

Supplementary information

Oxygen accelerated scalable synthesis of highly fluorescent sulfur quantum dots

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Materials. Sublimed sulfur, NaOH, polyethylene glycol (PEG, $M_n = 400$ Da), poly(vinyl alcohol) (PVA, $M_w = 90-98$ kDa, 90+% hydrolyzed), acrylamide (AM), methylene-bis-acrylamide (MBA), tetramethylethylenediamine (TEMED), and potassium persulfate ($K_2S_2O_8$) were purchased from Beijing Innochem Technology Co. Ltd. (Beijing, China) and used as received. High purity oxygen (O_2 , 99.999%) and argon (Ar, 99.999%) were purchased from Huaao Gas Co., Ltd. (Liuzhou, China). All other reagents were analytical grade and used as received. Milli-Q water (18.2 M Ω) was used throughout the experiments.

Characterizations. Photoluminescent spectra were collected using a Varian Cary 100 spectrometer. Transmission electron microscopy (TEM) was carried out on a JEOL-2010 TEM at 200 kV. Samples were prepared by placing a drop of dilute aqueous dispersion of SQDs on the surface of a copper grid. X-ray photoelectron spectroscopy (XPS) measurements were made on Kratos AXIS UltraDLD (Kratos Analytical Ltd.) with mono Al K α radiation ($h\nu = 1487.71$ eV) at a power of 75 W. Fourier transform infrared (FT-IR) spectra were recorded using a PE Paragon 1000 spectrometer (KBr disk). Absorption spectra were recorded on a UV-3600 UV-vis spectrophotometer (Shimadzu). Powder X-ray diffraction (XRD) spectra were collected on a Holland PANalytical X'Pert PRO X-ray diffractometer with Cu K α radiation. Confocal laser-scanning microscopy (CLSM) images were recorded on a Zeiss LSM 510 (Jena, Germany) CLSM with imaging software (Fluoview FV1000). Absolute photoluminescence quantum yields of the SQDs samples in aqueous solution (0.1 mg/mL) were determined on a FluoroMax-4 (HORIBA)

photoluminescence spectrometer with an integrating sphere, and the excitation wavelength is 400 nm. The elementary analysis measurement was performed on a Perkin-Elmer 240C Elemental Analytical Instrument. Raman spectra were recorded on a LabRam-1B Raman spectroscope with 532.05 nm incident radiation and a 50× aperture.

Preparation of fluorescent SQDs. In a typical procedure, 4 g of NaOH and 3 g of PEG were dissolved in 50 mL of water before adding 1.6 g of sublimed sulfur powder. The mixture was stirred at 90 °C for 10 h under pure O₂ atmosphere. The resulted SQDs were purified by dialysis against water (molecular weight cut off, 3500 Da) for at least three days and followed by freeze-drying. Elemental analysis result of the SQDs: S 38.78 wt%, H5.82 wt%, C 32.36 wt%, and O 23.04 wt% (calculated).

The product yield of SQDs was defined as follows:

$$\text{Product yield} = \frac{M_{SQDs} \times W_S \times 100\%}{M_{\text{sublimed sulfur}}}$$

where M_{SQDs} is the mass of freeze-dried SQDs, W_S is the weight content of S element according to the elemental analysis result, and $M_{\text{sublimed sulfur}}$ is the mass of used sublimed sulfur. For comparison, the preparation of SQDs under air and argon atmosphere was also performed using the same procedure as that under O₂ atmosphere.

Preparation of fluorescent PVA-SQDs composite film. The fluorescent and transparent PVA-SQDs nanocomposite film could be easily fabricated by the following procedure. Firstly, 0.98 g of PVA was dissolved in 10 mL of water to form a homogeneous solution. Then 0.02 g of SQDs was added and the mixture was stirred

for 10 min. Finally, the resulted mixture was casted into a petri-dish and followed by water evaporation at 50 °C.

