Structural Stability and Variable Dielectric Constant in Poly Sodium 4-Styrenesulfonate Intercalated Graphite Oxide

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The structural stability and dielectric constant of poly sodium 4-styrenesulfonate (PSS) intercalated graphite oxides (GOs) were investigated. We found that the interlayer distance of a PSS-treated graphite oxide increased by about 1 Å compared to that of the precursor graphite oxide. This increase in interlayer spacing was attributed to the intercalation of a monolayer of planar PSS into the graphite oxide interlayers facilitated by a \( \pi-\pi \) interaction between the aromatic rings of the graphite oxide and PSS. The PSS-intercalated graphite oxide had a higher structural stability than the pristine graphite oxide during thermal treatment because of the high melting point of PSS. Furthermore, the dielectric constant of the PSS-intercalated graphite oxide increased significantly at temperatures between 20 and 100 °C, and both of the GO and PSS–GO samples had dielectric constants that varied as a function of temperature due to their hydrophilicity.

I. Introduction

Graphite oxide has promise for use in the fabrication of supercapacitors.1 Because graphite oxide has an extended interlayer distance of up to 6–10 Å, its use in the electrodes of a supercapacitor could increase the capacitance of the device because of availability of intercalant electrolyte ions. However, a serious drawback is that the interlayer of the graphite oxide shrinks during the charging/discharging process,1 which results in a reduction of capacitance. The interlayer distance of the graphite oxide also decreases during the simple thermal annealing at 100 °C that is used in the manufacturing of supercapacitor electrodes.1 These processes cause the removal of some of the functional groups located between the graphite oxide interlayers.1

One approach to preventing interlayer shrinkage is to form a bridge between the interlayers that is chemically stable and inert during heat treatment. Since graphite oxide is water-soluble, the bridge material should be water-soluble as well. To maintain structural stability, a polymer with an aromatic ring structure could be utilized to enhance the \( \pi-\pi \) interaction with the layered graphite oxide. In our study, we introduced PSS to intercalate into the graphite oxide.

Poly sodium 4-styrenesulfonate (PSS) is a polymer based on polystyrene with a benzene ring that contains \( \text{SO}_3^- \) and \( \text{Na}^+ \) ions. The chemical formula of PSS is \( \text{C}_8\text{H}_7\text{NaSO}_3 \), and its molecular mass is 206. PSS has been used as a dispersant for dispersion of graphitic nanoplatelets in aqueous solution.2 Polymers with a benzene ring such as polyaniline, polyvinyl alcohol,8 poly(ethylene oxide),10 poly(vinyl alcohol),11 poly(allylamine hydrochloride),12 and poly(vinyl acetate)13 have also been used for this purpose. However, these chemicals are not proper intercalants for our purpose because they are not soluble in water,1,4,7 have low melting points,5,8–11,13 and high toxicity.5,9,12 On the other hand, PSS is water-soluble and has a higher melting temperature (460 °C) due to ionic bonding and the high polarity of sodium and sulfonate. Another advantage is that PSS is known to be nontoxic. Therefore, we chose PSS as an intercalant for graphite oxide to improve its structural stability during thermal treatment while maintaining its nontoxic nature.

II. Experimental Methods

Graphite oxide (GO) was synthesized from natural graphite flakes (99.999% purity, 200 mesh, Alfar Aesar) using a modified Brodie’s method.14 Graphite flakes (5 g) were oxidized by sodium chloride oxide (45.2 g, Sigma-Aldrich) in fuming nitric acid (100 mL, Matsunoen Chemicals Ltd. JAPAN) for 24 h at room temperature as described elsewhere.14,15 The graphite oxide obtained (200 mg) was dispersed in deionized water (250 mL) by dropwise addition of a 0.1 M NaOH aqueous solution until the pH was equal to 10 and then sonicated for 1 h. Figure 1a shows the well-dispersed graphite oxide solution. A PSS aqueous solution was made from2go fP S S (Sigma-Aldrich, MW = 18 000) and 200 mL DI water. The mixture was sonicated for 10 min for better dissolution (pH = 4.9). The two solutions (GO and PSS) were mixed and stirred for 12 h (pH = 8.0 ± 0.2). Then, the PSS–GO composite was formed into a thin film on a filter (0.1 μm, Anodisc 47, Whatman) by slow filtration for over 1 day (Figure 1b).

