Electronic Supporting Information (ESI) for:

Study of transfer of photo-excited charge carries within direct and inverted type-I heterojunction of CdS and ZnS QDs

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Figures

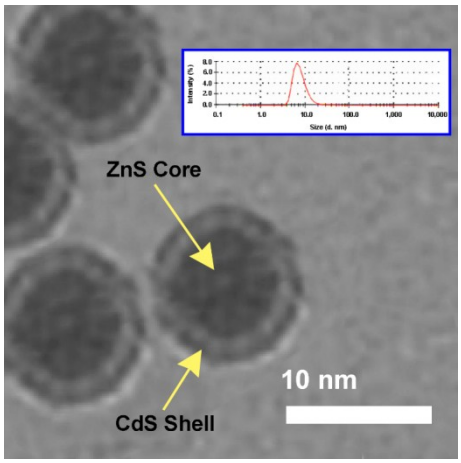

Fig. S1 TEM image of ZnS@CdS inverted type-I core/shell QDs. The inset shows the particle size distribution of ZnS@CdS inverted type-I core/shell QDs measured by DLS.

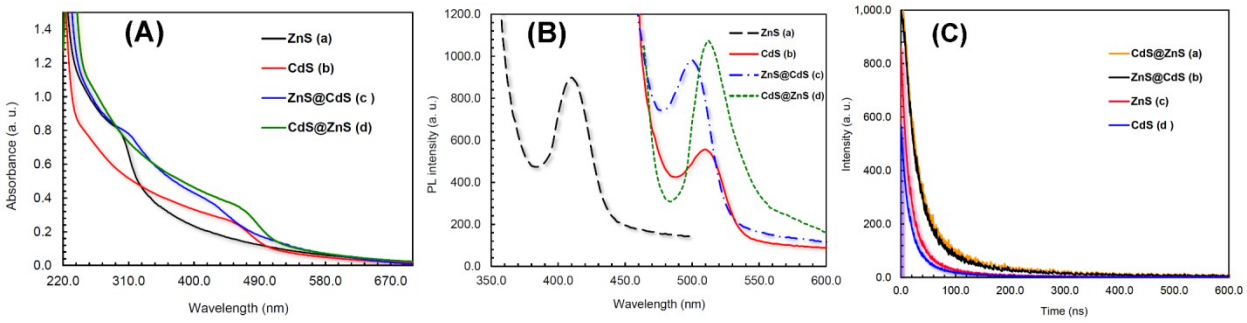

Fig. S2 (A) UV−vis and (B) PL spectra of the ZnS@CdS (c), CdS@ZnS (d), ZnS (a) and CdS (b). (C) Fluorescence emission decay curves of the above-mentioned QDs.

The first exciton absorption peak and the emission peak of ZnS QDs were 298 and 410 nm, respectively; while that for CdS QDs were 455 and 510 nm, respectively. The optical absorption spectra of the inverted core/shell QDs showed two bands at 310 and 425 nm for ZnS core and CdS shell, respectively. Interestingly, upon photoexcitation of the ZnS@CdS core/shell at 300 nm, only one PL peak appeared at 500 nm. The exciton absorption peak and the emission peak of CdS@ZnS QDs were 458 and 512 nm, respectively. We then studied the fluorescence decay of ZnS, CdS, CdS@ZnS and ZnS@CdS QDs at the wavelengths of 410 nm, 510 nm, 512 nm and 500 nm, respectively. The fluorescent lifetimes of 33.2 ns for the ZnS, 23.5 ns for the CdS, 120.8 ns for the CdS@ZnS and 111.3 ns for the ZnS@CdS QDs were calculated from the fitted decay curves using a multiexponential fit. The low lifetime of CdS and ZnS compared with CdS@ZnS and ZnS@CdS QDs is due to nonradiative quenching in the single phase QDs. Also, the longer emission lifetime of the nanohybrids confirms charge carrier transfer through the electronic coupling.

