Preparation Method Allowing Self-isolation of CdS Nanocrystals Emitting Intense Band-gap Luminescence

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Isolated CdS nanocrystals exhibiting intense luminescence can be prepared in aqueous solution, and combination of this new method with the previously developed size-selective photo-etching method produces fluorescent markers emitting desired wavelengths.

With their tunable size, semiconductor nanocrystals possess a wide range of potential applications. In particular, nanocrystals showing intense band-gap luminescence have attracted great interest as multicolor fluorescent markers for biological analysis and other purposes.[1] To prepare nanocrystals emitting a desired color, not only the crystal size but also surface must be controlled because the presence of surface defects causes emission of non-band-gap luminescence or extinction of emission. Core-shell nanocrystals such as $CdSe/ZnS$,[2] $CdSe/CdS$,[3] $CdS/Cd(OH)_2$,[4] and $CdS/HgS/CdS$[5] are capable of exhibiting band-gap luminescence. In most cases, however, the emissive nanocrystals must be present in solvent containing much amount of other dissolved species like stabilizing material because nanocrystals without such species coalesce in solution, generating nonluminescent bulk particles. If one would like to apply the semiconductor nanocrystals to fluorescent agents for labeling biomolecules like DNA, it is required to prepare isolated nanocrystals that emit without dissolved stabilizing materials.

The fundamental technique for preparation of CdSe-based core-shell nanocrystals developed by Bawendi et al.[6] is presently the sole method to produce a size-series of highly luminescent quantum dots that emit fluorescence stably without any specific species in solution. Then, it is attempted to prepare unique labeling agent by putting appropriate functional groups on the nanocrystal surfaces. This useful material is prepared by growing crystals in a mixed solvent of tri-*n*-octylphosphine (TOP) and tri-*n*-octylphosphine oxide (TOPO) at relatively high temperature. Although the synthetic route is not complicated, skilled techniques are required for handling toxic reagents in a closed reactor and to monitor crystal growth until the desired size. Such difficulties seem to deter researchers who are not familiar with cluster synthesis from preparing the valuable nanocrystals.

We here report the first method to prepare isolated CdS nanocrystals exhibiting intense band-gap luminescence in aqueous solution at room temperature. Since the resulting nanocrystals can keep their intense fluorescence even after separation from water, they can be used as seeds for preparation of labeling agents. Furthermore, it will be shown here that combination of this method with the size-selective photoetching method[7] provides easy method to prepare fluorescent markers emitting desired wavelengths.

The initial step of our synthesis method is mixing 0.2 mmol of $Cd(ClO_4)_2$ and 0.2 mmol of H_2S gas in 1 dm^3 water containing 0.1 mmol of $(NaPO_3)_6$ as a stabilizing material, producing the nanocrystals dispersed in the solution.[4] After vigorously stirring the solution for 1 h, 0.57 mmol of mercaptopropionic acid (MPA) is added to produce MPA-capped CdS nanocrystals. The resulting solution is subjected to filtration by an ultrafilter membrane (YM10, MWCO 10000) to remove $(NaPO_3)_6$ and other dissolved materials. Then the MPA-capped CdS nanocrystals dissolved in pure water is obtained. However, when pH of the solution is adjusted to 11 with NaOH and then left on a bench, a yellow fine flocculate gradually appears. This is fine enough to be easily dispersed by weak agitation and takes several tens of minutes for complete reappearance. Surprisingly, the flocculate was found to exhibit luminescence and its intensity increased gradually over several hours (see Figure 2c). Once the intensity reached the maximum value, it was kept for one month or more. Figure 1 shows a picture of solution under black light (15 W, $\lambda_{max} = 360$ nm) taken immediately after agitation. Fluorescence measurements with an excitation light of $\lambda_{ex} = 350$ nm gave a single fluorescence peak at 520 nm with a 25-nm peak width at half height. The fact that wavelength of the fluorescence peak was close to the onset wavelength of its absorption spectrum (525 nm) revealed that the observed fluorescence was assigned to the band-gap emission.

