

## Sonochemical Synthesis and Characterization of Amine-Modified Graphene/Conducting Polymer Nanocomposites

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**ABSTRACT:** The objective of this work is to modify graphene and study the effect of modification of graphene in thermal and electrical properties of graphene/polypyrrole and graphene/polyaniline nanocomposites. The amine functionalization of graphene was confirmed by Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy. The nanocomposites were prepared by *in situ* oxidative polymerization method using ammonium persulfate as oxidant. Field emission scanning electron microscopy and high-resolution transmission electron microscopy were used to study the morphology of the nanocomposites which indicates toward the better dispersion of modified graphene within the polymer matrices as compared to unmodified composites. The modification of graphene played an important role in the noticeable improvements in electrical conductivity of the prepared composites. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

**KEYWORDS:** graphene; polypyrrole; polyaniline; *in situ* polymerization

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### INTRODUCTION

Recently graphene has become the most promising material in nanoscience and nanotechnology due to its amazing electrical, mechanical, and thermal properties.<sup>1–3</sup> It has generated lot of research interest after its discovery in 2004 by Geim and co-workers.<sup>4</sup> The discovery of graphene brought the concept of single atomic component closer to reality. Graphene is a two-dimensional sheet of sp<sup>2</sup> hybridized carbon atoms, arranged in a honeycomb fashion. By stacking the graphene sheets one can make three-dimensional graphite, while by rolling the graphene sheets one can make one-dimensional carbon nanotubes. It is possible to make zero-dimensional fullerenes also by wrapping the graphene sheets.<sup>5</sup> Due to its high aspect ratio, high surface area as well as excellent electrical conductivity, graphene can be used as an efficient filler in polymer.<sup>6</sup> On the other hand, graphene sheets offer extraordinary electronic, thermal, mechanical properties, which lead it to be used in various applications such as sensors, batteries, supercapacitor, hydrogen storage systems as well as reinforcement fillers of nanocomposites. The appropriate modification of the nanofiller (CNT, graphene etc.) through perfect careful control of the surface chemistry can create a perfect incorporation of all components on polymeric matrices.

Great deal of researches has been done for the synthesis of graphene.<sup>7–10</sup> Now researchers are interested to modify the surface of graphene to improve the electrical, thermal as well as

mechanical properties. Si and Samulski<sup>11</sup> synthesized water-soluble graphene by incorporating —SO<sub>3</sub>H group in graphene. Niyogi et al.<sup>12</sup> functionalized graphene by octadecylamine to improve its thermal properties. Bai et al.<sup>13</sup> reported the noncovalent functionalization of graphene sheets by sulfonated polyaniline (PANI) to produce water-soluble and electroactive composites. Compton et al.<sup>14</sup> had proposed a one-pot synthetic procedure to produce electrically conductive “Alkylated” graphene paper through chemical reduction of amine-functionalized graphene oxide (GO) paper. Stankovich et al.<sup>15</sup> demonstrated the surface functionalization of GO with aliphatic and aromatic isocyanates derivatives through formation of amide and carbamate esters with carboxylic and hydroxylic groups, respectively, on the surface of GO. However, functionalization of graphene is essential to make a combination between reinforcing agent and the polymer matrices to get enhanced electrical, mechanical, and thermal properties. Though lot of researches has been done for the surface modification of graphene, still now it is an immense challenge for the scientists to functionalize graphene and incorporate in the polymer matrices to improve the properties of composites.

Among the conducting polymers, polypyrrole (PPy) and PANI are the most promising material for electrical applications due to the existence of various oxidation structures (doped state) as well as due to their easy synthesis, good processability, high electrical conductivity, good chemical, and thermal stability.

**Table I.** Composition of the Composites

Composition	Sample codes
Graphene + PPy	GP
Modified Graphene + PPy	MGP
Graphene + PANI	GA
Modified Graphene + PANI	MGA

Carbon nanotubes had been used as nanosized filler for conducting polymers to improve electrical properties<sup>16,17</sup> in last decade. As graphene has higher electrical conductivity than carbon nanotube, it can be considered as an effective nanofiller for conducting polymers.

The effectiveness of modified graphene/PANI nanocomposite as an electrode material for supercapacitor applications has been studied by us and reported earlier.<sup>18</sup> In this study, we have focused on the conductive nature of modified graphene/conducting polymer nanocomposite for various electronic applications.

The aim of this study is to achieve stable dispersion of graphene sheets into the polymer matrices to yield enhanced electrical as well as thermal properties.

