Cobalt Phosphide-Embedded Reduced Graphene Oxide as a Bifunctional Catalyst for Overall Water Splitting

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ABSTRACT: It is highly desirable to design high-efficiency stable and low-price catalysts in the electrocatalysis field. Herein, we reported a cobalt phosphate (Co,P)-loaded reduced graphene oxide (rGO) composite catalyst (rGO/Co,P) prepared via the convenient hydrothermal and H2 reduction methods. The rGO/Co,P catalyst reduced at 800 °C (rGO/Co,P-800) shows superior electrocatalytic activities for hydrogen evolution reaction and oxygen evolution reaction in 1.0 M KOH solution, achieving an overpotential of 134 and 378 mV, respectively, at a current density of 10 mA cm−2. Moreover, the catalyst can not only maintain stability for a long time in alkaline solution but also in acid media because of the protection of the rGO layers. The superior performance of this catalyst is attributed to the synergy between the carbon layer and transition-metal phosphides. The Co2P nanoparticles have a high degree of dispersion, which prevents agglomeration, thereby exposing more active sites. Moreover, rGO protects the exposed metal particles while providing more electroconductivity to the material. This work provides an efficient route for the development of bifunctional electrocatalysts with excellent performance and stability, which provides new ideas toward overall water splitting.

1. INTRODUCTION

With the depletion of global traditional energy sources and increase of environmental pollution, the urgent demand for clean and renewable energy sources is increasing.1,2 Hydrogen, as a renewable substitute to fossil fuels, has attracted widespread attention because of its great reserves and more environmentally friendly behavior.3,4 At present, among all hydrogen production methods, electrocatalytic water-splitting process is the most sustainable, effective, and environmentally friendly method. The theoretical voltage of water splitting is 1.23 V, and it is often below the required impressed voltage. This is caused by the sluggish dynamics of the anode and cathode.3,5 It is well known that noble metals work very well for hydrogen evolution reaction (HER) and oxygen evolution reaction (OER).6,7 Nevertheless, because they are relatively rare and expensive, their mass production and practical application are greatly limited.8 In addition, the use of diverse catalysts for the water-splitting reaction of the anode and cathode greatly increases operating procedures and production costs. Hence, there is an urgent need to design high-efficiency and cheap bifunctional catalysts for HER and OER simultaneously.9−11

At present, researchers are actively involved in the preparation of various transition-metal materials (such as Co−,12,13 Mo−,14,15 Ni−,16 based catalysts, etc.) and derivatives such as composites (e.g., −C=17−19−N−,20,21−S−, etc.) as HER and/or OER catalysts. Among these, metal oxides, hydroxides, and other metal compounds are used in OER.22,25 Metal phosphides, carbides, nitrides, and phosphates are used in HER.24,25 So far, cobalt-based catalysts,26 especially cobalt phosphate catalysts,27,28 have received wide attention because of their low-price advantage over noble metals. However, satisfactory results are difficult to be achieved with their catalytic activity and durability, and they are highly susceptible to corrosion in acidic media.29 Researchers are also widely concerned with carbon-based materials because of their high specific area, excellent conductivity, and good stability.30−32 The metal phosphate is embedded in the carbon material carrier, which can effectively prevent the loss of the metal.33 The strong adsorption capacity of the carbon material can prevent dissolved Co from falling into the electrolyte to a certain extent and plays a role in stabilizing Co. Among the carbon-based materials, the graphene-based material is an effective material for electrochemical energy storage and conversion.34−36 Moreover, the composites of carbon-based materials and transition metals will produce a synergistic effect and enhance the catalytic activity of the catalyst.37 Therefore, we propose a strategy to embed spherical Co2P nanoparticles into reduced graphene oxide (rGO) layers, which can well prevent the spherical Co2P nanoparticles from being corroded by the acidic electrolyte. The cobalt phosphate nanoparticles can be loaded on carbon layers to overcome these disadvantages. In addition, because of its unique delocalized

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ACS Omega 2020, 5, 6516−6522

https://dx.doi.org/10.1021/acsomega.9b04143

ACS Omega 2020, 5, 6516−6522

Published: December 5, 2019
Accepted: March 6, 2020
Published: March 23, 2020
conjugated electron system, graphene can strongly conjugate with a specific structure of the catalyst, thereby enhancing the activity of the catalyst. Therefore, using graphene as a carrier supporting a cobalt-based phosphide thereon can improve the catalytic activity. It facilitates the exposure of more active sites, enhances charge transfer, and improves cycle tolerance.

