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A bright white light emitting material based on CdSe QDs were prepared by a facile post-synthetic treatment of passivating the QDs by hyperbranched polyethyleneimine (PEI) in water. The CdSe@PEI aqueous solution emits white light with CIE coordinates (0.334, 0.347) and with a PLQY of (17.7 ± 0.1)%. White light emitting materials (WLEMs) attract much attention from both scientific and industrial society due to the fundamental importance to illumination, display, sensors, and so on.[1] Typically, white light is realized by either mixing three primary colors, i.e. red, green, and blue, or mixing at least two complementary colors with a suitable proportion. This means that at least two materials of different emission color are required to achieve white light emission. Recently, the development of WLEMs of a single emitter is in research blooming.[2] Among them, semiconductor quantum dots (QDs) are promising candidates.[3]

Colloidal QDs of unique optical properties, such as tuneable photoluminescence (PL), high thermodynamical stability, high color purity, and solution processibility, have been applied as nano-emissive materials in display, lighting, bioimaging, fluorescent probing, and photocatalysis.[4-5] The large surface-to-volume ratio of QD usually gives rise to dual emission of a band-edge exciton emission and a surface-trap emission.[6, 7] This PL spectral feature is prevalent in ultrasmall or magic-size CdSe QDs.[8, 9] By virtue of the unique dual emission, CdSe QD is considered as a potential single emitter WLEM and have been studied.[10-15] In 2005, Rosenthal et al. firstly reported a kind of ultrasmall (1.5 nm) CdSe nanocrystals (NC) exhibiting white light emission due to a broad PL profile throughout most of the visible light spectrum with a PL quantum yield (QY) of only 2-3%.[10] Later, they found that treatment of the ultrasmall CdSe NCs with organic acids enabled to dramatically improve QY.[11, 12] Kambhampati described that both temperature and surface ligand exchange alter ratio of band-edge and surface radiation of the ultrasmall CdSe NCs, high purity white light emission of the CdSe NCs can be achieved via temperature control.[13] The ultrasmall CdSe NCs used in above works were synthesized by precise controlling the size and the surface-to-volume ratio. This usually requires harsh synthetic conditions (high temperature and/or pressure) and precise time control in synthesis. Sardar and Khanna developed relative mild synthetic methods to prepare white light emitting CdSe NCs, however, scarce and cost organic Se-precursors are required.[14, 15]

In this communication, we report a facile post-synthetic method to prepare bright white light emitting CdSe QDs in an aqueous solution. The solo emissive component 3-mercaptopropionic acid (MPA) capped CdSe QDs used in this work were synthesized by a simple and mature aqueous synthetic protocol.[16] MPA-CdSe QDs prepared in aqueous solution usually exhibit poor PLQY and emits yellow light due to relative larger proportion of the surface-trap emission.[11] In this work, we employ a facile post-synthetic method that passivation of MPA-CdSe QDs by hyperbranched polyethyleneimine (PEI, Mw = 60k, Figure S1) in aqueous solution at room temperature. After passivation, the emission color of the QDs can be tuned from instinct orange-yellow to white. At an optimal condition (Figure 1a), a CdSe@PEI aqueous solution ([CdSe] = 3.30 × 10−5 M, [PEI] = 5.00 mg mL−1) shows bright white emission with CIE coordinates (0.334, 0.347), which is very close to the pure white point (0.333, 0.333). The PLQY of the system increased from (1.6 ± 0.1)% in the absence of PEI to (17.7 ± 0.1)%, a 10.8-time improvement is obtained. The CdSe@PEI isolated from the aqueous solution as gel still emits white light, and can be used as a solid WLEM. The white light emission of the CdSe@PEI aqueous solution is sensitive to CO2, and can be used as a reversible CO2 fluorescent sensor.
The MPA-CdSe QDs was synthesized according to a widely used method by heating CdCl₂, NaSeSO₃, and MPA in aqueous solution (Electronic Supplementary Information, ESI). The size of the MPA-CdSe QDs observed from TEM image (Figure 3a) is in a range of 1.8-1.9 nm. The QDs in an aqueous solution (Electronic Supplementary Information, ESI) shows two PL peaks at 462 nm (band-edge exciton emission) and 623 nm (surface-trap emission), demonstrating intrinsic dual emission. The QDs emits dim yellow light due to domination of the surface-trap emission (510-740 nm). The spectral evolution and plot the ratio of the band-edge exciton emission and surface-trap emission of the QDs is component-concentration-dependent and can be tuned rationally by component concentration control. The intrinsic emitting color of the QDs is enhanced obviously. The S₂/S₁ ratio increases from 0.34 before adding PEI to 0.76 at the end of PEI passivation.

