Hydrophilic tannic acid-modified WS$_2$ nanosheets for enhanced polysulfide conversion in aqueous media

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Abstract

Polysulfide-based organic battery systems have demonstrated great potential for large scale energy storage, but are restricted by the cost and the flammability of the organic solvents. It would be ideal to establish the aqueous-based polysulfide electrochemistry to enable cost-effective stationary energy storage. However, the sluggish reaction kinetics of polysulfide placed a serious fundamental barrier to implementation. Here we developed hydrophilic tannic acid-modified WS$_2$ nanosheets as polysulfide conversion electrocatalysts in alkaline aqueous solutions. The tannic acid not only acted as a negatively-charged surfactant to effectively delaminate the bulk WS$_2$ sheets, but also functionalised the delaminated WS$_2$ nanosheets through the attachment of tannic acid functional groups, resulting in greatly improved hydrophilicity. Using graphene as the conductive support, the tannic acid-modified hydrophilic WS$_2$ nanosheets demonstrated a promoting electrocatalytic activity for polysulfide oxidation and reduction in aqueous solution. The incorporation of tannic acid imposed the collective interactions between polysulfide and the WS$_2$ nanosheets via the hydrophilic molecules and the polar surfaces. With a 0.5 M Li$_2$S$_2$ electrolyte, the graphene and modified WS$_2$ mixture gave an areal specific capacity of 0.37 mAh cm$^{-2}$, compared to 0.27 mAh cm$^{-2}$ for the pure graphene.

1. Introduction

There is a critical demand for advanced large-scale energy storage systems that can contribute to the development of renewable energy technologies such as solar and wind systems, as they suffer from the random and intermittent nature. Lithium ion batteries (LIBs) have been dominant in such energy storage systems over the last two decades. Although substantial effort has been devoted to the improvement of LIBs and various vigorous studies toward further development still continue [1–5], the present Li-ion technologies cannot fulfill the ever-increasing requirements of the modern society, because of the limited energy density and expensiveness in the large-scale applications [6].

Sulfur (S), one of the most abundant elements in earth’s crust, provides not only the cost and non-toxicity advantages but also a promising candidate for high-energy battery systems. For example, S exhibits a high theoretical capacity of 1675 mAh g$^{-1}$ in non-aqueous electrolytes and constructs the organic electrolyte-based lithium–sulfur batteries with a theoretical specific energy of 2600 Wh kg$^{-1}$, which is about 5-fold higher than the current LIBs in energy density [7–10]. More significantly, S possesses high solubility in aqueous sulfide solutions, which makes it also attractive for aqueous electrochemical energy storage [11]. Different from organic electrolytes, where the S produces a series of polysulfides ($Li_2S_x\, 1 < x < 8$) during the reduction, the redox reaction of aqueous polysulfides is based on three main chemical species, i.e. $H_2S$ (aq.), $HS^-$ (the major monosulfide species) and $S_x^{2-}$ ($2 < x < 4$), whose formation can be affected by the pH [11, 12]. Given that economical and safe battery technologies are of major importance nowadays for commercial applications, polysulfide-based aqueous rechargeable batteries potentially could fulfill the criteria through the use of cost-
effective sulfur and non-combustible aqueous electrolytes. Water-based electrolytes are cheaper and safer than organic counterparts, and also low-cost salts and separators are available. Furthermore, the aqueous electrolytes deliver around two order of magnitude higher ionic conductivity than that of organic solvents [13, 14].

With these perspectives, there is tremendous interest in recent years in polysulfide-based aqueous battery research. Licht team proposed the use of polysulfides in aqueous system two decades ago and they constructed an aluminium sulfur battery based on concentrated polysulfide catholytes and an aluminium anode in an alkaline electrolyte [11, 12, 15]. Such battery possessed a theoretical energy density of 647 Wh kg$^{-1}$ with a voltage window of 1.79 V, even though only 1.3 V cell voltage and 110–170 Wh g$^{-1}$ energy density were demonstrated in practical tests. Subsequently, dissolved polysulfides were developed in combination with lithium metal/lithium ions in either hybrid or aqueous systems. A Li-ion/polysulfide cell utilising LiMn$_2$O$_4$ versus polysulfides in the Li$_2$SO$_4$-containing electrolyte was found to provide a 1.5 V open circuit voltage and 110 mAh g$^{-1}$ capacity with almost no fading over 100 cycles [13]. A hybrid lithium-polysulfide battery in which dissolved Li$_2$S$_4$/Li$_2$S redox couple in the aqueous LiOH electrolyte was used as the cathode and metallic lithium in the organic electrolyte was used as the anode separated by a ceramic membrane was reported for the first time by Li et al and co-workers [16]. The battery was found to deliver a reversible capacity of 1030 mAh g$^{-1}$ and a specific energy density of ~654 Wh kg$^{-1}$. Afterwards, they took advantage of solar energy to further improve the cell by oxidising S$^{2-}$ to polysulfides in aqueous solution with a Pt-modified CdS photocatalyst [17]. Moreover, S has drawn considerable attention in the field of redox flow batteries (RFBs). Unlike the enclosed configuration of the batteries (e.g. LiBs), the flow batteries are that the electroactive species are dissolved in liquid electrolytes and stored in the separate tanks [18–20]. The aqueous bromine-polysulfide RFB employs NaBr electrolyte in the positive half-cell and Na$_2$S$_x$ electrolyte in the negative half-cell [21, 22]. A cell voltage of about 1.5 V is given by such a system. A new ferri/ferrocyanide—polysulfide RFB was reported recently based on K$_2$Fe(CN)$_6$ at the positive side and Na$_2$S$_x$ at the negative side in the NaOH supporting electrolyte with a 0.91 V cell voltage [23]. Also, a polysulfide—poliodide flow battery was developed, which delivered an open circuit voltage of 1 V and utilised sodium working ions to balance the charge in both electrolytes [24].

