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Preparation and Conductivity of Polymer-Modified Graphene Films

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Article Information

ABSTRACT

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INTRODUCTION

Graphene, which is only one atom thick, has a unique planar structure in two dimensions, a very high specific surface area, and great barrier properties. Graphene has attracted extensive attention for its electrical (Kim, et al., 2017 and Mohan, et al., 2016) and thermal conductivity (Balandin, et al., 2008 and Pop, et al., 2012), optical (Schoche, et al., 2017) and mechanical properties (Liu, et al., 2012, Kordkheili, et al., 2013, Zhu, et al., 2010). Water could be used as a reducing agent, according to Stankovich S, Dikin D A et al., 2007. Hydrazine hydrate can turn graphene oxide (GO) into graphene with higher electrical conductivity. The electrical conductivity of the resulting graphene is similar to that of graphite. (Qi, X Y, Yan D, Jiang Z, et al., 2011) the GO made with the Hummer method was turned into graphene by heating it, and the graphene was then added to a polystyrene matrix. The graphene/polystyrene composite material was obtained. The research results found that: after adding a small amount of graphene to pure polystyrene, its electrical conductivity changed from 6.70×10-14S.m⁻¹ increased to about 3.49S.m⁻¹.

(Liu H Y, Kuila T, Kim N H, *et al.*, 2013) reported that polyethyleneimine (PEI) could reduce GO, and at the same time, PEI was grafted to the in situ generated stone. A water-soluble polymer-modified graphene PEI-GO was obtained on the graphene sheet. According to the conductivity test results, the PEI mass ratio is GO. The conductivity of the resulting PEI-GO can be greatly affected. Based on the research (Liu, H Y, Kuila T, Kim N H, *et al.*, 2013), this paper looks into how the reaction temperature affects how PEI breaks down GO. Under the premise of fixing the mass ratio of raw materials

The Hummers method was used to make graphite oxide, and ultrasonic exfoliation at 25°C and 90°C was used to make graphene oxide (GO). At a low temperature, polyethyleneimine (PEI) was used as a reducing and changing agent for graphene oxide (GO) to make dispersions of graphene that were modified with PEI. Optoelectronics' electron and infrared spectroscopy showed how temperature affected PEI's ability to break down GO. The results show that PEI can partially reduce GO at 25°C. At 90°C, the grafted PEI gradually dissociated from the GO sheet. The graphene dispersion was filtered and assembled into a PEI-GO film, and its conductivity was found to be 117S.m⁻¹, hopefully conductive material for graphene.

> PEI and GO by changing the reaction temperature, PEImodified graphene was prepared. The prepared PEImodified graphene aqueous dispersion was filtered into a composite film, and the graphene composite thin films obtained at different temperatures were investigated the conductivity of the film.

METHOD AND MATERIALS

Reagents and instruments

Sigma-Aldrich sold polyethyleneimine with an average relative molecular mass of Mn≈10000. Concentrated sulfuric acid (the mass fraction is 98%), potassium permanganate, sodium nitrate, hydrogen peroxide (30% by mass), and hydrochloric acid (38% by mass) were analytically pure reagents for further purification. The samples were tested by an AXIS-NOVAX-ray photoelectron spectrometer (Kratos Analytical Ltd., UK) elemental composition. The structural information of the samples was tested using a Nicolet 6700 infrared spectrometer (Thermo Scientific, USA). Product morphology tests were completed on the H-7650 TEM (Hitachi, Japan) and JSM-6701F SEM (JEOL, Japan). A Keithley 2000 type four-probe resistivity tester (Keithley Instruments Inc., USA) was used to test its electrical conductivity.

