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Gold nanorods and their plasmonic properties†

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Gold nanorods have been receiving extensive attention owing to their extremely attractive applications in biomedical technologies, plasmon-enhanced spectroscopies, and optical and optoelectronic devices. The growth methods and plasmonic properties of Au nanorods have therefore been intensively studied. In this review, we present a comprehensive overview of the flourishing field of Au nanorods in the past five years. We will focus mainly on the approaches for the growth, shape and size tuning, functionalization, and assembly of Au nanorods, as well as the methods for the preparation of their hybrid structures. The plasmonic properties and the associated applications of Au nanorods will also be discussed in detail.

1. Introduction

Gold has been regarded as one of the most precious matters in the world since its first extraction in the 5th century BC. It becomes more ‘precious’ when it is divided into fragments of sizes reaching down to ~ 100 nm. The electronic, optical, and catalytic properties of Au nanostructures are very different from those of their bulk counterpart. Most of these differences

originate from the large surface area-to-volume ratio and the spatial confinement of the free electrons of Au nanocrystals.¹ For example, the large surface area-to-volume ratio of Au nanocrystals introduces a large number of surface sites with high curvatures. These sites have more dangling bonds, which can substantially improve the chemical reactivities and surface bonding properties of Au nanocrystals.² The electron confinement in Au nanocrystals results in exotic properties, such as confinement-induced shifts of energy levels,³ nonlocal dielectric responses,^{4,5} and enhanced optical transition probabilities.⁶ All of these characteristics have greatly motivated the research efforts in Au nanocrystals, including their growth, characterization, and applications.^{1,7–12}

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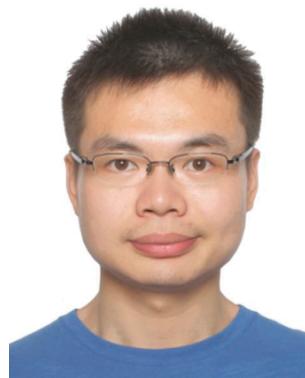
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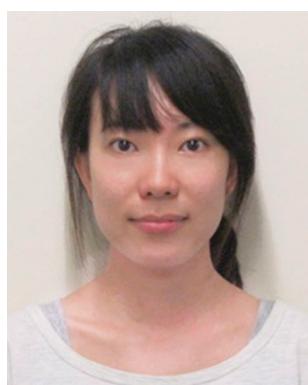
The shape of Au nanocrystals is also an important parameter in governing their physical and chemical properties. In comparison with spherical ones, nonspherical Au nanocrystals exhibit anisotropic optical and electronic responses that are determined by their topological aspects.¹³ Among various Au nanocrystals with nonspherical shapes, much attention has been paid to those with rod-like shapes, namely, Au nanorods. Because of their important applications in optical devices, biochemical sensors, and nanomedicine, the growth and characterization of Au nanorods have encountered an upsurge in research activities since their first discovery in 1991.^{1,14–16} Many growth methods have been developed over the past two decades with the consistent goal of improving the yield, aspect ratio, shape, and uniformity control of Au nanorods.^{1,7,15–17} Moreover, great efforts have also been made to study the physical and chemical properties of Au nanorods to cultivate their applications in photonics, electronics, catalysis, and biology.^{1,7}

The most intriguing property of Au nanocrystals is their localized surface plasmon resonances (LSPRs). LSPRs are electromagnetic modes associated with the collective oscillations of the free electrons confined to the nanoscale.^{18,19} Under resonant excitation, Au nanocrystals have the unique ability to concentrate the free-space optical field within subwavelength regions adjacent to their surfaces.^{8,20} This unique capability enables extremely large electric field enhancements around the nanocrystals, giving rise to a variety of light-matter interactions with new mechanisms, such as plasmon-enhanced spectroscopies,^{21,22} high-harmonic generation,²³ optical nanoantenna effect,⁸ plasmon-induced vacuum Rabi splitting,^{24,25} photothermal conversion,²⁶ and plasmon-assisted photochemical reactions.^{27,28} Driven by the utilization of these fascinating optical properties, LSPRs have become a flourishing new field in science as well as technology.

One remarkable feature of Au nanocrystals is that their LSPR properties can be tailored by synthetically tuning their sizes

and shapes. Compared to other nanocrystals, Au nanorods offer significant advantages in this aspect. There are two plasmon modes in Au nanorods. One is the longitudinal LSPR mode associated with the electron oscillations along the length axis, and the other is the transverse LSPR mode excited by light polarized along the transverse direction of the nanorod.⁷ The plasmon wavelength of the longitudinal mode can be synthetically tuned across a broad spectral range, covering the visible and near-infrared regions by tailoring their aspect ratios, that is, the ratio between the length and diameter.^{1,7,13} In the spectral regions far from the interband transitions of gold, which are below ~590 nm, the plasmon damping is very small. Au nanorods can therefore exhibit huge electric field enhancements under resonant excitation. Such enhancements are mainly located in the regions around the two ends of the nanorods. Their magnitudes and distributions can also be tailored by varying the head shape. Furthermore, Au nanorods can be assembled into a number of superstructures in different geometries, which results in even richer plasmonic properties owing to the anisotropic nature of Au nanorods. As a result, LSPRs in Au nanorods have been vigorously pursued during the last decade.^{1,7}

In this review, we will give a comprehensive introduction on Au nanorods, including their growth and assembly methods, shape and size tuning, functionalization, hybrid structures, plasmonic properties, and related applications. An outlook regarding the future developments in this ongoing hot field will be given at the end of this review. What should be mentioned is that there had already been many excellent review articles summarizing the research works on Au nanorods up to 2006, including, but not limited to, their growth and characterization,^{7,29} plasmonic properties,^{1,12} and biomedical applications.^{1,30} Even among Chemical Society Reviews, there have been at least two tutorial reviews concerning the growth and characterization of Au nanorods.^{11,12} Therefore, we will mainly highlight the research progress since 2006,



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although some works before 2006 will also be mentioned for the purpose of coherency and completeness. We apologize for not being able to include all of the important works in this field due to the space limitation.

2. Preparation

The preparation of Au nanorods is essential in this field because every Au nanorod-based application, whether it is optical, electronic, or catalytic, relies upon reproducible methods for producing Au nanorods in high yields, high uniformity, and with controlled geometries. In our discussion, the yield of Au nanorods refers to the ratio between the number of Au nanorods and the total number of Au nanocrystals in products. Great progress has been made in the preparation of Au nanorods during the past five years. That will be briefly discussed below.

2.1 Direct growth and fabrication

The first reported procedure for growing colloidal Au nanocrystals was performed in 1857 by Michael Faraday, who found that a beautiful ruby fluid composed of fine Au nanoparticles was obtained through the reduction of Au chloride by phosphorus.³¹ Since then, a number of methods have been developed for preparing or fabricating Au nanocrystals, such as chemical reduction, electrochemical reduction, photochemical reduction, and different physical methods.^{1,7} The obtained Au nanoparticles include nanospheres,¹⁵ nanorods,^{15,16} nanoplates,^{32,33} nanocubes,³⁴ nanoshells,³⁵ and anisotropic nanostructures with various protrusions.^{34,36,37} For Au nanorods, there are two general growth approaches, which are bottom-up and top-down methods. For bottom-up methods, Au nanorods are generated through nucleation in aqueous solutions and subsequent overgrowth, where Au salts are usually used to provide the Au source through reduction. In top-down methods, Au nanorods are obtained through a combination of different physical lithography processes and Au deposition.

Typical bottom-up methods for growing Au nanorods include wet-chemical,^{15,16,38} electrochemical,³⁹ sonochemical,⁴⁰ solvothermal,⁴¹ microwave-assisted,⁴² and photochemical reduction techniques.⁴³ In these methods, aqueous solvated Au salts are reduced by various reducing agents, such as sodium borohydride, ascorbic acid, and small Au clusters, under different external stimuli. The role of the stimulus is to trigger or enhance the reduction of the Au salt. In order to obtain elongated Au nanorods, one has to resort to a template, which serves to confine the growth along one direction during the reduction. The most widely used hard template for growing one-dimensional nanostructures is anodic aluminium oxide membranes, which possess randomly or self-organized cylindrical, monodisperse perpendicular pores with high densities and controllable pore sizes. Anodic aluminium oxide membranes have been widely utilized in various bottom-up techniques for growing Au nanorods^{44–46} since the pioneering work by Masuda *et al.*⁴⁷ and Martin.⁴⁸ Although the yield and uniformity of the nanorods obtained *via* the anodic aluminium oxide template is high, one needs to employ relatively complex techniques to

release the nanorods from the template and disperse them into solvents for subsequent applications. In addition, the nanorods usually have relatively large diameters (~ 100 nm), which hampers their plasmonic responses due to the retardation effect. In later research studies, people have developed techniques for growing freestanding Au nanorods that have much smaller diameters in the presence of various surfactants.⁷ The surfactants that are widely used in the colloidal growth of Au nanorods are cationic ammonium ones, among which cetyltrimethylammonium bromide (CTAB) is most common. Surfactants serve as the stabilizing agents to prevent the aggregation of the nanorods. They can also form micelles to direct the longitudinal growth of Au nanorods.⁴⁹ These micelles are often referred to as ‘soft templates’ (Fig. 1), although their exact roles in the formation of Au nanorods still need to be understood.

The most common method that utilizes ‘soft templates’ for growing Au nanorods is the so-called ‘seed-mediated’ growth (Fig. 1), which was developed independently by Murphy *et al.* and El-Sayed *et al.*^{15,16,49} Nearly monodisperse Au nanorods with very high yields and uniformity can be obtained using the seed-mediated growth method. In a typical growth, small Au nanoparticle seeds of ~ 1.5 nm in size are first prepared by reducing chloroauric acid with borohydride in an aqueous CTAB solution. A certain amount of the seed solution is then added into the growth solution, which is obtained by reducing Au(III) complex ions to Au(I) complex ions with ascorbic acid in an aqueous CTAB solution. The added seeds thereafter catalyze the further reduction of Au(I) complex ions to form Au nanorods. Another important aspect for producing Au nanorods in high yields is the addition of AgNO₃. For the growth without Ag⁺ ions, the products contain nanocrystals with many different shapes, including spheres, triangular plates, and rods.^{17,49} There are difficulties in increasing the yields of Au nanorods and tailoring their aspect ratios. In contrast, the presence of Ag⁺ ions can greatly improve the yields of Au nanorods in the products and allow for the rough control of their aspect ratios.^{16,50} Although the detailed mechanisms are still unclear, Ag(I) ions are believed to bond selectively to the higher-energy {110} facets of Au nanocrystals and slow down the growth rate on these facets. As a result, Au atoms will be predominantly deposited onto the {100} facets, leading to the longitudinal growth of the nanorods.^{49,50} The yields of the nanorods from the seed-mediated growth method can be as high as 99%.¹⁶ In addition, the size and shape of Au nanorods can be tailored by carefully adjusting the growth conditions, such as the composition of the surfactant, the pH of the growth solution, the amounts of the reagents, the growth temperature, and the structure of the seeds, in the seed-mediated growth process.^{15,16,29,50–58} A very recent study has demonstrated the seed-mediated growth of Au nanorods in high yields and uniformity through the use of aromatic additives in addition to CTAB.³⁸ The aspect ratios of the grown Au nanorods can be varied from 2.4 to 8.5. On the basis of these great efforts, a few start-up companies have been established as the commercial suppliers for high-quality Au nanorods, such as Nanopartz⁵⁹ and NanoSeedz.⁶⁰

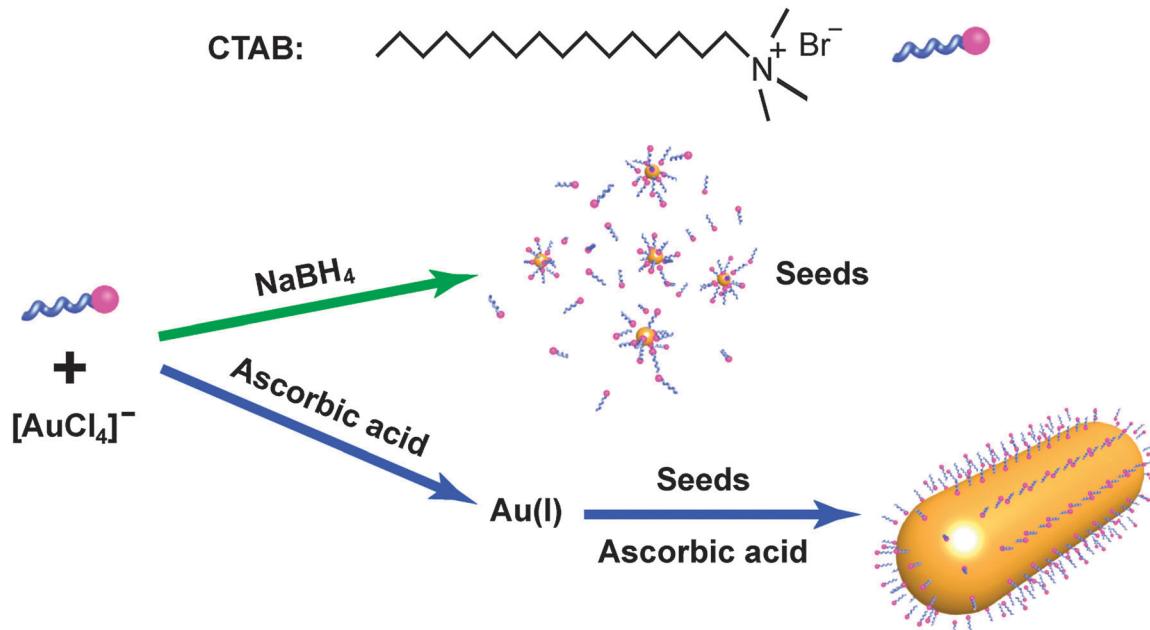


Fig. 1 Schematic illustration of the seed-mediated method for the growth of Au nanorods.

Although the bottom-up methods can give nearly monodisperse Au nanorods with small diameters and high uniformity, they suffer from several disadvantages that hinder the potential device applications. First, selective placement of Au nanorods at desired locations on substrates by the bottom-up methods has been very difficult owing to the random nature of the reduction of Au ions and the deposition of Au atoms in reaction solutions. Second, the shape and size of Au nanorods vary among different batches, even though the growths follow the same procedures. This variation will affect their optical and catalytic properties and applications. Third, there are extreme difficulties in placing Au nanorods into large-area, ordered arrays with the bottom-up methods. Top-down approaches are therefore developed as a complementary means to the preparation of Au nanorods. Top-down methods have the merit of producing homogeneous Au nanorods with controlled particle geometries and regular inter-particle arrangements, which is valuable for quantitative characterization as well as device applications.

There are mainly two types of top-down methods for the preparation of Au nanorods. The first refers to the removal of gold from pre-deposited Au films according to pre-designed patterns using focused ion beam or various etching techniques.^{61–63} The remaining structures are composed of Au nanorods located at pre-determined sites. The second type of top-down methods employs lithography techniques to make masks. A layer of gold is then deposited on the substrate that is covered with the mask through physical methods, such as thermal, electron-beam evaporation, or sputtering. Au nanorods are obtained after the lift-off process. The sizes of the nanorods fabricated using the top-down methods are usually limited by the resolution of lithography techniques. For example, traditional photolithography can only produce nanostructures with sizes in the range

of several hundred nanometers due to the diffraction limit of light. Electron-beam lithography is the most commonly used technique for the fabrication of Au nanorods with smaller sizes. Nowadays, state-of-the-art electron-beam lithography systems can produce Au nanorods of diameters ranging from ~10 nm to several hundred nanometers.⁶⁴ However, the top-down methods are usually time-consuming and have high cost, which makes them impractical for the fabrication of Au nanorods on large scales. In addition, the nanorods obtained from vacuum deposition techniques are usually composed of polycrystalline nanoparticles, which will degrade their plasmonic properties due to the electron scattering at the grain boundaries. These shortcomings prevent the top-down methods from practical device applications and limit them mostly to fundamental research.

2.2 Shape and size tuning

One of the great challenges in materials science is the fine tuning of the size and shape of nanostructures in a controlled manner. This is very important not only in the rational design of nanomaterials but also for their applications, because many optical, electronic, and catalytic properties of nanomaterials are strongly dependent on their shapes and sizes. For example, one of the most intriguing plasmonic properties of Au nanorods is that their longitudinal plasmon wavelength exhibits a nearly linear dependence on their aspect ratio.⁷ Moreover, even for Au nanorods with the same aspect ratio, the plasmon resonance properties are also strongly dependent on their head shape.

During the past five years, tremendous progress has been made on the shape and size tuning of Au nanorods. Most of them are based on the bottom-up methods, because such tuning usually occurs at scales of several to tens of nanometers, which is below the resolution limits of most top-down techniques. By using the seed-mediated growth method together with

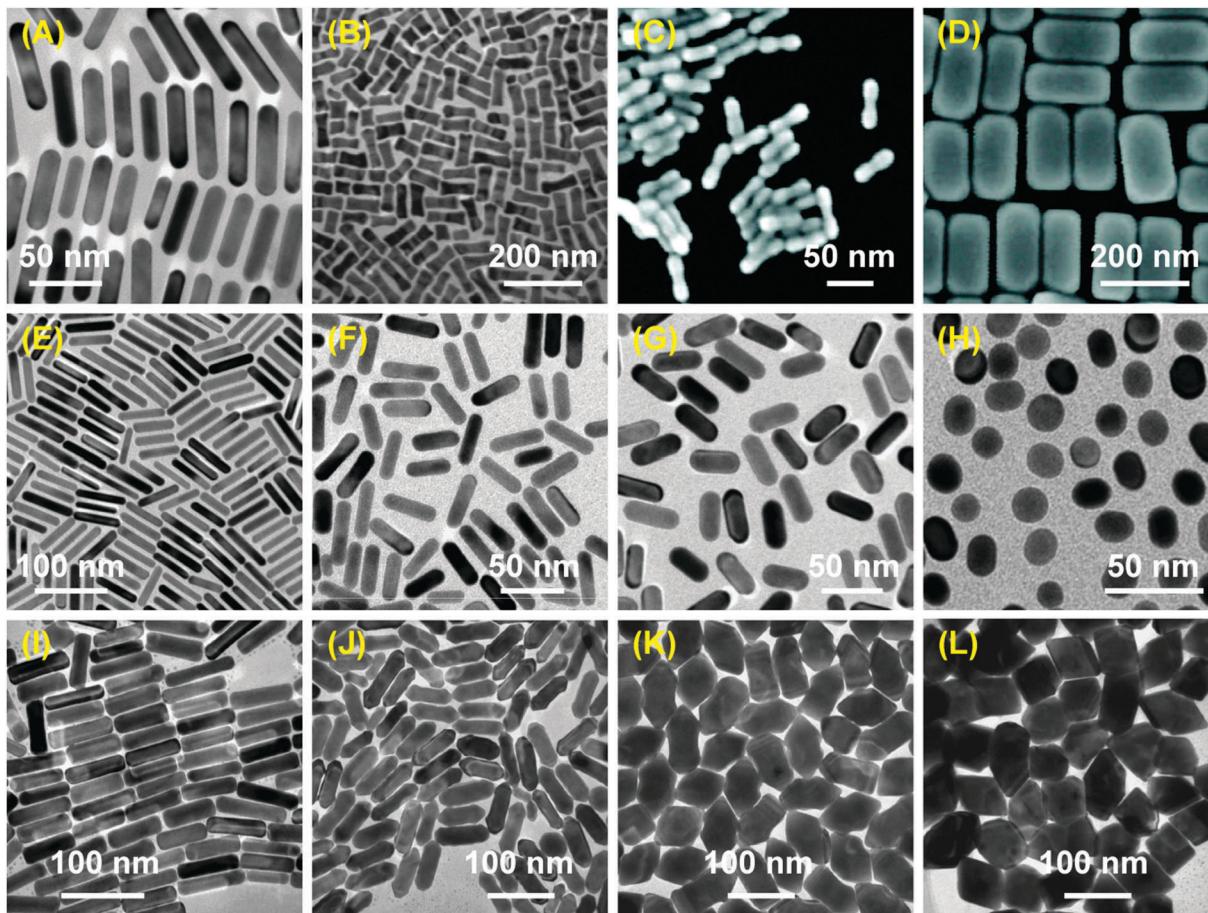


Fig. 2 Gold nanorods of various sizes and shapes. (A) Au nanorods with spherical heads. (B) Dogbone-like Au nanorods.⁶⁶ (C) Dumbbell-shaped Au nanorods.⁶⁷ (D) Au nanorods with a cuboidal shape.⁶⁷ (E–H) Au nanorods at various stages of anisotropic oxidation.⁷⁴ (I–L) Au nanorods at various stages of transverse overgrowth. Adapted from the data of the cited papers by permission from Wiley Interscience and The American Chemical Society.

subsequent chemical modifications, Au nanorods with various head shapes can be obtained. The as-grown Au nanorods using the seed-mediated method usually possess spherical heads (Fig. 2A). Close inspection of the heads indicates that they are enclosed with {110}, {111}, and {001} facets.⁶⁵ The head shapes can be tuned by subsequent overgrowth using the growth solution made of the reactants at varying concentrations. In the initial growth, if insufficient ascorbic acid is added, there will be excess Au ions left in the solution. Murphy *et al.* have shown that by further reducing the residual Au ions in the presence of pre-grown Au nanorods, dogbone-like nanorods with relatively flat heads are generated (Fig. 2B).⁶⁶ The formation of such structures is attributed to the site dependence of the CTAB binding strength on the surface of the nanorods. CTAB molecules are believed to preferentially bind to the middle of the nanorods. This preferential binding causes more Au atoms to be deposited at the ends, leading to the production of the dogbone-like nanorods. Huang *et al.* have extended the similar idea and found the detailed conditions for growing Au nanorods with many different head shapes. They have illustrated vividly their growths with an ‘evolutionary tree’.⁶⁷ Previous studies have shown that CTAB molecules tend to stabilize the

{100} facets of gold.^{68,69} The stabilizing power of CTAB can be reduced by decreasing its concentration as well as reducing the pH of the growth solution. As a result, dumbbell-shaped nanorods with spherical heads thicker than the waist (Fig. 2C) are obtained using less CTAB in the overgrowth process. In comparison, if the concentration of CTAB is the same as that used in the initial growth, the Au nanorods will undergo isotropic overgrowth. This isotropic overgrowth leads to the exposure of the {100} facets and therefore the formation of cuboidal Au nanocrystals (Fig. 2D). More interestingly, by carefully adjusting the CTAB concentration and pH of the growth solution, one is able to prepare Au nanostructures of various sizes and shapes using the same Au nanorods as the seeds.⁶⁷

The longitudinal plasmon resonance wavelengths of Au nanorods can be tailored to accommodate different applications by tuning their length-to-diameter aspect ratios. There are mainly two approaches for adjusting the aspect ratio. One is anisotropic oxidation, and the other is transverse overgrowth. In the anisotropic oxidation process, the aspect ratios of Au nanorods can be controlled by selectively shortening their lengths with thermal or laser heating, cyanide or Au(III) dissolution, or various oxidants, while keeping their diameters

nearly unchanged.^{70–72} The selective shortening of the nanorods is believed to originate from the smaller packing density of CTAB molecules at the two ends of the nanorods. We have developed a mild oxidation method using environmentally benign oxygen or hydrogen peroxide for such selective shortening.^{73,74} In a typical reaction, oxygen or controlled amounts of hydrogen peroxide are added into the Au nanorod solution *via* bubbling or injection, respectively. Br[−] ions coming from CTAB act as the complexing agent to ease the oxidation of Au(0) into Au(i) and thus ensure the progress of the oxidation reaction. Oxygen oxidizes Au nanorods into colorless AuBr₂[−] ions, while hydrogen peroxide generates yellow AuBr₄^{3−} ions due to its stronger oxidation power. The acid concentration and the reaction temperature are further found to be two pivotal parameters governing the oxidation rate. The anisotropic oxidation process can be monitored by measuring the extinction spectra of the nanorod solution as a function of time on large or miniature spectrophotometers and stopped by centrifugation. As a result, the aspect ratios of the nanorods can be synthetically tailored over a broad range without changing their diameters (Fig. 2E–H). What should also be mentioned is that another anisotropic shortening method has recently been developed, where the diameters of the nanorods are reduced while the lengths are kept nearly unchanged. In this method, preferential etching of the side surface of the nanorods is realized by selectively capping the ends of the nanorods with a Ag₂O protection layer.⁷⁵ This transverse oxidation method will be beneficial for applications, such as photothermal therapy, which require Au nanorods with longer plasmon wavelengths and smaller particle volumes.

The overgrowth method, in contrast to the anisotropic oxidation, tailors the aspect ratios of Au nanorods by selectively widening their diameters. This strategy was first proposed by our group⁷⁶ in 2007. Prior to the overgrowth, small thiol molecules, such as glutathione or cysteine, are bonded to the ends of the nanorods. The bonding of thiol molecules blocks the longitudinal growth. As a result, Au nanorods undergo transverse overgrowth by additionally supplying the growth solution, producing Au nanorods with larger diameters but lengths remaining nearly unchanged (Fig. 2I–L). The enlargement of the middle section when a large amount of the growth solution is provided is presumably caused by the development of the stable {111} facets. As a result, the transverse overgrowth will finally produce faceted Au nanostructures (Fig. 2L).

3. Functionalization

In order to make Au nanorods stable under different conditions and arm them with added functionalities for particular applications, the most common CTAB-capped Au nanorods should be functionalized with appropriate organic or inorganic species. Detailed information about the functionalization of Au nanorods can be found in a recent review by Zubarev *et al.*⁷⁷ Different methods have been developed for functionalizing CTAB-capped Au nanorods. The capping CTAB molecules form a partially-interdigitated bilayer on the surface of Au nanorods,

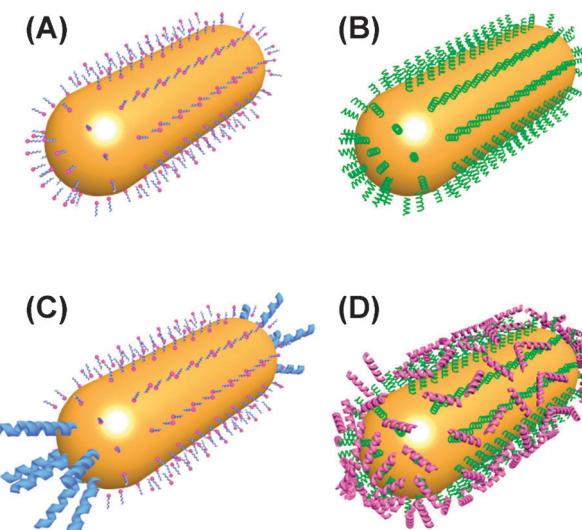


Fig. 3 Schematics of (A) CTAB bilayer-capped Au nanorods, (B) functionalized Au nanorods with the CTAB bilayer completely exchanged, (C) functionalized Au nanorods with the CTAB bilayer partially exchanged, and (D) secondarily functionalized Au nanorods.

similar to the structure of a vesicle or cell membrane (Fig. 3A).⁶⁸ The Au surface is believed to carry negative charges due to the adsorption of bromide or chloride ions. The positively charged ammonium head group binds tightly to the Au surface through electrostatic interaction, leading to the formation of the inner layer. Because the hydrophobic carbon-chain tail does not like to stay in water, another layer of CTAB molecules is formed, with the hydrophobic tails pointing inside and interacting with those of the inner layer and the ammonium groups pointing outside. The existence of the bilayer on Au nanorods in aqueous solutions has been proved by measuring the layer thickness.^{78,79} The CTAB bilayer makes Au nanorods positively charged⁸⁰ and therefore stabilized in aqueous solutions. The bilayer can be disrupted when the CTAB concentration is lower than its critical micelle concentration, organic solvents are added, the salt concentration in the solution is high, or some other external stimuli are applied to the Au nanorod solution.

