Electronic Supplementary Information (ESI)

Facile template-free approach for fabrication of flower-like CdS: the evolutionary process of the structure and the performance of photocatalytic activity

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Experimental section

Synthesis of flower-like CdS

All the reagents were analytical grade and used as received. Cadmium chloride ($CdCl_2$) and ammonia water ($NH_3 \cdot H_2O$) were purchased from Shanghai Chemical Reagents Co. Thioglycollic acid (TGA) was obtained from Shanghai Aladdin Reagents Co. A typical procedure is as follows. 0.015 mmol of $CdCl_2$ was dissolved in 40 mL distilled water. Subsequently, 0.5 mL of $NH_3 \cdot H_2O$ (25–28% w/w) and 10 μL of TGA were added slowly to the mixture with stirring until a clear solution was formed. The above solution was transferred to a Teflon-lined autoclave (50 mL capacity), which was sealed and heated in an oven at 160 °C for 4 h, and allowed to cool naturally to room temperature. The yellow products were isolated by centrifugation and cleaned by several cycles of centrifugation/washing/redispersion in distilled water and in absolute ethanol. Finally, the products were dried in a vacuum at 60 °C for 6 h.

Characterization

The products were characterized by powder X-ray diffraction (XRD) using a Bruker D8 ADVANCE X-ray diffractometer with graphite monochromatized $Cu_{K\alpha}$ radiation (λ = 1.5418 Å). Field emission scanning electron microscopy (FESEM) was performed on a Hitachi S-4800 scanning electron microscope. The energy dispersive X-ray (EDX) spectrum was recorded with a Hitachi S-4800 scanning electron microscope equipped with an INCAx-Sight OXFORD energy-dispersion X-ray fluorescence analyzer. The transmission electron microscopy (TEM) images, high-resolution transmission electron microscopy (HRTEM) images and the corresponding selected area electron diffraction (SAED) pattern were obtained using a FEI Tecnai G20 transmission electron microscope at an accelerating voltage of 200 kV. Nitrogen adsorption-desorption isotherms were measured by using a Quantachrome Nova 2000E sorption analyzer at liquid nitrogen temperature (77 K). Pore sizes distribution was calculated by the Barett-Joyner-Halenda (BJH) method. The specific surface area of the products was measured using the Brunauer-Emmett-Teller (BET) method. The

absorption spectrum was collected on a UV-vis spectrophotometer (U-4100, Hitachi). Photoelectrochemical measurement of the products was performed with a electrochemical work station (CHI 660C, Chenhua) in a standard three-electrode system with a Pt wire and an Ag/AgCl electrode as the counter electrode and reference electrode, respectively. The working electrode was prepared on indium-tin oxide (ITO) conductor glass. 6 mg of the products was ultrasonicated in 1 mL of ethanol to disperse it evenly to get a suspension. 30μL of the suspension was dropped onto the surface of an ITO glass, followed by drying at room temperature. A 0.2 M Na_2SO_4 aqueous solution was used as the electrolyte. A 500 W Xe arc lamp (Zolix LSH-X500, Beijing, China) with an ultraviolet cutoff filter was used as visible light source.

Photocatalytic test

The photocatalytic activity of the as-prepared flower-like CdS was measured by the degradation of methylene blue (MB), methyl orange (MO) and rhodamine B (RhB), respectively. A 500 W Xe arc lamp was used as the light source and equipped with an ultraviolet cutoff filter to provide visible light. The photocatalytic tests were performed as follows (using MB as the typical example): 30 mg flower-like CdS was suspended in a 40 mL MB aqueous solution (5 mg/L) with constant stirring. The suspension was stirred in the dark for 30 min to establish adsorption/desorption equilibrium and then exposed to a 500 W Xe arc lamp at room temperature. At the given irradiation time intervals, the suspension was collected and centrifuged to remove the photocatalyst, and was then analyzed by recording the UV-vis spectrum of MB. The photocatalytic degradation of aqueous MO and RhB solutions was also examined using the same processes.

