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Hierarchical micro & mesoporous silicon carbide flakes for high-performance electrochemical capacitive energy storage

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HIGHLIGHTS

- Hierarchical porous SiC flakes (SiCF) are obtained from waste Si wafer.
- Micropores are derived by partial evaporation of Si atoms during the carbonization.
- Mesopores are formed by the integration of neighboring micropores.
- SiCF are investigated as electrode materials for EDLC in 1 M KCl electrolyte.
- The material has specific capacitance of 203.7 F g^{-1} at a scan rate of 5 mV s^{-1}.

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ABSTRACT

Hierarchical micro/mesoporous silicon carbide flakes (SiCF) with a high surface area of about 1376 m^2 g^{-1} are obtained by one-step carbonization of waste Si wafer without any chemical or physical activation. The micropores are derived from the partial evaporation of Si atoms during the carbonization process and mesopores are formed by the integration of neighboring micropores. During carbonization process, the proportion of micro and mesopores in SiCF can be controlled by carbonization time by controlling the amount of partial evaporation of Si atoms. The SiCF electrode carbonized for 8 h at 1250 °C exhibits high charge storage capacity with a specific capacitance of 203.7 F g^{-1} at a scan rate of 5 mV s^{-1} with 87.3% rate performance from 5 to 500 mV s^{-1} in 1 M KCl aqueous electrolyte. The outstanding electrochemical performance can be the synergistic effect of both enhanced electric double layer properties caused by micropores and reduced resistant pathways for ions diffusion in the pores as well as a large accessible surface area for ion transport/charge storage caused by mesopores. These encouraging results demonstrate that the SiCF carbonized for 8 h at 1250 °C can be promising candidate for high performance electrode materials for supercapacitors.

1. Introduction

The growing energy demands and worsening global issues call for urgent development of clean alternative energies as well as advanced energy storage devices. Electrochemical capacitors, also known as supercapacitors, have drawn intensive research attention as ideal energy storage devices due to their significant advantages of high power density, long cycle-life and safety tolerance to high rate charge and discharge [1,2]. Supercapacitors can be classified as two types according to the energy stored mechanism, namely the electrical double-layer capacitor (EDLC) and the pseudocapacitor. The capacitance of the former arises from an electrical double layer at the interface between electrode and electrolyte, carbon materials are typical example [3,4]. The capacitance of the latter is due to fast and reversible Faradic reactions at electrodes surface, such as transition metal oxides [5,6]. Notably, as one of the most important building components of a supercapacitor device, the electrode materials play a dominant role in determining the performance of supercapacitors. Therefore, tremendous efforts have been focused on the development of advanced electrode materials, with the aim of fabricating novel electrodes for next generation high performance supercapacitors.

For the practical application for EDLC, activated porous carbon materials having high surface area (2000–3000 m^2 g^{-1}) are widely used as electrode materials in EDLC with a specific capacitance

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around 250–350 F g^{-1} [7–10]. Scientists have tried several interesting synthetic routes to obtain high quality carbon. These include carbonization of hierarchical porous carbon [11–13], organic/polymeric precursors [14,15], chemical vapor deposition [16,17], excimer laser ablation of graphitic targets [18,19], and sputtering/plasma based synthesis [20,21]. Recently, many researchers have started utilizing organic waste materials, such as food, agricultural wastes, and even insects, for the synthesis of carbon for specific absorbants or charge storage application [22–25]. Unfortunately, although there are a lot of industrial wastes produced by factories and the disposal of industrial waste is one of the big problems, most of the research has been on utilizing biomass waste materials to fabricate carbonaceous materials.

In semiconductor manufacturing companies, the edges of silicon (Si) wafer are cut off in the deposition process of semiconductor wafer surfaces. These Si wafer fragments are created in ton quantities and disposed as industrial waste with enormous cost. Therefore, the recycling of these Si wafer fragments for supercapacitor electrode materials would contribute to enhance cost competitiveness in energy supply markets, explore novel materials for long-term sustainable energy storage, reduce environmental impacts, and meet the urgent need for green and sustainable development strategies [22].

Recently, a few new approaches have been proposed that make use of semiconductors or cermet nanowires as EDLC electrode materials instead of traditional carbon-based materials [26–28]. Various types of EDLC materials such as silicon nanowires, silicon carbide nanowires, titanium nitride nanowires, titanium dioxide nanotubes, and nanowires have attracted considerable interest because of their high surface area and excellent electrical conductivity. Among these, β-polytype silicon carbide, especially nanowire-type silicon carbide, is considered as a promising EDLC material owing to the high electron mobility and low band gap with high surface area [29,30]. However, because the working materials are grown directly on the current collector, these nanowire structures are not ideal for the fabrication of hybrid composites consisting of metal oxide or conductive polymers and for application as macroscale supercapacitor electrodes. Therefore, recent studies have shown the β-polytype silicon carbide microsphere particles to have great potential as EDLC materials; however, the porous properties of these silicon carbide microsphere particles (such as surface area and pore volume) are not satisfactory, because of their non-porous structure; this results in a low capacitive performance, e.g., 72.4 F g^{-1} at a scan rate of 10 mV s^{-1} in Na_2SO_4 aqueous electrolyte [31–33]. Thus, in order to obtain a high surface area, silicon carbide particles with a porous structure need to be developed.

