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Advanced electrocatalytic properties of nano-CoWO₄ and CoWO₄/nitrogen-doped graphene oxide as the anode materials of water electrolysis

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ABSTRACT

The electrocatalytic performance of tungsten-based compounds was significantly enhanced via the crystal facets engineering, defect tuning, and combination with conductive 2D materials. Stating from Na₂WO₄·2H₂O and CoCl₂·6H₂O we synthesized two types of nano-CoWO₄ with different morphologies. The products were characterized by XRD, FE-SEM, HRTEM, XPS and EDS in details. The electrochemical performance of CoWO₄ nanorods was obviously superior to CoWO₄ nanodots due to the enhanced electrochemical active areas. Furthermore, CoWO₄ and nitrogen-doped graphene oxides (NGO) composites were obtained under the similar synthetic conditions. As expected, the CoWO₄/NGO composites showed significant improvement on electrochemical properties.

1. Introduction

The oxygen evolution reaction (OER) has attracted intensive research interests in the last decades, because of its critical role in various energy conversion and storage technologies, such as photocatalytic splitting or electrolysis of water for hydrogen production [1], regenerative fuel cells [2], rechargeable metal-air batteries, and many more [3,4]. The water electrolysis includes hydrogen evolution on cathode and oxygen on anode, and its reaction rate is mainly determined by the complex and kinetically sluggish 4-electron transfer process between electrodes and reactants [15]. The electrocatalytic activity of CoWO₄ has been very few reported.

On the other hand, graphene is a two-dimensional nanomaterials with a single-layer structure, and has unique properties such as good chemical stability, excellent electrical conductivity, and high surface area. The electrochemical performance of the materials can be greatly enhanced by electrochemical hydrogen generation, oxygen generation or reduction, and supercapacitors due to their unique electrochemical properties [11–13]. In recent years, cobalt tungstate CoWO₄ has been reported as a potential materials for corrosion resistant electrode [14], and anodic oxygen evolution electrocatalyst [16]. The OER reaction is a four-electron transfer process with complicated mechanism and slow kinetics. The main function of OER electrocatalyst is to adsorb reactants on the surface to form adsorption intermediates, to promote charge transfer between electrodes and reactants [15]. The electrocatalytic activity of CoWO₄ is closely related to its morphology. So far to our knowledge, the morphology-dependence of electrocatalytic oxygen production activity of CoWO₄ has been very few reported.

On the other hand, graphene is a two-dimensional nanomaterials with a single-layer structure, and has unique properties such as good chemical stability, excellent electrical conductivity, and high surface area. The electrochemical performance of the materials can be greatly enhanced by combinding with graphene [17,18]. However graphene has poor water solubility, and it is difficult to form homogeneous phase in solution. In contrast, graphene oxide can be uniformly dispersed in an aqueous solution due to the hydrophilic groups attached on surface. However, graphene oxide is easy to accumulate and agglomerate, resulting in a decreased effective specific surface area of the catalyst. In addition, the conductivity of graphene oxide is much weaker than that of graphene.

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Therefore, the electrochemical properties of tungstate composites constructed with graphene oxide may not be well expected.

In this work, we adopted nitrogen-doped graphene oxide (NGO) as the carrier, since doping the nitrogen atoms into the graphene oxide can increase its electrical conductivity to improve the electrochemical oxygen production performance of the composites [19]. We firstly synthesized two types of nano-CoWO4 with different morphologies: the nanodots and nanorods, then investigated the morphology-dependence of electrocatalytic oxygen evolution activity of the two different nano-CoWO4. The CoWO4 nanorod with better performance was selected to be compounded with NGO by one-pot method. The results showed that the performance of composite materials is significantly better than the pure CoWO4 nanorods. Our work may provide a useful reference for the design of high-performance CoWO4-based electrocatalytic oxygen evolution catalysts.

2. Methods

2.1. Materials

The Na2WO4⋅2H2O, CoCl2⋅6H2O, ammonia, anhydrous ethanol, potassium hydroxide, NaNO3, H2SO4, graphite powder, and KMnO4, all of analytical grade, were purchased from Aladdin Reagent Co., Ltd. The H2O2 of analytical grade and HCl of 38% were purchased from Sinopharm Reagent Co., Ltd. The high purity water were prepared on Elsi5-Milli-Q of Millipore Co., US.

