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Highly Active Catalyst of Two-Dimensional CoS₂/Graphene Nanocomposites for Hydrogen Evolution Reaction

Wei Xing^{1*}, Yu Zhang¹, Qingzhong Xue¹ and Zifeng Yan^{2*}

Abstract

Hydrogen evolution reaction (HER) by electrochemical water splitting using new promising non-precious metal catalysts shows great potential for clean energy technology. The design and fabrication of a high-performance electrode material based on cobalt disulfide/reduced graphene oxide (CoS₂/RGO) nanocomposites is reported by a one-step hydrothermal method. Benefiting from its structural advantages, namely, large amount of exposed surface, fast charge transfer, and synergistic effect between CoS₂ and RGO, the as-prepared nanocomposites are exploited as a catalyst for the HER. The results indicate that CoS₂/RGO-5 % exhibits the best performance of hydrogen evolution and the smallest overpotential of 159 mV to achieve a 15 mA cm⁻² current density, possessing the easiest releasing of hydrogen gas and the highest charge transfer rate, as well as remarkable stability.

Keywords: Hydrogen evolution reaction, Cobalt disulfide, Two-dimensional structure

Background

Hydrogen, as a new type of renewable energy source, has attracted extensive concern due to its potential application in powering vehicles or electric devices. A promising method to produce hydrogen is electrocatalytic reduction of water via the hydrogen evolution reaction (HER) [1–3]. The platinum catalysts exhibit extraordinary activity in catalyzing the hydrogen evolution, but the high cost and scarcity seriously impede their practical applications. These limitations prompt the intensive investigations on inexpensive and earth-abundant electrocatalysts, e.g., metal sulfide [4], carbide [5], boride [6], and phosphide [7]. Many efforts have been taken to synthesize inorganic metal sulfur complexes to create analogs to these active materials. Particularly, MoS₂ and WS₂ have been researched as HER catalysts for their lower cost and higher stability than other metal derivatives [8–10]. On the other hand, carbon materials with excellent electrical conductivity, such as carbon nanotube and active carbons, were generally applied as supports of HER

catalysts to enhance their stability and electrical conductivity [11]. Till now, only few reports were devoted to the study of 2D CoS₂/graphene catalysts, which can expand the category of catalytic materials fitting for efficient HER [12].

Herein, we report a novel strategy to synthesize 2D cobalt disulfide/reduced graphene oxide (CoS₂/RGO) nanocomposites with high HER activity by a hydrothermal method. In these nanocomposites, RGO serves as a matrix for the uniform growth of CoS₂ nanoclusters. The presence of RGO facilitates both electrical conductivity and ionic transportation during the HER. Besides, the homogeneous dispersion of CoS₂ nanoclusters on the surface of RGO could also incredibly increase the catalytic active sites [13]. Furthermore, the interaction between graphene and CoS₂ can also inhibit the aggregation of CoS₂ nanoclusters, resulting in improved cycling stability [14]. Benefiting from their high electrical conductivity, opened pore structure, excellent dispersion of CoS₂, and positive synergistic effect between CoS₂ and RGO, the CoS₂/RGO nanocomposites exhibit excellent performance for HER process.

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Fig. 1 Synthesis strategy and hydrogen evolution process of the CoS₂/RGO nanocomposites

Methods

Materials

Natural graphite was provided by Qingdao Ruisheng Graphite Company. Cobalt(II) acetate tetrahydrate (Co(Ac)₂·4H₂O), thiourea (H₂NCSNH₂), ethyl alcohol, hydrogen peroxide (H₂O₂), potassium permanganate (KMnO₄), concentrated sulphuric acid (H₂SO₄), and sodium nitrate (NaNO₃) were purchased from Sino-pharm Chemical Reagent Company and used without further purification. Nafion (5 wt%) water solution was purchased from Shanghai Yibang Technology Co., Ltd. Deionized water (DI) was prepared by a Millipore pure water system.

