Supporting Information

Ethylenediamine-Modulated Synthesis of Highly Monodisperse Copper Sulfide Microflowers with Excellent Photocatalytic Performance†

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Experimental Section

Materials**:** Copper chloride dihydrate ($CuCl_2·2H_2O$), poly(vinylpyrrolidone (PVP) and ethylenediamine (EDA) were obtained from Shanghai Chemical Reagent. Sulphur powder was purchased Sinopharm Chemical Reagent Company. Ethylene glycol (EG) was bought from Shanghai Chemical Reagent Company. Methylene blue (MB), rhodamine 6G (R6G) and methyl orange (MO) were obtained from Aladdin Chemistry Co. Ltd. Lead. Hydrogen peroxide (H_2O_2, 30%) was bought from Shanghai Chemical Reagent Company and used as received without further purification.

Preparation of the copper sulfide (CuS) microflowers and microspheres**:** The CuS microflowers were synthesized by a facile solverthermal process: 0.085 g (0.5 mmol) $CuCl_2·2H_2O$ and 0.4 g PVP were dissolved in 35 mL EG at room temperature. Then 20 μL EDA was added into the solution, stirring for 30 minutes to form a dark blue solution. After the solution was transferred into a Teflon-lined stainless steel autoclave (50 mL), 0.045 g sulfur powder was added into the solution and sonicated for 20 minutes. Subsequently, the autoclave was sealed, maintained at 433 K for 12 h, and then cooled naturally to room temperature. Finally, a dark product was collected *via* centrifugation at 9000 rpm for 10 min, further washed with deionized water and ethanol several times, and dried at vacuum at 333 K for 12 h. Also, the CuS microspheres and other CuS materials were synthesized using a similar procedure by varying the amounts of PVP and EDA as described in the text.

Characterization**:** XRD measurements were recorded on a Philips X'Pert Pro X-ray diffractometer using a monochromatized Cu Kα radiation source (40 kV, 40 mA) with a wavelength of 0.1542 nm and analyzed in the range $10° \leq 2\theta \leq 90°$. FE-SEM images were obtained on a Supra 40 operated at 5 kV. HR-TEM images and selected area electron diffraction (SAED) patterns were obtained with a JEF 2100F field-emission transmission electron microscope using an accelerating voltage of 200 kV. The nitrogen (N_2) adsorption and desorption isotherm was obtained employing Micrometrics ASAP 2020 system. UV-Vis diffuse reflectance absorption spectra were acquired using Shi-madzu DUV-3700 spectrophotometer at room temperature. UV-Vis spectra were measured on a Shimadzu UV 2401 spectrometer in the range 200–800 nm. Photoluminescence (PL) measurements were performed on a Perkin-Elmer Luminescence spectrometer L550B at room temperature (excited at 325 nm).

Photocatalytic measurements**:** The photocatalytic activities of the CuS materials for the degradation of MB, R6G and MO were evaluated by under visible light irradiation. In a typical experiment, 5 mg CuS material was added to a MB solution (30 ml, 5 $mg·L^{-1}$ in distilled water) and magnetically stirred in the dark for 60 min to ensure adsorption equilibrium between the MB solution and the photocatalyst. Subsequently, 0.5 mL 30% H_2O_2 was injected rapidly into the solution and irradiated under visible light for different time. Finally, the catalyst was separated by centrifugation (12000 rpm) and the supernatant solutions were analysed with UV-Vis spectroscopy.

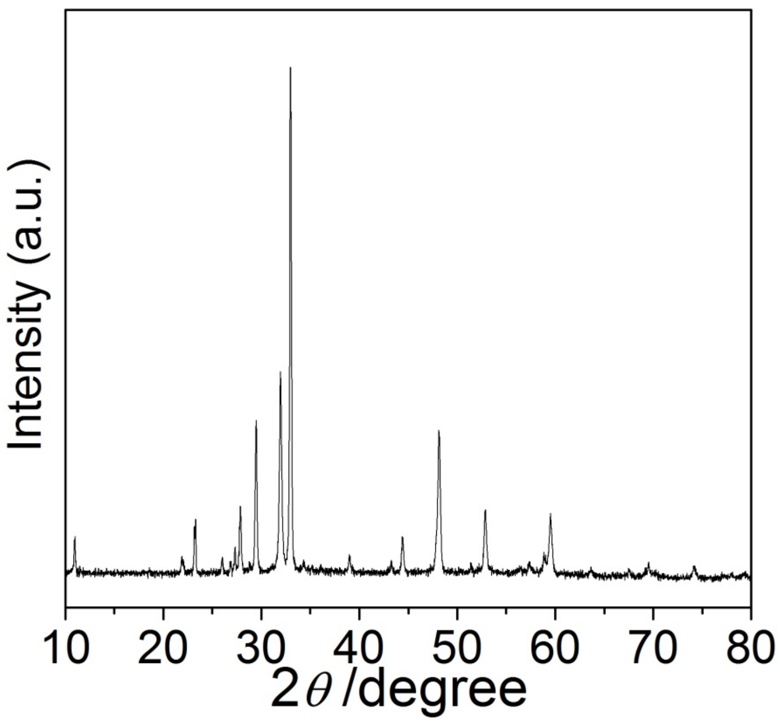

Fig. S1 The XRD pattern of the CuS material prepared at 433 K for 12 h in the absence of PVP and EDA.