This interesting phenomenon hints that emission color of the QDs is component-concentration-dependent and can be tuned rationally by component concentration control. The intrinsic dual emission of the CdSe QDs possesses a blue light band-edge exciton emission and a broad surface-trap emission spanning green to red regime in solar spectrum. The white light emission may be achieved by controlling concentration ratio of CdSe QDs and PEI. We therefore investigated the concentration effect of the system. By fixing CdSe QDs concentration at 1.00 × 10⁻⁵ M and adjusting PEI concentration from 0.50 mg ml⁻¹ to 9.00 mg ml⁻¹, the CIE coordinates of this series of sample shifts from yellow area to blue-white area (Figure S4b). The sample of 1.00 mg ml⁻¹ PEI gives rise to the closest CIE coordinates (0.336, 0.335) to the pure white point, the PLQY of the QDs in aqueous solution is (1.6 ± 0.1)%. By adding a certain amount of PEI (5.00 mg ml⁻¹) into an aqueous solution of the CdSe QDs (1.00 × 10⁻⁵ M), we found that both band-edge exciton emission and surface-trap emission of the CdSe QDs increased dramatically, and the PL spectrum evolutes temporally (ESI, Figure S3a). We monitored the spectral evolution and plot the ratio of the band-edge exciton emission area (S₂) to the surface-trap emission area (S₁) with time (Figure S3b). The S₂/S₁ ratio increases sharply in the first 10 hours and finally reaches a constant after 30 hours, indicating the finish of the passivation. The pH value of the solution kept in a range of 10.41 – 10.74 during passivation process. After the passivation, the band-edge exciton emission of the QDs is enhanced obviously. The S₂/S₁ ratio increases from 0.34 before adding PEI to 0.76 at the end of PEI passivation.

The CdSe@PEI system also shows pH-dependent emission. As shown in Figure 2c, the emission color of the CdSe@PEI system is sensitive to pH of the solution. In basic condition, the samples show white light emitting. By adjusting pH to acidic condition, the sample turn to yellow light emitting, which is the intrinsic emitting color of the QDs. As accompanying pH decreasing, the band-edge exciton emission peak diminishes and the total PL quenches (Figure 2b). This spectral change gives rise to a yellow light emission of the sample at acidic pH. For the CdSe aqueous solution without PEI, its PL also responds to pH, but the response is very weak and has no obvious regularity (Figure S6). We tested the response of the CdSe@PEI to pH under different PEI concentrations, and found that the results were consistent with the rules when the PEI concentration was 5 mg/mL (Figure S7, S8). We found that the white light emission of the system cannot be recovered by reversible adjusting pH from 4.9 to 10.4. This may cause by destroying electrostatic microenvironment on the surface of the QDs due to salt effect (NaOH and HCl were used to adjust pH).

To gain insights into the system, we firstly employed TEM concentration from 1.00 × 10⁻⁵ M to 3.30 × 10⁻⁵ M, the CIE coordinates (Figure S5b) shifts differently from blue-white area to yellow area. The PL intensities of these samples increase along with increasing QDs concentration from 1.00 × 10⁻⁵ M to 3.30 × 10⁻⁵ M, and decreases by further increasing QDs concentration due to self-quenching of the QDs at higher concentrations. The sample of 3.30 × 10⁻⁵ M QDs (Figure 1a, inset) shows bright white emission with CIE coordinates (0.334, 0.347). The PLQY at this condition increases up to (17.7 ± 0.1)%: a 10.8-fold improvement is obtained compared to the pristine CdSe QDs at the same concentration (3.30 × 10⁻⁵ M, Figure 1a, inset).