Here, we demonstrate the synthesis of high surface area hierarchical micro/mesoporous silicon carbide flakes (SiCF) by one-step carbonization of waste Si wafer without any chemical or physical activation and examine its properties for supercapacitor application. The activated carbon, which is most widely used electrode material for EDLCs, contains a large proportion of micropores with irregular pore size and structure. These irregular microporous structures are not easily wetted by the electrolyte, and the exposed surface of the irregular micropores cannot be utilized for charge storage. Moreover, even if the irregular micropores were wetted by the electrolyte, the ionic motion in such small pores would be so slow that a high-rate capability would not be achieved. Therefore, the dual-pore system combined with mesopores, which provide the ion-transport pathways with a minimized resistance, can be expected to provide a favorable electrochemical environment to achieve a fast ion-transport and high-charge storage capability. Therefore, considering the ideal charge/discharge properties of the dual-pore system combined with micro & mesopores with excellent electrical conductivity of β-polytype SiC, the strategy for recycling of waste Si wafer fragments to fabricate the β-polytype hierarchical micro/mesoporous silicon carbide flakes can largely influence to energy supply markets by economically and environmentally.

2. Experimental

2.1. Synthesis of hierarchical micro & mesoporous silicon carbide flake (SiCF-H)

The waste Si⟨100⟩ wafer fragments, as staring material, were pulverized to powder by ball milling process. The waste Si wafer fragments (3 g) were loaded in a steel milling vial with 20 zirconia balls (10 mm in diameter). The vial was sealed and filled with pure nitrogen gas at a pressure of 200 kPa above atmospheric pressure to avoid environmental contamination. The rotation speed of the planetary mill was set at 150 rpm for 48 h to generate rolling actions of the balls which apply shearing forces on the materials. The as-prepared Si flake (0.8 g) were loaded in a ceramic boat and put into the hot zone of a horizontal tubular furnace. Ethanol, which was used as carbon source, was ultrasonically sprayed using a home humidifier (60 MHz and 35 W) and carried by Ar gas into the horizontal tubular furnace at a flow rate of 60 sccm (standard cubic centimeter per minute). Then, the system was heated up to 1250 °C (5 °C/min) and held at this temperature for 4, 6, 8, 10 or 12 h. After the reaction was terminated and the furnace was cooled to room temperature, the products were exposed to air and heat at 600 °C for about 4 h to remove superfluous carbon. Finally, the both adsorbed SiO_2 layer on the surface of the SiCF particles and residual Si flakes was removed via treatment with hydrofluoric acid (HF). The obtained powder (10 g) was placed in 300 mL of 10% HF solution and stirred for 24 h. Subsequently, the sample was leached with distilled water until the pH of the leaching water reached 7–8. The resulting powder was collected and dried at 100 °C in a vacuum. The resultant hierarchical micro & mesoporous silicon carbide flakes (SiCF) materials are denoted as SiCF-*H*, where *H* indicates the carbonization time.

2.2. Characterization methods

X-ray diffraction (XRD) patterns were collected (New D8-Advance/Bruker-AXS) at a scan rate of 1° s^{-1} within the 2θ range 10°–80° using $CuK_{\alpha 1}$ radiation (0.154056 nm). The morphologies of the samples were observed using high-resolution transmission electron microscopy (HR-TEM, JEM-3010). X-ray photoelectron spectroscopy (XPS) analysis was performed on a VGMicrotech ESCA2000 system using a spectrometer with a Mg Kα X-ray source (1253.6 eV) and a hemispherical analyzer. During the curve fitting, the Gaussian peak widths were constant in each spectrum. Nitrogen sorption analysis was carried out using an ASAP 2020 accelerated surface area and porosimetry instrument (Micromeritics), equipped with an automated surface area at 77 K, using Brunauer–Emmett–Teller (BET) calculations for the surface area. The pore-size distribution plots were recorded from the desorption branch of the isotherms based on the nonlocal density functional theory (NLDFT).

2.3. Preparation and characterization of supercapacitors

The working electrodes were fabricated as follows. The SiCF-*H* powder was mixed with poly(tetrafluoroethylene) (60 wt% water suspension) to form an electrode consisting of 85 wt% active PSiCS materials, 10 wt% carbon black, and 5 wt% binder. The resulting mixture was then coated onto a stainless steel foil substrate