ATLANTIS PRESS

Advances in Engineering, volume 100

International Conference on Manufacturing Engineering and Intelligent Materials (ICMEIM 2017)

Facile Preparation of Few-layer MoS_2-NS by Liquid-Phase Ultrasonic Exfoliation

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Keywords: Few-layer MoS_2-NS, Liquid-phase Ultrasonic Exfoliation

Abstract: In recent years, two-dimensional layered nanomaterials have attracted wide attention due to their unique physical, chemical, electronic and mechanical properties. Among them, ultrathin molybdenum disulfide nanosheets (MoS_2-NS) are one of the important two-dimensional nano-functional materials. In this paper, ultrafine MoS_2-NS were prepared by a simple liquid-phase ultrasonic exfoliation. Molybdenum disulfide powder was used as the raw material, sodium hydroxide and N-methyl-2-pyrrolidone were added as the penetrant. After vacuuming, few-layer MoS_2-NS were prepared by ultrasonic method at ultrasonic power of 360W for 6h. The microstructure were observed by TEM, the phase structures were characterized using XRD and Raman spectrometer.

Introduction

Two-dimensional nano material is believed to have atomic level or molecular level thickness and infinite plane size of a new class of materials. In 2004 Novoselov and Geim by micro-mechanical stripping from the graphite peel off the graphene ,which is the most representative of the two-dimensional materials[1].Graphene is constituted by carbon atoms in a single layer with a honeycomb structure[2],The properties of Graphene are different from massive graphite such as mechanical properties, electrical properties, optical properties and thermal properties[3].Scientists are interested in the two-dimensional materials for example transition metal disulfides which have a graphene-like structure，because the two-dimensional structural material has bright prospects[4-5].

The graphene-like molybdenum disulfide (MoS2) is an important two dimensional layered material, molybdenum disulfide's crystal structure is hexagonal crystal system, but the single-layer MoS2-NS is constituted by three atomic layers by covalent bonds, Molybdenum atoms sandwiched between the upper and lower layers of sulfur atoms, similar to a sandwich structure[6].Few-layers MoS2 is constituted by a few monolayer MoS2 with a weak Vander Waals force. The distance between the layers is about 0.65 nm[7],So the interaction force is very strong, and the interaction between layer and layer is weak, this particular layered structure predetermines the excellent lubricating and catalytic properties of MoS2-NS[8-9].The band gap of MoS2-NS is about 1.2eV,and the energy band is changed from indirect band gap to direct band gap with the number of layers decreases, and the direct band gap transition of the monolayer MoS2 reaches a maximum value of about 1.9 eV. The graphene-like MoS2 has a controlled band gap and has a brighter prospect in optoelectronic devices[10-11].

However, it is difficult to prepare the graphene-like MoS2-NS with few layers by chemical and physical methods, the method of prepare molybdenum disulfide at home and abroad have the following categories: Micro mechanical stripping method、Lithium ion intercalation method、Liquid ultrasonic method 、 chemicalvapor deposition and Hydrothermal method. Micro-mechanical stripping method which use special adhesive tape to stripping nanosheet is a simple method of

obtaining two-dimensional materials. In 1965 Frindt[12] used a special tape to peel off a few layers of MoS2-NS,This method is very effective to prepare monolayer materials. The method is simple, rapid, and has a high stripping rate, and the stripped MoS2-NS has a high electron mobility. However, the micro-mechanical stripping method has a very low production efficiency. In 1986,Joensen[13] firstly prepare monolayers of MoS2-NS by lithium ion intercalation. This method is more complex, the reaction time is longer, and it also can changes the crystal structure of MoS2-NS.YShi[14] prepared graphene-like MoS2-NS on a graphene substrate by chemical vapor deposition (CVD).The advantage of this method is pure MoS2-NS product, the disadvantage is that the reaction conditions have a great impact on the product. Coehoorn R[15] prepare monolayer MoS2-NS by ultrasonic the N-methyl-2-pyrrolidone (NMP) and MoS2 mixed solution. Although liquid phase ultrasonic stripping method is inefficient, the product had a complete structure，this method can be used for large-scale production.

In this paper, we sought a suitable reproducible experimental condition by a large number of experiments, nd a simple liquid-phase ultrasonic exfoliation was used to prepare the ultra-thin molybdenum disulfide nano-sheets for other research in different fields .

