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pH-Dependent Network Formation of Quantum Dots and Fluorescent Quenching by Au Nanoparticle Embedding

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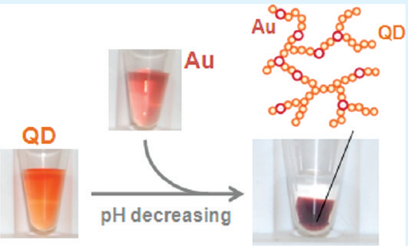
S *Supporting Information*

ABSTRACT: A simple approach to the creation of colloidal assemblies is in high demand for the development of functional devices. Here, we present the preparation of CdTe-QD (quantum dot) networks in as little as 1 day simply by pH modification without the use of oxidants. The QD network was tractable in water and casting from a droplet produced a porous networked film on both hydrophobic and hydrophilic solid substrates. Further, we found that citrate-protected gold nanoparticles (AuNPs, d = 5 nm) could be incorporated into the QD networks to afford a QD/Au composite network, and that the fluorescence from the QDs was largely decreased by the addition of a small proportion of AuNPs (QD:AuNP = 99.4:0.6), probably due to the efficient charge transfer through the network. These data indicate that our method is suitable for application to the creation of metal/QD hybrid materials that can be integrated into wet-based processes.



KEYWORDS: quantum dot, gold nanoparticle, self-assembly, fluorescence quenching, CdTe, nanoparticle assembly

Semiconductor nanoparticles have been one of the most important nanomaterials in a wide range of research fields because of their tunability to the desired luminescent wavelength, high luminescence efficiency, and redox potentials.[1,2] Recently, considerable progress has also been made in the study of QD organization in large structures, such as 1D, 2D, and 3D assemblies,[3−6] as these structured QDs are expected to generate collective new functions with applications to random lasers,[7,8] solar cells,[9−11] and electroluminescence devices (LEDs).[12,13] Several conventional approaches to the preparation of QD assemblies, including the layer-by-layer (LbL) method,[14−16] and incorporation into polymers[17,18] or gels,[19,20] have been reported. However, large gap between nanoparticles is thought to reduce the efficacy of interparticle energy or charge transfer.[21−23] We focus on a relatively new method, the gelation of QDs, as the gaps between QDs produced by this approach are relatively small, leading to highly efficient energy or charge transfer between the QDs. The instability of nanoparticle dispersion eventually results in their aggregation, and a transient state between chain formation and aggregation is known to generate a 3D colloidal network.[24,25] Brock et al. have explored the creation of QD-based aerogels and xerogels, which are made by the covalent connection (formation of Se−Se bonds) of QDs by removing capping ligands by oxidation or light irradiation.[26−30] Recently, Kotov et al. also reported the synthesis of a sol−gel reversible QD network by long-term irradiation (3 month) with white light.[31] In this paper, we report that charged QDs can be formed by controlling the pH of the solution, into noncovalent (not cross-linked) 3D networks of QDs. In our method, the QD network can be prepared within one day. Since our method is not based on photoinduced strong particle−particle connections, but pH-mediated weak assembly, the network is moldable in water and can produce porous thin films on solid substrates. It is noted that the cast film is homogeneously deposited on the substrate after evaporating the solvent without generation of the coffee ring pattern that is often observed during the drying process of colloidal solutions. These properties indicate that QD networks are a good precursor to the preparation of high-density, colloidal assemblies on solid substrates.

The close-coupling of QDs with different nanoparticles would significantly improve the electronic and optical functions or even express new properties, such as exiton-plasmon coupling.[32] Further we present that the QD/AuNPs composites can be produced in the process of the network formation and AuNPs efficiently quenched the photoluminescence (PL) from QDs. Very recently, Eychmuller and co-workers reported that tetrazole-coated CdTe and AuNPs can form mixed network structures by chelation-based cross-linking of particles in the presence of a large excess of cationic ions, such as Cd^{2+}.[33] However, there have been few reports on the integration of other particles into QD network without the use of cross-linking reagents, which could affect or disturb the electro-optical properties of the network. Our simple approach to making hybrid networks will expand the utility and functionality of these heterogeneous colloidal assemblies.

