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Talanta 69 (2006) 957–962
Talanta
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Preparation of cobalt hexacyanoferrate nanowires using carbon nanotubes as templates

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Received 1 July 2005; received in revised form 17 November 2005; accepted 23 November 2005
Available online 18 January 2006

Abstract

A simple and convenient method for preparation of cobalt hexacyanoferrate (CoHCF) nanowires by electrodeposition was reported. Multiwall carbon nanotubes (MWNTs) were used as templates to fabricate CoHCF nanowires. MWNTs could affect the size of CoHCF nanoparticles and made them grow on the sidewalls of carbon nanotubes during the process of electrodeposition. Thus CoHCF nanowires could be obtained by this method. Field-emission scanning electron microscopy, UV–vis spectroscopy, Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy were used to characterize these nanowires. These results showed the CoHCF nanowires could be easily and successfully obtained and it gave a novel approach to prepare inorganic nanowires.

Keywords: Carbon nanotubes; CoHCF; Nanowires; Electrodeposition

1. Introduction

Carbon nanotubes have been important materials since they were discovered [1,2]. With good physical and chemical properties, they have been widely used in electrochemistry, catalysis and so on [3–13]. Aligned carbon nanotubes can be assembled on electrode surface by chemical methods. At the same time, multilayer films of carbon nanotubes can be obtained by electrostatic assembled method [14–16]. Recently, nanowires prepared by carbon nanotubes as templates have attracted considerable interests because they may be used to fabricate nanodevices and nanoarray. Some papers reported that gold nanowires could be obtained by electrostatic assembled method with carbon nanotubes as templates [17–20]. Poly(diallyldimethylammonium chloride) (PDDA) was first adsorbed on the surface of carbon nanotubes pretreated by mixture of H_2SO_4 and HNO_3, and this resulted in the positive charged carbon nanotubes as templates for assembly of negative charged gold nanoparticles. Monolayer or multilayer silica-coated gold nanoparticles could also be assembled onto the sidewalls of carbon nanotubes [18]. Gold nanoparticles protected by hexadecyltrimethylammonium-bromide (CTAB) could be self-assembled on multiwall carbon nanotubes (MWNTs) [20]. It was reported that gold nanoparticles could be covalently bound onto carbon nanotubes modified by thiol groups [21]. Small Ag nanoparticles were electrochemically synthesized on the surface of MWNTs functionalized by 4-aminobenzene [22]. Organic–inorganic hybrid nanowires could also be produced using carbon nanotubes as templates. By acceptor and donor interaction, erbium phthalocyanine nanoparticles were assembled onto MWNTs to obtain organic–inorganic nanowires [23]. Compared with prime erbium phthalocyanines, the nanowires showed high and effective photosensitivity. Both aniline and pyrrole could also be electrochemically polymerized onto surface of carbon nanotubes [24–26].

Many inorganic materials especially the transition metal hexacyanoferrate have received much attention. Prussian blue has been widely studied among them and used in electrocatalysis [27–29]. It is reported that single wall carbon nanotubes could be chemically functionalized by Prussian blue nanoparticles because of the interaction between them [27]. Cobalt hexacyanoferrate (CoHCF) with the same properties is also an important transition metal hexacyanoferrate and its structure

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doi:10.1016/j.talanta.2005.11.053

and electrochemical properties have also been studied [30,31]. Recently, it has been reported that a carbon paste electrode modified by cobalt hexacyanoferrate films exhibited electrocatalytical oxidation for guanine and DNA [32].

Electrodeposition is an usual method to modify electrode surface. Many redox polymers and metal nanoparticles can be modified onto electrode surface by this method. But few papers reported that inorganic nanowires were prepared using carbon nanotubes as templates by electrodeposition. Here, a simple and convenient method for the preparation of CoHCF nanowires by electrodeposition was reported. As the templates, MWNTs could affect the size of CoHCF nanoparticles and made them grow on the sidewalls of MWNTs. In the absence of MWNTs, only big CoHCF particles were obtained. At last, field-emission scanning electron microscopy (FE-SEM), X-ray photoelectron spectroscopy (XPS), UV–vis spectroscopy and Fourier transform infrared spectroscopy (FTIR) were used to characterize these nanowires.

