Asian Journal of Chemistry; Vol. 34, No. 4 (2022), 1009-1014

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2022.23707

Exfoliation of MoS_2-RGO Hybrid 2D Sheets by Supercritical Fluid Process

MURTHY MUNIYAPPA[1], MAHESH SHASTRI[1,2], MANJUNATH SHETTY[3], VINAY GANGARAJU[1], JAGADEESH BABU SRIRAMOJU[4], SINDHUSHREE MURALIDHAR[1], MANIKANTA P. NARAYANASWAMY[1], MUDIKE RAVI[1], NAVYARANI MARLINGAIAH[5], PRASANNA D. SHIVARAMU[1], ANANDA KUMAR C S[1] and DINESH RANGAPPA[1,*]

[1]Department of Applied Science (Nanotechnology), PG Centre Bangalore Region, Visvesvaraya Technological University, VIAT, Muddenahalli, Chikkaballapur-562101, India
[2]Department of Electronics & Communication, Nagarjuna College of Engineering & Technology, Devanahalli, Bengaluru-562164, India
[3]Department of Aeronautical and Automobile Engineering, Manipal Institute of Technology, Manipal-576104, India
[4]Department of Physics, Malla Reddy Engineering College, Maisammaguda, Hyderabad-500100, India
[5]Department of Applied Sciences, Dayanand Sagar University, Kumar Swamy Layout, Bengaluru-560111, India

*Corresponding author: E-mail: dineshrangappa@gmail.com; dinesh.rangappa@vtu.ac.in

Received: 3 January 2022; *Accepted*: 19 February 2022; *Published online*: 10 March 2022; AJC-20747

Layered 2D transition metal dichalcogenides (TMD's) have been considered as an important class of materials in the field of energy and environmental applications. Therefore, it is desirable to fabricate 2D hybrid TMD's materials in simple solution processing methods. In this study, MoS_2-RGO hybrid 2D few layered sheets are produced by supercritical fluid process (SCF) by using ethanol as solvent at 250 ºC in a short duration of 0.5 h. Atomic force microscopy (AFM), transmission electron microscope (TEM) and scanning electron microscope (SEM) images confirmed the formation of 2D hybrid few layered sheets. The electrochemical impedance measurement indicates fivefold increase in conductivity of bulk MoS_2. This work presents rapid and one pot exfoliation of MoS_2 and simultaneous reduction of GO that can facilitate the production of 2D hybrid materials.

Keywords: 2D, Transition metal dichalcogenides, RGO, MoS_2, Supercritical fluids.

INTRODUCTION

Metal dichalcogenides are an attractive group of materials, which are being applied in catalysis, hydrogen generation, battery applications, sensors, transistors, solar cells, *etc*. [1-4]. Layered 2D transition metal dichalcogenides (TMD's) have chemical structure in the form of MX_2 where, M denotes transition metal and X denotes chalcogen atom. TMD's consists of layered structures bonded with weak van der Waals forces. However, transition metal and chalcogens are covalently bonded [5-7]. The electronic and optical properties of TMD's mainly depends upon the number of layers and phases [3,8]. Among various TMD's, the MoS_2 is non-toxic, stable and earth abundant material. It offers lot of applications in energy and environmental field such as photocatalysis, electrocatalysis, sensors, electrochemical energy storage and hydrogen generation [5-7,9-11]. Inspite of all these intriguing properties, MoS_2 shows some drawbacks in terms of its electrical and optical properties. Now a days for improving its electrical properties, one of the most trending carbon based 2D material, graphene has been composited with MoS_2 [3,12-16].

The MoS_2 can be synthesized by two approaches namely top down and bottom-up approach. In bottom-up approach, a chemical reaction occurs between salts of Mo and sulfur to form MoS_2 [17-19]. Some of the examples for bottom-up approach are chemical vapour deposition, hydro or solvothermal methods [9,20-22]. In top-down approach bulk materials are chipped in to smaller or thinner sheets by mechanical shearing or micro mechanical cleavage. Ultrasonication and intercalation of Li compounds between the layers of MoS_2 is carried out to separate each layer by suppressing the weak van der Waals forces [23]. Some of the challenges in these methods include high manpower, vacuum or inert atmosphere requirement, low yield, poor quality and time consumption [24-27]. To avoid these drawbacks, one has to look for facile solution based processing for obtaining high quality, large yield in less time consuming techniques.

These aspects require a supercritical fluid process (SCF) process because of its excellent physico-chemical properties. Rangappa *et al.* [28] reported exfoliation of pristine graphite into few layered graphene sheets under SCF process. Recently, Truong *et al.* [29] has studied exfoliation of few layered MoS_2 and MoSe sheets in dimethyl formamide as a supercritical fluid for Mg-ion battery application at 400 ºC for 1 h duration. Thangaswamy & Sathish [30] reported the exfoliation of MoS_2 nano-scrolls in DMF based SCF process for luminescent application. Here, reaction was carried out at temperature 400 ºC for 1 h duration. However, there are no reports on the simultaneous exfoliation and reduction of MoS_2 and GO 2D few layered sheets by SCF at low temperature and short reaction time.

