doi:10.1246/cl.2012.732

Preparation of Nanosheets by Ultrasonic Exfoliation with the Aid of Surfactant Poly(vinylpyrrolidone)

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Using poly(vinylpyrrolidone) (PVP) as a stabilizing agent graphite nanosheets (GNs) and molybdenum disulfide nanosheets (MNs) were conveniently obtained under ultrasound treatment. The two kinds of obtained nanosheets were detected by transmission electron microscopy (TEM) and atomic force microscopy (AFM) and analyzed by Raman spectroscopy. UV–vis spectrophotometric measurement was performed to test their typical absorption peaks.

In recent years, two-dimensional (2D) nanostructured materials have stimulated great interest due to their exceptional properties and potential applications in electronics, catalysis, and magnetic miniaturized devices.[1] Since the discovery of graphene by Geim in 2004, GNs have recently attracted much more attention for their excellent properties; usually viable and inexpensive carbon materials are used in many composites.[2] GNs have been obtained from the thermal expansion route; however, GNs resulting from this process contain hundreds of stacked graphene layers: average in thickness between 30 and 100 nm.

Molybdenum disulfide (MoS_2), a technologically important semiconductor compound, has earned intensive interest for its commercial applications, such as catalysts, transistors, energy storage, and solid electrolytes.[3] Compared to block materials, nanomaterials often exhibit remarkable and unique properties. As a result, much effort has been devoted to the fabrication of various MoS_2 nanostructures.[4] As a typical layered transition-metal sulfide, MoS_2 is composed of three stacked atom layers (S–Mo–S) held together by van der Waals forces.[5]

So far, the preparation of GNs and MNs using ultrasound treatment has been carried out and reported. Coleman et al. showed that graphite and molybdenum disulfide could be exfoliated in various organic solvents with a well-defined surface tension to produce mono- and few-layer nanosheets.[6] Although this process is insensitive to air and water and can potentially be scaled up to give large quantities of exfoliated material, unfortunately, it is not without its drawbacks. These solvents are expensive and require special care when handling. In addition, they tend to be nonvolatile, making it difficult to deposit individual monolayers on surfaces. Thereafter, the Zhang research group demonstrated a versatile and scaleable mixed-solvent strategy for stabilization of GNs and MNs, this strategy mainly changed the dielectric constant of the solvents in some certain cases.[7] Here, in our experiment, an alternative, liquid-phase process is demonstrated. Solvents in this work are compatible with safe, user-friendly, low boiling-point, preferably absolute ethanol and deioized water. The surfactant PVP was selected to make an initial survey for each material.

In this work, GNs and MNs were similarly obtained through a simple ultrasound method with the aid of PVP at room temperature. All the raw materials were analytical grade agents, purchased from Shanghai Sinopharm Chemical Reagent Co., Ltd., and used without further purification. In a typical procedure, the preparation of GNs and MNs involved the following three processes: first, the raw material powders were added into 100-mL cylindrical vial which was filled with 80 mL of absolute ethanol or deionised water with PVP at mole concentration of 0.001 M; second, the mixed solution was sonicated in a low-power sonic bath (Branson Sonifier S-450) with a horn probe sonic tip for different time, and then the dispersion was centrifuged at 10000 rpm for 10 min to remove residual aggregates. The supernatant (top two thirds of the centrifuged dispersion) was collected by a pipette, cinereous supernatant was for GNs and dark green supernatant for MNs. This result can be attributed to the entropy elasticity of polymer molecules chain and the osmotic pressure of macromolecular solutions. In addition, polymer chain in PVP can form an adsorption layer on the surface of GNs and MNs and, due to the adsorbed surfactant and two water affinity groups of the polymer chain such as pyrrole alkyl groups and hydroxy groups, can make GNs and MNs suspend in the ethanol or deionized water, they can be a very good protection.

Figure 1 shows the UV absorption spectra of GNs (a and b) and MNs (c and d) in different PVP–solvent solutions. As shown in Figures 1a and 1b, it can be seen that there is an obvious broad characteristic absorption peak located at the wavelength of 268 nm, which corresponds to π–π^* transitions of aromatic C–C bonds. From Figures 1c and 1d, the two typical absorption peaks