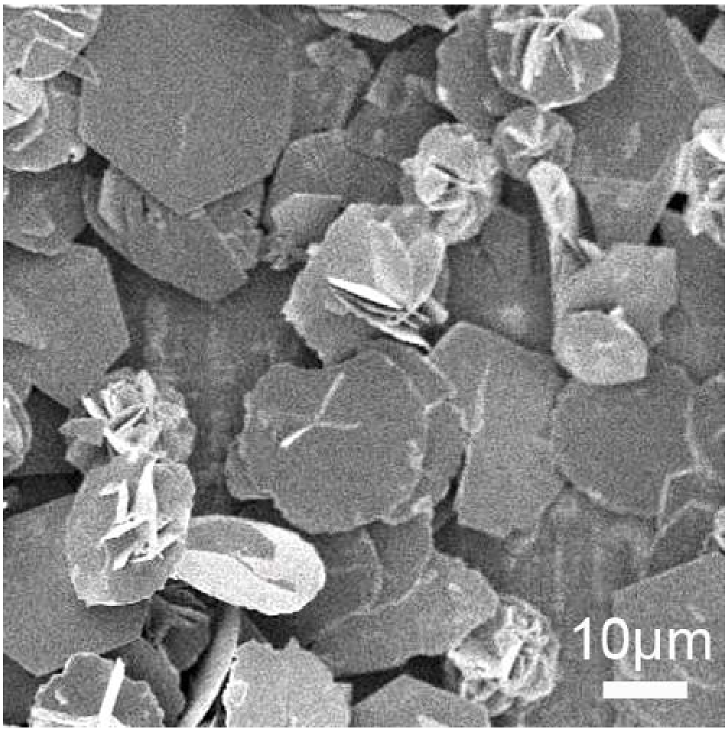

Fig. S2 The FE-SEM image of the CuS material prepared at 433 K for 12 h in the absence of PVP and EDA.

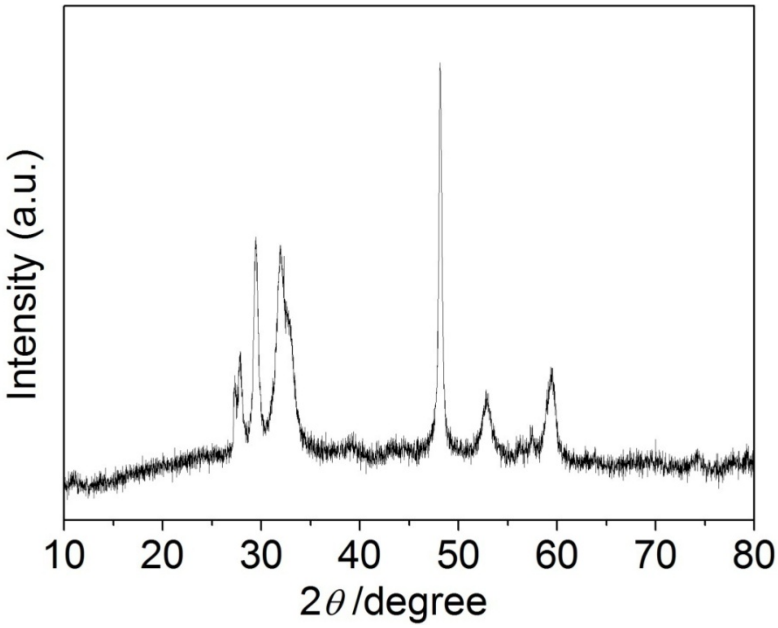

Fig. S3 The XRD pattern of the CuS material prepared at 433 K for 12 h in the presence of 0.4 g PVP without adding EDA.

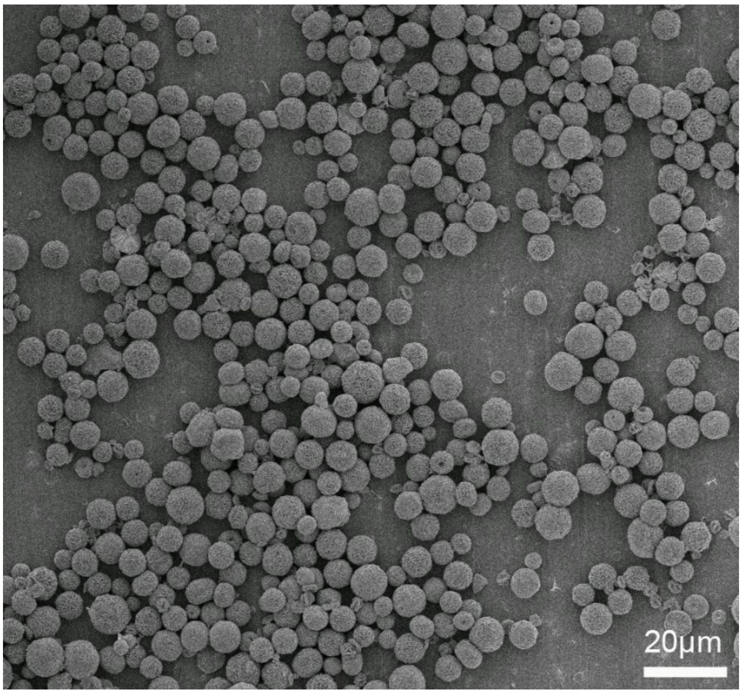

Fig. S4 The FE-SEM image of the CuS material prepared at 433 K for 12 h in the presence of 0.4 g PVP without adding EDA.

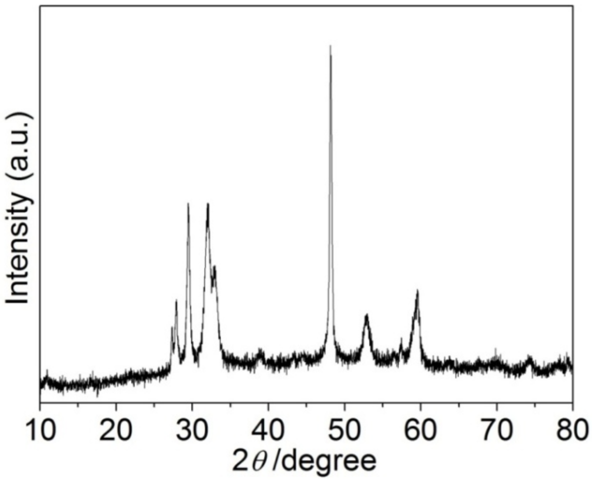

Fig. S5 (a) XRD pattern of the CuS material prepared at 433 K for 12 h in the presence of 0.4 g PVP and 10 μL EDA.

