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Colloidal synthesis of 1T' phase dominated WS₂ towards enduring electrocatalysis

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ABSTRACT

Transition metal dichalcogenide (TMD) nanomaterials have attracted tremendous attention due to their great potential for hydrogen evolution reaction (HER), especially with their metallic 1T/1T' phase, which possesses much higher HER activity than the 2H phase. But the metallic phase can transform to 2H phase accompanied by an undesirable degradation in HER activity. Currently, how to prepare the stable metallic phase TMD nanomaterials enabling an enduring HER is one of the main challenges for practical application. Herein, we establish an effective colloidal chemistry strategy for the controllable synthesis of metallic 1T' phase dominated WS₂ (1T'-D WS₂) nanostructures. Such 1T'-D WS₂ exhibits higher performance and more stable HER activity than 2H phase WS₂ in the H₂SO₄ electrolyte. The endurance half-life of 1T'-D WS₂ from stability testing under constant overpotential of 0.3 V vs. RHE and an initial current density of 41 mA/cm² is about 46 days, despite vigorous erosion due to continuous H₂ bubbling which exerts large capillary stresses on the atomic sheets. The facile preparation of highly stable 1T'-phase dominated TMD nanomaterials advances them as competitive sustainable HER electrocatalysts.

1. Introduction

Hydrogen evolution reaction (HER) through electrocatalysis is considered a key reaction for clean energy conversion [1]. Platinum (Pt) on carbon is the standard electrocatalyst, but earth's Pt resources might be insufficient if electrolyzer and fuel cell technologies are scaled up [2]. Huge efforts have been devoted to preparing non-Pt electrocatalysts with the enhanced HER performance. In recent years, among the non-Pt electrocatalysts, the layered transition metal dichalcogenide (TMD) nanomaterials, such as MoS₂ and WS₂, especially their metallic (1T/1T') phase [3–5], are considered promising candidates for HER electrocatalyst [3–9]. For instance, experimental studies have shown that the 1T phase MoS₂ and WS₂ fabricated from the lithium exfoliation method exhibited enhanced HER electrocatalytic performance compared to the corresponding 2H phase [3,4]. Chou et al. [10] confirmed that 1T' MoS₂ was the relatively more active phase towards HER since its active sites are distributed on both the basal planes and the edges, rather than just the edges of the 2H phase MoS₂. On account of this, different fabrication methods have been investigated for preparation of

the metallic phase TMD nanomaterials, including chemical exfoliation [3,4,11], solvothermal [12,13] and colloidal chemistry [14]. However, the aforementioned methods on the synthesis of the metallic phase TMD nanomaterials were restricted to incremental improvement on the cost and/or activity, but without addressing the stability issue. The nondurable performance is associated with the unstable features of metallic phase TMD nanomaterials, which easily transform to 2H phase, accompanying the undesirable degradation of catalytic activity [2,15]. We would therefore like to develop an effective strategy which not only can prepare high-ratio metallic phase of TMD nanomaterials but also can prevent the metallic phase transformation to 2H phase in water/air.

As an important member of layered TMD compounds, tungsten disulfide (WS₂) has wide applications in lubrication [16], field effect transistors [17], electrocatalysis [6] and photocatalysis [14,18]. However, the metallic phase WS₂ nanostructures, especially the 1T' phase, is much less explored. Recently, colloidal chemical synthesis was demonstrated to work impressively in that it retained the stability of synthesized metallic phase MoS₂ over 3 months, much longer than 12 days of chemically exfoliated MoS₂, which can reverse-transform from

