Supporting Information

Facile synthesis of highly fluorescent gelatin/Si nanocrystals composite film for optical detection of amines from water

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Experimental Section

1.1 Materials

Methanol (AR, 99.5%), toluene (AR, 99.5%) and aqueous hydrofluoric acid (AR, 40%) were purchased from Sinopharm Chemical Reagent Co. Ltd. Mestilylene (AR, 97%) was purchased from Aladdin, 1-dodecene (95%). Trifluoroacetic acid, 1,2-ethanediamine, 1,3-propanediamine, *n*-propylamine, butylamine, urea， block copolymer Pluronic F-127 were purchased from Sigma-Aldrich. Copper nitrate ($Cu(NO_3)_2$•$2.5H_2O$), ethanolamine ($NH_2CH_2CH_2OH$) (AE), glutaraldehyde (GA) (50 wt%), gelatin (from pork skin with 150 blooms) were purchased from Acros Chemicals. Nuclepore polycarbonate (PC) membranes of 2.5 cm with pore size of 200 nm were purchased from Whatman. Deionized water (18.2 MΩ) used throughout all experiments was produced by a Millipore Direct-Q System. All experiments were carried out at room temperature unless otherwise stated.

1.2 Synthesis of water-soluble Si NCs

Free-standing Si NCs were synthesized by using SiH_4-based plasma.[1-3] They were collected as a powder and dispersed in methanol by sonication. The Si-methanol dispersion was then transferred into a PTFE beaker and HF acid was added to remove the surface oxide. H-Si NCs were separated from the mixture by centrifugation at 10000 rpm for 3 min and re-dispersed in mestilylene, then transferred to a three neck round bottom flask and degassed with a Schlenk line. The hydrosilylation of Si NCs was then performed in a mixture of 1-dodecene and mestilylene in the atmosphere of argon at 165 °C. Rotary evaporation was used to remove excess capping agent and solvent. The dodecyl-terminated Si NCs were re-suspended in toluene with the concentration of 1mg/ml as a stock solution for further surface modification. In order to make Si NCs well dispersed in water, the dodecyl-terminated Si NCs were modified with the amphiphilic block copolymer F127 (PEO–PPO–PEO) [poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide)]. 1 ml of stock solution was added to 5 ml of F-127 aqueous solution (with the concentration of 10 mg/ml) and stirred for 12 hours until all solvent was completely evaporated. Finally, 5 ml of deionized water was added and sonicated for 15 min. The resulting dispersion (with the Si NCs concentration of 0.2 mg/ml) was filtered through a 0.45 μm membrane filter and kept under dark condition for further use.

1.3 Preparation of gelatin/Si NCs composite films

Firstly, ultrathin $Cu(OH)_2$ nanostrands (CHNs) solution was prepared by mixing an aqueous solution of 1.4 mM AE with an equal volume of 4 mM $Cu(NO_3)_2$ under vigorous stirring for about 1 min and then the mixture was aged for 1 or 2 days to form CHNs as described elsewhere.[4] Secondly, 3 ml of gelatin solution (0.33 mg/ml) was mixed with 400 μl Si NCs solution (0.2 mg/ml) under vigorous stirring for about 1 hours. Thirdly, the dispersion was filtered on a mesoporous CHNs layer, which was preformed by filtering 20 ml CHNs solution on a PC membrane. Subsequently, the gelatin/Si NCs composite filter cake was cross-linked by 3 ml 2.5 wt% GA aqueous solution for 2 hours. Finally, 5 mM HCl solution was used to remove CHNs and resulting in free-standing gelatin/Si NCs composite film. After peeling off the films from the PC in ethanol and washing with deionized water thoroughly, they were transfered onto quartz substrate for further optical investigation. The gelatin/Si NCs composite films prepared from 300 μl, 200 μl, 100 μl and 0 μl Si NCs solution (0.2 mg/ml) were also synthesized following the above route.

1.4 Fluorescence quenching detection of amines

The as-synthesized gelatin/Si NCs composite film prepared from volume ratios of 0.4 : 3 (Si NCs solution : gelatin solution) was put into 10 ml, 20 mM 1,2-ethanediamine, 1,3-propanediamine, butylamine, *n*-propylamine and ethanolamine aqueous solution for certain minutes, respectively. To study the PL recovery with TFA, the sample that had been quenched by 1,2-ethanediamine was put into 10 ml, 100 mM TFA solution for 8 hours. The reuse of the composite film was achieved by taking the film out of the TFA solution and stored in deionized water solution for 3 days, then repeat the same detection procedure. The quenching and recovery percentages were calculated based on the change in PL intensity. The absolute PL quantum yield was measured in an integrating sphere, with excitation provided by a 450W Xe lamp. A PMT (R928) was used for detection. Background and scatter were accounted by subtracting a spectrum obtained under identical conditions. Spectra were then corrected using the calibration data. Quantum yield calculation was achieved using F900 software. The excitation wavelength was 325 nm for all the samples.

