STUDY ON CONDUCTIVITY OF POLY (ANILINE SULFONIC ACID) (PAS)/GRAPHENE OXIDE (GO) COMPOSITES

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Abstract

The authors studied the effect of GO content and heat-treatment temperature on the conductivity of PAS/GO thin film composites and its action mechanism. Their conductivity increased with GO content and heat-treatment temperature (150 and 170 ˚C). Measurements of UV-Vis spectra and zeta-potential of PAS/GO/water dispersion suggested some physical interaction between PAS molecules and GO. It was found that the conductivity enhancement of PAS/GO thin film solids was due to not the π-π interaction between PAS molecules and GO surface (or rGO (reduced type GO)), but the increase of C=C(sp^2) bonds (possibly conjugated), where thermal reduction of GO were promoted by SO_3H groups in PAS at a higher temperature.

1. Introduction

Conductive polymers such as polyaniline doped with dodecyl benzene sulfonic acid ((PANI:DBSA), poly (3, 4-ethylenedioxythiophene) doped with polystyrene sulfonic acid (PEDOT:PSS) and self-doped poly (aniline sulfonic acid) (PAS) [1] shown in Fig.1 possess a good conductivity, transparency and environmental stability. They are promising materials to take the place of a conventional transparent conductive material, Sn-doped In_2O_3 (ITO). However the study on the conductivity improvement of such conductive polymers has been made, sinde they are inferior to ITO in conductivity.

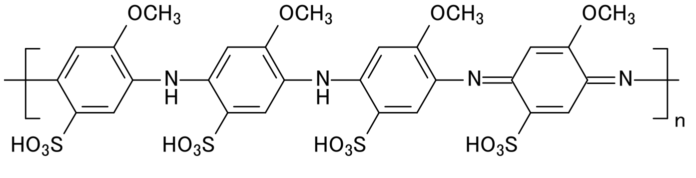

Figure 1. Chemical structure of poly (aniline sulfonic acid) (PAS) [1]

On the other hand graphene nano-particle (Gr) is also a promising material for transparent conductive films, since Gr has a high conductivity and good transparency. Since it is very difficult to prepare Gr directly from graphite by exfoliation method, graphene oxide (GO) and reduced GO (rGO) prepared from graphite with Hummers method are usually applied instead of Gr [2]. Figure 2 shows the synthetic diagram of Gr, GO and rGO from graphite.

Since PAS and GO (or rGO) have conjugated double bonds with rich π-electrons, π-π interaction between them which leads to the increase of currency is expected. So the authors have been studying

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the composite of PAS with GO (or rGO) in order to enhance its conductivity. In this paper the effect of GO content and heat-treatment condition on the conductivity of PAS/GO composite will be discussed.