### Materials

Graphene was obtained from Sinocarbon Materials Technology, China. Dicyclohexylcarbodiimide (DCC) was purchased from Spectrochem, Mumbai, (India). Ethylenediamine (EDA), ammonium persulphate (APS), and cetyltrimethylammonium bromide (CTAB) were supplied from Loba Chemie, Mumbai (India). Aniline and pyrrole were obtained from E. Merck (India). All the chemicals were used as received, without any further purification. Sonication for all the samples were carried out through a horn-type sonicator (Ultrasonic Processor, PR-250), provided by Oscar Ultrasonics, Mumbai (India).

### Synthesis of Composites

**Modification of graphene.** The surface modification of graphene was carried out by covalent attachment of amine group to the basal carbon atoms. Basically, the amine modification of graphene was carried out through mixed acid treatment route based on the path reported by Wang et al.<sup>19</sup> In a typical method, graphene was stirred at 60°C for 24 h with a solution of Conc. H<sub>2</sub>SO<sub>4</sub> and Conc. HNO<sub>3</sub> (weight ratio 3 : 1). The weight ratio of the mixed acid to graphene was 200 : 1. As prepared solution was centrifuged and washed with distilled water for several times and finally dried at 70°C for 12 h to get acid modified graphene. Amine modification was carried out by stirring the acid modified graphene with EDA/DCC/THF solution (weight ratio of EDA to DCC to graphene was 25 : 25 : 1) at room temperature for 48 h.

### Composites Preparation

Nanocomposites were prepared by *in situ* oxidative polymerization using APS as oxidant. For composite preparation, we have followed the same route as discussed in one of our previous work.<sup>20</sup> In this process, first of all, graphene/modified graphene (60 mg) was dispersed in distilled water by using CTAB as sur-

factant followed by sonication. After that monomer (0.6 mL) was added to the bulk solution followed by further sonication. In the last step, aqueous APS solution (2 g in 100 mL water) was added and further sonicated for 15 min. The whole reaction mixture was maintained at 0–5°C for 24 h for polymerization. The resulting black colored solution was filtered and washed with water and ethanol several times and dried at 70°C for 12 h to get nanocomposites.<sup>21</sup> The compositions of the composites are shown in Table I.

### Characterization Techniques

**Fourier Transform Infrared Spectroscopy.** Fourier transform infrared spectroscopy (FTIR) spectra of nanocomposites were carried out by using a NEXUS 870 FTIR (Thermo Nicolet).

**X-ray Photoelectron Spectroscopy.** Acid and amine-modified graphene was analyzed by X-ray photoelectron spectroscopy (XPS) (AXIS-NOVA, Kratos Analytical, UK).

### Field Emission Scanning Electron Microscopy

A Carl Zeiss-SUPRA<sup>TM</sup> 40 field emission scanning electron microscopy (FESEM) with an accelerating voltage of 5 kV was used to understand the morphology of the nanocomposites.

### High-Resolution Transmission Electron Microscopy

The nanocomposites based on both unmodified and modified graphene were analyzed by high-resolution transmission electron microscopy (HRTEM, JEOL 2100). A small amount of sample was dispersed in acetone by sonication for 30 min. A drop of the solution was poured on the copper grid to perform the HRTEM analysis.

### Thermogravimetric Analysis

Thermogravimetric analysis (TGA) of the composites was performed by using Dupont 2100 Thermogravimetric analyzer. The TGA measurements were conducted at a heating rate of 10°C/min under air from 30 to 800°C.

### Electrical Conductivity Measurements

The conductivity of the composites was measured using by four-electrode probe method (Lakeshore Resistivity and Hall measurement set up) using the following equation:

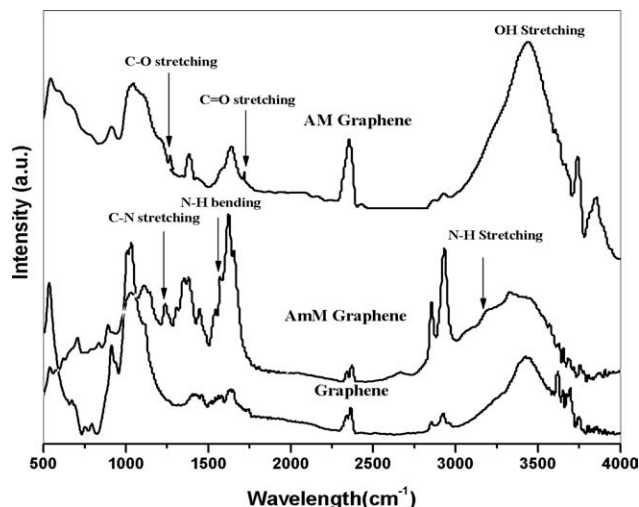
$$\begin{aligned} \text{Resistivity}(\rho, \text{ohm} - \text{cm}) &= \pi t / \ln 2(V/I) \\ &= 4.53 \times t \times (\text{resistance}) \\ \text{Conductivity}(\sigma, \text{S/cm}) &= 1/\rho. \end{aligned}$$

where,  $t$  is the thickness of the sample,  $V$  is the measured voltage, and  $I$  is the current applied.