Gold–thiol bonding chemistry is commonly utilized for completely or partially functionalizing the surface of Au nanorods (Fig. 3B and C). Small molecules are not preferred because the steric effect introduced by small molecules cannot overcome the large attractive force among Au nanorods. Therefore, the bonding of small thiol molecules often leads to poor dispersibility and irreversible aggregation of Au nanorods. Large thiol-terminated polymers with high molecular weights, such as poly(ethylene glycols) (PEGs) and DNAs, have instead been employed for functionalization. Thiol molecules have been found to preferentially bond to the two ends of Au nanorods at low concentrations, which has been attributed to the smaller packing density of CTAB at the highly curved ends.^{76,81} Thiol-terminated PEGs endow Au nanorods with high stabilities and improve their biocompatibilities. PEGylated Au nanorods are dispersible without aggregation in aqueous solutions and various types of polar organic solvents, including

ethanol, methanol, acetone, acetonitrile, dimethylformamide, dimethyl sulfoxide, and phosphate buffered saline solutions.⁸² Apart from Au–thiol interactions, disulfides and dithiocarbamates can also be utilized to bond to Au nanorods,^{83,84} which adds the flexibilities in functionalizing Au nanorods for various applications.

Secondary functionalization of Au nanorods is often needed for their assembly into a variety of superstructures and the inclusion of new functionalities. It can be realized by electrostatic attraction, antibody–antigen interaction, or DNA sequence recognition (Fig. 3D). For instance, polyelectrolytes can be directly attached onto CTAB bilayer-stabilized Au nanorods through a layer-by-layer deposition technique.^{85–87} Negatively and positively charged polyelectrolytes are sequentially deposited onto the positively charged surface of Au nanorods through electrostatic interaction. Polyacrylic acid and polystyrenesulfonate are often employed as negatively charged polyelectrolytes, while poly(diallyldimethylammonium chloride) and poly(allylamine hydrochloride) are often used as positively charged polyelectrolytes. The deposition cycle can be repeated multiple times. Biological polyelectrolytes and proteins can also be deposited onto the surface of CTAB-capped Au nanorods through electrostatic adsorption. This technique can also introduce functional groups, such as carboxylic acid and amine groups, for further functionalization.

4. Gold nanorod-based hybrid nanostructures

Preparation and characterization of Au nanocrystal-based hybrid nanostructures has long been an attractive research topic in materials science, not only due to their synthetic challenges but also because of the potential enhanced functionalities offered by the synergistic interactions among different components. For example, coating dielectric shells around Au nanorods enhances the light scattering of the hybrid nanostructures, which is beneficial for biomedical imaging.⁷ Integration of Au nanocrystals with semiconducting components leads to hybrid nanostructures with intriguing optical responses by taking advantage of the interactions between excitons and plasmon resonances.^{88–91} Studies of such interactions can further our understanding on the light–matter coupling at the nanoscale, as well as help in cultivating potential nonlinear optical applications.^{92,93} Moreover, preparation of Au nanocrystal-based multi-component metallic nanostructures can give rise to a wide range of nanostructures with exceptional catalytic properties.^{94–96} In this section, we will mainly focus on Au nanorod-based hybrid nanostructures and give a brief overview of them.

4.1 Gold nanorod core–silica shell nanostructures

Two promising biomedical applications of Au nanorods are *in vivo* bioimaging and photothermal cancer therapy. However, as-grown Au nanorods from the wet-chemistry methods are usually capped with surfactant molecules, such as CTAB. The presence of these molecules will not only affect the functionalities of Au nanorods, but also bring in toxicities to biological species at different levels.⁹⁷ In order to improve the

biocompatibility of the nanorods, one can replace the surfactant with other inert molecules, which requires very strict preparation conditions. Alternatively, one can coat Au nanorods with a dielectric shell that is biocompatible. The most common dielectric shell is silica. The protocol for coating a layer of silica on Au nanorods was first developed by Liz-Marzán *et al.* on the basis of the well-known Stöber method.^{98,99} In a typical preparation, Au nanorods are first wrapped in two layers of polyelectrolytes of low molecular weights by the layer-by-layer technique. The polyelectrolyte layer acts as a silane binding agent for enhancing the affinity of gold to silica. The deposition of silica onto the functionalized Au nanorods is achieved through the hydrolysis and condensation of tetraethyl orthosilicate (TEOS). The silica shell exhibits a dense structure with smooth surface (Fig. 4A). The thickness of the shell can be precisely controlled by changing the added amount of TEOS or prolonging the reaction time.⁹⁹

The key point in the method above for coating silica is the wrapping of the polyelectrolyte layers on Au nanorods by the layer-by-layer technique, which requires strict reaction conditions, such as proper concentrations of the polyelectrolytes, addition of salts to adjust the electrostatic interaction, and careful handling of the multistep processes. Matsuura *et al.* have developed a relatively simple single-step method for coating silica onto CTAB-capped Au nanorods.¹⁰⁰ In their method, the silica coating is conducted by injecting TEOS into the aqueous Au nanorod solution at a controlled CTAB concentration. The CTAB molecules adsorbed on Au nanorods act as templates for the deposition of the hydrolyzed TEOS species onto the nanorods. As a result, the obtained silica shell exhibits a mesostructure with disordered pores around 4 nm in diameter (Fig. 4B). The mesostructured silica coating can thereafter be employed as scaffolds for further TEOS deposition to increase the thickness as well as change the morphology of the silica shell.¹⁰⁰ Furthermore, the mesostructured nature of the silica shell allows for the encapsulation of other species, such as dye molecules, for different applications.^{101–104}

4.2 Gold nanorod–semiconductor hybrid nanostructures

Integration of Au nanorods with semiconducting materials is driven by the combination of multiple functionalities into one system for particular applications, such as light harvesting and photocatalysis. Moreover, the interactions between the plasmon resonances in Au nanorods and the excitons in semiconductors can greatly improve the overall application performance of the hybrid system and even generate new physical and chemical properties. The reported Au nanorod–semiconductor hybrid nanostructures can be generally divided into two categories: Au nanorod–metal oxide and Au nanorod–metal chalcogenide.

Enormous efforts have been made to combine metal nanocrystals with metal oxide semiconductors to form hybrid nanostructures with enhanced optical, catalytic, and magnetic properties.^{105–108} For example, studies have shown that light-induced charge separation can be improved due to the presence of metal ingredients in metal–TiO₂ hybrid nanostructures.^{109,110}

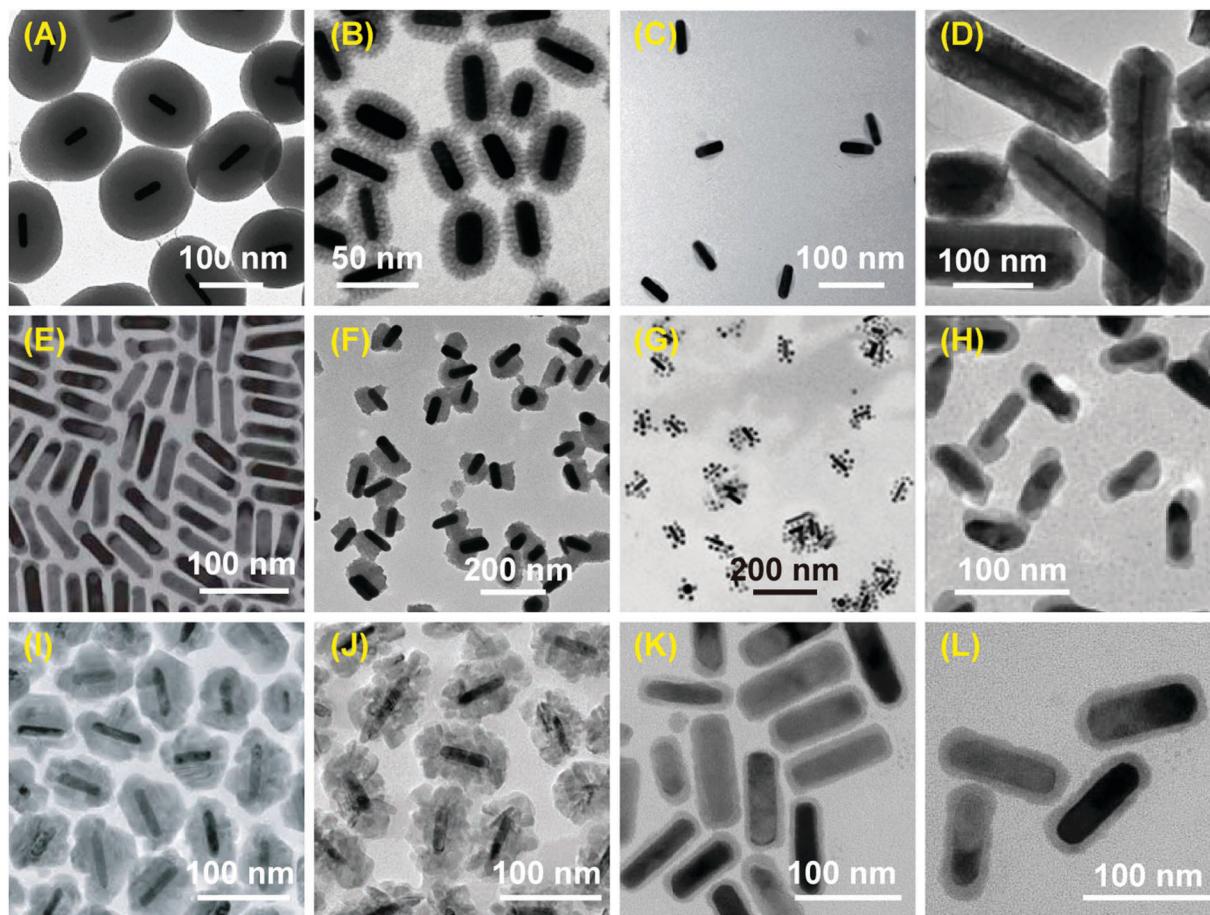


Fig. 4 Transmission electron microscopy (TEM) images of Au nanorod-based hybrid nanostructures. (A) Au nanorod core–silica shell nanostructures.⁹⁹ (B) Au nanorod core–mesostructured silica shell nanostructures.¹⁰⁰ (C) Au nanorod–TiO₂ heterostructures.¹¹¹ (D) Au nanorod core–Cu₂O shell nanostructures.¹⁰⁵ (E) Au nanorods capped with Ag₂O at the two ends.⁷⁵ (F) Au nanorod–superparamagnetic hematite heterostructures.¹¹³ (G) Au nanorod–Fe₃O₄ hybrid nanostructures.¹¹⁴ (H) Au nanorod–Cu_{2–x}S heterostructures.¹¹⁷ (I) Au nanorod core–CdS shell nanostructures.¹¹⁹ (J) Au nanorod core–ZnS shell nanostructures.¹¹⁹ (K) Au nanorod core–Ag₂S shell nanostructures.¹²⁰ (L) Au nanorod core–Ag₂Se shell nanostructures.¹²⁰ Adapted from the data of the cited papers by permission from The American Chemical Society, The Royal Society of Chemistry and Wiley Interscience.

The plasmon resonances of the metal nanocrystals can also enhance the light absorption in the adjacent semiconductors.^{89,90} These effects enhance the photocatalytic and light-harvesting efficiencies of the semiconductors. Most of these studies utilized spherical metal nanocrystals, which facilitates the uniform deposition of metal oxides owing to the highly symmetric geometry. For anisotropic nanocrystals like Au nanorods, difficulties still remain in coating metal oxides on their surface, as well as in precisely controlling the morphology and composition of the coated metal oxides. Han *et al.* have developed an approach for anisotropic growth of TiO₂ on Au nanorods.¹¹¹ In their experiment, a titanium precursor (titanium diisopropoxide bis(acetylacetone)) that has a very slow hydrolysis rate was employed. The use of this precursor helps in separating the nucleation and growth of TiO₂. Fig. 4C shows a typical result with TiO₂ concentrically coated around Au nanorods. By carefully adjusting the amount of the titanium precursor as well as controlling the experimental procedures, eccentric and Janus hybrid nanostructures can also be obtained. In a later study, they successfully prepared Au nanorod core–TiO₂ shell nanostructures with a modified procedure. The resultant

nanostructures exhibit improved photocatalytic activities by taking advantage of the strong light concentrated by the LSPR of the Au nanorod core.¹¹²

Other Au nanorod–metal oxide hybrid nanostructures have also been explored. Huang *et al.* have successfully prepared Au nanorod core–Cu₂O shell nanostructures through a facile aqueous solution approach.¹⁰⁵ Cu₂O is deposited onto Au nanorod cores by reducing CuCl₂ with NH₂OH·HCl as the reducing agent. Despite the large lattice mismatch between gold and Cu₂O, the resultant core–shell nanostructures exhibit excellent structural integrity (Fig. 4D). Moreover, the morphology of the hybrid structures can be tuned by varying the volume of the reducing agent. Close examination of the growth process suggests that Cu₂O is formed through a hollow-shell-refilled mechanism, where a hollow Cu₂O framework encapsulating a Au nanorod core is constructed at the early stage of the growth. The space between the core and the outer shell is thereafter filled by small Cu₂O nanoparticles. Continuous shell growth eventually leads to the formation of a crystalline shell structure. We have developed a method for selectively coating Au nanorods with Ag₂O

hydrothermally.⁷⁵ In a typical reaction, a thin layer of Ag_2S is first formed on the surface of the nanorods. This thin Ag_2S layer is then oxidized to form Ag_2O through the hydrothermal treatment. Interestingly, Ag_2O coating is reconstructed and converted from uniform coating around the entire nanorod to selective capping at the two ends of the nanorod (Fig. 4E) as the hydrothermal reaction time is increased.

Iron oxides having magnetic properties have been combined with Au nanorods. Au nanorod–superparamagnetic hematite heterostructures have been fabricated by hydrothermally decomposing ferric acetylacetone on the Au surface. The formed hematite nanoparticle aggregates are decorated on the surface of Au nanorods, forming porous coating (Fig. 4F).¹¹³ Au nanorods co-functionalized with PEG and amine molecules have been conjugated with Fe_3O_4 nanoparticles that are capped with carboxyl groups, using carbodiimide/*N*-hydroxysuccinimide chemistry, to yield Au nanorod– Fe_3O_4 heterostructures (Fig. 4G).^{114,115} Coprecipitation of iron salts has been employed to coat iron oxide nanoparticles on Au nanorods that are wrapped with polymers.¹¹⁶ These hybrid nanostructures exhibit both plasmonic and superparamagnetic properties. They therefore have great potential for various biotechnological applications, such as magnetic resonance imaging, magneto-motive imaging, bioseparation, and targeted photothermal therapy.

Coating of Au nanocrystals with metal chalcogenides has recently attracted much attention due to their intriguing optical properties and applications in plasmon-enhanced harvesting of solar energy. However, direct coating is generally difficult because of the large lattice mismatches between Au cores and metal chalcogenides. In 2009 we developed a general hydrothermal strategy for the preparation of Au nanocrystal core–metal sulfide shell heterostructures.¹¹⁷ The method is highly reliable and reproducible. Various metal thiobenzoates were used as the metal precursors. They were decomposed during the hydrothermal reaction under proper temperatures. A key factor in the deposition of metal sulfides is the addition of a small amount of Ag^+ ions. The presence of Ag^+ ions produces a very thin Ag_2S layer on the Au surface, which acts as an intermediate binder between the Au core and the shell material and therefore facilitates the further overgrowth of the shell. The thickness and integrity of the metal sulfide shell can be tailored by varying the concentration of Ag^+ ions. This method can be extended to the use of Au nanorods as cores. Fig. 4H gives an example of using copper thiobenzoate as the precursor. Copper sulfide is preferentially deposited on one side of each nanorod, resulting in Au nanorod–copper sulfide heterostructures. In a later study, a multistep route was proposed for the preparation of Au nanorod core–CdS shell nanostructures through a cation-exchange process.¹¹⁸ The obtained nanostructures exhibit superior two-photon-excited luminescence due to the plasmonic field enhancement of the Au nanorod core. On the basis of the method developed by us,¹¹⁷ Sun and Su *et al.* demonstrated a one-step hydrothermal approach for the preparation of Au nanorod core–metal sulfide shell nanostructures.¹¹⁹ By finely adjusting the ratio between the added metal thiobenzoate and

Ag^+ ions, core–shell nanostructures with Au nanorods encapsulated by CdS or ZnS are obtained (Fig. 4I and J). Owing to the spillover effect on the surface of Au nanorods, the core–shell nanostructures exhibit improved gas sensing performances compared to their pure metal sulfide counterparts. Guyot-Sionnest *et al.* employed a wet-chemistry method to coat a homogeneous layer of Ag_2S (Fig. 4K) or Ag_2Se (Fig. 4L) on Au nanorods.¹²⁰ The obtained nanostructures exhibit interesting plasmonic properties.

4.3 Gold nanorod-based multimetallic nanostructures

Integration of Au nanocrystals with other types of metals can lead to distinct physical and chemical properties in comparison to the dielectric and semiconductor materials described above. There exists Ohmic contact without an energy barrier at the interface between two metals, facilitating electron flows back and forth between the two metals. In addition, the real part of the dielectric function of metals is negative, which brings in interesting optical properties. Coating Au nanocrystals with a continuous metallic shell will usually give blue-shifted plasmon resonances due to the repulsion of the electromagnetic field outside the core.^{121–124} This is very different from the red-shift behaviors caused by the increase of the refractive index of the surrounding medium. Moreover, the electron diffusion between the core and shell can improve the catalytic performance through synergistic interactions. The stability of the shell during catalytic reactions can also be improved by using a chemically stable metal core.

Although there have been a number of studies on the preparation and characterization of Au nanocrystal-based multimetallic nanostructures, most of them utilize spherical Au nanocrystals as cores.^{125–130} Only in recent years researchers have paid more attention to the combination of Au nanorods with other metals. Silver is one of the most popular metals employed. The imaginary part of the dielectric function of silver is very small in the visible range. Ag nanocrystals therefore exhibit much weaker plasmon damping as well as larger light scattering compared to nanocrystals made of other metals. El-Sayed *et al.* have conducted comprehensive theoretical studies on the plasmonic responses of Au–Ag alloy nanorods.¹³¹ Their calculation results indicate that the plasmon linewidth, defined as the full width at half maximum of the extinction peak, decreases as the Ag content in the nanorods is increased, giving rise to enhanced light extinction and refractive index sensing performance. In a later study, Sönnichsen *et al.* showed that the ensemble plasmon linewidth of Au nanorods can be narrowed by 20% after coating a thin Ag shell.¹²¹ They attributed this phenomenon to the reduced inhomogeneous broadening of the plasmon resonance of the Au nanorod core–Ag shell nanostructures. This ‘plasmonic focusing’ provides a simple method for producing plasmonic nanocrystals with high-quality factors and tunable resonance wavelengths over a broad spectral range.

Coating silver on Au nanorods is usually based on wet-chemistry approaches, where Ag^+ ions are reduced by weak reducing agents, such as ascorbic acid, and deposited on the

surface of pre-grown Au nanorods. Depending on the reaction conditions, such as the pH, surfactant, and temperature, Ag shells in different morphologies can be obtained. For example, Niidome *et al.* have successfully prepared Au nanorod core–Ag shell nanostructures by reducing Ag^+ ions in cetyltrimethylammonium chloride (CTAC) solutions.¹³² Rapid nucleation and suppressed growth of the Ag shell in CTAC solutions are two pivotal factors for controlling the uniformity of the Ag shell. In addition, the Ag shell is highly uniform among the different core–shell nanostructures. On each nanorod, the thickness of the Ag shell in the transverse direction is larger than that in the longitudinal direction (Fig. 5A). The faster deposition in the transverse direction is ascribed to the molecular packing state of CTAC on the surface of Au nanorods. Preferential deposition of silver on the side surface of Au nanorods can also be realized by capping the nanorod ends with thiol molecules. Pastoriza-Santos *et al.* have shown that selective bonding of thiolated PEGs to the ends of Au nanorods completely blocks the Ag growth in the longitudinal direction and thereby induces the transverse growth of the Ag shell on Au nanorods.¹³³ The continuous Ag coating finally leads to the production of octahedron-shaped Au nanorod core–Ag shell nanostructures (Fig. 5B).

Vaia *et al.* have recently studied systematically the effects of various parameters, including the concentrations of Ag^+ ions, CTAB, and Au^{3+} ions, aging time of the precursor solution, pH, and reaction temperature on the morphologies of the Ag shell.¹³⁴ They performed Ag coating in aqueous CTAB solutions. Their study indicates that the molar ratio between CTAB and Ag^+ ions plays an important role in controlling the growth of the Ag shell. Ag^+ ions react with Br^- ions, which is from CTAB, to form freestanding Ag–Br complexes at low $[\text{CTAB}]/[\text{Ag}^+]$ ratios. These complexes are adsorbed on the surface of Au nanorods due to the positively charged CTAB bilayer, which leads to uniform nucleation of silver on the nanorods in the presence of ascorbic acid. As a result, the generated Ag shell has a conformal shape. Aging of the growth solution prior to the addition of ascorbic acid induces the formation of negatively charged Ag–Br clusters. Since the CTAB bilayer on the side surface of Au nanorods is denser, more Ag–Br clusters will be adsorbed on the side surface than at the ends. Therefore, more silver will be deposited in the transverse direction. If the size of the Ag–Br clusters is comparable to that of Au nanorods, anisotropic growth of the Ag shell occurs, resulting in boat-shaped asymmetric bimetallic nanostructures (Fig. 5C). The pH of the growth solution affects the deposition rate of silver on Au nanorods. When the pH of the reaction solution is low, the overall reduction rate of Ag^+ ions will be slowed down, which gives rise to uniform deposition of silver on Au nanorods. The obtained nanostructures have a cuboidal shape (Fig. 5A). In addition, the supply of a small amount of Au^{3+} ions can also change the morphology of the Ag shell. At appropriate concentrations of Au^{3+} ions, Ag^+ ions, and ascorbic acid, preferential deposition of silver at the ends of Au nanorods occurs, which produces dumbbell-like Ag shells with sharp tips (Fig. 5D).

Interestingly, coating Au nanorods with a Ag shell gives complex plasmonic resonance behaviors. Usually four plasmon

bands are observed on the extinction spectra of the bimetallic nanostructures.^{133,135,136} In several studies, numerical electrodynamic calculations were performed to simulate the optical responses of the core–shell nanostructures and ascertain the origins of the plasmon bands.^{135–137} However, there has been a lack of consensus on the nature of the plasmon bands. We have addressed this question in our recent study by simultaneously conducting extensive measurements of the plasmonic responses of Au nanorod core–Ag shell nanostructures and computational simulations.¹³⁸ We found that the lowest-energy resonance belongs to the longitudinal dipolar plasmon mode, the second-lowest-energy resonance is the transverse dipolar plasmon mode, and the two highest-energy resonances can be ascribed to octupolar plasmon modes. The octupolar plasmon modes result from the retardation effect and the interference between the excitations along the two transverse edge directions.

Palladium and platinum are two metals widely used in catalysis. Pd nanoparticles are an important type of hydrogenation catalysts. Pt nanoparticles are used in the petroleum industry as a catalyst in a number of separation processes. In recent years, researchers have shown great interest in coating Au nanocrystals with palladium and platinum, mainly because the bimetallic nanostructures show enhanced catalytic performances and stabilities.^{122,125,129,139–143} Yang *et al.* made the first effort to coat palladium on Au nanorods by reducing H_2PdCl_4 in aqueous CTAB solutions.¹²² The obtained bimetallic nanostructures are composed of Au nanorod cores surrounded by many small Pd nanoparticles. The large lattice mismatch between gold (4.08 Å) and palladium (3.89 Å) was thought to be responsible for the discontinuous morphology of the Pd shell. Wu and Xie *et al.* successfully coated continuous Pd shells uniformly on Au nanorods using a similar method with carefully tuned concentrations of the reactants.¹⁴³ Because the surface energy of the Pd {110} facets is higher than that of the {100} facets, the coated Pd shells exhibit predominantly the {100} facets in order to minimize the total surface energy. As a result, the bimetallic core–shell nanostructures possess a cuboidal shape (Fig. 5E). However, such a growth mechanism can be affected by halogen ions. A very recent study has shown that I^- ions can be selectively adsorbed on the Pd {110} facets, which accordingly causes the Pd shell to possess a clearly different morphology.¹⁴⁴

Coating of platinum on Au nanorods usually gives discontinuous shells that are made of small Pt nanoparticles (Fig. 5F).^{141,145} Liz-Marzán *et al.* have conducted a detailed study on the formation of Pt shells on Au nanorods.^{139,141} Their study shows that Ag^+ ions are crucial for controlling the morphology of the Pt shells. In the absence of Ag^+ ions, homogeneous coating of Pt nanoparticles on Au nanorods is obtained. Ag^+ ions can selectively bond to the side surface of the nanorods and thereby suppress the deposition of platinum. As a result, a dumbbell-like shape is obtained in the presence of Ag^+ ions, with Pt nanoparticles preferentially deposited on the tips (Fig. 5F). However, the discontinuous morphology possessed by the Pt shells has still remained unclear, given the small lattice mismatch on the {111} facets between gold (2.88 Å) and platinum (2.77 Å). Pd–Pt

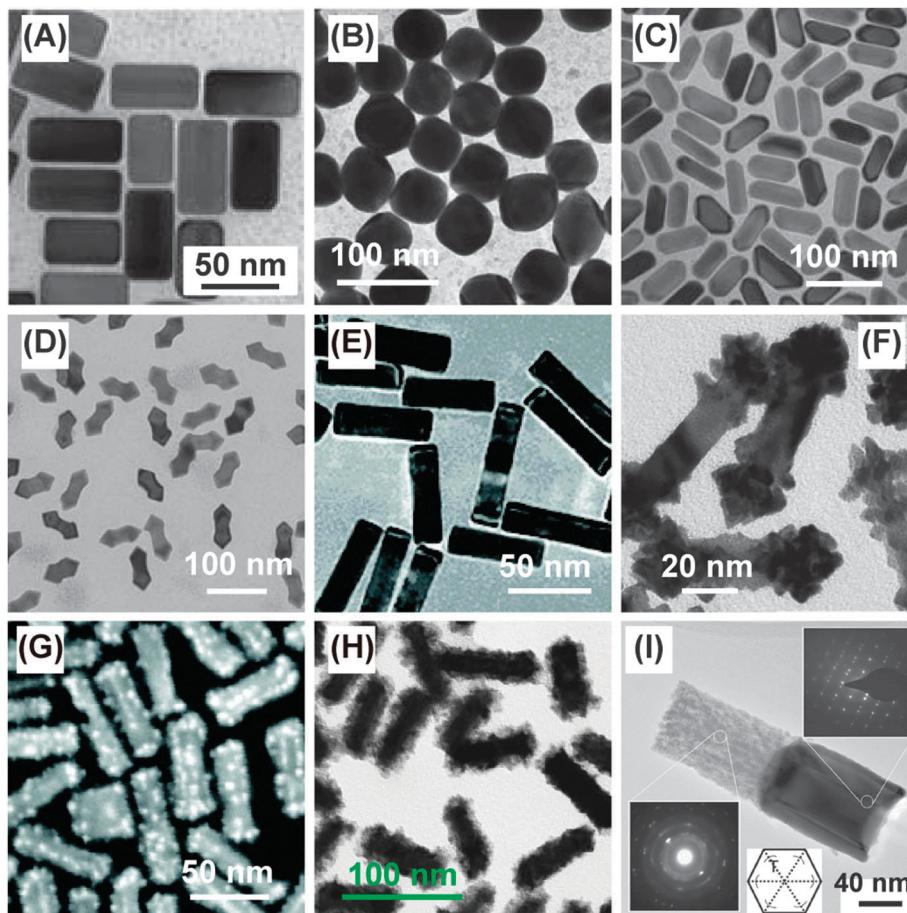


Fig. 5 TEM images of Au nanorod-based multimetallic nanostructures. (A) Au nanorod core–Ag shell nanostructures in a cuboidal shape.¹³² (B) Au nanorod core–Ag shell nanostructures in an octahedron shape.¹³³ (C) Au nanorod–Ag shell nanostructures in a boat shape.¹³⁴ (D) Au nanorod–Ag shell nanostructures in a dumbbell-like shape.¹³⁴ (E) Au nanorod core–Pd shell nanostructures in a cuboidal shape.¹⁴³ (F) Bimetallic nanostructures with Au nanorod cores decorated with Pt nanoparticles.¹⁴¹ (G) Trimetallic nanostructures made of Au nanorod cores decorated with Pd–Pt alloy nanoparticles.¹⁴⁶ (H) Bimetallic nanostructures with Au nanorod cores decorated with Ni nanoparticles.¹⁴⁷ (I) Trimetallic nanorod made of Au and FePt.¹⁴⁹ The insets at the top right corner and that at the bottom left corner are the selected-area electron diffraction patterns recorded on the Au and FePt segments, respectively. The inset in the bottom middle is the schematic showing the possible hexagonal, six-fold crystalline twinning from the cross-sectional view. Adapted from the data of the cited papers by permission from The Royal Society of Chemistry, The American Chemical Society and Wiley Interscience.

alloy coating on Au nanorods has recently been achieved through a similar growth method by Wu *et al.* The growth solution contains both PdCl_4^{2-} and PtCl_4^{2-} ions,¹⁴⁶ which are reduced simultaneously with ascorbic acid. The discontinuous growth manner of platinum leads to the formation of uniformly-distributed Pd–Pt alloy nanoparticles on Au nanorods (Fig. 5G). The molar ratio between palladium and platinum in the alloy nanoparticles can be synthetically tuned from 0.2 to 5 by simply changing the relative concentrations of the metal precursor ions. The obtained trimetallic nanostructures with attached Pd–Pt alloy nanoparticles exhibit excellent catalytic activities toward the oxidation of various chromogenic substrates.