2. Experimental

2.1. Chemicals and reagents

Potassium hexacyanoferrate, cobalt(II) chloride hexahydrate, potassium chloride were analytical grade and used without purification. Poly(diallyldimethylammonium chloride) (PDDA, high molecular weight, average M_w 400,000–500,000, 20 wt.%) was obtained from Aldrich. MWNTs (diameter, 20–40 nm; length, 0.5–500 μm) obtained from Shenzhen Nanotech Port. Co. Ltd. (Shenzhen, China) were shortened and purified by a reported method [33]. MWNTs were shortened and functionalized by ultrasonication in mixture of H_2SO_4 and HNO_3 (3:1, v/v) for 8 h. After that, this solution was purged into 100 ml double distilled water. The pH of the resulted solution was adjusted to neutral with concentrated NaOH. The shortened MWNTs were obtained by filtering the solution and thoroughly washing with water. At last, these MWNTs were dried at 60 °C for 12 h. FTIR gave two peaks at about 1716 and 1559 cm^{-1} corresponding to stretch mode of carboxylic and carbonyl groups, respectively. The obvious peak at about 3434 cm^{-1} was attributed to the presence of hydroxyl groups. The results indicated that there were many carboxylic acid groups on the surface of MWNTs. All chemicals and reagents used were of analytical grade. All solutions were prepared by double distilled water.

2.2. Apparatus and procedures

The field-emission scanning electron microscopy (FE-SEM) images were obtained on PHILIP XL-30 ERSEM and the accelerating voltage was 20 kV. The samples for FE-SEM were prepared on conductive indium-doped tin oxide (ITO) glasses. ITO glasses were rinsed with water and dried in nitrogen before the experiments. The clean ITO glass was immersed in 4% PDDA solution (containing 0.5 M NaCl) for 30 min. After rinsed with water and dried in nitrogen, it was dipped into the MWNTs solution (pH 9.0) for 30 min. This resulted in monolayer film of shortened MWNTs on the surface. The monolayer film was used as templates for electrodeposition. To prepare CoHCF nanowires using MWNTs as templates, CoHCF films were electrodeposited with cyclic scans from 0.0 to 1.1 V at a scan rate of 100 mV s^{-1} in mixed solution containing 2 ml 0.5 M KCl, 20 μl 0.1 M $CoCl_2$ and 10 μl 0.1 M $K_3Fe(CN)_6$ for 15 cycles. After that, the ITO glass was rinsed with water and dried in nitrogen.

Optical spectrum was acquired using a Cary 50 UV–vis NTR spectrometer (Varian, USA) with an ITO conductive glass substrate. The preparation of samples on the ITO glass surface was similar to that of FE-SEM experiments.

Fourier transform infrared spectroscopy (FTIR) was operated at BRUKER vertex 70 FTIR (German). Attenuate total reflection (ATR) spectroscopy was measured on a glassy carbon plate (3 mm thick, type 2, Alfa).

X-ray photoelectron spectroscopy (XPS) measurements were conducted with an ESCALAB MK II spectrometer (VG Co., UK).

Cyclic voltammetric experiments were carried out with a CHI 832 (Shanghai, China). In these experiments, a three-electrode