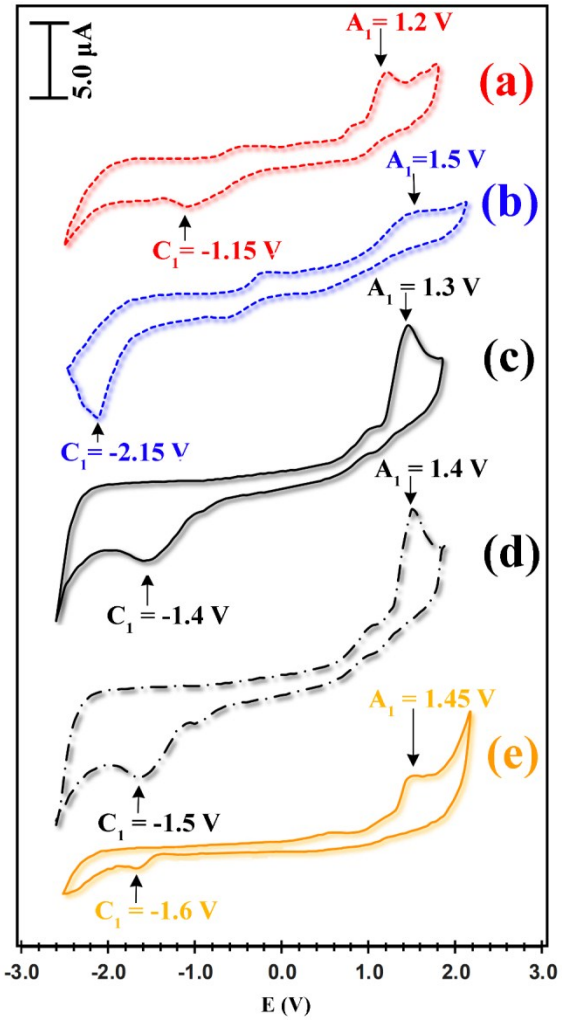

Fig. S3 CV curves of (a) CdS-CP, (b) ZnS-CP, (c) ZnS@CdS-CP and CdS@ZnS-CP electrodes in light condition. (e) Cyclic voltammogram of ZnS@CdS-CP and CdS@ZnS-CP electrodes in dark condition (both showed the same results).