Preparation of Graphene Oxide

First, graphite oxide was prepared according to the Hummers method (Lei, *et al.*, 2016). Under ice-water bath conditions, 50 ml of concentrated sulfuric acid was added to 1g of natural graphite and 0.5g of sodium nitrate and stirred to mix them evenly. Under magnetic stirring, take 3g of potassium permanganate, slowly add

Page 15

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it to the system, and continue stirring. After 10 minutes, the ice-water bath was removed, the reaction system was heated to 35 °C, and the stirring was continued for 30 minutes. At this point, the black reaction system became a brownish-yellow color, 40ml of deionized water was added to the reaction system, the temperature was raised to 95 °C, and the reaction was continued for 1h to obtain a golden vellow dispersion. Additions of 150ml of deionized water and 10ml of hydrogen peroxide with a mass fraction of 30% were mixed for 30 min, and then 50ml of 5% hydrochloric acid solution was added. Last, wash the sample with deionized water until the solution is neutral. The obtained product was filtered with suction to remove the solvent water, and the obtained sample was placed in a vacuum at 40°C. Dry to obtain dry graphite oxide. Weigh graphite oxide and disperse it in an appropriate amount of deionized water. 30 minutes of medium sonication to obtain 0.5 mg/ml. The graphene oxide solution is ready for use.

Preparation of polyethyleneimine-modified graphene

Dissolve 0.05 g of polyethyleneimine in 100 ml deionized water to obtain a PEI solution of 0.5 mg/ml. The PEI solution was placed in a three-necked flask, and 100 ml of GO solution (0.5 mg/ml) was added dropwise to the PEI solution via a constant pressure drop funnel while magnetic stirring at 25°C. The reaction was stirred for 4h to obtain a brown PEI-GO dispersion.

The GO dispersions were passed through a membrane (a cellulose filter membrane with a pore size of $0.2 \ \mu m$) suction filtration, with about 1 liter of deionized water added to wash the sample and remove the impurities. Separated PEI and PEI-GO films were obtained, respectively.

RESULTS AND DISCUSSION

Morphology analysis of the product

The GO sheet contains many epoxy groups, hydroxyl groups, carboxyl groups, and carbonyl groups at the edge of the sheet, and GO has good water solubility. It can be spread out evenly in solvent water to make a brownish-yellow GO solution. The GO solution was added to the polyethyleneimine solution at room temperature. After stirring for 4h, PEI-GO was obtained. In appearance, PEI-GO was not much different from GO, both of which were brown-yellow aqueous solutions. This is because, at 25 °C, PEI can't reduce GO very well, so it's grafted onto GO sheets instead. The amino group of PEI reacts with the epoxy group of GO to make PEI-GO with a modified branch linkage. When the reaction temperature was 90 °C, most of the amino groups of PEI were dissociated from the GO sheet, forming C=C, reducing GO.

It is graphene, which is consistent with the mechanism of hydrazine hydrate reduction of GO. (Song, P, Zhang X, Sun M, et al., 2012) used oxalic acid as a reducing agent and heated it at 75°C for 18h. The brown GO was also observed to transform into a black graphene dispersion. So that the shapes of GO and PEI-GO could be seen, their dispersions were taken and freeze-dried to make samples that looked like fluffy sponges. The field emission scanning electron microscope (FE-SEM) photo of the surface after gold spraying is shown in Figure 1. For GO, there are a lot of random wrinkles on the GO sheet, and the edges are easy to bend, showing that the GO sheet has good flexibility and toughness. Due to their very high specific surface area, the different GO sheets in PEI-GO are randomly stacked and cross over each other. However, the packing density of PEI-GO is slightly larger than that of GO because, at 25°C, GO has



(a) GO

(b) PEI-GO

Figure 1: Field Emission Scanning Electron Microscopes photos of GO and PEI-GO.

a higher packing density. PEI partially restored it. It can be observed that the graphene sheets have corrugated wrinkles due to their close packing with each other. This is because GO is effectively reduced to graphene by PEI at 90°C, due to the π - π interaction leading to Graphene sheets being tightly packed together.

To better show the morphology of the samples, another dispersion liquid was taken, dropped on the carbon film, and dried for transmission electron microscopy (TEM) analysis. The obtained TEM photos are shown in Figure 2. Figure 2a shows a TEM image of GO divided into two parts. It can be seen that graphene oxide has a finely layered structure with a large number of irregular wrinkles at the edges, which can reduce graphene oxide. The specific surface area reduces its surface energy, thereby making it stable. The TEM image of PEI-GO is shown in Figure. 2b with graphene oxide.