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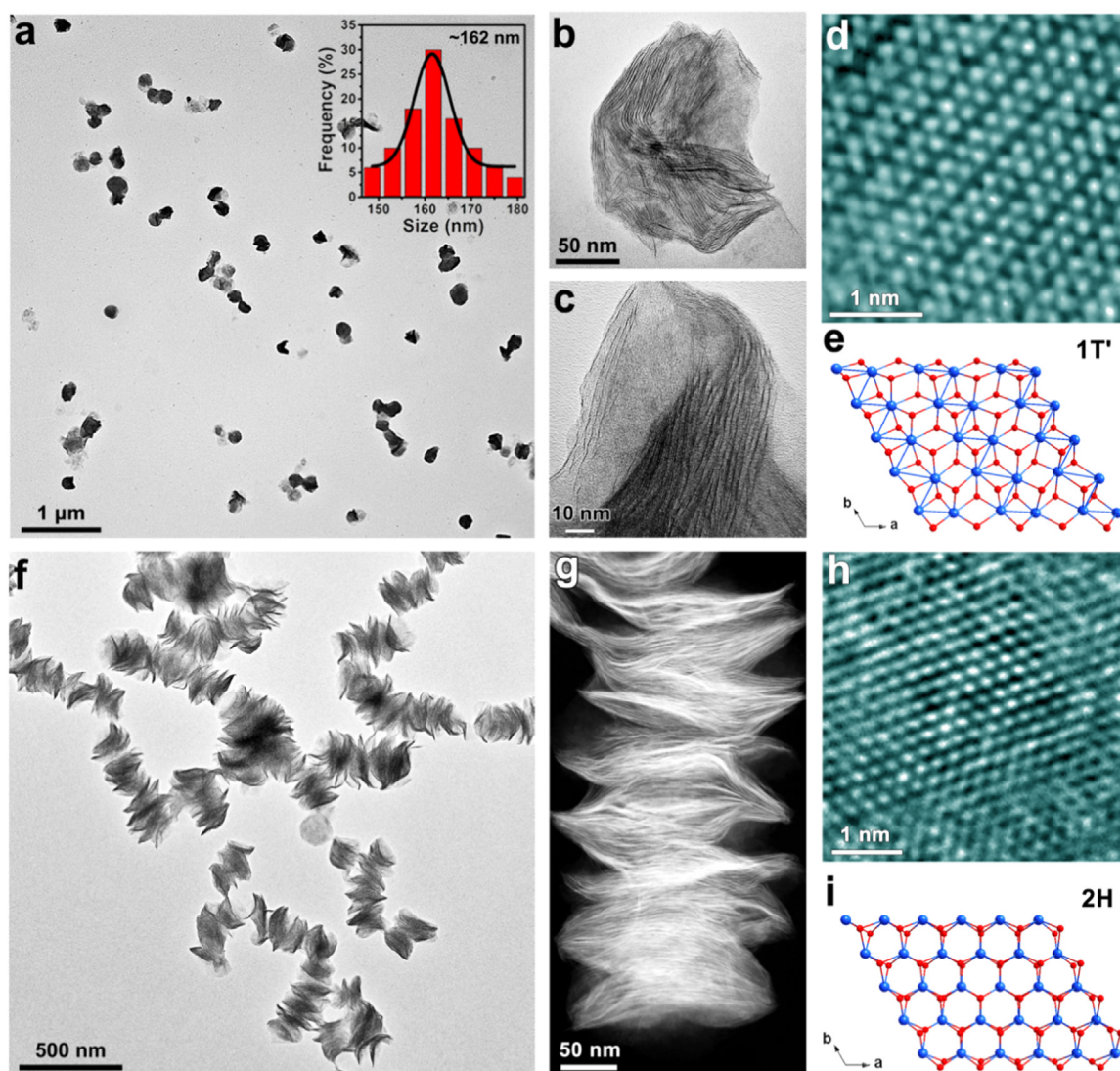


Fig. 1. (a) Typical low magnified TEM image of WS₂ NPs with a dominant size of ~ 162 nm (inset of a). (b) A single TEM image and (c) enlarged TEM image of the WS₂ nanoparticles (NP). HRTEM image of (d) WS₂ NPs, and (e) c-axis view of WS₂ NPs predicted based on structural optimization of the unit cell. Red and blue balls represent S and W atoms, respectively. (f) TEM and (g) HAADF-STEM images of WS₂ nanochains (NCs). HRTEM image of (h) WS₂ NCs and corresponding (i) c-axis view of atomic structure model.

1T to 2H [19–21]. Herein, we established a facile and effective one-pot colloidal chemical strategy to selectively synthesize stable 1T' phase dominated (mixed with 2H phase) and pure 2H phase (as control) WS₂ nanostructures, respectively, abbreviated to 1T'-D WS₂ and 2H WS₂. Compared to 2H WS₂, 1T'-D WS₂ exhibited superior HER performance, such as low overpotential of 200 mV at the current density (J) of 10 mA/cm², small Tafel slope of 50.4 mV/dec and excellent stability. As a proof-of-concept demonstration, a HER endurance half-life of 46 days from of 1T'-D WS₂ was first extracted by performing ultralong HER operation at static overpotential.

2. Results and discussion

The 1T'-D WS₂ was prepared by our one-pot colloidal synthesis approach (see details in Supporting Information). Briefly, 0.2 mmol (NH₄)₂WO₄ and 0.6 mmol thiourea in 20 mmol oleylamine (OM) were used for reaction at 280 °C for 90 min. As shown in the scanning electron microscope (SEM) image of Fig. S1a, the WS₂ sample has nanoparticle-like (NP) structure. The typical low-magnification transmission electron microscopy (TEM) image (Fig. 1a) shows the as-prepared WS₂ nanoparticles (NPs) are relatively monodisperse with a dominant size of

