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Synthesis of Silver Nanorods by Low Energy Excitation of Spherical Plasmonic Seeds

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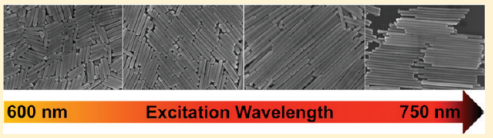
Supporting Information

ABSTRACT: Plasmon excitation of Ag seed particles with 600−750 nm light in the presence of Ag^+ and trisodium citrate was used to synthesize penta-twinned nanorods. Importantly, the excitation wavelength can be used to control the reaction rate and, consequently, the aspect ratio of the nanorods. When the excitation wavelength is red-shifted from the surface plasmon resonance of the spherical seed particles, the rate of Ag^+ reduction becomes slower and more kinetically controlled. Such conditions favor the deposition of silver onto the tips of the growing nanorods as compared to their sides, resulting in the generation of higher aspect ratio rods. However, control experiments reveal that there is only a range of low energy excitation wavelengths (between 600 and 750 nm) that yields monodisperse nanorods. This study further highlights the utility of using wavelength to control the size and shape of growing nanoparticles using plasmon-mediated methods.



KEYWORDS: Silver, nanorods, plasmon, synthesis, low energy excitation

Light can be a valuable tool for influencing nanoparticle growth and realizing anisotropic nanostructures.[1−3] Indeed, in early work, we demonstrated that silver spherical nanoparticles could be converted into triangular nanoprisms using visible light and plasmon excitation of the spherical seed particles.[1] One advantage of this photomediated process over subsequently developed thermal methods[4] is that irradiation wavelength can be used to exquisitely control the dimensions of the products, with longer wavelengths yielding larger nanoprisms.[2,5] Since the initial work with silver, others have shown that photostimulation of certain nanostructures can be used to direct their growth and assembly into larger and more exotic structures.[6,7] For example, a variety of groups have shown that irradiation of semiconductor nanorods with UV and visible wavelengths can be used to control the deposition of metal ions on the ends of the nanorods as opposed to the random deposition observed by the thermally controlled reduction process.[8−11] Kotov and co-workers have shown that photostimulation of semiconductor nanoparticles can be used to assemble them into twisted ribbon-like structures, which do not form in the absence of irradiation.[7]

Since the initial report of the photomediated synthesis of silver triangular nanoprisms,[1] there has been much interest in understanding how light and selective plasmon excitation can be used to direct the size and shape of a growing noble metal nanostructure. Despite the numerous studies on the growth of the triangular prism morphology,[1,2,5,12−21] there are only a limited number of other shapes that can be synthesized in high yield using photomediated methods. These include right triangular bipyramids,[22] tetrahedra,[23] and decahedra.[24,25] Mechanistic studies of these reactions have determined that plasmon excitation of silver nanoparticle seeds is responsible for photocatalytically reducing Ag^+ to Ag^0 by trisodium citrate.[3,26] Indeed, if the surface plasmon resonance (SPR) of the seed particles is not excited—due to either the absence of photostimulation or a mismatch between the excitation wavelength (λ_{ex}) and the SPR of the seeds—the reaction does not occur.[14] This phenomenon is partially responsible for imparting wavelength-controlled size effects in the triangular nanoprisms synthesis: as the prisms grow and their SPRs red shift from the excitation wavelength, the prisms absorb less light and their growth slows.[2,5,13,16,22] However, not all plasmon-mediated syntheses demonstrate such wavelength-dependent behavior, and considering the relatively few morphologies that can be accessed by plasmon-mediated methods compared to thermal methods,[27,28] there is a need to gain a better understanding of the physical and chemical reasons for how excitation wavelength influences the size and, importantly, the shape of a growing particle.

