Electronic Supplementary Material (ESI) for RSC Advances.

Mn-doped ZnS quantum dots with 3-Mercaptopropionic assembly as the ratiometric fluorescence probe for curcumin detection

Xiaojuan Zhao[a], Fengxia Li[a,b], Qingyan Zhang[a], Zengbo Li[a], Jun Yang[a], Yehong Zhou[a]，Chuan Dong[a]，Junping Wang[b] and Shaomin Shuang[a]*

[a]Department of Chemistry and Chemical Engineering, Shanxi University, Taiyuan 030006, People's Republic of China
[b]Shanxi Province People's Hospital, Taiyuan, People's Republic of China
Tel: +86-351-7018842 Fax: +86-351-7011688
*Corresponding author. E-mail: smshuang@sxu.edu.cn

Figure.S1 showed the average hydrodynamic size of Mn-doped ZnS QDs was 8.7 nm from the DLS measurement. The hydrodynamic diameter of nanoparticle obtained by DLS was larger than those by TEM due to presence of solvatation layer around the QDs in aqueous solution [1].

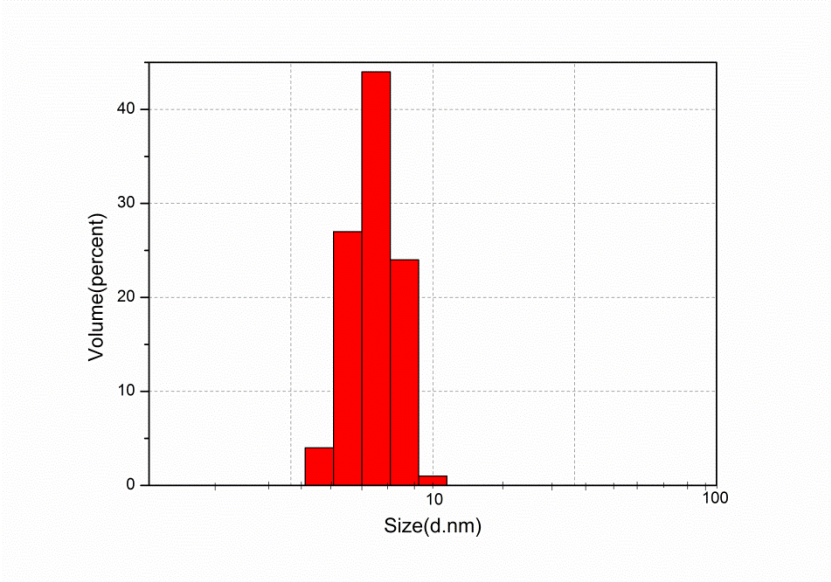

Figure S1. Particle size distribution of Mn-doped ZnS QDs

Figure. S2 demonstrated zeta potentials of MPA-capped Mn-doped ZnS QDs were negative in the pH range of 5~12. And it showed that an even-

lower pH value would quickly result in instability of MPA-capped QDs. This instability mainly originated from relatively low pKa values for 3-Mercaptopropionic acid, which in turn resulted in the depletion of ligands on QDs' surface [2].

