Exfoliated WS₂ nanosheets: optical, photocatalytic and nitrogen-adsorption/desorption characteristics

S J HAZARIKA and D MOHANTA*

Nanoscience and Soft Matter Laboratory, Department of Physics, Tezpur University, PO: Napaam, Tezpur, Assam 784028, India

*Author for correspondence (best@tezu.ernet.in)

MS received 19 January 2018; accepted 24 March 2018; published online 7 December 2018

Abstract. In this work, we report on structural, optical, photocatalytic and nitrogen adsorption–desorption characteristics of WS₂ nanosheets developed *via* a hydrothermal route. X-ray diffraction (XRD) studies have revealed a hexagonal crystal structure, whereas nanodimensional sheets are apparently observed in scanning and transmission electron microscopy (SEM and TEM) micrographs. As compared to the bulk counterpart, the WS₂ nanosheets exhibited a clear blue shift. Through Brunauer–Emmett–Teller (BET) surface area analysis, average surface area, pore volume and pore size of the NSs were calculated as 211.5 m² g^{−1}, 0.433 cc g^{−1} and 3.8 nm, respectively. The photocatalytic activity of the WS₂ nanosheets was also examined with malachite green (MG) as the target dye under both UV and day light (visible) illumination conditions. Accordingly, a degradation efficiency as high as 67.4 and 86.6% were witnessed for an irradiation time duration of 60 min. The nano-WS₂ systems have immense potential in optoelectronics, solid-lubrication and other next generation elements.

Keywords. Nanosheets; photocatalysis; TMDC; sorption process.

1. Introduction

Owing to their immense potential in the fields of optoelectronics, nanoelectronics and nanophotonics, graphene and other layered systems have captured a great deal of interest amongst material scientists and researchers [1]. Layered materials, especially the transition metal dichalcogenides (TMDCs) have unusually exciting properties when exist in layered form. While possessing the general formula MX₂ (where M = Mo, W, Ta, etc. and X = S, Se, Te, etc.), the systems characterize an indirect band gap in the bulk form, and turns into a direct band gap when exfoliated to a few layers or monolayer [2].

In the family of TMDCs, tungsten disulphide (WS₂) is a technologically important member with matchless power in the fields of optoelectronics, catalysis and lubrication [3]. One of the most remarkable applications of WS₂ is to use it as a photoactive material and as a photocatalyst. Being a narrow band gap semiconductor ($E_g = 1.9$ eV), WS₂ is responsive to both UV and visible light illuminations. This allows the nanoscale WS₂ to act as an advanced photocatalytic agent as compared to the traditional photocatalysts, such as TiO₂, SnO₂ and ZnO, which are generally efficient only under UV light irradiation [4]. One of the essential features of a good photocatalyst is large surface-to-volume ratio, which can be obtained by exfoliating the bulk WS₂ into its corresponding sheets [5]. However, obtaining micro- and nano-scale WS₂ systems was not easy due to lack of availability of a standard, cost-effective and user-friendly

route in spite of numerous efforts. Earlier, nanoscale WS₂ systems were synthesized using methods, such as chemical vapour deposition, magnetron sputtering, laser ablation, etc. [6], all of which come with much sophistication and with a need for high temperature. Synthesizing nanoscale WS₂ *via* a hydrothermal route does not require very high temperature processing and could offer products with less or no agglomeration, phase homogeneity and good crystallization [7]. Moreover, a surfactant-assisted hydrothermal route was also employed to fabricate WS₂ nanostructures [8].

In this work, we report on the processing of WS₂ nanosheets using a facile, hydrothermal route followed by effective ultrasonication. Morphological, photocatalytic and nitrogen adsorption–desorption properties were highlighted along with the scope for future investigation.

2. Experimental

2.1 Synthesis procedure and steps

First, a single-step hydrothermal process is attempted for the production of WS₂ and consequently, exfoliated into its nanosheets form with the help of repeated ultrasonication. The chemicals used in the synthesis were of analytical grade and were used without further purification. For synthesis, sodium tungstate (Na₂WO₄ · 2H₂O) (Rankem, 98% pure) was used as the source of tungsten, and thiourea (CH₄N₂S)

Figure 1. The block diagram of steps involved for synthesizing WS₂ nanosheets.

