Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Electronic Supplementary Information

Hierarchical dandelion-flower-like cobalt-phosphide modified CdS/reduced graphene oxide-MoS_2 nanocomposites as a noble-metal-free catalyst for efficient hydrogen evolution from water

D. Amaranatha Reddy, Jiha Choi, Seunghee Lee, Yu-jin Kim, Sangyeob Hong, D. Praveen Kumar and Tae Kyu Kim*

Department of Chemistry and Chemical Institute for Functional Materials, Pusan National University, Busan 609-735, Republic of Korea

*E-mail address: tkkim@pusan.ac.kr

1. Experimental section

(i) Synthesis of CdS nanospheres:

CdS microspheres were synthesized via a hydrothermal method. A typical synthetic process involved dissolving $Cd(CH_3COO)_2 \cdot 2H_2O$ (3.2 mmol), CH_4N_2S (16 mmol) at the required stoichiometry into de-ionized (DI) water in a 40 ml Teflon-lined autoclave. After stirring for 2 h, the autoclave was placed inside a furnace and heated at 140 °C for 24 h. After completion of the reaction, the autoclave was air-cooled to room temperature. The products were collected and washed several times with DI water to remove any impurities and then finally heated in air at 100 °C for 6 h to obtain the final products.

(ii) Synthesis of graphene Oxide (GO):

Graphene oxide (GO) was prepared from natural graphite flakes according to the modified Hummers method and similar to our earlier work [1-5]. Briefly, 69 mL of concentrated H_2SO_4 was slowly added to a mixture of graphite powder (3 g; 1 wt equiv) and $NaNO_3$ (1.5 g; 0.5 wt equiv) in a 500 mL beaker. The mixture was cooled to 0 °C in an ice bath and stirred for 1 h. Subsequently, $KMnO_4$ (9.0 g; 3 wt equiv) was added slowly in portions to keep the reaction temperature below 20 °C. The beaker was then placed in a 35 °C water bath, and the solution was stirred for about 1 h to form a thick paste, after which ultra-pure DI water (138 mL) was added slowly, producing a large amount of exothermic heat, which raised the temperature to 98 °C; this temperature was maintained for 30 min. A mixture of DI water (420 mL) and 30% H_2O_2 (10 mL) were added, producing another exotherm. Finally, the solution was filtered to collect the precipitate. The filter cake (graphite oxide) was washed (3–4 times) using HCl (30%) plus DI water. The GO suspension was subsequently obtained by sonicating the as-prepared solid in water under ambient conditions for 60 min.

(iii) Synthesis of Molybdenum disulfide (MoS_2):

MoS_2 nanosheets were synthesized via a hydrothermal method. A typical synthetic process involved dissolving Na_2MoO_4, (0.3 g) and C_2H_5NS (0.6 g) at the required stoichiometry into deionized (DI) water in a Teflon-lined autoclave. After stirring for 3 h, the autoclave was placed inside a furnace and heated at 200 °C for 24 h. After completion of the reaction, the autoclave was air-cooled to room temperature. The products were collected and washed several times with DI water to remove any impurities and then finally heated in air at 100 °C for 6 h to obtain the final products. The black precipitates were the MoS_2 nanosheets, which were synthesized.

(IV) Synthesis of CdS-RGO nanocomposites:

To synthesize CdS-RGO, the above synthesized GO was sonicated in 40 mL of DI water for 1 h to generate a clear brown dispersion. Then, required stoichiometry amount of $Cd(CH_3COO)_2{\cdot}2H_2O$ (3.2 mmol), CH_4N_2S (16 mmol) was added. The mixture was vigorously stirred for 2 h to obtain a homogeneous suspension. Then, this suspension was transferred to a 40 mL Teflon-sealed autoclave and maintained at 140 °C for 24 h. After completion of the reaction, the autoclave was air cooled to room temperature. The products were collected and washed several times with DI water to remove the impurities and finally heated in air at 100 °C for 6 h to obtain the final products. CdS with different GO contents was prepared following the same method with different wt % of GO as the reactant.