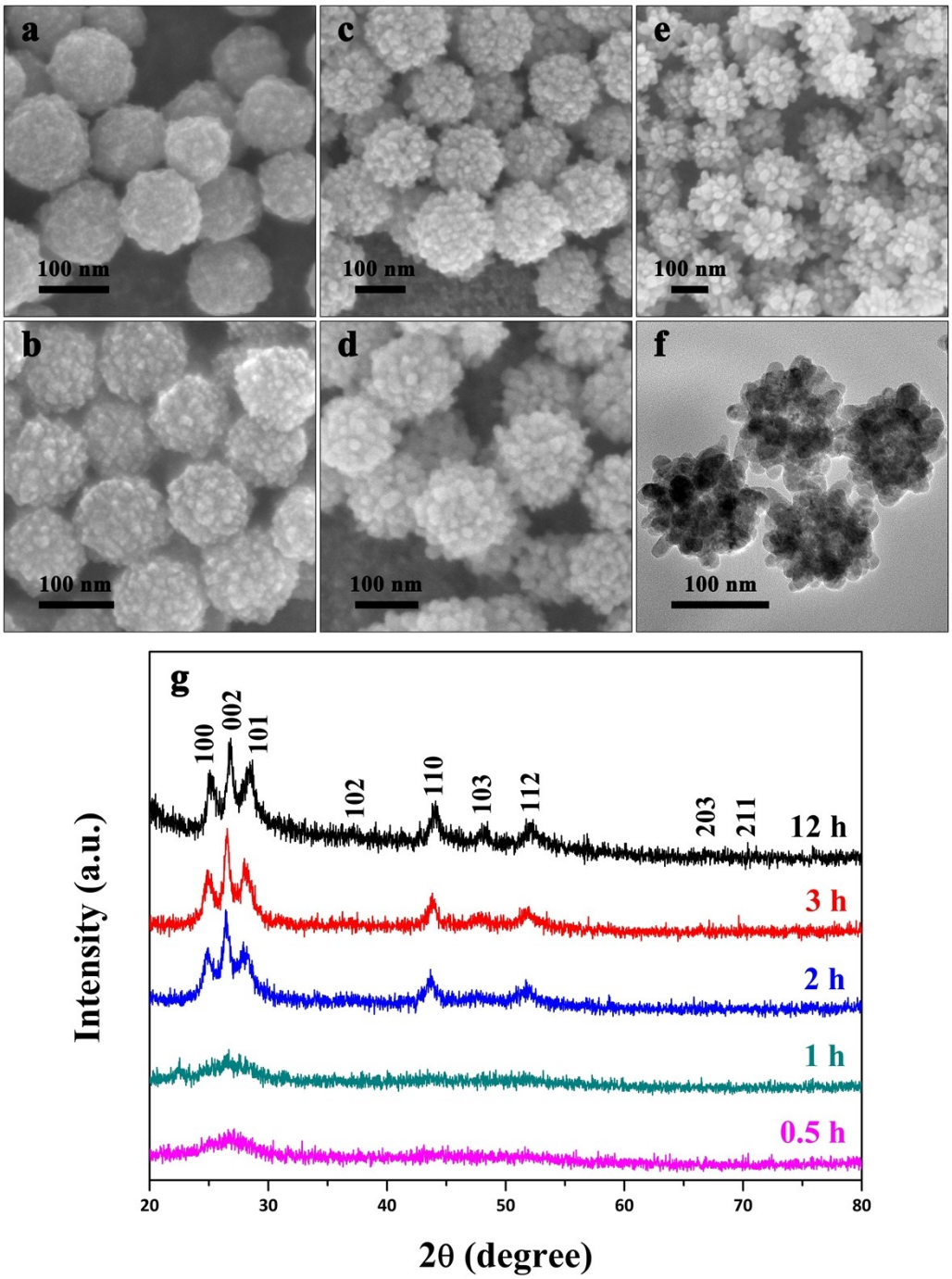

Fig. S1 Characterization of the products obtained from different reaction stages. (a-d) FESEM images observed from the products after reacting for 0.5, 1, 2, and 3 h, respectively. (e) FESEM image and (f) TEM image of the products obtained after a reaction time of 12 h. (g) XRD patterns of the products obtained from different stages of reaction time: 0.5, 1, 2, 3, and 12 h.

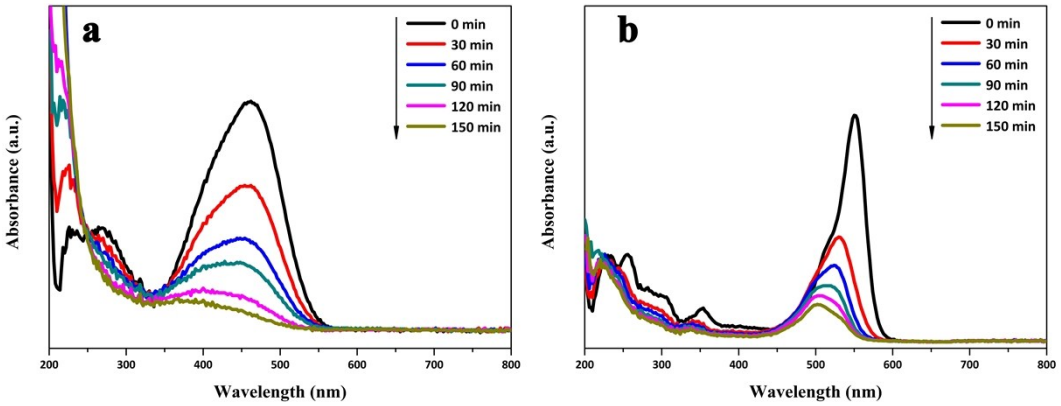

Fig. S2 The adsorption spectra of (a) MO and (b) RhB solutions in the presence of the flower-like CdS irradiated for various times.