~ 162 nm (inset histogram of Fig. 1a), suggesting the retention of capping ligands on the surface of nanostructures, as verified by Fourier transform infrared (FTIR) spectroscopy (Fig. S1b). The magnified morphology of an individual WS₂ NP (Fig. 1b and Fig. S1c–f) reveals that the entire WS₂ NP comprises of closely-stacked thin nanosheets, which is more discernible in the enlarged TEM image (Fig. 1c). The energy-dispersive X-ray spectroscopy (EDX) (Fig. S1g) confirms that stoichiometric WS₂ is formed with an atomic ratio of W/S ≈ 1/2, consistent with the inductive coupled plasma-optical emission spectroscopy (ICP-OES) data of 1/2.07. The detailed crystal structure of WS₂ NP was examined by high-resolution TEM (HRTEM, Fig. 1d), which was recorded from the planar orientation. It indicates that the crystal lattice of the synthesized WS₂ NP is dominated by the distorted 1T' phase structure with a feature of a zigzag chain of W atoms [4,14], which is consistent with the c-axis view of its corresponding atomic structure model (Fig. 1e). The ratio of 1T' phase vs 2H phase will be analyzed in the following section.

In addition, under the same conditions, except that 16 mmol OM and 4 mmol oleic acid (OA) were used as solvents for reaction at 280 °C for 60 min, our WS₂ features self-assembled chain-like nanostructures. The obvious ripples and corrugations shown in Fig. 1f,g and Fig. S2a

