Research Article

Prospects for Electrochemical and Energy Applications of Highly Stable 2D WS_2 Nanosheets

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Abstract:

The physical and electronic properties of ultrathin 2-dimensional (2D) layered nanomaterials highly related to their thickness. Few-to-monolayers and nanosheets of the TMDCs were proved to be one of the potential material due to their high specific surface area, good active contact areas and porous nature. Therefore, In the recent past, there has been a much interest in 2-dimensional (2D) nanomaterials for its use in the applications related to energy generation and storage. Herein, we have synthesized the nanosheets of WS_2 in the dispersion form via sonchemical exfoliation method. The morphology, microstructure of samples, absorption behavior and electrochemical measurements were performed to study the nanosheet dimensions and to understand the possible use of WS_2 nanosheets in the electrochemical applications.

Keywords: 2D Nanomaterials, WS_2 nanosheet, Electrochemical and energy applications

I. INTRODUCTION

Two-dimensional (2D) transition metal dichalcogenides (TMDCs) have emerged as promising candidates for next-generation electronic and optoelectronic applications in substitution to graphene. However, much of the research has focused on measuring and optimizing intrinsic properties on small samples of micromechanically exfoliated flakes under idealized conditions (Eunjeong,2015; Ravindra,2016). As far as the real-world devices and systems it is inevitably require large-area samples that are integrated with metal and semiconductor contacts to achieve up to the practical devices. These requirements are particularly challenging to realize for two-dimensional materials as their properties are highly sensitive to various factors including defects, surface chemistry etc. Hence, the frontier research is now focused on alternative method as solution-processed two-dimensional materials with an eye toward realizing scalable processing of large-area thin-films. Theoretical and experimental investigations of few-to-monolayer atomically thin two-dimensional (2D) materials and their quantum dots (QDs) have revealed that these systems can exhibit highly unusual behaviors. The outstanding property of reduced dimensionality, 2D QDs present opportunities for manifestation of concepts/phenomena that may not be so prominent or have not been seen in bulk materials. With van der Waals interactions between neighboring layers other 2D layered materials and metals can be flexibly integrated without the limitation of lattice mismatches. This in turn explores entirely new opportunities beyond the reach of existing materials in terms of integrating distinct properties at the atomic scale shaping qualitatively and quantitatively their electronic, transport and optical properties, and thus their potential for applications (Manish,2015). With van der Waals interactions between neighboring layers, different 2D layered materials can be flexibly integrated without the limitation of lattice mismatches. This approach therefore opens up vast possibilities for nearly arbitrarily combining multiple materials and

integrating distinct properties at the atomic scale, and thus enabling entirely new opportunities beyond the reach of existing materials. The unique properties of two dimensional (2D) transition metal dichalcogenides (TMDs) in their few-to-monolayer form has gained sufficient momentum in the semiconductor research, the ability to tune their optical and electrical properties by introducing local interactions with the surface offers even greater perspective (Xin,2016). These 2D TMDC materials seeking attraction as bulk form of these can exfoliated up to few- to monolayer from bulk form. Moreover, these arrangements are more favourable to achieve monolayer of it as there is van der Waals interaction between two such layer and internally transition metal and chalcogenide interacted covalently. A monolayer has the thickness of 6 – 7 Å which is defined here as a plane of metal atoms sandwiched between two hexagonally ordered planes of chalcogen atoms, where the chalcogen is providing the oxidation state of +4 and -2 (Damien,2016).

Two dimensional (2D) Semiconducting transition metal dichalcogenides (TMDCs) unlike graphene, exhibit numerous fascinating properties associated with their reduced thickness. The layer dependent transition in their band structure from an indirect to a direct band gap semiconductor immediately makes TMDCs attractive in electronics and optoelectronics. Therefore it has been a robust research area for the researchers (Butler, 2013) (Pati,2010) (Geim,2013) (Dong,2106). Out of the various synthesis mechanisms of monolayer TMDCs, liquid phase exfoliation using ultra-sonication in discrete organic solvents, aqueous surfactant solutions, or solutions of polymers in solvents took great interest as it provide high level feasibility for getting large scale yield of monolayer and Nano-crystals (Coleman, 2014) (John, 2014) (Wang,2012).

