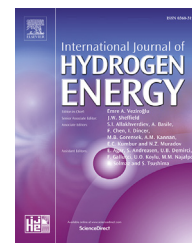




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Novel strongly coupled tungsten-carbon-nitrogen complex for efficient hydrogen evolution reaction

Syed Comail Abbas ^{a,b,1}, Jing Wu ^{a,1}, Yiyin Huang ^a, Dickson D. Babu ^a,
Ganesan Anandhababu ^a, Muhammad Arsalan Ghausi ^{a,b},
Maoxiang Wu ^a, Yaobing Wang ^{a,*}

^a CAS Key Laboratory of Design and Assembly of Functional Nanostructures, Fujian Provincial Key Laboratory of Nanomaterials, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China

^b University of Chinese Academy of Sciences, Beijing, 100190, China

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ABSTRACT

Alternatives to noble metal based electrocatalysts are vitally necessary to produce hydrogen from water at low overpotentials. Earlier research on tungsten based electrocatalyst has been mainly concentrated towards tungsten carbide (WC) and tungsten nitride (WN) as the potential electrocatalysts for hydrogen evolution reaction (HER), whereas tungsten carbide (W₂C) has been least focused upon. Herein, we report a highly active novel strongly coupled tungsten-carbon-nitrogen complex (W₂C-NC-WN complex) prepared by in situ carbonization method. This W₂C-NC-WN complex exhibits a remarkable electrochemical performance for HER with a small onset potential of 33 mV vs. RHE and requires an overpotential (η) of 145 mV vs. RHE to render -10 mA cm^{-2} current density. The Tafel analysis demonstrates a slope of 96 mV dec^{-1} which is much better than WN ($109.6 \text{ mV dec}^{-1}$) and WC ($142.4 \text{ mV dec}^{-1}$). The strong coupling of W₂C and WN within N-doped carbon (NC) framework brings about a significant enhancement in HER kinetics and faster electron transport due to the remarkable reduction in charge transfer resistance. The facile synthetic approach reported here, provides a powerful tool for the structurally controlled modification of the catalyst while simultaneously introducing active species.

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Introduction

Driven by global concerns over energy crisis and environmental issues, search of renewable energy resources represent the most dynamic scientific challenge [1–5]. Hydrogen, as an abundant environmental benign and sustainable fuel, is a promising energy carrier with high energy density to replace fossil fuels [6–8]. Electrochemical reduction of water to

hydrogen (H₂) via hydrogen evolution reaction (HER) is an attractive approach to obtain hydrogen with high purity in large quantities [9,10]. As a cathodic reaction, an efficient electrocatalyst for HER is required to afford a high energetic efficiency [11,12]. Although, noble metals such as Pt and its alloy based catalysts are the most active materials for HER, but their high costs, low natural abundance and instability in harsh conditions prevent their applications in industrial production of

* Corresponding author.

E-mail address: wangyb@fjirsm.ac.cn (Y. Wang).

¹ These authors contributed equally to this work.

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hydrogen [13–15]. Therefore, exploring low cost alternatives to replace noble metal electrocatalysts is a key technological task in the development of the hydrogen economy [16].

Transition metals (W, Mo, Co, Ni, and Fe) and derivative components (carbides, nitrides, sulfides, phosphides and borides) have been exploited over the past years towards efficient HER due to their low-cost, high abundance, environmental benignity, variable valence states and outstanding theoretical electrochemical activities [17–21]. Among these reported materials, transition metal carbides have received substantial interest owing to their superior electronic conductivity which make them suitable candidates for catalyzing the conversion of H^+ to H_2 [22,23]. Recently, tungsten carbides (WC/W_2C) have received considerable attention as efficient HER electrocatalysts because of their electrochemical stability and band structure resemblance to Pt [24,25]. Specifically, few recent reports clearly demonstrate that W_2C is a significantly more active HER electrocatalyst than WC, with much less negative Gibbs free energy of hydrogen adsorption (ΔG_{H^+}) and higher electronic density of states (DOS) at the Fermi level [26]. Although W_2C is indeed an active electrocatalyst for HER but it suffers from corrosion and instability under neutral and basic pH conditions [27]. To circumvent this issue, the introduction of heteroatom such as nitrogen in the form of nitrides can be a possible solution because the nitrides have the ability to resist against corrosion and improve the electrocatalytic activities of metal carbides. Interestingly, Nakanishi et al. synthesized nitrogen rich WCN nanocomposite in the presence of iron for efficient HER kinetics via pyrolysis [28]. Chen et al. reported the mutual incorporation of W_2C and WN species on graphene for the enhancement of HER electrocatalytic activities [29]. In these previous reports, they have clearly demonstrated that the nitrogen incorporation induces local charge density and accommodates the surface charge state due to its lone-pair electrons in 3p orbitals and vacant 3d orbitals which result in the promising activity of nitrides [30,31]. Furthermore, quantum mechanical calculations show that N-dopants create positive charge on neighboring carbon atoms which have the electron accepting ability [32]. In this regard, WN is another attractive candidate for HER electrocatalyst because it has the ability to resist against the corrosion in basic and neutral conditions. Such being the case, it is fair to infer that the combination of W_2C with WN could be more efficient for catalyzing HER [29,33].