Preparation of fluorescent polyacrylamide (PAM)-SQDs composite hydrogel. For preparing fluorescent PAM-SQDs composite hydrogel, two solutions were prepared. Solution A contains SQDs (25 mg), AM (1 g), MBA (0.2 g), TEMED (30 mg), and 9 mL of water. Solution B contains K₂S₂O₈ (15 mg) and 1 mL of water. Then solution A and solution B were mixed and the mixture was quickly cast to a glass beaker. After keeping the system at 45 °C for 8 h, fluorescent PAM-SQDs composite hydrogel was obtained.

Cytotoxicity evaluation. The cytotoxicity of SQDs was evaluated using the methyl-thiazolyldiphenyl-tetrazolium (MTT) assay. 293T human embryo kidney cells and MCF-7 breast cancer cells were seeded in 96-well plates at a density of 1×10^4 cells/mL, respectively. After 24 h of incubation, the medium was replaced by the aqueous dispersion of SQDs with concentrations of 100, 75, 50, 25, and 0 µg/mL and further incubated for 24 h. Subsequently, the wells were washed thrice with PBS buffer, and 100 µL of freshly prepared MTT (0.5 mg/mL) solution in culture medium was added to each well. The MTT medium solution was carefully removed after 3 h of incubation. Dimethyl sulfoxide (100µL) was then added into each well, and the plate was gently shaken for 20 min. The absorbance of MTT at 570 nm was recorded by the microplate reader. Cell viability was expressed by the ratio of absorbance of the cells incubated with SQDs to that of the cells incubated with culture medium only.

Cell imaging. MCF-7 cancer cells were cultured in the chambers at 37 °C. After 80%

confluence, the medium was removed and the adherent cells were washed twice with $1 \times$ PBS buffer. The SQDs suspension ($20 \mu\text{g}/\text{mL}$, 0.4 mL) was then added to the chamber. After incubation for 2 h, cells were washed three times with $1 \times$ PBS buffer and then fixed by 75% ethanol for 20 min, which was further washed twice with $1 \times$ PBS buffer and imaged by CLSM (Zeiss LSM 510, Jena, Germany) with imaging software (Fluoview FV1000).