It has been reported very confidently the uses of very thin TMDC in the several sorts of optoelectronic devices, namely photodetectors, photovoltaics,and light-emitting devices (Jariwala, 2014). Zongyou Yin et al. fabricated MoS_2 based phototransistorand investigate its electric characteristics and observed single-layer MoS_2 phototransistor gives a better photo responsivitythan does the graphene-based device with photocurrent generation and annihilationcan be switched promptphoto switching behaviour. In addition, it is proposed single layer MoS_2 transistors exhibited a higher photo responsivity (7.5 mAW^{-1}) than graphene FETs, presenting a potential application as a phototransistor(Yin, 2012). The single-layer MoS_2 has a unique quantum luminescence efficiency and exhibits a high channel mobility (~200 $cm^2 V^{-1} s^{-1}$) and current ON/OFF ratio (10^8) when it was used as the channel material in a field-effect transistor (FET) Radisavljevic, 2011). Later on the wavelength-dependent studies carried out which showed the photocurrent normally follows the absorption spectrum, which led to photocurrent generation due to inter-band absorption and carrier separation (Hee, 2012). Although Schottky junctions are the main source of the low bias photo response in most reports of MoS_2 phototransistors, the concept of a metal-semiconductor-metal (M-S-M) junction has been systematically exploited only recentlyb(Xin,2015). However, a p-n junction photodiode acquaints scopes for rapid photo detection and even heterojunction p-type Si and n-type TMDC now been ongoing trend of research. These materials based single wall carbon nanotubes and n-type MoS_2 shows good photo response having the rise time of less than 15 μs.(Jariwala, 2013) (Liu, 2016) (McCreary, 2016). Hence enhanced properties of few-to-monolayer TMDCs are still rich to study its potential commercialization versatile properties. The flexibility, stretch ability, and transparency are most promising mechanical properties of TMDC single layer which has thickness of < 1nm in comparison with bulk materials. Continuously the efforts are going on to improvise the electrical and mechanical properties of TMDCs. Late et al. described various uses of the TMDC in solar cell, super capacitor, Li-ion batteries, water splitting and energy harvesting which suggests the resurgence of the required study get the best out of it. These applications in various field tells the versatility of the TMD materials. With this, access to right-quality, large-area inorganic few-to mono-layer for any particular application is still growing interest and some issues in this regard yet to be addressed.(Late,2015). Mishra *et al*. introduced eco-friendly method to synthesis nano-sheets using simple detergent, this shows the demand of the cost effective production process at large scale. Using simple household detergent with ease peeling off the bulk materials in to nano scale is possible. Next, as this material shows strong absorption in visible range which further expands the doors of catalytic activity of it (Mishra, 2015) (Libraries, 2013) (Kaushik, 20104). These could be applicable in dye industries for degradation process of toxic chemicals. Kaushik et al. reported MoS_2 temperature based transistor characteristics with Schottky contacts of Au and Pd. Both Au and Pd exhibit n-type behavior on multilayer as well as monolayer MoS_2 transistors with Schottky

barrier heights of 0.126 eV and 0.4 eV (Deepesh, 2014). Deepesh Gopalakrishnan *et al.* studied a liquid exfoliation method for the synthesis MoS_2 nano-sheets. Mandar *et al.* and the group is engaged in the micro-mechanical exfoliation and device fabrication of TMDCs (Mandar, 2016).

METHODS/MATERIALS AND METHODS

Experimental Details

Materials

WS_2 powder (<2 µm, 99%, Aldrich) and 1-methyl-2-pyrrolidinone (NMP, 99%, Sigma-Aldrich) were used as received.

Dispersion of WS_2 Sheets

The dispersions of WS_2 were prepared for direct sonication in NMP, which is a commonly used solvent. An improved grinding assisted salt based sonication process was carried out for the exfoliation process. The dispersions were prepared using 50 mg WS_2 in 80 ml NMP with NaOH (0.25 mg/ml). The mixture was sonicated for 2 h using probe sonicator (Life care Probe sonicator, 40 kHz, 200W) with a cooling system to prevent overheating during sonication. After the sonication, the exfoliated solution was centrifuged several times at 10000 rpm for 30 minutes. The supernatant was collected and sediment was discarded to remove the unexfoliated WS_2 or thick flakes.

