



Full Length Article

Fabrication and electric heating behavior of carbon thin films from water-soluble poly(vinyl alcohol) via simple dry and ambient stabilization and carbonization

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ABSTRACT

In this study, the development of electrically-heatable carbon thin films (CTFs) from water-soluble poly(vinyl alcohol) (PVA) is described. CTFs are easily obtained by room-temperature and solid-state proton irradiation-induced stabilization of PVA thin films followed by carbonization at a high temperature. The results of the chemical, optical, and structural analyses reveal that polyene-network structures, enabling high-temperature dimensional stability, are effectively created in the PVA thin films by combined reactions of crosslinking and dehydration during proton irradiation; these structures are further converted to pseudo-graphitic CTFs by carbonization. The prepared CTFs exhibit the fluence and thickness-dependent electrical conductivity ranging from 0.8×10^2 to $2.63 \times 10^2 \text{ S cm}^{-1}$, and a very low surface roughness of below 0.41 nm. Moreover, the prepared CTFs show excellent electric-heating characteristics and the performance is clearly dependent on the thickness and fluence. The CTFs prepared in this study have good potential for application in the fabrication of automobiles, smart windows, and medical devices for deicing, defrosting, and warming.

1. Introduction

Carbon thin films (CTFs) are widely used in energy, environment, biomedical engineering, and electronics applications due to their excellent electrical and electrochemical properties as well as low cost. Carbon materials, such as graphene, carbon nanotubes, and carbon fibers, conducting polymers, and their composites are used as conductive carbon thin films due to their high electrical conductivity and good device performances [1–7]. However, their drawbacks, such as high surface roughness [8], low thermal and chemical stability [9,10], and complicated fabrication processes [11,12], are serious obstacles for their practical applications.

To overcome these drawbacks, CTFs have been prepared by the carbonization of various organic materials, such as polyacrylonitrile (PAN), pitch, poly(vinyl alcohol) (PVA), polyimide (PI), and polyaromatic compounds [13–16]. Among these organic materials, PVA, an eco-friendly water-soluble polymer, is considered as a promising material for the preparation of carbon fibers and films due to its high carbon content [17]. However, the carbonization yield of PVA, a critical

factor for both carbonization efficiency and dimension retention of the precursor after carbonization, is below 5 wt% by the direct carbonization of PVA without any pre-treatment or stabilization processes [18]. Therefore, stabilization before carbonization is necessary to create well-defined carbon structures with improved carbonization yield. Stabilization including pre-treatment (e.g., iodination) and incorporation of metal or metal oxide (e.g., Fe_3O_4) have been suggested to enhance the carbonization yield [18–20]. However, these processes have disadvantages in that they are wet processes requiring toxic and expensive chemicals, and they are time- and energy-consuming. Therefore, there is still a high demand for a simple, efficient, and cost effective strategy to produce PVA-derived CTFs for practical applications.

Proton irradiation is a promising route to improve both the carbonization yield and dimension retention of precursory polymer thin films during the production of CTFs. The room-temperature high energy transfer of energetic protons enables easy generation of networked sp^2 -hybridized carbon structures in solid-state polymer thin films without any chemicals [21,22]. Despite this distinct feature, to the best of our knowledge, this is the first report on the preparation of electrically-

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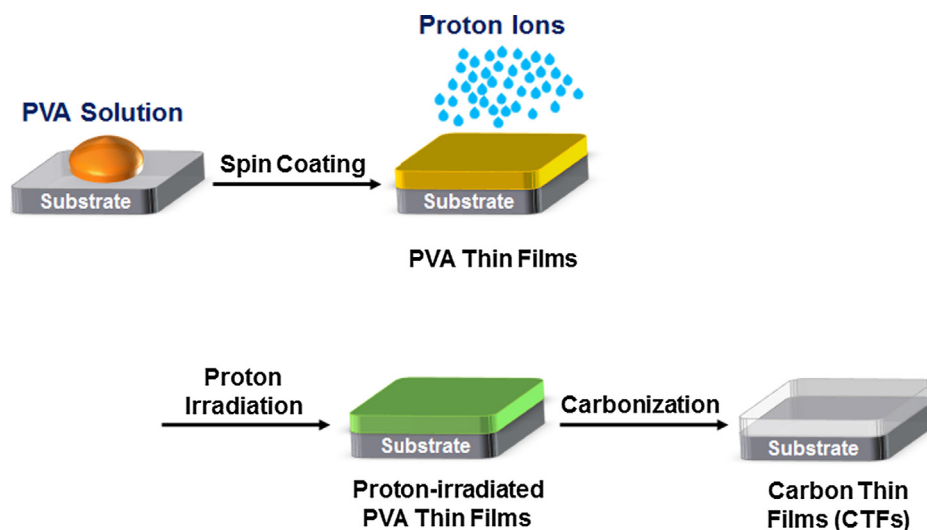


Fig. 1. Schematic illustration of the formation of CTFs by proton irradiation and carbonization.

heatable PVA-derived CTFs by the combination of proton irradiation-induced stabilization with carbonization.

