# Supplementary Information

# A facile strategy for the synthesis of hierarchical $TiO_2$/CdS hollow sphere heterostructures with excellent visible light activity

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## 1. Experimental section

### *1.1 Preparation of $SiO_2$ nanosphere:*

In a typical synthesis, 10 mL of ammonia (28 wt%), 20 mL of deionized water and 70 mL of ethanol were mixed and transferred to a three-necked flask. Then, 10 mL of tetraethoxysilicate (TEOS) were dissolved in 90 mL of ethanol, then; the solution was added into the former mixed solution and vigorously stirred at 40 °C for 2.5h. The obtained white suspension was separated by centrifugation and washed four times with ethanol, and then dried in air to form the final $SiO_2$ nanospheres.

***Preparation of $SiO_2$/$TiO_2$ core-shell nanosphere*:**

1.50 g of the as-prepared $SiO_2$ nanospheres were ultrasonically dispersed in 100 mL of ethanol, and then the mixture solution and a certain amounts of ammonia was transferred to a three-necked flask together. Next, 10.0 g tetra-n-butyl titanate (TBOT) were dissolved in 100 mL of ethanol and subsequently added to the former mixed solution, vigorously stirred at 60 °C for 3 h. The solid were separated by centrifugation and washed four times with deionized water, and then dried in an oven at 60 °C for 6 h. Finally, the sample was annealed at 550 °C for 2 h in air to obtain the crystallize $SiO_2$/$TiO_2$ core-shell nanosphere.

***Preparation of $SiO_2$/$TiO_2$/CdS core-shell nanosphere:***

The obtained $SiO_2$/$TiO_2$ core-shell nanospheres(0.30 g) were first ultrasonically dispersed in 150 mL of deionized water. Afterwards, 7.50 mL of 0.12M $CdCl_2$ solution, 10 mL of 0.1M sodium citrate solution and 15 mL of 0.12M thiourea solution were added to the solution under stirring gently for 5 min. A certain amount of ammonia (1.50 mL for C-B sample, 1.75 mL for D-B sample, 2.00 mL for E-B sample and 2.25 mL for F-B sample, respectively) were then dropwise added into the mixed solution and sonicated continuously at 65 °C for

1.5 h. The lemon-yellow suspension were separated by centrifugation and washed four times with deionized water, and then dried in an oven at 60 $^{o}$C for 6 h.

***Preparation of the hierarchical $TiO_2$/CdS hollow sphere heterostructures:***

The lemon-yellow solid powder were dispersed in 35 mL of 2.00M NaOH solution, and then the obtained lemon-yellow suspension was transferred to 50 mL Teflon-sealed autoclave and maintained at 80 $^{o}$C for 4 h. The resulting products were washed with deionized water four times and dried at 60 $^{o}$C under vacuum overnight to prepare the final hierarchical $TiO_2$/CdS hollow sphere heterostructures.

***Characterization:***

The phase composition was identified by X-ray diffraction (XRD; SHIMADZU, Lab X XRD-6000). Fourier transform infrared (FT-IR) spectra were recorded using a Nicolet avatar 360 FT-IR spectrometer with KBr as the reference sample. The morphologies and nanostructures of all the $TiO_2$/CdS hollow sphere heterostructures samples were performed by scanning electron microscopy ( FESEM; JEOL, JSM-6700F, 200kV) and transmission electron microscopy (TEM; JEOL, JEM-2100). The component of as-prepared samples was also detected by energy dispersive X-ray spectrometry (EDX). To investigate the optical properties, UV-vis diffuse reflectance spectra (DRS) were measured on a Hitachi U-4100 instrument employed with a lab-sphere diffuse reflectance accessory. The textural properties were studied by an ASAP-3000 adsorption apparatus undertaken at liquid nitrogen temperature (77K). The obtained specific surface area and pore size distributions plots of the photocatalysts were calculated by the Brunauer-Emmett-Teller (BET) method and Barrett-Joyner-Halenda (BJH) method, respectively. X-ray photoelectron spectroscopy (XPS; AXIS ULtrabld) was employed to examine the composition and the elemental contents on the surface of the as-prepared samples. It should be noted that, during the high-resolution XPS spectrum analysis, all the binding energies were calibrated using the C1s peak (284.6 eV) form contaminant carbon.

