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Quantum Dots

Fluxible Monodisperse Quantum Dots with Efficient Luminescence**

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Colloidal semiconductor nanocrystals, also referred to as quantum dots (Qdots), are currently of great fundamental and technical interest because of their unique size-dependent optical properties and flexible chemical processability, which are useful in biological labels, optical devices, and barcodes.[1–3] In these applications, Qdots are usually used in the form of a film, powder, or dispersion in aqueous/organic solvents. However, most organic solvents are not environmentally benign. Recently, Giannelis and co-workers[4] pioneered a new class of hybrids, termed nanoparticle ionic materials (NIMs), which comprise a nanoparticle core functionalized with a covalently tethered ionic corona. Solvent-free $CaCO_3$,[5] protein,[6] and carbon nanotube[7] liquids adopting this approach have been reported. In these sorts of NIMs, a cationic oligomeric corona is grafted onto the nanoparticle cores, and anionic surfactants act as a counterion to produce solvent-free nanoparticle ionic liquids.[8] Quantum dots–ionic liquid hybrids have been prepared by extracting cationic CdTe into low-molecular-weight ionic liquids[9] or passivating CdSe nanocrystals with ionic liquids.[10] Sun et al. also obtained lead salt quantum dot ionic liquids with infrared emission by ligand exchange.[11] Nevertheless, in all of the reported works, the methods for the preparation of NIMs are not accessible to solvent-free fluxible Qdots with narrow, symmetric photoluminescence (PL) spectra in the visible window (400–700 nm) owing to their different surface functional groups and photochemical instability. As a typical example, we reproduced the ionic behavior of CdSe Qdots based on the literal method of PbS Qdot ionic liquids.[11] However, the resulting CdSe Qdot ionic liquids always quenched during ligand exchange, and consequently, the valuable fluorescence could not be maintained.

Herein, we report a new type of NIM based on CdSe/CdS/ZnS core/shell/shell Qdots through a simple, rapid extraction method with commercially available reagents, in which the long chain cationic surfactant is grafted onto the anionic CdSe/CdS/ZnS Qdots. The ionic bonds between low-molecular-weight carboxylate grafted on the surface of Qdot core and cationic surfactant with polyethylene glycol chains pave a way to solvent-free fluxible Qdots (F-Qdots) with nonvolatility (weight loss $< 0.57\,\%$ below 200 °C), low melting point (0.12 °C), low viscosity (< 0.1 Pa s at 70 °C), narrow emission spectral width (28 nm), and high thermal stability (decompose at about 200 °C). In this strategy, both the steric hindrance of the quaternary ammonium salt $C_9H_{19}C_6H_4(OCH_2CH_2)_{10}O$-$(CH_2)_2N^+(CH_3)_3Cl^-$ (NPEQ) grafted on the F-Qdots and the electrostatic force between the Qdots and NPEQ make the F-Qdots monodisperse owing to the high grafting density (88 % organic content) of NPEQ, and thus fluxible Qdots with efficient luminescence are achieved.

Typically, highly fluorescent Qdots were synthesized according to the literature methods with a little modification.[12–14] Water-soluble Qdots were prepared by following a literature procedure,[15] passivated with mercaptopropionic acid (MPA), and then deprotonated by NaOH. NPEQ dissolved in chloroform was employed to extract anionic stabilized Qdots in water through ion exchange. The facile phase-transfer process is depicted in Scheme 1.