Herein, we report a promising strategy to rationally synthesize W_2C -NC-WN complex via *in situ* carbonization process for hydrogen evolution reaction (HER). The electrocatalytic tests show that the W_2C -NC-WN complex exhibits much better HER electrocatalytic performance with very low onset potential and small Tafel slope as compared to WC and WN in alkaline medium. Such excellent electrochemical performance for HER can be attributed to the synergistic involvement of W_2C and WN moieties in the NC framework.

Experimental

Synthesis of W_2C -NC-WN complex

200 mg of ammonium tungstate $(NH_4)_2WO_4$, Xilong Chemicals, China) and 800 mg of melamine ($C_3N_3(NH_2)_3$, Sinopharm

Chemicals, China) were directly mixed in ceramic crucible in 1:4 mass ratio of ammonium tungstate and melamine. The mixture was placed in quartz tube furnace, and pyrolyzed at 800 °C at the heating rate of 3 °C/min in argon atmosphere for 3 h. Then the furnace was cooled down to room temperature and black powder was obtained. In the mean time, a series of comparative experiments have been carried out in order to understand the relationship between structure and electrochemical catalysis. (i) Different experiments were carried out by changing the mass ratios of ammonium tungstate and melamine. The ratios of ammonium tungstate to melamine were 1:2, 1:4 and 1:8. In our experiments, we found 1:4 ammonium tungstate to melamine as the best mass ratio. (ii) After finding out the best ratio, we carried this experiment at different temperature such as 700, 800 and 900 °C for further optimization.

Characterizations

A JEOL-6700F scanning electron microscope was employed to investigate the morphology of the W_2C -NC-WN electrocatalyst. The structural morphology was characterized using transmission electron microscope (TEM, JEOL JEM-2010). The accelerating voltage of instrument was kept at 200 kV with a microanalyser having 129 eV resolution power. The contents and chemical valence state of W, N and C in the material were characterized by X-ray photoelectron spectroscopy (XPS, VG ESCALAB 250) with an Al/ K_{α} X-ray source at 1487 eV and the pressure of chamber was below than 3×10^{-10} mbar during analysis. Specific correction was performed by employing a C 1s binding energy of 284.8 eV. X-ray powder diffraction (XRD) characterization was carried out with a Philip X'Pert Pro MPP diffractometer. Radiation source for XRD was Cu/ K_{α} ($\lambda = 1.54 \text{ \AA}$) and the scan rate was 1° min^{-1} .

Electrochemical measurements

The electrochemical studies for HER were conducted in a three-electrode system by using CHI660e electrochemical working station (CH Instrument Inc.) at room temperature. The Pt slice (1 cm^2) and the Ag/AgCl saturated with KCl were used as the counter and reference electrodes, respectively. The Glassy carbon (GC) electrode covered with the as-prepared catalyst was used as the working electrode. For preparation of working electrode: 10 mg of the catalyst was homogeneously dispersed in a suspension containing 950 μL of isopropyl alcohol and 50 μL of 20 wt% Nafion solution (DuPont, USA) under ultrasonic stirring. 4 μL of the slurry was pipetted with a micro-syringe and spread on the polished GC electrode surface and the electrode was dried under the infra-red lamp (catalyst loading 0.2 mg cm^{-2}). 1 M KOH aqueous solution saturated with oxygen was employed as the electrolyte for HER. The potentials, measured against the Ag/AgCl electrode, were converted to the potentials vs. reversible hydrogen electrode (RHE), according to the equation:

$$E \text{ vs. RHE} = E \text{ vs. Ag/AgCl} + 0.203 + 0.059 \text{ pH}$$

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