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Molybdenum carbides embedded on carbon nanotubes for efficient hydrogen evolution reaction

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ABSTRACT

Molybdenum carbides embedded on carbon nanotubes are prepared via a simple hydrothermal method with subsequent post-treatment at high temperature. In order to optimize the electrocatalytic activity for hydrogen evolution reaction (HER), effects of hydrothermal and post-annealing temperature are systematically investigated. Electrochemical testing results indicated that Mo_2C/CNT prepared at a solvothermal temperature of 200 °C and 800 °C post heat-treatment exhibits the best HER activity with an overpotential of 125 mV in acid media and 93 mV in alkaline media at a current density of 10 mA cm^{-2}. Such enhanced catalytic activity may originate from high electro-conductivity and ECSA value, together with ultra-small particle size, which accelerates the electron transfer rate and provides large surface area and active sites, respectively.

1. Introduction

Hydrogen, a green and renewable energy source, has been intensely investigated as a promising alternative to conventional fossil fuels [1–3]. Recently, electrochemical water splitting to produce hydrogen has attracted tremendous attention [4–6]. Although Pt-group precious metals or alloy are mostly active and stable catalysts for the hydrogen evolution reaction (HER) [7,8], their scarcity and high cost made them impractical for global-scale applications. Much efforts have been made to develop cost-effective and earth-abundant *3d*–transition metal (TMs) based HER electrocatalysts, including carbides [9–11], nitrides [12,13], sulfides [14–17] and phosphides [18–21], et al. Among these catalysts, molybdenum carbides are considered as the effective non-Pt electrocatalysts for HER in both acidic and basic conditions, owing to their similar *d*-band electronic density with Pt [22,23], lower hydrogen-adsorption properties [10,24,25] and relative high chemical stability. However, although molybdenum carbides exhibit good electronic conductivity [26,27], the HER rate is restricted by the electron transfer rate. Therefore, a combination of carbon material is usually adopted to enhance the electronic conductivity. Recently, Wang and co-workers reported a facile, one-step synthetic route to obtain molybdenum carbide (Mo_2C) embedded in nitrogen-rich carbon layers by using ammonium molybdate and dicyandiamide as precursor [28]. Mo_2C nanoparticles decorated graphitic carbon sheets (Mo_2C/GCSs) were prepared via a one-step solid-state method, utilizing sodium alginate (ALG) as a low cost environmental friendly carbon source [29]. Latterly, graphene supported molybdenum carbide octahedral nanoparticles with porous and small size was derived via an in situ carburization of metal organic framework structure (MOFs) [30]. The HER activity was obviously improved via the incorporation of Mo_2C and carbon support. In addition, further improvement of HER activity would be acquired through a more intimate incorporation between molybdenum compounds and carbon support [31–32].

Herein, we report a facile, two-step synthetic route for the synthesis of molybdenum carbides embedded on carbon nanotubes. Pure phase molybdenum carbide compound (Mo_2C/CNT) are obtained via the solvothermal (within 180–240 °C) and post-annealing process (within 700–900 °C). Mo_2C/CNT synthesized via a 200 °C solvothermal with post annealing of 800 °C (Mo_2C/CNT_{S200}–800) exhibits the best HER activity compared with other catalysts prepared at different temperature. Such enhanced catalytic activity may originate from the low hydrogen binding energy, high electro-conductivity and the ultra-small particle size, which decrease the free-energy, accelerate the electron transfer rate and increase active sites, respectively.

2. Experimental part

2.1. Materials synthesis

2.1.1. Synthesis of MoO2/CNT composites

180 mg of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ was fully dissolved in a mixture solvent of 10 mL distilled water and 20 mL ethylene glycol by

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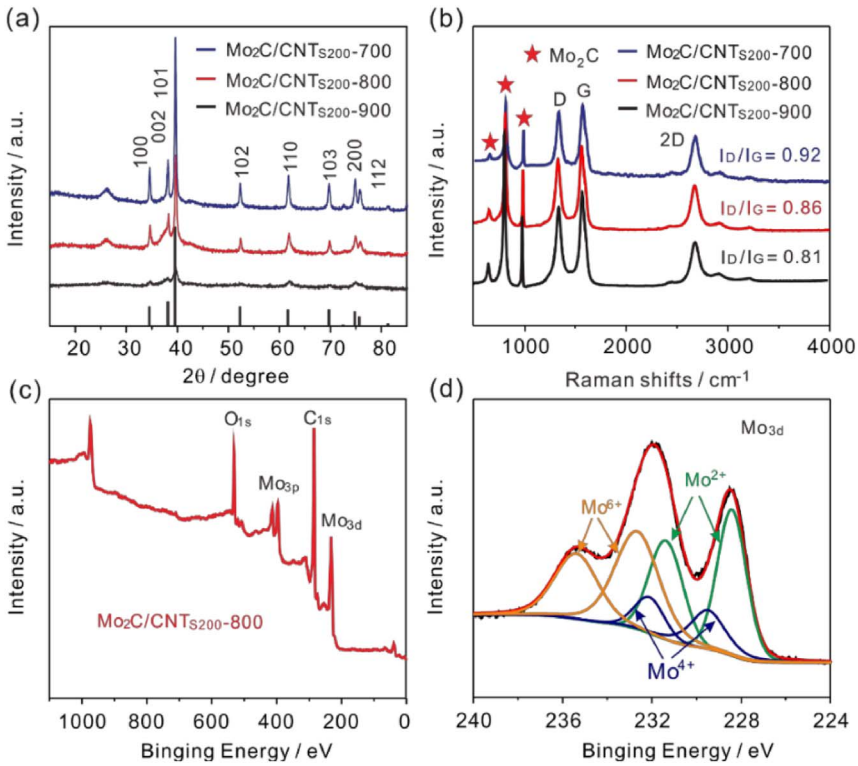

