Supplementary information

Super-stable Centimeter-scale Inverse Opal Belts Integrated with CdTe QDs for Narrow Band Fluorescence Optical Waveguiding

Xianyong Lu^{*a}, Lingmei Ni^{al}, Shimin Wu^{al}, Yanzi Wu^a, Hongyan Cai^a, Ke Ding^b, Lihong Jin^b, Yi Hou^b, , Ying Zhu^{*a}, Mingyuan Gao^b and Lei Jiang^{ab}

^aKey Laboratory of Bio-Inspired Smart Interfacial Science and Technology of Ministry of Education, Beijing Key Laboratory of Bio-inspired Energy Materials and Devices, School of Chemistry and Environment, Beihang University, Beijing 100191, PR China

^bInstitute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China

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^{*} To whom correspondence should be addressed: (X.Lu) xylu@buaa.edu.cn, (Y. Zhu) zhuying@buaa.edu.cn

Experimental Detail

1. Materials

Divinylbenzene (DVB-80, 80% divinylbenzene isomers, technical grade, Aldrich) was washed with 5% aqueous sodium hydroxide and deionized water, dried over anhydrous magnesium sulfate before use. Acrylic acid (AA, analytical grade, Beijing Chemical Regents Co) was purified further by vacuum distillation before polymerization. 2,2-Azobis(2-methylpropionitrile) (AIBN) (analytical grade, Beijing Chemical Regents Co.) was recrystallized from methanol. Acetonitrile (analytical grade, Beijing Chemical Regents Co.) was recrystallized from methanol. Acetonitrile (analytical grade, Beijing Chemical Reagents Co.) was dried over CaH₂ and purified by distillation before use. Thioglycolic acid (TGA, 90%) , tetraethoxysilane (TEOS) Cd(CH₃COO)₂.2H₂O (99.5%), NaBH₄ (96%) and potassium tellurite (K₂TeO₃, 98%) were purchased from Aldrich. Other chemicals of analytical grade were used as received without any further purification.

2. Synthesis of PAA submicrospheres by distilled- precipitation polymerization

High quality PAA submicrospheres with Divinylbenzene-80(DVB-80) as crosslinker were prepared by a modified distilled-precipitation polymerization. A typical procedure: DVB-80 (0.2 mL, 0.18 g, 1.40 mmol), acrylic acid (1.6 mL, 1.68 g, 23.3 mmol), AIBN (0.04 g, 0.24 mmol, 2.2 wt% relative to the comonomers) were dissolved in 80 mL of acetonitrile in a dried 100 mL two-neck flask attached with a fractionating column, Liebig condenser, and a receiver. Finally, PAA submicrospheres were dispersed in ethanol as stable colloidal solutions.

3. Centimeter-scale PAA colloidal crystal belts by CSNPVD strategy

The ethanol suspension of PAA colloids (2 mL, typical concentration of 0.016 g/mL) were placed in a 5 mL commercial cylindrical glass vial. Then the vial was vertically placed in a vacuum oven with well-controlled negative pressure of 4000 Pa and temperature of 40 °C. With ethanol evaporation, PAA colloids were deposited on the surface of glass vial. With increasing drying the latex film, regular belts were obtained. The array of belts was connected on the circle of three-phase line for ethanol gas, glass substrate and colloidal ethanol suspension. When ethanol was evaporated completely, separated centimeter-scale PAA colloidal crystal belts were

obtained.

4. Synthesis of TGA-capped CdTe QDs

In a typical synthesis, the molar ratio of $Cd^{2+}/TGA/TeO_3^2$ was 1.0 : 1.0 : 0.2, pH= 10.5~11.0. 1 mmol Cd(CH₃COO)₂.2H₂O was dissolved into 50 ml ultrapure water in a stand-up flask. Then 90 µL TGA was added and pH was adjusted with 1 M NaOH solution. After stirring for 5 min, 0.2 mmol K₂TeO₃ which was dissolved in 50 mL ultrapure water was added into the above-mentioned solution. Then 0.4 g of NaBH₄ was added into the precursor solution. After the reactions proceeded for another 5 minutes, the flask was attached to a condenser and refluxed at 100 °C under open-air conditions. Through controlling the reaction time, CdTe QDs with desired PL emission spectra can be obtained.

