Spherical ended and arrow ended gold nanodumbbells were synthesized by a simple approach of introducing gold nanorods to solutions of sodium hydroxide and ascorbic acid, respectively. From UV-visible absorption spectroscopy, the transverse and longitudinal surface plasmon resonance that corresponds to electron oscillations perpendicular and parallel to the gold nanorods showed either blue or red shift, depending on the concentration of the acid or alkali solution. The morphological change from gold nanorods to spherical ended and arrow ended dumbbells was assessed by transmission electron microscopic (TEM) analysis. A theoretical model using the volume integral equation method was used to simulate the surface plasmon resonance of the gold nanodumbbells, which was in good agreement with the experimental observations. From the experimental observations and numerical calculations, a new growth mechanism for gold nanodumbbells is proposed.

Introduction

One dimensional gold nanoparticles are scientifically intriguing due to their unique properties and wide application in materials science, molecular electronics, catalysts and sensors. The surface plasmon absorption bands of gold nanorods are different from those of gold nanoparticles. Gold nanorods exhibit transverse and longitudinal surface plasmon resonances (SPR) that correspond to electron oscillations perpendicular and parallel to the rod length, respectively. When plasmonic nanoparticles (gold or silver) are exposed to laser light resonant with their surface plasmon oscillation, they can strongly absorb the light and rapidly convert it into heat via a series of photophysical processes. This has been shown to be an effective photothermal therapeutic method for application in diagnostics of cancerous cells.

Another remarkable feature of plasmonic nanorods is their tunable optical properties, which can be realized through the tailoring of their nanostructure. The longitudinal modes of the SPR of gold nanorods are very sensitive to changes in the ratio of length to diameter. By tailoring the aspect ratio of nanorods, the longitudinal SPR peak can be red shifted or blue shifted. This can then be used to tune the wavelength position and intensity of surface plasmon absorption. The tailoring of the SPR to a particular wavelength is quite useful, for example in in vivo applications of tissue absorption, where the absorption window lies in the near-infrared region (650–900 nm), and thus is favorable to optimal light penetration. Therefore, considerable effort has been focused on tailoring the sizes and shapes of plasmonic nanorods. This has wide application in biochemical sensing, biological imaging, medical diagnostics, and therapeutics. The seed-mediated growth method is the most popular method for the synthesis of colloidal gold nanorods. Recently, this method has been modified by Nikoobakht and El-Sayed to produce a high yield of gold nanorods and reduce the output of spherical particles. On this basis, several tailored shapes and structures of gold nanoparticles, such as nanorings, nanoplates, dendrimer-like shapes, nanocubes, nanoprisms, crooked nanorods, nanodumbbells and nanonetworks have been synthesized and studied. Although nanodumbbells with arrow and spherical ends have already been synthesized using similar methods in previous papers, different reaction mediums were used (e.g. in ref. 32, glycine buffers are used and in ref. 35, only L-ascorbic acid is used). Here, two kinds of surfactants, benzyltrimethylammonium chloride hydrate (BDAC) and hexadecyltrimethylammonium bromide (CTAB) are used. The investigation in ref. 32 focused on the control of gold nanoparticle shape (from rectangular, 'dogbone'- and peanut-like outlines to branched multipods with corrugated surfaces) by varying the pH of the reaction medium, and ref. 35 mainly studied the synthesis of arrow-headed Au nanorods and Au nano-octahedra by using ascorbic acid (AA) and controlling the ratios of AA : Au$^{3+}$ and Au$^{3+}$: Ag$^+$, respectively. On the
contrary, the mechanism of the growth of the tailored nanostructure and its effect on surface plasma absorption bands is complex, and is not completely understood. However, the research aspect is of great significance for practical application in medical and biochemical sensing and medical diagnostics, and therefore it is important to assess these phenomena.

In this paper, gold nanorods with a uniform distribution of length to diameter ratios were synthesized. By the addition of different concentrations of ascorbic acid and sodium hydroxide to the gold nanorods, arrow and spherical ended gold nanodumbbells were produced with distinctive surface plasmon resonance. Based on the morphological change observed with transmission electron microscopy, and their optical absorption using UV-visible spectroscopy, the mechanism of the structural change was simulated by volume integral equation theory, and a new growth mechanism for the gold nanodumbbells is proposed. The theoretical model and numerical simulations were consistent with observed experimental results.