Therefore, it is imperative to concentrate on lower temperature supercritical solvents and short reaction time technique for obtaining hybrid MoS_2-RGO 2D few layered sheets. At supercritical temperature and pressure, solvents exhibit zero surface tension, high wettability, high diffusivity, low viscosity and high solvating power [31]. By inspiring with these fascinating properties, we demonstrate a direct, simple and one step approach for the preparation of hybrid MoS_2-RGO 2D few layered sheets. Electrochemical impedance spectra was carried out to determine the conductivity of the as prepared hybrid MoS_2-RGO 2D few layered sheets.

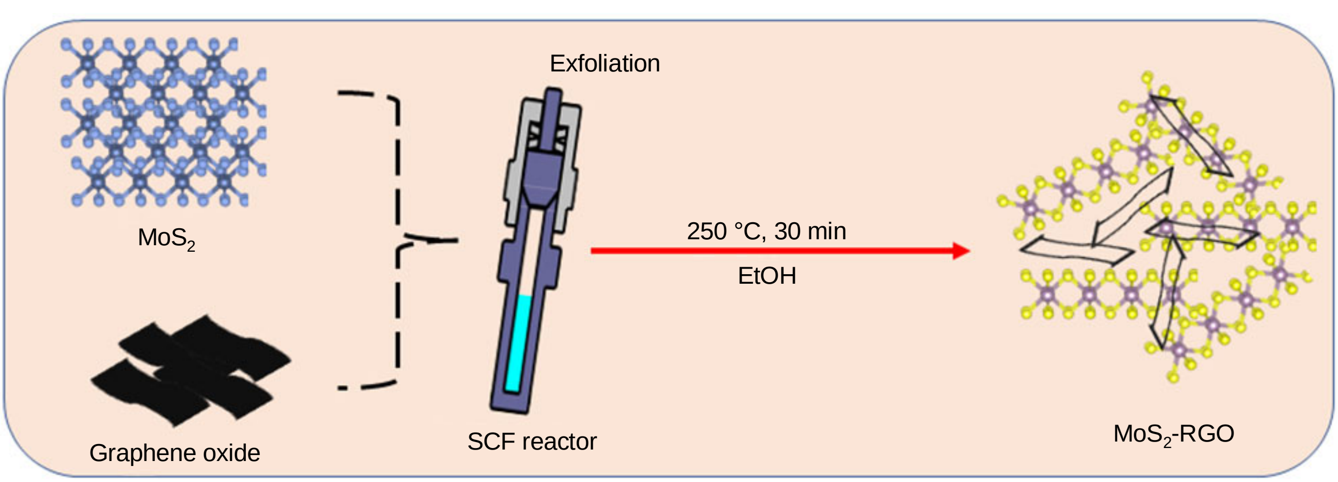
EXPERIMENTAL

The chemicals *viz.* ethanol, sodium nitrate, graphite powder, potassium permanganate, hydrochloric acid and hydrogen peroxide (100%) were purchased from Merck Chemicals. All the chemicals were used without further purification. Bulk MoS_2 were purchased from SRL Ltd., India and used without any purification.

Crystal structure and phase were identified by using powder X-ray diffractometer (XRD, Rigaku ultima-IV). The range of measurement was from 10º to 70º at 0.02 steps/s using Cu*K*α as X-ray source. The morphology of the samples were analyzed by using scanning electron microscope (SEM, SU1510) and transmission electron microscopy (JEOL, JEM 2100). The number of layers and surface topography were analyzed using atomic force microscopy (AFM, Park system). An absorbance spectrum was recorded by UV-VIS spectroscope (Perkin-Elmer, Lambda 750). To confirm the layered structure of as synthesized samples, Raman spectroscopy was carried out. Electrochemical impedance spectra were carried out in the range of 0.01-10^6 Hz in OrigaLys electrochemical workstation. All the measurements were made on a standard three-electrode system. The Ag/AgCl was used as a reference electrode, Pt wire was used as counter electrode and FTO coated sample (3 cm × 6 cm) were used as a working electrode with 0.1 M Na_2SO_4 as an electrolyte.

Preparation of graphene oxide (GO): Graphene oxide (GO) was prepared by using modified Hummer's method as reported in the literature [32]. Initially, a mixture of HNO_3 and HCl were taken in a beaker and placed in an ice bath on magnetic stirrer. Graphite powder (1 g) was added in to the above acid mixture followed by addition of 1 g sodium nitrate. After stirring the mixture for 0.5 h, 6 g of $KMnO_4$ was slowly added. It was observed that solution turns into pink colour after stirring vigorously for 1 h. The ice bath was removed and increases the hot plate to 50 ºC. Simultaneously, added 200 mL of deionized water followed by 30% H_2O_2. The formation of light-yellow bubbles confirmed the formation graphene oxide. Then the obtained GO was washed until it reaches to a neutral pH by repeated centrifugation.