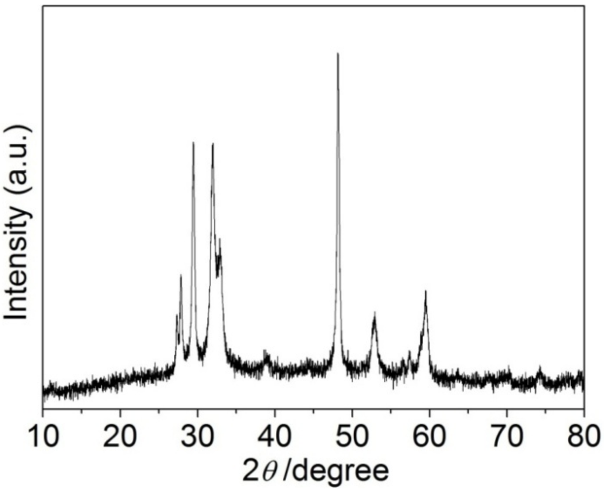

Fig. S5 (b) XRD pattern of the CuS material prepared at 433 K for 12 h in the presence of 0.4 g PVP and 40 μL EDA.

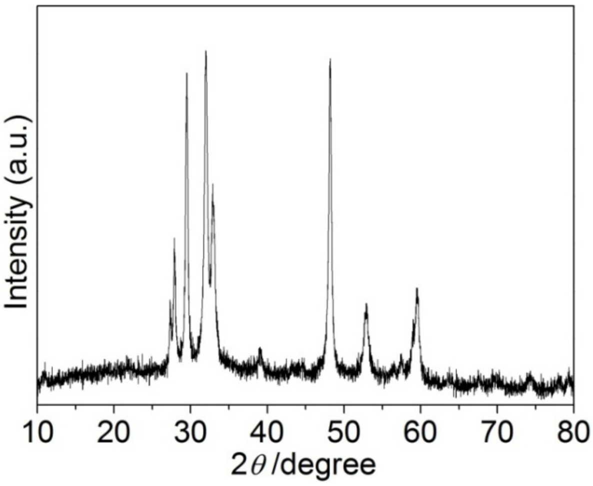

Fig. S5 (c) XRD pattern of the CuS material prepared at 433 K for 12 h in the presence of 0.4 g PVP and 60 μL EDA.

Fig. S6a and b shown the CuS sample consists of microflowers with diameters of about 5~6 μm and stacking nanosheets with a disc-like structure in the thickness range of 100~200 nm, when 10 μL of EDA was used. Further increasing the amount of EDA to 40 μL, the as-obtained CuS microflowers (Fig. S8c and d) have a similar monodisperse property as CuS-**1** shown in Fig. 1c, while the nanopetals show more intensive arrangement.

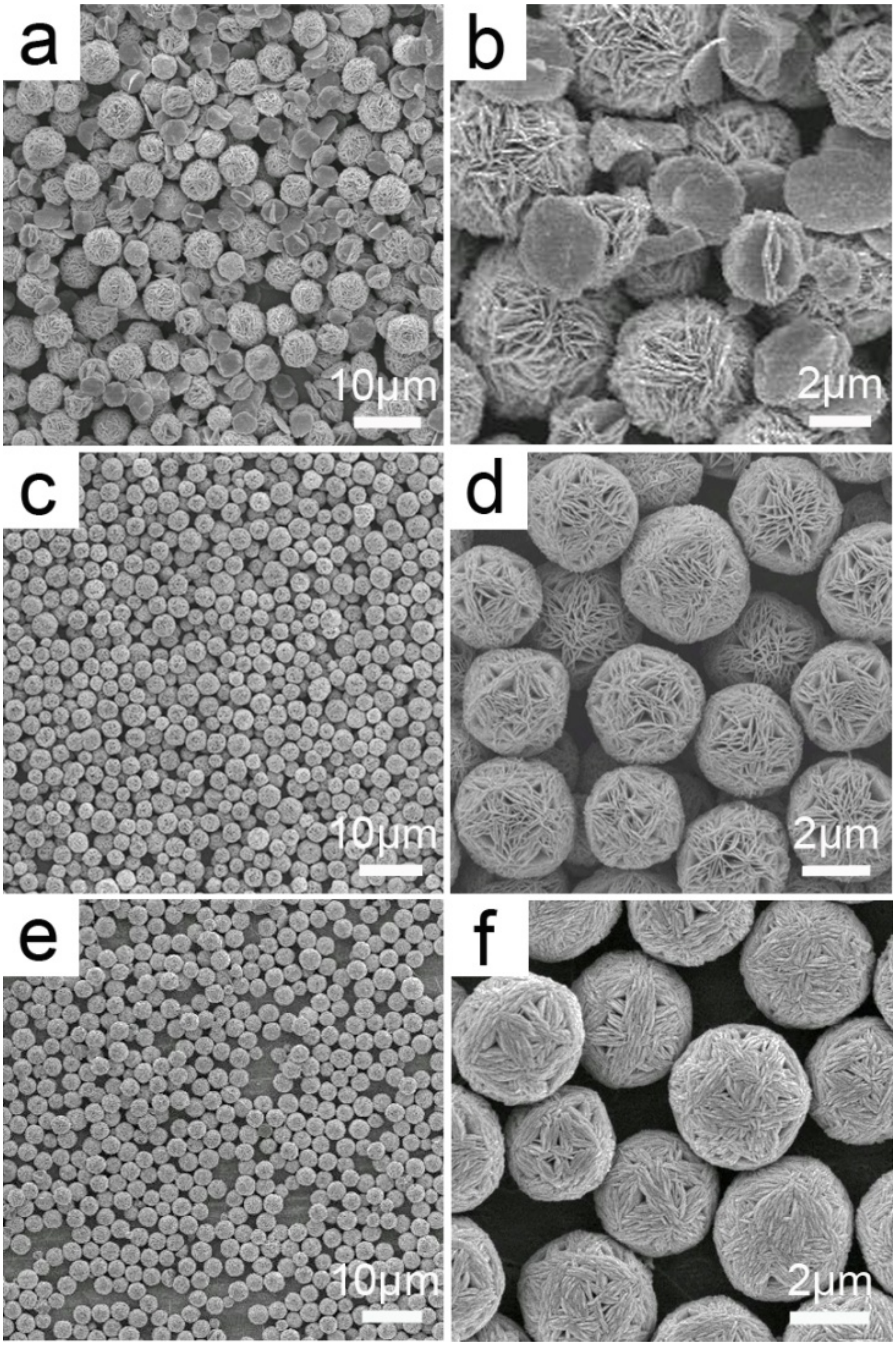

Fig. S6 The FE-SEM images of the CuS materials prepared at 433 K for 12 h in the presence of 0.4 g PVP and 10 (a, b), 40 (c, d) and 60 μL (e, f) EDA.

