

## Unique structure and photoluminescence of Au/CdTe nanostructure materials†

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**Unique nanostructure materials with highly ordered spherical aggregates have been obtained by self-organization of single CdTe nanocrystals using gold nanoparticles as seeds, and a red shift of the photoluminescence peak was observed.**

Nanostructure materials have received steadily growing interest as a result of their peculiar and fascinating properties, and applications superior to their bulk counterparts.<sup>1–2</sup> Now building and patterning of semiconductors nanocrystals into two- and three-dimensional organized and designed structures is an important goal in materials chemistry for the application of the ordered system in electronic, sensor, and photonic devices. CdTe nanocrystals are important II–VI semiconductor materials, which have been used in numerous applications, such as in light-emitting devices,<sup>3</sup> photonic<sup>4</sup> and biological labels.<sup>5</sup> Spontaneous organization of single CdTe nanocrystals into luminescent nanowires upon controlled removal of the protective shell of an organic stabilizer has been reported recently.<sup>6</sup> Radtchenko *et al.* developed a method to form core-shell structures by the solvent-controlled precipitation of luminescent CdTe nanocrystals on latex spheres.<sup>7</sup> Later, CdTe-labeled polystyrene beads of 925 nm diameter were prepared *via* the layer-by-layer assembly approach.<sup>5</sup>

We present here an approach to obtaining photoluminescent nanostructure materials by self-organization of single CdTe nanocrystals using gold nanoparticles as seeds. The formation mechanism is also discussed in this paper. It provides a new method for self-organized nanostructure materials and a red shift of the photoluminescence peak has been observed.

The synthesis process of 3-mercaptopropionic acid (MPA)-capped Au nanoparticles was followed by the reduction of tetrachloroauric acid with sodium borohydride in the presence of MPA.<sup>8</sup> The mean diameter of such MPA-capped Au nanocrystals was 2 nm, which has been confirmed by transmission electron micrographs (TEMs). Then 10 ml of 0.33 mM MPA-capped Au nanocrystals was diluted to 100 ml and placed in a three-necked flask. 0.1310 g of Cd(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O was added and stirred for 10 min. Then 53 μl thioglycolic acid (TGA) was added, and the solution was adjusted to pH 11 with 1 M NaOH, and de-aerated with N<sub>2</sub> for 30 min. After that, 0.15 mmol of oxygen-free 0.25 M NaHTe solution, which was freshly prepared from tellurium powder and NaBH<sub>4</sub> in water, was injected into the above solution under vigorous stirring. The solution was then heated and further refluxed for 8 h in an oil bath. For the purposes of comparison, the CdTe nanocrystals were all prepared in the similar conditions except when in the presence of Au seeds.

TEM and selected area electron diffraction (SAED) were recorded using a JEOL-2010 electron microscope operating at 200 kV. X-Ray photoelectron spectroscopy was conducted using a VG ESCALAB MK II spectrometer (VG Scientific, UK) employing a monochromatic Mg Kα X-ray source ( $h\nu = 1253.6$  eV). Peak positions were internally referenced to the C 1s peak at 284.6 eV.

† Electronic supplementary information (ESI) available: photoluminescence and UV-Vis spectra of Au nanoparticles, and XRD spectra of CdTe nanocrystals and Au/CdTe. See <http://www.rsc.org/suppdata/cc/b3/b314664b/>

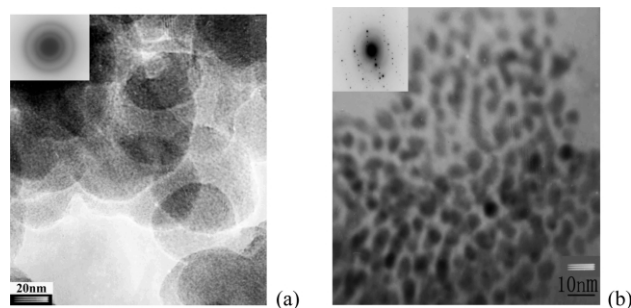
Fluorescence spectra data were obtained from FS920 steady state fluorescence spectrometer (Edinburgh Instruments, UK).

