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Layered tungsten-based composites and their pseudocapacitive and electrocatalytic performance†

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With the rapid development of heterostructured electrocatalysts, the potential application of transition metal dichalcogenide (TMD)-based composites for electrocatalysis have attracted intense attraction owing to their unique optical, electronic, and mechanical properties. Herein, a facile solvothermal method to obtain heterostructured composites consisting of TMD (WS_2) and graphitic carbon nitride ($g-C_3N_4$) is reported. DFT calculation results demonstrates that the interface interaction between $g-C_3N_4$ and WS_2 optimizes the electronic structure of composite materials and activates the active sites. The $WS_2-g-C_3N_4$ composites with surface sulfur and nitrogen vacancies exhibit high specific capacitance of 1156 F g^{-1} and excellent cycling stability with no capacitance loss over 2000 charge–discharge cycles, demonstrating huge potential in applications for pseudocapacitive energy storage. In addition, $WS_2-g-C_3N_4$ composites can attain excellent hydrogen production activity to reach a current density of 10 mA cm^{-2} at an overpotential of -0.170 V (vs. RHE) and Tafel slope of 59 mV dec^{-1} . This work provides an effective way for the synthesis of heterostructured electrocatalysts with efficient activity for energy conversion and storage.

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1. Introduction

Two-dimensional (2D) layered transition metal dichalcogenides (TMDs) have emerged as a promising class of catalysts due to their unique crystal structure and layer-dependent optoelectronic properties which offer great prospects for exploitation in applications ranging from photovoltaics, photocatalysis to electrocatalysis. Among TMDs, tungsten and its compounds (*i.e.*, WS_x) have been tested as electrocatalysts in their intrinsic

or hybrid form, because of their polymorphic nature and ability to participate in complex interatomic interactions with other materials *via* surface engineering. The structural features of WS_x , such as their lateral size, layer number and active sites *i.e.* step edges and atomic vacancies, have been shown to greatly influence their electrocatalytic properties and performance.¹ When the lateral size of WS_x is reduced within the nanoscale domain, unique mechanical and optoelectronic properties arising from quantum confinement effects have been observed.² Their individual sandwich layers made up of transition metal and chalcogen bound by weak van der Waals forces can also offer large surface area and permeable channels for ion adsorption and transport.³

Experimental and computational studies have established that exposed chalcogen edge sites of WS_x can facilitate improved electrocatalytic performance while the basal surfaces remain catalytically inert.^{3,4} Accordingly, WS_x can be supported on carbon nanostructures to increase the activity of the inert basal surface of TMD through increased defect sites created *via* the preferential bonding between the basal planes of WS_x and carbon surfaces. Carbon nanostructures can also serve as conductive supports to further augment the electrical conductivity while increasing contact resistance. Pure carbon and hybrids of graphitic carbon nitride ($g-C_3N_4$) have been reported to hold great promise as alternatives to expensive precious metal-based

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catalysts for water splitting and CO₂ reduction due to their tunable chemistry, high thermal and chemical stability, low cost, and non-toxicity.^{5,6}

Several strategies have been developed to tailor the structural features of g-C₃N₄ to enhance their electrochemical activity and durability. Improvements in electronic structure and energy band configuration of g-C₃N₄ based nanocomposites have been demonstrated by the functionalization of g-C₃N₄ at atomic and molecular levels *via* elemental doping and copolymerization, respectively. The content of heteroatomic species of nitrogen and sulfur are particularly useful for modifying surface functional groups and crystallinity which can increase charge carrier mobility with low diffusion barriers during cycling to enhance rate capability and electrochemical performance. For example, quaternary nitrogen has been reported to improve electrical conductivity which facilitates the charge/discharge process while pyrrolic and pyridinic nitrogen can introduce active sites and defects.^{7,8} Surface sulfur vacancies have been reported to alter the electronic structure of host materials by reducing the electron transition energy barrier and enhancing electrophilic adsorption.⁹ Other ways of improving the physico-chemical properties of g-C₃N₄ for target-specific applications include coupling with other semiconductors, metal/metal oxides as a cocatalyst or incorporation of carbonaceous materials to form hybrid nanocomposites. Since g-C₃N₄ possesses an analogous layered structure with finite exposed edges, the fabrication of an organic/inorganic hybrid nanocomposites with another layered material such as WS₂ can lead to the formation of surface heterojunctions for efficient charge collection and separation while exposing active sites required for electrocatalytic reactions. Understanding the effect of growing WS₂ on a g-C₃N₄ based support for electrocatalytic reactions is crucial, and yet remains to be explored.

Herein, we report the formulation of tungsten-based composites *via* the growth of WS₂ on an interconnected, macroscopic g-C₃N₄ scaffold using W₁₈O₄₉ derived from solvothermal treatment as a template. The presence of different heteroatomic surface species of nitrogen and sulfur were found to influence the rate capability and cyclic performance of the tungsten-based composites. DFT calculations confirm the importance of WS₂-g-C₃N₄ heterostructure design. Benefitting

from optimal specific surface area and nitrogen and sulfur content of 11 at% and 1.01 at%, respectively, the WS₂/g-C₃N₄ composite exhibits high specific capacitance of 1156 F g⁻¹ and excellent cycling stability with no capacitance loss over 2000 charge-discharge cycles, demonstrating huge potential in applications for pseudocapacitive energy storage. In addition, the WS₂/g-C₃N₄ composite can attain excellent hydrogen production activity to reach a current density of 10 mA cm⁻² at an overpotential of -0.170 V and Tafel slope of 59 mV dec⁻¹.

2. Experimental

2.1. Preparation of WS₂-g-C₃N₄ composites

The scheme for fabricating the WS₂-g-C₃N₄ composites is illustrated in Fig. 1. All chemical compounds and solvents used during synthesis were purchased from Sigma Aldrich. Solvothermal treatment, an easy and low-cost methodology, was employed to grow W₁₈O₄₉ on melamine (C₃H₆N₆) scaffold using the tungsten hexachloride (WCl₆, 0.075 g) - cyclohexanol (C₆H₁₂O, 50 mL) mixture, subjected to heat treatment for 6 h at 200 °C.¹⁰

Prior to sulfidation, the W₁₈O₄₉-C₃H₆N₆ composites were subjected to carbonization under argon atmosphere to yield W₁₈O₄₉-g-C₃N₄ composites at reaction temperatures of 400, 600 and 800 °C to derive samples, which were referred to as WS₂-400, WS₂-600 and WS₂-800, respectively. Once the reaction temperature mentioned above was attained, hydrogen sulfide gas was introduced into the reaction chamber for 50 min to initiate the sulfidation process for the samples. After sulfidation, most of the W₁₈O₄₉ grown on the g-C₃N₄ scaffolds were converted into WS₂, depending on the reaction temperature.