First, as-prepared water-soluble anionic Qdots are dispersed in the water layer above chloroform containing NPEQ (Scheme 1 a). An emulsion forms after vigorous stirring (Scheme 1 b), which supports that ion exchange occurred between NPEQ and carboxylate tethered on the surface of Qdots at water–chloroform interface (Scheme 1 c). As a traditional phase-transfer catalyst,[16] the quaternary ammonium salt can smoothly transfer hydrophilic anionic nanocrystals into the oil phase. During ion exchange, the generated NaCl is dissolved in water, and the Qdot-NPEQ ion pair is extracted into chloroform (Figure S1 in the Supporting Information). After stirring of the emulsion for 30 min and standing for about 10 min, the anionic stabilized Qdots are almost completely transferred to chloroform (Scheme 1 e). The light-yellow water layer indicates that unreacted NPEQ has been stripped from chloroform into water because of its amphiphilic nature. The water layer containing unreacted NPEQ is discarded and water-soluble anionic Qdots are again added steadily to ensure that all of the NPEQ molecules have reacted with Qdots. Repeated stripping of potential NPEQ from chloroform to water is necessary to purify the F-Qdots. The F-Qdots are obtained after evaporation of chloroform (Scheme 1 f,g), whose structure is depicted in Scheme 1 h. The resulting F-Qdots were loaded into a vial and irradiated by a UV lamp ($\lambda = 365$ nm). The fluidity of the F-Qdots and light emission were clearly observed (Scheme 1 i). The F-Qdots material is a homogeneous viscous and red fluid that shows liquidlike behavior at room temperature and emits bright orange light upon UV excitation. Additionally, the F-Qdots

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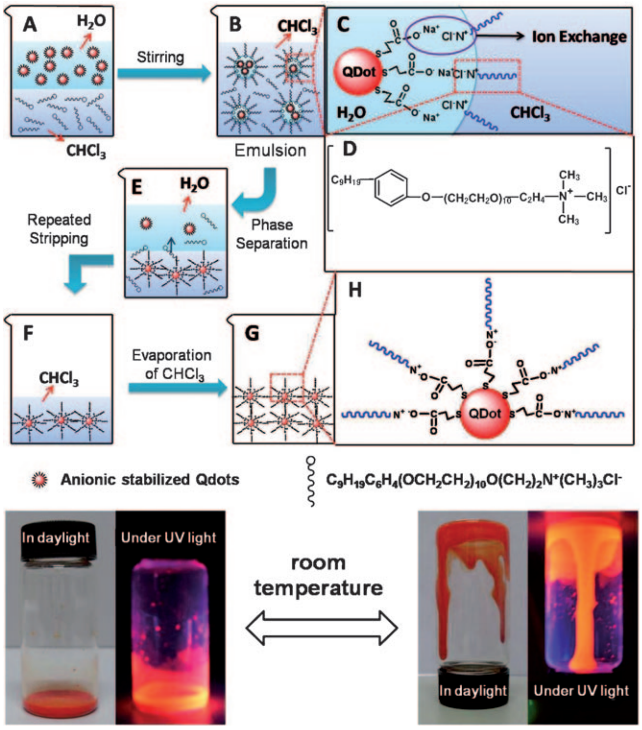

Scheme 1. A) Water-soluble Qdots and NPEQ in chloroform, B) emulsion of water in oil (W/O), C) ion exchange between the Qdots and NPEQ at the water–chloroform interface, D) molecular formula of NPEQ cationic surfactant, E) water layer containing unreacted Qdots and chloroform layer containing NPEQ functionalized Qdots, F) oil-soluble Qdots in chloroform, G) F-Qdots, and H) a single NPEQ-functionalized Qdot. I) Photographs of the fluidity of corresponding samples (in daylight and under UV light).

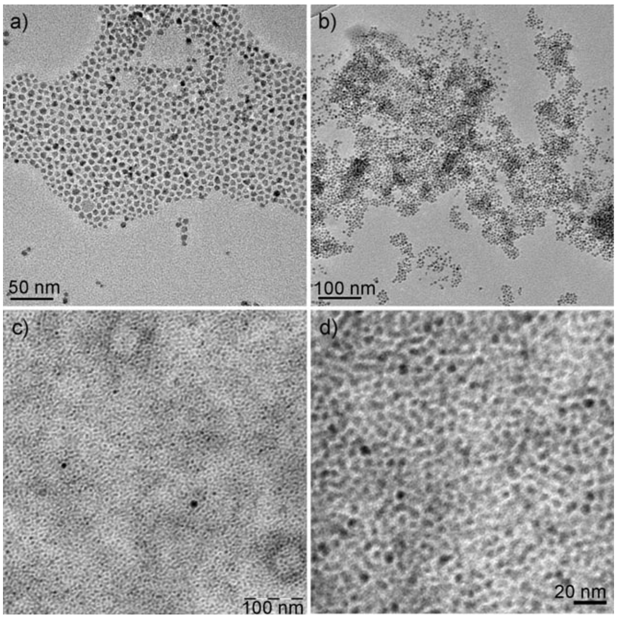

Figure 1. TEM images of a) synthetic Qdots, b) MPA-coated Qdots and c, d) F-Qdots.

