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High performance catalyst for electrochemical hydrogen evolution reaction based on SiO_2/WO_{3-x} nanofacets

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ABSTRACT

The electrochemical hydrogen evolution reaction (HER) was studied over silica/tungsten oxide nanofacets (SiO_2/WO_{3-x}) that was prepared by calcinations of electrospun polyacrylonitrile nanofibers containing silicotungstic acid under air atmosphere. It was found that the Keggin structure of precursor ($H_4SiW_{12}O_{40}.29H_2O$) was decomposed and transferred to crystalline monoclinic WO_3 after calcinations at 500 °C. The morphology of prepared catalyst after pyrolysis, observed by FE-SEM, was nanocrystals deposited on joined nanoparticles fiber. The size of nanocrystal increases with increasing annealing time. In addition, increasing annealing time also enhances interaction between SiO_2 and WO_{3-x}. The synthesized catalyst was employed as an electrocatalyst for HER. It was found that the catalyst annealed at 500 °C for 5 h showed 6.6 times higher HER activity than the bulk WO_3 and exhibits excellent electrochemical stability over 100 cycles.

1. Introduction

Global warming is caused by the emission of large amount of carbon dioxide gas (green house gas) in the atmosphere due to the combustion of hydrocarbon based fuels. It is now obvious that this has a great impact on the climate change [1]. In this regard, the development of alternative energy resources, especially non-carbon based fuel is highly desirable to resolve the problem. Hydrogen is the most abundant element in the universe and it has been considered as a potential fuel for polymer electrolyte membrane fuel cells. Fuel cell technology is promising and considered as an alternative energy technology due to its environmental friendly (water and heat as by products) and high specific energy density as well as higher efficiency compared to the conventional internal combustion engine technology [1]. Hydrogen can be produced by several processes such as reforming, electrolysis and auto-thermal process [1]. Hydrogen produced by reforming and auto-thermal processes requires high temperature and substantially causes the environmental pollution [1]. On the other hand, hydrogen produced by electrolysis is an environmental friendly process; this makes electrolysis has been attractive and promising process [2]. The H_2 production by electrolysis process is so called hydrogen evolution reaction in which the

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performance is strongly depending on the metal electrode. Platinum (Pt) is the most active electrode for HER [3,4]. However, the low abundance and high cost are the major problems impede the commercialization of electrolysis process. Therefore, enormous amount of research efforts have been devoted to develop a low cost and highly active electrode material for HER, including non-precious metal oxide, metal complexes as well as metal sulphide [3–5].

Tungsten oxide (WO_3), an n-type semiconductor with a band gap between 2.4 and 2.8 eV, is inexpensive, non-toxic, easy to prepare, and stable in the photocatalytic oxidation process; this compound has been investigated as an electrocatalyst for HER [6–11]. However, the HER activity of WO_3 diminished owing to its bulk structure [8]. This challenge can be remarkably overcome by suitably reducing the size to the nanometer scale. Nanostructured WO_3 in the form of nanorods, nanowires, nanoparticles, and nanofibers enhances HER activity of WO_3 due to the extremely high surface area; it also significantly altered the surface energies and quantum confinement effects [6–11]. These nanostructures have been successfully prepared by various synthetic approaches including template synthesis [6], hydrothermal method [7,9] and thermal evaporation [12]. Among numerous methods, template synthesis has been found to be very effective for the preparation of nanostructured WO_3; meso or nanoporous silica and anodic alumina membrane have been used as templates for the preparation of the nanostructured WO_3 [12]. However, use of such templates is expensive, and it must be eliminated by using hazardous chemicals such as HF, NaOH etc., Thus, the carbon based materials such as carbon microspheres and polymers can be easily removed by heating at elevated temperature in an oxygenated environment, is an alternative template for the preparation of WO_3. Zhao et al. have prepared SiO_2/WO_3 nanoparticles by calcining surfactant encapsulated polyoxotungstate, which serves as a template and a tungsten source, respectively. The surfactant was used to protect the framework structure of the polyoxotungstate and to promote the effective doping of silica particles [13]. However, the synthesis procedure is complicated, multi-step processes and requiring the surfactant to introduce SiO_2.