Coating Au nanorods with magnetic metals is another approach to the production of magnetically functionalized Au nanorods. The preparation of hybrid nanostructures containing Au nanorods and magnetic metals is usually difficult, since the growth of magnetic metal nanocrystals is typically carried out in organic solvents and requires proper catalysts. Liz-Marzán *et al.* developed a quasi-epitaxial growth of nickel shells on Au

nanorods in aqueous CTAB solutions by first selectively growing Pt nanocrystals on the tips of Au nanorods. The small Pt nanocrystals then act as catalysts for the preparation of Ni nanoparticles (Fig. 5H).¹⁴⁷ An alternative method for the preparation of Au nanorod core–magnetic metal shell hybrid structures is the use of hard templates. Porous alumina membranes can serve as a template for the electrochemical fabrication of Au core–nickel shell nanorods¹⁴⁸ and trimetallic Au–FePt heterostructured nanorods (Fig. 5I).¹⁴⁹ Since transition metals are usually unstable in aqueous solutions, methods for the preparation of magnetic metal core–Au shell nanorods are highly desired. One critical challenge for such preparations is how to transfer magnetic metal seeds from organic solvents to aqueous CTAB solutions for the growth of Au nanorods.

5. Assembly

Assembly of nanocrystals into oligomers or large-scale ordered superstructures can bring in various attractive properties due to

the simultaneous contributions from the individual components and the collective inter-particle coupling among the assembled components. Metal nanocrystals support LSPRs. When metal nanocrystals are placed adjacent to one another, their LSPRs are coupled together through electrostatic interaction. The plasmon coupling caused by arranging metal nanocrystals into ordered structures brings many interesting collective plasmon responses, such as extremely large electric field enhancements and distinct collective plasmon modes.^{150–154} For metal nanocrystals with reduced shape symmetries like Au nanorods, the plasmon responses of their assemblies are further enriched due to the anisotropic optical response of the individual nanorod. These fascinating properties are favorable for many potential optoelectronic and biomedical applications. Moreover, study of the optical properties of these ordered structures can help to further our understanding on light-matter interactions at the nanoscale. In recent years, growing interest has been shown in assembling Au nanorods into ordered superstructures and characterizing their optical properties. There have been mainly three strategies. They are solvent evaporation-induced assembly, assembly through small thiol molecules, and assembly through biological molecules and polymers.

5.1 Solvent evaporation-induced assembly

Solvent evaporation-induced assembly has been widely used to form large-scale ordered structures of metal nanocrystals in various geometries. It relies on the formation of liquid-crystalline phases of nanocrystals during solvent evaporation.¹⁵⁵ Gold nanorods grown from the wet-chemistry methods are usually capped with surfactants like CTAB for stabilization. The capping agents usually make Au nanorods charged. For example, zeta potential measurements show that the CTAB bilayer formed around Au nanocrystals usually makes them positively charged.^{80,156} The bilayers can induce van der Waals attraction, electrostatic repulsion, and interchain attraction between different Au nanorods when they approach each other. To trigger the self-assembly process, a small amount of the solution containing Au nanorods is usually dropped on a flat substrate (Fig. 6A).¹⁵⁷ As the solvent is progressively evaporated, Au nanorods will be carried toward the edge of the droplet by the outward solvent flow due to the capillary force. The concentration of Au nanorods at the edge therefore becomes higher and the spacing between different Au nanorods is reduced. The counterbalances among the van der Waals attraction, electrostatic repulsion, interchain attraction and capillary forces thereafter lead to the formation of liquid-crystalline phases of Au nanorods, once the nanorod concentration at the edge increases up to a certain point. The formed assemblies are distributed on the substrate after the solvent is completely dried (Fig. 6A). The formation of liquid-crystalline phases is thermodynamically stable due to a gain in the translational entropy that overrides the loss of orientational entropy associated with nanorod alignment.¹⁵⁸

El-Sayed *et al.* and Murphy *et al.* conducted the pioneering works using the solvent evaporation-induced assembly approach to fabricate ordered Au nanorod superstructures.^{155,156,159}

The obtained superstructures are similar to smectic-A liquid-crystalline phases with Au nanorods aligned parallel with each other in a layer-by-layer manner. The exact mechanism governing the parallel alignment remains to be further understood. One probable origin is that the capillary force along the length of a nanorod is larger than that along its width. Later studies have shown that the obtained Au nanorod superstructures are strongly dependent on their geometry.¹⁶⁰ Nanorods with small (<7) and large (>7) aspect ratios give an isotropic-smectic phase and an isotropic-nematic-smectic phase, respectively. In addition, by carefully choosing nanorods with different head shapes and aspect ratios, various superstructures, such as honeycomb structures, higher-order smectic two-dimensional structures, lower-order one-dimensional ribbon structures, or bundle structures, can be formed.

Most of the solvent evaporation-driven assembly experiments produce superstructures with lateral sizes and heights limited to a few micrometers and several layers, respectively. Generation of large-scale superstructures with three-dimensional ordering has remained rare. In 2009 we successfully demonstrated the formation of Au nanorod superstructures with three-dimensional geometries.¹⁶¹ The superstructures were obtained by solvent evaporation of a droplet of the aqueous dispersions of Au nanorods at high concentrations. The resultant Au nanorod assembly has an area of $0.1\text{--}0.8\text{ mm}^2$ and a depth of $1.7\text{--}2.2\text{ }\mu\text{m}$. Both of nematic- and smectic-phase nanorod superstructures are obtained in the circular ring area of the dried droplet (Fig. 6B and C). More interestingly, the assembly is shape-dependent, and mixtures of Au nanorods with other Au nanostructures can self-separate and form their own ordered superstructures. For example, binary mixtures of Au nanorods with different aspect ratios self-separate to form smectic superstructures (Fig. 6D). For mixtures composed of Au nanorods and spherical polyhedrons, alternating ordered superstructures are obtained (Fig. 6E).

Solvent evaporation-induced assembly is affected by several factors. The CTAB concentration has been shown to be an important parameter that governs the final nanorod superstructures.¹⁶¹ The CTAB concentration is believed to affect the coverage of the CTAB molecules on Au nanorods, which can in turn perturb the assembly process *via* the van der Waals attraction, electrostatic repulsion, and molecular interchain attraction. In addition, the temperature at which the solvent evaporates is also a pivotal factor. Ordered Au nanorod superstructures cannot form at temperatures above $\sim 60\text{ }^\circ\text{C}$.¹⁶¹ Higher temperatures lead to vigorous Brownian motion and fast solvent evaporation, which prevents Au nanorods to find their favorable anchoring sites. In a recent study, Guerrero-Martínez and Liz-Marzán *et al.* showed that the surfactant also plays an important role in the formation of the superstructures.¹⁶² In their study, cationic gemini surfactants with two hydrophobic tails and two hydrophilic head groups were utilized during the growth of Au nanorods. The gemini-capped Au nanorods self-assemble into highly ordered, multilayer three-dimensional islands on substrates. In comparison with those obtained with CTAB-capped Au nanorods, the nanorod islands are mostly composed of

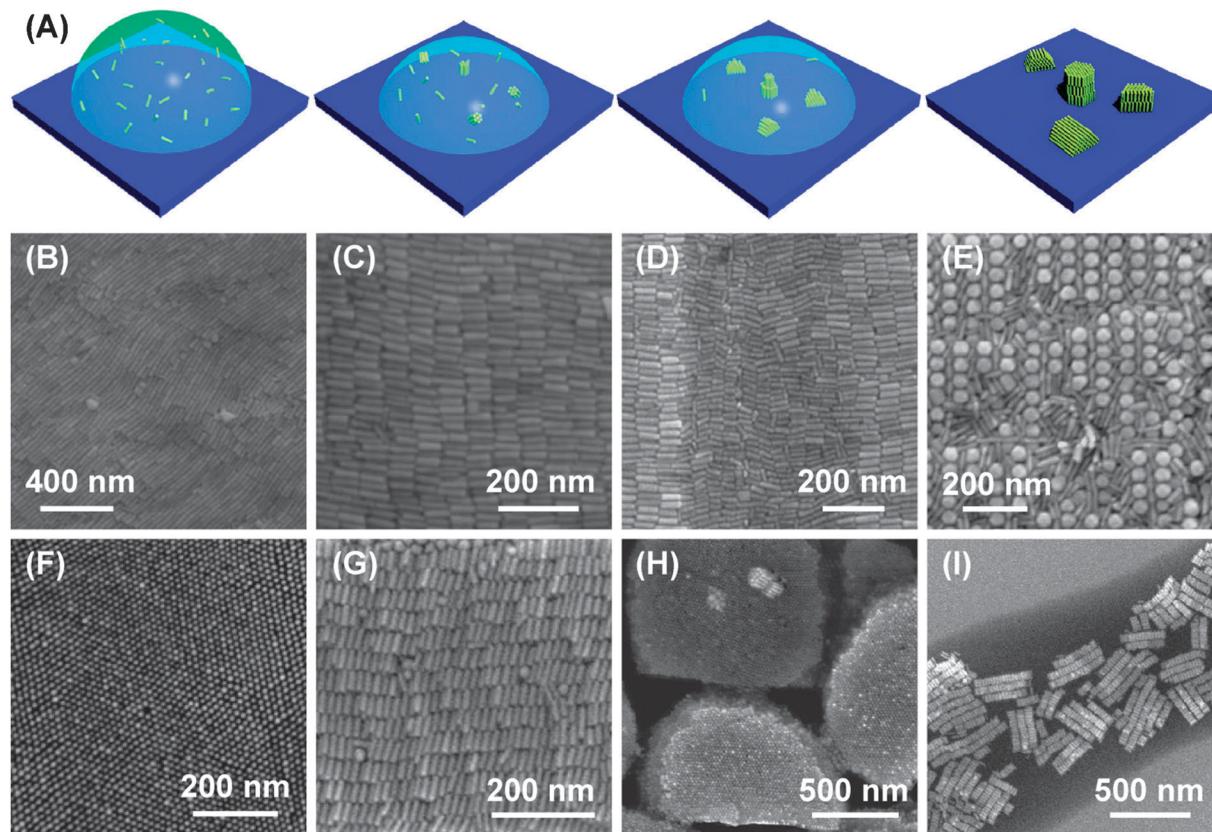


Fig. 6 Ordered Au nanorod superstructures formed by solvent evaporation-induced assembly. (A) Schematic showing the process of solvent evaporation-induced assembly of Au nanorods.¹⁵⁷ (B) Scanning electron microscopy (SEM) image of a nematic Au nanorod superstructure.¹⁶¹ (C) SEM image of a smectic-A Au nanorod superstructure.¹⁶¹ (D) SEM image of the self-separation and superstructure formation of a binary Au nanorod mixture.¹⁶¹ (E) SEM image of the self-separation and superstructure formation of a binary mixture of Au nanorods and polyhedrons.¹⁶¹ (F,G) SEM images of the top and side views of a smectic-A Au nanorod superstructure.¹⁶² (H) SEM image of circular and semicircular Au nanorod superstructures.¹⁵⁷ (I) SEM image of Au nanorod superstructures with a ribbon-like arrangement.¹⁵⁷ Adapted from the data of the cited papers by permission from The American Chemical Society and Wiley Interscience.

vertically aligned Au nanorods in a hexagonal arrangement (Fig. 6F). Each island can have up to fourteen layers of Au nanorods (Fig. 6G). Adopting a similar idea, Liu *et al.* replaced the CTAB molecules around Au nanorods with an OH-terminated hexa(ethylene glycol) alkanethiol, through which the repulsive force induced by the CTAB molecules can be tailored to become a steric force.¹⁵⁷ The balance between this repulsive steric force and the attractive depletion interaction during solvent evaporation gives rise to highly ordered, vertically aligned Au nanorod superstructures (Fig. 6H). In addition, the superstructures can be further controlled by changing the concentration of Au nanorods. For example, monodisperse Au nanorod superstructures consisting of ribbon-like nanorod chains were obtained by lowering the concentration of Au nanorods (Fig. 6I).

Other than their beautiful appearances, the highly ordered Au nanorod superstructures are of potential in optical and biomedical applications. The plasmon coupling among close-packed Au nanorods produces ‘hot spots’ with extremely large electric field enhancements in the superstructures. These ‘hot-spots’ can amplify various optical signals and give interesting surface-enhanced Raman scattering (SERS)¹⁶³ and two-photon-excited photoluminescence.¹⁶¹ In addition, the superstructures also

exhibit intriguing collective plasmon modes that can only be excited with polarized light.¹⁶² We foresee that with better control on the area, uniformity, as well as arrangement of the Au nanorod superstructures, more properties, applications, and even functional devices can be cultivated in the future.

5.2 Assembly through small thiol molecules

Small thiol molecules can be employed as linkers to assemble Au nanorods into oligomers or long chains. Molecules containing thiol groups are widely used to functionalize Au surfaces due to the formation of strong semi-covalent Au-S bonds.¹⁶⁴ The end or side surfaces of Au nanorods can be selectively functionalized for end-to-end or side-by-side assembly with dithiol molecules or thiol-containing bifunctional molecules. Alkanedithiols with different molecular lengths have been utilized to fabricate Au nanorod dimers and chains, as shown in Fig. 7A–C.^{80,165,166} The assembly behavior is controlled by the temperature, the concentrations of Au nanorods and thiol molecules. Bifunctional molecules like 3-mercaptopropionic acid and 11-mercaptoundecanoic acid induce the assembly of Au nanorods through intermolecular hydrogen bonding.¹⁶⁷ Other bifunctional molecules, such as glutathione and cysteine, connect Au nanorods through electrostatic interaction. The

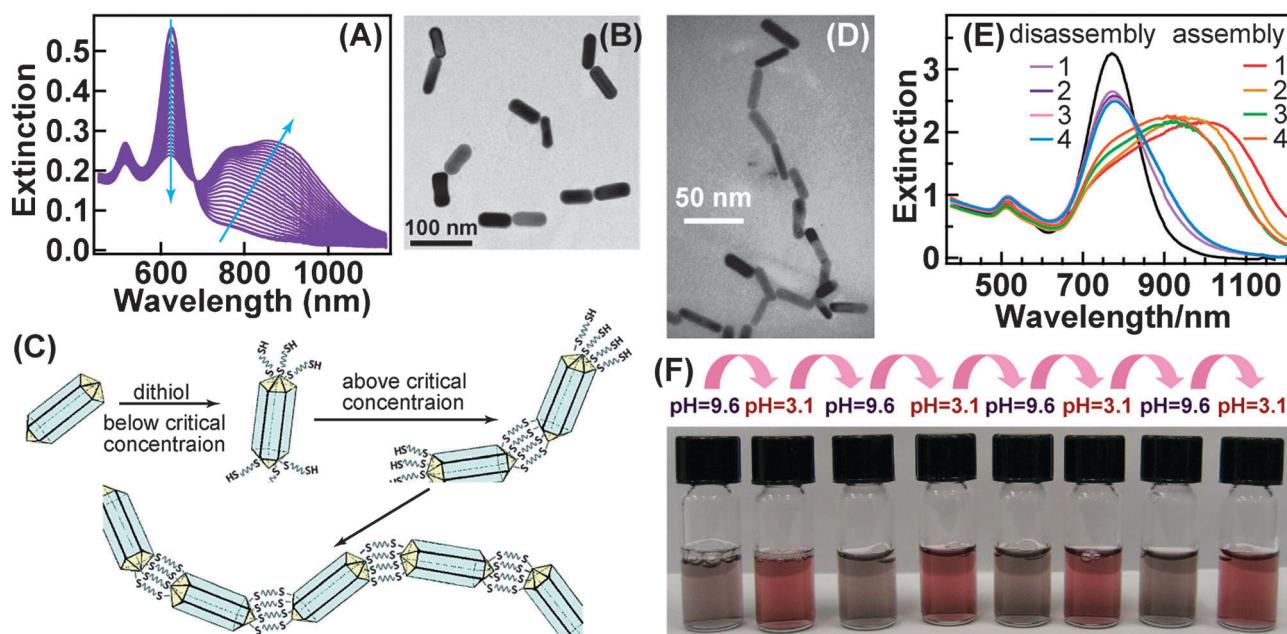


Fig. 7 Dithiol-induced assembly of Au nanorods: (A) time-dependent extinction spectra, indicating the assembly of Au nanorods;¹⁶⁵ (B) TEM image of Au nanorod dimers linked using 1,2-phenylenedimethanethiol molecules;⁸⁰ (C) schematic showing the stepwise formation of Au nanorod chains in the assistance of alkanedithiol molecules.¹⁶⁶ (D–F) pH-controlled reversible end-to-end assembly and disassembly of Au nanorods using 3-mercaptopropionic acid.¹⁶⁷ (D) TEM image of the end-to-end assembly of Au nanorods at pH = 9.6; (E,F) extinction spectra and photo showing the four cycles of the assembly and disassembly of Au nanorods. Adapted from the data of the cited papers by permission from The American Chemical Society and Wiley Interscience.

assembly realized by employing these thiol molecules is reversible. 3-Mercaptopropionic acid, glutathione, and cysteine preferentially bond to the ends of CTAB-stabilized Au nanorods at low concentrations of the thiol molecules and induce the end-to-end assembly of Au nanorods. The assembly and disassembly can be controlled by changing the pH value of the solution (Fig. 7D–F).¹⁶⁷ 11-Mercaptoundecanoic acid bonds to both the end and side surfaces of CTAB-stabilized Au nanorods. It induces either the end-to-end or side-by-side assembly at different pH values. Both the assembly manners are reversible by varying the pH values. Stimuli other than the solution pH have also been employed to control the assembly of Au nanorods in solutions in the presence of different bifunctional thiol molecules. Heat,¹⁶⁸ metal ions,^{169–171} peptides,¹⁷² and salts^{173,174} have been reported to function as the stimuli. On the other hand, because Au nanorods exhibit distinct plasmonic responses, the assembly and disassembly of Au nanorods can act as an indicator for different stimuli, leading to the fabrication of ultrasensitive sensors.^{174,175}

5.3 Assembly through polymers and biological molecules

The assembly of Au nanorods can also be realized by attaching polymers on the end or side surfaces of the nanorods. Kumacheva *et al.* have provided the details on polymer-induced assembly of Au nanorods in their recent review.¹⁷⁶ When the solubility of polymeric ligands is reduced, they produce attractive interaction. Region-selective polymeric ligands can therefore provide directionality in Au nanorod assembly. One can control the assembly of polymer-tethered Au nanorods by tuning the solubility of the polymeric ligands in different solutions.^{177,178} The assembly of

polymer-tethered Au nanorods can be manipulated by varying the position of the polymeric ligands, the volume ratio between the nanorod and the polymer blocks, and the solvent selectivity according to simulation results.¹⁷⁶ The size of the polymer chain can also be varied to control the assembly of Au nanorods. End-to-end and side-by-side assembly of Au nanorods have been achieved by selectively attaching polymers to the side and end surfaces of the nanorods, respectively (Fig. 8A). Au nanorods can be assembled to chains, rings, bundles, and even spheres. The assembly of Au nanorods has been quantitatively described by the kinetics and statistics of reaction-controlled step-growth polymerization,¹⁷⁸ which enables the prediction of the architecture of linear, branched, and cyclic assembled Au nanostructures, their aggregation numbers and size distributions.

Thiol-terminated biological molecules have been often utilized to assemble Au nanorods. The assembly is achieved through biorecognition between biological ligands, such as avidin and biotin,^{83,179,180} antibody–antigen,^{181,182} aptamer–protein,^{183,184} oligonucleotides–metal ions,¹⁸⁵ and DNA sequence recognition.^{186,187} DNA hybridization enables DNAs to act as templates to direct the assembly of Au nanorods. Au nanorod dimers with various predetermined inter-rod angles and gap distances have been prepared by DNA-directed assembly of Au nanorods (Fig. 8B).¹⁸⁷ DNA-mediated Au nanorod assembly has further been utilized to build close-packed lattices (Fig. 8C).¹⁸⁶

6. Plasmonic properties

LSPRs, the surface electromagnetic modes associated with the confined collective oscillations of the conduction electrons, are

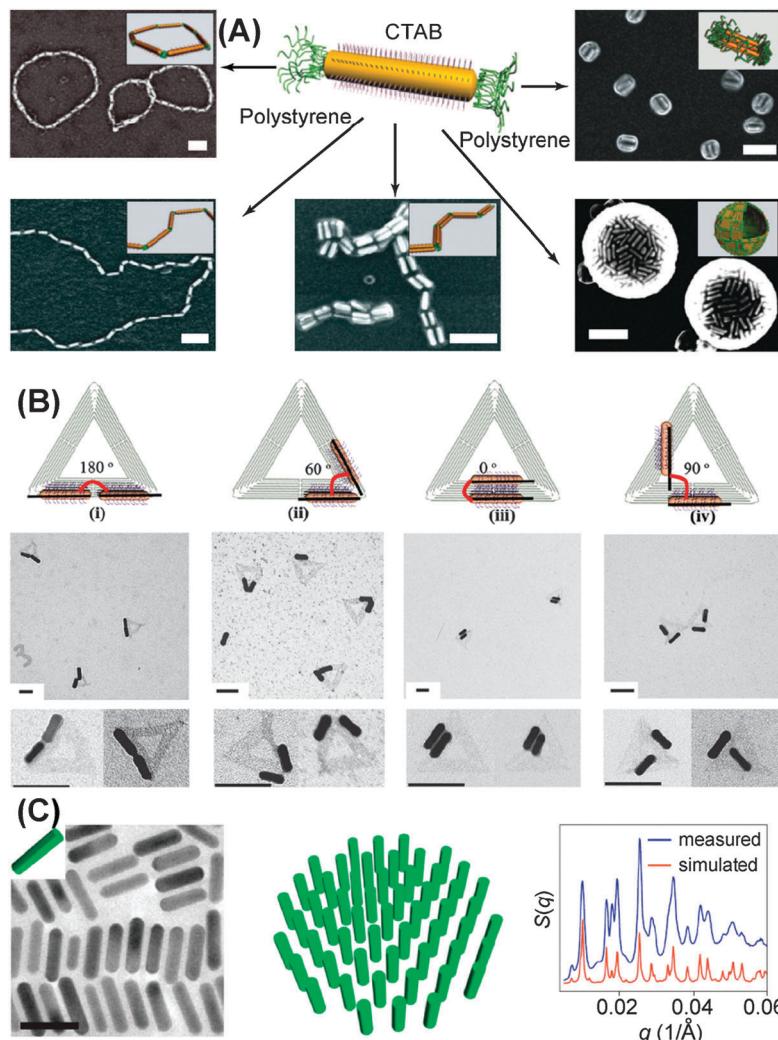


Fig. 8 (A) Assembly of polymer-tethered Au nanorods into different structures.¹⁷⁶ The rings and chains are assembled in dimethylformamide–water mixtures. The side-by-side aligned bundles and spheres are assembled in tetrahydrofuran–water mixtures. The scale bars are all 100 nm. (B) DNA-directed assembly of Au nanorods into dimers with various inter-rod angles and gap distances.¹⁸⁷ The scale bars are all 100 nm. (C) DNA-directed assembly of Au nanorods into lattices.¹⁸⁶ (Left) TEM image. The scale bar is 50 nm. (Middle) Schematic showing a hexagonal two-dimensional Au nanorod assembly. (Right) Experimental and simulated small-angle X-ray scattering spectra for the hexagonal-close-packed Au nanorod lattice. Adapted from the data of the cited papers by permission from The Royal Society of Chemistry, The American Chemical Society and Nature Publishing Group.

the most exceptional properties of metal nanostructures. Under resonant excitation, noble metal nanostructures concentrate free-space electromagnetic waves within the near-field regions (<100 nm) close to their surfaces. This unique property enables noble metal nanostructures with various splendid effects, such as extremely large electric field enhancements, nanoantenna characteristics, huge light scattering and absorption, and striking photothermal conversion capabilities. In addition, the plasmonic properties of metal nanostructures are strongly affected by their geometries. For example, the plasmon wavelengths, where the strong light absorption or scattering occurs, of spherical metal nanocrystals are determined by their diameters, giving rise to the vivid colors of their colloidal solutions. Elongation of metal nanocrystals lowers their geometrical symmetry and thereby enriches their plasmonic properties. Compared to their spherical

counterparts, Au nanorods exhibit anisotropic plasmon responses that are determined by the electron oscillation dynamics along different directions. In addition, such an anisotropic behavior also enables various intriguing plasmon coupling properties, which depend strongly on the arrangements of Au nanorods. Under the inspiration by all of these fascinating characteristics, tremendous research progress has been made on studying the plasmonic properties of Au nanorods during the past few years.

6.1 Individual Au nanorods

Gold nanorods with cylindrical symmetry usually exhibit two plasmon modes, a longitudinal LSPR mode associated with the electron oscillations along the length direction and a transverse LSPR mode arising from the transverse electron oscillations. Due to the longer path of the electron movements, the

longitudinal mode is located at the red side of the transverse one. Both modes are dipolar resonances and can be efficiently excited by external plane waves. Higher-order resonance modes, such as quadrupolar and octupolar modes, can also be supported. These higher-order resonances exhibit zero net dipole moments and therefore cannot be excited by plane waves or radiate into the far field. In order to excite and measure these higher-order modes, one has to resort to radiations with non-uniform electromagnetic field distributions, for example, a local dipole source.¹⁸⁸ Under the excitation of non-uniform electromagnetic fields, the electron oscillations in the nanorod contain multipolar components of all orders, enabling the examination of various higher-order plasmon modes.