The concentration of hydroxides and protons constantly changes because of water splitting. Further, compared to the high corrosion resistance of the catalyst in an alkaline electrolyte, acidic water electrolysis is of less advantage. Most catalysts can only perform well in either alkaline or acidic solution. Thus, it is necessary to prepare a high-efficiency, durable bifunctional catalyst that exhibits good performance over a broad range of pH. At the same time, the design of the electrolytic cell can be simplified and the production cost can be reduced.

In this work, we report the bifunctional electrocatalyst rGO/Co2P via the simple hydrothermal method and H2 reduction method. Because of the synergy of each component, the as-prepared materials show superior performances and stability not only in alkaline medium but also in acidic media. On the one hand, rGO can increase the electroconductibility and improve the dispersion of Co2P particles. On the other hand, Co2P nanoparticles can increase the electrocatalytic activity of carbon. This provides a low overpotential and high stability for HER and OER. The proposed rGO/Co2P is a highly active and low-cost bifunctional catalyst, which provides an exciting route for overall water splitting.

2. EXPERIMENTAL SECTION

2.1. Synthesis of GO. We adopt the modified Hummer method to synthesize graphene oxide (GO). Graphite powder (2.0 g) and sodium nitrate (NaNO3) (1.0 g) were transferred into a dry three-neck round-bottom flask (500 mL), and then concentrated sulfuric acid (H2SO4) (46 mL) was added. The above mixture was mixed intensely in an ice-water bath for 30 min. Potassium permanganate (KMnO4) (6.0 g) was slowly injected into the system, stirring at 20 °C for 1 h; then the ice bath was removed, stirred at 35 °C overnight, and deionized water (92 mL) was added under magnetic stirring. The solution immediately turned brown. After vigorous stirring, hydrogen peroxide (30 wt %, 20 mL) was added dropwise for 1 h. The mixture was then washed until pure. The finally obtained filter cake is naturally dried to obtain the desired product.

2.2. Synthesis of GO/Co3(PO4)2 Samples. For the preparation of GO/Co3(PO4)2, 0.029 g of cobalt nitrate hexahydrate (Co(NO3)2·6H2O), 0.10 g of sodium dodecyl sulfate, and 1.20 g of urea were ultrasonically dispersed in 10 mL of deionized water. Graphene powder (0.0050 g) was dispersed in 10 mL of deionized water and poured into the above mixed solution at room temperature. A 41 μL of phosphoric acid (H3PO4) was instilled to the mixture and stirred for 1 h until uniform dispersion. The solution was filled in a 20 mL polytetrafluoroethylene liner and transferred to an autoclave and then maintained at 80 °C for 12 h. The hydrothermal product was obtained by centrifugal washing with ethanol for three times and with deionized water once. After complete drying, GO/Co3(PO4)2 was obtained.

2.3. Synthesis of rGO/Co2P Catalysts. The rGO/Co2P catalyst is synthesized by high-temperature reduction. By tube furnace roasting reduction, the GO/Co3(PO4)2 precursors were reduced at 600, 700, 800, and 900 °C for 2 h under N2/H2, respectively. By adjusting the temperature of the tube furnace,
rGO/Co2P-600, rGO/Co2P-700, rGO/Co2P-800, and rGO/Co2P-900 catalysts are obtained without changing the other experimental conditions.

In the above steps, the comparative sample of Co2P is obtained without adding GO at a reduction temperature of 800 °C.

