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Nitrogen DC-pulse atmospheric-pressure-plasma jet (APPJ)-processed reduced graphene oxide (rGO)-carbon black (CB) nanocomposite electrodes for supercapacitor applications

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ABSTRACT

This study compares supercapacitors with reduced graphene oxide (rGO)-carbon black (CB) and CB nanocomposite coated carbon cloth electrodes. We use a nitrogen DC-pulse atmospheric pressure plasma jet (APPJ) to process the electrodes. The APPJ processing time is < 40 s. Nitrogen APPJ burns off organic binders to create nanoporous structures. Replacing part of the CB with rGO nano-flakes can increase the overall surface area to improve the supercapacitive performance. Specifically, by replacing 50 wt% of CBs with rGOs, the specific (areal) capacitance can be improved from 91.84 $\mathrm{F \cdot g^{-1}}$ (19.74 $\mathrm{mF/cm^2}$) to 162.68 $\mathrm{F \cdot g^{-1}}$ (29.16 $\mathrm{mF/cm^2}$), respectively, with 20 s APPJ processing time, as evaluated by cyclic voltammetry under a potential scan rate of 2 $\mathrm{mV \cdot s^{-1}}$. The nitrogen DC-pulse APPJ is demonstrated to be an ultrafast and highly economical tool for efficiently processing nanocomposite electrodes of supercapacitors.

1. Introduction

Atmospheric-pressure plasma (APP) is a highly economical and environmentally friendly technology because it can be operated under regular pressure without requiring any vacuum equipment. APP technology has been applied in various area thus far, including food processing [1, 2], surface modification [3, 4], and biomedicine [5, 6]. APPs have versatile characteristics depending on design of the electrode configurations and excitation methods, thus enabling the realization of plasmas with various charge densities and heavy particle temperatures. A nitrogen DC-pulse atmospheric-pressure plasm jet (APPJ) has been found to react violently with carbon-based materials, with the strong CN emissions being observable by optical emission spectroscopy (OES) during APPJ processing [7–11]. A nitrogen DC-pulse APPJ affords ultrafast processing capability with processing time < 30 s. Therefore, it is widely used for the rapid processes of rGOs and carbon nanotubes (CNTs) in supercapacitors [9–11], rGO counter electrodes of dye-sensitized solar cells [12, 13], and electrochemical sensor [14]. APPs have also been used for material etching [15, 16]. For example, Liu et al. etched and patterned the electrodes of multi-walled carbon nanotubes (MWCNTs) using a micro plasma-jet [17].

Supercapacitors have high power density and long cycle life, making them attractive as energy storage devices [18, 19]. Supercapacitors generally have one or two types of charge storage mechanisms: electrical double-layer capacitance (EDLC) which is usually seen in carbon-based materials and pseudocapacitance which is usually seen in metal oxides with multiple oxidation states and conducting polymers [20–23]. Carbonaceous materials such as graphene, CNTs, and CBs have been extensively used in supercapacitors [10, 22–28]. Graphene is an outstanding electrode for EDLC owing to its high surface area to volume ratio, excellent electrical conductivity, and good chemical stability. Graphene is frequently added to nanocomposites consisting of metal oxides, conductive polymers, and nano-carbons to improve the supercapacitive performance. For example, Lim et al. reported an SnO_2-graphene nanocomposite supercapacitor with specific capacitance of 363.3 $\mathrm{F\,g^{-1}}$ as measured by cyclic voltammetry (CV) [29]. Fan et al. fabricated a CNT-graphene sandwich-structured supercapacitor that showed specific capacitance of 385 $\mathrm{F\,g^{-1}}$ at scan rate of 10 mV/s in a 6 M KOH solution [30]. Wang et al. reported a solid-state supercapacitor with rGO-CB hybrid films with specific capacitance of

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112 F g^{-1} at scan rate of 5 mV/ s [26]. Fei et al. presented an all-solid-state supercapacitor with graphene-CB electrodes that had specific capacitance of 144.5 F g^{-1} at current density of 0.5 A g^{-1} [25].

In this study, we screen-printed pastes containing rGO, CB, terpineol, ethyl cellulose, and ethanol onto carbon cloth. Then, we used a nitrogen APPJ to process the rGO-CB and CB electrodes because this APPJ shows high reactivity with carbon-based materials. The APPJ process can efficiently remove organic binders and dope nitrogen into electrodes with a short processing time. Brunauer–Emmett–Teller (BET) surface area analysis shows that the replacement of 50 wt% rGO with CB can increase the total surface area. Electrochemical impedance spectroscopy (EIS) results indicate that the rGO-CB electrodes have lower charge transfer impedance. Therefore, the addition of rGO to CB improves the supercapacitor performance.

2. Experimental details

2.1. Preparation of screen-printing pastes

CB pastes were prepared as follows: 0.1 g of CB powder (purity: > 99%, diameter: < 30 nm, Golden Innovation Business Co., Ltd), 3.245 g of terpineol (anhydrous, #86480, Fluka), 1.75 g of 10 wt% ethyl cellulose (5–15 mPa·s, #46070, Fluka) ethanolic solution, 2.25 g of 10 wt% ethyl cellulose (30–50 mPa·s, #46080, Fluka) ethanolic solution, and 1.5 g of ethanol were mixed for one day using a magnetic stirrer. Subsequently, 4 ml of this mixture was condensed at 55 °C for 5 min using a rotatory evaporator. rGO-CB pastes were prepared by a similar process except that half of the amount CB powder (in wt%) was replaced with rGO nano-flakes (purity: 99%, sheet size: 0.1–5 μm, thickness: < 5 nm, Golden Innovation Business Co., Ltd); 0.05 g each of rGO and CB powders was used.

