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pTSA doped conducting graphene/polyaniline nanocomposite fibers: Thermoelectric behavior and electrode analysis

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Abstract
Highly conducting graphene/polyaniline (GN@Pani) nanocomposite was prepared by the in situ oxidative polymerization of aniline in the presence of GN and the surfactant, cetyltrimethylammonium bromide (CTAB). The micellar structure of CTAB assisted both, the formation of GN@Pani tubules and the dispersion of GN. Sheet-like GN was distributed uniformly in the Pani matrix, leading to high electrical conductivity because of the p–p interactions between Pani and GN. Studies of the thermoelectrical behavior using isothermal and cyclic aging techniques showed that GN@Pani possessed a high combination of electrical conductivity and thermal stability, even beyond 150 °C. GN@Pani was used as cathode active material in microbial fuel cells, and showed an enhanced power density and cell voltage, leading to better catalytic performance compared to plain carbon paper.

1. Introduction
The recent discoveries of carbon nanotubes (CNTs) and graphene (GN) by Iijima [1] and Geim and Novoselov [2], respectively, has triggered research towards nanosized carbonaceous materials throughout the scientific community. Among the different allotropes of carbon, GN has attracted considerable attention owing to its potential applications in a wide range of technologies, such as solar cells, fuel cells, sensors, and energy storage [3–6]. GN is a one atom thick sheet of sp² hybridized carbon atoms with a good combination of mechanical strength and conductivity, which is in contrast to the insulating properties of diamond, charcoal, etc. Accordingly, GN is considered as the next generation material because of its exceptional properties.

Recently, composites of GN with conducting polymers have attracted considerable attention because the resulting composite is expected to have enhanced additive properties. Among the different conducting polymers, polyaniline (Pani) has been widely explored most owing to its peculiar properties, such as low cost, ease of synthesis, and easy control of its redox states by simple acid–base chemistry [7]. In previous studies, Pani composites were
prepared using different metal oxides under different acidic conditions, and their electrical properties were examined under aging experiments [8–10]. The electrical conductivity and thermal stability were found to be dependent on the dopant acids and filler particles. Since GN exhibits good electrical conductivity and stability, composites of Pani with GN are expected to have high electrical conductivity and stability due to the synergism between constituents. These highly thermally-stable materials may find applications in advanced areas, such as sensors, electronics, and fuel cells [11–16].

The strong dependence on fossil fuels for energy demands is creating major problems because the burning of fossil fuels leads to the generation of gases linked to global warming [17]. The depletion of these resources is also an important issue of concern, which has encouraged scientists to search for economic and green energy production technology to meet growing demands. Microbial fuel cells (MFCs) are devices that utilize microorganisms as a catalyst for the conversion of organic substrates to electricity [18]. They generate electricity directly from a variety of waste materials, and have attracted increasing attention as alternative and relatively inexpensive energy source [19].

The limiting factor for power generation is the cathodic oxygen reduction rate, which has limited the use of MFCs for practical applications. Therefore, it is important to modify the cathode surface further and reduce the charge transfer resistance. Accordingly, in this study, highly conducting GN@Pani nanocomposite was prepared and coated on carbon paper (CP) to reduce the charge transfer resistance. The GN@Pani coated CP exhibited enhanced cathodic activity compared to plain CP. The electrical conductivity and thermal stability of the nanocomposites under aging conditions were also examined.

2. Experimental section

2.1. Chemicals and instrumentation

Aniline, para toluene sulfonic acid (pTSA) from Sigma Aldrich and GN was purchased from iljin Nano Tech, Seoul, Korea (thickness ~8 nm and average length ~500 nm). Potassium persulphate (PPS), cetyltrimethylammonium bromide (CTAB), HCl, and methanol were purchased from Duksan pure chemicals, Korea, and used as received. The water used in these experiments was de-ionized water used for a PURE ROUP 30 water purification system.

X-ray diffraction (XRD, PANalytical, X’Pert-PRO MPD) was performed using Cu Kα radiation (λ = 0.15405 nm). The surface morphology was examined by scanning electron microscopy (SEM, Hitachi-4200). The diffuse reflectance spectra (DRS) of GN@Pani were measured using a UV–VIS–NIR spectrophotometer (VARIAN, Cary 5000 U.S.A.). All measurements of the DC electrical conductivity (σ) were performed using a 4-in-line probe electrical conductivity measuring instrument with a PID controlled oven (Scientific Equipment, Roorkee, India). The calculations were performed using the following equation:

\[
\sigma = \frac{\ln(25W)}{2\pi S(V/I)}
\]

where I, V, W, and S are the current (A), voltage (V), film thickness (cm), and probe spacing (cm), respectively, and σ is the DC electrical conductivity (S cm⁻¹) [20].