Despite the advantages and potential of aqueous S-polysulfides in the energy conversion and storage systems, the kinetics behaviour of polysulfide chemical reactions is slow in the aqueous electrolyte, which crucially causes the low conversion efficiency and energy loss. It was demonstrated that the homogeneous rate of conversion between S$_2$$^{2-}$ and S$_4$$^{2-}$ and the rate of the heterogeneous chemical reaction of S$_2$$^{2-}$ ↔ HS$^-$ were both significant in determining the kinetics of polysulfides [25]. Carbon-based materials, due to the non-polar property, only possess physical van der Waals interaction with polar polysulfides species, which result in weak adsorption and easy detachment of polysulfides and hence, poor electrochemical performance [26]. This indicates that carbonaceous materials themselves cannot serve alone as an ideal host and thus suitable electrocatalysts are necessary to optimise the polysulfide reaction. Several electrocatalysts, e.g. Co, CoS, Co$_x$S$_2$ and MoS$_2$, have been demonstrated to accelerate the kinetics of polysulfide oxidation and reduction in the aqueous systems [16, 23, 25, 27–29]. However, the surface properties of these electrocatalysts need to be tailored to achieve appropriate activity in the aqueous systems.

Herein, we tailored WS$_2$ sheets to electrocatalyse the aqueous polysulfides redox reaction. WS$_2$, similar with MoS$_2$, is one of transition metal dichalcogenides, consisting of hexagonal layer of W atom sandwiched between two layers of chalcogen atoms [30]. The sandwich layers are coupled by the van der Waals forces. WS$_2$ has been studied extensively in terms of the catalytic property for electrochemical evolution of hydrogen [31–33] as well as the ion intercalation/deintercalation behaviour in LiBs and sodium ion batteries [34–37]. These investigations have shown that the surface chemistry of WS$_2$ is closely related toward high catalytic activity or high ion storage performance. More importantly, different forms of WS$_2$ as the electrocatalysts for polysulfide oxidation and reduction were studied, which reported that the catalyst activity was directly proportional to the number of edge planes at the catalyst surface [38]. Furthermore, transition metal dichalcogenides, owing to their strong chemical affinity with polar polysulfide species, are found to play an anchoring effect in the organic electrolyte-based lithium–sulfur batteries, which can introduce intimate contact with polysulfides and thereby facilitate the polysulfide redox reactivity [26, 39, 40]. The anchoring effect mainly originates from its chemical interaction with the Li atom in Li$_2$S$_x$ species, which overcomes the weak chemical adsorption by carbon substrate [26]. The transition metal dichalcogenides can induce remarkable but not too strong binding strength, which ensure the intact Li$_2$S$_x$ configuration and prevent its destruction and dissolution into the electrolyte. According to density functional theory simulations, WS$_2$ provides the binding energy of 0.52–1.45 eV for Li$_2$S$_x$ (the binding energy increases as the lithiation process continues until Li$_3$S) [41], whereas the chemical bonding energy of the non-polar carbon materials is only in the range of 0.1–0.3 eV [26].

Consequently, capitalising upon this knowledge base, in this work we design a facile and one-pot route to modify the WS$_2$ sheets, which aims to the optimisation of WS$_2$ electrocatalysts for aqueous polysulfide oxidation and reduction. The WS$_2$ nanosheets functionalised with tannic acid was obtained through sonication-assisted exfoliation and surface modification of bulk WS$_2$. Our results revealed that the dimension of modified WS$_2$ was
reduced, which created more active sites/edge planes; the hydrophilicity of modified WS2 was increased, which accelerated the ion transport to the electrode–electrolyte interfaces in the aqueous system. The chemical interaction with polysulfides was also strengthened by introducing the WS2, which enhanced the kinetics of polysulfide redox reactions. Thus, the graphene and modified WS2 mixture gave an areal specific capacity of 0.37 mAh cm$^{-2}$ in the 0.5 M Li$_2$S$_2$ electrolyte, while the pure graphene only delivered a capacity of 0.27 mAh cm$^{-2}$.

2. Experimental procedure

2.1. Materials
Tungsten disulfide (2 μm particle size), tannic acid, sulfur, lithium sulfide, lithium hydroxide, expandable graphite and Nafion perfluorinated resin (5 wt%) solution were purchased from Sigma-Aldrich.

