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## Supplementary Material

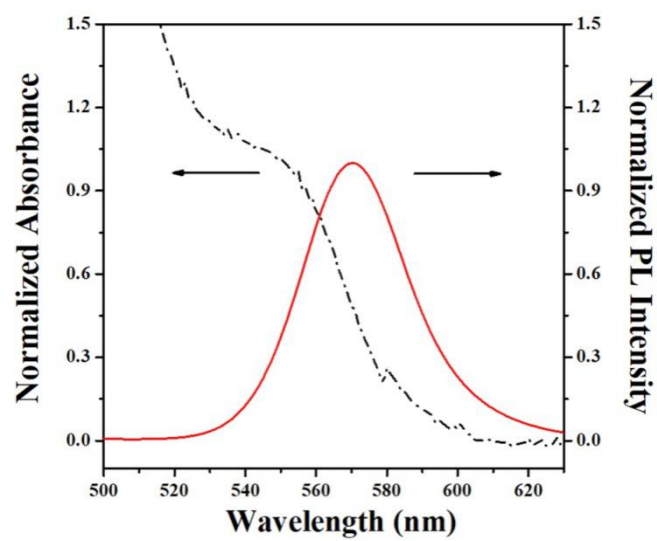
### ***para*-Hydroxy Thiophenol-Coated CdSe/ZnS Quantum Dots as a Turn-On Fluorescent Probe for H<sub>2</sub>O<sub>2</sub> Detection in Aqueous Media**

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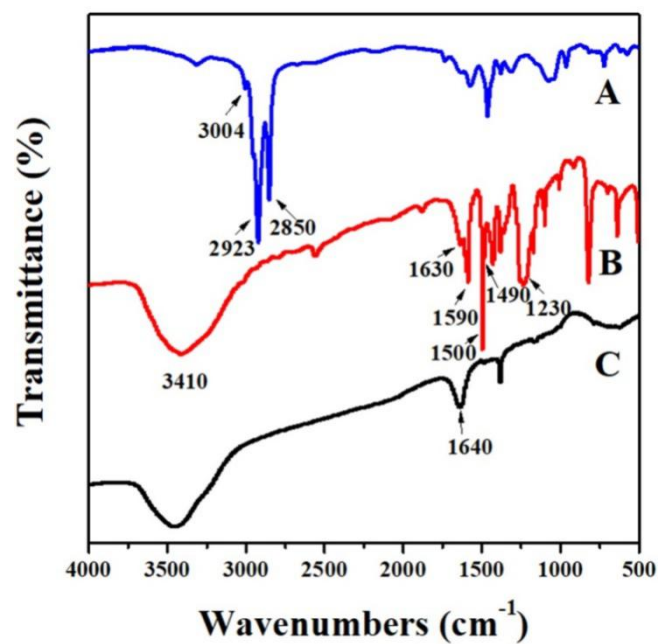
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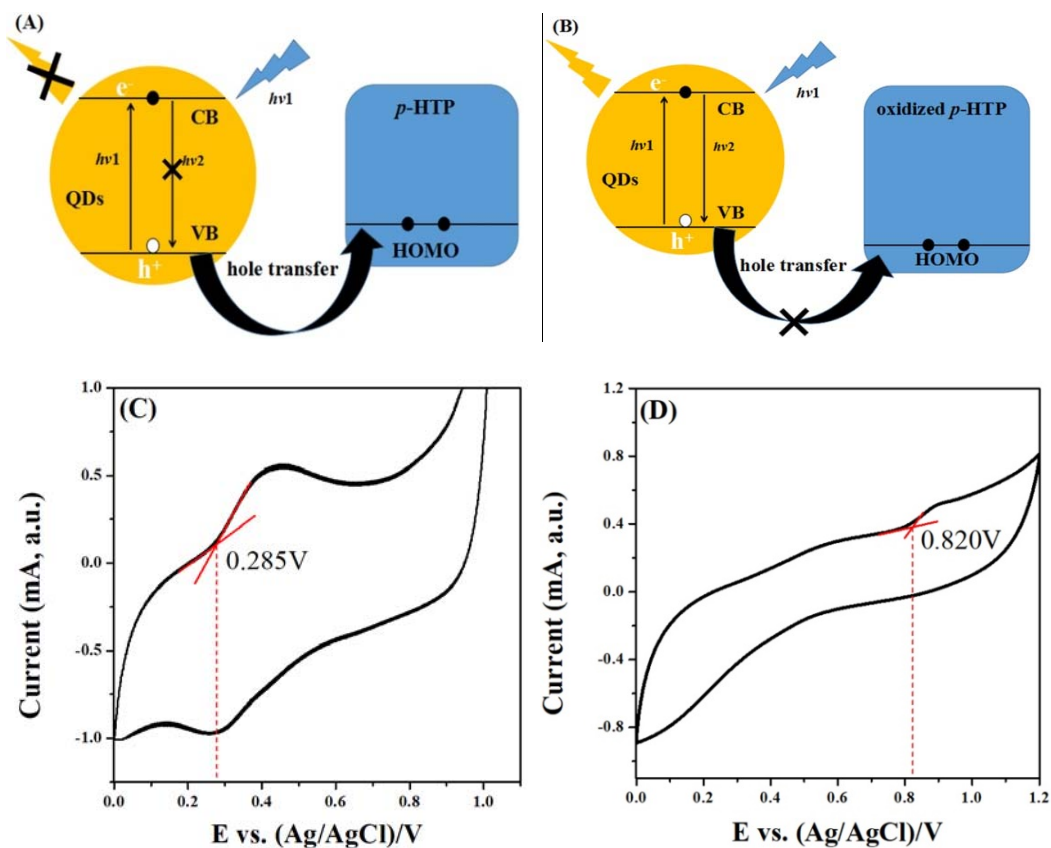
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**Fig. S1.** UV-vis absorption and fluorescence spectra of *p*-HTP-QDs in water



