Electronic Supplementary Information

For

Facile passivation of yellow light emitting CdSe QDs by polyethyleneimine in water to achieve bright white light emission

Bo-Yi Deng, Jin Wu, Jing Liu, Ying-Yi Ren, Feng Wang

Table of contents

1. Chemicals and synthesis

Sodium sulfite, mercaptopropionic acid, sodium hydroxide, polyethyleneimine (PEI) (Mw = 60000, 50% aqueous solution), quinine, benzylamine, Se power, cadmium chloride hydrate ($CdCl_2 \cdot 2.5H_2O$, 98%), sulfuric acid (H_2SO_4), hydrochloric acid (HCl) was purchased from commercial suppliers (Sinopharm chemical reagent co., LTD, Adamas, and Sigma-Aldrich) and used without further purification. N_2 (99.999%), CO_2 (99.99%) were purchased from commercial supplier (Huaerwen). All solvents of analytical grade were purchased from commercial suppliers and used without further purification.

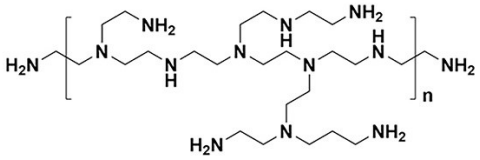

Figure S1. Graph of PEI structure

The synthesis of MPA-CdSe QDs

The MPA-CdSe QDs were synthesized according to the literature method with slight modification.[1] First, Na_2SeSO_3 aqueous solution was prepared by following steps. Selenium powder (40 mg) was added into Na_2SO_3 aqueous solution (100 mL, 1.50 mmol) and the mixture was stirred at 130 °C until the solid powder disappeared. In another flask, $CdCl_2 \cdot 2.5H_2O$ (92 mg) and 3-mercaptopropionic acid (52 μL) in deionized water (380 mL) was prepared. The pH of the solution was adjusted to 11 by NaOH (1 M) and then saturated by nitrogen. A 20 mL Na_2SeSO_3 solution was injected into the above solution. The mixture solution was stirred at 130 °C for 2.5 hours. The MPA-CdSe QDs as yellow solid was obtained

via subsequently participation by isopropanol, centrifugation, and drying in vacuum.

2. Instruments and methods

High-resolution TEM images were obtained by Titan G2 60-300 with an image corrector high-resolution transmission electron microscopy system (HRTEM) operating at 300 kV. The Confocal Microscope images were recorded by Chameleon LSM. The X-ray photoelectron spectroscopy (XPS) measurements were conducted using AXIS SUPRA+ spectrophotometer with Al-Ka radiation. UV-Vis absorption spectra were recorded on a Shimadzu UV-2600 spectrophotometer in the range of 200-700 nm. The photoluminescence (PL) measurements were carried out by a RF-6000. The fluorescence lifetimes were measured by the QuantaMaster 8000.The pH measurements were determined with a Model pHS-3C meter (Mettler Toledo FE28, Swiss). The zeta potentials was measured by the Nano ZS90.

CdSe@PEI solution preparation

The CdSe@PEI aqueous solution was prepared by physical mixing of PEI and MPA-CdSe QDs with certain amount. The solid CdSe@PEI gel was obtained by freeze-drying of CdSe@PEI aqueous solution.

PLQY measurments

The PLQY values in this work were determined by using quinine as a reference (in 0.5 M H_2SO_4 aqueous solution) and calculated according to the equation following:

$$\frac{\Phi_s}{\Phi_r} = \left(\frac{A_r}{A_s}\right) * \left(\frac{D_s}{D_r}\right) * \left(\frac{n_s}{n_r}\right)$$

Φ represents the quantum yield, A is the absorbance at the excitation

wavelength, D is emission area, and n is the refractive index. The reference quinine has a fluorescence quantum yield of 0.546 in a 0.5 M H_2SO_4 aqueous solution [2].

CO_2 fluorescent sensor experiments

The CO_2 fluorescent sensor experiments were carried out by cyclic bubbling CO_2 or N_2 into a CdSe@PEI aqueous solution ([CdSe] = 1.00×10^{-5} M, [PEI] = 5.00 mg mL^{-1}). The white light emission of the solution turns to yellow by bubbling CO_2 for 30s, the recovery of the white light emission needs to bubble N_2 for 50 mins.