Experimental

Growth of Au nanorods

Gold nanorods were prepared using the improved seed-mediated growth method. The synthesis steps are as follows: firstly, the seed solutions were prepared by the reduction of auric acid in the presence of (1-hexadecyl)trimethylammonium bromide (CTAB) by mixing 5 mL of 0.20 M CTAB with 5.0 mL of $5 \times 10^{-4}$ M HAuCl₄, followed by stirring. Then 0.6 mL ice-cold sodium borohydride (0.01 M) was added quickly with vigorous stirring of the seed solution for another 2 min, which resulted in the formation of a brownish yellow solution. The growth solution was prepared by adding 0.22 mL of 0.004 M AgNO₃ solution (the aspect ratio of gold nanorods can be controlled by adding AgNO₃ in the reaction) to 5 mL of a mixed solution of 0.2 M CTAB and 0.15 M benzylcetyltrimethylammonium chloride hydrate (BDAC). To this solution, 5.0 mL of 0.001 M HAuCl₄ was added and the solution was stirred. This was followed by the addition of 60 μL of 0.0788 M acid solution were mixed into the solution sequentially, after which the absorption spectrum of the sample was taken to measure the shift in the longitudinal surface plasmon resonance peak. Ascorbic acid was added until the position of the longitudinal surface plasmon resonance peak did not shift.

Structural and optical characterizations

The absorption (extinction) spectra of the Au nanorod solutions were taken using a UV-visible spectrophotometer (Lambda 35 101N605705, PerkinElmer). Transmission electron microscopy (TEM) images were taken at 80 kV using a Hitachi H-7650 transmission electron microscope path length on a Hitachi U-3501 UV visible/NIR spectrophotometer.

Results and discussion

A typical TEM image of the starting gold nanorods is shown in Fig. 1(a). The average length of the gold nanorods was 47.95 ± 7.55 nm and the diameter was 9.16 ± 1.28 nm, which gave an aspect ratio of 5.23. Fig. 1(b) shows a high-resolution TEM image of an Au nanorod, which revealed that the gold nanorods were confined by the {100} faces, and stacked along the {100} direction. Upon addition of sodium hydroxide to the gold nanorods, the morphology of the Au nanorods changed to spherical ended nanodumbbells. Fig. 1(c) shows the TEM image of spherical ended Au nanodumbbells prepared by the addition of sodium hydroxide to the gold nanorods. From the microstructure, the average length of the spherical ended dumbbells was found to be 56.53 ± 5.96 nm and the average diameter was 15.81 ± 1.45 nm, giving an aspect ratio of 3.61 ± 0.56. Compared
with the Au nanorods, it is evident that the length and diameter of the spherical ended gold nanodumbbells increased, whereas the aspect ratio decreased. On addition of ascorbic acid, the gold nanorods transformed from a cylindrical shape to arrow ended Au nanodumbbells. Fig. 1(d) shows the TEM image of the Au nanodumbbells prepared with the addition of ascorbic acid (C₆H₈O₆). The average length and diameter of the arrow ended dumbbells were found to be 63.71 ± 7.81 nm and 13.06 ± 1.38 nm, which gave an aspect ratio of 4.87 ± 0.56. The arrow heads had a length of 22.04 ± 1.41 nm. In comparison with the original gold nanorods, it is evident that the length and diameter of arrow ended dumbbells have increased, while the aspect ratio has decreased.

Different from spherical Au nanoparticles, the surface plasmon absorption bands of gold nanorods have two modes, namely transverse and longitudinal modes which correspond to electron oscillations perpendicular and parallel to the rod length direction, respectively.

The longitudinal surface plasmon wavelengths (LSPWs) are tunable from the visible to the infrared region by tailoring the microstructural shape. This tailoring process can be observed by UV-visible spectroscopy. Fig. 2(A) shows the UV-vis absorption spectra of the spherical ended gold nanodumbbells, on addition of different quantities of sodium hydroxide (NaOH) solution to the gold nanorods. In the UV-visible spectra in Fig. 2(A), a, b, c, and d correspond to 0 μL, 25 μL, 50 μL and 125 μL of sodium hydroxide (NaOH) solution added to the gold nanorods solution (the corresponding pH values are 7.0, 11.09, 11.39, and 11.76). It is evident from Fig. 2(A) that the intensity of the absorption peak corresponding to the SPR of the longitudinal mode is blue shifted from 930 nm to 802 nm.

According to Mie–Gans theory, the position of the maximum value of the longitudinal mode is mainly decided by the length to diameter ratio. Therefore, from the absorption spectra and the electron microscope observations in Fig. 1(c) and 2(A), it can be seen that the gold nanodumbbells grown on addition of sodium hydroxide predominantly grew thicker with an increase in diameter, thus resulting in a decrease in the length to diameter ratio.

By using the volume integral equation method, we simulated the absorption spectra which occur due to the change in the shape of the gold nanorods upon addition of sodium hydroxide. Fig. 2(B) shows the scheme of the simulation grid model, in which the progressive change from nanorods to nanodumbbells takes place. Shown in Fig. 2(B), the insets a, b, c, and d are the models of nanorods, dumbbell-1, dumbbell-2 and dumbbell-3.

