Aqueous dispersions of TCNQ-anion-stabilized graphene sheets

Rui Hao,† Wen Qian,† Luhui Zhang and Yanglong Hou*

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Aqueous dispersed graphene was successfully prepared *via* using 7,7,8,8-tetracyanoquinodimethane (TCNQ) anion as a stabilizer and expanded graphite as a starting material, which could provide a facile route to produce high quality water-soluble and organic solvent-soluble graphene sheets for various applications.

Graphene, as a new family member of carbon allotropes, has exhibited potential applications in microelectric devices, sensors, biomedicines and mechanic resonators due to its unique electronic and mechanic properties, which are attributed to the monolayer of carbon atoms densely packed into a honeycomb structure.[1–3] Several physical and chemical routes have been developed to produce graphene, for example, mechanical exfoliation,[1] heat treatment of silicon carbide wafers,[2] and epitaxial growth by chemical vapor deposition of hydrocarbons on metal substrates.[4] However, there are more challenges to obtain a flat graphene sheet in the free state because it easily tends to form a curved structure.[5] On the other hand, the hydrophobic property of as-synthesized graphene is limited for developing its applications. Therefore, preparation of an aqueous individual graphene sheet is of great significance for the fundamental and applied issues.[6,7] So far, graphene oxide[8,9] and expanded graphite[10] were used to prepare soluble graphene, however, only the former was reported to prepare an aqueous solution. Moreover, graphene oxide prepared from oxidized graphite includes significant oxygen functionality and contains irreversible lattice defects, which degrade the unique electronic properties, compared with pristine graphene.[11] It is worth noting that exfoliated pristine graphene derived from expanded graphite exhibits high quality and high electrical conductivity because it keeps the basic structure and has fewer defects.

Considering the similarity between graphene and carbon nanotube, it is possible, in principle, that the stabilizers for the functionalization of carbon nanotubes such as tetrabutyl-substituted phthalocyanin, alkyl-substituted porphyrins and anthracene[12] could also be effective for graphene. For example, 1-pyrenebutyrate[9] and poly(*m*-phenylenevinylene-*co*-2,5-dioctoxy-*p*-phenylenevinylene) (PmPV)[10] have been applied to modify the surface of graphene. From the viewpoint of their chemical structures, one can know that these stabilizers normally constitute two functional groups, one for adsorption, and the other for dispersion. However, the dispersion groups are usually insulated, which degrades the conductivity of functionalized graphene. 7,7,8,8-Tetracyanoquinodimethane (TCNQ) has a highly conjugated system and abundant π electrons, which can give effective electron delocalization, so that it is usually considered to be a powerful electron acceptor,[11] which could increase the electrical conductivity of the adsorbates.[12] In addition, TCNQ and its anion have exhibited excellent electrical and magnetic performances.[13,14] As a large aromatic molecule, TCNQ has strong π–π stacking interactions with carbon nanotubes.[15] On the other hand, TCNQ can be easily reduced to form the TCNQ anion, so negative charges of adsorbed TCNQ anion on graphene can effectively prevent the inter- or intra-π–π stacking of graphenes, leading to dispersion of functionalized graphenes. In this communication, we report the preparation of water-soluble/organic-solvent-soluble graphene by using TCNQ anion as a stabilizer and expanded graphite as a starting material.

In a typical procedure, expanded graphite was prepared by modifying the method of Dai *et al.*[10] Commercial expandable graphite[16] (average diameter of 300 μm, 99% purity, Beijing Invention Biology Engineering & New Material Co. Ltd, Beijing) was rapidly heated to 1000 °C and maintained for 60 s under the atmosphere of forming gas (4% H_2 and 96% Ar). The resulting expanded graphites (1 mg) were mixed with TCNQ (2 mg) by using a mortar and pestle for about 10 min,[17] then several drops of dimethyl sulfoxide (DMSO, ~0.5 mL) were added. Subsequently the mixture was maintained at room temperature for 12 h. Afterwards, the mixture was dried under vacuum at 80 °C for 6 h. The resulting solid powders were dispersed in deionized water solution (5 mL) consisting of KOH (50 mg), after sonication for 90 min, finally forming a black suspension. The non-fully exfoliated graphite and extra TCNQ were removed by centrifugation. The supernatant solution composed of single or few-layer graphene sheets was used for characterization.