Preparation of MoS_2/RGO 2D few layered sheets: In a typical experiment, 40 mg of bulk MoS_2 and 40 mg GO was added to 10 mL ethanol and mixed by magnetic stirrer. After complete dispersion of GO and MoS_2 the mixture was transferred to SCF reactor and placed in tubular furnace at 250 ºC for 0.5 h. Then, obtained black coloured solution was sonicated for 15 min and kept it for 2 min until unexfoliated bulk sheets were settled down. The dispersed black colour solution was washed in deionized water and ethanol to remove any impurities present in the sample. Then samples were dried overnight at 70 ºC. The formation or exfoliation mechanism is shown in **Scheme-I**. At supercritical fluid state, the ethanol displays high diffusivity and excellent wettability, hence it diffuses between the layers of both GO and bulk MoS_2 by overcoming the weak van der Waal's force separate the layers as shown in **Scheme-I**.



Scheme-I: Schematic of one step simultaneous MoS_2-RGO exfoliation and reduction process leading to hybrid 2D few layered sheets

RESULTS AND DISCUSSION

XRD studies: Formation of graphene oxide (GO) was confirmed by XRD analysis as shown in Fig. 1. The peak at 10.5º indicates successful oxidation of graphite powder into few layered graphene oxide. The crystal structure and phase purity of the obtained MoS_2-RGO hybrid 2D few layered sheets exfoliated by SCF process was confirmed by XRD measurement as shown in Fig. 2. The bulk MoS_2 diffraction were matched to 2H phase MoS_2 with lattice constants a = b = 3.1612 Å and c = 12.2985 Å. The XRD patterns were matching with PDF card no 9007660. The bulk MoS_2 exhibits high intensity peak that corresponds to 2θ values at 14.64º (002), 39.80º (103). Whereas, the SCFs treated MoS_2-RGO shows less intensity peaks (002) at 2θ 14.78º. The reduced intensity confirms the exfoliation of bulk MoS_2 into few layered MoS_2 [30]. The broad peak between 25º to 30º indicates successful reduction of GO into RGO.

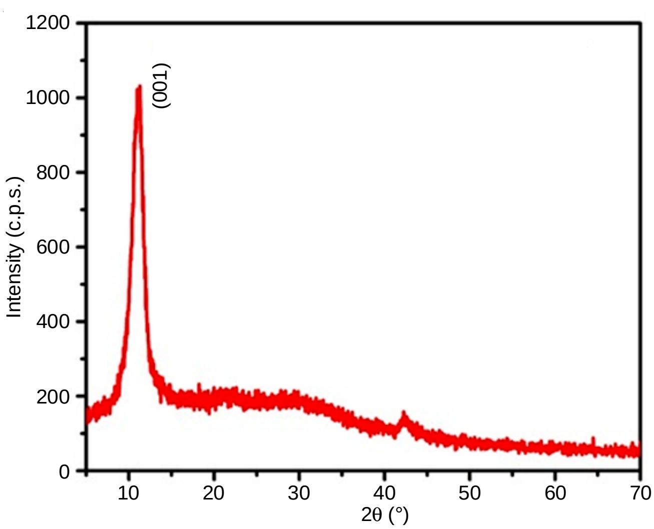


Fig. 1. XRD pattern of GO prepared by modified Hummer's route

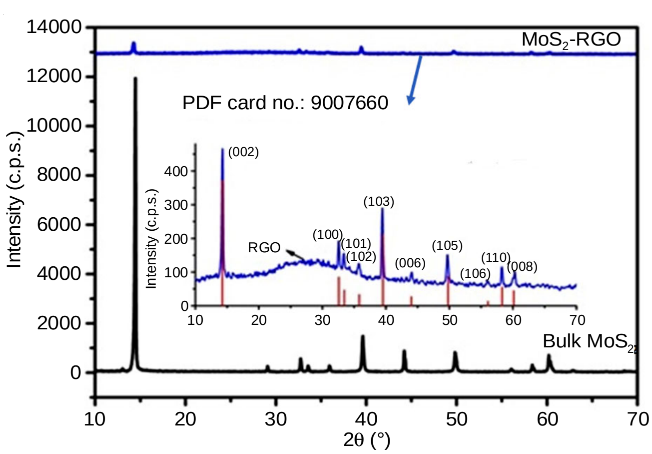


Fig. 2. XRD patterns of bulk MoS_2 and MoS_2-RGO hybrid 2D few layered sheets exfoliated by SCF process

Raman studies: In order to further assure successful exfoliation and formation of MoS_2-RGO few layered sheets, Raman spectroscopy analysis was carried out as shown in Fig. 3. In earlier reports, the vibrations modes E_{2g} (in plane) and A_{1g}

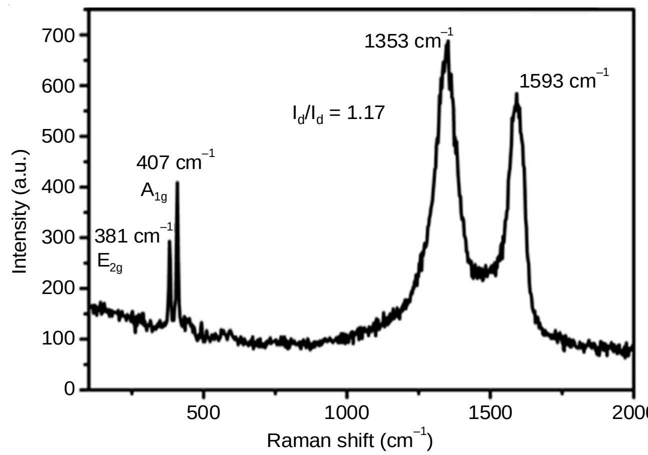


Fig. 3. Raman spectra of MoS_2-RGO hybrid 2D few layered sheets exfoliated by SCF process

