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Structural and electrochemical studies of tungsten carbide/carbon composites for hydrogen evolution

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ABSTRACT

In an attempt to develop high-activity and earth-abundant electrocatalysts for hydrogen evolution reaction (HER), tungsten carbide/carbon composites are prepared readily via annealing a polyaniline/tungstic acid hybrid precursor under vacuum condition. By simply changing the mass ratio of polyaniline and tungstic acid, a variety of products with different structures can be obtained. The varying mass ratio causes the change of crystalline sizes of carbides, existential state of carbon and carbides/carbon content of final products. The composite produced at mass ratio of 1/1 shows the worst HER activity among all the catalysts due to its minimal content of active ingredients and the lowest degree of graphitization. In the case of the mass ratio of 1/3, an excess of tungsten source results in increasing graphitic carbon layers and decreasing electrochemical active surface area, which leads to the limited charge transfer process and less exposed active sites for HER. The composite fabricated at the mass ratio of 1/2 presents favorable electrocatalytic activity and excellent stability in both acidic and alkaline solutions, indicating its great potential to serve as a HER catalyst for water splitting.

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Introduction

In consideration of finite amount of fossil fuel and deteriorating environmental pollution brought by fossil fuel burning, it is highly desirable to develop other clean and renewable energy source as substitute. Hydrogen has been received widespread attention to be a promising energy carrier in virtue of its high conversion efficiency, recyclability and eco-friendly nature [1–3]. At present, hydrogen production through reforming of natural gas or methane is the primary approach to satisfy fierce demand from industry [4]. However, natural gas is not a renewable energy source and this production process nevertheless gives rise to greenhouse gas

emissions [5]. Splitting water into hydrogen by sustainable energy sources has been considered as an environmentally friendly, carbon-free alternative for hydrogen production [6,7]. As the cathodic reaction of electrochemical water splitting, hydrogen evolution reaction (HER) is strongly uphill with large overpotential while the electrolysis efficiency is enhanced when platinum-group metals (i.e., Pt, Ir, Ru, Rh and Pd) are used as catalysts [8–12]. Up to now, Pt is the most efficient candidate to accelerate the electrochemical process of HER, but its high cost and limited world-wide supply rule out the possibility of using it for large scale commercialization [13,14].

Therefore, efforts have been devoted to casting about for alternative HER catalysts with vast reserve, low cost and high activity as well as excellent stability [15]. Although hydrogen

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evolution over precious-metal-free catalysts is, in general, a relatively slow process compared to platinum, various approaches have reduced this gap and stimulated research and development for the optimization of the performance of non-precious metal catalyst materials. Recently, numerous non-noble metal materials such as transition metal sulfides [16–19], nitrides [20–22], phosphides [23–26], carbides [27–29] and carbonaceous materials [30–32] have been studied for the purpose of replacing noble metal catalysts. Among these materials, transition metal carbides, such as tungsten carbide (WC) [33–37] and molybdenum carbide (Mo_2C) [38–41] have been reported possessing catalytic properties analogous to Pt-group metals owing to their unique d-band electronic structures [42]. In particular, WC stands out for its high corrosion resistance, superior electronic conductivity and low price, which make it an attractive candidate for electrocatalytic HER [43].

Recently, encapsulation of non-noble metal within carbon matrix has been proposed as an efficient strategy in improving catalytic performances. The improved HER catalytic activity is ascribed to the alteration of the texture structures and electronic properties of the carbon carriers or active metal components [44]. Although various transition metal and their derivatives encapsulated in carbon materials (iron-based carbon materials, cobalt-based carbon materials, nickel-based carbon materials, etc.) have been designed as novel electrocatalysts [45–48], limited studies on WC as the active coating component have been reported. Herein, we describe a facile approach to fabricate WC embedded carbon supports through chemical oxidative polymerization of aniline, co-precipitation of polyaniline and tungstic acid, followed by carburizing heat treatment. Furthermore, the intrinsic correlation between structure and electrocatalytic activity of the materials is investigated. Moreover, the as-prepared catalyst shows favorable electrocatalytic activity and excellent stability in both acidic and alkaline solutions, indicating its great potential to serve as a promising candidate toward HER.

