



Synthesis and Electrochemical Study of Nano Graphitic Mesoporous Carbon

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(Received 30 Aug. 2014; Final version received 20 Oct. 2014)

Abstract

In the present study, a type of graphitic mesoporous carbon (denoted as GMC) is synthesized and its structural properties were characterized by nitrogen physisorption isotherms, transmission electron microscopy and Raman spectroscopy. According to BET and BJH methods, the specific surface area (SBET) and the average pore diameter of GMC are estimated to be 720 m²/g and 3.4 nm, respectively. Transmission electron microscopy shows the mesoporous structure with stripe like patterns and less than 10 nm widths for GMC. Due to the large surface area and high crystallinity of GMC, we used it to modify the glassy carbon electrode (GCE). The electro catalytic behavior of modified electrode (GMC/GCE) was studied and successfully compared with a conventional carbon mesoporous modified electrode (CMK-3/GCE) and bare glassy carbon electrode (GCE). Cyclic voltammetry (CV) experiments displayed the best electron efficiency for GMC/GCE.

Keywords: Nano graphitic mesoporous carbon, CMK-3, Voltammetry, Electrochemical study.

Introduction

Recently, various studies have been focused on applying mesoporous carbon materials, owing to the large specific surface area, large pore volume, regular and tunable pore size, chemical inertness and good mechanical stability of carbon [1, 2]. Concerning these properties mesoporous carbon

within the CMK-3 network is well known as a good candidate for a wide range of applications including energy conversion and storage devices [3, 4], supporting matrix for catalysis [5, 6], electrode for electrochemical double layer capacitors [7, 8], electrode materials in lithium batteries [9, 10], electrochemical

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biosensor [11-13], and adsorbent for water and air purification [14, 15]. Despite its remarkable properties, conventional mesoporous carbon (CMK-3) generally possess amorphous pore walls with relatively low crystallinity and poor electrical conductivity [16, 17], which can limit its potential applications, mainly in the field of electrochemical sensors, solar cells, fuel cells and electronic devices. Therefore, development of mesoporous carbon materials with high crystallinity in their pore walls is highly desirable (i.e., graphitic character) [18, 19]. In this point of view, a variety of strategies such as chemical vapor deposition [20, 21], thermal treatment at high temperature [22] and use of fused-ring aromatic molecules as carbon precursors [23] have been proposed for the preparation of graphitic mesoporous carbon materials.

To our knowledge, there are few reports about the electrochemical behavior of graphitic mesoporous carbon. In the present study, a type of graphitic mesoporous carbon (denoted as GMC) was synthesized using Gokulakrishnan et al. method [24], and used for fabrication of a modified glassy carbon electrode (GCE). The electrochemical behavior of GMC/GCE was investigated and compared with a conventional carbon mesoporous modified electrode, CMK-3/GCE and bare GCE.

Experimental

Chemicals and reagents

Triblock copolymer P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, EO

= ethylene oxide, PO = propylene oxide, 5800) was supplied from Aldrich Co., and tetraethyl orthosilicate (TEOS, $\text{Si}(\text{OCH}_2\text{CH}_3)_4$), sucrose, NaCl, NaOH, HCl, acetone and ethanol were purchased from Merck Co. (Germany).

Apparatus

All the electrochemical experiences were performed via a PalmSens Instrument (Netherlands) with a conventional three electrode cell. The glassy carbon (2mm diameter, Azar electrode: Iran), an Ag/AgCl electrode (in saturated KCl solution) and a piece of Pt wire were served as working, reference and counter electrode, respectively. The sample solutions were purged with high-purity nitrogen gas for at least 15 min at the beginning of the experiments to remove oxygen. The nitrogen adsorption-desorption isotherms were measured at $-196\text{ }^\circ\text{C}$ using a Micromeritics ASAP 2000 analyzer. Prior to the characterization of textural properties by nitrogen sorption technique, sample was degassed for 5 h at $70\text{ }^\circ\text{C}$. The specific surface area was calculated according to the BET (Brunauer-Emmet and Teller) model [25], while the pore size and pore volume were calculated using the Barrett-Joyner-Halenda (BJH) formula [24] based on the desorption branch of the isotherm. Transmission electron microscopy (TEM) was performed on Philips (CM 120) electron microscope. Raman experiments were carried out at

room temperature with a Dilor micro-Raman spectrometer.