3. UV-Vis absorption and PL spectra

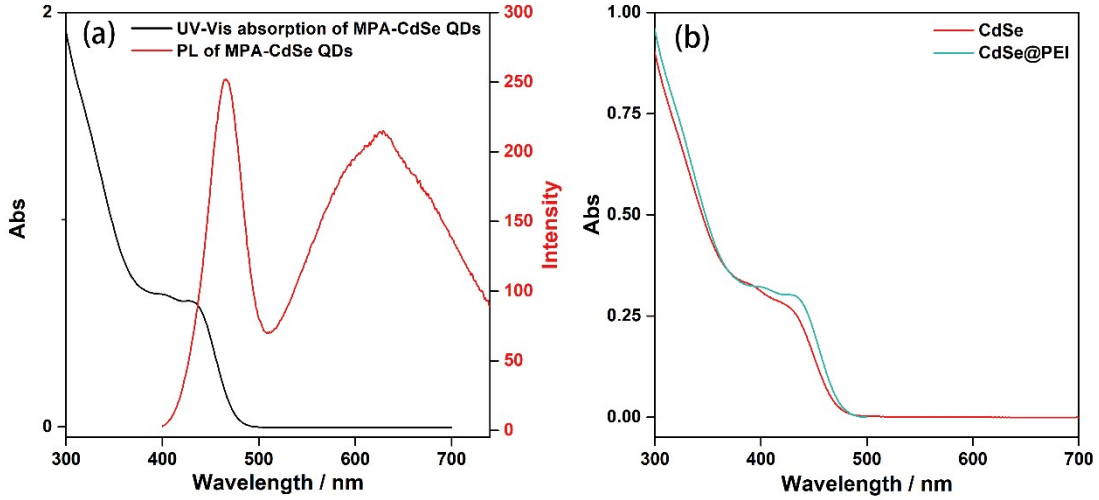

Figure S2. (a) UV-Vis absorption and PL spectra of MPA-CdSe QDs in water (1.00×10^{-5} M), excitation wavelength: 380 nm. (b) UV-Vis absorption of MPA-CdSe QDs (1.00×10^{-5} M) and CdSe@PEI ([CdSe] = 1.00×10^{-5} M, [PEI] = 5.00 mg mL^{-1}) in water.

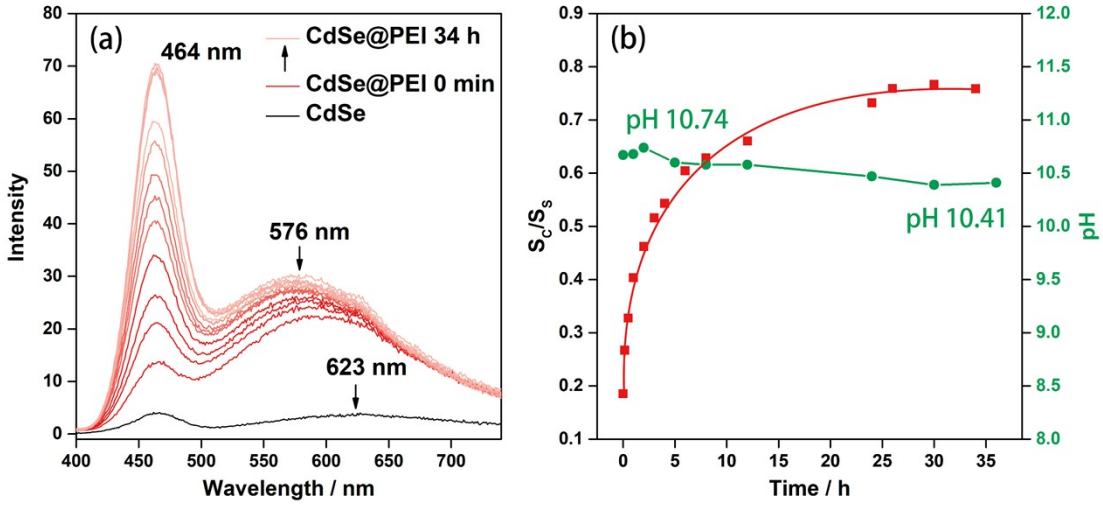

Figure. S3 Change of CdSe@PEI ([CdSe] = 1.00×10^{-5} M, [PEI] = 5.00 mg mL^{-1}) PL enhancement from 0 h to 34 h, excitation wavelength: 380 nm. (b) The ratio of the band-edge exciton emission area (S_1) to surface-trap emission area (S_2) plots to time, and pH change of the solution during passivation process.

