Microwave-assisted aqueous synthesis of Mn-doped ZnS quantum dots and their room-temperature phosphorescence detection of indapamide



Figure S1. (A) XRD patterns of the prepared Mn-ZnS QDs by reference S1. (B) XRD patterns of the prepared Mn-ZnS QDs by our microwave-assisted aqueous synthesis. Diffraction lines for cubic phases of bulk ZnS are shown for the guidance

Figure S2 showed the photoluminescence spectra of the Mn-doped ZnSe nanocrystals recorded at various Mn:Zn ratio in prepared QDs using an excitation wavelength of 310 nm. An increase in the doping level (from 0.13% to 1.14%) obviously leads to the increase in the PL intensity of the Mn^{2+} -related $_4T^1(4G) \rightarrow _6A^1(6S)$ transition. While with an increase in the Mn^{2+} concentration in the sample from 1.14% to 1.65%, decrease in the PL intensity of 585nm orange emission, perhaps because of enhanced Mn-Mn interaction^{S2}. Mn-Mn interaction only occured when Mn dopant concentration was very high for bulk samples.



Figure S2. Photoluminescence spectra of the Mn-ZnS QDs recorded at various Mn:Zn ratio using an excitation wavelength of 310 nm a:0.13%, b:0.38%, c:0.83%, d:1.14%, e:1.65%. The measurement conditions were identical in all cases and therefore relative intensities can be compared.

The carboxylic ligands at the surface of Mn-ZnS QDs play a role of recognition receptor to bind indapamide species through the acid-base pairing interaction. Moreover, the huge surface-tovolume ratio of the QDs greatly enhances the adsorption affinity to indapamide species. As shown in Figure S3, the bonding of indapamide onto the surface of the Mn-ZnS QDs was confirmed by the new vibration peaks (1656 cm⁻¹ for stretching vibrations of the C=O bond and 1608 cm⁻¹, 1538 cm⁻¹ and 1447 cm⁻¹ for stretching vibrations of the C=C bond from benzene ring skeleton) from indapamide in the infrared (IR) curve, while these peaks were not present in the IR curve from Mn-ZnS QDs only. Indapamide is inclined to be electron-deficient due to the strong electron-withdrawing effect of the carbonyl group (C=O) and sulfonyl group (O=S=O). When the Mn-ZnS QDs are optically excited, static electrons (electrons located in the valence band) become mobile (electrons located in the valence band) within the semiconductor matrix, leaving behind them holes in the valence band.^{S2} After the loading of indapamide, mobile electrons of the QDs

optically excited is inclined to be transferred to indapamide, due to the electron transfer, it was halted that the energy of a photogenerated electron-hole pair was transferred into the electronic d-d levels of the Mn²⁺ ions, resulting in the quenching of the photoluminescence of the Mn-ZnS QDs. Such an electron transfer from QDs to electron-deficient species has been reported.^{S3}



Figure S3. FT-IR spectrograms of the Mn-ZnS QDs capped with MPA, indapamide and the Mn-ZnS QDs/indapamide hybrids.



Figure S4. RTP and fluorescence spectra of urine (curves c and b) and serum (curves c and a).

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