Highly luminescent mono- and multilayers of immobilized CdTe nanocrystals: controlling optical properties through post chemical surface modification†

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The significant fluorescence enhancement of immobilized CdTe nanocrystals through chemical surface modifications is described, enabling us to fabricate stable, highly luminescent thin films and patterns of nanocrystal mono- and mutilayers.

Recently, CdTe nanocrystals functionalized with several functional molecules have been widely prepared,[1–4] and have found several applications in nanoscience and biotechnology.[5–8] Recent progress in device fabrication technology has motivated several attempts to use these CdTe nanocrystals as elemental building blocks for the next generation of nanodevices such as light emitting diodes,[9–11] solid-state sensors,[12,13] and solar cells.[14] In particular, much effort has been devoted to organizing nanocrystals into structures on solid substrates to form thin films[15,16] and patterns[17,18] using a variety of fabrication techniques.

Nanocrystal-based devices ultimately require the nanocrystals to be stably and selectively immobilized on a substrate. This can be achieved for specific layers including self-assembled monolayers[18] and/or functionalized polymers.[15] Post-treatment of immobilized nanocrystals is considered effective for creating film-type devices, because fluorescent quantum yield typically decreases during the immobilization process. However, although there are numerous reports on the fabrication of thin nanocrystal layers, there have only been a few reports on controlling the fluorescent properties of the immobilized nanocrystal layers by post-treatment procedures.[17] In the present study, mono- and multilayers of CdTe nanocrystals covalently immobilized on a glass substrate are fabricated, and their optical properties are systematically controlled through a post surface chemical modification using thiolate ligands.

The present process works by immobilization of CdTe nanocrystals on a glass substrate modified with monolayers bearing thiol moieties, followed by further nanocrystal surface modification using alkanethiol or dithiol molecules (Fig. 1A). In a typical procedure, CdTe nanocrystals were first prepared *via* the method reported by Yu *et al.*[19] We prepared tributylphosphine (TBP)-protected CdTe nanocrystals with diameters of about 3.7 nm and 3.2 nm, showing a weak emission peak at 613 nm (red-emitting nanocrystals) and 565 nm (green-emitting nanocrystals), respectively. Glass substrates were treated with a toluene solution of 3-mercaptopropyltrimethoxysilane (MPS, 40 mM) at room temperature for 1 h followed by heat treatment at 110 °C for 30 min to produce glass surfaces functionalized with –SH groups. After rinsing the substrate with toluene, the substrate was immersed into the toluene solution containing CdTe nanocrystals (30 μM) at room temperature for the appropriate times. The CdTe nanocrystals are immobilized and self-assembled on the glass surface due to the strong binding interactions between the CdTe nanocrystals and the –SH moieties, therefore resulting in the formation of CdTe monolayers, similar to the CdS monolayers reported on glass substrates.[20]

The average surface coverage of nanocrystals can be controlled simply by the immobilization duration (Fig. 2). UV-Vis spectroscopy of the substrate was used to monitor the immobilization of nanocrystal layers to the substrate. Absorbance at 530 nm, which corresponds to band edge absorption of CdTe nanocrystals, increases quickly at the initial stage of

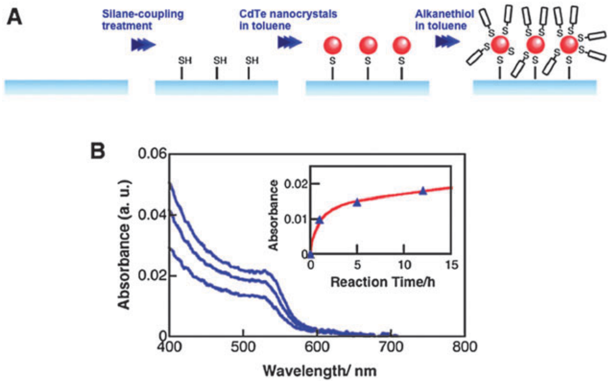

Fig. 1 (A) Schematic of the fabrication of immobilized CdTe monolayers and post-surface modification using alkanethiols. (B) Changes in optical absorption spectra for CdTe nanocrystals immobilized on glass substrate as a function of immersion time of the thiol-functionalized glass substrates in toluene solution containing CdTe nanocrystals. Inset: Plots of absorbance at 530 nm for CdTe nanocrystals with immersion time.