4. Component concentration effect and pH effect

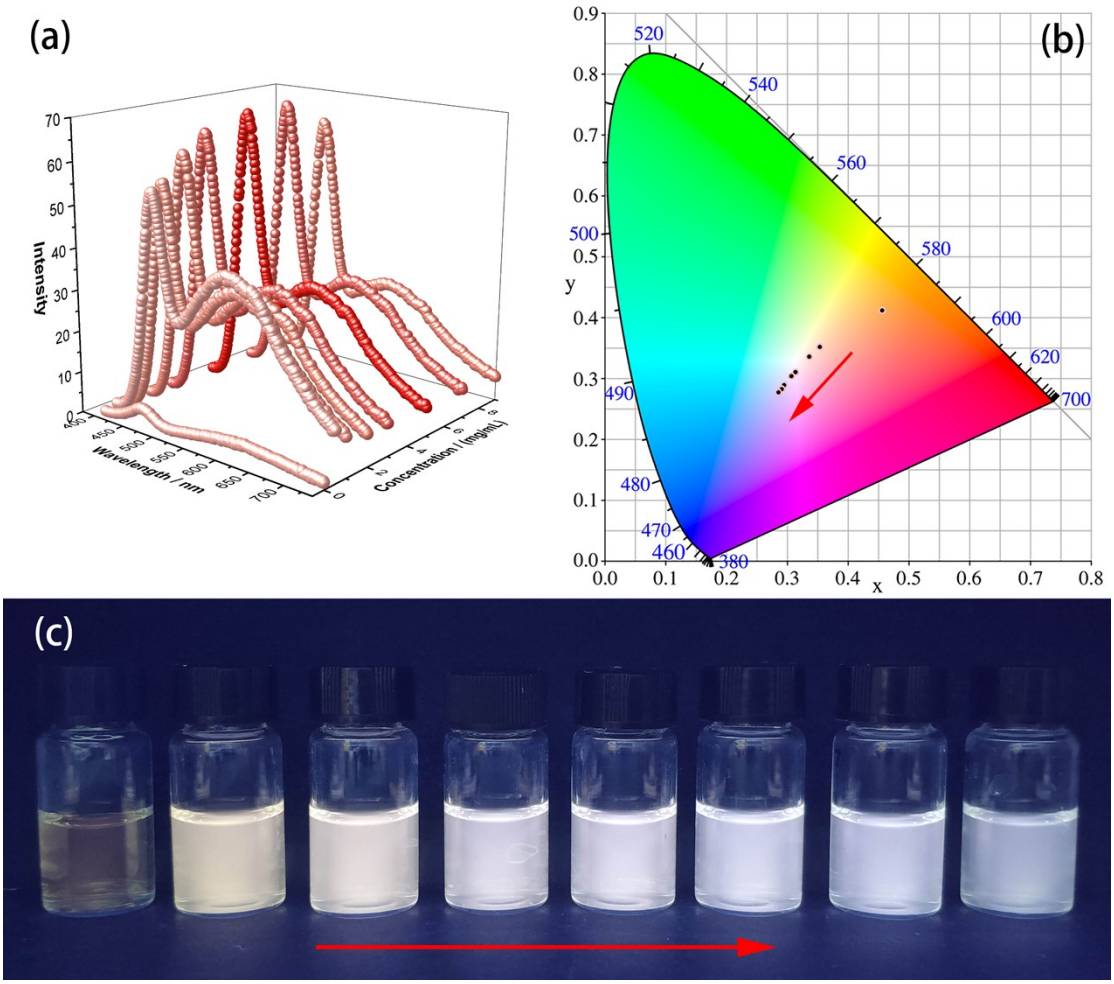

Figure. S4 (a) PL spectrum of the CdSe@PEI aqueous solution with different PEI concentrations (0, 0.50, 1.00, 2.00, 3.00, 5.00, 7.00, 9.00 mg mL^{-1}), excitation wavelength: 380 nm. (b) CIE coordinates of the samples. (c) The digital picture of the samples.