2.2. Materials characterization and electrochemical testing

The crystalline structure of the composites was characterized by X-ray diffraction (XRD) using a Bruker D8 Advance diffractometer (operated at 40 kV, 40 mA), with a Cu Kα radiation, at a step size of 0.02° and a dwell time of 1 s. The Raman spectra were acquired at room temperature using a Renishaw benchtop system, with 532 nm excitation wavelength and 24001 mm⁻¹ grating. Surface chemical analysis was performed on a Kratos Axis Ultra system with a monochromated Al Kr X-ray source

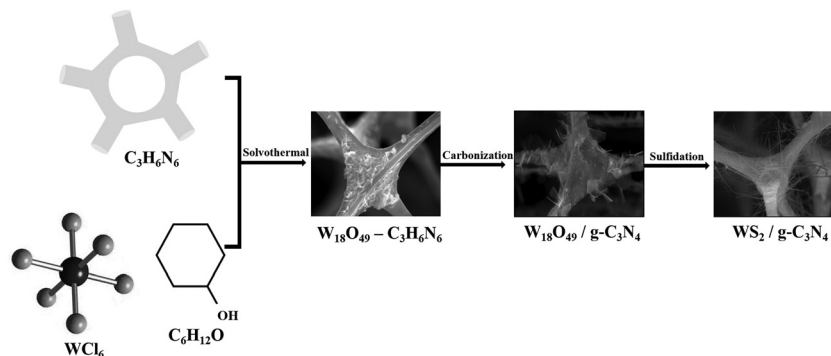


Fig. 1 Schematic of synthetic procedure for WS₂-g-C₃N₄ composites.



operated at 10 mA emission current and 15 kV anode potential. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were used to conduct the morphological and structural analyses. Elemental composition of WS₂-g-C₃N₄ composites was evaluated using scanning electron microscopy (Hitachi S3200N, Oxford instrument – SEM-EDS) and high-resolution transmission electron microscopy (JEOL-2100, HR-TEM), respectively. The Brunauer–Emmett–Teller (BET) surface areas and pore size distribution of the WS₂/g-C₃N₄ composites were measured with the Micromeritics ASAP 2020 nitrogen adsorption analyzer.

2.3. Electrochemical measurements

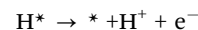
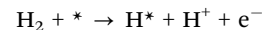
Electrochemical measurements for hydrogen evolution reaction (HER) and capacitance were performed at room temperature using a CHI-660E workstation coupled with a rotating disk electrode (RDE) system consisting of Ag/AgCl/KCl, platinum wire and glassy carbon rotating disk electrode (GCE) covered with catalyst ink as reference, counter and working electrodes, respectively. The working electrode was prepared by drop casting of catalyst ink prepared from a mixture of 5 μL of Nafion solution, 1 mL of ethanol/water solution and 3 mg of composite sample. The active mass loading of the electrodes was 0.21 mg cm⁻². For the HER, electrochemical measurements were carried out in a 0.5 M H₂SO₄ (Sigma Aldrich) electrolyte solution at different potentials and scan rates varying from 0 –0.8 V and 10–100 mV, respectively. The experimentally measured potential versus Ag/AgCl, $E_{\text{Ag/AgCl}}$, was calibrated with respect to the RHE (reversible hydrogen electrode), E_{RHE} , according to the Nernst equation; $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + E_{\text{Ag/AgCl}}^0 + 0.059 \text{ pH}$ (at 25 °C) where $E_{\text{Ag/AgCl}}^0 = 0.1976 \text{ V}$ at 25 °C. The acquired HER experimental values were generated in 0.5 M H₂SO₄ solution and corrected for iR loss. Chronoamperometric measurements were performed by applying the corresponding potential to support an initial current density of about 10 mA cm⁻² for 10 h for the HER. Electrochemical impedance spectroscopy measurements were carried out after applying the AC voltage with 10 mV amplitude at a frequency range of 0.05 Hz to 10 kHz, using the open circuit potential.

For specific capacitance (C_{sp}), galvanostatic discharge/charge (GCD) measurements were recorded at current densities ranging from 2 to 15 A g⁻¹. Specific capacitance (C_{sp}) was derived from GCD measurements using the equation: $C_{\text{sp}} = I/m(\Delta V/\Delta t)$ where I (A) is the discharge current, Δt (s) is the discharge time consumed in the potential window of ΔV (V) and m represents the mass of active material. The stability of the supercapacitor was evaluated by cyclic GCD measurements at current density of 15 A g⁻¹ for 10 000 cycles.

2.4. DFT Calculation parameters

In this work, the first-principles density functional theory (DFT) was applied by using the projector augmented wave method (PAW).¹¹ Additionally, the exchange–correlation function was approved by employing the Perdew–Burke–Ernzerhof generalized gradient approximation (PBE-GGA).¹² For the results, we

applied the wave functions with plane-wave expansion with 400 eV cutting off energy while force tolerance was set at 0.05 eV Å⁻¹ for relaxation. Also, certain surfaces of the (100) planes were chosen to build the heterostructure of WS₂-g-C₃N₄ nanocomposites. Furthermore, the WS₂ surface of (100) with 7 × 7 units of and the g-C₃N₄ surface (100) with 3 × 3 units were established to simulate the heterostructure of WS₂-g-C₃N₄. Since HER consists of four elementary reactions, the electron transfer for each reaction was supplemented by the process of proton expulsion, which can be indicated below:



where * and X* are demonstrated as an adsorption site and an adsorbed X intermediary on the reaction surface. The H⁺ + e⁻ can be shown as free energy of half formation energy of H₂ at 1 atm within 298 K. The reduction activity was calculated by using $\Delta G = \Delta E + \Delta \text{ZPE} - T\Delta S$ for the free energy where the ΔE was acquired by its geometric forms. Moreover, the ΔZPE and ΔS were defined by using the computational vibration frequency, combined with the standard tables of gas reactants. The entropy was assumed as zero at the adsorbed surface-active site.

3. Results and discussion

3.1. Structural and physicochemical properties

To investigate the structure–activity relationships, DFT calculations were applied to study the electronic structure of these catalysts. Here, g-C₃N₄, WS₂ and WS₂-g-C₃N₄ are considered as the model object to analyse the difference of electronic structure and catalytic mechanism. Density of states (DOS) and partial density of states (PDOS) of these materials are shown in Fig. 2.

The band gap of WS₂, g-C₃N₄, and WS₂-g-C₃N₄ are 1.63 eV, 1.21 eV, and 0.85 eV, respectively. The WS₂-g-C₃N₄ composite exhibits the lowest band gap energy, beneficial to electron transfer in catalytic process. Furthermore, atomic orbit such as N, S, and W of the WS₂-g-C₃N₄ composite is closer to the Fermi level compared with g-C₃N₄ and WS₂, which supports this finding. In addition, enhanced electron transfer at the interface of g-C₃N₄ and WS₂ can further facilitate the absorption of water molecules. Therefore, designing the heterostructure of WS₂-g-C₃N₄ has a positive effect for improving the catalytic activity of HER. To understand the catalytic process for HER reaction, the reaction energies of WS₂, g-C₃N₄, and WS₂-g-C₃N₄ at each step of the HER reaction are calculated. The Gibbs free energies of pristine g-C₃N₄, WS₂ and WS₂-g-C₃N₄ composite have been calculated to investigate HER activity (Fig. 3). As shown in Fig. 3, the Volmer–Heyrovsky reaction pathway of HER is that H⁺ was first adsorbed onto the surface of solid catalysts, then formed in the intermediate species H*, finally converted into hydrogen.

