

Graphene composites containing chemically bonded metal oxides

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Abstract. Composites of graphene involving chemically bonded nano films of metal oxides have been prepared by reacting graphene containing surface oxygen functionalities with metal halide vapours followed by exposure to water vapour. The composites have been characterized by electron microscopy, atomic force microscopy and other techniques. Magnetite particles chemically bonded to graphene dispersible in various solvents have been prepared and they exhibit fairly high magnetization.

Keywords. Composites; oxides; thin films; electron microscopy; magnetic properties.

1. Introduction

After the discovery of graphene (Novoselov *et al* 2004; Geim and Novoselov 2007; Rao *et al* 2009; Rao and Sood 2013), there has been considerable research in the area of two-dimensional materials, many of which are based on inorganic layered compounds (Novoselov *et al* 2005; Matte *et al* 2010; Coleman *et al* 2011). Several workers have prepared composites of these materials and studied their properties (Wang *et al* 2008; Cao *et al* 2012). An aspect of particular interest pertains to coating thin layers of metal oxides on the graphene surfaces to prepare useful composites. Such composites may indeed possess valuable properties, specially if the oxide layers are chemically bonded to graphene (Zhang *et al* 2010). The composites can be heated to high temperatures to generate thin oxide films. With this purpose, we have carried out the reactions of metal halide vapours with the oxygenated surfaces of graphene, followed by treatment with water vapour to prepare composites containing thin oxide films chemically bonded to graphene. By burning off the graphene, we obtain free-standing oxide nano-films. Thin films of metal oxides possess superior material properties (Miyachi *et al* 2002; Kamegawa *et al* 2011). We have also prepared nanoparticles of magnetite chemically bonded to graphene to yield composites which are dispersible in many solvents.

2. Experimental

Graphite oxide (GO) was synthesized by the modified Hummer's method (Hummer and Offeman 1958). Graphene

samples were obtained from graphite oxide by thermal exfoliation in a furnace preheated to 250 °C. Figure 1 shows schematic diagram of experimental set up used for coating metal oxides onto graphene (Gomathi *et al* 2005). It consists of three glass chambers, one to contain the metal halide (TiCl₄, SiCl₄, etc), the second for graphene and the third for water. High-vacuum stopcocks interconnect the chambers, which are connected to a vacuum pump. In a typical preparation, the sample chamber is evacuated for 15 min and the metal halide vapour from first chamber was allowed to enter

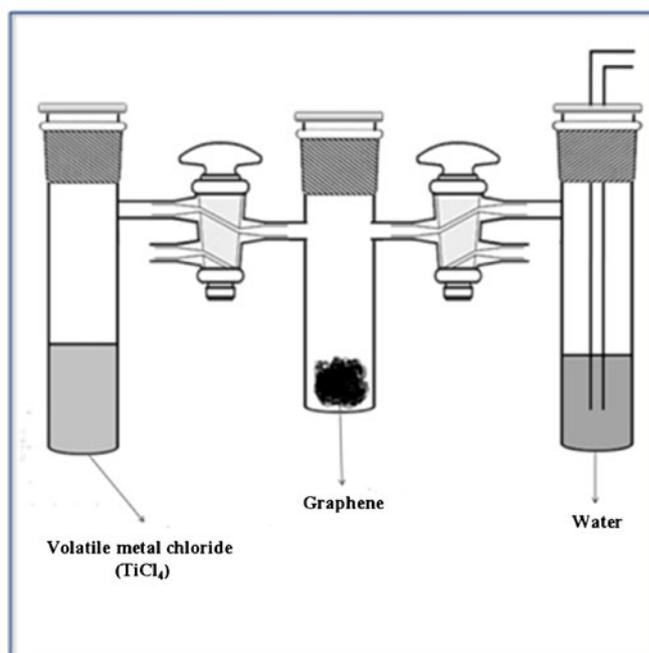


Figure 1. Schematic diagram of experimental set up.

