



Surfactant- and sonication- free exfoliation approach to aqueous graphene dispersion



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ABSTRACT

A $\text{Li}^+\text{-OH}^-$ exfoliation system was designed to prepare graphene in water without surfactants or sonication. Due to the positive charge transferred from intercalating Li^+ ions to adjacent C atoms, OH^- could add on the graphene sheets and further promote their affinity to water, resulting in efficient exfoliation of graphene in water. The as-prepared graphene concentration was up to $0.09 \text{ mg}\cdot\text{mL}^{-1}$, and sheet sizes range from 1 to $2 \mu\text{m}$. Detailed characterizations revealed the formation of high-quality and few-layer graphene sheets and confirmed the addition of hydroxyl groups on graphene sheets during exfoliation. This strategy has potential in scalable production of graphene in aqueous phase.

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1. Introduction

Graphene holds promising industrial applications due to its extraordinary electric, thermal, mechanical and optical properties [1]. For example, nanoporous graphene is an excellent membrane material for H/D/T isotope separation, and can be applied in tritium production for fusion power [2,3]. Since the original scotch tape mechanical exfoliation method [4], various physical methods and wet chemistry procedures have been developed [5,6]. Recently, exfoliation of intercalated graphite in liquid phase has received increasing attention because of its high scalability, low energy consumption and high economic efficiency [7]. To minimize environmental impacts, water-based exfoliation procedure is a natural choice for massive production of graphene. However, the hydrophobic nature of graphene surface prevents stable dispersion in water and results in aggregation. Moreover, the hydrophobic repulsion between graphene layers and water tends to increase the free energy of exfoliated sheets and hence compromises the exfoliation efficiency. A common solution is adding organic surfactants which lower the interfacial free energy via bonding in the graphene/solvent interface. However, surfactants should be sophisticatedly removed for some specific applications. Another strategy with lower manufacturing costs and environmental

impacts is to directly improve the hydrophilic property by introducing charge to graphene sheets. In this direction, some inspiring researches have been reported. For instance, Liu and co-workers stabilized exfoliated graphene in water by employing weakly basic solution ($\text{pH} = 10\text{--}11$) to promote the ζ -potential of sheets [8]. Drummond and co-workers demonstrated surfactant-free stable dispersion of negatively charged graphenide in degassed water [9].

Herein, we propose a simple procedure to prepare graphene in aqueous $\text{Li}^+\text{-OH}^-$ exfoliation system without surfactants. Generally, we use Li^+ intercalation to expend the spacing between graphite layers and OH^- addition to stabilize the exfoliated graphene sheets in water (Fig. 1a). Via introducing OH^- into the exfoliation system, hydroxyl groups can be added on the surface of graphene. The hydroxyl groups significantly increase the ζ -potential of the graphene sheets, and form hydrogen bonds with water molecules, which would stabilize the graphene-water mix [8]. On the other hand, the addition of hydroxyl groups turns some carbon atoms from sp^2 to sp^3 configuration, breaking the π conjugation and weakening the π - π stacking attraction between graphite layers. As predicted, aqueous graphene solution with concentration up to $0.09 \text{ mg}\cdot\text{mL}^{-1}$ was obtained without surfactants or sonication. Since sonication process was omitted, the prepared graphene sheets are relatively large ($1\text{--}2 \mu\text{m}$). This strategy provides a new pathway for scalable aqueous production of surfactant-free graphene in an environmentally sound manner with low cost.

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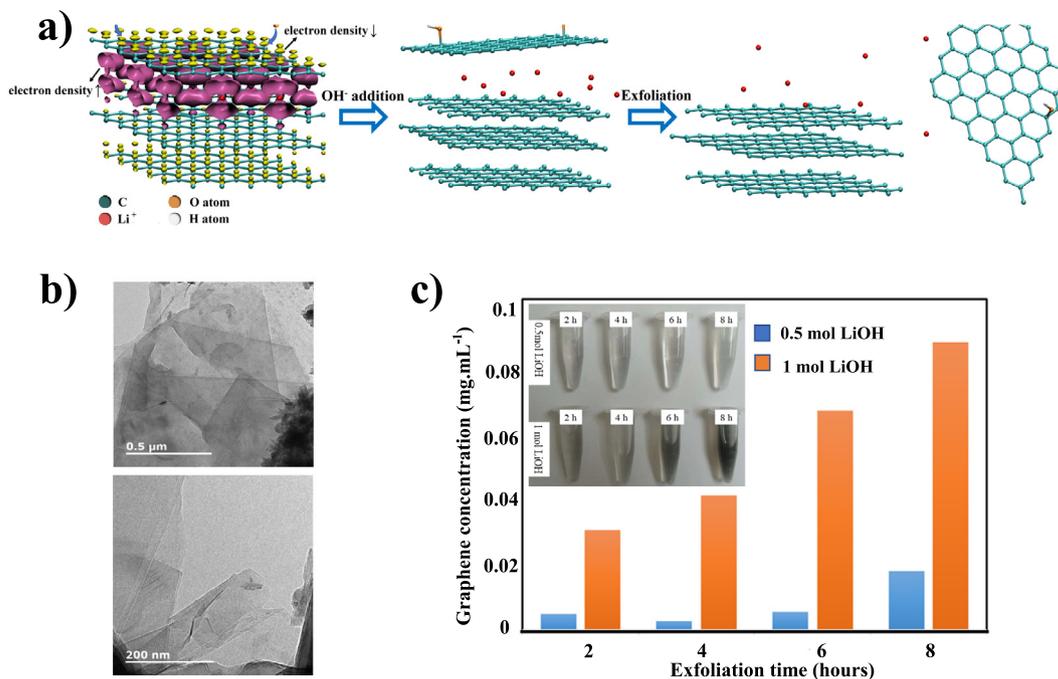


