Hydrogen generation *via* photoelectrochemical water splitting using chemically exfoliated MoS_2 layers

Cite as: AIP Advances **6**, 015315 (2016); https://doi.org/10.1063/1.4941062
Submitted: 26 July 2015 . Accepted: 18 January 2016 . Published Online: 26 January 2016

R. K. Joshi, S. Shukla, S. Saxena, G.-H. Lee, V. Sahajwalla, and S. Alwarappan

Hydrogen generation *via* photoelectrochemical water splitting using chemically exfoliated MoS_2 layers

R. K. Joshi,[1,a] S. Shukla,[2] S. Saxena,[2] G.-H. Lee,[3]
V. Sahajwalla,[1] and S. Alwarappan[4,a]
[1]*Centre for Sustainable Materials Research and Technology, School of Materials Science and Engineering, University of New South Wales, NSW 2052, Australia*
[2]*Department of Metallurgical Engineering and Materials Science, Indian Institute of Technology Bombay, Mumbai, India*
[3]*Department of Material Science and Engineering, Yonsei University, Seoul 120-749, Korea*
[4]*CSIR-Central Electrochemical Research Institute, Karaikudi 630006, Tamilnadu, India*

(Received 26 July 2015; accepted 18 January 2016; published online 26 January 2016)

Study on hydrogen generation has been of huge interest due to increasing demand for new energy sources. Photoelectrochemical reaction by catalysts was proposed as a promising technique for hydrogen generation. Herein, we report the hydrogen generation *via* photoelectrochecmial reaction using films of exfoliated 2-dimensional (2D) MoS_2, which acts as an efficient photocatalyst. The film of chemically exfoliated MoS_2 layers was employed for water splitting, leading to hydrogen generation. The amount of hydrogen was qualitatively monitored by observing overpressure of a water container. The high photo-current generated by MoS_2 film resulted in hydrogen evolution. Our work shows that 2D MoS_2 is one of the promising candidates as a photocatalyst for light-induced hydrogen generation. High photoelectrocatalytic efficiency of the 2D MoS_2 shows a new way toward hydrogen generation, which is one of the renewable energy sources. The efficient photoelectrocatalytic property of the 2D MoS_2 is possibly due to availability of catalytically active edge sites together with minimal stacking that favors the electron transfer. [http://dx.doi.org/10.1063/1.4941062]

Hydrogen is one of the promising energy sources beyond fossil fuel era because of its green, storable and high energy density characteristics.[1] Among the renewable energy technologies for hydrogen production, photoelectrochemical water-splitting has been widely studied as solar energy resources without environmental pollution.[2] Dissociation of water into hydrogen can be achieved *via* photoelectrochemical process that utilizes both light harvesting and solar fuel production. Recently, transition metal di-chalcogenides (TMDCs) consisting of few-atom-thick layers have emerged as an alternative of traditional materials in various applications due to their unique properties. TMDCs such as MoS_2 and WSe_2 have shown a great potential in immense applications of valleytronics,[3,4] flexible electronics,[5] high-mobility transistors[6–8] and optoelectronic devices.[9,10] Recently, it has been predicted that TMDCs are useful for photovoltaic applications due to their tunable band gap and strong photo-excitement.[11] The exfoliated MoS_2 exhibits high photoluminescence quantum yield and other unusual optical properties.[12,13] In addition, MoS_2 nanoribbons or nanoflakes have excellent catalytic effect at the highly reactant edges, resulting in superior photo-induced catalyzing abilities.[14–16] The strong electrocatalytic activity of the nanostructured 2D MoS_2 is attributed to the highly active edges of the MoS_2. From the first-principle calculations, nanostructured MoS_2 is preferred over bulk MoS_2 for photocatalytic application due to the larger availability of catalytically active edge sites.[17] Therefore, increasing the number of active edges in

[a]Corresponding author's email: r.joshi@unsw.edu.au (RKJ), alwarappan@cecri.res.in (SA)

the 2D MoS_2 is critically important to bring out an efficient hydrogen evolution reaction (HER).[18–20] In this work, we employed thin MoS_2 film with numerous active edges as an efficient photocatalytic material. Photo-catalytic hydrogen generation using 2D materials shows a promising way toward straightforward and cost-effective procedures of hydrogen production.