The formation of self-organized spherical aggregates can be directly visualized by TEM [shown in Fig. 1(a)]. It can be seen that highly ordered spherical aggregates with a mean diameter of 50 nm have been obtained. These spherical aggregates are composed of many intensely dark spots. Every nanoparticle with the size of about 2 nm shows a rather clear boundary in the spherical aggregates. The spherical aggregates are transparent and the intersection between two clusters can be clearly seen.

While the TGA-capped CdTe nanocrystals prepared without Au seeds are separated to show a mean size of *ca.* 3.2 nm [see Fig. 1(b)], SAED of the separated CdTe particles, inset of Fig. 1(b), shows that the CdTe nanocrystals have single crystalline character. When the CdTe nanocrystals were self-organized into spherical aggregates, the SAED pattern appears as broad diffuse rings [inset of Fig. 1(a)].

The elemental composition of the luminescent spherical aggregates was analyzed by XPS. The appearance of a characteristic Cd 3d<sub>5/2</sub> peak at 404.8 eV, Te 3d<sub>5/2</sub> peak at 572.2 eV, and S 2p peak at 163.2 eV confirms the existence of TGA-coated CdTe nanocrystals, which are the intensely dark spots in the individual spherical aggregates. However, the characteristic Au 4f peaks at 84.2 and 88 eV of the MPA-capped Au nanocrystals [Fig. 2(a)] were not obviously observed in the spherical aggregates [Fig. 2(b)], which indicates that the Au nanoparticles are inside the spherical aggregates, and do not exist either on the surface of the spherical aggregates or as free particles in the solution.

It is considered that the prevailing driving force for the formation of spherical aggregates is their dipole–dipole attraction. The presence of a large permanent dipole moment in the nanocrystals has been proved in previous reports.<sup>9</sup> The permanent dipole moment exists not only in the wurtzite CdSe nanocrystals,<sup>10,11</sup> but also in the zinc-blende materials such as CdTe and ZnSe.<sup>6,12</sup> It should be emphasized that the formation of spherical aggregates is considered to be a cooperative effect of dipole–dipole interaction and the nanocrystals growth in the given reaction environment. When the Cd<sup>2+</sup> ions were added to an Au colloid with a negative surface charge due to the MPA salt, the Cd<sup>2+</sup> ions could be attached to the Au colloidal surface *via* electrostatic binding. This stage is the formation of the aggregate of Au–Cd–thiolate clusters.<sup>13</sup> Then



**Fig. 1** TEM and SAED (inset) patterns of Au/CdTe nanostructures (a), and separated CdTe nanocrystals (b).

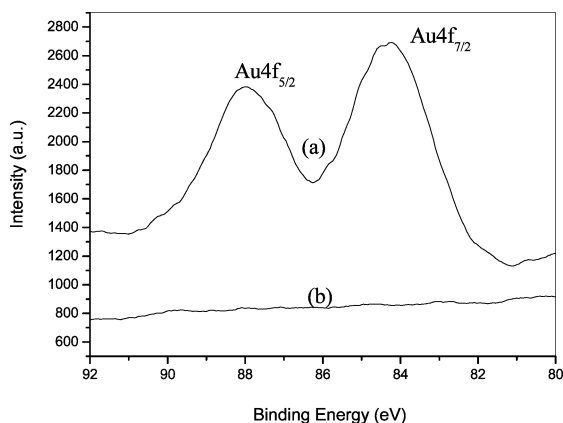
the Cd–thiolate clusters were formed around the Au core. The ratio of Au colloid and Cd<sup>2+</sup> ions is an important parameter for controlling such spherical aggregates. When the amount of Au doubled in this system, the expected aggregated structure could not be formed.

