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# Tungsten carbide/carbon composite synthesized by combustion-carbothermal reduction method as electrocatalyst for hydrogen evolution reaction

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## ABSTRACT

Tungsten carbide/carbon ( $WC_x/C$ ) composite was synthesized by combustion-carbothermal reduction method. Systematic experiments that vary the ratio of the carbon atom of glucose to the tungsten atom of ammonium tungstate (C/W ratio), temperature and holding time used generated to investigate the synthesis process. The morphology of the as-prepared powders is flake-like and the  $WC_x$  nanoparticles are embedded in the carbon matrix. This method is facile and easy to scale up. Electrochemical measurements demonstrate that the  $WC_x/C$  composite exhibits good hydrogen evolution reaction (HER) catalytic activity, giving a  $\eta_{10}$  (the overpotential for driving a current of  $10 \text{ mA cm}^{-2}$ ) of  $-264 \text{ mV}$  and Tafel slope of  $85 \text{ mV dec}^{-1}$  in acid solution ( $0.5 \text{ M H}_2\text{SO}_4$ ).

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## Introduction

With the increasing of the worldwide energy crisis, looking for the substitution of fossil fuels is imminent. Hydrogen, as a clean and renewable energy source, is considered a promising candidate because of its high energy density. There are currently three main pathways for hydrogen production industrially, that is, steam methane reforming, coal gasification and water electrolysis. Among these three hydrogen production pathways, water electrolysis still provides a hope that it is possible to produce hydrogen in a sustainable way, because its feedstock is water, which is abundant and

renewable hydrogen source [1]. It is well-known that platinum-group metals (PGMs) (Pt, Rh, Pd, etc.) are excellent catalysts as only low overpotentials are required for high reaction rates. Nevertheless, the scarcity and high cost of PGMs may limit the widespread technological use. Therefore, the low-cost, efficient production of hydrogen still remains a scientific and technological challenge [2]. Recently, several non-noble metal materials, such as transition-metal chalcogenides [3–5], carbides [6–9], nitrides [10] and phosphides [11,12] have been widely investigated as catalysts or supports for application in HER.

Among them, tungsten carbide has been reported to exhibit platinum-like behavior in catalysis of HER, first by

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Boudart's group in the 1970s [13]. It exhibits high thermal and electrochemical stability, which makes it a suitable candidate to replace PGMs catalysts in emerging renewable energy technologies, such as fuel cells and electrolyzers [6,7,14–20]. Traditionally, the bulky tungsten carbide materials synthesized by the direct carburization of tungsten or tungsten oxides at high temperature (1400–1600 °C) show much inferior catalytic capability because of their big size and poor specific surface area [21]. Therefore, present studies focus on tungsten carbides with nanoscale particle sizes, large pores, and a high surface area. Pure tungsten carbides are likely to agglomerate leading to poor electrocatalytic activity, so supports are needed to disperse them. Carbon materials are outstanding carriers. For example, Fan et al. reported the versatile approach that allowed for fabrication of a range of hybrid materials which had metal carbide nanoparticles rigidly embedded into the graphitic carbon nanosheets. The resulting two-dimensional nanosheets demonstrated high activity and stability as catalyst for electrochemical HER [22]. On the one hand, carbon materials can disperse the tungsten carbide particles, leading to the decrease of particle size and the rise of specific surface area; on the other hand, carbon materials have adequate electrical conductivity to act as pathway for the electron flow [23] and excellent corrosion resistance [24].

In this study, we obtain WC<sub>x</sub>/C composite by combining solution combustion synthesis (SCS) with in situ carbothermal reduction reaction. SCS is a versatile method for preparing metal oxide. This approach is time and cost efficient significantly, and can prepare the products with different morphology and composition in one step [25]. Morales et al. [26] used peroxotungstic acid and different fuels (glycine, urea or thiourea) to prepare nanocrystalline WO<sub>3</sub> by SCS. Our group prepared W<sub>18</sub>O<sub>49</sub> using metal acid radical ion ([H<sub>2</sub>W<sub>12</sub>O<sub>40</sub>]<sup>6-</sup>) as the metal source by SCS [27]. Due to the many advantages of this method, the tungsten oxide/carbon (WO<sub>3</sub>/C) composite that WO<sub>3</sub> particles dispersed uniformly on the carbon matrix was prepared by SCS in a short period of time. Then in situ carbothermal reduction reaction was performed to get WC<sub>x</sub>/C composite in an inert gas atmosphere. The as-made WC<sub>x</sub>/C composite exhibited good electrocatalytic activity in HER performance.

