

Uniaxial Plasmon Coupling through Longitudinal Self-Assembly of Gold Nanorods

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We report a new paradigm for tuning the optical properties of gold nanorods by organizing them longitudinally, using thioalkylcarboxylic acid based bifunctional molecules. The rationale behind the selection of the bifunctional molecule is based on the fact that the thiol group binds to the ends of the nanorods, which further assembles in a longitudinal fashion through cooperative hydrogen bonding between the carboxylic groups. A generalized procedure for uniaxial plasmon coupling through longitudinal self-assembly of Au nanorods, initially to dimers and further to linear assemblies, is presented. Uniaxial modulation of interplasmon coupling through stepwise self-assembly of Au nanorods will have application in nanoelectronics and plasmonics.

Nanotechnology is fundamentally changing the way in which materials are synthesized and devices are fabricated.¹ For example, hierarchical integration of nanoscale building blocks (nanoparticles, nanorods, nanotubes, etc.) into functional assemblies and further into multifunctional devices can be achieved through a “bottom up approach”.² Self-assembly of Au nanorods driven by surfactants,^{3a} DNA molecules,^{3b} and their preferential end to end assembly using biotin-streptavidin connectors⁴ have been demonstrated. Such closely packed metal nanoparticles and nanorods can, in principle, function as guides of electromagnetic radiation (waveguides) allowing miniaturization of devices below the diffraction limit.⁵ Tailoring the optoelectronic properties of nanomaterials through the stepwise integration of nanoscale building blocks is one of the major challenges in the area of nanotechnology. Herein we report a simple strategy for selectively tuning the longitudinal plasmon absorption band of Au nanorods by interconnecting them linearly, through cooperative hydrogen bonding.

Gold in its nanometric dimension possesses shape dependent optical and electronic properties. For example, Au nanorods possess two absorption bands, one at a shorter wavelength (~ 520 nm) and the other at a longer wavelength which undergoes a bathochromic shift with increasing aspect ratio.⁶ In the present study, gold nanorods of various aspect ratios were synthesized photochemically,⁷ and the TEM image obtained by drop casting Au nanorods (average aspect ratio 3) onto a carbon coated copper grid from a concentrated stock solution is presented in Figure 1A. The heavy capping of surfactant molecules keeps the nanorods well separated, and spacing between the nanorods are more or less uniform. A comparison of the absorption spectra of Au nanorods (aspect ratio 3) in water and acetonitrile–water mixture (4:1) is shown in Figure 1B. The spectral properties of Au nanorods remain unaffected on increasing the composition of acetonitrile and the rods were

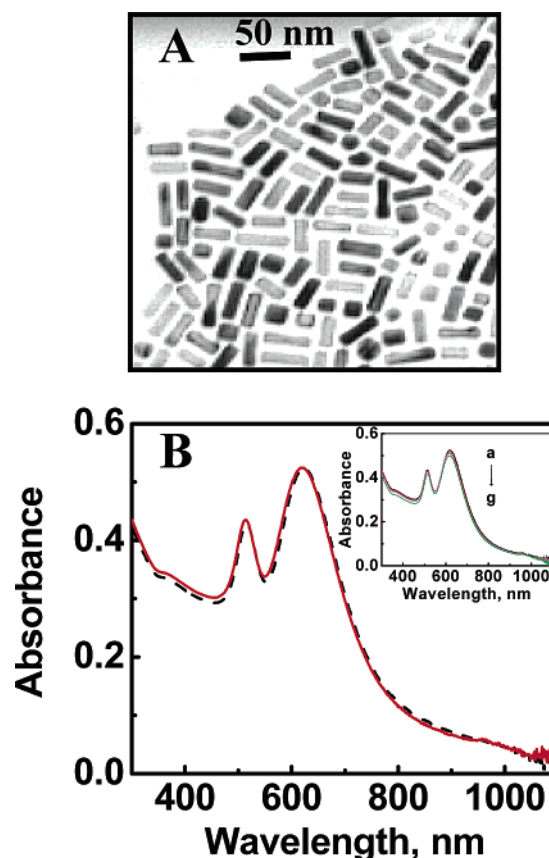


Figure 1. (A) TEM image of gold nanorods (aspect ratio 3) drop cast from a concentrated stock solution. (B) Absorption spectrum of Au nanorods (aspect ratio 3) recorded in water (solid line) and acetonitrile–water (4:1; dotted line). Inset shows the absorption spectrum of the nanorods in acetonitrile–water (4:1) (a) immediately and (b–g) at 2 h intervals from 1 to 11 h.

