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Porphyrin-stabilized CNT in nanofiber via non-covalent interaction for enhanced electrochemical performance

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ABSTRACT

Herein, a new fabrication method for CNT nanofiber composite (pPC-FP) through non-covalent interaction between porphyrin monomers with CNTs is reported. This led to the alleviated agglomeration of pristine CNT without acid pre-treatment, producing a highly porous material with high surface area of 444 m^2/g and narrow pore size distribution for all pPC-FP nanofiber composites. Enhanced performances of pPC-FP3 and pPC-FP5 (CNT nanofiber with porphyrin monomers) were brought about by the enhanced CNT dispersion, hence, better porosity as compared to pPC. Moreover, through the incorporation of porphyrin monomer, M-N–C bond was simultaneously formed and served as a contributor to the excellent capacitive performance of the material, resulting in the highest capacitance of 150 A/cm^2 at 0.25 mAh/cm^2 with 77 A/cm^2 at 2.5 mAh/cm^2. The composites also exhibited stable performance even after cycling at different current densities (0.25–2.5 mAh/cm^2) for 3000 cycles with almost 100% columbic efficiency. Through π-π stacking interaction, the agglomeration was prevented and CNT was aligned along the axis of the polymer which rendered the nanofibers highly porous resulting to a conductive composite material with excellent electrochemical performance.

1. Introduction

For the past few years, renewable energies such as solar cells, wind turbine, redox batteries and artificial photosynthesis have garnered a lot of attention for as one of the alternative energy source replacing fossil fuel [1–3]. The reason behind of the transition of energy source is due to the hazardous constituents that are emitted in utilization of fossil fuel [4]. Hence, the drastic change in the climate have accompanied due to the accumulation of greenhouse gases such as carbon dioxide, nitrogen oxides and particulate matter which are also known to have tremendous effect on human health [5,6]. In lieu of a cleaner emission, new technologies have recently been introduced that utilize non-toxic materials and environmentally appropriate reactants such as water for hydrogen production [7–9], methanol as direct fuel cell [10–12], oxygen in the metal-air batteries [13–16]. However, these technologies are still far from being materialization, thus, a more practical technology is in need. One of rising technology in energy storage is supercapacitor, which is known to have the capability of fast charge-discharge process as compared to the conventional capacitors and lithium-ion batteries [17,18].

Supercapacitors are categorized into two types of materials electric double layer capacitor (EDLC) and pseudocapacitors [19]. The former are carbon based materials and a lot of the reported literature focus on this kind of material by taking advantage of their high stability compared to pseudocapacitors [20–23]. They also have high surface area with tunable pore size distribution and good mechanical properties (tensile strength) for device application. One of the most commonly utilized material for EDLC are carbon nanotube (CNT) due to their excellent electrical conductivity. They are regarded as a good candidate material not only limited to supercapacitor but as well also to other area such as chemisensors [24,25], electrochemical reduction and oxidation reactions [26,27], photovoltaics [28–31] and so on. They also provide a sturdy support for the active materials and enhances the conductivity when necessary. However, pristine CNTs are hard to manipulate due to its excessive agglomeration [32–35] as a result of van-der-waals interaction [36], thus, poor dispersion in most solvents. Especially

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in nanofiber fabrication, agglomeration of CNT plays a significant role in determining the textural property of the material which might also affect negatively the overall performance of the composite by either the collapse in the surface area, uneven distribution and random orientation of CNT strands resulting to an insulating effect to the entire composite. So in order to overcome such drawback, a corrosive acid oxidation treatment is typically employed by functionalizing the surface of the CNT with hydrophilic oxygenated groups to improve its dispersion and prevent particle agglomeration [37–41]. Although acid oxidation step is commonly employed, it is only applicable for laboratory scale but highly undesirable for large-scale production as it creates a hazardous condition for handling and processing.

Another method employed for better dispersion of CNT is using surfactants which contain hydrophobic and hydrophilic moieties that can stabilize the CNT and prevent agglomeration. However, most of surfactants are ionic in nature and carry positive or negative charges. Hence, they can disrupt the fiber formation due to high charge density similar to reports of polymer fibers electrospun with ionic liquids [42].

One of the highly utilized property of the CNT is π-conjugation which allows interactions with conjugated organic molecules to attach onto the surface. Porphyrin, a conjugated macrocyclic compound, has an established interaction on CNT via non-covalent wrapping and this interaction with conductive material (graphene, CNT) has been exploited on many applications solely for the purpose of increasing the conductivity of porphyrin resolving its main drawbacks [43–46]. In this study, three major roles of the non-covalent interaction of porphyrin on CNT has been reported. 1) To increase the degree of dispersion in solvent for facile electrospinning fabrication, 2) to form M-N–C as a redox active material on the polymer fiber composite with excellent supercapacitive performance. And lastly, 3) to assist in the formation of a well aligned CNT within polymer matrix allowing the fabrication of a polymer fiber with high surface area after pyrolysis. Thus, supercapacitive performance of pristine CNT were enhanced via π-π stacking interaction with porphyrin and is the first report regarding on electrospun CNT nanofiber composite to have an intact nanofiber morphology with high degree of porosity without the need of an acid oxidation step.