Characterization

X-ray diffraction patterns of both bulk and exfoliated WS_2 nanosheets were collected using Bruker X-ray diffractometer with Cu Kα radiation, λ=1.5418 Å. The prepared nanosheets of WS_2 were drop casted on the P-type silicon wafer and left for drying at 200ºC for an hour and kept safe for the X-Ray Diffraction (XRD) analysis. UV−vis spectra of the WS_2 dispersion were recorded using UV-1800 spectrophotometer (Shimadzu, Japan). A quartz cell with a path length of 1.0 cm was used for absorbance. The lateral dimension and crystal structure of WS_2 nanosheets were characterized using HRTEM (JEM-2010F from JEOL, 200 KV). For High resolution Transmission electron microscopy (HR-TEM) analysis the sample was drop casted on the Cu coated carbon grid and kept for natural drying process for 24 hour and heated for a while to remove excess moisture or any other impurities at 200ºC. For UV-VIS (UV-1800 spectrophotometer,Shimadzu, Japan) and RAMAN spectroscopy (NXR FT-Raman Module,Thermo Scientific) the as synthesised QDs of WS_2 dispersions were used with dilution in the NMP if needed.

Electrochemical measurements

The electrochemical measurement was carried out with the standard three electrode system using electrochemical workstation CHI 600E instrument, USA in NMP/$TBAPF_6$. The platinum disk, a platinum wire, and a saturated Ag/Agcl were used as working, counter and reference electrode respectively. The peaks on the positive side are known as the oxidation peak, and the negative one is the reduction peak.

RESULTS

The dispersions of WS_2 nanosheets were prepared by a grinding assisted direct exfoliation of bulk WS_2 powder with NMP through sonication in NMP. Because of the weak vand der Waals interaction between the WS_2 layers, the use of NMP as the solvent could exfoliate the bulk flakes of WS_2 into few-to monolayer nanosheets in the dispersion form. The obtained stable dispersion was characterized by various methods discussed in the following section.

DISCUSSION

Figure 1 shows the X-ray diffraction (XRD) pattern of bulk WS_2 and the prepared exfoliated nanosheets of WS_2. The XRD spectra of pristine WS_2 powder is shown in the Figure 1 depicts sharp peaks at 2θ = 14.2, 28.7, 43.8 and 59.7 which are allotted to (002), (004), (006) and (008) respectively which shows high macro phase crystallization in bulk sample of WS_2 with Hexagonal structure (JCPDS35-0651). The peak located at 14.2 degree corresponding to the (002) plane disappeared in WS_2 nanosheet.

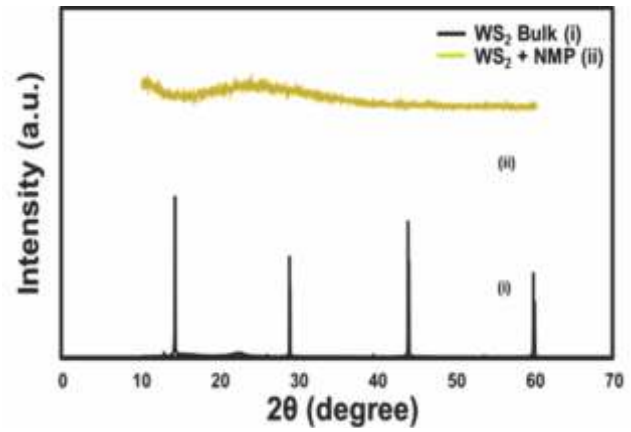

Fig. 1. XRD patterns of bulk WS_2 flakes and nanosheets

This could be due to the fact that, the synthesized WS_2 nanosheets are of few-to-monolayer in dimension and are highly exfoliated in nature. While making the sample preparation on Si substrate during the process of drying, a disordered re-stacking of layers results in almost incomplete crystallization is formed.

