A Novel Electrochemical Nitrobenzene Sensor Based on NiCu Alloy Electrode

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An electrochemical sensor of NiCu alloy was investigated for nitrobenzene detection based on nitrobenzene electroreduction. The bimetallic NiCu sensors were characterized by scanning electron microscope and X-ray diffraction, and their electrochemical behaviors for nitrobenzene reduction were investigated by polarization and current-time curves. The result showed that NiCu0.04 electrode exhibited a more sensitive response to nitrobenzene electroreduction possibly due to its higher Cu content and larger surface area. The detection limit of the NiCu0.04 sensor for nitrobenzene detection was 4×10^{-5} M (S/N= 3) with a correlation coefficient of 0.995. This opens a new way to develop a simple and novel sensor for fast detection of nitroaromatic compounds in the environment.

1. INTRODUCTION

Nitrobenzene ($C_6H_5NO_2$) is a well-known oral and dermic toxic chemical in the environment and mainly produced in large quantities in the leather industry and widely used as explosive, herbicide, insecticide, pharmaceutical and industrial feed stock chemical for dyes, etc [1]. As a common environmental contaminant, nitrobenzene has been listed as the second most characteristic of anthropogenic pollutants [2]. The demands in environmental protection and public health safety speed up the research and development efforts to detect ultratrace amounts of nitroaromatic compounds with many technologies including mass spectrometry, nuclear quadrupole resonance, X-ray diffraction,

fluorescence and luminescence [3-8]. Among these technologies, electrochemical methods for the detection of nitroaromatic compounds exhibits many merits[9-14]. For example, the instrument needed is relatively simple and suitable for constructing inexpensive and portable detectors [15]; the electrodes (sensors) can be designed and precisely controlled as expected, which can resort to the nanoscale or porous materials with high sensitivity, good stability and non-toxicity [10,16]. Exploring a simple and effective sensor is still highly desired in electrochemical detection of nitrobenzene.

Ni-based and Cu-based electrodes have been developed as cathode materials for hydrogen evolution reaction due to their high electrocatalytic activity [17-20]. It is possible to use Ni-based and Cu-based materials as electrocatalysts for the electrochemical hydrogenation of organic molecules, due to their high hydrogen absorbility [21,22]. For example, Ni-based and Cu-based electrodes have already been investigated to show a relatively high electrochemical activity for nitrobenzene reduction [23-25].

Bimetallic materials with nanoscale structure have drawn considerable interest due to their unique physical and chemical properties, and are of importance in a wide variety of applications including catalysis [24,25] and sensors [26,27]. Due to the low-cost, nontoxicity and relatively high catalytic activity, NiCu material is widely used as an electrochemical sensor for glucose detection [28] and a catalyst in chemical and electrochemical reactions including selective catalytic reduction of nitrogen oxides [29], H_2 production [30], ethanol electrooxidation [31] and hydrogen evolutioin [32]. However, to the best of our knowledge, the electrocatalytic properties of NiCu bimetallic nanostructures for the detection of nitrobenzene have not been investigated. In this paper, NiCu alloy film was constructed on a Cu substrate by a simple electrodeposition method and its potential application in nitrobenzene detection was probed.

2. EXPERIMENTAL

2.1 Catalyst preparation

NiCu alloy electrode was prepared by co-electrodepositing Ni^{2+} and Cu^{2+} onto a commercial pure (99.5%) Cu sheet (the other side was sealed with epoxy resin) at a constant current density of 20 mA/cm^2 for 10 min in a 0.2 M NiSO$_4$ and 0.04 M citric acid solution containing 0.01, 0.02, 0.04 or 0.1 M CuSO$_4$. Before electrodeposition, the Cu sheet was carefully dealt with mechanical polishing using 800$^\#$ and 1500$^\#$ sandpaper, followed by cleaning in an ultrasonic bath for 5 min and thorough rinsing with distilled water. The as-prepared NiCu electrode was designated as NiCux (x=0, 0.01, 0.02, 0.04 and 0.1), where x was referred to the concentration of Cu^{2+} in the electroplating solution.

2.2 Catalyst Characterization

The sample morphology was observed by an S-4800 field emission scanning electron microscope (SEM, Hitachi,Japan). The crystalline structure of the samples was measured by a

D/MAX-RB X-ray diffractometer (XRD, Rigaku, Japan) with Cu Kα radiation at a scan rate (2θ) of 0.05° s^{-1}, and the accelerating voltage and applied current were 40 kV and 80 mA, respectively.