2.2. Synthesis of tannic acid modified WS$_2$ (ta-$\text{WS}_2$)
The ta-$\text{WS}_2$ nanosheets were synthesised from bulk WS$_2$ by sonication-assisted liquid exfoliation in the aqueous tannic acid solution. In a typical procedure, the solid-state tannic acid was first dissolved in the deionised water (DI water) with the concentration of 20 mg ml$^{-1}$. Secondly, 100 mg of pristine WS$_2$ powder was added into 30 ml of the tannic acid solution and dispersed by probe sonication for 3 h (amplitude: 50%; pulse-on: 10 s; pulse off: 5 s). Thirdly, the dark green dispersion (after sonication) was treated by vacuum filtration to collect the treated WS$_2$ nanosheets and also rinsed by sufficient DI water to remove the excessive tannic acid. Finally, the as-obtained sample was dried in the oven at 120 °C, which was denoted as ta-$\text{WS}_2$. The ta-$\text{WS}_2$ was dispersed in water for further characterisations.

2.3. Preparation of aqueous lithium polysulfide solution and graphene
The aqueous lithium polysulfide solutions were prepared as follows: first, 0.5 M Li$_2$S was dissolved in aqueous solution containing 1 M LiOH, then 0.5 M, 1.5 M or 2.5 M sulfur was added into the solution for preparing the 0.5 M Li$_2$S$_2$, Li$_2$S$_4$, and Li$_2$S$_6$ solution, respectively. All solutions were applied with N$_2$ to remove the air for 20–30 min and then sealed airtight. Finally, the solutions were transferred to a 95 °C bath for a continuous stirring of about 1 h until the sulfur was totally dissolved. In terms of graphene, graphite was oxidised by the improved Hummer’s method. Then the oxidised graphite was annealed in the furnace at 900 °C for 5 min to obtain the graphene sample.

2.4. Characterisations
The size of bulk WS$_2$ and ta-$\text{WS}_2$ was determined by Malvern Zetasizer Nano ZS. Transmission electron microscopy (TEM) was performed on the Tecnai F20 field emission transmission electron microscope. Scanning electron microscopy (SEM) images of bulk WS$_2$ and ta-$\text{WS}_2$ were collected from the NanoSEM 230 field emission scanning electron microscope. X-ray diffraction (XRD) was carried out on a PANalytical Empyrean Thin-Film XRD System with a Cu Kα source. Raman spectra were obtained on a Renishaw inVia Raman Microscope from 300–450 cm$^{-1}$ using a green excitation laser (Ar, 514 nm). Fourier transform infrared (FTIR) spectroscopy was performed on the Varian 640 FTIR Spectrometer with a sensitive liquid nitrogen-cooled MCT detector. X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Scientific K-Alpha spectrometer with Al Kα radiation. The UV–visible absorption spectrum measurements for the aqueous lithium polysulfide solutions (Li$_2$S, Li$_2$S$_2$, Li$_2$S$_4$, and Li$_2$S$_6$) were performed using Shimadzu UV-3600. The BET specific surface area measurements were conducted by Micromeritics Tristar 3030.

2.5. Electrochemical measurements
The ink solutions including the pure graphene, pure ta-$\text{WS}_2$, 10:1, 5:1, 2:1 and 1:1 graphene+ta-$\text{WS}_2$ and 2:1 graphene+WS$_2$ were prepared as follows: 5 mg of samples or mixed samples were separately dispersed in 1 ml of diluted Nafion solution (DI water:ethanol:purchased Nafion = 8:2:1 by volume) by probe sonication for 2 min (amplitude: 20%; pulse-on: 10 s; pulse off: 5 s). Then the various ink solutions (the pure graphene: 4 μl; pure ta-$\text{WS}_2$: 4 μl; 10:1 graphene+ta-$\text{WS}_2$: 4.4 μl; 5:1 graphene+ta-$\text{WS}_2$: 4.8 μl; and 1:1 graphene+ta-$\text{WS}_2$: 8 μl; 2:1 graphene+ta-$\text{WS}_2$: 6 μl, which ensured the same mass of graphene loading) were drop-cast onto a glassy carbon electrode ($D = 0.4$ cm). The electrochemical properties of the samples were evaluated by using a three-electrode cell: a graphite counter electrode, a Hg/HgO reference electrode in 0.1 M NaOH solution, and a glassy carbon working electrode drop-casting with different samples stabilised in 0.5 M Li$_2$S$_2$ alkaline solution at the scan rates of 10, 20, 30, 40, 50, 80 and 100 mV s$^{-1}$ within $-1.1$ to 0.2 V. The electrochemical impedance spectroscopy (EIS) (10 mHz–600 kHz, 5 mV) was used to study the graphene, 2:1 graphene+ta-$\text{WS}_2$ and 2:1 graphene+WS$_2$ at the $-0.2$ V. The material stability of the graphene, 2:1...
graphene–ta-WS2 and 2:1 graphene–WS2 for the polysulfide reactions was tested individually within −1.1 to 0.2 V by cycling 5 times at 20 mV s⁻¹ and then 100 times at 100 mV s⁻¹. This unit process of cycling test was continuously repeated for 5 times. Moreover, the graphene, 2:1 graphene–ta-WS2 and 2:1 graphene–WS2 were further studied by linear sweep voltammetry (LSV) using the rotating disk electrode (RDE) in the same three-electrode set-up at 1600 rpm at 5 mV s⁻¹ from −0.65 V (open circuit voltage) to 0.2 V and from −0.65 to −1.1 V.