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found to be stable for several hours (inset of Figure 1B). The integrity of the rods, on dilution, was further confirmed through TEM studies.

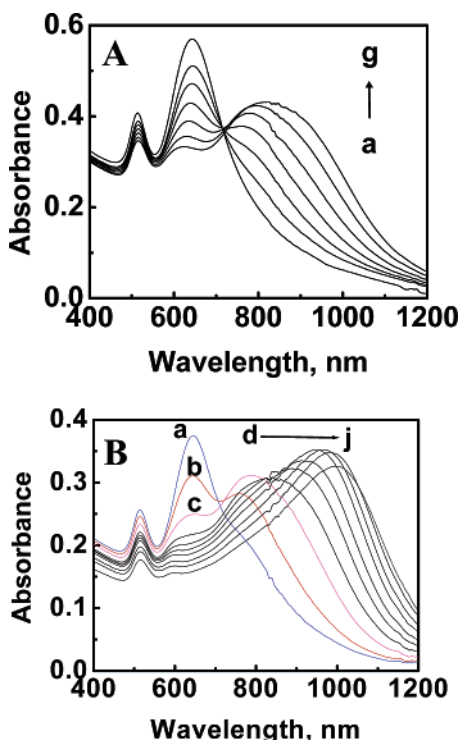


Figure 2. (A) Absorption spectra of gold nanorods (aspect ratio 3) in acetonitrile–water (4:1) recorded immediately after the addition of MPA. [MPA]: (a) 0, (b) 3.6, (c) 4.5, (d) 5.4, (e) 6.3, (f) 7.2, and (g) 8.1 μM . (B) Absorption spectra of gold nanorods in acetonitrile–water (4:1) at different time intervals after addition of 15 μM MPA; (a) 0, (b) 4, (c) 8, (d) 12, (e) 16, (f) 20, (g) 30, (h) 45, (i) 60, and (j) 120 min.

Nature adopts cooperative hydrogen bonding for assembling simple molecular units to supramolecular assemblies which performs many complex biological functions. In the present study, we have utilized the intermolecular hydrogen bonding ability of carboxylic acid derivatives, namely, 3-mercaptopropionic acid (MPA) and 11-mercaptoundecanoic acid (MUA), for assembling Au nanorods. The selection of these molecules is based on the rationale that the thiol group can bind to the surface of Au nanorods and the appended carboxyl groups assist in the self-assembly of nanorods through intermolecular hydrogen bonding.

Addition of varying amounts of MPA in acetonitrile–water (4:1) led to a decrease in the absorption of the long wavelength band, accompanied by the formation of a red-shifted absorption band. After each successive addition of MPA, the solution was kept for 5 min and the absorption spectra were recorded. The absorption spectra recorded immediately after the addition of a known amount of MPA exhibited a new red-shifted absorption band with an isosbestic point at 720 nm (Figure 2A).

The isosbestic point observed at 720 nm indicates the existence of Au nanorods in two different forms (expression 1)



Interestingly, the short wavelength band of Au nanorods remains unaffected upon addition of MPA. Similar results were also obtained when we employed MUA instead of MPA (see the Supporting Information). To obtain further insight into the interaction of these bifunctional molecules with Au nanorods, we investigated the absorption spectral changes as a function of (i) time, (ii) solvent polarity, and (iii) aspect ratio.

On addition of a known amount of MPA/MUA, first we observed the formation of a new red-shifted absorption band

with a clear isosbestic point at 720 nm (traces a to c in Figure 2B). The newly formed absorption band at 800 nm slowly shifted toward longer wavelength with increasing time (traces d to j in Figure 2B) and this time dependent bathochromic shift in the absorption is more pronounced at higher concentrations of MPA (or MUA). We attribute these changes to the further propagation of the linear assembly of Au rods. The initially formed dimer rods in MPA solution continue to grow through intermolecular hydrogen bonding to yield rod assemblies of different lengths. Since the nanorod assemblies of different lengths exhibit different spectral maximum, we see a collective response of broader absorption, without any isosbestic spectral features. Similar spectral changes were observed when water is used as solvent and also upon addition of MPA (or MUA) to Au nanorods of four different aspect ratios ranging 3.0–4.0. The half width of the newly formed absorption band increased with increasing aspect ratio (see the Supporting Information).

