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Short communication

Fabrication of hydrophobic, electrically conductive and flame-resistant carbon aerogels by pyrolysis of regenerated cellulose aerogels

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ABSTRACT

In this paper, we reported miscellaneous carbon aerogels prepared by pyrolysis of regenerated cellulose aerogels that were fabricated by dissolution in a mild NaOH/PEG solution, freeze–thaw treatment, regeneration, and freeze drying. The as-prepared carbon aerogels were subsequently characterized by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), nitrogen adsorption measurements, X-ray diffraction (XRD), Raman spectroscopy, and water contact angle (WCA) tests. The results showed that the carbon aerogels with pore diameters of 1–60 nm maintained interconnected three-dimensional (3D) network after the pyrolysis, and showed type-IV adsorption isotherm. The pyrolysis process leaded to the decomposition of oxygen-containing functional groups, the destruction of cellulose crystalline structure, and the formation of highly disordered amorphous graphite. Moreover, the carbon aerogels also had strong hydrophobicity, electrical conductivity and flame retardance, which held great potential in the fields of waterproof, electronic devices and fireproofing.

1. Introduction

Carbon aerogels with large specific surface area, high porosity and high electrical conductivity have been widely considered as promising high-performance materials for adsorbents, catalyst supports, artificial muscles, electrodes for electrical double-layer capacitors, and gas sensors (Li, Wang, Huang, Gamboa, & Sebastian, 2006; Moreno-Castilla & Maldonado-Hódar, 2005; Waghuley, Yenorkar, Yawale, & Yawale, 2008). Traditionally, carbon aerogels are synthesized by carbonization of organic aerogels, which are prepared by sol–gel procedure from polycondensation of different organic monomers (Moreno-Castilla & Maldonado-Hódar, 2005). Typically, resorcinol–formaldehyde system is the most extensively used raw materials for fabrication of carbon aerogels, and the resulting carbon aerogels have tunable surface properties related to the synthesis and processing conditions, which can design various materials with unique properties. Apart from the above-mentioned numerous merits, some defects of the resorcinol–formaldehyde organic aerogels, such as high density (100–800 mg cm^{-1}) (Fu et al., 2003; Wu, Fu, Dresselhaus, & Dresselhaus, 2006), fragility, toxicity and environmental pollution, dramatically hamper the development and industry application of this class of carbon aerogels. Recently, some novel carbon aerogels using natural polymers like glucose and bacterial cellulose as precursors have been prepared by pyrolysis, and show superior flexibility, adsorption properties, fire resistance, and electric properties (Chen et al., 2013; Liang, Guan, Chen, et al., 2012; Liang, Guan, Zhu, et al., 2012; Wu, Li, Liang, Chen, & Yu, 2013; Wu et al., 2014). Nevertheless, regenerated cellulose aerogels, composed of cross-linked three-dimensional (3D) network similar to bacterial cellulose, might also be ideal precursors for carbon aerogels.

Thereby, in this paper, versatile carbon aerogels were fabricated by pyrolysis of regenerated cellulose aerogels that were prepared following the procedures of dissolving cellulose in a green NaOH/PEG solution, freeze–thaw treatment, regeneration, and freeze drying. The as-prepared carbon aerogels were characterized by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), nitrogen adsorption measurements, X-ray diffraction (XRD), Raman spectroscopy, and water contact angle (WCA) tests. Moreover, the resulting carbon aerogels showed strong hydrophobicity, electrical conductivity and flame retardance.

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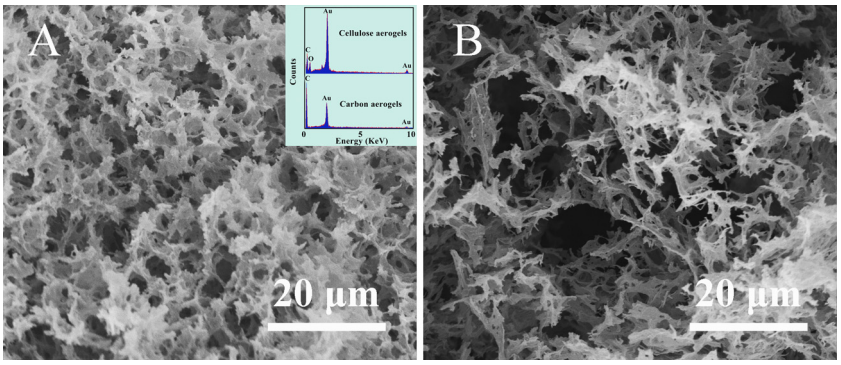

Fig. 1. SEM images of the cellulose aerogels (A) and the carbon aerogels (B). The inset showed the corresponding EDX spectra.