(Merck, 99% pure) for sulphur. In a typical synthesis, 1.65 g of sodium tungstate, 0.72 g of hydroxylamine hydrochloride (NH₂–OH · HCl) (Merck, 98% pure) and 1.17 g of thiourea were dissolved in 30 ml of deionized Millipore® water. The solution was stirred for 1 h until a clear solution is obtained, while maintaining the solution at pH = 6. The mixture was then transferred into a 50 ml Teflon-lined autoclave, and upon proper sealing, it was kept in oven at a temperature of 200 °C for 24 h. After allowing it to cool naturally, the obtained product was washed several times with deionized water and ethanol, and employed centrifugation (~4000 rpm) for 10 min. The precipitate was oven-dried at a temperature of 60 °C and consequently, a dark grey-coloured powder is acquired. The synthesized powder was labelled as S₁.

To obtain nanosheets out of the synthesized WS₂ powder, 0.2 g of the powder was added to 20 ml of 1-methyl-2-pyrrolidone (Merck, 99.5% pure) and then, subjected to ultrasonication bath (UD100SH: $f = 50$ Hz, $P = 100$ W) for 4 h. The solution was then centrifuged (~5000 rpm) for 10 min and two-third of the solution was considered for further centrifugation (~7000 rpm) for 15 min, followed by multiple washing with ethanol. The as-received precipitate was collected and then oven-dried (~60 °C) for 10 h. The resulting product that yielded WS₂ nanosheets was labelled as S₂. The whole synthesis steps are highlighted in a block diagram shown in figure 1.

2.2 Characterization techniques employed

To exploit the structural and crystallographic properties, X-ray diffraction (XRD) technique was employed using a Bruker AXS, Germany D8 focus X-ray diffractometer equipped with a CuK α source ($\lambda = 1.543$ Å). The morphological detail of the as-synthesized WS₂ nanosheets is revealed through both scanning electron microscopy (SEM; JEOL JSM, 6390LV) and transmission electron microscopy (TEM; FEI, Tecnai) imaging studies. The compositional analysis was performed through the energy-dispersive X-ray (EDX) spectroscopy studies. On the other hand,

phonon-assisted vibrational modes are studied through the Raman spectrometer (Renishaw, Wotton-under-Edge) using a Ar⁺ laser ($\lambda = 514$ nm line) as the excitation source. Information regarding nanosheet-surface area, pore size and pore distribution were evaluated through the Bruner–Emmet–Teller (BET, Quantachrome Nova 1000e, FL) analysis performed on the WS₂ nanosheets by way of studying N₂ adsorption/desorption response at liquid nitrogen temperature (~77 K). UV–Vis spectroscopy (UV 2450, Shimadzu Co.) study was employed to obtain energy gap as well as photocatalytic degradation efficiency.

2.3 Execution of photocatalytic experiment

To analyse the photocatalytic efficiency of the as-prepared WS₂ sheets, we have chosen malachite green (MG) as the target to be decomposed. MG is an organic compound that is used as a dye-stuff (triaryl methane dye) and controversial antimicrobial agent in aquaculture [9]. Recognized as class II health hazard, researchers are trying hard to find means to degrade these harmful dyes found in sea foods and pigment industry. The photoactivity of the nano-WS₂ samples was investigated both under UV and visible light illumination conditions. To perform the experiment, 60 mg l^{−1} of the WS₂ nanoparticles is first added to 20 mg l^{−1} of the MG, and then subjected to stirring for about 1 h in dark, then, the mixture is ultrasonicated for about half an hour. The collected solution is then placed inside a cabinet, which has the provision for UV lamp as well as the incandescent bulb, the latter being used as the source of visible light. The samples are kept at the base of the chamber and at a distance of about 12 cm from the UV source ($\lambda = 365$ nm) and the polychromatic light source used independently. The WS₂ nanocatalyst-loaded dyes are irradiated for different time durations: 15, 30, 45 and 60 min. Next, 5 ml of the MG solution is employed for the optical absorption analysis, knowing that the peak maximum for the initial absorption of MG normally appears at ~619 nm [10]. The percentage of decomposition of the target MG under

Figure 2. XRD patterns of un-exfoliated WS₂ (*S*₁) and exfoliated WS₂ nanosheets (*S*₂).