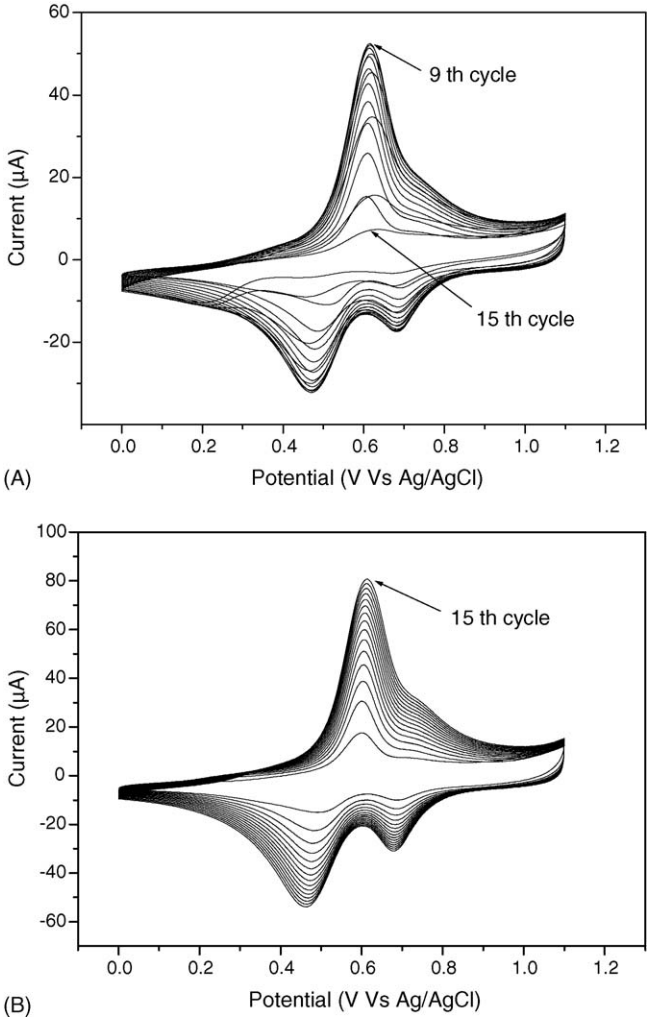

Fig. 1. Cyclic voltammograms of electrodeposited process on the electrode surface: (A) a bare GCE and (B) a GCE modified by monolayer film of MWNTs.

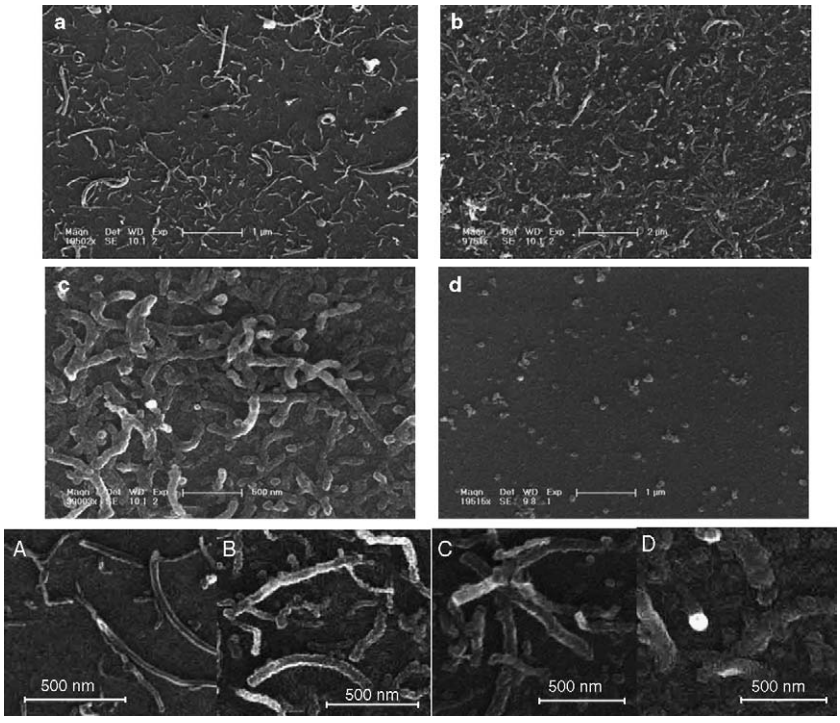

Fig. 2. FE-SEM images of the electrodeposited CoHCF film: (a) monolayer film of MWNTs before electrodeposition, (b) monolayer film of MWNTs after electrodeposition, (c) correspond to the magnification of nanowires and (d) in the absence of MWNTs; FE-SEM images of the electrodeposited CoHCF nanowires after different cyclic scans: (A) 1 cycle, (B) 3 cycles, (C) 15 cycles and (D) 20 cycles.

system was employed with a glassy carbon electrode (GCE) or ITO electrodes as working electrode, an Ag/AgCl (saturated potassium chloride) as reference electrode, a platinum foil as counter electrode. The GCE (diameter 3 mm) was polished with alumina slurry and ultrasonically cleaned with double distilled water to clean the electrode surface before experiments. Then it was put into 4% PDDA solution (containing 0.5 M NaCl) for 10 min. After rinsed and dried in nitrogen, it was immersed into the solution of MWNTs (pH 9.0) for 30 min to obtain monolayer film of MWNTs on the electrode surface.