The CdSe@PEI system also shows pH-dependent emission. As shown in Figure 2c, the emission color of the CdSe@PEI system is sensitive to pH of the solution. In basic condition, the samples show white light emitting. By adjusting pH to acidic condition, the sample turn to yellow light emitting, which is the intrinsic emitting color of the QDs. As accompanying pH decreasing, the band-edge exciton emission peak diminishes and the total PL quenches (Figure 2b). This spectral change gives rise to a yellow light emission of the sample at acidic pH. For the CdSe aqueous solution without PEI, its PL also responds to pH, but the response is very weak and has no obvious regularity (Figure S6). We tested the response of the CdSe@PEI to pH under different PEI concentrations, and found that the results were consistent with the rules when the PEI concentration was 5 mg/mL (Figure S7, S8). We found that the white light emission of the system cannot be recovered by reversible adjusting pH from 4.9 to 10.4. This may cause by destroying electrostatic microenvironment on the surface of the QDs due to salt effect (NaOH and HCl were used to adjust pH).
to observe morphology of the system. As shown in Figure 3a, the CdSe QDs are evenly monodisperse. In contrast, CdSe QDs are enwrapped by PEI to form irregular assemblies (Figure 3b). These assemblies were observed emissive from Confocal images (Figure S10). We next used X-ray photoelectron spectroscopy (XPS) to examine the interaction between PEI and CdSe QDs. As shown in Figure 3c, the XPS spectrum of CdSe QDs shows two distinct peaks at 405.3 eV and 412.0 eV, which are assigned to the signals of Cd 3d$_{3/2}$ and Cd 3d$_{5/2}$, respectively. These two peaks negatively shift to 404.3 eV and 411.1 eV in the XPS spectrum of the CdSe@PEI sample (original pH 10.4), indicating the coordination between Cd atom and amino groups in PEI occurs.\[19, 20\] The CdSe@PEI sample prepared at pH 4.9 shows that these two peaks slightly shift to 404.7 eV and 411.5 eV. This indicates that partial dissociation of amino groups from surface Cd of CdSe QDs due to protonation of amino groups in PEI at acidic condition. To verify above results, we measured surface zeta potentials (ξ) of the samples (Figure 3d). PEI in an aqueous solution is positively charged with a ξ value of 11.43 mV even in basic condition (original pH 10.4) because of its buffering property over a wide pH range.\[21\] By adjusting pH to 4.9, the ξ value of the PEI aqueous solution increased to 46.00 mV due to protonation of amino groups. Although CdSe QDs are negatively charged with a ξ value of -39.03 mV, the CdSe@PEI sample is positively charged with a ξ value of 9.06 mV at pH 10.4, and this value increases to 40.73 mV by adjusting pH to 4.93. These results indicate that the charge state of PEI dominates the overall surface zeta potential of the CdSe@PEI system.

The transient PL measurements were carried out to investigate kinetics of the CdSe@PEI system. After excitation by a 340 nm laser, the band-edge exciton emission of CdSe QDs biexponential decays with two lifetimes of 4.86 ns and 22.00 ns.\[7, 22-24\] The average lifetime ($\tau_{\text{AC}}$) of the band-edge exciton emission decay is 5.77 ns. The surface-trap emission of CdSe QDs also biexponential decays with two lifetimes of 35.72 ns and 267.57 ns, and the average lifetime ($\tau_{\text{AS}}$) of the surface decay is 163.06 ns (Figure 4). Likewise, both band-edge exciton emission and surface-trap emission kinetics of the CdSe@PEI sample dramatically increase in comparison to those of the CdSe sample. The average lifetimes of band-edge exciton emission and surface-trap emission decay of the CdSe@PEI sample are 89.98 ns and 183.96 ns, respectively. The $\tau_{\text{AC}}/\tau_{\text{AS}}$ ratio can be viewed as an indicator of population distribution of excitons at band-edge and surface-trap states in the QDs.\[7\] This ratio dramatically increased from 0.03 in the absence of PEI to 0.49 in the presence of PEI. This is consistent with the trend of the PL spectra changes of the system.