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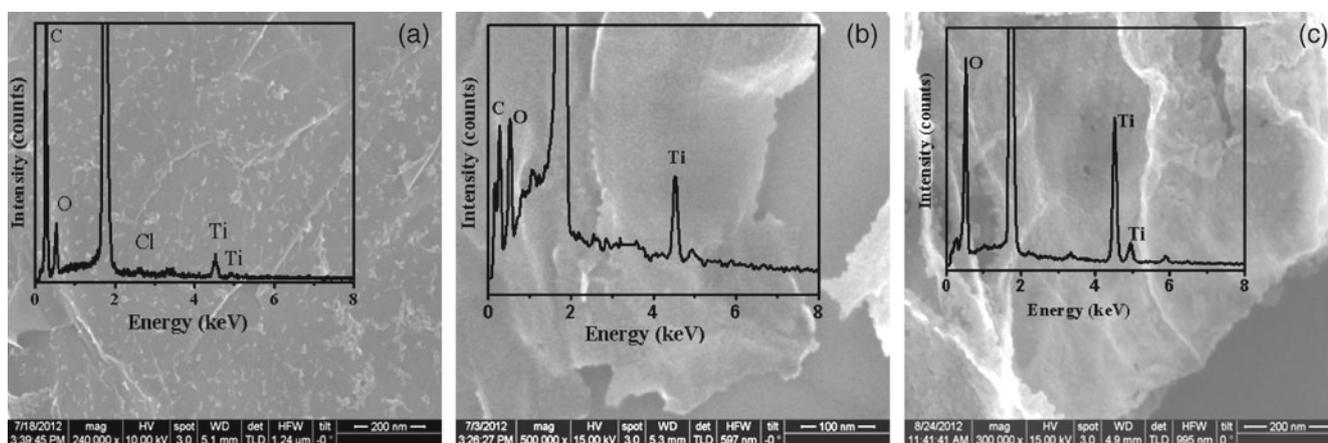


Figure 2. SEM images of (a) TiO₂-bonded graphene prepared at room temperature, (b) same sample after calcination at 350 °C and (c) TiO₂ nanosheets after removal of graphene at 600 °C. Insets show EDX patterns.

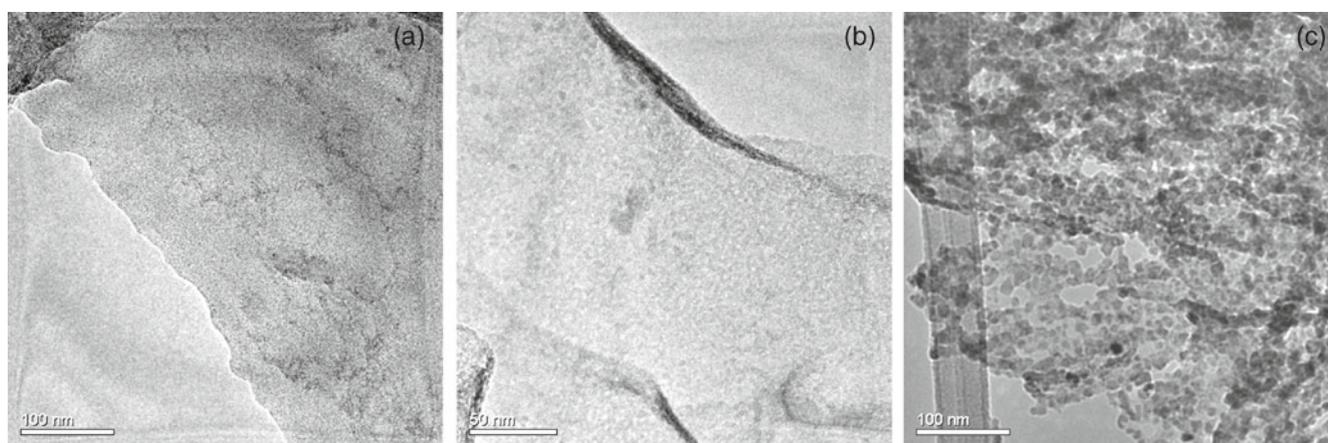


Figure 3. TEM images of (a) TiO₂-bonded graphene prepared at room temperature, (b) same sample after calcination at 350 °C and (c) TiO₂ nanosheets after removal of graphene at 600 °C.