Synthesis of SBA-15

SBA-15 was synthesized based on the reports of Zhao et al. [26]. In a typical synthesis, 2 g P123 was dissolved in 75 mL of 2 M HCl solution at 40 °C and 4.16 g of tetraethyl ortho silicate was then added. After magnetically stirring the solution at 40 °C for 24 h, the mixture was transferred to an autoclave, which was kept at 100 °C for 48 h under isothermal static condition. The resulting material was recovered by filtration and washing with distilled water. Subsequently, the sample was calcined at 550 °C in air for 6 h to remove the organic template P123 and to obtain SBA-15.

Synthesis of CMK-3

The mesoporous carbon (CMK-3) was prepared by using mesoporous silica material SBA-15 as hard template and sucrose as carbon source according to the process described by Jun et al. [27]. Briefly, one gram of SBA-15 was added to 5 mL aqueous solution containing 1.25 g sucrose and 0.14 g H₂SO₄. The resulting sludge was heated in an oven at 100 °C for 6 h and then 160 °C for another 6 h. In order to obtain fully polymerized and carbonized sucrose inside the pores of the silica template, 5 mL aqueous solution containing 0.8 g sucrose and 0.09 g

H₂SO₄ was added again and the mixture was subjected to the thermal treatment described above. Then, it was carbonized in an argon flow at 900 °C for 6 h with a heating rate of 5 °C min⁻¹. Finally, the mesoporous carbon (CMK-3) was obtained by removing the silica matrix using a 4 M NaOH solution (50 vol.% ethanol-50 vol.% H₂O) at room temperature followed by filtration, washing, and drying at 120 °C for 4 h.

Synthesis of the graphitic mesoporous carbon

The graphitic mesoporous carbon (GMC) was synthesized using 2,3-dihydroxy naphthalene (DHN) as the carbon source and SBA-15 as template according to the process described by Gokulakrishnan et al. [24]. In a typical synthesis, 0.5 g of the synthesized SBA-15 mesoporous silica, previously dried in vacuum at 150 °C for 3 h, was mixed with 2.3 g of DHN dissolved in 5 mL of acetone and stirred at room temperature for 24 h. After evaporation of the solvent, the DHN-SBA-15 composite material was treated at 300 °C for 2 h under nitrogen flow (50 mL min⁻¹) with a heating rate of 3.3 °C min⁻¹. Then, the resulting dark green solid was thoroughly washed with acetone to remove the free DHN molecules, followed by further carbonization at 900 °C for 5 h (heating rate of 3.3 °C min⁻¹) under nitrogen atmosphere (150 mL min⁻¹). Finally, the resulting material was treated with 35% aqueous HF to eliminate the silica template,

filtered, thoroughly washed with water and ethanol and dried at 100 °C.

Electrode preparation and electrochemical measurements

In this study, 2 mg of the prepared graphitic mesoporous carbon was dispersed in 10mL of N, N-dimethyl formamide (DMF) and the mixture was sonicated for 30 min to obtain a homogeneous black suspension. Prior to the surface modification, the glassy carbon electrode (GCE) was polished successively with 1 μ m, 0.3 μ m and 0.05 μ m alumina slurries, and then thoroughly rinsed with double-distilled water. After rinsed with nitric acid/acetone (1:1, v/v), and double-distilled water, the electrode was dried in air. Then 10 μ L of obtained suspension was casted on the GCE surface and allowed to dry at room

temperature. The resulting modified electrode was denoted by GMC/ GCE.

Results and Discussion

Characterization of the graphitic mesoporous carbon

Figure 1 displays the N₂ adsorption/desorption isotherms of CMK-3 and GMC. Both isotherms show a distinct hysteresis loop at 0.35-0.55 relative pressure, which indicates the mesoporous nature of the prepared materials [28]. According to BET method, the specific surface area (SBET) of CMK-3 and GMC is estimated to be 940 m²/g and 720 m²/g, respectively. As can be seen from Figure 2, the average pore diameter of CMK-3 and GMC calculated with BJH method found to be about 3.6 nm and 3.4nm respectively. These results

