Ultrathin exfoliated WS$_2$ nanosheets in low-boiling-point solvents for high-efficiency hydrogen evolution reaction

Y Q Qin$^{1,2,3}$, Y Q Peng$^1$, W F Yang$^1$, Y Wang$^1$, J W Cui$^1$ and Y Zhang$^{1,2}$

$^1$School of Materials Science and Engineering, Hefei University of Technology, Hefei 230009, China
$^2$Key Laboratory of Advanced Functional Materials and Devices of Anhui Province, Hefei 230009, China

E-mail: albon@hfut.edu.cn

Abstract. Two-dimensional mono- or few-layer WS$_2$, as a typical transition metal dichalcogenide, usually exhibits excellent electrocatalytic hydrogen evolution reaction (HER) activity. In this work, low-boiling-point solvents are adopted for the controllable preparation of ultra-thin WS$_2$ nanosheets by an improved liquid phase exfoliation process directly from the raw WS$_2$ powder. The thickness of as-obtained WS$_2$ nanosheets is about $\sim$1.5 nm with lateral size of $\sim$1.2 μm. Their HER performance was investigated by loading them onto a glass carbon electrode in 0.5M H$_2$SO$_4$ solution. The resulting polarization and Tafel curves indicate that the as-obtained WS$_2$ nanosheets are effective electrocatalysts for HER with a low onset potential of 65mV and a Tafel slope of 55mV/dec. The proposed liquid phase exfoliation technique is lucrative for exfoliating transition metal disulfide materials in various applications.

1. Introduction
With the increasing energy demand, new sources of renewable energy become very topical. In particular, hydrogen is regarded as a very promising energy carrier due to its perfect properties, such as pollution-free nature, high energy density, wide availability of raw materials, and high conversion rate [1-3]. There are several methods of preparing hydrogen [4], including its electrocatalytic production water by the electrocatalytic hydrogen evolution reaction (HER). It has attracted wide attention, because it needs only a continuous electric energy supply to generate hydrogen [5]. The key issue of electrocatalytic HER is to explore efficient catalysts with low cost. At present, a wide application of Pt catalysts with brilliant catalytic performance [6-7] is limited by their high cost and scarce reserves [8-9]. Therefore, finding earth-abundant, low-cost, and efficient catalysts became an urgent practical problem [10]. In this respect, thin two-dimensional (2D) layered transition metal dichalcogenides (TMDs) have gained wide interest because of their unique electrical and optical performance [11].

As a typical TMD, WS$_2$ became popular in recent years [12-13]. The structure of TMD consists of monolayer $M$ (X=W, Mo) atom in the middle of a two-layer S atom. Neighboring layers bind to each other loosely by the van der Waals force [14], so it can be easily laminated to form nanosheets through some physical or chemical procedures [15-18]. Vory et al. reported that WS$_2$ nanosheets have excellent HER performance, which onset potential is 80 mV [19]. Besides, WS$_2$ is earth-abundant and cost-effective, so that it can be a promising replacement for Pt-based electrocatalysts in the future [20].
Up to now, several methods have been explored to exfoliate TMDs into nanosheets, including top-down exfoliation methods (e.g., mechanical exfoliation [21-22] or liquid phase exfoliation [23]) and bottom-up process (e.g., chemical vapor deposition [24-25]). Unfortunately, the above methods are quite expensive, require complex equipment or provide a low yield, and not suitable for mass production.

Liquid phase exfoliation method is one common way for producing two-dimensional materials. For example, Hernandez et al. [26] exfoliated graphene nanosheets by liquid exfoliation method with high production. Liquid exfoliation method can also synthesize various layered materials of high specific surface area with simple operation and low cost. As for liquid exfoliation, it is crucial to develop an appropriate dispersion media. Organic solvent is widely used for liquid exfoliation. Unfortunately, this kind of solvent generally has high-boiling-point which might be difficult to be removed after exfoliation and the remained solvent has detrimental effect on catalyst. The toxicity of those solvent also limits the scalable production of two-dimensional materials. In this paper, we exfoliate WS$_2$ nanosheets in the iso-propyl alcohol and water mixed solvent (IPA: H$_2$O = 1:1, volume ratio), which has low-boiling-point rather than traditional high-boiling-point organic solvent, such as N, N-dimethylformamide (DMF) [27], N-methyl-2-pyrrolidone (NMP) [28]. In addition, our method can large-scale produce WS$_2$ nanosheets. The as-abtained WS$_2$ nanosheets show excellent electrocatalytic performance with a small onset potential of only 65 mV and a Tafel slope of 55 mV/dec. It is worth noting that the mesoporous structure of the as-obtained nanosheets increases the number of active sites, which further improves the electrocatalytic performance of the material.