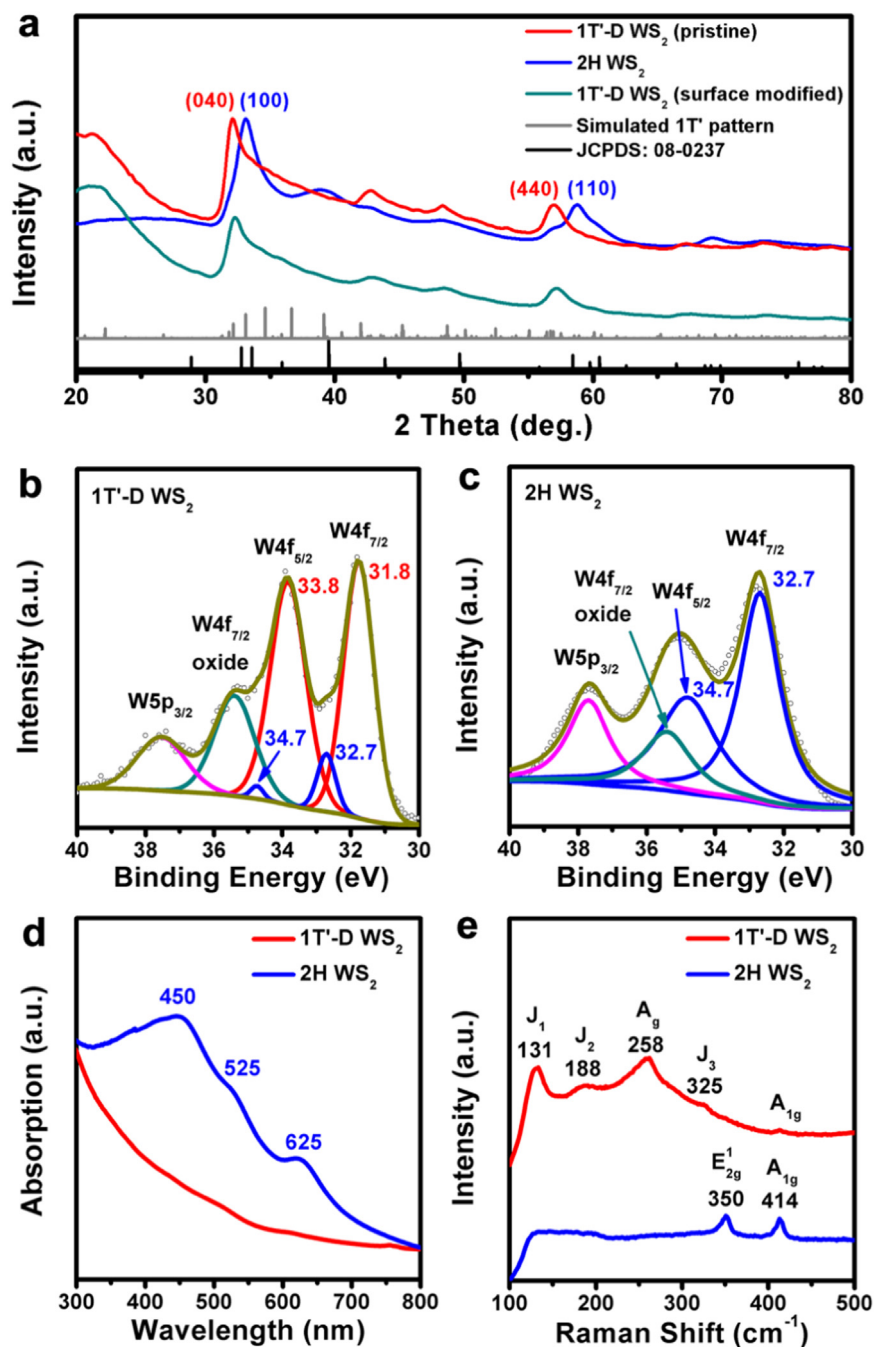


Fig. 2. (a) XRD patterns of pristine 1T'-D WS₂ nanoparticles (NPs), after surface modified 1T'-D WS₂ NPs and 2H WS₂ NCs. (b,c) XPS spectra of W signals recorded from 1T'-D WS₂ NPs and 2H WS₂ nanochains (NCs), respectively. (d) UV-vis spectra and (e) Raman spectroscopy of as-obtained 1T'-D WS₂ NPs and 2H WS₂ NCs samples.

suggest the WS₂ nanochains (NCs) were constructed from WS₂ nanosheets with a thickness of ~ 7.6 nm (about 11 WS₂ monolayers). The FTIR spectroscopy indicates the retention of OM and OA capping ligands on the WS₂ NCs surfaces (Fig. S2b). The HRTEM image (Fig. 1h) clearly shows the crystal structure of the WS₂ NCs is hexagonal, indexed to 2H phase WS₂ [3]. Viewed from the *c*-axis of atomic structure model (Fig. 1i), the 2H phase WS₂ hold the regular hexagonal structure feature, consistent with the HRTEM image.

X-ray diffraction (XRD) patterns, X-ray photoelectron spectroscopy (XPS), UV-vis and Raman scattering were used to further identify the 1T' and 2H phase of WS₂ nanostructures. The XRD patterns of WS₂ NPs and WS₂ NCs samples are presented in Fig. 2a, and both exhibit well-resolved diffraction peaks. The XRD peaks in regions of 31–32° and

56–59° can be used to identify 1T' phase or 2H phase WS₂. As shown in Fig. 2a, the XRD peaks of WS₂ NPs at 31.9° and 56.7° correspond to the (040) and (440) planes of the 1T' phase, while the peaks of WS₂ NCs at 32.9° and 58.5° correspond to the (100) and (110) planes of the 2H phase. In order to further confirm our conclusion, we annealed the WS₂ NPs at 200 °C for 2 h under the protection of N₂. During the thermal treatment, it was found that the XRD peaks at 31.9° and 56.7° of WS₂ NPs gradually shifted to 32.9° and 58.5° of 2H phase, as shown in Fig. S3a,b.

The core level peaks of W4f_{7/2} and W4f_{5/2} in XPS spectra is an efficient way to distinguish the metallic and 2H phase. As shown in Fig. 2b, double peaks located at 31.8 eV and 33.8 eV are ascribed to the core levels of W4f_{7/2} and W4f_{5/2} of 1T' phase WS₂, respectively

[4,12,14]. The ratio of 1T' phase and 2H phase occupies 66.4% and 5.8% in WS₂ NPs sample, respectively, indicating the formation of 1T'-D WS₂ nanocrystals. Two strong peaks of WS₂ NCs at 32.7 eV (W4f_{7/2}) and 34.7 eV (W4f_{5/2}) (Fig. 2c) are the characteristics of W for 2H phase WS₂, and 2H phase occupies 62% in WS₂ NCs sample. Meanwhile, the peaks at 37.5 eV and 35.4 eV corresponding to W5p_{3/2} and W4f_{7/2} (Fig. 2b,c) for both WS₂ samples can also be observed, which may originate from amorphous WO_x-like clusters on the surface of as-prepared WS₂ nanostructures [14]. The ratio of WO_x was 27.8% and 38% in the synthesized 1T'-D and 2H WS₂ samples, respectively. The UV–vis absorption spectra (Fig. 2d) give similar results to previously reported TMD nanocrystals, revealing the 1T' phase for WS₂ NPs and the 2H phase for WS₂ NCs (characteristic peaks at ~ 450 nm, 525 nm and 625 nm) [14]. The Raman shifting peaks of WS₂ NCs at 350 cm⁻¹ and 414 cm⁻¹ are observed (Fig. 2e), which are attributed to E_{2g} and A_{1g} of the characteristic 2H phase. The obviously different Raman shifting peaks of WS₂ NPs located at 131 cm⁻¹, 188 cm⁻¹, 258 cm⁻¹ and 325 cm⁻¹ in the lower frequency region correspond to J₁, J₂, A_g and J₃ peaks, respectively, unambiguously confirming the formation of 1T' phase WS₂ NPs [4,12].