GO Preparation and Purification

GO was synthesized by using modified Hummer's method. In a typical synthesis, 1 g of graphite, 1 g of NaNO₃, and 46 mL of H₂SO₄ were firstly mixed together in ice bath. Afterwards, 6 g of KMnO₄ was added, and the suspension was heated to 35 °C. After vigorous stirring for 60 min, 80 mL of deionized water was added, and the temperature

of solution was heated to 95 °C. Finally, 200 mL of water and 6 mL of H₂O₂ (30 wt%) was dropped into the solution, turning the color from dark brown to light yellow. Afterwards, the solution was filtered and washed thoroughly with deionized water. The filter cake was redispersed in water by strong mechanical agitation. After that, centrifugation was performed at 1500 rpm for four times until the solution is free of any visible particles. The supernatant was centrifuged at 8000 rpm for 20 min to remove tiny GO pieces. Finally, the precipitate was then redispersed in certain amount of water by sonication, resulting in an exfoliated GO solution (1 mg mL⁻¹).

Synthesis of CoS₂/RGO Nanosheets

Co(Ac)₂·4H₂O (0.01 mol) and H₂NCSNH₂ (0.02 mol) were added to 60 mL of GO solution (containing 12.3 mg GO that is weighed by drying the GO solution). The mixture was then treated by sonication for about 30 min, giving a clear solution. Then, the solution was poured to a Teflon-lined autoclave (100 mL) and heated in an oven at 180 °C for 12 h. During this

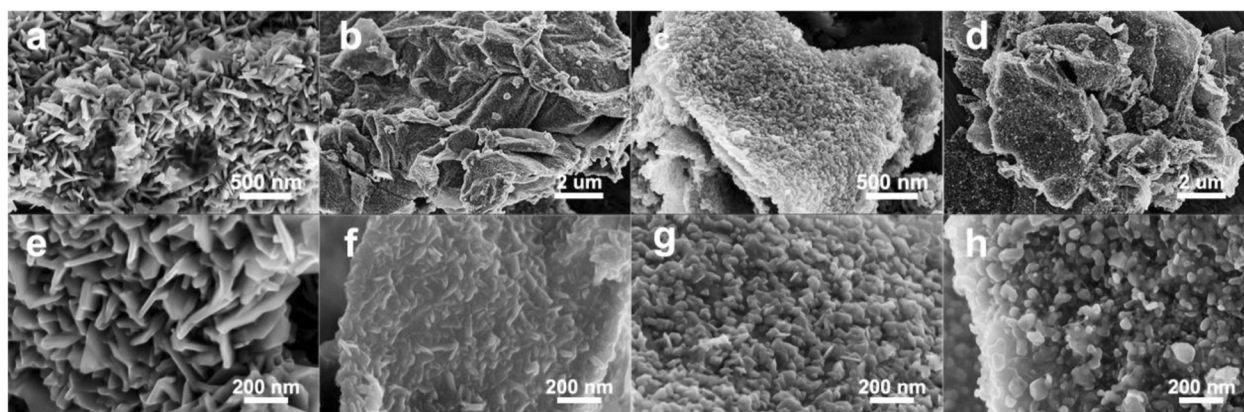


Fig. 2 SEM images of CoS₂/RGO-1 % (a, e), CoS₂/RGO-3 % (b, f), CoS₂/RGO-5 % (c, g), and CoS₂/RGO-15 % (d, h)

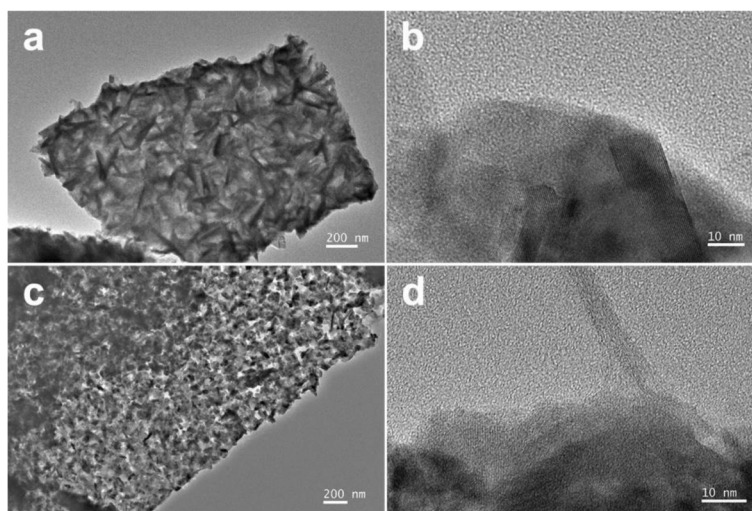


Fig. 3 TEM images of CoS_2/RGO -1 % (a, b) and CoS_2/RGO -5 % (c, d)

hydrothermal process, the GO was reduced to RGO. After being cooled to an ambient temperature, the resultant was separated by centrifugation, then washed with water and ethanol several times, and finally dried in an oven at 60 °C. For comparison, different GO dosages (36.9, 61.5, and 184.5 mg) were adopted in the preparation. The CoS_2/RGO composites were denoted as $\text{CoS}_2/\text{GO}-X$ ($X = 1, 3, 5, 15$ %), where X is the mass ratio of GO and CoS_2 . Pure CoS_2 was also synthesized under the same conditions in the absence of GO.