Regarding the specific capacity, the integral area of the oxidation peak was first produced from the cyclic voltammetric (CV) profiles. Then the integral area was divided by the corresponding scan rate and the electrode area (0.126 cm²), which thus obtained the specific capacity.

Diffusion coefficient (cm² s⁻¹) in the electrolyte was evaluated by cyclic voltammetry with different scan rates and calculated according to the Randles–Sevick equation:

\[ I_p = 2.69 \times 10^7 n^{3/2} A D^{1/2} C_v^{0.5} \]

in which \( I_p \) (A) is the peak current, \( n \) represents the number of electrons in the reaction (based on \( 2S_2^- \rightarrow 2e^- \rightarrow S_2 \), \( n = 2 \)), \( A \) (cm²) indicates the electrode area (0.126 cm²), \( C \) (mol ml⁻¹) means the ion concentration in the electrolyte, and \( v \) stands for the scanning rate (V s⁻¹).

The electrochemical rate constant \( k^0 \) (cm s⁻¹) was obtained through a Tafel plot by using the equation below:

\[ i_0 = FAk^0C_0. \]

The \( X \) value of the fitted Tafel plot at the potential of −0.55 V (versus Hg/HgO) gave the logarithm of the exchange current \( i_0 \) for each sample, which equals to \( FAk^0C_0 \), where Faraday’s constant \( F \) = 96 485 C mol⁻¹, electrode area \( A = 0.126 \) cm² and polysulfide concentration \( C_0 = 0.5 \) M.

3. Results and discussion

Tannic acid-modified WS2 (ta-WS2) nanosheets were prepared with a one-pot synthesis method by simply exfoliating bulk WS2 under probe sonication in the tannic acid solution, followed by removal of the excess tannic acid with vacuum filtration and washing. In this strategy, the tannic acid molecules were selected as a surfactant and the exfoliation time of the bulk solid WS2 was set to 3 h, which is comparable with that of exfoliation of bulk WS2 in other surfactant solutions, e.g. hexadecyltrimethylammonium bromide (CTAB) and N, N-dimethylformamide (DMF) [33, 42]. With the assistance of continuous ultrasonication, the bulk WS2 in the presence of tannic acid molecules was efficiently split into smaller nanosheets with the size reducing from about 2 μm to 450 nm, which was determined from the dynamic light scattering using the Zetasizer. The TEM images in figure S1 (supplementary material is available online at stacks.iop.org/JPENERGY/1/015005/mmedia) further confirmed the obvious reduction of the size in the ta-WS2 nanosheet. Additionally, the tannic acid molecules modified the surface of the bulk WS2, which resulted in the improved hydrophilicity of the ta-WS2 nanosheets. The water suspension of the ta-WS2 after being stored for 2 days under ambient environment was much more stable than that of the bulk WS2 (figure S2, supporting information). With regard to the mechanism of tannic acid-assisted exfoliation and modification of WS2 (figure 1(a)), the negatively charged tannic acid molecules, due to the ionisation in the water, should first approach toward the W atoms at the edge and the aggressive sonication functioned as a driving force to facilitate the intercalation of tannic acid molecules into the interlayer space of WS2. Such insertion of tannic acid molecules delivered enough repulsive steric forces to break the van der Waals interlayer interactions in WS2, which therefore helped to reduce the thickness of the WS2 sheets. Such inserted tannic acid molecules also helped to split the WS2 sheets into smaller sizes under the intense sonication, which reduced the plane dimension of the WS2 sheets. Also, after breaking the WS2 sheet, the defects were formed at the WS2 edge/surface, which accompanied the production of the unsaturated W species. These unsaturated W species provided the opportunity for the attachment of negatively charged tannic acid molecules on the WS2, resulting in the surface modification of the WS2, which thus increased the hydrophilic nature of the WS2 nanosheets.

Layered materials (transition metal oxides, sulfides and carbides) have been demonstrated to introduce strong binding interaction with polysulfide species in lithium–sulfur batteries for achieving long-cycling performance [26, 39, 43–45]. The WS2 was hence studied as the electrocatalyst in this work for aqueous polysulfide oxidation and reduction, on account of its strong chemical affinity with highly polar polysulfides. As depicted in figure 1(b), the ta-WS2 nanosheets were attached to the conductive graphene matrix. The graphene substrate could afford efficient electron pathways and trigger the electrocatalytic activity of the hydrophilic ta-WS2 nanosheets for aqueous polysulfide redox reactions. To be specific, the decreased dimension of ta-WS2, on one hand, helped to form high-effective charge-transfer junction between conducting graphene framework and ta-WS2 surface. This guaranteed the full utilisation of the polysulfide species that were adsorbed/captured by the ta-WS2 nanosheets. On the other hand, the ta-WS2 nanosheets provided a higher specific surface area
compared to the bulk WS$_2$, which, as a result, increased the exposed sulfphilic polar surface/active sites. The improved hydrophilicity of the ta-WS$_2$ in aqueous system also can accelerate the ion transport toward the electrode–electrolyte interface. However, even though the pristine WS$_2$ had the polar adsorption sites for polysulfone ions, the bulk size could block the electron pathways from the graphene to the WS$_2$, which caused the low utilisation of polysulfides (see figure 1(c)). The inferior wettability of the pristine WS$_2$ further negatively affected the electrochemical performance of polysulfide reaction.