1.5 Characterization

The morphologies and structures were characterized by using scanning eletronic microscopy (SEM) (Hitachi S-4800), a high-resolution transmission electronic microscopy (HR-TEM) (FEI F20), and TEM (Tecnai G2 F20 S-TWIN). SEM observation was conducted after coating a 2 nm thick platinum 30 layer by using a Hitachi e-1030 ion sputter at the pressure of 10 Pa and the current density of 10 mA. PL spectra were recorded using a FLS920 fluorescence spectrometer (Edinburgh Instruments) with a 325 nm He-Cd Laser as excitation source equipped with a variable attenuator. PL measurements were conducted at room temperature. The size of the Si NCs were measured by dynamic light scattering (DLS, Zetasizer Nano-ZS, Malvern Instruments Ltd) at room temperature with Polydiseperse Index (PdI) of 0.559, zeta potential (ZP) of -6 mV, mobility of -0.5237 μmcm/V_s, conductivity of 0.109 mS/cm.

1 X. D. Pi, Q. Li, D. Li, D. R. Yang, *Sol. Energy Mater. Sol. Cells.* 2011, **95**, 2941.
2 L. Mangolini, E. Thimsen, U. Kortshagen, *Nano Lett*. 2005, **5**, 655.
3 U. Kortshagen, *J. Phys. D: Appl. Phys.* 2009, **42**, 113001.
4 H. W. Huang, Q. Yu, X. S. Peng, Z. Z. Ye, *J. Mater. Chem*. 2011, **21**, 13172.

Additional figures:

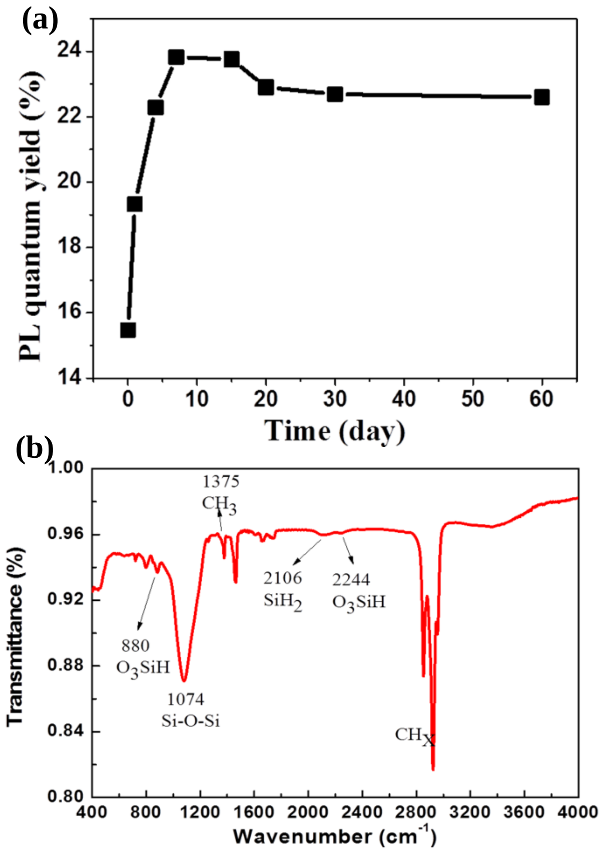

Figure S1 (a) Time-dependent quantum yield of water-soluble Si NCs dispersion. (b) The FTIR spectrum of dodecyl terminated Si NCs after storage for 20 days.

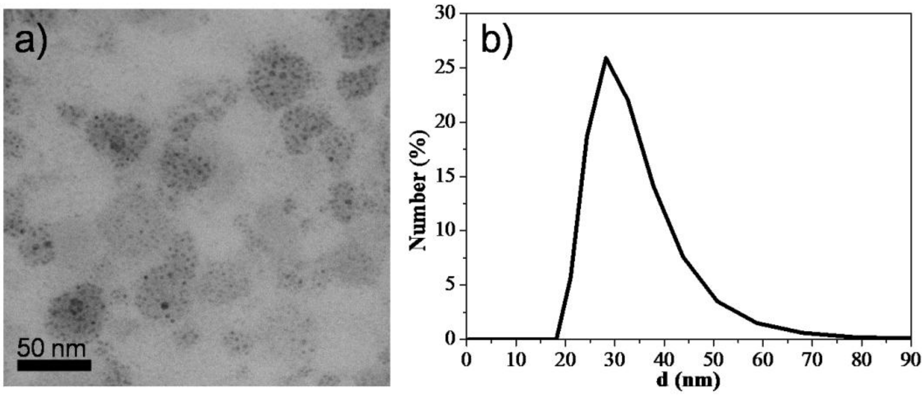

Figure S2 (a) TEM image of water-soluble Si NCs particles; (b) the corresponding DLS histogram.