3. RESULTS AND DISCUSSION

3.1. Preparation and Characterization of rGO/Co2P.

GO/Co(NO3)2·6H2O under hydrothermal conditions, and the rGO/Co2P catalysts are obtained by annealing at different temperatures and named as rGO/Co2P-temperature. The representative scanning electron microscopy (SEM) images of the rGO/Co2P samples present a sheet-like structure, with the metal phosphide particles evenly distributed on the rGO layers (Figure S1). Figures 1a and S2 show rGO/Co2P-600−900 samples have similar morphologies, but as the pyrolysis temperature increases, the size of Co2P nanoparticles increases. The sample of rGO/Co2P-800 has Co2P particles of size of around 16−18 nm that are uniformly distributed on the rGO surface (Figure 1b). The Co2P particles of other samples have a size of around 10−25 nm and are distributed at the center of the rGO surface. The high-resolution transmission electron microscopy (HRTEM) image shows that the lattice fringe spacing of 0.21 nm corresponds to the rGO plane (100) (Figure 1c). The elemental mappings are shown in Figure 1d−h, indicating that the spherical Co2P particles are uniformly distributed on the rGO layer. The electron energy spectrum (EDS) of the sample is shown in Figure 1i, further proving the existence of Co, P, C, and O, and the ratio of the elements Co and P is 2:1.

Figure 2a shows the X-ray diffraction (XRD) patterns of different materials. The 2θ value of 10.8° for pure rGO corresponds to the (100) crystal plane of GO (JCPDS 01-081-2220). Several distinct characteristic peaks of Co2P in the rGO/Co2P samples at 2θ of 30−50° are due to the (112), (211), and (020) crystal planes of Co2P (JCPDS: 98-006-6703). According to the characterization, the doping of rGO promotes the growth rate of Co2P along the [211] direction, which can increase the specific surface area and the exposure of active sites, as well as promote electron transfer. The Raman spectra of each catalyst as well as pure rGO and Co2P are shown in Figure 2b. The two different peaks at ~1341 and 1588 cm−1 are ascribed to the D band and G band, respectively. The rGO/Co2P-800 sample has the highest I_D/I_G intensity ratio of 0.98. The results show that more defects are produced during the preparation of rGO/Co2P, which are helpful for improving the electrochemical performance. The nitrogen adsorption−desorption isotherms are displayed in Figure 2c. The sharp peaks at the relative pressure P/P0 < 0.1 in the adsorption isotherms indicate that the rGO/Co2P-800 sample has abundant micropores. Meanwhile, rGO/Co2P-800 has higher Brunauer−Emmett−Teller surface area and pore volumes of about 49.53 m2 g−1 and 0.06 m3 g−1 than bare Co2P (15.53 m2 g−1 and 0.02 m3 g−1), respectively. These microstructures can facilitate the exposure of active sites, having a positive impact on the catalytic efficiency.

The interactions of each component were further studied by X-ray photoelectron spectroscopy (XPS) analysis. Figure 3a shows four main peaks located at 130.2, 284.4, 529.7, and 778.2 eV, corresponding to P 2p, C 1s, O 1s, and Co 2p, respectively. Figure 3b exhibits the C 1s spectra of pure Co2P and the rGO/Co2P-800 sample. The main peak at 284 eV is attributed to the sp2-hybridized graphitic carbon C=C and C−N50 bonds; the peak at 285.4 eV is relatively weak and belongs to the C=O and C−N50 bonds. The peak at 287.7 eV is attributed to the C=O bond. After combining with Co2P, the C 1s peak shifts toward the direction of low binding energy, indicating that Co2P is more likely to transfer electrons to the rGO layer. The Co 2p spectrum shows two peaks at about 779.12 and 793.96 eV that can be ascribed to Co 2p3/2 and Co 2p1/251 (Figure 3c). The Co 2p spectrum of rGO/Co2P-800 can be divided into four peaks. The peaks at 778.2 and 793.3 eV are ascribed to Co54. The peaks at 781.3 and 796.5 eV are related to Co55. The surface of the metal Co was oxidized, which is the reason for the existence of Co2+.52 The peaks at 785.8 and 802.1 eV are assigned to the satellite peaks from the shakeup processes.53 When combined with rGO,
the peaks corresponding to Co$^{2+}$ increase obviously. This shows that rGO can promote the reduction of Co$_2$P. As shown in Figure 3d, the two characteristic peaks at 129.9 and 130.4 eV are attributed to the 2p$_{3/2}$ and 2p$_{1/2}$ peaks of P.$^5$ After combining with rGO, the P 2p peaks move toward the direction of high binding energy. This is consistent with the XPS variation of the above Co element. Such changes of the Co surface electronic density demonstrate an interplay between Co$_2$P nanoparticles and rGO layers. Moreover, rGO is more likely to facilitate the adjustment and control of the electronic configuration of the rGO surface. In summary, the combination of rGO and Co$_2$P is beneficial to the improvement of the catalytic efficiency.