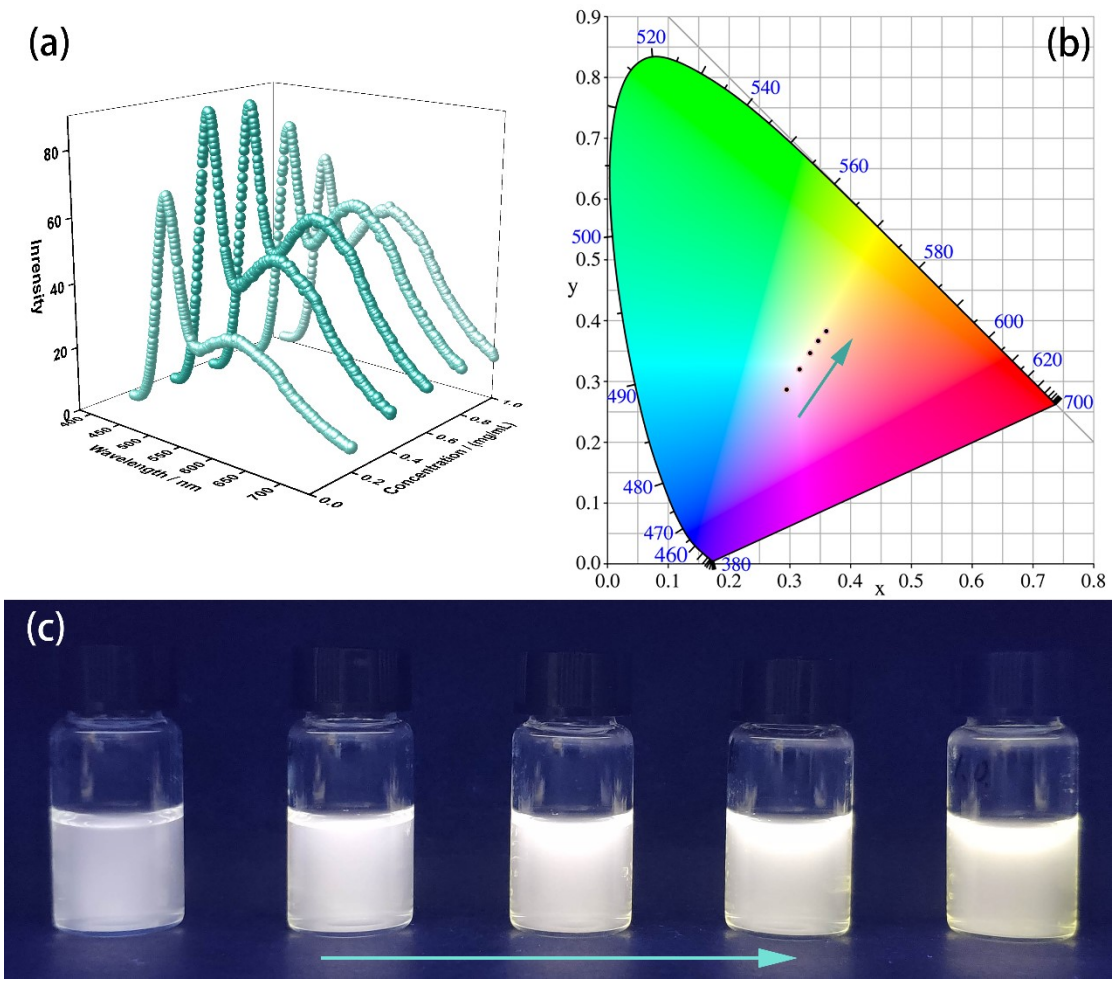

Figure. S5 (a) PL spectrum of the CdSe@PEI aqueous solution with different CdSe concentrations (1.00×10^{-5} M, 1.60×10^{-5} M, 2.14×10^{-5} M, 2.75×10^{-5} M, 3.30×10^{-5} M), excitation wavelength: 380 nm. (b) CIE coordinates of the samples. (c) The digital picture of the samples.