***Photocatalytic activity measurements:***

The photocatalytic activity of the hierarchical $TiO_2$/CdS hollow sphere heterostructures has been evaluated by using the Rhodamine B (RhB) and Methyl orange (MO) solution of 15mg/L as the model pollutant under visible-light irradiation and ambient conditions. Visible light source was provided by a 300 W Xenon lamp (Nbet, HSX-F/UV300, Beijing, China), equipping with a 420 nm cut-off glass filter to remove UV light. In a typical reaction, 0.07 g of the photocatalyst was dispersed in a glass vessel containing 70 mL of RhB solution. Before visible light irradiation, the suspension was stirred in the dark for 40 min to ensure that the mixed solution reached adsorption-desorption equilibrium. Then, 3 mL of suspension was removed from the reactor while visible light irradiation and

repeated the above described operation every 30 min during the photoreaction. The suspension was taken from the reactor and centrifuged (13000 rpm for 5 min) to remove the photocatalysts, and the concentration of the remaining RhB or MO solution was analyzed by UV-vis spectrophotometer (UV-1900PPC, Shanghai, China).

For the photocatalysis stability measurements, 0.1 g hierarchical $TiO_2$/CdS hollow sphere was dispersed in 100 mL of RhB solution (15 mg/L) and the photoactivity tested as described above, but the photoreaction time is certain for 90 min. After each photoreaction test, both the separated catalyst particles and the solution were returned to the reaction system, and each recycling test is conducted under the same conditions.

**Table S1** Calculation results of BET surface area, pore volume, average pore size as well as crystal size of $TiO_2$ and CdS for all samples.

| Samples | $S_{(BET)}$ ($m^2/g$) | Pore volume ($cm^3/g$) | Average pore size (nm) | Crystal size of anatase $TiO_2$ (nm) | Crystal size of hexagonal CdS (nm) |
|---|---|---|---|---|---|
| D-B | 104.48 | 0.18 | 7.04 | 17.51 | 17.98 |
| E-B | 90.04 | 0.12 | 5.29 | 20.29 | 28.04 |
| Pure $TiO_2$ | -- | -- | -- | -- | 25.28 |
| Pure CdS | -- | -- | -- | -- | 26.52 |

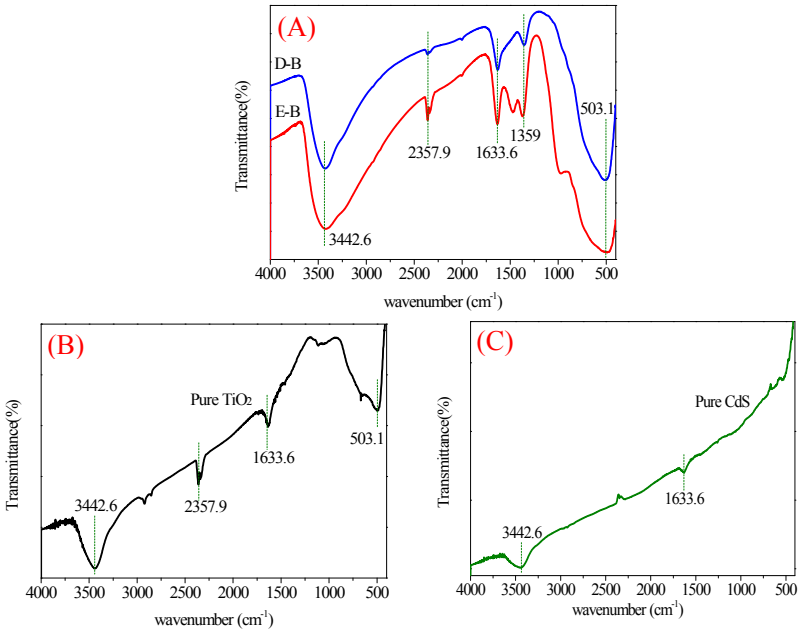


**Fig. S1.** (A) FT-IR spectra of the hierarchical $TiO_2$/CdS Hollow sphere heterostructures samples: (a) D-B, (b) E-B. (B) FT-IR spectra of pure $TiO_2$. (C) FT-IR spectra of pure CdS.