**Fig. S2** Solid-state FIRT spectra of OAm-capped CdSe/ZnS QDs (A), *p*-HTP-QDs (B), and oxidized *p*-HTP-QDs by H<sub>2</sub>O<sub>2</sub> (C)



**Fig. S3** The schematic illustration of the photo-induced hole transfer of *p*-HTP-QDs (A) and oxidization product *p*-HTP-QDs (B) by H<sub>2</sub>O<sub>2</sub> and Cyclic voltammograms of *p*-HTP-QDs (C) and *p*-HTP-QDs by H<sub>2</sub>O<sub>2</sub> (D) at scan rate 100mV/s

#### Possible mechanism of PL “off-on” in probing H<sub>2</sub>O<sub>2</sub> by *p*-HTP-QDs

For the PL quenching of *p*-HTP-QDs system in pH 6.0 conditions, an efficient energy transfer process was firstly excluded due to no spectral overlap between the absorption spectrum of *p*-HTP and CdSe/ZnS QDs emission spectrum (Fig. S6). The PL quenching should be ascribed to hole transfer or charge separation mechanism. In *p*-HTP-QDs system, the modifier *p*-HTP was considered as the real PL quencher after ligand exchange. For an effective quencher toward QDs PL, it needs to have the

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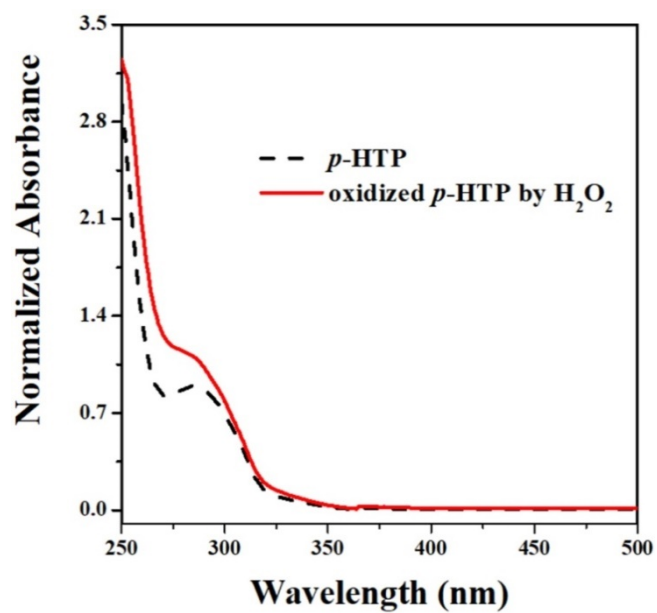
ability to directly interact with one of the QDs charge carriers, thereby disrupting the native radiative electron-hole recombination. For instance, a lysosome targetable fluorescent probe for endogenous imaging of H<sub>2</sub>O<sub>2</sub> in living cells, the fluorescence spectrum of receptor LyNC exhibits a weak fluorescence emission in aqueous buffer at pH 7.4 is due to photoinduced electron transfer from the catechol unit to the naphthalimide core.<sup>[1]</sup> In this work, we propose that the highest occupied molecular orbital (HOMO) of modifier *p*-HTP locates at a relatively higher energetic position above the valence band of CdSe/ZnS QDs and *p*-HTP serves the hole trapper to accept thermodynamically photogenerated holes from QDs. The resulting charge separation of QDs disturbs the intrinsic electron-hole recombination of QDs. The subsequent electron transfer from the conduction band of QDs to HOMO of *p*-HTP is followed and regenerates QDs and modifiers in initial states. Expectedly, the inhibition of the native electron-hole recombination of QDs results in the quenching of QDs PL (Fig. S3A). In the presence of H<sub>2</sub>O<sub>2</sub>, the structural