The optimal reaction parameters for colloidal synthesis of 1T'-D WS₂ and 2H WS₂ were screened, such as precursor concentration and the ratio of OM/OA surfactants, as detailed in the supporting information (Figs. S4 and S5). Normally, the phase of nanocrystals can be controlled by tuning the surfactants during the colloidal synthesis process [14,22]. In the present work, the combination of different surfactants was found to play a key role in obtaining 1T'-D WS₂ and 2H WS₂. Sole use of OM as surfactant produced 1T'-D WS₂. Notably, when adding a little amount of OA, the 1T'-D WS₂ would change to 2H phase. The reason for forming different phases of WS₂, changing from 1T' phase to 2H phase, can be explained by electrostatic interactions between the surface charge of [WS₂]⁻ species and the surfactants used [14,23]. For 1T'-D WS₂, the negatively charged [WS₂]⁻ species can be stabilized by the positively charged OM surfactant because of their strong interactions. For 2H WS₂, the added OA surfactant weakens the electrostatic interactions, which cannot prevent its transformation to the thermodynamically stable 2H phase. This can be further confirmed by the thermal treatment results (Fig. S3), the OM surfactant interaction with the 1T'-D WS₂ becomes less important with increasing temperature and leads to the transformation from 1T' phase to 2H phase.

There are three key known factors for achieving excellent HER electrocatalytic activity: active sites, intrinsic conductivity and clean surface. In order to generate a hydrophilic surface for electrocatalysis, we employed acid treatment to remove/modify the surfactant molecules at synthesized WS₂ nanostructures (see details in the experimental section of supporting information) [23,24]. Our experimental results showed that the 1T'-D WS₂ still remained in 1T' phase after acid treatment, which was confirmed by XRD pattern (Fig. 2a) and XPS spectra of W4f (Fig. S6a). This is ascribed to large adsorption energy of thioglycolic acid on 1T'-D WS₂ [23]. Note here, however, the 2H WS₂ changed to oxide (Fig. S6b) under the same condition probably due to the weak interaction between 2H WS₂ and thioglycolic acid, which does not give protection [23]. From above analysis, we can find that our synthesized 1T'-D WS₂ was more stable than 2H WS₂ during the surface modification process, which paved the way for the electrocatalysis applications.

The as-prepared 1T'-D WS₂ and 2H WS₂ were used to investigate the HER electrocatalytic performances. As shown in Fig. 3a, the polarization curves (*i*R corrected) showed the current density versus voltage (*J* versus *V*) for comparison of 1T'-D and 2H phase WS₂ along with Pt/C (20%) samples. Under the same current density of *J* = 10 mA/cm² for H₂ evolution, a low overpotential of 200 mV vs RHE is enough for 1T'-D WS₂ (Fig. 3a), while an overpotential of 290 mV vs RHE is required for 2H WS₂, suggesting a strong catalytic activity of 1T'-D WS₂. The superior HER activity was further proved by the smaller Tafel slopes of 1T'-D WS₂ (50.4 mV/dec) than that of 2H WS₂ (99.4 mV/dec),

indicating the kinetics of the electrochemical hydrogen evolution on 1T'-D WS₂ was much faster than the 2H WS₂ (Fig. 3b). The excellent HER performance of the synthesized 1T'-D WS₂ (e.g. low overpotential at *J* = 10 mA/cm² and small Tafel slope) is comparable to or even better than the reported WS₂ based electrocatalysts (Table S1).

As compared in Fig. S7, Nyquist plots revealed a decreased charge transfer resistance (*R*_{ct}) for the 1T'-D WS₂ relative to the 2H WS₂ for the same mass loading. The electrochemical impedance spectroscopy (EIS) results confirmed that 1T'-D WS₂ possesses much smaller impedance, benefiting faster hydrogen evolution. We also compared the electrochemical surface area (ECSA) of obtained WS₂ samples by measuring the double-layer capacitance (*C*_{dl}). Fig. S8a,b showed the typical cyclic voltammograms (CVs) of 1T'-D WS₂ and 2H WS₂ taken with various scan rates (20, 40, 60 mV/s, etc.) in the region of 0.1–0.3 V (vs. RHE) in 0.5 M H₂SO₄. Current density differences ($\Delta J = J_a - J_c$) at 0.2 V (vs. RHE) were plotted against scan rates. The electrochemical double-layer capacitances, equivalent to the linear slopes in Fig. 3c, were used to represent and compare the ECSA of 1T'-D WS₂ and 2H WS₂. It was noteworthy that the *C*_{dl} of 1T'-D WS₂ (18.8 mF/cm²) was higher than that of 2H WS₂ (8.9 mF/cm²) for the same mass loading, suggesting the 1T'-D WS₂ possessed much larger active surface area and more active sites for hydrogen production.