Experiments

Preparation of Few-layer of MoS_2 Nanosheets:

The chemical reagent of experiment are analytically pure, the MoS_2 powder was purchased in Shanghai Aladdin Biochemical Technology Co.,Ltd. the NMP was purchased from Tianjin DaMao Chemical Reagent Factory. The Sodium hydroxide (NaOH)was purchased from Tianjin Tianli Chemical Reagent Co.,Ltd.

Weighted in different MoS2/NMP/NaOH mass ratios, they were then dissolved in 40 ml of DI water, then the solution was vacuum-treated with a special vacuum pump, and the NMP penetrated sufficiently into the MoS2 sheet and let it rest for more than 48 hour. The solution was transferred to ultrasonic cleaner, then treated the solution with different ultrasonic power and different ultrasonic times. Followed by centrifugal separation (3500 r/min),the supernatant was collected and characterized.

Characterization:

Morphology of the samples were observed by transmission electron microscope (TEM, Hitachi G-7650).The phase structure of the final products was characterized using X-ray diffraction (XRD,BRUKER-AXS, Germany). In addition, a Raman spectrometer（LabRAM HR Evolution） was used to obtain the corresponding Raman spectra of the few-layer MoS2-NS.

Results and Discussion

It is known from the literature that the NaOH contributes to stripping of the graphene-like MoS2-NS.The graphene-like MoS2-NS sample were prepared at the content of NMP is constant,MoS2/NaOH with mass ratios of (a) 1 /0 (b) 2/1 (c)1/1 (d) 1/2.Representative TEM images of the graphene-like MoS2-NS sample are shown in Fig.1.As shown in Fig.1(a-c),With the increase of the amount of NaOH, the graphene-like MoS2-NS gradually becomes thinner, but after a certain proportion, the graphene-like MoS2-NS appears wrinkle, As shown in Fig.1(d).

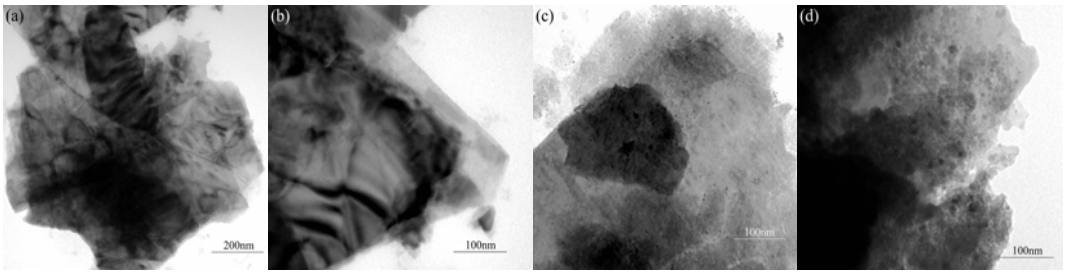

Figure 1. Representative TEM micrographs of MoS_2-NS with different mass ratios of MoS_2/NaOH:

(a) 1 /0 ,(b) 2/1 ,(c) 1/1,(d)1/2 .

