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Low-temperature exfoliation of multilayer-graphene material from $FeCl_3$ and CH_3NO_2 co-intercalated graphite compound†

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Microwave induced rapid decomposition of nitromethane at low temperature exfoliates the graphene sheets from the $FeCl_3$ and CH_3NO_2 co-intercalated graphite compound without creating many defects and functional groups. This approach provides a scalable method for high-quality graphene materials *via* low-temperature exfoliation of graphite under mild chemical conditions.

Since the discovery of the exceptional electronic properties of graphene in 2004,[1] the unique mechanical, thermal, electrical, and chemical properties of graphene materials have attracted the attention of researchers from different fields.[2,3] The large demand for high-quality graphene materials makes the synthesis of graphene one of the key steps to meet various research needs.[4] Graphenes are currently produced through bottom-up and top-down approaches. The bottom-up approach is the chemical synthesis from small molecules including chemical vapor deposition (CVD),[5–7] epitaxial growth,[8] and chemical reduction of ethanol followed by pyrolysis.[9] Although the chemical synthesis from small molecules could provide almost perfect large single sheets,[6–8] its scalability is hindered by either the use of catalytic substrates or harsh synthetic conditions.[9] The top-down approach uses graphite as starting materials. Large quantities of inexpensive graphite materials make massive production of graphene through exfoliation practical. The chemical or physical exfoliation of graphite is a straightforward method to produce graphene with least synthesis effort, since it takes advantage of the existing graphene structure in crystalline graphitic materials. Many research efforts focus on the exfoliation of graphite by weakening the van der Waals forces of adjacent graphene sheets through chemical reactions or intercalation. The generally practiced Hummers method[10] is an exemplary case of producing graphene sheets by chemically weakening the intermolecular interactions. In this method, the graphite is oxidized while breaking the aromaticity of graphene and functionalizing the honeycomb carbon framework with oxygenated groups. However, the strongly oxidizing conditions produce a significant amount of heteroatoms (oxygen, sulfur, nitrogen *et al.*) and other functional groups.[11–13] Even for a mild oxidative treatment (soaking in oleum), the oxidation is non-negligible.[14] The structural defects thus generated disrupt the electronic structure of graphene, resulting in an electrical conductivity several orders of magnitude lower than that of pristine graphene.[15] In addition, these defects cannot be removed completely, even after annealing at 1100 °C,[16,17] possibly due to the highly stable carbonyl and ether groups still residing in the material.[11]

We demonstrate herein, the exfoliation of graphite intercalation compounds (GIC)[18–21] by a method that circumvents the dramatic structural changes of graphene brought about by irreversible chemical functionalization. The method holds the promise for massive production of graphene with a low concentration of defects *via* a low-temperature, mild exfoliation approach.

We found that $FeCl_3$ and nitromethane (CH_3NO_2) co-intercalated graphite[22–24] can be readily exfoliated to graphene sheets at the boiling temperature of water by heating in a microwave (MW) oven. As a mild oxidant, $FeCl_3$ facilitates the intercalation of nitromethane into graphite without degrading the integrity of the graphene sheets.[22–24] The rapid heating to high temperature[19] is avoided; therefore, the resultant graphene sheets are likely less defective than those produced by thermal shock. The essence of this method is the rapid decomposition of nitromethane to gaseous products including NH_3, HCOOH, NO_2, H_2O and CO_2[25] expanding within the galleries of graphene sheets. The mechanical force from the gas expansion overcomes the already weakened van der Waals forces and thus leading to the formation of graphene sheets. Being an important explosive monopropellant, the decomposition of CH_3NO_2 has been widely studied.[25,26] At certain pressure conditions, CH_3NO_2 decomposes to NH_3, HCOOH, NO_2, H_2O and CO_2 and produces a shock-wave through intermolecular interactions and energy-transfer at low temperatures (<150 °C).[25] The confinement of nitromethane within the galleries of graphene sheets facilitates the intermolecular interactions and thus eases its decomposition.