(out of plane) for bulk MoS_2 was reported at 383.4 cm^{-1} and 409.1 cm^{-1} [30]. Whereas, after exfoliation the peaks were red shifted from 383.4 cm^{-1} to 381 cm^{-1} indicating successful exfoliation [30]. The decrease in the peak width infers the decreased number of layers. The D and G band peaks at 1353 cm^{-1} and 1593 cm^{-1}, respectively, indicates presence of carbon layers [33]. The ratio of D to G bands is greater than 1 indicates successful reduction of RGO [22]. The D/G ratio for the MoS_2-RGO few layered sheets was found to be 1.17, which indicates the successful reduction of RGO from GO.

SEM studies: Figs. 4a-b show the SEM images of bulk MoS_2 and Figs. 4c-d show exfoliated MoS_2-RGO 2D hybrid sheets. The morp-hology of the bulk MoS_2 powder shows the stacked layers of 5 to 10 µm size. After the SCF ethanol exfoliation, MoS_2 layers were crumbled into few layers of sheets with smaller thickness. The smaller exfoliated MoS_2 sheets were covered by reduced graphene oxide sheets (RGO).

TEM studies: Further, to confirm the exfoliation of bulk MoS_2 into few layered MoS_2 sheets along with reduction of GO to RGO, the TEM analysis has been carried out as shown in Fig. 5. From the TEM images it is very clear that few layers of MoS_2 sheets are present with sizes ranging from 20 to 30 nm. The MoS_2 layers were covered by transparent very thin layers of RGO, which is consistent with SEM analysis. Hence, formation of MoS_2-RGO 2D hybrid sheets under supercritical fluid process is confirmed.

AFM studies: Fig. 6 represents atomic force microscopy images and its corresponding line profile of the produced MoS_2-RGO 2D hybrid sheets. The presence of smaller sized sheets was confirmed in the AFM image. The line profiles of the sheets were found to be 16 nm. Around 20 to 25 single layers of MoS_2-RGO sheets piled to up to form 16 nm height of thesample by considering the thickness of MoS_2 is 0.65 nm and single layer reduced graphene oxide thickness is 0.35 nm. In AFM image, a presence of few bigger sized sheets was observed, which arises due to aggregation or stacking of sheets one above the other during the sample preparation therefore, excluded for line profile measurement.

UV-visible studies: Fig. 7 shows the UV-vis absorbance spectra of MoS_2-RGO 2D nanosheets prepared by SCF process.