The interlayer distances in the samples were measured by powder X-ray diffraction (XRD, Rigaku RotaFlex D/MAX system, Rigaku, Japan) with a Cu anode (1.54 Å). The physical structure was assessed by scanning electron microscope (SEM, JEOL JSM6700F) images that were acquired at 10 keV, while simultaneous compositional analysis was obtained in energy dispersive X-ray spectroscopy (EDX) mode. The functional groups in pristine graphite (PG), graphite oxide (GO), PSS, and...
the PSS–GO thin film were also identified by Fourier-transform infrared spectroscopy (FTIR spectroscopy, Bruker IFS-66/S). Samples of PG, GO, and PSS were ground with KBr to make pellets, but the PSS–GO thin film was used in its unmodified form. Chemical bonding between the functional groups and carbon atoms was confirmed by X-ray photoelectron spectroscopy (XPS, ESCA2000, VG Microtech, England). The samples were put in a vacuum chamber at a base pressure of 1 × 10⁻⁶ Torr for the thermal treatment. The chamber was filled with argon gas (550 mTorr), and the samples were heat-treated at 200 °C at a heating rate of 50 °C/min for 10 h. The dielectric constants of the samples were measured with a dielectric spectrometer (DES, Seiko Exstar 6000, Japan) in the temperature range from 25 to 100 °C and in the frequency range from 10 to 100 kHz.

### III. Results and Discussion

The uniform thin film of PSS-intercalated graphite oxide (Figure 1b) was first characterized by X-ray diffraction along with the PG and GO, as shown in Figure 1c. The X-ray (002) peak of the pristine graphite was observed at 2θ = 26.4° indicating an interlayer distance of 3.37 ± 0.002 Å. This peak shifted to 12.5° after the 24-h oxidation treatment, indicating that the interlayer distance in the graphite oxide increased to 7.09 ± 0.156 Å. The interlayer distance in the graphite oxide was expanded by the presence of epoxide, carboxyl groups, and water molecules between the graphene oxide layers, which made the graphite oxide hydrophilic. This increase is mentioned again in the FTIR section. The peak shifted again to 10.9° in the PSS–GO sample, indicating an interlayer distance of 8.08 ± 0.277 Å. The interlayer distance increased by 1 Å compared to that of the precursor GO. This can be explained by the removal of water molecules driven by the intercalation of PSS. We can conjecture that the 2.8 Å³ space vacated by the removal of the water molecule is easily taken up by the intercalating PSS, expanding the interlayer distance of the PSS–GO to 8 Å. The intercalation of PSS is possible when a monolayer of planar PSS lies parallel to the GO sheets. This structural transformation will be discussed in the FT-IR and XPS analysis section.

Sample morphology was investigated by SEM (Figure 2). The SEM image of pristine graphite shows a chunky layered structure (Figure 2a). After oxidation treatment for 24 h, the layered structures were exfoliated and some of the flakes were cleaved further (Figure 2b). The PSS powder had spherically shaped particles of various sizes (Figure 2c). However, the PSS–GO composite maintained layered structures which were severely corrugated. The spherical PSS was dissolved in solvent and intercalated into graphite oxide. The qualitative compositions of the samples were simultaneously obtained using EDX analysis in the field emission scanning electron microscope (FESEM; Table 1). The pristine graphite consisted of mostly carbon with an oxygen content of 3 at %, which may be contributed by the carboxyl groups at the edges of the flakes. The oxygen content increased to 20 at % in the graphite oxide. The relative oxygen content measured by EDX varied slightly from batch to batch. The atomic ratios of C, O, Na, and S in PSS (C₈H₉Na₂SO₄) and PSS–GO were 70:16:7:7 and 72:20:5:3, respectively, as shown in Table 1. Since sodium was added to the PSS–GO while adjusting pH and the oxygen amount varied with moisture, the invariable component was the ratio of sulfur to carbon backbone. The S/C ratios for PSS and the PSS–GO were 0.1 and 0.04, respectively. This implies that the PSS content in PSS–GO was 40%, which is 0.04 divided by 0.1.