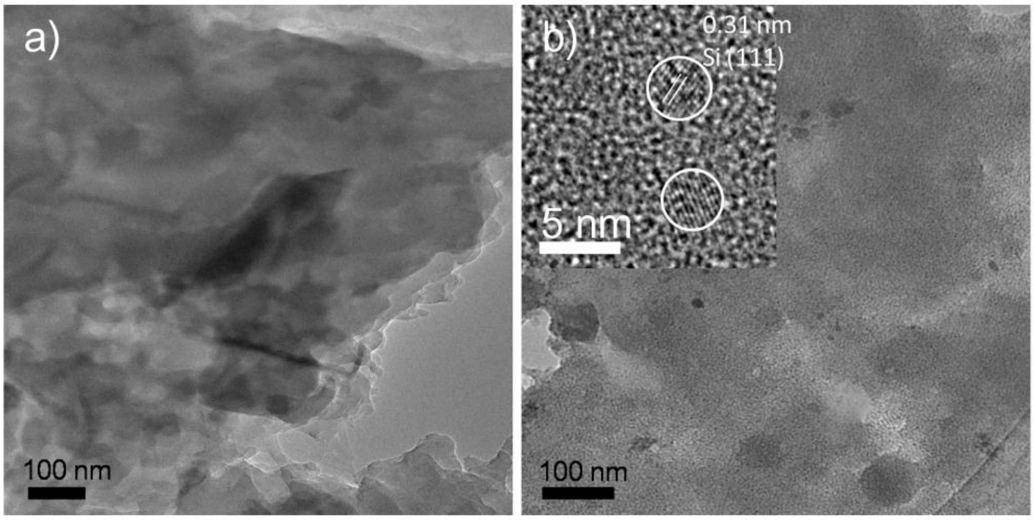

Figure S3 TEM image of (a) pure gelatin film; (b) gelatin/Si NCs composite film from 0.4 ml Si NCs (0.2 mg/ml) and 3 ml gelatin (0.33 mg/ml). Inset in (b) presents the HRTEM image of single Si NCs.

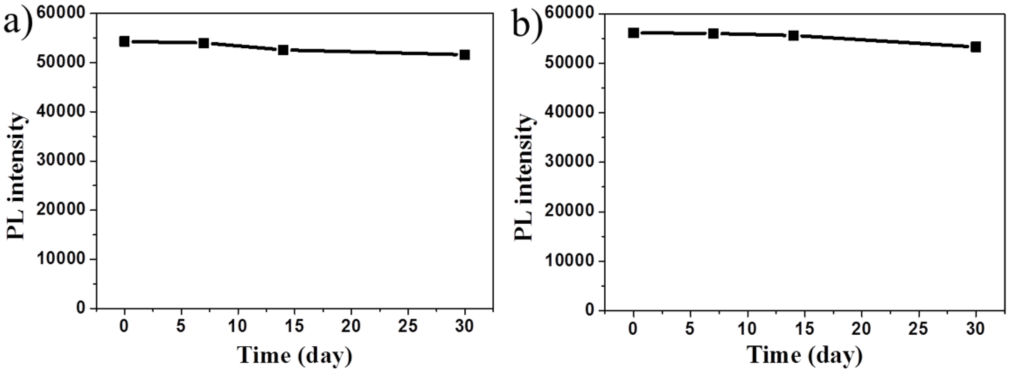

Figure S4 The evolution of PL intensity when the gelatin/Si NCs composite film is stored in (a) ambient air and (b) deionized water. The exposure time is from 0 to 30 days.