UV and visible light illuminations can be evaluated through the formula:

$$\% \text{ Degradation} = \frac{C_0 - C_t}{C_0} \times 100\%, \quad (1)$$

where C_0 and C_t represent concentration of MG solution before and after irradiation [11].

3. Results and discussion

3.1 Structural and morphological analysis

Figure 2 shows the XRD patterns of the as-prepared WS₂ samples (un-exfoliated and nanosheets). The samples exhibit diffraction peaks at nearly same positions and no shift in the peak position was observed. The diffraction peaks positioned at $2\theta = 28.76, 32.66, 33.42, 35.26, 39.57, 44.28, 49.65, 55.53$ and 60.31 correspond to (004), (100), (101), (102), (103), (006), (105), (106) and (008) planes of the hexagonal (H) structure of WS₂, respectively [7]. The prominent peak located at $2\theta = 14.38^\circ$ signifies the (002) plane of 2H-WS₂ (JCPDS file no. 08-0237). The remarkable difference between the XRD patterns of the two samples is in the intensity of the peaks with the nanosheets possessing a relatively lower value due to lack of adequate atomic planes participating in the diffraction process. The lowering of the peak intensity is attributed to the decrease in crystallinity of the nanosheet as compared to the un-exfoliated WS₂ powder [12]. The diffraction peaks in the XRD pattern of WS₂ sheets are also tend to get broadened, which suggests the exfoliation of the WS₂ powder into the sheets of nanoscale form [13]. No peak either due to impurities or oxide phase was witnessed in the diffractograms, thus, indicating the formation of the phase-pure WS₂ product in this case.

The micrographs of the un-exfoliated (*S*₁) and nanosheet (*S*₂) WS₂ powder captured on a HRSEM machine are shown

Figure 3. The SEM micrograph of (a) un-exfoliated WS₂ powder and (b) exfoliated WS₂ nanosheets. (c) The EDX micrograph of the un-exfoliated WS₂ powder.

Figure 4. TEM micrograph of (a) WS₂ nanosheets, (b) magnified view of the sheets, (c) lattice fringe pattern captured at the surface and (d) SAED pattern indicating diffused diffraction rings.

in figure 3a and b, respectively. Figure 3b shows the EDX micrograph of the as-synthesized WS₂ powder. The presence of the elements W and S can be clearly seen in the EDX spectrum. Intensity-based calculations gave the ratio of S to W to be 1.90:1. Moreover, the exfoliated sheets are visualized at a higher magnification through TEM imaging (figure 4a, b). The nanosheets indicating a higher surface area coverage can be noticed with a few kinks and folds. The lattice fringe pattern captured at the edge of the WS₂ nanosheets is shown in figure 4c. Using ImageJ software[®] [14], the average fringe width defining lattice spacing of the nanosheets was calculated to be ~ 0.62 nm. Moreover, the observation of diffused ring like patterns is an indicative of the polycrystalline content present in the synthesized WS₂ product (figure 4d).

3.2 Optical absorption response and Raman active vibrational features

In the optical absorption spectra shown in figure 5, two absorption peaks located at 536 and 633 nm can be observed for the un-exfoliated WS₂ system (*S*₁). The absorption peak at

536 nm is ascribed to the transitions from spin-split valence band to the conduction band [15], whereas the peak at 633 nm corresponds to *d*–*d* type transitions at the centre of the Brillouin zone [16]. The corresponding peaks are blue-shifted to 519.6 and 620.7 nm on exfoliation as observed for the nanosheets (*S*₂). Earlier, the blue-shifting of the absorption peaks was viewed as a consequence of quantum confinement effect [16]. Consequently, the optical band gap would increase for the exfoliated WS₂ nanosheets, as compared to its un-exfoliated form. Moreover, the second peak is effectively suppressed for the nanosheets owing to a lowered value of *d*–*d* transitional probability.

Figure 6 highlights the Raman spectra of the as synthesized WS₂ systems. Apparently, two distinct peaks corresponding to the *E*_{2g}¹ and *A*_{1g} Raman active modes can be seen [17]. The *E*_{2g}¹ mode represents an in-plane optical mode, whereas the *A*_{1g} mode signifies the out-of-plane vibrations of the sulphur atoms [18]. We also noticed a small blue-shifting in the Raman peaks from 351.26 (417.32) to 356.07 (421.66) cm^{−1}, as *S*₁ was converted to *S*₂ through exfoliation.