With the assistance of continuous sonication in the presence of tannic acid, the bulk solid material was split into smaller structures. The SEM images of the WS$_2$ before and after tannic acid processing, as displayed in figures 2(a) and (b), unveiled a marked difference in the size between the pristine and the treated WS$_2$. The raw WS$_2$ sheets exhibited clear flake shape and are highly crystalline. By contrast, owing to the surface modification with tannic acid molecules, the microstructure of the ta-WS$_2$ remarkably became smaller and more disintegrated, compared to the bulk WS$_2$. The size reduction of ta-WS$_2$ contributed to higher specific area, which was advantageous to catalyse the polysulfide redox reaction. Also, thanks to the decreased dimension of the ta-WS$_2$, the effective electron pathway with the graphene substrate can be formed, which facilitated the full utilisation of polysulfides. The HR-TEM images provided further evidence of the effect of the tannic acid on the microstructure of ta-WS$_2$, particularly at its terminated edge. The as-obtained sample showed a ribbon-like edge, composed of many loosely assembled small pieces of WS$_2$ nanosheets (see figure S3(a)). The tannic acid treatment introduced abundant defects such as edge planes into the final product. Such defects created more catalytic sites, which were responsible for the aqueous polysulfide conversion. The pristine WS$_2$, however, retained a platelet-like edge plane, which was angular and faceted (figures S3(b) and (c)). Furthermore, the lateral plane of the ta-WS$_2$ nanosheets was observed in figure 2(c) with the ordered lattice fringes that exhibited an interlayer distance of around 0.68 nm. This was corresponded to the (002) peak in the XRD data. Figure 2(d) depicted a uniform lattice matrix on the basal plane of the ta-WS$_2$, where the thickness was three layers.

The XRD patterns of the bulk WS$_2$ and ta-WS$_2$ are shown in figure 2(e). The diffraction peaks corresponded to the hexagonal phase (2H) of WS$_2$. For ta-WS$_2$, the intensities of (002), (004), (006) and (008) peaks, which were indexed to the layer stacking along the c direction, decreased after ultrasonication with tannic acid, indicative of the reduced thickness and the decreased degree of crystallisation of the ta-WS$_2$ slices while the crystalline 2H phase of WS$_2$ was still retained. The XRD results confirmed the mechanism of tannic acid-assisted exfoliation of WS$_2$, as exhibited in figure 1(a). The tannic acid molecules did intercalate into the interlayer space of WS$_2$ under the intense sonication driving force, which thus broke the van der Waals interactions to reduce the thickness of WS$_2$. In terms of Raman spectrum, the first-order E$_{2g}^1$ and A$_{1g}$ optical modes represented the in-plane phonon mode and the out-of-plane phonon mode for the 2H-WS$_2$, respectively, as illustrated in the inset of figure 2(f). The typical Raman spectra of the pristine WS$_2$ and ta-WS$_2$ are displayed in figure S4 with the range from 100 to 800 cm$^{-1}$. When using 514 nm excitation, although the second-order Raman peak, the 2LA(M) mode at 352 cm$^{-1}$, overlaps with the first-order E$_{2g}^1$ mode at 355 cm$^{-1}$, the Lorentzian peak fitting in figure 2(f)
clearly separates their individual contributions [46]. It was reported that when decreasing the number of WS₂ layers, the peak frequency of A₁₈ mode decreased and the relative intensity E₂LA/A₁₈ (at 514 nm excitation) increased correspondingly [46]. The softening of the A₁₈ mode resulted from the weaker phonon restoring force caused by van der Waals interlayer contributions [46]. Based on the Raman spectra for the pristine WS₂ and ta-WS₂, the A₁₈ peak frequencies and intensity ratios of E₂LA/A₁₈ are displayed in figure 2(f). It is clearly observed that the ta-WS₂ had a decreased peak frequency of A₁₈ and an increased intensity ratio of E₂LA/A₁₈ as compared to the bulk WS₂, suggesting that the ta-WS₂ was in a more lamellar structure. The Raman results further demonstrated that the thickness of ta-WS₂ was reduced after sonicated with tannic acid molecules.