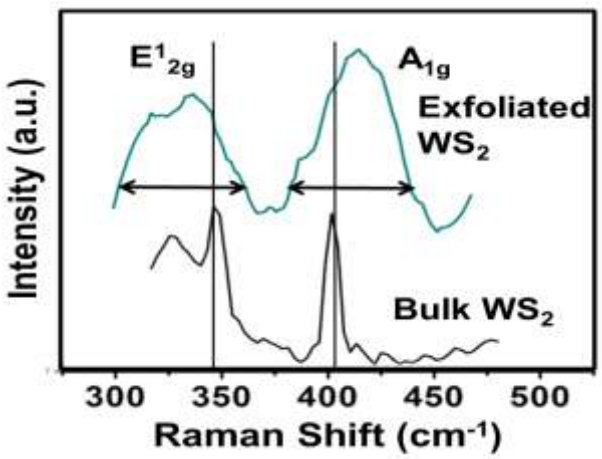

Fig. 2. Raman spectra of bulk WS_2 flakes and the exfoliated nanosheets

Raman spectroscopy employed to characterize the structure and shape of bulk (i.e. multi-layered) WS_2 and 2D layered WS_2 nanosheets revealed in figure 2. The schematic representation of two distinguished modes of WS_2 such as $\mathbf{E^1_{2g}}$ **and** $\mathbf{A_{1g}}$ where $\mathbf{E^1_{2g}}$ represents the in-plane vibratioin mode of W and sulfur atoms while $\mathbf{A_1g}$ out-of-plane vibration mode of sulphur atoms as shown in figure 2. The results demonstrated the successful synthesis of the WS_2 nanosheets of few-to monolayers. It could be concluded that, the sharp peaks of the multi-layered WS_2 become broader and resulting very weak interaction between the layers suggests successful exfoliation and the conversion of WS_2 QDs. The obtained results are consistent with other reported results (Ravindra, 2016). Further, the phonon modes are expected to soften due to the decreasing number of layers and weakening the interlayer interactions as the exfoliation of bulk WS_2 to nanosheets and monolayers occurs. Due to this, from bulk to monolayer, a red-shift is observed to the A_{1g} mode. While an anomalously has been observed in the represents the out-of-plane vibration mode of sulphur atoms as shown in figure 2. The results demonstrated the successful synthesis of the WS_2 nanosheets of few-to monolayers. It could be concluded that, the sharp peaks of the multi-layered WS_2 become broader and resulting very weak interaction between the layers suggests successful exfoliation and the conversion of WS_2 QDs. The obtained results are consistent with other reported results (Ravindra, 2016). Further, the phonon modes are expected to soften due to the decreasing number of layers and weakening the interlayer interactions as the exfoliation of bulk WS_2 to nanosheets and monolayers occurs. Due to this, from bulk to monolayer, a red-shift is observed to the A_{1g} mode. While an anomalously has been observed in the $\mathbf{E^1_2g}$ mode with a minor blue-shift for the monolayer. Similar behaviour is also observed in other TMDCs such as MoS_2 (Weijie, 2013; Changgu, 2010)

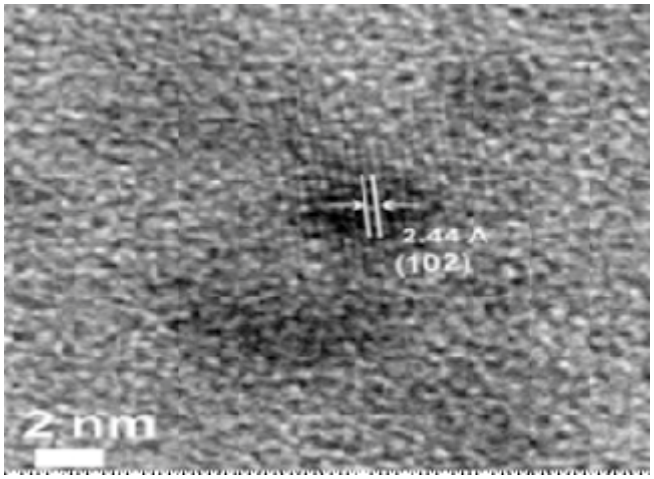

Fig. 3. TEM image of the exfoliated WS_2 nanosheets

Transmission electron microscopy (TEM) image was employed to characterize the exfoliation of WS_2 to few-to-monolayer WS_2 nanosheets. As shown in the figure 3 it is clear that clusters of WS_2 are formed due to dominating surface energy of NMP and that the bulk powder is uniformly exfoliated in to WS_2 nanosheets claiming the average size of 3±0.5nm.

