

## Supplemental information for “Green Synthesis of Highly UV-Orange Emitting ZnSe/ZnS:Mn/ZnS Core/Shell/Shell Nanocrystals by a Three-step Single Flask Method”

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### Experimental

#### Chemicals

Manganese (II) acetate ( $\text{Mn}(\text{OAc})_2$ ) ( $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ , 99.99%), zinc acetate ( $\text{Zn}(\text{OAc})_2$ ) ( $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ , 99.99%) and sodium sulfide ( $\text{Na}_2\text{S}$ ), 3-mercaptopropionic acid (MPA, 99+%), sodiumborohydride ( $\text{NaBH}_4$ , 96%), selenium powder (99.5%), 2-propanol (HPLC grade). All the chemicals are of analytical grade and purchased from Sigma-Aldrich. Deionized water (DI water) used in all synthesis was high purity grade with a conductivity of 18.2  $\text{M}\Omega$  cm.

#### Apparatus and characterization

UV-vis absorption spectra were obtained using an Optizen 2120UV spectrophotometer (Science and Technology Development). The obtained nanocrystals (NCs) were dispersed in water to check dynamic light scattering (DLS) (Scatteroscope I model by Qudix company) with suitable concentration to test the distribution relative size of NCs. Fluorescence measurements were performed using WGY-10 fluorescence spectrophotometer. All optical measurements were carried out at room temperature. The photoluminescence quantum yield (PL QY) of NCs was measured according to the method described in Crosby and Demas [S1- S3]. PL QYs were determined by comparing the integrated emission of the NCs samples in water with that of fluorescent dye rhodamine 6G (PL QY = 95% in ethanol) with identical optical density (0.05-0.1) at the excitation wavelength. X-ray diffraction measurements were performed on a D/Maxrnt 2000 powder X-ray diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The X-ray photoelectron spectra (XPS) were taken on a Thermo Scientific K-alpha electron energy spectrometer using  $\text{Al K}\alpha$  (1486.6 eV) as the X-ray excitation source (VG Multi-lab ESCA 200 System model). The samples used for XRD, TEM and XPS were prepared as follows: the NCs solution was firstly concentrated to one-tenth of the original volume, and then the NCs were precipitated with 2-propanol and collected via centrifugation, finally the colloidal precipitate was dried in a vacuum drying oven. High resolution transmission electron micrographs (HRTEM) images were acquired using a JEM 2100F transmission microscope with acceleration voltage of 200 kV. TEM samples were prepared by dropping the samples dispersed in water onto carbon coated copper grids with excess solvent

evaporated. The selected area electron diffraction (SAED) pattern was taken with a camera length 20 cm. The average size of NCs was determined using imageJ software from TEM images.

### Preparation of ZnSe/ZnS:Mn/ZnS Nanocrystals

Using 3-mercaptopropionic acid (MPA) as capping ligand in the preparation of ZnSe or other II-IV semiconductor NCs in the aqueous route due to its preferable binding capacity [S2]. An aqueous colloidal ZnSe solution was prepared using the reaction between  $\text{Zn}^{2+}$  and NaHSe solution following the literature method.

+ NaHSe was produced by reaction between  $\text{NaBH}_4$  and Se powder as previous report [S4]. The  $\text{Zn}^{2+}$  precursor solution was prepared by dissolution of 10 ml of zinc acetate 0.1 M in 90 ml of DI water, and 40 ml of MPA 0.1 M in three-neck flask, then the pH of this system was adjusted to pH = 6.5 using NaOH 2 M with vigorous stirring. This three-neck flask was degassed by  $\text{N}_2$  bubble in 30 minutes, and the NaHSe solution was injected into the  $\text{Zn}^{2+}$  precursor solution at room temperature under oxygen-free. The system was heated to 90-100 °C and refluxed for 3 hours for complete ZnSe core growth.

+ The flask was cooled to room temperature, then the mixture of 7.9 ml of zinc acetate 0.1 M and 9.28 ml of manganese acetate 0.01 M (11.7% related to Zn in the first shell) was dropwised at 1 drop/second (the volume and concentration of manganese acetate were adjusted to get the desired  $\text{Mn}^{2+}$  at.% relative to  $\text{Zn}^{2+}$  of the first shell from 11.7, 25.0, 35.0 and 45.0% in order to consider the affect of Mn doping concentration). After vigorous stirring for 20 minutes, the pH was adjusted by NaOH 2 M to 11.1, the temperature was raised to 80 °C. At this point, 9.21 ml solution of  $\text{Na}_2\text{S}$  0.1 M was injected slowly for metal sulfide NCs crystalline formation, the flask was continuously stirred for one and half hours (at this point the faint orange emission ( $\lambda = 587$  nm) was visible under UV light with 365 nm wavelength).

+ The reaction system was keep on stirring at 80 °C, 8.3 ml of zinc acetate 0.1 M was added slowly. After 20 minutes of stirring, 8.3 ml of  $\text{Na}_2\text{S}$  0.1M was injected to get ZnS complete crystallization at the outer shell by rapid stirring and refluxing for 1 hour. The flask system was cooled down to room temperature to terminate reaction. The as-prepared NCs solution was purified by centrifugation and decantation with 2-propanol.

[S1] Y. He, H. T. Lu, L. M. Sai, W. Y. Lai, Q. L. Fan, L. H. Wang and W. Huang, *J. Phys. Chem. B*, 2006, **110**, 13370-13374

[S2] J. N. Demas and G. A. Crosby, *J. Phys. Chem.*, 1971, **75**, 991-1024

[S3] Measurement of Fluorescence Quantum Yields, Michael W. Allen, Thermo Fisher Scientific, Madison, WI, USA

[S4] A. Shavel, N. Gaponik and A. Eychmüller, 2004 *J. Phys. Chem. B* **108**, 5905-5908

**Table 1.** Nominal Mn concentration used in the synthesis and PLQYs of various samples of ZnSe/ZnS:Mn (cs) and ZnSe/ZnS:Mn/ZnS (css) NCs

Mn at.% relative to Zn	ZnSe/ZnS:Mn cs	ZnSe/ZnS:Mn/ZnS css
	PLQY (%)	PLQY (%)
11.7	28.7	31.7
20.0	30.3	34.2
35.0	32.1	35.3
45.0	35.6	42.9