In the Volmer–Heyrovsky reaction, the generation of intermediate species H* is the important rate determining step in



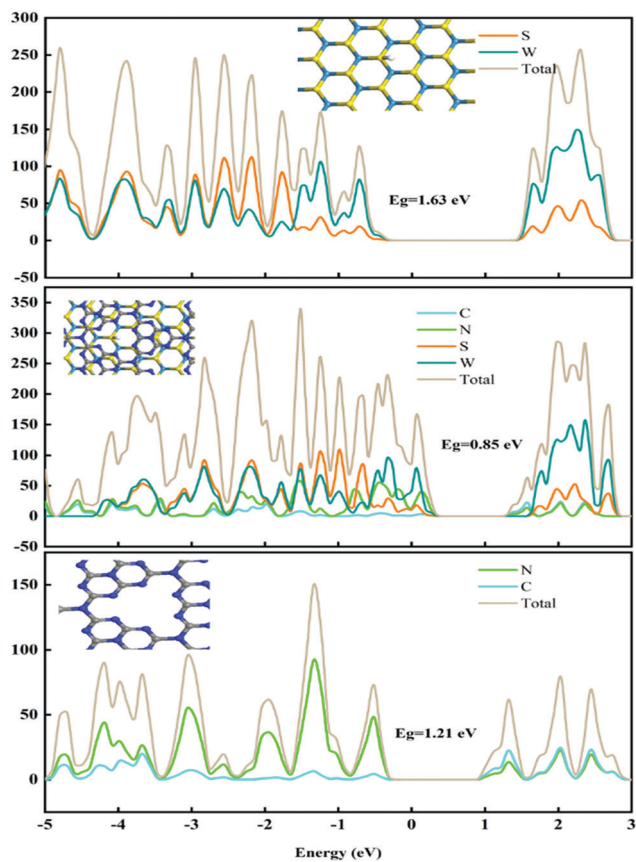


Fig. 2 Theoretical calculation of the density of states (DOSs) near the Fermi level.

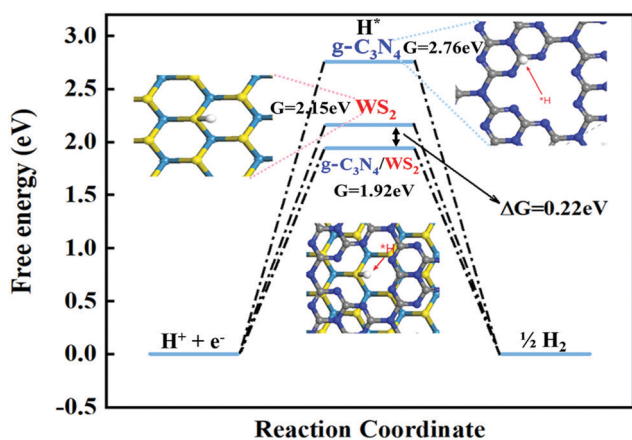


Fig. 3 Free-energy diagram for the HER with Volmer–Heyrovsky reactions on pristine $g\text{-C}_3\text{N}_4$, WS_2 and $\text{WS}_2\text{-}g\text{-C}_3\text{N}_4$ composite.

the HER reaction and needs to overcome some reaction energy barriers. Fig. 3 displays the calculated Gibbs free energy (ΔG^*) of hydrogen adsorption (0.22 eV) and the Gibbs free energy of C_3N_4 , WS_2 and $\text{C}_3\text{N}_4/\text{WS}_2$, which are 2.76 eV, 2.14 eV and 1.92 eV, respectively, which is in line with previous reported values.¹³ The $\text{WS}_2\text{-}g\text{-C}_3\text{N}_4$ composite shows the lowest activation barriers than those of WS_2 and $g\text{-C}_3\text{N}_4$, indicating

that the $\text{WS}_2\text{-}g\text{-C}_3\text{N}_4$ possesses the highest electrocatalytic HER activity. Our calculation results also demonstrate that the interface interaction between $g\text{-C}_3\text{N}_4$ and WS_2 optimizes the electronic structure of composite materials *via* the promotion of more electrochemical active sites and improved charge transfer kinetics required for optimal electrochemical performance. These calculation results confirm the importance of $\text{WS}_2\text{-}g\text{-C}_3\text{N}_4$ heterostructure design.

As shown in Fig. 4a and Fig. S1 (ESI[†]), a sparse to dense mat of nanowires was grown on the $g\text{-C}_3\text{N}_4$ scaffolds when the calcination temperature increased from 400–800 °C, respectively. The average thickness and length of the nanowires were between 10–30 nm and $\leq 1 \mu\text{m}$, respectively. Low- and high-resolution TEM images show homogeneous, layered, spindle-shaped structures of varying width and length stacked on top of each other in different directions (Fig. 4b). The interplanar spacing of the spindle shaped structures are 0.38, 0.32 and 0.27 nm which matched the d spacing values for (002), (002) and (100) planes of $g\text{-C}_3\text{N}_4$, orthorhombic (β) WO_3 and hexagonal WS_2 , respectively.¹⁴ The presence of WO_3 is due to the reaction of some $\text{W}_{18}\text{O}_{49}$ nanoparticles with residue oxygen during the reduction reaction in $\text{H}_2\text{S}/\text{Ar}$ atmosphere between 400–800 °C. The phase transformation of $\text{W}_{18}\text{O}_{49}$ is expected to initially proceed through the formation of WS_3 *via* the substitution of oxygen atoms with sulphur atoms.¹⁵ Further reaction leads to the formation of WS_2 with residual orthorhombic WO_3 nanoparticles due to oxidation occurring during sulfidation. The presence and homogeneous distribution of C, N, W, O and S was clearly confirmed from the elemental mapping of $\text{WS}_2/800$ (Fig. 4d–i) which is consistent with the XRD and XPS results, to be described below.