6.1.1 Plasmonic properties described by quasistatic theory.

The plasmonic responses of metal nanostructures can be precisely simulated by various rigorous numerical algorithms, such as finite-difference time-domain (FDTD) methods, boundary element methods (BEMs), and discrete dipole approximation (DDA). However, these numerical procedures cost large amounts of computational resources without capturing the underlying physics. On the other hand, for metal nanostructures with sizes much smaller than the incident wavelength, quasistatic theories can be employed for describing the plasmonic properties associated with dipolar modes. Within the framework of quasistatic approximation, the electromagnetic field is treated to be the same throughout the entire particle. It is then solely determined by the scalar potential. Gans theory is the most famous quasi-static theory for calculating the light scattering and absorption of nanocrystals with an ellipsoidal shape. In order to utilize Gans theory to calculate the plasmonic responses of Au nanorods, one has to approximate the nanorod as a prolate spheroid (Fig. 9A). This approximation does not affect the main conclusions drawn on the plasmonic properties of Au nanorods, yet it retains the necessary underlying physics. By solving Laplace's equation in the ellipsoidal coordinate system, the scattering, absorption, and extinction cross-sections of a Au ellipsoid excited along different axes can be obtained as:¹⁸⁹

$$C_{\text{sca},i} = \frac{k^4}{6\pi} |\alpha_i|^4 \quad (1)$$

$$C_{\text{abs},i} = k \operatorname{Im}(\alpha_i) \quad (2)$$

$$C_{\text{ext},i} = C_{\text{sca},i} + C_{\text{abs},i} \quad (3)$$

$$\alpha_i = 4\pi abc \frac{\varepsilon_1 - \varepsilon_m}{3\varepsilon_m + 3L_i(\varepsilon_1 - \varepsilon_m)} \quad (4)$$

In the equations above, k is the wavevector, α_i is the polarizability of the metal nanocrystal, ε_m and ε_1 are the dielectric functions of the surrounding medium and the metal. The parameter L_i is the depolarization factor. It is calculated according to:

$$L_a = \frac{abc}{2} \int_0^\infty \frac{dq}{(a^2 + q)f(q)} \quad (5)$$

$$L_b = \frac{abc}{2} \int_0^\infty \frac{dq}{(b^2 + q)f(q)} \quad (6)$$

$$L_c = 1 - L_a - L_b \quad (7)$$

$$f(q) = \{(q + a^2)(q + b^2)(q + c^2)\}^{1/2} \quad (8)$$

In these equations, a , b , and c are the half lengths of the ellipsoid along the three major axes. The LSPR peaks can thereafter be extracted from the scattering, absorption, or extinction spectra using the above equations.

From Gans theory, one can clearly see that the scattering or absorption cross-sections and plasmon wavelengths vary with the size and shape of the nanorod. By progressively increasing the aspect ratio of the nanorod with a fixed diameter, the extinction cross-sections of both the longitudinal and transverse plasmon modes will be enlarged (Fig. 9B and C). In addition, the plasmon wavelengths of these two modes will also be changed. For the transverse mode, its wavelength exhibits a small blue shift of only 8 nm when the aspect ratio is increased by 4 (Fig. 9D). On the contrary, the longitudinal mode of the nanorod exhibits a much more sensitive behavior. It red-shifts by up to several hundred nanometers for the same change in the aspect ratio. The much larger dependence of the longitudinal plasmon wavelength on the aspect ratio results from the higher polarizability of the nanorod at the longitudinal plasmon resonance. The polarizability usually determines how easily a nanocrystal can be polarized. Nanocrystals with higher polarizabilities can induce more polarization charges, leading to larger plasmon shifts as their geometry is changed. Moreover, the longitudinal plasmon wavelength is nearly linearly dependent on the aspect ratio of the nanorod (Fig. 9E). Such a linear behavior is expected from Gans theory by considering the nearly linear dependence of the real part of the Au dielectric function on the wavelength in the visible range.¹⁹⁰

As shown by eqn (1)–(4), the scattering cross-section of the nanorod is a quadratic function of the particle volume while the absorption cross-section exhibits a linear dependence. Therefore the scattering, absorption, and extinction cross-sections of the nanorod show nonlinear dependences on the diameter of the nanorod even if their aspect ratio is fixed (Fig. 9F). This is also corroborated by rigorous FDTD calculations by considering nanorods with cylindrical geometry (Fig. 9G).¹⁹¹ The discrepancy between the results obtained by these two methods is due to the retardation effect for nanorods with diameters larger than 30 nm.¹⁹² This effect is not considered in quasistatic theory. The electric field distribution around the nanorod can be computed from the gradient of the electric potential, whereby the electric field enhancement can be obtained. Regions with high curvatures, such as the two ends of the nanorod, can concentrate electrons at higher volume densities and therefore lead to higher electric field enhancements (Fig. 9H and I).¹⁹³ The electric field enhancement is also a function of the nanorod geometry. By extracting the maximum electric field enhancement around the nanorod at the longitudinal plasmon resonance, one can clearly see that the field enhancement grows monotonically with the aspect ratio of the nanorod (Fig. 9J). This dependence arises from the red shift of the longitudinal plasmon resonance into regions far away from the interband transition of gold, which reduces the damping of the plasmon resonance.¹⁹⁴ Rigorous numerical calculations have

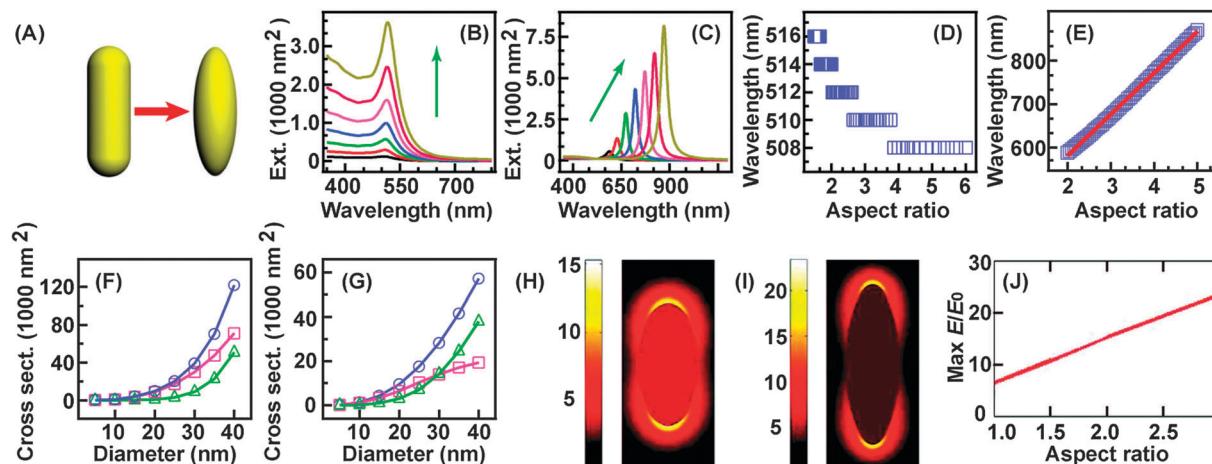


Fig. 9 Plasmonic properties of Au nanorods described by Gans theory. (A) Schematic showing the geometry of a Au nanorod used in Gans theory. (B) Dependence of the extinction spectra on the aspect ratio under transverse excitation. (C) Dependence of the extinction spectra on the aspect ratio under longitudinal excitation. The aspect ratio of the nanorod is changed from 1.5 to 6 while its diameter is fixed at 5 nm. The green arrows in (B) and (C) indicate the increasing direction in the aspect ratio. (D) Dependence of the transverse plasmon wavelength on the aspect ratio. (E) Dependence of the longitudinal plasmon wavelength on the aspect ratio. (F) Extinction (circles), scattering (triangles), and absorption (squares) cross-sections versus the diameter calculated according to Gans theory. (G) Extinction (circles), scattering (triangles), and absorption (squares) cross-sections versus the diameter obtained from FDTD calculations.¹⁹¹ The aspect ratio of the nanorod in (F) and (G) is 2.4. (H) Electric field enhancement contour¹⁹³ of a nanorod with aspect ratio of 2. (I) Electric field enhancement contour¹⁹³ of a nanorod with aspect ratio of 3. (J) Change of the maximum electric field enhancement as a function of the aspect ratio at the longitudinal plasmon resonance.¹⁹³ Adapted from the data of the cited papers by permission from The American Chemical Society.

shown that the electric field enhancement can also be affected by the head curvature as well as the volume of the nanorod.^{195,196}

Once the plasmon resonance is excited, it will decay rapidly mainly by the generation of electron–hole pairs, thermalization with the lattice through Joule heating, and emission of photons (Fig. 10A). These three decay channels govern the plasmon damping dynamics and thereby the linewidth of the plasmon resonances. Feldmann *et al.* have shown that plasmon damping is drastically reduced in Au nanorods compared to that in Au nanospheres, which is due to the suppression of the electron–hole pair formation through interband transitions.¹⁹⁴ The reduced plasmon damping leads to much narrower scattering peaks from individual Au nanorods (Fig. 10B). In a later study, Zhu utilized quasistatic approach to elucidate the effects of the nanorod shape on its plasmon damping.¹⁹⁷ The calculated results indicate that with the increase of the aspect ratio, the full width at half maximum of the longitudinal plasmon resonance becomes larger quadratically (Fig. 10C). This result is ascribed to the increase in the radiation damping for nanorods with larger aspect ratios. On the other hand, for nanorods with sizes approaching the mean free path of the electrons in metal (~ 30 nm for gold), the plasmon damping caused by the electron scattering on the surface of the nanorod becomes prominent. Mulvaney and Hartland *et al.* have conducted comprehensive investigations on the contributions from the radiation damping and surface scattering to the linewidth of the longitudinal plasmon band of Au nanorods.¹⁹⁸ Their studies indicate that for Au nanorods with diameters smaller than 20 nm, the plasmon damping is governed by electron–surface scattering, while for nanorods with larger diameters, the radiation damping overwhelms and dominates the

plasmon linewidth. By combining the contributions from the bulk damping of gold, surface scattering, and radiation damping, the theoretical prediction on the plasmon linewidth agrees very well with the experimental measurements (Fig. 10D). When the sizes of the nanorods approach the quantum region (< 10 nm), various damping mechanisms originating from the many-body effect, such as electron–electron correlated and exchange interactions, electron–electron scattering, will become important. In this regime, one needs to employ quantum theory for describing the plasmon damping, which is still a challenge in theoretical research as well as experiments.

Besides the geometry, the electron density is also an important factor that affects the plasmon resonances of Au nanorods, although not much attention has been paid to it. From Gans theory, one can derive the longitudinal plasmon wavelength of a nanorod as:

$$\lambda_{\text{plasmon}} = \lambda_p \sqrt{\epsilon_\infty + \left(\frac{1}{L} - 1 \right) \epsilon_m} \quad (9)$$

$$\lambda_p = \sqrt{\frac{2\pi^2 c^2 m^* \epsilon_\infty}{N e^2}} \quad (10)$$

In eqn (9), ϵ_∞ is the high-frequency dielectric constant of gold, and L is the depolarization factor along the length axis of the nanorod. In eqn (10), c is the speed of light, m^* is the electron effective mass in gold, e is the elemental charge, and N is the conduction electron density. The expressions above show clearly that the longitudinal plasmon wavelength of Au nanorods can be strongly affected by the change in the electron density. An increase in the number of free electrons will result in a blue shift of the plasmon resonance due to the enhanced

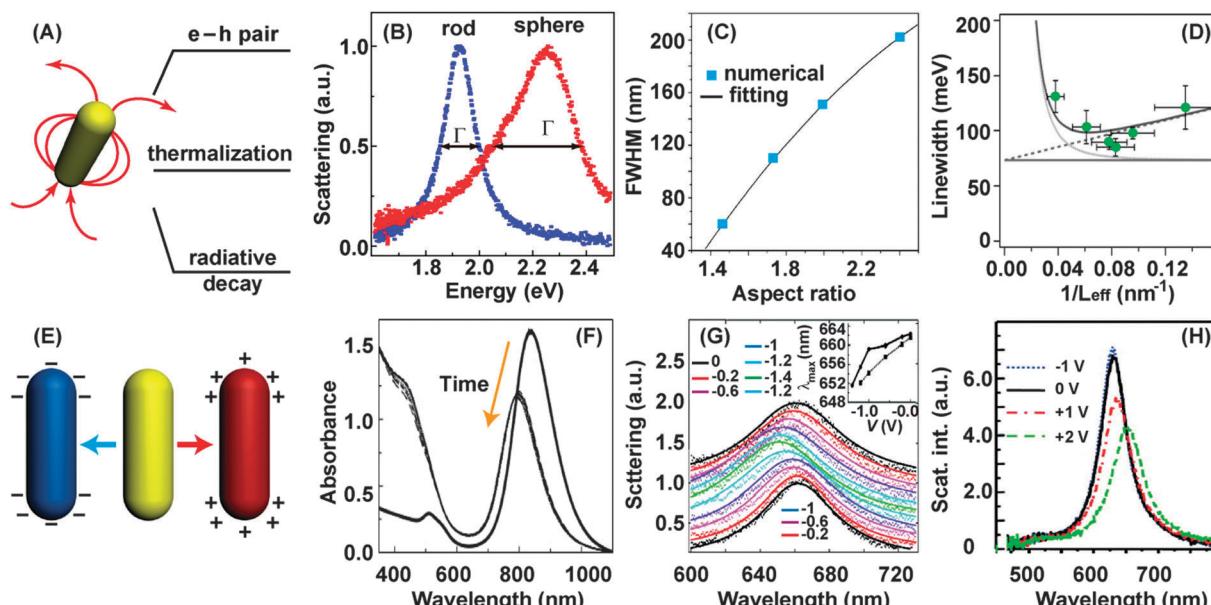


Fig. 10 Plasmonic properties of individual Au nanorods. (A) Schematic showing the major plasmon damping pathways of a single Au nanorod. (B) Comparison of the scattering spectra of an individual Au nanosphere (60 nm in diameter) and Au nanorod (64 nm by 32 nm). (C) Dependence of the full width at half maximum (FWHM) of the longitudinal plasmon mode of Au nanorods on the aspect ratio.¹⁹⁷ (D) Change of the plasmon linewidth with the inverse of the effective path length of free electrons ($1/L_{\text{eff}}$) for Au nanorods with aspect ratios between 2 and 4. The lines show the calculated linewidths from bulk scattering (horizontal line), bulk plus surface scattering (dashed line), and bulk plus radiation damping (dotted line). The solid line illustrates the total linewidth.¹⁹⁸ (E) Schematic of charging of a single Au nanorod. (F) Evolution of the extinction spectra of Au nanorods after the addition of NaBH₄.¹⁹⁹ (G) Normalized scattering spectra of a single Au nanorod at different electrochemical potentials. The inset shows the dependence of the plasmon peak wavelength on the electrochemical potential.²⁰⁰ (H) Scattering spectra of a single Au nanorod at different applied potentials.²⁰¹ Adapted from the data of the cited papers by permission from Elsevier, The American Chemical Society and The Royal Society of Chemistry.

restoring force (Fig. 10E). Mulvaney *et al.* have studied the effect of electron injection by adding reducing agents in Au nanorod solutions.¹⁹⁹ Addition of a reducing agent can introduce extra electrons to the nanorods, leading to blue shifts of the longitudinal plasmon resonance (Fig. 10F). The electron charging effect was examined in a later study using single-particle measurements by ruling out the inhomogeneous broadening effect.²⁰⁰ Electron charging and discharging were realized electrochemically. The longitudinal plasmon resonance exhibits a clear and reversible blue shift by applying different electrochemical potentials (Fig. 10G). For large plasmon shifts, the color changes of the scattering image from individual Au nanorods can even be observed by eyes. In this study, only the scattering spectra of the nanorods at different potentials were provided, from which one cannot elucidate the effect of the electron charging on the plasmon intensity. The changes in the plasmon intensity and plasmon linewidth can be used to characterize the plasmon damping induced by the electron charging. A very recent study has been devoted to the plasmon damping mechanisms for individual Au nanorods under applied potentials.²⁰¹ Besides the plasmon shift, the electron charging of a nanorod can induce large damping of its longitudinal plasmon resonance, which is manifested by suppressed scattering and clear spectral broadening (Fig. 10H). Further theoretical calculations suggest that the damping stems from the excitation of the surface-trapped electrons by the plasmon resonance of Au nanorods. The charging-induced

plasmon shifts of Au nanorods provide an alternative route for designing actively controlled plasmonic devices, which are strongly desired for future novel optoelectronic applications.

6.1.2 Refractive index-dependent plasmon resonance. The plasmon resonance of Au nanorods is highly sensitive to the surrounding dielectric environment. This can be readily understood from eqn (9), which shows that the plasmon peak of Au nanorods varies with $(\epsilon_m)^{1/2}$. This dependence can be understood from a physics point of view. Increase of the dielectric constant, or in other words, the refractive index, of the nanoenvironment surrounding the nanorod can induce more polarization charges around the nanorod. Under external electromagnetic excitation, there will be an increased screening of the Coulombic restoring force that acts on the free electrons in the nanorod (Fig. 11A). The reduced restoring force therefore results in a red shift in the plasmon resonance. The red shift can be more clearly seen from the calculated extinction spectra of the nanorod in solutions with different refractive indices (Fig. 11B). Both the longitudinal and transverse plasmon modes red-shift with increasing refractive indices. The plasmon shift of the longitudinal mode can be up to 120 nm for an increment of 0.4 in the refractive index. Furthermore, the longitudinal plasmon shift follows a linear relationship with the refractive index (Fig. 11C). This linear relationship has been corroborated by a number of experimental measurements.^{196,202–206}

The refractive index-induced plasmon shift has received increasing attention due to its potential for designing

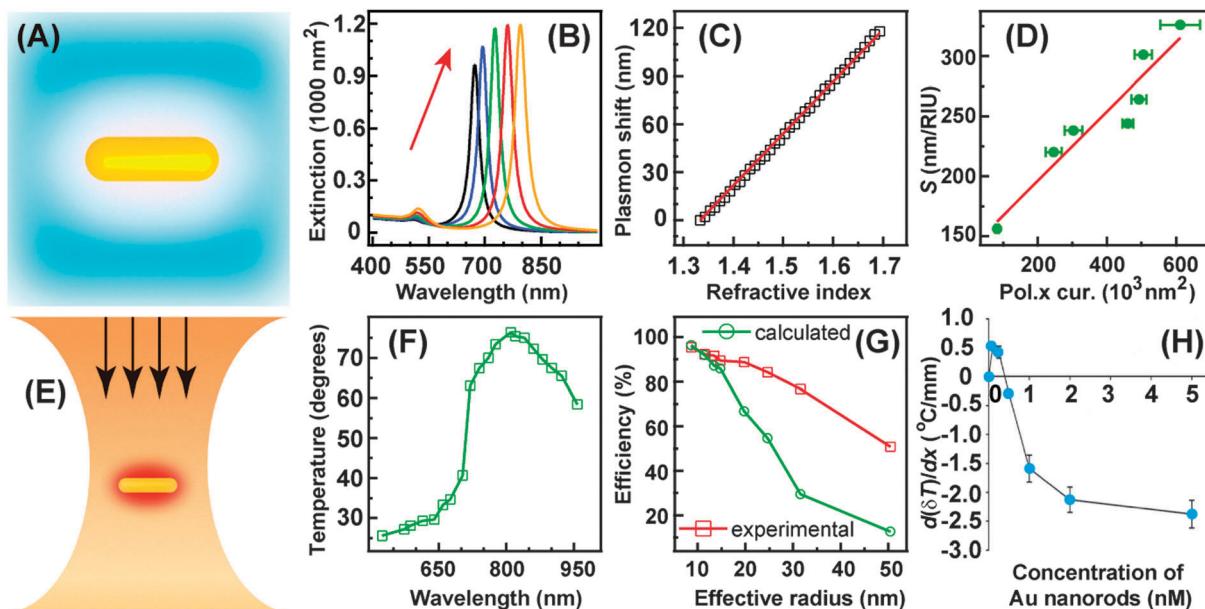


Fig. 11 Refractive index dependent-plasmon resonances and plasmonic photothermal conversion properties of Au nanorods. (A) Schematic of a Au nanorod immersed in a solution. (B) Calculated extinction spectra of a Au nanorod in solutions with different refractive indices. The nanorod has an aspect ratio of 3. The refractive index of the solution is increased from 1.3 to 1.7 at a step of 0.1. (C) Dependence of the longitudinal plasmon shift on the refractive index of the solution. (D) Refractive index sensitivity, the plasmon shift per refractive index unit (RIU), as a function of the product between the polarizability and the end curvature of elongated Au nanocrystals with different end shapes.¹⁹⁶ (E) Schematic showing the plasmonic photothermal conversion of a Au nanorod. (F) Dependence of the end temperature on the nanorod longitudinal plasmon wavelength.⁷⁴ (G) Dependences of the measured and calculated photothermal conversion efficiencies on the effective particle radius of Au nanorods.⁷⁴ (H) Effect of the Au nanorod concentration on the gradient of the temperature increase along the depth of the microcentrifuge tube containing Au nanorods.²²⁴ Adapted from the data of the cited papers by permission from The American Chemical Society and Wiley Interscience.

ultrasensitive biomedical sensors.^{10,207} One important parameter that determines the sensing performance of metal nanocrystal-based plasmonic sensors is the refractive index sensitivity, which is defined as the plasmon shift per refractive index unit. The extent of the red shift of the plasmon resonance is governed by the amount of the polarization charges, which is determined by the local electromagnetic field distribution around the nanocrystal and the polarizability of the nanocrystal. These two factors are the functions of the material and geometry of the metal nanocrystal. Great efforts have been made in previous studies to identify the pivotal structural and material parameters for refractive index sensitivities.^{131,196,202,203,206,208–211} El-Sayed *et al.* have conducted systematic studies on the refractive index sensing behaviors of Au–Ag alloy nanorods with different Ag contents using numerical simulations.¹³¹ The calculated results indicate that the index sensitivities of Au, Ag, and Au–Ag alloy nanorods with the same geometry are similar to one another. They ascribed this result to the fact that noble metals have similar dispersions of their real dielectric functions. However, their study did not pay much attention to the effect of the plasmon wavelength. We have addressed this issue by comparing the index sensing performance of Au nanorods with plasmon wavelengths ranging from the visible to near-infrared regions.²⁰⁶ The index sensitivities of Au nanorods were found to generally increase as their plasmon wavelengths become longer. This finding indicates that the index sensitivities are generally larger for Au nanorods with longer plasmon wavelengths. Such a

characteristic can be ascribed to the fact that the dispersion of the real part of the dielectric function of gold is larger in the longer-wavelength region. Therefore, the plasmon shift will be larger for nanorods with longer plasmon wavelengths. In order to reveal how the index sensitivities of nanorods depend on their shapes, we determined the refractive index sensitivities of elongated Au nanocrystals with different shapes and sizes but the same longitudinal plasmon wavelength in a later study.¹⁹⁶ The index sensitivity is observed to increase as the polarizability-curvature product is increased (Fig. 11D), indicating that both the polarizability and the shape of metal nanocrystals play important roles in the index sensitivity. Although this is an empirical relationship, it is rather understandable because the displacement of the free electrons in a nanocrystal depends on its polarizability and the local electric field around its surface, with the latter determined by the curvature of the nanocrystal.

6.1.3 Plasmonic photothermal conversion. Decay of the plasmon resonances in Au nanocrystals through thermalization with the lattice will generate heat, which can thereby cause temperature rises in the surrounding environment (Fig. 11E). This ability of converting light into heat through the excitation of plasmonic resonances has made Au nanocrystals excellent candidates for killing cancer cells,^{212–216} controllable gene release^{217,218} and delivery of drugs.^{219–221} Au nanorods offer additional merits as photothermal conversion agents. Their plasmon wavelengths can be synthetically tuned into the near-infrared region where organic tissues show small light

absorption.²²² Furthermore, compared with other light-absorption species, such as organic dye molecules, semiconductor nanocrystals, and spherical Au nanoparticles, Au nanorods exhibit much stronger light absorption at their plasmon resonances.²²³ Therefore, in recent years, studies of the photothermal conversion properties of Au nanorods and their related applications have gained much interest.

The photothermal conversion efficiency of plasmonic metal nanocrystals is the most critical factor for photothermal conversion-based applications. As the photothermal conversion of metal nanocrystals is governed by the competition between the radiative and non-radiative decays of the plasmon resonance, the photothermal conversion efficiency is straightforwardly expected to be strongly dependent on the geometries and plasmonic properties of metal nanocrystals. We have shown that the photothermal conversion will be highest for Au nanorods with longitudinal plasmon wavelengths very close to the incident laser wavelength (Fig. 11F).⁷⁴ Under this condition, the incident laser can efficiently excite the plasmon resonance of the nanorods, through which its energy can be effectively converted into heat. In addition, by growing rod-shaped Au nanocrystals with various particle volumes but the same longitudinal plasmon wavelength, we were able to elucidate the effect of the particle volume on the photothermal conversion properties. Both experimental measurements and theoretical simulations have shown that the photothermal conversion efficiency decreases as the particle volume of Au nanocrystals gets larger (Fig. 11G). Its origin is ascribed to the reduced radiative decay of the plasmon resonance in small nanocrystals, whereby the absorbed light energy is mainly converted into heat.

As most of the applications utilizing photothermal conversion rely on heating induced by Au nanorod ensembles, the concentration of Au nanorods is expected to play an important role in their photothermal conversion behaviors. On the other hand, for applications such as photothermal therapy, the temperature distributions in the target tissues are also important. Such information can help in controlling the dose of the nanorods as well as the laser power to achieve the optimal curative effects. Recently, Choi *et al.* have addressed this issue by investigating the effect of Au nanorod concentration on the temperature distribution caused by photothermal heating.²²⁴ Au nanorods are suspended in a polyacrylamide phantom, which is contained in a 2 mL microcentrifuge tube. Their results show that the concentration of Au nanorods strongly affects the temperature rise along the depth of the tube containing Au nanorods. The temperature is nearly uniform in the tube at low nanorod concentrations (<0.5 nM), while temperature gradients develop and get larger as the concentration of Au nanorods is increased (Fig. 11H). This finding will be useful for clinical applications that require uniform temperature distributions in tissues.

For applications requiring localized heating in tiny regions, such as catalysis, microfluidics, and localized tissue repair, to know the heat generation and temperature distribution around an individual Au nanocrystal is very important. Many efforts

have been made on this aspect, with most of them being theoretical studies and mainly focusing on spherical nanoparticles. A recent comprehensive theoretical study has explored the nanoscale temperature distribution around a single Au nanorod using BEM.²²⁵ They also calculated the temperature distributions of Au nanocrystals with arbitrary geometries. Despite the progress on theoretical simulations, direct experimental measurements of the local temperature distributions around individual Au nanorods are still challenging. Such measurements are mainly limited by the lack of nanoscale temperature probes. Only until recently, have Quidant *et al.* established a milestone in this aspect by utilizing a novel thermal microscopy technique.²²⁶ Their technique enables the imaging of the heat distribution around a single Au nanorod by recording molecular fluorescence polarization anisotropy. The temperature distribution around the nanorod is found to be fairly uniform. The thermal ‘hot spots’ usually do not coincide with the optical ‘hot spots’ of the plasmon mode. However, the spatial resolution of the thermal imaging (~300 nm) is still not high enough for the quantitative analysis of the plasmonic photothermal heating and its induced thermal diffusion at the nanoscale.

6.2 Plasmon coupling

Au nanorods can support both the longitudinal and transverse plasmon modes, with the plasmon resonances polarized along and orthogonal to the length axis of the nanorod. When two Au nanorods are placed in a close proximity to, but not in contact with each other, the plasmon resonances carried by the two nanorods will interact to form different collective plasmon modes, according to the plasmon hybridization model.³⁵ Due to the geometrical anisotropy and the synthetically tailorabile longitudinal plasmon energy of Au nanorods, coupled Au nanorods exhibit extremely rich spectral responses. The plasmon coupling of Au nanorods also provides much larger electric field enhancements than individual Au nanorods. These unique properties brought by coupled plasmonic Au nanorods offer great potential in a variety of applications, such as highly sensitive biological and chemical sensors, optical switches, plasmon-enhanced spectroscopies, high harmonic signal amplification, nanometric optical tweezers, and metamaterials for manipulating light at the nanoscale.