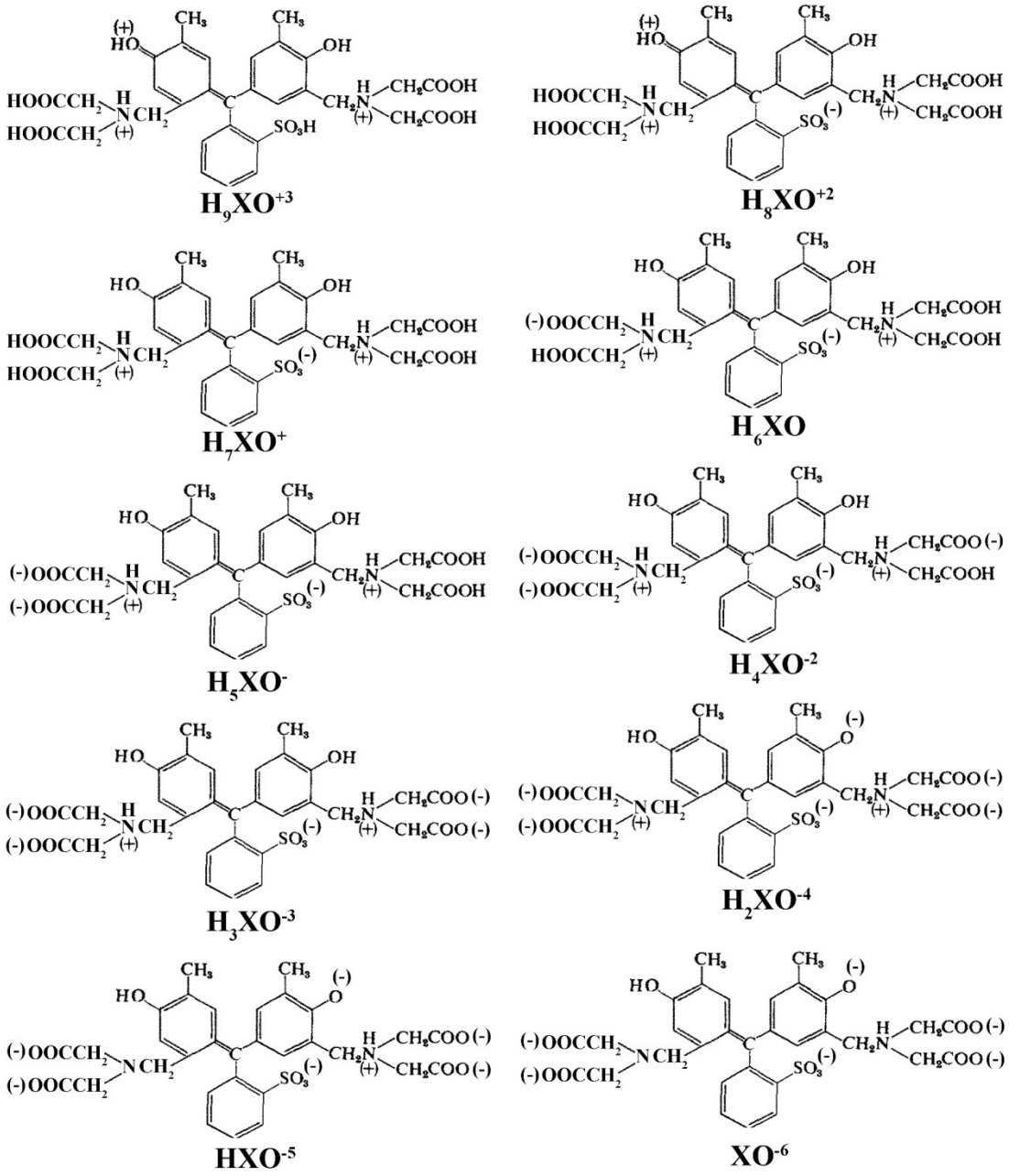

Fig. S4 Proposed species involved during XO acidity equilibria.

Table S1 Protonation constants of XO [1].

XO species	Functional group	pK_a
$HXO^{-5} \leftrightarrow XO^{-6}$	$\equiv NH^{+}$	12.23
$H_2XO^{-4} \leftrightarrow HXO^{-5}$	$\equiv NH^{+}$	10.35
$H_3XO^{-3} \leftrightarrow H_2XO^{-4}$	-OH	6.7
$H_4XO^{-2} \leftrightarrow H_3XO^{-3}$	-COOH	2.85
$H_5XO^{-} \leftrightarrow H_4XO^{-2}$	-COOH	2.32
$H_6XO \leftrightarrow H_5XO^{-}$	-COOH	1.40
$H_7XO^{+} \leftrightarrow H_6XO$	-COOH	---
$H_8XO^{+2} \leftrightarrow H_7XO^{+}$	$=OH^{+}$	---
$H_9XO^{+3} \leftrightarrow H_8XO^{+2}$	$-SO_3H$	---

[1] B. J. Colston and V. J. Robinson, *Analyst*, 1997, **122**, 1451.