To further investigate the mechanism for the higher catalytic performance of 1T'-D WS₂, we applied first-principles density functional theory (DFT, see the Supporting Information for details) to calculate the ΔG_{H^*} , the adsorption free energy of H* on surface and edge sites for 1T' WS₂ and edge sites for 2H WS₂ (the surface for 2H WS₂ was not taken into account as active sites only distribute on the edge for 2H phase TMD) [10], which is an appropriate parameter to describe the HER performance. The optimal ΔG_{H^*} value of HER catalyst should approach zero, which could facilitate the charge transfer processes for both H* intermediate and H₂ formation [25]. As shown in Fig. 3d, the H atoms adsorb on the protruding S of 1T' WS₂ in the surface region, and on both S and W in the edge region of 1T' and 2H WS₂. The calculated ΔG_{H^*} patterns of 1T' and 2H WS₂ are shown in Fig. 3e. The ΔG_{H^*} values for both surface and edge of 1T' WS₂ are closer to zero, which explain a better HER initial activity from 1T' WS₂ than 2H WS₂, consistent with the experiment results.

Additionally, we investigated the stability of 1T'-D WS₂ and 2H WS₂ by continuous HER operation for 12 h. As shown in Fig. 4a, the current density of 1T'-D WS₂ shows a slight 8% drop after a long period of 12 h of continuous operation under static overpotential of 0.3 V vs. RHE. By comparison, the 2H WS₂ electrocatalyst exhibits a continuous decrease of 26% in HER activity after 12 h (Fig. 4a) under static overpotential of 0.45 V vs. RHE. Note here, the initial current density on 1T'-D WS₂ electrode is 41 mA/cm², higher than the 37 mA/cm² on the 2H WS₂ electrode. The possible reason for the dramatic decrease of 2H WS₂ HER activity resulted from oxidation of WS₂ to WO_x as HER proceeded, which was confirmed by the XPS spectra of W after stability testing (Fig. S9a). And we verified that the obtained WO_x by direct oxidation of 2H WS₂ displayed poor HER performance (Fig. S9b). In stark contrast, the XPS spectra of 1T'-D WS₂ after 12 h HER stability testing showed no obvious changes of the chemical state for W (Fig. S9c), indicating the 1T'-D WS₂ catalyst still maintained the 1T' phase, and hence the excellent HER stability.

1T'-D WS₂ exhibited impressive HER stability, but what is curious about this material is why it still got 8% drop in performance after 12 h stability testing. In order to investigate the reason behind the slight HER degradation of 1T'-D WS₂, we compared the *ex-situ* XPS spectra of S recorded from 1T'-D WS₂ (Fig. 4b) at different times during the course of HER stability testing. Compared with pristine 1T'-D WS₂, it was found that a new strong peak appears at 169.1 eV after HER stability testing. The new peak is attributed to sulfonate. The formation of sulfonate can be further demonstrated by the FTIR spectra (Fig. 4c). The peaks at 1105 cm⁻¹ and 987 cm⁻¹ were indexed to S=O stretch and S-O stretch of sulfonate, respectively. However, we used Nafion