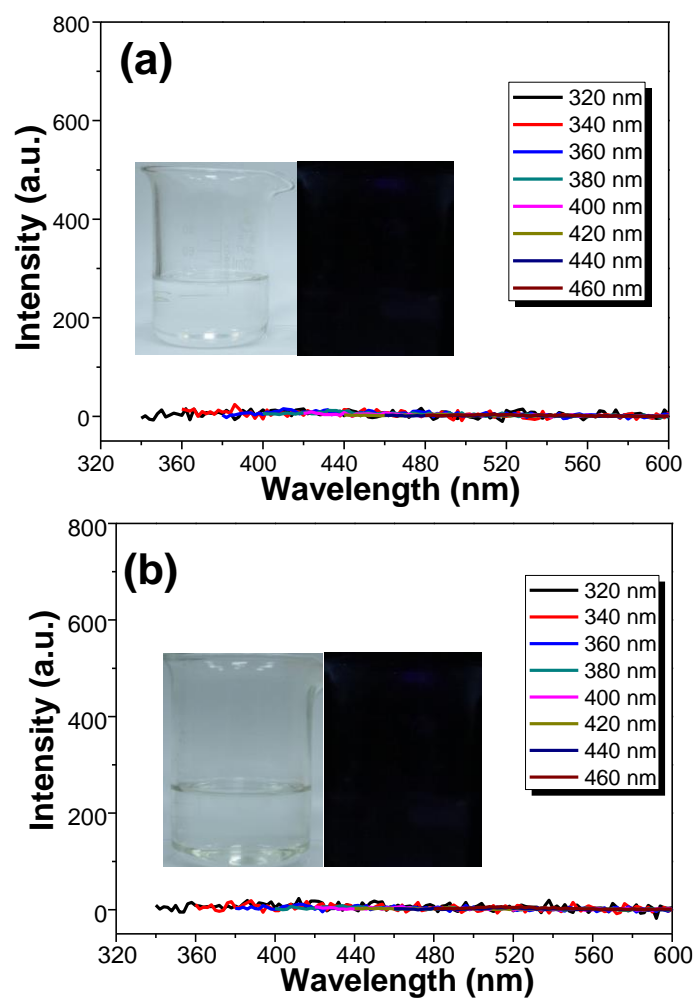


Fig. S1. Emission spectra of the mixture of PEG and NaOH before (a) and after (b) stirring at 90 °C for 10 h under O₂ atmosphere. Insets: photographs of the mixture of PEG and NaOH before (a) and after (b) stirring at 90 °C for 10 h under O₂ atmosphere under daylight (left) and 365 nm UV lamp (right).