are well soluble in nonpolar solvents and no longer soluble in polar solvents (Figure S2). This behavior indicates that the outer layer of the Qdot-NPEQ hybrids is coated with hydrophobic NPEQ chains and suggests that the reaction of ion exchange between cationic NPEQ and anionic stabilized water-soluble Qdots has occurred.

The water-soluble Qdots passivated with MPA was confirmed by the well-resolved infrared absorption bands (Figure S3). The $C{=}O$ stretching band is located at 1706 cm^{-1}, and the peak at 3415 cm^{-1} corresponds to their hydroxy groups. The ion exchange by the NPEQ was confirmed by the benzene skeleton vibration at 1456, 1512, and 1610 cm^{-1}.

Figure 1 shows the transmission electron microscopy (TEM) images of the original Qdots in hexane, anionic stabilized water-soluble Qdots in water, and the resulting F-Qdots in chloroform. In agreement with the reported results,[14] the as-synthesized original hydrophobic CdSe/CdS/ZnS core/shell/shell Qdots (Figure 1 a) are monodisperse without any aggregation. However, after being passivated with MPA, the water-soluble Qdots become agglomerative owing to the lack of steric hindrance between nanocrystals (Figure 1 b). Interestingly, after ion-exchange with NPEQ, the F-Qdots exhibit perfect monodispersity (Figure 1 c), and no aggregation of F-Qdots can be observed even in a wide field view (Figure S4). Figure 1 d shows that the dense Qdot-NPEQ hybrids loaded on the copper grid are well dispersed by NPEQ. The monodispersity of Qdots in the NPEQ continuous phase is attributed to the electrostatic force among the ions and steric stabilization between Qdots. Both the long polymer chain of NPEQ and ionic bilayer structure facilitate the dispersion of Qdots. The extraction strategy makes sure that individual Qdots can be densely grafted by NPEQ.

A differential scanning calorimetry (Figure 2 a) trace of F-Qdots shows that the ligands on the surface of Qdots crystallize at −12 °C and melt at 0.12 °C. No other phase-transition temperature was observed for the F-Qdots material, which indicates that the F-Qdots have excellent fluidity at room temperature. Thermogravimetric analysis (TGA) (Figure 2 b) shows that the decomposition temperature of the F-Qdots is about 200 °C. Notably, the organic content of F-Qdots is up to 88 % w/w. To the best of our knowledge, this is the first example of extremely high organic content in reported NIMs.[4] If the size of Qdot core is assumed to be 5 nm, the calculated organic content of the F-Qdots should be 86.85 % (Figure S5), which demonstrates further that the 88 % organic content is attributed to the dense coating of NPEQ on individual Qdots and to the small size of the Qdots.

The flow properties of the F-Qdots were observed in an inverted vial and measured by a parallel plate rheometer. When passivated with MPA, the Qdots appear as a solid. After ion exchange with NPEQ on the surface of anionic stabilized Qdots, the solvent-free Qdot–NPEQ hybrids behave in a liquid manner. This behavior was also confirmed by the fact that the shear loss modulus G'' is higher than the storage modulus G' from room temperature to 70 °C (Figure 3 a). Also, the viscosity of the F-Qdots decreases with increasing temperature and is as low as 0.1 Pa s at 70 °C (Figure 3 b). Generally, the viscosity of the F-Qdots is affected by the grafting density and chain length of the ligands on the