Fig. 1 schematically illustrates the formation process of aqueous dispersion of chemical exfoliated graphene sheets. First of all, the expandable graphite was heated at 1000 °C to obtain the loose expanded graphite. With the aid of intensive polar solvent (DMSO), which could dissolve TCNQ effectively, TCNQ was diffused to the inter-layer of expanded graphite and adsorbed on the surface by π–π stacking interactions. Finally, upon addition of KOH aqueous solution, TCNQ was reduced to TCNQ anion.[18] After sonication, single and few-layered graphene peeled off from expanded graphite, TCNQ anion could adsorb with graphene sheets and stabilize them in water. Furthermore, the functionalized graphene could also be stably dispersed in other intensive polar solvents such as *N*,*N*-dimethylformamide (DMF) and DMSO, but was not soluble in anhydrous ethanol (Fig. 1d). The adsorbed TCNQ anions lead to the solubility of graphene in polar solvents. According to the report,[10] ~0.5 wt% of the

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Department of Advanced Materials and Nanotechnology, College of Engineering, Peking University, Beijing, 100871, China. E-mail: hou@pku.edu.cn; Fax: +86 10-82529028

† These authors contributed equally to this work.

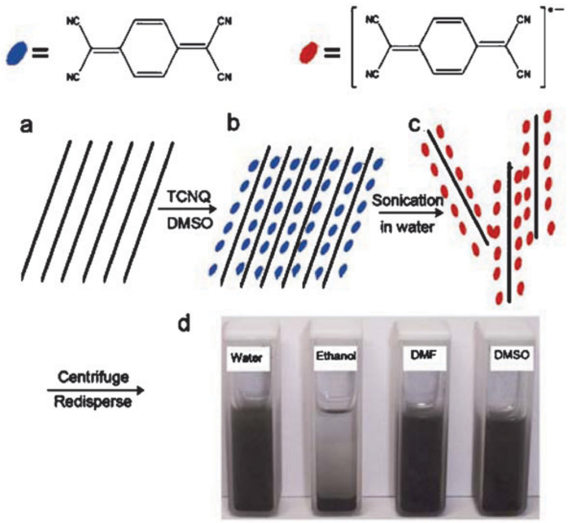

Fig. 1 Schematic illustration of aqueous graphene dispersions stabilized with TCNQ anion. (a) pristine expanded graphite by heating expandible graphite at 1000 °C; (b) TCNQ insertion into the intercalated graphite by the aid of DMSO; (c) after durative sonication, TCNQ-anion-stabilized graphene in water; (d) photograph of TCNQ anion adsorbed graphene dispersed in different solvents: water, ethanol, DMF, DMSO.

expanded graphite can be converted to small pieces of single and few-layer graphene. In our case, the yield of aqueous graphene depends on the output of graphene sheets exfoliated from expanded graphite. By measuring the weight of centrifuged samples, the concentration of graphene redispersed is estimated to be about 15 ~ 20 μg mL^{-1} in each solvent. What is more important is that we propose an effective way to produce aqueous dispersed graphene using TCNQ anion as a stabilizer.

Transmission electronic microscopy (TEM) and electron diffraction (ED) images of typical TCNQ-stabilized graphene sheets are shown in Fig. 2. Large amount of isolated graphene sheets with various dimensions were observed and some of them overlapped on the edges (Fig. 2a). Small quantities of graphene nanoribbons were also obtained (Fig. 2b). The corresponding ED pattern clearly reveals the typical six-fold symmetry diffraction patterns, which is ascribed to graphite/graphene (Fig. 2c).[19] TEM images indicate that durative sonication could mechanically break the graphene sheets into small pieces, and then we are able to make homogenous dispersions of graphene with the aid of adsorbed TCNQ anion. Note that there is no apparent coiled graphene sheet, which is also attributed to the adsorbed TCNQ anion.

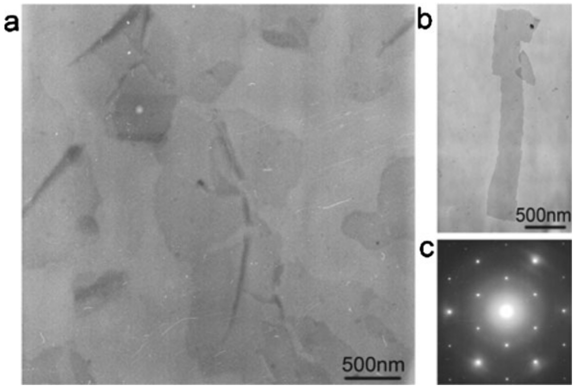

Fig. 2 TEM and ED images of graphene sheets: (a) several isolated graphene sheets; (b) a typical graphene ribbon; (c) the corresponding ED.

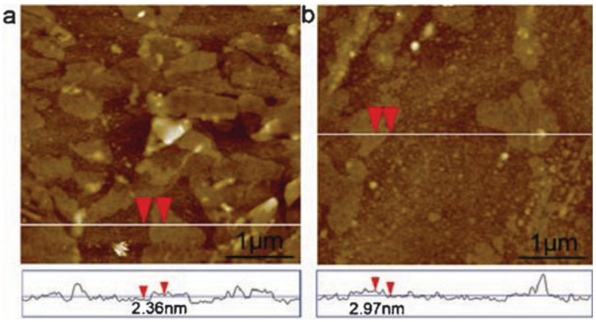

Fig. 3 AFM height images of numerous graphene sheets by tapping mode. (a) one of these graphene sheets is about 2.36 nm thick; (b) another graphene sheet is about 2.97 nm thick.