2.2. Synthesis of nano-CoWO4 and anode materials

2.2.1. CoWO4 nanodots

The CoCl2⋅6H2O of 1 mmol was dissolved in 20 mL water solution (labeled as A); the Na2WO4⋅2H2O was dissolved in 20 mL water to form transparent solution (labeled as B). The B was added into A to form a purple suspension, which was then transferred into a high pressure reactor with Teflon liner (V = 50 mL). The reactor was then placed in oven at 180 °C. After 12 h reaction, the product was cooled to room temperature, and rinsed several times by high purity water and anhydrous ethanol, and then placed in vacuum drier ready for use.

2.2.2. CoWO4 nanorods

The CoCl2⋅6H2O of 1 mmol was dissolved in 20 mL water solution (labeled as A); the Na2WO4⋅2H2O was dissolved in 20 mL water to form transparent solution (labeled as B). The B was added into A to form a purple suspension, which was then transferred into a high pressure reactor with Teflon liner (V = 50 mL). Ammonia of 0.5 mL was then added into the reactor. With continuous mixing, the reaction was proceeded at 180 °C for 12 h. The product was cooled to room temperature, rinsed several times by high purity water and anhydrous ethanol, and placed in vacuum drier ready for use.

2.2.3. Graphene oxide

The graphene oxide was prepared from graphite powder by improved Hummers method. The graphite of 10 g and sodium nitrate of 5 g was added into 230 mL cold concentrated sulfuric acid, then 30 g KMnO4 was slowly added into solution with the system in continuously stirred ice water bath, where the temperature of the mixture was controlled below 20 °C. After stirring the mixture for 35 min at 35 °C, 460 mL deionized water was slowly added in to raise the temperature to 95 °C and maintained for 1 h. Then 80 mL 30% H2O2 and 720 mL deionized water were added into at the same time. Filtered the solution while it was still hot, then the solid product was washed with 1 M HCl solution several times until it was sulfate free. After washing with deionized water 3-4 times, the product was centrifuged at 6000 RPM for 10 min to remove the residue. The graphene oxide solution was then collected and dispersed in aqueous solution (10 mg mL −1) and ready for use.

2.2.4. Nitrogen-doped graphene oxide

The graphene oxide solution (5 mg mL −1) of 0.25 mL, 0.5 mL and 1 mL were added into the Teflon liner of high pressure reactor (V = 50 mL) respectively, and mixed with high purity water of 35 mL. The system was processed by ultrasonic dispersion for 1 h. Then 0.5 mL ammonia was added into and stirred for 15 min. The reactor was then tightly sealed and put into oven at 180 °C for 12 h. After reaction, the product was cooled to room temperature, rinsed several times by high purity water and anhydrous ethanol, and placed in vacuum drier ready for use.

2.2.5. CoWO4/NGO composite

The graphene oxide solution (5 mg mL −1) of 0.25 mL, 0.5 mL, 1 mL were added into the Teflon liner of high pressure reactor (V = 50 mL) respectively, and mixed with high purity water of 35 mL. The system was processed by ultrasonic dispersion for 1 h. The CoCl2⋅6H2O of 1 mmol was added and stirred to be even, then Na2WO4⋅2H2O of 1 mmol was added and stirred for 15 min, followed by adding 0.5 mL ammonia into the reaction kettle with another 15 min stirring. After removing the magnetic stirrer, the reactor was tightly sealed and put into oven at 180 °C for 12 h. After reaction, the product was cooled to room temperature, rinsed several times by high purity water and anhydrous ethanol, and placed in vacuum drier ready for use.

2.3. Preparation of electrode

2.3.1. Preprocessing of the glassy carbon electrode

Glassy carbon electrode (diameter = 3 mm) was polished by metallographic sandpaper, and then polished by Al2O3 powder with the particle size of 0.3 μm and 0.05 μm respectively. After washing away the dirt on the surface, the electrode was washed by secondary distilled water several times. At last, the electrode was treated by ultrasonics for 5 min by anhydrous ethanol and secondary distilled water respectively. The dried electrode was then placed in vacuum drier ready for use.