The FT-IR spectra of all samples are shown in Fig. S1 (A, B and C), the peaks at 3442.6 $cm^{-1}$ and 1633.6 $cm^{-1}$ are attributed to the surface adsorption of water molecules.[1] In comparison with the spectra of CdS, the broad peak in the region of 400-800$cm^{-1}$ in Fig. S1 (A and B) are due to the Ti-O stretching and Ti-O-Ti bridging stretching modes.[2]


1 J. Fu, B. Chang, Y. Tian, F. Xi and X. Dong, *J. Mater. Chem. A*, 2013, **1**, 3084.

2 G. Yang, B. Yang, T. Xiao and Z. Yan, *Appl. Surf. Sci.*, 2013, **283**, 402-410.

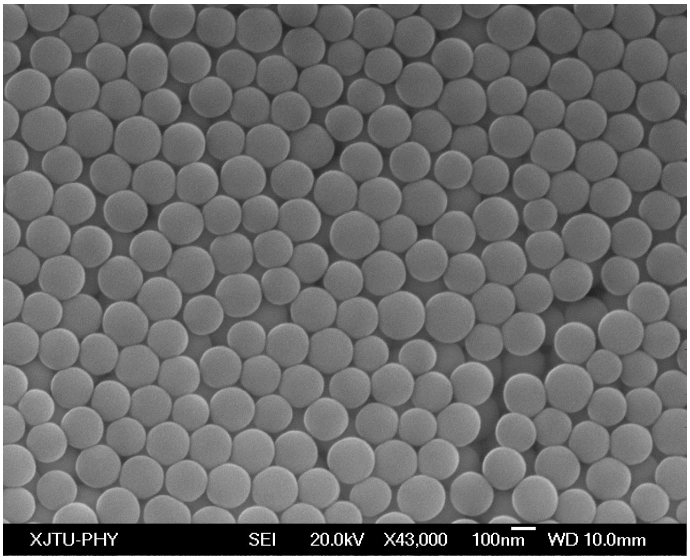


**Fig. S2.** SEM image of the obtained $SiO_2$ nanospheres

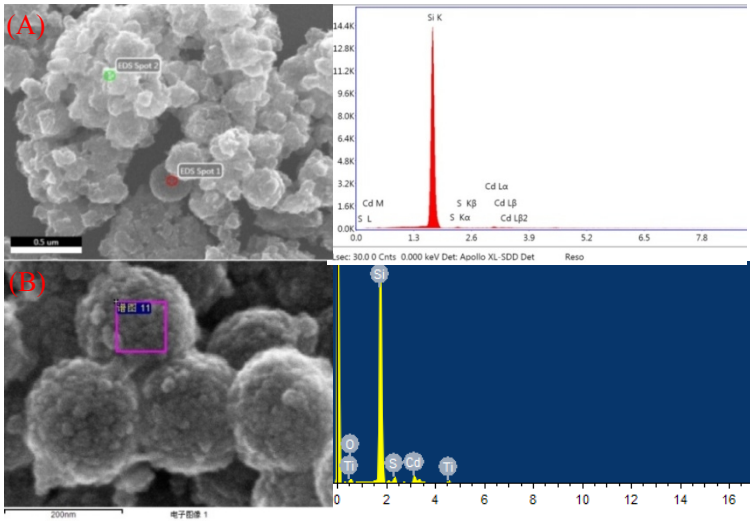


**Fig. S3.** EDX spectrum of all samples: (A) sample D-B. (B) sample E-B.

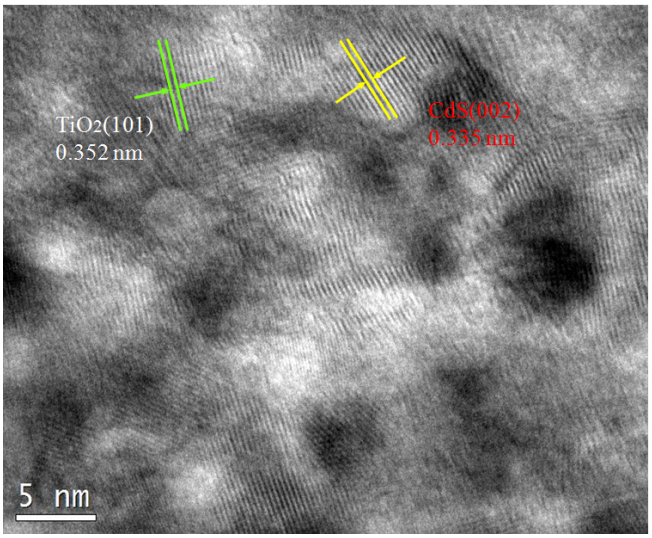


**Fig. S4.** High resolution TEM image of as-prepared sample E-B.

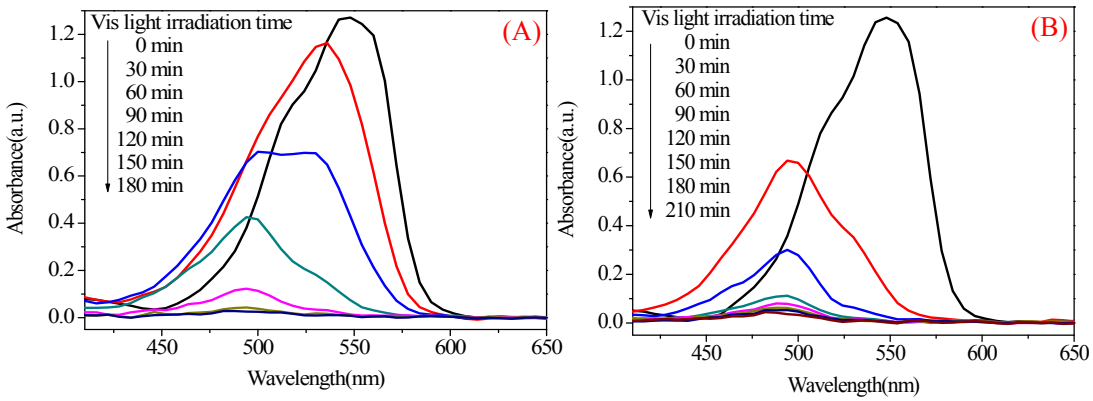