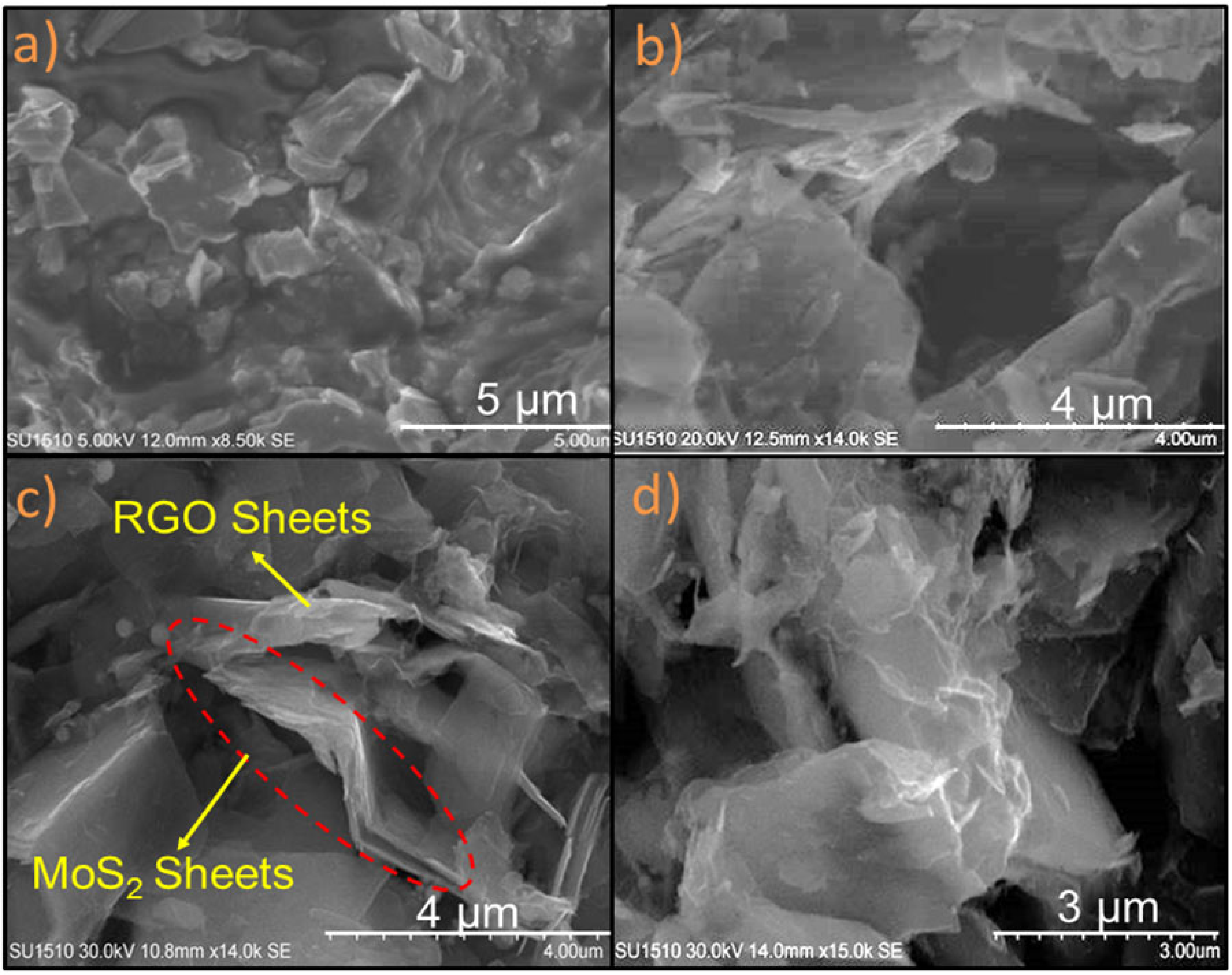


Fig. 4. SEM images of (a-b) bulk MoS_2, (c-d) MoS_2-RGO hybrid 2D few layered sheets exfoliated under SCF process

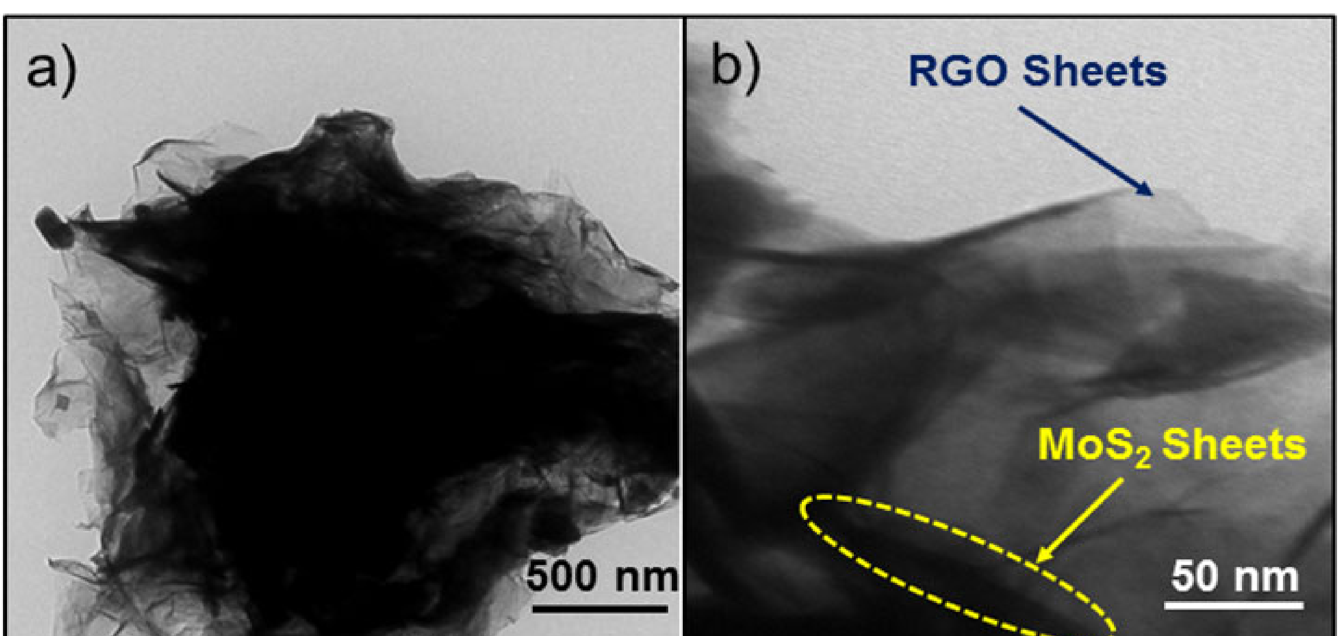


Fig. 5. TEM images of (a-b) MoS_2-RGO hybrid 2D few layered sheets exfoliated under SCF process