The XRD patterns of the as-synthesized $\text{WS}_2\text{-}g\text{-C}_3\text{N}_4$ composites prepared after thermal treatment at 400–800 °C are shown in Fig. 5a. Phase characterization indicates that the samples are crystalline and in good agreement with orthorhombic (β) WO_3 (JCPDS card no. 20-1324), $g\text{-C}_3\text{N}_4$ (JCPDS no. 87-1526), and hexagonal WS_2 (JCPDS card no. 08-0237). The diffraction peaks at $2\theta = 32.8^\circ$, 33.6° , 35.3° , 55.9° and 57.6° are indexed to (100), (101), (102), (106) and (110) planes of hexagonal WS_2 , respectively. The diffraction peak at 27.6° is attributed to the (002) plane of $g\text{-C}_3\text{N}_4$ linked to the interplanar stacking of conjugated aromatic systems.¹⁶ The peaks of $\beta\text{-WO}_3$ and WS_2 become sharper with the increase of reaction temperatures. Raman spectra in Fig. 5b have revealed the characteristic peaks of the $\text{W}_{18}\text{O}_{49}$ and WS_2 in the 200–1000 cm^{-1} range and the D (1348 cm^{-1}) and G (1587 cm^{-1}) bands for $g\text{-C}_3\text{N}_4$ in the $\text{WS}_2\text{-}g\text{-C}_3\text{N}_4$ composites prepared at different temperatures. The peak intensity ratios of the disordered amorphous carbon (D band) to graphitic carbon (G band) are calculated to be 1.33, 1.23 and 1.07 for $\text{WS}_2/400$, $\text{WS}_2/600$ and $\text{WS}_2/800$, respectively. The absence of 2D band linked to the second-order two-phonon process of graphene and low degree of graphitization is ascribed to the presence of structural defects and high nitrogen content.

Only $\text{WS}_2/400$ presents a Raman band at 129 cm^{-1} , which is assigned to the $\beta\text{-WO}_3$ phase. This confirms that some oxidation reaction occurred during the growth of WS_2 on the $g\text{-C}_3\text{N}_4$



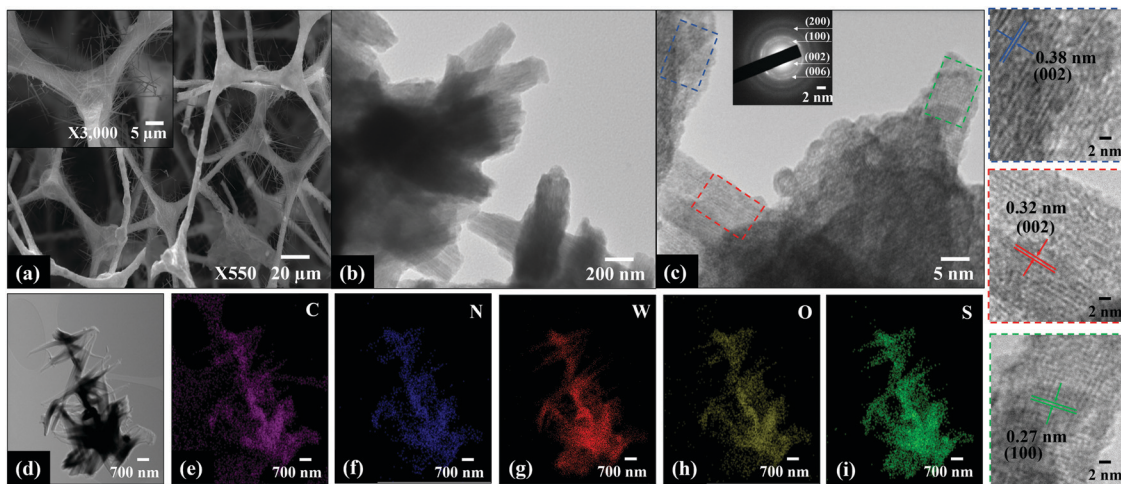


Fig. 4 (a) SEM image of WS_2 - $\text{g-C}_3\text{N}_4$ composites prepared at 800°C (WS_800), with inset high-resolution image showing the nanowire morphology of WS_800. TEM analysis of WS_800: (b) low magnification image, (c) high-resolution images showing lattice planes of $\text{g-C}_3\text{N}_4$, WO_3 and WS_2 . (d–i) TEM images with corresponding elemental mapping of WS_800.

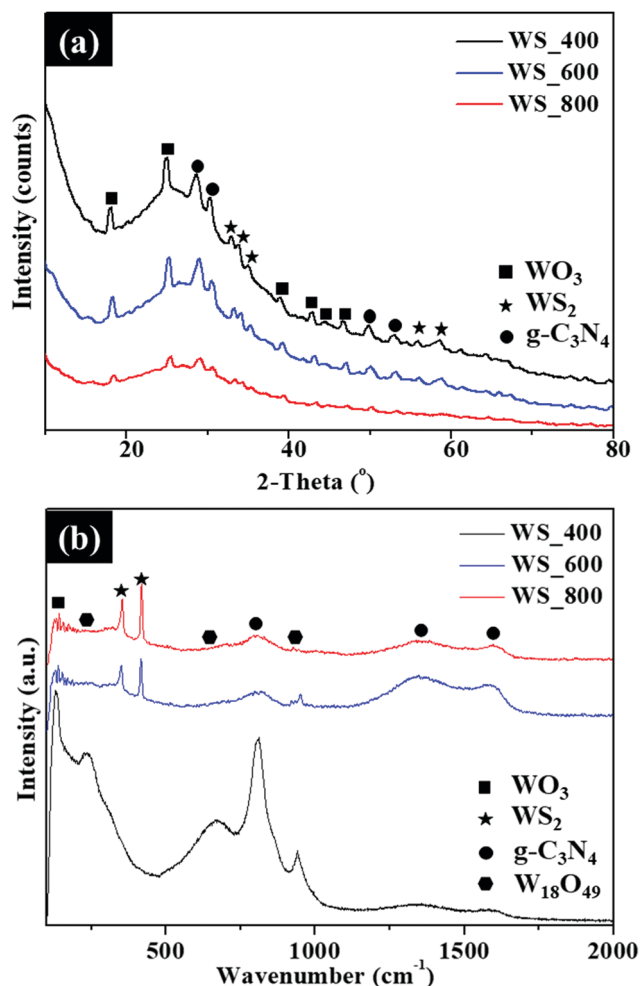


Fig. 5 (a) XRD patterns and (b) Raman spectra of the WS_2 - $\text{g-C}_3\text{N}_4$ composites prepared at different temperatures.