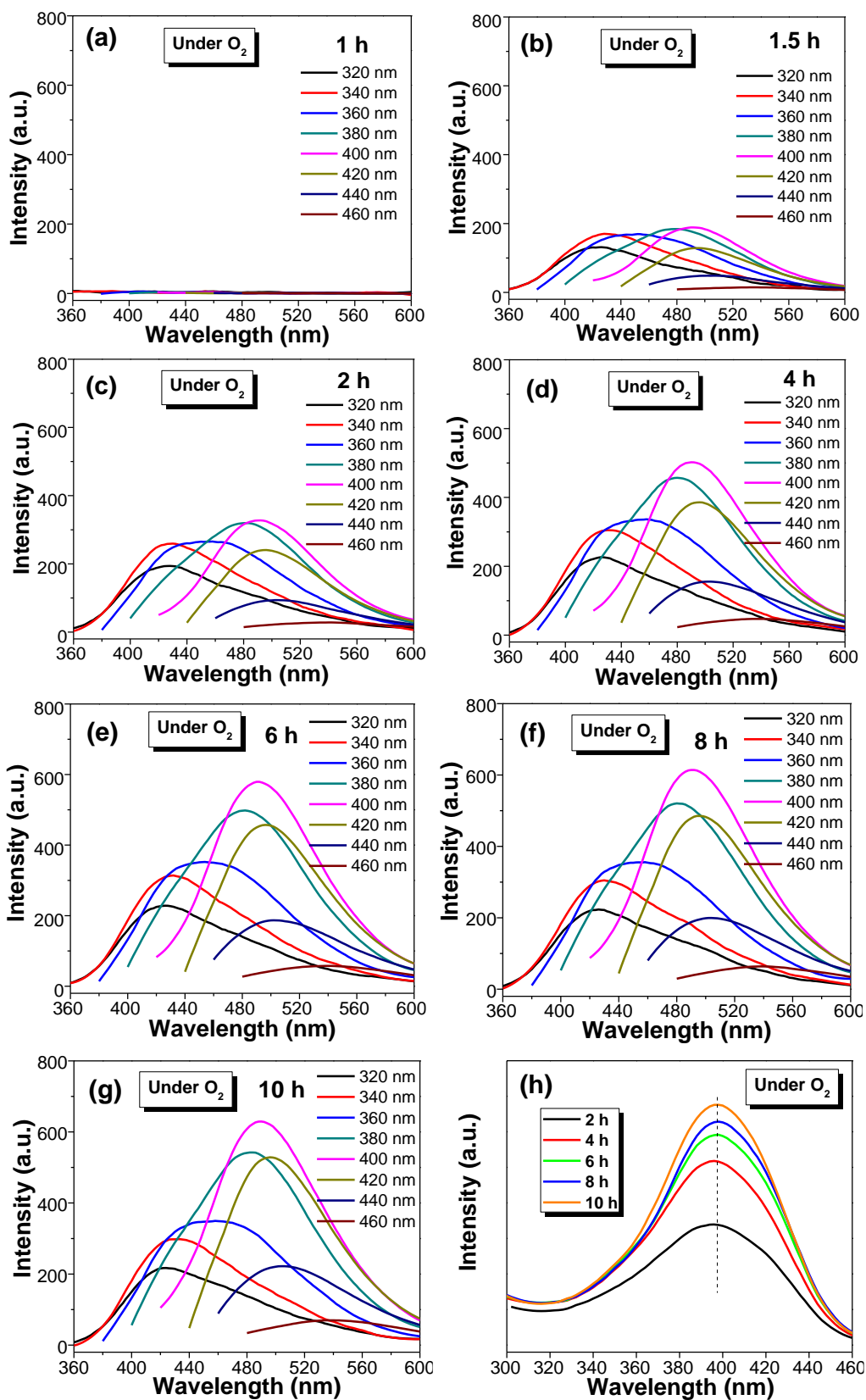


Fig. S2. Emission (a-g) and excitation ($\lambda_{em} = 490$ nm) (h) spectra of the reaction mixture after stirring for different time under O_2 atmosphere.

