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Hierarchically porous carbon nanosheets derived from alkali metal carbonates and their capacitance in alkaline electrolytes

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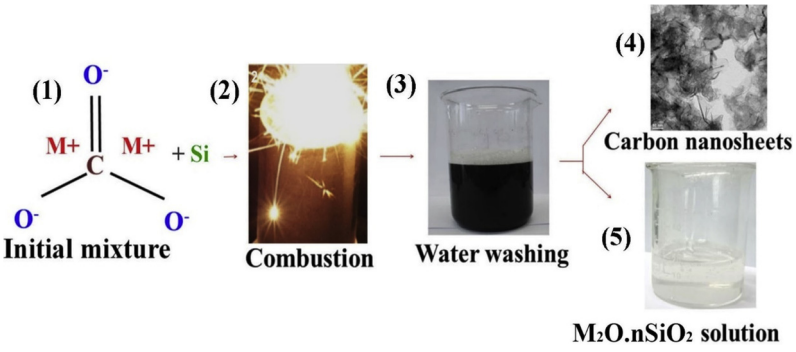
HIGHLIGHTS

- The combustion process in M_2CO_3 (Me is Na and K) + Si system was investigated.
- The formation of hierarchically porous carbon nanosheets was observed in the temperature range of 1000–1400 °C.
- Carbon nanosheets exhibited 178.6 –860 $m^2 g^{-1}$ surface area and 0.09 –1.94 $cm^3 g^{-1}$ pore volume.
- The maximum capacitance of carbon was 240 F g^{-1} under the scan rate of 10 mV s^{-1}.

GRAPHICAL ABSTRACT



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ABSTRACT

With the assistance of alkali metal carbonate M_2CO_3 (M is Na and K) as a carbon source and silicon as a displacement agent, an exothermic and self-sustaining reaction to produce two-dimensional (2-D) hierarchically porous carbon nanosheets (denoted as HP-CNSs) was achieved. The combustion reaction developed a temperature in the range of 1100–1400 °C and resulted in a two-phase product consisting of HP-CNSs and alkali metal silicate ($M_2O{\cdot}nSiO_2$). After dissolving the $M_2O{\cdot}nSiO_2$ in distilled water, a black carbon powder was formed. Despite the simple synthesis process, the HP-CNSs had a BET surface area of about 178.6–860 $m^2 g^{-1}$ and a pore diameter in the range 0.5–150 nm. HP-CNSs based capacitors showed a specific capacity of about 85–240 F g^{-1} and good cyclic performance for over 1000 cycles.

1. Introduction

Porous carbon materials have attracted great attention in fundamental research during the last few decades due to their improved electronic, photonic, and mechanical properties [1–3]. Engineering the morphology of the carbon materials and their pore

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structures is thus vital to improving the performance by providing a better electrolyte permeability, ion transport/diffusion and electron-transfer path as well as a higher charge-induced ion-adsorbing surface area [4]. Examples of these carbon nanostructures are interconnected hierarchical porous structures with well-distributed micro–meso–macropores [5–8], mesoporous carbons [9] and two-dimensional (2-D) carbon nanosheets [10,11]. Benefitting from the distributed interconnected micro–meso–macropores where these pores function as either active sites for ion adsorption, ion-transport paths, or ion reservoirs, the hierarchical porous carbon has a higher capacitance and a significantly improved rate capability than that of activated carbon due to the higher utilization of micropores with a nanometer ion-transport distance from adjacent mesopores and macropores [12].

Since the discovery of single-layer graphene (SLG), tremendous progresses have been made in developing/redeveloping various types of techniques for synthesizing both SLG and multilayer graphene (MLG) sheets, such as epitaxial growth on both SiC and metallic substrates [13–17], reduction of graphite oxide (GO) [18], chemical vapor deposition (CVD) [19–22], electrical discharge [23], etc. Compared to SLGs, MLGs are more immune to the influence of the external environment. The hierarchically porous multilayer carbon nanosheets (HP-CNSs) can be considered advantageous among carbon materials due to their interconnected hierarchical porous structure, high conductivity and aspect ratio for electron transfer in graphene-based sheets, and ion-transport capability across the electrodes in structure-engineered graphene. Currently, a few approaches have been developed for the synthesis of 2-D porous carbons with greatly improved ion-transport properties. Among the known synthesis approaches, the following can be highlighted: templating, biomass carbonization and biomass carbonization–activation. Graphene oxide [24], metal oxides [25–27], metal salts [28,29], and layered materials like montmorillonite have been used as templates for the generation of 2-D porous carbons. The addition of template materials resulted in a layered carbon structure with a specific surface area of 300–1000 $m^2 \cdot g^{-1}$. The specific surface area of the carbons derived from biomass precursors (seaweeds [30], dead leaves [31], waste coffee [32] and amaranthus waste [33] can be as high as 100–1400 $m^2 \cdot g^{-1}$ with a pore volume of 1.6 $cm^3 \cdot g^{-1}$.

