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Letter to the editor

Graphene and graphene-analogue nanosheets produced by efficient water-assisted liquid exfoliation of layered materials

ABSTRACT

We report the efficient productions of single- and few-layered graphene and molybdenum disulphide (MoS_2) nanosheets using a surfactant-free, water-assisted liquid-phase exfoliation (LPE) of graphite and MoS_2 bulk powders in N-methylpyrrolidinone (NMP). Extensive absorption spectroscopic study and materials characterizations indicate that the addition of water to NMP was not only effective on the exfoliation yields but also the stability of the colloidal dispersions of exfoliated nanosheets in the water-NMP mixed solvent upto 18 months. Detailed micro Raman spectroscopic analysis suggests the defects of the exfoliated graphene nanosheets were reduced using the developed water-assisted LPE in NMP.

The nanosheets of graphene and graphene-analogues such as molybdenum disulphide (MoS_2) have been demonstrated promising materials with exceptional properties for various applications [1]. However, it is still challenging to synthesize these materials with high purity in a bulk quantity [2]. Among various preparation methods including micromechanical and electrochemical exfoliations and chemical vapour deposition [3], the liquid phase exfoliation (LPE) with appropriate solvents and chemical additives including surfactants and organic compounds has been reported as an effective and potentially scalable approach to produce graphene and graphene-analogues nanosheets with the advantages of simple operation, low defects on produced nanosheets, and minimal environmental impact [2,3]. However, the use of surfactants may degrade the intrinsic properties of the exfoliated nanosheets [3]. In addition, the organic compounds used in the LPE are either solid or having high boiling points [4], which are difficult to be removed from the exfoliated nanosheets.

Here we demonstrate a facile and scalable preparation of single- and few-layer graphene and MoS_2 nanosheets by a surfactant-free, water-assisted LPE using N-methylpyrrolidinone (NMP). The recent demonstrations on the efficiency of mixed solvents in LPE [5,6] and the uniqueness of water-NMP mixed solvents to stabilize high concentration graphene oxide dispersions [7] motivated us to employ water as the cosolvent with NMP in a LPE. To our best knowledge, there is no report to demonstrate the possibility to exfoliate layered materials with water-assisted LPE using NMP. We found that with the mass fraction (m_w) 0.2 of water in NMP, the exfoliated concentrations of graphene and MoS_2 nanosheets were enhanced almost by 2.5 times than those obtained in pure NMP. Detailed absorbance and micro Raman spectroscopic studies revealed that the developed water-NMP solvents not only increased the exfoliation yields but also reduced the defects in the exfoliated graphene nanosheets caused by sonication. The colloidal dispersions of exfoliated graphene and MoS_2 nanosheets were highly stable for 18 months.

Fig. 1 shows the representative photographs, UV-visible absorption spectra, absorbance and concentrations profiles as functions of water mass fraction, m_w of as-exfoliated graphene and MoS_2 nanosheet dispersions. At appropriate m_w, black and dark green colloidal dispersions of graphene (Fig. 1a) and MoS_2 nanosheets (Fig. 1d), respectively were obtained. Graphene nanosheets exhibited a peak at 266 nm (Fig. 1b) and MoS_2 nanosheets exhibited three peaks at 669, 608 and 396 nm (Fig. 1e), which are consistent with previous report [6]. The absorbance values presented in Fig. 1b and e (as inset) are average of five individual experiments. The exfoliated concentration (mg ml^{-1}) of the materials (Fig. 1c and f) were determined by filtration and weighing method [2,8] (Section S2, supporting information). The exfoliated concentration increased initially with increase of water m_w in NMP, and the optimal m_w for maximum exfoliation were found to be 0.2 for both the materials. At this NMP-water composition, the final dispersion concentrations of graphene and MoS_2 nanosheets obtained after centrifugation were 0.43 and 0.48 mg ml^{-1}, respectively, which are almost 2.5 times of concentrations obtained in case of pure NMP for both the materials. We also noticed that sonication time directly influenced in the increase of exfoliation yield. The water-NMP mixed solvent at optimal m_w of 0.2 gives rise to better yield for every sonication time (Figure S1).

Transmission electron microscopy (TEM) was used to characterize the thicknesses and morphologies of the exfoliated graphene and MoS_2 nanosheets, shown in Fig. 2 and Fig. S2. TEM images indicate single and few-layer graphene and MoS_2 nanosheets. The statistical analysis from TEM observations revealed that the majority