scaffold. The 226 cm^{-1} band could be assigned to the O–W–O bending mode of bridging oxygen for $\text{W}_{18}\text{O}_{49}$. The characteristic Raman bands for $\text{W}_{18}\text{O}_{49}$ observed at 667 and 812 cm^{-1} are assigned to the asymmetric and symmetric stretching vibration modes of O–W–O, respectively. The Raman bands at 812 cm^{-1} can be attributed to the out-of-plane N–C–N bending of $\text{g-C}_3\text{N}_4$. This band at 920 – 1000 cm^{-1} corresponds to the W=O stretching vibration mode of a terminal oxygen and has been used as the characteristic shifts for $\text{W}_{18}\text{O}_{49}$ nanowires.¹⁷ The intensity of this band was observed to decrease with increasing temperatures, due to the conversion of most of the $\text{W}_{18}\text{O}_{49}$ into WS_2 . The disappearance of the 129 , 225 and 667 cm^{-1} characteristic bands of $\beta\text{-WO}_3$ and $\text{W}_{18}\text{O}_{49}$, respectively, was observed for the WS_600 and WS_800 samples. As shown in Fig. 5b, additional bands were observed for WS_600 and WS_800 at 297 , 350 and 416 cm^{-1} which corresponds to the E_{1g} , E_{2g}^1 and A_{1g} modes of WS_2 , respectively. The E_{2g}^1 mode is linked to the in-plane, while A_{1g} mode correspond to out-of-plane phonon mode of WS_2 . Additionally, the A_{1g} mode undergoes a slight red shift as the reaction temperature was increased from 600 to 800°C . This shift triggered by the temperature increase is expected, due to the decrease in the interlayer van der Waals interaction resulting in weak restoring forces during lattice vibration. The BET surface area of the WS_2 - $\text{g-C}_3\text{N}_4$ composites and pore size distribution of WS_600 is shown in Fig. S2 (ESI[†]). The resulting specific surface areas of WS_400, WS_600 and WS_800 was 61 , 86 and $47\text{ m}^2\text{ g}^{-1}$, respectively. As shown in Fig. S2b (ESI[†]), WS_600 possesses mesopores with pore sizes of less than 37 nm which can facilitate efficient ion transport and accommodate the potential volume changes during the repeated charge–discharge processes.

As shown in Fig. 6, the chemical composition and valence state of the composites are characterized by XPS. The atomic percentage of all samples, with the calculated atomic ratios for N/C, pyridinic N [C–N–C]/pyrrolic N [N–(C)₃], W/S and WO_3/WS_2 are summarized in Table S1 (ESI[†]). The survey scan spectrum in



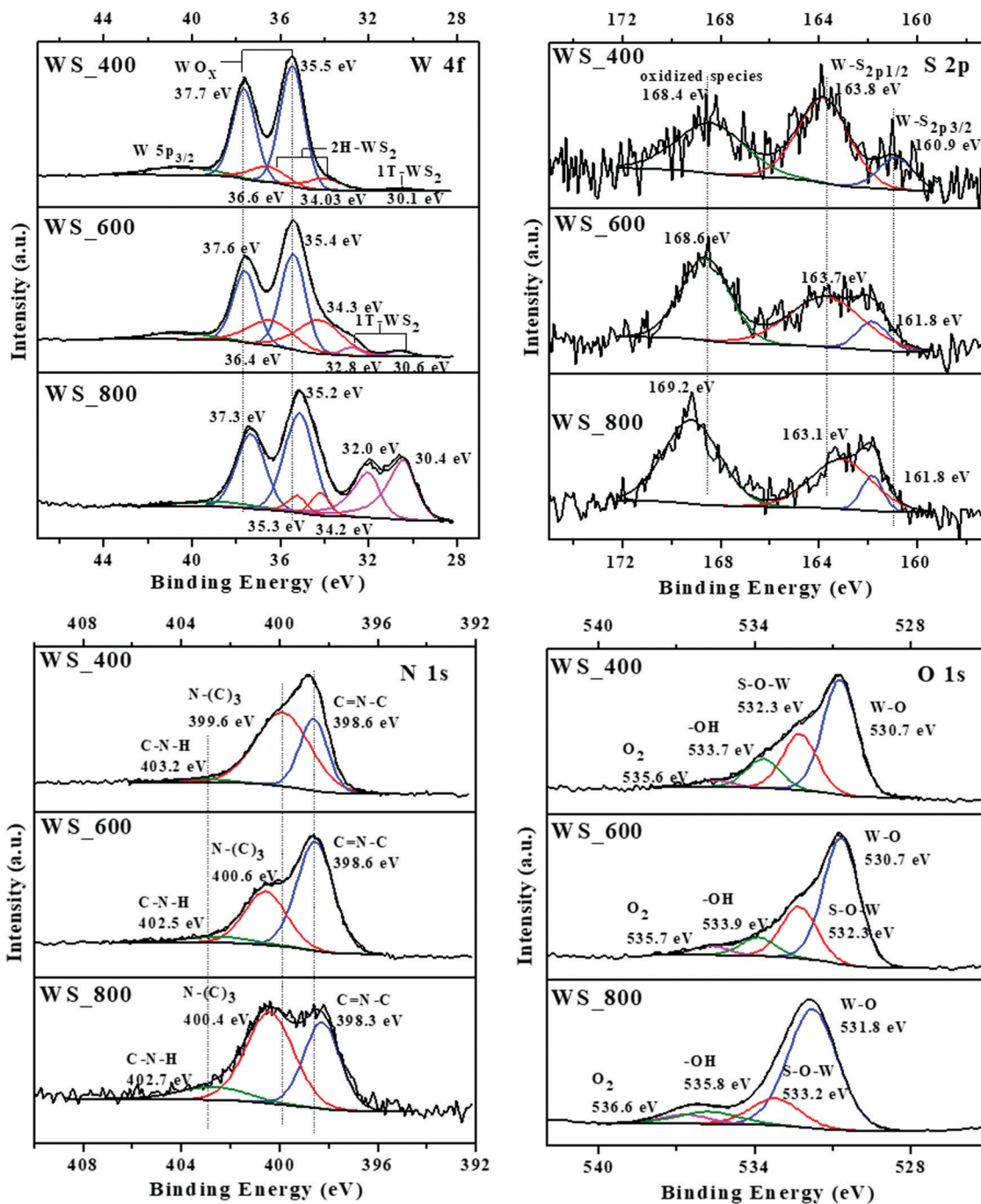


Fig. 6 High-resolution XPS spectra of W 4f, S 2p, N 1s and O 1s for all samples.

Fig. S2a (ESI[†]) confirms that C, N, O, W and S elements exist in WS₆₀₀. Considering the W 4f spectra of all samples, the binding energy at about 35 and 37 eV were generally attributed to W⁶⁺ species of tungsten oxide (WO_x). Two peaks of W 4f_{7/2} and W 4f_{5/2} at about 34 and 36 eV can be observed, indicating the semiconducting nature of the 2H phase WS₂. The peak locations are positively shifted to higher binding energies compared with the reference for 2H-WS₂ which is matched with the peak of W⁵⁺ in the WO_x structure.¹⁸ However, the peak of one layer per (Trigonal) unit cell (1T) structure is observed in

all samples. Together with the XRD results and TEM element mapping, these peaks are therefore assigned to 2 layers per hexagonal unit cell (2H)-phase of WS₂. The peak shift is linked to an incomplete transfer structure from WO_x to WS₂, and to the presence of W⁵⁺ species inside the WO_x structure.

