Journal of Physics and Chemistry of Solids 91 (2016) 122–127

Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids

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

A simple synthesis method to produce metal oxide loaded carbon paper using bacterial cellulose gel and characterization of its electrochemical behavior in an aqueous electrolyte

Naoya Miyajima [a,*], Ken Jinguji [b], Taiyu Matsumura [b], Toshihiro Matsubara [b], Hideto Sakane [b], Takashi Akatsu [c], Osamu Tanaike [d,*]

[a] *Center for Instrumental Analysis, University of Yamanashi, Takeda, Kofu, Yamanashi 400-8551, Japan*
[b] *Graduate School of Medicine and Engineering, University of Yamanashi, Takeda, Kofu, Yamanashi 400-8511, Japan*
[c] *Graduate School of Engineering, Saga University, 1 Honjo-machi, Saga, 840-8502, Japan*
[d] *National Institute of Advanced Industrial Science and Technology, 4-5-1 Nigatake, Sendai, Miyagi 983-8551, Japan*

ARTICLE INFO

Article history:
Received 10 August 2015
Received in revised form
18 November 2015
Accepted 7 January 2016
Available online 7 January 2016

Keywords:
Carbon paper
Porous carbon
Bacterial cellulose
Cellulose gel
Pseudocapacitance

ABSTRACT

A simple synthetic chemical process to produce metal oxide loaded carbon papers was developed using bacterial cellulose gel, which consisted of nanometer-sized fibrous cellulose and water. Metal ions were successfully impregnated into the gel via aqueous solution media before drying and carbonization methods resulting in metal oxide contents that were easy to control through variations in the concentration of aqueous solutions. The papers loaded by molybdenum oxides were characterized as pseudocapacitor electrodes preliminary, and the large redox capacitance of the oxides was followed by a conductive fibrous carbon substrate, suggesting that a binder and carbon black additive-free electrode consisting of metal oxides and carbon paper was formed.

1. Introduction

Fibrous carbon is often possible to be shaped into carbon paper without binder, which has been expected for many applications. Such carbon paper not only has the characteristics of typical paper morphologies, such as gas/liquid permeability and excellent formability, but also characteristics of carbon materials such as good conductivity and high surface area. One of the most promising applications of carbon paper is in the gas diffusion layer of the polymer electrolyte fuel cell, which can utilize both the excellent conductivity of carbon and the gas permeability of paper [1–4]. Carbon nanotubes, as well as other fibrous carbons, have been also manufactured into paper without using a binder. These simple papers may be used as electrodes for the electric double layer capacitor in which the relatively large surface area and high conductivity are suitable for electrodes with a large electric double layer and low internal resistivity [5,6].

Various types of fibrous carbons have been used for manufacturing carbon paper, including industrial polymer-based carbons [7,8] and natural-resource-based carbons [9,10]. In the present study, we focused a bacterial cellulose-based fiber as a material for producing carbon paper. Bacterial cellulose is a natural cellulose fiber with very small diameters in the order of several micrometers and is produced by *Acetobacter xylinum* through fermentation of sugars such as glucose [11]. It is commonly available as an aqueous gel where water molecules are present between fine cellulose fibers and is often known as the main component of the food material “Nata de Coco”. Attempts to utilize the paper obtained by drying the gel have been carried out for use in industrial applications, such as production of fine paper sheets for electronic device substrates [12,13] or biomedical materials [13,14].

The cellulose fiber gel is expected also for a precursor of fine carbon paper. Actually the carbon paper produced through carbonization of the bacterial cellulose paper has been also reported [15–18], in which the usually disordered and porous carbon paper is formed based on the typical nature of cellulose as a carbon precursor. For some industrial applications such as catalysis and production of electrochemical capacitors, it is certainly valuable to disperse particles of inorganic active materials on high surface area carbons. In this study, a simple synthesis route for metal oxide loaded carbon paper is examined using bacterial cellulose gel, because the gel of cellulose fiber has some merits that carbon

* Corresponding authors.
E-mail addresses: miyajima@yamanashi-u.jp (N. Miyajima), o-tanaike@aist.go.jp (O. Tanaike).

