Materials Letters 188 (2017) 224–227

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

# Graphene-like $MoS_2$ prepared by a novel intercalation-detonation method

Fan Yang[a,b], Ping Hu[a,b,c,*], Kuai-She Wang[a,b,*], Zhen-Yu Chen[a,b], Bo-Liang Hu[a,b], Rui Song[a,b], Qing-Wei Li[a,b], Wei-Cheng Cao[c], Dong-Xin Liu[c], Geng An[c], Zhou-Yue Jiang[a], Yi-Fei Li[a], Alex A. Volinsky[d]

[a] School of Metallurgy Engineering, Xi'an University of Architecture and Technology, Xi'an 710055, China
[b] State Local Joint Engineering Research Center for Functional Materials Processing, Xi'an 710055, China
[c] Jinduicheng Molybdenum Co., Ltd., Xi'an 710068, China
[d] Department of Mechanical Engineering, University of South Florida, Tampa 33620, FL, USA

ARTICLE INFO

*Keywords:*
Graphene-like $MoS_2$
Intercalation-detonation
Exfoliation
Crystal structure
Structural

ABSTRACT

Graphene-like $MoS_2$ has attracted significant interest because of its unique electronic, optical and catalytic properties with two-dimensional lamellar structure. A novel intercalation-detonation method was used to prepare monolayer and multilayer graphene-like $MoS_2$. $MoS_2$ was first completely intercalated by abundant oxygen-containing functional groups bonded to the sulfur atom layer in basal planes of the $MoS_2$ structure, increasing the layer spacing and decreasing the Van-der-Waals' force between the layers. Then, the intercalated $MoS_2$ was rapid exfoliated by high energy of detonation. Characterization results indicate that the graphene-like $MoS_2$ was successfully prepared by the explosion method. This type of processing is simple, highly efficient and generates fewer impurities.

## 1. Introduction

Graphene-like molybdenum disulfide ($MoS_2$) is a new two-dimensional (2D) layered material, which has recently attracted considerable attention because of its unique structure, optical and electronic properties [1]. Unlike conductive graphene, bulk crystalline $MoS_2$ is a semiconductor with an indirect band gap of about 1.2 eV, which gradually increases with the reduction of the number of layers. Atomically layered $MoS_2$ is a semiconductor material with direct band gap, and the single-layer $MoS_2$ band gap is 1.9 eV [2].

Due to the adjustable band gap, graphene-like $MoS_2$ has a bright future for applications in photoelectronic devices. However, it is hard to obtain layered graphene-like $MoS_2$ by using conventional chemical or physical methods. Recently, micromechanical exfoliation [3], $Li^+$ intercalation [4], liquid ultrasonic [5], hydrothermal method [6], and chemical vapor deposition [7] have been used to prepare graphene-like $MoS_2$. Still, some deficiencies hinder the development of this attractive material, such as poor repeatability, time consumption, low efficiency and product quality, etc. Thus, reproducible production of graphene-like nanosheets in bulk quantities is still a challenge.

Here, we report a novel intercalation-detonation method to prepare graphene-like $MoS_2$. It is the first time to use oxygen-containing groups as intercalation compound of layered structure $MoS_2$ and take advantage of explosion technology to exfoliate intercalated $MoS_2$. As-prepared graphene-like $MoS_2$ is systematically characterized, and the exfoliation mechanism is proposed.

## 2. Materials and methods

### 2.1. Materials preparation

Raw materials, $MoS_2$ powder, picric acid (PC), $NaNO_3$ and $KMnO_4$ were pure AR grade, and 98% concentrated sulfuric acid was used to oxidize bulk $MoS_2$. Typical preparation procedure is as follows. 5 g of $MoS_2$ powder and 2.5 g $NaNO_3$ were dissolved in 200 ml of 98% concentrated sulfuric acid. The reaction flask was placed in an ice bath with violent stirring, and 15 g $KMnO_4$ was added slowly to avoid sudden increase in temperature. After 2 h reaction, the flask was heated to 35 °C and 90 °C held for 30 min in series. The reactive solution was diluted during stirring. The solution was filtered and thoroughly washed with deionized water until the pH of the filtrate became neutral. After filtration, the intercalation $MoS_2$ was obtained. The intercalation $MoS_2$ slurry was dried in a vacuum oven at 60 °C before use.