2.3.2. Preparation of the working electrode

The catalyst of 5 mg was dispersed in 1 mL the 2 : 1 water and iso-propanol solution, and the 35% (mass percentage) perfluoropolymer sulfonic acid solution (Nafion) of 40 μL was added, followed by a 30 min ultrasonic treatment to reach a homogenous system. Dripped this solution of 5 μL onto the surface of glassy carbon electrode to form a catalyst layer with a load density of about 0.34 mg/cm2, and the electrodes were naturally dried in the air.

2.4. Characterization

The Raman spectra was carried on the Raman instrument of Renishaw, UK. The scanning electron microscopy (SEM) was carried on NanoSEM2000 of FEI, US. The X ray diffractometer (XRD) was carried on Advanced D8 of Bruker Co., Germany. The high resolution transmission electron microscopy (HREM) and X ray energy dispersive spectroscopy (EDS) were carried on JEOL-2100F of JEOL Co., Japan. The specific surface area test (BET) was carried on ASAP2020 of Micromeritics Instrument Co., US. The X ray photoelectron spectroscopy (XPS) was carried on ESCALAB 250 of Thermo Fisher Co., US. Electrochemical test of cyclic voltammetry (CV) and linear sweep voltammetry (LSV) was carried on CHI660D of Beijing Hua Pu Tian Technology Co., China. The three electrode system was adopted: a platinum electrode with diameter of 1 mm was used as the counter electrode, a calomel electrode as the reference, and a glassy carbon electrode with diameter of 3 mm as the working electrode. The electrode is 0.5 M KOH (pH = 13.7), and the sweep speed is 10 mV/s. The electrode potential accorded to the RHE standard, E(RHE) = E(SCE) + 0.242 + 0.059 × pH.
3. Results and discussion

3.1. The morphology and structure of the two types of nano-CoWO₄

We firstly need to figure out which type of nano-CoWO₄ is better for the application on anode. The morphology and structure of CoWO₄ nanodots and nanorods were characterized as illustrated respectively in Fig. 1 and Fig. 2. Fig. 1a presents the SEM graph of nano-CoWO₄ prepared without ammonia, and particles with an even size of about 50 nm can be observed. Fig. 1b is the high-resolution TEM picture at the edge of CoWO₄ particles, which reveals the clear crystal lattice. Element scanning diagrams show that the elements of Co, W and O evenly distribute throughout the sample, as shown in Fig. 1d–f.

Fig. 2a is the SEM graph of nano-CoWO₄ prepared with ammonia. The final product can be observed as nanorods with the length of about 200–400 nm, and the diameter of about 20 nm. Fig. 2b is the HRTEM at the edge of nanorods, similarly the well observable crystal lattice implies a good crystallinity. Element scanning shows that the elements of Co, W and O are also evenly distributed throughout the nanorods, as shown in Fig. 2d–f.

The XRD was carried on in order to identify the phases of two different products. Fig. 3 presents the XRD patterns of nanodots and nanorods. The main diffraction peaks in the diagram can be characterized as monoclinic crystal, which is consistent with the standard card (JCPDS No.15–0687). And there are no other miscellaneous peak, such as Co₃O₄ or WO₃, indicating that the phase of two samples are sufficiently pure.

We have done the X-ray energy dispersive spectroscopy to determine the elements composition and stoichiometric ratio of the two types of nano-CoWO₄. Fig. 4a and b shows the EDS of CoWO₄ nanodots and nanorods, the spectra confirm that both are composited by W, Co and O with the ratio of 1:1:4.

The XPS element analysis was done to confirm the valence state of elements in two types of nano-CoWO₄. The spectra of Co 2p, W 4f and O 1s are presented in Fig. 5a–c. In Fig. 5a, there are two strong peaks at 783.2 eV and 797.1 eV, corresponding to Co 2p₃/₂ and Co 2p₁/₂, which agrees to the binding energy of Co²⁺ [20]. In Fig. 5b, two strong peaks at 35.3 eV and 37.5 eV can be observed, corresponding to W 4f₁/₂ and W 4f₃/₂, which agrees to the binding energy of W⁶⁺ [20]. The XPS results basically confirm the similar valence states of nanodots and nanorods.