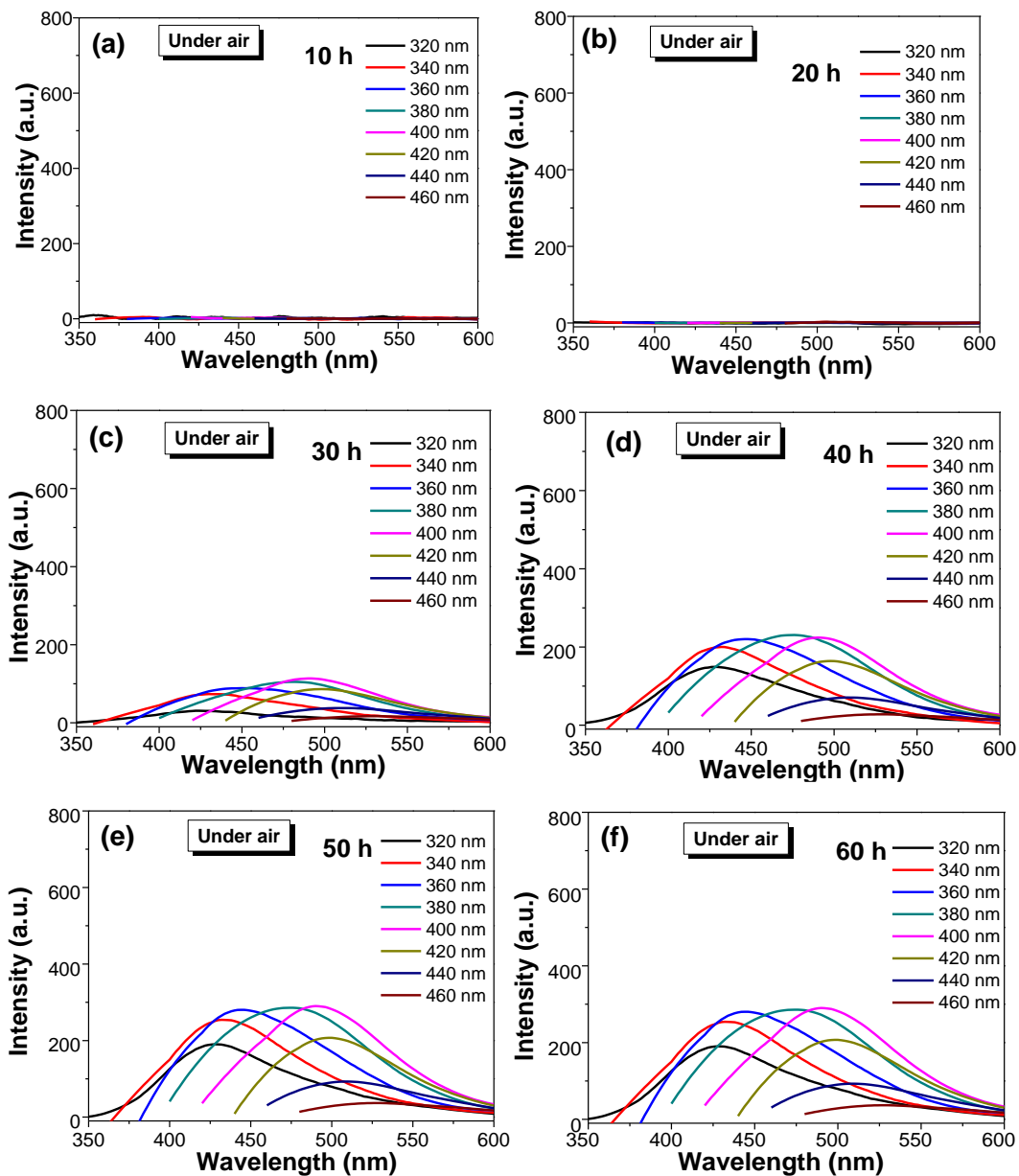


Fig. S3. Emission spectra of the reaction mixture after stirring for different time under air atmosphere.

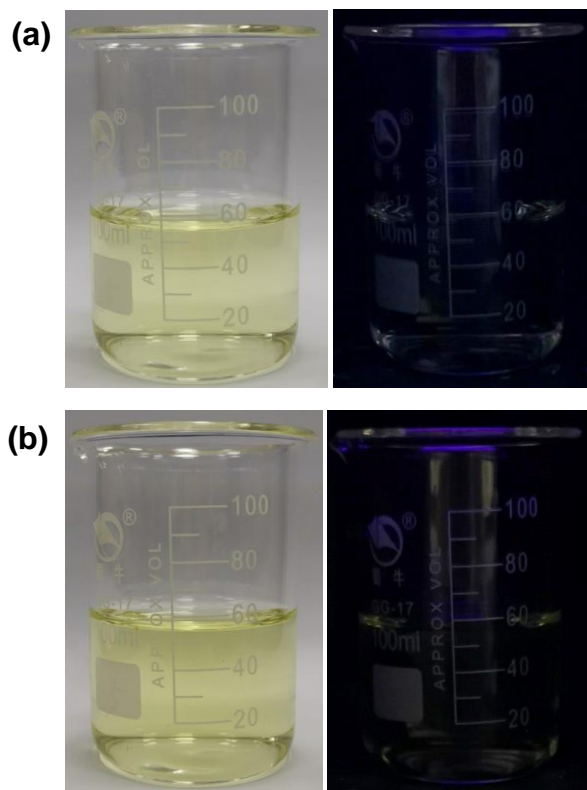


Fig. S4. (a) Photographs of the reaction mixture after stirring at 90 °C for 20 h under air atmosphere under daylight (left) and 365 nm UV lamp (right). (b) Photographs of the reaction mixture after stirring at 90 °C for 60 h under Ar atmosphere under daylight (left) and 365 nm UV lamp (right).