## RESULTS AND DISCUSSION

### FTIR Analysis

FTIR analysis of the pure graphene, acid-modified, and amine-modified graphene are represented in Figure 1. In the FTIR spectrum of acid-modified graphene, peaks found at 1276, 1710, and 3432 cm<sup>-1</sup> are attributed to the C—O stretching, C = O stretching, and O—H stretching vibration, respectively.<sup>19</sup> The absence of peaks of epoxy group in acid-modified graphene confirms that the acid treatment on graphene could not convert graphene to GO. However, peaks at 1238, 1576, and 3258 cm<sup>-1</sup> could be assigned to C—N stretching, N—H bending, and N—H

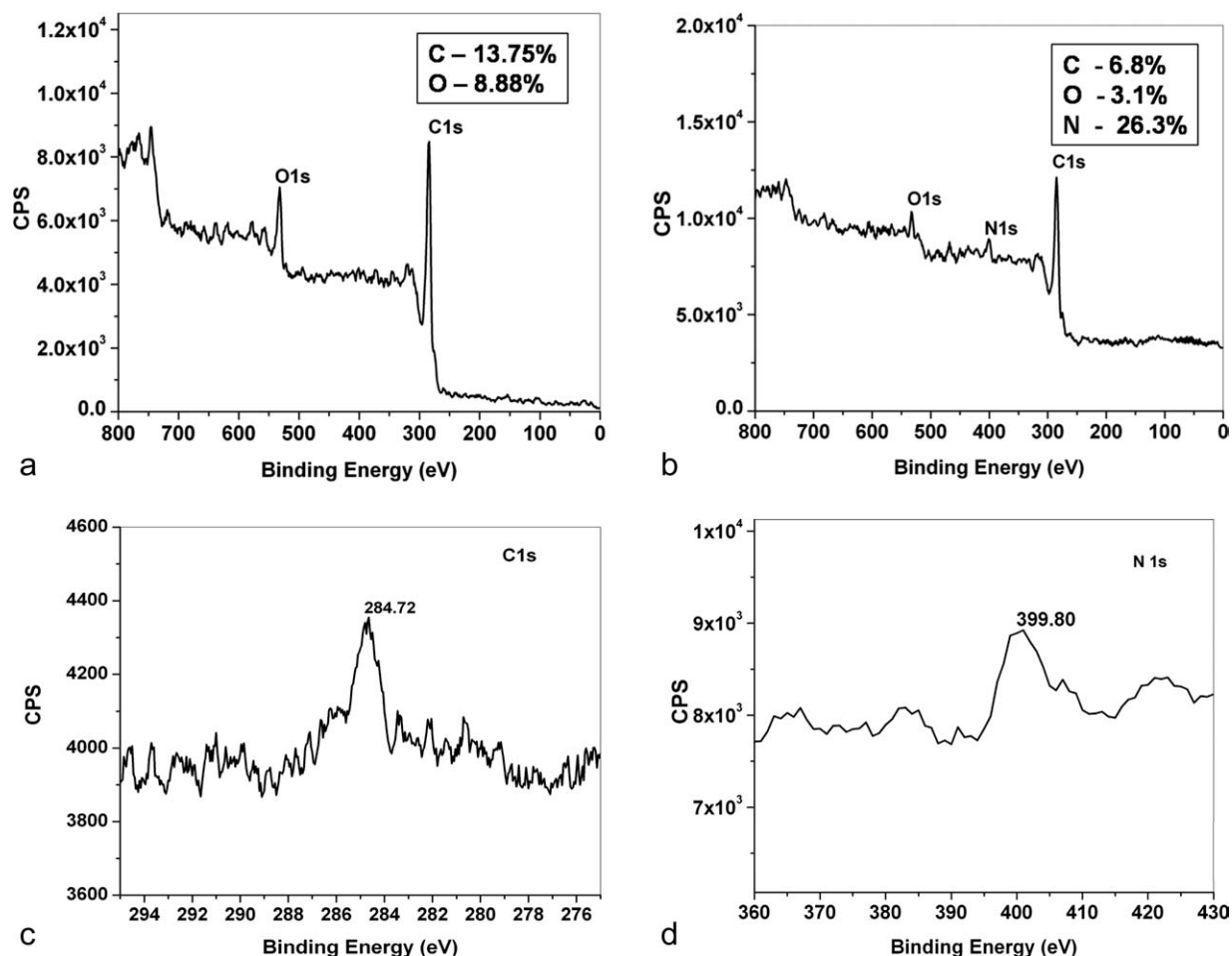


**Figure 1.** FTIR spectrum of graphene, acid-modified graphene (AM graphene), and amine-modified graphene (AmM graphene).

