Supplementary data

Graphene oxide induced fast curing of amino novolac phthalonitrile

Temina Mary Robert*, Dhanya Augustine, SatheeshChandran M, Dona Mathew and C.P. Reghunadhan Nair

^{*a*} Polymers and Special Chemicals Group Vikram Sarabhai Space Centre, Trivandrum-695022

Email: temirobert@gmail.com Tel:+91-0471-2564777 Fax: +91-0471-2564203

Synthesis of graphene oxide

Graphene oxide was synthesized from graphite flakes via a modified Hummer's method [1, 2]. The graphite flakes (3g, 2–5mm in lateral size) were first incubated in H2SO4 (98%, 12 ml) at 80°C for 3 h. It was cooled and sonicated in a water bath for 2 h and the solution was diluted with de-ionized (DI) water. The pre-oxidized graphite powder was extracted by filtering the solution in deionized water using 150nm Nylon Millipore filters, followed by repeated washing with DI water and dried. The pre-oxidized graphite (3.0g) was added to KMnO4 (20.0g) and NaNO3 (2.5g) and cooled to 4°C followed by slow addition of H2SO4 (80.0g) under ice-bath cooling and stirred for 2 h. The solution was then diluted in deionized water (250 ml), and H2O2 (50 ml, 30%) was added at room temperature and allowed to settle. The supernatant was collected by centrifugation. The metal ions existing in the GO powders were removed by treating with dilute HCl (10% by volume) followed by centrifugation. The GO powder so collected was washed several times with DI water to remove the excess acid. Finally the product was collected by centrifugation and dried under vacuum at 80°C for 24 hr. The product was characterized by FTIR, Raman Spectroscopy, XRD and TEM.

Characterization of graphene oxide

The FTIR spectrum of graphene oxide (Fig. 1) confirms the presence of epoxy and hydroxyl groups and Graphite shows practically any absorption. The absorptions corresponding to O–H,-C-H and C–O stretching vibrations were observed at 3437 cm⁻¹, 2927 cm⁻¹ and 1031 cm⁻¹ respectively. Absorption at 916cm⁻¹ confirms the presence of epoxy groups.



Fig 1. FT-IR spectrum of Graphite and GO

A Nd /YAG laser source of 532nm wavelength with an optical power density of 24Mw and a spot size of 1 µm² were used to record the Raman spectra for both the samples at room temperature and 5-7 accumulations per sample were collected with a grating system of 600grooves/mm. The Raman spectrum of GO(Fig 2.) showed the existence of D and G band, which are ascribed to the breathing mode of k-point phonons of A1g symmetry and the first order scattering of the E2g phonon of sp² C atoms respectively[3]. The spectrum of graphite shows peaks at 1348 cm⁻¹ (corresponding to D band), 1580 cm⁻¹ (corresponding to G band) and 2722 cm⁻¹ (corresponding to 2D band) whereas the GO exhibited peaks at 1342, 1569, 2666 cm⁻¹ corresponding to D, G and 2D bands respectively. The prominence of D band at 1340cm⁻¹ due to the breaking of symmetry is evident in the GO as expected. The 2D peak of graphene oxide has undergone a red shift from 2722(of graphite) to 2669cm⁻¹ [4]. The intensity ratio ID/IG between the D band and G band is often used to quantify the defects in graphitic materials. Graphite shows a small D band and a strong G band, with an ID/IG ratio of 0.03. For graphene oxide, an increased ID/IG ratio (0.34) and I2D/IG ratio (0.31) were observed compared to pristine

graphite. Attachment of organic functional groups changes some carbon atoms from sp² to sp³ and therefore results in an increased ID/IG ratio, which indicates successful covalent functionalization [5, 6, 7].



Fig 2. Raman spectra of (a) Precursor graphite flakes and (b) GO

XRD patterns of graphite flake and GO are shown in Fig. 3. In the X-Ray diffractogram, the intense 20 peak at 26.2 ° observed in the case of graphite has diminished and a sharp 20 peak appeared at 10.8° for GO which corresponds to an interlayer spacing of $d= 8.10 \text{ A}^\circ$. The enlargement in interlayer distance in GO by around 2.45 folds when compared with pristine graphite (d=3.31 A°) is an evidence for the introduction of oxygen-containing functional groups on the surface of graphite on oxidation resulting in an expansion of the layered structure.



Fig 3. XRD of Graphite and GO

Fig 4shows the TEM images of folded graphene oxide sheet, and the regularly ordered selected area diffraction

pattern indicates that it is monolayered.



Fig 4. a) TEM image of a single folded sheet of GO and b) selected area electron diffraction (SAD)

patterns for single-layer GO

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