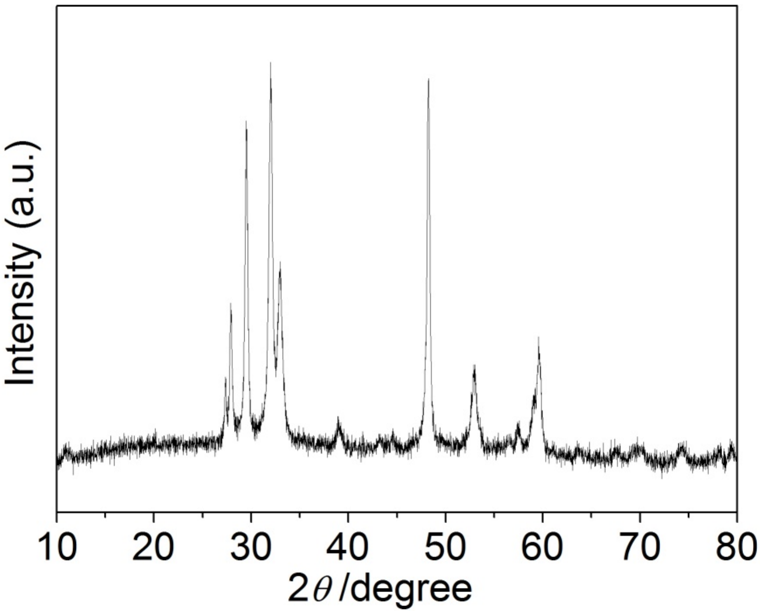

Fig. S7 The XRD pattern of the CuS material prepared at 433 K for 12 h in the presence of 0.4 g PVP and 80 μL EDA.

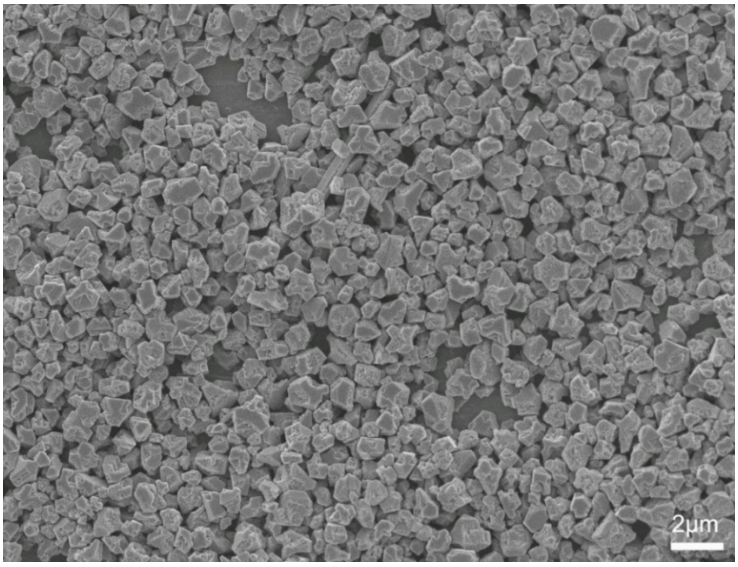

Fig. S8 The FE-SEM image of the CuS material prepared at 433 K for 12 h in the presence of 0.4 g PVP and 80 μL EDA.

Additionally, when only a small amount of EDA (60 μL) was introduced into the reaction system, we noticed that random aggregate structure of the hexagonal CuS crystal phase (Fig. S9) with a diameter of less than 1 μm was fabricated by self-assembly of numerous 2D nano-square sheets with sides of 300 nm and a thickness of 100 nm (Fig. S10)

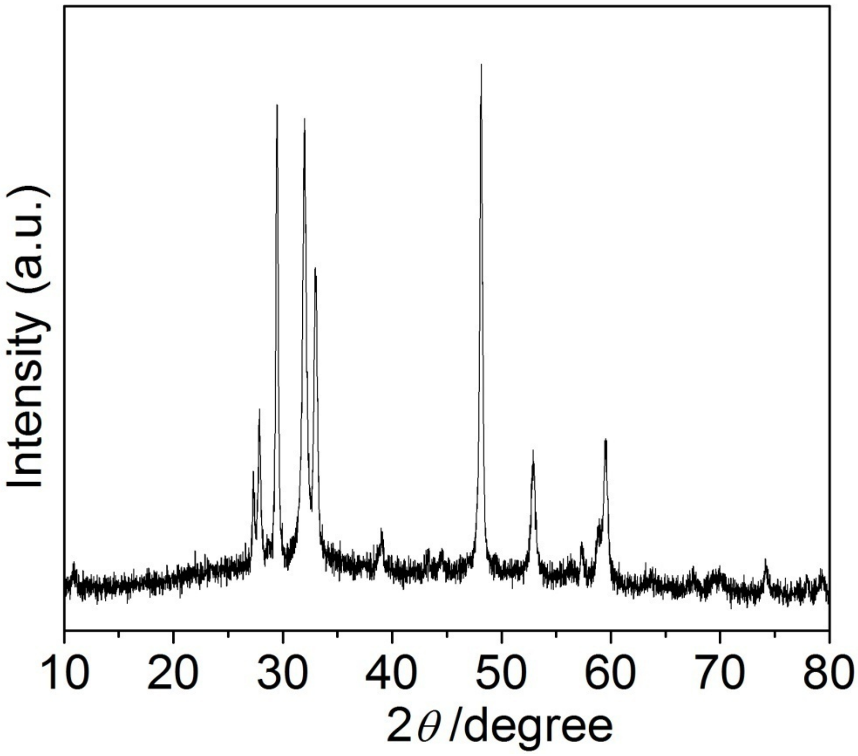

Fig. S9 The XRD pattern of the CuS material prepared at 433 K for 12 h in the presence of 60 μL EDA without adding PVP.