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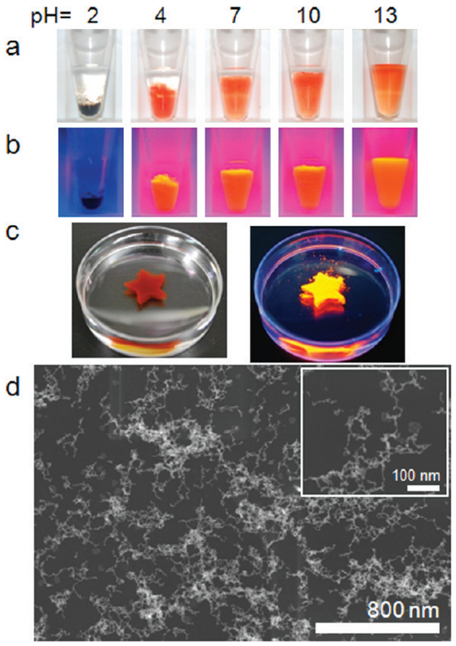

Figure 1. (a) Photographs and (b) fluorescence images of MPA-QDs prepared at pH 2, 4, 7, 10, and 13. (c) Photographs and fluorescence images of shaped networked QDs. (d) STEM images of networked QDs. The excitation wavelength is 365 nm.

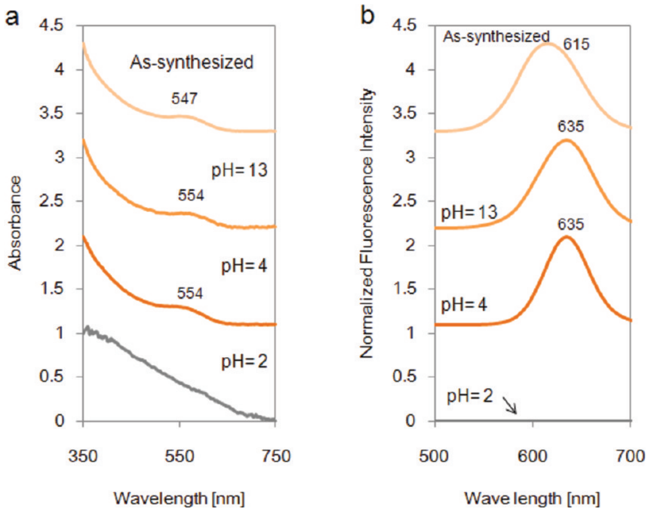

Figure 2. (a) Absorbance and (b) fluorescence spectra of as-synthesized, dispersed (pH 13), networked (pH 4) and aggregated (pH 2) QDs. The excitation wavelength is 365 nm.

The synthesis of 3-mercaptopropanoic acid (MPA)-stabilized CdTe QDs was carried out according to the literature.[34] Stokes diameter and ζ potential of the MPA-QDs were 6.0 nm and −44.4 mV, respectively. In order to increase the instability of QDs, excess ligands in the QD solutions were removed by repeated centrifugal filtration (× 5; 30 kD). The resultant QDs were resuspended in pure water and the pH of the solution was adjusted by the addition of HCl or NaOH (pH 2, 4, 7, 10, or 13). The solution was then left to stand for 24 h in a dark at room temperature (final concentration; 2.7 nM). Each QD dispersion state after standing for 24 h is shown in parts a and b in Figure 1.

Under strongly basic conditions (pH 13), MPA-QDs were well-dispersed. By decreasing the pH, QDs became separated from the water phase to form an assembled structure, with the QD density in the structure reaching a maximum level at pH 4.0. The QDs could be redispersed in the water by sonication or increasing the pH. This means that the QD self-assembly at pH 4.0 proceeds through noncovalent particle−particle interactions. Under strongly acidic conditions (pH 2), MPA-QDs were aggregated and formed an irreversible black precipitate. Scanning transmission electron microscopy (STEM) images of the phase-separated state were taken for a cast film on a carbon-coated TEM grid. For this assembled state (prepared at pH 4.0), a network structure, but not an aggregated form, was observed over a wide area (Figure 1d). This fluorescence QD network is not covalently connected; instead it behaves in a manner similar to a physical gel-like colloidal assembly. In fact, networked QDs are moldable in water. The precursor networked QD solution was poured into a star shaped mold, and the solution was left to stand for 12 h. The networked QDs maintained their star-shape for several weeks after removal from the mold (self-standing, Figure 1c). Because the networked QDs do not disperse in water, they have great advantages for use in extrusion molding. The QDs in a networked state showed clear fluorescence, even though the fluorescence intensity is reduced to 15% of that in the dispersed state (see Figure S1 in the Supporting Information). In contrast, aggregated QDs formed at pH 2 did not show any fluorescence.

