



ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/hydro

Facile in-situ formation of high efficiency nanocarbon supported tungsten carbide nanocatalysts for hydrogen evolution reaction

Cheng Liu ^{a,1}, Yan Wen ^{a,1}, Liangxu Lin ^{b,c,*}, Haijun Zhang ^b, Xifei Li ^d, Shaowei Zhang ^{a,**}

^a College of Engineering, Mathematics and Physical Sciences, University of Exeter, Exeter EX4 4QF, UK

^b The State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan 430081, China

^c Institute of Advanced Materials and Nanotechnology, Wuhan University of Science and Technology, Wuhan 430081, China

^d Institute of Advanced Electrochemical Energy, Xi'an University of Technology, Xi'an 710048, China

ARTICLE INFO

Article history:

Received 22 March 2018

Received in revised form

10 June 2018

Accepted 14 June 2018

Available online xxx

Keywords:

Tungsten carbide

Molten salt synthesis

Electrocatalyst

Hydrogen evolution reaction

ABSTRACT

Electrochemical hydrogen evolution reaction (HER) is one of the key techniques for hydrogen production. Much great effort has been made so far to develop highly efficient HER catalysts to replace expensive precious metals (e.g. Pt). Unfortunately, the synthesis processes were generally not cost-effective and/or scalable. So it is highly desirable to develop a facile technique to enhance HER activity of conventional inexpensive but less active materials. In this work, monodispersed tungsten carbide (WC) nanoparticles (<5 nm) were in-situ formed/anchored on nanosized carbon black (CB) and carbon nanotube (CNT) via a simple low temperature molten salt synthesis technique. Owing to this special hybrid structure, both the exposed surface area of active species and the electrical conductivity of the catalysts were increased effectively, making the catalysts perform considerably better in HER than pure WC and WC based catalysts prepared via other conventional routes. WC nanocrystals in-situ formed/anchored on CNTs showed small onset overpotential (90 mV), low Tafel slope (69 mV dec⁻¹), high current density (93.4 and 28 mA cm⁻² at 200 and 300 mV, respectively) and excellent stability (remaining stable even after 3000 cycles). Such a performance is one of the best among those of WC based electrocatalysts developed to date. We demonstrate here significantly improved HER performances of inexpensive tailored WC materials, along with a facile synthesis strategy which could be also readily extended to prepare a range of other types of mono-dispersed nanocatalysts for more potential applications.

© 2018 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

* Corresponding author. The State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan 430081, China.

** Corresponding author. College of Engineering, Mathematics and Physical Sciences, University of Exeter, Exeter EX4 4QF, UK.
E-mail addresses: L.Lin@wust.edu.cn (L. Lin), s.zhang@exeter.ac.uk (S. Zhang).

¹ The authors contributed equally to this work.

<https://doi.org/10.1016/j.ijhydene.2018.06.087>

0360-3199/© 2018 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

As an alternative to traditional fossil fuels, hydrogen (H_2) is considered as a promising future clean energy source with high energy density [1–7]. Compared to many other H_2 production techniques [8–10], the electrochemical hydrogen evolution reaction (HER) has several advantages, in particular the relatively high production efficiency [2]. However, high overpotential with this direct water splitting process still causes much energy loss and hinders further improvement in the overall efficiency [3,5,6]. One strategy commonly adopted to tackle this problem is the use of a highly efficient catalyst with a low free-energy of the adsorbed H [11]. Unfortunately, the most efficient HER electrocatalysts that have been developed so far are still precious metal based (e.g. Pt), which are expensive and unsustainable.

