Deoxygenation of Exfoliated Graphite Oxide under Alkaline Conditions: A Green Route to Graphene Preparation**

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Graphene[1] – a flat monolayer of carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice – is the basal building block in all graphitic materials.[2] Since it was first reported in 2004,[1] graphene has attracted great interest because of the unique electronic,[3–10] thermal,[11] and mechanical properties[12,13] arising from its strictly 2D structure, and to its potential technical applications.[2,13–16] However, producing graphene on a large scale using existing mechanical methods is still unfeasible. Searching for alternative chemical approaches is an urgent matter.[17] However, the hydrophobic nature of graphene and its strong tendency to agglomerate in solvents[13] present a great challenge to the development of fabrication methods, and severely restrict its promising applications. Although the mechanism involved remains unproven,[18] the chemical reduction of readily available exfoliated graphite oxide (GO) with reducing agents such as hydrazine and dimethylhydrazine is a promising strategy in the large-scale production of graphene.[13,18,19] Unfortunately, the reducing agents involved are very hazardous, and the graphene obtained presents irreversibly agglomerated features in solvents that do not contain polymer surfactants.[13] Here, we report a new green route for the synthesis of processable graphene on a large scale.

We observed that a stable graphene suspension could be quickly prepared by simply heating an exfoliated-GO suspension under strongly alkaline conditions at moderate temperatures (50–90 °C) (Figure 1a). Our initial purpose was to introduce functional groups to exfoliated GO by free-radical addition.[20] Surprisingly, the addition of NaOH to the GO suspension – to improve the solubility of the alkyl free-radical initiator, which is carboxyl-terminated – was accompanied by a fast, unexpected color change (from yellow-brown to homogeneous black). Careful experiments revealed that exfoliated GO can undergo fast deoxygenation in strongly alkaline solutions, resulting in stable aqueous graphene suspensions (Figure 1b). Typically, 150 mL of exfoliated-GO suspension (0.5–1 mL mg⁻¹) and 1–2 mL NaOH or KOH solution (8 M) were loaded into a jacketed vessel, with hot water circulating through the outer chamber (Figure 1S, Supporting Information). The temperature of the circulating water was constantly controlled by a temperature circulator, and the whole vessel was subjected to mild sonication (25 W, 40 KHz). The yellow-brown exfoliated-GO suspension became black after it was kept at the desired temperature (e.g. 80 °C) for a few minutes.

The 13C NMR spectrum of the GO (Figure 2a) confirms the presence of abundant epoxide and hydroxyl groups,[21] which should align perpendicular to the basal-plane carbon atoms. The carboxyl groups, which are located at the edges of the basal plane, are too few for 13C NMR detection, in agreement with previous studies[21] on GO prepared by the Hummers method.[22] After the reaction, however, the exfoliated GO (Figure 2b) showed a significant reduction in the amount of epoxide and hydroxyl groups present. In addition, plentiful sp² carbon atoms were introduced, as indicated by the increase in the peak at 90–150 ppm, suggesting the formation of graphene-based materials. This result is confirmed by X-ray photoelectron spectroscopy (XPS) analysis (Fig. 3), which shows that the O/C ratio in the exfoliated GO decreases remarkably after the reaction (Figure 3a, b), and that most of the epoxide and hydroxyl functional groups were successfully removed (Figure 3c, d). Remarkably, the π → π* shake-up satellite peak around 291.5 eV (C 1s spectrum, Figure 3d), a characteristic of aromatic or conjugated systems, resumes after reaction. These results, combined with X-ray powder diffraction (XRD) and thermogravimetric analysis (TGA) (Figures 3S and 4S in the Supporting Information), indicate the formation of graphene.

The graphene suspensions obtained showed impressive long-term stability (several days), which is desirable for processing. Considering the incomplete removal of the negatively charged oxide functional groups, this stability can be attributed to a strengthened electrostatic stabilization under alkaline conditions, as the repulsion between negatively charged graphene sheets should increase at higher pH values. Similar results have been observed recently by Wallace et al.[23]

The single-sheet nature of the graphene obtained is confirmed by atomic force microscopy (AFM, Figure 4). The thickness of the graphene sheet obtained is about 0.8 nm, matching well with the reported apparent thickness of
single-sheet graphene. Note that this value is smaller than the thickness of the exfoliated graphene oxide before deoxygenation (about 1.2 nm, Figure 6S in Supporting Information), as a result of the removal of the oxide groups. However, this value is still somewhat larger than the theoretical thickness for a perfectly flat sp²-carbon-atom network, which is attributed to the intrinsic out-of-plane deformation of graphene as well as to the instrumental offset arising from different interaction forces between the AFM probe, the graphene sheet, and the substrate.

Although the underlying mechanism remains unclear, the deoxygenation of exfoliated GO under alkaline conditions appears to be the reverse of the oxidation reaction of graphite in strong acids. This mechanism is supported by the pH dependency of this deoxygenation reaction – the higher the pH of the exfoliated-GO suspension, the faster the reaction. Notably, the reaction can even start at temperatures as low as 15°C when the pH of the suspension is high enough (Supporting Information). This interesting reaction provides...
an explanation for the “chemical reduction” of exfoliated GO, as the reducing agents used (e.g., hydrazine and dimethylhydrazine)\cite{5,13,18,19,23,28} are intrinsically strong alkalis.

In summary, we found that exfoliated GO can undergo quick deoxygenation in strong alkali solutions at moderate temperatures. This interesting reaction provides a green route to the synthesis of graphene with excellent dispersibility in water. Considering that sodium hydroxide of nontoxic nature is readily available, this study opens an exciting opportunity for the production of graphene on an industrial scale.

### Experimental

#### Preparation

GO was prepared and purified according to the Hummers method [21]. A suspension was obtained by dispersing purified GO in distilled water (concentration 2 mL mg\(^{-1}\)) with the aid of intensive sonication (100 W, 40 KHz, 1 h). To prepare an aqueous graphene suspension, 150 mL of the yellow-brown exfoliated-GO suspension (0.5–1 mL mg\(^{-1}\)) and 1–2 mL NaOH or KOH solution (8M) were loaded into a jacketed vessel (Figure 1S) with hot water circulating through the outer chamber. The temperature was strictly controlled by a constant temperature circulator, and the whole vessel was subjected to mild sonication (25 W, 40 KHz). The original yellow-brown suspension turned black after it was heated for a few minutes at the desired temperature (50–90 °C). The final suspension was then allowed to cool to room temperatures. Solid graphene samples for characterization were obtained by intensive centrifugation (23 000 \(g\), 2 h) of the final suspension, followed by washing with distilled water, and freeze-drying.

#### Characterization

\(^{13}\)C NMR (300 MHz) spectra were collected using a Varian Infinity Plus 300WB. XPS was performed using a PHI 1600 spectrometer (Perkin–Elmer). AFM images were acquired in tapping mode in air using a Digital Instrument Dimension 3100. XRD was carried out in a PANalytical X’Pert PRO X-ray diffractometer with Co Kα radiation. TGA was performed on a NETZSCH TG 209 under nitrogen flow with a heating rate of 10 °C min\(^{-1}\). The pH values of the suspensions were measured using a pH meter (Ecoscan pH6).

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