2. Experiments

2.1. Synthesis of WS$_2$ nanosheets

This paper adopts an improved liquid phase exfoliation technique for synthesizing ultra-thin WS$_2$ nanosheets. Firstly, a certain amount of raw WS$_2$ powder was immersed into liquid nitrogen for certain time. After liquid nitrogen pretreatment (LNP), a certain amount of raw WS$_2$ powder was dispersed in the IPA and water mixed solvent (IPA:H$_2$O=1:1, volume ratio), then the dispersion was ultrasonicated for 1-13 h. Finally, the dispersion was centrifuged with 6000 rpm (rounds per minute) for 30 min in order to remove the non-exfoliated WS$_2$ powder. The ultrathin WS$_2$ nanosheets were obtained from the upper suspension. Further insight into the effect of ultrasonication time towards WS$_2$ electrocatalytic activity was investigated, setting 4 hours as a gap from 1 to 13 h. Abbreviations WS$_2$-1, WS$_2$-5, WS$_2$-9, and WS$_2$-13 refer to the ultrasonication time of samples (1, 5, 9, and 13h, respectively).

2.2. Characterization

The morphology and composition of the specimen were characterized by field emission scanning electron microscopy (FESEM, Hitachi-SU8020, Japan), atomic force microscope (AFM, Bruker Dimension) and transmission electron microscopy (TEM, JEOM-2100F, Japan). X-ray diffraction (XRD, D/MAX2500 V, Rigaku, Japan) with Cu-Kα radiation (0.15418 nm) operating at 40 kV was carried out for the structures test. The elemental status analysis was analyzed by X-ray photoelectron spectroscopy (XPS, Thermo-ESCALAB250Xi, US) with a monochromatic Al Kα (1486.6 eV) X-ray source.

2.3. Electrochemical Measurement

A typical three-electrode electrolytic cell was designed for the electrochemical measurements on electrochemical workstation (CHI660D) at room temperature. Platinum wire, saturated calomel electrode, and a 5mm-diameter glassy carbon electrode were used as counter electrode, reference electrode, and working electrode, respectively. The as-obtained WS$_2$ nanosheets were loaded with controllable mass onto the glassy carbon electrode (loading 120 μg cm$^{-2}$ catalyst), and the tests were performed after drying the working electrode. The HER activity was measured by linear sweep voltammetry (LSV) in 0.5M H$_2$SO$_4$ electrolyte at a scan rate of 50 mV/s. The electrochemical stability
of the catalyst was tested by cycling the electrode for 1000 cycles. All potentials were calibrated to a reversible hydrogen electrode (RHE) and all data have been corrected for a small ohmic drop. The Nyquist plots were tested in the frequency range from 10-1 to 105 Hz with an overpotential of 100 mV. A cyclic voltammeter was run at the potential range from 0.1 V to 0.2 V vs. RHE at various scan rates (20-200 mV s⁻¹), in order to estimate the electrochemical active surface area.