2.3 Electrochemical Methods

The electrochemical tests were performed with a model LK-2000 microcomputer-based Electroanalysis System (LANLIKE, Tianjin, China). In these tests, a classical three-electrode cell was used. The prepared NiCux (x=0, 0.01, 0.02, 0.04 or 0.1) electrode with a geometrical surface area of 0.1 cm^2 was served as the working electrode and Pt foil with a big surface was used as the counter electrode, in addition to an Hg/HgO reference electrode. All reagents used were analytical grade, and all measurements were carried out at room temperature.

3. RESULTS AND DISCUSSION

Distinct from a silver nickel deposit (NiCu0), all obtained NiCux (x=0.01, 0.02, 0.04 and 0.1 M) deposits are characterized by a darkred and mat surface. It can be presumably believed that the reactions of Cu^{2+} + 2e$^-$ → Cu ($E^{\ominus}$=0.339 V) and Ni^{2+} + 2e$^-$ → Ni ($E^{\ominus}$ = -0.236 V, vs SHE) occur on the Cu substrate during the electrolysis process. The phase compositions of the NiCux (x=0.01, 0.02, 0.04 and 0.1 M) electrodes are shown in Figure 1.
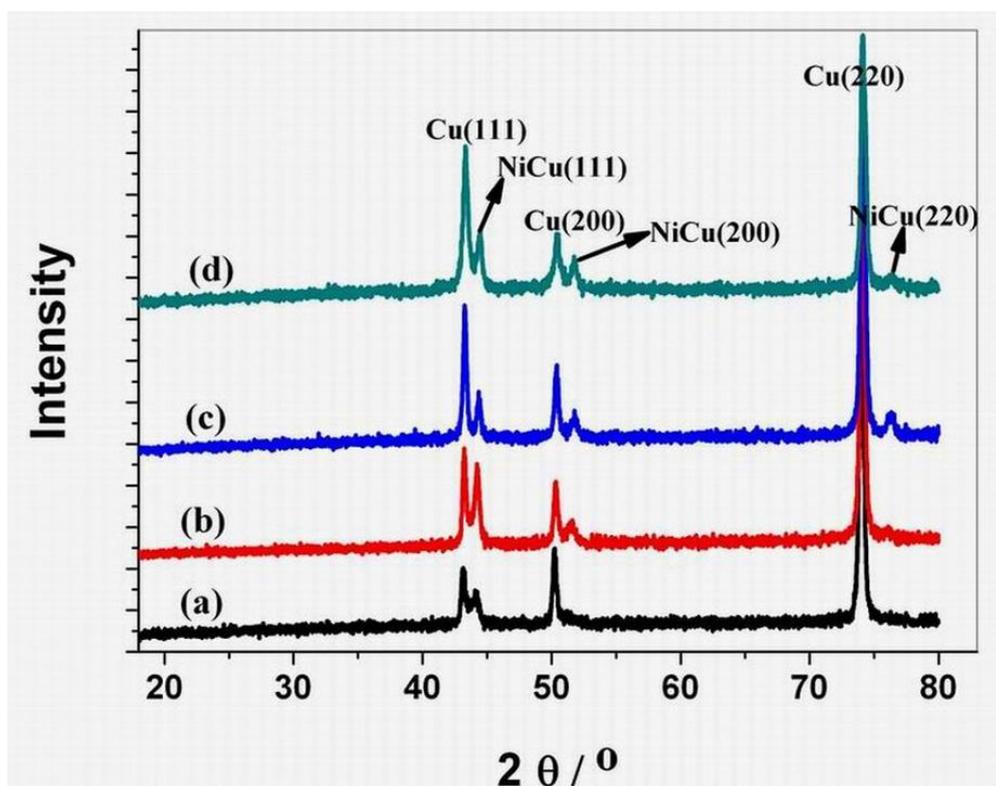
Figure 1. XRD patterns of NiCu0.01 (a), NiCu0.02 (b), NiCu0.04 (c) and NiCu0.1 (d).