2. Materials and methods

2.1. Materials

Sixty-mesh powder of wheat straw after grinding and sieving was collected and dried in a vacuum at 60 °C for 24 h before used. All chemicals were supplied by Shanghai Boyle Chemical Co. Ltd. and used without further purification.

2.2. Fabrication of carbon aerogel via a pyrolysis method

The purified cellulose from the wheat straw powder was referred to our previous report via a chemical pretreatment process (Li, Wan, Lu, & Sun, 2014); meanwhile, the α-cellulose content of the obtained cellulose was determined by a modification of the TAPPI Method No. T 203 08-61 (Antrim, Chan, Crary, & Harris, 1980). The preparation of homogenous cellulose solution could be referred to the method based on the green NaOH/PEG solution (Yan and Gao, 2008). Briefly, the purified cellulose was mixed with a NaOH/PEG-4000 aqueous solution (9:1 by weight) with magnetic stirring for 6 h to form a 2 wt% cellulose solution. After being frozen at −15 °C for 12 h, the solution was thawed out at ambient temperature under vigorous stirring for 30 min, and the following homogenous cellulose solution was obtained. After being frozen at −15 °C for 3 h again, the frozen cellulose solution underwent a regeneration process by solvent exchange with 1% hydrochloric acid, distilled water and tert butyl alcohol in sequence until the formation of hydrogel without residual chlorine anions. Afterwards, the hydrogel was subjected to a freeze drying process at −35 °C for 48 h in a vacuum, and the following cellulose aerogel was pyrolyzed at 1000 °C under argon atmosphere to generate black carbon aerogel.

2.3. Characterizations

Micromorphology and surface chemical compositions were determined by SEM attached with EDX (FEI, Quanta 200). Nitrogen adsorption measurements were run on an accelerated surface area and porosimetry system (3H-2000PS2 unit, Beishide Instrument S&T Co. Ltd.), and pore characteristic parameters were calculated based on the Brunauer–Emmet–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods. Crystal structures were identified by XRD (Rigaku, D/MAX 2200). Raman spectra were performed using a Raman spectrometer (Renishaw, inVia). The wetting properties were characterized by a WCA analyzer (JC2000C).