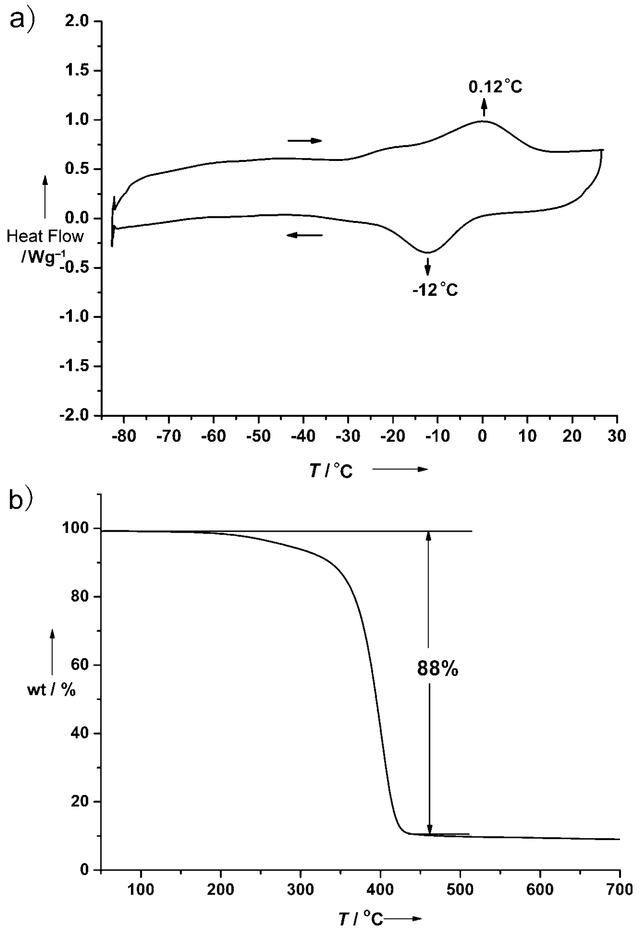

Figure 2. a) DSC trace recorded after one thermal cycle for the F-Qdots. The sample crystallized at −12 °C and melted at 0.12 °C. b) TGA trace of F-Qdots showing an organic content of 88% w/w and decomposition temperature of about 200 °C.

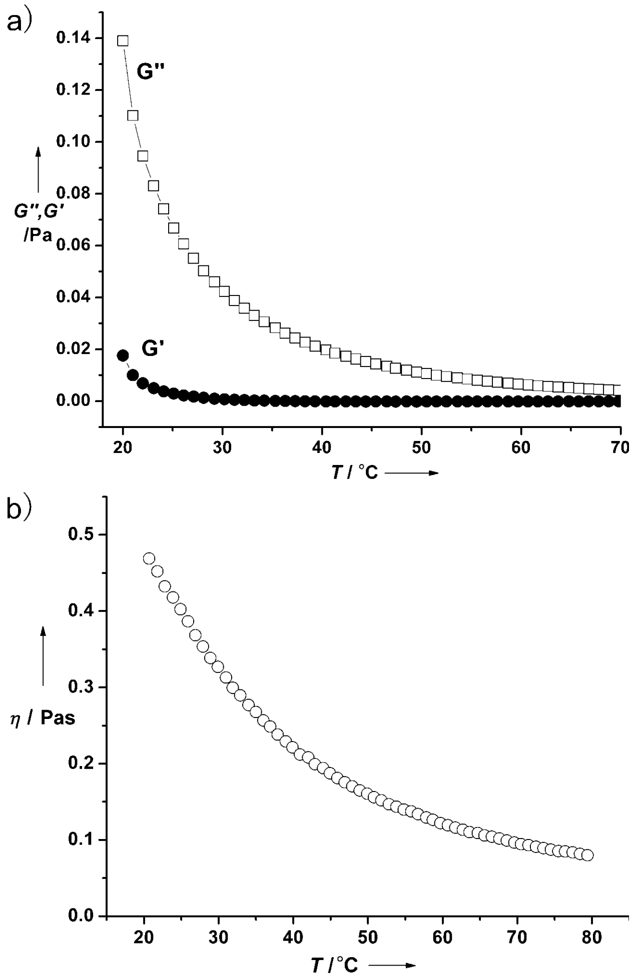

Figure 3. a) Modulus (*G*′, *G*″) and b) viscosity (*η*) versus temperature trace of F-Qdots.

surface of Qdots.[8,17] The 88 % organic content of the F-Qdots hybrids indicates that the NPEQ grafting on the Qdots acts as a continuous suspending medium and results in hybrids with low viscosity.