Exfoliation was performed by placing premixed intercalation $MoS_2$ (2 g) and picric acid (2 g) in a sealed stainless steel pressure vessel.

* Corresponding authors at: School of Metallurgy Engineering, Xi'an University of Architecture and Technology, Xi'an 710055, China.
*E-mail addresses:* huping1985@126.com (P. Hu), wangkuaishe888@126.com (K.-S. Wang).

http://dx.doi.org/10.1016/j.matlet.2016.11.005
Received 17 August 2016; Received in revised form 1 November 2016; Accepted 2 November 2016
Available online 05 November 2016
0167-577X/ 

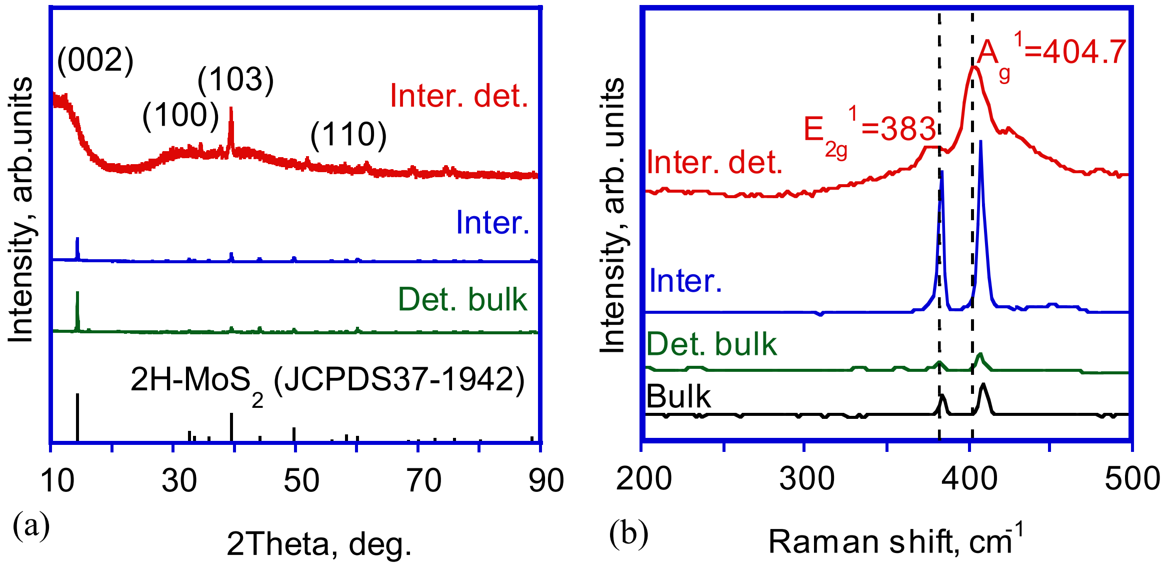


**Fig. 1.** (a) XRD patterns and (b) Raman spectra of detonated bulk $MoS_2$, intercalation $MoS_2$ and intercalation-detonation $MoS_2$ samples.

Detonation was induced by rapid heating at 50 °C/min to 400 °C. After detonation, the vessel was cooled in air, and generated gaseous products were released, while solid products were collected as the final sample of graphene-like $MoS_2$. The exfoliation sample of bulk $MoS_2$ was prepared using the same procedure.

### 2.2. Characterization

As-prepared samples were characterized by X-ray diffraction (XRD, Bruker, Germany), Raman spectroscopy (Jobin Yvon HR-800), atomic force microscopy (AFM, Bruker, Germany), high resolution transmission electron microscopy (HR-TEM, Fischione M3000) and X-ray photoelectron spectroscopy (XPS, PHI-5400, USA). The samples for AFM and HR-TEM examinations were dispersed in ethanol with ultrasonic treatment for 30 min before loading onto the carrier.