transformation of phenol ring to  $\alpha$ -hydroxyl ketone derivative, which reduced the energetic level of HOMO of *p*-HTP after H<sub>2</sub>O<sub>2</sub> oxidation and thus reverses the relative energetic positions of HOMO of *p*-HTP and QDs valence band. The new resulting energy levels is no longer suitable for hole transfer. Therefore, QDs PL is switched on (Fig. S3B). Similar hole transfer has been recently utilized in a QDs-based fluorescence probe for Zn<sup>2+</sup> detection.<sup>[2]</sup> In order to verify the above hypothesis, the electrochemical test of *p*-HTP-QDs and oxidized *p*-HTP-QDs by H<sub>2</sub>O<sub>2</sub> was performed by cyclic voltammetry. As shown in Fig. S3C and S3D. There exhibit two irreversible redox curves. The most distinctive changes in CV diagram are that the oxidation potential was shifted from 0.285 to 0.820 V from *p*-HTP-QDs to oxidized *p*-HTP-QDs by H<sub>2</sub>O<sub>2</sub>, which essentially reflects the change in energy level of HOMO of *p*-HTP before and after adding H<sub>2</sub>O<sub>2</sub>. The similar CV behavior of *p*-HTP and oxidized *p*-HTP was observed in a previous report.<sup>[3]</sup> The CV results support the above hole transfer mechanism. From the CV data, the vacuum energy level of HOMO of *p*-HTP-QDs was estimated to

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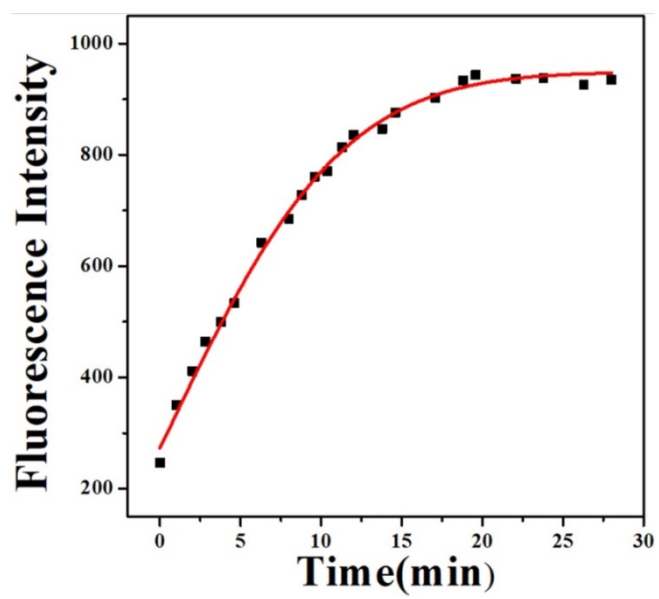
–5.01 eV by empirical formula  $E_{\text{HOMO}} = -(E_{\text{ox}} + 4.72)$  eV. Similarly, the vacuum energy level of HOMO of *p*-HTP-QDs after H<sub>2</sub>O<sub>2</sub> oxidation was downregulated to –5.54 eV. By using  $E_{\text{CB}} = -1.57$  eV vs. NHE for *ca.* 3.0 nm CdSe QDs<sup>[4,5]</sup> and band gap (2.25 eV, estimated from the UV-vis absorption spectrum) of CdSe/ZnS QDs used in this work, one can get the vacuum energy level of  $E_{\text{VB}}$  of QDs (–5.18 eV). The overall free energy changes ( $\Delta G$ ) for a hole transfer from *p*-HTP to QDs can be estimated according to the equation:  $\Delta G = E_{\text{VB}} - E_{\text{HOMO}}$ . The negative  $\Delta G$  value of –0.17 eV in *p*-HTP-QDs (comparing with the positive  $\Delta G$  of 0.36 eV in *p*-HTP-QDs by H<sub>2</sub>O<sub>2</sub> oxidation) indicates that the hole transfer is a thermodynamically favourable process.