2.2. Synthesis of GN@Pani nanocomposites

The GN@Pani nanocomposite was prepared in the presence of the surfactant CTAB by the in situ oxidative polymerization of aniline with GN using PPS as an oxidizing agent. The molar ratio of Pani/CTAB/oxidant was 1/0.25/0.5 in all experiments. GN (3% of aniline monomer wt. by wt.) was dispersed in a CTAB solution prepared in 1 M HCl and ultrasonicated for 15 min. Aniline was then added to the above dispersion, and stirred vigorously to allow proper adsorption on GN, which was later polymerized by the addition of oxidant prepared in 1 M HCl solution. The reaction mixture was stirred constantly for 24 h. The resulting mixture transformed slowly into a greenish black slurry, which was filtered and washed thoroughly with double distilled water to remove the excess acid and PPS until the filtrate became colorless. The nanocomposite after washing was dedoped in a 1 M ammonia solution, followed by washing with methanol to remove the Pani oligomers. Subsequently, the prepared emeraldine base form of the GN@Pani nanocomposite was doped with 500 mL of 1 M pTSA by stirring the nanocomposite in the wet stage for 5 h. The pTSA-doped GN@Pani nanocomposite was filtered and dried at 60 °C for 24 h in an air oven, converted to a fine powder and stored in a desiccator for further experiments.

2.3. Studies and measurements

The electrical conductivity was measured using pelletized samples of GN@Pani (0.1 g) with the assistance of a hydraulic pressure instrument at a 50 kN pressure for 10 min. The stability of the nanocomposite was examined in terms of their retention of the DC electrical conductivity using isothermal and cyclic aging techniques under ambient conditions. In isothermal aging experiments, pellets of the nanocomposites were heated to 50, 70, 90, 110, and 130 °C in a PID controlled temperature oven. The electrical conductivity was measured at 10 min intervals. In the cyclic aging experiments, the DC electrical conductivity was measured at temperatures ranging from 40 to 150 °C for five times at 45 min intervals. The GN@Pani was annealed before the aging studies to remove the volatile impurities and adsorbed moisture, which might affect the electrical properties. Fig. S1 shows the digital photograph depicting the working conditions of the 4-in-line probe electrical conductivity measuring instrument. The UV-visible diffuse absorbance spectra of GN@Pani was measured at room temperature (~25 °C) and at wavelengths ranging from 200 to 800 nm. The GN@Pani nanocomposite was also examined as a cathode-active material in the MFCs. Details of the experimental setup is given in the supplementary section (Fig. S2) and are reported elsewhere [21].

3. Result and discussion

3.1. Preparation of GN@Pani nanocomposite

Fig. 1 presents the synthesis scheme of the GN@Pani nanocomposite. In the system of a fixed polymer concentration and varying surfactant concentrations, two critical conditions appear. The first is when the surfactant concentration is below a critical micelle concentration (cmc), i.e. the onset of the association of the surfactant with the polymer. At this concentration, the adsorption or aggregation of the surfactant occurs on the polymer surface. Under the second condition, normal micellization of the surfactant occurs when the polymer is saturated with a surfactant, i.e. beyond the cmc limit [22,23]. The GN@Pani nanocomposite was prepared in the presence of CTAB as the surfactant. As CTAB has a very long alkyl chain of 16 carbons, and its concentration was well above the cmc (>0.0009 mol/L), it self-aggregated into the supermolecular structures when dissolved in the aqueous phase to form micelles [24]. CTAB, when dissolved in water, appears to form tubular micelles (Fig. 1a). The tubular micelle in the presence of anilinium cations acts as a template for the formation of nanostructures (Fig. 1a).
The fraction of aniline/aniline adsorbed on GN, which becomes polymerized inside the template, forms fibrous/tubular structures. The remaining aniline, which does not have a template, forms flake-like structures. The presence of GN (Fig. 1b) provides the template for micelle formation by CTAB. Therefore, the polymerization of Pani occurs in a highly confined environment. Such condition leads to the formation of nanocomposites with a highly interconnected fibrous and tubular network with a lower likelihood of forming a flaky morphology. Some long tubular structures combine and generate bundles composed of several to dozens of tubular nano-aggregates, leading to the formation of a network structure. Fig. 1c shows a cross section view of a micelle over GN.