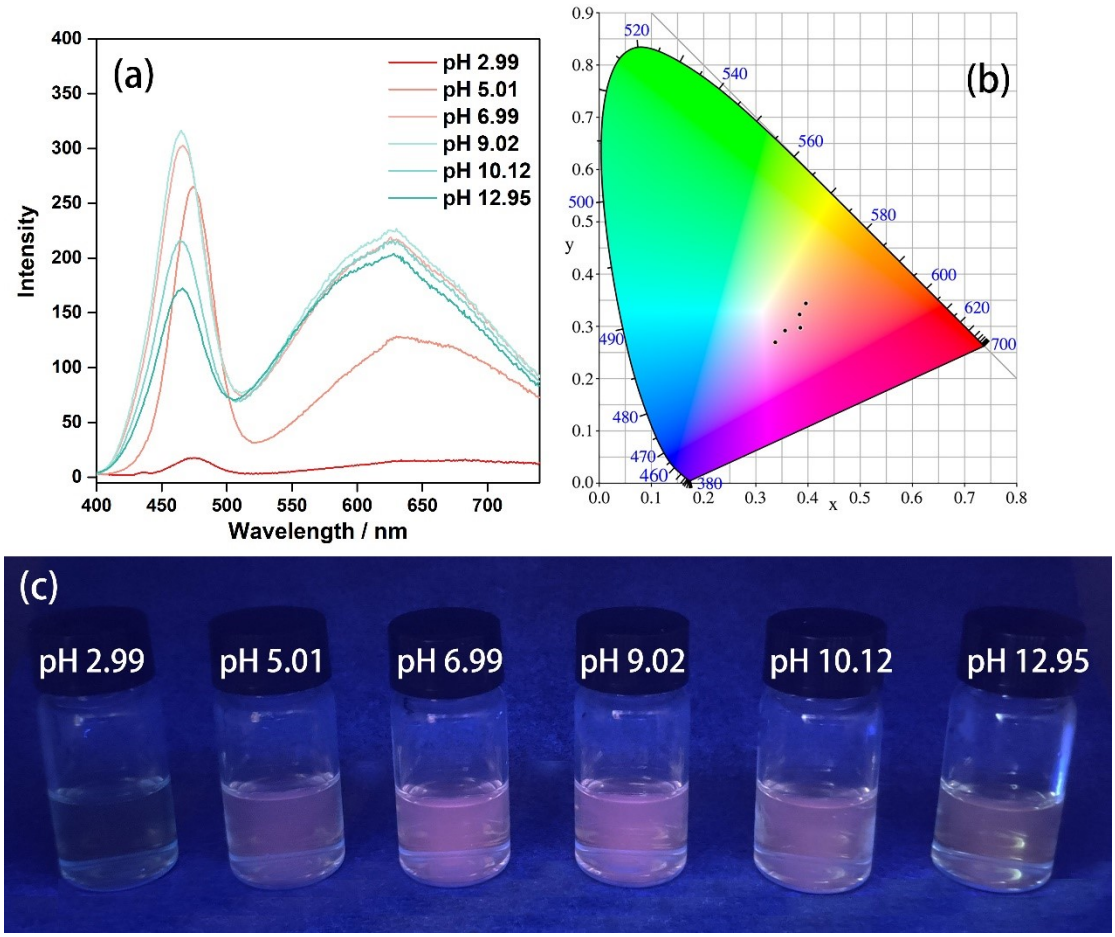

Figure. S6 (a) PL spectrum of the CdSe aqueous solution (1.00×10^{-5} M) at different pH, excitation wavelength: 380 nm. (b) CIE coordinates of the samples. (c) The digital picture of the samples.