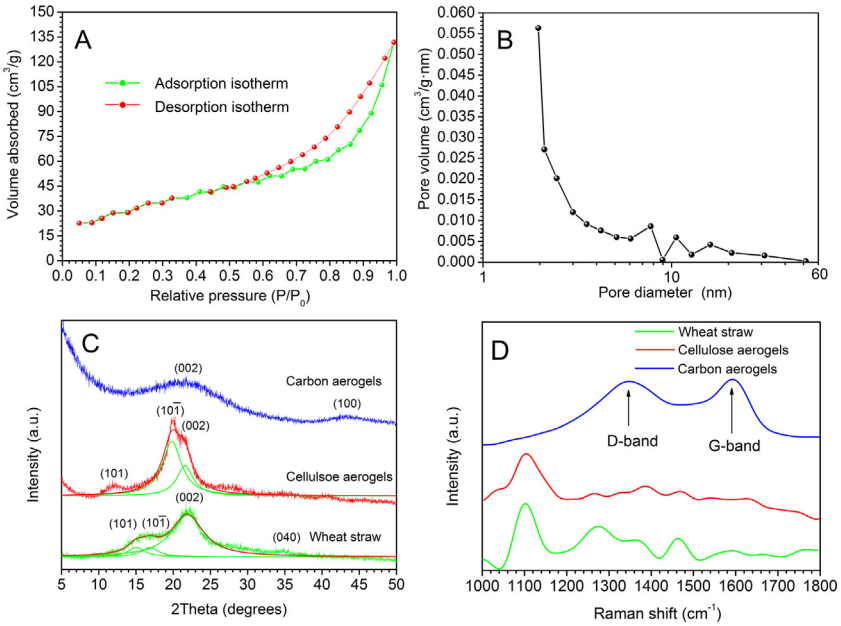

Fig. 2. (A) N_2 adsorption–desorption isotherms and (B) pore size distribution of the carbon aerogels. (C) XRD patterns and (D) Raman spectra of the wheat straw, the cellulose aerogels and the carbon aerogels.

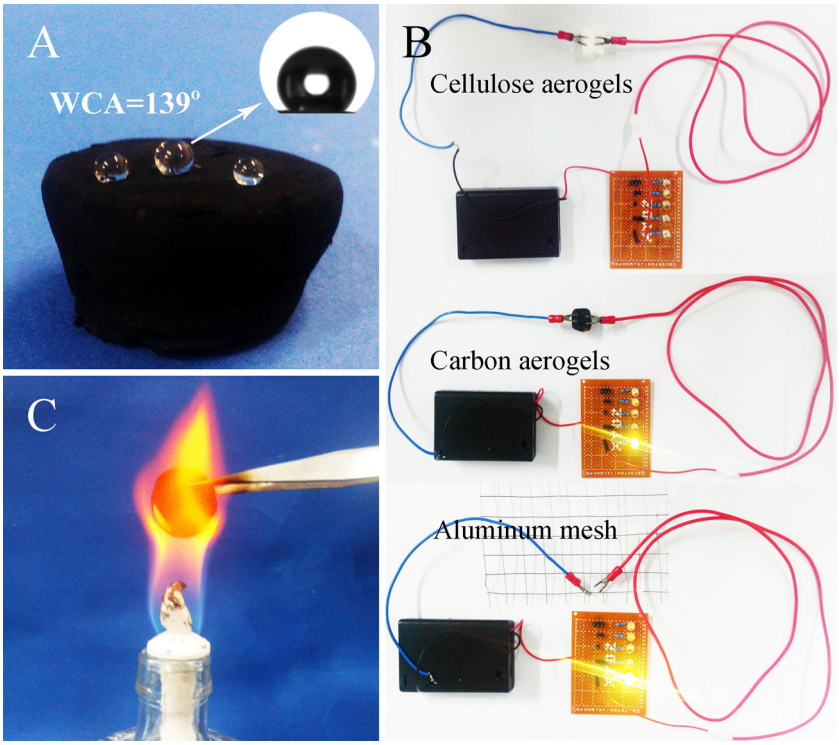

Fig. 3. (A) Hydrophobic carbon aerogels with several water drops on the surface, and the inset showed the water contact angle measurement. (B) Electrical conductivity tests of the cellulose aerogels, the carbon aerogels and the aluminum mesh. (C) Digital photograph of the carbon aerogels in a hot flame of an alcohol burner.

3. Results and discussion

The as-prepared cellulose after the chemical pretreatment had high α-cellulose content of 90.03% because of the massive removal of hemicellulose and lignin, indicating high purity for the cellulose samples. Moreover, the cellulose aerogels and the carbon aerogels from the cellulose-NaOH/PEG solution were also successfully fabricated. SEM images of the cellulose aerogels and the corresponding carbon aerogels were shown in Fig. 1. Typical 3D network structure of the cellulose aerogels could be clearly found, whose pore sizes ranged from approximately dozens of nanometers to several microns. After the pyrolysis process, the cross-linked nanoporous 3D network was maintained for the carbon aerogels, whereas the network became relatively tenuous and uneven. Moreover, compared with the cellulose aerogels, the oxygen peak in the EDX spectrum of carbon aerogels was almost entirely disappeared (inset in Fig. 1A), and the carbon peak improved sharply, which indicated the severe decomposition of oxygen-containing functional groups during the pyrolysis contributing to the formation of hydrophobicity.