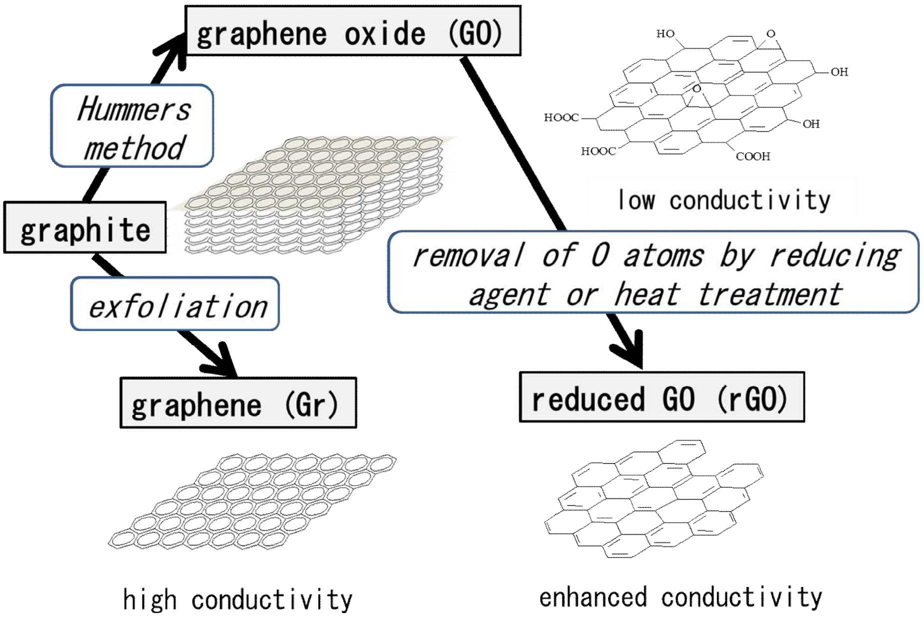

Figure 2. Synthetic diagram of GO, rGO and Gr

2. Experimental

2.1. Materials

GO/water dispersion (conc.; 1.0 wt%) was purchased from Nishina Material company in Okayama University in Japan [2]. The aqueous PAS/water solution (conc.: 5.0 wt%) was supplied with Mitsubishi Rayon Co., Ltd in Japan. 2-methoxy aniline-5-sulfonic acid (MeASA) [1] was purchased from Tokyo Chemical Industry Co., Ltd. (TCI) . Commercial pure water was used for the preparation of PAS/GO composites and measurements of zeta-potential and UV-Vis spectra of PAS/GO/water dispersion. A pre-cleaned micro slide glass with the size of 76 mm×26 mm and the thickness of 0.9-1.2 mm was used as a substrate for the preparation of PAS (or MeASA)/GO thin film composites.

2.2. Preparation of PAS/GO and MeASA/GO thin film composites

The mixtures of GO/PAS with a different GO/(GO+PAS) weight ratio were dispersed with ultrasonic waves for 20 min, and a small amount of the resulting mixtures were dropped with a syringe on the slide glass. The coated slide glasses were dried under the conditions of 100, 150 and 170˚C for 1.0 hour in air. The thickness (t) of the dried PAS/GO composite layer was controlled to be around 2.0 μm, and its actual thickness was calculated from the weight of the dried layer. The preparation and characterization of MeASA/GO composites with a different GO/(GO+MeASA) weight ratio were carried out in the same way.

2.3. Measurement

The size and zeta-potential of GO in the dispersion with its concentration of 0.020〜0.10wt% were measured by the zeta-potential & size analyzer with a titrator, ELS-Z (Photal Otsuka electronics Co.

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Ltd in Japan). Its zeta potential change (conc.; 0.060 %) with the addition of PAS was measured by ELS-Z.
UV-Vis spectra of PAS/GO/water suspension were measured by UV-Vis spectrometry (JASCO UV-650). Raman spectra of PAS/GO composites were measured with Raman spectroscopy (JASCO NRS-1000) under the following conditions; wave length: 532nm, output: 10mW, exposure time: 60sec.
XPS spectra of heat-treated PAS/GO, MAS/GO and GO were measured with automated X-ray imaging photoelectron spectrometer (SHIMADZU KRATOS NOVA).
Surface resistivity (Rs, Ω/□) of PAS/GO and MAS/GO thin film composites on the glass plate was measured with Lowresta (Mitsubishi Chemical Co. Ltd.) under the following condition; temperature: 20-25 ˚C, humidity: 45-60 %, voltage: 100 V. Volume resistivity (ρ) was calculated according to the following equation.

$$\rho\ (\Omega\cdot\ \mathrm{cm}) = Rs\ (\Omega/\square) \times t\ (\mathrm{cm})$$

3. Results and Discussion

3.1. Characterization of GO in water

The average diameter and zeta-potential of GO were estimated to be 7×10^3 nm and -29 mV. Good dispersion of GO in water was ascribed to its hydrophilic property and coulomb repulsive force, which resulted from a large absolute zeta-potential value.

3.2. Characterization of PAS/GO dispersion mixed in water

Fig 3 shows the zeta potential change of GO in water with the titration of PAS. Its zeta-potential gradually changed with the increase of PAS from -29 mV to -34 mV (PAS/GO weight ratio= 2.0), which suggested the adsorption of PAS molecules on GO. Since the surface of GO has a large minus charge (-29 mV) and hydrophilic groups such as OH and COOH groups, GO adsorbed self-doped PAS molecules with -NH^+=C (emeraldine salt) and -NH- groups by coulomb interaction and hydrogen bonding, which possibly brought about such zeta-potential change.

