

Laser-Induced Fabrication of Au@CdS Core–Shell Nanowires

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Au@CdS core–shell nanowires have been fabricated readily by exciting the surface-plasmon resonances of gold nanospheres, which were priorly connected to each other by 1,5-pentanedithiol (PDT) and coated with CdS, using picosecond laser pulses at room temperature. Gold nanospheres were cross-linked by PDT molecules to form gold nanostrands, which were then fixated and protected by CdS shells to yield Au@CdS core–shell nanocomposites. The irradiation of the nanocomposites loaded on a grid of transmission electron microscopy with 532 nm pulses of 30 ps has produced Au@CdS core–shell nanowires. The thermalized photon energy of surface-plasmon excitation has induced gold nanospheres to fuse together within CdS shells.

Introduction

The design and fabrication of nanostructured materials having functional properties have been widely explored due to potential applications in catalysis, optoelectronics, and transistors.^{1–5} In particular, core–shell nanocomposites have been extensively investigated because they provide diverse opportunities for the development of novel nanomaterials having improved physical and chemical properties against single-component counterparts.^{6,7} It is great progress that metal/semiconductor nanocomposites have been created by combining metals with semiconductors.^{7–11} Metal@semiconductor core–shell nanomaterials attract considerable attention because of their unique optical, electrical, and catalytic properties.^{7–14} The presence of an interface within a metal@semiconductor core–shell nanostructure may promote charge transfer and charge separation.^{8,15,16} Moreover, the semiconductor shell can protect the metal core from chemical poisoning, corrosion, and dissolution, although metal nanoparticles alone tend to react or aggregate on account of their poor stability in a medium.^{17,18}

Among metal@semiconductor core–shell nanocomposites, in particular, Au@CdS core–shell nanostructures have been recognized importantly because not only CdS nanoparticles can be applied to photocatalysts and light-emitting diodes due to anion vacancies possessing a high electron affinity,^{8,19,20} but also gold nanoparticles can be employed as chemical or biological sensors based on surface-enhanced Raman scattering and surface-plasmon resonances.^{21,22} Nevertheless, although the syntheses of Au@CdS,^{7,8} Au@CdSe,^{9,10} Au@TiO₂,¹⁴ and Ag@TiO₂^{15,16,23} core–shell composite nanoparticles have been already reported, the preparation and the characterization of Au@CdS core–shell nanowires have been hardly reported yet.

We present that a Au@CdS core–shell nanowire has been prepared by exciting the surface-plasmon resonances of gold nanospheres, priorly connected by dithiol molecules of 1,5-pentanedithiol (PDT) and coated with a CdS shell, using picosecond laser pulses at room temperature (Figure 1). Despite efforts to synthesize metal@semiconductor composite nanomaterials,^{8–23} no report has so far dealt with the preparation of Au@CdS core–shell nanowires at room temperature. We have analyzed the optical properties of gold nanoparticles connected by the PDT, demonstrated the preparation of Au@CdS core–shell

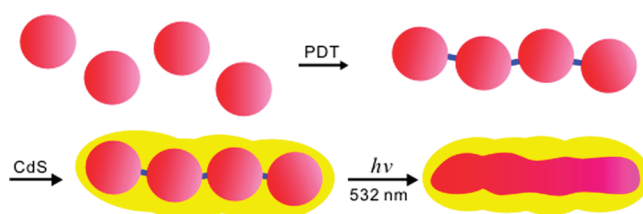


Figure 1. Schematic description for the laser-induced fabrication of a Au@CdS core–shell nanowire.

nanocomposites, and described the laser-induced fabrication of Au@CdS core–shell nanowires. Laser irradiation can melt or reshape metal nanoparticles without causing any significant perturbations in surrounding media.^{24–30} Because heating via laser irradiation is a selective process, the laser-induced transformation of metal nanoparticles has provided a simple mean to modify the shape of the nanoparticles. It has been reported that not only the mutual transposition of the core and the shell of a Au@Pt core–shell nanosphere but also the excavation of the silver core of a Ag@Pt core–shell nanosphere can be obtained by exciting the surface-plasmon resonances of platinum with picosecond laser pulses to produce new nanostructures of a reversed Pt@Au core–shell nanosphere²⁵ and a hollow platinum nanosphere,²⁶ respectively. The laser-induced formation mechanism of metal nanoparticles is not understood well yet, although the laser-induced size and shape alterations of metal nanoparticles in water have been explained to occur through melting and vaporization.^{31–33}