Detailed pore features of the carbon aerogels were investigated by nitrogen adsorption measurements. As shown in Fig. 2A, the nanoporous carbon aerogels with specific surface area ($113\,m^2\,g^{-1}$), average pore size (7.2 nm) and total pore volume ($0.21\,cm^3\,g^{-1}$) exhibited type-IV adsorption isotherm according to the IUPAC classification, and the hysteresis loop was generally attributed to the capillary condensation occurring in the mesopores. Moreover, it was observed in Fig. 2B that the pore diameters of the carbon aerogels were within the scope of 1–60 nm, which suggested that the aerogels were primarily composed of mesopores (2–50 nm).

The XRD pattern of the wheat straw exhibited typical cellulose I crystalline structure (Fig. 2C) due to the characteristic peaks at around 15.1°, 16.9° and 21.9° corresponding to the (1 0 1), (1 0 $\bar{1}$) and (0 0 2) planes. As the result of NaOH treatment, the cellulose aerogels showed strong peaks at 12.0°, 19.8° and 21.6°, indicating the generation of cellulose II. After the pyrolysis at 1000 °C, the cellulose characteristic peaks were completely disappeared, revealing that the cellulose crystalline structure was destroyed, and two new broad peaks centered at around 22.0° and 43.3° were corresponding to the (0 0 2) and (1 0 0) planes of graphite, which demonstrated that amorphous carbon was formed (Wu et al., 2013). From the Raman spectra as shown in Fig. 2D, the characteristic peaks of the wheat straw and the cellulose aerogels at around 1101, 1378 and $1460\,cm^{-1}$, which were primarily originated from cellulose components (Agarwal & Ralph, 1997), were all disappeared in the Raman spectrum of the carbon aerogels; instead, the graphitic D- and G bands at $1346\,cm^{-1}$ and $1594\,cm^{-1}$ related to graphitic sp^2-bonding were generated. Especially, the shift of the G-peak from a value of $1581\,cm^{-1}$ to $1594\,cm^{-1}$ revealed the presences of nanocrystalline (highly disordered) graphite and aromatic cluster (Sevilla & Fuertes, 2009). Meanwhile, the broad D-peak also suggested disorder in the graphite structure.

Some unique macro-properties of the carbon aerogels were presented in Fig. 3. Fig. 3A showed that carbon aerogels with a WCA of 139° could stably hold several water drops on the surface, indicating the formation of strong hydrophobicity, which might be used as high-performance separating or adsorbing materials for cleanup of oil spillage and chemical leakage. Moreover, it was observed in Fig. 3B that the cellulose aerogels had inferior conductivity when connected to a closed circuit system, and could not support current flow leading to no luminescence of the bulb. On the contrary, the carbon aerogels were good electrical conductors, which allowed current flow to pass through and lighted the bulb, and the brightness of the bulb was comparable with that of the bulb in the circuit with aluminum mash, which may find applications in electronic devices. The carbon aerogels were also superior fire retardants, which did not support any burning and

release obvious smoke all the time when exposed to a flame of an alcohol burner (Fig. 3C). Thus, as previously reported carbon aerogels based on bacterial cellulose with similar strong hydrophobic properties, electrical conductivity, fire resistance, and adsorption properties (Liang, Guan, Chen, et al., 2012; Liang, Guan, Zhu, et al., 2012; Wu et al., 2014), this class of carbon aerogels in this study generated from the regenerated cellulose aerogels might also be expected to be exploited more excellent performances. Furthermore, the detailed adsorption, thermal, and electrical properties of the carbon aerogels would be intensively studied in our future research.

4. Conclusions

In conclusion, we successfully fabricated miscellaneous carbon aerogels by pyrolysis of regenerated cellulose aerogels. After pyrolysis, the nanoporous carbon aerogels maintained cross-linked 3D network, and exhibited type-IV adsorption isotherm, which was mainly composed of mesopores. Moreover, the pyrolysis process resulted in the decomposition of oxygen-containing functional groups, the destruction of cellulose crystalline structure, and the formation of highly disordered amorphous graphite. Meanwhile, the carbon aerogels also displayed strong hydrophobicity, electrical conductivity and flame retardance, which might be useful for waterproof materials, electronic devices and flame retardants.

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