The diffraction peaks of all the samples are ascribed to the diffraction peaks of crystalline Cu and NiCu phases [28], which are marked with Cu and NiCu, respectively. The diffraction peaks of the NiCu phase are from the electrodeposits, and that of crystalline Cu phase from Cu substrate. The XRD result indicates that the bimetallic NiCu deposits can be successfully obtained by a simple electrodeposition method.
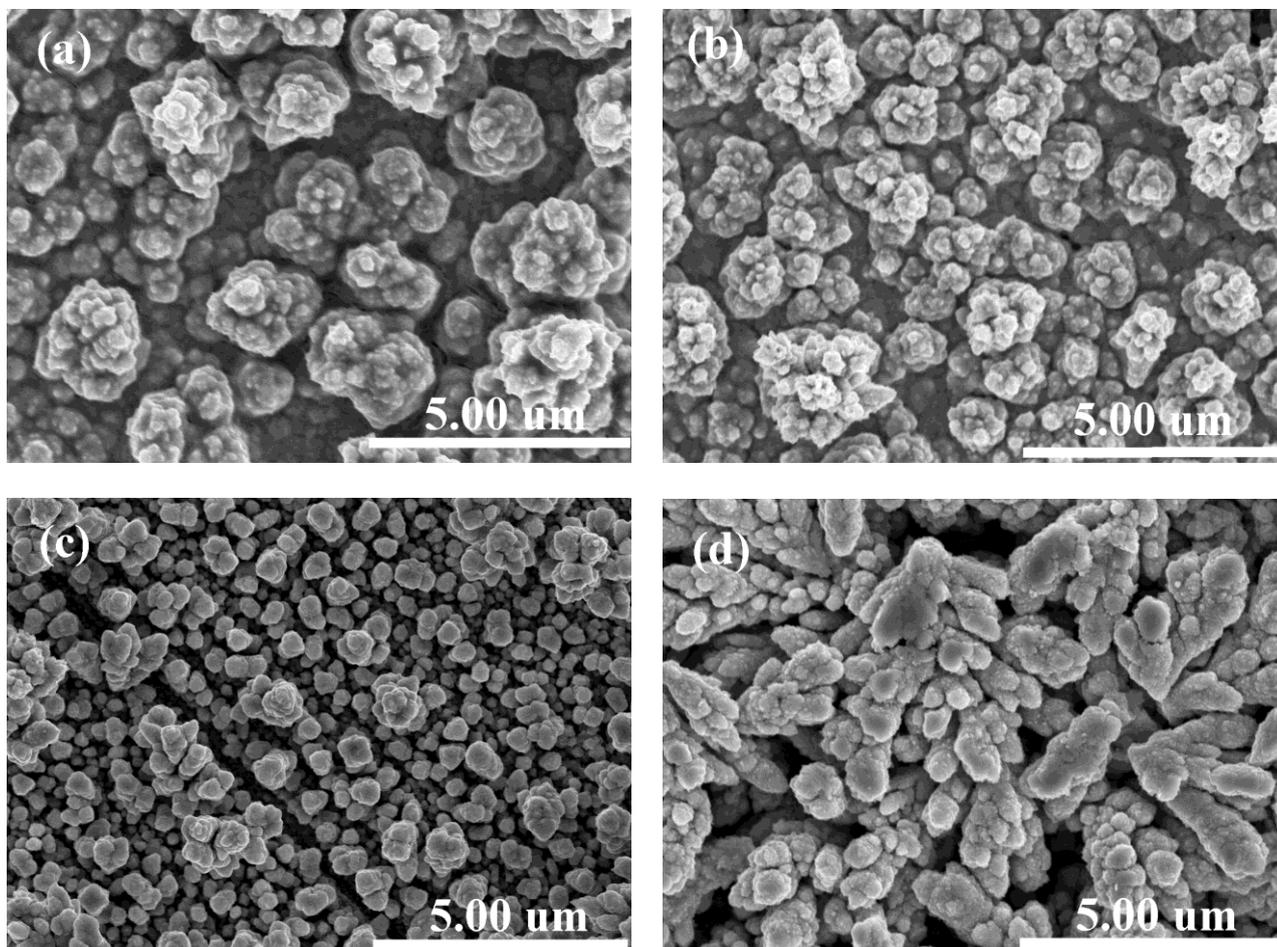
Figure 2. SEM images of NiCu0.01 (a), NiCu0.02 (b), NiCu0.04 (c) and NiCu0.1 (d).

Electrochemical reactions are essentially surface reactions, relying on the intrinsic electrocatalytic activity and active surface area of the electrode. In the case of this study, it is difficult to determine the real surface areas of the NiCux (x=0.01, 0.02, 0.04 and 0.1 M) electrodes. However, SEM can be at least used for a qualitative estimation of the real surface areas of the NiCu nanostructures. Figure 2 shows SEM images of the NiCux (x=0.01, 0.02, 0.04 and 0.1 M) electrodes. It can be observed that all the electrodeposited NiCu films exhibit high surface roughness and hence could result in a high electrocatalytic activity. Further observation shows that the bimetallic NiCu film consisted of agglomerated particles with the nanoparticle size of ca. 50-100 nm. The agglomerated particle size decreased firstly, and then increased as the Cu^{2+} concentration in the solution increased from 0.01 M to 0.1 M. The smallest size of the agglomerated NiCu particle was obtained in the