Herein, we report that under appropriate conditions silver nanorods can be selectively synthesized using 600−750 nm light. Nanorods have not been previously accessible by plasmon-mediated reactions in high yield.[29] We also demonstrate that λ_{ex} can be used to effectively control the aspect ratio of the nanorods. Importantly, we show that the further λ_{ex} is from the SPR of the spherical seed particles, the slower and more kinetically controlled the reaction becomes. Such conditions result in the preferred reduction of Ag^+ onto the ends of the nanorods as compared to their sides, resulting in higher aspect ratio rods. Control experiments reveal that excitation wavelengths longer than 750 nm result in incomplete reactions due to the extremely small extinction coefficient of the silver seed particles within this region, while excitation wavelengths shorter than 600 nm give poor yields due to the growth of other nanoparticle shapes such as bipyramids. These results highlight

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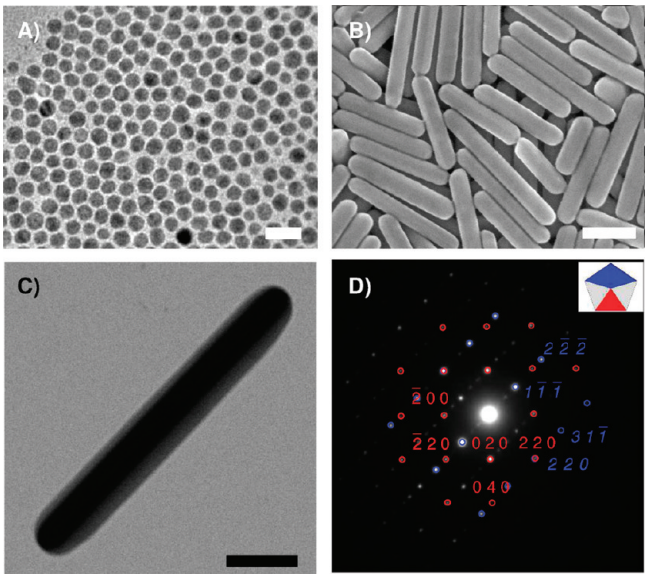

Figure 1. (A) TEM image of the silver seed nanoparticles. (B) SEM and (C) TEM images of silver nanorods synthesized with a bandpass filter centered at 600 ± 20 nm. (D) Selective-area electron diffraction (SAED) pattern of a single silver nanorod, showing the interpenetrating [100] (red) and [112] (blue) zone patterns. (Scale bars: 100 nm).

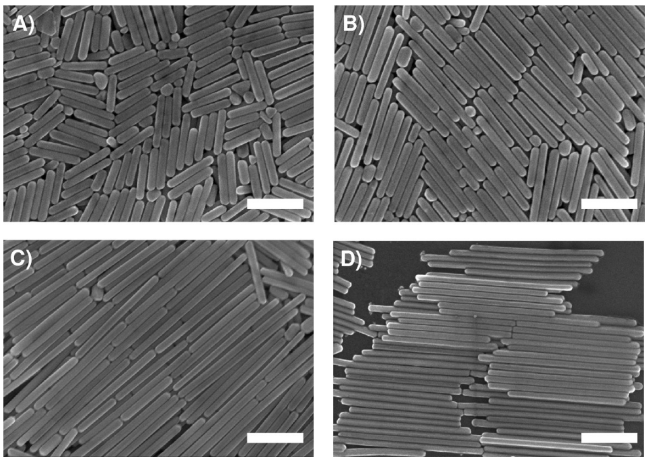

Figure 2. SEM images of the silver nanorods (scale bars: 400 nm) generated with the bandpass filter centered at (A) 600 ± 20, (B) 650 ± 20, (C) 700 ± 20, and (D) 750 ± 20 nm.

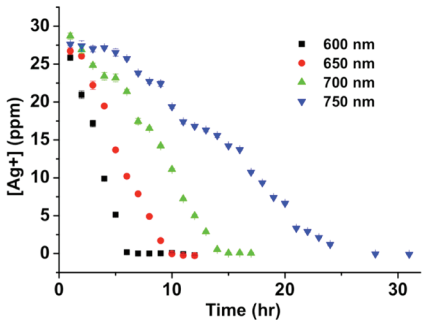

Figure 3. ICP-OES data monitoring the change in the concentration of unreacted Ag^+ for reactions at different λ_{ex}.

both the utility and limitations of using λ_{ex} to control product morphology in plasmon-mediated reactions. Indeed, there is only a range of low energy excitation wavelengths ($600 \leq \lambda_{ex} \leq 750$ nm) that yield monodisperse nanorods.