Furthermore, the surface modification of WS₂ with tannic acid molecules was verified by XPS and FTIR measurements. The FTIR spectrum of the ta-WS₂ (see figure 3(a)) showed the characteristic absorption peaks in the wavenumber range from 1800 to 800 cm⁻¹, which were consistent with the peak signals of the tannic acid.
molecule that represented the regions of aromatic compounds and substituted benzene rings, correspondingly [47, 48]. This confirmed the successful functionalisation of the WS2 with tannic acid during the ultrasonication process. The further evidence was provided by XPS. The pristine WS2 and ta-WS2 exhibited the similar high resolution W 4f and S 2p core-level spectra of XPS. To be specific, as shown in figure S5(a), the binding energies of W 4f7/2 and W 4f5/2 for W4+ in both bulk WS2 and treated ta-WS2 were located at 33.1 and 35.3 eV, respectively [42, 49]. The peaks at about 36.3 and 38.6 eV were assigned to the binding energy of W6+ in WO3, which possibly result from the tiny oxidation of W edges. Meanwhile, the peaks at around 164.0 and 162.8 eV were ascribed to the coexistence of S 2p1/2 and S 2p3/2 for S2− in figure S5(b) [42, 50]. A main difference between the bulk WS2 and ta-WS2, as presented in figure 3(b), was observed in the deconvolution of the C 1s peak. The small amount of carbon occurring in the pristine WS2 might originate from the adsorption of CO2 in air on the surface of the sample. After the treatment, the carbon content of ta-WS2 obviously increased from 6.14%–28.63% and the peaks at 284.6, 287.3 and 289.0 eV corresponded to carbon atoms attached to different oxygen-containing moieties, which indicated the existence of tannic acid. This can be explained as below. Thanks to the continuous vigorous ultrasonication, the size and the thickness of the WS2 was reduced with the assistance of the tannic acid, during which abundant defects on the WS2 edge/surface can be formed. These defects accompanied the production of the unsaturated W species that could adsorb the negatively charged tannic acid molecules. Meanwhile, the substitution of S by the oxygen functional groups of the tannic acid molecules could happen during the sonication. Thus the attachment of the tannic acid molecules on the ta-WS2 was found, which was confirmed by FTIR and XPS results. Moreover, the contact angle study was used to ascertain the hydrophilicity of the untreated and treated WS2, as seen in figures 3(c) and (d). The contact angle θ through the water droplet on the ta-WS2 was smaller than that of the bulk WS2, which indicated the increased wettability of the ta-WS2 due to the occurrence of the hydrophilic function groups from tannic acid molecules.

The synthesised ta-WS2 as the electrocatalyst for polysulfide oxidation and reduction was investigated in a three-electrode system in the 0.5 M Li2S2 electrolyte by the CV tests. Elemental sulfur cannot dissolve in aqueous solution, however, is soluble in aqueous sulfide solutions [11]. The aqueous Li2S2 solution was prepared by 1:1 sulfur to Li2S solution in the 1 M LiOH, where the LiOH supporting electrolyte was used to prevent the formation of H2S. The existence of S2− ions in the solution was verified by the UV–vis in figure S6. The ta-WS2 nanosheets were first mixed with the graphene in the different ratios, in order to determine the optimal condition for the polysulfide redox reaction, as shown in figure 4(a). As the ta-WS2 is non-conductive, different mixing proportions of the graphene to ta-WS2 were studied to find out the condition in which the addition of ta-WS2 cannot block the efficient electron transfer pathway of the conductive material so as to maximise the performance of the polysulfide reaction. In order to compare these samples equally, the graphene, as the conductive material for the polysulfide reaction, was loaded in the same quantity, i.e. 0.02 mg, with different proportions of ta-WS2, which was then studied in the polysulfide electrolytes with the same concentration and volume. Graphene, due to the non-polar C–C bond, provides a poor electrical contact with the high-polar
polysulfides, which can lead to slow redox kinetics and high charge transfer resistance for polysulfide reactions \[39\]. Thus, the pure graphene electrode gave the lower current density than the graphene incorporated by the sulphilic ta-WS\textsubscript{2} in the proportions of 10:1, 5:1 and 2:1. The increase of the current densities with the increasing mass of ta-WS\textsubscript{2} can be observed, indicating that the ta-WS\textsubscript{2}–polysulfide interaction not only indeed exists but also dynamically accelerate the electrochemical reactions of polysulfides. Due to the poor electrical conductivity of the WS\textsubscript{2}, the 1:1 graphene + ta-WS\textsubscript{2}, where the amount of ta-WS\textsubscript{2} further increased, showed the worst performance (the current density was only half of that of the pure graphene), which was caused by the improved resistance of the electrode. The CV curves of the graphene + ta-WS\textsubscript{2} in various proportions are shown in figure S7 and it is clearly showed that the 2:1 ratio of graphene to ta-WS\textsubscript{2} was the optimal electrode with the highest current response for the polysulfide redox reaction. Additionally, given that the carbon material used in the experiment was a kind of reduced graphene, a small number of function groups existed on the surface of the

Figure 4. (a) Column diagram of current densities based on different ratios of graphene to ta-WS\textsubscript{2} in the 0.5 M Li\textsubscript{2}S\textsubscript{2} at 50 mV s\textsuperscript{−1}; (b) CV curves of the pure graphene, pure ta-WS\textsubscript{2}, graphene + ta-WS\textsubscript{2} and graphene + WS\textsubscript{2} in the 0.5 M Li\textsubscript{2}S\textsubscript{2} at −1.1 to 0.2 V versus Hg/HgO at 20 mV s\textsuperscript{−1}; (c) rate capability within −1.1 to 0.2 V versus Hg/HgO at 20, 50, 80 and 100 mV s\textsuperscript{−1}; (d) EIS of the pure graphene, graphene + ta-WS\textsubscript{2} and graphene + WS\textsubscript{2} electrodes in the 0.5 M Li\textsubscript{2}S\textsubscript{2} electrolyte; (e) CV profiles of graphene + ta-WS\textsubscript{2} at Cycle 1, 200, 500 at 20 mV s\textsuperscript{−1} and (f) cycling performances at 20 mV s\textsuperscript{−1} of the pure graphene, graphene + ta-WS\textsubscript{2} and graphene + WS\textsubscript{2} electrodes in the 0.5 M Li\textsubscript{2}S\textsubscript{2} electrolyte.
graphene (see the XPS survey spectrum in figure S8), which was beneficial to anchor the polar ta-WS2 nanosheets.