Fluorescence spectra obtained from dispersed QDs after removal of excess ligands showed a red shift of 20 nm compared to that of QDs in the presence of excess MPA (as-synthesized QDs) (Figure 2). Although the fluorescence intensity of the networked QDs decreased, the process of network formation did not affect the wavelength of the fluorescent peak. Previous reports have indicated that QDs tend to recrystallize into nanowires, causing a red shift of the fluorescence.[25] However, judging from the STEM images and fluorescence shift, no significant growth of nanoparticles could be observed after the formation of the network state. Importantly, thioglycolic acid (TGA)-coated QDs, which have a short alkyl chain (C2), were well-dispersed in water and did not form a gel network under the same experimental conditions. This implies that the slight increase in the hydrophilicity of the ligand molecules affects the network formation of QDs, probably because of the balance between electrostatic repulsion and van der Waals attraction force.

We also tested the pH-dependent network formation of 2-mercaptoethanolamine (MA)-coated QDs, which possess a positively charged ligand (see Table S1 in the Supporting Information), to expand the generality of this network phenomenon. MA-QDs formed a similar gel-like structure by increasing the pH up to 13 to neutralize the amine residues (see pictures in Figure S2 in the Supporting Information). These data suggested that cationic QDs can also form a stable network by changing the pH of the solution, and this network can be kept for more than one week without irreversible aggregation.

Because the QD networks in this study are not covalently connected solids, they are expected to be candidates for colloidal inks used in directed writing.[20] Thus, we applied the QD network to create a film precursor on solid substrates. Controlling the distribution of nanoparticles during the drying process is a key step in the production of homogeneous cast films. We deposited the QD network onto hydrophobic and hydrophilic glass substrates. Regardless of the substrate properties, the QD network

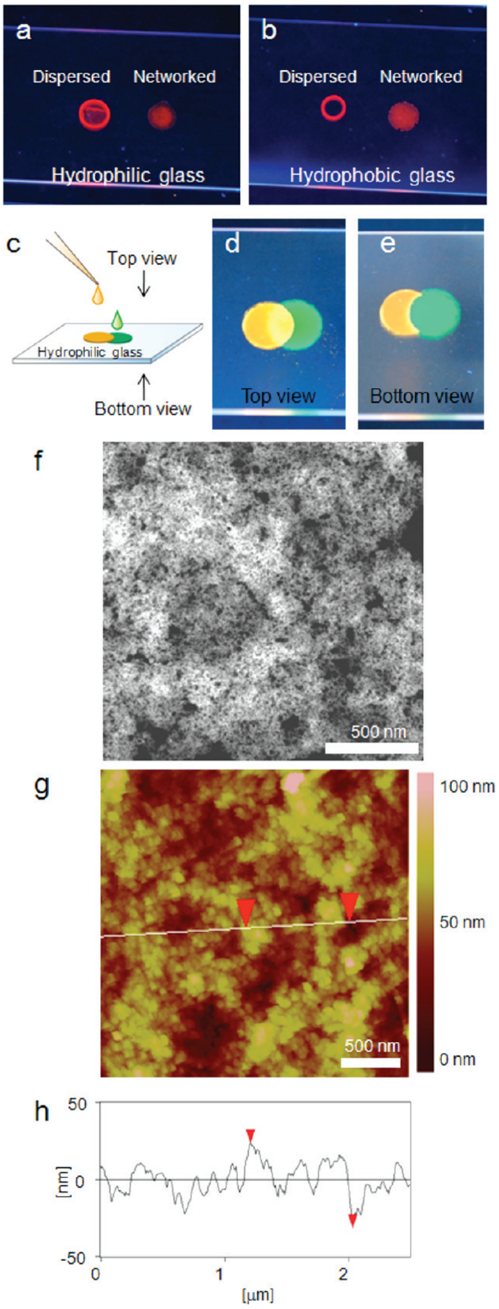

Figure 3. Fluorescence images of dried droplets of dispersed and networked QDs on (a) hydrophilic and (b) hydrophobic glass substrates under UV light. (c) Preparation of networked QD layers on a hydrophobic glass plate. The yellow QD network was deposited on the dried green QD network. (d, e) Fluorescence images of the QD layer under UV light. (f) STEM, (g) AFM, and (h) cross-section images of networked QD films of b.