Similar to graphene, ultrathin MoS_2 flakes can be obtained using mechanical or chemical exfoliation methods. Here MoS_2 layers were prepared using chemical exfoliation method in solvent. For this purpose, a mixture of MoS_2 powder and N-Methyl-2-pyrrolidone (NMP) solvent was ultra-sonicated for 10 hours. The solution was further centrifuged repeatedly three times at 10, 000 RPM for 10 minutes. The final product contains the few layered MoS_2 flakes. In order to produce the thin MoS_2 film for water splitting and other electrochemical experiments, MoS_2 dispersion was sprayed on the chosen substrates. For over-pressure observation experiments, 1μm-thick MoS_2 film was prepared on an alumina template using a vacuum filtration. Current-voltage measurements were conducted to study the photocatalytic hydrogen generation from these layers.

Figure 1 represents the typical transmission electron microscopy (TEM) micrograph, selected area electron diffraction (SAED) pattern, Raman spectrum and photoluminescence spectrum of the chemically exfoliated MoS_2 layers used for photocatalytic hydrogen generation. Figure 1(a) shows the morphology of the exfoliated MoS_2 layers. The rolled-up edges are evidently observed. The inset of Figure 1(a) is the high resolution TEM image of the exfoliated MoS_2, indicating that a typical hexagonal pattern of MoS_2 is maintained without any defects in the grain. The spacing of 2.7 Å corresponds to the inter-atomic spacing of MoS_2 can be seen. The SAED of Figure 1(b) shows that the exfoliated MoS_2 sample has a single crystal structure. In the Raman spectrum of bulk MoS_2, two distinct vibrational modes can be noticed at 383 cm^{-1} for in-plane mode (E^1_{2g}) and at 408 cm^{-1}