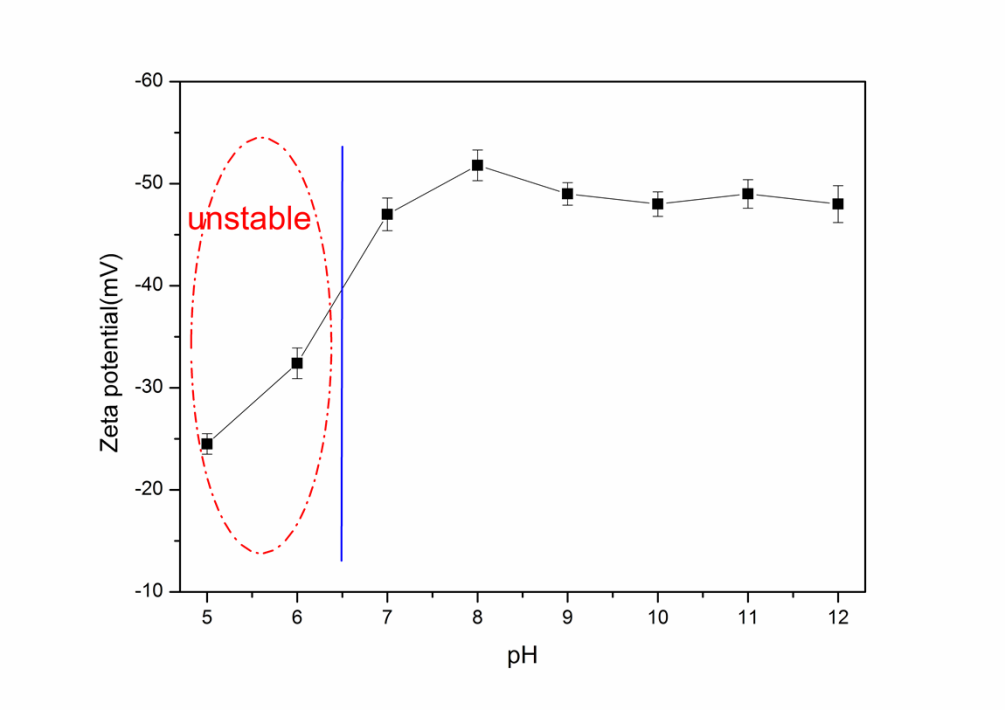

Figure S2. Zeta potential of Mn-doped ZnS QDs under different pH values.

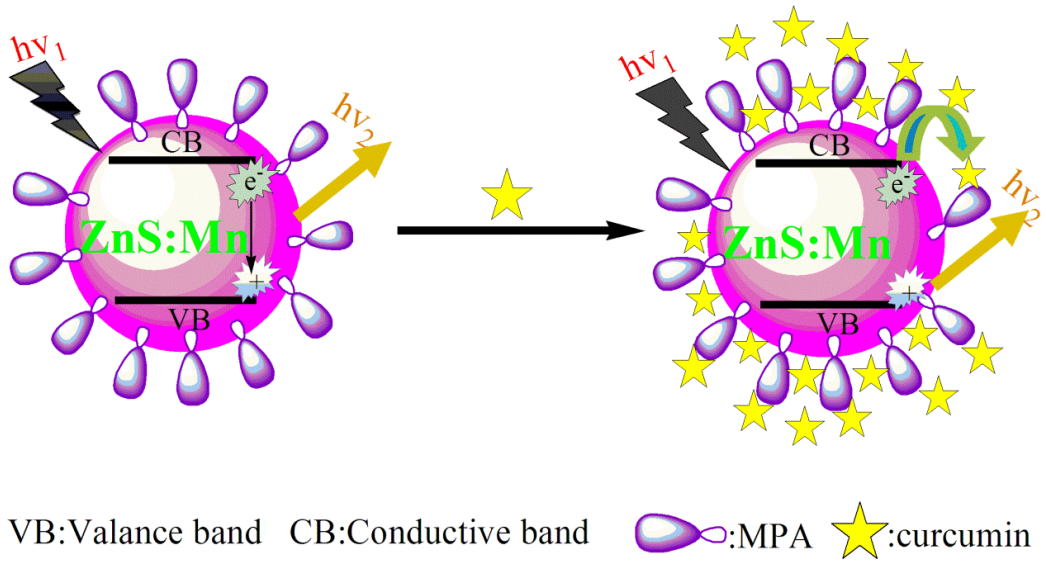

Figure S3. Schematic illustration of the photoinduced electron transfer (PET) of QDs after the addition of curcumin

Lifetime Measurements were recorded on an Edinburgh Analytical Instruments FLS-920 using laser as light source and 315 nm as excitation wavelength. Decay curves of lifetime measurement for Mn-doped ZnS QDs were monitored at 458 nm. The time decay curves at 458 nm under 1μM curcumin added were shown in Figure. 13.