the reaction chamber and allowed to react for 10 min, the unreacted metal halide vapour being removed by evacuation. In this step, the metal halide reacts with the oxygen functionalities on graphene giving out HCl. Water vapour from the third chamber was then passed onto the sample chamber for hydrolyzing the remaining unreacted chlorines of the metal halide. These two procedures were repeated several times. The graphene samples so obtained were heated to 350 °C to produce metal oxide coatings. In the case of TiO₂, the samples obtained after calcination at 350 °C and 600 °C for 12 h are designated as G-TiO₂-350 and G-TiO₂-600, respectively. The sample heated to 600 °C burned off the carbon giving only a thin free-standing film of TiO₂.

To prepare graphene chemically bonded to Fe₃O₄, nanoparticles of Fe₃O₄ were prepared by the method reported in the literature (Zhang *et al* 2011). In a typical synthesis, 6.5 g of 1,6-hexadamine, 2.0 g of sodium acetate and 1.0 g of FeCl₃ were vigorously stirred in 30 ml of ethylene glycol at 50 °C until a clear yellow solution was obtained. The resultant solution was transferred into a teflon-lined

stainless-steel autoclave and kept at a temperature of 200 °C for 6 h. The amine-coated Fe₃O₄ nanoparticles so obtained were reacted with graphene containing acid chloride groups (G-COCl). G-COCl was prepared by refluxing graphene oxide with excess of thionyl chloride for 12 h, the excess thionyl chloride being removed under vacuum. In a typical reaction, 20 mg of the amine-coated Fe₃O₄ was dispersed in 10 ml dry DMF and sonicated for 10 min. The suspension was added to G-COCl, sonicated for 10 min and refluxed at 70 °C for 12 h under nitrogen. The resultant solution was centrifuged and the solid product washed with water and ethanol and dried in vacuum.

X-ray diffraction (XRD) patterns were recorded with CuK α radiation using a Rich-Siefert XRD-300-TT diffractometer. FTIR spectra were recorded with KBr pellet using Bruker Tensor 27. Scanning electron microscopic (SEM) images were recorded with a FEI NOVA NANOSEM 600. Transmission electron microscopic (TEM) images were viewed with a JEOL TEM 3010 instrument fitted with a Gatan CCD camera operating at an accelerating voltage of