## 3. Results and discussion

### 3.1. XRD and Raman spectroscopy

XRD patterns were used to detect the phase change of $MoS_2$ samples, as shown in Fig. 1(a). In general, the exfoliation of $MoS_2$ results in the significantly reduction of the (002) reflection intensity, and even causes this peak to disappear. The spectra in Fig. 1(a) show that the (002) reflection was almost not present for the intercalation-detonation $MoS_2$, while other main peaks can be indexed to the 2H polytype of $MoS_2$ crystal structure (JCPDS 37-1492). Besides, the peaks can be indexed to the 2H polytype of $MoS_2$ crystal structure while the (002) peaks present strong intensity for detonated bulk and intercalation $MoS_2$. This indicates that the processing procedure didn't change the hexagonal crystal structure of $MoS_2$, and few- or mono-layer $MoS_2$ was obtained after the intercalation-detonation process.

Raman spectra are shown in Fig. 1(b). $MoS_2$ nanosheets have peaks at 383 $cm^{-1}$ and 405 $cm^{-,1}$ corresponding to the vibrational modes of $E^1{}_{2\,g}$ and $A^1{}_g$, which is consistent with previous results [8]. From Fig. 1(b), it can be seen that Δk for the intercalation-detonation $MoS_2$ sample is 21.7 $cm^{-1}$, indicating that the few-layer $MoS_2$ nanosheets were obtained. However, Δk for the detonated bulk and intercalation $MoS_2$ samples are larger than 25 $cm^{-1}$, revealing the multilayer characteristics of $MoS_2$.

### 3.2. TEM and AFM morphology

Fig. 2. shows TEM and AFM images of the intercalation-detonation $MoS_2$ samples. A large area of the single layer structure can be seen at the edge of the sample in Fig. 2(a), exhibit multi-layer structure of the graphene-like $MoS_2$ nanosheet. In addition, high resolution TEM morphology in Fig. 2(b) and (c) exhibits high crystallinity of the layered $MoS_2$ with the 6.2 Å interplanar spacing. Selected-area electron diffraction pattern is shown in the inset of Fig. 2(b) and is well-indexed as a pure hexagonal $MoS_2$ phase.

AFM morphology in Fig. 2(d) shows the thickness image of the as-prepared intercalation-detonation $MoS_2$ samples. The 2 nm calculated average thickness indicates the presence of 3 layers, where the thickness of $MoS_2$ sheets is 0.65 nm per layer, also indicates that the layered structure of graphene-like $MoS_2$ was obtained.

### 3.3. XPS spectra

XPS measurements were carried out to characterize the chemical nature of the intercalation and intercalation-detonation $MoS_2$ samples. The XPS survey spectra show the co-existence of Mo, S, O and C elements, as seen in Fig. 3(a). High-resolution Mo 3d and S 2p spectra show peak locations corresponding to the Mo $3d_{3/2}$, Mo $3d_{5/2}$, S $2p_{1/2}$ and S $2p_{3/2}$ components of $MoS_2$, respectively (Fig. 3(b) and (c)) [9].

From Fig. 3(d), the high-resolution O 1s spectrum of intercalation $MoS_2$ shows that the peak at 533 eV is related to the S–OH bond [10], which indicates that the oxygen-containing functional groups were bonded to the surface or sulfur atom layer of $MoS_2$ during intercalation process. The O 1s spectrum of intercalation-detonation $MoS_2$ shows peaks at 531.4 and 533.3 eV, which are ascribed to the hydroxyl groups and S–OH, respectively [10]. Additionally, the peak intensity at 533.3 is much smaller than that of 531.4 eV, which proves that most of S–OH bonds were decomposed and converted to hydroxyl groups during detonation process.