The peaks at 30 and 32 eV can be attributed to metallic 1T-WS₂ structures or sulphur vacancies in the crystal structure,¹⁹ which are present in both WS₆₀₀ and WS₈₀₀ samples. However, a shadow peak of the 1T phase WS₂ is also presented at 30.1 eV for WS₄₀₀ samples. The peak of W 5p_{3/2} at 40.5 eV is



attributed to the unavoidable surface oxidation of the samples. The S 2p spectra were deconvoluted into 3 peaks for all samples, which include S 2p_{3/2} peak at ~161 eV, S 2p_{1/2} peak at ~163 eV and the oxidized species at ~169 eV. The oxidised sulphate groups were generated from residues after reaction or intermediate products formed during the transformation of WS₂ from WO_x.²⁰ The peak percentage areas for both S 2p_{3/2} and S 2p_{1/2} in the sample decreased with increased temperature from 400 to 800 °C, *i.e.*, WS₄₀₀ to WS₈₀₀. As shown in Table S1 (ESI[†]), S content of the composites decreases with increasing calcination temperature. The same decreasing trend was observed for the atomic ratios of W to S, implying the absence of surface sulphur atoms Fig. 6.

The O 1s spectra of mixed WO_x/WS₂ nanostructures can be assigned into 4 peaks with binding energies of about 530, 532, 533 and 535 eV.⁶ The peak at 530 eV is attributed to binding state of W⁶⁺ or W⁵⁺ corresponding to the lattice oxygen in WO_x; while the peak at 533 eV is from O₂ adsorbed on the WO_x/WS₂. The peak at 535 eV is assigned to OH-groups and water molecules, which can be chemisorbed on the defects and vacancies of the WO_x/WS₂ nanostructures. The peak at 322 eV can be associated with the O atom bonded to W atoms, which corresponded to S–O–W bonds indicating that an interfacial bond exists in the nanostructures.²¹

According to the high resolution XPS spectra of N 1s, three peaks at about 398, 399 and 402 eV correspond to the sp²-bonded pyridinic N (C=N–C), pyrrolic N (N–(C)₃) groups and quaternary N (C–N–H), respectively.²² The composites possess high N contents between 5.31 and 17 at%, showing that high N amounts are present in the final structures after calcination at 800 °C. As shown in Table S1 (ESI[†]), the N/C atomic ratio was observed to decrease from 0.24 to 0.065 with increasing calcination temperature. The same decreasing trend was observed for atomic ratios of pyridinic and pyrrolic N species where the atomic ratios decreased from 1.99 to 0.73 for WS₄₀₀ to WS₈₀₀, respectively. Conversely, an increasing trend was observed for the quaternary N (Fig. S4, ESI[†]). The decreasing N content can be linked to the introduction of N-vacancies while preferential loss of pyridinic N atoms over pyrrolic N atoms occurs due to unsaturated coordination which creates charge imbalance due to missing pyridinic N atoms.²³ The type and content of pyridinic, pyrrolic and quaternary N species have been reported to play a key role in influencing the structure (*i.e.*, defects and active sites) and electrochemical performance (*i.e.*, electron transport and conductivity).^{7,23} As shown in Fig. S4 (ESI[†]), the WS₂-g-C₃N₄ composites possess a high content of pyridinic and pyrrolic N species, which can provide active sites for redox reactions, resulting in improved electrochemical performance.

As shown in Fig. S3b (ESI[†]), the core level spectrum of C 1s can be fitted with 4 peaks with positions around 284, 285, 287 and 290 eV, which are corresponding to the C–C, C–O/C–S, N=C–N and C–N bonds, respectively.²⁴ Therefore, all the structure analyses suggest that the WS₂-g-C₃N₄ composites contain mainly 2D WS₂ with residual amounts of WO_x. The amount of WS₂ (2H-phase) in the samples increased with the

increases of temperature from 400 to 600 °C while the amount of WS₂ (2H-phase) in the 800 °C sample decreased, due to phase transformation of 2H to 1T. Overall, the total WO₃/WS₂ atomic ratio of the composites decreased with increased calcination temperature (Table S1, ESI[†]). The peaks of N and C confirmed the presence of graphitic carbon nitride within these samples.

Based on the XPS results, it is confirmed that WO_x/WS₂ was grown on the g-C₃N₄ surface and connected *via* van der Waals bonds. In addition, the 2H-WS₂ matrix contained S-vacancies due to WO_x-WS_x or 2H-1T phase transitions. This is supported by O 1s peak at about 322 eV, 1T (which can also refer to defects of WS_x structure) and oxidized species peaks from S 2p spectra.²⁵ Overall, the preferential bonding between the basal planes of WS₂ and g-C₃N₄ optimizes the electronic structure of the composite materials and activates the active sites.

3.2. Electrochemical performance evaluation

The electrochemical performance of the WS₂-g-C₃N₄ composites for supercapacitors was evaluated by using a three-electrode cell configuration in 0.5 M H₂SO₄ electrolyte. Fig. 7 and Fig. S5 (ESI[†]) show the electrochemical performance of the WS₂-g-C₃N₄ composites. As shown in Fig. 7a, Fig. S4a and c (ESI[†]), all WS₂-g-C₃N₄ composites possess a convex quasi-rectangular CV shape at potential windows of 0.2 to 1.0 V at various scan rates ranging from 10 to 100 mV s⁻¹, which is indicative of the pseudocapacitive behavior, due to the electric double layer capacitance (EDLC) and faradaic reactions of g-C₃N₄ and WS₂, respectively.

The shape of the well-defined CV curves is maintained at different scan rates, which indicates the capacity of the WS₂-g-C₃N₄ composites for fast charge transfer and improved rate performance. The galvanostatic charge/discharge profiles of WS₄₀₀, WS₆₀₀ and WS₈₀₀ electrodes at current densities between 2–15 A g⁻¹ were measured and presented in Fig. 7b, Fig. S5b and d (ESI[†]), to evaluate the potential use of these composites as supercapacitors. The quasi-triangle shape of galvanostatic charge/discharge profiles is asymmetrical, suggesting the presence of some EDLC and faradaic reactions, which is consistent with the reported CV results. The WS₆₀₀ electrode exhibited a longer discharge time compared with other electrodes, supporting an optimal pseudocapacitive performance. The specific capacitance was calculated from the galvanostatic charge/discharge profiles of the WS₂-g-C₃N₄ electrodes, to highlight the rate capability which represents a measure of the charge and discharge capability of supercapacitors. The calculated specific capacitance values of WS₂-g-C₃N₄ electrodes at different current densities are shown in Fig. 7c. The electrodes of samples WS₄₀₀, WS₆₀₀ and WS₈₀₀ reveal specific capacitance values of 256, 1156 and 997 F g⁻¹ when the N content was 17, 11.78 and 5.31 at%, respectively at a current density of 2 A g⁻¹. The specific capacitance values show that the nitrogen content must be kept around 11.78 at% to obtain optimal specific capacitance values. WS₆₀₀ electrode with N and S content of 11 at% and 1.01 at% had the maximum specific capacitance compared with other electrodes. Its specific capacitance remained as high as 832 F g⁻¹ at a maximum current density of 15 A g⁻¹, due to its



