



Electrochemical preparation, characterization and application of electrodes modified with nickel–cobalt hexacyanoferrate/graphene oxide–carbon nanotubes



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ARTICLE INFO

Article history:

Received 24 May 2015

Received in revised form 10 July 2015

Accepted 2 August 2015

Available online 5 August 2015

Keywords:

Graphene oxide

Multi-walled carbon nanotubes

Nickel–cobalt hybrid hexacyanoferrate

Hydroxylamine

ABSTRACT

A nanohybrid of graphene oxide and multiwalled carbon nanotubes (GO–CNTs) was synthesized through π – π interaction. The nickel–cobalt hybrid hexacyanoferrate decorated GO–CNTs (NiCoHCF/GO–CNTs) was prepared by electrodeposition of NiCoHCF in different ratios of Co^{2+} to Ni^{2+} solution on GO–CNTs. The characterization was performed by UV–vis, FT-IR, Raman spectroscopy, and SEM. The electrochemistry behavior of NiCoHCF/GO–CNTs was studied by cyclic voltammetry. The NiCoHCF/GO–CNT modified GCE (NiCoHCF/GO–CNT/GCE) exhibited greatly improved electrocatalytic activity towards electrooxidation of hydroxylamine. The modified electrode exhibited a wide linear range from 0.2 μM to 150 μM and a low detection limit (LOD) of 0.08 μM .

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1. Introduction

Graphene oxide (GO) possesses many unique advantages, such as good hydrophilicity, low toxicity, high surface area, and excellent biocompatibility [1]. But, its poor electrical conductivity limits its direct application as electrically active materials. Nanohybrid or nanocomposites can combine the advantages of each component and exhibit improved properties [2–4]. Carbon nanotubes (CNTs) are also very attractive in electroanalysis [5], so combining one-dimensional CNTs with two-dimensional GO and using the hierarchical carbon nanohybrid in the electrochemical determination is worthwhile. Not only can the combination of CNTs and graphene increase the conductivity of GO, but the synergy between CNTs and GO can enhance the electrocatalysis properties of nanohybrid over CNTs or GO alone [6–8].

Metal-hexacyanoferrates (MHCs) belong to a class of polynuclear inorganic compounds. The hybrid hexacyanoferrates, such as nickel–cobalt hexacyanoferrate [9], copper–cobalt hexacyanoferrate [10,11], nickel–palladium hexacyanoferrate [12], cobalt–iron hexacyanoferrate [13,14], and nickel–iron hexacyanoferrate [15] have been studied. These hybrid MHCs possess unique electrochemical property to mediate electrochemical reactions such as electro-catalyzed oxidation of hydrazine [10], cysteine [11], isoniazid [13], and H_2O_2 [14]. They can improve the stability and have a different electrochemical behavior

compared to single component [16]. Recently, the combination of graphene and MHCs for construction of electrochemical sensor has been proposed [17–19]. Due to the synergic electrocatalytic action between graphene and MHCs, the nanocomposites of graphene and MHCs were proved to expand their applications in electroanalytical field [18,19].

In this study, the nanohybrid of GO nanosheets and carboxylated CNTs (GO–CNTs) was prepared through π – π interaction. The nickel–cobalt hybrid hexacyanoferrate (NiCoHCF) was used to decorate the GO–CNTs by electrodeposition process for the first time. The morphology and the electrochemical behavior of the NiCoHCF decorated the GO–CNT nanohybrid (NiCoHCF/GO–CNTs) were characterized. The nanohybrid was used for the electrochemical detection of hydroxylamine with low detection, wide linear range and good selectivity.

2. Experimental

2.1. Reagents and materials

Graphene oxide was purchased from Nanjing XFNANO Materials Tech Co., Ltd (China). Multi-wall carbon nanotubes (CNTs >95% purity, diameter 10–20 nm, length 5–10 μm) were bought from Aladdin Industrial Inc. Nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), hydroxylamine, and potassium ferrocyanide ($\text{K}_4\text{Fe}(\text{CN})_6$) were obtained from Shanghai Chemical Reagent Co. (China). All other materials and solvents were of analytical grade and

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used without further purification if not mentioned. Doubly distilled water was used for the preparation of solutions. The supporting electrolyte was 0.1 M KCl and 0.1 M phosphate buffer solution, which was prepared with $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$.