### 3.4. Exfoliation mechanism

Based on the above analysis, the exfoliation mechanism of bulk $MoS_2$ is proposed in Fig. 4. First, $MoS_2$ was completely intercalated into intercalation $MoS_2$, resulting in abundant oxygen-containing

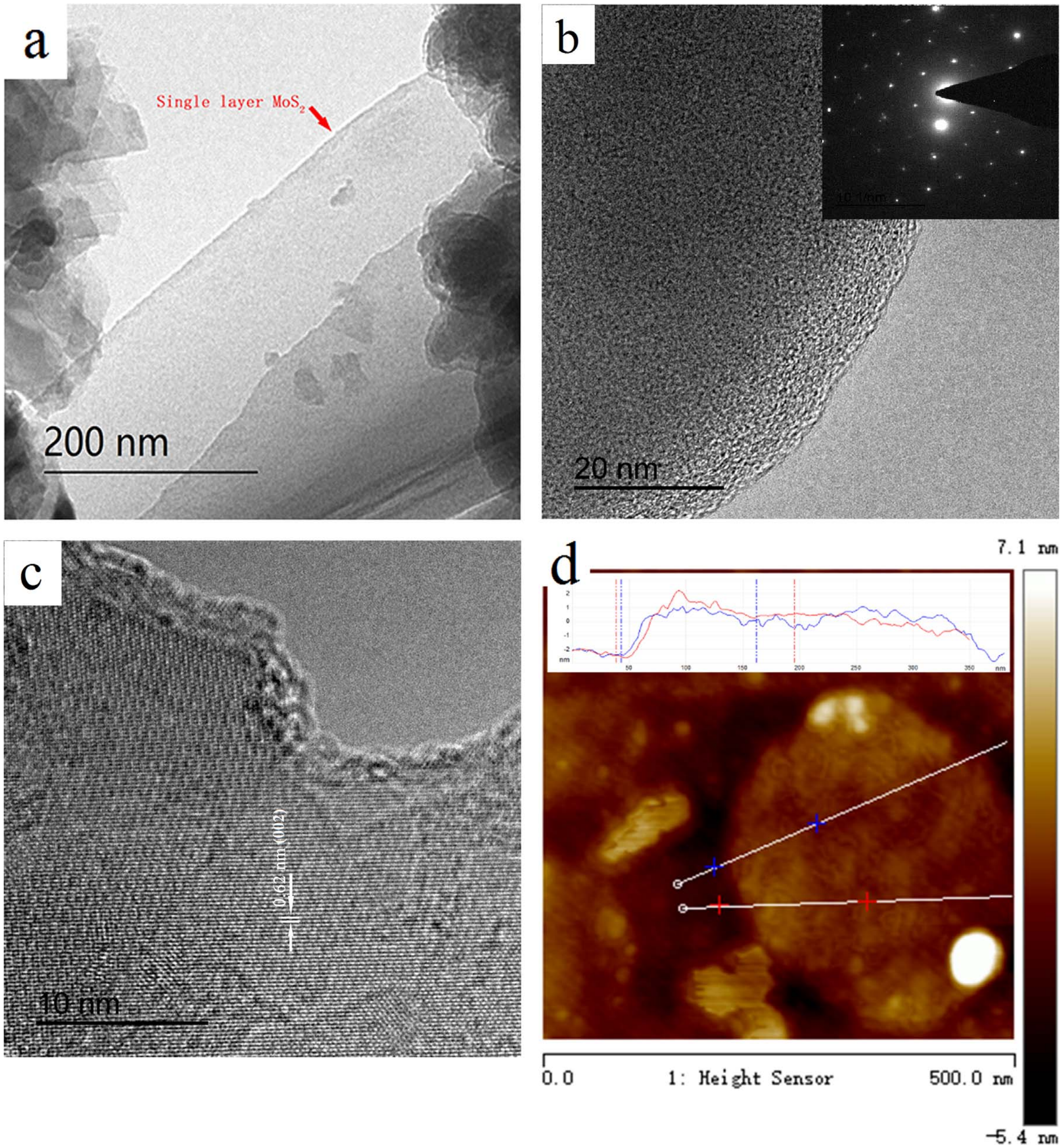


**Fig. 2.** (a–c) TEM and (d) AFM morphology of the intercalation-detonation $MoS_2$ sample.

functional groups bonded to the sulfur atom layer in basal planes of the $MoS_2$ structure. Then, the detonation was induced by rapid heating and the intercalation $MoS_2$ was rapidly heated to high temperature, inducing its oxygen-containing functional groups to be decomposed into $CO_2$ and $H_2O$. Expansion of the gases evolved into the interstices between the adjacent $MoS_2$ sheets resulted in the $MoS_2$ exfoliation.