Table S1 Fluorescence lifetime data of the Mn-doped ZnS QDs probe in the absence and presence of curcumin

Substrate	Emission lifetimes[a]/ns		Average lifetime(τ_{av})[b]/ns
	τ_1	τ_2	
Mn-doped ZnS QDs	2.5971(39.3%)	15.3924(25.68%)	14.13
Mn-doped ZnS QDs + curcumin	2.2215(49.23%)	11.8174(50.77%)	10.34

[a]The FL decay was analyzed using the express $F(t) = a_1\exp(-t/\tau_1) + a_2\exp(-t/\tau_2) + a_3\exp(-t/\tau_3)$, where τ_1 and τ_2 were the lifetimes. The values in parentheses indicate the fraction (%) of the corresponding lifetime component. [b]The average lifetime values was calculated using the expression $\tau_{av} = \sum a_i\tau_i^2/\sum a_i\tau_i$.

LC-MS were recorded on a Shimadzu Instruments LCMS-8030 with (+) ESI. The analytical column C18 (Agilent SB, 2.1mm×50mm×1.8μm) was used. The mobile phase was a mixture of acetonitrile/water (50:50, v/v) with 0.1% acetic acid. The injection volume was 1 μl; run time was 3min; flow rate was 0.3ml/min. During the analyses, the ESI parameters were set as follows: ion source voltage, 4.5kV; ion source temperature, 300 ◦C; atomizer, N_2，3L/min; and drier, N_2，15L/min.

The multiple reactions monitoring pair monitored was m/z 369/177 for curcumin. As shown in Fig. S4, curcumin $[M + H]^+$ m/z 369 and fragment ion 177 were detected, which suggested that a little curcumin

was present in urine sample. Moreover, we also conducted the blank and control assay, which indicated blank urine showed no significant interfering peaks at the retention time of curcumin Fig. S5.