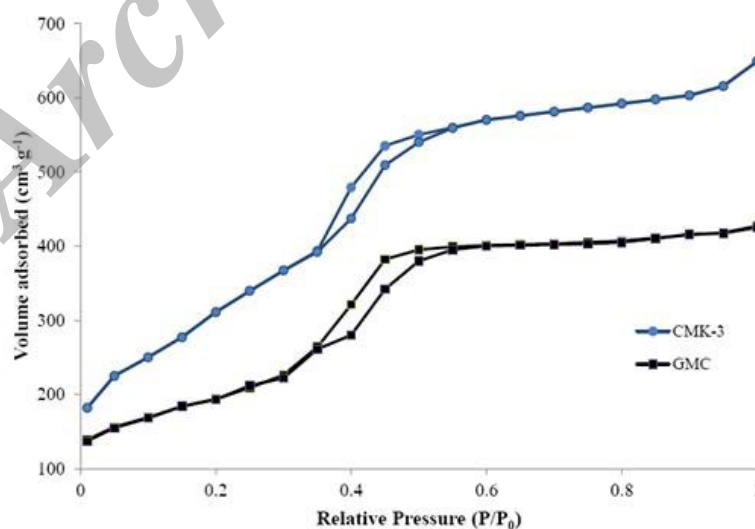


Figure 1. Nitrogen adsorption–desorption isotherm.

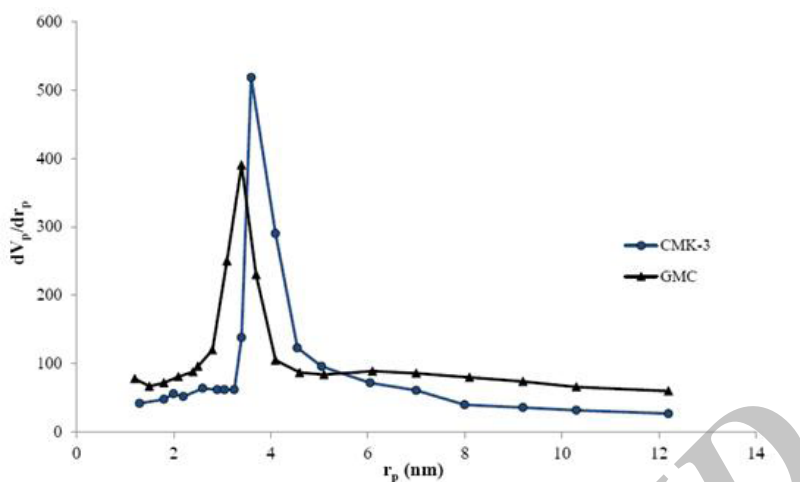


Figure 2. Pore size distribution of CMK-3 and GMC.

indicate that the prepared graphitic mesoporous carbon with an almost similar pore diameter possesses an inferior specific surface area than CMK-3. Transmission electron microscopy of GMC (Figure 3) shows the mesoporous structure with stripe like patterns in less than 10 nm width in large domains. The Raman spectroscopy was carried out to examine the

graphitic structure of the prepared carbon materials. As can be seen in the Figure 4, both of the carbon materials show two characteristic peaks of D and G bands at around 1340 and 1595 cm^{-1} , respectively. G band is related to the optically active E_{2g} , which is due to the stretching vibration modes of C=C bonds of typical graphite layers.

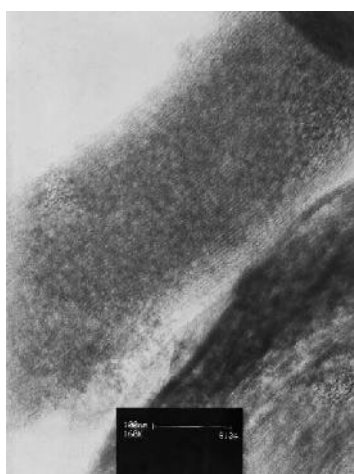


Figure 3. TEM image of GMC.

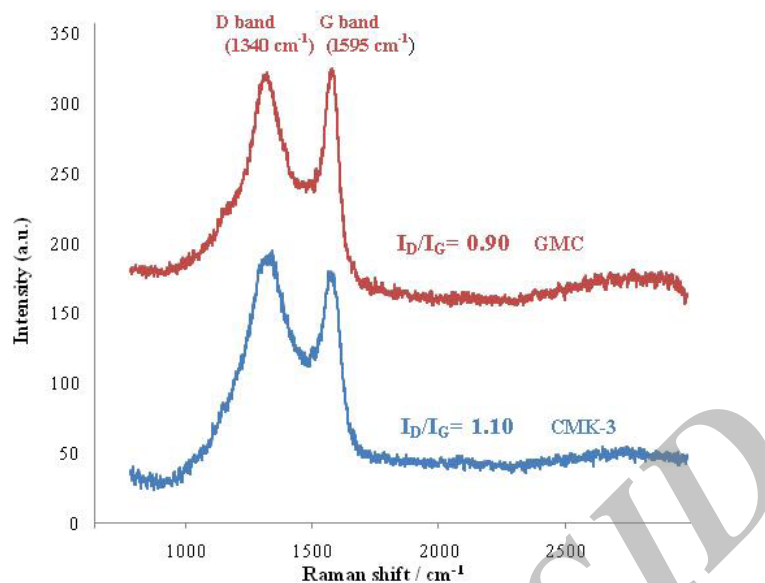


Figure 4. Raman spectrum of CMK-3 and GMC in the 800–3000 cm^{-1} region.