2.2. Fabrication of supercapacitors

CB and rGO-CB pastes were deposited on carbon cloth (W0S1002, without microporous layer and PTFE, CeTech Co. Ltd) with area of 1.5 cm × 2 cm using a screen-printing machine. The printed area was processed by a DC-pulse nitrogen APPJ for 0, 20, and 40 s. Fig. 1(a) shows the schematic of the DC-pulse APPJ equipment. The temperature reached ~550 °C within a short duration after the APPJ was turned on, as shown in Fig. 1(b). The temperature was measured using a K-type thermocouple. The APPJ operation parameters are described in detail elsewhere [31].

The gel-electrolyte was prepared by mixing 1.5 g of polyvinyl alcohol (PVA) into 15 ml 1-M H_2SO_4 by magnetic stirring at 80 °C for 4 h. The preparation process was considered complete when the gel-electrolyte became clear. Then the PVA-H_2SO_4 electrolyte was coated on the electrode and dried at room temperature for one day. This process was repeated three times. Finally, two pieces of gel-coated electrodes were assembled together on the gel-electrolyte sides to form a sandwich-type supercapacitor.

2.3. Characterization of materials and supercapacitors

The APPJ was characterized by OES (USB4000, Ocean Optics). A scanning electron microscope (SEM, Nova NanoSEM 230, FEI) was used to inspect the surface morphology of the CB and rGO-CB electrodes. A goniometer (Model 100SB, Sindatek Instruments Co., Ltd.) was used to measure the water contact angle. X-ray photoelectron spectroscopy (XPS, VGS Thermo Scientific spectrometer) was used to analyze the surface chemical state. A porosimetry system (Micromeritics ASAP 2010) was used to determine the specific surface area.

The electrochemical performance of the supercapacitors was evaluated by CV, galvanostatic charging/discharging (GCD), EIS, and cycling stability using an electrochemical workstation (Zahner Zennium). CV was measured at scan rates of 2, 20, and 200 mV·s^{-1}. The CV cycling stability was performed at a scan rate of 200 mV·s^{-1} for 1000 cycles. GCD was conducted at different constant currents. The potential scan range was 0–0.8 V for CV and GCD measurements. EIS was conducted with amplitude of 5 mV in the frequency range of 100 kHz to 0.1 Hz.

3. Results and discussion

Fig. 2(a) and (b) show the emission spectra during APPJ processes of CB and rGO-CB electrodes. The CN violet system ($B^2\Sigma \rightarrow X^2\Sigma$) is observed clearly at around 358.39, 385.09, 415.24 and 450.22 nm. Wavelengths longer than 530 nm, seen in Fig. 2(c) and (d), are attributed to N_2 1st positive emissions ($B^3\Pi_g \rightarrow A^3\Sigma_u^+$). Fig. 3 shows the OES spectra of CB and rGO-CB electrodes. The CN emission intensity increases and then decreases as the APPJ processing time increases. Both CB and rGO-CB samples show strong CN emission systems that are indicative of reactions between reactive nitrogen species and carbon-based materials. For the same processing time, the rGO-CB sample shows higher CN intensity than the CB one, indicating more violent interaction of reactive nitrogen plasma species with rGOs.

Fig. 4 shows 30,000× magnification SEM images of screen-printed CB and rGO-CB on carbon cloth without/with APPJ processing. CB and rGO-CB have ball and mixed ball-flake morphology, respectively. The as-deposited nanocomposite electrodes were wrapped by organic binders. The addition of rGOs increases the total BET surface area from 0.59 m^2 (CB) to 0.97 m^2 (rGO-CB). The higher surface area increases the

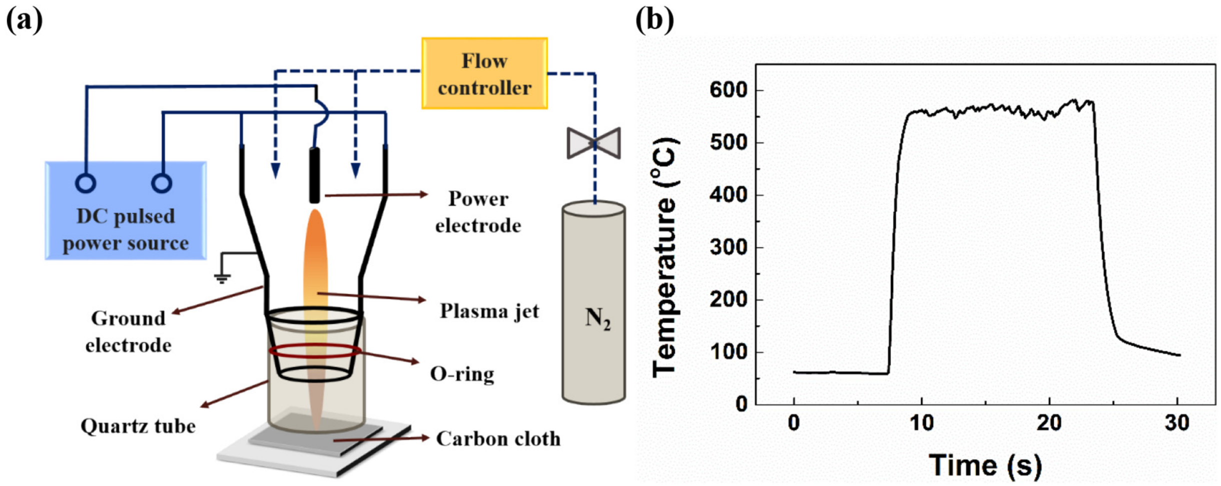

Fig. 1. (a) Schematic of DC-pulse APPJ setup, and (b) surface temperature of sample under APPJ operation.

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