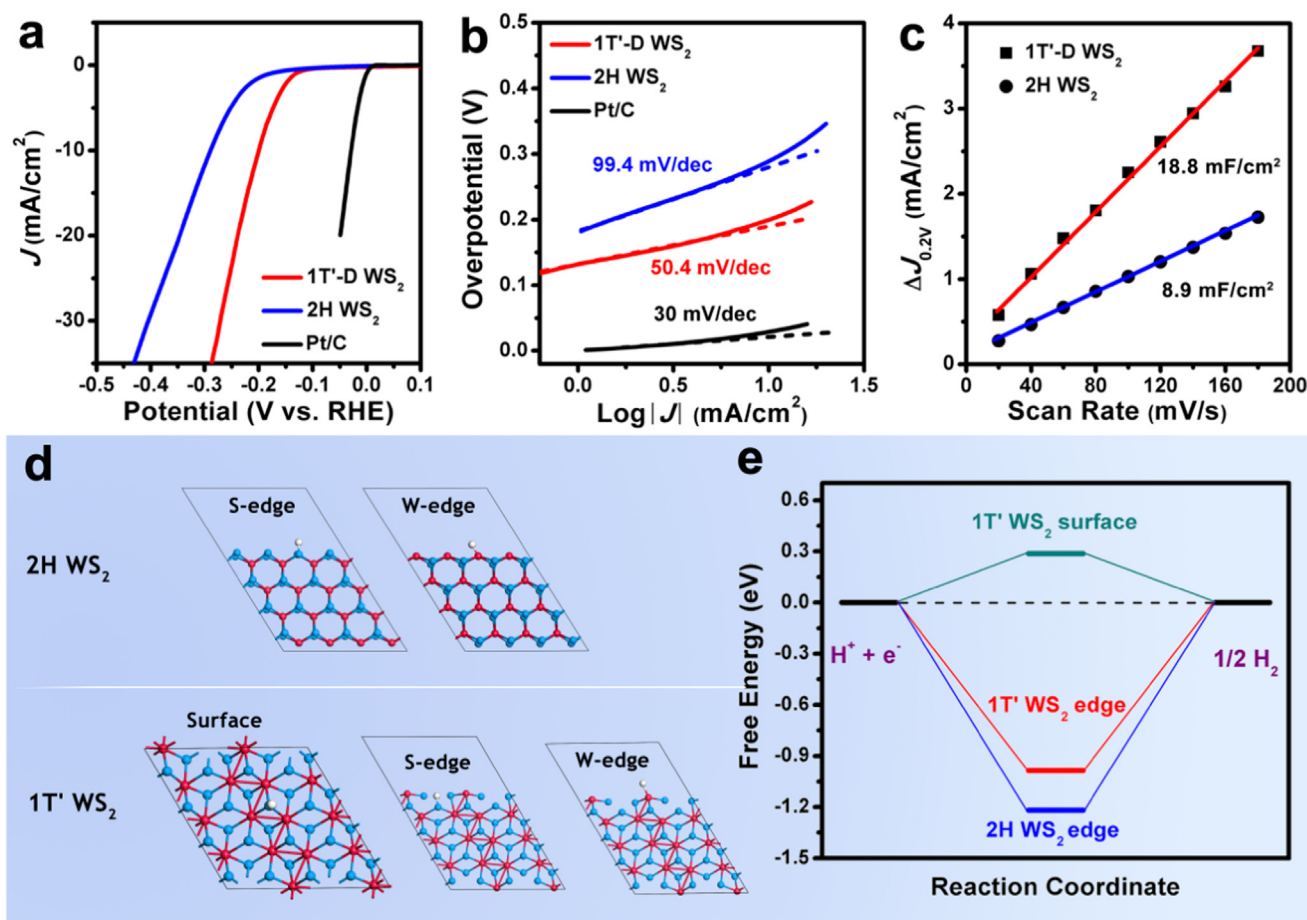


Fig. 3. (a) Polarization curves of 1T'-D WS₂, 2H WS₂, and commercialized Pt/C (20%) for comparison. “J” represents the current density. (b) The corresponding Tafel curves for catalysts derived from (a). (c) The electrochemically active surface area estimated from the voltammograms at various scan rates (20–180 mV/s, Fig. S8). (d) Surface and edge view of 1T' and 2H phase WS₂. Red, blue and white balls represent W, S and H atoms, respectively. (e) The calculated free-energy diagram of HER for surface/edge of 1T' and 2H phase WS₂.

(perfluorosulfonic acid-PTFE copolymer) as the fixative in the HER experiments. In order to rule out the possibility of sulfonate group from Nafion, we also studied PTFE (polytetrafluoroethylene) as fixative instead of Nafion in the HER experiment. As shown in Fig. 4c, we found that with either Nafion or PTFE, sulfonate could be generated during HER testing, thus it is not due to the fixative. The sulfonate may come from the reaction between WS₂'s surface WO_x components and H₂SO₄ in 0.5 M H₂SO₄ electrolyte. Furthermore, during the HER operation, there still exists the transformation of 1T'-D phase to 2H phase (Fig. 4b). Therefore, the aforementioned causes the slight HER degradation of 1T'-D WS₂ after 12 h operation.

As a proof-of-concept demonstration, we implemented HER endurance testing to calculate the endurance half-life of electrocatalyst. As shown in Fig. 4d, the catalyst exhibited a relative stable HER activity in the first 5 days and then gradually decreased in course of HER stability testing (Fig. 4d). The high decrease rate after 15 days may result from WS₂ catalyst's mechanical peeling off the electrode after long-time immersion in the electrolyte, accelerated by erosion due to continuous H₂ bubbling from catalyst as observed from experiments that exert large capillary forces on the atomic sheets. The half-life of this HER could be calculated by the following Eq. (1):

$$t_{1/2} = \frac{t}{\log_2 \left(\frac{N(t)}{N_0} \right)} \quad (1)$$

where $t_{1/2}$ and t represent half-life and the variable of time, respectively. $N(t)$ and N_0 stand for the current density at time t and initial current density, respectively. Based on the definition of Eq. (1), the

calculated half-life of 1T'-D WS₂ was about 46 days under constant overpotential of 0.3 V vs. RHE and an initial current density of 41 mA/cm². The XPS spectra of W and S recorded from the 1T'-D WS₂ catalyst after HER endurance testing over one month indicated that there were only WO_x species (Fig. S10a) and sulfonate left (Fig. S10b). This reveals another cause of HER performance degradation under high-current-density testing for 1T'-D WS₂ (Fig. 4d). As far as we know, this is the first long-term HER endurance test to evaluate the half-life of TMD electrocatalyst, which provides valuable experimental information on device lifetime and cost/performance tradeoff, thus benefiting the future research efforts towards industrialization.