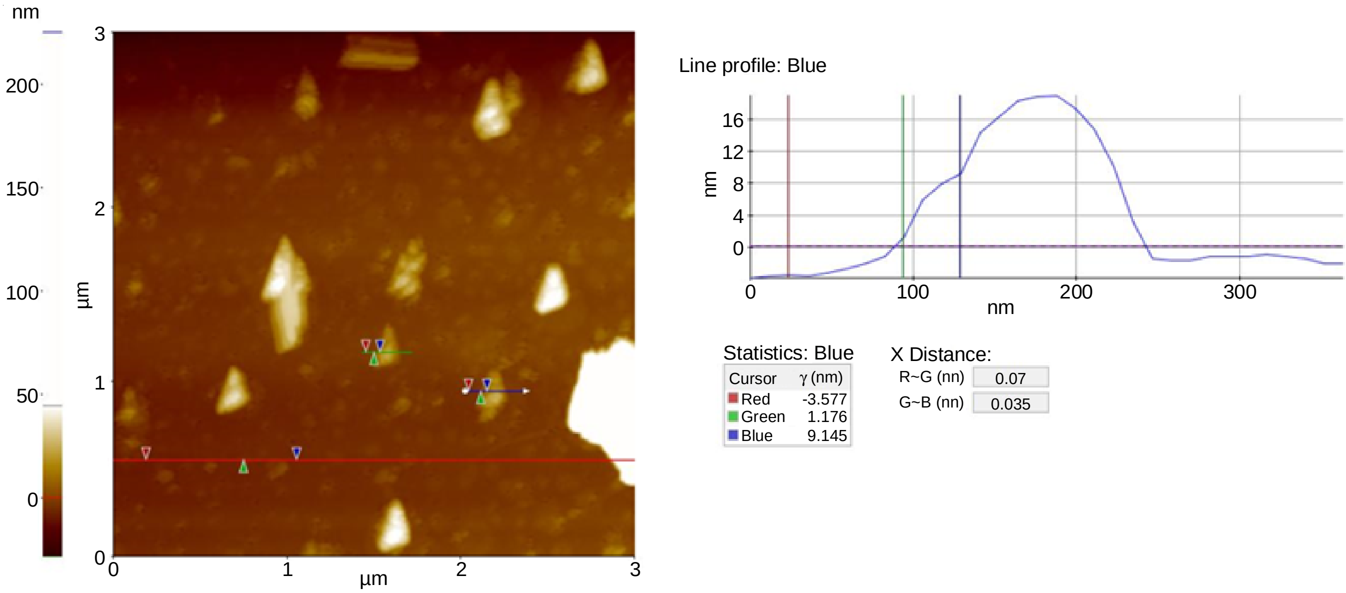


Fig. 6. AFM Image and corresponding line profile of MoS_2-RGO hybrid 2D few layered sheets exfoliation by SCF process

According to previous reports the peak at 328 nm indicates presence of MoS_2 and peak at 280 nm indicates presence of RGO, which confirms the successful reduction of GO into RGO [30,32]. Probably, the two peaks were submerged in to a single peak, which indicates the successful exfoliation of MoS_2-RGO 2D sheets.

Electrochemical studies: Fig. 8 represents electrochemical impedance spectra of bulk MoS_2 and MoS_2-RGO hybrid 2D few layered sheets exfoliated by SCF process. In the impedance plot, the semicircle represents the charge transfer resistance. In the plot of bulk MoS_2, the arc was found to be around 300 ohms, whereas in MoS_2-RGO hybrid 2D few layered sheets it decreased to 65 ohms. Approximately, five folds of charge transfer resistance was decreased after loading with RGO. Therefore, inclusion of RGO in MoS_2-RGO hybrid 2D few layered sheets improves the conductivity of the hybrid 2D sheets, which is useful in the applications where, charge transfer or conductivity plays a crucial role.

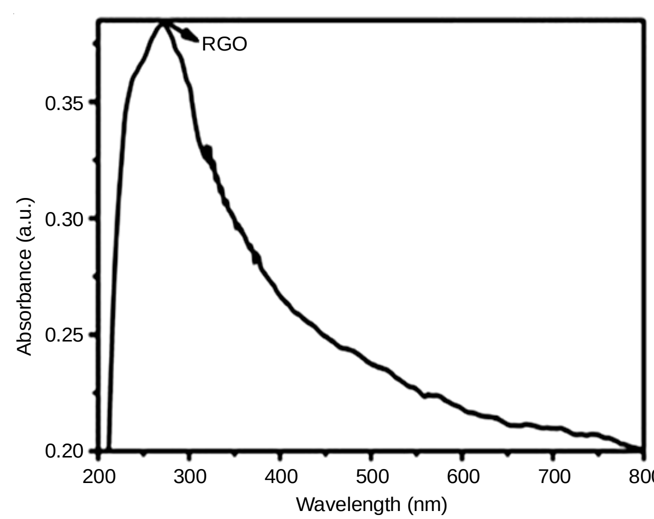


Fig. 7. UV-Vis spectroscopy of MoS_2-RGO hybrid 2D few layered sheets exfoliation by SCF process