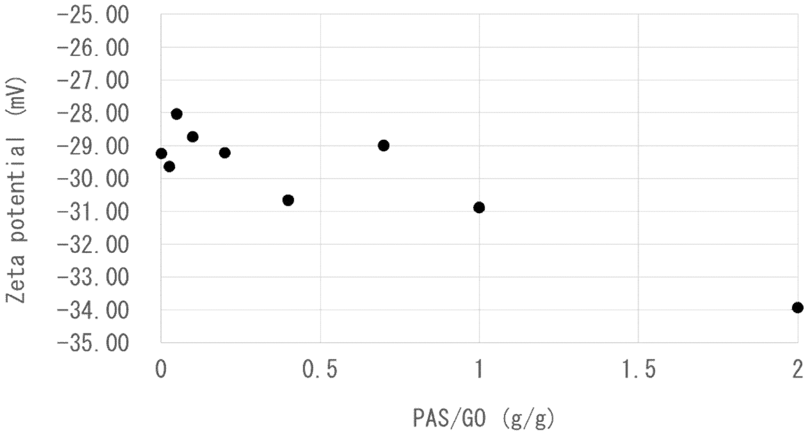

Figure 3. Zeta potential of GO titrated with aqueous PAS solution

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Fig.4 shows the UV-Vis spectra of different PAS/GO mixtures in water, changing GO/PAS ratio 0, 0.05, 0.1, 0.25, 0.5 and 1. The absorption peak at 474 nm is assigned as a polaron bond [3, 4]. The peak at 474 nm decreased and new shoulder peak at a little shorter wave length appeared, which possibly resulted from the decrease of the self-doping ability of SO_3H to –N=C- in PAS molecule or a small conformational change of PAS molecule caused by an access of OH, COOH groups on GO to –N=C- bond in PAS molecule. There is possibly a weak interaction between PAS molecules and GO in water.

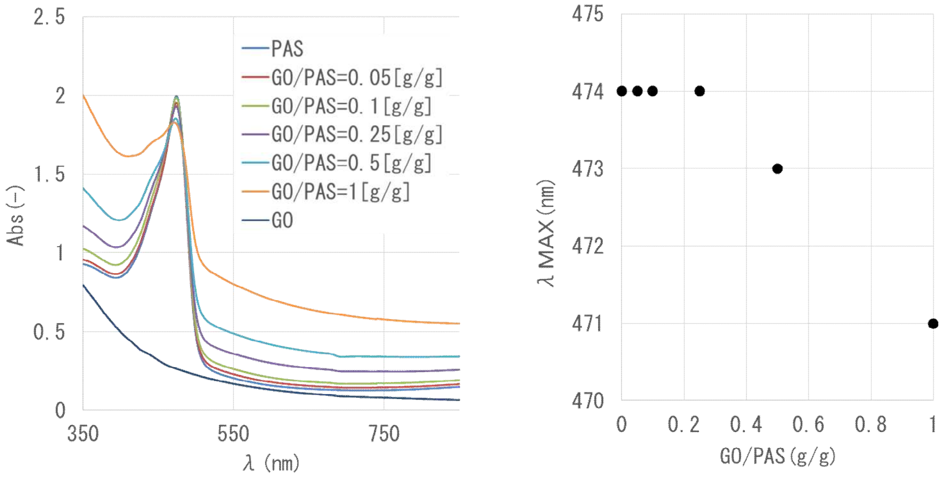

Figure 4. UV-Vis spectra of GO/PAS/water dispersion (PAS conc.: 0.06 %)

3.3. Effect of GO content on volume resistivity (ρ) of PAS/GO thin film composites

Fig.5 shows the ρ values of the PAS/GO thin film composites with the different weight ratio of GO/(GO+PAS), which were heat-treated at 100, 150 and 170 ˚C. The ρ value change of PAS/GO composites was dependent on the heat treatment temperature. The ρ values of PAS/GO composites heat-treated at 100 ˚C increased with the weight ratio of GO/(GO+PAS), but heat-treatment at 150 and 170 ˚C decreased their ρ values gradually with the GO content, which was lower than that of GO thin film heat-treated at each temperature. This behavior is almost the same with that of PANI:DBSA/GO as mentioned before [5].