Fig. 1. (a) The diagram of the synthesis strategy with $\text{Li}^+\text{-OH}^-$ exfoliation system. The purple and yellow surfaces in the left panel represent the $+0.002$ and -0.002 e/Bohr^3 isosurfaces of electron density difference caused by Li^+ intercalation. (b) TEM images of the exfoliated graphene sheets. (c) Graphene concentration as a function versus the concentration of LiOH and exfoliation time. The inset is the prepared aqueous graphene suspension.

2. Methods

100 mg of graphite and 0.5–1.0 mol of LiOH were added into a flask with 100 mL of deionized water. The mixture was kept boiling under stirring for 2–8 h. Then the mixture was centrifugated at 2,000 rpm for 5 min. The supernatant fraction was collected for further characterization.

The density functional theory (DFT) calculations were performed within the generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof (PBE) parametrization implemented in Abinit software package [10]. The projected augmented wave method was used to describe the electron–ion interaction; and the van der Waals interaction was described by DFT-D2 method [11].

3. Results and discussion

The proposed preparation procedure is diagrammatically shown in Fig. 1a. The DFT-calculated electron density difference caused by Li^+ intercalation is depicted in the left panel. The purple and yellow isosurfaces represent the regions with increased and decreased electron densities respectively. Bader charge analysis reveals that 12% of the positive charge of Li^+ transferred to graphite, which would greatly favor the addition of negative-charged OH^- on graphene sheets. As shown in the transmission electron microscope (TEM) images (Fig. 1b), the size of prepared graphene sheets ranges from 1 to 2 μm . The concentration of dispersed graphene was evaluated from the optical absorption at 660 nm. [12] The results are displayed in Fig. 1c as a function versus the amount of LiOH precursor and exfoliation time. Varying with the reaction conditions, the graphene concentration in the as-prepared suspension is in the range from 0.005 to 0.09 $\text{mg}\cdot\text{mL}^{-1}$, and roughly proportional to the exfoliation time. Increasing the amount of LiOH from 0.5 to 1.0 mol can significantly improve the production of graphene. Similar results were also observed in organic phase exfoliation systems with surfactants [13].

Fig. 2a presents the Raman spectra of graphite precursor and exfoliated products. The G peak at 1580 cm^{-1} and 2D peak at 2700 cm^{-1} are well resolved. Compared to graphite precursor, the as-prepared graphene exhibits a more symmetrical 2D peak with less distinct shoulder, which is signal of structural transformation from graphite to graphene [13]. The ratio of the intensity of D peak at 1355 cm^{-1} to that of the D' peak at 1620 cm^{-1} [$I(\text{D})/I(\text{D}')$] can be employed to determine the dominating types of defects in graphene. The $I(\text{D})/I(\text{D}')$ ratio of (1.67 ± 0.5) in our sample suggests that the disorder-induced bands arise from the edge of sheets [14]. This ratio also indicates no significant in-plane defects for which the $I(\text{D})/I(\text{D}')$ ratio is larger than 6.0 [14]. In addition, the broad peak at about 26.6° in X-ray diffraction patterns (Fig. 2b) of prepared samples implies few-layer graphene sheets [15]. The above results suggest that low-defect and few-layer graphene sheets were produced with the designed procedure.

Then we employed X-ray photoelectron spectroscopy (XPS) experiments in conjunction with Fourier transform infrared spectroscopy (FT-IR) to elucidate the addition on hydroxyl groups on graphene sheets. As shown in Fig. 3a, the C 1s XPS spectrum of the pristine graphite can be well deconvoluted into a pronounced peak around 284.2 eV corresponding to C–C bonds, and a peak at 285.5 eV that can be assigned to C–O bonds [16]. For the prepared graphene sheets, a higher intensity of C–O peak was recorded. And the survey scans also reveal a higher oxygen atomic concentration. A new peak at 282.4 eV corresponding to C–Li bonds emerged. It can be interpreted by that the ionized hydroxyl groups reduced the electrostatic potential on the surface of graphene and more Li^+ were adsorbed on the sheets. Moreover, in the FT-IR spectra, for the $800\text{--}1300\text{ cm}^{-1}$ range contributed by C–O stretching and the $3000\text{--}3700\text{ cm}^{-1}$ range arising from O–H stretching [17,18], the prepared graphene exhibits more intense absorption. These above results lend solid evidence to our hypothesis that the hydroxyl groups were added on the graphene sheets during the exfoliation. The hydroxyl groups can also be almost completely removed by annealing above 300°C , if necessary [17].

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