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Graphene with cobalt oxide and tungsten carbide as a low-cost counter electrode catalyst applied in Pt-free dye-sensitized solar cells

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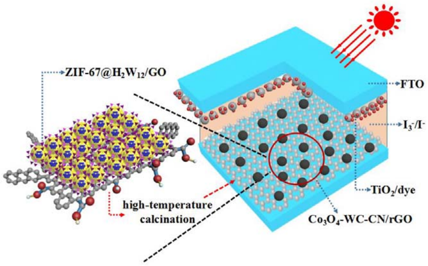
HIGHLIGHTS

- The preparation method of new compounds was economic, non-toxic and simple.
- A strategy for simultaneous breaking of MOF and POMs to obtain nanomaterial.
- Homogeneous dispersion of Co_3O_4 and WC composite on graphene is achieved.
- The catalytic activity of Co_3O_4-WC-CN/rGO as CE is higher than that of Pt.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, the nanomaterial Co_3O_4-WC-CN/rGO (CN is nitrogen-doped carbon; rGO is reduced graphene oxide), as an efficient alternative to platinum for the counter electrode (CE), has been prepared by the high temperature calcination of the $Na_6H_2W_{12}O_{40}{\cdot}H_2O$ (H_2W_{12}) embedded metal-organic framework in argon gas and air atmosphere. It shows high catalytic activity as the CE in the dye-sensitized solar cells (DSSCs), which is due to the excellent catalytic activity of Co_3O_4-WC and high conductivity of rGO. The photoelectric conversion efficiency (PCE) of DSSC with Co_3O_4-WC-CN/rGO as the CE is 7.38%, which is superior to that of Pt as the CE (η = 6.85%).

1. Introduction

With the development of modern society, the energy crisis is one of the key issues that mankind will face at present. A very straightforward way to solve the energy crisis is to make full use of solar energy, which is rich, pollution-free and economical [1–5]. Through the efforts of countless scientists, solar energy can be effectively converted into heat and electricity using excellent heat conduction and photoelectric conversion devices. DSSCs and perovskite solar cells (PSCs) are two promising photoelectric conversion devices. After several years of development, PSCs have undergone rapid development, the efficiency of which is now an impressive 22.1% [6]. Nevertheless, after more than 20 years of development, DSSCs has its own advantages. The production process of DSSCs is simple, non-toxic, pollution-free, and does not require high energy consumption such as vacuum preparation process. More importantly, DSSCs have a long working life due to their good stability. Therefore, DSSCs meet the needs of photovoltaic industry for low-cost solar cell technology, and have broad application prospects [7]. Since M. Grätzel et al. firstly reported the DSSCs in 1991, the energy conversion efficiency of DSSCs has been reached up to 13% over the past few years [8,9]. The DSSCs mainly include the following four parts: photoanode (mainly including TiO_2 or ZnO), dye (mainly including bipyridine metal complexes, carboxylic acid polypyridyl phthalocyanine, porphyrins), redox electrolyte (mainly including I_3^-/

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I^-) and CE (mainly including Pt) [10]. At present, two major issues in the DSSCs should be resolved until it is realized commercialize. On one hand, the preparation of high efficiency and noble metal-free dyes is still a major challenge [11,12]. Another important aspect, the resources of Pt as CE existed on the earth is very limited, and looking for a kind of catalyst material which can replace scarce Pt is urgent to be solved. The CE materials in the DSSCs must show excellent catalytic activity for the reduction of I_3^- and good electrical conductivity [13,14]. Co_3O_4 is an excellent catalyst, which has been widely applied in the electrocatalytic water oxidation, supercapacitor, lithium ion batteries and so on [15]. However, the Co_3O_4 applied in the CE of DSSCs is rare. Sharma et al. prepared Co_3O_4 nanoparticles by green synthesis method, the PCEs of the DSSCs was 0.66% [16]. In 2016, the Co_3O_4 was loaded on the graphene as the CE of DSSCs, the PCEs was raised to 5.79% [17]. Recently, WC materials have been widely used in electrocatalysis and DSSCs due to its Pt-like properties. Ma et al. employed large-grained WC as the CE material and the PCE of DSSCs was 5.35%, while that of the Pt-based DSSCs is 7.89%. But they loaded WC on the mesoporous carbon, the PCE of the DSSCs was improved to 8.18% [18]. Lee et al. synthesized the small particle size WC by two different methods, and the specific surface area of the synthesized WC was greatly enlarged. The PCEs of the DSSCs reached 7.01% and 6.61% [19]. Therefore the key of obtaining the efficient DSSCs is to get high dispersion WC or Co_3O_4 nanomaterials. On the basis of the above research, we find that it is an opportunity to develop a way to prepare the composite using synergistic catalysis between Co_3O_4 and WC nanomaterial. In addition, the electrode material should be a nanomaterial with porous characteristic, which ensured that more active spots can be exposed to obtain relatively high catalytic activity. So it is also a challenge to get Co_3O_4 and WC nanomaterials at the same time.