(V) Synthesis of CdS/RGO-MoS_2 nanocomposites:

To synthesize CdS/RGO-MoS_2, the synthesized GO (5 wt.%) and desired wt.% of MoS_2 (1, 2, 3, 4 and 5) of bare MoS_2 nanosheets were dispersed in 20 mL of DI water in a separate beaker and both of the samples were sonicated for 30 minutes. After sonication, MoS_2 suspension was mixed with the GO solution very slowly under vigorous magnetic stirring for 1 h at room temperature. Then, required stoichiometry amount of $Cd(CH_3COO)_2 \cdot 2H_2O$ (3.2 mmol), CH_4N_2S (16 mmol) was added. The mixture was vigorously stirred for 2 h to obtain a homogeneous suspension. Then, this suspension was transferred to a 40 mL Teflon-sealed autoclave and maintained at 140 °C for 24 h. After completion of the reaction, the autoclave was air cooled to room temperature. The products were collected and washed several times with DI water to remove the impurities and finally heated in air at 100 °C for 6 h to obtain the final products. CdS-RGO with different MoS_2 contents was prepared following the same method with different wt.% of MoS_2 as the reactant.

(VI) Preparation of hierarchical dandelion-like Cobalt phosphide (CoP) nanostructures:

Dandelion-like CoP nanostructures were synthesized via a thermal phosphidation chemical reaction using $Co(OH)_2$ nanostructures as the precursor material. In a typical synthesis procedure mixed solution of ethylene glycol (20 mL) and de-ionized water (20 ml) was used as the solvent. 2 mmol of $Co(NO_3)_2 \bullet 6H_2O$ and 10 mmol of urea as the reactants. The above precursor's mixture was vigorously stirred for 2 h to obtain a homogeneous suspension. Then, this suspension was transferred to a 40 mL Teflon-sealed autoclave and maintained at 90 °C for 12 h. After completion of the reaction, the autoclave was air cooled to room temperature. The products were collected and washed several times with DI water to remove the impurities and finally heated in air at 60 °C for 6 h to obtain the final products. For CoP synthesis the obtained $Co(OH)_2$ nanostructures (50 mg) and 250 mg of NaH_2PO_2 were mixed thoroughly and placed in a quartz boat of the tube furnace and heated at 300 ^oC for 1h with a heating rate of 2 $^oC/min$ under Ar atmosphere. Finally obtained black solid was washed subsequently by water and ethanol three times to get the final CoP nanostructures.

(VII) Synthesis of CdS-RGO-MoS_2@CoP nanocomposites:

For the formation of the CdS-RGO-MoS_2@CoP nanocomposite, desired wt.% (5, 10, 15, 20, 25 and 30) of bare CoP nanostructures and CdS/RGO-MoS_2 were dispersed in 40 mL of DI water in a separate beaker and both of the samples were sonicated for 30 minutes. After sonication, CoP suspension was mixed with the CdS/RGO-MoS_2 solution very slowly under vigorous magnetic stirring for 10 h at room temperature. Then the precipitate was collected by centrifugation, washed with DI water and dried for 8 h at 80 °C. CdS/RGO-MoS_2 with different CoP contents was prepared following the same method with 5, 10, 15, 20, 25 and 30 wt.% of CoP respectively.

(VIII) Synthesis of CdS/RGO-CoP nanocomposites:

For the formation of the CdS/RGO-CoP nanocomposite, optimized 20 wt.% of CoP nanostructures and CdS/RGO (5 %) were dispersed in 40 mL of DI water in a separate beaker and both of the samples were sonicated for 30 minutes. After sonication, CoP suspension was mixed with the CdS/RGO solution very slowly under vigorous magnetic stirring for 10 h at room temperature. Then the precipitate was collected by centrifugation, washed with DI water and dried for 8 h at 80 °C.

2. Characterization

The morphologies and average particle sizes were measured using a Hitachi S-4800 field emission scanning electron microscope (FESEM) equipped with an Inca 400 energy-dispersive spectrometer from Oxford Instruments. The microstructure properties were measured using a JEOL JEM-2100F transmission electron microscope (TEM) with an accelerating voltage of 200 kV. Phase determination of the as-prepared powders was performed using a Bruker D8 Advance X-ray diffractometer with a Cu Kα X-ray source. X-ray photoelectron spectroscopy (XPS) was performed using a monochromated Al Kα X-ray source (hν = 1486.6 eV) at an energy of 15 kV/150 W. The optical absorption measurements were performed using a Shimadzu UV-1800 double-beam spectrophotometer. Photoluminescence (PL) measurements were performed at room temperature using Hitachi F-7000 fluorescence spectrophotometer.