## Experimental section

### Preparation of the precursor

All the WO<sub>3</sub>/C composite were synthesized by mixing different amount of ammonium tungstate ((NH<sub>4</sub>)<sub>6</sub>W<sub>7</sub>O<sub>24</sub>·6H<sub>2</sub>O) (9.44 g (0.005 mol), 5.70 g (0.003 mol), 3.87 g (0.002 mol) and 1.89 g (0.001 mol)), 6.0 g (0.1 mol) of urea (CO(NH<sub>2</sub>)<sub>2</sub>), 19.2 g (0.24 mol) of ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>) and 11.9 g (0.06 mol) of glucose (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>) in 100 mL of deionized water (denoted as CW10, CW17, CW25, CW50, respectively. The numbers represent C/W ratio). All the chemicals were bought from Sinopharm Chemical Reagent and Guangfu Chemical Reagent. The commercial 20% Pt/C catalyst was purchased from Alfa Aesar. The beakers containing preconfigured solution were transferred to an electric furnace. With heating the solutions evaporated into gels and foamed. Then, the mixtures

swelled dramatically and fierce combustion ensued. Then the products of these reactions were collected and grinded.

### Synthesis of WC<sub>x</sub>/C composite

The as-prepared precursors were heated up to setting temperature at the rate of 5 °C/min and then carbonized for different time in the presence of purity argon flow in a tube furnace. The final products were cooled down to ambient temperature naturally.

### Characterization

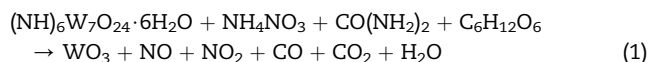
WC<sub>x</sub>/C composite was characterized by X-ray diffraction (XRD) on a Rigaku UltimaIV X-ray diffractometer, which uses a Cu-Kα source with a wavelength of 0.5406 Å. TGA experiments were accomplished on a Linseis STA PT 1600 at a heating rate of 10 °C/min in the air. Field-emission Scanning electron microscopy (FESEM) pictures were collected on a FEI Quanta FEG450. Transmission electron microscopy (TEM) images were captured on a FEI G2 F20 S-TWIN instrument. XPS measurements were made with a Thermo escalab 250Xi system using Al Kα radiation. Specific surface area (BET) were determined by N<sub>2</sub> adsorption at 77 K with the BET method using a volumetric unit (Quadrastorb SI).

### Electrochemical measurements

Approximate 3 mg of sample was mixed with 145 μL of deionized water, 45 μL ethanol and 10 μL 5 wt% Nafion in 5 mL vial. Then the mixture was ultrasonic dispersed for 30 min in order to completely scatter the sample. Yet 5 μL mixed solutions were dropped into a diameter 3 mm smooth glassy carbon electrode (0.0707 cm<sup>2</sup>), giving 1.05 mg/cm<sup>2</sup> mass loading of catalyst, and dried in air. Electrochemical measurements were performed on a Princeton VersaSTAT 4, and used three electrode system: the reference electrode (saturated calomel electrode, SCE), counter electrode (smooth Pt foil (1 cm<sup>2</sup>)) and working electrode (glassy carbon electrode). The electrolytes were 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. The scan rate for linear sweep voltammetry is 2 mV s<sup>-1</sup>.

## Result and discussion

The WC<sub>x</sub>/C composites were realized by combustion-carbothermal reduction method (Scheme 1). Firstly, the WO<sub>3</sub>/C composites were synthesized with four foolproof chemicals by SCS that were completed in a very short period of time (Equation (1)). Then in situ carbothermal reduction method was used to prepare WC<sub>x</sub>/C composites.



To obtain a good understanding of solution combustion process, the reactions were characterized using thermogravimetry (TG) –differential scanning calorimetry (DSC) as shown in Fig. 1. Obviously, the spontaneous combustion

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