

Low-density graphitic films prepared from iodine-doped enzymatically synthesized amylose films as carbonization precursors



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ABSTRACT

We have developed a novel approach for preparing low-density graphitic films using iodine-doped enzymatically synthesized amyloses (ESAs) with strictly controlled molecular weights as carbonization precursors. All of the iodine-doped ESA films retained their film structures and morphologies, even after the heat-treatment at 800 °C and 2600 °C. Therefore, iodine doping plays an indispensable role in retaining film structure and morphology during the carbonization of ESA polysaccharides. It was also elucidated that the carbonization yields of the ESA films can be controlled by changing the conditions of iodine doping process. The bulk densities of the graphitic films are varied from 0.08 to 0.42 g/cm³ dependent on the doping level. In addition, the capacitance performances of the graphite films prepared from the ESAs are investigated using cyclic voltammetry and galvanostatic charge/discharge procedures. The potential utility of the carbonized and graphitized ESA films for supercapacitors was revealed. This approach may broaden the application and even the swill processing of polysaccharides.

1. Introduction

Polysaccharide is a biological polymer that plays important roles in the storage of energy and in the composition of the structures of organisms. Cellulose, starch, and chitin have been widely studied as the most abundant homopolysaccharides because of their biodegradability. Cellulose-chitosan (Hasegawa, Isogai, Onabe, Usuda, & Atalla, 1992; Wu et al., 2004) and chitosan-amylose (Cervera, Heinamaki et al., 2004; Cervera, Karjalainen et al., 2004; Zhai, Zhao, Yoshi, & Kume, 2004) blend films are attractive materials with preeminent antibacterial and mechanical properties. However, these studies have been conducted on composite films with chitosan acid salts and plasticizers. An additive-free film must be studied to understand the physicochemical properties of these polysaccharides.

Nearly monodisperse (Kitamura, Yunokawa, Mitsuie, & Kuge, 1982; Kitamura, 1996; Waldman, Gyax, Bendnarski, Shangraw, & Whitesides, 1986) amylose with no branching (Kitamura, Kobayashi, Tanahashi, Ozaki, & Kuge, 1989) was enzymatically synthesized using maltooligosaccharide as a primer and glucose 1-phosphate as a substrate. The molecular weight of the enzymatically synthesized amylose (ESA) was strictly controlled through the concentration of

maltooligosaccharide and glucose-1-phosphate and/or the reaction time. This successful synthesis indicates that ESA is a suitable material for basic research, such as that into the solution physics of amylose. Furthermore, the films prepared from water-soluble ESA with high molecular weights exhibited high transparency and favorable gas barrier properties, implying that they could be used as food wrapping and optical films.

We have succeeded in synthesizing one-component mechanically strong graphite films with distinguished electrically and thermally properties from iodine-doped stretchable polyacetylene (PA) films (Kyotani et al., 2008; Matsushita, Yan, Kyotani, & Akagi, 2016) as heat-treatment precursors using a novel carbonization method named “morphology-retaining carbonization” (Matsushita, Kyotani, & Akagi, 2011; Matsushita, Yan, Yamamoto, Jeong, & Akagi, 2014; Matsushita & Akagi, 2015; Yan, Matsushita, Suda, & Akagi, 2015; Yan, Matsushita, & Akagi, 2016; Yan, Matsushita, & Akagi, 2017). The stretchable PA film was prepared through the solvent evacuation method (Akagi et al., 1989; Akagi, Sakamaki, & Shirakawa, 1992). Iodine doping process was demonstrated to be indispensable in suppressing thermal decomposition and keeping the fibril structure and morphology of the original PA film as precursor (Kyotani et al., 2008; Matsushita, Yan, Kyotani, &

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Akagi, 2016; Matsushita, Kyotani, & Akagi, 2011; Matsushita & Akagi, 2015). Recently, iodine-doped cellulose papers were used as carbonization precursors for preparing functionalized carbon papers via morphology-retaining carbonization at 2600 °C (Kyotani, Matsushita, Kimura, & Akagi, 2012). The iodine dopant in the cellulose paper acted as an important role for suppressing thermal decomposition of the cellulose and keeping the microfibril morphology.

Amylose is a linear polymer made up of glucose units with α -1,4 linkages. It forms a helical structure owing to intrachain hydrogen bonding, where one helical pitch corresponds to six α -glucose units. Amylose is also known to exhibit a so-called iodo-starch reaction in which the color of amylose changes from red to blue depending on the helical chain length because iodine molecules penetrate into the amylose coil to form charge transfer complexes between the amylose coil and I_3^- or I_5^- . The use of iodine as a stabilizer for producing carbon products from potato starch and chitosan was reported by Miyajima and co-workers (Miyajima et al., 2010). However, it is well established that natural amylose has a slightly branched structure (Takeda, Shitaazono, & Hizukuri, 1990). Therefore, to use ESA with no branching is a good approach for preparing advanced carbon materials. In this study, iodine-doped ESA with a strictly controlled molecular weight was used as a carbonization precursor for preparing carbon and graphite films (Scheme 1). The relation between the iodine doping conditions for the precursor and the carbonization yield is discussed, and the possibility of applications in supercapacitors is examined. The present approach might be useful for broadening the application or even the swell processing of polysaccharides.