### 3.2. Scanning electron microscopy

The morphology of GN@Pani was analyzed by FESEM at different magnifications, as shown in Fig. 2. The morphology was mostly tubular with some flaky-like structures because polymerization had been performed in both a partially-confined environment, i.e., in a template channel of CTAB, and a non-confined environment. The presence of GN provides a template for micelle formation by CTAB, so a Pani coating over GN can be observed (Fig. 2). Such condition leads to the formation of nanocomposites with highly interconnected fibrous and tubular network morphology. In

**Fig. 1.** Schematic diagram of the mechanism of GN@Pani nanocomposite formation.

**Fig. 2.** SEM images of GN@Pani nanocomposite at different magnifications.

**Fig. 3.** XRD pattern of GN@Pani nanocomposite.
addition, these conditions do not allow a flake-like morphology. The growth of Pani on the GN surface is difficult to observe because of the much smaller dimensions of GN (≈8 nm × ≈500 nm) [25].

3.3. X-ray diffraction

The XRD pattern of GN@Pani (Fig. 3) revealed a single broad amorphous peak for Pani at 19.5° 2θ, owing to the periodicity parallel to the polymer chain [26]. The sharp peak was observed at 26.5° 2θ, which was assigned to graphite with a typical d-spacing of 0.33 nm, and smaller peaks were observed at a higher angle (44°, 55°, 77° and 84° 2θ), indicating the presence of GN in the nanocomposite [27]. This suggests that GN had been incorporated successfully into Pani, and the polymerization condition did not result in the modification of GN, which is important for the successful translation of the properties of both constituents into the GN@Pani nanocomposite. The XRD pattern of GN@Pani after the aging experiments (Fig. S3, supplementary information) showed peaks corresponding to Pani (a shoulder at ~19.5° 2θ) and GN (26.5°, 44°, 55°, 77° and 84° 2θ). This confirmed that no structural deformity had occurred during the aging experiments and GN@Pani is highly stable at temperatures as high as 150°C.

3.4. UV-visible diffuse absorbance spectroscopy

The prepared GN@Pani nanocomposites showed strong absorption in the UV-visible region with some extension in the near IR region. The UV-visible spectra showed three absorbance peaks at λ = 320, 410 and 670 nm, which originated from a π-π transition of the benzenoid rings, the polaron–π transition, and π-polaron transition, respectively. The peak at ~670 nm was assigned to protonated Pani in the prepared nanocomposites (Fig. 4) [28]. The reflectance spectra (Fig. 4 inset) showed a similar tendency of light interactions, as in the absorbance spectra. The reflectance peak at 470 nm could be assigned to the localized polarons in protonated Pani.

3.5. Electrical conductivity

The GN@Pani nanocomposite were prepared using an in situ oxidative polymerization method in the presence of CTAB. CTAB cannot act as a doping agent for Pani because of large size of its cation. Therefore, the nanocomposite was doped with pTSA. This is in contrast to the Pani composites with multi walled CNT prepared in the presence of dodecyl-benzene-sulphonic-acid (DBSA), where DBSA acts as both a doping agent and surfactant [20].

The initial room temperature electrical conductivity of the as-prepared pTSA-doped GN@Pani was 26.5 S/cm, which was much higher than Pani doped with inorganic acids [19]. The high electrical conductivity might be due to the following: (a) an increase in the metallic regions in the nanocomposite, (b) a decrease in the hopping/tunneling distance, and (c) an increase in the density of charge carriers [29]. Another factor is the incorporation of GN (conductivity of pTSA-doped Pani under similar conditions was measured to be ~6 S/cm), the increase in electrical conductivity might be due to the additive/synergistic effect of both Pani and GN because both GN and Pani are conducting. In addition, the incorporation of GN forms a more efficient network for charge transport. Saini et al. [30] reported that the GN@Pani composites are richer in quinoid structures, and the π bonded surface of GN might interact with the conjugated structure of Pani, particularly through the quinoid structure. This interaction might facilitate the charge transfer process, thereby increasing its conductivity. Fig. 5 presents a schematic diagram of the movement of charge carriers related to the increase in electrical conductivity.

The electrical conductivity of GN@Pani was examined before and after annealing at 150°C, as shown in Fig. 6a. The electrical conductivity decreased after annealing but the conductivity showed a uniform increase at higher temperatures. The decrease in electrical conductivity might be due to the loss of (a) moisture, (b) dopant, (c) impurities, etc. [8]. The ordered alignment of Pani chains might occur during the annealing process, which also contributes to the uniform electrical conductivity behavior.