The preparation of CdS flocculate under different conditions allowed us to notice that room light was important factor for generation of luminescent CdS nanocrystals. In other words, increase in luminescence intensity can be accelerated by intentional irradiation of the CdS solution. In the case of putting the sample under the above-mentioned black light, it takes only ca. 30 min to obtain the maximum intensity of luminescence.
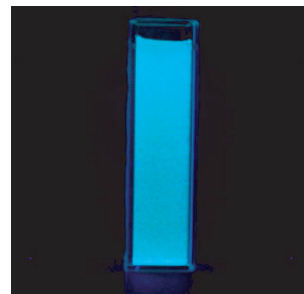

Figure 1. Emitting CdS nanocrystals dispersed in aqueous solution (pH = 11) under irradiation by a black light ($\lambda_{max} = 360$ nm). The picture was taken after agitation.
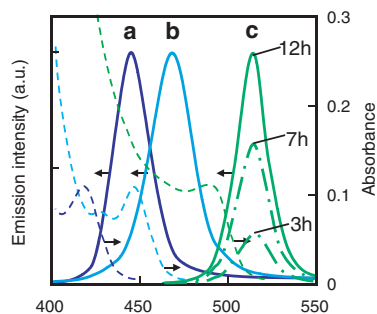
Figure 2. Absorption spectra (broken lines) and normalized fluorescence spectra (solid lines) taken with $\lambda_{ex} = 350$ nm for the CdS original nanocrystals (c) and nanocrystals subjected to the size-selective photoetching at 458 nm (a) and 476 nm (b). Increase in fluorescence with time for the original crystals is dipicted by alternate long and dash lines.

The fact of formation of CdS flocculate suggests strongly that MPA molecules adsorbed on CdS nanocrystals are desorbed in a weak alkaline solution. At the same time, the naked CdS becomes $CdS/Cd(OH)_2$[4] resulting in formation of fluorescent flocculate. Probably, negative charges on the crystal surfaces prevent coalescence of nanocrystals in the absence of any stabilizing material. The photocatalytic activities of CdS could help occurrence of the events. Investigations clarifying the reaction mechanism and structure of the resulting nanocrystals are underway.

The method of preparing CdS nanocrystals developed in this study can be combined with the size-selective photoetching technique that we have previously developed.[7] After preparation of CdS nanocrystals in aqueous solution containing $(NaPO_3)_6$, 0.05 mmol of methyl viologen (MV) is dissolved, followed by O_2 bubbling for 10 min. The MV works as an electron quencher for accelerating the potoetching. Then, the solution is irradiated with monochromatic Ar laser light. An absorption spectrum of the original solution shows absorption due to CdS nanocrystals with an onset at 520 nm. When light at wavelengths below the onset is used, a photoetching reaction ($CdS + 2O_2 \rightarrow Cd^{2+} + SO_4^{2-}$) takes place, resulting in smaller CdS nanocrystals. The quantum size effect gives blue-shift of the onset of the absorption spectrum. When the onset wavelength becomes the same as that of laser beam, photoetching is automatically ceased. It took ca. 30 min until the reaction was finished when laser beams of 476 nm (30 mW) and 457.9 nm (15 mW) were employed.

After addition of MPA, the resulting solution is then subjected to ultrafiltration and the alkaline treatment. Figure 2 shows fluorescence spectra of an original CdS nanocrystal-dispersed solution (c) and the solutions subjected to size-selective photoetching at 457.9 nm (a) and 476 nm (b). The quantum yields (QY) estimated by comparison of those spectra with a fluorescence spectrum obtained for quinine sulfate (QY = 54.6%) are greater than 30%, which are high enough for practical application as fluorescent markers. As recognized from the spectra shown in Figure 2, fluorescence agents exhibiting desired colors can be produced by simply tuning the wavelength of light used for the photoetching.

The CdS nanocrystals precipitated in alkaline solution maintain their intense fluorescence after filtration or centrifugation. It was found that the nanocrystals were completely dissolved in
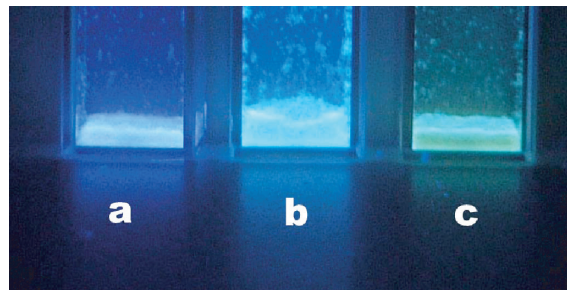

Figure 3. Picture of precipitation of CdS nanocrystals taken under irradiation by a black light. The CdS nanocrystals showing fluorescent spectra given in Figure 2 kept emitting intense luminescence even after precipitation.

ammonia water and aqueous solutions containing amine or ammonium salt, suggesting again that the nanocrystal surfaces are negatively charged. The coating of the nanocrystals with alkylamine would be useful as a method to introduce functional groups on the nanocrystal surfaces. For example, adsorption of 1-aminodecane on the CdS nanocrystals produces the CdS fluorescence markers that are dissolved in organic solvent like heptane. By utilizing these techniques, development of the multicolor fluorescence agents that are suitable for chemical and biochemical analysis, and other purposes are underway.

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