Human hair-derived hollow carbon microfibers for electrochemical sensing

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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 N2 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.

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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 N2 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 electrokinetonic particle manipulation [15]. Fabrication of three-dimensional (3D) microstructures with very high aspect ratios is easy and has led to a...
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 N2 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% polymers, 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 shirvel 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 N2 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/SiO2 substrate using SU-8 2002 for SEM imaging. The chemical composition of samples was examined by Raman spectroscopy (inVia Qantor, 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 cm2) 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 N2 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,
while the G-band is characteristic of graphite. The intensity ratio of the D-band to G-band \( \frac{I_D}{I_G} \) marks the degree of structural order with respect to a perfect graphitic structure. The \( \frac{I_D}{I_G} \) of hair-derived hollow carbon fibers was 0.99, which indicates that the structure is mostly glassy carbon [33]. This value is similar to the one \( \frac{I_D}{I_G} = 1.1 \) in previous research that human hair-derived carbon flake was used for fabricating supercapacitors [29].

According to the EDS data, the natural human hair that we used in this research was composed of carbon (66.57 atom%), oxygen...
(16.19 atom%), nitrogen (7.94 Atom%), sulphur (9.14 atom%), and a little amount of minerals such as calcium (0.16 Atom%) (See Fig. 4 and Table 1). After the pyrolysis, most of the nitrogen and sulphur was removed whereas the percentage of carbon significantly increased to 80.84 atom%. Additionally, 14.83 atom% of oxygen and a small amount of calcium (0.21 atom%) were found. Considering the amount of removed elements (nitrogen and sulphur), the little increase in relative amount of calcium is reasonable. It is likely that most of the oxygen in the hair is removed during the pyrolysis, because the amount of oxygen detected from the sample after the pyrolysis (14.83 atom%) is almost consistent with that from the Si/SiO2 wafer substrate [34]. The presence of inorganic elements such as sodium (0.21 atom%) and calcium is consistent with the results reported in the literature, that show varied distribution of inorganic elements in human hair samples collected from several scalp regions of different people [35]. We also measured 1.82 atom% and 3.69 atom% of silicon from the hair samples before and after the pyrolysis, respectively, due to the Si/SiO2 substrate on which the samples were attached [34]. These results showed that the hair samples were successfully transformed into glassy carbon in the pyrolysis process.

By pre-arranging the hairs before the pyrolysis, various patterns of carbon microfibers were created as shown in Fig. 5a and b. Coiled structures could be obtained by applying a torsion to the hair before the pyrolysis (See Fig. 5c and d). The hollow carbon microfibers were sometimes broken or collapsed due to the high tensile stress during the pyrolysis process (See Fig. 5e and f). These results show that desired patterns of carbon microfibers can be achieved by precise positioning and patterning of human hair samples before the pyrolysis. Combining this method with the well-established C-MEMS technology, a variety of carbon microelectrode structures could be fabricated from human hair for diverse applications including electrochemical sensors and energy storage devices.

In this research, we applied the hair-derived carbon fibers to electrochemical sensing of ascorbic acid and dopamine. We prepared screen printed carbon electrodes and coated the surface of the working electrode with ground hair-derived carbon (See Fig. 6a). The surface morphology of the working electrode before

<p>| Table 1 | Chemical composition determined by EDS for human hair before and after pyrolysis. |
|---------|---------------------------------|---------------------------------|</p>
<table>
<thead>
<tr>
<th>Element</th>
<th>Before pyrolysis</th>
<th>After pyrolysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>66.57 Atomic %</td>
<td>80.84 Atomic %</td>
</tr>
<tr>
<td>Oxygen</td>
<td>16.19 Atomic %</td>
<td>14.83 Atomic %</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>7.94 Atomic %</td>
<td>0 Atomic %</td>
</tr>
<tr>
<td>Sulphur</td>
<td>9.14 Atomic %</td>
<td>0.21 Atomic %</td>
</tr>
<tr>
<td>Calcium</td>
<td>0.16 Atomic %</td>
<td>0.21 Atomic %</td>
</tr>
<tr>
<td>Sodium</td>
<td>0 Atomic %</td>
<td>0.22 Atomic %</td>
</tr>
<tr>
<td>Silicon</td>
<td>1.82 Atomic %</td>
<td>3.69 Atomic %</td>
</tr>
</tbody>
</table>

Fig. 5. Scanning electron microscopic images of various patterns of hair-derived hollow carbon microfibers. (a, b) Aligned straight carbon fibers. Scale bar = 50 μm. (c, d) A coiled carbon fiber. Scale bars = 20 and 100 μm, respectively. (e, f) A broken carbon fiber. Scale bars = 50 and 10 μm, respectively. (A colour version of this figure can be viewed online.)
and after placing hair-derived carbons was characterized by SEM. The SEM images of unmodified and modified working electrodes are shown in Fig. 6b and c. The electrochemical sensing performance of the sensors coated with the hair-derived carbons was compared with the bare working electrodes or CNT-coated working electrodes. Cyclic voltammograms were recorded for 100 μM dopamine and 100 μM ascorbic acid in 0.1 M phosphate buffer solution of pH 7.4 using a scan rate of 100 mV/s (See Fig. 6d and e). The oxidation peaks for dopamine were measured at 333 mV, 266 mV, and 96 mV, for the unmodified carbon electrode, the electrode modified with the hair-derived carbon, and the electrode modified with the CNTs, respectively (See Fig. 6d). The peaks attributed to oxidation of ascorbic acid were observed at 414 mV, 455 mV and 297 mV with the screen printed carbon electrodes unmodified, modified with the hair-derived carbon, and modified with the CNTs, respectively (See Fig. 6e). No reduction peaks appeared for ascorbic acid since the oxidation of ascorbic acid is an irreversible process, as previously reported [36].

When the working electrode was coated with the hair-derived carbons or the CNTs, the peak potential for dopamine was shifted towards more negative and its peak current increased, while the peak potential for ascorbic acid was shifted positively and its peak current decreased. This might be because the surface of the hair-derived carbon is slightly negatively charged, attracting positively charged dopamine [37,38]. These results imply that the electrode modified with human hair-derived hollow carbon microfibers is suitable for dopamine sensing in the presence of ascorbic acid, which is the main interferent. The electrochemical sensing performance of the electrode modified with the hair-derived carbon was better than the unmodified electrode, although the CNTs-coated electrode showed the best performance in our experimental conditions. Although the hair-derived carbon microfibers have less surface-area-to-volume ratio than CNTs, the extremely low cost and ease of fabrication are the main advantages of using human hair-derived carbon microfibers over CNTs. The electrochemical sensing performance would be enhanced with further treatment or functionalization of the human hair samples before and after pyrolysis.

4. Conclusions

In this research, hollow carbon microfibers in various patterns were fabricated by the pyrolysis of human hairs. The unique coaxial structure of human hair leads to long hollow carbon fibers fabricated with a simple pyrolysis process. The chemical composition of pyrolyzed hair was mostly glassy carbon according to the Raman scattering and EDS analyses. Various patterns of glassy carbon fibers could be fabricated by pre-arranging human hair samples. The glassy carbon derived from human hair was successfully applied for electrochemical sensing of dopamine and ascorbic acid.

The extremely low cost and ease of fabrication of our method would suggest a new way of using hair waste for manufacturing 3D carbon microelectrodes for diverse applications. The hair-derived glassy carbons could be modified to achieve yet better performance for electrochemical sensing or in energy storage devices. Different types of hairs from nature could also be utilized for obtaining a variety of carbon nano- and microstructures.

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