3. Results and discussion

3.1. Process of electrodeposition on electrode surface

It was reported that CoHCF film could be prepared on electrode surface by electrodeposition. To further study the effect of MWNTs, a GCE was used for the electrodeposition of CoHCF films by cyclic scan. The process could be described by steps (2) and (3) as followed [34]:

$$2.5CoCl_2 + 2K_3[Fe(III)(CN)_6] \rightarrow Co(II)_{1.5}[Fe(III)(CN)_6] + KCo(II)[Fe(III)(CN)_6] + 5KCl \quad (1)$$

$$Co(II)_{1.5}[Fe(III)(CN)_6] + e^{-1} + K^+ \rightarrow KCo(II)_{1.5}[Fe(II)(CN)_6] \quad (2)$$

$$KCo(II)[Fe(III)(CN)_6] + e^{-1} + K^+ \rightarrow K_2Co(II)[Fe(II)(CN)_6] \quad (3)$$

Step (1) gave a preceding equation showing the mixture of initial hexacyanoferrate products formed. Fig. 1A showed the cyclic voltammogram of electrodeposited process of the CoHCF film on a bare GCE at a scan rate of 100 mV s^{-1}. Two couple of redox peaks appeared from 0.4 to 0.6 V and from 0.6 to 0.8 V, respectively. They corresponded to the steps (2) and (3). The peak currents increased continuously indicating the CoHCF film was produced on the electrode surface. But the peak currents decreased and the shape of redox peaks began to change after nine cycles. It was possibly attributed to the produced thick film of CoHCF, which resulted in the resistance of electron transfer. The GCE modified by monolayer film of MWNTs was also used to electrodeposite CoHCF. The cyclic voltammogram of the process was showed in Fig. 1B. The peak currents were enhanced with increasement of cyclic scans. Moreover, the currents did not decrease during 15 cycles and they were obviously large compared with that from the bare GCE. This showed the modified GCE had a higher surface area than the bare GCE and this resulted in more CoHCF nanoparticles deposited on the surface.

3.2. FE-SEM images of CoHCF nanowires

Because the ITO glasses or GCE exhibited negative charges, positive charged PDDA molecules could be assembled onto the electrode surface by electrostatic attraction [35]. There were

many carboxylic acid groups appeared on the surface of MWNTs and MWNTs could be shortened after ultrasonication in mixture of H_2SO_4 and HNO_3. This resulted in MWNTs with more negative charges and they could further be assembled onto the surface. Small bundles of carbon nanotubes could be obviously observed in FE-SEM image of monolayer film of MWNTs prepared by electrostatic assembled method (Fig. 2a). These MWNTs were used as templates for the electrodeposition of CoHCF. Fig. 2b corresponded to the image after electrodeposition. Diameter of MWNTs became big compared with that of MWNTs before electrodeposition. Moreover, CoHCF almost electrodeposited on the sidewalls of MWNTs. Fig. 2d showed the image of the CoHCF film directly electrodeposited on ITO surface. CoHCF particles with diameter of about 70–140 nm could be observed. Fig. 2c gave the magnification of these nanowires. All sidewalls of MWNTs were coated by CoHCF nanoparticles and the diameter of them was about 70–100 nm. It was more larger than that of MWNTs before electrodeposition (about 20–40 nm). This indicated that CoHCF nanoparticles was successfully electrodeposited on the sidewalls of MWNTs. FE-SEM has a resolution of 10 nm in the experiment, so the higher resolution images of CoHCF nanowires could not be obtained. Moreover, all sidewalls of MWNTs were completely coated by CoHCF nanoparticles after 15 cycles (about 5 min). So these MWNTs could be used as "nanowire backbone" to prepare inorganic nanowires.

To further study the process of electrodeposition, Fig. 2A–D gave the FE-SEM images of CoHCF nanowires prepared by different cyclic scans. Fig. 2A corresponded to that after one cyclic scan, no obvious change was observed for these MWNTs compared with bare ones. But after 3 and 15 cyclic scans, the diameter of MWNTs became large with cyclic scans increasing (Fig. 2B and C). When more cyclic scans were conducted, more CoHCF nanoparticles were deposited on sidewalls of MWNTs (Fig. 2D). During the process of electrodeposition, CoHCF seeds firstly appeared on the sidewalls of MWNTs. After that, these seeds grew into large CoHCF nanoparticles and all sidewalls were coated by them. This resulted in CoHCF nanowires on the ITO surface. So MWNTs could be used to prepare CoHCF nanowires and MWNTs could affect the size of CoHCF nanoparticles. Moreover, these nanoparticles could grow on the sidewalls of MWNTs and this resulted in CoHCF nanowires. The size of CoHCF was a function of the diameter of the MWNTs and the cyclic scans. Both of them could be used to control the size of CoHCF nanowires.