3. Photocatalytic hydrogen Production

The photocatalytic hydrogen evolution experiments were performed in a Pyrex flask (containing 12 ml of DI-water, 3 ml of lactic acid as sacrificial agent and 1 mg of photo-catalyst) at ambient temperature and atmospheric pressure. The openings of the flask were sealed with silicone rubber septum. A solar simulator equipped with an AM 1.5G filter and 150 W Xe lamp (Abet Technologies) was used as the light source. The output light intensity was adjusted to 1 sun (100 W/m^2) using 15151 low-cost calibrated Si reference cell (ABET technologies). Before irradiation, the system was evacuation and bubbled with Ar for 30 min to remove the air inside. The hydrogen gas evolved was determined using an off-line gas chromatograph (Young Lin Autochro-3000, model 4900) equipped with thermal conductivity detector.

The apparent quantum efficiency (QE) was measured according to the equation below.

$$\mathrm{QE} = \frac{\text{nuber of reacted electrons}}{\text{number of incident photons}} \text{ x } 100\ \%$$

$$= \frac{\text{number of evolved } H_2 \text{ molecules x } 2}{\text{number of incident photons}} \text{ x}100\%$$

Here the QE was measured under the same photocatalytic hydrogen evolution experimental conditions except the irradiation source, here 150 W Xe lamp with 425 nm band pass filter having optical density greater than 4 in the rejection band and slope factor less than 1 %, were used as light sources, instead of the solar simulator. The output light intensity was measured using 15151 low-cost calibrated Si reference cell (ABET technologies). The liquid level is ~16 cm far from the window of lamp and the illuminated area is 21.24 cm^2.

4. Photo-electrochemical measurements

Photo-electrochemical measurements were performed in a three-electrode system using a CHI 617B electrochemical workstation. A solar simulator equipped with an AM 1.5G filter and 150 W Xe lamp (Abet Technologies) was used as the irradiation source to produce monochromatic illuminating light. The output light intensity was adjusted to 1 sun (100 W/m^2) using 15151 low-cost calibrated Si reference cell (ABET technologies). The reference and counter electrodes were Ag/AgCl and platinum wire, respectively, and Na_2SO_4 aqueous solution served as the electrolyte. To prepare the working electrode, the as-synthesized 10 mg of CdS and CdS/RGO-MoS_2@CoP nanocomposites were first dispersed into ethanol (450 µl) and 50 µl Nafion mixtures using soft ultrasonic stirring to obtain a uniform suspension. The solution containing the catalyst (30 µl) was dropped onto the pretreated indium–tin oxide (ITO) conductor glass substrate, which was then dried in an oven at 100 °C for 3 h. Photo-responses were measured at 0.0 V during on-off cycling of the solar simulator. Electrochemical impedance spectroscopy (EIS) was carried out at open-circuit potential over the frequency range of 10^5 and 10^{-1} Hz with an AC voltage magnitude of 5 mV.

