Surface Modification of Photoluminescent CdS Nanocrystals Inducing Spontaneous Phase Transfer Reaction

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A facile one-step method to modify the surface of luminescent CdS nanocrystals by alkylamines, without their luminescence intensity loss, was established. The interfacial modification inducing spontaneous transfer of the CdS from an aqueous to a non-polar organic phase was found to be controlled simply by choosing the alkyl group of the amine. Analysis of the absorption and emission spectra revealed the phase transfer yield of ca. 100%.

Semiconductor nanocrystals have recently revealed magnificent versatility for technological applications such as biological sensors,[1,2] solar cells,[3,4] and luminescence devices.[5,6] These unique applications were developed by introducing functionalities on the surface of the nanocrystals. In particular, the surface-coated nanocrystals dispersed in organic solvents can readily be utilized in preparing films, super-lattice structures and nanocomposite materials.[4,7,8]

The nanoparticle surface modification is easily confirmed by monitoring the surface hydrophilicity and hydrophobicity. For example, the nanocrystals modified by octadecanethiol[9] or alkylammonium surfactants[10,12] were extracted from an aqueous to an organic solution. Polymers with charged terminates[13] or aliphatic chains[14] are used for transferring nanocrystals between aqueous and non-polar solvents. In general, however, these functional groups largely reduce the photoluminescence intensity. Ideally the properties optimized in the aqueous solution are maintained or enhanced even after the surface modification. In this paper, we present modification of the luminescent CdS nanocrystals by alkylamine as an alternative candidate for the surface coating agent, altering the surface hydrophilic property to hydrophobic without any high photoluminescence intensity loss. One-step modification reaction is instigated at a water–oil interface, inducing spontaneous phase transfer reactions.

Photoluminescent CdS nanocrystals were obtained by the method we have developed recently.[15] In summary, an aqueous CdS colloidal solution was prepared by mixing $Cd(ClO_4)_2$ and H_2S gas with $(NaPO_3)_6$ stabilizing material, with the size selective photoetching appropriately investigated.[16] The CdS was coated with mercaptopropionic acid to ensure thorough washing with pure water. The pH of the solution was adjusted to 11 using NaOH, this causes the nanocrystals to be flocculated from the solvent, and subsequently the photoluminescent intensity increased to a quantum yield of, at least, 13% compared with quinine sulfate (QY = 54.6%) as a reference.

Phase transfer reactions of the photoluminescent CdS nanocrystals were performed by coating the surface with alkylamines at a water–oil interface. Hexylamine (0.2 mL, Wako Pure Chemical Ind.) and hexane (2 mL) were added to the 2 mL aqueous solution containing CdS precipitation. Two different phases were immediately formed; the upper hexane phase and the lower water phase, and then the solution was vigorously agitated for a few minutes.

Prior to the amine addition, the CdS was identified in the aqueous phase, see Figure 1a. The left photograph was taken in room light whereas the green light emission in the right photo-

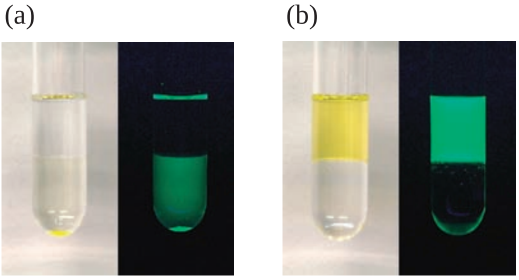

Figure 1. Photographs of the phase transfer processes. (a) Initially the CdS nanocrystals are located at the lower phase. (b) Hexylamine addition results in transfer of the nanocrystals to the hexane solution.

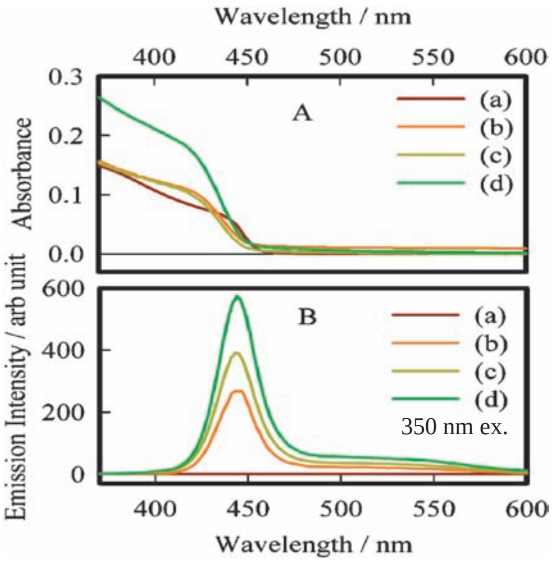

Figure 2. Absorption (A) and emission (B) spectra of the CdS nanocrystals capped with mercaptopropionic acid (a). For photoluminescent CdS dispersed in the aqueous solution after NaOH addition (b). For the hexylamine capped CdS in 2 mL hexane after the phase transfer (c). After the phase transfer to 1 mL hexane (d).