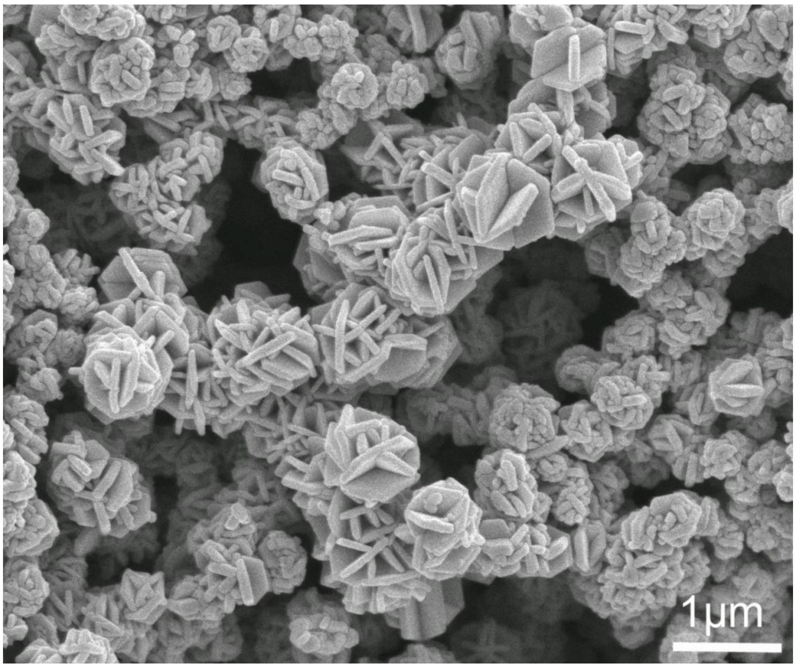

Fig. S10 (a) The FE-SEM image of the CuS material prepared at 433 K for 12 h in the presence of 60 μL EDA without adding PVP.

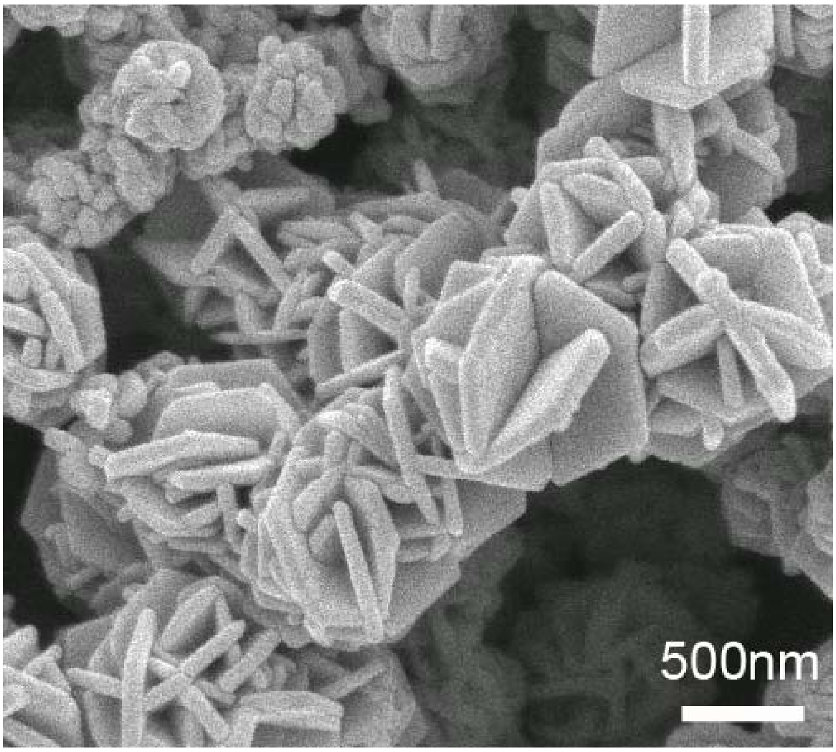

Fig. S10 (b) The FE-SEM image of the CuS material prepared at 433 K for 12 h in the presence of 60 μL EDA without adding PVP.

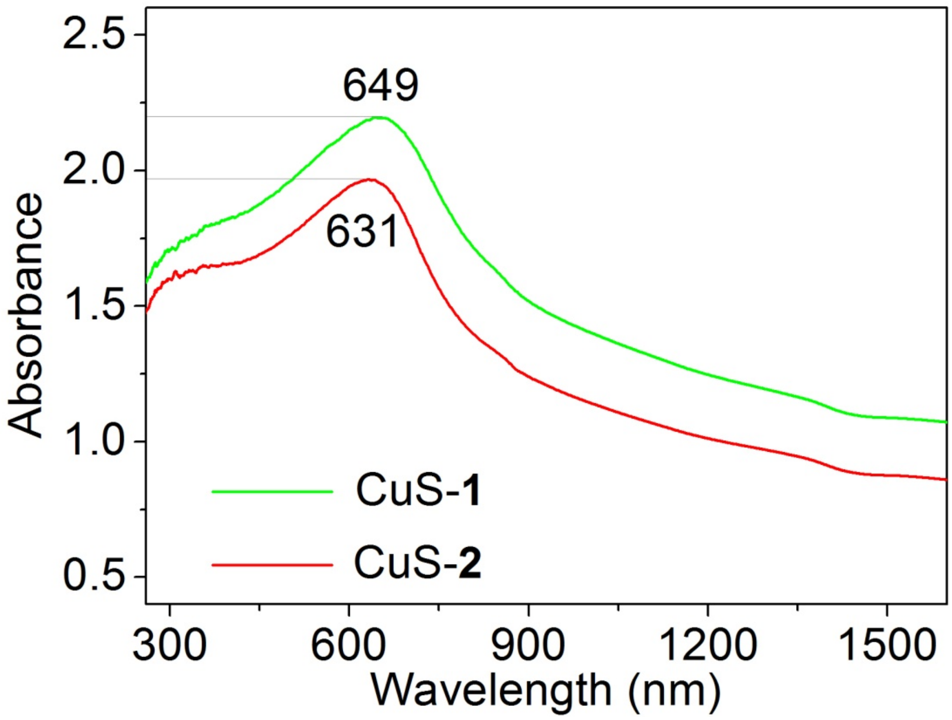

Fig. S11 UV–Vis diffuse reflectance spectra of the as-obtained CuS-**1** and CuS-**2**.