Fig. 1. XRD, Raman and XPS spectra of Mo_2C/CNT catalysts calcined at different temperature after 200 °C solvothermal process. (a) Powder XRD patterns of Mo_2C/CNT_{S200}–700, Mo_2C/CNT_{S200}–800 and Mo_2C/CNT_{S200}–900; (b) Raman spectrum of Mo_2C/CNT_{S200}–700, Mo_2C/CNT_{S200}–800 and Mo_2C/CNT_{S200}–900; XPS spectra of Mo_2C/CNT_{S200}–800 (c) and corresponding high-resolution spectra of Mo 3d (d).

sonication. Then 120 mg of CNT was added into the mixed solution. The mixture was stirred at room temperature for approximately 20 min until a homogeneous solution was achieved. Then the solution was transferred to a 50 mL Teflon-lined stainless steel autoclave and heated in an oven at 200 °C for 10 h. The solvothermal product was collected after being washed with DI water and ethanol for several times, and then dried via the freeze dryer.

2.1.2. Synthesis of Mo_2C/CNT composites

The solvothermal product was annealed in H_2 (5%)/Ar (95%) atmosphere at 700 °C, 800 °C and 900 °C for 2 h at a heating rate of 10 °C min^{-1}, respectively. The obtained molybdenum compounds were denoted as Mo_2C/CNT_{S200}–700, Mo_2C/CNT_{S200}–800 and Mo_2C/CNT_{S200}–900. In order to explore the difference of the obtained materials in solvothermal process, the solvothermal temperature was investigated at 180 °C, 200 °C, 220 °C and 240 °C for 10 h, and then annealed in H_2/Ar atmosphere up to 800 °C for 2 h with a heating rate of 10 °C min^{-1}, respectively, The resulting powder was denoted as Mo_2C/CNT_{S180}–800, Mo_2C/CNT_{S200}–800, Mo_2C/CNT_{S220}–800 and Mo_2C/CNT_{S240}–800, respectively. The obtained materials were kept in 5 mL centrifuge tube immediately, which were filled with nitrogen before sealed.

2.2. Material characterization

The crystal structure was determined using X-ray diffraction, and diffraction patterns were collected using Cu Kα (λ = 1.5406 Å) radiation at a scanning rate of 4° min^{-1}. Raman spectra were collected by a LabRam HR800 spectrometer with a 532 nm laser excitation. The morphologies were measured by scanning electron microscopy (SEM, Sirion200), Transmission electron microscopy (TEM) images were recorded by a JSM-2100 transmission electron microscopy (JEOL, Japan) at an acceleration voltage of 200 kV. Further, the chemical states of the elements in catalysts were studied by XPS using an AXIS-ULTRA DLD-600 W Instrument, and the binding energy of the C 1s peak at 284.6 eV was taken as an internal reference.

2.3. Electrochemical measurements

5 mg of catalyst and 1 mL of Nafion solution (1 wt‰) were sonicated to form a homogeneous ink. Then 16.5 μL of the catalyst ink was loaded onto a glassy carbon electrode (5 mm in diameter), the loading is 420 μg/cm^2. For comparison, the electrodes were also modified with Pt/C. All electrochemical measurements were performed using a Autolab PGSTAT302N electrochemical workstation in a three-electrode setup with modified glass carbon working electrodes, reversible hydrogen electrode (RHE) as reference, carbon rod as a counter electrode. 0.5 M H_2SO_4, 1 M KOH and 1 M phosphate buffer (pH = 7) solution were used as electrolyte and are deaerated with nitrogen. The electrocatalytic activity of the catalysts towards HER was evaluated by using linear sweep voltammetry (LSV) in 0.5 M H_2SO_4 and 1 M KOH at a scan rate of 5 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) measurements were conducted at overpotential of 100 mV from 10^5 Hz to 0.01 Hz.

3. Results and discussion

The crystal structure of molybdenum-based materials was confirmed by the XRD measurement. MoO_2 phase was first obtained via solvothermal process (XRD patterns in Fig. S1). After the subsequent annealing treatment at 700 °C, 800 °C and 900 °C, Mo_2C/CNT was obtained which can be seen in Fig. 1a. The small diffraction peak located at 26° is ascribed to (002) plane of the carbon nanotubes, while the diffraction peaks located at 34.4°, 37.8°, 39.4°, 52.1°, 61.5°, 69.6°, 72.4°, and 74.6°, are indexed to (100), (002), (101), (102), (110), (103), (200) and (112) lattice planes of Mo_2C (JCPDS NO. 01-035-0787) [33]. Typical for Mo_2C/CNT solvothermal in 200 °C, annealing at 800 °C (denoted as Mo_2C/CNT_{S200}–800), the additional structural information was obtained from Raman spectroscopy measurements. The full-range Raman spectra showed characteristic peaks of molybdenum carbide (Fig. 1b) located at 670 cm^{-1}, 840 cm^{-1} and 990 cm^{-1}, which is consistent with the XRD pattern in Fig. 1a [30]. Moreover, it can be seen that D band located at 1350 ± 20 cm^{-1} and G band located at 1575 ± 20 cm^{-1}, which are corresponding to the disordered graphitic