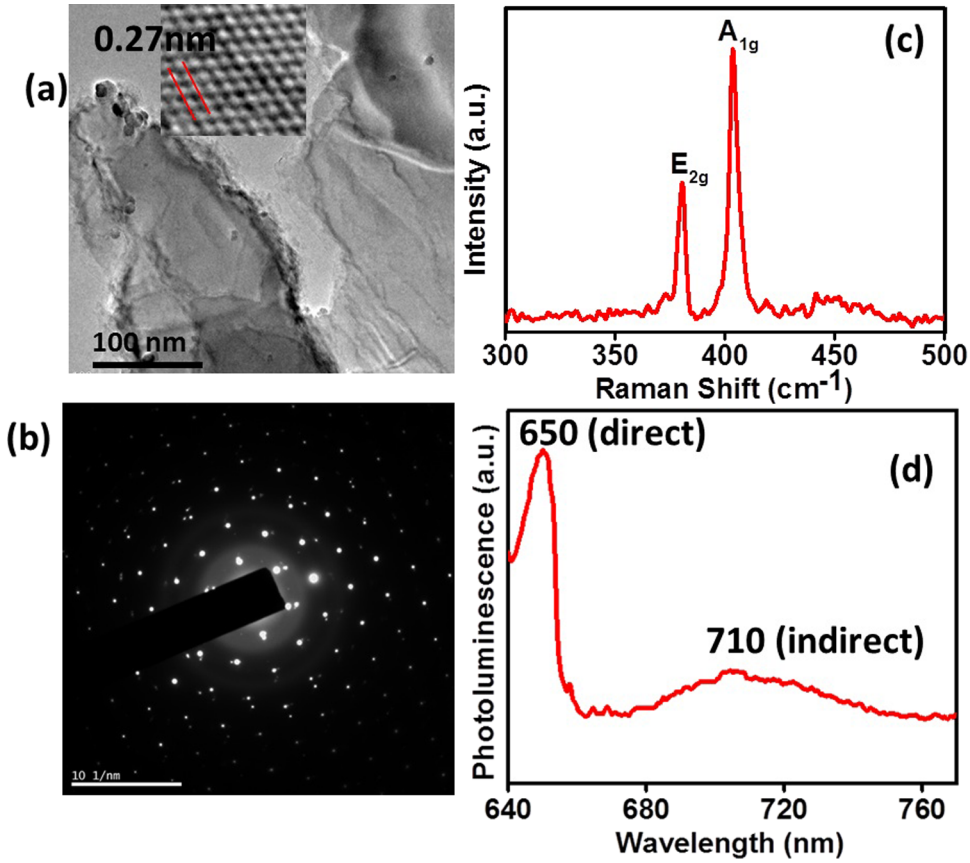

FIG. 1. Structural and optical characteristics of chemically exfoliated MoS_2 layers: (a) TEM micrograph of the exfoliated MoS_2. The inset shows high resolution TEM image in atomic scale. (b) SAED pattern (c) Raman spectrum and (d) photoluminescence spectrum of the MoS_2 layers.

out-of-plane mode (A_{1g}).[21] Of these two vibrational modes, the interlayer vibrational mode is the fingerprint of the material that corresponds to the chemical composition of the material synthesized. Furthermore, their position is directed by the number of atomic layers present in the material. In the present work, the MoS_2 layers synthesized exhibited a peak centered at 388.6 cm^{-1} and 403.1 cm^{-1} due to the $E^1{}_{2g}$ and A_{1g} modes respectively. Our experimental values upon comparison with the theoretical values reported in the literature,[21] with frequency difference of 22.5 cm^{-1} suggest few (3) layered samples. Photoluminescence (PL) measurement was performed on the selected MoS_2 samples. Figure 1(d) shows two emission peaks around 650 nm and 710 nm, which correspond to direct (1.90eV), and indirect (1.74eV) bandgap transition, respectively suggesting presence of exfoliated layers. Enhancement in bandgap suggests the possible photocatalytic application using chemically exfoliated layers.

First principle calculations using density functional theory suggests direct optical transition at the K point in the Brillouin zone corresponds to the peak marked by a red arrow in the electronic band structure for mono-layered MoS_2 as shown in figure 2. This band gap is found to decrease and the lowest band (green) becomes doubly degenerate at the K point in bulk MoS_2. First principle calculations were performed using density functional theory as implemented in the Vienna Ab-initio Simulation Package (VASP). The details of calculations have been described elsewhere.[22] K-points mesh of 16x16x8 and was generated using Monkhorst-Pack scheme to sample the reciprocal space for electronic structures calculations.

In order to measure the amount of the photocatalytically generated hydrogen through the MoS_2 film, we fabricated the simple set-up of figure 3. The thin film of exfoliated MoS_2 coated on the porous alumina template by a vacuum filtration was immersed in a container filled with a deioned water. Top of the container was sealed with a thin rubber baloon, which can be blown up as hydrogen is generated. Upon exposure to visible light (60 W-AM 1.5) at a distance of 10 cm from the MoS_2 film, the baloon starts to expand and. The size of baloon increase with time and formation of bubbles on the MoS_2 film surface was observed. This confirms that hydrogen generation occurs through water spliting initiated by photocatalytic activity of MoS_2 films. The size of the baloon is evantually saturated after a day and maintained unchanged for three weeks. It should be noted that this experiment was conducted only for 3 weeks. To confirm the photocatalytic effect of the exfoliated MoS_2, we also performed the same experiment with bulk MoS_2 (before exfoliation) bare alumina template, or nothing in a water container with the sealed baloon on its top. No bubbles or gas generation was found in these three conditions.