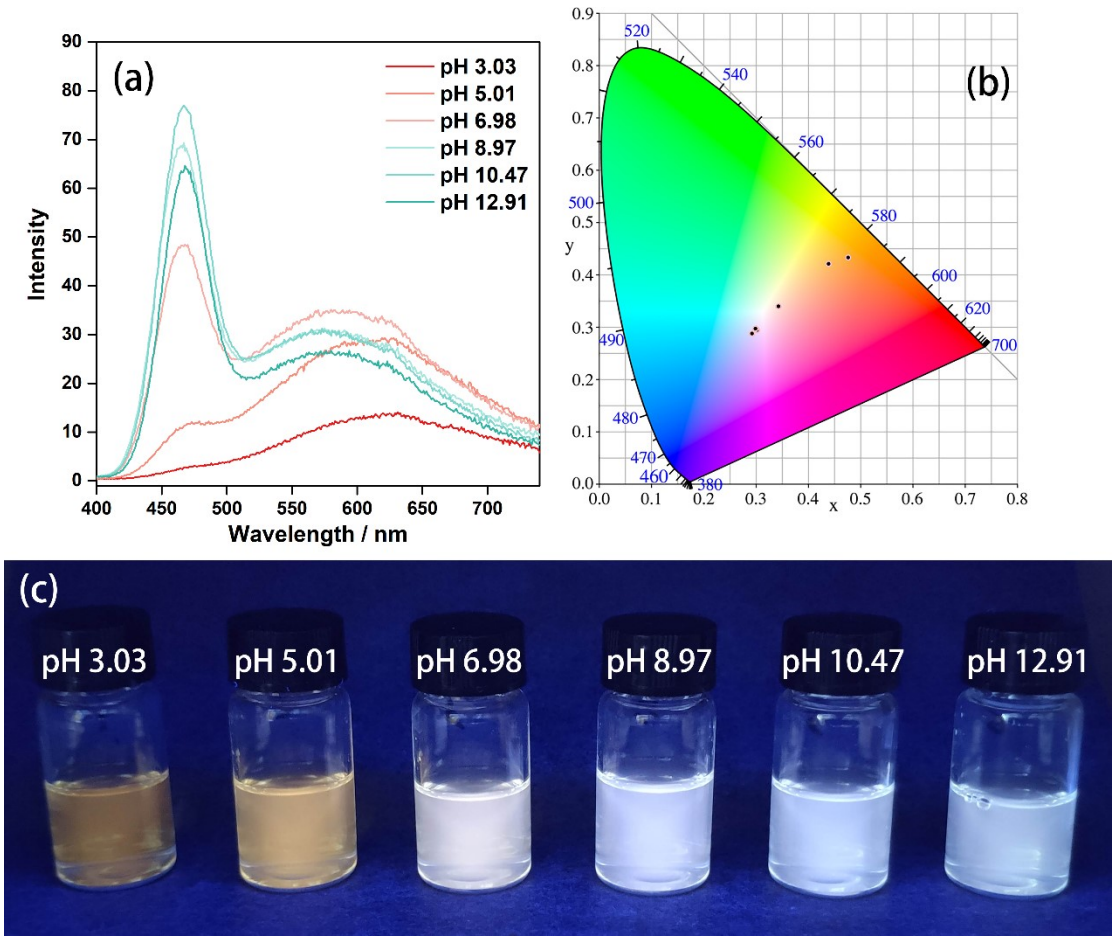

Figure. S7 (a) PL spectrum of the CdSe@PEI aqueous solutions ([CdSe] = 1.00×10^{-5} M, [PEI] = 2.00 mg mL^{-1}) at different pH, excitation wavelength: 380 nm. (b) CIE coordinates of the samples. (c) The digital picture of the samples.

