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Nanocrystalline graphite-like pyrolytic carbon films as electrodes for electrochemical sensing application

Mojtaba Hadi [a], Ahmad Rouhollahi [a,*], Mohammad Yousefi [b]

[a] Department of Chemistry, Faculty of Sciences, K.N. Toosi University of Technology, Tehran, Iran
[b] Department of Petrochemicals, Iran Polymer and Petrochemical Institute, Tehran, Iran

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ABSTRACT

Pyrolytic carbon films (PCFs) were deposited on graphite substrates by methane pyrolysis at temperature range of 1000–1100 °C. The fundamental electrochemical behaviors in relation to the surface microstructural properties were investigated to ascertain the potential use of these carbon film electrodes for electroanalytical applications. Cyclic voltammetry were performed to examine the residual current and capacitance and the kinetics parameters were obtained in the presence of $\mathrm{Fe(CN)}_6^{3-/4-}$ as a model redox system. Beside, the effects of electrochemical pretreatment were examined using cyclic voltammetry and electrochemical impedance spectroscopy. $\mathrm{Fe(CN)}_6^{3-/4-}$, $\mathrm{Co(phen)}_3^{3+/2+}$, $\mathrm{Fe}^{3+/2+}$, and hydroquinone were the redox systems employed to evaluate the electrochemical behavior of the PCF electrodes after pretreatment. Raman spectroscopy, scanning electron microscopy (SEM), and polarized light optical microscopy (PLOM) were carried out to explain the microstructural and morphological properties. Low and stable residual currents toward anodic activation and high electron transfer kinetics specifically after anodic activation were the attractive features of those carbon film electrodes prepared at the higher part of the processing temperature range.

1. Introduction

Nanostructured graphitic carbon materials such as carbon nanotubes (CNTs) and nano-graphene layers have attracted high interest from the research community and have been found useful to develop new applications for the electrochemical sensing and biosensing [1–3]. A high density of electrochemically active edge sites at the edges of tubes and graphene layers, excellent electrical conductivity, and a high surface area are more likely the reasons for their unique electrochemical performances though in some cases remaining metallic impurities in CNTs [4], large residual currents [5], and a weak adhesion of the solvent-cast carbon films to the surface of electrode substrate could be the major drawbacks.

Pyrolytic carbon films (PCFs) structurally consist of many graphene sheets stacked together, which are deposited onto the surface of substrate by thermal decomposition of various hydrocarbons [6–9]. The extremely small size of graphene layers of about 1–3 nm and defect sites within these layers provide a high portion of electrochemically active edge sites on the surface; possibly the main reason why the PCF electrodes demonstrate good potentials for electrochemical sensing applications [10–13]. The favorable mechanical properties, high structural stability, high electrical conductivity due to the graphitic nature, surface smoothness, absence of any metal impurities due to the non-catalytic nature of the production process, and a high adhesion to the surface of substrate are the other features making the PCFs suitable for this purpose. Our group is developing PCFs for electrochemical sensing and biosensing applications. Using the PCFs as electrode substrates, we reported electrochemical detections of some important analytes such as ascorbic acid [10], hydrazine [11], cysteine, homocysteine, *N*-acetyl cysteine [12], dopamine, uric acid [14], and lead ions [15] in real environments while high sensitivity, electrochemical stability, and low capacitive currents were the attractive features of these electrodes.

Like other carbon materials, PCFs exhibit a wide range of microstructural features from isotropic to lamellar anisotropic depending on the processing conditions and some research works have been directed toward understanding these correlations [16–19]. In this respect, due to the interrelation between the surface microstructure and electrochemical properties [20–22], our approach in developing the PCF electrodes should inevitably consider a tripartite relationship between preparation conditions, surface microstructures, and the electrochemical performances. In this work, by suitable adjustment of the pyrolysis conditions, PCFs were obtained at different processing temperatures. As an important processing variable, temperature has shown to have serious effect on PCFs microstructure [6,8,9,16–19]. The study was

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* Corresponding author. Address: Faculty of Sciences, No. 41, Kavian St., Mojtabaee St., Seyyed Khandan Bridge (N.), Shariati Ave., P.O. Box 16315-1618, 15418-49611 Tehran, Iran. Tel.: +98 21 2285 3308; fax: +98 21 2285 3650.
E-mail address: rouhollahi@kntu.ac.ir (A. Rouhollahi).

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followed by examining the fundamental electrochemical behaviors such as residual current, double-layer capacitance, electrochemical activity toward $Fe(CN)_6^{3-/4-}$ redox system, and electron transfer resistance which were investigated in terms of how these properties may be affected by the surface morphologies and microstructures of the resulting carbon films. Examination of the effects of anodization was also the other attempt that has been made in this study. Electrochemical pretreatment via anodization is an important and well-known technique to improve the electro-activity of carbon-based electrodes [13,21–25]. But, the increase in the electrode sensitivity after anodic activation coincides with increase in the residual current and decrease in potential windows [13,22,23,26], which are not desirable in electroanalysis, as the major drawbacks of this pretreatment technique. As a result, part of this study was focused on assessing the electrochemical stability of each different carbon film through the application of high anodization potentials. Finally, the anodized PCF electrodes were evaluated for their electron transfer reactivity with some benchmark redox systems with different sensitivity to the surface chemistry, including $Fe(CN)_6^{3-/4-}$, $Co(phen)_3^{3+/2+}$, $Fe^{3+/2+}$, and hydroquinone. A satisfactory combination of good electrode sensitivity with stable and small residual current demonstrates the applicability of PCFs as electrodes to electroanalytical chemistry.