The heating by microwave radiation could be another factor leading to the decomposition of nitromethane. In this reaction,

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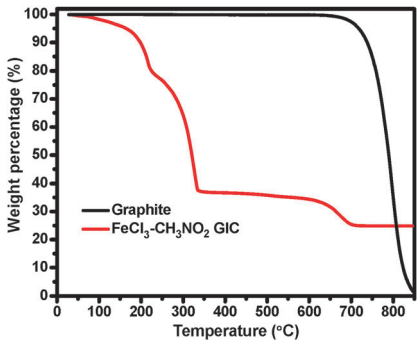

Fig. 1 Thermogravimetric analysis of natural graphite (black line) *vs.* $FeCl_3$–CH_3NO_2 GIC (red line) in air at 10 °C min^{-1}.

the temperature was controlled at the boiling temperature of water by dispersing the $FeCl_3$–CH_3NO_2 GIC in deionized water where the particles were microwaved. The low temperature character of the microwave wet-heating process is crucial since microwave-heating of the dry particles would lead to an uncontrollable combustion of the $FeCl_3$–CH_3NO_2 GIC. The heating by microwave radiation has a prominent effect on the exfoliation of the $FeCl_3$–CH_3NO_2 GIC. Heating of the $FeCl_3$–CH_3NO_2 GIC in boiling water or in a tube furnace that was ramped at 10 °C min^{-1} to 500 °C does not produce thin sheets of graphene. The $FeCl_3$–CH_3NO_2 GIC loses weight in a broad temperature range while graphite is stable up to 650 °C (Fig. 1). The first weight loss of $FeCl_3$–CH_3NO_2 GIC starts at 85 °C corresponding to the vaporization of CH_3NO_2 absorbed on the carbon surface or the interstitial spaces formed during the intercalation.[24] Signals of CH_3NO_2, HCOOH, NO_2, H_2O and CO_2 were detected at temperatures below 325 °C by a mass spectrometer that was attached at the exhaust of the TGA (Fig. S1, ESI†). Apparently, these chemical species are the debris of the thermally decomposed CH_3NO_2. The GIC loses about 20% of weight at a temperature below 216 °C. The most significant loss of the GIC sample occurs from 216 to 325 °C, which is considerably higher than the boiling temperature of nitromethane. Given the high volatility of nitromethane, the retarded evolution of nitrogen containing gaseous species is a piece of strong evidence of the intercalation of nitromethane in graphite.

It is noteworthy that the exfoliation of the $FeCl_3$–CH_3NO_2 GIC by microwave radiation occurs at the boiling temperature of water, which is much lower than that of the decomposition of nitromethane at TGA heating condition. We believe that the decrease of the decomposition temperature of the intercalated CH_3NO_2 under microwave radiation is caused by the pressure built up through rapid heating of the solvent trapped within the interstitial spaces of the partially exfoliated graphite layers. At high pressure, CH_3NO_2 decomposes explosively at much lower temperatures.[25] Therefore, the rapid heating under microwave radiation induces the decomposition of nitromethane at lower temperature and favors the exfoliation of graphite. The weight loss at a temperature higher than 325 °C is attributed to the decomposition of $FeCl_3$. Complete gasification of carbon is observed at temperatures between 600 and 700 °C. The 25% residual mass remaining after the TGA analysis is Fe_2O_3. There is no doubt that excess $FeCl_3$ exists and mixes with the GIC. Long time heating of graphite in concentrated $FeCl_3$/nitromethane solution at the refluxing temperature of nitromethane results in partial exfoliation of graphite as observed by Hooley.[24] It is possible that the excess $FeCl_3$ resides in the interstitial spaces of particles.