Materials and methods

Synthesis of tungsten carbide

Tungsten carbide (WC) was synthesized from polyaniline (PANI) and tungstic acid (H_2WO_4) via chemical oxidative polymerization combined with co-precipitation methods, followed by carburizing heat treatment. Briefly, pre-arranged aniline monomer which had been distilled under reduced pressure was dissolved in aqueous hydrochloric acid (HCl, 1 M) in a three-neck flask. The mixture solution was stirred in ice bath for 30 min. Subsequently, 50 ml ammonium persulfate solution (APS, 1 M) as a polymerization catalyst and a certain amount of sodium tungstate (Na_2WO_4) as tungsten source were added slowly to avoid overheating. The resultant mixture was stirred continuously during the polymerization reaction. The formed dark green precipitates which composed of PANI and H_2WO_4 were filtered and washed with distilled water for several times. Finally, the sediments were dried under vacuum at 60 °C overnight. The obtained precursors were heated in a vacuum furnace at 1200 °C for 2 h with a heating rate of 5 °C min^{-1} , and then

cooled down to room temperature. For comparative studies and uncover the interplay between the structures and the electrocatalytic activity of the catalysts, three different samples were prepared by varying the weight ratio of the precursors while keep all other factors constant. The mass ratio of aniline over Na_2WO_4 were controlled at 1/1, 1/2 and 1/3, and the obtained materials were denoted as WC-1/1, WC-1/2 and WC-1/3, respectively.

Sample characterizations

Powder X-ray diffraction (XRD) measurements of the materials were carried out by using a Bruker DX-1000 Discovery instrument ($\text{Cu K}\alpha$, $\lambda = 1.5418 \text{ \AA}$). Raman measurement was performed on a Raman spectrometer (Renishaw Corp., UK) with a laser wavelength of 532 nm. X-ray photoelectron spectroscopy (XPS, Kratos, XSAM 800) were used to detect the surface elemental composition. Thermogravimetry (TG) of the samples was carried out by using a simultaneous thermal analyzer (Netzsch, STA 449/C) in the temperature range of 50 °C–900 °C in air at a heating rate of 10 °C min^{-1} . The micro-morphology of the products were characterized by scanning electron microscopy (SEM, Hitachi S-4800) with an integrated energy dispersive spectrometer (EDS) and transmission electron microscope (TEM, Tecnai G²F20S).

Electrochemical measurements

The electrochemical measurements were carried out with a conventional three-electrode cell using a CH instrument (model 660E). A saturated calomel electrode (SCE) and a graphite rod were used as reference electrode and counter electrode, respectively. To prepare the working electrode, 5 mg of catalysts and 30 μl of 5 wt % Nafion solution were added into 0.50 ml of ethanol and 0.50 ml of H_2O , and ultrasonic dispersed for 1 h to form a homogeneous ink. Then 10 μl of the catalyst ink was drop-casted onto a glassy carbon electrode (GCE) with a diameter of 5 mm, yielding a catalyst loading of 0.25 mg cm^{-2} . By using this electrode as the working electrode, electrochemical measurements were conducted in 0.5 M H_2SO_4 (pH = 0.3), 0.1 M phosphate buffer (pH = 7) and 1 M KOH (pH = 14), which were prepared using highly purified water and all the electrolytes were saturated by N_2 prior to the measurements. For Linear Sweep Voltammetry (LSV) measurements, the scan rate was set to be 5 mV s^{-1} . The stability tests of the catalysts were performed by potential cycling between -0.4 V and 0.2 V at a sweep rate of 100 mV s^{-1} for 1000 cycles. The long-term (10 h) stability was also tested at the overpotential for the current density of -10 mA cm^{-2} . The electrochemical impedance spectroscopy (EIS) was carried out at η of -0.4 V from 10^5 Hz down to 10^{-1} with 5 mV AC amplitude. To investigate the electrochemical active surface area (ECSA) of the samples, the double-layer capacitance (C_{dl}) was analyzed by cyclic voltammetry in the potential range of 0.2–0.4 V under a series of sweep rates (20–200 mV s^{-1}). All the potentials reported in the work were quoted with respect to reversible hydrogen electrode (RHE), according to $E_{\text{vs RHE}} = E_{\text{vs SCE}} + E^{\circ}_{\text{SCE}} + 0.059 \text{ pH}$. All the electrochemical measurements were conducted at room temperature.

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