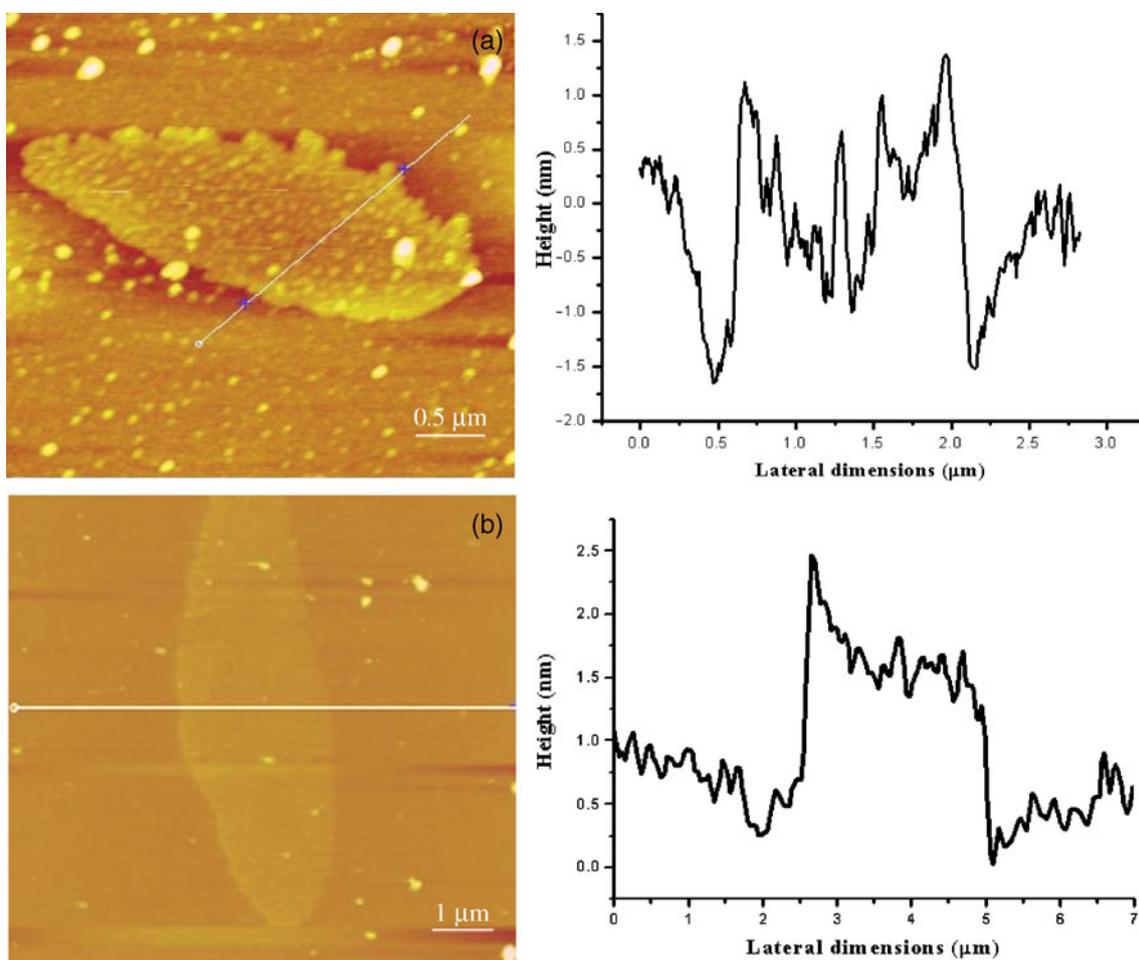


Figure 4. AFM images of (a) graphene-TiO₂ composite after calcination at 350 °C and (b) TiO₂ nanosheets after removal of graphene at 600 °C. Height profiles are given.

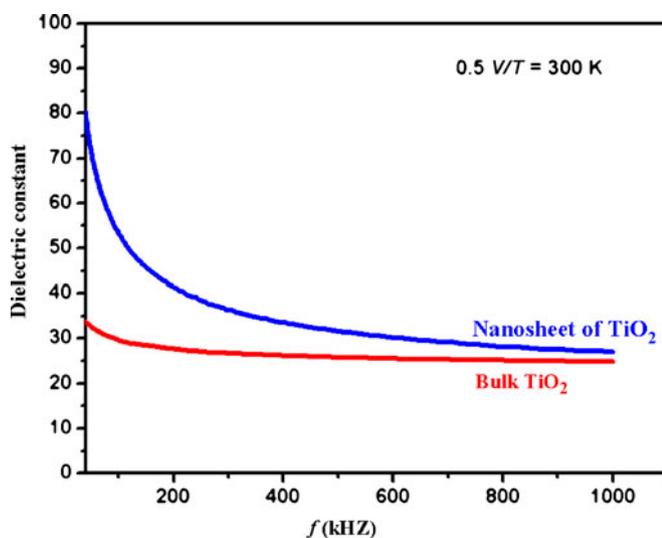


Figure 5. Frequency-dependent dielectric constant of TiO₂ nanosheets compared to bulk TiO₂.

300 kV. Atomic force microscope (AFM) measurements were performed using an Innova atomic microscope. $M-H$ measurements were performed via superconducting quantum interface device (SQUID) magnetometer at 300 K.