The catalytic effect of ta-WS2 was further studied in comparison with the pristine WS2 by CV within the potential range of −1.1 and 0.2 V versus Hg/HgO at 20 mV s$^{-1}$, as exhibited in figure 4(b). Even though the pure ta-WS2 itself does not deliver any decent CV signal for the polysulfides, the ta-WS2 nanosheets mixed with the graphene indeed greatly enhance the electrochemical reactivity of the polysulfide ions with the higher peak current densities by comparing the CV curves of the graphene with and without the ta-WS2. However, when introducing the pristine WS2 in the same condition, the graphene + WS2 electrode gives lower current response, that is, worse electrochemical performance than that of the pure graphene. The redox reaction of S$_x$~$^{2−}$/S$_x$~$^{2−}$− couple follows the electrochemical equation (1) given below. In the aqueous system, the S$_x^2$~$^{2−}$ ions cannot be formed, as the disproportionation of S$_6^2$− to S$_7^2$− and S$_7^2$ is present, which is demonstrated by the UV–vis (see figure S6). It is worth noting that multiple electron transfers happen in the CV curves obtained on the graphene, graphene + ta-WS2 and graphene + WS2, as indicated by two oxidation peaks at −0.55 V (small) and −0.2 V (broad) and two reduction peaks at −0.7 and −0.85 V (broad, overlapped). Theoretically, both oxidation and reduction peaks are corresponding to the reactions based on the electrochemical equations (2) and (3). It is however possible that the polysulfides experience more complicated electrochemical reactions with the involvement of more polysulfide species, such as S$_x^2$~$^{2−}$ (x = 1, 2, 3, 4, 6, etc) [23]. In addition, rate capability based on the areal specific capacity with various scan rates in the range of 20−100 mV s$^{-1}$ is illustrated in figure 4(c). It is obvious that the specific capacity of the graphene + ta-WS2 outperforms those with the pure graphene and graphene + WS2 electrodes at all scan rates. The graphene + WS2 electrode is found to exhibit comparable performance with the pure graphene at the higher scan rates. This is probably because the introduction of WS2 generates an elevated binding energy with the polysulfides, resulting in the improved reaction kinetics

\[
\begin{align*}
2S_2^2− & \rightarrow 2e− \leftrightarrow S_4^2− \quad (1) \\
3S_2^2− & \rightarrow 2e− \leftrightarrow 2S_3^2− \quad (2) \\
4S_3^2− & \rightarrow 2e− \leftrightarrow 3S_4^2− \quad (3)
\end{align*}
\]

Figure 4(d) shows the EIS for the graphene electrodes without and with ta-WS2/WS2 in the Li$_2$S$_2$ electrolyte. The semicircle in the Nyquist plots represents the charge transfer resistance ($R$$_t$) at the electrode-polysulfide interfaces. The fitting $R$$_t$ results are 110.6, 97.5, 130.7 ohm for pure graphene, graphene + ta-WS2 and graphene + WS2, respectively. The ta-WS2 is engineered to provide strong ta-WS2 interaction, relieving the kinetic barrier from polysulfide redox transformation. This thus allows the polysulfide to reach dynamic equilibrium more easily. By introducing the sulphilphic ta-WS2, the high efficient charge transfer junction can be formed, which accelerates the polysulfide redox reaction. When the ta-WS2 nanosheets are attached to conductive graphene matrix, easy access can be provided for electrical charge to reach ta-WS2-polysulfide interface, thereby triggering the polysulfide electrochemistry. Consequently, the charge transfer at ta-WS2-polysulfide interface is faster than at graphene-polysulfide interface, suggesting that the redox kinetics of polysulfides in the aqueous system (Li$_2$S$_2$ ↔ Li$_2$S$_0$) is enhanced by incorporating the sulphilphic ta-WS2 hosts. However, due to the large dimensional size and hydrophobicity of the pristine WS2, the efficient electron pathways can be blocked, thereby increasing the charge transfer resistance. Furthermore, stability of the electrode materials for the aqueous polysulfide reaction was investigated at the alternant scan rates of 20 and 100 mV s$^{-1}$. As given in figure 4(e), by comparing the CV profiles of the graphene + ta-WS2 composite electrode at Cycle 1, Cycle 200 and Cycle 500 at 20 mV s$^{-1}$ during which cycling at 100 mV s$^{-1}$, the shape does not change obviously, which demonstrates the stable composite material for the polysulfide reactions. The specific capacities of the graphene, the graphene + ta-WS2, the graphene + WS2 are compared throughout the cycling in figure 4(f) and clearly, the graphene + ta-WS2 composite electrode exhibits the best specific capacities. This can be expected that when adding the ta-WS2 into the electrode, it not only improves the polysulfide redox reaction with the higher capacity, but also shows a stable cycling performance in the polysulfide-based batteries.