Figure 5. UV-Vis optical absorption spectra of the (S_1) un-exfoliated WS_2 powder and (S_2) exfoliated WS_2 nanosheets.

The exfoliation causes a weak layer interaction, leading to an appreciable peak shifting towards higher wavenumber [19]. The ratio of the intensities of the E_{2g}^1 and A_{1g} peaks was calculated to be 0.68 for the nanosheets, which is comparatively higher than the bulk WS_2 [20]. A blue shift of Raman peaks was observed in case of the nanosheets as compared to the un-exfoliated WS_2 , owing to phonon confinement effect.

3.3 Photocatalytic activity of WS_2 nanosheets on MG dye

The photocatalytic performance of the WS_2 nanosheets is examined on a harmful organic dye (MG). The extent of degradation was observed under both UV and visible light illumination and for different durations of time. With an increase in time duration of the UV exposure, the WS_2 nanosheet-loaded dye showed a steady fall in the absorption response at $\lambda = 619$ nm (figure 7A (a–c)). We also observed a rapid fall in the absorbance under visible light illumination (figure 7A (d–f)). In other words, the WS_2 nanosheets tend to exhibit a better catalytic efficiency under visible light. This is because of its narrow band gap, which acts as a facilitator to activate the redox reaction necessary for the production of hydroxyl radicals, which play a vital role in the photocatalytic activity. A scheme illustrating photocatalytic activity of WS_2 nanosheets is shown in figure 7B and the mechanism as detailed below.

Upon light irradiation, the WS_2 nanosheets are believed to be photo-excited releasing electrons and holes. The electrons are lifted to the conduction band leaving behind holes in the

Figure 6. Raman spectra of the (S_1) un-exfoliated WS_2 nanopowder and (S_2) exfoliated WS_2 nanosheets.

valence band. The e–h pairs are likely to be captivated in the active W^{4+} and S^{2-} defect sites, otherwise, it is likely that recombination of these carriers would take place to dissipate energy [21]. These carriers would migrate to the nanocatalyst surfaces, resulting in the formation of intermediate reactants. The light-induced holes and the reactive hydroxyl radicals are extremely important for the stimulation of the redox reaction necessary for decomposition of water. The target MG, being in aqueous form, the water molecule is believed to come in contact with the surfaces of the nanocatalyst. The active sites of the nanocatalyst readily trap the OH group, or superoxide $O_2^{\cdot -}$, latter being a consequence of the electrons being transferred to the adsorbed oxygen [22]. Water and hydroxyl groups are transformed to hydroxyl radicals by the photo-generated holes. The superoxide and hydroxyl radicals are readily responsible for the decomposition of the organic dyes into harmless entities [23].

The characteristic photocatalytic features shown in figure 7A (a–f) suggest an increase in photodegradation of the MG with irradiation time duration, notably, for an exposure time of 60 min. The WS_2 nanosheets under UV illumination gives a 67.4% decomposition of MG. But visible light could decompose as high as 86.6% of the MG dye. In a recent work, we have discussed the photodegradation activity of the inorganic fullerene (IF) type WS_2 nanoparticles, which exhibited 45 and 71.2% degradation of the dye under respective illumination conditions, but for a larger duration of time [21]. Thus, the photoactivity of the WS_2 nanosheets, owing to its relatively high specific surface area, is drastically enhanced. A higher surface area with mesopores would allow

(A)

(B)

Figure 7. (A) UV–Vis optical absorption spectra of MG and WS₂ nanocatalyst (nanosheet)-loaded dye with different irradiation times, percentage of photodegradation and pseudo-first-order plots: (a–c) UV light illumination and (d–f) visible light illumination. (B) The schematic diagram representing the formation of nanosheets and the mechanism of photocatalysis.

more MG molecules to get adsorbed into the active sites under visible light irradiation. The performance of the UV illumination is relatively less due to the band gap excitation led possibility of photo-oxidation at the pores and interfaces. The kinetics of photocatalytic degradation of MG at the nanocatalyst (WS₂ nanosheets) surface can be evaluated qualitatively

by employing a simple Langmuir–Hinshelwood (L–H) model [24].

