Carbon 107 (2016) 872–877

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

Human hair-derived hollow carbon microfibers for electrochemical sensing

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ARTICLE INFO

Article history:
Received 22 April 2016
Received in revised form
21 June 2016
Accepted 22 June 2016
Available online 24 June 2016

ABSTRACT

Glassy carbon has been widely used for various applications including electrochemical sensors and energy storage devices. Here we introduce a novel way to fabricate glassy carbon microfibers based on human hairs. The coaxial structure of hair shafts results in long hollow glassy carbon structures upon pyrolysis at 900 °C in a N_2 atmosphere. The morphology of human hair samples before and after pyrolysis was characterized using scanning electron microscopy. The chemical composition of natural and pyrolyzed human hairs was also characterized using Raman spectroscopy and energy-dispersive X-ray spectroscopy. Screen printed carbon electrodes were modified with the hair-derived carbons and applied for electrochemical sensing of dopamine and ascorbic acid. The hair-derived carbons significantly improved the performance of the electrochemical sensors compared to the unmodified sensors. This method provides an easy, simple, and inexpensive way to fabricate hollow 3D glassy carbon microelectrodes.

1. Introduction

Carbon is one of the most abundant materials in nature and has been widely used in various applications for many decades. Carbon has many allotropes with very different physicochemical properties enabling its usage in a variety of applications [1–4]. Depending on the particular application one can choose from one of the following allotropes: diamond, graphite, coke, amorphous carbon, carbon nanotubes (CNTs), and glassy carbon. Among those allotropes, glassy carbon is one of the most promising candidates for applications where the following physical properties are required: high isotropy, good electrical conductivity, impermeability to gases, and low coefficient of thermal expansion. Its high corrosion resistance and inertness make glassy carbon ideal for applications in extremely corrosive environments, such as crucibles for decomposition of ores. It has also been widely used as an electrode material for electrochemical applications as it resists both strong acids and bases [5,6]. Microfabrication of carbon devices is a relatively new field. Use of focused ion beam [7,8] or reactive ion etching [9], is an expensive and time-consuming process to that end. In contrast Schueller et al. first demonstrated a more practical carbon microfabrication technique using organic polymer precursors [10]. They applied standard soft lithography based on polydimethylsiloxane (PDMS) to pattern and transfer a precursor polymer structures to a substrate, followed by pyrolysis of the microstructures at high temperature [11]. UV photolithography has also been utilized to fabricate glassy carbon microelectrodes [12]. UV curable polymer precursors such as SU8 photoresists were patterned and the polymer structures were carbonized at high temperature (900–1100 °C) in an oxygen-free environment. At the elevated temperature in vacuum or a N_2 atmosphere, all the non-carbon elements are removed and only carbon remains. This technique, developed by some of the current team, is called carbon-based microelectromechanical systems (C-MEMS) technology and has received much attention due to its simplicity and its cost-effectiveness to implement many applications such as electrochemical sensing [13], energy storage [14], and electrokinetic particle manipulation [15]. Fabrication of three-dimensional (3D) microstructures with very high aspect ratios is easy and has led to a

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http://dx.doi.org/10.1016/j.carbon.2016.06.095
0008-6223/

wide variety of C-MEMS-derived carbon electrodes to replace noble metal electrodes in a variety of applications [13,14,16–18].

Natural and waste hydrocarbon precursors have been applied for the synthesis of carbon-based nanomaterials [19]. Plant-derived precursors and wastes such as seeds, fibers, oils, and bagasse have yielded different forms of carbon via pyrolysis. It has been known that high-quality graphene, single-walled CNTs, multi-walled CNTs, and carbon dots can be produced by thermal decomposition of turpentine oil, sesame oil, neem oil (*Azadirachta indica*), eucalyptus oil, palm oil, jatropha oil, camphor, tea-tree extract, waste food, insects, agro waste, and food products [20–23]. Liang et al. found a cost-effective way to prepare porous carbon microfibers by utilizing a silk cocoon as a precursor material [24]. They obtained the biopolymers from a silkworm *Bombyx mori* that spins silk microfibers to form a cocoon around itself. The one dimensional (1D) silk microfibers were collected and carbonized at 900 °C under N_2 flow to generate carbon microfibers.

Human hair is a rather interesting waste material. Waste hair has plenty of applications in industry and academic research. It has a unique chemical composition and comes with several interesting properties, such as very slow degradation, high tensile strength, high thermal insulation, high elastic recovery, and it has a scaly surface. These listed properties lead to diverse applications. Human hair is made up of approximately 91% polypeptides, which contain more than 50% carbon, and the rest are elements such as oxygen, hydrogen, nitrogen, and sulphur [25]. Waste hair has been used in agriculture as fertilizer because it is one of the highest nitrogen containing organic materials in nature [26]. Hair has also been used for reinforcing clay-based constructions due to its high tensile strength and high friction coefficient [27]. It has also been used in traditional medicine in several cultures; *i.e.* carbonized human hair has been used in traditional Chinese medicine [28]. Recently, human hair has been utilized to prepare carbon flakes employed for supercapacitors [29].