formed a homogeneous thin film (5 mm in the diameter) after drying (Figure 3a, b) and the films remained intact even after rinsing with water (see Figure S3 in the Supporting Information). In contrast, the cast from the dispersed QD solution on the substrates resulted in a circular pattern with the QDs concentrated at the edge due to the coffee ring effect.[35] We deposited QD networks of different colors (yellow and green) step-by-step on a hydrophobic glass substrate to make a layered QD assembly (Figure 3c; the yellow QD network was deposited on the dried green QD network). Figure 3d-e shows photographs of the QD assembly on the glass plates under UV irradiation. This data clearly indicates that each QD network was layered without any mixing during the deposition process, demonstrating the robustness of the networked film after drying. To date, QD assemblies have generally been made using a layer-by-layer (LbL) method.[14−16] This LbL method requires the addition of polymers or dendrimers, and the thickness of the QD layers is hard to regulate. However, our method does not need any such additional compounds that may reduce the conductivity between the QDs, and the thickness of each QD layer can be easily modulated by changing the amount deposited. These features might be important to obtain maximum efficiency in solar cells by adapting to the wavelength of sunlight. Based on these observed properties, we concluded that the QD network is a good precursor for the formation of colloidal assemblies on desired substrates using a wet process. STEM images reveal that the film surface is quite rough with pores derived from the network structure (Figure 3f). AFM images confirm that the surface roughness is about 50 nm, and this supports the idea that a xerogel-like network is maintained in this film (Figure 3g, h).

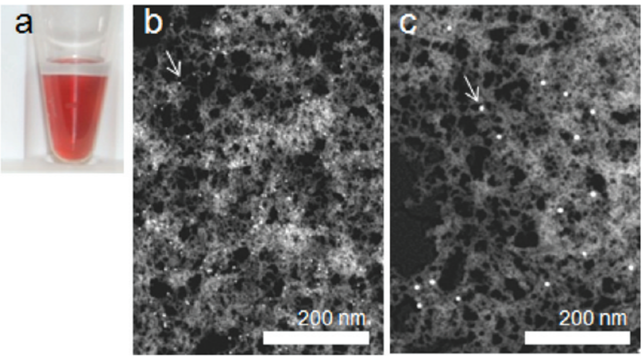

Figure 4. (a) Photograph and (b) STEM images of the MPA-QD network into which 5-nm AuNPs were embedded (number ratio; QD: Au = 99.4:0.6). (c) The MPA-QDs network with 0.1% of 10 nm AuNPs. The excitation wavelength is 365 nm. White arrows in the STEM images indicate (b) 5 and (c) 10 nm AuNPs, respectively.

Next, we made colloidal assemblies blending heterogeneous nanoparticles into the QD networks. MPA-QD assembly in the presence of AuNPs (Particle number ratio; QD: AuNPs = 99.4:0.6) was carried out. Surprisingly, upon network formation, the supernatant was colorless and negligible UV−vis absorption (no surface plasmon-originated color) was observed, indicating that the AuNPs ($d = 5$ nm) were completely trapped within the QD networks (Figure 4a). STEM images of the networked QDs demonstrated that the AuNPs were homogeneously embedded into the QD networks to afford the networked QD/Au composite (Figure 4b). This QD/Au composite can be made for 10 nm AuNPs (Figure 4c). Even when the number ratio of AuNPs to QDs was increased up to 9%, AuNPs were incorporated into the QD networks (see Figure S4 in the Supporting Information).