Experimental Section

The analytical grade chemicals of HAuCl₄(s), CdCl₂(s), Na₂S(s), sodium citrate dihydrate(s), and PDT(l) were used as purchased from Sigma-Aldrich. Deionized water with a resistivity of greater than 18 MΩ cm, from a Millipore Milli-Q system, was used throughout the experiments. Surfactant-free gold nanospheres dispersed in water, having an average diameter of 17.6 nm and the absorption maximum of surface-plasmon resonances at 527 nm, were prepared by the citrate reduction of HAuCl₄.^{34,35} The concentration of gold nanoparticles was determined to be 3.6 nM by taking the dependence of the extinction coefficient on the nanoparticle size into consideration.³⁶ Gold nanospheres were capped with PDT by mixing 2

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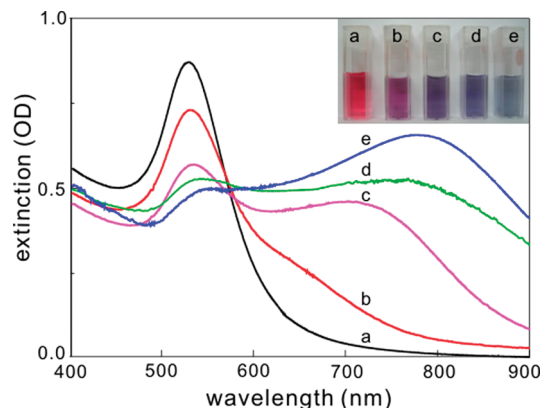


Figure 2. Extinction spectra of gold nanoparticles connected by PDT at VRs of (a) 0, (b) 0.05, (c) 0.1, (d) 0.2, and (e) 0.4. Inset shows the corresponding hydrosol colors.

mL of the cooled gold hydrosol with an indicated volume of a 1% PDT aqueous solution. The volume ratio (VR) of 1% PDT(aq) to the gold hydrosol was varied from 0.0 to 0.4. Upon addition of the PDT solution, the color of the colloidal solution changed from pinkish-red to purplish-blue. Five milligrams of CdCl_2 , 20 mg of Na_2S , and 15 mL of the PDT-capped gold hydrosol were mixed to prepare Au@CdS composite nanostructures.

Absorption spectral changes of surface-plasmon resonances for a 2 mL colloidal solution of PDT-connected gold nanoparticles contained in a quartz cell having a path length of 10 mm were monitored by measuring absorption spectra at scheduled intervals during laser irradiation using a UV/vis spectrophotometer (Scinco, UVS3100). Transmission electron microscopy (TEM) grids loaded with gold colloidal solutions were irradiated to weld gold nanoparticles by using laser pulses having a duration of 30 ps from a mode-locked Nd:YAG laser (Quantel, YG701) run at 10 Hz. The spot diameter of the irradiation beam was 4 mm. Energy dispersive X-ray (EDX) profiles and high-resolution transmission electron microscopy (HRTEM) images were measured with a JEOL JEM-3000F microscope, while TEM images were measured with a JEOL JEM-2000 microscope.

Results and Discussion

The bifunctional molecules of PDT were chosen to connect gold nanoparticles to one another because the short chain length of PDT would adequately prevent the attachment of both thiol groups of a PDT molecule to the same gold nanoparticle. Gold is known³⁷ to form a strong thiolate bond, leading to the self-assembled monolayer of dithiol molecules on a gold nanoparticle. Terminal thiol groups could chemisorb on another gold nanoparticle, thereby leading to the cross-linking of gold nanoparticles. This can be easily monitored by measuring optical extinction spectra. We first tried to determine the optimal concentration of PDT required to prevent the precipitation of gold nanoparticles via covering the gold surface. The surface-plasmon absorption of gold nanoparticles shifted to the red by 20 nm with the increment of VR, the volume ratio of 1% PDT(aq) to the gold hydrosol (Figure 2). Figure 2 also shows that the addition of PDT induces the surface-plasmon resonances of gold nanoparticles at 526 nm to disappear gradually, while it causes a new broad surface-plasmon resonance band above 700 nm with the increment of VR. The extinction band above 700 nm is shifted to the red increasingly with the increment of VR due to the aggregation of PDT-connected gold nanoparticles.³⁸ While dispersed colloid extinction arises from absorption, aggregate

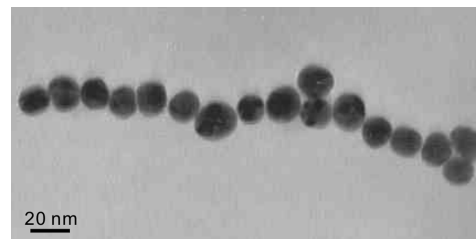


Figure 3. TEM image of gold nanospheres connected by PDT at VR = 0.1.