Our photoinduced synthesis is based on a seed-mediated approach. First, monodisperse spherical seed nanoparticles with an average diameter of 7.9 ± 0.9 nm were prepared by irradiating an aqueous solution containing $AgNO_3$, bis(*p*-sulfonatophenyl)-phenylphosphine dihydrate dipotassium salt (BSPP), trisodium citrate, and sodium hydroxide with 254 nm light (Figure 1A, see Experimental Section in Supporting Information for details). Note that this synthetic method yields spherical particles with pentagonal twin structures (*vide infra*), which are significantly different from the seed particles used in previous nanoprism syntheses that have planar twin defects.[1,2,5] To synthesize silver nanorods, the penta-twinned seed particles (0.5 mL) were added to an aqueous growth solution containing $AgNO_3$ (0.2 mM) and sodium citrate (1.0 mM) and then irradiated for 24 h using a 150 W halogen lamp and a bandpass filter to selectively tune the λ_{ex} from 600 to 750 nm.

The photomediated reaction (λ_{ex} = 600 nm) yields nanorods with uniform diameters (67 ± 5 nm) and lengths (330 ± 85 nm) (Figure 1, panels B and C). These nanorods have pentagonal cross sections and are multiply twinned along their long axes, as indicated by the electron diffraction patterns showing either interpenetrated [112] and [100] zone patterns or [111] and [110] zone patterns from an face-centered cubic structure (Figure 1D and Figure S2, Supporting Information), which is characteristic of a pentagonal multiple twinned structure.[30,31] The penta-twinned structure of the silver nanorods can be partially attributed to the structure of the seed particles, which also have a pentagonal multiple-twinned structure, as shown by high-resolution TEM (Figure S3, Supporting Information). The importance of the seed morphology was confirmed by several control experiments where either no silver seeds or silver seeds of different sizes and structures were used. In all cases, silver nanoparticles that differed in shape, including spheres, rods, triangular prisms, and plates were generated (Figure S4, Supporting Information).

Remarkably, the length and the diameter of the nanorods are highly tailorable through λ_{ex}. Reactions mediated by 650 ± 20, 700 ± 20, and 750 ± 20 nm light generated silver nanorods with lengths of 460 ± 130, 870 ± 250, and 1010 ± 230 nm, and diameters of 66 ± 6, 61 ± 5, and 51 ± 5 nm, respectively (Figure 2 and Figure S5, Supporting Information). Therefore, the aspect ratio of the silver nanorods increases as the λ_{ex} increases from 600 to 750 nm. This indicates that in this photomediated synthesis, λ_{ex} can indeed be used as a parameter to control the dimensions of the resulting nanoparticles, similar to the synthesis of nanoprisms[2,5,13] and triangular bipyramids.[22]

To investigate the wavelength-dependent growth process, we examined the reaction kinetics by monitoring the concentration of Ag^+ during the entire course of the reaction using inductively coupled plasma optical emission spectroscopy (ICP-OES) (Figure 3). The depletion rate of Ag^+ decreases as λ_{ex} becomes longer, indicating that as the reaction rate is slowed the aspect ratio of the nanorods increases. (Note that the intensity of the excitation light is fixed at all four wavelengths.) This is likely due to the reactions becoming more kinetically controlled as the λ_{ex} is red-shifted from the SPR of the seeds. While the spherical seed

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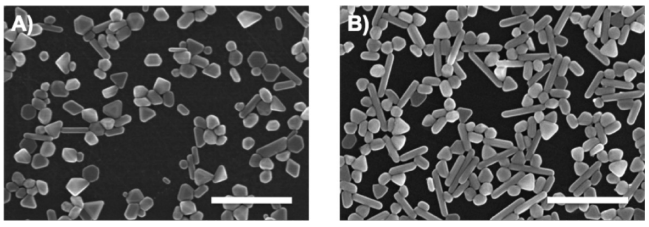

Figure 4. SEM images of the nanoparticles (scale bars: 400 nm) generated at different λ_{ex}: (A) 500 nm; (B) 550 nm.