2.2. Apparatus

The characterization of nanocomposites was performed by UV–vis adsorption spectroscopy (Hitachi U-4100), laser-Raman spectrometer (Laboram-010, France), Fourier transform infrared spectroscopy (FT-IR, WQF-410, Beijing, China), and scanning electron microscopy (SEM, JSM-5610L, JEOL). All the electrochemical experiments were carried on a CHI 760C electrochemical workstation (Chenhua Corp. Shanghai, China). A three-electrode system consisted of modified glassy carbon electrode as a working electrode, platinum wire as an auxiliary electrode and a saturated calomel electrode (SCE) as a reference electrode. All electrochemical measurements were performed at room temperature.

2.3. Preparation of GO-CNT nanohybrid

Prior to use, CNTs were treated as the carboxylation of CNTs. The process is as the following [20]: CNTs were refluxed with mixed concentrated HNO_3 and concentrated H_2SO_4 ($V/V = 1:3$) for 6 h, then filtered and rinsed with water until the filtrate was neutral, and finally dried at 80°C in a vacuum oven. 1 mg mL^{-1} of treated CNTs dispersion was prepared by ultrasonication as segmentation for 40 min. Then, it was mixed together with 1 mg mL^{-1} of GO aqueous solution ($V/V = 1:1$) and sonicated for 20 min. Excessive CNTs were removed by centrifugation at 6000 rpm. The unreacted GO was separated at 12,500 rpm. The obtained sediment was dried at 50°C .

2.4. Preparation of different modified electrodes

The bare glassy carbon electrode (GCE) was polished on fine emery paper, and then 1.0 and $0.05\ \mu\text{m}$ alumina powder until obtaining a mirror-like surface. It was then rinsed with double-distilled water thoroughly and sonicated in 1:1 nitric acid, acetone, NaOH, and doubly distilled water for 5 min, respectively. After that, $6\ \mu\text{L}$ of GO-CNT dispersed solution was dropped on the cleaned electrode and dried it at normal temperature to obtain GO-CNT modified GCE (GO-CNT/GCE). The nickel-cobalt hybrid hexacyanoferrate nanoparticle (NiCoHCF) modified electrode was electrodeposited onto GO-CNT/GCE in the solution containing 0.10 M of KCl, 0.5 mM of $\text{K}_4[\text{Fe}(\text{CN})_6]$, 0.5 mM of NiCl_2 , and 0.5 mM of CoCl_2 by applying cyclic voltammetry at a scan rate of 50 mV s^{-1} for 10 cycles. The electrode was recorded as NiCoHCF/GO-CNT/GCE. Furthermore, the CoHCF/GO-CNT modified electrode (CoHCF/GO-CNT/GCE) and NiHCF/GO-CNT modified electrode (NiHCF/GO-CNT/GCE) were also prepared by the above similar way. The NiCoHCF/GO-CNT/GCE with different component ratios of Co^{2+} to Ni^{2+} was also constructed by depositing NiCoHCF hybrid in containing different ratios of NiCl_2 and CoCl_2 solution.

3. Results and discussion

3.1. Characterization of GO-CNTs

The UV–vis absorption spectrum was used to demonstrate the nanohybrid. As could be seen in Fig. 1A, GO showed a strong absorption at 229 nm and a shoulder peak at 303 nm, which corresponded to $\pi \rightarrow \pi^*$ transitions of aromatic $\text{C}=\text{C}$ bond and $n \rightarrow \pi^*$ transition of $\text{C}=\text{O}$ bond, respectively. The curve of CNTs showed a strong absorption peak at 249 nm and a shoulder peak at 377 nm. They were almost the same as the reported [21]. For the GO-CNTs, the curve showed a strong bathochromic-shift peak at 256 nm and a shoulder peak at 377 nm.

