Electronic Supplementary Material (ESI) for RSC Advances.

In situ formation of metal $Cd_xZn_{1-x}S$ nanocrystals on graphene surface: A novel method to synthesis sulfide-graphene nanocomposites

Yansong Zhou, Gang Chen,*Yaoguang Yu, Zhonghui Han, Jian Pei, Jingxue Sun, Fang He

Department of Chemistry, Harbin Institute of Technology, Harbin, 150001, PR China. E-mail: gchen@hit.edu.cn; Fax: +86-451-86403117; Tel: +86-451-86403117; zys@hit.edu.cn

I. Experimental Section

Chemicals. Chemical reagents including graphite flakes (Nanjing XFNANO Materials Tech Co., Ltd), $Cd(CH_3COO)_2 \cdot 2H_2O$ (Aladding Chemistry Co. Ltd), $Na_2S \cdot 9H_2O$ (West Long Chemical Co. Ltd), Na_2SO_3 (Sinopharm Chemical Reagent Co., Ltd), $Zn(CH_3COO)_2 \cdot 2H_2O$ (Sinopharm Chemical Reagent Co., Ltd), sublimed sulfur (Sinopharm Chemical Reagent Co., Ltd) were used without further treatment.

Preparation of graphene suspension. 0.5 g of graphite flakes was added into 300 mL N-methylpyrrolidone (NMP). To obtain a single layer graphene sheet, the mixture was sonicated for 3 h. The obtained mixture was centrifuged (10000 rpm for 5 min), and the bulk graphite was decanted away. The supernatant was further sonicated for 0.5 h and centrifuged (10000 rpm for 5 min). The final concentration of graphene suspension was measured to be 0.067 mg/mL.

Preparation of sodium polysulfide solution. Na_2S_x solution was prepared by dissolved 1.5 g of elemental S in to in the Na_2S solution (Na_2S 24.2 g, water 20 mL) and stirred with a magnetic stirrer for about 12 hours at room temperature. Then the solution was diluted to 500 mL for the next progress.

Preparation of sulfur/graphene composites. The sulfur/graphene (S/G) composite was prepared by a chemical deposition method in an aqueous solution. In a typical process, 200 mL of Na_2S_x solution was added into a certain amount of graphene suspension. The weight ration of S and graphene in sulfur/graphene was controlled by changing the amount of graphene suspension. The mixture was stirred for 5 minutes and the formic acid (18%) was added into the mixture drop by drop till the orange aqueous solution turned to be colorless. Then, the mixture was centrifuged and washed with water repeatedly to remove the remained impurities. Finally, the solid was dried at 50℃ in a drying oven for 12 h.

Synthesis of the CZS(0.4)-G(ω). CZS(0.4)-G(ω) was prepared by a solvothermal method. In a typical process, 0.227 g of $Zn(CH_3COO)_2 \cdot 2H_2O$, 0.413 g of $Cd(CH_3COO)_2 \cdot 2H_2O$ was dissolved in 5 mL N,N-dimethylformamide (DMF) to form a clear solution Then 0.145 g of the as-prepared sulfur/graphene (S/G) powder and 10 mL triethanolamine was added into the solution. After being stirred for 5 minutes, the mixture was totally transferred into an autoclave (Teflon cups with 20 mL inner volume). The autoclave was maintained at 200℃ for 24 h and then air-cooled to room temperature. The product was collected by centrifugation, washed several times with absolute ethanol, and finally air dried. The pure CZS(0.4) were prepared by the same method except using elemental sulfur to take the place of sulfur/graphene (S/G) composites.

As comparison, a facile method that has been reported for the preparation of the CdS/graphene has also being used for the preparation of CZS(0.4)/graphene composites.[1] In our work $Cd(CH_3COO)_2·2H_2O$ and $Zn(CH_3COO)_2·2H_2O$ were used to take the place of $Cd(CH_3COO)_2·2H_2O$ in the reference. Graphite oxide for this work was prepared from flake graphite by a modified method[2] reported by Marcano et al.[3]

II. Characterization

The structures of the samples were characterized with a powder X-ray diffractometer (XRD, Rigaku D/max-2000) using Cu-Kα radiation (λ= 0.15406 nm, 45 kV, 50 mA) at a scanning rate of 5° min-1 in the 2θ range 5-90°. Field-emission scanning electron microscope (FESEM, FEI, Quanta 200F) and transmission electron microscopy (TEM, FEI, Tecnai G2 S-Twin, operating at 300kV) were employed to observe the morphology of the samples. The Raman spectra were obtained with a MODEL BX41TF Raman system using an excitation source of 532 nm. The Cd : Zn ratio was determined by inductively coupled plasma atomic emission spectrometry (ICP, Perkin Elmer Optima 5300DV).

III. Photocatalytic reactions

The photocatalytic reaction was performed in a closed gas-circulation system with a side window. The photocatalyst powder was dispersed ultrasonicly in an aqueous solution (300 mL) containing Na_2S (0.1 mol/L) and Na_2SO_3 (0.1 mol/L) for 10 min. The reaction was carried out at 278 K by irradiating the suspension with light from a 300 W Xe lamp (Trusttech PLS-SXE 300, Beijing) which was equipped with an optical filter ($\lambda >$ 400 nm). The amount of produced H_2 was measured by gas chromatography (Agilent 6820) with a thermal conductivity detector (TCD) and Ar was used as the carrier gas.