3. Results and discussion

The method employed by us to prepare graphene chemically bonded to metal oxide films, by employing the experimental set up shown in figure 1, gives rise to $M-O-C$ bonds. Reaction with water vapour results in hydrolysis of the unreacted chlorine, which on calcination gives oxidic species. Thus, in the case of TiCl₄, we obtain a coating of TiO₂ film on graphene by this means. The thickness of the oxide layers depends on the number of times we carry out the reaction with the metal halide. In figure 2, we show SEM images of TiO₂ chemically bonded to graphene (G-TiO₂) obtained after the reaction of TiCl₄ with graphene at room temperature and subjected to calcination at different temperatures. The energy-dispersive X-ray analysis (EDX) pattern given in the inset of figure 2(a) shows presence of Ti, O and Cl in the sample prepared at room temperature. Chlorine is absent

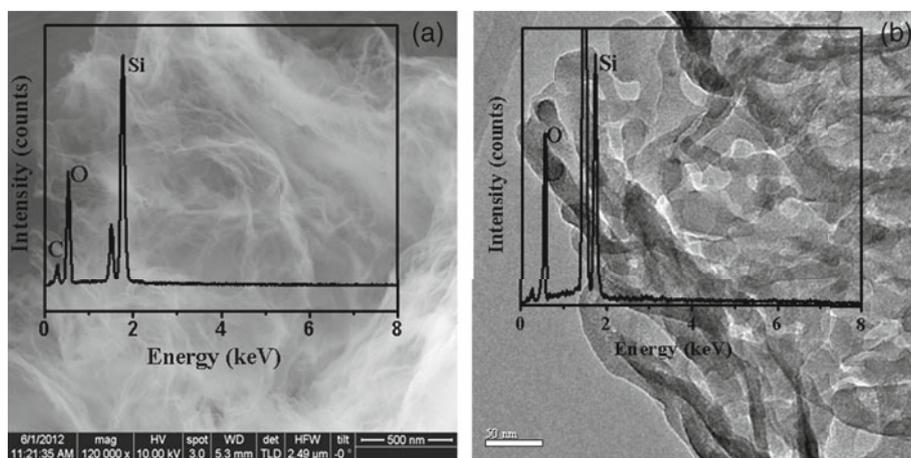


Figure 6. (a) SEM image of SiO₂-bonded graphene calcined at 350 °C and (b) TEM image of SiO₂ nanosheets obtained after calcination of SiO₂-bonded graphene at 600 °C. Insets show EDX patterns.