Evidence for the exfoliation of the $FeCl_3$–CH_3NO_2 ternary GIC is the complete disappearance of peaks in the powder X-ray diffraction (XRD) (Fig. S2, ESI†). The characteristic graphite [002] and [004] peaks disappeared after intercalation, suggesting the native graphite stacking structure was not retained, further confirming the low stage number of $FeCl_3$–CH_3NO_2 ternary GIC estimated by TGA, although mixed phases of stage 3 are observed in the Raman spectra (Fig. 2 and Fig. S3, ESI†).[22]

The Raman spectrum of the graphene sheets from the exfoliated $FeCl_3$–CH_3NO_2 GIC confirms that this graphene material has a low level of defects (Fig. 2).[27,28] A typical spectrum of single graphene is mainly characterized by the D, G and 2D bands.[28,29] Similar to the starting natural graphite, the absence of a D band in the spectrum of GIC indicates that the intercalation process does not result in detectable defects on the graphitic basal plane. A barely noticeable D band was observed after microwave treatment. This D band peak is likely arising from the edges of the randomly distributed graphene sheets or small defects (if there are any) generated during the exfoliation process.[30] This small D band also proves that the resultant graphene material has a very low level of functional groups. The low level of functional groups is attributed to the low-temperature process and the mild chemicals evolved during the reaction that could not react with the graphene sheets. The G band of the natural graphite shows one single peak whereas the G band of the resulting $FeCl_3$–CH_3NO_2 GIC splits into two peaks with the major peak upshifted by about 30 cm^{-1}. Although the split G band indicates the presence of stage 3 or upwards compounds,[22,31,32] the intensity ratio of the upshifted peak to the base peak is 3.2, which is higher than the theoretical value of the stage 3 compound. Therefore, the resulting $FeCl_3$–CH_3NO_2 GIC is a mixed phase of stage 3 and lower stage compounds.[31–33] After microwaving and repeated HCl washing, the exfoliated GIC shows a singlet G band, indicating the complete removal of intercalants. It is interesting that even trace amount of the residual intercalants in the exfoliated GIC could result in the G band splitting. This phenomenon could be useful for checking the purity of the exfoliated graphene

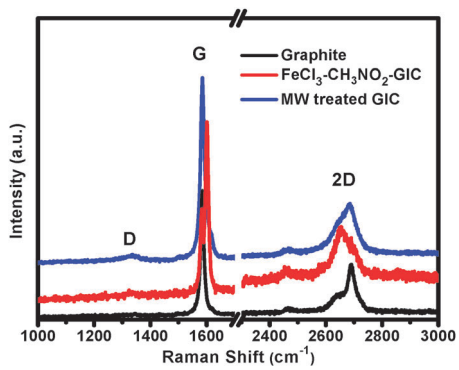

Fig. 2 Raman spectra of natural graphite, $FeCl_3$–CH_3NO_2 GIC and exfoliated GIC.

material (Fig. S3, ESI†). The 2D band (also known as G′ band in literature) is well known as a "fingerprint" area for identification of graphene.[28] The 2D band of the exfoliated sample distinguishes itself from its precursors, the natural graphite and the GIC. Although the 2D band of graphite, GIC, and exfoliated sample show asymmetric peaks that can be well fitted by two Lorentzian components (Fig. S4, ESI†), the intensity ratio of the components are different. The number of graphene layers is correlated to the symmetry and the position of the 2D band. The position and symmetry of 2D band of the exfoliated sample suggests that the number of graphene layers in the material is around five (see ESI†).[29] The restacking of graphene layers after the deinsertion and the high stage number impurity phases of GIC are most likely the cause of the multilayered graphene material resulting from this ternary intercalation compound. The exfoliation of GIC is also confirmed by micrographs presented in Fig. S5 and described in ESI†).

In summary, we have demonstrated a convenient, scalable method for the production of high-quality graphene material through the exfoliation of $FeCl_3$–CH_3NO_2 GIC using microwave heating. The use of mild chemicals and a low processing temperature are crucial to the formation of graphene sheets with low quantities of defects or functional groups. The method was realized by taking advantage of rapid decomposition of nitromethane, confined in the galleries of graphite, through microwave radiation. The decomposition temperature of nitromethane in $FeCl_3$–CH_3NO_2 GIC varies with the heating method. The rapid heating of the GIC by microwave radiation decreases the decomposition temperature of nitromethane by about 100 °C. At such a low temperature the chemicals used in this synthesis could not react with graphene. Hence, the graphene materials are less defective and almost free of functional groups. This approach therefore provides a scalable route to large quantities of low-defect, high-quality graphene.

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