Fluorescence properties of the QD/Au composite were then measured to clarify the interaction between the AuNPs and QDs. As a control to the network structure, we prepared a dispersed QD solution with the same concentration as that of the networked QDs. Since the solid volume of the QD network was one-third of that of the original QD solution, the original QD solution was simply concentrated (not networked) 3-fold. Spectra a and b in Figure 5 show the absorbance and fluorescence spectra

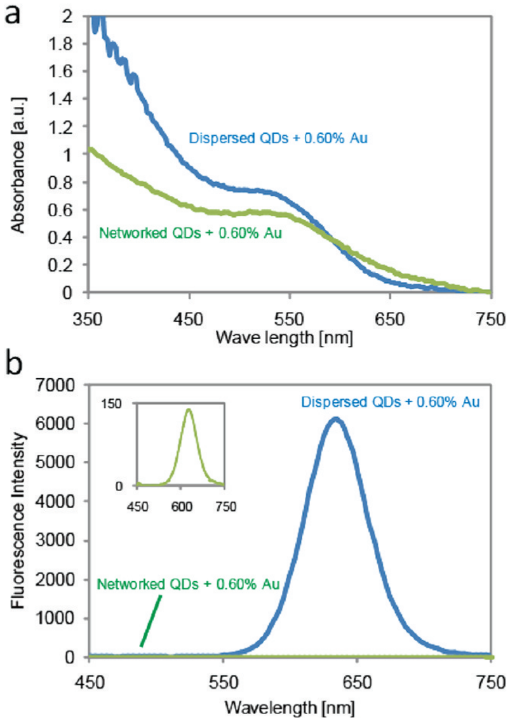

Figure 5. (a) Absorbance and (b) fluorescence spectra of dispersed and networked QDs mixed with 5 nm AuNPs. The excitation wavelength is 365 nm. Density (number of particles) of the dispersed QD solution is equal to that of the networked QDs. Inset shows the enlarged spectra of networked QD mixed with 5 nm AuNPs.

of the networked and concentrated QD/Aus. Interestingly, the fluorescence of QD/Au network was too small to be detected. In contrast, the concentrated solution produced clear fluorescence. Because the concentrations (numbers) of AuNPs and QDs were the same in both samples, this fluorescence quenching is thought to be derived from the network structure. The absorbance spectra corresponding to the Au plasmon resonance (~520 nm) became weaker and were broadly red-shifted for the networked structure. We measured the fluorescence decay of the QD/Au network (see Figure S5 in the Supporting Information). The fluorescence lifetime of the networked and dispersed QD/Aus were 2.4 and 7.4 ns, respectively (see Table S2 in the Supporting Information). This also indicated that the effective fluorescence quenching of QDs is due to the networked structure. The photoluminescence quenching was previously observed for CdSe/Au binary superlattice structures (number ratio: CdSe:Au = 1:0.7) because of exciton-plasmon interactions.[32] In addition, there are a number of reports of the fluorescence quenching of semiconductor nanocrystals when in contact with AuNPs, probably due to electron transfer[36] and energy transfer[37−39] from the semiconductor to the AuNPs. For example, the dipole-based energy transfer process was reported to induce QD quenching in QD-DNA-AuNP hybrid systems.[37−39] Similarly, the broad, red-shifted and weakened plasmonic peak was reported for the CdS-Au conjugation, because of the suppression of plasmon resonance.[40] However, in this network, the number ratio of AuNPs to QDs is ca. 1%, which is much lower than that in previous reports, so this large fluorescence quenching implies that the efficient electron or energy transfer from QDs to AuNPs might occur through QD networks.

In summary, we explored a method for pH-dependent QD network formation and demonstrated the potential applications of such QD networks. The network condition is simple, and no chemical reagents, such as detergents and oxidants, are necessary. AuNPs could be incorporated into the QD network, indicating that the process of network formation is suitable to the creation of the metal/QD nanoparticle composite materials. In addition, it was clarified that the network structure causes efficient photoluminescence quenching, implying that the efficient charge or energy transfer from the QDs to AuNPs through the network. The QD network can be formed into a thin porous film on solid substrates after evaporation of the solvent. This demonstrates its possible application to printing and wet processes using colloidal assembly. Therefore, we are currently engaged in research toward the coating of QD layers onto ITO or conductive polymer substrates to make light-emitting diodes (LEDs) or solar cell devices based on the benefits of networked QDs.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Fluorescence spectra, photographs of dispersed and networked QDs. This material is available free of charge via the Internet at http://pubs.acs.org

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