For quantitaive analysis of the photocatalytic effect of exfoliated MoS_2, photo-current generated by the MoS_2 was measured. The MoS_2 suspension was sprayed on Si substrates of 1×1 cm^2. The current-voltage (I-V) characteritics was measrued in a dark condition or under visible light illumination. I-V characteristics from positive to negative bias clearly indicated that the MoS_2 film

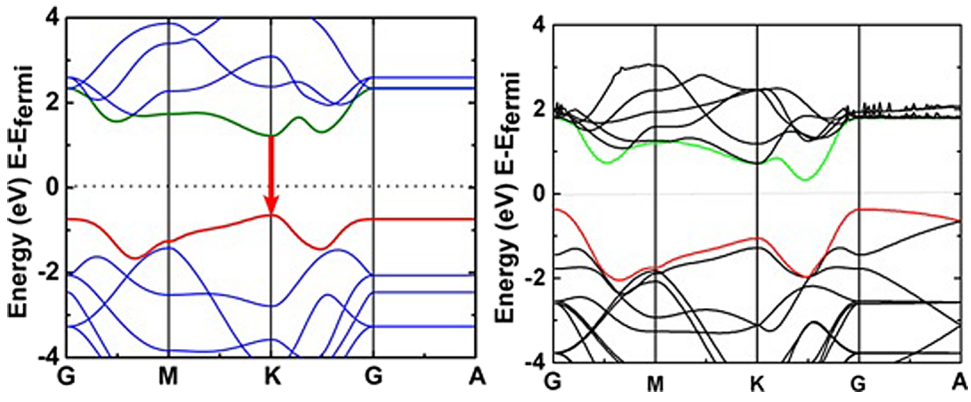

FIG. 2. Electronic band structure of mono-layer MoS_2 along the high symmetry directions(left). The lowest conduction band and the highest valence band are marked in green and red, respectively. Emission corresponding to ~705 nm as observed in the (right) electronic band diagram of bulk MoS_2 showing indirect bandgap.

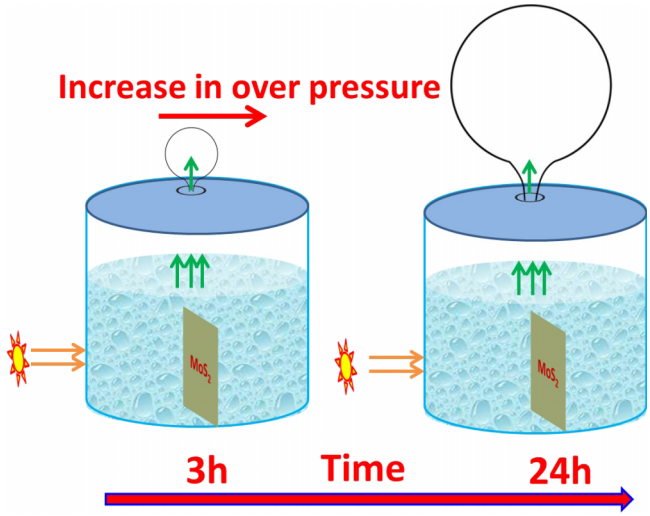

FIG. 3. Schematic of the water-spliting experimental setup. The over pressure was measured by observing blowing- up of a baloon as a function of time when the MoS_2 film in water was exposed to visible light.

is highly sensitive to the visble light. In contrats, no such photo-current was measured for bulk MoS_2. With no external voltage applied, the visible light creates enough carriers on the surface of semiconducting MoS_2, corresponding to a current of approximately 0.2μA, which is roughly three magnitude of orders higher than that under no illumination of the light. To measure the photoelectochemical resposne of the exfolidated MoS_2 film, we set up the experiment of figure 4(a). The MoS_2 film deposited on the gold substrate of 1 x 1 cm^2 was used as anode and platinum plate was employed as cathode. When the MoS_2 film is exposed to a visble light, electron-hole pairs are generated. Then, photo-excited electrons in MoS_2 are transferred to the Pt counter electrode. On the Pt electrode, H^+ ions are reduced, leading to generation of hydrogen bubbles, as reported in the typical photoelectrochemical experiments.[23–27] During the experiment, bubble formation was clearly detected in a water. The holes in the MoS_2 electrode oxidize the OH^- ions so that a current flows through photoelectrochemical reaction. The photoelectrochemical current curves of Figure 4(a) show that the MoS_2 film on Au are more efficient than the bare Au electrode when exposed to the visible light. To verify the dynamic optical response in photo-current, the electrical current was mesured at 0.5 V under the periodic illumination. Figure 4(b) shows the photo-current ratio of I/I_o, where I and I_o is the photo-currents under illumination and in dark, respectively. Under, the photo-current ratio reaches over 10, which indicates the high efficiency of hydrogen generation