6.2.1 End-to-end and side-by-side alignment. Both theoretical and experimental results have revealed that the plasmonic interactions between two Au nanorods depend strongly on their relative configurations.^{165,227–229} A detailed hybridization diagram has been developed to identify the energies of all the coupled plasmon modes.²²⁷ Under the excitation of light polarized along the length axis of Au nanorods, linearly, end-to-end assembled Au nanorod homodimers have been experimentally found to support a largely red-shifted coupled plasmon mode, while side-by-side assembled homodimers support a slightly blue-shifted coupled plasmon mode.⁹ The plasmon coupling can be well understood and predicted by the hybridization model, similar to the case for the molecular orbital theory (Fig. 12A).²³⁰ The coupled plasmon mode for the linear, end-to-end

homodimer has a bonding nature and that for the side-by-side homodimer has an antibonding nature, similar to the formation of a σ bond and a π^* bond, respectively. The charge distributions on the Au nanorods exhibit an attractive manner for the end-to-end bonding plasmon mode and a repulsive manner for the side-by-side antibonding mode, respectively. Owning to the symmetry of the entire structure, the other two modes, the antibonding plasmon mode (σ^* bond) for the end-to-end homodimer and the bonding mode (π bond) for the side-by-side homodimer, cannot be excited by far-field light and therefore are ‘dark’ plasmon modes, since there are no net dipole moments for the entire homodimer. The plasmon coupling between the transverse plasmon modes carried by Au nanorods is usually very weak. Moreover, a universal scaling behavior of the distance-dependent decay of the plasmon coupling, which is expressed by the fractional wavelength shift after coupling, is applicable for Au nanorod homodimers aligned along the length axis when the gap distance is not very small.^{228,229,231} The universal scaling behavior can be described by the following formula:

$$\frac{\Delta\lambda}{\lambda} \approx Ae^{-(s/D)/\tau} \quad (11)$$

In this equation, λ is the plasmon wavelength of the uncoupled Au nanorod, $\Delta\lambda$ is the plasmon wavelength shift caused by the plasmon coupling, s is the gap distance, D is the length of the nanorod, τ is the decay constant, and A is the maximal fractional plasmon wavelength shift. A and τ are usually determined from fitting and vary for the homodimers made of differently sized Au nanorods. We later found that by replacing the term s/D in eqn (11) with $(s/D)^{1/3}$, A and τ are nearly the same for homodimers of Au nanorods with different aspect ratios.²³¹ This is because the use of the power of 1/3 can better describe the competition between the inter-particle near-field interactions and the intraparticle Coulombic restoring force. The universal scaling formula therefore becomes more powerful. It can be used as a guideline for various plasmonic applications. The empirical exponential decay formula does not hold any more when the gap distance between two Au nanorods becomes very small and the ratio s/D is less than 0.09.²²⁸ When the gap distance is smaller than ~ 0.5 nm, quantum tunnelling effect should be taken into account.¹⁹³ When the two nanorods get in contact, the coupled bonding plasmon mode undergoes an abrupt large blue shift, and a new charge-transfer plasmon mode appears in the near-infrared region (Fig. 12B).²³²

6.2.2 With symmetry breaking. The geometrical symmetry breaks when the two nanorods in a dimer have different orientations or a size mismatch. For Au nanorod homodimers, when one nanorod is rotated around its center to form an angle of θ from its original orientation in linear alignment, the fractional wavelength shift exhibits approximately a $\cos^2\theta$ dependence.²²⁹ When two differently sized Au nanorods are coupled together, the ‘dark’ plasmon modes can also be excited due to the symmetry breaking caused by size mismatch.²³² For

linearly end-to-end assembled Au nanorod heterodimers, the excitation of both the subradiant antibonding plasmon mode and the superradiant bonding plasmon mode can be clearly extracted from the charge plots (Fig. 12B). The plasmon energy of the bonding plasmon mode for linearly end-to-end assembled Au nanorod heterodimers presents an anticrossing behavior in the coupling energy diagram, which is found to also follow a universal scaling relationship. The coupled bonding plasmon energy can be described by a simple hyperbolic scaling formula (Fig. 12C and D):²³¹

$$E_{12} \approx \frac{1}{2}(E_1 + E_2) - \frac{1}{2}\sqrt{(E_1 - E_2)^2 + [(E_1 - E_{11}) + (E_2 - E_{22})]^2} \quad (12)$$

In the equation above, E_{12} is the coupled bonding plasmon energy of the heterodimer, E_1 and E_2 are the longitudinal plasmon energies of the two differently sized Au nanorods, E_{11} and E_{22} are the coupled bonding plasmon energies of the homodimers composed of the two differently sized nanorods, respectively. The symmetry breaking present in the linear, end-to-end heterodimers made of two differently sized Au nanorods also causes the occurrence of Fano resonance at a higher energy than that of the coupled bonding plasmon mode (Fig. 12C). The Fano resonance is attributed to the interference between the dipole–dipole bonding plasmon mode and a dipole–quadrupole bonding one.²³¹

When two Au nanorods of the same size are assembled together at their ends and have different orientations, new plasmon modes can also be excited. The end-to-end assembled Au nanorod homodimers with varying angles between the length axes of the two nanorods support both an attractive bonding plasmon mode and a repulsive antibonding plasmon mode (Fig. 12E and F). The scattering spectra are very sensitive to the nanorod angle. The scattering intensity ratio between the two plasmon modes varies systematically as a function of the nanorod angle.^{165,228}

Symmetry breaking can also be achieved by introducing another Au nanocrystal that is much smaller than the Au nanorod. Fig. 12G shows the plasmon coupling between a Au nanorod and a small Au nanosphere. The spatial perturbation of the nanosphere results in distinct spectral changes of the heterodimer. When the nanosphere moves from the end to the side of the nanorod, the nanosphere dipole rotates around the nanorod dipole to achieve favorable attractive interaction for the dipole–dipole bonding mode.²³³ The dips on the scattering spectra of the heterodimers in Fig. 12G also come from the Fano interference between the dipole–dipole bonding plasmon mode and a dipole–quadrupole bonding one. We have found that the spectral shape and the Fano interference in the heterodimers are highly sensitive to the gap distance and vary with both the vertical and lateral displacements of the nanosphere relative to the nanorod. The Au nanorod–nanosphere heterodimers therefore provide a useful means for measuring the conformation transformations of macromolecules in soft-matter systems.

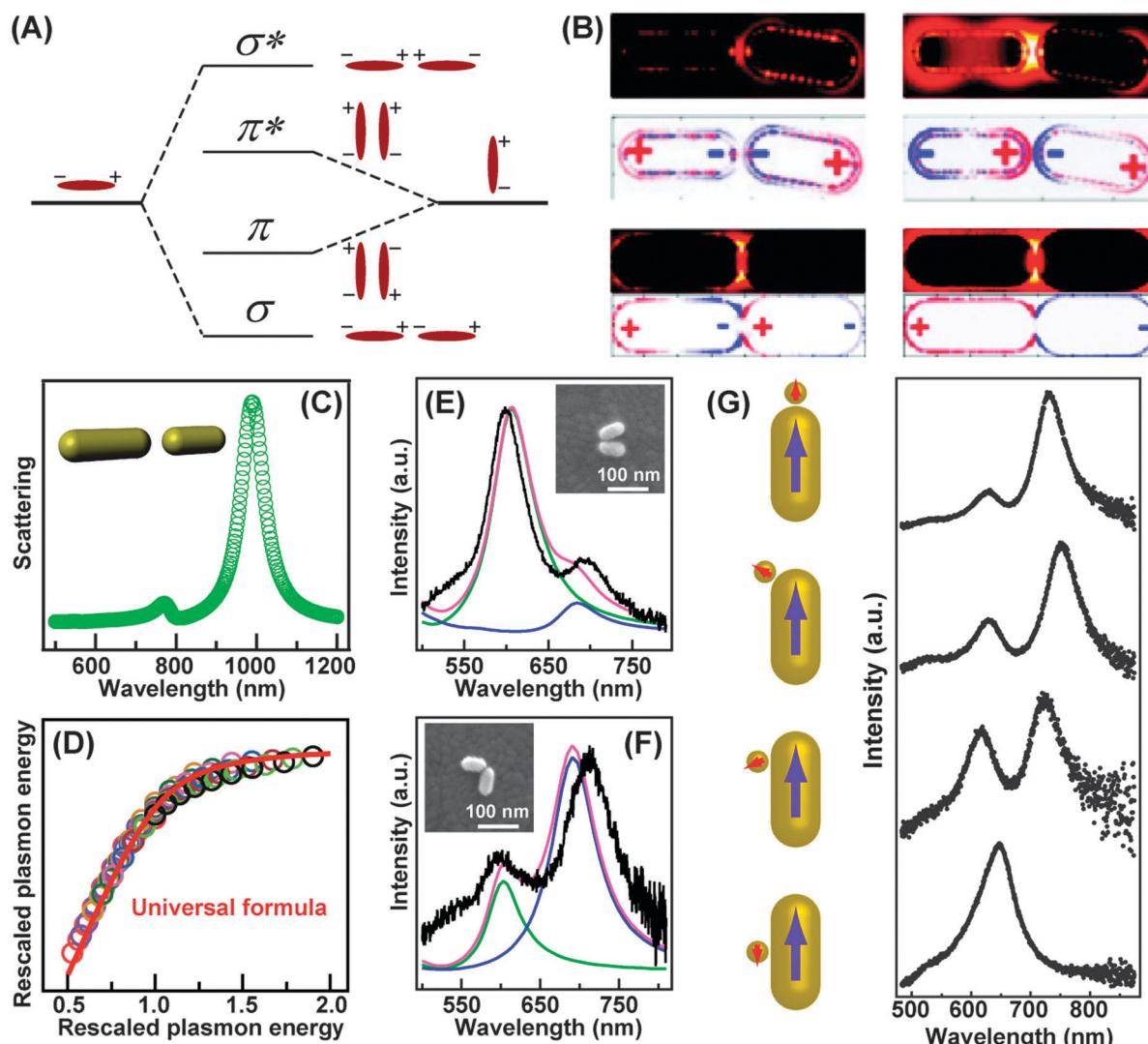


Fig. 12 Plasmon coupling in Au nanorod dimers. (A) Electromagnetic analogy to molecular orbital theory: hybridization model showing the basic picture of the coupled longitudinal plasmon modes of end-to-end and side-by-side assembled Au nanorod homodimers.²³⁰ (B) FDTD-calculated electric field enhancement contours (upper) and charge distributions (lower) of linear end-to-end nanorod homodimers at the antibonding mode, the bonding mode, the conductive coupled bonding mode, and the conductive coupled charge-transfer plasmon mode.²³² (C) Calculated scattering spectrum of a linearly aligned Au nanorod heterodimer. The inset shows the schematic of the heterodimer.²³¹ (D) Universal scaling behavior in the energy diagrams of the plasmon coupling in heterodimers consisting of linearly aligned, differently sized Au nanorods.²³¹ (E,F) Plasmon coupling in Au nanorod homodimers with the nanorod angles at $\sim 30^\circ$ and $\sim 87^\circ$, respectively.¹⁶⁵ (G) Plasmon coupling between a Au nanorod and a small Au nanosphere located at different positions on the nanorod.²³³ Adapted from the data of the cited papers by permission from The American Chemical Society.

The extremely sensitive dependence of the plasmon coupling behavior and associated rich spectral responses^{231,233,234} allow for the fabrication of high-performance nanoscale sensors, optical metamaterials with narrow transparency windows, and active optical devices such as optical switches, nano-optomechanical systems, and electro-optical modulators. The challenges lie in the development of low-cost, reproducible, high-resolution fabrication techniques, whether they are bottom-up or top-down.

6.2.3 Substrate effects. A number of plasmonic devices require the deposition of metal nanocrystals on various substrates, including metals, semiconductors, and insulators. The presence of substrates will bring in symmetry breaking of the

dielectric environment surrounding each metal nanocrystal, which can greatly modify the plasmonic properties of supported metal nanocrystals. In the case of dielectric substrates, excitation of the plasmon resonances of a supported metal nanocrystal can induce image charges in the substrate. The image charges in turn interact with the free electron oscillations in the nanocrystal and affect their dynamic processes. Moreover, the substrate can mediate the interaction between different plasmon modes in the nanocrystal through their corresponding image charges, giving rise to efficient plasmonic hybridization in the nanocrystal.^{235–238} On the other hand, for a metal nanocrystal supported on a metal substrate, besides the image charge effect, strong coupling between the LSPRs

of the nanocrystal and the propagating plasmons of the metal film can be induced.²³⁶ Depending on the relative energies of the localized and propagating plasmons, either red or blue shifts in the plasmon resonances of the nanocrystal can occur as the nanocrystal approaches the metal substrate along the normal direction.

Coupling between metal nanocrystals and substrates gives rise to rich plasmonic properties of the hybrid systems, such as large red shifts of the plasmon resonances, appearance of new plasmon modes, rich Fano-like resonances, directional far-field emission, and intriguing far-field scattering patterns.^{235–242} In addition, the free-space electromagnetic field can be funnelled into the small spacing between the nanocrystal and substrate to form a ‘hot spot’ with an extremely large field enhancement, which is highly desirable for various surface-enhanced spectroscopies.^{241,243} A number of previous studies have revealed the effects of substrates on the plasmonic properties of metal nanocrystals with a spherical shape. Distinct plasmonic resonance behaviors induced by substrates are likely to be more pronounced for anisotropic metal nanocrystals such as Au nanorods. Due to their intrinsic anisotropic optical responses, the plasmonic response of a Au nanorod supported on a substrate is determined by three excitation manners. One is the excitation polarized perpendicular to the substrate, and the other two are excitations with the electric fields polarized along the nanorod length and width axes, respectively (Fig. 13A). The multipolar plasmon modes of the nanorod can hybridize and give intriguing plasmonic properties if the three excitation manners act simultaneously.

The induced image charges are determined by the dielectric properties of the substrate. Therefore, the plasmonic properties of a nanorod are strongly dependent on the dielectric properties of the supporting substrate. We have found that the presence of a substrate can greatly change the far-field scattering pattern of a Au nanorod.²⁴⁴ For Au nanorods deposited on substrates with small dielectric constants, such as glass, the longitudinal plasmon resonance overwhelms the other resonances. Therefore, far-field scattering of the nanorods appears as solid bright spots (Fig. 13B). In contrast, if the dielectric constant of the substrate is large enough, such as Au films, the longitudinal electron oscillations in the nanorods will be cancelled by their out-of-phase image charges in the substrate. The vertical electron oscillations will dominate and give rise to doughnut-shaped scattering patterns (Fig. 13C). Further studies indicate that whether the solid bright spot or doughnut-shaped scattering patterns occurs is determined by the $|\epsilon|^{-2}$ of the substrate (Fig. 13D), where ϵ is the complex dielectric function of the substrate.

For Au nanorods supported on dielectric substrates, their plasmon resonances usually red-shift without obvious distortion of their spectral line shapes (Fig. 13E).²⁴⁵ Although this result has been widely observed in experiments, there has been still a lack of general theoretical methods for predicting the plasmon shift of Au nanorods on various substrates. The difficulty comes from rigorous solving of Maxwell's equations with complex boundary conditions. Numerical simulations can

provide excellent solutions on this problem, but they provide little insight into the underlying physics governing the interaction between the nanorod and the substrate. By resorting to quasistatic approximation, Vernon *et al.* have developed a theory for calculating the plasmon wavelength of a nanocrystal with an arbitrary geometry deposited on dielectric substrates.²⁴⁵ The predicted plasmon shifts of Au nanorods with various aspect ratios are in excellent agreement with experimental measurements as well as numerical simulations (Fig. 13F). However, their theory is inadequate for the nanorods with large sizes due to the applied quasistatic approach. Large Au nanorods possess strong higher-order multipolar plasmon resonances due to the retardation effect. Therefore, the hybridization among different plasmon modes mediated by the substrate will be more efficient compared to that for small Au nanorods, especially when the nanorods are supported on substrates with large dielectric constants. We have recently shown that for Au nanorods having a large size and deposited on silicon substrates, a Fano line shape can be observed on the scattering spectra owing to the interference between the broad octupolar and narrow quadrupolar plasmon modes of the nanorods (Fig. 13G).²⁴⁶ The Fano resonance is found to be of a near-field nature, which only takes place when the spacing between the nanorod and the substrate is smaller than 8 nm.

6.2.4 Arrays. The plasmon coupling between noble metal nanocrystals can be further enriched by forming periodic arrays (Fig. 14A). Metal nanocrystals in arrays can interact with one another through coherent scattering processes and therefore support collective plasmon resonances. The collective plasmon resonances will be sharpened, shifted, and enhanced owing to the coupling with the diffraction, as predicated theoretically.¹⁵³ Specifically, the long-range radiative dipolar coupling in Au nanorod arrays with large lattice constants leads to blue shifts in the plasmon resonance (Fig. 14B and C).²⁴⁷ With small lattice constants, the near-field dipolar coupling results in red shifts. Multipolar plasmon resonances, on the other hand, do not exhibit apparent wavelength shifts in comparison to those of individual Au nanorods. Moreover, constructive dipolar coupling can compensate for the plasmon damping to generate extremely narrow collective plasmon resonances.²⁴⁸ When the lattice constant is close to the excitation wavelength, narrow spectral features, as shown in Fig. 14D, are observed close to the diffraction edge introduced by the periodic arrangement of Au nanorods. Such Fano-like spectral features come from the interference between the directly transmitted light and the light scattered by the array.¹⁵⁰

In addition, the diffractive coupling of Au nanorods can enable the excitation of the lattice surface mode, as indicated by the sharp spectral peak around 900 nm in Fig. 14C. The lattice surface mode causes a drastic redistribution of the near field with a much larger enhancement in between Au nanorods (Fig. 14E and F).^{248,249} The large electric field enhancement is superior for biosensing applications. The plasmon coupling in metal nanocrystal arrays has been found to be strongly dependent on the inter-particle spacing, nanocrystal shape, and excitation condition (polarization and wavevector direction) (Fig. 14G).²⁴⁹ Therefore, the collective plasmon resonances can be controlled by

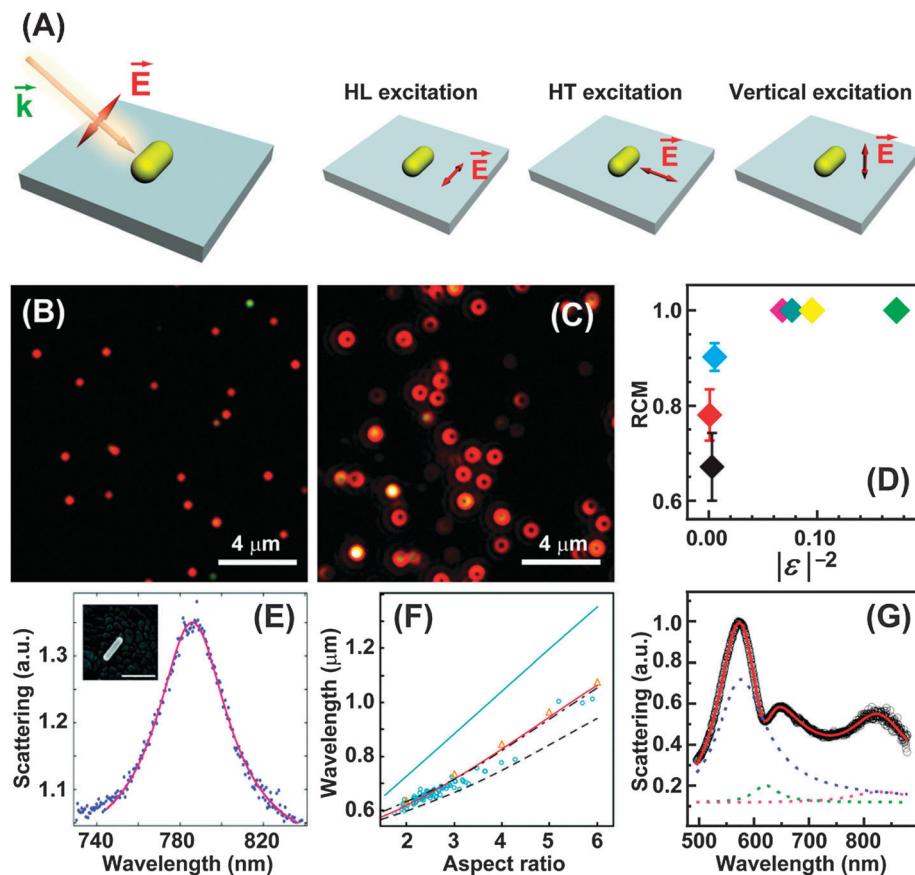


Fig. 13 Effects of substrates on the plasmonic properties of Au nanorods. (A) Schematic showing the three different excitation manners. HL excitation: the electric field is parallel to the substrate plane (horizontal) and along the length axis of the nanorod (longitudinal). HT excitation: The electric field is parallel to the substrate plane (horizontal) and perpendicular to the length axis of the nanorod (transverse). Vertical excitation: the electric field is perpendicular to the substrate plane.²⁴⁴ (B,C) Far-field scattering images of Au nanorods deposited on a glass slide and a Au film, respectively.²⁴⁴ (D) Dependence of the ratio between the light intensity at the center of the scattering pattern of Au nanorods and the maximum intensity (RCM)²⁴⁴ on $|\epsilon|^{-2}$. (E) Scattering spectrum and SEM image (inset) of a single Au nanorod supported on an ITO-coated glass substrate. The scale bar in the inset is 100 nm.²⁴⁵ (F) Plasmon wavelength of Au nanorods on an ITO-coated glass substrate as a function of the aspect ratio. The circles represent the experimental data points. The solid blue line and dashed black line are the theoretical predictions using homogeneous media with permittivities of 2.25 and 1, respectively. The solid red line and dot-dashed black line stand for the theoretical predictions obtained from quasistatic theory. The triangles are the results obtained from electromagnetic numerical simulations.²⁴⁵ (G) Experimental scattering spectrum of a single Au nanorod supported on a silicon substrate and the theoretical fitting with the 3-pole Fano interference model. The red line is the fitting result. The black circles represent the experimental spectrum. The green, blue, and pink curves are the contributions from the three resonances.²⁴⁶ Adapted from the data of the cited papers by permission from The American Chemical Society.

varying these parameters. Other parameters that have been overlooked are the lattice symmetry and the use of metal nanocrystal oligomers as the building unit. The collective plasmon resonances are expected to be controllable by employing arrays of different symmetries. The use of nanocrystal oligomers as the unit will dramatically increase the flexibility and complexity in tuning the array structures to achieve desired plasmonic properties. The employment of colloidal metal nanocrystals and oligomers can potentially greatly reduce the fabrication cost by electron beam lithography, although the particle monodispersity and homogeneity achieved by lithography methods have to be sacrificed. In addition, enormous challenges still remain in the construction of large-area highly ordered arrays of colloidal plasmonic metal nanocrystals with controllable lattice constants.

6.3 Plasmonic–molecular resonance coupling

Over the past few decades, researchers have witnessed great progress in producing electronic and optoelectronic devices

using organic materials. These devices are impressive for their low cost, flexibility, and facile fabrication techniques. However, the developments of organic devices are currently hindered by several drawbacks, such as small charge mobilities, chemical and physical instability, and low light absorption. A promising strategy for solving these problems is by conjugating organic materials with inorganic ones. Understanding fundamentally the interactions in the hybrid nanostructures is the starting point for building practical functioning devices. For metal nanocrystals exhibiting plasmonic resonances, their coupling with organic molecules can significantly modify the optical processes of the molecules, resulting in their enhanced light absorption, fluorescence, and nonlinear optical properties. Moreover, new hybrid excited states can be formed by the energy exchange between the metal nanocrystal and the organic molecules, especially when the absorption of the molecules is nearly degenerate with the plasmon band of the metal nanocrystal. This intriguing phenomenon, known as plasmonic–molecular resonance coupling,

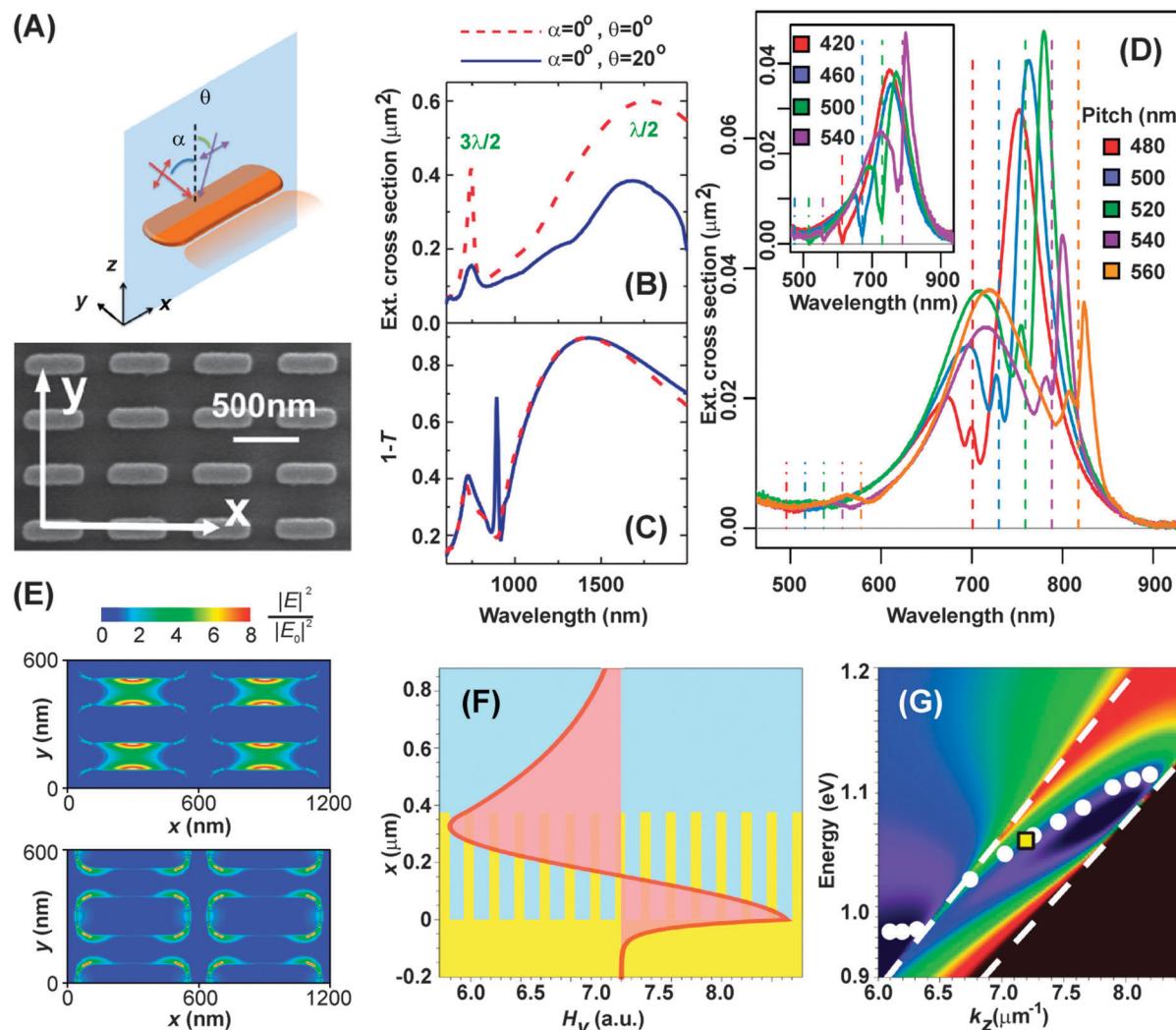


Fig. 14 Plasmon coupling in Au nanorod arrays. (A) Schematic of an individual Au nanorod and SEM image of a lithographically fabricated Au nanorod array.²⁴⁷ α and θ define the angles of incidence. (B) Extinction spectra of a single Au nanorod.²⁴⁷ The $\lambda/2$ and $3\lambda/2$ modes represent a dipolar and a multipolar resonance, respectively. (C) Extinction spectra of a Au nanorod array.²⁴⁷ (D) Extinction spectra of Au nanorod arrays with different lattice constants. The diffraction edge sweeps through the particle resonance. The inset shows the extinction spectra of another series of Au nanorod arrays with a different unit size.¹⁵⁰ (E) Near-field distributions of a Au nanorod array at the wavelengths of the lattice surface mode (upper) and the longitudinal plasmon mode (lower), respectively.²⁴⁸ (F) Electromagnetic field distribution of the collective plasmon mode in a Au nanorod array.²⁴⁹ (G) Dispersion of the collective plasmon mode in a Au nanorod array. The color plot is from numerical simulations. The circles are experimental results. The dashed lines stand for the dispersion of light in air (top left) and the substrate (bottom right). The yellow square corresponds to the collective plasmon mode at which the electromagnetic field distribution of the Au nanorod array is shown in (F).²⁴⁹ Adapted from the data of the cited papers by permission from The American Physical Society and Nature Publishing Group.

has attracted much attention in recent years due to their great importance in both the fundamental understanding of light-matter interactions and practical technological applications.^{87,250–260} The resonance coupling stems from the near-field interactions between the dye molecules and the metal nanocrystal. Excitation of the plasmon resonances in the metal nanocrystal leads to extremely concentrated electric fields in the affinity of the nanocrystal. For the molecular transitions in resonance with the plasmons, energy exchange will occur between the excited molecules and the plasmon resonances of the metal nanocrystal. As a result, both plasmonic and molecular absorption properties are dramatically altered, producing hybridized states and giving distinct scattering or extinction spectra from those of the separate constituents.^{87,250–254} This effect

should be taken into account for applications involving plasmon-molecule hybrid nanostructures, especially for those relying rigorously on the plasmon wavelengths of the nanocrystal, such as various plasmon-enhanced spectroscopies.

