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A hierarchically structured urchin-like anode derived from chestnut shells for microbial energy harvesting

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ABSTRACT

Electrode materials that have rich carbon contents and high specific surface areas are crucial for high power generation in microbial fuel cells (MFCs). A novel low-cost carbonized chestnut shell electrode (CSE) is examined as the anode for MFCs. The prepared CSE possesses a hierarchically structured urchin shape not only at the macroscopic level but also at the microscopic level. Electrochemical and bioelectrochemical properties of thorny CSEs and thornless CSEs were evaluated by impedance spectroscopy and cyclic voltammetry techniques. CSEs can achieve power densities of 759 ± 38 mW m^{-2} and coulombic efficiencies of $75\% \pm 12\%$, which are comparable to those of traditional electrode materials. This superior performance would be primarily due to a larger surface area on the CSE resulting from the microscopic/macroscopic three-dimensional urchin-shaped structure which increased the attachment of microorganisms. This study introduces a promising method for solving the environmental issues caused by chestnut shell disposal and offer new possibilities for value-added applications for chestnut shells by preparing CSEs.

1. Introduction

The microbial fuel cell (MFC) is a technology that utilizes exoelectrogenic microorganisms to directly convert organics into electrical energy. In the anode chamber of the MFC, bacteria oxidize organic material to produce electrons and protons. Then, the electrons flow through an external circuit from the anode to cathode, producing an electrical current [1]. One promising application of MFCs is power support for wastewater treatment and ocean equipment [2,3]. However, the high cost and the non-renewable nature of electrode materials seriously hinder the commercialization of MFCs [4]. In general, the electrodes in MFCs should possess biocompatibility, stability, low resistance, high surface area and low cost [5]. Various carbon-based materials, such as carbon cloth and carbon nanotubes, have been investigated because of their high qualities for the aforementioned properties [6]. Toward the aim of developing low-cost and high-efficiency electrodes, several sustainable natural materials, such as loofah sponge, kenaf stems, corn stems, hollow fibers and spongy pomelo peels, have recently been reported [5,7–9]. Natural materials exhibit excellent biocompatibility and are inexpensive; furthermore, after carbonization, these materials have high conductivities and high specific surface areas, which are responsible for their high electrochemical performance.

Chestnut is a fruit that has large plantation areas (5.5×10^5 ha) around the world. In China, the annual production of chestnut is ca. 1.65×10^6 tons (in 2013), which is 82% of the total global chestnut production [10]. The shell is separated as a residue during the chestnut peeling process, and it has no significant industrial or commercial uses; therefore, chestnut shells are an environmental issue [11]. To solve the pollution problems resulting from its disposal and to support its valorization, reutilizations of chestnut shells as fuels, adsorbents for heavy metal and organic pollution removal, and as an extracted raw material for pigments and antioxidants were analyzed in previous studies [12–14]. To our knowledge, no investigations on the utilization of chestnut shells as an electrode material in MFCs have been conducted. Studies in which the chestnut shell was used as a heavy metal adsorbent demonstrated that chestnut shells have a porous structure and high surface area [15], and previous works have shown that chestnut shells are carbon rich and contain up to 60% fixed carbon

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after carbonization [16], suggesting the great potential of this material for use as an electrode in a MFC.

Based on the above, the objective of this study was to convert chestnut shells into anodes for MFCs. To investigate the importance of the thorn, both thorny and thornless chestnut shells were carbonized into carbon balls. The structure, morphology and surface composition of the carbon ball were determined to analyze its intrinsic properties. Then, the carbon ball was fabricated into a carbonized chestnut shell electrode (CSE), and its electrochemical performance was measured in MFCs. Our results provide a type of value-added application for chestnut shells.

2. Materials and Methods

2.1. Preparation and characterization of the CSE

Chestnut shells (*Castanea mollissima Blume*) were obtained from a local farm (Guangzhou, China). After washing with distilled water and drying, the whole chestnut shell was carbonized in a high-temperature furnace at 900 °C for 1 h under a N_2 atmosphere. After cooling to room temperature, the carbonized chestnut shell was washed with distilled water until the pH of the effluent became neutral. Then, the carbonized shell was dried at 60 °C for 12 h, and an urchin-shaped carbon ball was obtained. Finally, titanium wire was connected to the carbonized shell, and the CSE was obtained (2.7 cm in diameter) (Fig. 1A and C). A control sample without thorns on the surface of the chestnut shell was prepared by removing all of the thorns using scissors prior to carbonization and then fabricated into a thornless CSE (2.3 cm in diameter) following the steps for the thorny CSE.