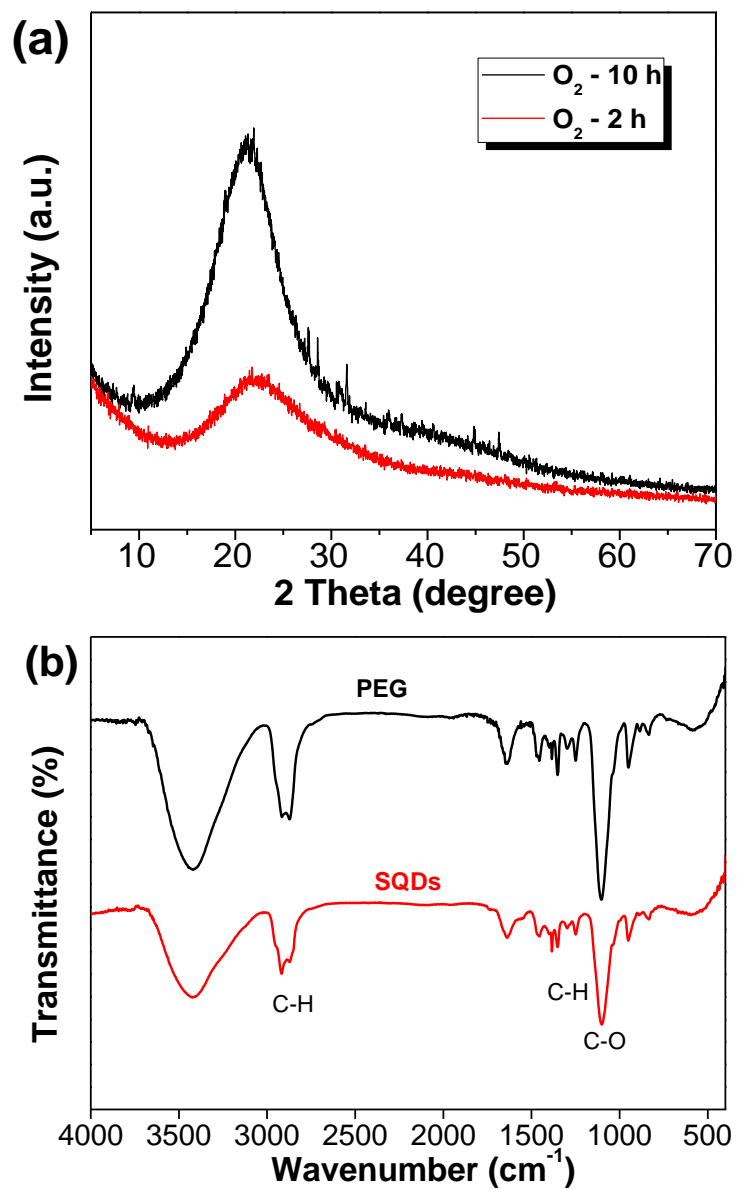


Fig. S5. (a) XRD patterns of SQDs prepared with different reaction time under O₂ atmosphere. (b) FTIR spectra of SQDs and pure PEG.

