Catalysis Communications 10 (2008) 267–271

Contents lists available at ScienceDirect

Catalysis Communications

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

Simple synthesis of graphitic porous carbon by hydrothermal method for use as a catalyst support in methanol electro-oxidation

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ARTICLE INFO

Article history:
Received 8 March 2008
Received in revised form 15 August 2008
Accepted 20 August 2008
Available online 12 September 2008

Keywords:
Carbon
Electrocatalyst
Hydrothermal method
Graphitic
Methanol

ABSTRACT

Graphitic porous carbon (GP-carbon) was prepared using non-toxic and economical carbon precursor (sucrose) by a simple hydrothermal method under a relatively low pyrolysis temperature. Uniform silica particles (100 nm) were used as pore-forming templates and etched by HF solution after carbonization. The GP-carbon exhibited highly graphitic properties with surface area of 425 m^2/g and pore volume 0.42 cm^3/g. The GP-carbon showed superior performance as a catalyst support in methanol electro-oxidation. The enhanced activity would be closely related to advantageous properties resulting from highly-developed graphitic structure of the GP-carbon.

1. Introduction

Graphitic carbons have attracted much attention by many scientists and engineers in practical and fundamental researches for use in hydrogen storage, catalysis and electrochemistry, due to their high electronic conductivity and mechanical strength. Practically, graphitic carbon materials, such as graphite powder, carbon nanotube (CNT) and graphitic carbon nanofiber (GNF), have high conductivities and unique electronic properties which affect electron transfer and metal orientation. They showed the enhanced electrochemical performance in many reactions [1,2]. Although there are superior electronic properties and electrochemical performance, the use of the graphitic carbons have been limited due to the disadvantageous characteristics, such as low surface area and uncontrollable morphologies [3]. In addition, synthetic methods are complex and preparation conditions are uneconomical and severe. Thus, many researchers have made effort to fabricate graphitic carbon with various morphologies using economical methods.

Generally, graphitic carbons have been prepared by pyrolysis using graphitizable carbon precursors such as polymer [3], aromatic hydrocarbon [4] or mesophase pitches [5,6] at an extremely severe condition. Yu et al. reported that ordered macroporous carbon with a graphitic framework was synthesized from a mesophase pitch as carbon precursor through pyrolysis at 2500 °C [6]. Although the ordered macroporous graphitic carbon was prepared, the pyrolysis temperature was still high. Several research groups have also reported preparation methods for graphitic carbons under mild conditions. Hyeon and co-workers prepared graphitic carbon nanocoils by carbonizing resorcinol–formaldehyde gel doped with metal salt, at a relatively low temperature. The prepared graphitic nanocoil showed higher performance than commercial carbon black for use as catalyst support in methanol electro-oxidation [7].

Hydrothermal synthesis is a simple and easy process for the preparation of powder materials using aqueous solution as a starting material. This method is also suitable for the control of crystal growth and mass production at a low temperature. Recently, nanostructured carbon materials, such as carbon sphere and porous carbon, have been synthesized by the hydrothermal synthesis route [8–10]. However, few investigations have been reported for the preparation of graphitic carbon materials which have a variety of morphologies.

In this work, an economical and easy method for the preparation of GP-carbon under mild synthesis conditions is reported. We prepared highly graphitic GP-carbon using a simple hydrothermal method with templating route. The resulting material was characterized by SEM, HR-TEM, XRD and Raman spectroscopy, and examined for use as a catalyst support in methanol electro-oxidation.

2. Experimental

The GP-carbon was prepared by a simple hydrothermal method using uniform-sized silica particles as templates under mild

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doi:10.1016/j.catcom.2008.08.031

pyrolysis conditions. Uniform-sized silica particles were synthesized as described by Stöber et al. [11]. Fig. 1 illustrates the preparation scheme for GP-carbon synthesized in this study. Silica particles (100 nm diameter) were well dispersed in de-ionized water by ultrasonication for 3 h. Sucrose (Aldrich) and iron salt ($Fe(NO_3)_3 \cdot 9H_2O$, Sigma) were dissolved into the above aqueous solution under vigorous stirring. The aqueous solution was charged in a teflon-coated stainless steel autoclave. The autoclave was placed in a convection oven at 190 °C for 10 h with vigorous stirring. After cooling down the autoclave at room temperature, the black precipitates were filtered and dried to obtain polymer–silica composites. These polymer–silica composites were carbonized at 900 °C for 5 h and then carbon–silica composites, which contained the graphitic structure, were formed. Final GP-carbon was obtained by dissolution of the silica template and removal of Fe species with diluted HF and HNO_3 solutions, respectively. For comparison purposes, sucrose was polymerized under ambient conditions without hydrothermal treatment to obtain amorphous porous carbon (AP-carbon).