Next, the clusters reacted with the Te<sup>2-</sup> ions to form a CdTe colloid, followed with nanocrystal growth. The growth was controlled possibly by either a diffusion-controlled growth or the higher chemical reactivity of the smaller nanocrystals in the solution.<sup>14</sup> According to the theory of diffusion-controlled growth, every nucleus gathers the neighboring primary particles within the individual attraction field. The attraction field is extended as a circular area around a spherical particle with a defined distance from the center of the particle.<sup>15</sup> Even a few smaller Cd–thiolate clusters might be formed beyond the Au core, the smaller nanocrystals in the solution would shrink due to the higher chemical reactivity. On the other hand, TGA molecules adsorb and desorb rapidly from the nanocrystal surface, enabling the addition (as well as removal) of atoms from the crystallites at the growth temperature. The dipole–dipole attraction means that the CdTe nanocrystals are close to each other, while the mutual electrostatic repulsion of the nanoparticles from the TGA molecules depresses the proximity. Equilibrium between the two forces was established to lower the energy of this system, resulting in the formation of such spherical aggregates.

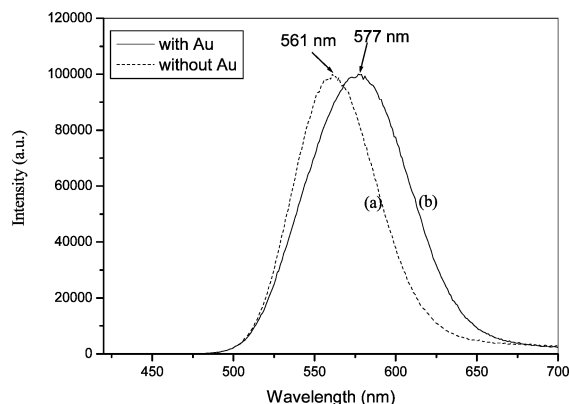
To demonstrate that the spherical aggregates must be formed in the nanocrystal growth process, we simply mixed the Au nanoparticles with CdTe nanocrystals in the same ratio, and refluxed, whereupon the spherical aggregate structures could not be found; moreover, the emission of CdTe was quenched. This experiment also indicated that such a structure is an important requirement for the strong luminescence.

Fig. 3(a) shows the photoluminescence spectrum of separated CdTe prepared without Au seeds. The excitonic photoluminescence peak appears at 561 nm. However, the excitonic photoluminescence peak of CdTe nanocrystals in the spherical aggregates shifts to 577 nm [Fig. 3(b)]. In addition, the full width at half-maximum is broadened compared with the separated CdTe.

It is well-known that the photoluminescence peak of CdTe nanocrystals shifts to longer wavelength with increasing particle size.<sup>14</sup> But our result shows that the photoluminescence peak of much smaller ‘spots’ in the aggregate has a longer wavelength emission. The mechanism behind this phenomenon is not very clear yet. We consider that the unique structure of the Au/CdTe nanocomposites is related to their photoluminescence. In the



**Fig. 2** X-Ray photoelectron spectra of the characteristic Au 4f peaks: (a) pure MPA-capped Au nanoparticles, and (b) Au/CdTe nanostructures.



**Fig. 3** Photoluminescence spectra of separated CdTe (a), and Au/CdTe nanostructures (b).

spherical aggregates, the distance between the CdTe nanocrystals is very small. There is a strong dipole–dipole interaction between the CdTe nanocrystals, which leads to the formation of so-called exciton states, which are delocalized over several CdTe nanocrystals. For CdTe nanocrystals, further investigation is necessary to confirm this speculation, although similar results have been confirmed in the pigment–protein complexes.<sup>16,17</sup>

In summary, CdTe nanocrystals were self-organized into spherical aggregates using Au as seeds. The formation mechanism is considered to be a cooperative effect of dipole–dipole interaction and the nanocrystal growth in the given reaction environment. Since the permanent dipole moment is an intrinsic characteristic for many types of semiconductors, it can be used and developed for the self-organization of various superstructures. The strong dipole–dipole interaction between the CdTe nanocrystals also leads to the red shift of the luminescence peak.

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