The dimensions of models a and d were taken from experimental observations, whereas b and c were generated theoretically (see the ESI† Fig. S1; Table S1 lists the specific parameters used in the simulations and the resulting band positions).

Fig. 2(B) shows the simulated absorption spectra with the models of the nanorods and dumbbells 1, 2 and 3. It is evident that the longitudinal surface plasmon absorption band (which is located in the longer wavelength range) is blue shifted, which is due to the decreasing of ratio of length to diameter. Also, the intensity of the SPR bands is enhanced as the bulk volume increases due to the structural change from nanorods to nanodumbbells. Additionally, it is observed that the transverse mode SPR is enhanced, which could be related to the growth of the spherical ends of the nanorods.

In contrast to the spherical ended nanodumbbells, addition of ascorbic acid to the gold nanorods resulted in the formation of arrow ended nanodumbbells, and the UV spectra were found to be different. Fig. 3(A) (a–n) show the changes in the SPR position of the nanorods upon addition of various quantities of 0.0787 mol L⁻¹ ascorbic acid. From the UV-visible spectra it is observed that the transverse surface plasmon absorption band is red shifted from 516 nm to 550 nm, and its full width half maximum (FWHM) broadens, after which the band blue shifts to 531 nm and its FWHM narrows. There is also an initial red shift in the absorption band of the longitudinal surface plasmon absorption from 930 nm to 996 nm on addition of 150 μL of ascorbic acid, after which a continuous blue shift occurs until 884 nm. On further addition of ascorbic acid (>700 μL), as shown in Fig. 3(B), no change in the absorption band of SPRs occurred. From this observation, we can conclude that on addition of ascorbic acid to the gold nanorods, initially there is an increase in the length of the nanorods, which is followed by a predominant increase in diameter, thus leading to a decrease in the aspect ratio.

Fig. 2  (A) UV-vis absorption spectra of gold nanodumbbells prepared with an increasing amount of sodium hydroxide (NaOH) solution (the corresponding pH values of solutions of a, b, c, and d are 7.0, 11.09, 11.39 and 11.76). (B) Simulated spectra of gold nanorods and spherical ended gold nanodumbbells. Inset images are the simulated models of nanorods (a), dumbbell-1 (b), dumbbell-2 (c) and dumbbell-3 (d), respectively. The parameters of the simulated nanorods and dumbbells are listed in the ESI.†
The growth mechanism of gold nanodumbbells

Experimentally we have successfully shown that, by the addition of acid or alkali, the morphology of gold nanorods can be tailored to form spherical ended or arrow ended gold nanodumbbells. As shown in Fig. 4, high-resolution TEM images (a) and (c) demonstrate that the spherical ended Au nanodumbbells and the arrow ended Au nanodumbbells are well grown single crystal rather than amorphous. This also can be seen from Fig. 4(b) and (d); the fringes with a lattice spacing of 0.209 nm can be indexed as the {100} planes of face-centered cubic (fcc) Au, and 0.24 nm is spacing between the {111} planes. However, the question remains as to how the acid and alkali change the morphology of the gold nanorods. It is known that during the growth of gold nanorods, the surfactant CTAB plays an important role. Here BDAC/CTAB co-surfactants are used in the reaction, which was found to be more suitable for Au NR synthesis. These surfactants form a soft micelle template which can be used to control the microscopic size and shape of the gold nanorods. The shape of gold nanoparticles in general are octahedral, decahedral, and dodecahedral, which are confined by the low energy and relatively stable {100} and {111} facets. In comparison, gold nanorods are confined by the {100}, {110} side facets and the {111}, {110} top end facets in a pentatwinned structure with the growth direction of [001]. This is consistent with the TEM image observations in Fig. 1(b), where the fringes with a lattice spacing of 0.204 nm can be indexed as the {100} planes of face-centered cubic (fcc) Au.

The presence of the {110} facets is a unique feature of Au nanorods and is not commonly observed, because the {110} facet has a higher energy than the {111} and {100} facets. A combination of these facets controls the shape formation. When the surfactant is removed, the {110} facet becomes unstable, while the free gold nanoparticle at the {110} surface will continue to grow. The gold nanorod structure coated by surfactant double layers is stable. Under certain conditions, such as upon addition of acid or alkali, the cylindrical colloidal templates are destroyed. The micelle charge density is then reduced, and thus the geometry of the micelle templates will change, which changes the morphology of the nanorods to form a nanodumbbell-like structure. Based on our results, we propose two different growth mechanisms of the dumbbells on addition of acid or alkali. Fig. 5 demonstrates the scheme of the reaction, and the structural changes on addition of different compounds.
The growth mechanism of spherical ended Au nanodumbbells

On addition of sodium hydroxide solution to the gold nanorods seed solution, there is an increase in the pH, which plays an important role in the growth mechanism. It was previously shown by Wang et al. that pH had a strong influence on the reducing power of ascorbic acid, which determines the shape of the gold nanostructure. At low pH values, the reducing power of ascorbic acid is very weak, so the reduction rate of gold ions was very slow, yielding small numbers of gold atoms, which deposited equivalent amounts of gold on the \{111\} and \{110\} facets of the gold nanorods. On increasing the pH value by addition of alkali to the growth solution, the reducing power of ascorbic acid and the reduction rate of the gold ions increased, and resulted in the formation of gold nanoclusters which attached to the surface of the gold nanorods evenly, forming smooth spherical structures at both ends of the gold nanorods.