Based on above results, a mechanism for the white light emitting of the CdSe@PEI system can be explained. CdSe QDs of small size shows intrinsic dual emission, a band-edge exciton emission resulting from band-edge radiative relaxation and a surface-trap emission resulting from surface-trap radiative relaxation. The latter is red-shift compared with the former due to the lower energy level.\[7\] Upon excitation, electrons populate in both band-edge state and surface-trap state. The emission color of the QDs is dominated by the exciton population and radiative decay at these two states. The smaller $\tau_{\text{AC}}/\tau_{\text{AS}}$ ratio of the MPA-CdSe QDs indicates that radiative relaxation at surface traps dominates, this leads an orange-yellow light emission of the MPA-CdSe QDs. The PL of the QDs is sensitive to the surface chemical environment.\[25-27\] Hyperbranched PEI contains abundant primary, secondary, and tertiary amines. The amine ligands, such as small organic amines, are capable to coordinate to unpassivated surface cadmium sites.\[28-32\] XPS analysis revealed that the coordination between amino groups of PEI and surface cadmium of CdSe occurs. This results in two obvious PL spectral changes. First, the overall PL intensity improves. Second, the $S_1/S_0$ ratio increases. For above phenomenons, the analysis proceeds in steps. First, the unpassivated surface cadmium sites are considered as nonradiative electron traps.\[29\]
The passivation of both these sites by PEI leads to enhance radiative relaxation of the electrons, which are evidenced by longer lifetimes of both band-edge exciton emission and surface-trap emission of the CdSe@PEI system. Second, due to spectral overlap between absorption and emission spectra of the QDs (Figure S2a), photoinduced energy transfer (PET) between QDs is inevitable. The structure of the QDs enwrapping into PEI matrix and the viscosity increasing of the solution suppress PET. These contribute to the overall PL increase. Finally, surface passivation by PEI decreases surface traps and thus suppresses electron transfer from the band-edge state to surface-trap state. A larger portion of excitons relax from the band-edge state and thus gives rise to a well-balanced ratio of band-edge emission and surface-trap emission. This is the key reason of the white light emitting of the system.

We therefore make a white light LED by coating the CdSe@PEI gel on a blue light LED bead (Figure 5b). The coated LED bead emits bright white light when powered on (Figure 5d). The CEI of the white light LED is (0.311,0.335) (Figure S9). And the original lumen value of the LED is 30-50 lm. This model emits bright white light when powered up (Figure 5d). The CEI band-edge emission and surface-trap emission. This is the key property, we propose the CdSe@PEI aqueous system can be potentially used as a CO₂ absorvent. The amino groups in PEI enable to reversibly adsorb CO₂. Based on this property, we propose the CdSe@PEI aqueous system can be used as a CO₂ fluorescent sensor. To verify this assumption, we bubble CO₂ into a CdSe@PEI aqueous solution for 30 second. As shown in Figure 5e, the initial white light emission of the CdSe@PEI aqueous solution turns yellow light emission, showing high sensitivity to CO₂. The pH decreases from 10.42 to 6.75. We then bubbling N₂ into the solution for 50 minutes, the emitting color can be recovered to white, and pH increases to 8.71. The Sₗ/Sₚ ratio and pH (8.71) of the solution cannot recover to the initial values. Presumably, CO₂ cannot be expelled from the solution completely under such manipulation. However, the changes of emitting color and pH of the system show good reversibility and stability in the next cycles. Under CO₂ atmosphere, CO₂ is chemically adsorbed by amino groups of PEI (2R-NH₂ + CO₂ ↔ R-NHCO₂⁻ + NH₃·R). This leads dissocation of amino groups from the QDs, therefore the QDs emits distinct orange-yellow light. CO₂ desorbs from amino groups when N₂ is saturated in the solution. The free amino groups in PEI re-passivate the QDs, thus white light emission recovers. This phenomenon further confirms the analysis described above.

Conclusion

In summary, our work demonstrates that the emission color of the MPA-CdSe QDs synthesized in aqueous solution can be tuned from original orange-yellow to white via a facile post-synthetic treatment of adding hyperbranched PEI. The surface passivation of MPA-CdSe QDs by PEI results in increase of both band-edge exciton emission and total PLQY. These provide chance to tune emission color the CdSe QDs by rational components concentrations control. At an optimal condition, the CdSe@PEI aqueous solution shows bright white light emission with CIE coordinates closing to pure white and with a PLQY up to (17.7 ± 0.1%). The method has several advantages of facile preparation, aqueous processibility, no need harsh synthesis of CdSe QDs. The CdSe@PEI gel/aqueous solution can be potentially used as solid white light emitting material as well as a reversible CO₂ fluorescent sensor.

Conflicts of interest

There are no conflicts to declare.

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