## References

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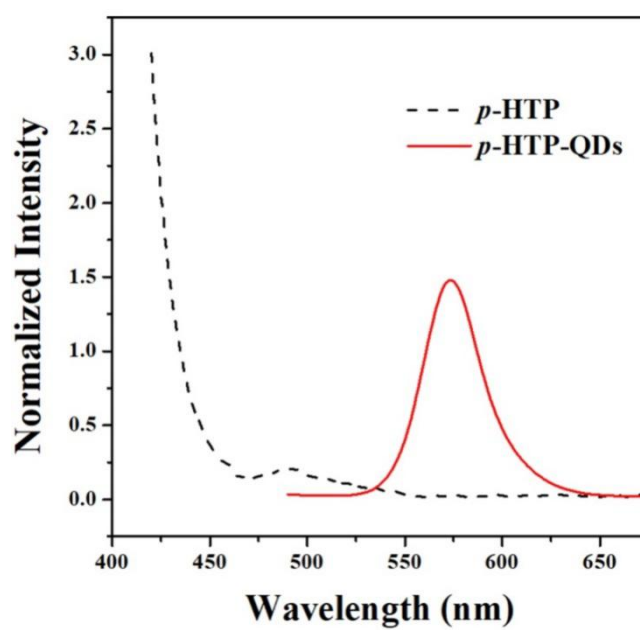


**Fig. S4** The UV-vis spectra of *p*-HTP-QDs before (black dash line) and after (red solid line) adding H<sub>2</sub>O<sub>2</sub>

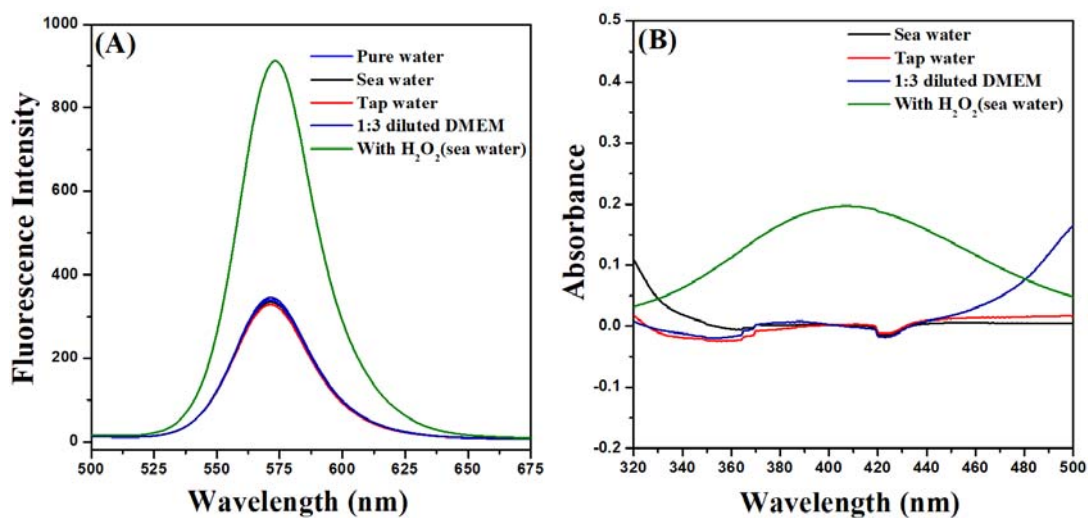


**Fig. S5** The PL response time of *p*-HTP-QDs suspension toward H<sub>2</sub>O<sub>2</sub> at pH 6.0





**Fig. S6** Absorbance spectrum of *p*-HTP and PL spectrum of *p*-HTP-QDs ( $\lambda_{\text{ex}} = 399$  nm) in aqueous media



**Fig. S7.** The fluorescence spectra of *p*-HTP-QDs to various real water samples without artificial regulation by H<sub>2</sub>O<sub>2</sub> (A) and UV-Vis absorption spectra of the real water samples in the absence of H<sub>2</sub>O<sub>2</sub> using standard colorimetric method (B). The corresponding response spectra in the presence of H<sub>2</sub>O<sub>2</sub> (1.65 mM) are provided for comparison