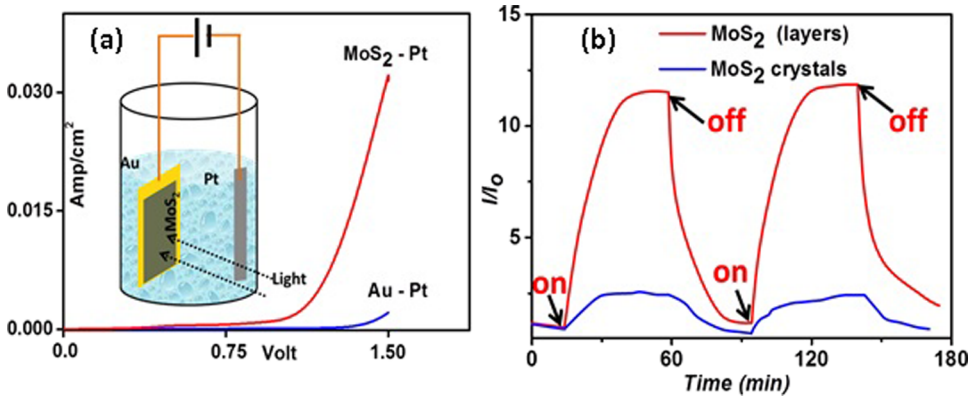

FIG. 4. (a) Current-voltage (I-V) characteristics under illumination. Schematic of the inset shows experimental set-up. (b) Photo-current ratio of I/I_o under periodic illumination for exfoliated MoS_2 film and bulk MoS_2 film.

by photoelectrochemical activity of the MoS_2 film. This result shows that 2D MoS_2 can be used as an active catalyst for hydrogen generation. It is expected that the larger area monolayer film of the exfoliated MoS_2 will have the more enhanced photocatalytic behaviour due to increased area of MoS_2 film, indicative of more ractive MoS_2 edges.

In conclusions, we have developed a straightforward procedure to study hydrogen generation through water-spliting by the photoelectrochemical activity of 2D MoS_2. The chemically exfolaited MoS_2 layers were characterized for their structural quality prior to their use for hydrogen generaion experiment. The over-presure created by formation of hydrogen *via* water splitting by MoS_2 catalyst was investigated by measuring the blowing-up of the baloon. In the quantitative anlysis of photocatalytic effect, a large amount of photo-current in exfoliated MoS_2 film, which is higher than that in bulk MoS_2, was observed under the illumination of visible light. Our work shows a new way toward hydrogen generation by 2D MoS_2, which is required for our future energy plan.

ACKNOWLEDGEMENT

RKJ acknowledges Prof. A. K. Geim and Dr V. J. Kravets of the University of Manchester. This work in part was funded by faculty start up research grant of the University of New South Wales. SA acknowledges CSIR for supporting this research through the grant CSC0101 (MULTIFUN). G.H.L. acknowledges support from the Basic Science Research Program (NRF-2014R1A1A1004632) through the National Research Foundation (NRF) funded by the Korean government Ministry of Science, ICT and Future and in part by the Yonsei University Future-leading Research Initiative of 2014.