electrolyte containing 0.04 M Cu^{2+}, indicating the largest active surface area and highest electroactivity of the NiCu0.04 electrode.
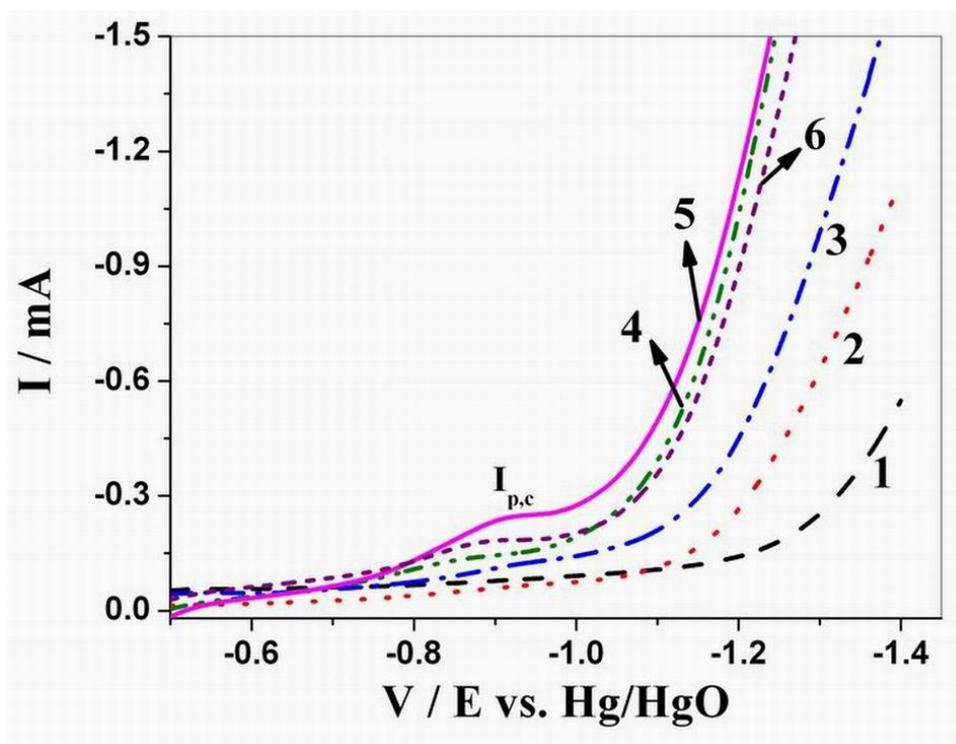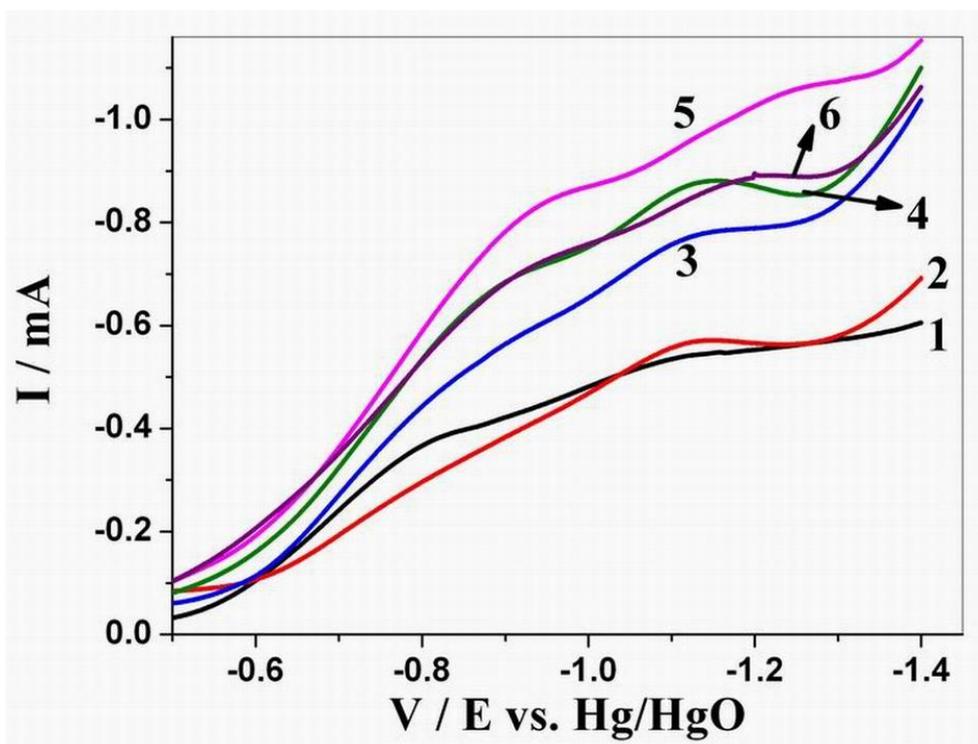