The electrical conductivity of annealed GN@Pani examined under cyclic aging conditions revealed an increase in electrical conductivity at higher temperatures (Table 1), which is normal thermal activation behavior (Fig. 6b). At higher temperatures, the mobility of the charge carriers increases via the Pani–Pani chains or through the π–π interaction of GN and Pani, resulting in an increase in the electrical conductivity. Fig. 6b shows that the electrical conductivity was similar, even after several cycles. The initial electrical conductivity showed slight loss (0.86 and 0.59 S/cm in 2nd and 3rd cycle respectively) initially, after which it became constant (Fig. 7a). Fig. 7b shows the loss/gain in electrical conductivity after each cycle. GN@Pani showed a gain in electrical conductivity in all cycles. This became almost constant in the 3rd and 4th cycles, which is semiconducting behavior. Therefore, the nanocomposite showed excellent semiconducting behavior after annealing repeatedly at higher temperatures.

The electrical conductivity of the annealed GN@Pani was also examined under isothermal aging conditions (Table 2). The change in the relative electrical conductivity during each experiment was divided by the experimental duration (30 min) to obtain the relative electrical conductivity loss/gain per minute of heating according to the following equation:

\[
\text{Change in relative electrical conductivity/minute} = \frac{\text{Final relative electrical conductivity} - \text{Initial relative electrical conductivity}}{\text{Duration of experiment (30 min)}}
\]
GN@Pani showed very small loss (~10^{-3} S/cm) at almost all temperatures. The loss at higher temperatures was similar. These results confirm the semiconducting behavior of GN@Pani (Fig. 8).

These results suggest that ptTSA has a major effect on the DC electrical conductivity stabilization because the loss of dopant is minimized at higher temperatures. Reports of HCl-doped Pani nanocomposite with TiO_2, GN and ZnO showed stability until ~130 °C, after which a loss of electrical conductivity was observed at higher temperatures [8,26]. In the present case, GN@Pani exhibited high conductivity at room temperature as well as remarkable stability up to 150 °C with no apparent loss in conductivity.

Therefore, the presence of GN and ptTSA increases the electrical conductivity and thermal stability. The loss of ptTSA was minimized at higher temperatures compared to HCl, which produced nanocomposites with high thermal stability.

### 3.6. Application of GN@Pani in microbial fuel cell

MFC is well known for power generation, and depends on the material for cathodes. The highly conducting materials showed better performance in MFC. Therefore, GN@Pani was used as a cathode active material in MFCs owing to its good combination of conductivity and environmental stability. Fig. 9a and b shows the comparative polarization and power density curves of CP and GN@Pani in MFCs. The performance of the MFCs was evaluated by varying the external resistance. The performance of the MFCs was evaluated using a power density curve, from which the power produced was calculated at different resistances. The current and power was calculated using the following equations:

\[
I = \frac{V}{R}
\]

\[
P = R \times I^2
\]

where \(I\) (A) is the current, \(R\) is the applied external resistance to the system in ohms (Ω), \(V\) (volt) is the voltage produced, and \(P\) (watt) is...
the power produced by the MFC. As shown in Fig. 9a and b, GN@Pani exhibited the highest OCV of 0.593 compared to plain CP (0.492 V). The order of the maximum power density for the MFCs was GN@Pani > CP. GN@Pani showed a two fold increase in the maximum power density to 0.01795 W m$^{-2}$ compared to the 0.00921 W m$^{-2}$ achieved in the case of CP. Therefore, GN@Pani coated on CP showed better performance than plain CP owing to its high conductivity, high catalytic activity and greater surface area, which eventually increases the rate of oxygen reduction. Plain CP produced lower power production due to smaller surface area and lower catalytic activity. Therefore, the GN@Pani cathode exhibited higher catalytic activity and improved power generation and is expected to find better applicability in MFC compared to CP.

4. Conclusions

The GN@Pani nanocomposite was synthesized successfully using an in situ polymerization technique in the presence of GN, followed by doping with pTSA to render it conducting. The nanocomposite showed high electrical conductivity owing to the high mobility of the charge carriers through a π−π interaction between Pani and GN. The DC electrical conductivity examined using isothermal and cyclic aging techniques showed conductivity retention, even after repeated use. The GN@Pani nanocomposite used...
as an alternative cathode in MFCs had higher density because of the high conductivity of GN@Pani. The maximum power density of GN@Pani achieved was 0.01795 W m\(^{-2}\) compared to that of plain CP (0.00921 W m\(^{-2}\)). pTSA doped GN@Pani is believed to be a suitable replacement for Pani in a range of electrical and electronic devices because of its better thermoelectric and electrode performance.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2013.12.033.

References