In contrast, PEI-GO is still a finely layered structure, and its darker color may be due to the PEI grafted on the surface of GO. The folded state of graphene at the edge





(b) PEI-GO

Figure 2: TEM view of GO and PEI-GO

is clearly seen in the graphene sheet, and there are more random wrinkles. This is because the graphene sheets π - π interact, making wrinkles more likely. More wrinkles also indicate that the graphene oxide sheets are reduced to graphene sheets. (Xu, L Q, Liu Y L, Neoh K G, et al., 2011) reported that due to the modification of graphene sheets and graphene oxide sheets showed similar TEM morphologies.

Structural Analysis of the Product

X-ray photoelectron spectroscopy (XPS) was done on the samples to determine how the temperature affected PEI's ability to break down GO. Figure 3 depicts the spectrum of a spectroscope (XPS) analysis. For GO, its XPS spectra have two main peaks, corresponding to sp. carbon (281.4 eV) and oxygen (530.5 eV), which is consistent with the conclusion of the (Chua, C K et al., 2012). Except for the carbon and oxygen peaks, the XPS spectrum of PEI-GO is at 398 eV. A nitrogen peak appeared at the position of GO, which means that the polyethyleneimine molecular chain was grafted onto the GO sheet. Carbon and oxygen peaks of PEI-GO and GO are compared. It has been found that the former oxygen peak is less strong than it used to be. This may be because the PEI molecular chain absorbs the oxygen from the epoxy group in the GO sheet. The nitrogen of the amino group is substituted to form a nitrogen-containing three-membered ring. It

PEI-GO Intensity (a.u.) GO 0 200 400 600 800 1000 1200 Binding energy (eV)

Figure 3: XPS spectra survey of the GO and PEI-GO



Figure 4: FT-IR spectra survey of the GO and PEI-GO

means that even at 25°C, the amino group of the PEI molecular chain can interact with the GO sheet. PEI-GO was created by reacting the epoxy groups and grafting them onto the GO sheet. In (Li, X et al., 2009), GO was heated in a nitrogen atmosphere to prepare nitrogendoped graphene, also found a nitrogen peak at 398 eV in the XPS spectrum.

Figure 4 shows the three samples' Fourier transform infrared (FT-IR) spectra. For GO, the broad and strong blunt peak at 3100-3500cm⁻¹ is the stretching vibration peak of the associated hydroxyl group, and the peak in the 1734cm⁻¹ figure is the C=O stretching vibration peak at 1640 cm-1. The spikes correspond to the C=C stretching vibration peak, 1388 cm-1. The absorption peak is the bending vibration peak of the hydroxyl group at 1246 cm⁻¹. The absorption peak is the CO stretching vibration peak of the epoxy group. The appearance of these oxygen-containing functional groups is consistent with the (Gao, Y, Liu L Q, Zu S Z, et al., 2011), which says that Ming graphite was successfully oxidized, and graphene oxide was obtained after ultrasonic exfoliation. In contrast, the FT-IR curves of PEI-GO are not related. The hydroxyl stretching vibration peak was replaced by the PEI molecular chain. The N-H stretching vibration peak is strong and sharp, indicating that the PEI molecular chain is branched to the GO sheets. It is worth noting that in PEI-GO 1734 cm⁻¹. Still exist C=O vibration



peak, only the intensity compared to the decrease of GO shows that PEI can only partially reduce GO at 25 °C but cannot completely reduce GO to graphene. The C-O stretching vibration of the epoxy group in the GO curve's dynamic peak (1246 cm⁻¹) disappeared completely in PEI-GO, proving that the epoxy group of GO was not affected by the reaction of the amino group of PEI. The effect of reaction temperature means that PEI molecular chains can also be grafted onto GO at 25°C.