3.2. Electrochemical Performance of HER and OER. We used a three-electrode system to study the electrocatalytic performance of HER and OER in 1 M KOH, 0.5 M H$_2$SO$_4$, and 1.0 M phosphate-buffered saline (PBS) electrolytes. First, we tested and measured a series of rGO/Co$_2$P samples in 1.0 M KOH. Figure 4a shows that the rGO/Co$_2$P-800 catalyst exhibits a high catalytic performance with overpotentials of 134 and 304 mV at 10 and 100 mA cm$^{-2}$ (defined as $\eta_{10}$ and $\eta_{100}$), respectively. The rGO/Co$_2$P-600, rGO/Co$_2$P-700, and rGO/Co$_2$P-900 samples are also prepared for comparison. They provide overpotentials of 206, 188, and 178 mV at $\eta_{10}$ higher than that of rGO/Co$_2$P-800. In addition, 20 wt% Pt/C, bare rGO, and Co$_2$P are also tested for comparison. The overpotential of the composite catalyst is greatly improved relative to the comparison samples of rGO (492 mV) and Co$_2$P (478 mV), and compared with similar non-noble metal phosphides, it also has better catalytic activity (Table S1). Figure 4b exhibits the Tafel plots of the rGO/Co$_2$P samples in alkaline solution. Compared to rGO/Co$_2$P-600 (99 mV dec$^{-1}$), rGO/Co$_2$P-700 (62 mV dec$^{-1}$), and rGO/Co$_2$P-900 (64 mV dec$^{-1}$), rGO/Co$_2$P-800 shows a more lower Tafel slope of 58 mV dec$^{-1}$, which is close to that of commercial Pt/C (37 mV dec$^{-1}$).

Besides, the catalyst is further examined in the acid electrolyte (0.5 M H$_2$SO$_4$, pH = 0). Figure 4b exhibits that the rGO/Co$_2$P-800 sample has a low $\eta_{10}$ of 189 mV, which is superior to the $\eta_{10}$ values of rGO/Co$_2$P-600 (235 mV), rGO/Co$_2$P-700 (216 mV), rGO/Co$_2$P-900 (209 mV), and Co$_2$P (345 mV). When Co$_2$P is combined with rGO, the catalytic activity is significantly increased. Such an improved catalytic performance is likely because of the following reasons: (a) in terms of components, the Co$_2$P particles formed by phosphating treatment can effectively increase the defects and produce a high density of active centers; (b) structurally, Co$_2$P nanoparticles are beneficial with the exposure of active sites because of their uniform size and high dispersion on the rGO layers, and a high temperature can increase the interaction between Co$_2$P and rGO; and (c) rGO can effectively improve the conductivity of materials.

Electrochemical impedance spectroscopy (EIS) is performed in an alkaline solution to further investigate the interfacial electron-transfer kinetics of the catalyst for HER (Figure S6a). rGO/Co$_2$P-800 has the lowest charge-transfer resistance ($R_n$) of 25.2 $\Omega$ compared to rGO/Co$_2$P-600 (58.1 $\Omega$), rGO/Co$_2$P-700 (34.1 $\Omega$), and rGO/Co$_2$P-900 (39.3) (Table S2). It is shown that the sample of rGO/Co$_2$P-800 can substantially improve the interfacial intrinsic HER dynamics.

Stability is an important criterion to judge whether an electrocatalyst can be used in practice. The durability of rGO/Co$_2$P-800 was tested by recording the polarization curves at 1st, 1000th, 2000th, 4000th, 8000th, and 10,000th cycles (Figure 4c). The result shows the excellent durability of the rGO/Co$_2$P-800 catalyst after 1000 cyclic voltammetry (CV) cycles; the overpotential of each cycle has no obvious attenuation compared with the previous one, not only in alkaline solution but also in the acidic electrolyte. Pure Co$_2$P was examined under the selfsame conditions (Figure S7), and the results showed that the stability of the samples after compounding with rGO was significantly improved. In addition, the stability of rGO/Co$_2$P-800 was evaluated using chronometric technology. After 48 h of unceasing operation at 10 mA cm$^{-2}$, the current density remained almost unchanged. The result also indicates that rGO/Co$_2$P-800 has excellent durability and stability. These two tests were carried out in acidic media, and the superior durability and stability of rGO/Co$_2$P-800 were also confirmed (Figures 4f and 5c). To illustrate, we attach a TEM image of the sample catalyzed in an acid electrolyte (Figure S8), which is not significantly different from that before catalysis; this also shows that the sample has excellent stability.

