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The role of metal dopants in WS_2 nanoflowers in enhancing the hydrogen evolution reaction

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ABSTRACT

We demonstrate a facile and efficient method for the synthesis of a metal-doped WS_2 nanoflower (NF) catalyst. We also report its application for the electrocatalytic hydrogen evolution reaction (HER). The flower-like WS_2 particles were produced by a hydrothermal reaction, and, subsequently, the WS_2 was doped with metal chlorides such as $AuCl_3$, AgCl, $PtCl_2$, and $PdCl_2$, followed by reduction with sodium borohydride to form metal-doped WS_2 NFs. The Pd-doped WS_2 NF catalyst showed a high HER performance, having a Tafel slope of 54 mV/dec and an overpotential of -175 mV at $-10\,mA\,cm^{-2}$. The improvement is attributed to the energy band alignment near the H^+/H_2 reduction potential and the large surface area of the WS_2 NFs.

1. Introduction

Recently, energy production and fossil fuel use have become issues of concern, and many researchers are trying to find alternative, non-fossil fuel sources of energy. Hydrogen is one of the most well-known flammable gases and is considered an excellent replacement fuel for the efficient and environmentally friendly production of energy. Furthermore, the use of hydrogen would reduce the greenhouse emissions [1,2]. Electrochemical hydrogen production *via* water splitting is a facile and efficient way to produce hydrogen [3]. However, this method is a high-energy process, and platinum, an expensive and non-earth abundant metal, is often used as a catalyst [3,4].

Transition metal dichalcogenides (TMDs) such as MoS_2, WS_2, $MoSe_2$, and WSe_2 have been used by many scientists to catalyze the hydrogen evolution reaction (HER). TMDs have unique catalytic properties and are earth-abundant, which would allow the production of hydrogen in a facile and low-cost manner [5–9]. WS_2 is a stable and highly active catalyst for the HER. For example, Wu et al. used WS_2 nanosheets as a catalyst for the HER [10]. WS_2 nanosheets were synthesized *via* mechanical activation from WO_3 and sulfur, and the Tafel slope was 72 mV/dec. However, despite the relatively high Tafel slope, the proposed method involves an annealing process, as well as a complicated synthetic method [11–13]. Therefore, new, simpler methods to synthesize and modify WS_2 are required so that it can be used as a catalyst in HER applications.

To modify the catalytic activity of WS_2, doping can be used; this is a facile method to enhance the HER performance. For example, Sun et al. used nitrogen as a dopant in WS_2 to improve the HER catalytic activity. The catalyst was prepared by the sol-gel method. Using this N-doped WS_2 nanosheet as a catalyst for the HER, a low onset potential of 197 mV and Tafel slope of 69.69 mV/dec were obtained. Modification of the surface by forming other shapes, such as hollow spheres and flowers, can also enhance the HER activity. In fact, there are a larger number of active sites at the edges of the WS_2 layers compared to the surface of a WS_2 nanosheet. Thus, the formation of flower-shaped or spherically shaped particles can provide more active sites and a higher surface area, increasing the HER properties.

Here, we propose a new and facile method to form flower-like WS_2 particles for use in the HER. This is the first time that WS_2 NFs have been prepared *via* a hydrothermal method, which is a controllable process. First, WS_2 nanoflowers (NF) were synthesized by the hydrothermal process, and, subsequently, a metal chloride, such as $AuCl_3$,

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AgCl, $PtCl_2$, or $PdCl_2$, was added to the WS_2 NF solution as a dopant to improve the HER performance. We also tested different concentrations of the metal chloride solution (5%, 10%, 15%, 20%, 25%, and 30%) to investigate the effect of the doping level. Next, the produced precursor was reduced using sodium borohydride to form metal-doped WS_2 NFs. We found that the optimized Pd-doped WS_2 NF catalyst exhibits high performance for the HER because of the efficient band alignment of the catalyst near the hydrogen separation energy level in water. Therefore, the WS_2 NF catalyst with a very small amount of metal dopant is an excellent candidate for highly efficient electrochemical hydrogen production.

2. Experimental section

2.1. Synthesis of WS_2 NFs

Tungsten (VI) chloride 99.9% and thioacetamide (98%) (TAA) were purchased from Sigma–Aldrich and used without any purification. WS_2 nanoflowers were prepared hydrothermally following a previously reported method with some modifications [14]. Briefly, 0.4 g WCl_6 was mixed with 0.375 g TAA in 10 mL of de-ionized (DI) water with stirring at room temperature for 1 h. After a uniform dark-blue solution had been obtained, the solution was placed in a 20-mL Teflon-lined stainless-steel autoclave in a furnace. The temperature of the furnace was increased to 280 °C over the course of 1 h (5 °C min^{-1}). Then, the temperature was maintained for 24 h, followed by natural cooling to room temperature. A black powder was obtained at the bottom of the Teflon-lined autoclave. Finally, the black product was washed by dispersion in DI water followed by centrifugation (three times). Then, the product was dried at 60 °C in an oven. A schematic of the preparation process is shown in Fig. 1.