Apparent quantum yields (AQY) for hydrogen evolution were measured under the same experimental condition, except for the addition of band pass filters with wavelength of 420 nm. The apparent quantum yields are defined by following eqs:

$$
\begin{aligned}
\mathrm{AQY}(\%) &= \frac{\text{Number of reacted electrons}}{\text{Number of incident photons}} \times 100 \\
&= \frac{2 \times \text{number of } \mathrm{H_2} \text{ molecules evolved}}{\text{Number of incident photons}} \times 100
\end{aligned}
$$

The number of incident photons was measured by a radiometer (Photoelectric Instrument Factory, Beijing Normal University)

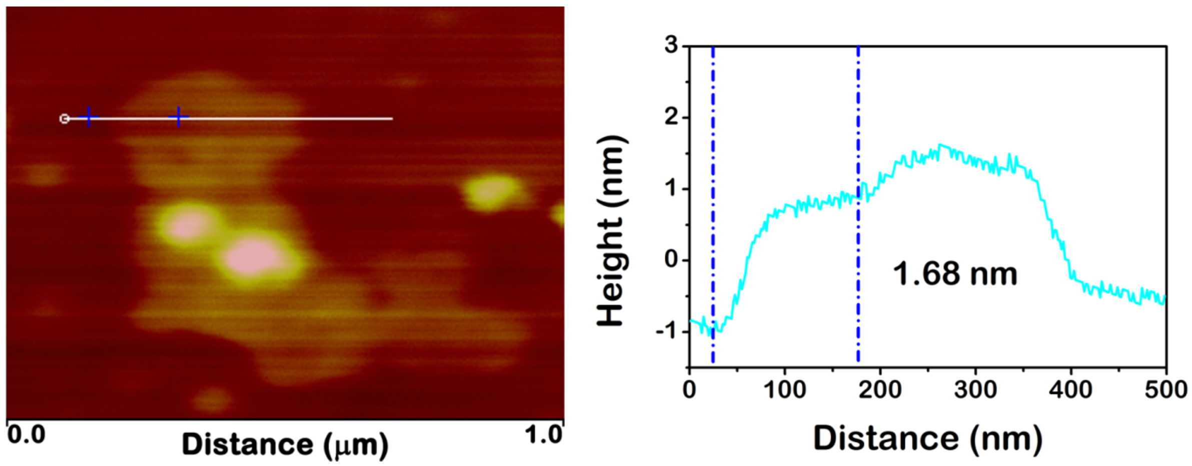

Fig. S1. AFM image of graphene sheets obtained from the liquid-phase exfoliation with thickness about 1.68 nm (approximately 5 layers).

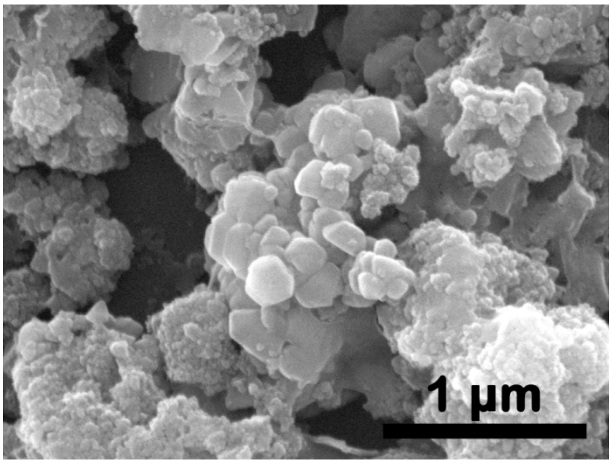

Fig. S2. SEM image of pure CZS(0.4). Significant aggregation of nanoparticles is observed in the sample of pure CZS(0.4)

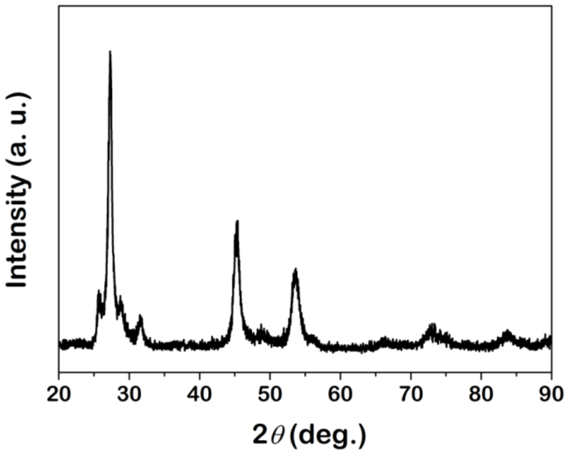

Fig. S3. XRD pattern of the as-prepared CZS(0.4)-G(0.5). XRD analysis reveals that the CZS(0.4)-G is corresponding to wurtzite CZS (JCPDS No. 89-2157).