5. Supporting Figures

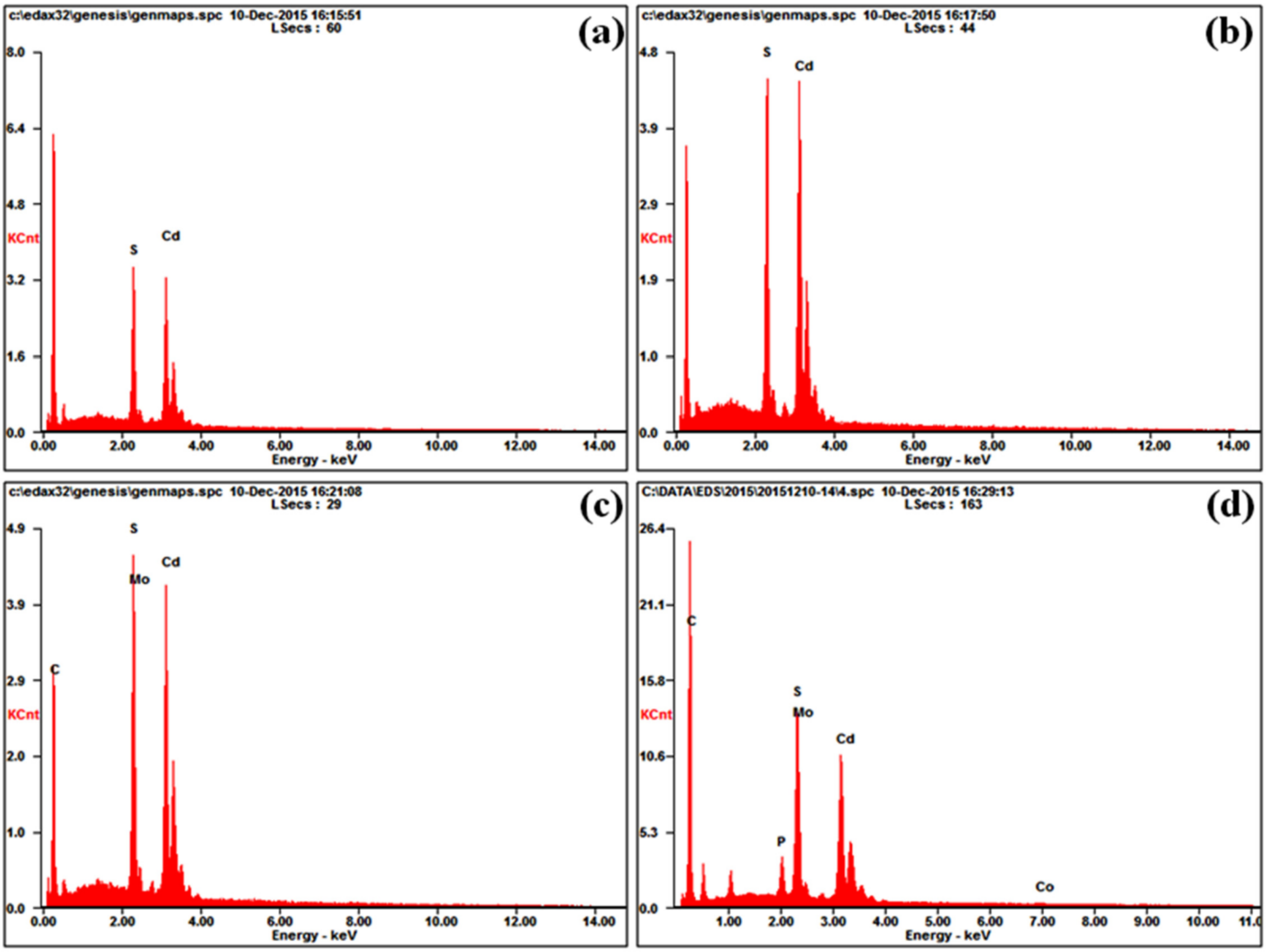

Fig.S1: EDS spectra of (a) CdS (b) CdS-RGO (c) CdS/RGO-MoS_2 and (d) CdS/RGO-MoS_2@CoP nanocomposites.