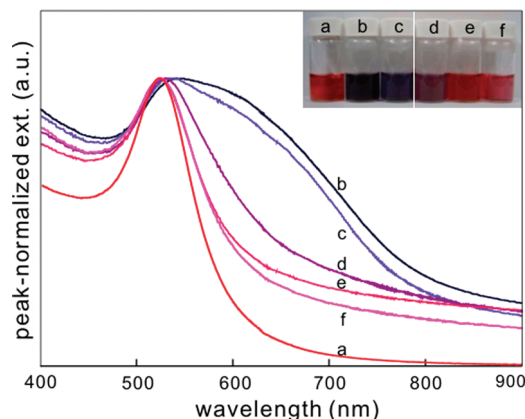


Figure 4. Extinction spectra of (a) bare gold nanoparticles and (b–f) gold nanoparticles connected by PDT at VR = 0.08. Samples were irradiated for 20 min with 532 nm pulses of 30 ps having pulse energies of (a) 0, (b) 0, (c) 0.2, (d) 0.8, (e) 1, and (f) 5 mJ. Inset shows the corresponding hydrosol colors.

colloid both scatters and absorbs visible light.^{38–40} The aggregate scatters light on the long wavelength side of the shifted plasmon band, although the absorption peak is also red-shifted from the dispersed colloid location.^{39,40} Thus, both scattering and absorption contribute to the red-shifting and broadening of the extinction band for PDT-connected gold nanoparticles.³⁹ In addition, the inset of Figure 2 shows that the color of the gold hydrosol has been changed from pinkish-red to purplish-blue by the aggregation of PDT-connected gold nanoparticles.

The TEM image of Figure 3 shows that gold nanospheres having an average diameter of 17.6 nm have been connected via PDT molecules to form a gold nanostrand. Both Figures 2 and 3 suggest that the cross-linking of gold nanoparticles takes place via capping gold nanospheres with the dithiol molecules of PDT. We infer that the induced dipole–dipole interactions of PDT-capped gold nanospheres drive the aggregation process favorably to produce gold-nanosphere strands. Diverse TEM images show that the nanostrands of aggregated gold nanospheres do not coalesce into large aggregates of aggregates.

Figure 4 indicates that the shoulder absorption band of PDT-capped gold nanospheres around 670 nm decreases gradually with the pulse energy of irradiation light. Extinction decrease around 670 nm by irradiation is attributed to the laser-induced desorption of PDT molecules from the surfaces of gold nanospheres.^{41,42} Thus, the nanostrands of PDT-linked gold nanospheres disappear upon laser irradiation. This suggests that a nanostrand of PDT-connected gold nanospheres should be protected by a semiconductor shell to be welded together via laser irradiation to produce a nanowire.

The TEM image of Figure 5a shows that CdS surrounds PDT-connected gold nanospheres to form a Au@CdS core–shell nanocomposite. PDT has been found to be very essential for the fabrication of Au@CdS core–shell nanostructures. Figure S1 in the Supporting Information indicates indeed that Au@CdS

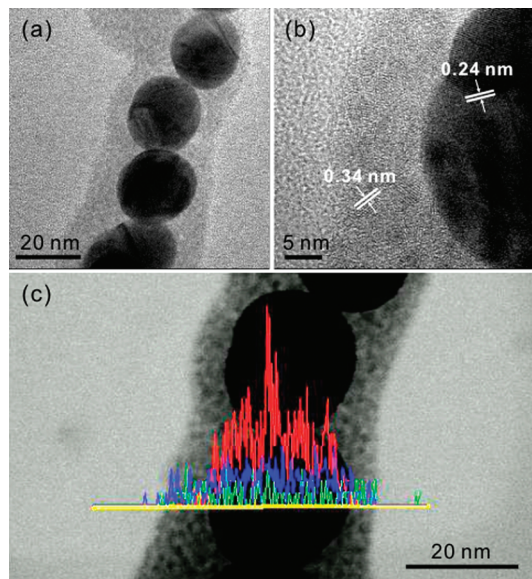


Figure 5. (a) TEM image of a Au@CdS core-shell nanocomposite. (b) HRTEM image of a Au@CdS nanocomposite showing lattice plane distances. (c) EDX line-scanned intensity profiles of Au (red), Cd (green), and S (blue) for a Au@CdS nanocomposite.