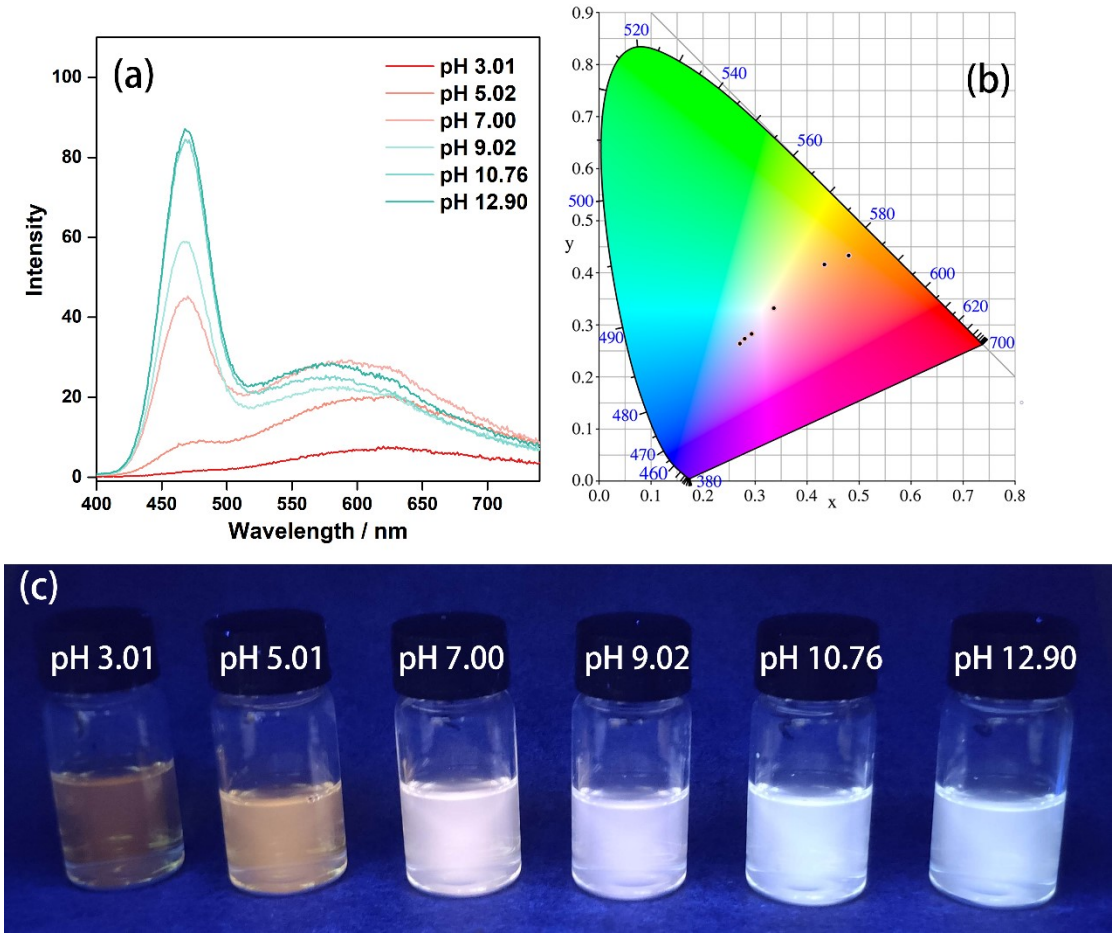

Figure. S8 (a) PL spectrum of the CdSe@PEI aqueous solutions ([CdSe] = 1.00×10^{-5} M, [PEI] = 7.00 mg mL^{-1}) at different pH, excitation wavelength: 380 nm. (b) CIE coordinates of the samples. (c) The digital picture of the samples.

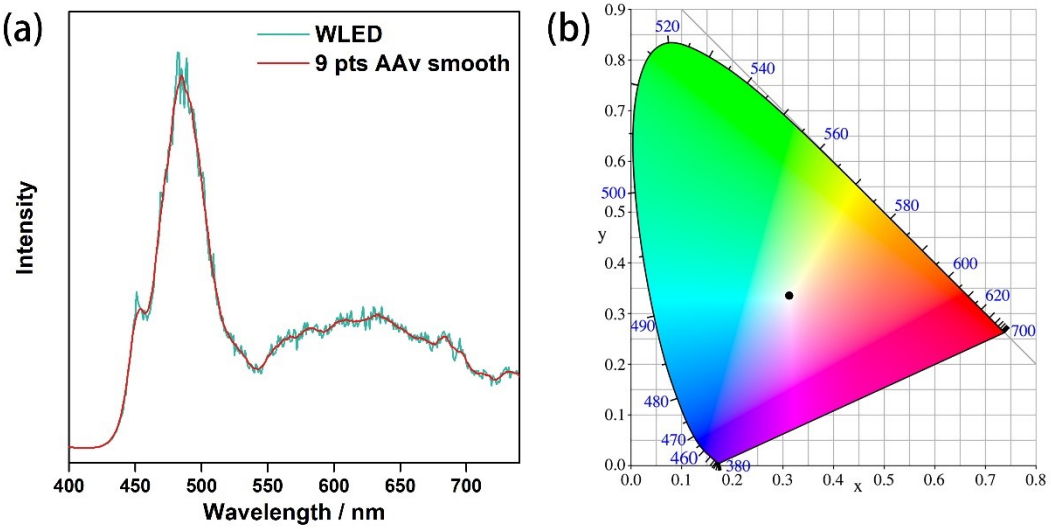

Figure. S9 (a) Emission spectrum of the white light LED. (b) CIE coordinates of the white light LED.