Material Characterizations

The morphology of the CoS_2/RGO nanosheets was observed by field emission scanning electron microscope

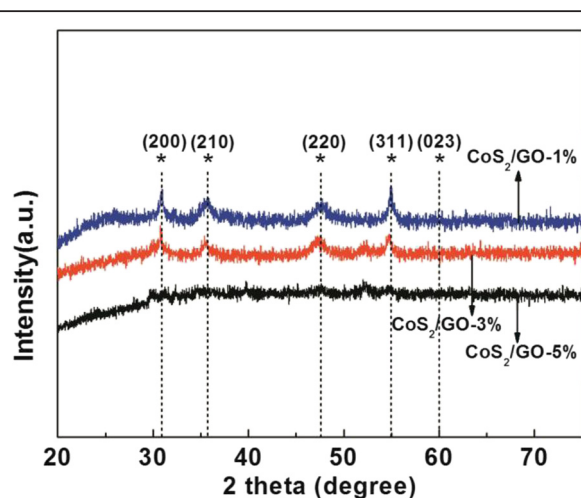


Fig. 4 XRD patterns of CoS_2/RGO -1 %, CoS_2/RGO -3 %, and CoS_2/RGO -5 %

(SEM, FEI Sirion 200) and transmission electron microscope (TEM, JEM 2010, JEOL, Japan). Crystal phase analysis was performed on a PANalytical X-ray diffractometer (XRD). Nitrogen sorption isotherms were determined at 77 K using a porosity analyzer (Tristar 3000, Micromeritics, USA). The Brunauer-Emmett-Teller (BET) area of the samples was obtained using the adsorption branch within the relative pressure (P/P_0) ranging from 0.06 to 0.3. Pore size distribution (PSD) curve was obtained from the desorption branch by the BJH (Barrett-Joyner-Halenda) method.

Electrochemical Measurements

All electrochemical studies were conducted on a CHI660D electrochemical work station in a three-electrode setup using the as-prepared samples as working electrode, a calomel electrode as the reference electrode, and a platinum foil as a counter electrode in 0.5 M H_2SO_4 electrolyte. The oxygen dissolved in the electrolyte was removed by purging with nitrogen for 10 min prior to the experiments. Linear sweep voltammetry was used to determine the electrocatalytic activities of the as-prepared samples (with an active area of 0.5 cm^2) towards the HER at room temperature. HER measurement was also performed using a carbon counter electrode to preclude any Pt contamination. The results showed that the polarization curves from either counter electrode are almost the same. All the potentials were referred to the reversible hydrogen electrode (RHE) without specification.

Results and Discussion

The strategy for the synthesis of the CoS_2/RGO nanosheets is illustrated in Fig. 1. CoS_2 nanoclusters were in situ grown on the RGO surface through a facile hydrothermal process.

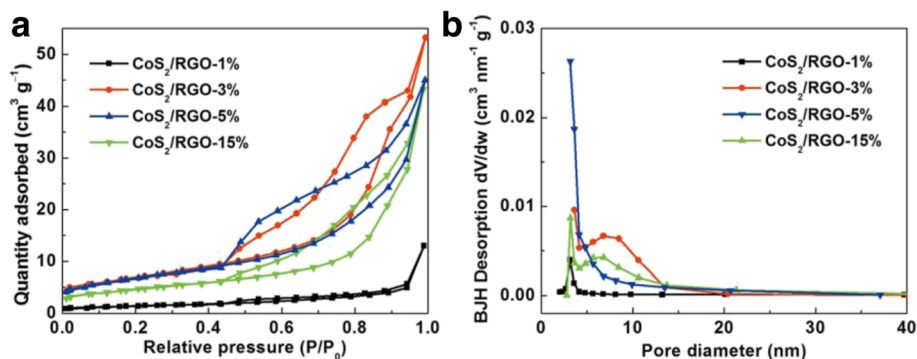


Fig. 5 Nitrogen adsorption-desorption isotherms (a) and PSD curves (b) of CoS₂/RGO-1 %, CoS₂/RGO-3 %, CoS₂/RGO-5 %, and CoS₂/RGO-15 %

In the structure of CoS₂/RGO nanocomposites, the highly conductive graphene and the 2D structure of the composites are beneficial for electron transfer and proton transport, respectively. This is supposed to facilitate the proton reduction at the catalyst/electrolyte interface. Besides, the high dispersion of CoS₂ nanoclusters on the surface of graphene will increase drastically the catalytic active sites for the hydrogen evolution reactions [15–17].