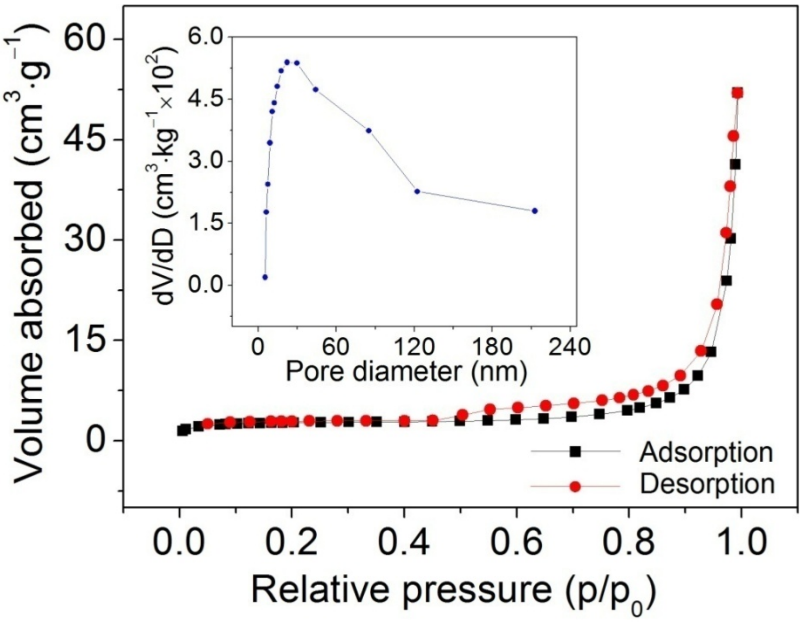

Fig. S12 N_2 adsorption-desorption isotherm and pore size distribution of the CuS-**1**.

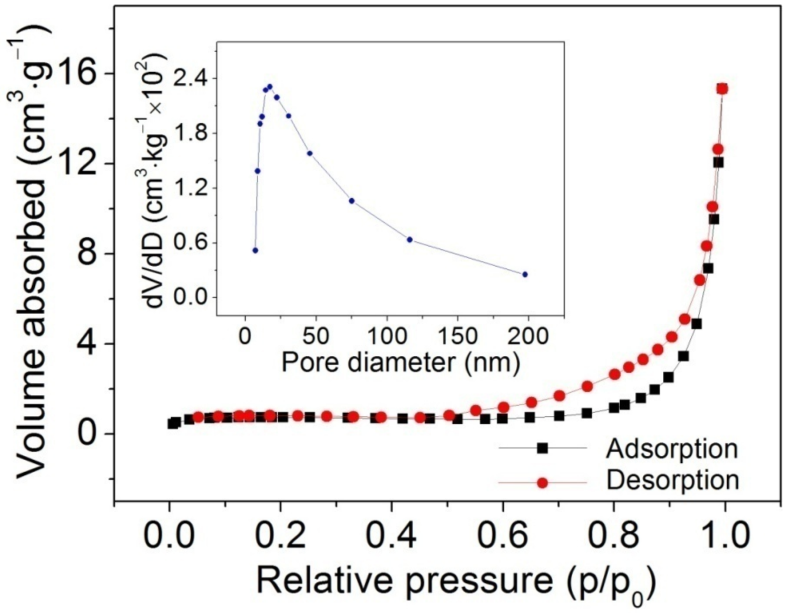

Fig. S13 N_2 adsorption-desorption isotherm and pore size distribution of the CuS-**2**.

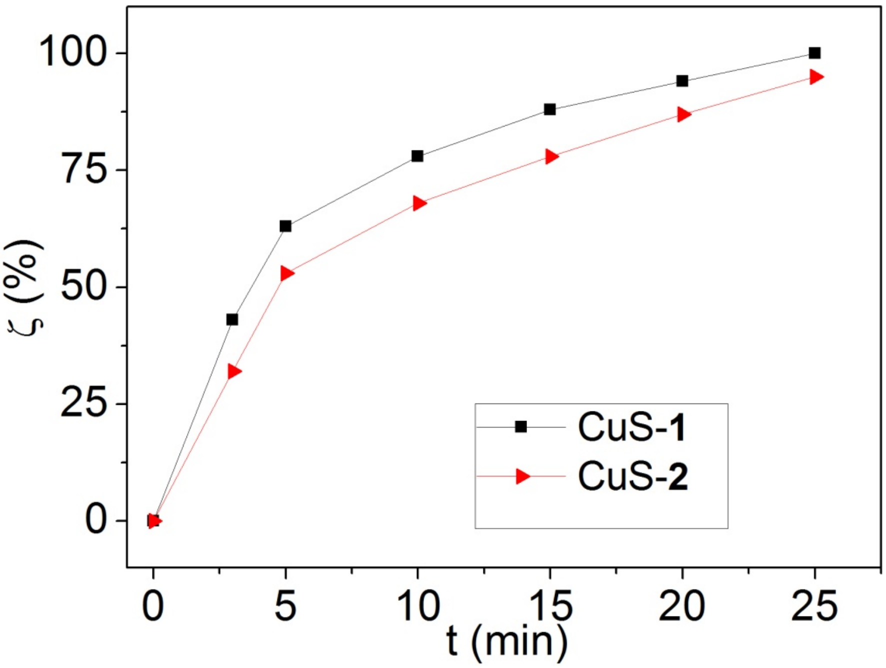

Fig. S14 The photodegradation degrees (*ξ*, %) of MB in the presence of different photocatalysts under visible-light irradiation.