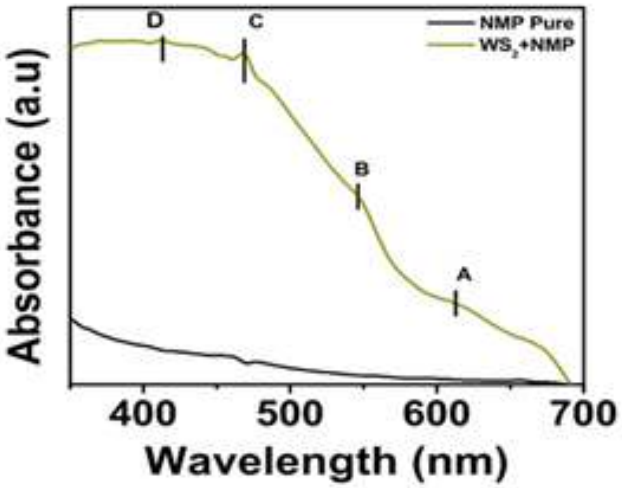

Fig. 4. Optical spectra of exfoliated WS_2 nanosheets in dispersion

Figure 4 shows the UV-vis absorbance spectra of WS_2 nanosheets in NMP. There are four absorption peaks of WS_2 nano-sheets are observed at ~620 nm, ~530 nm, ~464 nm and ~410 nm. The A and B peaks are termed as the excitonic peaks at k point in Brillouin zone and the remaining two (B and C) are the direct transition from valance band to conduction band. The results shown here are in good agreement with the reports. The shaping of WS_2 nanaosheets from bulk tends to modify the optical property very interestingly.

Recent progress of TMDCs in electrochemical and energy storage devices

Graphene based layered structures are commercially used in the lithium-ion batteries (LIBs) technology for much of the applications, such as consumer electronics, artificial satellites, military equipment, renewable energy storage for smart grids, and electric vehicles. However, the increasing demand of LIBs, researchers are putting efforts to explore new anode materials delivering a high performance. Recent past witnessed the development of TMDCs based anode materials which is analogous to graphene with high lithium storage capacity (ca. 670 mAh g−1). Numbers of different synthesis technologies have been evolved to overcome the structural deterioration and low intrinsic electrical conductivity between two adjacent X−Mo−X sheets (c-direction), which together lead to a poor cycling performance and inferior rate capability which, limits its practical application. Out of TMDC class of materials, MoS_2 based compounds such as Graphene-like MoS_2/amorphous carbon composites, MoS_2 nanosheet/active carbon fiber, MoS_2 microspheres encapsulated porous carbon etc. have been studied by the investigators for its successful use as table anode for Li-ion batteries (Chang, 2011; Wang, 2014; Zhang, 2014; Liu, 2014; and Kalluri, 2015). Among graphite group, graphene has found more suitable because of its high electrical conductivity, mechanical properties and large specific surface area in the monolayer form. Hence in combination with TMDCs, fast electrode kinetic and stable cycling performance could be achieved during lithiation /delithiation reaction. TMDCs in the nanosheets from with a larger specific surface area than the sheet structure, could increase the active material /electrolyte interface reaction to take place and provide a shorter diffusion distance for both lithium ions and electrons.

Table 1. Use of TMDCs in recent past for its application in electrochemical and energy storage devices