## 4. Conclusions

In conclusion, crystalline graphene-like $MoS_2$ nanosheets were exfoliated from bulk $MoS_2$ through the novel intercalation-detonation procedure. Characterization by XRD, Raman and XPS spectroscopy, TEM and AFM indicates that the as-prepared samples have high crystallinity, layered graphene-like $MoS_2$ nanosheets structure with a single or few layers. The new method of detonation is a simple and highly efficient way to exfoliate substantial materials, which exhibits good prospects for various applications. This preparation method of graphene-like $MoS_2$, might be applied to other 2D layered materials.

## Acknowledgments

This work was supported by the Outstanding Doctorate Dissertation Cultivation Fund of Xi'an University of Architecture and Technology (2016), National Natural Science Foundation of China (NSFC) (51404181), the Youth Science and Technology New Star Project of Shaanxi Province Innovation Ability Support Plan (2017KJXX-35), the China Postdoctoral Science Foundation (2016M600770), and the postdoctoral work centre in Jinduicheng Molybdenum Co., Ltd. (2016-19).

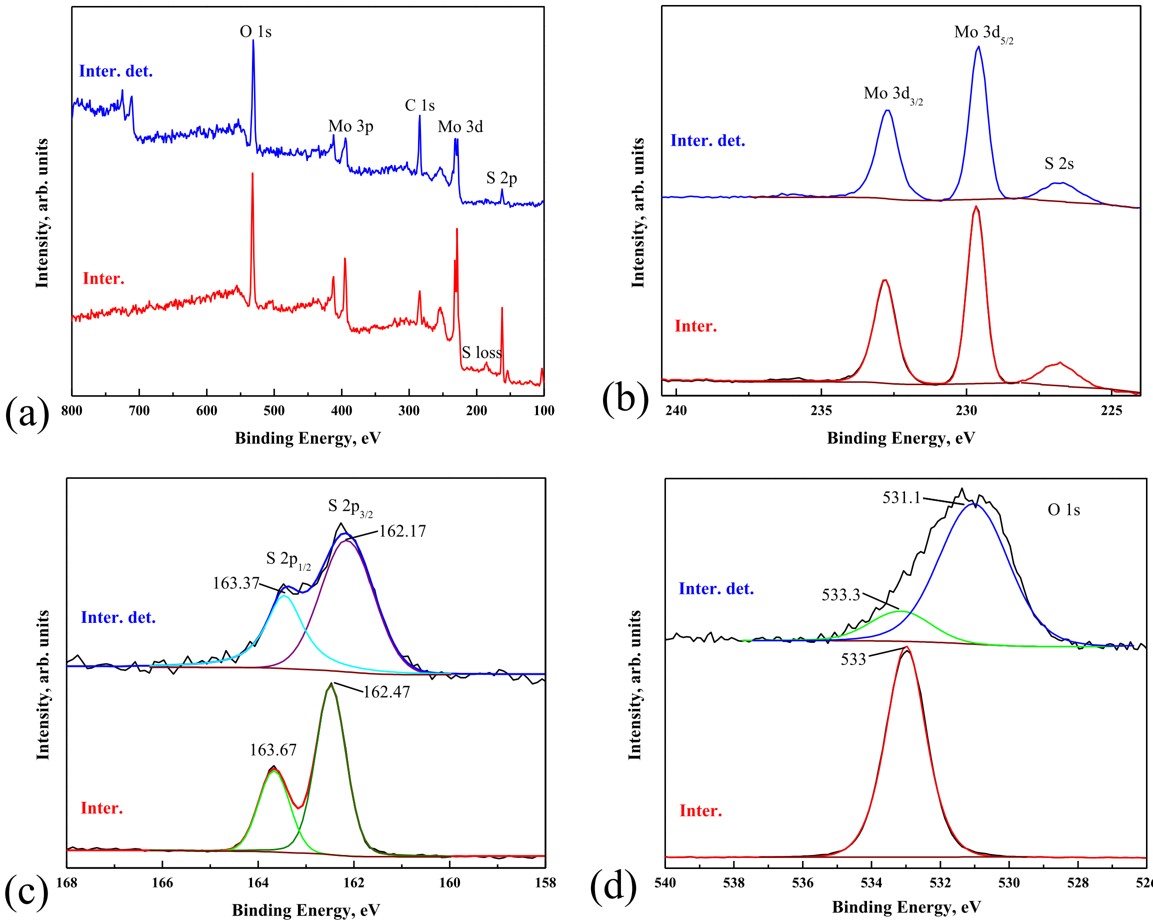


