Liquid exfoliation of 2D nano materials MoS_2 and its composites with polymer

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Introduction

Post graphene discovery, single-layered transition-metal dichalcogenides such as MoS_2, have attracted great attention as next generation 2D materials owing to their large intrinsic bandgap, which is particularly attractive in view of the gapless nature of graphene. Single-layer MoS_2 has attractive attributes such as a direct bandgap (1.9 eV), large in-plane mobilities (200–500$cm^2V^{-1}s^{-1}$), high current on/off ratios(exceeding 10^8), as well as remarkable mechanical and optical properties. These properties are of great interest for applications in optoelectronic devices such as thin film solar cells, photodetectors, flexible logic circuits and sensors. Researches have shown that these single-layered nanosheets can increase the modulus and strength of polymer ,as well as bring new properties to the polymer.

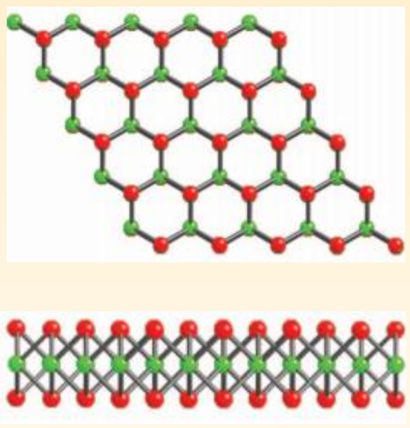

Fig. 1.The top view and side view of MoS_2.

One of the oldest methods to exfoliate MoS_2 is using n-butyl lithium to form Li_xMoS_2, then reacts with deionized water, releasing H_2 into the space between two layers to make them separated. In 2011, Coleman used a point probe sonic tip (VibraCell CVX: 30% of 750 W) to exfoliate MoS_2 in combinations of different kinds of solutions and polymers. In this system, polymer plays as a role of stabilizer and it also provides a method to make 2D nanosheets-polymer composites. New methods like using sodium naphthalene, ice expansion and shear vibration have come out.