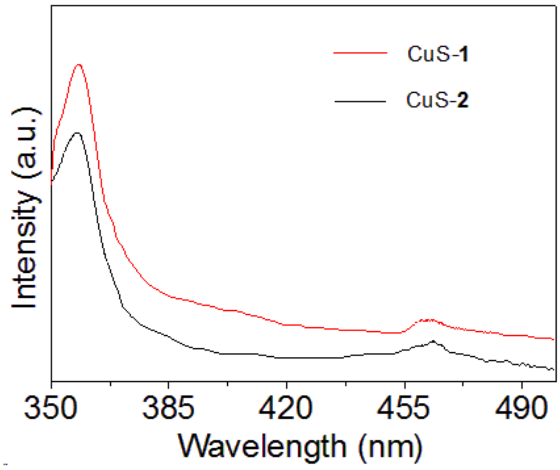

Fig. S15 The PL spectra of the prepared CuS-**1** and CuS-**2**.

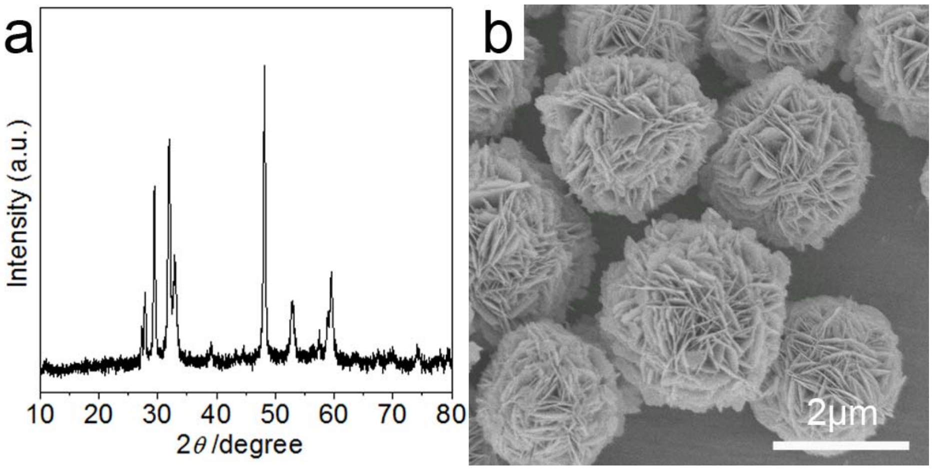

Fig. S16 The XRD pattern (a) and SEM image (b) of the CuS-**1** photocatalyst over the first three cycles.

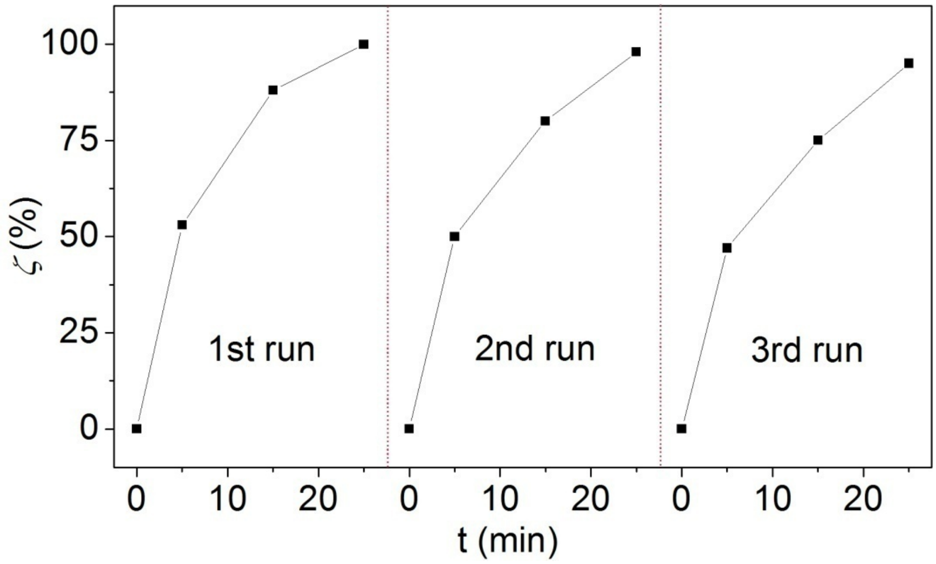

Fig. S17 The photodegradation degrees (ξ, %) of MB in the first three cycles using the CuS-**1** as the photocatalyst under visible-light irradiation.

Table S1. Comparison of photocatalytic activity of different materials for degradation of MB.

Materials	Catalyst (mg)	Concentration (MB mg/L)	Volume (MB /mL)	Time (min)	Photodegradation degree (ξ, %)	Reference
CuS microflowers	5	5	30	25	98	The present work
CuS microspheres	5	5	30	25	95	The present work
CuS hierarchical structures	30	20	40	90	87	1
CuS plates	10	3	30	30	80	2
CuS nanoparticles	20	0.16	50	90	94	3
hollow CuS microspheres	20	11.3	106	48	74	4
CdS hollow nanospheres	50	14	50	60	87	5
Fe_2O_3/ZnO hollow spheres	50	5	100	50	95.2	6