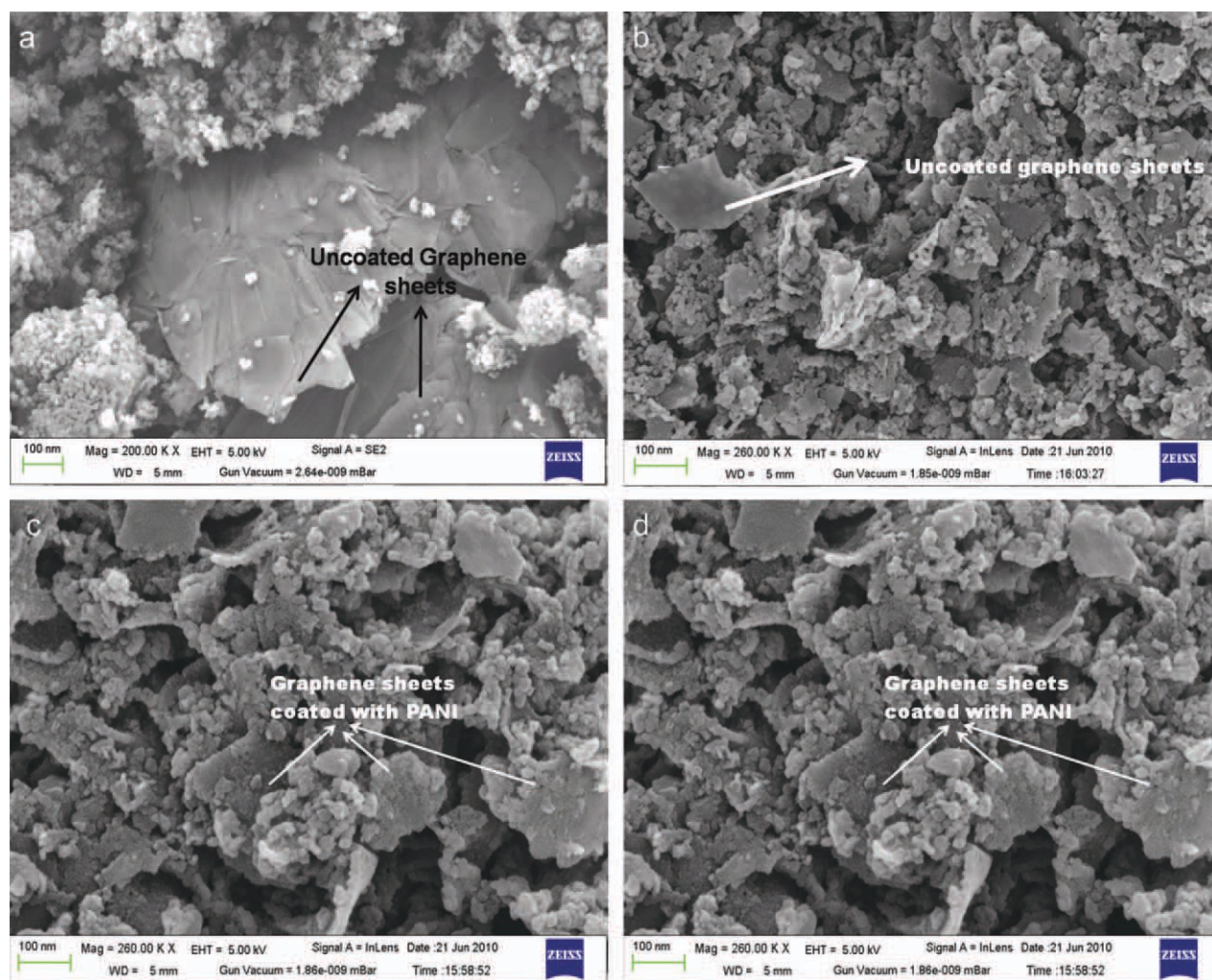
stretching vibration in amine-modified graphene.<sup>19</sup> The FTIR analysis confirmed the amine modification of graphene. For further conformation, we have done the XPS analysis.