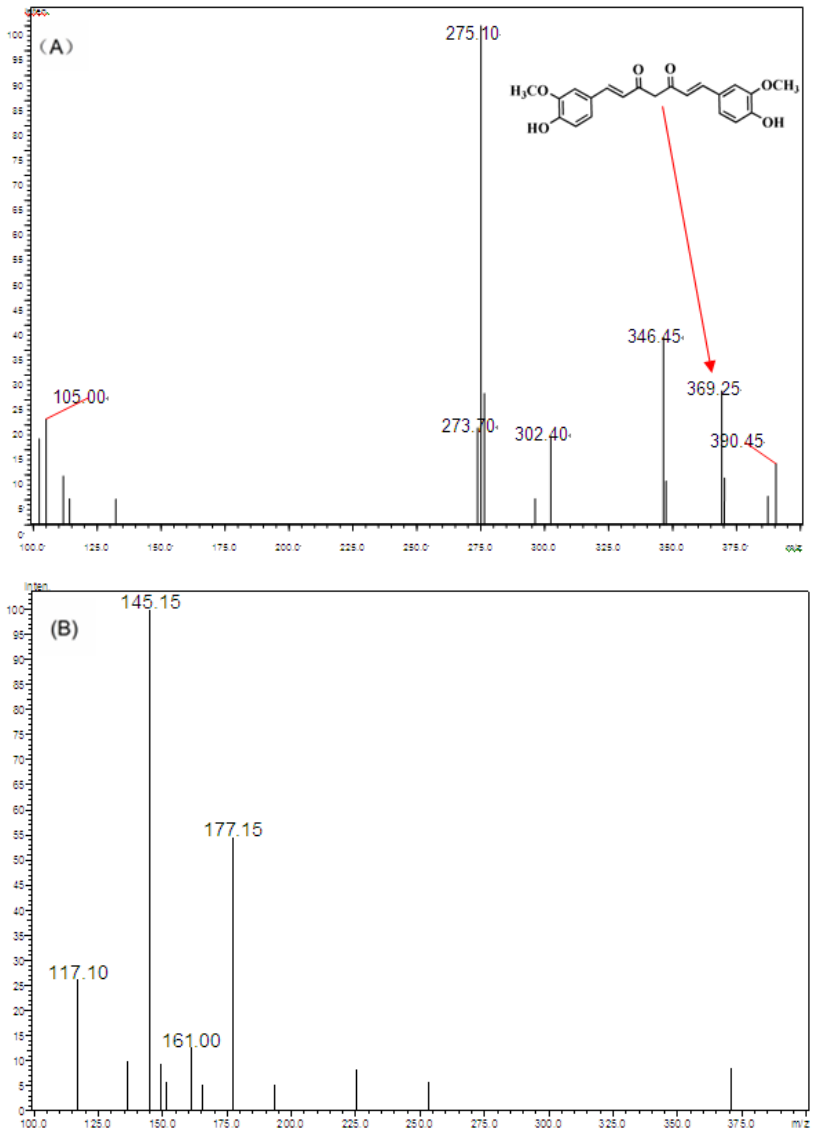

Figure S4 Curcumin (A) MS and (B) MS/MS spectrums in urine sample

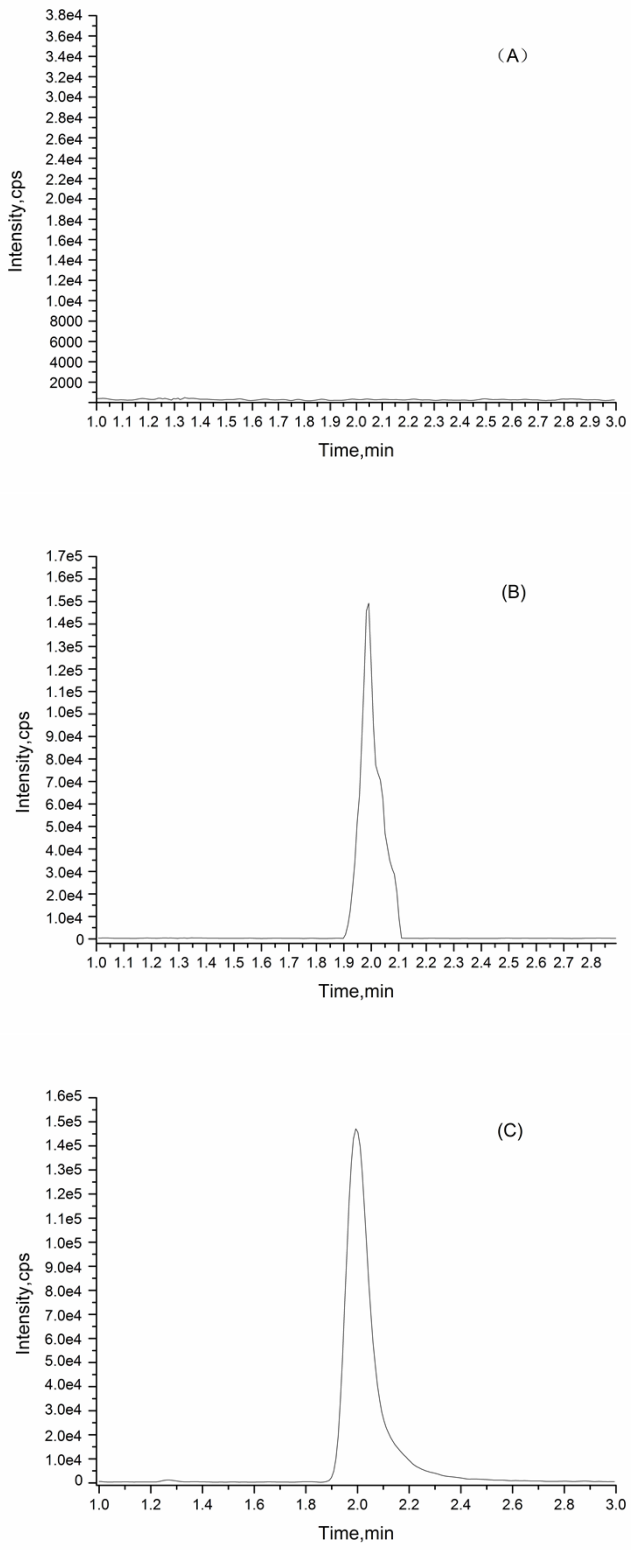

Figure S5 MRM spectrum of curcumin: (A) blank urine, (B) urine sample, (C) curcumin reference substance

References

1 K.M.K. Selim, I. Kang and H.Q. Guo, Macromolecular Research.,

2009,17, 403.

2 S.H, Xu, C.L. Wang, H. Zhang, Z.Y. Wang, B. Yang and Y.P. Cui, Nanotechnology., 2011, 22, 315703.