excellent rate capability and electrochemical performance. In comparison, the specific capacitance values of WS₄₀₀ and WS₈₀₀ electrodes are 639 and 131 F g⁻¹ at the same current density of 15 A g⁻¹. The specific capacitance retention of the WS₆₀₀ electrode was estimated to be 12.5% and 41% higher than those of WS₄₀₀ and WS₈₀₀, respectively, revealing the superior rate capability of WS₆₀₀ electrode. The specific capacitance of all the samples decreases with increasing current density due to the difficulty in ion transport at high current densities. In addition, the electrochemical stability was evaluated *via* cyclic galvanostatic measurements at a current density at 15 A g⁻¹. The stability of the WS₆₀₀ electrode over 10,000 cycles at 15 A g⁻¹ is shown in Fig. 7d. The WS₆₀₀ electrode exhibited excellent cyclic stability. After 10,000 cycles, the WS₆₀₀ electrode retained 82% of its initial specific capacitance. The specific capacitance of WS₆₀₀ is superior to the recently reported tungsten-based supercapacitors^{26–32} (Table S2, ESI[†]). Overall, the WS₆₀₀ electrode possessed the optimal specific capacitance, improved rate capability and cyclic performance, against the WS₄₀₀ and WS₈₀₀ electrodes. The improved performance of WS₆₀₀ electrode is linked to the contributing effects of optimal surface area, surface defects (*i.e.*, sulfur vacancies in WS₂ and nitrogen vacancies in g-C₃N₄) as active sites, and both EDLC and redox reactions from the WS₂ and g-C₃N₄, which together facilitated the improved charge storage. The layered structures of WS₂ embedded in the g-C₃N₄ scaffold provided shorter pathways

for a fast and efficient ion transport, while the porous feature could accommodate the potential volume changes during the repeated charge–discharge processes.

Besides utilization as supercapacitors, the WS₂-g-C₃N₄ composites also demonstrated interesting performance in hydrogen evolution reaction, which is a key process in the electrochemical water splitting. The electrocatalytic HER activities of the WS₂-g-C₃N₄ composites were evaluated using a three-electrode configuration in an acidic (0.5 M H₂SO₄) electrolyte, as shown in Fig. 8. The linear sweep voltammetry (LSV) curves of 20 wt% Pt/C and WS₂-g-C₃N₄ composites are displayed in Fig. 8a. The WS₆₀₀ electrode again showed a small onset potential of -0.06 V (*vs.* RHE) against other WS₂-g-C₃N₄ based electrodes, and was slightly higher than that of 20 wt% Pt/C. After which a sharp increase in the cathodic current was observed under negative potentials for all samples. The operating potential at a standard current density of 10 mA cm⁻² was adopted in this study, for comparison purpose. This value is representative of the current density expected for a solar water splitting device operating at 12.3% efficiency.³³ WS₆₀₀ electrode exhibited excellent catalytic activity with a low overpotential of -0.170 V (*vs.* RHE) to drive a current density of 10 mA cm⁻².

In comparison, the WS₄₀₀ and WS₈₀₀ electrodes possessed higher overpotentials of -0.440 and -0.260 V (*vs.* RHE), respectively, to attain the same current density. These results affirmed the exceptional HER electrocatalytic activity of WS₆₀₀ amongst all samples.

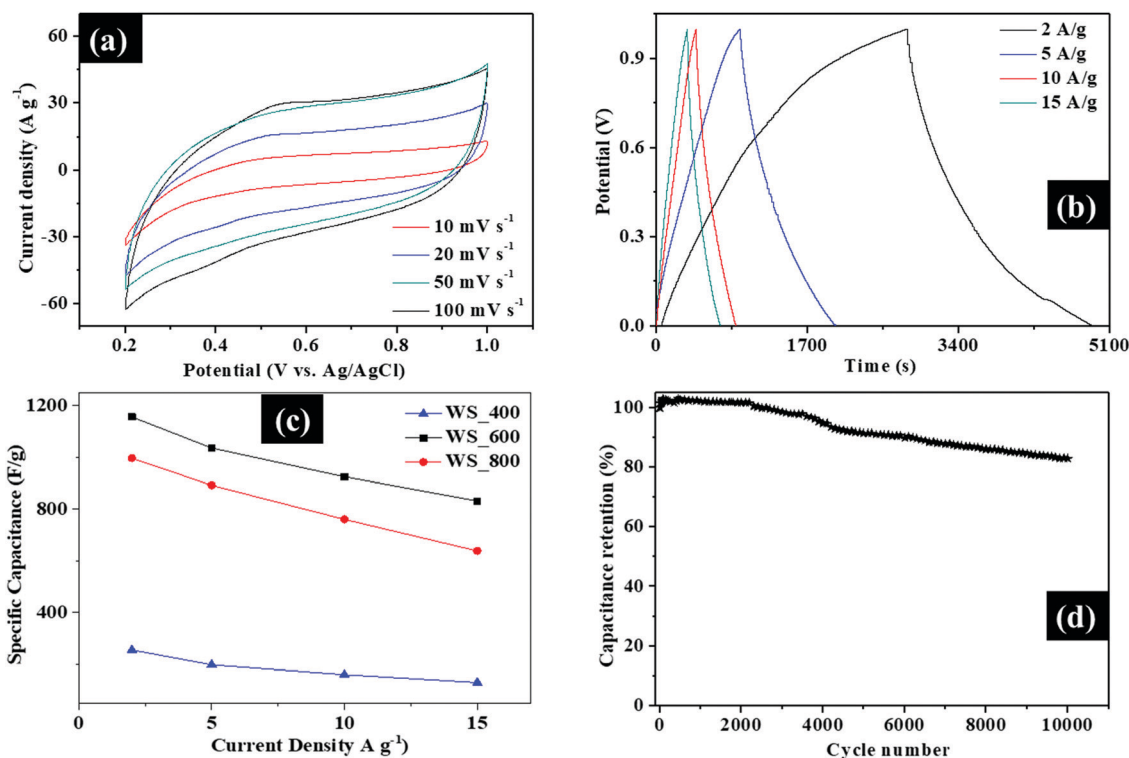


Fig. 7 (a) CV curves of the WS₆₀₀ electrode at various scan rates from 10 to 100 mV s⁻¹, (b) Galvanostatic charge discharge curves of WS₆₀₀ electrodes at different current densities, (c) Specific capacitance of WS₂-g-C₃N₄ composites as a function of current densities, and (d) Cyclic performance of WS₆₀₀ electrode at 15 A g⁻¹.