The introduction of ta-WS2 into the carbon substrate shows the enhanced performance in terms of aqueous polysulfide redox reactivity, which can be explained in three main ways. First, the dimension of ta-WS2 is obviously reduced, which increases the specific surface area and thereby provides more active sites/edge planes for efficiently electrocatalysing the polysulfide reactions. The specific surface area of ta-WS2 was 75.5 m$^2$ g$^{-1}$, while the pristine WS2 merely possessed a surface area of 15.6 m$^2$ g$^{-1}$. Because the catalyst activity was directly proportional to the number of edge planes at the catalyst surface for polysulfide redox reactions [38], the ta-WS2 with the higher specific surface area accompanied more active sites or edge planes, which greatly improved the catalytic performance in the polysulfide system. Also, the smaller size of ta-WS2 is beneficial to form effective electron pathways from conductive framework to the electrocatalyst surface, which results in the lower charge transfer resistance and ensures the higher utilisation of polysulfides. Second, the hydrophilic property of ta-WS2
is improved due to the attachment of the tannic acid molecules. This can increase the wettability of ta-WS₂ electrocatalyst and thereby accelerate the ion transport to the electrode–electrolyte interfaces. The ion diffusion coefficient was evaluated by a series CVs with various scan rates and was calculated by the Randles–Sevick equation (see figure 5(a)). The diffusion coefficients for graphene, 2:1 graphene+ta-WS₂ and 2:1 graphene+WS₂ were determined to be $2.80 \times 10^{-7}$, $5.69 \times 10^{-7}$, and $1.53 \times 10^{-7}$ cm$^2$ s$^{-1}$, respectively. It is clearly showed that the graphene+ta-WS₂ composite electrode possesses an almost two-time higher diffusion coefficient than that of the pure graphene, which is ascribed to the introduction of the ta-WS₂ with improved wettability. In contrast, when loading the bulk WS₂ into the graphene, due to the inferior hydrophilicity of the bulk WS₂, the ion diffusion efficiency is deteriorated. In the third aspect, the polysulfide adsorption capability of WS₂, due to the strong chemical affinity, affords high electrocatalytic activity for fast polysulfide redox reactions. The chemical binding energy of the WS₂ sheets for polysulfide ions was simulated to be 0.52−1.45 eV [41], while the non-polar carbon materials only provided the binding energy of 0.1−0.3 eV for polysulfides [26]. The stronger interaction between the WS₂ and the polysulfides ensures that the WS₂ can more easily adsorb or capture the polysulfide ions in the electrolyte, functioning as the electrocatalyst to accelerate the reaction kinetics of the polysulfides. The improved polysulfide redox kinetics was verified by LSV using the RDE, as shown in figures 5(b) and (c). It is known that the lower the current density, the more sluggish the kinetics. According to the current densities of the samples, the kinetics increased in the following order: graphene < 2:1 graphene+WS₂ < 2:1 graphene+ta-WS₂. Moreover, the fitted Tafel plots (shown as the dotted lines in figure 5(d)) yield the electrochemical rate constants of $8.20 \times 10^{-4}$, $9.89 \times 10^{-4}$, and $1.87 \times 10^{-3}$ cm s$^{-1}$ for graphene, 2:1 graphene+WS₂ and 2:1 graphene+ta-WS₂, respectively. Obviously, the incorporation of WS₂ or ta-WS₂ can dynamically enhance the polysulfide redox reactions and the better performance of ta-WS₂ is because of the reduced size with the higher specific area and the increased hydrophilicity.

Figure 5. (a) Relationship between peak current and $v^{1/2}$ for cyclic voltammograms of graphene, 2:1 graphene+ta-WS₂ and 2:1 graphene+WS₂ in the 0.5 M Li₂S₂ solution at different scan rates; kinetics study of graphene, 2:1 graphene+ta-WS₂ and 2:1 graphene+WS₂ in the 0.5 M Li₂S₂ solution by linear sweep voltammetry using the RDE at 1600 rpm at 5 mV s$^{-1}$ (b) from −0.65 V (open circuit voltage) to 0.2 V and (c) from −0.65 to −1.1 V; (d) the plots of potential versus the logarithm of kinetic current and the corresponding fitted Tafel plots (dotted traces) for graphene, 2:1 graphene+ta-WS₂ and 2:1 graphene+WS₂.
4. Conclusions

A facile and one-pot procedure to fabricate tannic acid modified WS$_2$ nanosheets with improved wettability has been developed. The synthesis route is very straightforward and can be scaled up or extended to other similar covalent-network materials. With the aid of tannic acid, the exfoliation efficiency of WS$_2$ is not only greatly improved, but also the hydrophilicity is obviously enhanced due to the functionalisation of tannic acid molecules. Such ta-WS$_2$ nanosheets are proved to show excellent electrocatalytic capability for aqueous polysulfide oxidation and reduction. The enhanced polysulfide redox reactions are achieved by tailoring the ta-WS$_2$ electrocatalysts with increased activation sites/edge planes, fast ion diffusion at the electrode–electrolyte interfaces and strong interaction with polysulfides. This work may open the way to preparation of optimal electrocatalysis of polysulfide redox reactivity and further improvement could be anticipated by engineering the hydrophilic electrocatalyst quantum dots or employing the nitrogen-doping into the electrocatalysts for development of polysulfide-based aqueous energy storage applications.

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Conflicts of interest

There are no conflicts to declare.

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