Plasmonic-molecular resonance coupling has been extensively studied using a variety of metal nanostructures, including thin metal films,^{261,262} nanostructured metal island films,²⁶³ spherical nanocrystals,^{255,256,264} and core-shell nanostructures.^{254,265} Compared to these nanostructures, the resonance coupling is expected to be more distinct for elongated metal nanocrystals due to their anisotropic optical responses and largely enhanced electric fields around them. We carried out the pioneering work on the plasmonic-molecular resonance

coupling using freestanding Au nanorods.^{87,252} Through the electrostatic layer-by-layer technique, we successfully constructed hybrid nanostructures consisting of Au nanorod cores adsorbed with dye molecules, HITC, which have a major absorption peak at 734 nm (Fig. 15A and B). The interaction between the longitudinal plasmon of the nanorod and the optical transition of HITC molecules induces split resonance modes that are manifested on the extinction spectra of the hybrid nanostructures. Such a phenomenon is usually known as ‘plasmon splitting’, which only occurs in the strong coupling regime.^{257,262,266} It is a classical analogy of vacuum Rabi splitting usually observed in quantum mechanical systems. The plasmonic Rabi splitting occurs due to the exchange of photons between the plasmonic field and the dye molecules, giving rise to new coherent hybrid light-matter states. This type of resonance coupling has been shown to be strongly dependent on the spectral overlap between the molecular absorption and the plasmon resonance. The measured extinction peak position and intensity vary systematically as a function of the energy difference between the longitudinal plasmon and the major absorption peak of HITC. An anticrossing behavior is clearly observed in the coupling energy diagram of the hybrid nanostructures (Fig. 15C). The coupling-induced plasmon shift can be up to 120 nm when the molecular absorption is degenerate with the longitudinal plasmon of the nanorod. Similar anticrossing phenomena have also been observed on other systems composed of different metal nanostructures and dyes.^{254,263,267}

The coherent interactions between the nanorod and dye molecules are mediated by the near field in the vicinity of the nanorod surface. They only occur when the spacing between the nanorod and dye molecules is smaller than 5 nm.⁸⁷ Furthermore, the coupling strength is sensitively dependent on the number of the adsorbed dye molecules on the nanorod, the pH of the solution, and the presence of external metal ions.²⁵² Most interestingly, by measuring the plasmon splitting of hybrid nanostructures made of Au nanorods and various dyes, the plasmon shift has been found to increase as the molecular volume-normalized absorptivity is increased.²⁵² This empirical relationship suggests that besides the number of adsorbed dye molecules, the molecular oscillator strength can also affect the resonance coupling. All of these characteristics offer great opportunities for the construction of resonance coupling-based ultrasensitive sensing devices through careful design of Au nanorod-dye molecule hybrid nanostructures.

Plasmonic–molecular resonance coupling is usually studied by measuring the collective responses of an ensemble of the hybrid nanostructures. Such ensemble measurements often produce ambiguities due to extrinsic factors, such as the inhomogeneous size distribution of metal nanocrystals, the background absorption from excess unadsorbed dye molecules, and the aggregation of metal nanocrystals. Therefore, further thorough understanding of intrinsic plasmonic–molecular interaction has to rely on the optical measurements at the single-particle level. Such studies, however, have long remained challenging due to the difficulties in measuring the optical

spectra of a single nanocrystal before and after dye adsorption. In 2010, we successfully observed the resonance coupling on individual Au nanorods using the dark-field scattering technique.²⁵³ Au nanorods are embedded in thin agarose gel matrices for dye adsorption and the optical measurements. Our results indicate that the scattering peak position and intensity induced by the resonance coupling vary systematically as a function of the original longitudinal plasmon wavelength of the nanorods. Most interestingly, because the used dye exhibits two absorption peaks due to the formation of H-aggregates on the nanorod surface, three peaks, which result from the hybridization, are observed when the plasmon band is situated in between the two absorption bands of the dye (Fig. 15D). Such a phenomenon, which is buried under the strong background in the ensemble measurements, unambiguously proves the formation of hybrid excited states. Our single-particle studies have also shown that the resonance coupling can be switched if the absorption properties of dyes are altered through laser illumination. For example, laser illumination can bleach the dye absorption and suppress the resonance coupling. The decoupling induced plasmon shift can reach up to 70 nm, indicating again the high potential for developing novel optoelectronic devices with active control on the basis of the resonance coupling. A demonstration of such applications has been shown by embedding Au nanorods into matrices containing photochromic dye molecules, where a plasmonic photoswitch is realized by monitoring the plasmon shift under laser illumination. The modulation depth of the switches can reach up to 7.2 dB.²⁶⁸

Once the hybrid nanostructures are excited, the energy will be shared by the plasmon resonance of the nanorod and the excited molecules. In other words, the excited states of the hybrid nanostructures have both plasmonic and molecular natures. In order to elucidate the physics underlying such a coherent process, one has to resort to ultrafast spectroscopy. Recently, Misawa and Sun *et al.* looked into the hybrid-state dynamics of Au nanorods coated with J-aggregates of dye molecules.²⁵ In their study, the femtosecond pump–probe technique was utilized to measure the decay of the resonance coupling-induced hybrid states of the nanostructures. Decay of the hybrid excited states was found to be governed by the thermal dissipation of the nanorods under non-resonant excitation. In contrast, under resonant pumping, the transient dynamics of the hybrid states clearly showed the coherent energy exchange between the molecular states and the plasmon of the nanorods. The coherent coupling only exists in short durations of ~100–200 fs (Fig. 15E). Such an understanding of the dynamics of the excited states can not only broaden our knowledge on light-matter interactions at the nanoscale, but also help to design novel nanodevices with coherent functionalities that are of great potential in future quantum computing and processing applications.

Despite its quantum mechanical nature, the resonance coupling can be described within the classical electrodynamic framework through various theoretical approaches. Numerical simulations can give precise predictions on the spectral properties of the

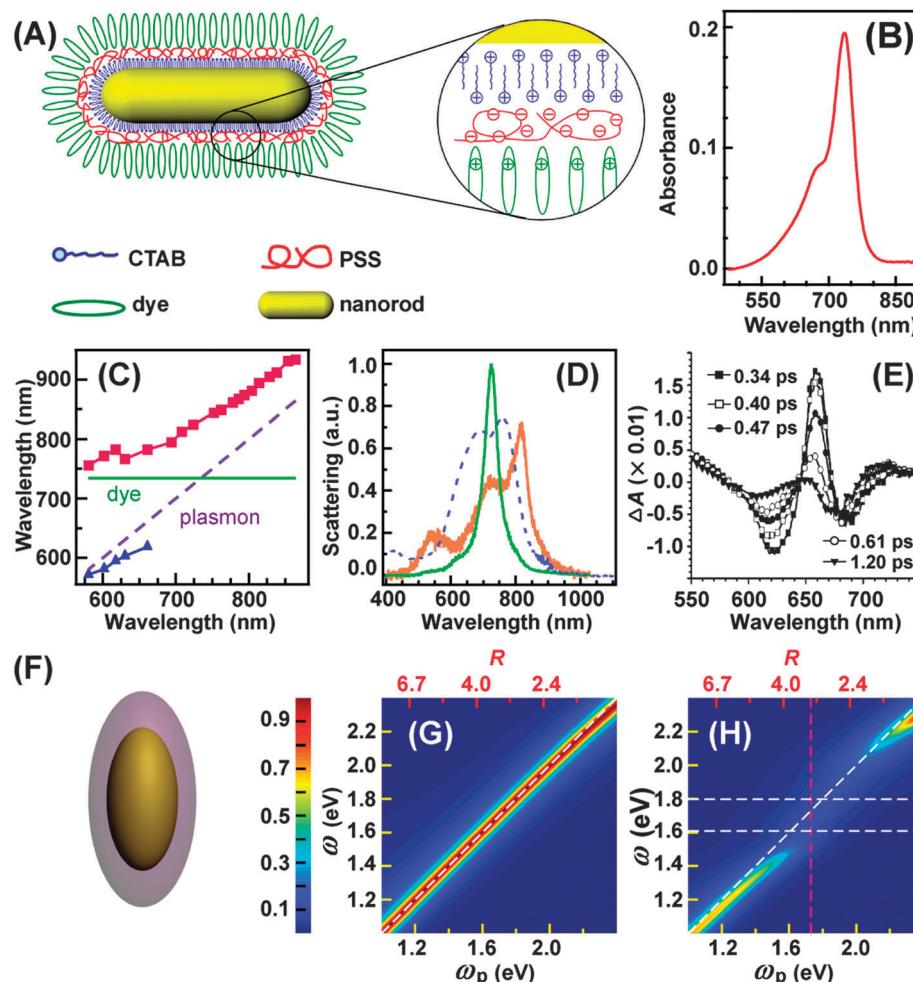


Fig. 15 Plasmonic–molecular resonance coupling of Au nanorods. (A) Schematic showing a Au nanorod–HITC hybrid nanostructure.⁸⁷ (B) Absorption spectrum of HITC in an aqueous solution.⁸⁷ (C) Energy diagram of the resonance coupling.⁸⁷ (D) Scattering spectrum of a single Au nanorod before (green) and after (orange) HITC adsorption. The absorption spectrum of HITC adsorbed on a glass slide is also included (blue).²⁵³ (E) Transient absorption spectra of a hybrid structure solution under resonant excitation.²⁵ (F) Schematic showing the model of a nanorod–dye hybrid nanostructure used in the quasistatic calculations. (G) Calculated energy diagram for Au nanorods without adsorbed HITC molecules.²⁵³ (H) Calculated coupling energy diagram for Au nanorod–HITC hybrid nanostructures. The two horizontal lines represent the two molecular resonance energies of HITC.²⁵³ Adapted from the data of the cited papers by permission from The American Chemical Society and Wiley Interscience.

resonance coupling. In addition, the energy transfer process between the adsorbed molecules and the nanorods can be monitored using time-domain algorithms such as the FDTD method. Through these sophisticated numerical techniques, one can conduct in-depth studies on the coherent dynamics of plasmonic–molecular resonance coupling. On the other hand, analytical electromagnetic models can be easily employed to calculate the scattering, absorption, and extinction spectra of the hybrid nanostructures. They can provide intuitive physical pictures without performing a large amount of calculations. The most widely used analytical model is based on quasistatic approximation, where the hybrid nanostructure is treated as an ellipsoidal Au nanorod core coated with a dye layer (Fig. 15F). The molecular transition, depending on the number of the absorption bands, is described as being composed of several Lorentz oscillators. The calculated energy diagrams of Au nanorods before and after the adsorption of dye molecules match well with the experimental measurements. The plasmon

wavelengths of the nanorods obey linear dependence on the aspect ratio (Fig. 15G). The introduction of dye coating modifies the plasmon spectrum and induces plasmon splitting when the plasmon band is degenerate with the molecular absorption (Fig. 15H). Depending on the number of molecular absorption bands, multiple splitting modes can be observed on the scattering spectra of the hybrid nanostructures. The quasistatic model can further enable the scrutiny of the effects of molecular properties, including the transition oscillator strength, transition linewidth, dye thickness, and spacing between dye molecules and the surface of the nanorod, on plasmonic–molecular resonance coupling.²⁶⁹

7. Applications

The splendid plasmon-related properties of Au nanocrystals have significantly propelled their wide applications in biomedical sensing and imaging, cancer therapy, drug delivery, nanophotonics, and optoelectronics. In addition, the anisotropic

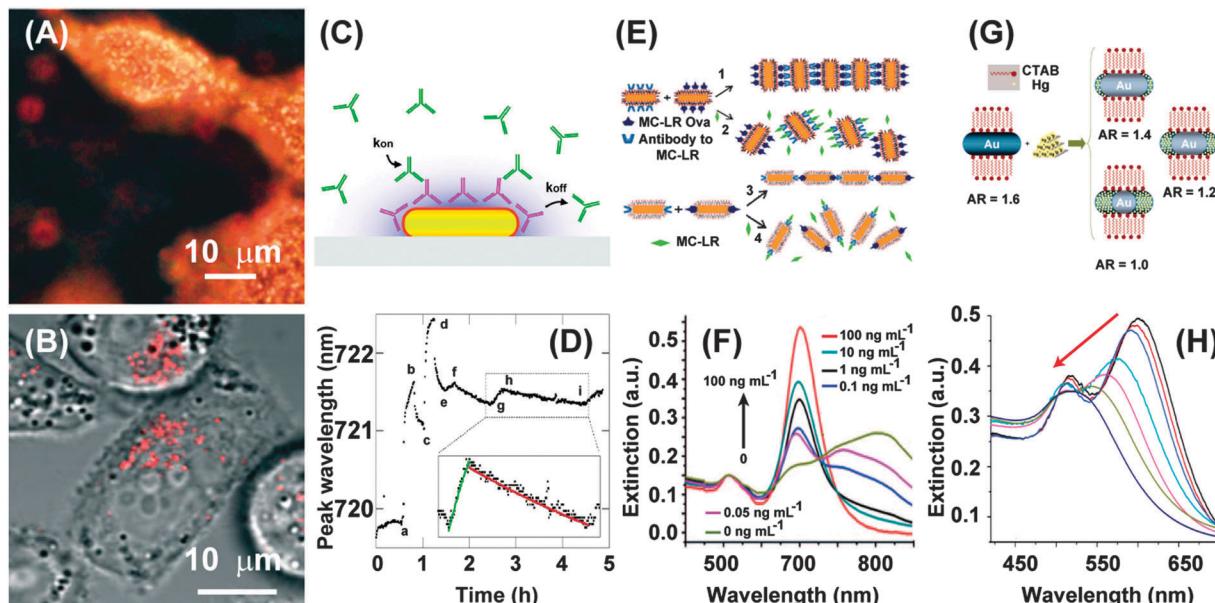


Fig. 16 Bioimaging and plasmonic sensing with Au nanorods. (A) Dark-field scattering image of cancerous hematopoietic stem cells with anti-EGFR-conjugated Au nanorods located on cytoplasm membranes.²¹² (B) Two-photon-excited photoluminescence imaging of KB cancer cells with internalized folate-conjugated Au nanorods.²⁷⁴ (C) Schematic showing Au nanorod-based plasmonic sensing.²⁸⁷ (D) Kinetic immunoassay monitored by the plasmon peak wavelength of an individual Au nanorod.²⁸⁷ (E) Schematic showing the toxin detection method with side-by-side and end-to-end Au nanorod assemblies.²⁸⁹ (F) Evolution of the extinction spectra of Au nanorods as the concentration of microcystin-LR (MC-LR) is increased for the end-to-end assemblies.²⁸⁹ (G) Schematic showing the detection of Hg^{2+} with Au nanorods.²⁹² (H) Spectral evolution of Au nanorods as a function of the Hg^{2+} concentration. The red arrow indicates the spectral change with the increase in the Hg^{2+} concentration.²⁹² Adapted from the data of the cited papers by permission from The American Chemical Society and Wiley Interscience.

plasmonic responses have provided great opportunities for Au nanorod ordered assemblies to be built up as metamaterials by exploiting their collective plasmonic responses. Such assemblies offer great potential in nanoscopic optical signal processing, manipulation, and transduction. The research works over the last two decades on the fundamental aspects of plasmonics and the development of various plasmon-based applications have opened up a new branch in nanophotonics, that is, nano-plasmonics. In the following sections, we will give a brief introduction to the various applications of Au nanorods.

7.1 Biotechnological applications

7.1.1 Labelling and imaging. The scattering cross-sections of Au nanorods at their plasmon resonances can be 4–5 orders of magnitude higher than those of conventional dye molecules,^{223,270} making them excellent candidates for biomedical labelling and imaging using reflectance confocal microscopes or dark-field scattering microscopes. Besides the large light-scattering capability, there are at least three other merits for employing Au nanorods as bioimaging agents. First, the synthetically tunable plasmon wavelengths of Au nanorods make them feasible for imaging with different excitation wavelengths, especially for those using near-infrared techniques. Second, the nanorods do not suffer from photobleaching as encountered with traditional dyes and semiconductor nanocrystals under the same conditions of light illumination, which makes them the most stable imaging agents. Third, as discussed in the sections above, the nanorod surfaces can be easily functionalized with a variety of chemical or biological

groups to enable targeted imaging, as well as integration with other imaging modalities. By using dark-field scattering imaging, antibody-labelled Au nanorods have been demonstrated for cancer diagnosis by their selective binding to cancer cells through recognition of the over-expressed EGFR on the cell surface (Fig. 16A).²¹² Similar techniques have been utilized for monitoring the dynamics of the cellular uptake and targeted delivery of Au nanorods.^{271,272} The dependence of the plasmon wavelength of Au nanorods on the aspect ratio also enables multiplexed imaging. By using Au nanorods with different aspect ratios, the simultaneous imaging of several biomarkers on the surface of human breast epithelial cells has been achieved.²¹² Moreover, the anisotropic optical response of Au nanorods provides the opportunity for tracking the motions of objects in cellular environments. Fang *et al.* have demonstrated the capability to resolve the three-dimensional rotational motions of Au nanorod-contained vesicles with Nomarski-type differential interference contrast microscopy, whereby the transport dynamics of nano-objects in live cells can be disclosed.²⁷³

Au nanorods exhibit intriguing nonlinear optical properties owing to extremely enhanced electromagnetic fields around their surface. This feature can act as an alternative technique for bioimaging using ultrashort laser pulses. Compared to the linear scattering imaging, the spatial resolution of the nonlinear imaging technique can be greatly improved. For example, Wei and Cheng *et al.* have shown that two-photon-excited photoluminescence of Au nanorods can well differentiate their targeting of cancer biomarkers on cytoplasm membranes

(Fig. 16B).²⁷⁴ Similar strategies have been employed for *in vivo* imaging of the blood vessels of mouse ears,²⁷⁵ cancer cells,²⁷⁶ and cellular uptake processes.⁸⁴ In recent studies, two-photon-excited luminescence imaging with Au nanorods has been extended to three-dimensional imaging.²⁷⁷ The above two imaging techniques rely on the radiative properties of the nanorods. There are also absorption-based bioimaging approaches that take advantage of the strong light absorption properties of Au nanorods. For example, Au nanorods have been utilized to greatly enhance both *in vitro* and *in vivo* imaging contrast in photoacoustic tomography, which is based on the optical absorption contrast in tandem with ultrasonic detection.^{278–281} In a very recent study, integrin-targeted Au nanorods were utilized for near-infrared imaging of glioblastomas by exploiting their strong plasmonic absorption in this spectral range.²⁸²

7.1.2 Plasmonic sensing. Adsorption of analytes on the surface of Au nanocrystals will change their local dielectric environment and lead to red shifts of the plasmon resonances. This refractive index change-induced plasmon shift has been widely used in the fabrication of ultrasensitive, light-weight, and remote chemical and biomedical sensors. The first example of the ‘real life’ applications of such biosensors was realized by immobilizing Au nanocrystals on glass substrates for detecting hormone stanozolol. A detection limit at the pM level has been achieved.²⁸³ Due to their larger electric field enhancements and polarizabilities, Au nanorods are more advantageous than their spherical counterparts for plasmonic sensing. Chilkoti *et al.* have successfully fabricated a label-free biosensor by conjugating biotin to Au nanorods. The binding of streptavidin to biotin can be monitored by measuring the plasmon shift of the nanorods. The detection limit of this sensor reaches down to ~20 nM in serum.²⁸⁴ Plasmonic sensing based on the single-particle modality enables ultrasensitive detection with high spatial resolution, where individual binding events can be monitored by choosing proper biomarkers. In a later study, Chilkoti *et al.* successfully detected the binding of streptavidin to an individual Au nanorod with a detection limit down to 1 nM.²⁸⁵ A very recent study even improved the sensing limit of prostate specific antigens to as low as the attomolar scale using a single Au nanorod.²⁸⁶ Moreover, the capability of single-particle measurements also allows for investigating the dynamic process of antibody–antigen interactions. By conjugating the surface of a Au nanorod with rabbit immunoglobulin, Hafner *et al.* have demonstrated the observation of the kinetic binding processes of anti-rabbit immunoglobulin (Fig. 16C and D).²⁸⁷ With real-time analyses, various binding and unbinding constants can be determined by monitoring the initial steps in the conjugation process (Fig. 16D). On the other hand, high-performance biosensors with real-time, parallel monitoring, and high miniaturization require the exploration of multiplex sensing. Irudayaraj *et al.* have made great efforts on this aspect by conjugating different antibodies to Au nanorods with various aspect ratios.²⁰² Multiplex sensing of different proteins is realized by monitoring the spectral shifts of the differently conjugated Au nanorods in the presence of the protein targets.^{202,288}

An alternative strategy for plasmonic sensing is to make use of the aggregation or assembly of Au nanorods. It is based on the spectral shift due to the plasmon coupling by bringing different Au nanorods close to each other. Xu and Kotov *et al.* have utilized Au nanorods for environmental toxin sensing by employing their side-by-side and end-to-end assemblies.²⁸⁹ In their study, Au nanorods were first functionalized with microcystin-LR antibodies and microcystin-LR-OVA antigens to induce the side-by-side or end-to-end assembly (Fig. 16E). Increase of the toxin MC-LR concentration in the solution will break the conjugation between the MC-LR antibodies and antigens, leading to the disassembly of the nanorods. By monitoring the spectral change of the nanorod solution, the presence of the toxin as well as its concentration can be obtained (Fig. 16F). The sensitivity of the end-to-end assembly modality reaches up to 0.03 ng mL⁻¹. This sensitivity is an order of magnitude better than that of the side-by-side assembly. By carefully choosing Au nanorods and their assemblies, this technique can even enable sensing through the observation of the color changes by naked eyes, which is similar to colorimetric sensing approaches.

The plasmonic sensing principle can be extended for non-biological species that threaten our daily life, such as heavy metal ions and nitrites.^{290–292} Campiglia *et al.* reported the detection of Hg²⁺ ions in tap water by taking advantage of the amalgamation of mercury with gold.²⁹² The adsorbed Hg²⁺ ions amalgamate with Au nanorods, leading to the reduction of the aspect ratio (Fig. 16G). Therefore, the concentration of Hg²⁺ ions can be determined from the blue shift of the longitudinal plasmon resonance of the nanorods (Fig. 16H).

7.1.3 Photothermal conversion-based therapy and drug/gene release. Hyperthermia therapy that relies on the plasmonic photothermal conversion of metal nanocrystals realizes the killing of cancer cells without using any conjugated drugs by inducing local heating at targeted sites. The use of Au nanocrystals for photothermal conversion-based therapy can be traced back to 2003 when spherical Au nanocrystals and nanoshells were utilized for cancer treatment.^{293,294} As a photothermal agent, Au nanorods have the advantages of small sizes, strong light absorption especially in the near-infrared range, high photothermal conversion efficiencies, and facile conjugation with targeting molecules and drugs. The first example of using Au nanorods for photothermal cancer therapy was presented by El-Sayed *et al.* in 2006, where Au nanorods were selectively bound to human oral cancer cells.²¹² Under the irradiation of a near-infrared continuous-wave laser, the cancer cells are killed through the photothermal heating of the nanorods. Following their pioneering study, many efforts have been made towards using Au nanorods in cancer cell treatments. Recently, Rege and Heys *et al.* studied the spatiotemporal temperature distribution and cell death induced by irradiating Au nanorods with a near-infrared laser.²⁹⁵ On the basis of the experimental measurements, they developed theoretical models for predicting the spatial and temporal variations in cell death and injury by the photothermal conversion of the nanorods. Such models will greatly facilitate the choice of optimal parameters for the photothermal therapy using Au nanorods.

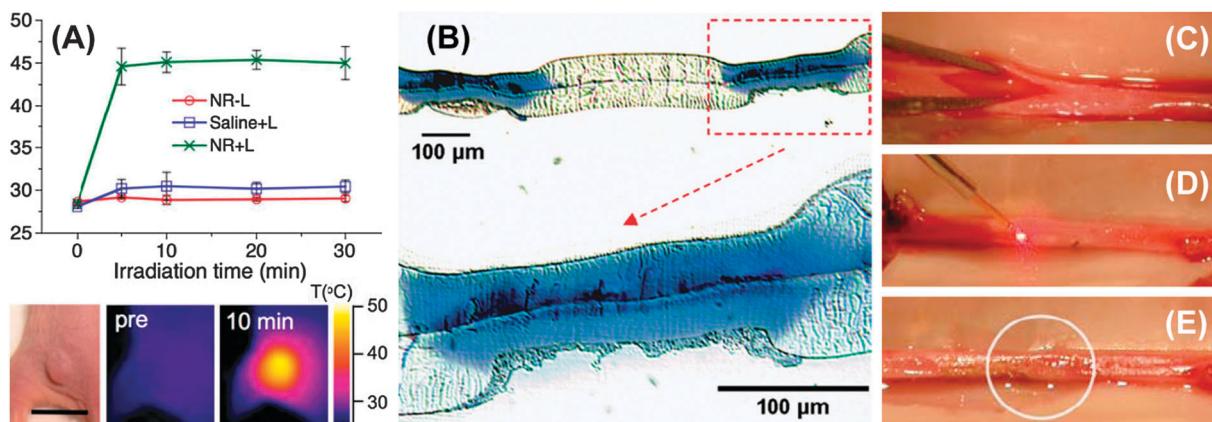


Fig. 17 Photothermal conversion-based therapy using Au nanorods. (A) Upper: temperature traces induced by localized laser irradiation of mice injected with Au nanorods. Tumor-bearing mice were injected intravenously with either Au nanorods (NR + L) or saline (saline + L). The trace labelled with 'NR-L' is a control where the nanorods were injected but the laser irradiation was not applied. Lower: infrared thermographic maps of the tumor region, showing the temperature distributions obtained after the laser exposure for the indicated periods of time. The scale bar is 1 cm.²⁹⁶ (B) Histological section of a laser-welded sandwich of anterior lens capsules (toluidine blue stain) using Au nanorods.²⁹⁷ (C–E) Sequence of images recorded during the laser welding procedure of a rabbit carotid artery using Au nanorods.²⁹⁸ Adapted from the data of the cited papers by permission from The National Academy of Sciences of USA, Elsevier and The International Society for Optics and Photonics.