2.2. Synthesis of metal-doped WS_2 NFs

Metal-doped WS_2 NFs were prepared by mixing the WS_2 NFs with a metal chloride solution (see Fig. 1). In a typical preparation, 2 mg of WS_2 NFs was mixed with 1 mL of dimethylformamide (DMF) solution and stirred for a few minutes. Next, 1 mg of each metal chloride was dissolved in 10 mL of DMF and vigorously stirred until a well-dispersed mixture was obtained. Different metal chloride concentrations (5%, 10%, 15%, 20%, 25%, and 30%) were tested to find the optimum doping amount for each metal chloride solution. Subsequently, $NaBH_4$ (0.3 M, 1 mL), which was used as a reducing agent, was added to the WS_2 NF solution, which was ultra-sonicated for 30 min. The final product was obtained as a homogeneous metal-doped WS_2 NF solution.

2.3. Characterization

X-ray photoelectron spectroscopy (XPS, VG Scientific Ltd., England) was carried out under a vacuum greater than 1×10^{-5} mbar. Mg-$K\alpha$ radiation (1250 eV) was used with a constant pass energy of 50 eV. The crystallographic composition of the thin film samples was examined by X-ray diffraction (XRD) analysis (Bruker D8 Advance X-ray diffractometer) with Cu-$K\alpha$ radiation ($\lambda = 0.1542$ nm). Raman spectra (Horiba, Japan) were taken at an excitation wavelength of 514 nm. Field-emission scanning electron microscopy (FE-SEM, Zeiss 300 V P) images were obtained at an acceleration voltage of 50 kV. Transmission electron microscopy (TEM) images were obtained on a (JEOL, Japan) instrument. The transmittance spectra were measured using a UV–Vis spectrophotometer (V-670).

2.4. Electrochemical measurements

Electrochemical measurements were performed in 0.5 M H_2SO_4 with a three-electrode quartz electrochemical cell connected to a potentiostat (Ivium 5612, Netherlands). The cell contained the catalyst coated with Nafion (5 wt%) on a glassy carbon electrode as the working electrode, and a calomel electrode (in saturated KCl) and Pt mesh wire were applied as the reference and counter electrodes, respectively. The potential was converted using E (*vs.* RHE) = E (*vs.* calomel) + 0.059 pH + 0.241. Linear sweep voltammetry (LSV) measurements were obtained at a scan rate of 60 mV s^{-1}. The cyclic

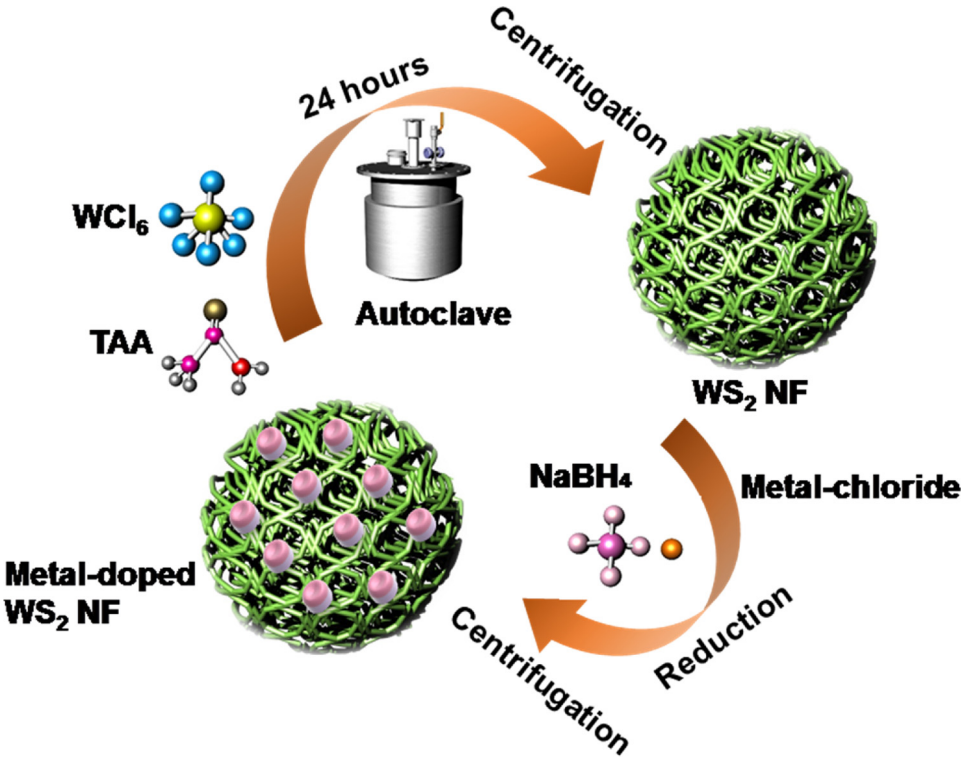

Fig. 1. Schematic of the synthesis of WS_2 NFs and metal-doped WS_2 NFs.