http://dx.doi.org/10.1016/j.jpcs.2016.01.007
0022-3697/

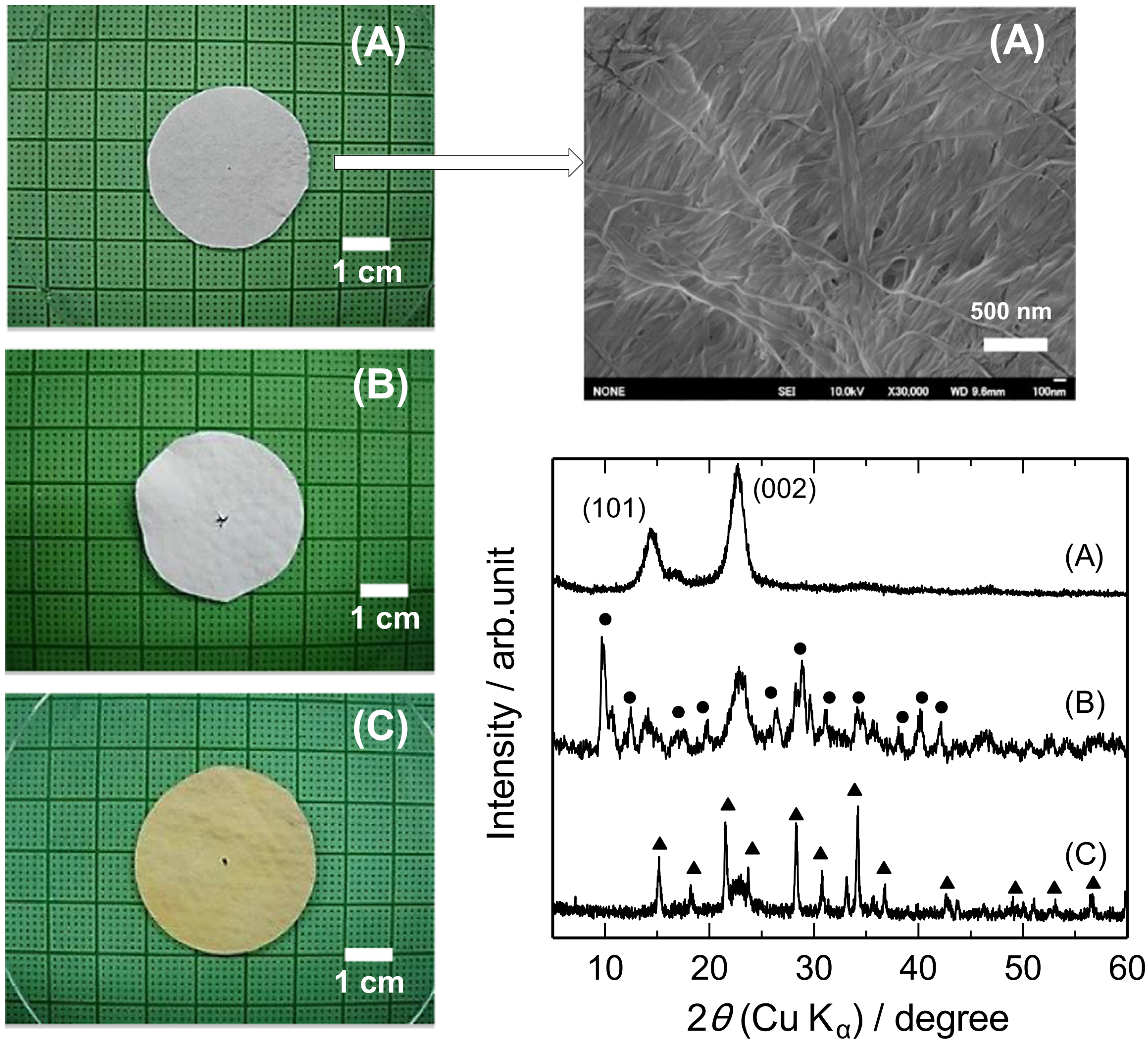

Fig. 1. Photographs of the cellulose papers before carbonization, their XRD patterns and SEM images of the paper of (A). (A) Without immersion, (B) with immersion in 0.05 mol/L of ammonium heptamolybdate tetrahydrate aqueous solution, (C) with immersion in 0.05 mol/L of ammonium metavanadate aqueous solution. ●: $(NH_4)_6Mo_7O_{24}$, ▲: NH_4VO_3.

paper without any binder is easily possible and content of metal compounds excluded is expected to be controlled by simple experimental condition of concentration of aqueous solution. In the present experiments, some metal ions were first simply impregnated into the gel through aqueous media. Then, the gel was dried and carbonized to obtain carbon paper containing metal oxides. The metal oxides were synthesized and remained even in an inert atmosphere during the carbonization without excess reduction by carbon, which could occur owing to the oxidative gas released from thermal decomposition of cellulose. The content of metal oxides supported on the carbon paper was easily controlled by varying the concentration of the aqueous solution of metal ions impregnating the gel. The final product of the metal oxide infused carbon paper was electrochemically characterized by cyclic voltammetry in an aqueous electrolyte solution to estimate the potential for its use as a binder-less porous carbon electrode for electrochemical applications.

2. Experimental

2.1. Preparation of carbon papers

Bacterial cellulose gel was purchased from FUJICCO Co., Ltd., as an intermediate product of food grade for making sweets. The gel was shipped as cubes that were 10 mm^3 in size and preserved in acetic acid. The impregnating solutions used for the gels were consisted of 0.01, 0.025 and 0.05 mol/L aqueous solutions of ammonium metavanadate (NH_4VO_3) or hexaammonium heptamolybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$). The gel was first washed in distilled water for several times until the pH of the rinsed solution reached 7. Next, 20 pieces of the gel cube was immersed in the above-listed aqueous solutions for 24 h to sufficiently impregnate the ions into the gel. The gel impregnated by metal ions was crushed with ethanol using a mixer, filtered by a Buchner funnel under vacuum to produce a filter shaped cellulose fiber paper containing metal ions. The paper was natural dried at room temperature to remove any residual water and ethanol remaining in the paper, and finally, the paper was sandwiched between graphite plates and carbonized at 700–1000 °C under nitrogen flow with 10 °C/min of heating rate using a tubular electric furnace.

2.2. Characterization of carbon papers

The papers were characterized before and after carbonization by X-ray powder diffraction (XRD; Rigaku, RINT2100 Ultima$^+$) measurement to determine the structures of carbon or cellulose