Fabrication of carbon microcoil/polyaniline composite by microemulsion polymerization for electrochemical functional enhancement

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1. Introduction

Carbon microcoil (CMC) is an amorphous carbon fiber which takes a spiral microstructure with 1–10 μm coil diameter and possesses good elastic property [1–5]. This type of novel material has some unique properties like absorption of high electromagnetic wave, stereospecific nature of magneto resistance, high electrical conductivity, high hydrogen adsorption, etc. [6–10]. Therefore CMC with unique characteristics has attracted much attention of researchers for their technological promising applications as electromagnetic absorbers, tactile sensors and so on. CMC embedded in silicone rubber matrix has been developed as a potential tactile sensor with high sensitivity to distinguish the weak force based on the extension and contraction as the force is applied [11].

CMC has stimulated multi- and inter-disciplinary research activities of the carbon materials like carbon nanotube. With highly promising potentials for applications, the CMC is an attractive building block for developing the advanced hybrid materials and devices of great practical importance. One strategy to achieving this goal is the fabrication of CMC/polymer composite with enhanced mechanical properties that alter the electrical properties according to the transformation mechanism of mechanical signal to electrical signal. Recently Adhikari et al. [12] have reported the fabrication of CMC/poly(vinyl alcohol) composite material with enhanced mechanical property and electrical conductivity. In addition of the formation of conducting CMC network, these types of composites are potential for applications to electronics. Therefore matrices of conjugated polymers are fabricated with CMC to increase conductivity and mechanical and thermal stability for applications to optoelectronics.

Polyaniline (PANI) is one of the important conducting polymers because of its relatively facile processability, high electrical conductivity and environmental stability [13,14]. Nanostructured conducting PANI has been proved to be an excellent electrode material which is applicable to various biosensors, because of its beneficial features that include a large surface area, homogeneity, unique redox property, a high electrical conductivity, and a strong adhesion to the electrode surfaces [15,16]. However, the thermal decomposition or desorption causes the release of the conducting polymer chain, and this phenomenon will affect the electrical conductivity of polymer. The mechanical envelopment of the highly oriented polymeric structure is well known to stop desorption of dopant from the polymer backbone. Therefore the PANI composites materials are required to induce an ordered structure. Last few years several studies have highlighted the PANI-decorated carbon nanotube composite for advancing electrical properties [17–20].

Meanwhile the spiral structure of CMC with flexible mechanical properties attracts a great deal of interest as a scaffold material of PANI composite for novel electronic applications. In the present work CMC/PANI composite was synthesized and characterized. An effective utilization of the CMC, as a filler material for either conductive or mechanical property, can be achieved only with...
homogeneous dispersion within the matrices, without damaging their integrity. Such dispersibility can be optimized by coating the individual CMC with a PANI layer, creating the core–shell microwire by microemulsion polymerization. The microemulsion aids the reduction in the agglomeration and entanglement of CMC in the aqueous solution, so that the polymerization of aniline on the surface of CMC can proceed with a significantly reduced concentration of initiator. The morphology and microstructure of the CMC/PANI composite are characterized by using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The thermal stability of the synthesized CMC/PANI composite is analyzed by thermogravimetric analysis (TGA). The electrochemical performance of the composite is studied and compared with the oxidized CMC. Then the utility of the composite such as an electrode material for super capacitor should be possible. The possible merit to use CMC as one of components of the electrode is its wide surface area and ultra-lightweight as a support of the electric conduction material.

2. Experimental

2.1. Reagents

CMC was prepared according to previously reported procedure [21]. Aniline monomer, ammonium persulfate (APS), sodium dodecyl sulfate (SDS), nitric acid, and KOH were purchased from Acros Organics. All reagents were of analytical grade and used without further purification. Ultra pure (Millipore Milli-Q) water was used for all synthesis and in the cyclic voltammetric (CV) study. Nickel foam substrate-150 μm (0.5 mm thickness) was purchased from Mitsubishi Materials Corporation, Japan.

2.2. Oxidation of CMC

The oxidation of CMC was performed according to the previous procedure [22]. The pristine CMC (100 mg) was suspended in concentrated HNO3 (50 cm3) and refluxed in a round-bottomed flask with a reflux condenser. The reaction was carried out at 90 °C for 10 h in an oil bath with slow stirring. The oxidized CMC was filtered using a 0.2 μm Teflon filter paper. Then the residue on filter paper was washed with plenty of water until the filtrates remain neutral and dried at 60 °C under vacuum for 24 h.