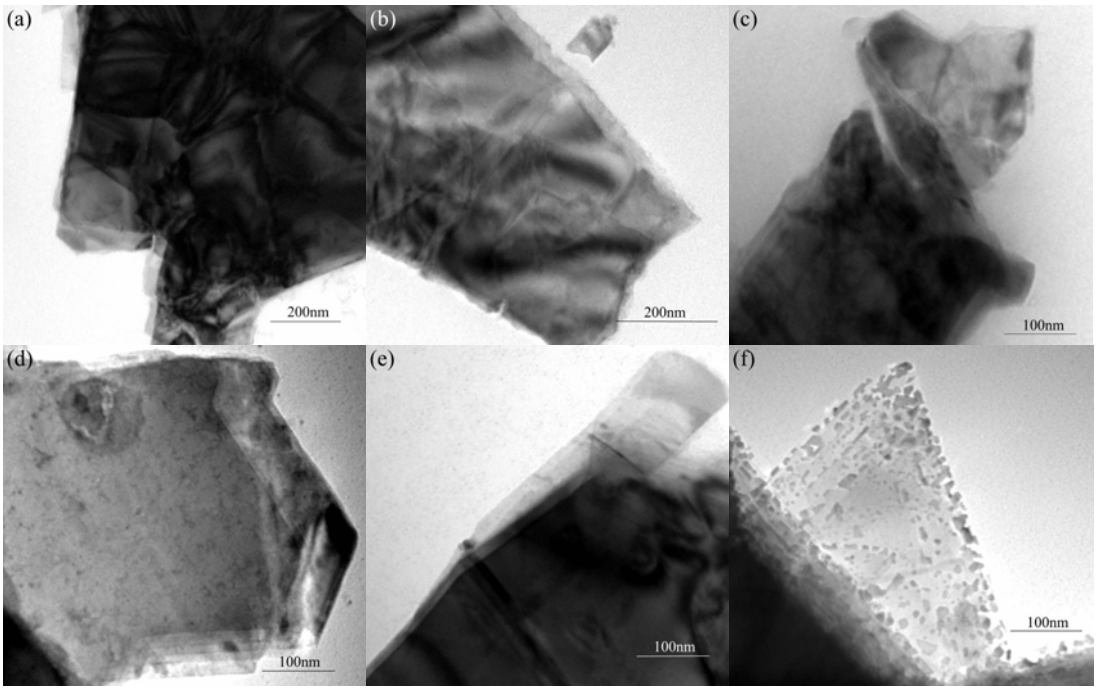

Figure 2. Representative TEM micrographs of MoS_2-NS with different Ultrasonic power

(a)180w,(b)240w,(c)300w,(d)360w,(e)480w,(f)600w.

The ultrasonic cleaner will cause the liquid to vibrate and produce tens of thousands of tiny bubbles. the collapse of the bubbles during the longitudinal propagation of the ultrasonic waves creates a tremendous pressure that will damage the surface of the material. In this experiment, the ultrasonic wave transferred to the NMP in MoS2 layer, and made the NMP explode that a series of small explosions were also produced to impact the MoS2 layer gradually to separate the MoS2 layer from the MoS2 block. As show in Fig.2,the ultrasonic power has a great influence on the peeling of MoS2-NS.With the increase of the ultrasonic power, the number of the peeling layers decreases gradually, but when the ultrasonic power reaches a certain value, the stripping effect will be destroyed sample. As shown in Fig.2(a),when the ultrasonic power is 180w,the molybdenum disulfide samples prepared are relatively thick as a whole, there is no obvious change; As shown in Fig.2(b),when the ultrasonic power of 240w,the whole began to thin; As shown in Fig.2(c),when the ultrasonic power of 300w;As shown in Fig.2(d),when the ultrasonic power is 360w,the whole thinning; As shown in Fig.2(e),when the ultrasonic power of 480w only local thinner, the majority is still thick; As shown in Fig.2(f),When the ultrasonic power of 600w ultrasound, due to the power is too large, the thin part of the shattered, the sample is destroyed.

If the ultrasonic time is short, the effect of peeling can not be achieved; and if the ultrasonic time is too long, the stripped MoS2-NS will be shattered. As shown in Fig.3 (a-d),the thin layer of graphene-like MoS2-NS is gradually thinned with the increase of ultrasonic time, but the edge of

sample will be damaged when the ultrasonic time is too long.

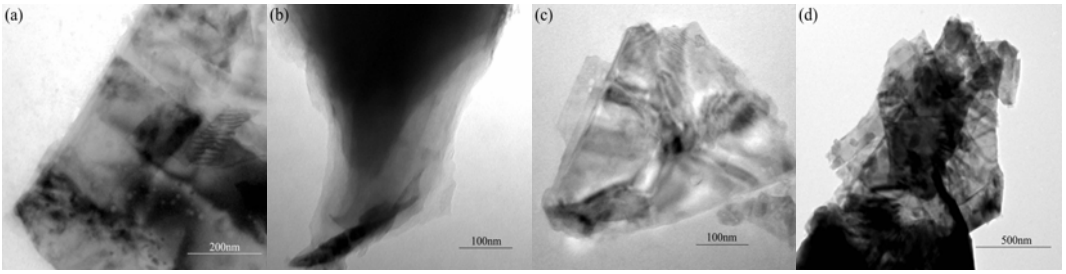

Figure 3. Representative TEM micrographs of MoS_2-NS with different Ultrasonic time

(a)360w1h,(b)360w 2h,(c)360w 6h,(d)360w10h.

After all the experiments were repeated to sum up the optimal parameters, a graphene-like MoS2-NS sample was prepared by a simple liquid-phase ultrasonic exfoliation and characterized by transmission electron microscopy (TEM),as shown in Fig.4,using a simple liquid-phase ultrasonic exfoliation to produce a few or even a single layer of graphene-like MoS2-NS.Through experiments we can see that we can see that graphene-like MoS2-NS can be prepared by ultrasonic for 6h under ultrasonic power of 360W under the condition of controlling the mass ratio of MoS2/NaOH was 1/1.