5. TEM and CLSM images

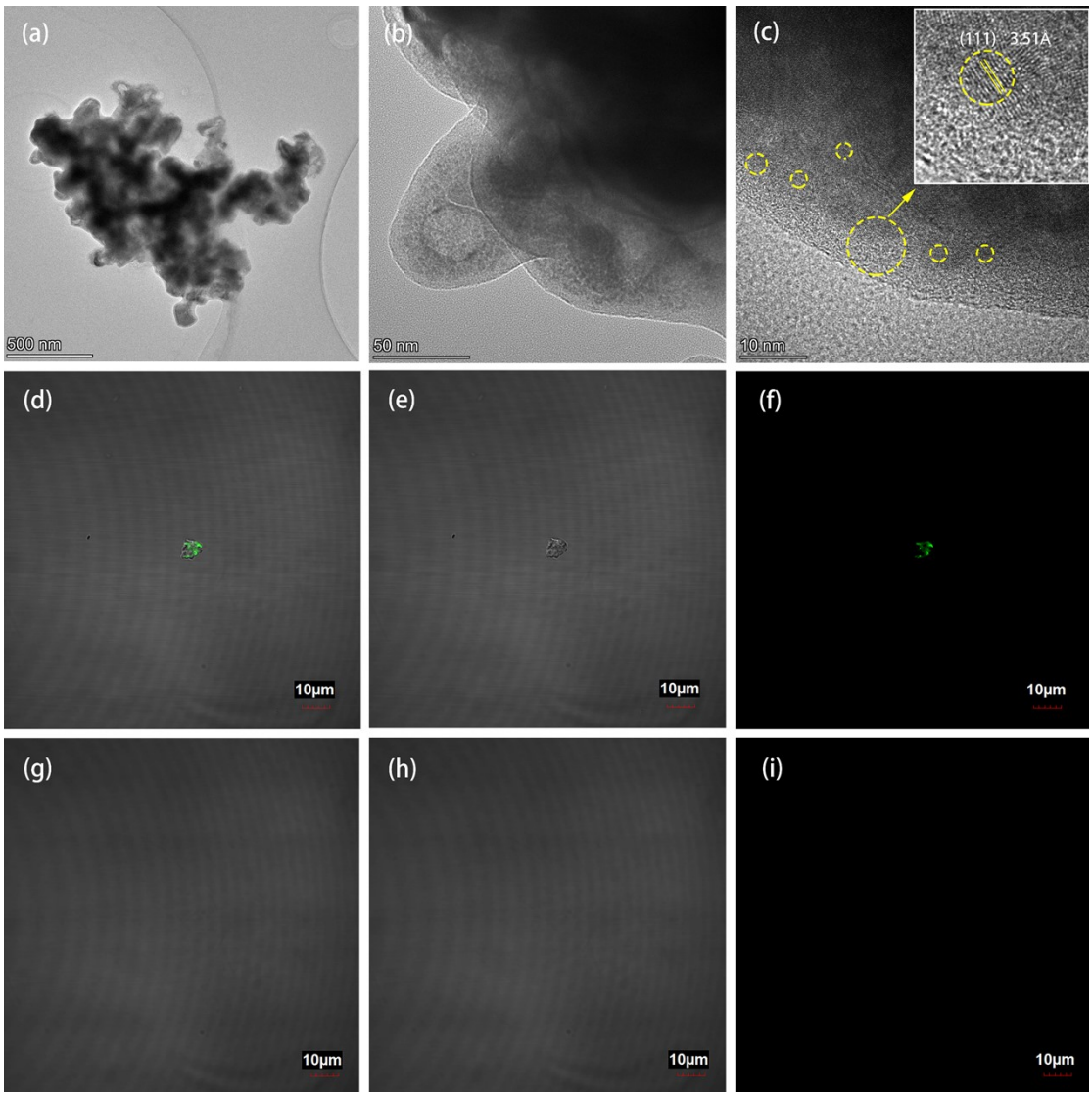

Figure. S10 (a-c) TEM images of CdSe@PEI ([CdSe] = 1.00×10^{-5} M, [PEI] = 5.00 mg mL^{-1}). (d-f) Confocal images of CdSe@PEI ([CdSe] = 1.00×10^{-5} M, [PEI] = 5.00 mg mL^{-1}) in an aqueous solution. (g-i) Confocal images of MPA-CdSe (1.00×10^{-5} M) in an aqueous solution.

6. Lifetimes

Table S1. The fitting lifetimes of MPA-CdSe and CdSe@PEI in aqueous solutions

Entry	λ / nm	τ_1 / ns	A_1	τ_2 / ns	A_2	τ_{av} / ns
CdSe	462	4.86	11.54	22.00	0.14	5.77
	602	35.72	0.73	267.57	0.12	163.06
PEI-CdSe	464	26.56	1.16	134.61	0.32	89.98
	562	50.00	0.70	227.90	0.47	183.96

7. Reference

[1] Y.-S. Park, A. Dmytruk, I. Dmitruk, A. Kasuya, Y. Okamota, N. Kaji, M. Toeshi, Y. Baba, *J. Phys. Chem. C*, 2010, **114**, 18834-18840.

[2] C. Wang, H. Zhang, J. Zhang, N. Lv, M. Li, H. Sun, B. Yang, *J. Phys. Chem. C*, 2008, **112**, 6330-6336.