### XPS Analysis

XPS is a direct method of determining the composition of elements, present in the surface of a material. XPS spectra of both acid- and amine-modified graphene are shown in Figure 2(a–d). Carbon 1s core level region of acid-modified graphene was recorded and two peaks are observed [Figure 2(a)]. The main peak at 284.5 eV is the characteristic peak of C–C bonds of graphene. The second peak at 286.7 eV is attributed to C–O bond. Oxygen 1s core level region of acid-modified graphene also shows two peaks [Figure 2(b)]. Peak at 534.2 eV binding energy is associated with C=O bond, present in the acid-modified graphene. The additional peak at 532.1 eV is assigned to “O–C–O” bond, which may arise due to oxygen atoms bound to carbon at the graphene edges.<sup>22</sup> However, XPS survey spectrum of acid-modified graphene confirms the presence of carbon 1s and oxygen 1s (O1s) peaks in acid-modified graphene [Figure 2(c)]. Beside this, XPS survey spectrum of amine-modified graphene reveals N1s peaks (SI) at 399.8 eV [Figure 2(d)]. The presence of O1s peak in amine-modified graphene may be due to the presence of some acid-functionalized graphene. From the elemental analysis (from XPS), it can be observed that the percentage of “C” and “O” are 13.75 and 8.88 for acid modified graphene, whereas the percentage of the same are 6.8 and 3.1,



**Figure 2.** (a) Photoemission spectra and fit of the C1s core level region of acid-modified graphene, (b) Photoemission spectra and fit of the O1s core level region of acid-modified graphene. (c) XPS survey spectrum of acid-modified graphene. (d) XPS survey spectrum of amine-modified graphene.



**Figure 3.** FESEM image of (a) GA, (b) GP, (c) MGA, (d) MGP. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

respectively, for amine-modified graphene. In addition, the percentage of “N” in amine-modified graphene is found to be 26.3, which clearly indicates toward the amine modification of graphene. Therefore, XPS confirms the amine functionalization of graphene.