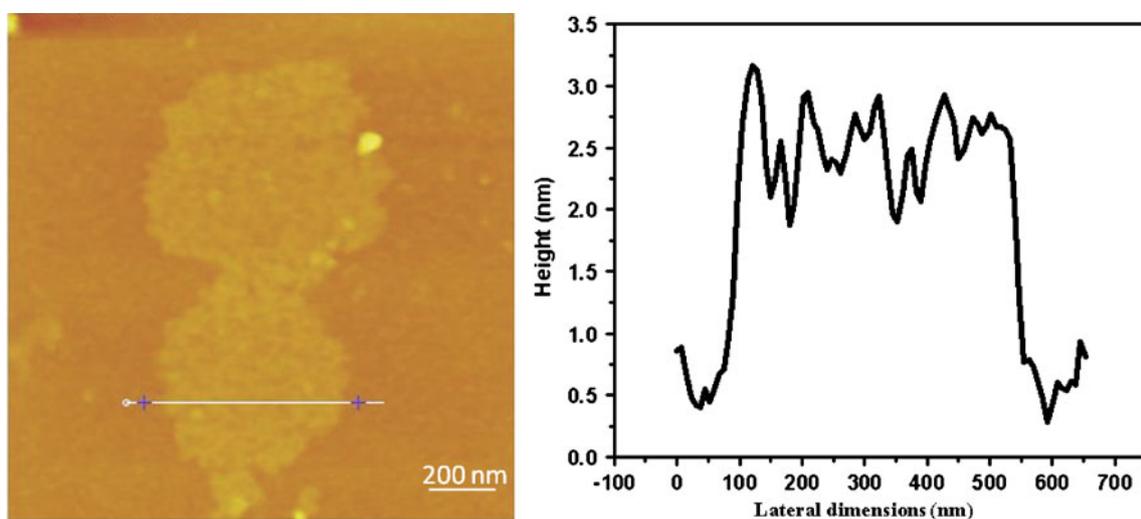


Figure 7. AFM image of SiO₂ nanosheets obtained after calcination of SiO₂-bonded graphene at 600 °C. Height profile is shown.

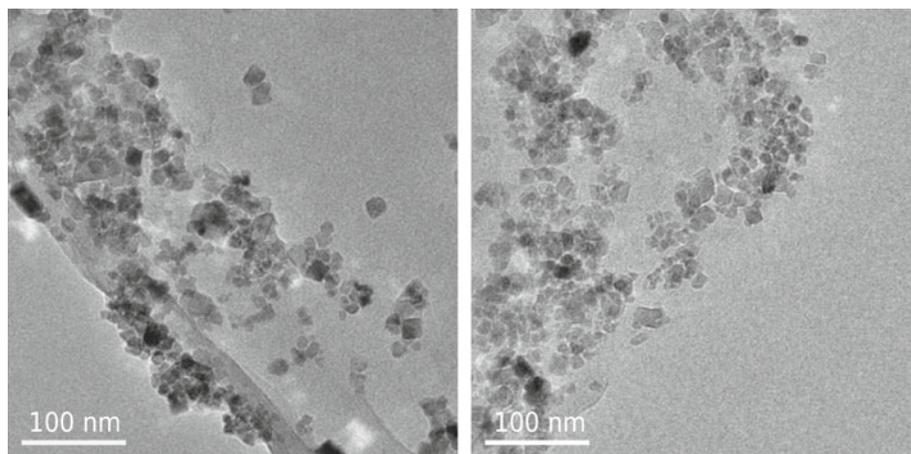


Figure 8. TEM images of GO-Fe₃O₄ composite.

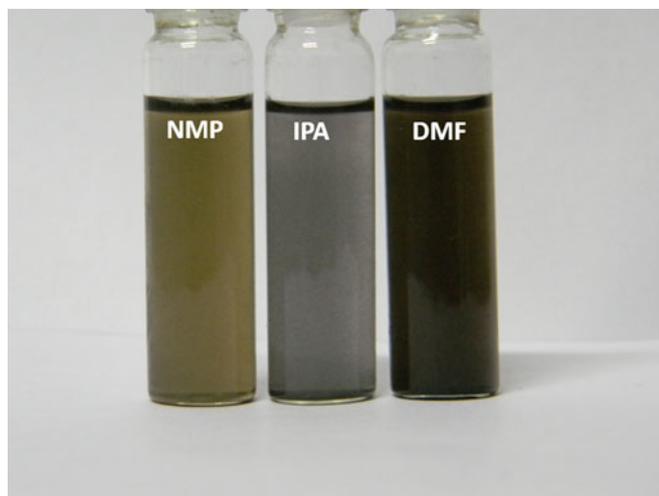


Figure 9. Dispersions of GO-Fe₃O₄ composite in different solvents.

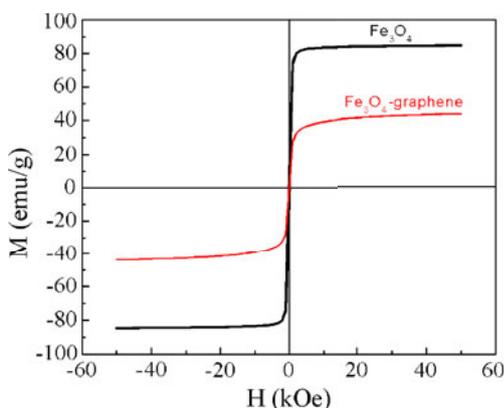


Figure 10. M - H curve of amine-functionalized Fe₃O₄ and GO-Fe₃O₄ composite.