2. Materials and methods

2.1. Materials

Chemical compounds were purchased from commercially available sources and were used as received. Potassium chloride (KCl) was purchased from Nacalai Tesque, Inc. Nickel plate was purchased from Nilaco Co., Ltd. The platinum (Pt) wire counter electrode was purchased from Metrohm Autolab. Ag/AgCl reference electrode for neutral aqueous solutions was purchased from BAS, Inc.

2.2. Characterization

2.2.1. Thermal behavior

Thermal behavior of A-900 was investigated by heating it at a rate of 10 °C/min under flowing nitrogen gas, using a thermogravimetry-differential thermal analysis (TG-DTA) apparatus (DTG-60, Shimadzu) with an alumina pan.

2.2.2. Film thickness

Film thickness was measured using a Nikon Digimicro digital length measuring system consisting of a DIGIMICRO MH-15 M, a DIGIMICRO

STAND MS-5C, and a DIGITAL READOUT UC-101.

2.2.3. X-ray diffraction

X-ray diffraction (XRD) measurements were performed with a Rigaku ultra X18 diffractometer. XRD patterns were recorded with an X-ray generator using Ni filtered $CuK\alpha$ radiation (40 kV/300 mA; $\lambda = 1.54 \text{ \AA}$) and a flat-plate camera (RINT2500, Rigaku). The exposure time was 1–2 h. The diffraction pattern was recorded on an imaging plate and scanned by a RAXIA-Di imaging plate reader at 100 μm resolution.

2.2.4. Ultraviolet–visible and circular dichroism spectra

Ultraviolet–visible (UV–vis) and circular dichroism (CD) spectra were measured using JASCO V570 and JASCO J820 spectrometers, respectively.

2.2.5. Infrared absorption spectra

The infrared (IR) absorption spectra of the A-900 films were measured of powders using a JASCO FT (Fourier transform)-IR 4200 spectrometer in a transmission mode.

2.2.6. Tensile tests

Tensile tests of the A-900 films were performed at room temperature using a TENSILON RTG-1210 (A&D) with a load cell of 500 N at a displacement rate of 0.05 mm/min. The specimens for the tensile tests were 4–12 mm wide (w), and the chuck distance (L_c) was 5 mm. The tensile strength (σ_t) and modulus (ϵ_t) were calculated using $\sigma_t = f_t/wt$ and $\epsilon_t = f/\delta$, respectively, where f_t is the maximum load, t is the specimen thickness, and f/δ is the initial linear slope of the load displacement curve.

2.2.7. Scanning electron microscopy

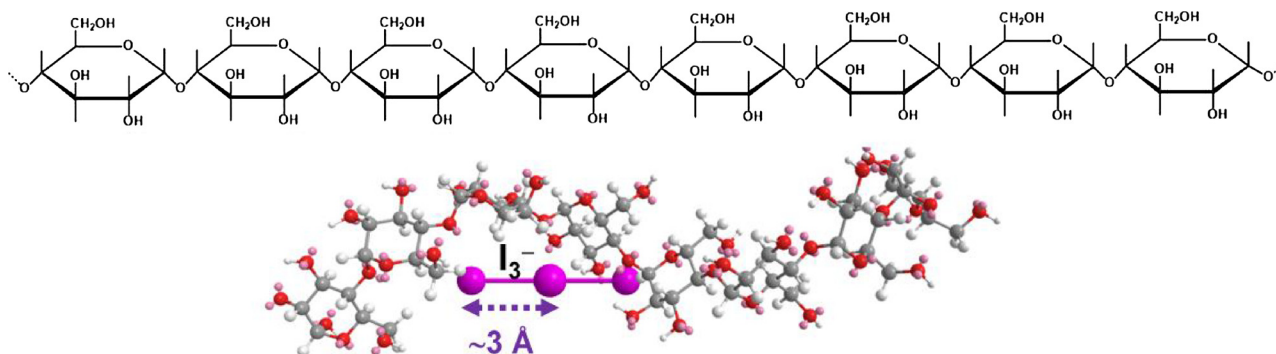
The accelerating voltage of field emission (FE)-SEM (JSM-7500F, JEOL) was 2–10 kV. Before being measured by SEM, the A-900 films were coated with Pt or a Pt-Pd alloy using a JFC-1600 (JEOL) ion coater. The coating thickness was evaluated to be ca. 5 nm.

2.2.8. Carbonization and graphitization

The carbon films were prepared using an electric furnace (KDF75, Denken). The graphite films were prepared using a graphitization apparatus [SCC-U-80/150 (2P), Kurata-giken]. The carbonization and graphitization yields were evaluated using the following equations, respectively: (weight of carbonized A-900)/(weight of A-900) \times 100 and (weight of graphitized film)/(weight of carbon film) \times 100.

2.2.9. Cyclic voltammetry and galvanostatic charge/discharge measurements

Cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) measurements were performed with a μ AUTOLAB III potentiostat/galvanostat.



Scheme 1. Iodine doped amylose (described as octamer) used as carbonization precursor.

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