It can be expressed in the form of a first-order reaction for a dilute solution (mM) ($C \ll 1$):

$$C_t = C_0 e^{-k_r t}, \quad (2)$$

where C_0 is the initial concentration of the MG solution, t the illumination time and k_r the pseudo-first-order rate constant.

At $t = 0$, one obtains where $C_t = C_0$, the initial concentration of the target before irradiation. The degradation trends of the MG dye can be found in figure 7A (b and e). Similarly, the curves of C_t/C_0 vs. t for different exposure conditions are shown in figure 7A(c and f). The exponential decay trend would help to determine the pseudo-first-order rate constant, k_r involved in the reactions under UV and visible light illuminations. The k_r values are estimated as, 0.11 and 0.16 min^{-1} , respectively. An improved rate constant under visible light exposure suggests an improved photoactivity owing to induction of maximal redox reaction at the nanosheet surfaces through release and participation of free carriers, formation of superoxide radicals, etc. Moreover, the possibility of photo-oxidation is largely avoided in this case, as compared to the UV photo-excitation condition.

3.4 BET surface area and pore-size analysis using N_2 adsorption–desorption curve

Surface analysis of nanoscale materials is an important aspect as it offers sound information regarding surface coverage and particularly, specific surface area, pore size, pore volume, etc. In this regard, earlier N_2 adsorption and desorption isotherms were employed for studying mesoporous WS_2 [25]. The type of isotherm is identified as type IV profile, which is the characteristic of a mesoporous material with pore diameter typically in the range of 2–50 nm [26]. Essentially, adsorption on mesoporous solids occurs *via* multilayer adsorption phenomena mediated *via* capillary condensation that results in type IV and V isotherms [27]. Here, figure 8 represents the characteristic N_2 adsorption/desorption isotherm of our hydrothermally processed and exfoliated WS_2 nanosheets. The initial part of the type IV isotherm is attributed to monolayer–multilayer adsorption, since it follows the same trend as the

corresponding part of a type II isotherm obtained with the given adsorptive on the same surface area of the adsorbent in a nonporous form. The hysteresis loop is appeared to be of the type H2 according to IUPAC classification, which indicates disordered distribution of pore size and shape. The hysteresis loop is found to occur at a magnitude above ~ 0.5 of relative pressure P/P_0 . The BJH pore-size distribution graph for the same sample is shown in the inset of figure 8. The BET surface area of the nanosheets is found to be $211.5 \text{ m}^2 \text{ g}^{-1}$. Using the BJH model, the pore volume and the average size of the pores are evaluated to be 0.433 cc g^{-1} and 3.8 nm, respectively.

The Kelvin's equation [28] is:

$$\ln \frac{P}{P_0} + \frac{4\gamma V_m}{dRT} = 0, \quad (3)$$

where P and P_0 represent actual and saturated vapour pressures, V_m molar volume, γ the surface tension of liquid N_2 and $d (=2r, r$ being radius) the size of the droplet. The symbols R and T signify universal gas constant ($8.31 \text{ J mol}^{-1} \text{ K}^{-1}$) and working temperature (77 K); respectively. Applying the respective values, we obtain the diameter of the drop that desorb out of the pores as $d = 2r = 2.1 \text{ nm}$. However, a relatively larger pore size ($2r \sim 3.8 \text{ nm}$) predicted through the experimental analysis and shown as inset of figure 8, might have arisen due to the existence of interconnected pores on the surfaces of the nanosheets. Earlier we also predicted similar pore sizes in case of nanoscale TiO_2/PbS network [29].

4. Conclusion

We have demonstrated spectroscopic, photocatalytic and sorption characteristics of WS_2 nanosheets derived through a hydrothermal route and exfoliation. While possessing a hexagonal crystal structure, the nanosheets exhibited a lattice spacing of 0.63 nm. Raman measurement on the WS_2 nanosheets has revealed E_{2g}^1 and A_{1g} modes with an intensity ratio of ~ 0.68 , which is higher than its value for the bulk counterpart. The BET N_2 adsorption–desorption curve gives a type-IV pattern with an open hysteric feature. Exhibiting a high specific surface area, the nanosheets are believed to have mesopores with an average pore dimension of $\sim 3.8 \text{ nm}$. Moreover, the photodegradation of the MG dye under visible light illumination was seen to be more effective than under UV light condition. The band gap excitation led photo-oxidation might hinder the redox reactions at the nanocatalyst surface sites in the latter case. More analysis with inclusion of C-dots [30] and also emphasizing on irradiation aspect is in progress.