Recently, electrospinning that is a continuous polymer fiber spinning technique utilizing a high voltage power supply, has shown potential for use in the fabrication of nanostructure templates for the synthesis of various nanofibers due to its relative advantages of simplicity, scalability, versatility and low cost [6].

In this study, we introduce a simple and versatile method to synthesize the nanostructured SiO_2 incorporated WO_3. This has been accomplished by first electrospinning a homogenous solution of polyacrylonitrile (PAN) containing silicotungstic acid ($H_4SiW_{12}O_{40}$, SiW) and then subsequently performing pyrolysis of the nanofiber under air atmosphere. PAN was used as the electrospinning carrier; SiW was used as the precursor for WO_3. The employed synthetic route is very simple, cost effective, and surfactant free; it can also be performed at a relatively low temperature for the synthesis of WO_3. The yield of WO_3 was about 90% with respect to silicotungstic acid. The novelty of this study relies on the *in-situ* synthesis of SiO_2 incorporated mixture of nanoparticles and nanofacets WO_{3-x}. Subsequently, the as-synthesized SiO_2/WO_{3-x} was used to investigate the electrochemical hydrogen evolution reaction. It was found that, compared to commercial WO_3 and synthesized WO_3 in the literature, the synthesized SiO_2 incorporated WO_{3-x} nanostructures exhibited superior HER activity.

2. Experimental

2.1. Preparation of electrospun (e-spun) PAN/SiW composites nonwoven web

Silicotungstic acid with amount of 0.39 g was completely dissolved in 1.70 g of *N*,*N*-dimethylformamide (DMF) by using ultrasonic cleaner (UC-10, LAB-companion). Polyacrylonitrile (M_w = 150 000 g/mol) and DMF with amount of 1.30 g and 7.00 g, respectively, were then added into SiW solution and the mixture was stirred at 70 °C until a clear homogenous solution was observed. The electrospinning process is described elsewhere [14]. The solution was electrospun under conditions: traveling distance between spinneret to collector of 15 cm, high voltage power supply of 15 kV, volume feed rate of 0.8 ml/h and rotating speed of 300 rpm under 25 °C and 20–30 %RH.

2.2. Preparation of tungsten oxide nanostructures

Tungsten oxide (WO_3) nanostructures were prepared by calcining the as-spun PAN/SiW composite nonwoven web in a tubular furnace (Wisd Laboratory Instruments) at 500 °C for 1 h, 3 h and 5 h. The calcination process was carried out in air atmosphere in which the composite nonwoven web was stabilized at 250 °C for 1 h to remove an organic materials then heating to 500 °C with different time. The heating rate was 5 °C per minute.

2.3. Characterizations

The morphology of the samples was observed using a field-emission scanning electron microscope (FE-SEM) (Hitachi, S-4800II) with an accelerating voltage of 3 kV. Before the observations, the samples were coated with osmium. The microstructures and lattice fringe of samples were determined by field-emission transmission electron microscope (FE-TEM) (Hitachi, HF-3300) with an acceleration voltage of 300 kV. For TEM analysis, samples were ultrasonically dispersed in ethanol, and then a drop of dispersion was deposited on carbon copper grid and dried under UV lamp.

The crystal structure of calcined samples was investigated by powder X-ray diffraction (XRD, Panalytical, Empyrean) using Cu Kα radiation at a generator voltage of 40 kV and a tube current of 30 mA. The structure analysis was also investigated by Raman spectrometer using the 514.5 nm line of an Ar ion laser as the excitation source. The chemical functional group of samples was analyzed using an attenuated Fourier-transform infrared spectrometer (ATR FT-IR, JASCO, 6100).

Elemental analysis was performed by X-ray photoelectron spectroscope (XPS, Thermo Fisher Scientific, ESCALAB250 XPS system, Theta Probe XPS system) using monochromated Al K-alpha source at 15 kV and 150 W. Binding energy values were