2. Experimental

2.1. PCFs fabrication

Fig. 1 shows a schematic diagram of the CVD apparatus for deposition of carbon films on graphite substrates. The inside diameter of the reaction tube was 4 cm and the isothermal zone was about 10 cm high. All deposits were made on rectangular-shaped graphite platelets of 7 cm length, 3 cm width, and 0.5 cm thickness. As it may be observed in Fig. 1, a thin hole was made in the upper-central part of graphite substrates to be held inside the central space of the reactor hot zone. Before being introduced into the reactor tube, the surface of each graphite substrate was carefully polished with emery papers up to 2000 grit and then it was further polished on a polishing cloth with 0.5 μm alumina pastes. Then, the polished surface was thoroughly cleaned by ethanol and deionized water in ultrasonic bath and lastly dried in a vacuum oven for about 12 h at 100 °C. Methane gas was used as the carbon source, with helium as the carrier gas. The total flow rate was 1200 cm^{-3} min^{-1} and the concentration of methane was 20% in all the experiments. The depositions were performed at ambient pressure and the reaction temperature was varied from 1000 to 1100 °C. The deposition time was fixed at 240 min.

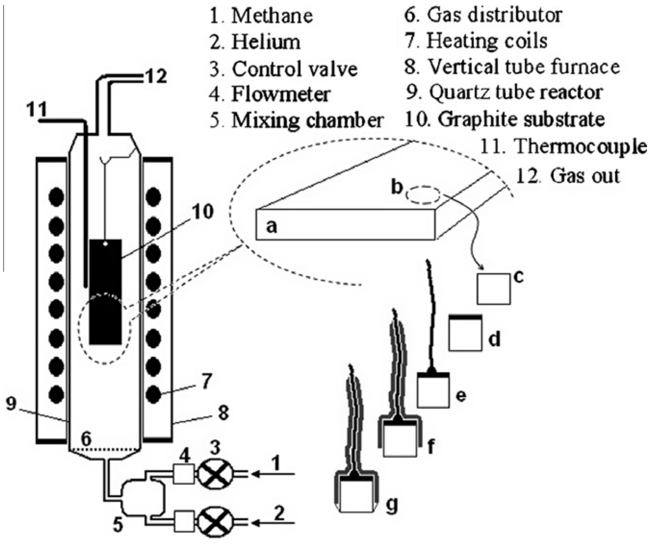

Fig. 1. Schematic diagram of CVD deposition apparatus and preparation of PCF electrode.

2.2. PCF electrodes preparation

As illustrated in Fig. 1, cylinder shapes of 3.9 mm diameter were cut from the graphite substrates with carbon coating by wire-cut technique (Fig. 1a–c). A thin layer of copper was electrodeposited on one of the two faces of graphite rod (Fig. 1d) to establish an appropriate electrical connection by solder connection of a copper wire (Fig. 1e). The sidewalls of graphite rod and the solder connection were covered by heat shrinkable tubing (Fig. 1f) and the gaps were sealed with silicone paste at the edge side of electrode surface (Fig. 1g). The PCF electrode geometry was thus a planar disk with a diameter of 3.9 mm.

2.3. PCFs characterization

Surface morphology and fracture cross-section of the carbon films were analyzed using a Cambridge-S360 scanning electron microscope (SEM).

The microstructures of the carbon coatings were observed under polarized light using an optical microscope equipped with polarizer and analyzer [27,28]. The samples were prepared by polishing transverse cuts of the substrates with carbon coating by polishing machine after being mounted in a matrix of epoxy resin. The ultimate stage of the polishing procedure was accomplished with 0.5 μm alumina paste on a polishing pad. The polished cross-section of the coating was then observed under the polarized light.

The carbon films were also characterized by Raman spectroscopy using a Thermo NicoletaImega Dispersive Raman spectrometer equipped with a second harmonic 532 nm laser line in a backscattering configuration.

2.4. Electrochemical measurements

All electrochemical measurements were performed with Autolab potentiostat (PGSTAT30) controlled by GPES 4.9 software for cyclic voltammetric experiments and electrochemical impedance spectra were recorded using Frequency Response Analyzer (FRA 2) module controlled by FRA 4.9 software. The electrochemical studies were performed in a single-compartment cell containing an Ag/AgCl (3 M KCl) reference electrode and a graphite rod as counter electrode. All potentials were reported with respect to the Ag/AgCl (3 M KCl) reference electrode. Electrochemical impedance spectroscopy was performed in 0.1 M KCl solution and the impedance data were analyzed using Randles equivalence circuit model [29,30]. The frequency range from 100 kHz to 0.01 Hz was scanned with an alternating voltage of amplitude 0.01 V, superimposed on the chosen applied potential of 0.0 V. Edge-plane pyrolytic graphite (EPPG) and basal-plane pyrolytic graphite (BPPG) electrodes were used as working electrodes for comparative purposes. Pyrolytic graphite pieces were machined into 3.9 mm diameter disks, with the faces parallel with the edge-plane or basal-plane for preparation of EPPG and BPPG electrodes, respectively [31]. The EPPG electrode was first polished on emery polishing papers of 2000 grit to obtain a smooth and shiny surface and then it was further polished on a polishing cloth with successive slurries of 1.0 and 0.05 μm alumina in distilled water. The electrode was finally sonicated in distilled water for 10 min. The surface of BPPG was renewed by pressing an adhesive tape onto the electrode surface and peeling away the top few layers of graphite [31].