**Fig. S5.** UV-vis spectral changes of RhB (15 mg/L) in aqueous solution of the hierarchical $TiO_2$/CdS Hollow sphere heterostructures. (A) D-B sample, (B) E-B sample.

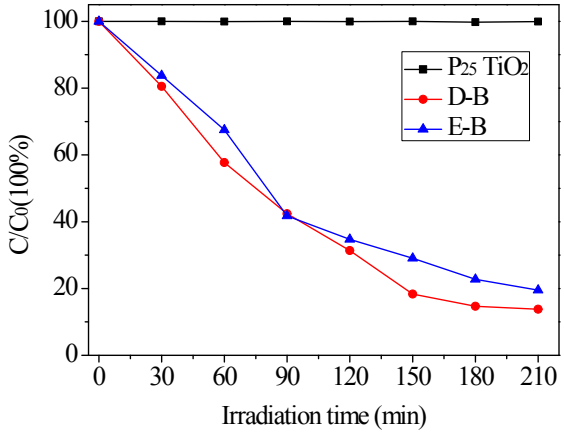


**Fig. S6** Plots of the decomposition of MO solution concentration versus irradiation time by different samples under visible-light irradiation ($\lambda \geq 420$ nm). The original concentration of MO solution is 15 mg/L.

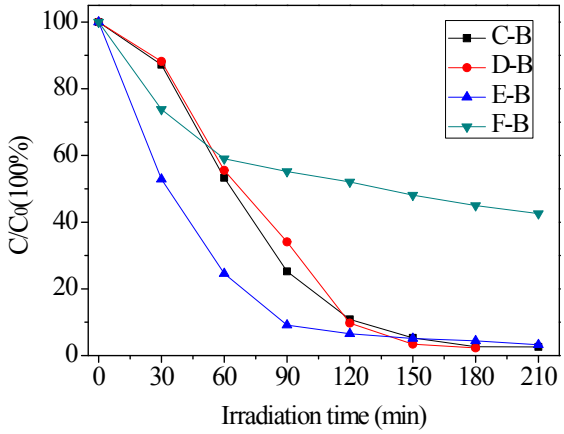


**Fig. S7** Plots of the decomposition of RhB solution concentration versus irradiation time by samples prepared with four different ammonia contents under visible-light irradiation (λ≥420 nm). The original concentration of RhB solution is 15 mg/L. the amounts of Ammonia: C-B: 1.50 mL; D-B: 1.75 mL; E-B: 2.00 mL; F-B: 2.25 mL;