3. Conclusion

In summary, we have established a one-pot colloidal synthesis method for selectively preparing metallic 1T'-D and semiconducting 2H phase WS₂ nanostructures with a high degree of monodispersity. After acid treatment, 1T'-D WS₂ largely remained and exhibited superior HER performance, such as low overpotential of 200 mV at current density 10 mA/cm², a small Tafel slope of 50.4 mV/dec and outstanding stability, compared with 2H WS₂. While the raw-materials cost limit of WS₂ (~ \$100/kg) is much cheaper than that of Pt (~ \$30,000/kg), if the endurance time of 1T'-D WS₂ is very short, it will never be able to compete with Pt-based HER catalysts. Here we have shown that at a very high current density of 41 mA/cm², our 1T'-D WS₂ catalyst is still super enduring, despite vigorous mechanical erosion by the bubbling H₂ gas and unavoidable chemical transformations to WO_x and

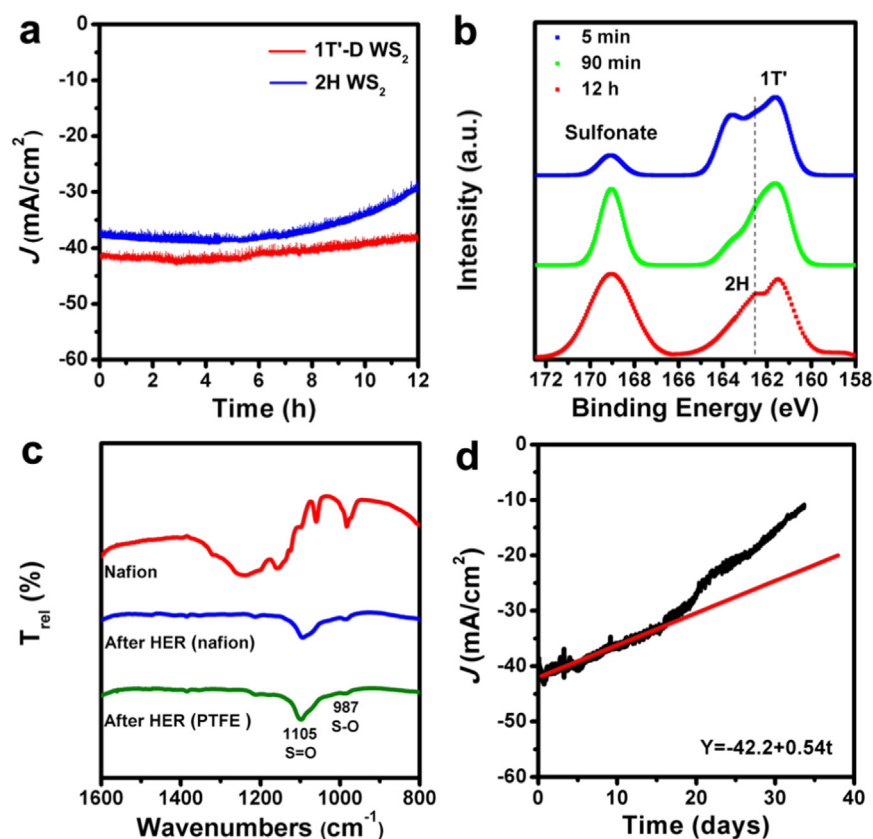


Fig. 4. (a) Continuous HER recorded from 1T'-D WS₂ and 2H WS₂ coated carbon fibre cloth (CFC) as working electrodes at a static overpotential of 0.3 V and 0.45 V vs. RHE, respectively. XPS spectra of (b) S2p recorded from 1T'-D WS₂ at different time in course of HER stability testing. (c) FTIR spectra of Nafion and 1T'-D WS₂ after HER test using Nafion and PVDF as a fixative. (d) Half-life time calculated by analysis continuous HER stability testing of 1T'-D WS₂ at a static overpotential of 0.3 V vs. RHE.

sulfonate. We believe our facile and scalable approach could be extended to selectively preparing 1T' and 2H phases for other TMDs materials with various properties, in pursuit of cost-effectiveness for a wide range of applications, including the hydrogen economy.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.nanoen.2018.05.019>.

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