The surface properties of the CSE were determined. The Brunauer-Emmett-Teller (BET) surface areas of the CSEs were obtained from N_2 adsorption at 77 μK using a Quantachrome Autosorb-IQMO002-2. Fourier transform infrared (FTIR) spectra were recorded between 4000 cm^{-1} and 400 cm^{-1} using a Hitachi EPI-G2 infrared spectrophotometer in transmission mode. For Raman spectroscopy, the MRG suspension was spread on a glass substrate and dried under vacuum. Raman spectra were recorded using a Nicolet Almega XR dispersive Raman spectrometer (laser wavelength of 488 nm). X-ray diffraction (XRD) measurements were carried out using an Empyrean diffractometer operating at 40 kV and 40 mA with an X-ray tube providing Cu Kα radiation (λ = 0.15418 nm) at room temperature [17]. The elemental composition of CSE was determined using energy-dispersive X-ray spectroscopy (EDS, Quanta 400 FEG). The morphologies of the CSE and biofilms were studied using Scanning electron microscopy (SEM) (FEI SIRION, Netherlands) as the procedure used by Yuan et al. [7]. The biomass attachment onto the anodes was determined with the BCA Protein Assay Kit after the microbes were separated from the anodes by bead beating for 30 seconds with sterile glass beads to ensure cell disruption.

2.2. MFC construction and operation

Single-chamber cubic-shaped MFCs with a liquid volume of 28 mL were constructed as previously described [17]. The cylindrical MFC chamber was composed of poly(tetrafluoroethylene) and had a length of 4 cm and diameter of 3 cm. The anode was the CSE or the thornless CSE, which was positioned in a concentric manner at the core of the cylindrical chamber (Fig. 1B). The cathode was a 30% water-proofed carbon cloth (7 cm^2 in total surface area, 3 cm in diameter) with platinum (0.5 mg cm^{-2}) and four diffusion layers coating [18]. A MFC equipped with a graphite

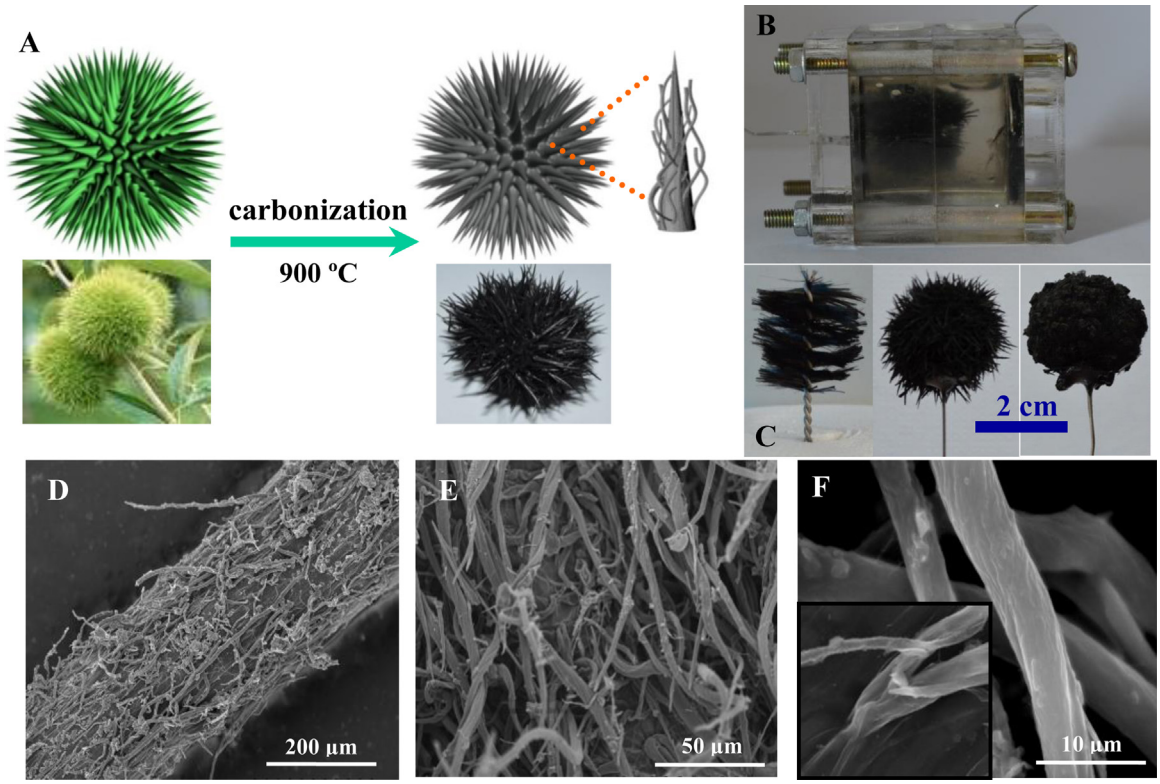

Fig. 1. Morphology characteristics of the CSE. (A) Schematic illustration of the preparation of CSE; (B) a photograph of the MFC equipped with the CSE; (C) photographs of the brush, CSE and thornless CSE; (D) SEM image of the thorns on the CSE; (E) high-resolution SEM image of the thorns on the CSE; and (F) SEM image of the fibers grown on the surface of the thorns on the CSE.