![Fig. 1. The SEM image of CoWO₄ nanodots synthesized without ammonia (a), the HRTEM image recorded on the edge of a single CoWO₄ nanodots (b), the STEM image (c), and the element mapping of CoWO₄ (d–f).](image-url)
Fig. 2. The SEM image of CoWO₄ synthesized with use of ammonia (a), the HRTEM image recorded on the edge of a single CoWO₄ nanodots (b), the STEM image (c), and the element mapping of CoWO₄ (d–f).

Fig. 3. The XRD pattern of two types of nano-CoWO₄ and their respective standard data obtained from JCPDS No. 15-0867.
3.2. Electrochemical properties of the two types of CoWO₄ nano particles

Fig. 6a shows the LSV performance of two types of nano-CoWO₄, and it is clear that the nanorods is better on oxygen evolution than the nanodots, the current density of the former can reach 10 mA cm⁻² at 1.89 V (vs RHE), while the latter one only reached 6.42 mA cm⁻², and also the overpotential of nanorods is lower. Moreover, Fig. 6b and c shows the LSV test on the two samples before and after 500 cycles, which indicates the electrochemical stability of both materials.

It is reasonable to hypothesize that the morphologies of two nano-CoWO₄ caused the different oxygen evolution properties. To further verify this, we compared the specific surface area and electrochemical active area of two materials. The pore size distribution is shown in Fig. 7a, and Fig. 7b is the nitrogen adsorption desorption curve. The specific surface area of CoWO₄ nanodots is 17.6 m²/g, while it is 30.9 m²/g for nanorods. In addition, we tested the electrochemical active area by cyclic voltammetry in the range of 0–0.05 V (vs SCE) at scan speeds of 20–100 mV/s, and the results are shown in Fig. 8a-b. It can be seen that the electrode has no oxidation reduction peak in the range of test interval, and the current density of anode and cathode are basically symmetrical with a good reversibility. Five linearly related data points as shown in Fig. 8c at 0.025 V (vs SCE). The slope is the Cidl of electrode.
the surface roughness of which can be calculated by 
\[ R_f = \frac{C_{dl}}{(60 \times 10^{-6} / \text{cm}^2)} \]. The electrochemical active area of nanorods is calculated to be 1.35 times larger than that of nanodots (Please refer the fitting details in the Fig. 8c.). In this way, the data of specific surface area and electrochemical active area may confirm that the morphology of nano-CoWO_4 significantly impacts the electrocatalytic oxygen generation performance.

3.3. The characterization of graphene oxide and NGO

The XRD analysis on GO is shown in Fig. 9. A strong peak can be observed at \( \theta = 11.6^\circ \), and it gives the distance between GO layers \( d = 0.78 \text{ nm} \) by the Bragg equation. Comparing to the \( d = 0.34 \text{ nm} \) of standard graphite layers, this larger distance is due to the oxygen-containing functional groups inserted in the layers during the oxidization.

Fig. 10 shows the SEM graph of GO and NGO. Clearly the surface of GO is relatively more smooth than NGO, which has obvious wrinkles and the pieces are more fractal, this is because the nitrogen doping destructs and twists the graphene plane. Furthermore, we observed discharging phenomenon during the SEM photographing on GO but not on NGO, meaning a better conductivity of NGO. And both the factors of larger surface area and higher conductivity imply a better electrochemical performance.
To further investigate the chemical composition of GO and NGO we prepared, the XPS analysis has been done and the result of C 1s of GO is shown in Fig. 11a, and the N 1s of NGO is shown in Fig. 11b. The fitting analysis in Fig. 11a indicates four states of carbon: C=C (284.7 eV), C–N (285.8 eV), C–O (286.5 eV) and O–C–O (289.9 eV) [17]. Meanwhile, the fitting analysis in Fig. 11b indicates three states of nitrogen: the pyridine nitrogen at 398.3 eV, the pyrrole nitrogen at 399.8 eV, and the graphitized nitrogen at 400.9 eV [18,19]. Pyridine and pyrrole N is due to the substitute of carbon atom by nitrogen on the graphene net. The existence of these three types of N confirms the formation of C–N bond during the reaction, and the nitrogen was successfully doped into the GO.