As shown in Fig. 2a–d, CoS₂ nanoclusters grow uniformly on both sides of the graphene sheets with a size of several micrometers, and the size of nanoclusters is about 50–80 nm. It also can be found from Fig. 2e–h that the morphology of CoS₂ nanoclusters changes from vertically dispersed nanosheets to uniformly distributed nanoparticles with the increase of GO dosage. This is because the amount of CoS₂ is only enough to form crystal nucleuses at the large dosage of GO. Higher GO dosage would be beneficial for better dispersion of CoS₂ nanoclusters, contributing to more exposed CoS₂ surface for HER. The high-resolution TEM images demonstrate that most of the CoS₂ nanosheets stand vertically on graphene for CoS₂/RGO-1 % sample (Fig. 3a, b). When the GO dosage was increased to 5 wt%, the shape of CoS₂ turns from nanosheets to nanoparticles. (Fig. 3c, d). The SEM and TEM observations agree with each other.

The crystal phase of the CoS₂/RGO composites was detected by X-ray diffraction, as is presented in Fig. 4. It is shown that all the peaks are attributed to the cubic CoS₂ phase (JCPDS number 41-1471), which should be an active phase for HER. The peak intensity decreases with the rise of GO dosage because of better dispersion of CoS₂ on more RGO. No diffraction peaks for RGO can be hardly detected in the spectrum due to its low content.

The pore texture of the as-prepared samples was determined by nitrogen sorption measurement at 77 K. As shown in Fig. 5a, all the CoS₂/RGO nanocomposites

show typical type IV isotherm and obvious hysteresis loop, revealing their mesoporous nature. The BET specific surface area of CoS₂/RGO-5 % is 26.2 m²g⁻¹ (Table 1), which is the highest among these samples. The larger porosity of CoS₂/RGO-5 % sample is also manifested by the PSD curves in Fig. 5b. The large surface area and pore volume are also supposed to facilitate its catalytic activity to HER.

The as-prepared CoS₂/RGO catalyst coated on glassy carbon was applied as a working electrode for the HER. Pure CoS₂ was also evaluated for comparison. As shown in Fig. 6a, the polarization curves is measured in 0.5 M H₂SO₄ electrolyte with a voltage sweep rate of 5 mV s⁻¹. The polarization curve of CoS₂/RGO-5 % sample shows a small overpotential of 143, 173, and 346 mV at the current densities of 10, 20, and 100 mA cm⁻², respectively, indicating a good HER activity. In contrast, pure CoS₂ exhibits overpotential of 414 mV at a current density of 20 mA cm⁻², which is apparently larger than the overpotential detected for CoS₂/RGO composites, suggesting its worse HER activity. On the other hand, at the potential of 300 mV, the CoS₂/RGO-5 % shows a large cathodic current density of 78.8 mA cm⁻² which is about nine times that of the CoS₂/RGO-1 % electrode (9.0 mA cm⁻²) and far larger than the pure CoS₂ electrode (6.0 mA cm⁻²). The Tafel slope of CoS₂/

Table 1 Surface area and pore volume of the as-prepared catalysts

Samples	S _{BET} ^a m ² g ⁻¹	S _{Micro} ^b m ² g ⁻¹	S _{Meso} ^c m ² g ⁻¹	Pore volume ^d cm ³ g ⁻¹
CoS ₂ /RGO-1 %	5.0	0.7	4.3	0.021
CoS ₂ /RGO-3 %	24.9	0.9	24	0.082
CoS ₂ /RGO-5 %	26.2	0.6	25.6	0.087
CoS ₂ /RGO-15 %	16.4	1.1	15.3	0.067