3.3. UV–vis, FTIR and XPS characterization of CoHCF nanowires

UV–vis spectroscopy and FTIR were used to further characterize the CoHCF nanowires prepared by electrodeposition (Fig. 3). There was no peak of absorbance in the range of 350–800 nm for MWNTs monolayer film (curve a). The CoHCF film exhibited two peaks at about 376 and 560 nm corresponded to reduced and oxidized film (curve b) [34]. After electrodeposition with MWNTs as templates, two peaks at about 370 and 560 nm were still observed (curve c). This confirmed that

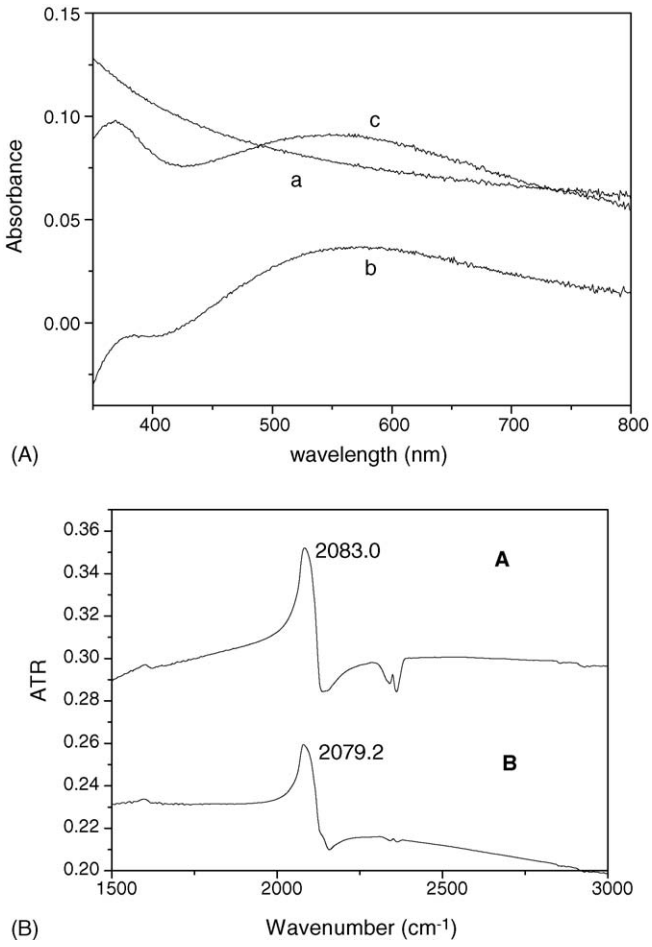

Fig. 3. UV–vis spectra of (a) monolayer film of MWNTs, (b) directly electrodeposited CoHCF film and (c) electrodeposited CoHCF nanowires; FTIR–ATR of the electrodeposited CoHCF film: (A) electrodeposited CoHCF nanoparticles without templates and (B) electrodeposited CoHCF nanowires using MWNTs as templates.

CoHCF could be successfully electrodeposited on the surface of MWNTs and their optical properties were not affected by MWNTs. The results of FTIR–ATR experiments only showed a strong peak at about 2083.0 cm^{-1} in the region from 1500 to 3000 cm^{-1} for CoHCF film electrodeposited on a bare glassy carbon slide (curve A). It was attributed to CN stretching in CoHCF film. The peak negatively shifted to 2079.2 cm^{-1} (about 3.8 cm^{-1}) for CoHCF nanowires (curve B). It could be explained by the π–π stacking interaction between MWNTs and CoHCF. It was reported that XPS could examine functional groups and various elements present on the surface of carbon nanotubes. CoHCF nanowires were also characterized by XPS analysis. Fig. 4 corresponded to the XPS results of N, Fe and Co elements. There was an obvious peak at about 397.9 eV in the specific nitrogen region, resulting from functional groups of CN. Two peaks at about 782.9 and 789.0 eV were attributed to Co(II) ($2p_{3/2}$) and Co(II) ($2p_{1/2}$) (Fig. 4B). This was consistent with that of $CoCl_2{\cdot}6H_2O$, indicating the presence of Co(II). Fig. 4C corresponded to the signal of Fe(II) and two obvious peaks of 708.8 and 721.7 eV could be observed. The peak position of Fe ($2p_{3/2}$) slightly positively shifted by about 1 ev compared with that of