The photoluminescence properties of Qdots are closely correlated to the surface state. The quantum yield (QY) of the original CdSe/CdS/ZnS Qdots can be as high as 70 %.[14] The QY of anionic stabilized water-soluble Qdots is decreased to 42 %, which is consistent with a prior report.[14] The considerable decrease of QY after water-solubilization with MPA possibly results from the increase of surface defects of Qdots and trapping of the photogenerated hole on the thiol groups.[18] Notably, the fluorescence intensity of Qdots is visibly enhanced after extraction from aqueous phase into chloroform, and the QY of F-Qdots increases to 54 %. The remarkable enhancement of F-Qdots in PL QY relative to that of anionic stabilized water-soluble Qdots probably results from excellent protective environment of NPEQ coated on the surface of Qdots. In the continuous suspending medium, the MPA-coated Qdots are confined in the NPEQ host by ionic bonds and the ionic bilayer structure can effectively suppress the generation of surface defects. The monodispersity of F-Qdots prepared by the extraction strategy makes each single Qdot be well protected by NPEQ and thus enhances the fluorescence intensity.

The desirable fluorescence can be demonstrated by the absorption and emission spectra of synthetic Qdots in hexane and F-Qdots in chloroform (Figure 4). The first excitonic absorption peak of the Qdots is $\lambda = 586$ nm, and no noticeable change of the absorption spectra is observed between the as-prepared Qdots and F-Qdots (Figure 4 a). This result indicates that the size of the Qdots does not change after being coated with NPEQ. Figure 4 b shows that after two phase-transfer cycles, the emission wavelength for the orange-emitting Qdots shifts from $\lambda = 607$ nm (in hexane) to $\lambda = 606$ nm (in chloroform). Importantly, the profile of the emission peak is not affected, which is indicative of the good attainment of the Qdots sizes and size distribution. The full-width at half-maximum of the F-Qdots emission spectra is 28 nm and is narrower than the reported Qdot ionic liquids.[19]

In conclusion, we developed a simple, reproducible, and effective approach to obtain solvent-free Qdot fluids with efficient luminescence. The extraction method is general and can be readily extended to prepare other solvent-free semiconductor nanocrystals (ZnS, InAs) and noble-metal nanoparticles (Au, Ag). The fluidity, low viscosity, high thermal

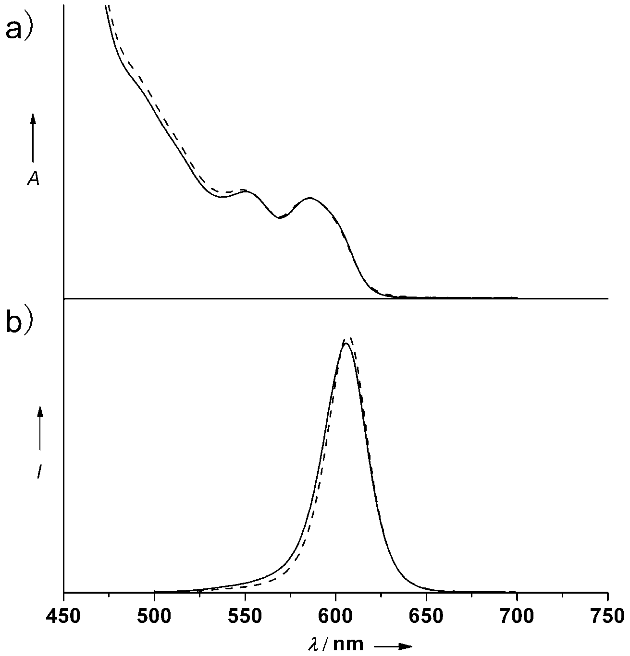

Figure 4. a) Absorption and b) photoluminescence spectra of synthetic Qdots in hexane (-----) and F-Qdots in chloroform (——).

stability, and efficient fluorescence of the F-Qdots make it an excellent candidate in the application of photovoltaic devices and electroluminescent materials.

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