One of the ultimate goals for biomedical applications of Au nanorods is their *in vivo* photothermal therapy. Compared to other types of thermal absorbers, such as dye molecules and carbon nanotubes, Au nanorods can possess simultaneously several imaging and therapy functions for *in vivo* applications. In 2008, El-Sayed *et al.* conducted the first investigation on using Au nanorods for *in vivo* photothermal cancer therapy, where the growth of squamous cell carcinoma in mice was effectively suppressed.²¹³ In later studies, Sailor *et al.* demonstrated that PEG-functionalized Au nanorods tended to accumulate in the tumor region of mice after intravenous injection. Effective *in vivo* photothermal heating of the tumor was realized by applying near-infrared laser irradiation (Fig. 17A).²⁹⁶ The photothermal conversion-induced temperature increase on the surface of the tumor can even be imaged by infrared cameras. Sailor *et al.* also prepared similar hybrid nanostructures by coating Au nanorods with Raman-active molecules. The obtained hybrid nanostructures allow for simultaneous *in vivo* near-infrared detection *via* Raman scattering and photothermal therapy of tumors in mice.²⁹⁶

The use of lasers to seal accidental and surgical wounds has become increasingly attractive as a minimally invasive and sustainable alternative to the conventional suturing and stitching approach in biomedicine. Laser welding is traditionally realized by use of organic dye molecules with near-infrared absorption. However, such dyes often suffer from several drawbacks, including low light absorption efficiencies, poor stability, and marked diffusiveness in biological environments. Plasmonic metal nanocrystals, although not much attention has been paid to them for this application, should be promising substitutes for organic dyes. Pini *et al.*, for the first time, explored the use of Au nanorods as light absorbers for laser welding of anterior lens capsules excised *ex vivo* from a porcine model.²⁹⁷ The operations simulated transplants in a sandwich assembly, where a patch of the anterior capsule of a donor was pasted

onto that of a recipient. The welding was realized through photothermal heating of Au nanorods stained at the interface between them. Their results indicate that the adhesion between the two capsules is strong enough to withstand a certain extent of mechanical traction (Fig. 17B). In a later study, they extended their welding technique to *in vivo* laser soldering applications.²⁹⁸ Specifically, a Au nanorod solution was first applied above and inside the cut of the carotid artery of a rabbit. Laser irradiation of the cut was then performed by slowly scanning the laser beam across the wounded artery. By adjusting the laser power and exposure time, an excellent closure of the cut edges was generated (Fig. 17C–E). These studies have opened up great opportunities for using Au nanorods in various surgery operations.

Precise control of drug/gene delivery and release in live cells or organic tissues is in high demand for biomedical therapeutics as well as for studying the evolution pathways in biological systems. Nano-platforms enabling loading and releasing of drugs/genes under remote triggers are foremost for this technique. In this context, Au nanorods have caught much attention during the past few years due to their excellent photothermal responses and facile conjugation chemistry.^{1,30} For realizing controlled drug/gene delivery, Au nanorods are usually functionalized or capped with desired drugs/genes through biochemical conjugation. Under the illumination of laser light in resonance with their longitudinal plasmon resonance, the functionalized Au nanorods release the contents through photothermal heating or reshaping. The near-unity photothermal conversion efficiency of Au nanorods allows drug/gene release to be activated with minimum optical exposures, therefore resulting in negligible damage to cells or tissues. In the study of Lee *et al.*, a Au nanorod-based switch is proposed for interfering with gene expression in live cells with nanometer-scale resolution and precise temporal control.²¹⁷ Prior to laser illumination, Au nanorods were conjugated with

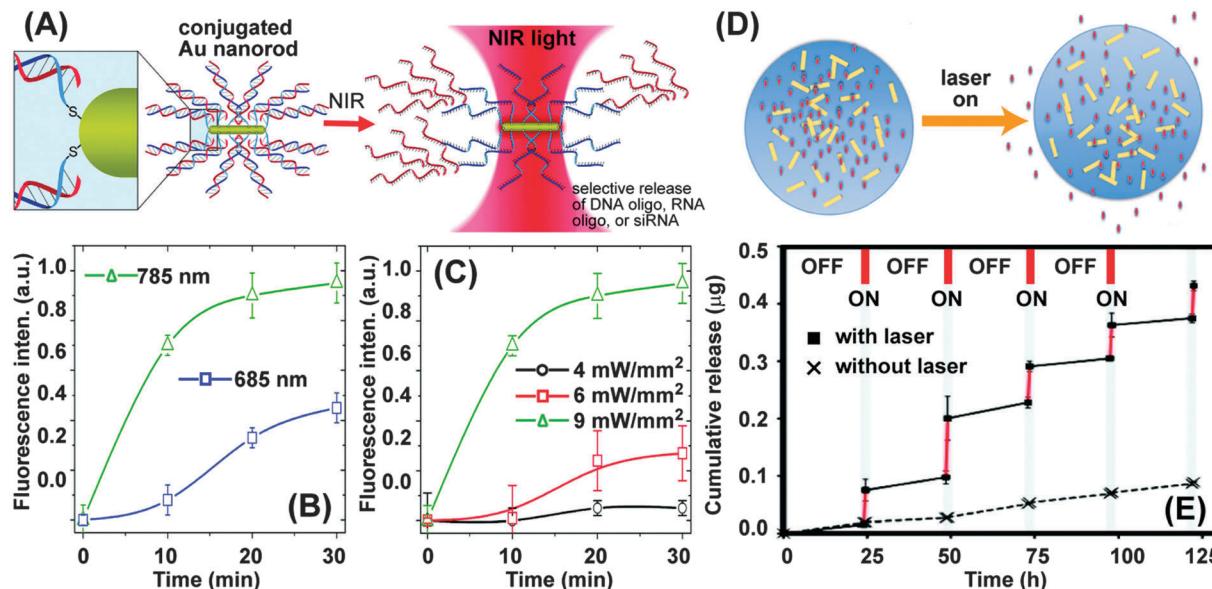


Fig. 18 Photothermal conversion-based drug/gene release using Au nanorods. (A) Schematic showing the release of antisense oligonucleotides from Au nanorods activated by laser illumination.²¹⁷ (B) Comparison of the photothermal gene release under the on- and off-resonance excitation conditions, with the laser wavelengths of 785 nm and 658 nm, respectively.²¹⁷ (C) Comparison of the photothermal gene release at different excitation laser power densities.²¹⁷ (D) Schematic showing the use of Au nanorods in a composite material to enable light-triggered drug delivery.³⁰ (E) Experimental results showing the dependence of the drug release on laser irradiation.³⁰³ Adapted from the data of the cited papers by permission from The American Chemical Society and The Royal Society of Chemistry.

double-stranded oligonucleotides, where antisense oligonucleotides were labelled with fluorescent dye molecules to visually monitor their release. They estimated that about 250 copies of oligonucleotides can be released from a single Au nanorod. After the functionalized Au nanorods were swallowed by cells, which were BT474 breast carcinoma cells in their study, laser irradiation was employed to induce the melting of the double-stranded oligonucleotides and therefore liberate the antisense oligonucleotides from the nanorods (Fig. 18A). The released antisense oligonucleotides then bound to a portion of ERBB2 mRNA and inhibited its gene translation. The photothermal release was found to be highest at the plasmon resonance wavelength (Fig. 18B). In addition, the gene release efficiency rises with the increase of the laser power (Fig. 18C). The minimum energy for reaching the required melting temperature of the oligonucleotides can be as low as 2 mJ cm^{-2} . Recently, mesoporous silica-coated Au nanorods have emerged as an effective drug/gene release agent, which is motivated by several advantages of the hybrid nanostructures.^{299–301} The mesoporous nature of the silica shell can increase the loading amount of drugs/genes. In addition, the silica shell can prevent the aggregation of the nanorods in the intracellular environment, which otherwise will degrade the photothermal conversion efficiency of the nanorods. Furthermore, the biocompatibility of the silica shell makes the hybrid nanostructures most suitable for *in vivo* applications.

An alternative drug/gene release strategy is to incorporate Au nanorods into composite materials. The nanorods act as the light absorber while the composites are drug carriers. Under laser illumination, the photothermal conversion of the nanorods heats up the surrounding composites, causing their structural changes and thereafter the release of the embedded

drugs/genes. In this way, Au nanorods can be seen as ‘nanoheaters’. In the work by Chen *et al.*, a proof-of-concept study has been demonstrated by embedding Au nanorods and an anticancer drug, paclitaxel, inside polyelectrolytes.³⁰² The composites were applied for the *in vitro* therapy of breast cancer cells. The release of paclitaxel was initiated by laser illumination. The inhibition rates of the cells exhibited strong dependence on the illumination modes and time. Moreover, multiple releases of paclitaxel from the composites can be controlled by switching on and off laser illumination. In a later study, Burdick *et al.* successfully controlled and enhanced the release of a molecular drug by taking advantage of the thermally induced glass transition of a polymer matrix.³⁰³ In their study, Au nanorods were encapsulated into a polymer matrix together with the drug. Under laser illumination, the nanorods heat up the matrix, inducing the glass transition of the polymer and therefore the release of the drug from the polymer matrix (Fig. 18D). By controlling laser illumination, the release of the drug can be repeated over several cycles (Fig. 18E).

At the end of this section, we would like to stress an important point for the biological and medical applications of Au nanorods: their toxicities. Previous studies have indicated that while Au nanorods themselves are safe for cells and organic tissues, the free CTAB molecules desorbed from the surface of Au nanorods are highly cytotoxic and can disrupt cell membranes.^{97,304} In this regard, replacing the CTAB molecules on the nanorod surface or covering the nanorods with other biocompatible molecules or materials, such as PEGs,^{304,305} phosphatidylcholine,³⁰⁶ poly(diallyldimethylammonium chloride),³⁰⁷ and poly(4-styrenesulfonic acid),³⁰⁷ will be crucial. This should be seriously taken into account, especially when Au nanorods are employed for *in vivo* applications.

7.2 Plasmonic modulation of optical signals

The nanoscale confinement of the electromagnetic field by the plasmonic resonances of metal nanocrystals allows for their integration with other nanoscale components, such as fluorophores, semiconductor nanocrystals/nanowires, and two-dimensional atomic crystals, to study the interactions of plasmons with other physical processes. On the one hand, the remarkably strengthened electric fields in the vicinity of metal nanocrystals can be utilized for enhancing the optical transitions of the adjacent various optical species. On the other hand, the excitation of the plasmon resonances strongly modifies the localized density of photonic states around metal nanocrystals, whereby the interactions between the nanocrystals and the adjacent species can produce distinct optical responses in comparison to their isolated components. For Au nanorods, these interactions and the resultant phenomena are even more enriched owing to their anisotropic plasmonic properties.

7.2.1 Plasmonic nanoantennas. Photonic and optoelectronic devices are all based on the in-coupling of free-space electromagnetic waves into the device regions for signal processing and the out-coupling of the signals into free-space radiation for transmission and detection. For devices with sizes much larger than the incident wavelength, these can be easily realized with traditional optical elements, such as lenses, mirrors, filters, waveplates, objectives, and gratings. However, as devices shrink down to the nanoscale, their efficient coupling with free-space light will become increasingly difficult due to the diffraction limit, let alone optical signal processing. Plasmonic metal nanostructures, which possess strong light absorption/scattering capabilities and relative narrow linewidths, can act as nanoantennas and thereby open up the possibilities for controlling and manipulating light-matter interactions at the nanoscale.

Plasmonic nanostructures, as nanoantennas, can function as a transducer between far- and near-field light signals. Free-space radiation can be captured by a plasmonic antenna and transferred to a nanoscale object (Fig. 19A).³⁰⁸ Due to the relative narrow linewidths of plasmonic metal nanostructures, only the radiation in resonance with the plasmon can be efficiently coupled with the nanoantenna. In 2008, we demonstrated a dipolar nanoantenna based on a single Au nanorod.¹⁰¹ The nanorod is encapsulated with a silica shell containing randomly distributed fluorescent dye molecules (Fig. 19B). Due to the dominant longitudinal plasmon resonance, the nanorod antenna selectively couples the light that is polarized along the nanorod length axis. The in-coupled light thereafter excites the fluorescent molecules in the silica shell (Fig. 19C). As mentioned above, the capture of light by plasmonic nanoantennas causes strong confined electromagnetic fields around them, which can not only enhance the optical transitions of adjacent nano-objects, but also allow for nanoscale optical signal processing. Experimental demonstration of such localized electric field distributions around a Au nanorod antenna was made by Quidant *et al.* using a two-photon-excited luminescence technique.³⁰⁹

According to the reciprocity principle, plasmonic nanoantennas can also transfer the localized near-field radiation from a nano-object into far-field detectable optical signals

(Fig. 19D). Due to the modified local density of photonic states by plasmonic nanostructures, the far-field radiation will be stamped with the characteristics of the plasmon, such as the frequency, polarization, and spatial radiation direction. By using the hybrid nanostructure similar to that shown in Fig. 19B, we have shown that the emission polarization of the nearby fluorophore molecules is modulated along the nanorod length axis irrespective of their random orientations (Fig. 19E and F).¹⁰² This modulation behavior is anticipated to be very important for future quantum computations, where coherent nanoscale light sources are greatly demanded. In addition, the local density of photonic states associated with the longitudinal plasmon mode of the nanorod enables the modulation of the decay dynamics of excited quantum emitters, giving rise to enhanced/suppressed fluorescence intensities and distinct fluorescence spectra. These phenomena are traditionally well known as the Purcell effect for atomic transitions confined in quantum cavities. Our recent study has examined this effect by using the hybrid nanostructures shown in Fig. 19B and E. The emission spectra of the fluorophore molecules distributed in the silica shell are strongly dependent on the longitudinal plasmon wavelength of the nanorod (Fig. 19G and H).¹⁰³ A new peak nearly overlapping with the plasmon resonance peak appears in addition to the intrinsic emission peak. This new peak stems from the decay of the excited molecules with the transition energy equal to that of the longitudinal plasmon. Under such a circumstance, the energy is transferred from the fluorophore molecules to the Au nanorod and thereafter emitted out from the hybrid nanostructure. Therefore, the polarization of the new emission peak follows that of the longitudinal plasmon mode, which is linearly polarized along the length axis (Fig. 19H). In contrast, the intrinsic emission peak remains unpolarized (Fig. 19G), suggesting that it arises from the direct radiative decay of the fluorophore molecules. This spectral reshaping has also been observed in other plasmonic systems, including individual metal nanocrystals, Au nanosphere dimers, and metamaterials.^{310–312}

Plasmonic nanoantennas can also steer the dipolar emission of nanoscale optical species, whose emissions usually have broad spatial distributions, into desired directions with small divergence. This can be done by carefully designing plasmonic nanostructures. Yagi-Uda nanoantennas, which consist of differently sized nanorods as feeds, reflectors, and directors, are one example of such nanostructures.³¹³ Previous studies have shown that Yagi-Uda nanoantennas can realize the unidirectional transmission of the incident light.^{313,314} In 2010, van Hulst *et al.* demonstrated the unidirectional emission of a single quantum dot by placing it besides the feed of a Yagi-Uda nanoantenna made of Au nanorods (Fig. 19I).³¹⁵ The resultant emission from the quantum dot is strongly polarized and highly directed into a narrow forward angular cone (Fig. 19J). Their results can be seen as a milestone in nanophotonics, where directional coupling of light at the nanoscale has always been a big challenge. In later studies, near-field electromagnetic field amplitudes as well as optical phases were studied using a homodyne amplification technique.³¹⁶ Recently, new types of

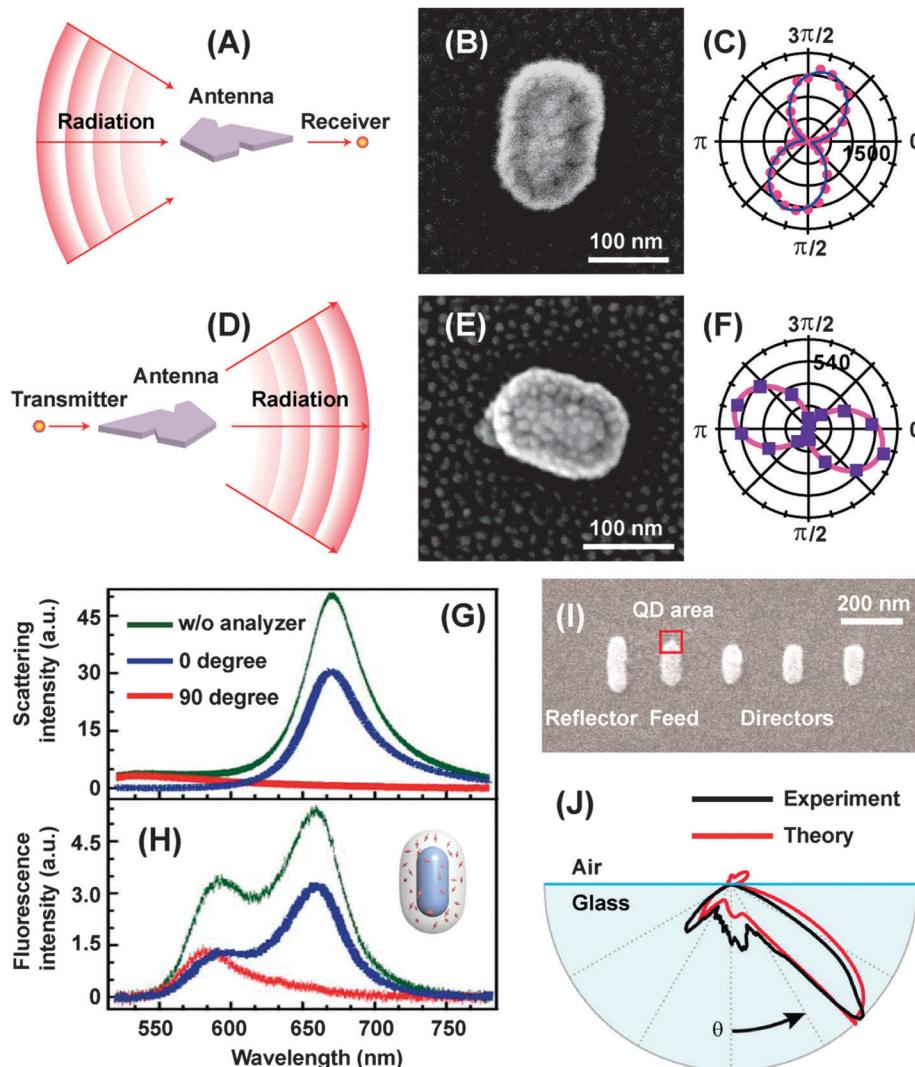


Fig. 19 Gold nanorod-based plasmonic nanoantennas. (A) Schematic showing the receiving antenna.³⁰⁸ (B,C) Excitation polarization-dependent fluorescence intensity from a hybrid nanostructure, which is composed of a Au nanorod core and a silica shell embedded with fluorophore molecules.¹⁰¹ (D) Schematic showing the transmitting antenna.³⁰⁸ (E,F) Linearly polarized emission from a hybrid nanostructure similar to the one shown in (B).¹⁰² (G) Scattering spectra of a hybrid nanostructure similar to those shown in (B) and (E). The green, blue, and red spectra were recorded in the absence of a polarization analyzer and in the presence of a polarization analyzer with its polarization axis aligned parallel and perpendicular to the nanorod length axis, respectively.¹⁰³ (H) Corresponding fluorescence spectra recorded on the same nanostructure as in (G).¹⁰³ (I) SEM image of a Yagi-Uda nanoantenna. A quantum dot is attached to one end of the feed element, as indicated by the red box.³¹⁵ (J) Experimental and theoretical angular radiation patterns from the quantum dot modulated by the Yagi-Uda nanoantenna.³¹⁵ Adapted from the data of the cited papers by permission from Nature Publishing Group, The American Chemical Society, The Royal Society of Chemistry and The American Association for the Advancement of Science.

Yagi–Uda nanoantennas with three-dimensional geometry have also been proposed.³¹⁷

A very important issue for the future applications of plasmonic nanoantennas is their integration with state-of-the-art silicon-based microelectronics techniques, whereby light-weight, highly compact, and wavelength-dependent functional optoelectronic devices can be designed and fabricated. In this context, plasmonic nanoantennas can act as light harvesting components. Halas *et al.* made the first effort in this direction by inventing a novel type of photodetectors with active optical antennas.³¹⁸ In their study, Au nanorod antennas are fabricated on n-type doped silicon wafers (Fig. 20A). The antennas strongly absorb incident light and generate hot electrons. These hot

electrons thereafter overcome the Schottky barrier at the antenna–semiconductor interface and are injected into the silicon substrate, contributing to a detectable photocurrent (Fig. 20B). The responsivity of this device reaches 8 nA mW^{-1} under resonant excitation. More interestingly, the photocurrent response of the device is strongly dependent on the plasmon resonance of the antenna (Fig. 20C and D). These devices are anticipated to function as tiny, on-chip spectrometers by using Au nanorods of different aspect ratios.

Although significant progress, as described above, has been made on the use of Au nanorods as efficient nanoantennas, their device applications in nanophotonics are still severely hindered by the strong light absorption of the metal itself.

Excitation of the plasmon resonances in these nanoantennas will inevitably dissipate the light energy through Ohmic loss, which attenuates the amplitudes of the optical signals as well as affects their coherence. Introducing a gain medium adjacent to the nanorod is a possible solution but rather cumbersome.^{319,320} An alternative is to explore semiconductor-based plasmonic materials, where the Ohmic loss can be negligible. The exploration of the plasmon resonances in semiconductor nanomaterials has just started as a new research front in the field of plasmonics.^{321,322}

2.7.2 Surface-enhanced Raman scattering. SERS can be seen as the first example of the plasmonic applications of metal nanostructures. Due to its significance for future chemical analysis and clinical diagnosis, tremendous efforts have been made to design and fabricate SERS substrates with strong Raman enhancements, high stability, and excellent signal uniformity, reproducibility and recyclability ever since its discovery. In comparison with other nanostructures, the strong electric field enhancements and well-developed synthetic tunability of the plasmon resonances in a wide spectral range to match with excitation lasers have made Au nanorods excellent SERS substrates. A large number of experiments have demonstrated the exceptional SRES performance of Au nanorods. We focus here only on the progress made in the recent years.

The SERS mechanism has been generally accepted to involve mainly the contributions from electromagnetic field enhancements and chemical enhancements, with the former being dominant for excitation in resonance with the plasmon mode of metal nanostructures. Strong field enhancements at the ends of Au nanorods due to the high curvature have been demonstrated experimentally, which is consistent with the theoretical predictions.³²³ The field enhancements can be further increased by bringing two nanorods close to each other. The gap region between the nanorods forms a 'hot spot' with extremely large electric field enhancements and therefore can give unprecedented SERS signals for molecules in between (Fig. 21A). Thomas *et al.* have demonstrated this effect by linking Au nanorods with dithiol derivatives.³²⁴ The Raman signal of the molecules in the gaps between the nanorods has been shown to be enhanced by $\sim 1.4 \times 10^5$. This value is not as high as those observed in single-molecule measurements.³²⁵ The smaller signal is ascribed to the use of laser excitation far away from the plasmon resonance of the coupled nanorods and the inhomogeneities in both the nanorod monomers and dimers.

A similar concept has been extended to Au nanorod aggregates, where the plasmon coupling among the nanorods produces numerous 'hot spots' for SERS. For example, Jana *et al.* have shown that the Raman enhancement factor of nanorod aggregates is 10^2 – 10^3 times larger than that from the polydisperse counterparts.³²⁶ In a different study, El-Sayed *et al.* induced the assembly of Au nanorods on cancer cells through bioconjugation. The resultant nanorod assemblies generate highly enhanced, sharp, and polarized SERS signals from cancer cells.³²⁷ For these nanorod aggregates and assemblies, a natural question arises. How does the SERS performance correlate with the number as well as the orientations of the nanorods in the

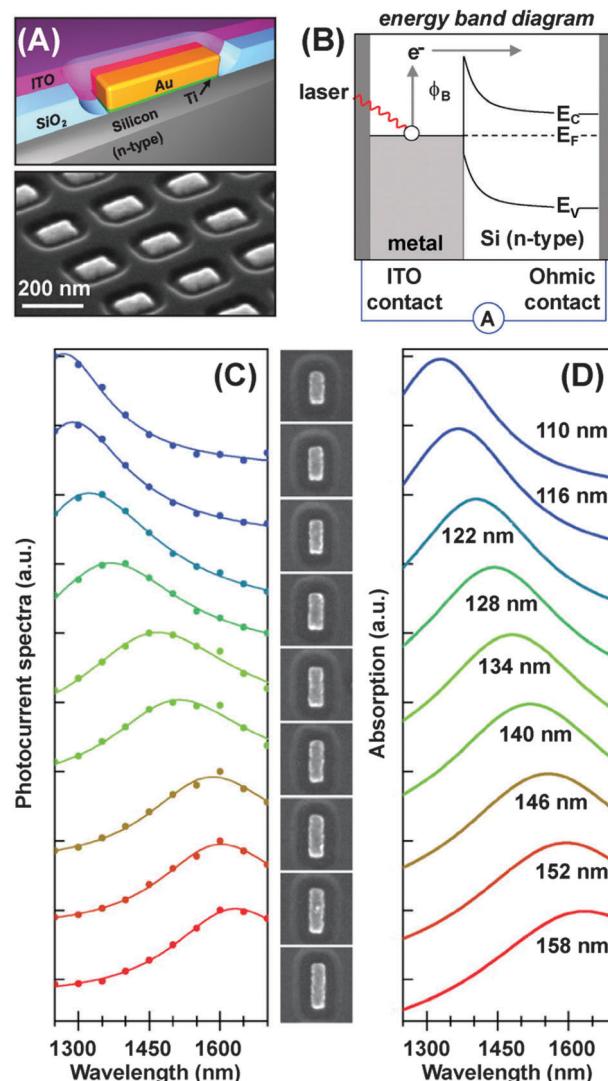


Fig. 20 Photodetectors based on Au nanorod antennas. (A) Schematic and SEM image of the Au nanoantennas on an n-type silicon substrate. (B) Energy band diagram for hot electron injection over the metal–semiconductor Schottky barrier by exciting the plasmon resonance. (C) Photocurrent spectra and SEM images of the nanoantenna-based photodetectors. (D) Corresponding calculated absorption spectra of the Au nanorods.³¹⁸ Adapted from the data of the cited papers by permission from The American Association for the Advancement of Science.

aggregates? A full understanding of this question, although still remains elusive, can provide the design rules for the fabrication of stable and reproducible SERS substrates for various biomedical applications. In addition, it can also provide important insights into the properties of the 'hot spots' in ordered metal nanostructures. In a very recent study, Kumacheva *et al.* have quantified the dependence of the SERS signal on the number of nanorods in a nanorod chain.³²⁸ By controllably fabricating the different chain assemblies (Fig. 21B–D), they were able to correlate the ensemble-averaged SERS intensity to the number of nanorods and the extinction of the chain assemblies. The SERS intensity is not monotonically dependent on the nanorod number, but it nearly follows the extinction product, which is

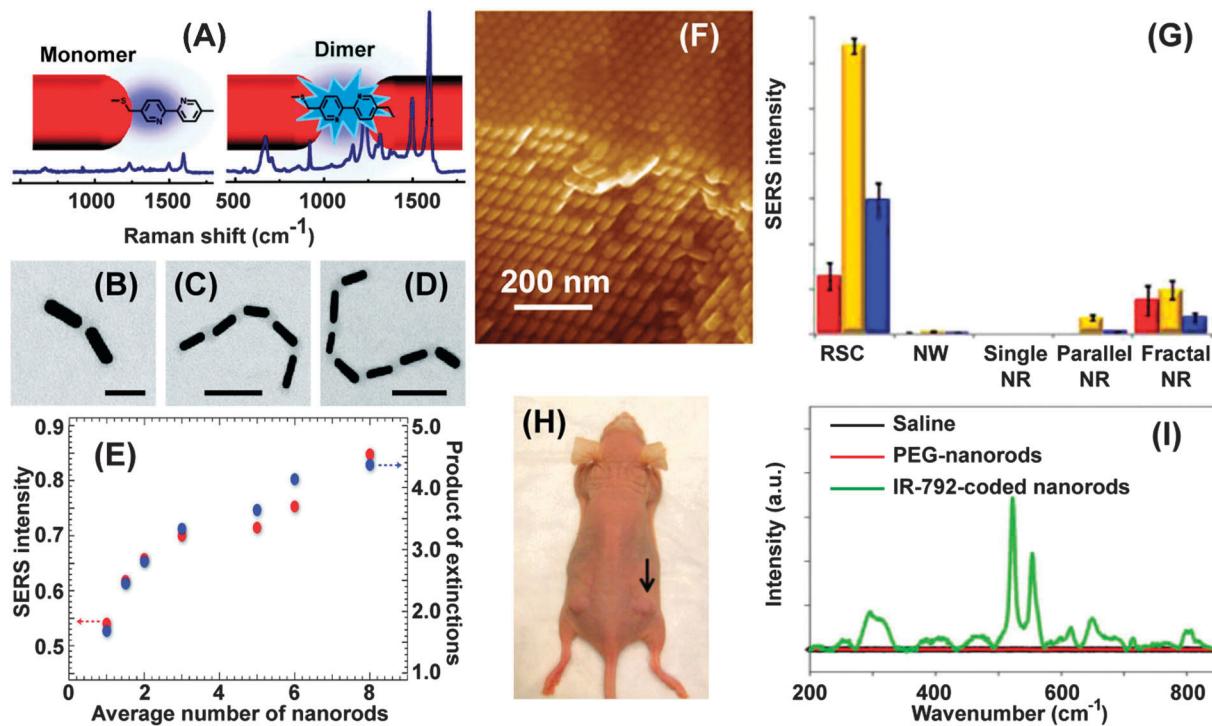


Fig. 21 SERS involving Au nanorods. (A) SERS from a Au nanorod monomer (left) and dimer (right).³²⁴ (B–D) Representative TEM images of Au nanorod chains with different numbers of nanorods.³²⁸ The scale bars are 40 nm. (E) Dependence of the normalized SERS intensity (red circles) and the product (blue circles) of the extinctions at the excitation and Raman scattering wavelengths as a function of the average nanorod number in the chains.³²⁸ (F) Typical SEM image of an ordered Au nanowires (NW). single Au nanorods (single NR), parallel and fractally aggregated Au nanorods (parallel NR and fractal NR, respectively). The red, yellow, and blue colors indicate the results obtained at excitation wavelengths of 633 nm, 785 nm, and 830 nm, respectively.¹⁶³ (H) Athymic mice bearing bilateral human MDA-MB-435 tumors were injected intratumorally with SERS-coded Au nanorods (arrow) to evaluate the potential for *in vivo* detection.²¹⁴ (I) *In vivo* Raman spectra of IR-792 perchlorate-coded Au nanorods, PEG-nanorods, and a saline solution.²¹⁴ Adapted from the data of the cited papers by permission from The American Chemical Society, National Academy of Sciences and Wiley Interscience.

defined as the product between the extinctions of the assemblies at the excitation and Raman scattering wavelengths (Fig. 21E). This correlation indicates that the SERS performance of the nanorod assemblies indeed originates from the inherent electromagnetic property of the nanostructures, rather than chemical effects. In a different study, Zhang *et al.* designed bifunctional PEG molecules to obtain controlled Au nanorod assemblies with varying orientations, including side-by-side, end-to-end, and their combinations.³²⁹ Among them, the end-to-end nanorod assembly gives the highest Raman enhancement, suggesting that the orientation of the nanorods in the assemblies plays an important role in determining its SERS performance.