Generally, the G peak in Raman spectra presents the sp2 hybridization on plane, and D peak presents the sp3 hybridization in tetrahedron and disordered carbon, and the sp2 hybridization at the edge of graphite, and the ratio of intensity of D and G peak (ID/IG) are considered to characterize the degree of disorder in graphite-type materials, a larger ratio implies more defects and disordered atoms. The Raman spectra of GO and NGO are shown in Fig. 12, it can be seen that, for GO the D peak at 1350 cm\(^{-1}\) and G peak at 1570 cm\(^{-1}\) are relatively smaller, and the 2D and D + G peaks are also not obvious, meaning a less defective GO structure, comparing that for NGO the D and G peak are much higher with a blue shift, and the 2D peak is more obvious. This confirms that the nitrogen atoms are doped into the GO and make it more defective.

### 3.4. The characterization of the CoWO\(_4\) nanorod and NGO composite

The samples which loaded 0.25 mL, 0.5 mL and 1 mL NGO solution of 5 mg/mL were labeled as sample S1, S2 and S3. To confirm that the addition of NGO of decent amount does not alter the crystal phase of nano-CoWO\(_4\), we performed the XRD tests on three samples, and the results are shown in Fig. 13. It can be seen that, regardless of the amount of NGO added, the main diffraction peaks accord well to the JCPDS No. 15–0687, which is the monoclinic phase of CoWO\(_4\). Fig. 14 shows the SEM graphs and S1, S2, and S3 and the CoWO\(_4\) nanorods, the direct observations on the pictures also confirms that the addition of NGO does not affect the morphology too much.

Furthermore, it maybe helpful to present for the audience’s reference that: we have also prepared the CoWO\(_4\) and GO composite, however found it showing non-intriguing property comparing to the NGO, just like the low performance of GO presented in the previous section, therefore we choose to discard the results of CoWO\(_4\) and GO composite, including the characterization and morphology in this section, and OER performance in the next section.
3.5. Electrochemical OER performance of the two types of nano-CoWO4/NGO composite

The LSV results shown in Fig. 15 clearly indicate that the attendance of NGO significantly improves the electrochemical performance of CoWO4 nanorods, however not in a proportional way. The current density increases with amount of NGO below 0.5 mL, and decreases after that, which yields the S2 to be the optimal sample. The ultra thin thickness and conjugated $\pi$ bond may increase the charge transportation and subsequently the oxygen evolution reaction speed [17]. On the other hand, more percentage of NGO may occupy too much space and the surface area of nano-CoWO4, and therefore reversely obstruct the electrochemical performance.

4. Conclusion

Starting from CoCl$_2$\cdot6H$_2$O and Na$_2$WO$_4$\cdot2H$_2$O we synthesized two different nanoparticles of CoWO$_4$: the nanodots and nanorods. The results were characterized by XRD, FE-SEM, HRTEM, XPS and EDX. The experimental results showed a better electrochemical OER performance of CoWO$_4$ nanorods. The CoWO$_4$/NGO composites were synthesized in the similar process, and the composite materials showed a better
electrochemical performance than the pure CoWO₄ nanorods, due to the excellent electrical properties of NGO.

Data availability

The data will be delivered upon request.

Credit author statement

Zhuping Nie: Experiments, Writing - Original Draft; Weiwei Ding and Boxin Zhou: Experiments assistance; Ran Huang: Writing- Reviewing and Editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors state that there is no competing interests.

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Fig. 14. The FE-SEM images of CoWO₄ nanorods (a), S1 (b), S2 (c) and S3 (d).

Fig. 15. The LSV curves of S1, S2, S3 and the pure CoWO₄ nanorods.
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