2.3. Synthesis of CMC/PANI composite

The CMC/PANI composite was synthesized by emulsion polymerization. First O/W (1:24) microemulsion was prepared using 0.2 M SDS in water (1 M HCl) and chloroform with vigorous stirring. Then the oxidized CMC (10 wt% based on the aniline concentration) was dispersed in the microemulsion solution with ultrasonication for 5 min. The 0.25 M aniline monomer was added to the CMC microemulsion with constant stirring. The polymerization process was allowed to proceed by adding a 0.25 M APS solution and the reaction solution was slowly stirred for 8 h at 0–5 °C. The polymerization was terminated by pouring the reaction mixture into acetone, and the CMC/PANI composite was precipitated. The precipitated CMC/PANI composite was washed with water, acetone, ethanol and 1 M HCl until the filtrate was colorless to remove the unreacted aniline monomer, low molecular weight PANI, APS and SDS. Then the composite was dried in vacuum oven at 60 °C for 24 h.

2.4. Characterizations

The microstructure of the samples was investigated by a SEM (JEOL JSM-6500F) and a TEM (Hitachi H-7000 with a CCD camera attachment). A Nicolet 6700 (Thermo scientific) FT-IR spectrometer was used for FT-IR analysis of the samples. TGA experiments were carried out using a Q500 equipment (TA Instruments, USA), where powders (4–5 mg) were heated at a scan rate of 10 °C/min from 25 to 800 °C under N2 atmosphere.

2.5. Electrochemical study

The electrochemical study was carried out in a 6 M KOH solution by three electrodes setup using Ni-foam as a working electrode, Ag/AgCl as a reference electrode and Pt foil as a counter electrode. The cyclic voltammogram (CV) was measured by an Hz-3000 automatic polarization system (Hokuto Denki, Japan). The working electrode was prepared by mixing CMC/PANI composite material and poly(tetrafluoroethylene) (PTFE) (95:5 mass ratio) and by dispersing them in ethanol. Then the resulting mixture was coated on the Ni-foam substrate (1 cm2) and finally dried at 100 °C under vacuum for 12 h. The prepared electrode contains 10 mg electroactive composite with binder material. The current in CV analysis was reduced into per unit mass of electroactive CMC/PANI composite material.

3. Results and discussion

3.1. Fabrication of CMC/PANI composite

The fabrication of CMC/PANI composite was carried out on the basis of the emulsion polymerization reaction. The overall reaction process for the synthesis of CMC/PANI composite by microemulsion polymerization is shown in Scheme 1. First SDS surfactants form the O/W microemulsion in the chloroform/water system. The polar head group of the SDS surfactant on the outer surface of the O/W microemulsion stabilizes the system. In the second step the oxidized CMC is added into the microemulsion system and then some microemulsions are adsorbed on the polar surface of the oxidized CMC. In the third step aniline monomer is added into the microemulsion system, and the addition of APS initiator is followed. Aniline and APS molecules are diffused into two sites due to their hydrophobic nature: (1) inside the microemulsion droplet and (2) on the hydrophobic surface of oxidized CMC. During the polymerization process the growth rates in the droplet are suppressed, because monomer diffusion is balanced by a high osmotic pressure of the hydrophobe. The diffusion could occur between droplet and the CMC, as in suspension polymerization. As the polymerization proceeds preferably on the surface of the CMC, the monomer will diffuse from the droplet onto the CMC surface. The insoluble polyaniline oligomers and polymers are then deposited on the surface of CMC.

3.2. Characterization of CMC/PANI composite

Characterization of CMC/PANI composite was performed using a FT-IR spectroscopy. Fig. 1 shows the FT-IR spectra of pristine CMC, oxidized CMC, CMC/PANI (10 wt%) composite and PANI. While no significant characteristic bands were observed in pristine CMC, oxidized CMC exhibits a band at 1730 cm−1 ascribed to the characteristic C=O stretching vibration mode of COOH group. FT-IR spectra of PANI and CMC/PANI composite were nearly identical: The significant characteristic IR bands at 2920, 1300, and 1150 cm−1 are assigned to a stretching mode of the C–H bonds in the phenyl rings and the bending modes of C–N bonds in the benzene and quinone rings, respectively. The C=C vibration bands at 1590 and 1490 cm−1 in the benzene and quinone groups on an IR spectrum of PANI are shifted to lower wavenumbers, 1580 and 1487 cm−1, respectively, on CMC/PANI. This is because of hydrogen bonds and electrostatic interactions, improving the conjugation degree of the PANI chains at the CMC surface. Another reason is the configurational change of
PANI from a coiled chain to an extended chain. The most noticeable change on an IR spectrum from oxidized CMC to that of CMC/PANI is the disappearance of a characteristic C=O stretching vibration band (1730 cm\(^{-1}\)) of COOH group. This indicates that COOH groups on oxidized CMC are exhausted on the process of the synthesis of CMC/PANI. Thus FT-IR spectroscopic results confirm the successful synthesis of CMC/PANI composite.