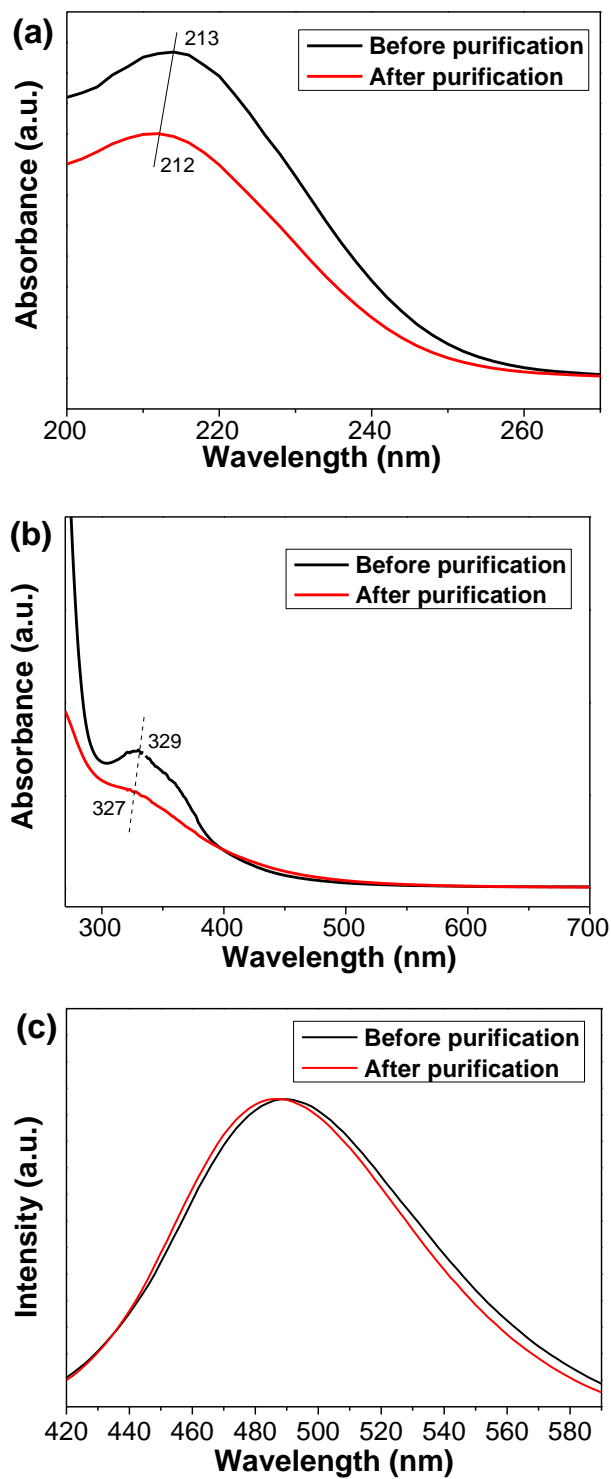


Fig. S6. UV-vis absorption (a,b) and emission (c) spectra of the SQDs before and after purification.

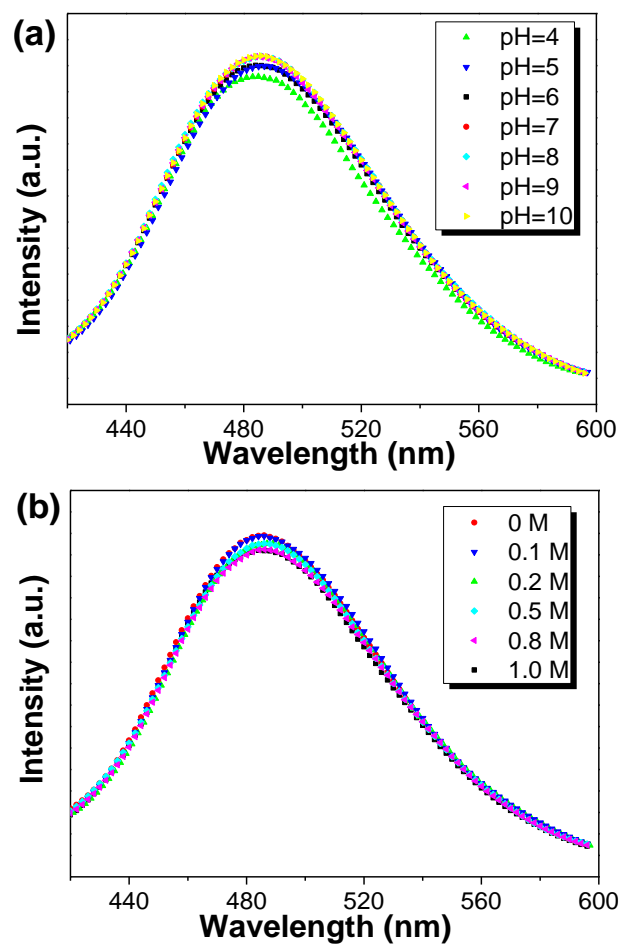


Fig. S7 The effects of solution pH (a) and concentration of NaCl (b) on the fluorescent intensity of the aqueous dispersion of SQDs.

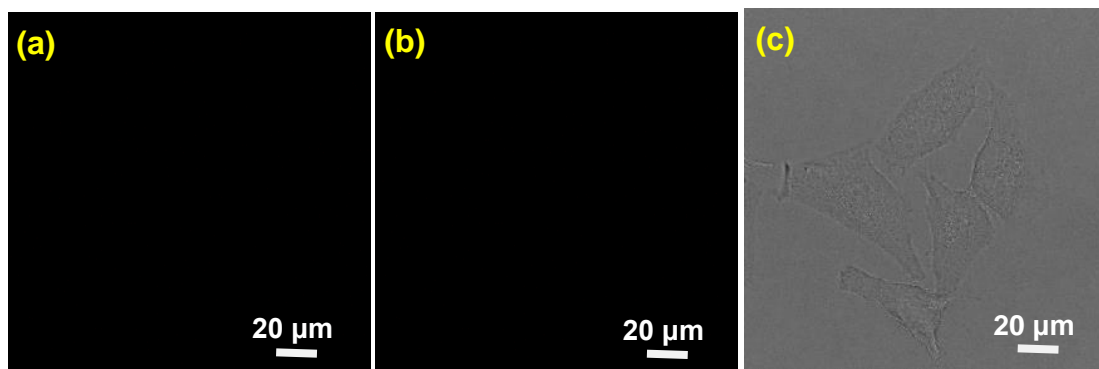


Fig. S8. Confocal fluorescence image by excitation at 458 nm (a) and 514 nm (b), and merged image of MCF-7 cells without incubation of SQDs.