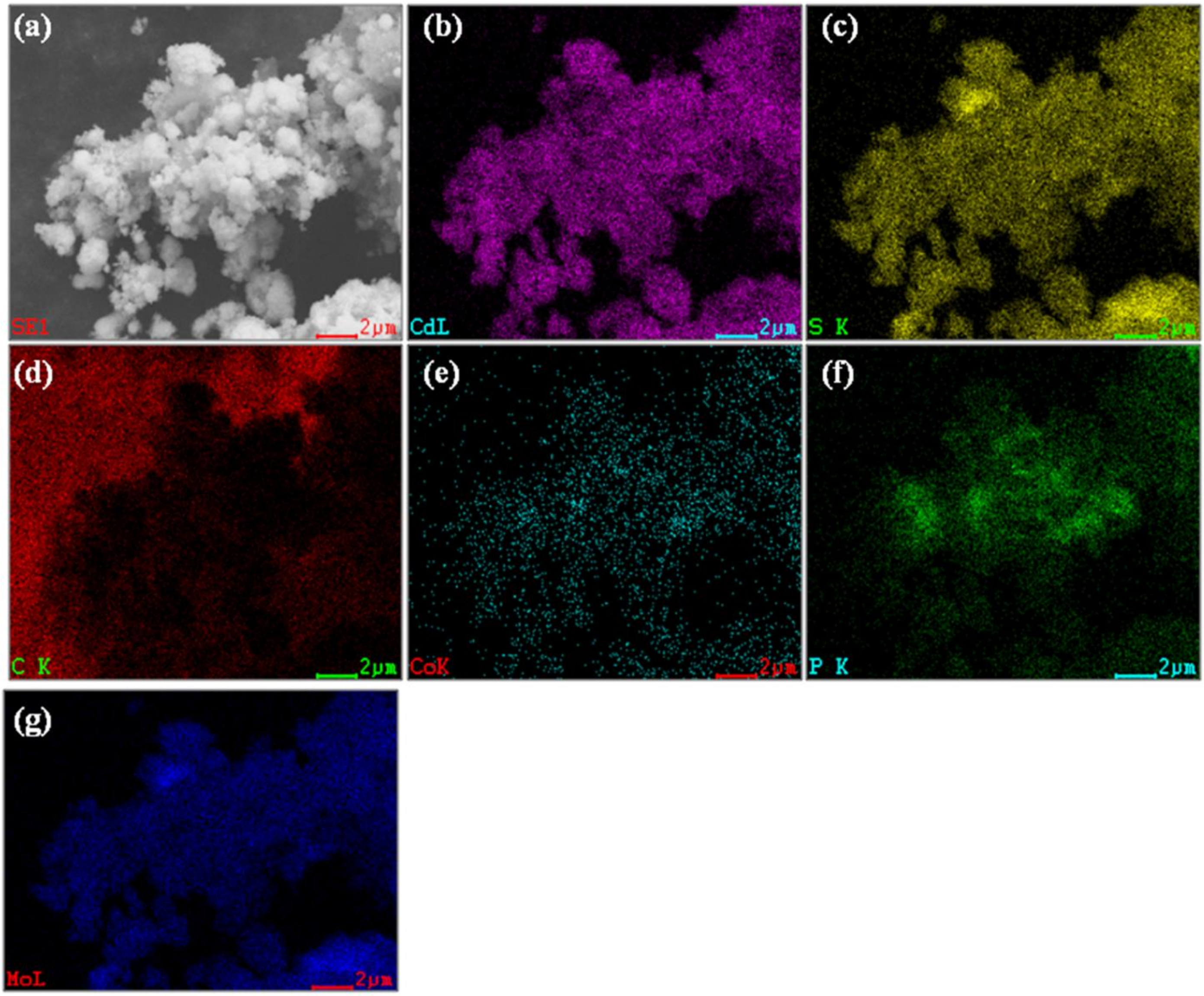

Fig.S2: (a) Electron micrograph and elemental mapping of CdS/RGO-MoS_2@CoP nanocomposite showing the presence of (b) Cd (c) S (d) C (e) Co (f) P and (g) Mo elements, respectively.

Table 1: Elemental composition of as-synthesized nanostructures from EDS analysis

Sample Name	**Estimated Composition in Wt.%**					
	Cd	S	C	Mo	Co	P
CdS	78.85	21.15	-	-	-	-
CdS/RGO-1	77.55	21.33	1.12	-	-	-
CdS/RGO-3	76.86	21.05	2.09	-	-	-
CdS/RGO-5	75.57	20.27	4.16	-	-	-
CdS/RGO-7	74.22	19.96	5.82	-	-	-
CdS/RGO-10	73.90	18.75	7.35	-	-	-
CdS/RGO-MoS_2-1	75.08	20.29	4.11	0.52	-	-
CdS/RGO-MoS_2-2	74.63	20.17	4.08	1.12	-	-
CdS/RGO-MoS_2-3	74.22	20.07	3.95	1.76	-	-
CdS/RGO-MoS_2-4	73.54	20.04	4.11	2.31	-	-
CdS/RGO-MoS_2-5	72.78	20.27	3.95	1.76	-	-
CdS/RGO-MoS_2@CoP-5	69.24	19.66	4.01	2.22	3.17	1.70
CdS/RGO-MoS_2@CoP-10	64.74	19.89	3.98	2.30	5.85	3.24
CdS/RGO-MoS_2@CoP-15	59.35	20.09	3.89	2.19	9.62	4.86
CdS/RGO-MoS_2@CoP-20	54.28	19.98	4.10	2.31	12.52	6.81
CdS/RGO-MoS_2@CoP-25	51.62	18.98	3.96	2.09	15.25	8.10
CdS/RGO-MoS_2@CoP-30	47.39	18.52	4.06	2.29	18.12	9.62

References

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