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Shell-core MoS_2 nanosheets@Fe_3O_4 sphere heterostructure with exposed active edges for efficient electrocatalytic hydrogen production

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ABSTRACT

Rational design and constructing advanced materials with intriguing nanostructures towards highly efficient and sustainable energy conversion and storage have received focused research efforts, but exploring effective strategies to accomplish this mission is still challenging. Aiming at this goal, we construct MoS_2 nanosheets on Fe_3O_4 nanospheres via a SiO_2 shell assisted sacrifice template method for the first time. The shell-core structured MoS_2@Fe_3O_4 catalyst is well characterized by XRD, Raman, TEM, SEM, and XPS techniques. SEM and TEM show that MoS_2 nanosheets possess edge exposed feature and defect-rich structure, assuring the maximum active sites for electrochemical hydrogen evolution reaction (HER). Raman characterization reveals the chemical coupling between MoS_2 and Fe_3O_4, indicating the formation of MoS_2@Fe_3O_4 heterostructure at the shell-core interface. High-resolution TEM (HRTEM) shows abundant defects at the heterostructures, which supplies more catalytic sites. The improved catalytic sites are proved by electrochemical capacitance measurements, and the enhanced catalytic activity over each site is also probed. Therefore, MoS_2@Fe_3O_4 exhibits remarkably enhanced catalytic activity for water splitting due to the above mentioned benefits.

1. Introduction

Energy sustainable production and storage are central to the sustainable development of human society. Molybdenum disulfide, possessing a typical two-dimensional (2D) layered structure of stacked S-Mo-S monolayer, has been considered as a promising candidate for applications in energy conversion and storage [1–3]. Due to the low onset potential and specific structural features, MoS_2 based catalysts have received intensive research interests for electrochemical hydrogen evolution reaction (HER) [4–26]. Previous reports have demonstrated that, the catalytic site numbers and electrical conductivity are key factors that determine the HER catalytic property. Carbon materials, such as graphene, carbon nanotubes and et al., have been reasonably employed as conductive substrate to enhance the catalytic activity of MoS_2 [5–12]. On the other hand, various MoS_2 based catalysts with defect-rich structures or exposed edges have been developed to pursue improved catalytic active sites [13–20]. For instance, defect-rich MoS_2 nanosheets with robust HER activity have been prepared via a solvothermal method [15]. Xie and co-workers have developed vertically aligned MoS_2 nanowalls with exposed edge sites to achieve improved HER catalytic activity [20]. Recently, both computational and experimental studies have demonstrated that, doping transition metals (Fe, Co, Ni et al.) into MoS_2 or constructing the hybrids of MoS_2 with other metal sulfides could tune its electronic and structural features, thus boosting the HER catalytic performance [21–26]. Unfortunately, the studies on these kinds of transition metal doped MoS_2 catalysts are limited by the rational structure design and proper component selection.

Constructing shell-core structured materials has been believed as an effective approach to achieve improved electrochemical properties, because of the structural advantages and the potential synergistic effect between different components [27]. Recently, some carbonous materials, such as N-doped carbon nanoboxes,

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carbon nanotubes, and polyaniline nanowires, have been used to support MoS_2 for the fabrication of shell-core structures and applications for electrochemical water splitting [7,28,29]. Besides, the shell-core structured $MoS_2|NiS|MoO_3$ nanowires with high intrinsic activity have also been synthesized as good electrocatalysts [30]. Therefore, selection of proper materials with motivating effect (e.g. oxides/sulfides of Fe, Co, Ni) to support MoS_2 nanosheets as shell-core structured catalysts could reasonably obtain both synergistic effect and structural advantages of highly exposed active centers and large surface area for HER. However, the design and construction of such MoS_2 based shell-core structures have rarely been reported and are desirable to be explored.

In the present work, we rationally design and develop the SiO_2 shell assisted sacrifice template method to construct MoS_2 nanosheets@Fe_3O_4 nanosphere shell-core nanostructures as advanced materials for electrochemical HER. The Fe_3O_4 sphere serves as the support for anchor of edge exposed MoS_2 nanosheets and enhances the charge transfer. The SiO_2 sacrifice template synthesis strategy assures the well anchor of MoS_2 nanosheets on the surface of Fe_3O_4 nanospheres. The successful formation of heterostructure between MoS_2 and Fe_3O_4 induces defect-rich feature and rapid charge exchange. Therefore, enhanced HER catalytic activity is reasonably obtained from the present hybrid catalyst.