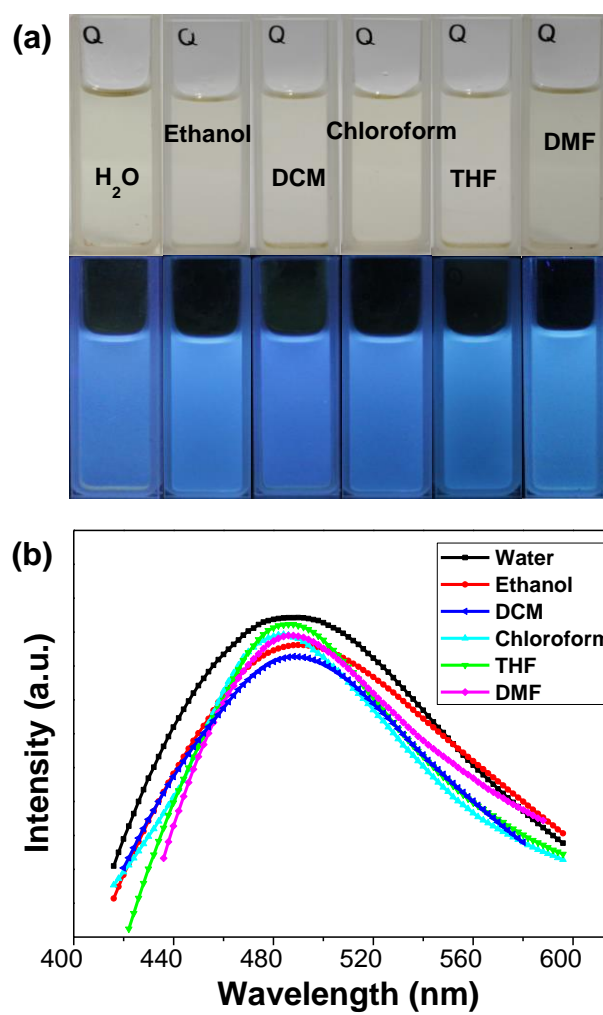


Fig. S9. (a) Photographs of SQDs in various solvents under daylight (top) and 365 nm UV lamp (bottom). (b) Emission spectra of SQDs in various solvents ($\lambda_{\text{ex}} = 400$ nm).

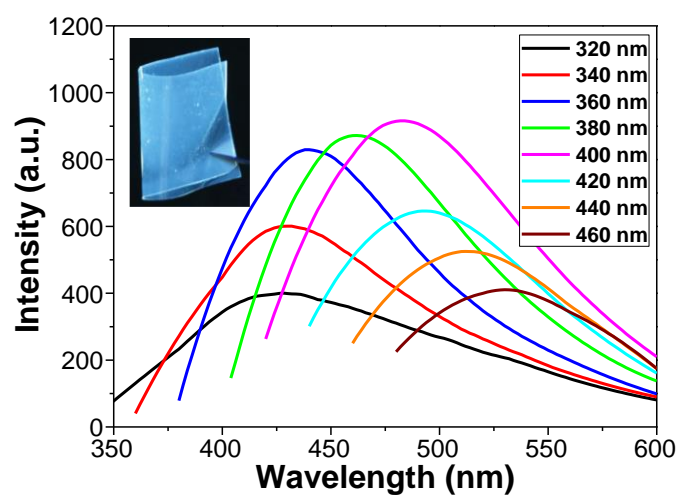


Fig. S10. Emission spectra of PVA-SQDs composite film with diverse excitation wavelength. Inset: photograph of PVA-SQDs composite film under 365 nm UV lamp.