Sr.No.	Electrode type	Specifications	References
1.	L-Cysteine-Assisted Synthesis of Layered MoS_2/Graphene	Specific capacity of 1100 $mAhg^{-1}$	Chang,2011
2.	Graphene-few-layer WS_2 composites	current density from 100 mAh g^{-1} to 5000 mAh g^{-1}	Chen,2013
3.	Honeycomb-like MoS_2 nanosheets anchored into 3-D graphene foam,	Discharge capacity of 1050 mAh g^{-1} at a current density of 200 $mAhg^{-1}$ after 60 cycles.	Wang,2014
4.	MoS_2/graphene nanocomposite	Reversible capacity of 1300−1400 mAh g^{-1}	Liu,2014
5.	Lamellar WS_2 nanosheet electrodes upon intercalation of single-walled carbon nanotubes	792 mAh g^{-1} capacity at a current density of 0.1 Ag^{-1} after 10 cycles	Yu Liu,2014
6.	VS_2/Graphene Nanocomposites	528 mAh g^{-1} capacity after 100 cycles at 200 mAh g^{-1}	Fang,2015
7.	Nanostructured WS_2/rGO	565 mAh g^{-1} capacity after 100 cycles when cycled at 0.1 Ag^{-1} and 337 mAh g^{-1} capacity at 2 A g^{-1}	Li, 2015
8.	Spray-Dried Molybdenum Disulfide-Graphene Hierarchical Microspheres	1300 $mAhg^{-1}$ and 640 $mAhg^{-1}$ at 0.1 A g^{-1}; 250-500 cycles	Sujith, 2015
9.	MoS_2 Nanosheets Vertically Grown on Graphene Sheets	907 mAh g^{-1} at 1000 mAh g^{-1} after 400 cycles	Teng,2016
10.	WS_2 nanosheets-carbon composites	Reversible lithium storage capacity of 322 $mAhg^{-1}$ at 200 mAh g^{-1} after 100 cycles	Junming Li, 2016
11.	WS_2-3D graphene nano-architecture	748 $mAhg^{-1}$ after 500 cycles	Lim,2016
12.	WS_2 nanosheets grown on graphene-wrapped electrospun carbon nanofibers	Charge capacity of 1128.2 $mAhg^{-1}$ at a current density of 0.1 A g^{-1}	Zhang,2016
13.	WS_2/CNT-rGO Aerogel	Specific capacity of 749 $mAhg^{-1}$ at 100 $mAhg^{-1}$	Wang,2016

Sr.No.	Electrode type	Specifications	References
14.	SnSe Nanoparticles Confined in Graphene	Specific capacity of 590 $mAhg^{-1}$ at 0.050 Ag^{-1}, a rate capability of 260 $mAhg^{-1}$ at 10 Ag^{-1}, over 120 cycles	Xu Yang, 2015
15.	Ge/MoS_2 nanocomposites	Specific capacity of 1362 $mAhg^{-1}$ cycled at 0.2 Ag^{-1} after 50 cycles	Hsieh,2017

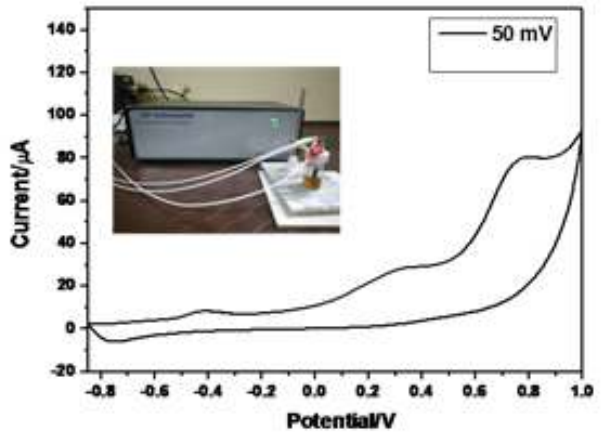

Fig. 5. Cyclic voltammetry measurements of WS_2 nanosheets

In order to evaluate the electrochemical activity of the WS_2 nanosheets, cyclic voltammetry (CV) measurements were carried out at a scan rate of 0.1 mV s−1, and the recorded curves are plotted in Figure 5. The scale ranging for CV reading was -1.0 to 1.0 V vs Ag/AgCl. The CV of WS_2 nanosheet was carried out at a scan rate of 50mv as shown in figure5. A small oxidation peak arefound at -0.41V and major oxidation peaks are at around 0.32V and 0.78V and associated reduction peak around -0.74V with a scan rate of 50mv, pointing towards its electrochemical application in the organic solar cell energy storage devices. The potential in this field is yet be studied.

CONCLUSIONS

The application of WS_2 few-to-monolayer nanosheets synthesized via sonochemical exfoliation method in the electrochemical applications has been studied. Sonochemical exfoliation synthesis method was proven to be the best method for the preparation of stable dispersions TMDCs nanosheets by studying its structural, microscopic and spectroscopic tools including XRD, TEM, UV-Vis and Raman spectroscopy. In order to confirm the use of 2D-WS_2 nanosheets for its potential use in energy storage devices, the electrochemical measurements of the WS_2 nanosheets have been studied.

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