core-shell nanocomposites cannot be produced in the absence of PDT. As VR increases, the CdS shell thickness of a Au@CdS core-shell nanocomposite also increases. Thus, we have been able to control the shell thickness of the nanocomposite by adjusting VR. The HRTEM image of Figure 5b reveals the detailed crystallographic structure of a Au@CdS core-shell nanocomposite, where numerous CdS quantum dots of 3 nm in diameter encompass PDT-connected gold nanospheres. An interlayer spacing of 0.24 nm observed in the core region agrees well with the literature value (0.2355 nm) of separation between the (111) lattice planes of the fcc Au crystal (JCPDS 04-0784). However, an interlayer spacing of 0.34 nm was observed in the shell region, complying with the lattice spacing (0.3367 nm) of the (002) planes of the wurtzite CdS (JCPDS 06-0314). The EDX line-scanned intensity profile of Figure 5c also designates that the gold and the CdS of the composite nanostructure are located in the core and the shell positions, respectively. Detailed EDX analysis indicates that the atomic percentage of sulfur is substantially larger than that of cadmium. We attribute this to the sulfur atoms of PDT, which was used to cap and connect gold nanospheres.

Figure 6 shows that, whereas the irradiation of PDT-connected bare gold nanospheres on a TEM grid with 532 nm pulses has produced featurelessly fused gold agglomerates, the irradiation of Au@CdS nanocomposites, where PDT-connected gold nanospheres were surrounded by CdS, under the same conditions has yielded Au@CdS core-shell nanowires. This indicates that nanostrands of PDT-connected gold nanospheres have been protected well by CdS shells during the laser welding process to produce CdS-surrounded gold nanowires. However, Figure S2 in the Supporting Information reveals that the irradiation of the same Au@CdS core-shell nanocomposites with 355 nm pulses, instead of 532 nm pulses, has demolished CdS shells without producing Au@CdS core-shell nanowires. Recall that because CdS is a high-bandgap semiconductor, CdS shells absorb light strongly at 355 nm, but they do hardly at 532 nm (Figure S3 in the Supporting Information).⁶ However, 532 nm light is all absorbed by the core gold nanospheres because its energy is not large enough to excite the CdS shells. Thus, these suggest that we can fabricate Au@CdS core-shell nanowires

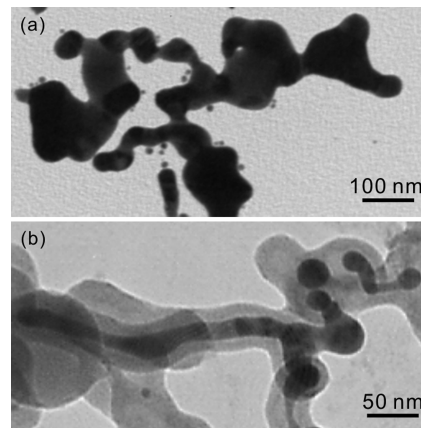


Figure 6. TEM images of (a) gold nanoparticles connected by PDT and (b) Au@CdS core-shell nanocomposites after irradiating samples on TEM grids with 532 nm pulses of 30 ps and 2 mJ for 30 min.

by exciting the surface-plasmon resonances of gold nanospheres connected by PDT and protected by CdS shells using picosecond laser pulses of 532 nm. The thermalized photon energy of surface-plasmon excitation induces gold nanospheres to melt and fuse together within CdS shells, producing Au@CdS core-shell nanowires. Figure S4 in the Supporting Information reveals that laser irradiation with a high power density induces core gold nanospheres to melt and effuse through CdS shells, producing hollow CdS nanostructures.

Conclusion

The addition of PDT induced the surface-plasmon resonances of gold nanospheres at 526 nm to disappear gradually while it brought about a new broad surface-plasmon absorption band above 700 nm, suggesting that gold nanospheres were cross-linked by PDT molecules to form gold nanostrands. The laser-induced desorption of PDT molecules from the surfaces of gold nanospheres has suggested that a nanostrand of PDT-connected gold nanospheres should be protected by a semiconductor shell to be welded together via laser irradiation to produce a nanowire. PDT-connected gold nanospheres were then fixated and protected by CdS shells to yield Au@CdS core-shell nanocomposites, where numerous CdS quantum dots of 3 nm in diameter encompass the core gold nanostrands. The irradiation of Au@CdS core-shell nanocomposites loaded on a TEM grid with 532 nm pulses of 30 ps has produced Au@CdS core-shell nanowires at room temperature. The thermalized photon energy of surface-plasmon excitation has induced gold nanospheres to fuse together within CdS shells, generating CdS-coated gold nanowires.

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Supporting Information Available: Additional TEM images and extinction spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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