3. Results and discussion

3.1. Characterization of WS₂ nanosteets
As schematically depicted in figure 1, after LNP, the raw WS₂ powder were liquid phase exfoliated into nanosheets through ultrasonication treatment in the IPA and water mixed solvent (IPA: H₂O = 1:1, volume ratio) for a certain time. LNP can effectively weaken interlayer van der Waals force of WS₂ and form small cracks. Then the WS₂ powder after ultrasonication can be easily exfoliated into ultrathin WS₂ nanosheets. The thickness and lateral size of the as-obtained WS₂ nanosheets were characterized by atomic force microscope (AFM). The specimen was dropped onto mica substrate, then dried in a vacuum oven before testing. As shown in figure 2(a), the typical height of obtained WS₂ nanosheets is measured to be ~1.5 nm with lateral size about ~1.2 μm, indicating the mono- or bilayer nanosheets. After statistical analysis from some selected area, the WS₂ nanosheet thickness distribution range of is 0.86~3.62 nm. Interestingly, some mesoporous structure can be found on the plane of the WS₂ nanosheets, providing more active sites for electrocatalytic performance of HER. After LNP, the interlayer van der Waals force of WS₂ powder was weakened and formed small cracks. Then the WS₂ powder after ultrasonication for certain time exfoliated into ultra-thin WS₂ nanosheets with a mesoporous structure. The transmission electron microscopy (TEM) is used to investigate the morphology and structure. It can be seen in figure 2(b) that the lattice spacing of about 0.31 nm can correspond to (004) planes of the WS₂ crystal. The selected-area electron diffraction pattern in the insert of figure 2(b) reveals a well-indexed pure hexagonal structure of 2H-WS₂ with a good crystallinity.

Phase identification of the obtained WS₂ nanosheets is evaluated by X-ray diffraction. Figure 3(a) presents the measured XRD patterns of bulk WS₂ and the exfoliated WS₂ nanosheets. The diffraction peaks at 2θ = 14.3, 28.9, 43.9, and 60° can be referred to the crystal planes of (002), (004), (006), and...
Comparing to bulk WS₂, the as-prepared WS₂ nanosheets have a strong diffraction peak (002). What's more, other diffraction peaks of the obtained WS₂ nanosheets are weak or even disappeared, indicating the exfoliated WS₂ nanosheets are mono-layered or few-layered. The XRD spectrum of the prepared WS₂ nanosheets with different LNP time is presented in figure 3(b). As can be seen from the XRD results that the intensity of (002) is quite weak with a short LNP time. With the increasing of LNP time, the intensity of peak becomes stronger, indicating that the concentration of WS₂ nanosheets increases. However, when the LNP time reaches 13h, the lateral size of WS₂ nanosheets is decreased. Besides, there are no obvious diffraction peaks of WO₃ in figure 3(a), indicating that no oxidization occurred during the LNP and exfoliation process.

Figure 3(c) and (d) show the W4f core-level and S2p XPS spectra. Two strong peaks of the W4f core-level spectrum are at 35.0 eV and 32.9 eV, which are assigned to W4f5/2 and W4f7/2 core levels respectively. It is confirmed the W⁴⁺ are present in WS₂ [29]. The S2p core-level spectra shows two strong peaks of S2p1/2 and S2p2/3 at 163.7 and 162.5 eV, respectively, which indicates the S²⁻ state in WS₂ [29]. Sulfur atom has not been oxidized, since no oxidation peaks can be found near 168 eV [18].

3.2. Electrocatalytic activity of HER
The HER of catalysts were measured using the standard three-electrode in the 0.5 M H₂SO₄ electrolyte. Figure 4(a) shows the polarization curves of the samples. It can be observed that the exfoliated WS₂ nanosheets showed much higher electrocatalytic performance with a low overpotential of 65 mV at a current density of 10 mA cm⁻², which is much lower than that of the raw WS₂ powder (280 mV). As the control group, the polarization curve of the glassy carbon electrode displays a straight line, indicating negligible catalytic activity of the glassy carbon. The results show that obtained WS₂ nanosheets exhibit higher catalytic activity of HER. Comparing to literature focused on WS₂ nanosheets before, e.g. Han GQ et. al [27] reported WS₂ nanosheets (overpotential of 80~100 mV) prepared by liquid exfoliation method in DMF, the WS₂ nanosheets produced by our work exhibit better HER activity (overpotential of 65 mV). Han GQ et. al investigated HER performance of nanosheets through loading them onto a glass carbon electrode in 0.5 M H₂SO₄ solution as well as our work. They exfoliate WS₂ nanosheets in the DMF. During electrode preparation, glass carbon electrode with nanosheets usually need to be dried in high temperature oven to remove DMF, but the nanosheets was easy to form re-aggregation and oxidation under high temperature, resulting in
decrease of HER activity. However, we exfoliate WS$_2$ nanosheets in the low-boiling-point organic solvent, thus avoid the above-mentioned problems.