5. Centimeter-scale SiO₂ inverse opal integrated with CdTe QDs

The PAA colloidal crystal belts were placed in a desiccator together with two open glass vessels containing about 2 ml of tetraethoxysilane (TEOS) and aqueous ammonia solution, respectively. The desiccator was closed again and chemical vapor deposition (CVD) of TEOS was carried out for 24 h. Similar to a Stöber reaction, silica is formed by hydrolysis and condensation of TES catalyzed by ammonia. PAA cores thermally degrade and <u>carbon dioxide and/or carbon monoxide</u> diffuses through the silica shell during calcinations under 600°C for 2 h in air. Then, centimeter-scale SiO₂ inverse opal belts were obtained. The SiO₂ inverse opal belts were immersed in the TGA-capped CdTe QDs solution for 8 h. After that, excess CdTe QDs were removed by the water with pH=9.0 three times. After vacuum dried, SiO₂ inverse opal belts dotted with QDs were obtained.

6. Characterizations

SEM studies were done with Hitachi S-4800 microscope at an accelerating voltage of 10 kV. Transmission electron microscopy was performed on the JEM-2100 with accelerating voltage 200 kV. True-color and fluorescence images of SiO₂ inverse opal belts dotted with CdTe QDs were recorded with an inverted Olympus Fluorescence Microscope (IX-70). The optical waveguide was measured in a Witec-Alpha scanning near-field optical microscope with 405 nm excitation. Dynamic light scattering (DLS)

measurements were carried out at 298.0 K with a Nano ZS (Malvern) equipped with a solid-state He-Ne laser ($\lambda = 633$ nm) for measuring the hydrodynamic size of the resulting PAA submicrospheres. The Fourier transform infrared (FTIR) spectroscopy was taken on a Bruker EQUINOX55 FT-IR spectrometer under ambient conditions. The digital photos were taken by Panasonic LUMIX GF2 cameras.



Fig. S1 Dynamic light scattering (DLS) size of PAA submicrospheres obtained by CSNPVD method. From Fig. S1, the DLS size of PAA colloids is 207.8 nm with polydispersity index_(PDI) 0.049 . The low PDI indicates that PAA microspheres have monodispersed size.



Fig. S 2 Bright-field images a) and fluorescence images b) of inverse opal belts, whereas, green emitting, yellow-emitting, red-emitting and pure SiO_2 inverse opal belts, (from left to right), respectively.



Fig. S3 PL spectra of a) SiO_2 inverse opal belts integrated with red CdTe QDs; b) SiO_2 inverse opal belts integrated with red CdTe QDs kept under ambient condition over 2 years.

The PL band of SiO_2 inverse opal belts integrated with red CdTe QDs is located at 636 nm. In contrast, the PL band of this sample stored under ambient condition over 2 years is located at 641 nm. A small red shift with 5 nm indicates that SiO_2 inverse opal belts integrated with red CdTe QDs have super-stable fluorescently property under ambient condition.



Fig. S4 a)Optical waveguiding in SiO₂ inverse opal belts integrated with Yellow-emission CdTe QDs detected by NSOM. b) PL spectrum detected with the NSOM collection tip held at the terminus of SiO₂ inverse opal belts integrated with Yellow-emission CdTe QDs.



Fig S5) PL spectra detected with the NSOM collection tip held at the terminus of red emission CdTe@SiO₂ inverse opal belts and with the excitation laser beam at side with angle of 45 °.

We have studied the PL spectra detected with the NSOM collection tip held at the terminus of red emission CdTe@SiO₂ inverse opal belts and with the excitation laser beam at side with angle of 45 °. The PL spectra of two peak are all located at 636 nm with different peak intensity, which indicates the optical loss of the waveguide.