Fig. 1B shows FT-IR spectra of GO, CNT, and GO-CNT nanohybrid. The bands that appeared at about 3420 cm^{-1} for all samples were assigned

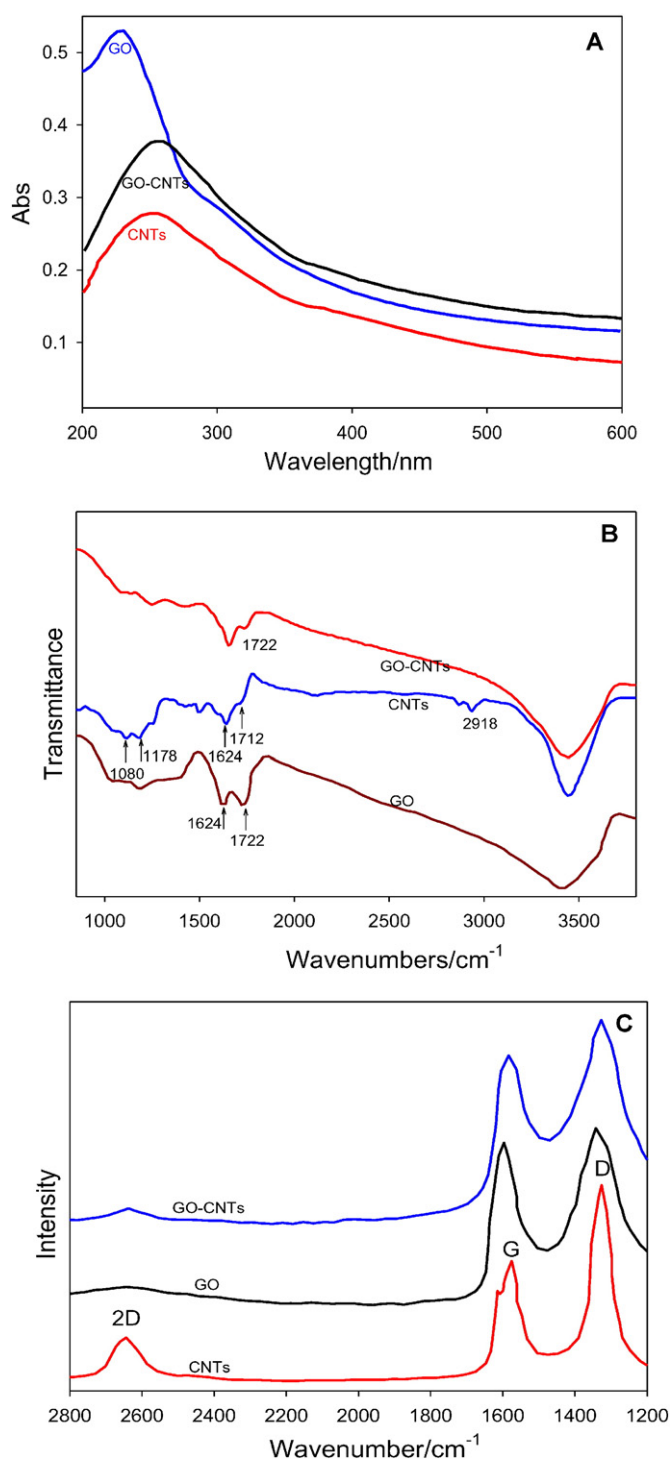


Fig. 1. UV–vis spectra (A), FT-IR spectra (B), and Raman spectra (C) of GO, CNTs, and GO-CNTs.

to the $-\text{OH}$ stretching vibration due to the existence of surface hydroxylic groups and chemisorbed water. The spectrum of GO exhibited the characteristic peaks at 1080 cm^{-1} , 1624 cm^{-1} and 1722 cm^{-1} . The CNTs showed the characteristic peak of $\text{C}-\text{O}$ vibration of various oxygen-containing groups (1080 cm^{-1}) and $\text{C}=\text{O}$ stretch of the carboxylic acid group (1712 cm^{-1}), which showed that CNTs were carboxylated very well. It also contained the peaks of $\text{C}-\text{OH}$ (1178 cm^{-1}) and $\text{C}=\text{C}$ skeletal stretching (1624 cm^{-1}). It was consistent with the reference [21]. For the spectrum of GO-CNTs, it displayed the characteristic peaks both GO and CNTs. The intensity of characteristic peak at about

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