Supporting Information

Magnetic-Room Temperature Phosphorescent Multifunctional Nanocomposites as Chemosensor for Detection and Photo-Driven Enzyme Mimetics for Degradation of 2,4,6-Trinitrotoluene

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State Key Laboratory of Analytical Chemistry for Life Science, School of Chemistry & Chemical Engineering and Center of Materials Analysis, Nanjing University, 22 Hankou Road, Nanjing 210093, China **Synthesis and Characterization of MEA Capped Mn-Doped ZnS QDs.** Mn-Doped ZnS QDs was prepared according to the reported procedures in literatures.^[1,2] Briefly, 12.5 mmol of ZnSO₄, 1 mmol of MnCl₂ and 40 mL of DDW were placed into a 100 mL flask. After the mixture was stirred under nitrogen at room temperature for 30 min, 10 mL of 12.5 mmol of Na₂S aqueous solution was added dropwise, and the mixture was kept stirring for another 30 min. The resultant bare Mn-doped ZnS QDs were centrifuged and washed with DDW and absolute ethanol several times. For the further surface modification, 0.1 g of bare Mn-doped ZnS QDs was redispersed in 50 mL of absolute ethanol and then purged with nitrogen for 30 min to exclude the oxygen in ethanol. An amount of 2.5 mmol of MEA was dissolved into the above solution, and the mixture was stirred for 24 h in a sealed flask. The resultant MEA-capped Mn-doped ZnS QDs were centrifuged and washed with DDW several times to remove the residue of MEA and were redispersed in DDW for use.

The HRTEM image revealed MEA capped Mn-doped ZnS QDs with spherical shape and almost uniform size in diameter about 3.5 nm (Figure S1-A₁). The selected area electron diffraction (SAED) patterns (Figure S1-B₁) showed the outer diffraction rings of the cubic structure of the MEA capped Mn-doped ZnS QDs. The XRD pattern of MEA capped Mn-doped ZnS QDs exhibited a cubic structure with peaks for (311), (220) and (111) planes (Figure S1-C₁). The FT-IR band at 1625 cm⁻¹ appearing in curve 1 and 2, associated with –NH bending (scissoring) vibration, testified MEA successfully grafted onto the surface of bare Mn-doped ZnS QDs (Figure S2).^[3]

Synthesis and Characterization of PPA Coupled Fe₃O₄ MNPs. Fe₃O₄ MNPs was prepared according to reported procedures^[3,4] with slight modification. Typically, 2 mmol of FeCl₃ and 12 mL DDW were placed into a 50 mL flask. After the solution was ultrasonicated under nitrogen for 30 min, 1 mmol of FeCl₂ and 0.125 mmol of PPA were added, then the resultant mixture was heated to 80°C. Subsequently about 6 ml of 28% ammonia solution was injected into the flask and ultrasonication was continued for another 30 min for the growth of nanoparticles. The solution was finally cooled to room temperature and the resulting MNPs were centrifuged and repeatedly washed in turn with DDW and ethanol.



Fig. S1 HRTEM images (A₁), SAED patterns (B₁) and XRD patterns (C₁) of MEA capped Mn-doped ZnS QDs; HRTEM images (A₂), SAED patterns (B₂) and XRD patterns (C₂) of PPA coupled Fe_3O_4 MNPs.

The HRTEM image revealed that Fe_3O_4 MNPs are almost spherical and uniform, and of a significantly narrow size distribution (approximately 6~8 nm in diameter) (Figure S1-A₂). SAED pattern indicated the polycrystalline nature of the as-prepared MNPs. The individual planes identified from the SAED pattern correlate well with those of the XRD pattern (Figure S1-B₂). The XRD pattern of the MNPs matched well with that of spinel magnetite (JCPDS card no. 75–1610) with peaks for (311), (220), (400), (440) and (511) planes (Figure S1-C₂)^[5]. The FT-IR spectra of the nanocomposite showed a strong band around 575 cm⁻¹, which is the characteristic of Fe–O vibration related to the magnetite core. A broad peak around 975 cm⁻¹ in both curves accounts for Fe–O–P and P=O stretching bands superimposed on one another (Figure S2).^[3] The above bands both indicated that PPA coupled Fe₃O₄ MNPs were successfully prepared.



Fig. S2 FT-IR spectra of MNPs/QDs NCs (curve 1), and TNT self-assembled on its surface (curve 2).

Spectroscopic Measurement. Spectral measurements were carried out with excitation and emission slit width both of 10 nm for synchronous mode, and with excitation and emission slit width of 10 nm and 20 nm, respectively, for phosphorescence mode. For photomultiplier tube voltage, 400 V and 950 V were used for synchronous and phosphorescence, respectively. Phosphorescence at an emission wavelength of 580 nm were monitored at an excitation wavelength of 316 nm, and RLS spectra were recorded by scanning simultaneously the excitation and emission monochromators ($\Delta \lambda = 0$) of the F-4600 spectrophotometer.

Emission property of MNPs/QDs NCs. Mn-doped ZnS QDs as one kind of the most interesting luminescent nanomaterials can emit fluorescence and RTP while the spectrofluorometer setting as fluorescence and phosphorescence modes, respectively.^[1,6,7] When the as-prepared MNPs/QDs NCs was also excited with 316 nm wavelength, the peaks at 430 nm and 580 nm for fluorescence, and at 580 nm for phosphorescence were observed, respectively (Figure S3-A). The phosphorescence lifetime of 2 ms for the MNPs/QDs NCs was evaluated from the decay curve of its phosphorescence emission (Figure S3-B). The emission at 430 nm observed in fluorescence but disappeared in phosphorescence mode is

ascribed to a defect-related emission. The orange emission at 580 nm observed both in phosphorescence and fluorescence modes is known to result from the ${}^{4}T_{1}$ - ${}^{6}A_{1}$ transition of Mn^{2+} impurities incorporated into the ZnS host lattice excited *via* energy transfer from the ZnS host.^[8] RTP intensity of the mixture containing 5 mg/L Mn-doped ZnS QDs and 25 mg/L Fe₃O₄ MNPs was not observed obvious change in comparison to that of only existence of the former (data not shown). Therefore, the congeries induced by electrostatic interaction between Mn-doped ZnS QDs and Fe₃O₄ MNPs did not result in the generation of local electric field, which would lead to enhancement of RTP.^[9-11] It can be inferred that the MNPs/QDs NCs have the same feature.



Fig. S3 Fluorescence (curve 1) and phosphorescence (curve 2) spectra of 5 mg/L MNPs/QDs NCs aqueous solution (A); The decay curve of phosphorescence (B).

References

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