Conductivity Analysis of the Product

The degree of reduction of GO has a lot to do with how well graphene conducts electricity. Because the GO sheet contains many hydroxyl, epoxy, and carbonyl groups, the carboxyl group destroys the conjugated structure of graphene, so GO is a non-conductive substance. When the reducing agent is added, the oxygen-containing groups of the GO sheet undergo partial or full reduction, and graphene restores the conjugated structure, thus helping to improve the electrical conductivity of the product. The higher the GO reduction degree, the better the graphene obtained and the higher the conductivity. Graphene's electrical conductivity, on the other hand, can demonstrate the degree of reduction in GO. It means that the degree of GO reduction is greater. GO and PEI-GO were assembled into membranes by suction filtration, respectively. The acupuncture method was used to calculate the electrical conductivity according to the method (Jun, et al., 2015).

Since GO is a non-conductive substance, the conductivity of the obtained GO thin film is 0.002 S·m-1. Such a low conductivity also explains why the graphene oxide prepared by this method is rich in oxygen-containing functional groups, which is consistent with the results of FT-IR and XPS. At 25°C, GO was added dropwise to PEI, and PEI was grafted onto the GO sheet through the reaction between the amino group of PEI and the GO epoxy group, resulting in a PEI-GO dispersion liquid. It was assembled into a PEI-GO film by suction filtration, and its conductivity was 0.103 S.m⁻¹. The specific conductivity of GO has increased, indicating that PEI reduced the oxygen-containing groups. (XU, Z, Bando y, Liu L, et al., 2011) found that the influence of epoxy groups on the electrical conductivity of graphene materials is much greater than that of hydroxyl groups, and the dissociation of epoxy groups from the GO sheet is preferential to that of the hydroxyl group, which is consistent with the results in this paper. At 25°C, due to the amino groups in the PEI molecular chain and the GO sheet. The layer epoxy group reaction made GO more conductive. Still, since the surface-grafted PEI molecular chain was not conductive, the increase in conductivity of PEI-GO was not very high. Conjugated structure of graphene, due to the departure of the non-conductive substance PEI and the recovery of the conjugated structure.

CONCLUSION

The temperature of the reaction has a big effect on how

well polyethyleneimine can break down graphene oxide. At 25°C, PEI can only partially reduce GO and connect. At 90°C, PEI effectively reduced GO to graphene, resulting in surface-modified graphene PEI-GO. This conclusion has some implications for reducing GO with other reducing agents. The films assembled from PEI-GO dispersions have, it has high electrical conductivity and is expected to be used in graphene-conductive composites.

Declaration of Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

REFERENCES

- Balandin, A. A., Ghosh, S., Bao, W., Calizo, I., Teweldebrhan, D., Miao, F., & Lau, C. N. (2008). Superior thermal conductivity of single-layer graphene. *Nano letters*, 8(3), 902-907. https://doi. org/10.1021/nl0731872
- Chua, C. K., Ambrosi, A., & Pumera, M. (2012). Graphene oxide reduction by standard industrial reducing agent: thiourea dioxide. *Journal of materials chemistry*, 22(22), 11054-11061. https://doi.org/10.1039/ C2JM16054D
- Gao, Y., Liu, L. Q., Zu, S. Z., Peng, K., Zhou, D., Han, B. H., & Zhang, Z. (2011). The effect of interlayer adhesion on the mechanical behaviors of macroscopic graphene oxide papers. *ACS nano*, 5(3), 2134-2141. https://doi.org/10.1021/nn103331x
- Jun, Y. S., Sy, S., Ahn, W., Zarrin, H., Rasen, L., Tjandra, R., ... & Yu, A. (2015). Highly conductive interconnected graphene foam based polymer composite. *Carbon, 95,* 653-658. https://doi.org/10.1016/j. carbon.2015.08.079
- Kim, K. W., Kim, J. H., Cho, S., Shin, K., & Kim, S. H. (2017). Scalable high-performance graphene paper with enhanced electrical and mechanical properties. *Thin Solid Films*, 632, 50-54. https://doi. org/10.1016/j.tsf.2017.04.039
- Kordkheili, S. H., & Moshrefzadeh-Sani, H. (2013). Mechanical properties of double-layered graphene sheets. *Computational Materials Science*, 69, 335-343. https://doi.org/10.1016/j.commatsci.2012.11.027
- Liu, Y., Xie, B., Zhang, Z., Zheng, Q., & Xu, Z. (2012). Mechanical properties of graphene papers. *Journal* of the Mechanics and Physics of Solids, 60(4), 591-605. https://doi.org/10.1016/j.jmps.2012.01.002
- Liu, H., Kuila, T., Kim, N. H., Ku, B. C., & Lee, J. H. (2013). In situ synthesis of the reduced graphene oxide–polyethyleneimine composite and its gas barrier properties. *Journal of materials chemistry a*, 1(11), 3739-3746. https://doi.org/10.1039/C3TA01228J
- Lei, L., Xia, Z., Zhang, L., Zhang, Y., & Zhong, L. (2016). Preparation and properties of aminofunctional reduced graphene oxide/waterborne



