A New Strategy for the Synthesis of Semiconductor-Metal Hybrid Nanocomposites: Electrostatic Self-Assembly of Nanoparticles

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CdS-Au hybrid nanoparticles are synthesized through electrostatically self-assembling of the pre-formed monodisperse CdS and Au nanoparticles via the interaction between ammonium ions and carboxylate ions which were modified on CdS and Au nanoparticle surface, respectively.

The synthesis of semiconductor-metal nanocomposites provides a new way to tailor the optical and electronic properties of the semiconductor or metal nanoparticles.[1-6] Recently, we showed that the strength of excitonic absorption band of ZnO nanoparticles can be reversibly controlled through the formation of hybrid ZnO-Ag nanoparticles, providing a new methodology applicable to non-linear optics.[1] Other novel optical properties have also been observed in the hybrid systems. For example, a new absorption band peaked at 650-900 nm was found for Au-coated Au_2S nanoparticles.[2,3] Surface-enhanced Raman scattering of CdS particles was detected through the formation of Ag-CdS hybrid particles.[4] However, in these studies direct evidence for the well-defined hybrid structure is still lacking, researchers in a recent study[6] even questioned the formation of rather Ag-Ag_2S particles than Ag-CdS in the previous research of Reference 4. Therefore, the formation of well-defined hybrid particles will set the base for future application of these materials. In all the previous strategies,[1-6] synthesis was conducted through the direct chemical reaction of the second phase in the presence of the first kind of nanoparticle as the nucleus, making it difficult to prevent nucleation and growth of the second separated nanophase. To overcome this problem, here we present a new approach to self-assemble the pre-formed monodisperse CdS and Au nanoparticles into hybrid particles, based on the electrostatic interaction between the amine-covered CdS and carboxylate-covered gold nanoparticles. This method possesses the advantages in that we can precisely control the size, monodispersity as well as structure of the components of the hybrid particles. Furthermore, it is versatile and can be used for the synthesis of other kinds of hybrid particles such as metal-metal or semiconductor-semiconductor systems.

All the chemicals used in this research are of reagent grade and purchased from Wako. Amine-modified CdS nanoparticles were prepared as follows: a vigorously stirred solution containing 1.33 g (5 mmol) of cadmium acetate dihydrate, 1.42 g (12.5 mmol) of 2-mercaptoethylamine hydrochloride and 0.47 g (6.25 mmol) of thioacetamide in 250 ml water was aged for 5 h at 40 ℃ and 60 ℃, respectively. After that, the cooled solution was filtrated, and concentrated to about 10 ml using a rotary evaporator. 20 ml of 2-propanol was then added, resulting in a turbid solution. The light-yellow precipitate separated from this solution by centrifugation at 9840×g (corresponding to 10000 r.p.m. with the centrifuge tube used) for 5 min, was then dissolved again with 5 ml of water, re-precipitated with 2-propanol (repeated further twice). At last, the precipitate was dried yielding light-yellow solid CdS (0.52 g) which can be easily dissolved in water. The whole process was monitored through the UV-Vis spectroscopy. An excitonic peak located at 368 nm indicated the formation of 2.5 nm CdS particles.[7] Powder X-ray diffraction showed that they belong to zinc blende structures. High-resolution images revealed that most of the particles have 8-10 (111)· lattice planes corresponding to particle size of 2.4-3.0 nm (right in the insert of Figure 1), which is consistent with the estimate from absorption spectra.

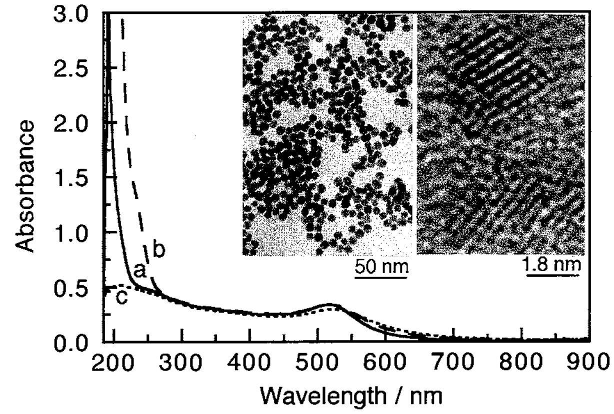

Figure 1. The absorption spectra of (a) Au particles stabilized by citrate, (b) Au particles mixed with mercaptosuccinic acid solution, and (c) the solution (b) after dialysis. The total concentration according to Au is $[HAuCl_4] = 1.15 \times 10^{-4}$ M. The insert shows the TEM photo of mercaptosuccinic acid stabilized gold particles (left) and high-resolution image of two CdS particles (right).