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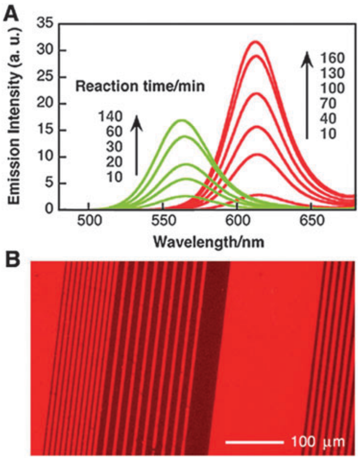

Fig. 2 (A) Fluorescence spectra of immobilized CdTe nanocrystals of 3.7 and 3.2 nm diameter as a function of reaction time with decanethiols. (B) Fluorescent image of micropatterns of red-emitting CdTe nanocrystal monolayer immobilized on glass substrate selectively functionalized with thiol functional groups.

the reaction and approaches a nearly constant value after 12 h. This observation demonstrates the ability to control the number density of the CdTe nanocrystals on the surface simply by immobilization duration. Indeed, higher concentration of the nanocrystals resulted in higher deposition rate.[21] In the current work, a 12 h reaction time produced a density of about 1.6×10^{-11} and 2.2×10^{-11} mol cm^{-2} for 3.7 and 3.2 nm nanocrystals, respectively.[22] These values are nearly consistent with those expected for a densely packed superlattice. The fluorescent quantum yield (QY) of both as-prepared CdTe nanocrystals in solution was below 1%.

Upon immersion of the substrates with the CdTe monolayers into toluene solution of decanethiol (DT) at 80 °C, initial less-fluorescent monolayers became strongly fluorescent; the fluorescent intensity from red- and green-emitting nanocrystals increased as a function of time (Fig. 2A). Since the number of immobilized CdTe nanocrystals remained intact (dissociation of the nanocrystals was not observed from ICP measurements for solution obtained after reaction), this observation suggests an increase in fluorescence QY of the immobilized CdTe nanocrystals.[23] This effect can be caused by molecular exchange of weakly bound TBP with alkanethiol molecules, as has been previously demonstrated for surface modification of CdTe nanocrystals in solution.[24] This process results in compensation for surface defects that are responsible for the nonradiative recombination of excitons. After the reaction for 160 min, QY of 30% was achieved for red emitting nanocrystals functionalized with DT. We note that the present simple surface modification process is applicable to the fabrication of fluorescent micropatterns (Fig. 2B) by a combination with lithographic techniques[22] (thiol treatment "embosses" the fluorescent patterns) as well as to other thiolate molecules with different functional groups.

It is important to recognize that the use of pre-treated CdTe nanocrystals (with QY of 60%, prepared before immobilization by reaction of the nanocrystals with DT molecules in solution) did not provide sufficient control of the nanocrystal immobilization nor the optical properties. Although such DT-protected CdTe nanocrystals could also be immobilized on the SH-terminated surface through a ligand exchange reaction, much longer times were necessary for complete immobilization (typically several days). In addition, the QYs of the nanocrystals decreased after immobilization and, more importantly, further chemical treatment using DT molecules no longer provided an increase in QYs. When surface "attachment" of thiol ligands is completed, then ligand exchange reaction between bound thiols and thiols in solution occurs, making nanocrystal surface defective again due to "thiol exchange" at the surface. This trend was generally observed when the semiconductor nanocrystals were already protected by molecules with strong binding affinities to the nanocrystal surface. Therefore, it is crucial that nanocrystals weakly-protected by TBP (or other molecules) are subjected to the immobilization process, and subsequently subjected to post surface modification using functional molecules with a strong binding affinity to the nanocrystals.

Interestingly, the degree of increase in fluorescent intensity was found to be dependent on the type and length of the molecules used for the surface modification. Typically, a greater increase in fluorescent intensity was achieved for dithiol molecules with shorter chain lengths than for monothiol molecules (Fig. 3). The rate of increase in the intensity for shorter dithiols was also found to be greater than that for longer dithiols. Shorter molecules are thought to effectively attach to the nanocrystal surface due to decreased steric hindrance. We have performed EDX elemental analysis for functionalized CdTe nanocrystals on the substrates during reaction with dithiol molecules. Consequently, the nanocrystals showing higher emission intensity (using shorter dithiols) were found to be functionalized with greater number of thiols as compared to the nanocrystals showing lower emission (using longer dithiols). Number of dithiol ligands attached to CdTe nanocrystals estimated from the intensity ratio (Cd-Lα and S-K X-ray lines) was *ca.* 24, 48 and 62 dithiols per nanocrystal for $HSC_{10}H_{29}SH$ (after 60 min reaction), $HSC_6H_{17}SH$ (after 60 min), HSC_3H_8SH (after 30 min), respectively, the values of which are relatively smaller than those for CdTe nanocrystals fully functionalized with monothiols (*ca.* 90 thiols per nanocrystal).[4] The results demonstrate that degree of surface attachment, which is affected by chain length of thiols, determines emission properties of the nanocrystals. Therefore, efficient surface coverage on the nanocrystal surface gives high QYs. In a current unoptimized system, QYs