Experiment Method

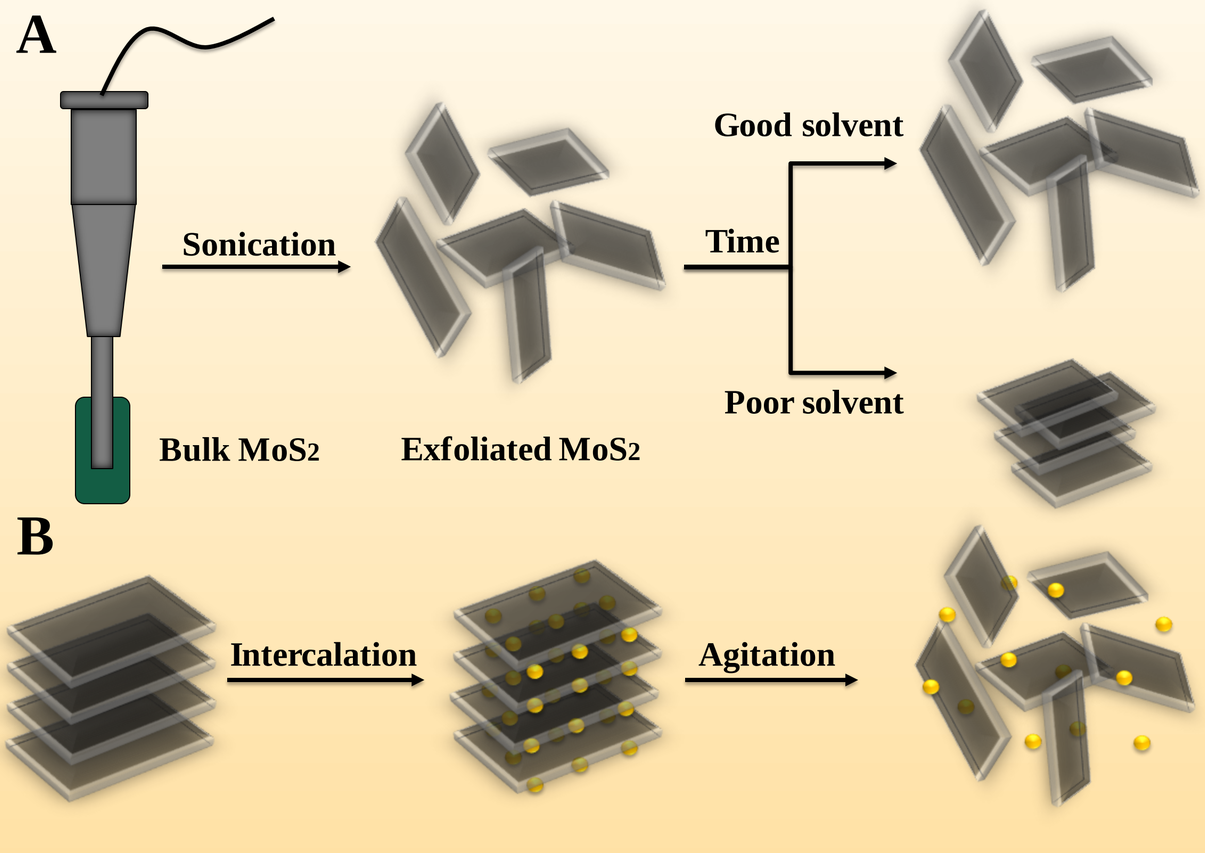

Fig. 2. Schematic of exfoliation of MoS_2 in liquid. (A) Sonication assisted exfoliation. (B) Ion intercalation.

In picture A, the layered crystal is sonicated in a solvent, resulting in exfoliation and nanosheets formation. In good solvents, those with appropriate surface energy—the exfoliated nanosheets are stabilized against reaggregation. Otherwise, for poor solvents reaggregation and sedimentation will occur. This mechanism also describes the dispersion of graphene oxide in polar solvents, such as water. After sonication, the dispersions were allowed to settle for ~24 hours before centrifuging them at 1500rpm for 45 minutes. The top 3/4 of the dispersion was collected by pipette.

In picture B, ions (yellow spheres) are intercalated between the layers in a liquid environment, swelling the crystal and weakening the interlayer attraction. Then, agitation (such as shear, ultrasonication, or thermal) can completely separate the layers, resulting in an exfoliated dispersion.

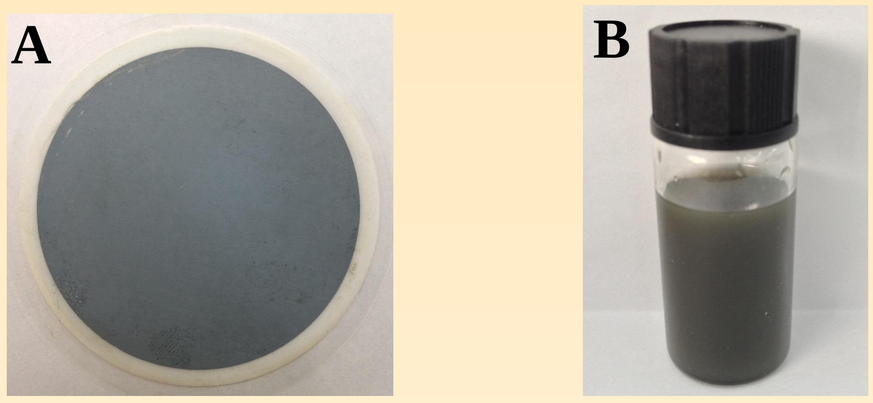

Fig. 3.(A) Exfoliated MoS_2 on the filter paper substrate; (B) The supernatant after sonication of MoS_2 in the solvent NMP.