For these reasons, considerable efforts have been made to develop alternative efficient HER catalysts, some of which were monolayered transition metal chalcogenides and their porous counterparts with tailored structures and improved electrical conductivity [12–19]. Nevertheless, their preparation processes generally were complex, not cost-effective and/or not scalable. In recent years, low cost transition metal carbides have also attracted a great deal of attention because of their great potential for HER applications [20–25], including molybdenum carbide [26–31] and tungsten carbide (WC) nanomaterials [25,32]. In the case of a WC nanomaterial, onset overpotentials of 165–323 mV and Tafel slopes of 85–119 mV dec^{-1} could be achieved via loading WC on a carbon substrate [33,34]. Diverse methods have been used to prepare such WC catalysts. The conventional solid-solid reaction process commonly exhibits several disadvantages, in particular, a high firing temperature and a long reaction time, resulting in uncontrollable sintering/heavy agglomeration of product particles and poor catalytic activity [35]. To avoid these problems, some other techniques relying on gaseous carbon sources have been attempted [36–41]. By using urea [36], CH_4 [37], acetone [38–40] and CO [41] as carbon sources, the synthesis temperatures could be reduced to 800, 1000, 600 and 800 °C respectively. However, a carbon film was always deposited on the WC catalyst nanoparticles (NPs), which separated them from the reactant species, reducing their catalytic activity. For instance, an Mo_2C -C nanocomposite [42] prepared at 600 °C using polypropylene as a carbon source only exhibited onset overpotential of 101.4–140 mV and Tafel slope of 79.5–100.4 mV dec^{-1} . Recently, Hunt et al. [43] have managed to fabricate well-dispersed WC NPs free from carbon covering by using the “removable ceramic coating method”. Nevertheless, this method still suffers from several drawbacks such as a complicated process, long processing time, the use of hazardous material precursors and low production yield. On the basis of the above review, it can be considered that development of an alternative facile fabrication method for WC catalysts is key to their performance and future application in efficient HER.

In the present work, highly efficient nanocarbon-supported WC nanocatalysts with substantially improved HER performance were fabricated via a novel one-step low temperature molten salt synthesis (MSS) technique. As

illustrated in Fig. 1, WC NPs were formed *in-situ* and firmly anchored on nanocarbon substrates (nanosized carbon black/CB or carbon nanotube/CNT). Differently from other synthesis techniques, the present MSS used only common raw materials and required a relatively low firing temperature. Such simple preparation process and the resulted unique catalyst structure conferred dramatically increased surface area and electrical conductivity on the catalyst, improving greatly the overall catalytic performance in HER. We report here the excellent HER electrocatalytic activity and stability of tailored WC nanocatalysts, along with a facile synthesis strategy potentially applicable to future commercial productions of a range of nanocatalysts for various important applications.

Experimental

Raw materials and sample preparation

0.29 g WO_3 (<100 nm), 0.12 g Mg (>99% purity), and 0.06 g multi-walled carbon nanotube (CNT, > 95% purity) or carbon black (CB, N990) (i.e., in the molar ratio of $WO_3:Mg:C = 1:4:4$) were ultrasonically dispersed for 1 h in ethanol, and dried in an oven at 80 °C for 2 h. The dried powder was further mixed with 15 g KCl (>99% purity) and contained in an alumina crucible. A tube furnace protected by following Ar was used to fire the alumina crucible to 950 °C (5 °C min^{-1}). After 4 h at this temperature, the crucible was allowed to cool in the furnace to room temperature. The solidified mass in the crucible was repeatedly washed with distilled water and 1 mol L^{-1} HCl solution. The resultant powder sample free from residual salt and byproduct MgO was further dried at 80 °C overnight and characterized as described below.

Sample characterization

A Siemens D500 X-ray diffractometer (Cu $K\alpha$, $\lambda = 0.154$ nm, 40 mV, 40 mA) was used to identify crystalline phases in samples (from 20° to 80° (2 θ) with a scan rate of 2.4°/min and step size of 0.04°), and an SSI S-Probe X-ray photoelectron Spectrometer to record their X-ray photoelectron spectra (XPS, samples in this case were pressed to form a thin pallet).

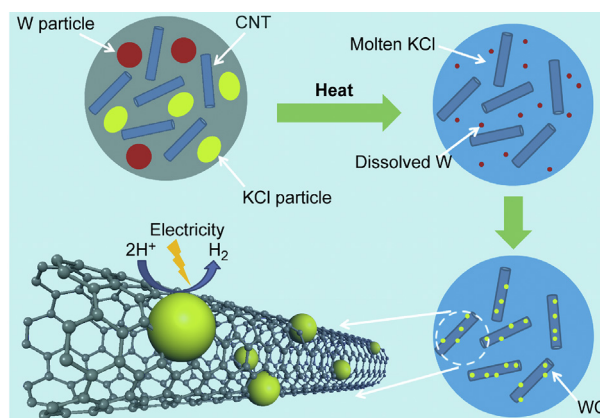


Fig. 1 – Schematic of the molten salt synthesis process used in the present work.

Download English Version:

<https://daneshyari.com/en/article/8961255>

Download Persian Version:

<https://daneshyari.com/article/8961255>

[Daneshyari.com](https://daneshyari.com)