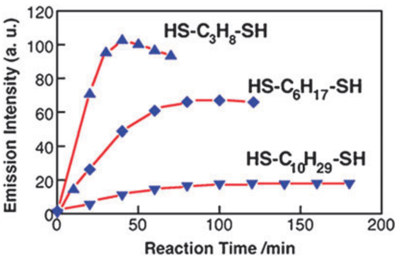

Fig. 3 (A) Effect of chain length for alkanedithiols on changes in emission intensity of immobilized red-emitting CdTe (3.2 nm) nanocrystals.

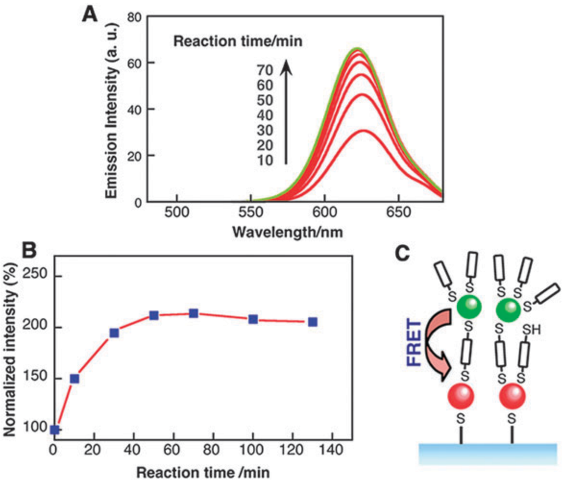

Fig. 4 (A) Fluorescence spectra of immobilized CdTe nanocrystal bilayer as a function of reaction time with decanethiols. (B) Plots of normalized emission intensity from red-emitting nanocrystals in the bilayer (set to 100% before reaction) as a function of reaction time. (C) Schematic of the bilayer consisting of first red-emitting nanocrystal layer and second green emitting nanocrystal layer, in which each layer is connected by decanedithiols.

over 80% were achieved for nanocrystals after reaction with propanedithiol for 60 min.

The present process is expected to be effective to construct multilayers of nanocrystals with controlled emission properties. In the current set of experiments, a second layer of smaller nanocrystals (3.2 nm, green-emitting nanocrystals) was immobilized on the first layer of nanocrystals (red-emitting nanocrystals) after modification of first layer using dithiol molecules (Fig. 4). In this case, further surface treatment for the "second" nanocrystal layer using thiol molecules results in an increase in emission intensity of the "first" nanocrystal layer (Fig. 4A and 4B), with no detectable emission of the second nanocrystal layer. These experiments were carried out after surface modification of first layers until the increase of emission intensity was saturated. Therefore, further increase of emission intensity in this first layer can be caused by fluorescent energy transfer from the second green-emitting nanocrystal layer to the first underlying red-emitting nanocrystal layer (Fig. 4C). As the QY of green-emitting nanocrystals increases through attachment of thiol molecules, the emitted light that is being adsorbed by red-emitting nanocrystals through energy transfer increases, thus resulting in an increase in emission intensity of the red-emitting nanocrystals. This technique enables the emission intensity of the first red-emitting nanocrystals to become over two orders of magnitude greater than that of the as-immobilized nanocrystals, allowing formation of very thin, bright nanocrystal layers that are potentially useful for light-emitting devices.

Herein, we have shown that the emission of pre-immobilized nanocrystal monolayers and energy transfer properties in the multilayered structures can be controlled by post surface chemical treatment. This process not only offers control of the optical properties, but also enables modification of the surface chemistry for the immobilized semiconductor nanocrystals. Such control is expected to have great potentials for fabricating dense nanocrystal-based devices, such as light emitting diodes and solar cells with energy-gradient internal microstructures.[15]

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22 See supplementary information (ESI†).
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