The unusual absorption spectral changes observed in the present system is explained on the basis of interplasmon coupling phenomenon. When an electromagnetic radiation interacts with Au nanoparticles, its electric vector displaces electron cloud with respect to the nuclear framework. A restoring force arises due to the Coulombic attraction between the electron cloud and nucleus, which establishes an oscillation.^{8a} Surface plasmon absorption originates when this frequency of oscillation resonates with the frequency of the incident radiation. Various factors such as size and shape of nanoparticles and the charge distribution on particles influence the plasmon absorption. Electric field alignment studies have shown that the short wavelength band (~ 520 nm) originates from the transverse mode of vibration and the long wavelength band from the longitudinal mode of vibration.^{8b} Selective decrease in the intensity of longitudinal plasmon absorption band and the formation of a new red shifted band (Figure 2) suggest that the isolated Au nanorods organize linearly upon addition of MPA or MUA. Such an organization allows uniaxial plasmon coupling in a longitudinal fashion.

To verify the linear organizational aspect, TEM images of gold nanorods were recorded in the absence and presence of MPA under similar experimental conditions. TEM samples were prepared by drop casting the solution used for spectroscopic investigation onto a carbon coated copper grid. These solutions are relatively dilute compared to the one employed in Figure 1A. The sample deposited from a suspension that does not include MPA shows a random distribution of Au nanorods (Figure 3A). On the other hand, MPA bound rods are self-assembled longitudinally (Figure 3B–D). Isolated linear arrays of gold nanorod::MPA assemblies could be seen throughout the grid, and the images from three different regions of the grid are shown in Figure 3.

Similar alignment of rods in an end to end fashion was recently observed in the biotin capped Au nanorod–streptavidin system.⁴ As indicated in this study, thiol derivatives preferentially bind to the {111} ends of the rods exposing the carboxylic acid of the MPA for further interactions through intermolecular hydrogen bonding. The intermolecular dimerization of carboxylic acids is known to occur in nonpolar hydrophobic environments. In the present case, the long alkyl chains of CTAB (cetyltrimethylammonium bromide) create a hydrophobic microenvironment near the surface of gold nanorods. Such a nonpolar local environment is favorable for the dimerization of appended carboxylic acids (inset of Scheme 1). Thus, the carboxyl groups appended at the ends of Au nanorods dimerize

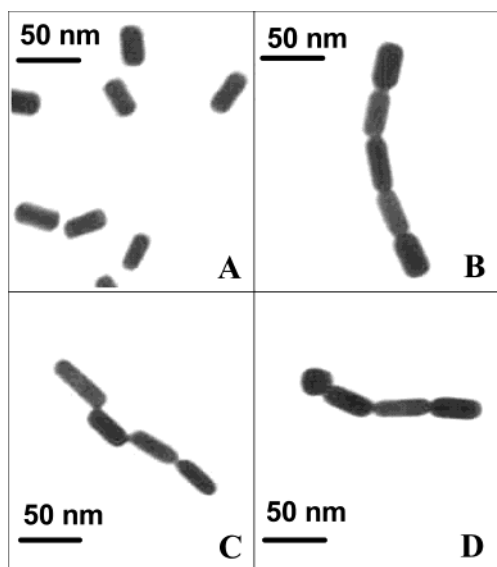
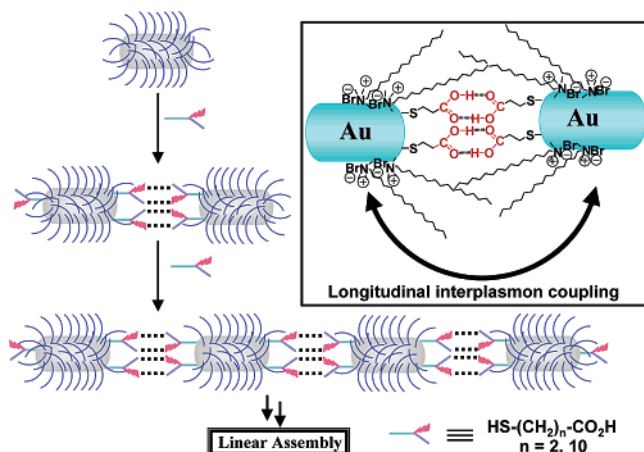


Figure 3. TEM images of (A) Au nanorods in the absence of MPA. Parts B–D are three separate examples of linearly assembled Au nanorods in the presence of MPA.

SCHEME 1: Pictorial Representation of the Linear Self-assembly of Gold Nanorods^a



^a The inset shows the intermolecular hydrogen bonding between MPA on adjacent nanorods.

through intermolecular hydrogen bonding, assisting the linear organization of Au nanorods.