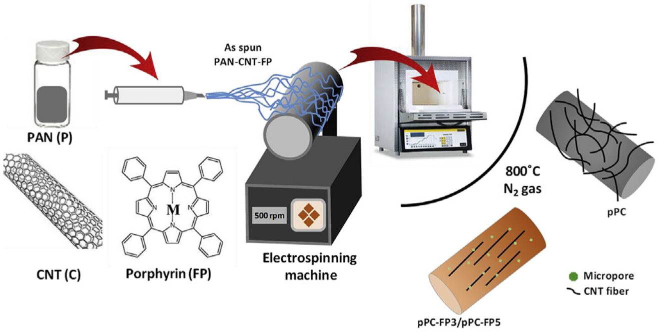
2. Experimental section

2.1. Materials and reagents

Iron Poprhyrin (FP) was synthesized similar to previous literature [47]. Multi-Walled Carbon Nanotube (CNT, 10–15 μm, 50–85 nm diameter) was purchased from Graphene Supermarket. The polyacrylonitrile (PAN, Mw = 150,000) was purchased from Sigma–Aldrich, Korea. N, N′-Dimethylformamide (DMF, Daejung), N-methylpyrrolidone (NMP, Daejung) were used as solvents. Nafion D-521 (5% w/w in water and 1-propanol, ≥0.92 meq/g exchange capacity) was purchased from Alfa Aesar. All materials were used as purchased without further purification.

2.2. Fabrication of as-spun polymer fiber (PAN-CNT-FP)

In a typical experiment (Scheme 1), 30–50 mg of FP was dissolved in DMF together with 10 mg of CNT and sonicated for an hour prior to the addition of PAN to obtain 10 wt% polymer solution. The solution was kept stirring overnight at 50 °C to maintain a homogeneous solution. The dope solution was transferred into a polypropylene syringe with 0.51 mm inner diameter needle tip. The syringe pump (Model: EP100, NanoNC) flow rate was kept 4 mL/h with an applied voltage (HV Power Supply, HV30, NanoNC) of 15 kV to form the nanofibers collected on an aluminum foil. The drum-type collector (Model: DC90, NanoNC) and needle tip distance was 10 cm. The fabricated polymer fibers were vacuum dried at 50 °C overnight and used as desired.



Scheme 1. Schematic representation of the fabrication of polymer fiber composite.

2.3. Pyrolysis of nanofiber (pPC-FP)

The fabricated polymer fibers were stabilized at 280 °C with a rate of 1 °C/hr and held for an hour and increased the temperature to 800 °C under nitrogen atmosphere with a rate of 5 °C/hr and held for an hour before cooling down to room temperature. The pyrolyzed nanofibers were used as required for characterization and electrochemical analysis.

2.4. Preparation of CNT-FP composite

In a 10 mL DMF, CNT and FP was dissolved in a ratio of 1:5 to ensure the optimized amount of interaction of the two material. The solution was ultra-sonicated for 1 h before collecting via centrifugation. The solids were continuously washed using different solvents such as dichloromethane, tetrahydrofuran and acetone until the solution became clear and then the solids were air dried and used as required.

2.5. Materials characterization

The phase and morphology of the material were characterized by powder X-ray diffractometer (XRD, Shimadzu XRD-6000) with Cu K-alpha irradiation (λ = 1.5406 Å), Field emission scanning electron microscopy (FE-SEM, Sigma S-4000) and transmission electron microscopy (TEM, Philips CM 200). Infrared spectra of the prepared CMPs were obtained using FTIR spectroscopy (Agilent, Cary 630). The elemental composition and oxidation state were analyzed using X-ray photoelectron spectroscopy (XPS Thermo, Esca lab 250xi). The specific surface area and pore size distribution of the materials were all studied by a Belsorp mini -II (BEL, Japan) instrument with the method of Brunner-Emmet-Teller (BET) and micorpore analysis for surface area and pore size distribution analysis, respectively. Prior to the actual absorption experiment, the samples were degassed at 100 °C for 12 h.

2.6. Electrochemical characterization

All the electrochemical tests were carried out on a ZIVE SP1 electrochemical workstation (Won-A-Tech Co. LTD, South Korea) by using prepared electrode material. The electrochemical tests were performed using three-electrode cell system in aqueous 1 M H_2SO_4 solution as the electrolyte with glassy carbon (GC, 3 mm diameter), Pt wire, and saturated Ag/AgCl as working, counter, and reference