The presence of functional groups in the samples was confirmed by FTIR spectra. The pristine graphite showed a W1 peak around 3442 cm⁻¹ in Figure 3, which is ascribed to O–H stretching vibrations from water. Nevertheless, in the graphite oxide, the peak near 3500 cm⁻¹ can be assigned to both the hydroxyl groups (H1) and water peak (W1). Additional peaks in the graphite oxide spectra are assigned to an O–H deformation of water near 1620 cm⁻¹ (W2), an in-plane O–H deformation of the hydroxyl group near 1363 cm⁻¹ (H2), and an epoxide near 1063 cm⁻¹ (E), as seen elsewhere. The PSS spectra show water peaks near 3500 cm⁻¹ (W1) and 1645 cm⁻¹ (W2), CH₂, CH₃, and 1,4-benzene peaks (B1, B2, B3, B4, and B5), and three SO₃ peaks near 1410, 1233, and 1040 cm⁻¹. One asymmetric stretching CH₃ (2960 cm⁻¹) and two symmetric and symmetric stretching CH₂ related peaks (2922 and 2860 cm⁻¹) are also observed. Peak B1 near 3061 cm⁻¹ indicates a stretching vibration of the ring C–H bonds. Peak B2 near 1920–1808 cm⁻¹ represents a C–H out-of-plane bending overtone from 1, 4-benzene. Peak B3 at 1643, 1496, and 1449 cm⁻¹ is ascribed to a ring C–C stretching vibration, and peak B4 at 1130 cm⁻¹ and peak B5 at 1009 cm⁻¹ are assigned to an aromatic C–H in-plane deformation vibration. The spectra of the PSS–GO show a combination of peaks derived from graphite oxide and PSS, except for peak B3. In the graphite oxide and PSS, as shown by the arrows in Figure 3, the water peak (W2) and the aromatic ring C–C stretching vibration (B3) overlapped with each other. However, the PSS–GO spectra show a clear separation of these two peaks (W2 at 1640 cm⁻¹ and B3 at 1600 cm⁻¹), with peak B3 shifted down due to the π–π interaction. No extra or missing peaks besides the π–π interaction-shifted peaks just noted are observed in the PSS–GO composite sample but not in the isolated component samples. This indicates that the π–π interaction between the PSS and graphite oxide in the composite is the driving force in the creation of the laminated PSS–GO composite.

Other evidence for the π–π interaction in the PSS–GO can be inferred from the XPS spectra. The S 2p spectra of the PSS and PSS–GO showed similar 2p₁/₂ and 2p₃/₂ peaks with the same binding energies, but with different intensities (Figure 4a). The Na 1s spectra of the PSS and PSS–GO were similar as well (Figure 4b). This indicates that no additional chemical bonding related to sulfur or sodium was generated in the PSS–GO. However, the C1s spectra indicate a slight π–π interaction, since the binding energy of the sp² peak in the PSS–GO spectra decreased from 285.0 eV in the graphite oxide (Figure 4d) to 284.9 eV in the PSS–GO (Figure 4e). This is a
relatively small change compared to that seen in the FTIR spectroscopy because the XPS is surface-sensitive, while the FTIR spectroscopy measures a rather deep region of the sample. Therefore, we conclude that the $\pi-\pi$ interaction is the major interaction between the PSS and the graphite oxide in the PSS–GO composite and no extra functional groups were generated. Other deconvoluted peaks of C1s in the graphite oxide originated from hydroxyl, epoxide, and carboxyl groups as seen elsewhere.\textsuperscript{14,18–20} The intensities of the three deconvoluted peaks of C1s increased after the intercalation of PSS into the graphite oxide due to the broad C1s peak of PSS.
The thermal stabilities of the graphite oxide and PSS-GO were further tested by heat treatment at 200 °C for 10 h under ambient Ar. Figure 5 shows that the interlayer distances in the graphite oxide after annealing for 10 h decreased to 6.0 (2θ = 14.68°) and 3.9 Å (∼22.9°). Some functional groups such as epoxide and/or hydroxyl groups were removed to some degree as evidenced by the peak of the differential thermogravimetric analysis (TGA) at 237.8 °C (Figure 6c), causing the interlayer distances to contract. This thermal instability has been problematic in supercapacitor applications. On the other hand, the interlayer distance in annealed PSS-GO (PSS-GO_10h) seen in the XRD was split into 11.0 Å (∼26.3°) and 4.9 Å (∼18°). The interlayer distance contraction to 4.9 Å was attributed to the removal of the hydroxyl groups from the graphite oxide, while the main PSS layers remained unchanged based on the TGA results (Figure 6b–d). The other peak at 11.0 Å (∼26°) in PSS-GO_10h, which was expanded further compared to 8.1 Å for the pristine PSS-GO, was attributed to the reconstruction of PSS in the interlayers of the graphite oxide. The reconstructed PSS maintained the interlayer distance despite the removal of functional groups from the graphite oxide. The existence of PSS in the annealed PSS-GO sample is a key factor in maintaining the interlayer distances, as indicated in Figure 6d.