on heating up to 350 °C. SEM image (figure 2b) of G-TiO₂ heated at 350 °C (G-TiO₂-350) for 12 h, gives an EDX pattern (see inset of figure 2b) showing the presence of only Ti and O and does not show any chlorine. In figures 3(a) and (b), we show TEM images of G-TiO₂ obtained at room temperature and at 350 °C, respectively. On calcining the TiO₂-bonded graphene composite at 600 °C for 12 h (G-TiO₂-600), the graphene sheets get oxidized, yielding TiO₂ nanosheets as shown by SEM and TEM images in figures 2(c) and 3(c), respectively. EDX pattern (inset of figure 2c) of the calcined sample confirms the presence of Ti and O. XRD patterns reveal the formation of TiO₂ in the anatase phase ($a = 3.785 \text{ \AA}$ and $c = 9.514 \text{ \AA}$) after calcination at 600 °C for 12 h.

AFM image of G-TiO₂-350 shown in figure 4(a) obtained by the calcination of the composite at 350 °C corresponds to that of graphene sheets ($\sim 0.8 \text{ nm}$) covered with TiO₂. AFM image of G-TiO₂-600 shows thickness of the oxide film to be ~ 1 – 2 nm . TiO₂ is a well known dielectric material (Hu *et al* 2010) with the bulk sample having dielectric constant

of 20–30. TiO₂ nanosheets obtained by us has a much higher dielectric constant as shown in figure 5.

Encouraged by the success of preparing TiO₂-bonded graphene, we prepared graphene bonded to SiO₂ films by using SiCl₄ as the reagent. In figure 6(a), we show a SEM image of SiO₂-bonded to graphene prepared after 10 cycles of coating and calcined at 350 °C. EDX pattern shows presence of only silicon and oxygen (see inset of figure 6a). A TEM image of SiO₂ nanosheets obtained after calcination of SiO₂-bonded graphene sheets at 600 °C is shown in figure 6(b). EDX pattern in figure 6(b) shows presence of only silicon and oxygen (see inset of figure 6b). AFM image of SiO₂-bonded graphene heated up to 350 °C gives ~ 5 – 6 nm thick film. SiO₂ nanosheets were amorphous and SiO₂ sheets obtained by calcination at 600 °C were $\sim 2 \text{ nm}$ thick (figure 7). We have also been able to bond Al₂O₃ to graphene by using AlCl₃ as the reactant. The oxide film was amorphous after calcination at 600 °C.

We have prepared chemically bonded magnetic Fe₃O₄ nanoparticles to graphene by functionalizing Fe₃O₄ by amine, then reacting it with graphene functionalized with acid chloride groups, resulting in the formation of an amide bond between the two. IR spectrum clearly shows the presence of amide carbonyl stretching band in the graphene-Fe₃O₄ composite. The morphology of GO-Fe₃O₄ composite particles is shown by TEM images in figure 8. Dense Fe₃O₄ particles are found at the edge of the sheets since graphene oxide has most carboxyl functional groups at the edges. The particle size of Fe₃O₄ is in the range of 10–15 nm. The GO-Fe₃O₄ composite can be dispersed in various solvents as can be seen from the photographs in figure 9. In figure 10, we show M - H curves of the GO-Fe₃O₄ composite. The saturation magnetization (M_s) of GO-Fe₃O₄ is 43.18 emu/g which is smaller than the M_s value of amine functionalized Fe₃O₄ (84.28 emu/g) (Li *et al* 2011).

4. Conclusions

Nano films of metal oxides such as TiO₂ and SiO₂ have been chemically bonded to the graphene surface to yield novel composites. Such composites may have potential applications worthy of exploration. Fe₃O₄ particles chemically bonded to graphene exhibit satisfactory magnetization values for use in diagnostics and other applications.

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