



Research paper

Effect of light source and applied potential in the electrochemical synthesis of Prussian blue on carbon nanotubes



Denise Tofanello Gimenes, Edson Nossol*

Instituto de Química—Universidade Federal de Uberlândia, Av. João Naves de Ávila, 2121, Uberlândia, MG, Brazil

ARTICLE INFO

Article history:

Received 13 April 2017

Received in revised form 14 June 2017

Accepted 23 August 2017

Available online 26 August 2017

Keywords:

SWCNT

Prussian blue

nanocomposite

photoelectrosynthesis

ABSTRACT

In this study it was investigated the application of different potentials range and distinct light sources in the formation of Prussian blue (PB) on single walled carbon nanotubes (SWCNT) thin films. The carbonaceous films were deposited through liquid-liquid interface method, with posterior voltammetric cyclic technique been employed for PB deposition and consequent formation of the SWCNT/Prussian blue nanocomposite. The range of applied potential has a great influence on the amount of electrosynthesized PB nanocubes, with the potential window of -0.3 to 1.4 V leading to the maximum formation of product. The process of Prussian blue film formation is accelerated by both UVA, UVC and white light radiation. UVA radiation provided the best condition for hexacyanoferrate dissociation, with consequent increase in current and PB deposition. The Prussian Blue/SWCNT films were characterized by different spectroscopic, microscopic, and electrochemical techniques and exhibit high electrochemical stability.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

The study of external effects modifications (temperature, pressure, magnetic and electric fields, light irradiation) on structural, electronic and magnetic properties of materials is a key area of research in chemistry. In feature, incidence of materials by light can lead to optically induced phase transitions, as appropriate atomic or molecular units are selectively photoexcited and through some cooperative interaction can condense in a new structure, with different electronic and/or magnetic properties and formation of nanoparticles with different sizes [1,2].

In this context, the family of Prussian blue analogues, $A_xM^II_y[M^III(CN)_6] \times nH_2O$ (A=alkali metal; M and M' =divalent and trivalent transition metal ions), respectively, can be highlighted, specially cobalt hexacyanoferrate [3], presenting metallic ions in which light can induce a charge transfer between two spin configurations centered on the metal [2,4,5]. The potassium ferric hexacyanoferrate ($KFe^III Fe^II(CN)_6$), called Prussian blue, is a well-know electrochromic material, and can change its absorbance ability of incident radiation upon an external applying agent [6]. Prussian blue has a face-centered cubic lattice structure, with ferric (Fe^{3+}) and ferrous (Fe^{2+}) ions alternating on the cubic lattice sites,

coordinated to nitrogen and carbon atoms by cyanide groups, respectively [7].

The electrochemical behavior of PB thin films deposited from aqueous precursors solutions onto conducting substrates was first described by Neff [8]. Prussian blue film can be reduced in the so-called Prussian white in the presence of potassium ions, and oxidized to the Berlin green or to the fully oxidized form, Prussian yellow [9]. This behaviour opens up a vast variety of applications, such as electrochromic material [10], active component in batteries [11], electrocatalysts [12] and sensors [13].

However, the lower electrochemical stability of PB films and the subsequent lower operational stability at neutral solution [9,14,15] limit the application of this material in the field of sensors. In view of the limitations for applications of Prussian blue, one of the most promising ways to increase stability, in addition to providing synergistic effects in the final material, consists of preparation of nanocomposites between Prussian blue and carbon based materials [16,17]. Carbon nanotubes (CNTs) are considered to be good components for Prussian blue –modified electrodes, because of their good electric conductivity, chemical stability, and the property of being particle carriers [17–19].

The preparation of modified electrodes with PB can be carried out by electrochemical deposition [20–23], chemical approach [24], and the self-assembling method [25–27]. In relation to electrochemical deposition, a method described by Zarbin et al. [28–33] has been gaining prominence in the scientific community. This approach is based on a heterogeneous reaction between iron

* Corresponding author. Fax: 55 34 3239 4208; *Tel.: 55 34 329 6341.

E-mail address: enossol@ufu.br (E. Nossol).

species presented on the CNTs and ferricyanide ions in aqueous solutions. This method presents the advantage of the production of a nanocomposite in which both CNTs and PB nanoparticles are in a maximized contact, increasing the performance and stability of Prussian blue.

Literature describes some studies regarding the influence of experimental parameters in Prussian blue electro-synthesis. Abbaspour et al. studied the influence of various parameters on Prussian blue formation, such as supporting electrolyte, electrode material, potential range, pH and ferricyanide concentration [34]. According to the authors, the best conditions for the material electrodeposition occur on gold electrode surface, at pH 2.3 and using a $2.0 \times 10^{-3} \text{ mol L}^{-1}$ ferricyanide solution. The deposition time was evaluated by Lin and Liao [6]. For electrodeposition, the authors related that redox charge capacities of the thin films increased with the increasing of deposition time. Husmann, Nossol and Zarbin checked the effect of the number of cycles on the stability and performance of PB electrodes applying 300, 500, 600 or 700 cycles [32]. According to the authors, the intensity of all redox peaks increase gradually with the increase of the cycle number, with the high stability obtained for the electrode modified by 500 voltammetric cycles.

Therefore, in this present paper, it was investigated two important factors for electrochemical deposition of Prussian blue on carbon nanotubes films: i) potential window and ii) irradiation source. To the best of our knowledge this is the first report on study of these parameters in the electro-synthesis of the CNTs/Prussian blue nanocomposites, since literature reports photo studies only for post-prepared electrodes based on PB [35] and related composites (containing polypyrrole [36] and TiO_2) [37–40]. In addition, the characterization of these films through Raman spectroscopy, cyclic voltammetry, scanning electron microscopy and energy dispersive X-ray spectroscopy were also performed.

