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Thermodynamic investigation of ferrocyanide/ferricyanide redox system on nitrogen-doped multi-walled carbon nanotubes decorated with gold nanoparticles

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ABSTRACT

Films consisting of nitrogen-doped multi-walled carbon nanotubes (N-MWCNTs) were fabricated by means of chemical vapor deposition technique with decomposition of acetonitrile. The N-MWCNTs-based films were modified with gold nanoparticles (AuNPs) with diameter either 5 or 35 nm and applied for the electrochemical investigation of ferrocyanide/ferricyanide, $[Fe(CN)_6]^{3-/4-}$ redox system in the temperature range of 283.15–303.15 K. The findings demonstrate that on N-MWCNT films modified with AuNPs (further denoted as N-MWCNTs/AuNPs) the $[Fe(CN)_6]^{3-/4-}$ redox system is quasi-reversible and its reversibility is improved with increasing temperature. Namely, it was established that with the rise in temperature the barrier for interfacial electron transfer decreases leading to an enhancement of kinetics of charge transfer reaction. The Gibbs free energies display that the exergonic redox process occurring on N-MWCNTs/AuNPs is shifted toward formation of $[Fe(CN)_6]^{3-}$ with increasing temperature. With the increase of diameter of AuNPs a slight improvement of kinetics of redox process occurs.

1. Introduction

Electrodes consisting of multi-walled carbon nanotubes were widely used in electroanalysis the last years [1,2]. The interest in these studies was mostly focused on understanding the factors that improve the electrochemical response and the electron-transfer kinetics of redox processes occurring on these carbon nanotubes-based electrodes. Specifically, it was already established that the use of carbon nanotubes as electrode materials in electrochemistry consequences to enhanced mass transport and high current densities. It is well known that fast electrode kinetics can be achieved onto carbon nanotubes-based electrodes due to their nanometer critical dimensions [3–5]. It was already established that the creation of specific structures on surface of carbon nanotubes-based electrodes through the appropriate modification leads to improved response and faster electron transfer kinetics. Namely, it was demonstrated that the surface modification seems to be critical to the performance and the stability of the electrodes as well as the reproducibility of obtained results. The surface modification of carbon nanotubes, especially their decoration with metal nanoparticles, has recently attracted significant attentions from both the fundamental and technological points of view, since the metal nanoparticles affect significantly their hydrophilic properties [6]. It is, thus, not surprising that the electrodes consisting of carbon nanomaterials modified with metal nanoparticles represent the most exciting area in nanotechnology, since they exhibit numerous advantages, such as extremely high reactivity, sensitivity, and selectivity [7,8].

Our research interest was currently focused in synthesis of films consisting of vertically-aligned N-MWCNTs and their application for electrochemical investigation of electroactive compounds [9–11]. Specifically, N-MWCNTs films were produced by means of chemical vapor deposition technique with decomposition of acetonitrile using ferrocene as catalyst, and used for electrochemical sensing of redox systems at the room temperature. The obtained results were found to be very promising, and therefore, a further investigation in larger temperature range in order to determine the thermodynamic parameters is required. Thus, in the present work we extend our research activity into investigation of electrochemical and thermodynamic properties of ferrocyanide/ferricyanide, $[Fe(CN)_6]^{3-/4-}$ redox system on fabricated N-MWCNTs films modified with AuNPs at the temperatures of 283.15, 293.15, and 303.15 K. For this purpose the cyclic voltammetry and the electrochemical impedance spectroscopy (EIS) techniques were used. From the extracted electrochemistry results the thermodynamic

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parameters of studied redox systems were estimated and discussed. The $[Fe(CN)_6]^{3-/4-}$ redox couple was selected as standard system for studying the electrochemistry of N-MWCNTs/AuNPs films since is an ideal Nernstian system with relative insignificant interaction ability with electrode's material.

2. Experimental

2.1. Reagents

Potassium hexacyanoferrate(III), $K_3Fe(CN)_6$ (~99.0%), potassium hexacyanoferrate(II) trihydrate, $K_4Fe(CN)_6 \cdot 3H_2O$ (>98.5%), and potassium chloride, KCl (>99.0%) were purchased from Sigma–Aldrich and used as received without any further purification. The $K_3Fe(CN)_6/K_4Fe(CN)_6$ (1.0 mM) solutions were prepared by dissolving the appropriate amounts of electroactive compounds in aqueous solutions of KCl (0.1 M). The solutions were prepared immediately prior the electrochemical experiments by using double-distilled water.

2.2. Apparatus and procedures

The electrochemical measurements were performed on electrochemical working station Zahner (IM6/6EX, Germany). The obtained results were analyzed by means of Thales software (version 4.15). A three electrode system consisted of N-MWCNTs/AuNPs as working electrode, platinum as auxiliary electrode, and Ag/AgCl (saturated KCl) as reference electrode was used for the electrochemistry measurements. The electrochemical impedance spectra were recorded in the frequency range from 0.1 Hz to 100 kHz at the half-wave potential of the studied redox system $[Fe(CN)_6]^{3-/4-}$. All experiments were carried out at the temperatures of 283.15, 293.15, and 303.15 K (±0.05 K). In all measurements, the solutions were deoxygenated by purging with high-purity nitrogen. Details regarding the electrochemistry experiments were already reported in previous published articles [12–14].