polyurethane hybrid emulsions. *Progress in organic coatings*, *97*, 19-27. http://dx.doi.org/10.1016%2Fj. porgcoat.2016.03.011

- Li, X., Wang, H., Robinson, J. T., Sanchez, H., Diankov, G., & Dai, H. (2009). Simultaneous nitrogen doping and reduction of graphene oxide. *Journal of the American Chemical Society, 131*(43), 15939-15944. https://doi. org/10.1021/ja907098f
- Mohan, V. B., Jayaraman, K., Stamm, M., & Bhattacharyya, D. (2016). Physical and chemical mechanisms affecting electrical conductivity in reduced graphene oxide films. *Thin Solid Films*, 616, 172-182. https:// doi.org/10.1016/j.tsf.2016.08.007
- Pop, E., Varshney, V., & Roy, A. K. (2012). Thermal properties of graphene: Fundamentals and applications. MRS bulletin, 37(12), 1273-1281. https:// doi.org/10.1557/mrs.2012.203
- Qi, X. Y., Yan, D., Jiang, Z., Cao, Y. K., Yu, Z. Z., Yavari, F., & Koratkar, N. (2011). Enhanced electrical conductivity in polystyrene nanocomposites at ultra-low graphene content. ACS applied materials & interfaces, 3(8), 3130-3133. https://doi.org/10.1021/ am200628c
- Schöche, S., Hong, N., Khorasaninejad, M., Ambrosio, A., Orabona, E., Maddalena, P., & Capasso, F. (2017). Optical properties of graphene oxide and reduced graphene oxide determined by spectroscopic ellipsometry. *Applied Surface Science*, 421, 778-782.

https://doi.org/10.1016/j.apsusc.2017.01.035

- Stankovich, S., Dikin, D. A., Piner, R. D., Kohlhaas, K. A., Kleinhammes, A., Jia, Y., ... & Ruoff, R. S. (2007). Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. *carbon*, 45(7), 1558-1565. https://doi.org/10.1016/j. carbon.2007.02.034
- Song, P., Zhang, X., Sun, M., Cui, X., & Lin, Y. (2012). Synthesis of graphene nanosheets via oxalic acidinduced chemical reduction of exfoliated graphite oxide. *Rsc Advances*, 2(3), 1168-1173. https://doi. org/10.1039/C1RA00934F
- Zhu, Y., Murali, S., Cai, W., Li, X., Suk, J. W., Potts, J. R., & Ruoff, R. S. (2010). Graphene and graphene oxide: synthesis, properties, and applications. *Advanced materials*, 22(35), 3906-3924. https://doi. org/10.1002/adma.201001068
- Xu, L. Q., Liu, Y. L., Neoh, K. G., Kang, E. T., & Fu, G. D. (2011). Reduction of graphene oxide by aniline with its concomitant oxidative polymerization. *Macromolecular rapid communications*, 32(8), 684-688. https://doi.org/10.1002/marc.201000765
- Xu, Z., Bando, Y., Liu, L., Wang, W., Bai, X., & Golberg, D. (2011). Electrical conductivity, chemistry, and bonding alternations under graphene oxide to graphene transition as revealed by in situ TEM. ACS nano, 5(6), 4401-4406. https://doi.org/10.1021/ nn103200t