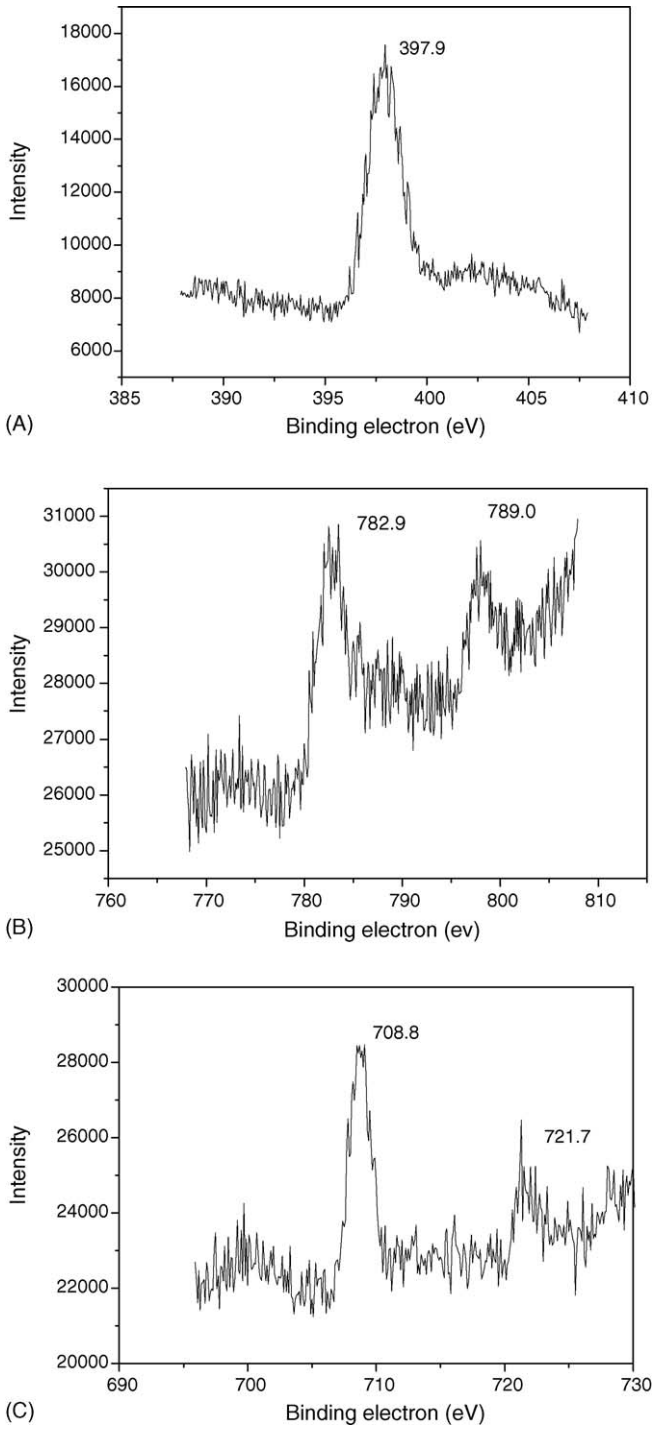

Fig. 4. XPS results of electrodeposited CoHCF nanowires using MWNTs as templates.

standard Fe(II) ($2p_{3/2}$). This suggested that there was Fe(III) and Fe(II) in the structure of CoHCF nanowires. The conclusion was consistent with that obtained from UV–vis spectroscopy.

4. Conclusion

In conclusion, CoHCF nanowires were produced by electrodeposition with MWNTs as templates. MWNTs had important effects on the preparation of CoHCF nanowires and only big CoHCF particles were observed in the absence of MWNTs. The CoHCF nanoparticles could grow on the sidewalls of MWNTs during the process. These nanowires were characterized by UV–vis spectroscopy, FTIR and XPS. The results confirmed that CoHCF nanowires could be successfully prepared by this method. The presence of MWNTs increased amount of deposited CoHCF nanoparticles. This method offered a simple and convenient approach to prepare CoHCF and other inorganic nanowires on the surface. Because CoHCF nanowires were obtained with MWNTs as templates, which had good electronic and electrochemical properties, these nanowires would be widely used in many fields of electrochemistry and electroanalysis.

Acknowledgement

This work was supported by the National Nature Science Foundation of China (No. 20335040) and the National Key Basic Research Development project research on Human Major Disease Proteomics (no. 2001CB5102).

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