In this paper, for the first time, we present a one-step combustion approach for the fabrication of 2-D hierarchically porous multilayer carbon nanosheets. The procedure for the fabrication is simple and involves the combustion of an alkali metal carbonate (M_2CO_3)-silicon (Si) solid mixture in an argon atmosphere and the subsequent washing away of the reaction by-product by water. It is worth noting that these carbon materials can be produced easily and in ways that are ecologically friendly by using as precursors widely available, cheap substances. When used as a capacitor electrode, this material exhibits a high capacitance and good cycling performance (>90% capacitance retention for 1000 cycles).

2. Materials and methods

2.1. Materials

In the preparation process, chemical grade Na_2CO_3 and K_2CO_3 (purity of 99%) were purchased from Samchun Chemicals and Metals Co., Ltd., Korea. Silicon powder (98% pure, particle size: 10–50 μm) was obtained from Junsei Chemicals Co. Ltd, Japan. The raw materials were used without any further processing. High purity argon gas (99.999%) was used to provide an inert medium for the combustion reaction.

2.2. Combustion synthesis

In a typical experiment, 1 mol Na_2CO_3, (or 1 mol K_2CO_3 or 0.5 mol ($Na_2CO_3 + K_2CO_3$)), was hand mixed with 1 mol Si powder using a ceramic mortar and pestle. The reaction mixture was compacted by hand into a paper cup (diameter: 4.0 cm; height: 8–9 cm). During the compaction, two thermocouples were placed inside the sample near the center. Approximately 2–3 g of Ti+0.9C (black soot) +0.1[$(C_2F_4)n$] mixture was placed on top of the reaction sample for a fast ignition. The cup containing the reaction mixture and the thermocouples was subsequently placed under a nickel/chromium coil in a combustion chamber. The reactor was tightly closed, and the air was pumped out with a vacuum pump, after which it was filled with argon to a pressure of 0.5 MPa. Local ignition of the reaction sample was achieved within 1–2 s using a nickel-chromium filament electrically heated to 900–1000 °C. After the combustion, the sample was cooled to room temperature prior to the removal from the combustion chamber.

2.3. Product purification

The surface layer of the combusted sample was mechanically removed, and the remaining solid was ground by hand and put into a 500-mL beaker for washing with water. About 300 mL of water was added to dissolve the metal silicate. After dissolution, a transparent liquor was formed containing black solid particles. The transparent liquor was filtered off from the black solid residue. The filtration residue was washed several times with distilled water and dried at 100 °C in air.

2.4. Capacitance measurement

A nickel micro mesh was rolled into ~20–25 mm long tube with a diameter of 5 mm. About 0.15–0.2 g of hierarchically porous carbon nanosheets prepared by the combustion method was mixed with 0.015–0.02 g of liquid binder (Teflon slurry) and compacted into the Ni tube to produce an electrode. The capacitance-voltage (CV) performance of the electrode was investigated in a three-electrode cell system using Ag/AgCl as a reference electrode and a graphite rode as a counter electrode. The electrolyte was 6 M aqueous solution of KOH. The CVs were recorded at different scan rates using an “Autolab” potentiometer. All experiments were carried out at room temperature. The specific capacitance in $F \cdot g^{-1}$ was calculated from the average anodic current recorded at different voltages divided by the potential scan rate and weight of the active electrode material taken in grams. The calculation was done by the following equation:

$$Cs = \frac{1}{2m\Delta V} \int_{V_{in.}}^{V_{fin.}} \frac{I}{dV/dt} dV. \quad (1)$$

Here, C_s ($F \cdot g^{-1}$) is the specific capacitance; m(g) is the mass of the active materials in the electrode; $\Delta V(V)$ is a potential window; $V_{in.}$ and $V_{fin.}$ are the starting and end potential in one cycle; I (A) is the instantaneous current at a given potential, and dV/dt is the potential scanning rate.

2.5. Characterization methods

Temperature-time profiles in the combustion wave were monitored by tungsten-rhenium thermocouples (WR-26/WR-5) connected to a computer-assisted data logger (GL100A, Graphtec Co., Japan). The crystal structures and morphology of the final