Gold nanoparticles were prepared according to the established method.[8] Briefly, 106 ml of 2.2 mM sodium citrate is brought to a boil for 10 min and 1 ml of 24.3 mM $HAuCl_4$ is added under rapid stirring. After the color of the solution changed to red within 3 min, the solution was further boiled for 15 min. Eighty ml of the cooled solution was then vigorously mixed with 80 ml of 6 mM mercaptosuccinic acid solution, followed by sealed into a Visking tube and dialyzed against distilled water for 3 days with 6 times exchange of water during dialysis. The pH of the solution changed from 3.8 to 6.9. After dialysis, the UV bands in the absorption spectra which belong to citrate or mercaptosuccinic acid disappeared showing that pure caboxylate-modified gold particles were formed (Figure 1, compared c to a or b). These particles have a mean diameter of 5.8 nm and coefficient of variation of 13% (left in the insert of Figure 1).

Hybrid CdS-Au nanoparticles are prepared by mixing the dialyzed gold particles with CdS particles in neutral solution (pH ~7). From the pK_a of succinic acid (~5) and the pK_b of ethyl amine (~3.4), it can be judged that the surface of Au particles will be negatively charged due to the formation of carboxylate ions whereas that of CdS will be positively charged due to the generation of ammonium ions. The concentrations were adjusted

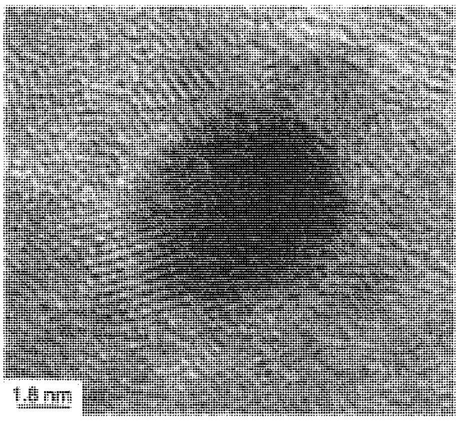

Figure 2. High-resolution TEM photo of one hybrid CdS-Au nanoparticle prepared from the solution of condition d in Figure 3.

to ensure the formation of hybrid particles traced by the fluorescence spectra.

Figure 2 shows the typical high-resolution image of one CdS-Au hybrid particle. The lattice distance on the black particle is 2.35 Å, corresponding to the (111) planes of fcc Au. In the periphery of the gold particle, separate small particles with 8-10 (111) lattice planes of zinc blende CdS (d_{111} = 3.36 Å) can be clearly seen. The (111) planes of different CdS particles oriented at different directions but contacted intimately with the gold particle, clearly confirmed the formation of CdS-Au hybrid particle.

The efficiency of CdS-Au particle formation through electrostatic assembly was illustrated by fluorescence spectra as shown in Figure 3. The amine-modified CdS particles have a broad fluorescence band peaked at 540 nm. This band, which is normally related to the surface defects such as sulfur vacancies or Cd atoms located on the particle surface[9], will be quenched when gold particles combine with CdS. Therefore, from the decrease in fluorescence intensity of CdS as shown in the insert of Figure 3, it can be estimated that more than 30% of the CdS particles have combined with gold particles in the condition d. If free Au particles absorb the fluorescence from CdS, the decrease in luminescence intensity will be a linear function of Au concentration. In addition, the absorption spectra during the increase in the concentration of gold particles (not shown) are only the arithmetic sum of that of respective CdS and Au, showing that Au particles have no effect on the excitonic peak position of CdS particles. This is different from the case when Ag nanoparticles were formed on hydroxyl covered ZnO particle surface, where quenching of the excitonic peak of ZnO occurred due to the formation of Ag_2O.[1] The formation of hybrid CdS-Au system through electrostatic combination here should be different from the chemical deposition of metal in the previous case.

In summary, a new strategy through self-assembling of pre-formed nanoparticles was demonstrated for the synthesis of hybrid semiconductor-metal particles. This method is versatile and can be applied for the design and development of other hybrid systems. It is noteworthy that one will also be able to control the combining intensity between nanoparticles through adjusting the modifiers on the particle surface, and thus further control the optical or electronic properties of the hybrid systems.

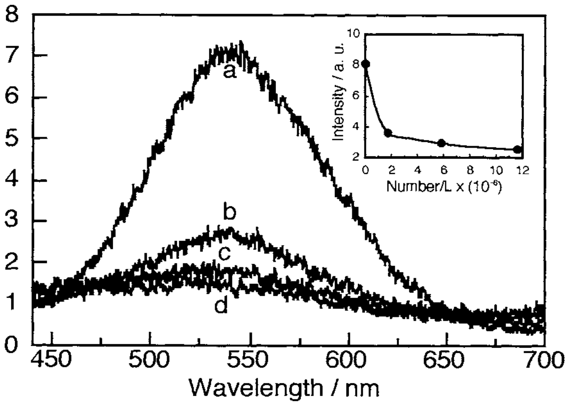

Figure 3. Fluorescence spectra of the CdS nanoparticle suspensions (7.8 mg/L) in the absence (a) and presence (b, c, and d) of gold particles. The total concentration according to Au is [$HAuCl_4$] = 1.70×10^{-5} M (b), 5.68×10^{-5} M (c), and 1.14×10^{-4} M (d). The insert shows the change of the fluorescence intensity (440-650 nm) with the increased concentration of the gold particles. The excitation wavelength is 370 nm.

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