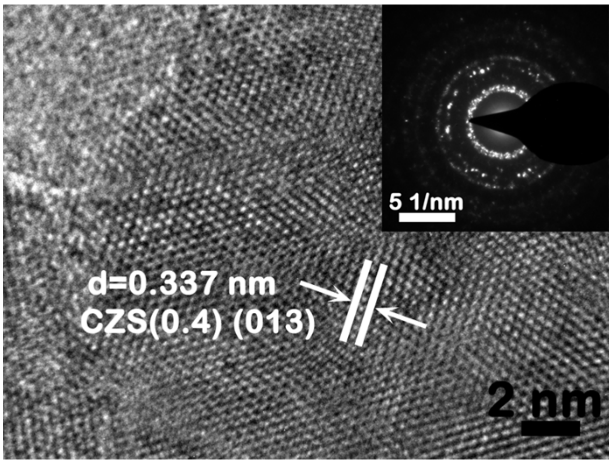

Fig. S4 HRTEM image of CZS(0.4)-G(0.5). The inset of (f) shows the SAED pattern of graphene sheet decorated with CZS(0.4) nanocrystals.

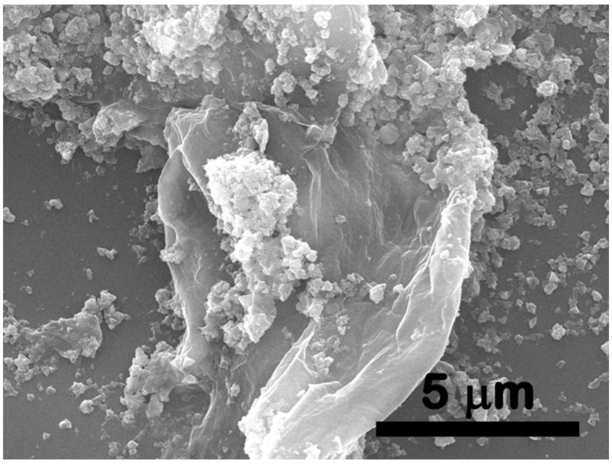

Fig. S5. SEM image of the sample prepared by using elemental sulfur and graphene dispersion as precursor. Significant aggregation of the particles and graphene sheets mixed with each other rather than *in situ* formation of the nanoparticles on the surface.

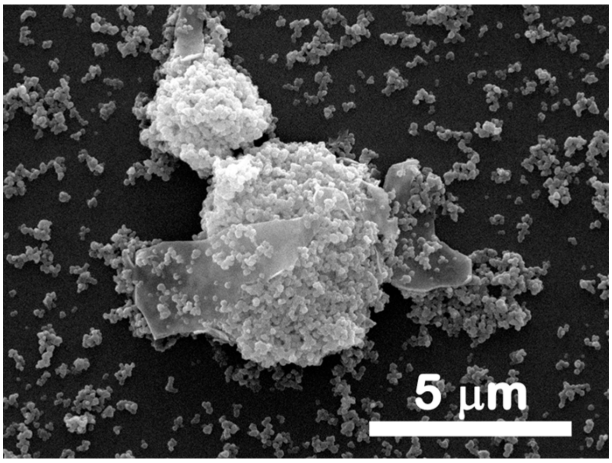

Fig. S6. SEM image of the sample prepared through the reported method.

Table S1. Compositions of final products for CZS(0.4)

Sample	Atom percentage (%)		Atomic ratio of Cd/Zn
	Cd	Zn	
CZS(0.4)	41.37	58.63	4:5.7

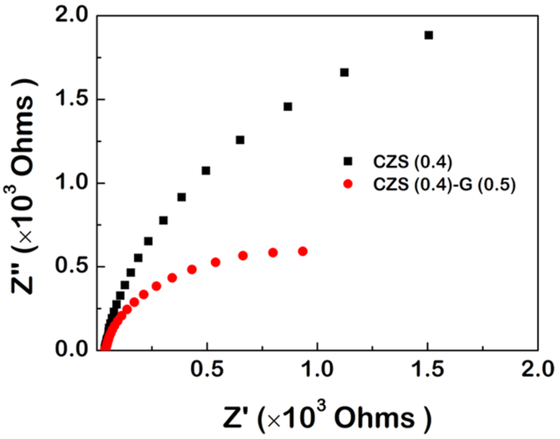

Fig.S7. EIS Nyquist plots of CZS(0.4)-G(0.5) and CZS(0.4). A smaller arc radius in EIS Nyquist plots for CZS(0.4)-G(0.5) corresponds to more effective separation of photogenerated electron−hole pairs.

References:

1. A. Cao, Z. Liu, S. Chu, M. Wu, Z. Ye, Z. Cai, Y. Chang, S. Wang, Q. Gong and Y. Liu, *Adv. Mater.*,, 2010, **22**, 103-106.

2. R. C. Jin, G. Chen, J. Pei and C. S. Yan, *New J. Chem.*, 2012, **36**, 2574-2579.

3. D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L. B. Alemany, W. Lu and J. M. Tour, *ACS Nano*, 2010, **4**, 4806-4814.