Compared to the aggregates and assemblies, supercrystals with high long-range ordering exhibit more exquisite field-enhancement properties. The plasmon coupling among a number of Au nanorods with different orientations and spacings gives collective plasmon resonances that spread throughout the supercrystals. The collective plasmon resonances generate large-area homogeneous ‘hot spots’ with a coherent nature. Recently, Liz-Marzán *et al.* systematically investigated the SERS performance of three-dimensional Au nanorod supercrystals (Fig. 21F).¹⁶³ Their results have elucidated the great potential of such supercrystals as stable and ultrasensitive SERS substrates for rapid

detection of scrambled prions, a traditional hard-to-detect infectious agent that causes various fatal neurodegenerative diseases in mammals. Compared to individual Au nanorods and other nanorod aggregates without long-range ordering, the supercrystals produce much stronger SERS signals for the prions (Fig. 21G). The Raman enhancement persists even for laser excitation that is not in resonance with the plasmon mode of the supercrystals, which is due to the spectral broadening induced by the collective coupling in the supercrystals. In addition, the supercrystals also show the ability of direct detection of the prions in complex biological media such as serum or blood, paving the way for fast online pre-symptomatic detection in biomedicine.

Raman spectroscopy has emerged as a promising approach for *in vivo* biosensing and biodetection, where Raman active molecule-coded nanomaterials are transferred to organic tissues and thereafter detected by measuring Raman scattering signals. In these applications, strong Raman signals from the coded nanomaterials are required. From this point of view, the SERS of Au nanorods is an attractive alternative for *in vivo* biological applications. In the study by Bhatia *et al.*, Au nanorods were coded with several Raman-active molecules, such as IR-792 perchlorate, DTTC-765, and DTDC-655, and then injected into the mice implanted with bilateral human

MDA-MB-435 tumors (Fig. 21H).²¹⁴ The Raman active molecule-coded Au nanorods were found to give intense *in vivo* Raman signatures with concentrations down to attomoles (Fig. 21I) under near-infrared illumination. This remote sensing ability in tandem with the photothermal conversion-based therapy has made Au nanorods an excellent multiplex biomedical platform.

7.2.3 Other related optical signals. The exquisite plasmonic responses of Au nanorods have impacted other areas of applications that rely on optical excitations. One interesting example is the enhanced nonlinear optical response of Au nanorods upon the excitation of their plasmon resonances. In 2005, Wiederrecht *et al.* showed that the strong two-photon-excited photoluminescence from individual Au nanorods originates from the radiative decay of its longitudinal plasmon resonance.³³⁰ The two-photon-excited luminescence spectra follow those of the scattering spectra of the individual nanorods (Fig. 22A). In addition, the emission intensity of an individual nanorod exhibits a strongly anisotropic dependence on the incident light polarization, which is in accordance with the anisotropic nature of the longitudinal plasmon mode of the nanorods (Fig. 22B and C). These results have stimulated the design of a new type of sensors that can detect different dielectric media or molecular adsorbates with high spatial resolution and small background interference. Fatti *et al.* utilized an ultrafast pump-probe setup in tandem with far-field spatial modulation spectroscopy to investigate the nonlinear optical response of a single Au nanorod. Their studies indicate that the third-order bulk metal nonlinearity can be enhanced by the excitation of the longitudinal plasmon mode, giving rise to the exotic extinction changes from the Au nanorod.³³¹

The enhanced optical near field around Au nanorods at the plasmon resonance can be employed for patterning through photopolymerization, a process resembling those used in traditional photolithography techniques but with much higher spatial resolution. This strategy has been conceptually demonstrated by embedding Au nanorods into a commercial photoresist SU-8.³³² Under the excitation of a laser pulse in resonance with the longitudinal plasmon mode of the embedded nanorods, SU-8 absorbs the laser energy through its two-photon absorption. The absorption is greatly enhanced by the plasmon resonance. The light absorption causes the thermal crosslinking of SU-8. The plasmon-enhanced photopolymerization process produces small bumps around the nanorods (Fig. 22D–G). Because the near field is maximized at the ends of the nanorods, the SU-8 bumps first appear near the two ends of the nanorods and then gradually spread towards the middle segment. As a result, this near field-induced patterning is strongly dependent on the exposure dose of the incident laser. The proposed plasmon-enhanced photopolymerization also provides a facile approach for rapid qualitative imaging of the nanoscale near-field distribution around Au nanorods.

Illumination of Au nanorods with a laser leads to the accumulation of heat around the nanorods due to the photothermal conversion. Therefore, the nanorods will undergo geometrical reshaping for laser energies above their damage

threshold. The optical responses of the reshaped nanorods will be distinct from those of the original ones. This characteristic is expected to be of great potential in optical data storage that utilizes laser patterning and writing. On the basis of this concept, Gu *et al.* have demonstrated a novel multiplex optical recording approach that can increase the storage capacity by several orders of magnitude.³³³ In their study, Au nanorods were embedded in multilayers of polymers with random distributions in each layer. The laser writing was initiated by the photothermal reshaping of the nanorods in the focal volume of the objective (Fig. 22H). The reshaping is selective in terms of the aspect ratio and orientation of the nanorods. Only the laser pulse polarized along the length axis and with the wavelength close to the longitudinal plasmon wavelength of the nanorods can induce the reshaping (Fig. 22H). Therefore, the nanorods act as optical recording media that are five-dimensional, including the wavelength and polarization of the writing laser and the three spatial axes. The readout of the recording was realized through the two-photon-excited photoluminescence of the nanorods. The luminescence was excited using the laser with the same wavelength and polarization as those used during the recording. Regions undergoing the laser writing gave weaker luminescence signals owing to the depletion of the nanorods with their longitudinal plasmon in resonance with the readout laser (Fig. 22I). The demonstrated five-dimensional laser writing and luminescence reading strategy enables cross-talk-free and high-density optical data storage and encryption.

Optical circular dichroism (CD), originating from the chirality of molecules, is a very intriguing phenomenon of biomolecules. CD signals are usually employed to detect biological species with chiralities as well as their conformational changes. In this sense, the accuracy of CD spectroscopy relies on the intensity of CD signals. In recent years, the plasmon resonances of metal nanostructures have been found to be able to enhance the electronic transition of adjacent chiral molecules and thereafter enhance their CD signals.^{334–336} These findings have opened up new opportunities for traditional CD spectroscopy and brought up a new research branch in this area, that is, plasmonic CD spectroscopy. Most of the previous studies have mainly focused on plasmonic CD signals induced by isolated metal nanocrystals. In view of future applications that require ultrasensitive detection, the use of the plasmon coupling in nanocrystal assemblies to enhance CD signals is highly desired. Very recently, Tang *et al.* made the first step in this direction.³³⁷ In their study, Au nanorods were first functionalized with double-stranded DNAs. Upon cooling the solution to 20 °C, the nanorods aggregated with each other through the sticky ends of the DNAs (Fig. 22J). The plasmon coupling between the assembled Au nanorods in the aggregates generates many electromagnetic ‘hot spots’. The chiral optical transitions of the DNAs are strongly coupled with the assembled nanorods, leading to a stronger CD response than that for the isolated ones (Fig. 22K). The aggregation of the nanorods was destroyed by increasing the solution temperature to 60 °C, which is above the melting temperature of DNAs. As a result, the plasmonic CD responses of Au nanorods can be controlled reversibly by adjusting the temperature of the solution (Fig. 22J).

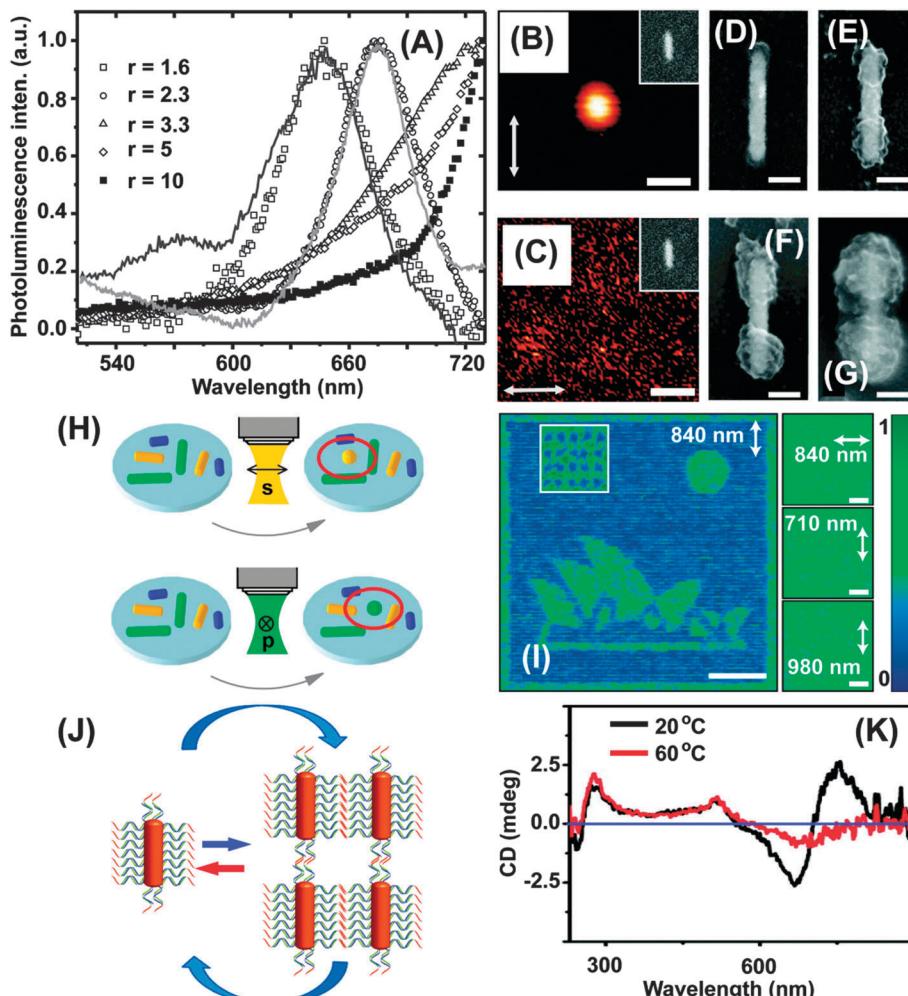


Fig. 22 Various optical applications of Au nanorods. (A) Two-photon-excited photoluminescence spectra from individual Au nanorods with different aspect ratios. The solid lines correspond to the scattering spectra of Au nanorods with aspect ratios of 1.6 and 2.3, respectively.³³⁰ (B–C) Confocal two-photon-excited luminescence images of individual Au nanorods (insets). The white arrows indicate the polarization directions. The scale bars stand for 300 nm.³³⁰ (D–G) SEM images of Au nanorods after exposure at increasing doses and development. Before the exposure, the Au nanorods were embedded in thin films of epoxy-based negative photoresist SU-8.³³² (H) Schematic illustrating the mechanism for the photothermal patterning of a Au nanorod film.³³³ (I) Normalized two-photon-excited luminescence raster scan of an image patterned using one laser pulse per pixel at the different laser wavelengths and polarizations. The scale bars are 20 μm .³³³ (J) Schematic showing the reversible plasmonic circular dichroism responses based on the dynamic assembly and disassembly of Au nanorods modified with double-stranded DNA at different temperatures.³³⁷ (K) Plasmonic circular dichroism spectra of Au nanorods.³³⁷ Adapted from the data of the cited papers by permission from The American Physical Society, The American Chemical Society and Nature Publishing Group.

7.3 Metamaterials

Metamaterials are artificial materials engineered to have optical properties that cannot be found in nature. This type of materials usually mainly gains their properties from structures rather than their compositions.³³⁸ Traditional metamaterials are usually composed of dielectric units with different spatial arrangements. They can modify the wavefronts of incident waves and redirect their propagation, giving rise to various unprecedented electromagnetic phenomena, such as negative refraction, photonic band gaps, cloaking, and electromagnetic induced transparency.^{339–342} In recent years, plasmonic metamaterials with metal nanostructures as building blocks have attracted much attention, because they are expected to work in the visible range due to the plasmon resonances of metal nanostructures. Zhang *et al.* have proposed a structure that exhibits a plasmonic resonance similar to electromagnetic

induced transparency by taking advantage of the interference between the different plasmon modes in metal nanorods.³⁴³ The building unit is a dolmen-style structure composed of two identical metal nanorods aligned parallel to each other and a third nanorod placed perpendicular to the two parallel ones with a small lateral displacement (Fig. 23A). Due to the retardation effect, the dipolar plasmon resonances in the two parallel nanorods are out of phase with each other, which leads to destructive interference. Therefore, the two nanorods exhibit a quadrupolar resonance with a net dipole moment of zero, which cannot couple to the far-field radiation. They are termed as the ‘dark mode’. In contrast, the dipolar resonance of the third nanorod can effectively couple with the far-field radiation. It is termed as the ‘bright mode’. Under the excitation polarized along the longitudinal direction of the third nanorod, the bright dipolar mode will first be excited. The excited dipolar

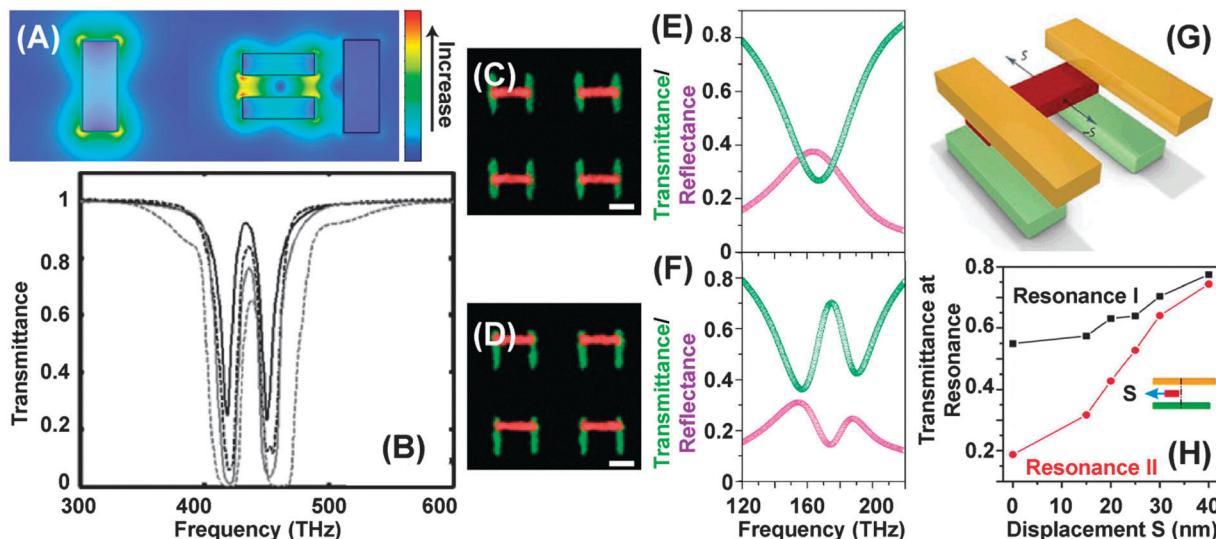


Fig. 23 Metamaterials made of Au nanorods. (A) Electromagnetic field distributions of an uncoupled Au nanorod (left) and the building unit of the metamaterial (right) at the frequency of the transmission window.³⁴³ (B) Transmission spectra of the metamaterials.³⁴³ (C,D) False color SEM images of metamaterials made of Au nanorods. The scale bars are 200 nm.³⁴² (E,F) Transmittance and reflectance spectra of the corresponding structures shown in (C) and (D), respectively.³⁴² (G) Schematic showing the three-dimensional plasmon ruler.³⁴⁶ (H) Evolution of the plasmonic resonances as a function of the displacement of the middle nanorod.³⁴⁵ Adapted from the data of the cited papers by permission from The American Physical Society, Nature Publishing Group and The American Association for the Advancement of Science.

mode then transfers its energy to the dark mode sustained by the other two nanorods, where the interference between the two modes occurs through the near-field electromagnetic interaction. This interference results in a transmission window on the extinction spectrum of the metamaterial (Fig. 23B), a phenomenon resembling electromagnetic induced transparency observed in atomic physics. This plasmon-induced transparency has been successfully observed in a later experimental study, where similar structures were fabricated out of Au nanorods with electron-beam lithography.³⁴⁴ The scattering spectrum from an individual dolmen-style structure exhibits a dip at the resonance of the quadrupole mode.

By adopting a similar concept, Giessen *et al.* have successfully fabricated arrays of the dolmen-style structures consisting of Au nanorods using electron-beam lithography.³⁴² In comparison to the structure shown in Fig. 23A, a small difference was made in their study by stacking the nanorod supporting the dipolar plasmon resonance on top of the two parallel nanorods (Fig. 23C and D). For symmetrical structures, where the upper nanorod is placed at the center of the two parallel nanorods (Fig. 23C), the quadrupolar resonance cannot be excited and therefore the transmittance and reflectance spectra of the array resemble that of the dipolar plasmon resonance (Fig. 23E). Displacement of the upper nanorod away from the center brings symmetry breaking in the system (Fig. 23D). The symmetry breaking allows the quadrupolar plasmon mode to be efficiently excited, leading to the electromagnetic coupling between the dipolar and quadrupolar resonances. As a result, the dipolar resonance is suppressed by transferring its energy to the quadrupolar resonance, giving rise to a sharp peak of nearly perfect transmission within the broad absorption profile (Fig. 23F). In this circumstance, the narrow linewidth of the transmission

window is solely limited by the fundamental nonradiative Drude damping of Au nanorods. These features pave the way for slow-light photonic devices with ultralow losses.

Because plasmonic nanostructures enable large field strengths within small mode volumes, plasmonic metamaterials have great potential in the fabrication of compact sensors with extremely high sensitivities. By arranging Au nanorods in highly ordered arrays, the refractive index sensitivity of the obtained metamaterials has been shown to reach up to 30 000 nm per index unit due to the strong plasmon-mediated energy confinement inside the arrays.²⁴⁹ In biological applications, the ability to monitor nanoscale conformational changes is very important for studying and understanding many important dynamic processes of macromolecules and proteins in biological environments. However, this has still remained a great challenge, as most of current plasmonic sensing techniques rely on one- or two-dimensional configurations. In a very recent study, Liu *et al.* have made the first attempt toward this direction by extending the dolmen-style structures into three-dimensional domains.^{345,346} Their proposed structure is made by embedding a single Au nanorod in between two pairs of parallel Au nanorods (Fig. 23G). The coupling between the dipolar plasmon resonance of the middle nanorod (red) and the quadrupolar plasmon resonances of the two pairs of nanorods generates two transmission windows on the transmittance spectrum of the structure. The spectral positions of these two windows are strongly dependent on the lateral (Fig. 23H) as well as vertical displacements of the middle Au nanorod. In addition, the geometries of the two pairs of nanorods and their relative orientations can also place great impact on the transmission windows of the coupled structure. Therefore, the proposed plasmonic structure can act as a three-dimensional ruler for measuring the configuration changes of

adjacent objects, although the fabricated structure units, on the order of several hundred nanometers, are currently larger than many biological molecules.

7.4 Plasmon-assisted photochemical reactions

The plasmon resonances of metal nanostructures, owing to their strong light absorption capabilities, can benefit various photochemical reactions. Plasmon-enhanced photochemical reactions can be achieved by integrating metal nanocrystals with traditional photocatalysts, such as TiO_2 and iron oxides. On the one hand, the strong near field around metal nanocrystals under resonant excitation can accelerate the generation of electron–hole pairs in the adjacent semiconductors, whereby the related photochemical reactions can be enhanced. On the other hand, the reaction environment around metal nanocrystals can be heated up due to the plasmonic photothermal conversion. In addition, the collective electron oscillations associated with the plasmon resonance can decay into hot electrons through electron–electron scattering. These energetic electrons can thereafter participate in the reaction processes. These two photothermally related effects are important driving forces for enhancing photochemical reactions. In recent years, plasmon-assisted photochemical reactions have attracted much attention due to their great prospects in highly efficient utilization of solar energy, which is a promising solution to the worldwide energy crisis.^{347,348}

In comparison to commonly used spherical metal nanocrystals, the much larger electric field enhancements and synthetically tunable plasmon wavelengths of Au nanorods have made them excellent alternatives for applications in photochemical reactions. However, only until recently have people paid attention to the employment of Au nanorods in such applications.^{28,349} Misawa *et al.* have demonstrated plasmon-assisted water oxidation by fabricating Au nanorod arrays on the surface of TiO_2 electrodes.²⁸ Under the excitation of the longitudinal plasmon resonance of the nanorod array, the enhanced local field around the nanorods promotes water oxidation. As a result, the generation of O_2 and H_2O_2 is achieved using near-infrared light with energies far below the band gap of TiO_2 . The total yields of O_2 and H_2O_2 reach up to 82% in the presence of the light irradiation.

8. Conclusions and outlook

We have critically reviewed the current research status of Au nanorods, including their growth, functionalization, hybrid nanostructures, assembly, plasmonic properties, and related applications. From the review above, one can clearly see that Au nanorods possess various excellent chemical and physical properties, which are expected to enable their extensive applications in chemical/biomedical sensing and detection, optical and optoelectronic devices. To unleash their full potential as novel functional nanomaterials, in our opinion, future research should focus on the following directions.

The first is to overcome the energy loss in Au nanorods due to Ohmic dissipation. The Ohmic loss has placed great

limitations on the quality factors of the plasmon resonances of Au nanorods. The low quality factors will severely hinder the utilization of Au nanorods in future quantum computation and processing applications, where coherent control of optical signals is strongly needed. A few studies have suggested that bringing gain media in close proximity to metal nanostructures can efficiently compensate for their Ohmic losses. Regardless of its complexity, this strategy is promising for improving the quality factors of Au nanocrystals. However, for Au nanorods, there is still lack of experimental evidence.

The second future research direction should be the development of nanorod-based active plasmonic devices. Future optical processing and communication require ultrafast control of the optical and optoelectronic responses of various functional elements. The development of nanorod-based plasmonic devices that can be actively controlled by electric/magnetic fields, mechanical forces, and especially light will therefore be essential.

The third direction for future research is the development of effective procedures for controlled assembly of Au nanorods that are grown from the wet-chemistry, seed-mediated methods. Many optoelectronic devices require Au nanorod assemblies with different ordering and alignments. Nowadays only time-consuming, high-cost top-down methods can produce nanorod arrays with controlled nanorod geometries and orientations. However, the nanorods obtained from lithography methods are usually composed of small Au nanoparticles. Such a polycrystalline nature causes severe plasmon damping and therefore degrades the plasmon resonances of the nanorods. In contrast, the nanorods obtained from the wet-chemistry methods are mostly single-crystalline. Therefore, facile, highly controllable methods for assembling the colloidal nanorods are strongly desired for future device applications.

The fourth direction concerns the underlying mechanisms governing plasmon-assisted photochemical reactions. Although there have been several reports showing the promising future of using Au nanorods for enhancing photochemical reactions, the underlying physical and chemical processes are still unknown and controversial. Studying and understanding these mechanisms will undoubtedly help to design and fabricate nanorod-based hybrid nanostructures for efficiently utilizing solar energy in the near future.

For the biomedical, especially the *in vivo* applications of Au nanorods, a great amount of efforts should be made to elucidate the toxicity of Au nanorods in biological environments at different levels. The responses of the immune system to circulating Au nanorods should be understood and minimized, which will benefit their selective targeting. In addition, to efficiently clear and degrade Au nanorods has remained unexplored. Understanding the long-term effects of Au nanorods in biological species will be a great challenge.

Last, from a fundamental point of view, the development of analytical theoretical models that can rigorously describe the plasmon coupling in Au nanorod assemblies is very important for the use of assembled Au nanorods in various applications. Compared to the sophisticated numerical methods, theoretical

models can provide the necessary physics underlying various plasmon coupling phenomena and offer instincts in discovering new plasmon-related phenomena and applications.

To sum up, we strongly believe that devotion of great efforts to the six directions given above will undoubtedly expedite the research progress on Au nanorods. Many exciting scientific discoveries and technological applications will certainly come up along with the progress in this exciting and promising field.

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