graph was observed under UV light irradiation. As previously reported,[15] the photoluminescence was observed near the bottom of the test tube due to the particle flocculation. After hexylamine was added into the solution, the nanocrystals were remarkably transferred to the hexane phase as displayed in Figure 1b. The bright luminescence was maintained even after the phase transfer reaction. The fact that the flocculent CdS can be dispersed in hexane indicates the absence of any strong bond between nanoparticles in the flocculent region.

We have recently demonstrated[15] that multi-color luminescent CdS in aqueous solutions can be prepared in combination with the size selective photoetching technique.[16] These color selected nanocrystals can also be transferred into the hexane by the amine addition (see the graphical abstract). The extracted CdS can readily be used for several direct applications such as multi-color light emitting diodes or lasers.

Figure 2 compares the optical properties of the CdS photoetched at 450 nm. The nanocrystals capped with mercaptopropionic acid (spectra a) clearly indicate complete luminescence quenching. This is in agreement with the results reported by Bawendi et al.[17] in which the thiol attachment on the surface modifies the electronic states, resulting in charge trapping to quench the luminescence. We have then obtained bright photoluminescent nanocrystals by adding NaOH to this solution (emission spectrum b). Subsequently, the phase transfer results in the nanocrystals dispersed in hexane (spectra c). Analysis of these spectra revealed the phase transfer efficiency of ca. 100%. In addition, the absorption and emission spectral shapes are almost identical before and after the phase transfer, implying no modulation in the CdS electronic states, i.e. the amine does not interact with the surface. This is not consistent with the results obtained by McLendon et al.[18] where the amines binding to the nanocrystal results in their absorption and emission spectral shape change. Note that slight improvement of the photoluminescence intensity after the phase transfer was observed (compare spectra b and c). This is probably due to less impurity, such as thiols or ions, in hexane since these impurities may partially interact with the CdS.[1]

The phase transfer was further investigated by using amines with a different alkyl length as indicated in Table 1. When propylamine was used, a phase transfer did not proceed, indicating that the capped CdS surface possesses relatively strong hydrophilicity. In contrast, when dodecylamine was used, the nanocrystals were assembled at the water–hexane interface. Addition of methanol assisted the transfer from the interface to the hexane phase with a yield of ca. 100%. This is probably due to difficulty in forming the nanocrystals fully capped by the amine with a longer alkyl chain at the interface. The methanol addition improves the dodecylamine solvation in the aqueous phase, assisting the amine attachment at the interface. Thus, this study demonstrates that the surface hydrophobicity can easily be controlled by the alkyl length of the amine.

We propose additional advantages introduced by this interfacial surface modification method. Firstly, a sound purification method for the luminescent nanocrystals from the aqueous solution which contains impurities, e.g. thiol molecules or ions, causing the photoluminescence intensity loss, while the conventional method required several washing and drying processes to obtain pure nanocrystals. Secondly, the CdS–hexane concentration can be controlled by adjusting the amount of hexane added for the reaction. For example, curves d in Figure 2 show the absorption and emission spectra when the CdS–hexane solution was concentrated by a factor of two, i.e. half the amount of hexane was used. Thirdly, the amine capped CdS can be used for solid state photoluminescence devices, for example the CdS in powder form strongly emits luminescence when hexane was completely dried. Finally, the photoluminescence stability of the extracted nanocrystals in hexane is remarkable. The preliminary experiment indicates that the photoluminescence intensity for the crystals in hexane has been unchanged for several months in comparison to the aqueous solution whose intensity gradually decreases within a few days. We are currently investigating the factors affecting the photostability and the results will be published shortly.

Table 1. Amine alkyl length dependence on phase transfer yield

Amine type	Phase transfer yield/%
Propylamine	0
Hexylamine	~100
Dodecylamine	~100 (with methanol addition)

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