After 400 s of operation at 1.0 M KOH, the poisoning tests were performed in a mixed solution of 1.0 M KOH and sodium thiocyanate. Figure S9 shows that rGO has no obvious attenuation. Because of the absence of a carrier support, the current density of Co$_2$P falls from 10 mA cm$^{-2}$ to approximately 0 mA cm$^{-2}$. The current density of the rGO/Co$_2$P material shows less attenuation because of the protection of the carbon layers. In addition, the C-based support contributes to the dispersion of Co$_2$P nanoparticles, producing highly active sites to catalyze water electrolysis.

The overall water decomposition requires excellent OER catalytic performances, and OER is measured in 1.0 M KOH. Commercial RuO$_2$ was used as the sample for comparison. The $\eta_{10}$ values of rGO/Co$_2$P-600, rGO/Co$_2$P-700, rGO/Co$_2$P-800, and rGO/Co$_2$P-900 were 432, 409, 378, and 405 mV,
Co2P-800 catalyst shows a relatively higher performance. The voltage gap of rGO/Co2P-800 (1.78 V) is close to that of RuO2 (1.64 V) and Pt/C (1.72 V) (Figure 6). rGO/Co2P-800 shows a higher TOF value (0.041 s−1) for HER and 387 mV for OER. The sample shows superior catalytic activity, which is reflected in its TOF value (η100 of 0.5 and 0.62 s−1 for HER and η100 of 0.041 s−1 for OER). Meanwhile, the sample also maintains excellent electrochemical stability after long cycle tests, which is ascribed to its unique carbon ring protection. This work proposes an exciting new route to develop high-active and stable bifunctional electrocatalysts for renewable clean energy systems.

4. CONCLUSIONS

In conclusion, we successfully prepared highly efficient rGO/Co2P catalysts with superior catalytic performances and stability for overall water splitting using the convenient hydrothermal and H2 reduction methods. We explored different reduction temperatures and found the optimum one (rGO/Co2P-800). Through the synergistic effect between rGO and Co2P, the catalytic performance is significantly improved. rGO/Co2P-800, as a bifunctional catalyst, displays small η10 of 134 mV (in 1 M KOH) and 189 mV (in 0.5 M H2SO4) for HER and 387 mV for OER. The sample shows superior catalytic activity, which is reflected in its TOF value (η100 of 0.5 and 0.62 s−1 for HER and η100 of 0.041 s−1 for OER). Meanwhile, the sample also maintains excellent electrochemical stability after long cycle tests, which is ascribed to its unique carbon ring protection. This work proposes an exciting new route to develop high-active and stable bifunctional electrocatalysts for renewable clean energy systems.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b04143.

Materials characterization instrument; parameter details of electrochemical measurements; SEM images of bare rGO, Co2P, and rGO/Co2P-600–900 samples; TEM images of rGO/Co2P-600, rGO/Co2P-700, and rGO/Co2P-900; XPS spectra and EIS Nyquist curves of rGO/Co2P-600–900 samples in 1.0 M KOH; current–time curves of the samples before and after the addition of SCN− ions; CV curves; chronopotentiometry testing of pure Co2P; metal-based electrocatalysts for HER and for OER in 1.0 M KOH solution; and electrochemical and electrocatalytic properties toward HER and OER of catalysts in 1 M KOH solution and 0.5 M aqueous H2SO4 solution (PDF)

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Figure 6. Polarization curves of rGO/Co2P-800, 20 wt % Pt/C, and RuO2 for overall water splitting performance in the three-electrode system.
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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
Financial supports were from the National Natural Science Foundation of China (nos. 51871090, U1804135, U1671080, U1471065, 21403053, and U1404503). Leading talents of science and technology innovation in Henan Province (194200510019) and Key projects of Henan Education Committee (19A150025) are acknowledged.

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