Acknowledgements

We acknowledge IUAC, New Delhi, for the financial support (Project: UFR-56322/2014 and 62312/2017). The

Figure 8. The nitrogen gas adsorption–desorption curve of the WS_2 nanosheets. The BJH pore size distribution curve is shown as inset.

initial assistance of Ms Mayuri Bora during experimental work is acknowledged. Further, we thank SAIC, Tezpur University, for extending several analytical facilities.

References

- [1] Chhowalla M, Shin H S, Eda G, Li L-J, Loh K P and Zhang H 2013 *Nat. Chem.* **5** 263
- [2] Wang Q H, Kalantar-Zadeh K, Kis A, Coleman J N and Strano M S 2012 *Nat. Nanotechnol.* **7** 699
- [3] Tenne R 2006 *Nat. Nanotechnol.* **1** 103
- [4] Mishra A K, Lakshmi K V and Huang L 2015 *Sci. Rep.* **5** 15718
- [5] Vattikuti S V P, Byon C and Reddy Ch. Venkata 2016 *Mater. Res. Bull.* **75** 193
- [6] Tang G, Tang H, Li C, Li W and Ji X 2011 *Mat. Lett.* **65** 3457
- [7] Shang Y, Xia J, China Zhude Xu and Chen W 2005 *J. Disp. Sci. Technol.* **26** 635
- [8] Cao S, Liu T, Hussain S, Zeng W, Peng X and Pan F 2014 *Mat. Lett.* **129** 205
- [9] Srivastava S, Sinha R and Roy D 2004 *Aquat. Toxicol.* **66** 319
- [10] Rabieh S, Bagheri M, Heydari M and Badiei E 2014 *Mater. Sci. Semicond. Process.* **26** 244
- [11] Paul N, Deka A and Mohanta D 2014 *J. Appl. Phys.* **116** 144902
- [12] Mao X, Xu Y, Xue Q, Wang W and Gao D 2013 *Nanoscale Res. Lett.* **8** 430
- [13] Lin H, Wang J, Luo Q, Peng H, Luo C, Qi R *et al* 2017 *J. Alloys Compd.* **699** 222
- [14] <http://imagej.nih.gov/ij/>
- [15] Ghorai A, Bayan S, Gogurla N, Midya A and Ray S K 2017 *ACS Appl. Mater. Interfaces* **9** 558
- [16] Nguyen T P, Choi S, Jeon J-M, Kwon K C, Jang H W and Kim S Y 2016 *J. Phys. Chem. C* **120** 3929
- [17] Nguyen T P, Sohn W, Oh J H, Jang H W and Kim S Y 2016 *J. Phys. Chem. C* **120** 10078
- [18] Molina-Sanchez A and Wirtz L 2011 *Phys. Rev. B: Condens. Matter* **84** 155413
- [19] Le Q V, Nguyen T P and Kim S Y 2014 *Phys. Status Solidi RRL* **8** 390
- [20] Berkdemir A, Gutiérrez HR, Botello-Méndez Andrés R, Perea-López Néstor, Elías Ana Laura, Chia C-I *et al* 2013 *Sci. Rep.* **3** 1755
- [21] Hazarika S J and Mohanta D 2017 *Appl. Phys. A* **123** 381
- [22] Bingham S and Daoud W A 2011 *J. Mater. Chem.* **21** 2041
- [23] Peng T, Zhao D, Song H and Yan C 2005 *J. Mol. Catal. A* **238** 119
- [24] Gaya U I and Abdullah A H 2008 *J. Photochem. Photobiol. C* **9** 1
- [25] Vattikuti S V and Byon C 2015 *Sci. Adv. Mater.* **7** 2639
- [26] Alothman Z A 2012 *Materials* **5** 2874
- [27] Kruk M and Jaroniec M 2001 *Chem. Mater.* **13** 316
- [28] Butt H-J, Graf K and Kappl M 2006 *The Kelvin equation: physics and chemistry of interfaces* (Weinheim: Wiley-VCH)
- [29] Dutta N, Mohanta D and Choudhury A 2011 *J. Appl. Phys.* **109** 094904
- [30] Hazarika S and Mohanta D 2019 *J. Luminescence* **206** 530