**Fig. 3.** (a) XPS survey spectrum of intercalation-detonation $MoS_2$ and high resolution scans of (b) Mo 3d, (c) S 2p and (d) O 1s.

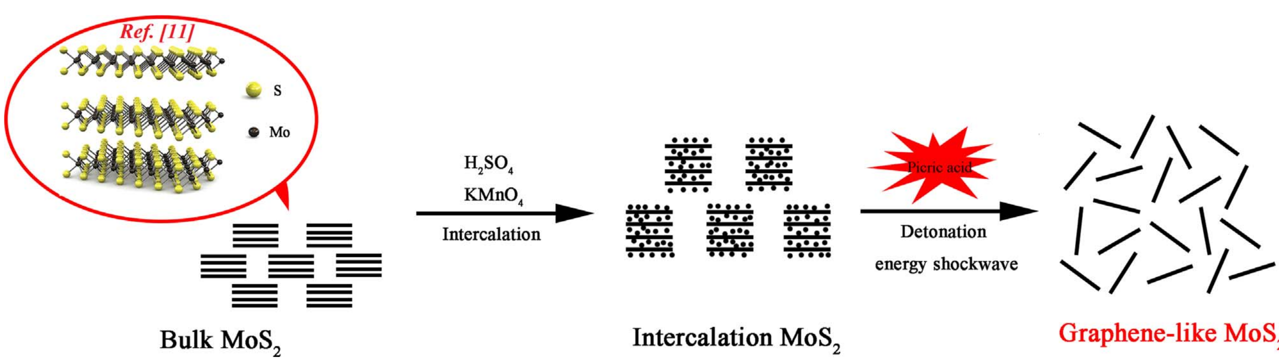


**Fig. 4.** Schematic illustration of the $MoS_2$ exfoliation mechanism [11].

## References

[1] D. MacMahon, A. Brothers, K. Florent, S. Kurinec, Mater. Lett. 61 (2015) 96–99.
[2] A. Splendiani, L. Sun, Y.B. Zhang, T.S. Li, J. Kim, et al., Nano Lett. 10 (2010) 1271–1275.
[3] Y. Yoon, K. Ganapathi, S. Salahuddin, Nano Lett. 11 (2011) 3768–3773.
[4] P. Joensen, R.F. Frindt, S.R. Morrison, Mater. Res. Bull. 21 (1986) 4.
[5] K.K. Liu, W. Zhan, Y.H. Lee, Y.C. Lin, M.T. Chang, et al., Nano Lett. 12 (2012) 1538–1544.
[6] H. Luo, C. Xu, D.B. Zou, L. Wang, T.K. Ying, Mater. Lett. 62 (2008) 3558–3560.
[7] V.G. Pol, S.V. Pol, P.P. George, A. Gedanken, J. Mater. Sci. 43 (2008) 1966–1973.
[8] J.N. Coleman, M. Lotya, A. O'Neill, S.D. Bergin, P.J. King, et al., Science 331 (2011) 568–571.
[9] P.P. Wang, H. Sun, Y. Ji, W. Li, X. Wang, Adv. Mater. 26 (2014) 964–969.
[10] Y. Zhang, P. Chen, F.F. Wen, B. Yuan, H.G. Wang, J. Electroanal. Chem. 761 (2016) 14–20.
[11] B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, A. Kis, Nat. Nanotechnol. 6 (2011) 147–150.