^aBET specific surface areas

^bMicropore surface areas calculated by t-plot method

^cMesopore surface areas equal to S_{BET} minus S_{Micro}

^dTotal pore volume calculated at the relative pressure of 0.99

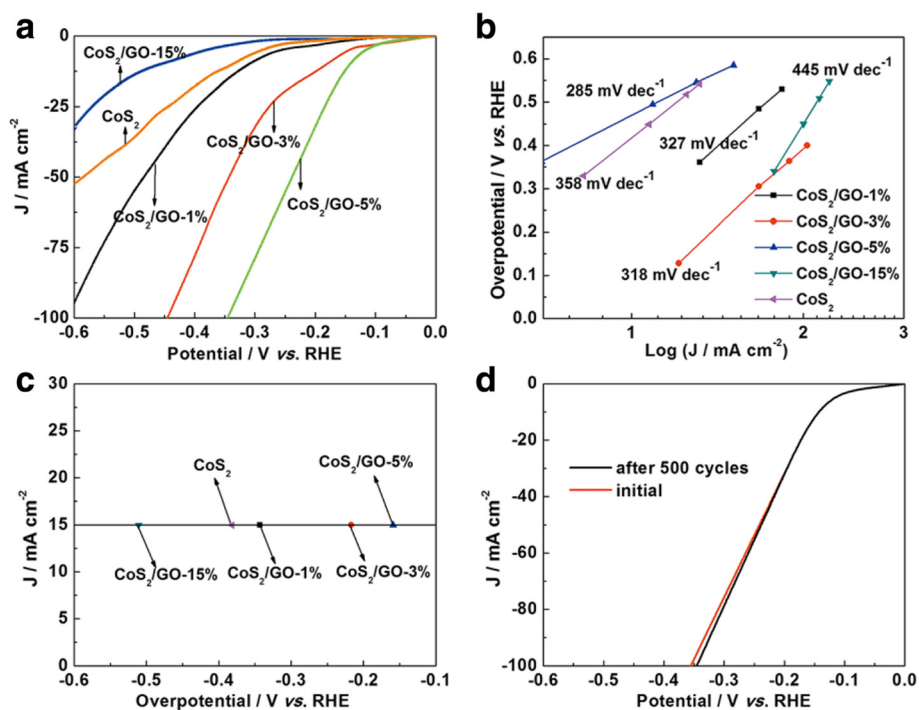


Fig. 6 **a** The HER polarization curves, **b** corresponding Tafel plots, and **c** the HER current density at 15 mA cm^{-2} versus overpotential. **d** Stability test for the CoS_2/RGO -5 % electrode

RGO-5 % in Fig. 6b is 285 mV dec^{-1} , thus leading to a faster increment of the HER rate with increasing overpotential. The polarization curve recorded on CoS_2/RGO -5 % displays the lowest overpotential of 159 mV to get a 15 mA cm^{-2} current density (Fig. 6c), which is smaller than those of the other samples. Therefore, the CoS_2/RGO -5 % with the smallest slope shows the highest activity in the HER. The excellent catalytic performance of CoS_2/RGO -5 % is due to its large surface area, which leads to high dispersion of CoS_2 nanoparticles and more active sites. Compared with pure CoS_2 , the better performance of CoS_2/RGO composites (1, 3, 5 %) also indicates the positive synergistic effect between CoS_2 and RGO for HER.

To evaluate the stability of the CoS_2/RGO -5 % catalyst, the electrode is operated continuously for 500 cycles of potential scans (scan rate 5 mV s^{-1}). The results show that there is no apparent recession of the activity, demonstrating robust catalytic durability of the CoS_2/RGO -5 % catalyst in acidic electrolyte (Fig. 6d). This should be attributed to the interaction between CoS_2 and RGO, which stabilize the CoS_2 nanoparticles in HER process.

Conclusions

In conclusion, we have proposed a novel method to synthesize active CoS_2/RGO nanocomposites by hydrothermal treatment. The obtained sample can be employed

as a catalytic material for the hydrogen evolution reactions. The synergistic effect of CoS_2 and RGO contributes to the good HER activity of these nanocomposites. Besides, this effective synthesis method could be extended to manufacture more promising electrode materials for fuel cell, Li-ion or Na-ion batteries, and supercapacitors.

Competing Interests

The authors declare that they have no competing interests.

Authors' Contributions

WX synthesized the nanocomposites materials and drafted part of the manuscript. YZ conducted the electrochemical assessment of the materials. QX participated in the design of the study and discussion of the results. ZY conceived of the study, participated in its design and coordination, and helped to draft the manuscript. All authors read and approved the final manuscript.

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