2. Experimental

2.1. Samples preparation

The shell-core structured MoS_2@Fe_3O_4 is prepared using SiO_2 shell as sacrifice template, which is schematically shown in Fig. 1. Firstly, $FeCl_3\cdot 6H_2O$ (3.3 g), sodium citrate (0.6 g), and anhydrous sodium acetate (6 g) are dissolved into 60 mL of ethylene glycol with vigorous stirring, which is then transferred into a Teflon-lined autoclave (100 mL) for heating at 200 °C for 10 h. After cooled to room temperature, the resultant black precipitates of Fe_3O_4 are harvested by centrifugation, washed with water and ethanol, and vacuum dried at 80 °C. Secondly, the obtained Fe_3O_4 nanosphers (0.2 g) are dispersed into a mixed solution containing 80 mL of ethanol and 16 mL of deionized water. After 4 mL of ammonia solution (30%) is added, 2 mL of tetraethylorthosilicate is then added in 15 min under ultrasonic. After 3 h, the products of shell-core structured SiO_2@Fe_3O_4 are harvested by magnet and vacuum dried. Finally, SiO_2@Fe_3O_4 (0.1 g), $Na_2MoO_4\cdot 2H_2O$ (0.16 g), and thioacetamide (0.15 g) are dissolved in 60 mL of water. After ultrasonic-treatment of 1 h, the suspension is added with NH_4F (0.022 g) and then transferred into a Teflon-lined autoclave (100 mL) for heating at 200 °C for 12 h. The precipitates of MoS_2@Fe_3O_4 are harvested, washed, and vacuum dried at 80 °C. And the SiO_2 sacrifice template is etched by HF that is generated from NH_4F during the hydrothermal process. Pristine MoS_2 is prepared via a similar method using $Na_2MoO_4\cdot 2H_2O$ and thioacetamide for comparison.

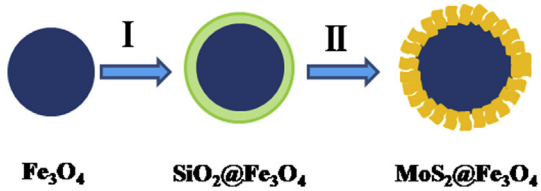

Fig. 1. Schematic illustration of SiO_2 template-assisted synthesis of shell-core structured MoS_2@Fe_3O_4. (I) Coating Fe_3O_4 spheres with SiO_2 shell via a facile Stöber method; (II) deposition of MoS_2 nanosheets on Fe_3O_4 and simultaneously etching SiO_2 with NH_4F.

2.2. Materials characterization

The crystallographic information of MoS_2@Fe_3O_4 is collected from X-ray powder diffraction (XRD, Philips X'-pert X-ray diffractometer). Raman spectroscopy is performed on a confocal microprobe Raman system (LabRam-e010, 632 nm as the excitation source). Scanning electron microscope (SEM) is obtained on a JEOL JSM-7500F. Transmission electron microscope (TEM) is conducted on a JEOL, JEM-2100. The composition contents of MoS_2@Fe_3O_4 composite are determined by inductively coupled plasma atomic emission spectrometry (ICP-AES, Perkin-Elmer Optima 3100 XL). X-ray photoelectron spectroscopy (XPS) is performed on a RBD upgrade PHI-5000c ESCA system (Perkin Elmer) with Mg Kα radiation ($h\nu = 1253.6$ eV).

2.3. Electrochemical HER measurements

The electrochemical HER experiments are conducted on CHI760D (CH Instruments, Shanghai, China) with a three-electrode cell. The MoS_2@Fe_3O_4 (4 mg) is dispersed into a mixed solution containing 50 μL Nafion solution (5 wt%) and 1.25 mL water under ultrasonic to obtain the catalyst ink. A portion of 5 μL ink (containing 20 μg of catalyst) is drop-casted on a glassy carbon electrode (GCE, 3 mm in diameter), which is used as the working electrode after dried at room temperature. The counter electrode and reference electrode are a graphite rod and a saturated calomel electrode (SCE), respectively. Linear sweep voltammetry are tested in 0.50 M H_2SO_4 with a scan rate of 5.00 mV s^{-1} (purged with pure N_2). Electrochemical impedance spectroscopy (EIS) is obtained at the frequency ranging from 0.1 Hz to 100 kHz in 0.5 M H_2SO_4 at the overpotential of 300 mV. All the potentials are calibrated to a reversible hydrogen electrode (RHE) to assess the HER performance of catalysts.

2.4. Electrochemically active surface area measurements

The electrochemical capacitance measurements are performed over the potential between 0.025 and 0.325 V versus RHE at varied scan rates of 20, 40, 60, 80, 100, 120, and 140 mV s^{-1}. The electrochemically active surface area (ECSA) is calculated based on the obtained specific capacitance [31]. And the per site turnover frequency (TOF) is also determined by the specific current density [31].

Calculation of electrochemical active surface area:

$$A_{ECSA} = \frac{\text{specific capacitance}}{40\ \mu F\ cm^{-2}\ \text{per}\ cm^2_{ECSA}}$$

Calculation of TOF:

$$TOF = \frac{\left(3.12\times 10^{15}\frac{H_2/s}{cm^2}\ \text{per}\ \frac{mA}{cm^2}\right)\times |j|}{\left(1.42\times 10^{15}\text{atoms}/cm^2_{real}\right)\times A_{ECSA}}$$

3. Results and discussion

Fig. 1 illustrates the schematic synthesis of MoS_2@Fe_3O_4. The SiO_2 shell sacrifice template method is developed to construct the designed shell-core MoS_2@Fe_3O_4. In the present synthesis strategy, SiO_2 shell plays an important role for the controlled deposition of MoS_2 nanosheets on the surface of Fe_3O_4 spheres, assuring the specific shell-core architecture as well as good coupling between them.