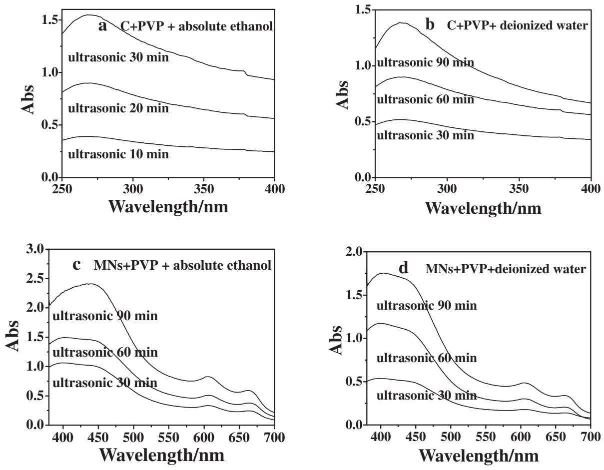

Figure 1. Typical UV–vis spectra of GNs (a and b) and MNs (c and d) in different PVP–solvent solution.

of MoS_2 suspension are observed clearly at 627 and 672 nm, it is in good agreement with previous work reported in the literature.[7] These two peaks indicate the existence of MNs dispersed in different single solvents with PVP existence.

From the comprehensive analysis of the UV absorption spectra of GNs and MNs, using absolute ethanol as solvent, the absorbance of GNs and MNs can reach a bigger value in a relatively short time under ultrasound treatment. Selecting deionized water as solvent for GNs, the yield of nanosheets at 30 min sonication is only half of that using absolute ethanol as solvent. However, no matter which solvent is selected, the yield of nanosheets increases gradually with the ultrasound treatment time increasing. And the conversion rate mainly depends on the ratio of the raw material powder and solvent and ultrasonic power and time. When 0.1 g of graphite powders was added into 100-mL cylindrical vial which was filled with 80 mL of absolute ethanol with PVP at mole concentration of 0.001 M, about 4.5% of graphite powders is converted into GNs under the conditions of ultrasonic power 280 W and ultrasonic time 30 min, and the highest concentration of nanosheets obtained reaches about 0.05 mg mL^{-1}, whereas no nanosheets can be obtained without PVP. Meanwhile, we also find that the average lateral size of the nanosheets reduced by prolonged sonication time, the results were analyzed using dynamic light scattering (DLS) method shown in Supporting Information.[12]

The morphology and structure of the GNs and MNs were observed by TEM analysis. Typically, a drop of a given dispersion was placed on a holey carbon grid and dried in ambient conditions. Under the TEM, large quantities of two-dimensional objects were detected, which revealed that the majority of the nanomaterials are present as two-dimensional nanosheets in the dispersions. A selection of the nanosheets observed is confirmed in Figures 2a and 2b for GNs and Figures 2c and 2d for MNs. It can be seen that the GNs and MNs exist in the PVP–solvents with sizes varying from 200 nm to several micrometers. Meanwhile, it is clear that the size of nanosheets obtained in ethanol is larger than in deionised water. In view of this, we also employed AFM with tapping-mode to certify the morphology of GNs and MNs dispersed separately in PVP–ethanol solution. The sample was prepared by drop-casting a dilute dispersion onto mica, and the results are given in Figures 3a and 3b. The single layer for GNs (Figure 3a) and MNs (Figure 3b) deposited separately on fresh mica has been observed, which provides a facile approach to obtain single GN and MN for device fabrication or studies on the properties of individual sheets. Here, we thought that PVP plays an important role in the formation of the nanosheets. PVP is absorbed onto the nanosheets surface in a random fashion and formed a protection layer so as to stabilize the nanosheets dispersions and inhibit the restack of the nanosheets.[8]

Raman spectroscopy is used widely to characterize carbon materials and also inorganic graphene analogues. Here, it was employed to further confirm the existence of GNs and MNs. Raman scattering of GNs and MNs was obtained by exciting the samples with the He/Ne 5140-Å laser line from an argon ion laser. Highly ordered graphite has only a couple of Raman-active bands visible in the spectra, the in-phase vibration of the graphite lattice (G band) at 1581 cm^{-1} as well as the disorder band caused by the graphite edges (D band) at approximately 1355 cm^{-1}. Both the G and the D bands undergo significant changes upon amorphization of graphite because amorphous carbon contains a certain fraction of sp^3 carbons.[9] As shown in Figure 4a, when graphite is exfoliated into GNs, higher disorder in graphite leads to a broader G band, as well as to a broad D band of higher relative intensity compared to that of the G band. Additionally, the G band shifts to higher frequencies, while the D band displays a shift to lower frequencies. According to the literature, G band generated from the ring or long chain of carbon atoms in the stretching vibration mode, which corresponds to atomic vibrations within the graphite layer.[10] Herein, isolated double bonds in GNs resonate at higher frequencies than the G band of graphite. D band resulted from the breathing vibrational mode of carbon atom ring. When graphite is exfoliated into GNs, the energy of breathing vibration becomes lower, so that D band moves to the lower frequencies.