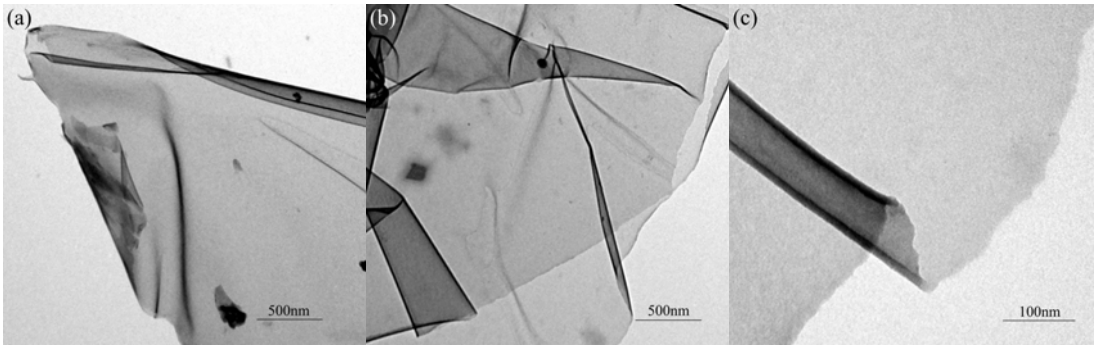

Figure 4. Representative TEM micrographs of MoS_2-NS with optimum conditions

Raman spectroscopy is the most effective tool to characterize lamellar compounds. The MoS2 Raman spectra can be judged directly by measuring the wave number corresponding to Raman peaks. The MoS2 Raman spectra have two basic vibration modes: E12g Mode and A1g mode.E12g is the in-plane vibrational mode, which is the vibration of the two S atoms and the middle Mo atoms in the opposite direction.A1g is the interlayer vibration mode, which is the vibration of S atoms and Mo atoms in the direction perpendicular to the layer. As the number of atomic layers decreases, the MoS2 Raman vibrational mode E12g blue-shift,A1g red shift, which can identify the MoS2 layers. As shown in Fig.5(a),the number of layers of the graphene-like MoS2-NS prepared by the simple liquid-phase ultrasonic exfoliation was decreased. From Fig.5(b),the peak position of MoS2 is consistent with the peak position of MoS2 powder. The diffraction peaks of MoS2 powder correspond to 2H-MoS2(JCPDS No.87-2416) The diffraction peak of (002) plane is lower than that of undissolved MoS2,and the diffraction peak is obviously widened.

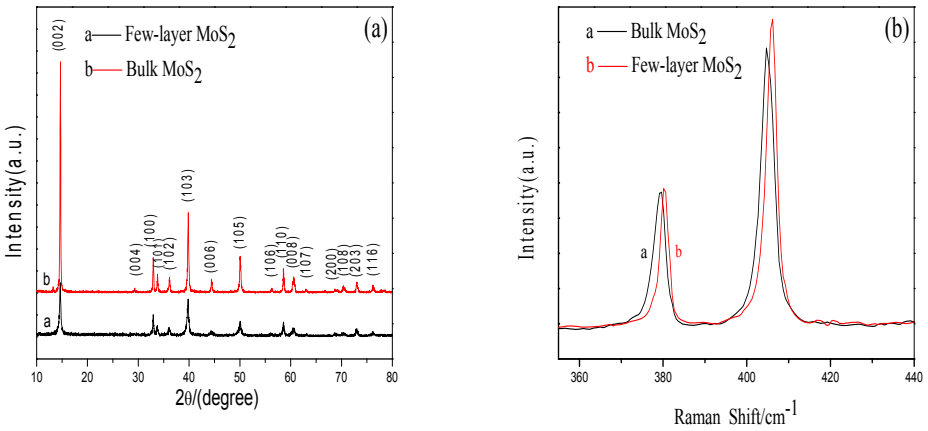

Figure 5. The XRD and Roman of MoS_2 with different scales

Conclusion

The results of TEM and Roman analysis show that the ultrasonic power, ultrasonic time and the amount of NaOH added directly affect the preparation of MoS_2-NS.With different test conditions, the degree of peeling of the prepared MoS_2-NS varies greatly. The optimal experimental parameters were obtained by comparing the experimental results.MoS_2 powders were placed in NMP and subjected to multiple pumping treatments. The ultrasonic power was 360w and the ultrasonic time was 6h.

Acknowledgments

This work was supported by the National Natural Science Foundation of China under Grant No.51272110.

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