The present study was intended to investigate the formation of water-soluble PVA-derived CTFs by ambient and dry proton irradiation-induced stabilization and subsequent carbonization, and to further demonstrate them as thin film heaters. To elucidate the formation of CTFs, PVA thin films spin-coated on a substrate were stabilized by proton irradiation at various fluences and then were subjected to carbonization. The resulting CTFs were investigated in terms of their remaining thickness, chemical structure and compositions, crystalline structure, and electrical properties. Furthermore, the electric heating behavior of the prepared CTFs was investigated to demonstrate the feasibility of the CTFs as promising thin-film heaters.

2. Experimental

2.1. Materials

PVA (Mw: 89,000–98,000 g/mol, degree of hydrolysis: > 99%, Sigma-Aldrich) was used as a precursor for the preparation of CTFs.

2.2. Preparation of CTFs

PVA films were formed on a substrate by spin-coating of PVA solutions with various concentrations in a distilled water and drying on a hot plate at 70 °C for 2 min. The resulting PVA thicknesses ranged from 5 to 400 nm. The prepared PVA films were irradiated with proton ions with an energy of 150 keV at a current density of $0.5 \mu\text{A cm}^{-2}$. The fluence of proton irradiation ranged from 6.0×10^{15} to 1.7×10^{16} ions cm^{-2} . After proton irradiation, the irradiated PVA films were placed in a tubular furnace (Lindberg Blue M, USA), heated to 1000 °C at a heating rate of $5 \text{ }^\circ\text{C min}^{-1}$ under a nitrogen atmosphere, maintained at 1000 °C for 1 h, and then naturally cooled to room temperature. The prepared carbon films were named CTF_X_Y, where X and Y denote the precursor thickness and fluence, respectively.

2.3. Characterization

The thickness was measured by using an Alpha Step IQ surface profiler (KLA Tencor, USA). The surface morphology was observed by using an atomic force microscope (AFM, XE-100, Park System, Korea). The UV–visible absorption spectra were measured by UV–vis spectrophotometer (S-3100, Scinco, Korea). The chemical structure and compositions were analyzed by using a FT-IR spectrometer (Varian 640,

Australia) and an XPS (MultiLab 2000, ThermoElectron Corporation, England) employing Mg-K α radiation. XRD analysis was carried out on an X-ray diffractometer (X'Pert Pro Multi-Purpose, PANalytical, Netherlands) with CuK α radiation in the range of $2\theta = 5\text{--}60^\circ$. Raman spectroscopy was performed on a Raman spectrometer (LABRAM-HR JobinYvon LabRAM system, Horiba Scientific, UK) with an Ar-ion laser at an excitation wavelength of 514.5 nm. To measure the current–voltage (I – V) characteristic of the prepared carbon thin films, silver electrodes with dimensions of 100 μm (length) \times 200 μm (width) \times 0.1 μm (height) were thermally deposited at both edges of the formed CTFs and the average distance between the electrodes was about 8000 μm . The I – V curves were recorded on a probe station (MST-4000A) equipped with a Keithley 2400 source meter. The electrical conductivity was measured by using a four-point probe measurement system (SR-1000N, Advanced Instrument Technology, Korea). Electric heating behaviours of the prepared CTFs under various applied voltages of 1–100 V were characterized using an IR camera (SE/A325, FLIR Systems Inc.) equipped with a Keithley 2400 source meter.

3. Results and discussion

3.1. Characterization of CTFs

To provide fundamental insight into the formation of CTFs, the changes in the chemical structures in the PVA during protons irradiation and carbonization depicted in Fig. 1 were investigated by FT-IR spectroscopy, and the results are shown in Fig. 2. As seen in Fig. 2(a), the characteristic peaks for the pristine PVA were identified at 3100–3500 (--OH), 2854–2918 and 1426 (aliphatic --CH_2), and 1000–1200 cm^{-1} (C--O--C). For the proton-irradiated PVA shown in Fig. 2(b), the peaks assigned to the C=O and C=C groups newly appeared at 1710 and 1630 cm^{-1} , respectively, while the peak intensities of OH, aliphatic C--H_2 , and C--O were markedly reduced, providing clear evidence for the formation of the polyene structure in the PVA film caused by proton beam-induced crosslinking, dehydration, and oxidation [23,24]. On the other hand, in the case of the CTFs (Fig. 2(c)), a prominent peak, indicative of the existence of the graphitic carbon structure, was clearly present at 1630 cm^{-1} (aromatic C=C), implying the successful formation of graphitic carbon structures in the CTFs [22,23,25]. From these results, it can be concluded that crosslinked polyene structures formed by proton irradiation without any pre-treatment and stabilization process are converted to graphitic carbon structures by carbonization.

To gain further insight into the changes in the chemical structures

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