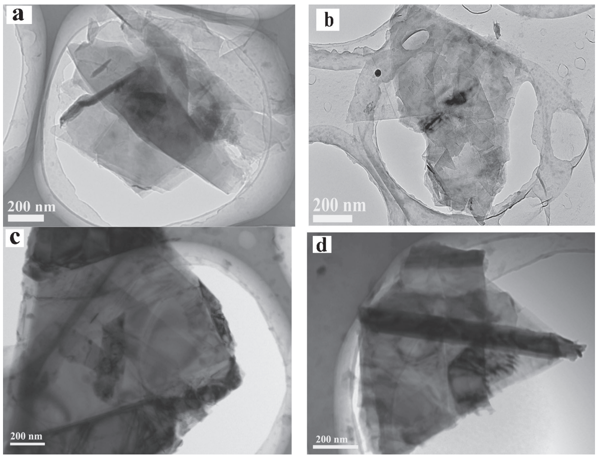

Figure 2. TEM images of GNs (a) in PVP–absolute ethanol, (b) in PVP–deionized water; MNs (c) in PVP–absolute ethanol (d) in PVP–deionized water respectively.

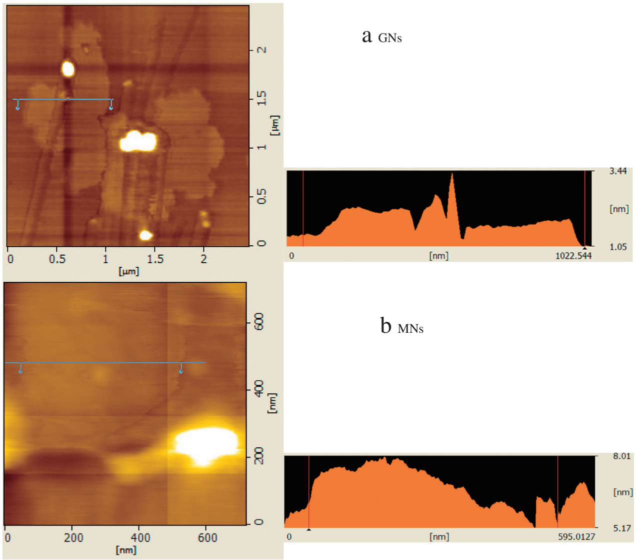

Figure 3. Tapping-mode AFM images with a height profile of (a) GNs and (b) MNs dispersed in PVP–absolute ethanol respectively.

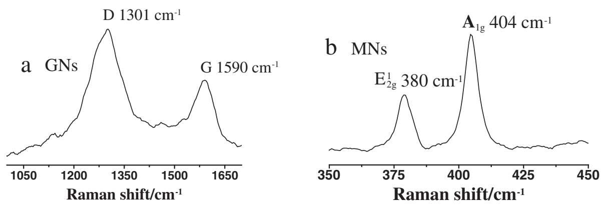

Figure 4. Raman spectra of the PVP-stabilized (a) GNs and (b) MNs dispersed in absolute ethanol separately under ultrasound treatment.

As inorganic graphene analogues, MNs were also confirmed by Raman mapping, shown in Figure 4b. According to the previously reported work, the bulk sample shows two main bands at 408 and 383 cm^{-1} due to the A_{1g} and $E^1{}_{2g}$ modes. And Raman spectra of nanoflower-like MoS_2 generated red shift.[11] Interestingly, the $A_{1g}(\Gamma)$ (404 cm^{-1}) mode of MNs is enhanced, and the relative intensity of the $A_{1g}(\Gamma)$ to $E^1{}_{2g}(\Gamma)$ (380 cm^{-1}) increases. Additionally, $A_{1g}(\Gamma)$ and $E^1{}_{2g}(\Gamma)$ peaks of MNs shift to lower energies more obviously. The difference in the Raman spectra may be also attributed to the MNs structure, and it once again conforms that MNs in the PVP–solvents were obtained successfully.

In conclusion, this work offered an effective and facile liquid-phase synthesis of GNs and MNs. PVP is thought to play an important role to stabilize the nanosheets in different single solvent. It can be thought that this facile exfoliation method may be used to obtain the nanosheets of other similar layered compound.

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12 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.