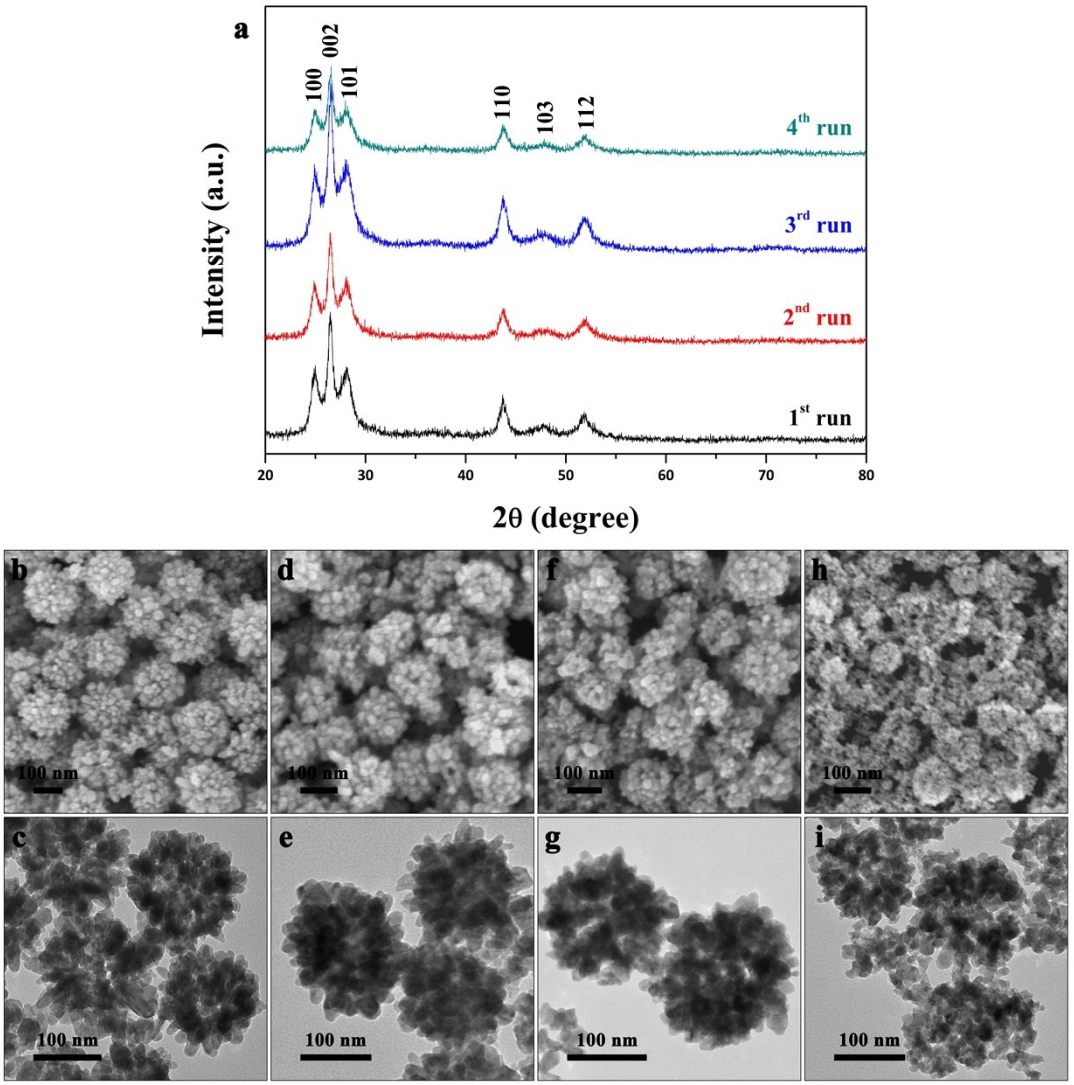

Fig. S3 (a) XRD patterns of the flower-like CdS after the every cyclic test of photocatalytic activity. FESEM and TEM images of the products after cyclic test of (b-c) 1st, (d-e) 2nd, (f-g) 3rd, (h-i) 4th.