Raman and UV Tests

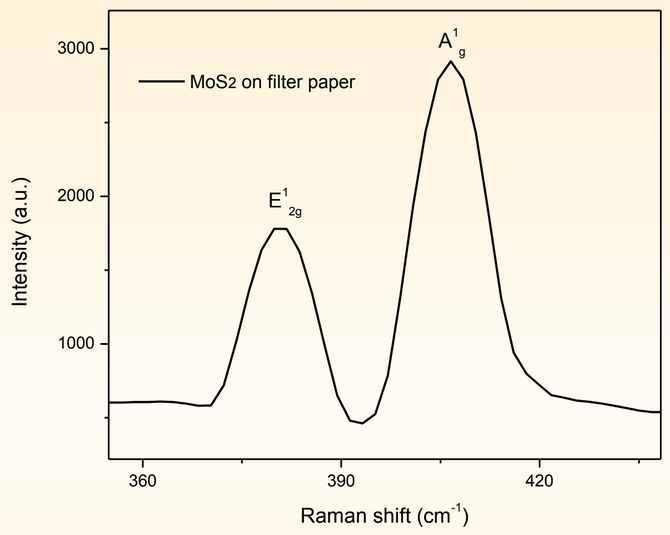

Fig.4.Raman spectrum of MoS_2 on the filter paper substrate

The Raman spectrum is tested using a laser of 514nm and the location of two main modes, E^1_{2g} and A^1_g ,will judge the number of layers of MoS_2.The sample of fig.3.A gives a D-value of about 24cm^{-1} of two modes, which means the number of layers is 4-5.

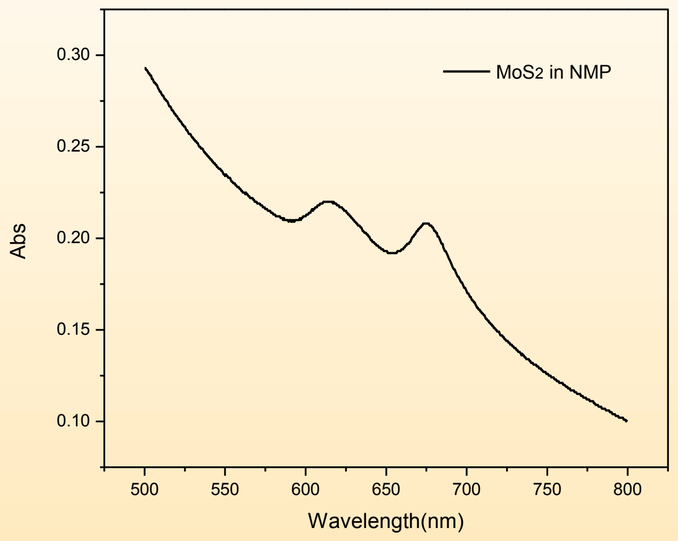

Fig.5.UV spectrum of MoS_2 in NMP

The UV absorption spectrum is tested in the solvent of NMP. The sample of fig.3.B gives two peaks in the wavelength of 615nm and 675nm, which means that the MoS_2 is exfoliated, while the degree of it is indistinct.

Result and Discussion

Several Raman spectrums and the UV abs spectrum of MoS_2 using the ultrasonication method shows that the flake thicknesses is between 1 to 10 layers with a mean of 4-5, even the supernatant is centrifuged with a high speed of 5000rpm.The intercalation method may have a higher yield of exfoliation of single layers, but the probability of success is not that high. As soon as the single-layered MoS_2 is obtained, the composites of polymer with it will be easily made in the liquid condition.

The attempt of obtaining pure single-layered MoS_2 is to bring the significant property of it into the polymer matrix. In the next work, we will exfoliate the nanosheets with existence of polymer, which plays a role as stabilizer. Different kinds of 2D nanosheets can be stacked layer-by-layer via filtration through a nitrocellulose membrane with a pore size of 20nm. If the separation of different layers is under controlled, we will know the effect of number of layers on the properties of polymer-nanosheets composites.

Acknowledgement: This work is supported by the National Natural Science Foundation of China (51325301, 51120135002, 51227801, U1232128, 51473151). The experiment is carried out in National Synchrotron Radiation Lab (NSRL).