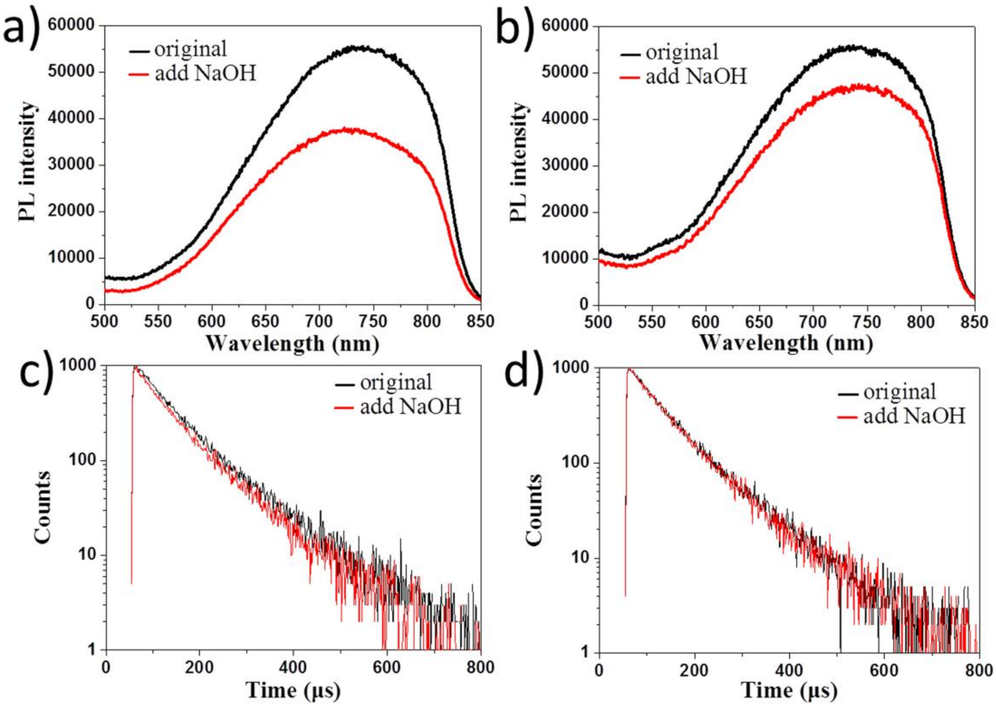

Figure S5 The PL spectra of gelatin/Si NCs composite films before and after immersing in NaOH solution with pH value of (a) 11.76 and (b) 10.79 for 30 minutes. The decay curves of gelatin/Si NCs composite films before and after immersing in NaOH solution with pH value of (c) 11.76 and (d) 10.79 for 30 minutes.

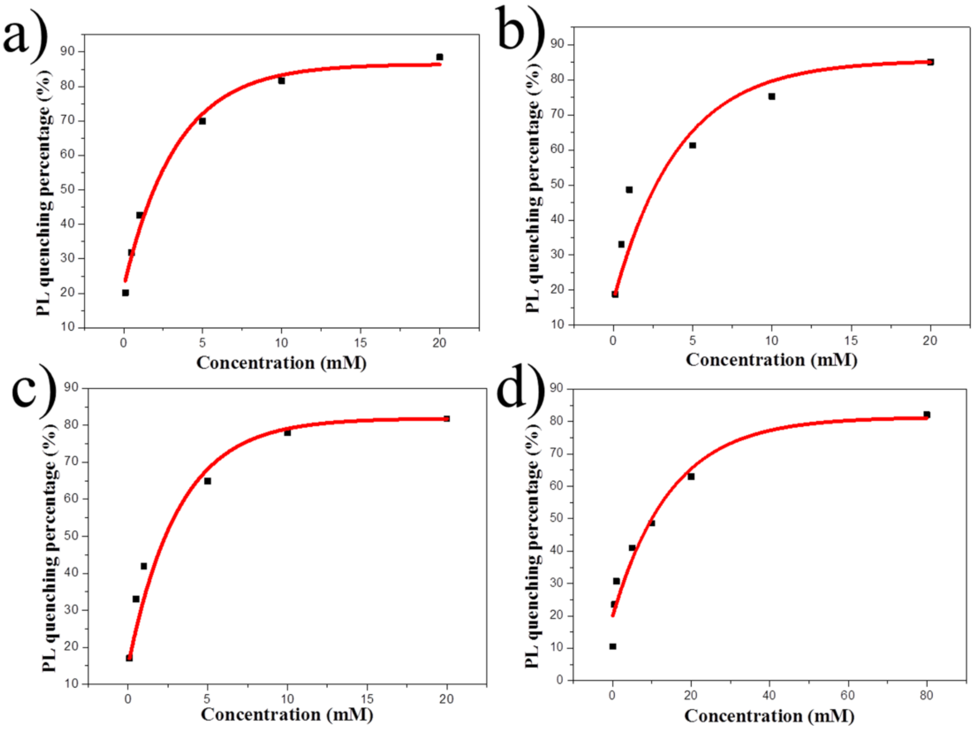

Figure S6. The quenching percentage of different concentration of (a) 1,3-propanediamine, (b) butylamine, (c) *n*-propylamine, and (d) ethanolamine solution, the immersing time is 30 minutes.