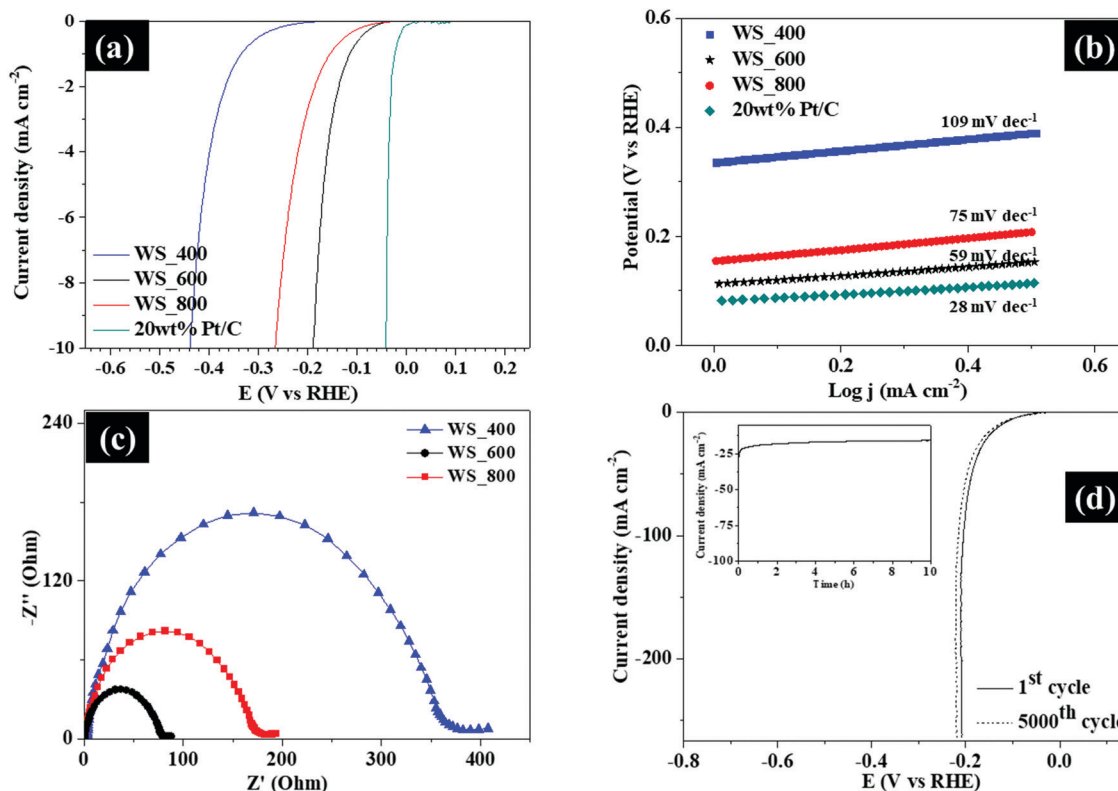


Fig. 8 (a) Polarization LSV curves, (b) Tafel plots, (c) EIS Nyquist plots and (d) LSV curves of WS₆₀₀ before and after cyclic studies (inset shows chronoamperometric measurements of WS₆₀₀).

The Tafel slopes of the samples were plotted to estimate the reaction kinetics and the rate-determining step for the HER process. As shown in Fig. 8b, the Tafel slope of WS₆₀₀ was 59 mV dec⁻¹, much lower than 75 and 109 mV dec⁻¹ for WS₈₀₀ and WS₄₀₀, respectively, indicative of its faster kinetics. The low Tafel slope of WS₆₀₀ confirmed the favorable HER kinetics, which is linked to its layered structure providing more pathways for easy ion transportation. Hydrogen production for the samples was facilitated through a Volmer–Heyrovsky mechanism due to their Tafel slope values being within the range of 40 and 120 mV dec⁻¹, where electrochemical desorption and formation of hydrogen molecules occurred, respectively. The transition from the Volmer to Heyrovsky pathway is the rate limiting step for this mechanism. The excellent HER performance of WS₆₀₀ with low overpotential and Tafel slope is comparable to other previously reported tungsten-based electrodes in the literature^{1,26,34–38} (Table S3, ESI†). The reaction kinetics occurring at the electrode/electrolyte interface was evaluated by EIS. Fig. 8c shows the Nyquist plots where the WS₂-g-C₃N₄ based electrodes showed semi-circles at high frequency region, a little intercept at the real part and a line with large slope at low frequencies which is attributed to the charge transfer resistance (R_{ct}), intrinsic resistance (R_e), and the diffusion resistance (W), respectively. The WS₂-g-C₃N₄ based electrodes exhibit low resistance and fast ion transfer, which enhanced pseudocapacitance. The WS₆₀₀ exhibited a lower R_{ct} compared with other samples, due to

better HER kinetics and enhanced ion transport at the electrode/electrolyte interface. The EIS plots of WS₆₀₀ before and after cycling (Fig. S6, ESI†) has a similar trend, where a slight increase of the R_{ct} and R_e was observed after 5000 cycles confirming the stability of WS₆₀₀.

The durability of WS₆₀₀ was investigated by cyclic linear potential sweeps and chronoamperometry measurements at the current density of 20 mA cm⁻². The polarization curve of WS₆₀₀ after continuous 5000 cycles at a scan rate of 5 mV s⁻¹ exhibited only a small decay benchmarked against the initial cycle (Fig. 8d). The current–time curve showed that WS₆₀₀ was stabilized after 10 h with no attenuation in its current density. These observations indicated that the WS₆₀₀ possessed superior cyclic and long-term stability for the HER. Overall, the excellent electrochemical performance was attributed to WS₂-g-C₃N₄ composites, which provided more electroactive sites at electrolyte/electrocatalyst interface to facilitate effective ion transport and possessed ample active sites to allow intensive electrochemical reactions.

4. Conclusions

In summary, WS₂-g-C₃N₄ composites with surface vacancies were successfully prepared by using a facile solvothermal method followed by sulfidation. Experimental and computational studies revealed the preferential bonding and interfacial interaction



between the basal planes of WS₂ and g-C₃N₄, which optimizes the electronic structure, improves charge transfer and electrochemical performance. In comparison with other electrocatalysts, the WS₆₀₀ electrode showed excellent specific capacitance of 1156 F g⁻¹ at the current density of 2 A g⁻¹, compared with 256 F g⁻¹ for WS₄₀₀. The WS₆₀₀ electrode retained 82% of its initial specific capacitance after 10 000 cycles. In addition to demonstrating excellent specific capacitance, the WS₆₀₀ electrode also exhibited an excellent catalytic activity, with a low overpotential of 0.170 V (vs. RHE) capable of driving a current density of 10 mA cm⁻² and a good stability after 8 h of testing. Overall, the WS₆₀₀ electrode possessed optimal specific capacitance, improved rate capability and cyclic performance, benchmarked against other samples due to the contributing effects of optimal specific surface area, surface defects (*i.e.*, sulfur vacancies in WS₂ and nitrogen vacancies in g-C₃N₄) as active sites, and both EDLC and redox reactions from the WS₂ and g-C₃N₄, which together facilitated the improved charge storage.

Conflicts of interest

There are no conflicts to declare.

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