particles have an extinction maximum at 395 nm, the colloid extinction spans the entire visible range, with a decreasing absorbance at longer wavelengths.[3] Because the seeds are only able to absorb a small amount of incident light at such low energy wavelengths, the plasmon-mediated reduction of Ag^+ occurs extremely slowly. Such kinetically controlled reaction conditions favor deposition onto the highest energy locations of the nanostructures, which in the case of the nanorods is at the tips due to the high curvature and presence of twin defects.[32] At longer λ_{ex} the seeds absorb less light and the reaction proceeds more slowly, resulting in an increased preference for reduction onto the tips as compared to the sides of the nanorods, ultimately yielding nanorods with higher aspect ratios. Similar behavior was observed for the plasmon-mediated synthesis of silver right triangular bipyramids and prisms where a slower reaction rate induced by a low pH results in preferred deposition onto twin defects to yield planar triangular nanoprisms.[33] This conclusion is also consistent with the thermal synthesis of silver nanorods where the aspect ratio is controlled through chemical parameters that influence the reaction rate. Typically, a slower reaction rate, induced by a lower seed concentration,[32] temperature,[34] or pH,[34] yields nanorods/nanowires with a higher aspect ratio. We note that Kitaev and coworkers have previously reported a thermal method to prepare penta-twinned silver nanorods by the regrowth of well-defined silver decahedral seeds in a 95 °C aqueous solution containing citrate and poly(vinylpyrollidone).[35] They are able to control the diameter and length of the resulting nanorods by controlling the size of the decahedral seeds and the amount of Ag^+ added to the reaction, respectively. In the plasmon-mediated method presented herein, both the diameter and the length of the resulting nanorods are affected by λ_{ex}. Therefore, this plasmon-mediated method provides a nice complement to the thermal preparation by Kitaev and coworkers.

However, the ability to control the product shape exclusively through λ_{ex} is limited. In control experiments where shorter λ_{ex} such as 500 and 550 nm are used, only a small amount of nanorods form and they are mixed with other morphologies such as triangular plates and truncated bipyramids (Figure 4). Structurally, penta-twinned nanorods grow from penta-twinned seeds, while triangular plates and truncated bipyramids grow from planar twinned seeds. The diverse growth pathways observed at shorter wavelengths can be tentatively attributed to the different growth kinetics of different seed morphologies under the present experimental conditions. Upon low energy excitation, Ag is preferentially deposited onto penta-twinned seeds, while at shorter λ_{ex} Ag is preferentially deposited onto other structured seeds (such as planar-twinned seeds). Typically, shape control is chemically achieved by reaction conditions such as pH,[31,36] reagent concentration,[37] or additives[23,25] that can effectively control the reaction kinetics and, consequently, the product morphologies. In plasmon-mediated syntheses, excitation wavelength, when combined with appropriate reaction conditions, has been used to control nanoparticle size and shape in the context of triangular prisms[2,5,13] and right triangular bipyramids.[22] Recently, researchers have suggested that λ_{ex} could be used as a single variable for directing nanoparticle shape.[24,29] For example, silver nanoparticles, under identical conditions, yield decahedra when irradiated at λ_{ex} = 455 or 465 nm but triangular nanoprisms when irradiated at λ_{ex} = 505 or 519 nm.[24,29] Taken together, these data show that wavelength can be a powerful shape modulator in plasmon-mediated nanoparticle syntheses.

In conclusion, we have demonstrated that photomediated methods can be used to effectively prepare silver nanorods in a controllable manner. Upon low energy excitation, the penta-twinned seeds particles can grow into nanorods with different aspect ratios depending on the λ_{ex}. A study of reaction kinetics reveals that λ_{ex} affects the reduction rate of Ag^+ and, consequently, controls the aspect ratio of the nanorods. Slower and more kinetically controlled reactions induced by lower energy λ_{ex} result in the generation of higher aspect ratio nanorods due to preferred reduction onto the tips as compared to the sides. Previous mechanistic studies involving the conversion of spherical seeds into triangular prisms have concluded that plasmon excitation is responsible for facilitating the reduction of Ag^+ by citrate, although the physical nature of this process is not well understood.[3,26] The present study further emphasizes that when combined with suitable conditions, λ_{ex} can be used to finely tailor the kinetics of the plasmon-mediated reduction reaction and thus provides an elegant method for controlling the architectural parameters of the resulting silver nanostructures.

■ ASSOCIATED CONTENT

Supporting Information. Experimental details; UV/vis/NIR spectra of the nanorods in D_2O; selective-area electron diffraction (SAED) pattern of a single silver nanorod; a high-resolution TEM image of the silver seed particles; SEM images of the products obtained from the reactions with no seeds, and with seeds synthesized by different methods; statistical analysis of the length of the nanorods. This material is available free of charge via the Internet at http://pubs.acs.org.

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