3.3. Thermal stability of CMC/PANI composite

The thermal stability of pristine CMC, oxidized CMC, CMC/PANI (10 wt%) composite and PANI under nitrogen atmosphere was examined by TGA as shown in Fig. 2. Pristine CMC is very stable and no decomposition was observed in temperature range of 30–800 °C. The weight loss (10 wt%) of oxidized CMC started from 30 °C and continued up to 800 °C. This loss is due to the decomposition of the functionalized carboxylic groups on the surface of CMC. Fig. 2c shows the 2 step thermal degradation of CMC/PANI (10 wt%) composite. The first 12% weight loss was observed from 30 to 100 °C, mainly arising from the release of adsorbed water and/or small molecules which are trapped in the composite. The second weight loss at the temperature range 200–800 °C was around 48%.

This loss is caused by the decomposition of PANI on the CMC surface. The TGA curve of CMC/PANI can be compared with that of PANI in Fig. 2d. Although the first small weight loss from 30 to 100 °C by absorbed water/molecules on the PANI is only 4%, the second weight loss from 200 to 270 °C was 33% and attributed to the loss of acid dopant in PANI which is not observed in CMC/PANI. Finally significant amount (38%) of weight loss due to the thermal degradation of PANI was observed from 270 to 800 °C. Since the thermal degradation of both PANI and PANI in CMC/PANI occurs through wide temperature region, it is obvious that this degradation is not a single-step reaction but a multi-steps reaction.

3.4. Morphology of CMC/PANI composite

Microscopy is a good tool for direct visualization of morphology. The SEM images of microstructures of pristine CMC, oxidized CMC, and CMC/PANI (10 wt%) composite were taken, as illustrated in Fig. 3. The pristine and oxidized CMCs are clearly evident as the spiral structure with smooth surface in SEM images (Fig. 3A and B). In contrast, for the CMC/PANI composite, remarkable
changes in the structural morphology were observed: The surface roughness of spiral CMC was visualized by the deposition of PANI.

The deposition of PANI can be elucidated even from TEM images. Fig. 4 shows TEM images of oxidized CMC and CMC/PANI (10 wt%) composite. Against the smooth surface of CMC (Fig. 4A), the TEM observation (Fig. 4B) of CMC/PANI (10 wt%) composite reveals the less dense veil on CMC, indicating that the spiral CMC microstructure is coated with PANI. The veil thickness of the PANI can be estimated to be ∼200 nm.

3.5. Electrochemical performance of CMC/PANI composite

Fig. 5 shows CV analysis curves of the synthesized composite material in comparison with PANI and oxidized CMC. The oxidation and reduction processes were denoted as positive and negative currents in the curves. There are a couple of redox peaks in CV curves of PANI, oxidized CMC and CMC/PANI (10 wt%) composite, although their currents from PANI are very weak. The voltammogram of oxidized CMC is indicative of rectangular shape, due to the capacitive property of its spiral mesoporous microstructure. Different from PANI and oxidized CMC, the CMC/PANI composite presents larger response currents driven from the semiconducting and conducting states of PANI. This kind of pseudocapacitance property comes from the surface faradic reaction of the electroactive materials and the CMC promotes such property.

CV results of CMC/PANI (10 wt%) composite at different scan rates are shown in Fig. 6. It was clearly observed that the cathodic peak shifts positively and the anodic peak shifts negatively with increasing scan rates from 10 to 50 mV s⁻¹. This phenomenon results from the resistance property and the rate capability of the composite electrode. Thus the CV results of the CMC/PANI
composite with large current density indicate the higher capacitive behavior than the PANI and oxidized CMC.

4. Conclusions

CMC/PANI composites were prepared by emulsion polymerization in the presence of O/W microemulsion and CMC. The synthesized PANI uniformly coated on the surface of spiral CMC to form a stable suspension, dispersing the CMC. This bottom-up polymerization method provides a novel surface modification procedure for helical 2-dimensional CMC and can be extended to other polymer/2-dimensional layer systems. The polyaniline-coated CMC revealed the enhanced electrochemical property. Therefore the CMC/PANI composite can be projected as a promising thermally stable electrode material such as for capacitor.

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References