Such a linear assembly of nanorods helps us to explain the origin of the new red-shifted band by means of a dipolar interaction mechanism. The perturbed charge distribution on assembled Au nanorods in the presence of external electromagnetic radiation results in an additional attractive force between the polarized negative and positive charges on adjacent rods. This additional attractive interaction, in turn, decreases the frequency of longitudinal plasmon oscillation, and such interparticle plasmon interactions were observed in closely spaced Au nanoparticles deposited on ITO glass plates⁹ and quartz.¹⁰ In the present case, the spectral interconversions are observed through an isosbestic point (Figure 2A and traces a–c in Figure 2B) indicating the existence of two different forms. Thus, the newly formed red shifted absorption band, observed upon addition of MPA or MUA, is assigned to the longitudinally

coupled plasmon absorption originating from the dimerized form of Au nanorods (Scheme 1). The time dependent bathochromic shift of the absorption to the NIR region indicates that these dimerized nanorods further interact in a linear fashion, through stepwise self-assembly and form oligomers, as indicated in Scheme 1. Such large shifts in longitudinal plasmon absorption were observed for Au nanorods of a large aspect ratio.¹¹

To check the reversibility of hydrogen bonding, absorption spectral changes were studied by varying the temperature (25–70 °C) which indicated that the Au nanorod:::MPA assembly precipitates at a higher temperature. Addition of acetic acid has no influence on plasmon absorption bands of Au nanorods, whereas both of the plasmon bands got dampened on addition of alkanethiol such as dodecanethiol, possibly due to aggregation (see the Supporting Information).

In conclusion, we have demonstrated that the longitudinal plasmon absorption of Au nanorods can be selectively modulated through their linear assembly, assisted by the cooperative intermolecular hydrogen bonding of anchored carboxylic acids. Approaches presented here for connecting nanomaterials into desired shapes and thereby tuning their optoelectronic properties may have wide-range application in nanotechnology, particularly in nanoelectronics and plasmonics.

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Supporting Information Available: Experimental section includes the photophysical studies of Au nanorods of different aspect ratios with MPA/MUA in water and CH₃CN–H₂O mixtures (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) Roco, M. C.; Williams, R. S.; Alivisatos, P., Eds.; *Nanotechnology Research Directions*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2001.
- (2) (a) Shipway, A. N.; Katz, E.; Willner, I. *ChemPhysChem* **2000**, *1*, 18. (b) Shenhar, R.; Rotello, V. M. *Acc. Chem. Res.* **2003**, *36*, 549. (c) Thomas, K. G.; Kamat, P. V. *Acc. Chem. Res.* **2003**, *36*, 888. (d) Kamat, P. V. *J. Phys. Chem. B* **2002**, *106*, 7729.
- (3) (a) Nikoobakht, B.; Wang, Z. L.; El-Sayed, M. A. *J. Phys. Chem. B* **2000**, *104*, 8635. (b) Dujardin, E.; Hsin, L.-B.; Wang, C. R. C.; Mann, S. *Chem. Commun.* **2001**, 1264.
- (4) Caswell, K. K.; Wilson, J. N.; Bunz, U. H. F.; Murphy, C. J. *J. Am. Chem. Soc.* **2003**, *125*, 13914–13915.
- (5) Maier, S. A.; Brongersma, M. L.; Kik, P. G.; Atwater, H. A. *Phys. Rev. B* **2002**, *65*, 193408.
- (6) Link, S.; Mohammed, M. B.; El-Sayed, M. A. *J. Phys. Chem. B* **1999**, *103*, 3073.
- (7) Kim, F.; Song, J. H.; Yang, P. *J. Am. Chem. Soc.* **2002**, *124*, 14316.
- (8) (a) Kelly, K. L.; Coronado, E.; Zhao, L. L.; Schatz, G. C. *J. Phys. Chem. B* **2003**, *107*, 668. (b) Felidj, N.; Aubard, J.; Levi, G.; Krenn, J. R.; Schider, G.; Leitner, A.; Aussenegg, F. R. *Phys. Rev. B* **2002**, *66*, 245407.
- (9) Rechberger, W.; Hohenau, A.; Leitner, A.; Krenn, J. R.; Lamprecht, B.; Aussenegg, F. R. *Opt. Commun.* **2003**, *220*, 137.
- (10) Su, K.-H.; Wei, Q.-H.; Zhang, X.; Mock, J. J.; Smith, D. R.; Schultz, S. *Nano. Lett.* **2003**, *3*, 1087.
- (11) Jana, N. R. *Chem. Commun.* **2003**, 1950.