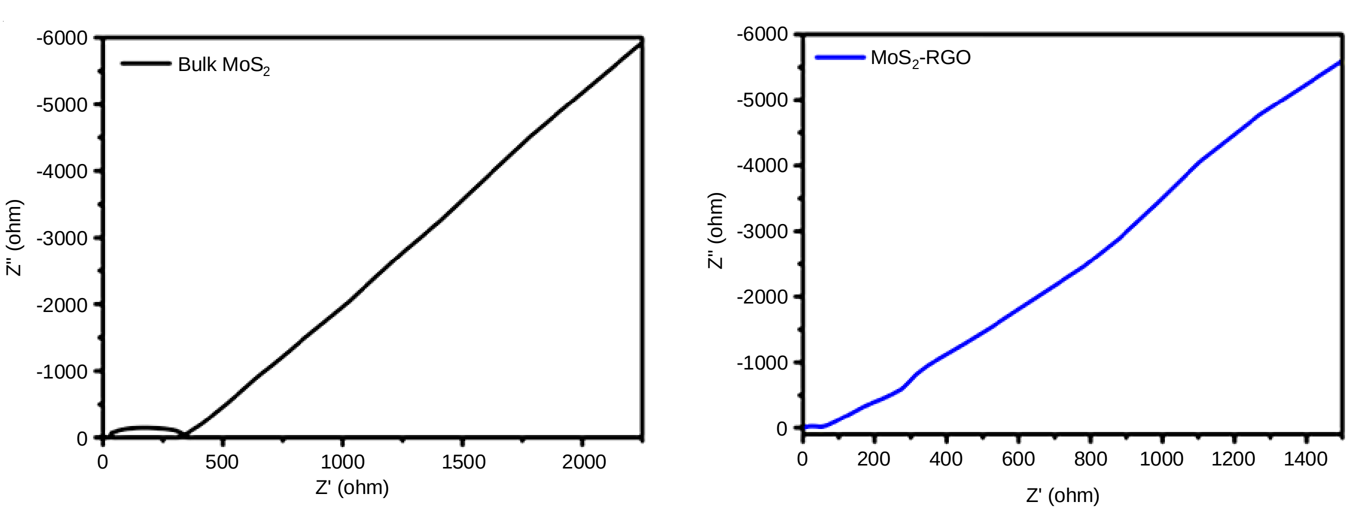


Fig. 8. Impedance spectra of bulk MoS_2 and MoS_2-RGO hybrid 2D few layered sheets exfoliated by SCF process