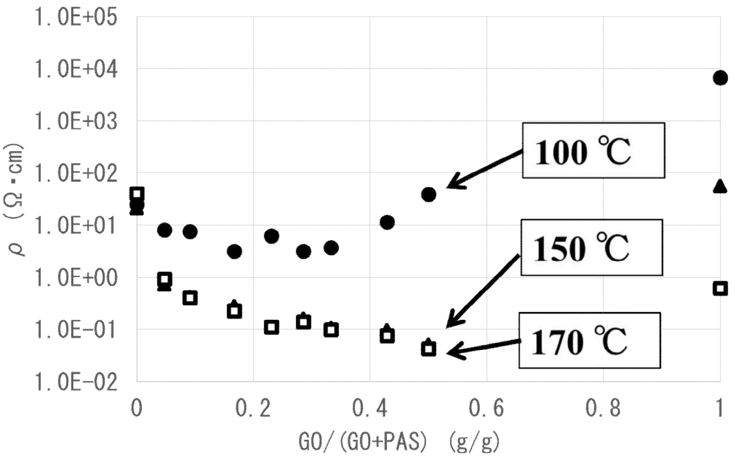

Figure 5. Effects of GO addition ratio and heat treatment on ρ values of PAS/GO thin film composites (heat-treatment conditions: 100, 150, 170 ˚C × 1 hour)

Fig.6 shows the Raman spectra of the PAS/GO thin film composites heat-treated at 170 ˚C for 1 hour. The G-band peak of heat-treated GO observed around 1580 cm^{-1} did not shift with PAS content, which suggested that the electronic state of GO in the heat-treated PAS/GO was not influenced by the PAS molecules. There is no electronic interaction between GO and PAS in the heat-treated PAS/GO solid.

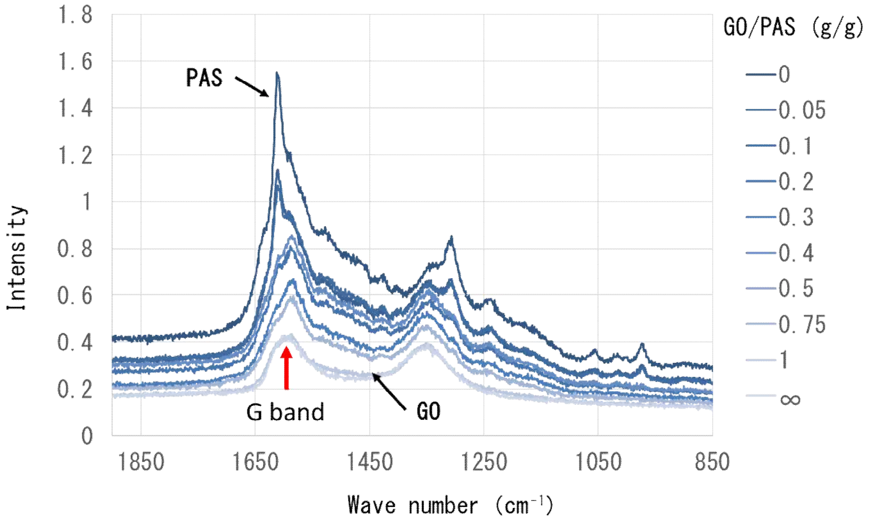

Figure 6. Raman spectra of PAS/GO thin film composites heat-treated at 170 ˚C for 1 hour

3.4. Mechanism of heat-treatment effect on conductivity enhancement of PAS/GO composites

The authors reported before that the conductivity enhancement of PANI:DBSA/GO composites by heat-treatment was ascribed to the thermal reduction of GO to rGO acceralated by DBSA dopant with a strong acidity [5]. Then the authors studied the effect of PAS monomer, 2-methoxyanilin-5-sulfonic acid (MeASA), on the thermal reduction of GO.

