Synthesis of Carbon Dots from the Biomass Products for Supercapacitor Applications

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Abstract. Biomass-derived CDs were prepared via a green one-step synthetic method. The orange juice biomass was used as a CD precursor. The resulting CDs were mixed with rGO under the hydrothermal condition to prepare rGO/CD composites with the variation of rGO:CD mass ratio. The composites were characterized through both physical and electrochemical methods. Moreover, the capacitive property of rGO/CD composites in 2 M KOH aqueous electrolyte was studied by cyclic voltammetry, galvanostatic charge-discharge measurements, and electrochemical impedance spectroscopy. The rGO/CD composite with a 4:1 mass ratio exhibits the high specific capacitance with 184.8 F g⁻¹ at a current density of 0.5 A g⁻¹. The rGO/CD 4:1 composite retains 97.3% of its initial capacitance after 1000 cycles at the current density of 10 A g⁻¹ in 2 M KOH electrolyte solution.

1. Introduction

Supercapacitors (SCs), also known as ultracapacitors or electrochemical capacitors, have many advantages for energy storage due to their high power densities, long cycle life, low maintenance cost, and environmentally eco-friendly nature. In general, SCs can be classified into three categories such as the electrical double-layer capacitors, pseudocapacitors, and hybrid capacitors. Each class is dependent upon its unique mechanism for storing charges [1]. In terms of carbon materials, carbon dots (CDs), a zero-dimensional carbon material, have attracted tremendous interest owing to their outstanding electronic properties, quantum confinement, and edge effects. CDs are used for several practical applications such as supercapacitors, batteries, optoelectronics, and biomedical field. Recently, several carbon sources, including small chemical molecules, have been employed for CD synthesis. One interesting challenge is to use CDs obtained from the sustainable resource. Biomass products are considered to be one of the most competent candidates for CD synthesis. Advantages of biomass energy are in terms of reducing chemical exposure, reducing waste, cheap and eco-friendly synthesis, and abundant sources [2].

Herein, rGO/CD composites were prepared by using a hydrothermal method and their electrochemical properties were systematically investigated. CDs were synthesized by using orange juice as a biomass-derived source. The effect of rGO:CD ratio on the electrochemical performance of the composites was also presented.
2. Experimental

2.1. Preparation of CDs by using orange juice
40 mL of the pulp-free orange juice and 300 µL of ethylenediamine were mixed into a 125 mL Teflon-lined stainless steel autoclave and heated at 160°C for 4 h. After cooling, the dark brown solution was centrifuged at 10000 rpm for 30 min to remove large particles. The dark brown supernatant was collected and filtered through a 0.22-μm syringe filter. After that, the solution was washed with excess dichloromethane to extract unreacted organic species. Subsequently, the yellowish brown aqueous solution was dialyzed in DI water using a tubular dialysis bag with the molecular weight cut-off of 3.5 kDa for 24 h. The purified CD aqueous dispersion was pre-concentrated and freeze-dried.

2.2. Preparation of rGO/CD composites
GO was prepared by using modified Hummers’ method [3]. Then, 100 mg of as-prepared GO was dissolved in aqueous solution and sonicated for 1 h. Variable amounts of CD were added to GO solution with continuous stirring to establish a homogeneous solution. After that, the reaction solution was hydrothermally heated in the autoclave at 180°C for 9 h. After cooling, the rGO/CD composites were centrifuged at 10000 rpm for 10 min and then washed with DI water. Finally, the composites were vacuum-freeze dried. The rGO/CD composites with different rGO:CD mass ratio of 6:1, 4:1, 2:1, and 1:1 were systematically denoted as rGO/CD 6:1, rGO/CD 4:1, rGO/CD 2:1, and rGO/CD 1:1, respectively.

2.3. Electrochemical measurements
The electrochemical performance of all samples was evaluated by using a conventional three-electrode system. Three-electrode setup was composed of a working electrode (electroactive material), reference electrode (Ag/AgCl in 3 M KCl), and counter electrode (Pt sheet) in a 2 M KOH aqueous electrolyte. The active material was prepared by mixing rGO/CD, PVDF binder, and conducting carbon black with 80:10:10 mass ratio. The specific capacitance can be calculated from the galvanostatic discharge of a supercapacitor by using the following equation; \( C_s = \frac{I\Delta T}{m\Delta V} \), where \( C_s \) is the specific capacitance (F g\(^{-1}\)), \( I \) is the discharge current (A), \( \Delta t \) is the discharge time (s), \( \Delta V \) is the discharge potential window (V), and \( m \) is the mass of active material (g).

2.4. Material characterization
The morphology of all samples was characterized by scanning electron microscopy (SEM, QUANTA 450) and transmission electron microscopy (TEM, JEM-3100F). The X-ray photoelectron spectrum was recorded using the PHI 5000 Versa Probe II XPS system (ULVAC- PHI, Japan) with Al Kα (1486.6 eV) as an X-ray source. Raman spectra were collected on a Raman microscope (InVia, Renishaw) with a laser excitation at 514 nm.