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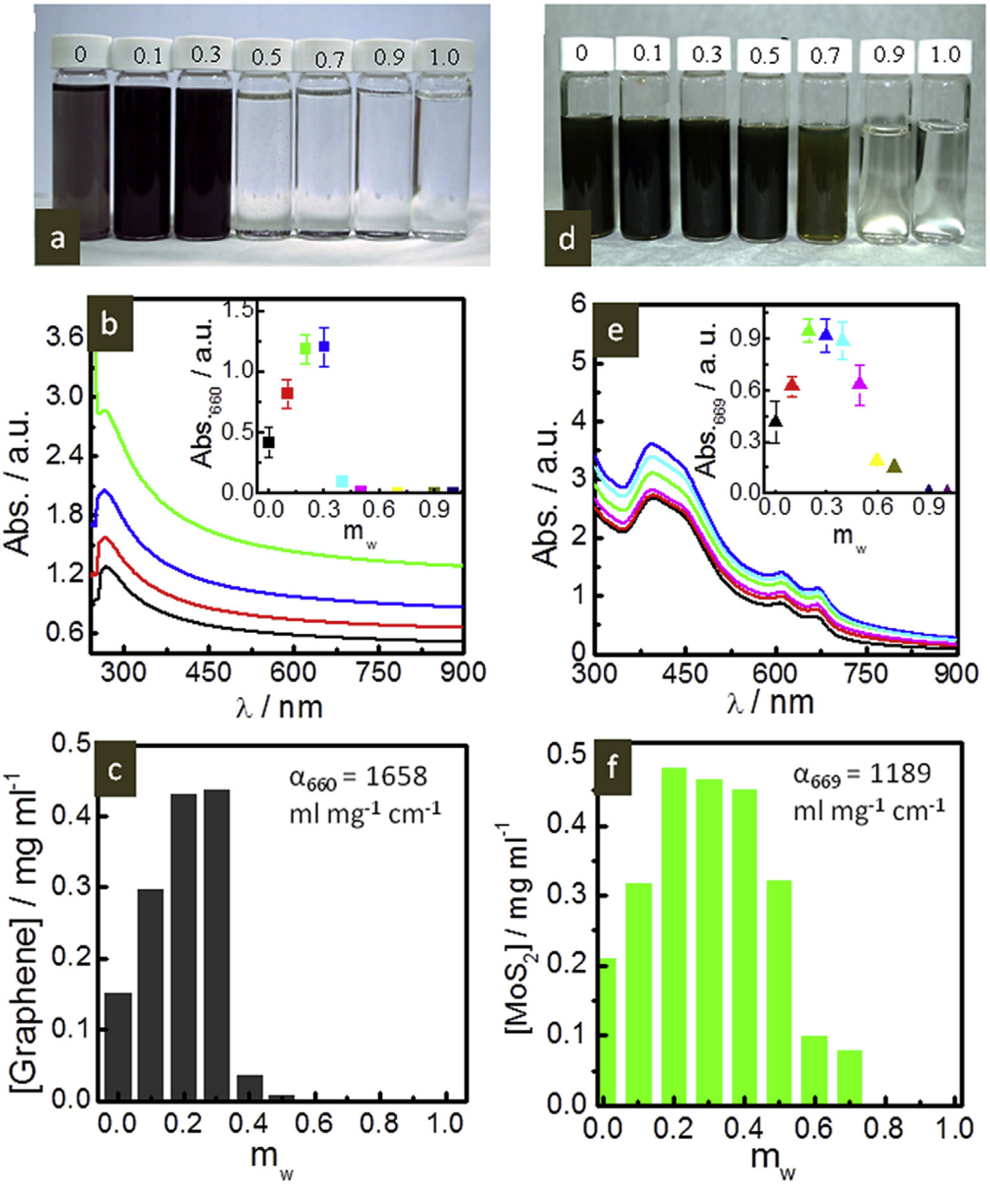

Fig. 1. (a, d) photographs, (b, e) UV–visible spectra, inset: corresponding absorbance profiles and (c, f) concentration profiles of graphene and MoS_2 nanosheet dispersions as a function of water mass fraction (m_w) in NMP-water solvents. (a, b, d, e) different m_w of water are mentioned in the corresponding figures. The absorption spectra were recorded using six time diluted graphene and MoS_2 dispersions, whereas, the concentrations of exfoliated dispersions are original. The absorption coefficients (α) of graphene and MoS_2 have been mentioned in figures (c, f).(For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

of the exfoliated graphene and MoS_2 nanosheets have lateral size of 500–2000 nm and 50–200 nm, respectively (Fig. S3), which were smaller than the nominal size of the bulk materials (325 mesh). The smaller sizes of the exfoliated nanosheets could be explained by that the raw bulk materials were polycrystalline with grain sizes smaller than the nominal size of bulk materials (325 mesh) [2], that is supported by the scanning electron microscopy (SEM) observations of the bulk graphite and MoS_2 powders showing polycrystalline nature of the bulk materials (Figure S4). The layer numbers in the exfoliated nanosheets were estimated by the analysis of edges of the nanosheets [2] (Fig. S2(d) and (h)). Reasonable numbers of monolayer, folded monolayer, and few-layer nanosheets were found for both the exfoliated graphene and MoS_2 materials. HRTEM images display that both the exfoliated graphene (Fig. 2b) and MoS_2 (Fig. 2d) nanosheets retain hexagonal atomic structures, indicating no severe distortion from regular crystalline structure during our LPE [2,8].

X-ray photoelectron spectroscopy (XPS) was performed for the bulk materials and exfoliated nanosheets to study the chemical modification if occurred during LPE (Fig. 3(a) and (c), and Fig. S5). XPS wide scan spectra of both the materials with critical discussion are given in Fig. S5 and Section S3 in supporting information. The peak at 286 eV (Fig. 3a and Fig. S5a) can be assigned to C(1s) peak for graphene and graphite. Mo($3d_{3/2}$), Mo($3d_{5/2}$), S(2s), S($2p_{1/2}$), and S($2p_{3/2}$) peaks were observed at 232, 229, 226, 163 and 162 eV, respectively for MoS_2. The binding energy for graphitic carbon, Mo, and S were found to be in good agreement with previous reports [8,9]. Moreover, the low intense oxygen peaks of both exfoliated nanosheets as well as corresponding bulk powders in the XPS wide scan spectra suggest no oxidation occurred during the exfoliation process (Section S3 and Fig. S5). Peaks observed along with the peak for graphitic carbon (Fig. 3a) can be assigned