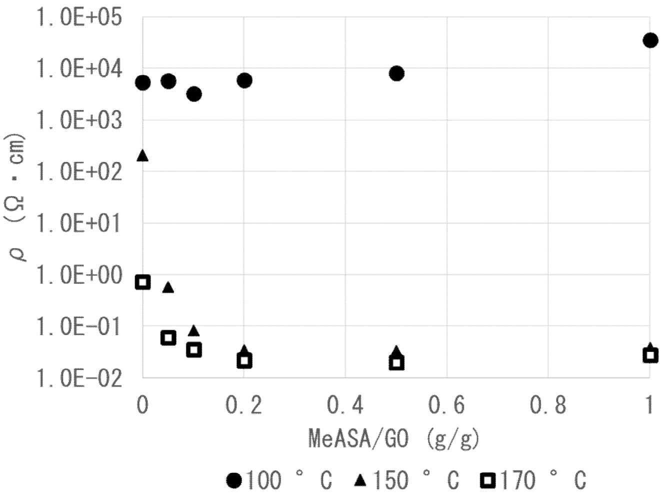

Figure 7. Effect of MeASA and heat-treatment on ρ values of MeASA/GO

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Fig. 7 shows the relationship between the content of MeASA and ρ values of MeASA/GO composites heat-treated at 100, 150 and 170˚C. Their ρ values decreased with the increase of MeASA and the heat treatment temperature. The MeASA/GO solids with its ratio of 0.5 heat-treated at 150 and 170 ˚C showed the lower ρ value, 0.037 and 0.028 Ω cm, which were lower than ρ values of PAS/GO composites corresponding to them (150 ˚C:0.051, 170 ˚C:0.043) as shown in Fig. 5. Conductivity enhancement of PAS/GO composites is ascribed to the sulfonic acid groups in PAS molecules, which possibly works as an accelerator of thermal reduction of GO to rGO.

Fig.8 shows the XPS spectra of GO, PAS/GO and MeASA/GO thin film solids heated-treated at 170 ˚C. There were no difference in XPS spectra among them, of which the large peak observed at 284.5 eV was ascribed to C=C(sp^2) bond. XPS spectra indicated that there were no difference in the chemical structures of the products (graphene-like compounds with conjugated C=C bonds) after the heat-treatment among them, which were produced from C-O bonds on GO by the thermal reduction [6]. There are some reports that GO sheets can be readily reduced under a mild condition using hydrohalic acid [7] or L-ascorbic acid (L-AA) [8]. It is concluded that conductivity enhancement of PAS/GO is not caused by the electronic interaction such as π-π stacking between GO (or rGO) and PAS, but mainly by the increase of C=C(sp^2) bonds owing to the acceleration of thermal reduction by SO_3H groups in PAS molecule.

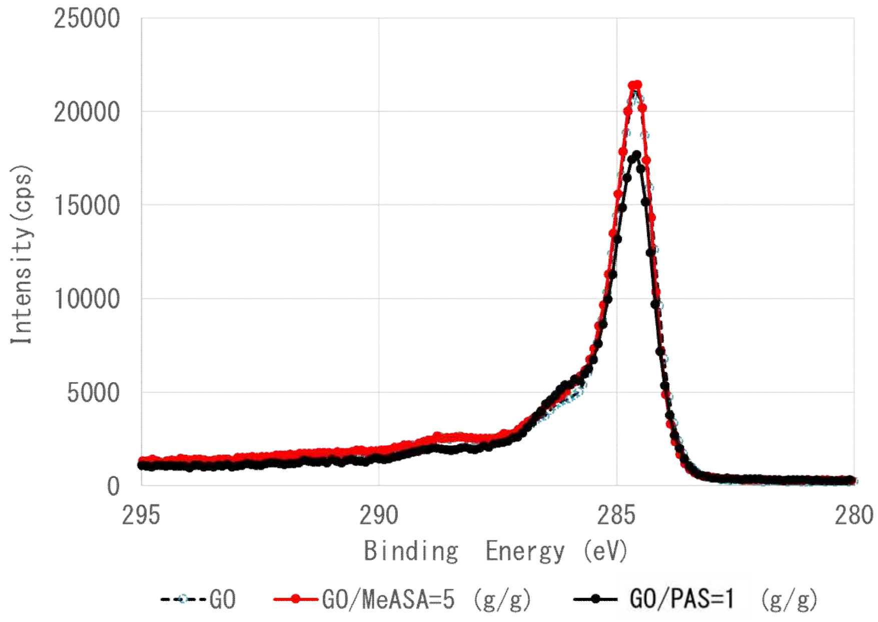

Figure 7. XPS spectra of GO and GO/MeASA or PAS heat-treated at 170 ˚C for 1 hour

4. Conclusions

The conductivity of PAS/GO thin film composites increased with GO content and heat-treatment temperature (150 and 170 ˚C). Measurements of UV-Vis spectra and zeta-potential of PAS/GO/water dispersion suggested some physical interaction between PAS molecules and GO. The conductivity enhancement of PAS/GO thin film solids was due to not the π-π interaction between PAS molecules and GO surface (or rGO (reduced type GO)), but the increase of C=C(sp^2) bonds (possibly conjugated), where thermal reduction of GO were promoted by SO_3H groups in PAS at a higher temperature.

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Acknowledgments

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