3. Results and discussion
As shown in Figure 1a, the spherical CDs were mainly observed in TEM with monodisperse particle and lattice fringe of 0.21 nm, corresponding to the (1 0 0) plane of graphitic carbon [4]. The size distribution of CDs ranges from 2.5 - 5.5 nm with the average size of 4.0 nm. Figure 1b presents a high-resolution C 1s XPS spectrum of CDs. The spectrum was deconvoluted into five distinct carbon components at the binding energy of 284.0, 285.5, 287.2, 288.4, and 291.7 eV, which is consistent with the presence of C–C/C=C, C=O/C–N, C=O, O–C=O, and π–π* transition, respectively [5]. It suggests that the hydrophilic group is abundant in the CD structure. Moreover, the morphology of rGO in Figure 2a exhibits crumpled sheets with random aggregation. Upon incorporation of CDs, the composite exhibits more open structure and the aggregation of rGO sheets was prevented as shown in Figure 2b. The TEM image of selected rGO/CD 1:1 in Figure 2c exhibits transparent thin rGO nanosheets with small CD aggregates.
Figure 1. (a) TEM and high resolution (inset) images and (b) C1s XPS spectrum of CDs.

Figure 2d reveals the Raman spectra of GO, rGO, and rGO/CD 4:1. For GO, the In/Ig ratio was calculated to be 1.76, which suggests a relatively low graphitic sp² carbon in the structure. After reduction, the In/Ig ratio of rGO is decreased to 1.61. For rGO/CD 4:1, the In/Ig ratio is slightly lower than that of rGO, indicating that the composite contains the larger extent of graphitic-sp² carbon.

Figure 2. SEM images of (a) rGO and (b) rGO/CD 4:1 (c) TEM image of rGO/CD 1:1 and (d) Raman spectra of GO, rGO, and rGO/CD 4:1.

Figure 3a shows the CV plots of all samples at a scan rate of 200 mV s⁻¹. The CV curve of rGO is distorted from the rectangular shape. The reversible anodic and cathodic humps between -0.4 and -0.8 V originate from the combined contribution of the electrical double layer and faradaic redox capacitances. In comparison with rGO, CV curves of all as-prepared rGO/CD also show the distorted rectangular shape. The area under the CV curves of rGO/CD 4:1 is slightly larger than that of the other samples, suggesting the enhanced specific capacitance of the composite. Furthermore, the observed current of rGO/CD 4:1 in Figure 3b gets increased with increasing the scan rate, which is ascribed to the increasing concentration of electroactive ions at the electrode-electrolyte interface at the higher scan rate. The galvanostatic charge/discharge curves of electrodes with different rGO/CD mass ratio are compared at a current density of 0.5 A g⁻¹ as shown in Figure 3c. The specific capacitance of rGO is 171.3 F g⁻¹. Meanwhile, the rGO/CD composites provide the enhanced specific capacitance with 183.8 F g⁻¹ for rGO/CD 6:1 and 184.8 F g⁻¹ for rGO/CD 4:1. However, the specific capacitance declines to 158.7 F g⁻¹ for rGO/CD 2:1 and 140.9 F g⁻¹ for rGO/CD 1:1 with an exceeding amount of CDs. This improved electrochemical behaviour is due to the positive effect of decorated CDs. The presence of CDs can shorten the transport pathways for electrons and ions and provides accessible edges [6]. However, the exceeding amount of CDs has an adverse impact on the electrochemical performance because of the blockage of ion channels [7]. Figure 3d illustrates the Nyquist plots of rGO and rGO/CD 4:1. Rs of the composite is lower than that of rGO, suggesting the lower intrinsic resistance. Nevertheless, the semicircles of both samples at the high frequency region were not clearly observed, indicating that both
samples have a small electron transfer resistance and the mass transfer dominates on the Nyquist plot. Figure 3e illustrates the cyclability performance of rGO and rGO/CD 4:1 at the current density of 10 A g⁻¹. The result suggests that rGO/CD 4:1 can retains 97.3% of its initial capacitance, whereas the rGO only maintain 93.4% of its initial capacitance after 1000 cycles. The improved electrochemical stability of rGO/CD 4:1 composite is ascribed to the stable porous structure, which is beneficial for the ion transport during the charge/discharge process.

Figure 3. CV curves of (a) rGO and rGO/CD composites at the scan rate of 200 mV s⁻¹, (b) rGO/CD 4:1 at different scan rates, (c) Galvanostatic charge/discharge curves of rGO and rGO/CD composites, (d) Nyquist plots of rGO and rGO/CD 4:1 and their magnified portion at high frequency (inset), and (e) Capacitance retention of rGO and rGO/CD 4:1 composite at the current density of 10 A g⁻¹.

4. Conclusions
We successfully synthesized CDs from orange juice biomass. The average particle size of CDs is 4.0 nm and CDs were used to prepare rGO/GO composites via facile hydrothermal treatment. The addition of CDs could hinder the rGO re-stacking, increase additional pseudo-capacitance, and enhance the electron transport. The rGO/CD 4:1 exhibits the superior specific capacitance of 184.8 F g⁻¹ at the current density of 0.5 A g⁻¹ and retains high capacitance retention of 97.3% after 1000 cycles.

5. References
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