On the other hand, D band is associated with the presence of defects in the graphite layer. It can be noted that the relative intensity ratio of D and G bands (I_D/I_G ratio) is proportional to disorder in graphite material and increases with higher defect sites in the graphite carbon [29, 30]. The I_D/I_G ratio of CMK-3 and GMC is 1.10 and 0.90, respectively, indicating the better graphitic structure of GMC than CMK-3.

Electrochemical behavior of GMC-GCE

In order to investigate the electrochemical properties of the synthesized graphitic mesoporous carbon (GMC), the cyclic voltammetry (CV) responses of GMC/GCE

were compared with CMK-3/GCE as a typical mesoporous carbon modified electrode and also a bare glassy carbon electrode. The cyclic voltammetry experiments were performed in 1mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ / 0.1 M KCl solution with a scan rate of 50 mV/s and the obtained results are shown in Figure 5. As shown in this figure, the electrochemical response current at the GMC/GCE is higher in comparison with CMK-3 modified electrode and bare glassy carbon electrode.

Furthermore, the difference in potential between the anodic and cathodic peaks (ΔE_p) is 65, 95 and 118 mV

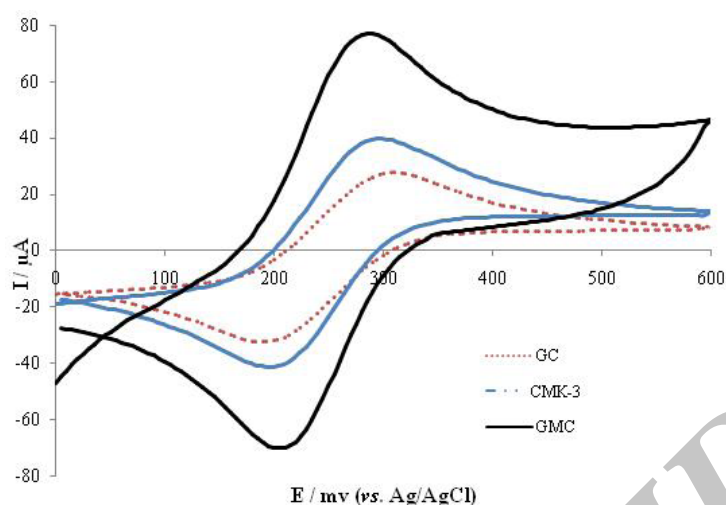


Figure 5. CVs obtained at bare GCE, CMK-3 and GMC electrodes in 1mM $K_3Fe(CN)_6$ /0.1 M KCl solution at a scan rate of 50 mV s^{-1} .

(versus $Ag|AgCl$) for GMC/GCE, CMK-3/GCE and bare GCE, respectively. Therefore, the order in terms of electron transfer efficiency is $GMC/GCE > CMK-3/GCE > \text{bare GCE}$, confirming the better electron transfer kinetics and catalytic activity in the case of graphitic mesoporous carbon modified electrode. The greatly enhanced electro catalytic behavior of the graphitic mesoporous carbon used in this study is attributed to its high crystallinity observed through Raman spectroscopy (Figure 4).

Conclusion

In this work, a kind of nano graphitic carbon mesoporous material (GMC) was synthesized and its electro catalytic activity was compared with a conventional carbon mesoporous (CMK-3) and also glassy carbon electrode. According to BET and BJH method, the specific surface area (SBET) and the average pore diameter of prepared GMC are estimated

to be $720 \text{ m}^2/\text{g}$ and 3.4 nm , respectively. Despite of rather lower specific surface area than CMK-3, GMC remarkably enhanced the oxidation and reduction peaks of $K_3[Fe(CN)_6]$ probe. The results show that the graphitization improves the electrocatalytic properties of carbon mesoporous materials.

Acknowledgement

Authors thank the Office of the Vice-President for Research Affairs at Islamic Azad University, South Tehran Branch for the financial support for this research project.

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