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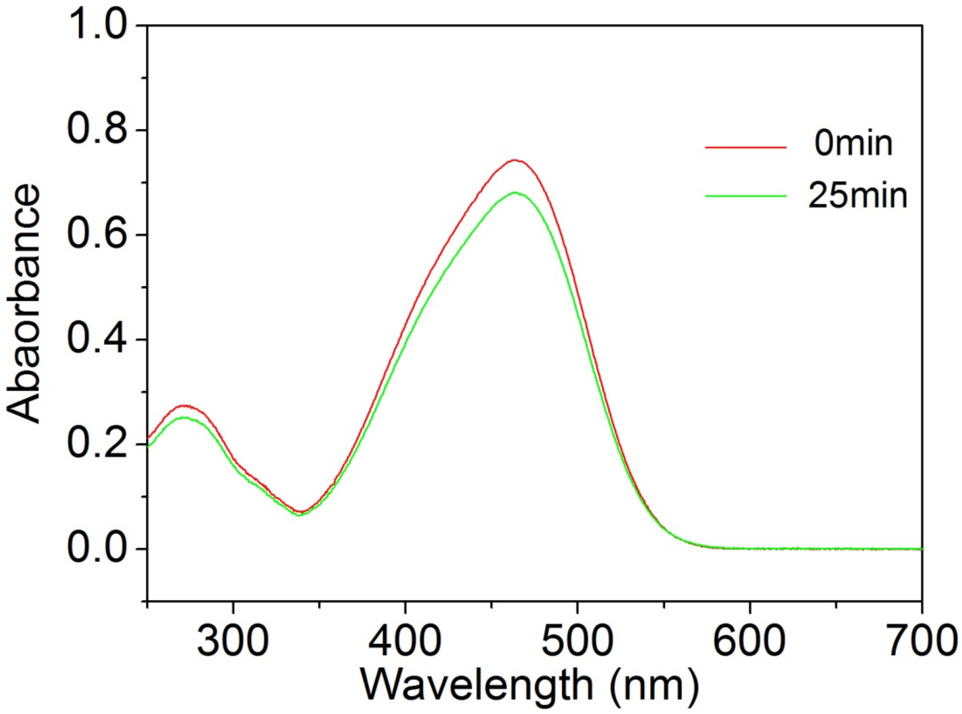

Fig. S18 UV–Vis absorption spectra of the MO solutions after being treated by the CuS-**1** using different time intervals: 0 and 25 min.

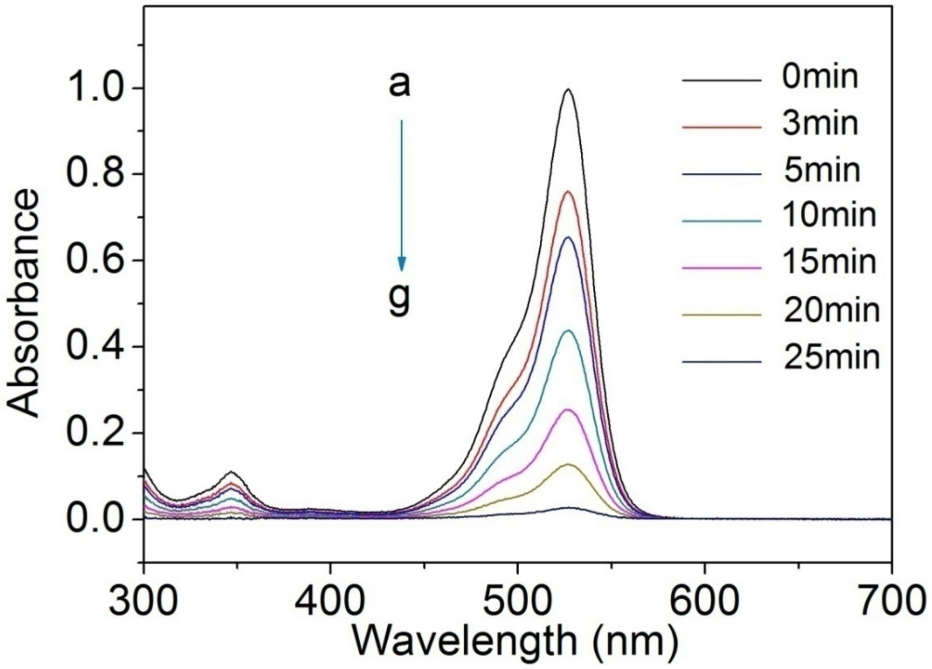

Fig. S19 UV–Vis absorption spectra of the R6G solutions after being treated by the CuS-**1** using different time intervals: 0 (a), 3 (b), 5 (c), 10 (d), 15 (e), 20 (f) and 25 min (g).

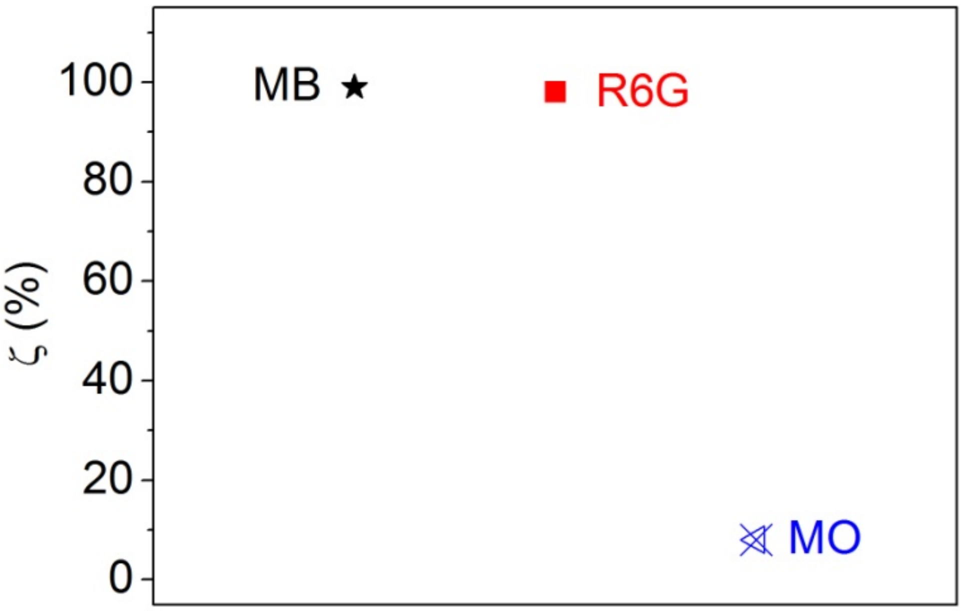

Fig. S20 Photodegradation degrees (ξ, %) of different organic dyes at the same initial concentration (5 mg·L^{-1}) of the CuS-**1** after an irradiation of 25 min.