[1] N.S. Lewis and D.G. Nocera, Proc. Natl. Acad. Sci. **103**, 15729 (2006).
[2] M.G. Walter, E.L. Warren, J.R. McKone, S.W. Boettcher, Q. Mi, E.A. Santori, and N.S. Lewis, Chem. Rev. **110**, 6446 (2010).
[3] H. Zeng, J. Dai, W. Yao, D. Xiao, and X. Cui, Nat.Nanotechnol. **7**, 490 (2012).
[4] K.F. Mak, K.L. McGill, J. Park, and P.L. McEuen, Science **344**, 1489 (2014).
[5] S. Bertolazzi, J. Brivio, and A. Kis, ACS Nano **12**, 9703 (2011).
[6] R. Kappera, D. Voiry, S. E. Yalcin, B. Branch, G. Gupta, A. D. Mohite, and M. Chhowalla, Nature Mat. **13**, 1128 (2014).
[7] B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, and A. Kis, Nat.Nanotech. **6**, 147 (2011).
[8] X. Cui, G-H. Lee, Y.D. Kim, G. Arefe, P.Y. Huang, C-H. Lee, D.A. Chenet, X. Zhang, L. Wang, F. Ye, F. Pizzocchero, B.S. Jessen, K. Watanabe, T. Taniguchi, D.A. Muller, T. Low, P. Kim, and J. Hone, Nature Nanotech. **10**, 534 (2015).
[9] C. Petit, C. Taleb, and M.P. Pileni, J.Phys.Chem B **103**, 1805 (1999).
[10] C.H. Lee, G-H. Lee, A.M. van der Zande, W. Chen, Y. Li, M. Han, X. Cui, G. Arefer, C. Nuckolls, T.F. Heinz, J. Guo, J. Hone, and P. Kim, Nature Nanotech. **9**, 676 (2014).
[11] K.F. Mak, C. Lee, J. Hone, J. Shan, and T. F. Heinz, Phy.Rev.Lett. **105**, 136805 (2010).
[12] E.S. Kadantsev and P. Hawrylak, Solid state Commun. **152**, 909 (2012).
[13] A. Splendiani, L. Sun, Y. Zhang, T. Li, Y. Kim, C-Y. Chim, G. Galli, and F. Wang, Nano.Lett. **10**, 1271 (2010).
[14] Q. Xiang, J. Yu, and M. Jaroniec, J. Am. Chem. Soc. **134**, 6575 (2012).
[15] F.A. Frame and F.E. Osterloh, J.Phys.Chem C **114**, 10628 (2010).
[16] J.V. Lauritsen, J. Kibsgaard, S. Helveg, H. Topsoe, B.S. Clausen, E. Laegsgaard, and F. Besenbacher, Nat. Nanotech. **2**, 53 (2007).
[17] Y. Li, Y-L. Li, C.M. Araujo, W. Luo, and R. Ahuja, Cat.Sci.Technol. **3**, 2214 (2013).
[18] M. Wang, L. Chen, and L. Sun, Energy.Environ. Sci. **5**, 6763 (2011).
[19] P. Du and R. Eisenberg, Energy.Environ. Sci. **5**(2012), 6012 (2012).
[20] S. Min and G. Lu, J.Phys.Chem. C **116**, 25415 (2012).
[21] C. Lee, H. Yan, L.E. Brus, T.F. Heinz, J. Hone, and S. Ryu, ACS Nano **4**, 2695 (2010).
[22] S. Saxena and T.A. Tyson, ACS Nano **4**, 351 (2010).
[23] A. Fujishima and K. Honda, Nature **238**, 37 (1972).
[24] P.J. Boddy, J. Electrochem.Soc.: Solid sate Science **115**, 199 (1968).
[25] A. Fujishima and K. Honda, Bull. Chem. Soc. **44**, 1148 (1971).
[26] F. Osterloh and B.A. Parkinson, MRS Bulletin **36**, 18 (2011).
[27] D. Voiry, M. Salehi, R. Silva, T. Fujita, M. Chen, T. Asefa, V. B. Shenoy, G. Eda, and M. Chhowalla, Nano Lett. **13**, 6222 (2013).