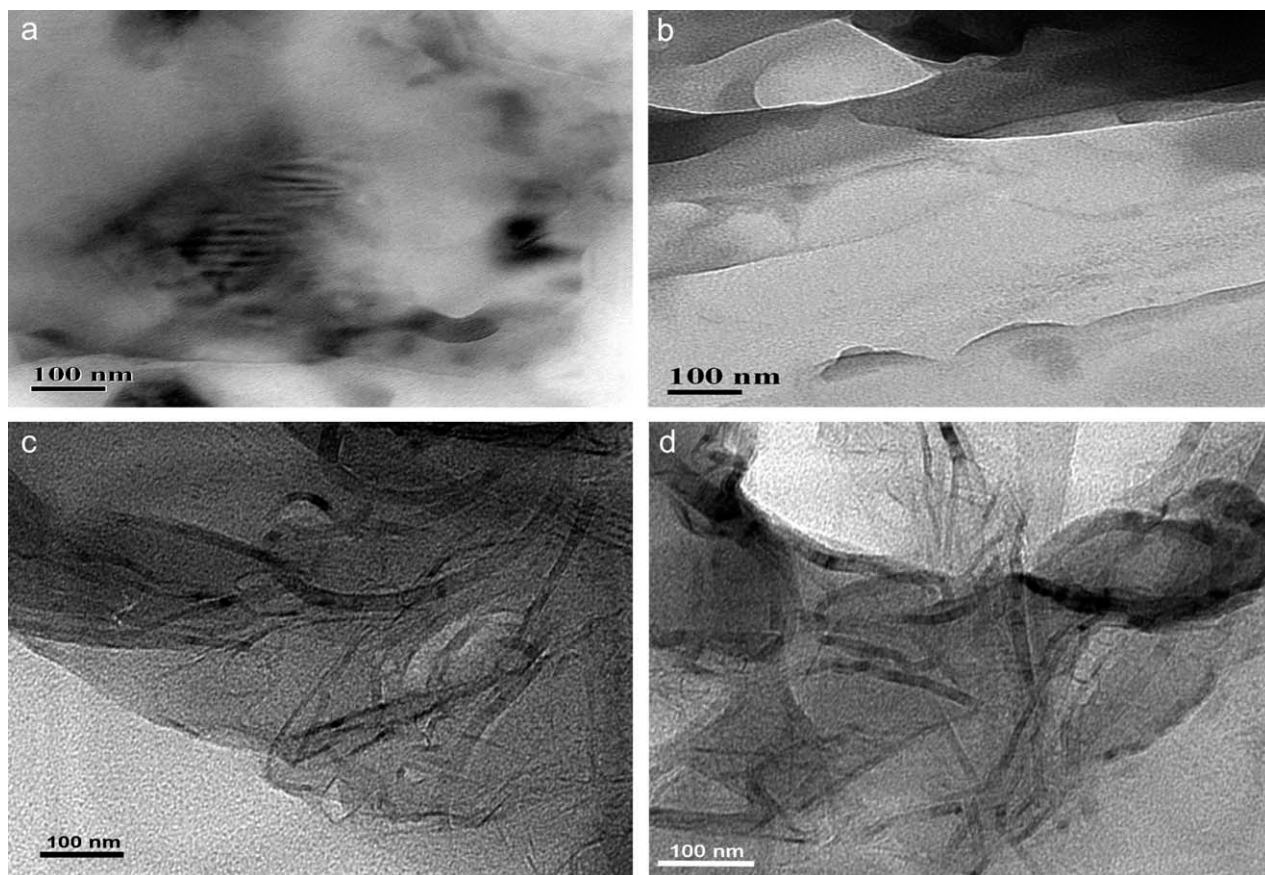
### Morphological Study

The morphology of graphene-based nanocomposites was analyzed by FESEM and HRTEM and the images are presented in Figures 3(a–d) and 4(a–d). The morphology of graphene shows smooth surface. However, the morphology of the nanocomposites is totally different from the granular morphology of polymer (PPy and PANI) and also that of graphene. FESEM images of GA and GP clearly show the presence of some uncoated graphene sheets. However, in case of modified graphene-based nanocomposites, the absence of any uncoated graphene sheets indicates toward the better compatibility between modified graphene and the polymer. The uniform coating of polymers on the modified graphene sheets may be due to the better interaction between the amine groups of modified graphene and conducting polymers. In case of modified graphene-based

nanocomposites, the monomers are attracted toward the amine group due to the H-bonding effect or  $\pi$ - $\pi$  stacking effect and during *in situ* polymerization process, these leads to the uniform coating of polymer on the graphene sheets. The graphene sheets are found to be thicker in case of MGP for the presence of amine group and displacement of  $sp^3$ -hybridized carbon atoms outside their original position.<sup>23</sup> HRTEM images support the FESEM data. HRTEM image of composites confirms the presence of graphene nanosheets in the composites. SAED (Selected Area Electron Diffraction) images of graphene and the graphene-based composites are shown in Figure 5. A perfect six-membered ring pattern is observable in the SAED image of graphene, which arises due to the crystalline nature of graphene. Similar kind of morphology was also observed by Zhang et al.<sup>24</sup> However, the absence of this ring pattern in both unmodified and modified graphene-based composites indicates the uniform cover up of polymers on the graphene sheets.

### Mechanism of Composites Formation

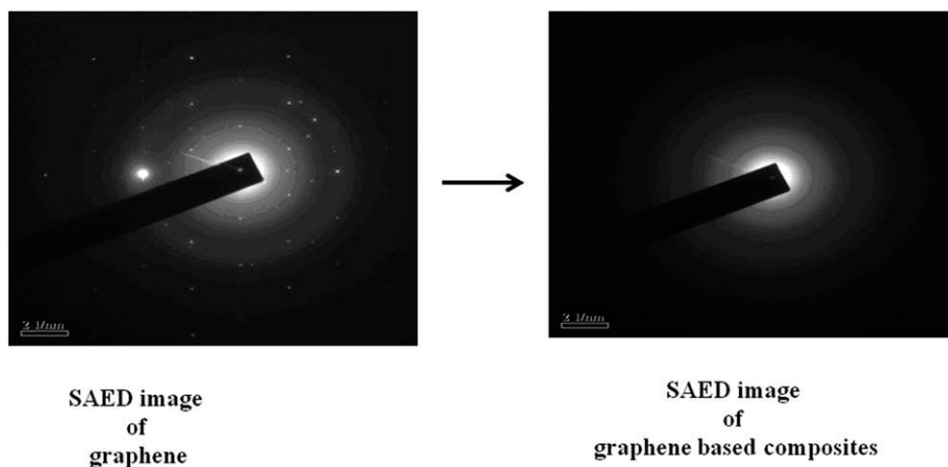
*In situ* polymerization technique is one of the most effective techniques for nanocomposite preparation. To understand the



**Figure 4.** HR-TEM image of (a) GA, (b) MGP, (c) MGA, (d) GP.

mechanism of nanocomposites preparation, we have demonstrated a schematic diagram (Figure 6) based on the physical and morphological study of the nanocomposites, which clearly illustrates various steps of composite preparation. Sonication leads to the separation of the graphene sheets from their aligned orientation.<sup>25–27</sup> Further, addition of monomer leads to the easy adsorption of the monomers in the graphene surface due to the electrostatic interaction between graphene and monomers (gra-

phene is good electron acceptor and monomers are better electron donor). After addition of oxidant (APS) into the reaction mixture, the adsorbed monomers initiates to polymerization. However, as observed from the morphological study, in case of unmodified graphene, few graphene sheets remained uncoated as well as polymerization occurred also in outside of the graphene sheets. Uniform thin coating of polymer on graphene surface is observed for modified graphene-based



