



Paragenesis of Mo₂C nanocrystals in mesoporous carbon nanofibers for electrocatalytic hydrogen evolution



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ARTICLE INFO

Article history:

Received 27 November 2017

Received in revised form

9 April 2018

Accepted 11 April 2018

Available online 12 April 2018

Keywords:

Mo₂C

Mesoporous carbon nanofibers

Electrospinning

Nanocrystals

Hydrogen evolution reaction

ABSTRACT

Cost-effective Mo₂C nanocrystals homogeneously distributed in interconnected mesoporous carbon nanofibers are prepared through an electrospinning route combined with a subsequent pyrolysis process. The crystal phases of the Mo₂C nanocrystals are controllable and their phase-dependent electrocatalytic activities for the hydrogen evolution reaction (HER) are explored. The nanocomposite catalyst made of the hexagonal-phase Mo₂C nanocrystals in carbon nanofibers exhibits outstanding electrocatalytic kinetics and high activities for the HER in both acidic and basic media. It is found that the overpotentials are 160 mV in 0.5 M H₂SO₄ and 92 mV in 1 M KOH at a current density of 10 mA cm⁻². The Tafel slopes of 66 mV dec⁻¹ in 0.5 M H₂SO₄ and 63 mV dec⁻¹ in 1 M KOH are achieved. Also, the as-obtained Mo₂C/C electrocatalyst shows long-term durability.

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1. Introduction

Hydrogen has been regarded as both an ideal energy carrier and a clean alternative energy source to displace fossil fuels because of its eco-friendly, renewable, and abundant features [1,2]. Electrolysis of water has been considered as a low-cost and effective strategy for hydrogen generation, compared to traditional methods [3–5]. However, this is often subjected to limitations since the electrocatalysts for the hydrogen evolution reaction (HER) during the hydrogen generation process do not have a high enough efficiency, and noble-metal catalysts are generally used [6–9]. Therefore, it is highly desirable that non-noble metal catalysts with high performances are designed and synthesized for the electrochemical HER.

Molybdenum (Mo)-based materials have aroused much interest because of their unique conductivity, chemical and thermal stability, and comparable catalytic properties to the Pt-group metals [10–14]. In particular, molybdenum carbide (Mo₂C), a kind of interstitial alloys, is usually produced by incorporation of carbon atoms into the lattices of the transition-metal Mo. Mo₂C possesses metallic-like properties, and is demonstrated as one of the most attractive catalysts for the HER [15]. Nanostructuring is an

important consideration in the catalyst design because it can offer sufficient active sites and improve the molecular transport of reactants and products. Since the pioneering work on commercial Mo₂C by Vrabel and Hu in 2012 [16], considerable effort has been made for the fabrication of Mo₂C-based catalysts for hydrogen generation. For instance, Mo₂C/CNT [17], Mo₂C nanoparticles decorated graphitic carbon sheets [18], nanoporous molybdenum carbide nanowires [19], nitrogen and sulfur co-doped molybdenum carbide nanosheets [20], Mo₂C coupled with nitrogen-rich nanocarbon [21], hierarchical β-Mo₂C nanotubes [22], iron-doped molybdenum carbide [23], three-dimensional (3D) hierarchical porous Mo₂C [24], and molybdenum carbide/reduced graphene oxide [25] have been reported for the HER. Among them, well-defined 1D porous architectures have received much attention, benefiting from plenty active sites, accelerated mass transfer, and the moderate Mo-H bond strength [26–29]. Despite these advances, however, successful controlled synthesis of Mo₂C-based nanostructures for electrocatalytic HER applications by facile and reliable techniques still remains a challenge to materials scientists.