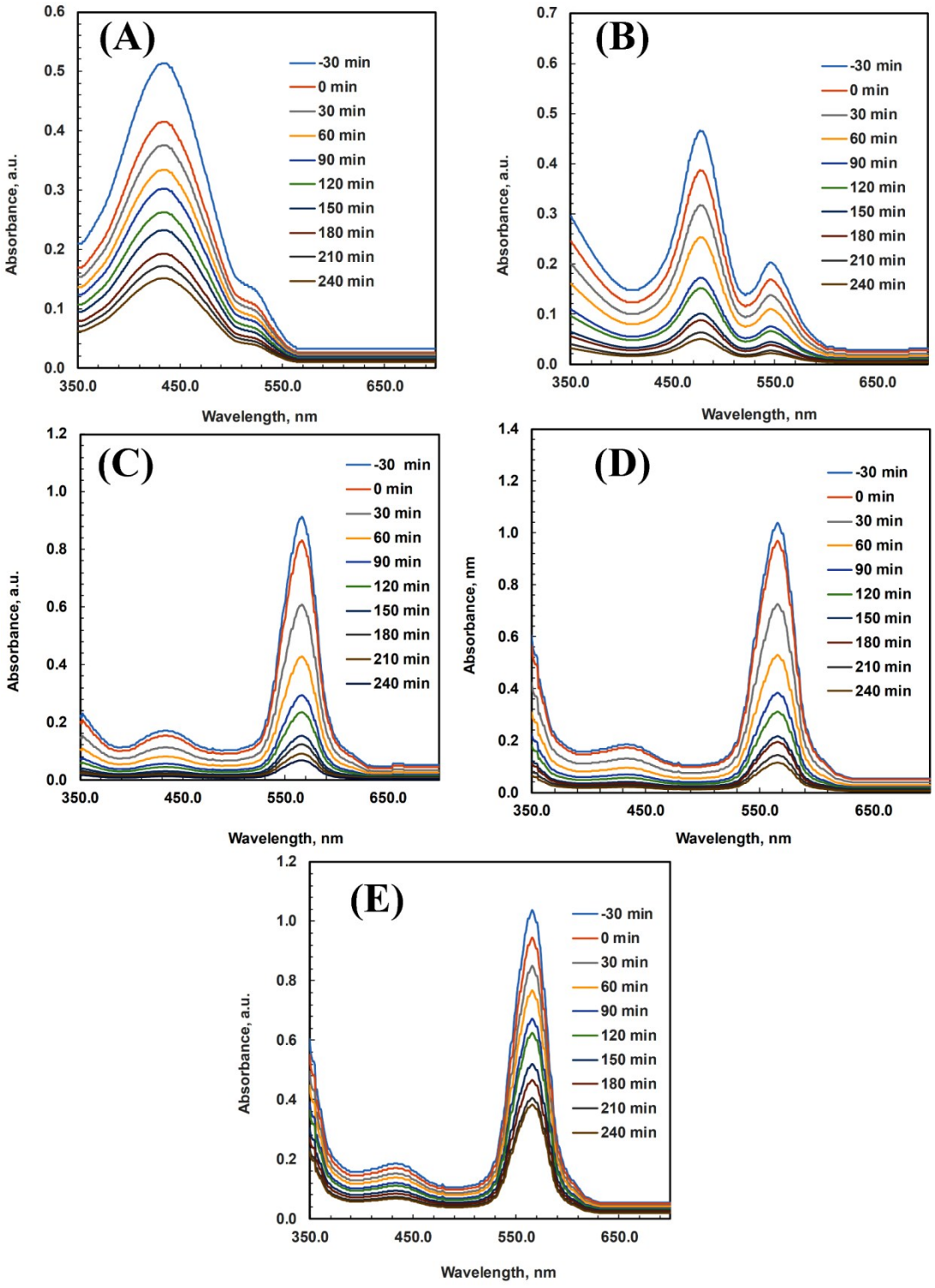

Fig. S5 Spectra of XO photodegradation solution at different pH values: (A) pH=2, (B) pH=5, (C) pH=7, (D) pH=9 and (E) pH=12.

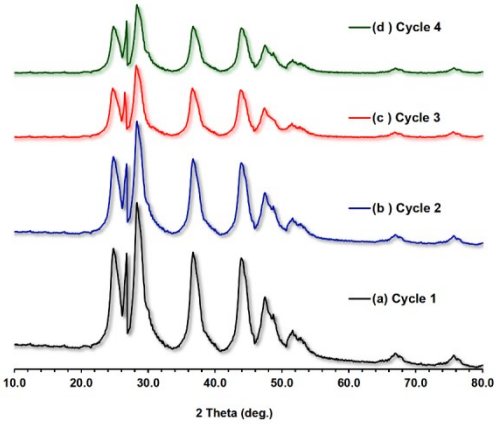

Fig. S6 XRD patterns of ZnS@CdS QDs acquired after each cycle.

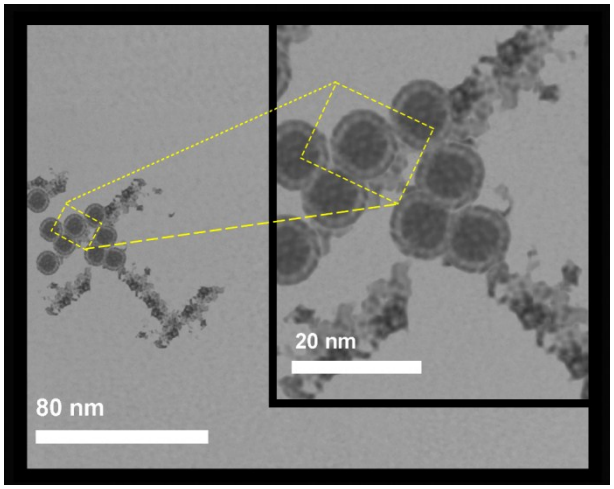

Fig. S7 TEM of ZnS@CdS QDs after the 4th cycle.