**Figure 5.** SAED images of graphene and graphene-based composites.

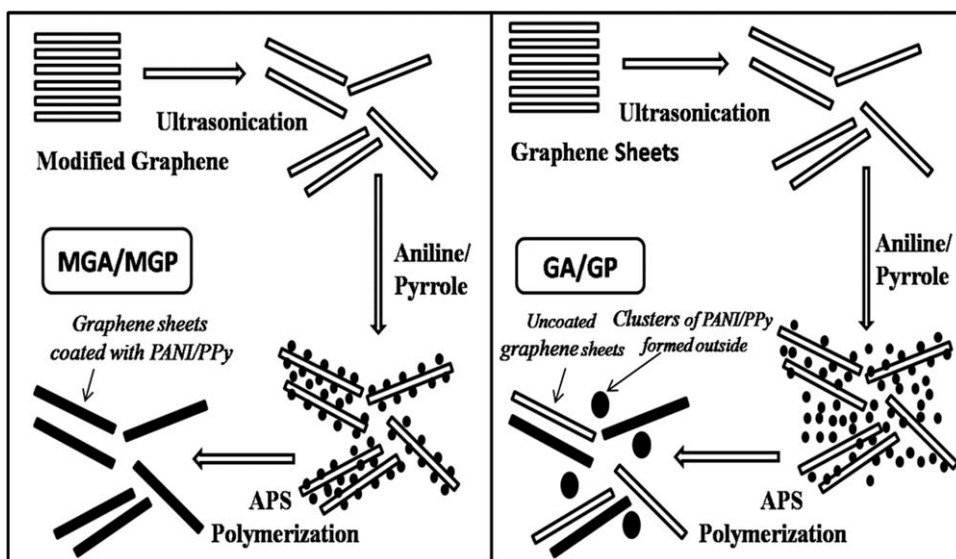


Figure 6. Schematic diagram of the composites preparation.

nanocomposites. The reason behind this observation is the better compatibility between modified graphene and polymer.

#### Thermal Analysis

Thermal stability of the composites is shown in Figure 7(a, b). For all the composites, nearly 7% weight loss has occurred at 100°C, which is due to moisture evaporation. A major weight loss has been found for all the composites, which arises due to the decomposition of polymer from the composite. However, the delayed degradation of MGA may be caused by the better compatibility between the modified graphene and PANI. Finally at 450°C, weight loss for unmodified graphene-based composites is more than that of modified graphene-based composites.<sup>28</sup> The magnified section, shown in Figure 7(a), indicates the second degradation step, that is, the degradation of PPy. The degradation of PPy starts at around 248°C in case of GP, whereas the degradation of the same starts at around 260°C for MGP. From the TGA analysis of the composites, it is confirmed that modified graphene-based composites showed higher thermal stability than unmodified graphene-based composites. The thermal properties of graphene and modified graphene based nanocomposites are shown in Table III.

#### Measurements of Electrical Conductivity

Electrical conductivity is one of the most important properties of the composites for various applications in electronic devices. In recent years, researchers are very much interested to develop nanocomposites based on conducting polymer and graphene/GO/graphite oxide with improved physical properties, mainly enhanced electrical conductivity. Bose et al.<sup>28</sup> found maximum conductivity of 7.93 S/cm for graphene/PPy nanocomposite, prepared by *in situ* oxidative polymerization method. On the other hand, Gu et al.<sup>29</sup> successfully prepared graphite oxide/PPy nanocomposite by *in situ* polymerization method and found maximum capacitance of 6.86 S/cm. Polymer nanocomposites based on PANI and graphene nanosheets (GNS) modified by poly(sodium 4-styrenesulfonate) (PSS) were prepared by Tung et al.<sup>30</sup> He found maximum electrical conductivity of 4.96 S/cm