Figure 4. (a) Polarization curves. (b) Tafel plots of samples. (c) and (d) Cyclic voltammograms of raw WS$_2$ and WS$_2$ nanosheets at various scan rates (20-200 mV/s). (e) The electrochemical active surface area. (f) Nyquist plots of raw WS$_2$ and WS$_2$ nanosheets.

The Tafel slope of catalyst is calculated by the Tafel equation $\eta=a+b \log (j)$, where $j$ is the current density and $\eta$ is the overpotential of the electrode. It provides an important evaluation of the electrocatalytic activity towards the HER. Figure 4(b) presents Tafel plots of all samples. The Tafel slope of commercial Pt catalysts is 29 mV/dec, which approaches the result reported in [30]. The Tafel slope of exfoliated WS$_2$ nanosheets (57 mV/dec) is much lower than that of bulk WS$_2$ (125 mV/dec), demonstrating that the exfoliated WS$_2$ nanosheets have a faster kinetics of HER with increasing overpotential. In our work, the thickness of obtained WS$_2$ nanosheets is very thin (about ~1.5 nm) with large lateral size of ~1.2 μm, resulting in large specific surface area. Besides, the mesoporous structure of WS$_2$ nanosheets are also beneficial to HER activity. In our work, we exfoliate WS$_2$ nanosheets in the low-boiling-point rather than traditional high-boiling-point organic solvent, preventing the remaining solvent cover WS$_2$ nanosheets to inhibit the HER activity.

Cyclic voltammograms of exfoliated WS$_2$ nanosheets and raw WS$_2$ powders in the non-Faradaic region of 0.1-0.2V vs. RHE are shown in figure 4(c) and 4(d). The CV test is selected to analyze the double-layer electric capacity as a way to estimate the effective electrode surface area. As can be seen from figure 4(e), the double-layer capacitance (Cdl) of exfoliated WS$_2$ nanosheets (1.65 mF cm$^{-2}$) is larger than that of bulk WS$_2$ (0.56 mF cm$^{-2}$). This result indicates the increase of exposed active edges after the exfoliation of bulk WS$_2$, which enhances the HER activity.

Conductivity is an important factor, which affects the electrocatalytic performance of HER. In order to investigate the catalytic performance further, the electrochemical impedance spectroscopy (EIS) was used for electrode kinetics characterization of HER. Figure 4(f) presents the EIS of WS$_2$ before and after exfoliation, with the overpotential of 100 mV. The Nyquist plots show an obvious charge transfer resistance reduction for exfoliated WS$_2$ nanosheets, as compared to non-exfoliated ones, indicating the higher conductivity of exfoliated WS$_2$ nanosheets. The enhancement of conductivity is caused by the increment of surface area and active edges after the exfoliation.
Exchange current density is another judgment of catalytic activity [31], which represents the velocity of the whole HER process. It is calculated to be 0.50 mA cm\(^{-2}\) for WS\(_2\) nanosheets in this work. High exchange current density is due to the increase in the number of active sites, which benefit from the exposed edges as the ultrathin nanosheets.

4. Conclusion

In this study, ultrathin WS\(_2\) nanosheets were successfully produced by the improved liquid phase exfoliation process in a low boiling-point solvent. The developed process can be easily operated with low cost. The resulting thickness of obtained WS\(_2\) nanosheets is about ~1.5 nm with a lateral size of ~1.2 \(\mu\)m. Moreover, the optimized WS\(_2\) nanosheets exhibit excellent catalytic properties with a small onset potential of 65 mV, a Tafel slope of 55 mV/dec.\(^1\) and remarkable stability (after 1000 cycles). The synthesis method of WS\(_2\) nanosheets proposed in this paper is simple and environment-friendly, which makes it instrumental in preparing various TMD nanosheets.

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