Herein, we report the design and fabrication of unique hybrid Mo₂C/C electrocatalysts, whereby with a 3D architecture composed of ultrafine Mo₂C nanocrystals distributed in mesoporous carbon nanofibers via a facile electrospinning and pyrolysis route. The phase-controllable Mo₂C nanocrystals are embedded within the 3D carbon framework with tunable carbon contents. It is found that

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the as-obtained hexagonal-phase Mo_2C nanocrystals in carbon nanofibers (denoted as H- $\text{Mo}_2\text{C}/\text{C}$) exhibit excellent electrocatalytic activities and kinetics for the HER in both basic and acidic media. The catalytic activity of H- $\text{Mo}_2\text{C}/\text{C}$ is comparable to that of the commercially available Pt/C catalyst. The Tafel slopes are 66 mV dec^{-1} in $0.5 \text{ M H}_2\text{SO}_4$ and 63 mV dec^{-1} in 1 M KOH , and the outstanding long-term durability has been achieved.

2. Experimental section

2.1. Materials synthesis

In a typical procedure, the precursor solution for electrospinning was prepared by using a certain amount of bis(acetylacetonato)dioxomolybdenum ($\text{C}_{10}\text{H}_{14}\text{MoO}_6$, aladdin), polyacrylonitrile (PAN, average $M_w = 150,000$, Aldrich), polyvinylpyrrolidone (PVP, average $M_w = 1,300,000$, Aldrich), poly(methyl methacrylate) (PMMA, aladdin) and N,N-dimethylformamide (DMF, Sinopharm Chemical Reagent). The weight of PAN, PVP and PMMA was fixed at 0.8, 0.2 and 0.3 g, respectively. The amount of $\text{C}_{10}\text{H}_{14}\text{MoO}_6$ was 3, 6, 7, or 11 mmol for preparing different samples. A plastic syringe with a stainless steel nozzle (20-gauge) was used to load the above mixed solution. A high voltage of 18 kV and a constant flow rate of 0.8 mL h^{-1} were conducted by a regulated DC power supply and a syringe pump during electrospinning. The distance was set to be 15 cm between the collector (aluminum foil) and the electrospinning jet. The as-electrospun 1D nanofibers were stabilized in air at 170°C for 5 h, and then annealed at different temperatures and atmospheres for 3 h (heating rate: 1°C min^{-1}). Eventually, the products of highly dispersed ultrafine nanocrystals encapsulated in 1D interconnected mesoporous carbon networks were obtained. Hexagonal Mo_2C nanocrystals distributed in carbon nanofibers were prepared by carbonizing the as-electrospun precursor (containing the molybdenum source of 7 mmol) at 800°C under Ar/H_2 (5 wt% H_2). Under the similar condition except replacing Ar/H_2 (5 wt% H_2) with N_2 for carbonization, cubic-phase Mo_2C nanocrystals in carbon nanofibers were prepared. For comparison, pure carbon nanofibers without involving Mo_2C nanocrystals were also prepared under the same condition. The detailed conditions for other control samples with different crystallinities, phases and particle sizes are listed in Table S1 (see Supporting Information).

2.2. Materials characterization

X-ray diffraction (XRD) patterns were collected on a PANalytical Multi-Purpose Diffractometer with high-intensity $\text{Cu } K_{\alpha 1}$ irradiation ($\lambda = 1.5406 \text{ \AA}$). The morphology and microstructures were characterized using a field-emission scanning electron microscope (FE-SEM, FEI Sirion 200) and a field-emission transmission electron microscope (Tecnaï G2 F30, Holland). Nitrogen adsorption/desorption isotherms were measured at 77 K. Thermogravimetric (TG) analysis and differential thermal analysis (DTA) were conducted using a PerkinElmer Diamond TG/DTA apparatus. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a VG MultiLab 2000 system with a monochromatic $\text{Al } K_{\alpha}$ X-ray source (Thermo VG Scientific). All spectra were calibrated to the C 1s line for carbon at a binding energy of 284.0 eV.