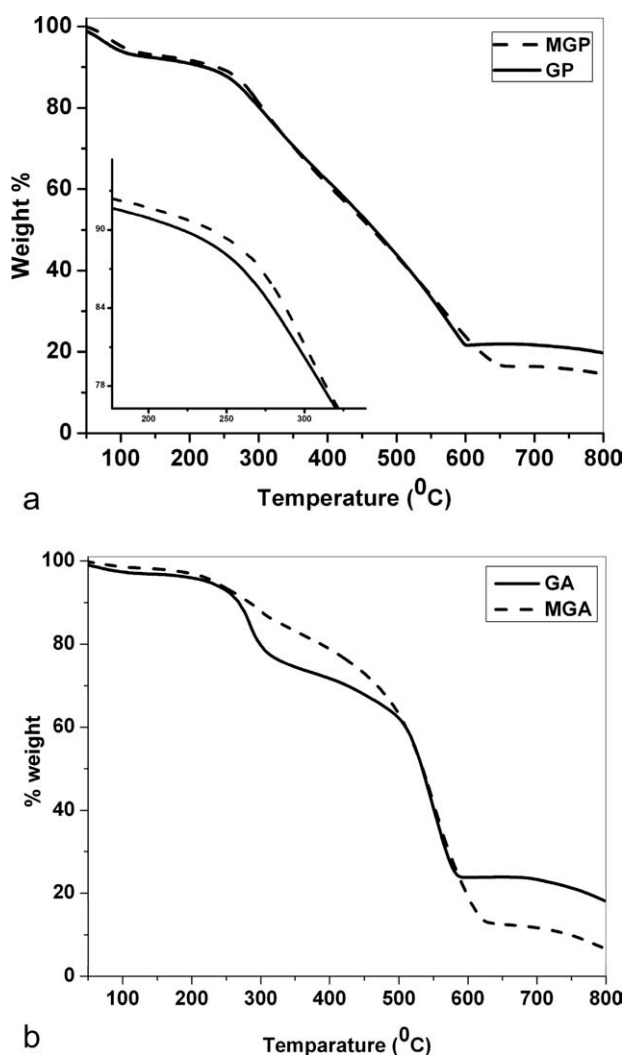


Figure 7. TGA of (a) GP and MGP, (b) GA and MGA.

**Table II.** Conductivity Measurements

Sample	Thickness (d, cm)	Resistance (ohm)	Resistivity ( $\rho$ , ohm-cm)	Conductivity ( $\sigma$ , S/cm)
GP	0.05	0.763	0.173	5.78
MGP	0.05	0.571	0.129	7.72
GA	0.05	0.728	0.165	6.05
MGA	0.05	0.543	0.123	8.12

**Table III.** Thermal Stability Data of Different Composites Extracted from TGA Plots

Composite	Weight loss at temperature (%)				
	100°C	200°C	300°C	400°C	450°C
GA	2.9	4.2	20.4	28.4	32.0
MGA	1.5	2.9	12.1	21.1	27.0
GP	6.7	8.2	20.5	37.5	46.3
MGP	5.5	9.5	19	40	48.5

for PANI/PSS-GNS with 5% PSS-GNS. However, the electrical conductivities ( $\sigma$ ) of GA, MGA, GP, and MGP composites were determined by four-point probe measurement system and the values are represented in Table II. Among all the nanocomposites, the highest electrical conductivity of 8.12 S/cm was found for MGA. This value is higher than the electrical conductivity value of nanocomposites reported by Bose et al., Gu et al., and Tung et al.<sup>28–30</sup> The high electrical conductivity of graphene-based composites may be due to the  $\pi$ - $\pi$  stacking between the graphene layers and polymer.<sup>28</sup> The increase in the magnitude of electrical conductivity for modified graphene-based composites may be due to better interaction and better compatibility between modified graphene and monomer. The presence of amine group in the graphene improves the charge transport properties of the composites, which increases conductivity.<sup>31</sup> The increment of electrical conductivity of modified graphene-based nanocomposites may be caused by the uniform coating of polymer on the modified graphene sheets, which is observed in the FESEM images of composites. The substantial improvement of conductivity in presence of graphene may be due to the high aspect ratio and large specific surface area of graphene. However, one of the reasons behind this enhanced conductive nature of modified graphene-based nanocomposites is their good dispersion in nanocomposites, as observed from the morphological study of the composites. In general, better the dispersion of graphene/modified graphene in nanocomposites, higher will be the electrical conductivity of the composites.<sup>32</sup> However, these exceptional conductive natures of the nanocomposites make them superior for various device applications.

## CONCLUSION

Nanocomposites based on modified and unmodified graphene were prepared by *in situ* oxidative polymerization method. The

amine modification of graphene was confirmed by XPS and FTIR analysis. The morphological study of the modified graphene-based nanocomposites showed homogeneous nature. Such composites exhibited a high value of conductivity, which may be attributed to the high aspect ratio and large specific surface area of the graphene nanosheets in polymer matrix. Modified graphene-based composites also showed superior thermal stability rather than the unmodified graphene-based composites.

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