The dielectric constants of the PSS-GO and graphite oxide were investigated as a function of temperature and frequency (Figure 7). The dielectric constant of the PSS-GO (Figure 7a) was higher than that of the precursor GO (Figure 7b) since the hydrophilic PSS was intercalated into the graphite oxide. What is more intriguing is the temperature dependence of the dielectric constants, particularly in the low frequency region. At frequencies below 1 kHz, the dielectric constant of the PSS-GO sample increased rapidly, showing a maximum near 42 °C, and then increased again after 70 °C. Although a similar peak was observed for the GO sample, the position of the maximum peak increased to 52 °C and no increase was observed after 70 °C. It has been reported that the dielectric constants for a silica tube and a polyimide composite film have a maximum around 50 °C caused by water evaporation.21 The same reasoning could be applied to the PSS-GO composite and graphite oxide. However, the change in the dielectric constant in the silica tube and polyimide composite was between 3.5 and 4. It is worth noting that the structure of the PSS-GO sample was stable up to 180 °C, as seen in the TGA results in Figure 6. It is unlikely that the desorption of the epoxide and hydroxyl groups plays a role in the abrupt change in the dielectric constant when the temperature is below 100 °C. The dielectric constant of the PSS-GO sample at low frequencies in the static limit exceeded 18 and decreased rapidly at frequencies above 100 Hz (Figure 7c). A similar phenomenon was also observed in the graphite oxide sample, but its dielectric constant was not as high as that of the PSS-GO sample. The high dielectric constant of the PSS-GO can be attributed to the enhanced π–π interaction. By assuming that the conductivity of the PSS-GO and graphite oxide follows the simple metallic Drude model, \( \varepsilon_{\text{eff}} = \varepsilon_{\infty} + \frac{i\omega}{\sigma_{\text{eff}}} \), one can extract useful information. Figure 7c shows the dielectric constant as a function of frequency with the Drude model fittings at the temperature of maximum dielectric constant. This indicates that the important physical properties of graphite oxide are similar to those of metallic graphite, even though graphite oxide is severely structurally distorted by the presence of oxygen and hydrogen atoms. The real conductivities of the PSS-GO and graphite oxide determined from the fitting were...
1.97 × 10⁻⁶ and 2.16 × 10⁻⁹ S/m. The π–π interaction was enhanced in the PSS–GO compared to the GO, and this interaction was temperature-sensitive below 100 °C. This indicates the possibility of monitoring the π–π interaction by simply measuring the dielectric constant. Evaluating this requires a further detailed study. It is expected that these materials will be useful in many smart materials applications.

IV. Conclusion

The structural stability and dielectric constant of poly sodium 4-styrenesulfonate (PSS) intercalated graphite oxides (GOs) were investigated using XRD, SEM, EDX, FTIR, XPS, TGA, and dielectric spectrometry. A monolayer of planar PSS was oriented parallel to the graphite oxide sheets and bound between the graphite oxide layers by a π–π interaction. The PSS–GO has a higher structural stability than graphite oxide during thermal treatment for 10 h at 200 °C and a higher dielectric constant that varies with temperature from 0.5 to 18. The maximum dielectric constant always occurred at 42–52 °C, and its position was frequency-independent. Therefore, this composite can be used in new applications as a smart material.

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