The shaft of human hair is composed of three major components: the cuticle, the cortex, and the medulla. The outermost part, the cuticle, is made of tightly arranged compact cells that protects and anchors the inner hair structures. The cortex forms the bulk of the hair shaft and is composed of keratinized cells forming long fibers. Pigment granules, mainly melanin, are found in this part. The medulla, if present, comprises only a small percentage of mass in human hair. The medullar cells are loosely packed, but they shrivel up leaving a series of vacuoles along the fiber axis during dehydration [30]. The medulla may either be completely absent, continuous along the fiber axis, or discontinuous, and in some instances, a double medulla may also be present. The medulla has a negligible contribution to the mechanical and chemical properties of human hair [31].

In this research, we propose a simple and cost-effective way to fabricate hollow carbon microfibers based on human hair. We demonstrate that the unique anatomy of human hair leads to electrically-conductive glassy hollow fibers upon pyrolysis. The change in chemical composition of hair before and after pyrolysis was characterized by Raman spectroscopy and energy-dispersive X-ray spectroscopy (EDS). The hair-derived carbon was applied for electrochemical sensing of ascorbic acid and dopamine.

2. Experimental

2.1. Fabrication of hollow carbon microfibers

Some hair strands from a healthy donor were used as a starting material for the fabrication of hollow carbon microfibers. The hair was pyrolyzed in a furnace (PEO 601, ATV Technologie GmbH, Germany) at 900 °C. The furnace was filled with a continuous flow of ultrapure grade N_2 gas (6 l/min) to ensure that the furnace tube environment was completely free of oxygen. The temperature was increased from room temperature to 900 °C at a 5 °C/min ramp rate and kept constant at that temperature for 1 h. After that, the temperature was lowered to the room temperature at a 10 °C/min rate.

2.2. Characterization

The physical structure of hair and hair-derived carbon hollow fibers were visualized by using a scanning electron microscopy (SEM; EVO MA25, Zeiss, Germany). The hair samples were attached on a Si/SiO_2 substrate using SU-8 2002 for SEM imaging. The chemical composition of samples was examined by Raman spectroscopy (inVia Qontor, Renishaw plc, UK) with a 514 nm Ar laser source, and EDS (XFlash 6, Bruker Corporation, Billerica, MA, USA) with a 20 kV accelerating voltage.

2.3. Electrochemical sensing

For electrochemical sensing, screen printed carbon electrodes were first prepared. Carbon and silver inks (Jujo Chemical, Japan) were printed on a polystyrene-base film using a screen printer (BANDO Industrial, South Korea). Ag/AgCl was used as the reference electrode and carbon as the working and the counter electrodes. The surface of the working electrode (area = 0.07 cm^2) was modified with hair-derived carbon and CNTs (Hanwha Chemical Corp., South Korea), respectively, using a simple drop coating method. A 5 μL of hair-derived carbon or CNTs solution was dropped onto the electrode surface and then the solvent was allowed to evaporate at 30–35 °C by putting the screen printed carbon electrodes in an oven for 30 min. The voltammetric experiments were conducted with a potentiostat/galvanostat (PT-1, Kosentech, South Korea). A drop of dopamine or ascorbic acid solution was placed on the screen printed carbon electrodes, and a linear potential sweep from −200 mV to 600 mV were applied to the working electrode with a scan rate of 100 mV/s.

3. Results and discussion

Human hair was utilized to fabricate hollow carbon fibers via pyrolysis at 900 °C in N_2 environment (See Fig. 1). The hair samples are collected and used for pyrolysis without performing any pretreatment. During the pyrolysis, the hair shrank significantly from a diameter of 82.88 ± 0.003 μm to 31.42 ± 0.003 μm, since non-carbon atoms were removed and only C–C chains remained. After pyrolysis the imbricated pattern of hair disappeared and the surface became rough (See Fig. 2a and b). Interestingly, the carbon fibers derived from the human hair had a hollow structure with a 2- to 4-μm-thick wall (Fig. 2c and d). The unique coaxial structure of human hair, composed of medulla, cortex, and cuticle, resulted in a hollow structure of carbon fibers through pyrolysis. While the medulla, in the middle of the hair fibers, is loosely packed and contains no keratins, the cortex and cuticle are composed of more carbon rich precursors and have a relatively high mechanical stiffness. After the pyrolysis, the medulla disappears whereas the cuticle and the cortex combine to make long hollow carbon fibers.

The chemical composition of the hair and the hair-derived carbon fibers was determined using Raman spectroscopy and EDS. Raman spectra of the hair before and after the pyrolysis are shown in Fig. 3. The Raman spectrum of natural human hair before the pyrolysis showed many peaks, representing lipid and amino acids [32]. On the other hand, after pyrolysis, only two broad peaks were found at around 1366 cm^{-1} and 1586 cm^{-1}, corresponding to the D- and G-bands, respectively. The D-band is attributed to defects,