2.3. Fabrication of N-MWCNTs/AuNPs

N-MWCNTs were fabricated by means of chemical vapor deposition technique onto oxidized porous silicon wafer using acetonitrile as carbon source material in the presence of ferrocene as catalyst. The fabrication process was performed in furnace at 900 °C using argon as carrier gas. The scheme of pyrolysis apparatus and more experimental details were reported in previous published article [15]. The N-MWCNTs films were decorated with AuNPs having diameters either 5 or 35 nm according to the following procedure: the N-MWCNTs films were immersed in aqueous solution of sodium citrate (2.5 mM) and left in solution for about ten minutes. After the treatment, the films were dried in the air for about 120 min at the room temperature. Afterwards, AuNPs with diameters either 5 or 35 nm were dropped onto treated N-MWCNTs films using a micropipette and let for drying under room conditions (24 h). Finally, the films were carefully washed with distilled water and dried in the air for about 24 h. The AuNPs of different sizes used for the decoration of N-MWCNTs films were fabricated with reduction of metal salt of chloroauric acid at the surface of seed particles by using ascorbic acid. More details regarding the fabrication of AuNPs were already reported in previous published article [16]. The study of the surface of fabricated N-MWCNTs/AuNPs films as well as the elemental analysis of deposited onto the surface AuNPs, was carried out by means of combined scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS) techniques. Representative SEM images are shown in Fig. 1. In order to construct the N-MWCNTs/AuNPs working electrodes for the electrochemistry measurements, the films were connected to copper wire by using silver conducting coating (silver paint). Once the silver coating was dried (after about 24 h), the silver conducting part of the films was fully covered with varnish protective coating (nail enamel). As soon as the varnish protective coating was dried (after about 12 h) the films were ready to be used for the electrochemical measurements. It must be mentioned that the fabricated N-MWCNTs/AuNPs films were quite stable and no detachment of electrode's contacting occurred during the measurements. The repeatability and reproducibility of N-MWCNTs/AuNPs films were evaluated by means of CV technique. The reproducibility of method was studied by measuring the electrochemical response of 5 different N-MWCNTs/AuNPs films toward $[Fe(CN)_6]^{3-/4-}$. In all cases reproducibility of less than 3% was estimated. Furthermore, the repeatability of the method was studied by monitoring the current response of same N-MWCNTs/AuNPs film toward $[Fe(CN)_6]^{3-/4-}$ for 10 different successive measurements. The repeatability of less than 3.5% estimated for N-MWCNTs/AuNPs film can be also considered quite acceptable. The findings demonstrate the good repeatability and reproducibility of N-MWCNTs/AuNPs films.

3. Results and discussion

The effect of variation of either scan rate or temperature on electrochemical behavior of $[Fe(CN)_6]^{3-/4-}$ (1.0 mM) in KCl aqueous solution (0.1 M) was investigated on N-MWCNTs/AuNPs films having AuNPs with diameters either 5 or 35 nm. Representative CVs recorded for the studied redox system on MWCNTs/AuNPs films are shown in Fig. 2. The obtained results are shown in Table 1. In recorded CVs, a couple of well-defined symmetric redox peaks were observed in whole investigated range of scan rate and temperature for both studied N-MWCNTs/AuNPs films. It is noticeable that the ratio of cathodic (i_p^{red}) and anodic (i_p^{ox}) peak currents tends to reach unity with increasing temperature on both studied films (Table 1). The findings demonstrate that the amounts of oxidized and reduced forms of studied redox system are equal and are not consumed in coupled chemical reaction, confirming that the charge-transfer process occurring on N-MWCNTs/AuNPs can be considered as Nernstian [17]. The variation of peak current (i_p) with the square root of scan rate ($\nu^{1/2}$) was found to be linear in the investigated temperature range of 283.15–303.15 K (Fig. 3), demonstrating that the electrochemical process is diffusion-controlled and verifying the Nernstian response of investigated redox couple $[Fe(CN)_6]^{3-/4-}$ on both N-MWCNTs/AuNPs films [18].

As was expected the film's oxidation current response toward $[Fe(CN)_6]^{3-/4-}$ tends to increase with increasing temperature (Fig. 4). However, no significant differences were observed in current responses of different N-MWCNTs/AuNPs films measured at the same temperature (Table 1), demonstrating that the diameter of AuNPs does not really affect the film's current response. The half-wave potential ($E_{1/2}$) of studied redox system $[Fe(CN)_6]^{3-/4-}$, determined as the average value of the oxidation and reduction peak potentials, was comparable within experimental potential error (±0.005 V) on different N-MWCNTs/AuNPs films tested (the potential appears to be independent on diameter of AuNPs). Furthermore, $E_{1/2}$ was found to be independent of applied scan rate (in the range from 0.05 to 0.10 V s^{-1}), as was expected for reversible redox system. However, $E_{1/2}$ was found to be strongly dependent on the temperature, namely, it was observed that $E_{1/2}$ shifts to less positive (less anodic) potentials with increasing temperature. These findings demonstrate that the equilibrium of the redox process $[Fe(CN)_6]^{3-} + e^- \leftrightarrow [Fe(CN)_6]^{4-}$ shifts to the left direction with the rise in temperature. Specifically, the obtained results exhibit that with increasing