The supported Pt catalyst (Pt/GP-carbon) was prepared by formaldehyde reduction method reported by Zhou et al. [12]. The Pt precursor (H_2PtCl_6, Acrose) was dissolved in 500 ml of de-ionized water and the prepared carbon support was well dispersed by ultrasonication. The concentrated formaldehyde solution as a reducing agent was added dropwise to the above solution and the batch was heated up to 70 °C under vigorous stirring for 5 h. The black precipitates were filtered, washed with copious amount of de-ionzed water and dried at 80 °C in vacuum conditions. The Pt loading was adjusted to 60 wt.% in the final catalyst.

X-ray diffraction (XRD) patterns were recorded using a M18XHF-SRA diffractometer (MAC science). The macroscopic morphology and lattices of carbon support were investigated by field emission scanning electron microscopy (FE-SEM, JEOL, JSM-6700F) and high resolution transmission electron microscopy (HR-TEM, JEOL, JEM-3010). Raman spectroscopy (Raman, RM 1000 Renishaw) was carried out to investigate the degree of crystalline structure of carbon support.

The electrocatalytic activity in methanol electro-oxidation was investigated in a conventional half cell by cyclic voltammetry using EG&G 263A potentiostat. Pt gause and saturated calomel electrode (SCE) were used as a counter and a reference electrode, respectively. The working electrode was prepared by coating the catalyst ink on a disk-type glassy carbon electrode. Cyclic voltammograms were recorded in 0.5 M H_2SO_4 solution containing 1 M CH_3OH at room temperature.

3. Results and discussion

Fig. 2 shows SEM and HR-TEM images of the prepared GP-carbon. As shown in Fig. 2a, partially broken pores were randomly distributed in the carbon framework, and the carbon had an open-pore structure. The spherical pores with an average pore diameter of 100 nm were easily observed in the high magnitude SEM image (Fig. 2b). As described in Fig. 1, pores were formed by silica-templating route. During the hydrothermal process, the sucrose was polymerized on the surface of randomly distributed silica particles in the synthetic solution and silica templates were located in the polymer framework after polymerization of sucrose. After carbonization and silica etching, silica particles were removed by HF solution and regular spherical pores were generated. It should be noted that the pore of support material has an important role in many catalytic reactions. In electrocatalytic reaction, large pore of carbon support has many advantages. It is well known that electrocatalysis in a electrochemical system, such as fuel cells and battery, is taken place in the interfaces of the reactant, the catalyst surface and the electrolyte, i.e., a triple-phase boundary [13]. The triple-phase boundary would be easily formed in the relatively large pore, compared to micropore of support materials because the conventional polymer electrolyte has large molecular size. Thus, the carbon support with regularly large pore is more desirable in view of the mass transfer and would show considerably high performance in practical fuel cells.

The (002) lattice fringes of the graphitic structure are clearly observed in HR-TEM images indicating that GP-carbon has highly graphitic characteristics (Fig. 2c). The d_{002} was measured and found to be ca. 3.4 Å. In addition, the GP-carbon exhibited a relatively high surface area (425 m^2/g) and a large pore volume (0.42 cm^3/g).

X-ray diffraction patterns of the prepared carbons are shown in Fig. 3. In the XRD patterns of Vulcan XC-72 (Cabot) and AP-carbon, a broad peak at ca. $2\theta = 25°$ was observed, while the GP-carbon showed a sharp peak at the same angle which was caused by the (002) diffraction plane of the hexagonal structure of graphitic carbon [9,10]. The graphitic crystalline size was measured using Scherer formula and d_{002} spacing for G-carbon was calculated to be 9.8 nm and 3.35 Å, respectively. The d_{002} spacing value of G-car-

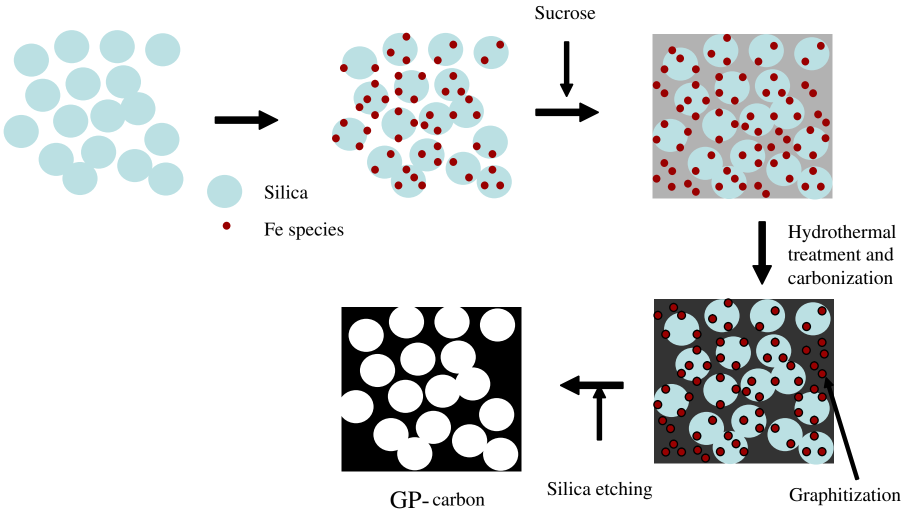

Fig. 1. Scheme of preparation procedure for GP-carbon.