2. Experimental

2.1. Reagents

All reagents utilized in this work were analytical grade and used with no further purification. All solutions were prepared freshly with deionized water (18 M Ω cm) obtained from a Milli Q water purification system (Millipore, Bedford, MA, USA). Potassium ferricyanide $\text{K}_3[\text{Fe}(\text{CN})_6]$ (Proquimios, 99.0%), KCl (Synth, 99.0%), cyclohexane (Alphatec) and chloroform (Vetec, 99.5%) were used as received.

Single-walled carbon nanotubes (SWCNT) (OCSiAl – Tuball™, 75%) with a diameter of 1.5 nm and a length of 5 μm were used without purification.

2.2. Preparation of carbon nanotube dispersions and film deposition

The CNT films were prepared by a liquid-liquid interfacial method, based on previous reports [41,42]. Initially, a suspension of carbonaceous material was prepared by adding SWCNTs (0.15 mg) to 20 mL of chloroform and sonicating the mixture using an 130 W ultrasonic tip (Cole-Parmer) for 10 min at 40% amplitude, with a sonication pulse rate of 30 s ON and 8 s OFF. The dispersion was maintained in an ice-bath to prevent solvent evaporation. The resulting dispersion was mixed with deionized water (20 mL) in a 50 mL round-bottom flask. The system was then stirred for 24 h at room temperature. Afterward, the magnetic stirring was interrupted, and a thin self-sustaining film was assembled at the organic/aqueous interface. For better film removal, the positions of the phases were switched. Chloroform was replaced by cyclohexane, and the two phases (organic and aqueous) were removed and replaced three times to remove any undispersed material. The CNT

film was entirely transferred to a beaker containing water and the indium tin oxide substrates fixed on a copper hast. The film was deposited over lifting the substrate using the copper haste in the direction of the film. Next, the substrate with the film was maintained for 24 h at room temperature. After this time, it was heated for 2 h at 150 °C.

2.3. Preparation of the carbon nanotubes/Prussian blue films

Electrochemical deposition of PB on CNT films was performed using a conventional three-electrode cell. The working CNT films electrode, a mini Ag/AgCl saturated with KCl (3.0 mol L^{-1}) [43] and a platinum wire were employed as the reference and auxiliary electrodes, respectively. The Prussian blue synthesis is based on a heterogeneous electrochemical reaction between the iron species presented in the CNTs and $[\text{Fe}(\text{CN})_6]^{3-}$ ions in solution [30–32,42]. For this purpose, cyclic voltammetric was performed at scan rate of 50 mV s^{-1} in a solution of $1.0 \times 10^{-3} \text{ mol L}^{-1} \text{ K}_3[\text{Fe}(\text{CN})_6]$ in 0.1 mol L^{-1} KCl. After 100 cycles, the films were copiously washed with distilled water and dried at 150 °C for 2 hours. Three different potentials range starting from -0.3 V were evaluated: 1.2, 1.3 and 1.4 V.

2.4. Photoelectrochemical studies

For photoelectrochemical synthesis, cyclic voltammograms were recorded from -0.3 to 1.3 V using the same electrolyte conditions described above. Experiments were carried out in a sealed box under the presence of three different light sources (UVC, UVA and white light) placed at the top of the open cell at 2.0 cm above the solution. For UVC irradiation, was used a 15 W (Sanyi) lamp with $\lambda_{\text{max}} = 185 \text{ nm}$ and irradiance of 0.73 W cm^{-2} . A 25 W (Avant) UVA fluorescent black light with $\lambda_{\text{max}} = 365 \text{ nm}$ (irradiance of 6.02 W cm^{-2}) and a fluorescent white light lamp (25 W – Avant), with radiance of 0.33 W cm^{-2} , were used as light sources.

2.5. Instrumentation

All electrochemical measurements were performed using an Autolab PGSTAT 12 potentiostat/galvanostat connected to a personal computer and controlled by NOVA Software version 2.0.

Raman spectroscopy measurements were carried out using a Horiba LabRAM HR Evolution. A He-Ne laser (633 nm) was used with 2.5 mW incidence potency over the $200\text{--}3500 \text{ cm}^{-1}$ region. Several spectra were acquired from different areas of the film surface, before and after the Prussian blue formation.

Powder X-ray diffraction patterns were recorded on a Shimadzu XRD-6000 equipment, with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) at 40 kV/20 mA. The XRD patterns were collected over the 2θ range of $10^\circ\text{--}80^\circ$, at a scan rate of 2° min^{-1} .

Morphology and composition of the samples were analyzed by scanning electron microscopy (SEM) using a Vega3 TESCAN equipped with an energy dispersive spectrometer (EDS) model INCA X-ACT standard, Oxford.

For irradiance measurements was used a radiometer (PMA 2100 Solar Light Co.) with UVA sensor in spectral range of 320–400 nm. The equipment was placed at the same angle and distance of incidence of radiation in the electrochemical cell.

3. Results and discussion

3.1. Single walled carbon nanotubes/Prussian blue nanocomposite film characterization

As previously described, the carbonaceous material used in this work is pristine single-walled carbon nanotubes. The species

Download English Version:

<https://daneshyari.com/en/article/6469961>

Download Persian Version:

<https://daneshyari.com/article/6469961>

[Daneshyari.com](https://daneshyari.com)