In comparison, in our experiments, the relatively large amounts of OH\(^-\) ions in the alkaline solution formed ion pairs with the CTA\(^+\) of CTAB experiments, the relatively large amounts of OH\(^-\)/C0\(^+\) on the surface of the gold nanorods, the CTAB falls off, and the gold nanorods are better protected along the length, and the ends are exposed. At the beginning of the growth process, free gold particles are evenly attached to both ends on the \{111\} and \{110\} surface, forming a spherical surface. Then, due to the combination of CTA\(^+\) and OH\(^-\) on the surface of the gold nanorods, the CTAB falls off, which leads to a large amount of free gold particles being attached to the surface of the gold nanorods. This results in an increase in the diameter of the nanorods, and a decrease in the aspect ratio. Our experiment, shown in Fig. 4(b), demonstrates that the growth direction along the axis of the Au nanorods is the [001] direction, and the spherical ends of nanodumbbell are well confined by the \{111\} planes. These observations are consistent with the above proposed growth mechanism.

The growth mechanism of arrow ended Au nanodumbbells

On addition of ascorbic acid to the gold nanorods, the stable structure of the surfactant is destroyed to a certain extent. However, in acidic environments, the bilayer structure of the surfactant is less damaged than in an alkaline environment. In particular, the amount of surfactant adsorbed on both the ends and the surfaces decreases, as demonstrated in Fig. 5. The large amount of free gold ions are reduced on addition of ascorbic acid, and preferentially attach to the ends of the nanorods due to the lower concentration of surfactants. At the ends of the nanorods, the gold atoms easily attach on the four unstable \{110\} facets, which grow quickly and finally disappear, leading to the growth of four \{111\} facets. These facets enlarge with time and meet to form the arrow ended structure. The newly formed arrow ended structure therefore has four \{111\} facets with a pointed end at the top and a square at the bottom. With time, the length of the arrow head increases, leading to an increase in the aspect ratio. After a certain time, the growth of the arrows at both ends stops as no more gold atoms can be attached to the \{110\} surface. Instead, the gold atoms deposit on the four \{110\} surfaces along the length of the nanorods until they meet the four \{100\} surfaces to form four prism structures, with the disappearance of the original four \{110\} surfaces. These predictions were confirmed by observation of the high resolution image of the arrow ended nanorods oriented along the \{111\} facets, as shown in Fig. 4(d). The fringes with a lattice spacing of 0.24 nm can be indexed as the \{111\} planes of face-centered cubic (fcc) Au. Therefore, an increase in the diameter of the nanorods occurs which then decreases the aspect ratio. This phenomenon is observed from the microstructure in Fig. 1(f), wherein the length of the dumbbell is longer and thicker than the original gold nanorods. Also, from the UV spectroscopic analysis in Fig. 3, an initial red shift followed by a blue shift is observed, which corresponds well with the proposed growth mechanism.

Conclusions

In summary, we have shown that by the addition of alkali or acid, the SPR and the morphology of gold nanorods can be tailored to form spherical ended and arrow ended nanodumbbells. The TEM and UV-visible spectroscopic analysis confirmed that the morphological change results in prominent shifts in the SPR peaks.

By this method, the products of the reaction process are unique (only spherical ended or arrow ended gold nanodumbbells were synthesized, and no other intermediate, e.g. dogbone, appeared in the reaction process); this intermediate process is confirmed by our TEM observations and the plasmonic spectra (for detailed discussion on this please see the ESI†). From the experimental analysis combined with the theoretical model using the volume integral equation method, a new growth mechanism for the gold nanodumbbells was proposed. It was found that chemical reagents change the surfactant double-layer structure of the gold nanorods, which causes the formation of spherical ended and arrow ended nanodumbbells by preferential stripping and deposition processes. The chemical surfactant plays an important role in controlling the microscopic size, the morphology of the rod ends, and the shape of the nanorods by mediating the surface energy. This is vital for understanding the surface energies of these nanorods. It provides new insights into the growth mechanism of gold nanodumbbells, with profound implications for controlling their morphology.

Acknowledgements

We acknowledge the support of this research by the National Natural Science Foundation of China (Grant No. 21073124 and 10904171).

Notes and references
