Supporting Information

Highly luminescent porous metamaterial based on mixture of gold and alloyed semiconductor nanoparticles

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S1. Synthesis of CdZnSeS/ZnS quantum dots and Au nanoparticles

1. Chemicals

Cadmium oxide (CdO, 99.99 %), zinc oxide (ZnO, 99.9 %, powder), sulfur (99.9 %, powder), selenium (99.99%, powder), sulphur (99.99%, powder), trioctylphosphine (TOP, 90 %), oleic acid (OlAc, 90 %), 1-octadecene (1-ODE, 90 %) were used as purchased from Aldrich.

2. Synthesis

Preparation / Synthesis of alloyed CdZnSeS/ZnS quantum dots

QDs were prepared by one-pot synthesis with slight modification according to Bae et al. (Multicolored light-emitting diodes based on all-quantum-dot multilayer films using layer-by-layer assembly method. Nano letters, 2010, 10, (7), 2368-2373). Briefly, 0.2 mmol of CdO and 4 mmol of ZnO were placed with 5 ml of OlAc and 15 ml of 1-ODE in 100 ml of flask, heated to 150 °C and evacuated for 30 min. The reaction flask was heated up to 300 °C maintaining the reaction vessel under Ar atmosphere condition to acquire clear mixed solution of Cd(oleate)₂ and Zn(oleate)₂. At 300 °C 2 ml of TOP dissolving 0.1 mmol of Se and 4 mmol of S was rapidly injected into the reaction vessel. The reaction was proceeded at 300 °C for 10 min in order to produce QDs with chemical composition gradient. After 10 min the temperature of final solution was lowered to room temperature to quench reaction. The obtained QDs were purified bv dispersing the in chloroform/precipitating with excess amount of acetone several times and dispersed in chloroform for further experiments.

Synthesis of Gold Nanoparticles.

The synthesis of Au NPs stabilized by mPEG-SH was carried out according to Dubavik et al. (Dubavik, A., Lesnyak, V., Gaponik, N., & Eychmüller, A. (2011). One-phase synthesis of gold nanoparticles with varied solubility. Langmuir, 27(16), 10224-10227). Briefly, at a molar ratio of gold/stabilizer =1/1, 10 mL of deionized water solution containing 0.3 mmol of mPEG350-SH was vigorously mixed with 0.3 mmol of HAuCl₄×3H₂O dissolved in 30 mL of H₂O for 10 min at room temperature. Shortly afterwards, 30 mL of the freshly prepared 3 mmol NaBH₄ aqueous solution chilled by ice was added to the mixture and left stirring overnight. The thus-prepared gold colloid was filtered in order to separate large aggregates of NPs. The Au NPs were isolated from the supernatant by evaporation of water on a rotary evaporator. The nanocrystals synthesized were redispersed either in polar or nonpolar solvents. The growth of Au NPs via Ostwald ripening was realized by heating at 150-160°C in mesitylene for 1 hour, similarly to the approach reported by Shimizu et al. (Shimizu, T.; Teranishi, T.; Hasegawa, S.; Miyake, M., Size evolution of alkanethiol-protected gold nanoparticles by heat treatment in the solid state. J. Phys. Chem. B 2003, 107 (12), 2719-2724)



Figure S1.1. TEM images of (a) CdZnSeS/ZnS quantum dots and (b) Au nanoparticles. Scale bar is of 50 nm.



Figure S1.2. Optical spectra of CdZnSeS/ZnS quantum dots and Au nanoparticles

S2. SEM images of sample QD1



Figure S2.1. SEM image of spiky flowers from QD1 sample.



Figure S2.2. SEM image of globular flowers from QD1 sample.



Figure S2.3. SEM image of spheres from QD1 sample.



Figure S2.4. SEM images of spheres on the edge of the substrate from QD1 sample.



Figure S2.5. Histograms of size distribution for size of typical structures formed in QD1: (a) flowers, (b) spheres.



S3. The destabilization of nanocrystal colloidal solution scheme

formation of spiky flowers structures QD aggregates superstructure nuclei

formation of

formation of globular flowers structures



formation of spherical structures



falling of different superstructures on vial and substrate bottom

Figure S3. Schematic presentation of nanocrystal assembly stages

S4. SEM images of samples QD-Au1 and QD-Au2



Figure S4.1. SEM image of the superstructures formed by QDs and Au NPs in samples QD-Au1 (high magnification).



Figure S4.2. SEM image of the superstructures formed by QDs and Au NPs in samples QD-Au1 (low magnification).



Figure S4.3. SEM image of the superstructures formed by QDs and Au NPs in samples QD-Au2 (high magnification).



Figure S4.4. SEM image of the superstructures formed by QDs and Au NPs in samples QD-Au2 (low magnification).



Figure S4.5. Histograms of size distribution for size of typical structures formed in (a) Au-QD1 and (b) Au-QD2.

S5. Optical properties of samples



Figure S5. PL spectra (upper panel) and PL decay (lower panel) for samples QD1 (green), Au-QD1 (blue) and Au-QD2 (red)