Metal-organic frameworks (MOFs) are a class of crystal mesoporous material possessing high specific surface area. In recent years, numerous excellent carbon nanomaterials/metallic oxide catalysts are derived from MOFs [20]. Although MOFs materials have these advantages, the materials derived from MOFs show a relatively poor conductivity. Graphene oxide (GO) is often used as the carrier for these materials in order to solve this problem. GO has good electrical conductivity and stability, which can ensure that the composite nanomaterials have excellent catalytic properties with their respective advantages [21].

In this paper, the ZIF-67 (Co(Hmim)$_2$, Hmim = 2-methylimidazole) was used as the template and cobalt source, H_2W_{12} as the tungsten source, and GO as the conducting substrate, so the metal oxide composite ZIF-67@H_2W_{12}/GO was prepared by a non-toxic, simple constant temperature stirring method in water solution. Besides, we propose a strategy for the simultaneous breaking of MOFs and POM using GO as conducting substrate to obtain composite nanomaterials under high temperature calcination conditions. Through further calcining in the argon and air, we synthesized new composite nanomaterial Co_3O_4-WC-CN/rGO, and Co_3O_4-WC composite was highly dispersed on graphene and retained sheetlike morphology of GO (Scheme 1). The composite nanomaterial is applied in the CE of the DSSCs, and it exhibits better catalytic activity than Pt. In general, the PCEs of DSSCs can be achieved 7.38% with the composite nanomaterial Co_3O_4-WC-CN/rGO as the CE, which is superior to the Pt based-DSSCs (η = 6.85%).

2. Experimental section

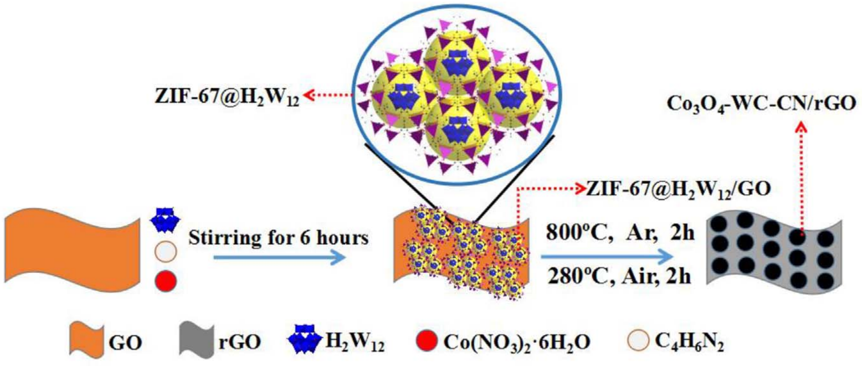
2.1. Materials and methods

ZIF-67 was synthesized following a method used in the previous report [22]. The H_2W_{12} was purchased from Alfa Aesar. The $Co(NO_3)_2 \cdot 6H_2O$, 2-Methylimidazole, anhydrous methanol, anhydrous ethanol, $KMnO_4$, KNO_3 were received from Sinopharm Chemical Reagent Co., Ltd (Beijing, China). All of the reagents were used without further purification. IR spectra were recorded using KBr pellets on a Bruker AXS TENSOR-27 FTIR spectrometer in the range of 4000-400 cm^{-1}. Thermogravimetric Analysis was recorded on a PerkinElmer TGA7 instrument at a heating rate of 10 °C per minute from 30 °C to 600 °C in the air. The Bruker AXS D8 Advance diffractometer was used to collecte X-ray powder diffraction datas using Cu K_α radiation (λ = 1.5418 Å) in the 2θ range of 5-80°. High resolution transmission electron microscope (JEOL-2100F) was used to characterize the nanomaterial Co_3O_4-WC-CN/rGO at an acceleration voltage of 200 KV. The morphology of nanomaterials is obtained by a Hitachi S-4800 scanning electron microscope at an accelerating voltage of 25 KV. The cyclic voltammetry and electrochemical impedance were measured by the Gamry Reference 3000 electrochemical workstation, and the cyclic voltammetry were recorded using a three electrode system comprising of prepared counter electrodes as the working electrode, a Pt wire as the counter electrode and Ag/AgCl electrode as reference electrode. All photoelectrochemical experiments were performed on the Gamry Reference 3000 electrochemical workstation at room temperature equipped with Xenon lamp as the light source.

2.2. Synthesis

2.2.1. Synthesis of GO

GO was prepared from graphite powder via a modified Hummers method [23]. Graphite powder (1.0 g) and $NaNO_3$ (1.0 g) were stirred in a solution of concentrated H_2SO_4 (46 mL) in an ice bath for 10 min $KMnO_4$ (6 g) was added slowly to the reaction mixture with vigorous stirring over 1 h. The mixture was stirred at 36 °C for 2 h. Then distilled water (80 mL) was added and the mixture was kept at 98 °C for another 30 min. The reaction was terminated by addition of water (200 mL) and 30% H_2O_2 (6 mL). The resulting mixture was washed by repeated centrifugation until the solution showing neutral, and the final precipitate was dried at 60 °C for 24 h in a vacuum oven. The suspension of GO (0.5 mg ml^{-1}) was dispersed and sonicated in distilled water for 30 min by using an ultrasonicator.



Scheme 1. Illustration of the preparation process for the Co_3O_4-WC-CN/rGO.