We used atom force microscope (AFM) to measure the thickness of exfoliated graphene sheets, the topographic heights were between 2 and 3 nm, as shown in Fig. 3. Considering the TCNQ anion adsorbed on both sides, and the monolayer crumpled ripples owing to thermal fluctuations,[20] the exfoliated graphene sheets were about 2–3 layers. The lateral dimensions of graphene range from several hundred nanometres to a few micrometres.

Raman spectroscopy is usually used to investigate the vibrational properties of carbon structures, it allows us to determine its crystallization. The peak at ~1582 cm^{-1} (G band) corresponding to an E_{2g} mode of graphite is related to the vibration of sp^2-bonded carbon atoms in a 2-dimensional hexagonal lattice, while the peak at ~1352 cm^{-1} (D band) is assigned to the defects and disorders in the hexagonal graphitic layers.[21] The Raman spectrum of the expanded graphite displays very small D bands, indicating the perfect crystallization (Fig. 4b). However, as to the exfoliated graphene sheets, the value of I_D/I_G is significantly reduced (Fig. 4a), it might be due to the structural defects resulting from the increase of the boundary edges of graphene sheets.

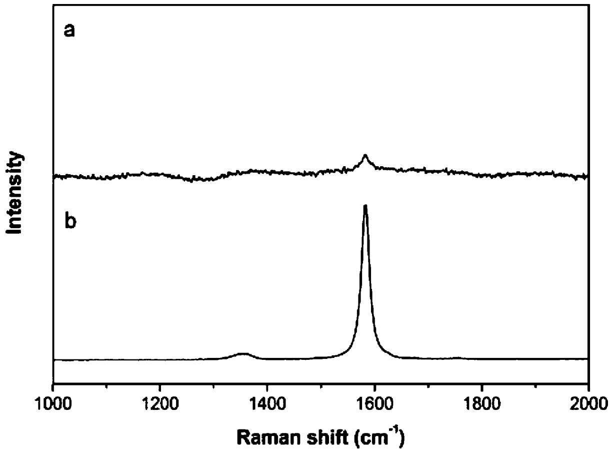

Fig. 4 Raman spectra of TCNQ-adsorbed graphene and expanded graphite: (a) TCNQ-adsorbed graphene; (b) expanded graphite.

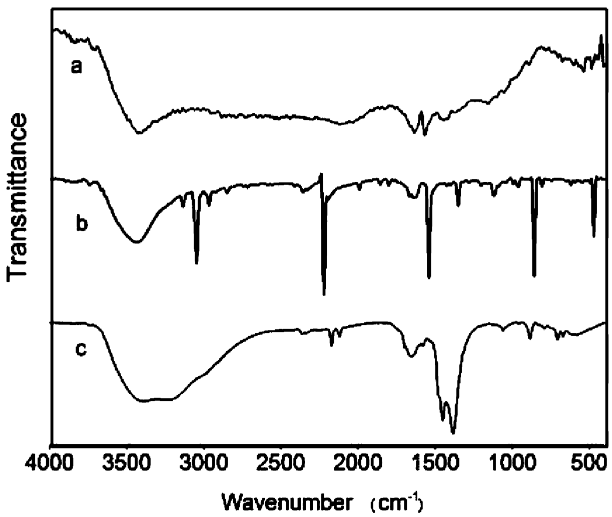

Fig. 5 FTIR spectra of (a) pristine expanded graphite; (b) TCNQ; (c) TCNQ-anion-adsorbed graphene.

To investigate the adsorption of TCNQ on the graphene, FTIR characterization is performed. In the FTIR spectrum of pristine expanded graphite (Fig 5a), TCNQ (Fig 5b) and TCNQ-anion-stabilized graphene (Fig 5c), one can see that the neutral TCNQ exhibits the characteristic vibration frequencies of the cyanic group at 2223 cm^{-1}, while for the TCNQ-anion-functionalized graphene, we observed two peaks for cyanic group at 2170 cm^{-1} and 2118 cm^{-1}, indicating the presence of the TCNQ anion.[22] The peak at 1388 cm^{-1} was assigned to the vibration of the C–H bond of TCNQ. Broadening of the peak may be due to the adsorption to graphene.

In summary, we present a chemical route to prepare the TCNQ-anion-stabilized graphene sheets, which can be dispersed in water, and other highly polar organic solvents such as DMF and DMSO. Our method provides a facile production route for high quality water-soluble and organic-solvent-soluble graphene sheets from expanded graphite. Considering the unique electrical and magnetic properties of both TCNQ and graphene, the composites could exhibit enhanced physical properties. A performance study of TCNQ-stabilized-graphene is underway.

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