Conclusion

A direct, simple and one step supercritical fluid process (SCF) process was demonstrated for the preparation of hybrid MoS_2-RGO 2D few layered sheets. This process offers low temperature and short reaction time for simultaneous exfoliation and reduction of hybrid MoS_2-RGO 2D few layered sheets. Formation of few layered MoS_2 and reduction of GO was confirmed XRD, TEM and AFM analysis. The addition of RGO in to MoS_2 increases five folds conductivity of bulk MoS_2 which, opens up scope for many applications in the field of energy and environment.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. M. Chhowalla, H.S. Shin, G. Eda, L.J. Li, K.P. Loh and H. Zhang, *Nat. Chem.*, **5**, 263 (2013); https://doi.org/10.1038/nchem.1589
2. A.K. Geim and I.V. Grigorieva, *Nature*, **499**, 419 (2013); https://doi.org/10.1038/nature12385
3. D. Jariwala, V.K. Sangwan, L.J. Lauhon, T.J. Marks and M.C. Hersam, *ACS Nano*, **8**, 1102 (2014); https://doi.org/10.1021/nn500064s
4. Q.H. Wang, K. Kalantar-Zadeh, A. Kis, J.N. Coleman and M.S. Strano, *Nat. Nanotechnol.*, **7**, 699 (2012); https://doi.org/10.1038/nnano.2012.193
5. H. Li, Z. Yin, Q. He, H. Li, X. Huang, G. Lu, D.W.H. Fam, A.I.Y. Tok, Q. Zhang and H. Zhang, *Small*, **8**, 63 (2012); https://doi.org/10.1002/smll.201101016
6. L. Cao, Y. Yu, S. Huang and W. Yang, Layer-dependent Electrocatalysis of MoS_2 for Hydrogen Evolution Layer-Dependent Electrocatalysis of MoS_2 for Hydrogen Evolution, Department of Materials Science and Engineering, North Carolina State University, Raleigh NC (2014).
7. S. Bertolazzi, J. Brivio and A. Kis, *ACS Nano*, **5**, 9703 (2011); https://doi.org/10.1021/nn203879f
8. K.F. Mak, C. Lee, J. Hone, J. Shan and T.F. Heinz, *Phys. Rev. Lett.*, **105**, 136805 (2010); https://doi.org/10.1103/PhysRevLett.105.136805
9. C. Lee, H. Yan, L.E. Brus, T.F. Heinz, J. Hone and S. Ryu, *ACS Nano*, **4**, 2695 (2010); https://doi.org/10.1021/nn1003937
10. L. Wei, Y. Chen, Y. Lin, H. Wu, R. Yuan and Z. Li, *Appl. Catal. B*, **144**, 521 (2014); https://doi.org/10.1016/j.apcatb.2013.07.064
11. A. Sobczynski, *J. Catal.*, **131**, 156 (1991); https://doi.org/10.1016/0021-9517(91)90332-X
12. H. Wang, H. Feng and J. Li, *Small*, **10**, 2165 (2014); https://doi.org/10.1002/smll.201303711
13. X. Wang, Z. Zhang, Y. Chen, Y. Qu, Y. Lai and J. Li, *J. Alloys Compd.*, **600**, 84 (2014); https://doi.org/10.1016/j.jallcom.2014.02.127
14. H.Y. Chang, S. Yang, J. Lee, L. Tao, W.S. Hwang, D. Jena, N. Lu and D. Akinwande, *ACS Nano*, **7**, 5446 (2013); https://doi.org/10.1021/nn401429w
15. Q. He, Z. Zeng, Z. Yin, H. Li, S. Wu, X. Huang and H. Zhang, *Small*, **8**, 2994 (2012); https://doi.org/10.1002/smll.201201224
16. M. Latorre-Sánchez, I. Esteve-Adell, A. Primo and H. García, *Carbon*, **81**, 587 (2015); https://doi.org/10.1016/j.carbon.2014.09.093
17. W. Zhou, X. Zou, S. Najmaei, Z. Liu, Y. Shi, J. Kong, J. Lou, P.M. Ajayan, B.I. Yakobson and J.-C. Idrobo, *Nano Lett.*, **13**, 2615 (2013); https://doi.org/10.1021/nl4007479
18. A.M. Van Der Zande, P.Y. Huang, D.A. Chenet, T.C. Berkelbach, Y. You, G.H. Lee, T.F. Heinz, D.R. Reichman, D.A. Muller and J.C. Hone, *Nat. Mater.*, **12**, 554 (2013); https://doi.org/10.1038/nmat3633
19. J.D. Tobias, *Anesthesiology*, **96**, 1522 (2002); https://doi.org/10.1097/00000542-200206000-00039
20. H. Li, J. Wu, Z. Yin and H. Zhang, *Acc. Chem. Res.*, **47**, 1067 (2014); https://doi.org/10.1021/ar4002312
21. O. Lopez-Sanchez, D. Lembke, M. Kayci, A. Radenovic and A. Kis, *Nat. Nanotechnol.*, **8**, 497 (2013); https://doi.org/10.1038/nnano.2013.100
22. A. Winchester, S. Ghosh, S. Feng, A.L. Elias, T. Mallouk, M. Terrones and S. Talapatra, *ACS Appl. Mater. Interfaces*, **6**, 2125 (2014); https://doi.org/10.1021/am4051316
23. Z. Zeng, Z. Yin, X. Huang, H. Li, Q. He, G. Lu, F. Boey and H. Zhang, *Angew. Chem. Int. Ed.*, **50**, 11093 (2011); https://doi.org/10.1002/anie.201106004
24. G.S. Bang, K.W. Nam, J.Y. Kim, J. Shin, J.W. Choi and S. Choi, *ACS Appl. Mater. Interfaces*, **6**, 7084 (2014); https://doi.org/10.1021/am4060222
25. J.N. Coleman, M. Lotya, A. O'Neill, S.D. Bergin, P.J. King, U. Khan, K. Young, A. Gaucher, S. De, R.J. Smith, I.V. Shvets, S.K. Arora, G. Stanton, H.-Y. Kim, K. Lee, G.T. Kim, G.S. Duesberg, T. Hallam, J.J. Boland, J.J. Wang, J.F. Donegan, J.C. Grunlan, G. Moriarty, A. Shmeliov, R.J. Nicholls, J.M. Perkins, E.M. Grieveson, K. Theuwissen, D.W. McComb, P.D. Nellist and V. Nicolosi, *Science*, **331**, 568 (2011); https://doi.org/10.1126/science.1194975
26. K.R. Paton, E. Varrla, C. Backes, R.J. Smith, U. Khan, A. O'Neill, C. Boland, M. Lotya, O.M. Istrate, P. King, T. Higgins, S. Barwich, P. May, P. Puczkarski, I. Ahmed, M. Moebius, H. Pettersson, E. Long, J. Coelho, S.E. O'Brien, E.K. McGuire, B.M. Sanchez, G.S. Duesberg, N. McEvoy, T.J. Pennycook, C. Downing, A. Crossley, V. Nicolosi and J.N. Coleman, *Nat. Mater.*, **13**, 624 (2014); https://doi.org/10.1038/nmat3944
27. A. Shmeliov, M. Shannon, P. Wang, J.S. Kim, E. Okunishi, P.D. Nellist, K. Dolui, S. Sanvito and V. Nicolosi, *ACS Nano*, **8**, 3690 (2014); https://doi.org/10.1021/nn5003387
28. D. Rangappa, K. Sone, M. Wang, U.K. Gautam, D. Golberg, H. Itoh, M. Ichihara and I. Honma, *Chem. Eur. J.*, **16**, 6488 (2010); https://doi.org/10.1002/chem.201000199
29. Q.D. Truong, M. Kempaiah Devaraju, Y. Nakayasu, N. Tamura, Y. Sasaki, T. Tomai and I. Honma, *ACS Omega*, **2**, 2360 (2017); https://doi.org/10.1021/acsomega.7b00379
30. P. Thangasamy and M. Sathish, *J. Mater. Chem. C Mater. Opt. Electron. Devices*, **4**, 1165 (2016); https://doi.org/10.1039/C5TC03630E
31. K. Chang and W. Chen, *Chem. Commun.*, **47**, 4252 (2011); https://doi.org/10.1039/c1cc10631g
32. M.N. Rani, M. Murthy, N.S. Shree, S. Ananda, S. Yogesh and R. Dinesh, *Ceram. Int.*, **45**, 25020 (2019); https://doi.org/10.1016/j.ceramint.2019.04.195
33. Y. Zhan, Z. Liu, S. Najmaei, P.M. Ajayan and J. Lou, *Small*, **8**, 966 (2012); https://doi.org/10.1002/smll.201102654