2.3. Electrochemical measurements

A typical three-electrode configuration was used to study the electrochemical properties of the catalysts. 5 mg of the active material in a mixture of $30 \mu\text{L}$ 5 wt% Nafion solution and $470 \mu\text{L}$ ethanol was dispersed under ultrasonication for about 20 min to generate a

homogeneous suspension. For preparing the working electrode, $5 \mu\text{L}$ of the suspension was transferred onto a glassy carbon electrode with a diameter of 5 mm by employing a micropipette. The electrode was dried at room temperature for several hours before use. The loading of the catalyst on the working electrode is calculated to be 0.255 mg cm^{-2} . A graphite rod and a saturated calomel electrode (SCE) were used as the counter electrode and the reference electrode, respectively. The catalytic HER performance was carried out on a CHI 760E electrochemical workstation by a linear sweep voltammetry (LSV) technique. In $0.5 \text{ M H}_2\text{SO}_4$, the LSV measurements were performed at a scan rate of 2 mV s^{-1} in the potential range from -0.05 to -0.7 V vs. SCE . In 1 M KOH , the LSV measurements were carried out at a scan rate of 2 mV s^{-1} in the potential range from -0.95 to -1.7 V vs. SCE . Both the acid and basic media were purged with the Ar/H_2 flow for 1 h before testing. The electrochemical double layer capacitance (EDLC) was obtained by cyclic voltammograms (CV) at different scan rates from 10 to 100 mV s^{-1} in the potential range of 0.35 – 0.45 V vs. RHE . The electrochemical impedance spectroscopy (EIS) measurements were conducted at frequencies from 0.1 to 1 MHz, and the amplitude of 5 mV is used for getting the electron transfer resistance (R_{ct}). The durability tests of the catalysts were carried out for 2000 cycles in the potential range between -0.14 and -0.44 V vs. SCE in acid and between -1 and -1.2 V vs. SCE in basic at a scan rate of 100 mV s^{-1} . The potentials against a SCE electrode were converted to a reversible hydrogen electrode (RHE) according to the formula $E \text{ (vs. RHE)} = E \text{ (vs. SCE)} + E^{\circ}_{\text{SCE}} + 0.059 \text{ pH}$. The Tafel plots for analyzing the HER mechanism were gained by transforming the LSV curves.

3. Results and discussion

The electrospun precursor was annealed at different temperatures and under different atmospheres to generate 1D interconnected mesoporous $\text{Mo}_2\text{C}/\text{C}$ nanofibers with controlled phases, crystallinities and particle sizes. Cubic-phase Mo_2C nanocrystals

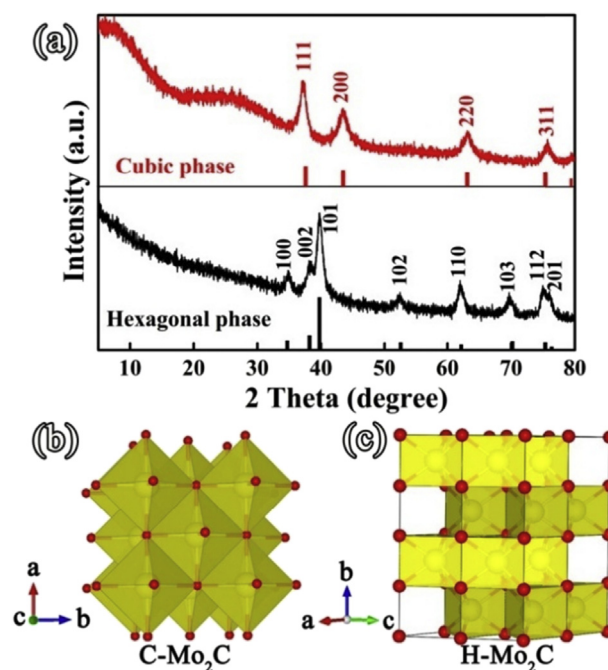


Fig. 1. (a) XRD patterns for the samples of C- $\text{Mo}_2\text{C}/\text{C}$ (top) and H- $\text{Mo}_2\text{C}/\text{C}$ (bottom). The crystal structures of C- Mo_2C (b) and H- Mo_2C (c). (Red and yellow balls stand for C and Mo atoms, respectively.). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

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