Figure 3. Polarization curves for different electrodes in 0.1 M NaOH water-ethanol (3:1, v/v) solution at the scan rate of 10 mV/s (1 → 6: Cu substrate, NiCu0, NiCu0.01, NiCu0.02, NiCu0.04 and NiCu0.1, respectively).

Figure 3 shows the polarization curves of NiCux (x=0.01, 0.02, 0.04 and 0.1 M) and a pure Cu electrodes in water-ethanol (3:1, v/v) solution containing 0.1 M NaOH in the absence of nitrobenzene. At the potential negative to ca.-1.1 V, a growing cathodic current attributed to hydrogen evolution is observed on the polarization curves of all electrodes. A broad current peak ($I_{p,c}$) appears obviously on NiCu0.04 and NiCu0.1 electrodes, which can be attributed to the absorption of hydrogen atom. Compared with the pure Cu electrode, the electrodeposited electrodes exhibit a higher current and a lower onset potential of hydrogen evolution, indicating that Ni and/or Cu electrodeposition on the Cu substrate can promote the hydrogen evolution reaction. Further observation is found that the onset potential of hydrogen evolution decreases firstly, and then increases with increasing Cu^{2+} concentration in the electroplating solution. The NiCu0.04 electrode exhibits the largest peak current of hydrogen atom absorption, the lowest onset potential and the highest current of hydrogen evolution. It indicates that NiCu0.04 electrode might possess a good performance of electrochemical hydrogenation of organic compounds.

Figure 4 shows the polarization curves for different electrodes in water-ethanol (3:1, v/v) solution containing 0.1 M NaOH and 10 mM nitrobenzene. Two poorly defined current peaks related to nitrobenzene electroreduction are observed at ca. -0.8 V and -1.1 V on all the electrode attributed to

the formation of hydroxylamine and amine, respectively [2], followed by a rapid increasing current of H_2 evolution at more negative potential (ca.-1.3 V).


Figure 4. Polarization curves for different electrodes in water-ethanol (3:1, v/v) solution containing 0.2 M NaOH +10 mM nitrobenzene at the scan rate of 10 mV/s (1 → 6: Cu, NiCu0, NiCu0.01, NiCu0.02, NiCu0.04 and NiCu0.1, respectively).

The current and onset potential of H_2 evolution in the presence of nitrobenzene visibly decreases and shifts to a more negative value, respectively, probably due to that the adsorption hydrogen atoms favor to participate in the reaction of nitrobenzene reduction on NiCux (x=0.01, 0.02, 0.04 and 0.1 M) electrodes. The current of H_2 evolution has little change, due to that nitrobenzene usually occurs via direct electron transfer on the copper cathode [2]. According to the decrease of the current of H_2 evolution, nitrobenzene reduction can be inferred mainly via indirect electron transfer from the atomic hydrogen on NiCux (x=0.01, 0.02, 0.04 and 0.1 M) electrodes. It indicates that Ni-containing can change the reduction process of nitrobenzene on the copper cathode. The peak currents related to nitrobenzene electroreduction on the NiCux (x= 0.01, 0.02, 0.04 and 0.1) electrodes are higher than those on the Cu and NiCu0 electrodes. The nitrobenzene reduction is strongly dependent upon the Cu^{2+} concentration in the electrodepositing solution. An increase in the current of nitrobenzene reduction is observed with increasing Cu^{2+} concentration presumably due to the increasing Cu content of the electrodeposited electrode and the high electrocatalytic activity of Cu [25]. However, when Cu^{2+} concentration reaches to 0.1 M, the current of nitrobenzene reduction decreases. The highest current of nitrobenzene electroreduction is obtained in the electrodepositing solution containing 0.04 M Cu^{2+}. It indicates that the NiCu0.04 electrode shows the most sensitive

response to nitrobenzene reduction, which can be attributed to its largest active surface area, as substantiated by SEM result.

Figure 5 displays current-time plots of the NiCu0.04 electrode with successive concentration of nitrobenzene. At each concentration of nitrobenzene, the current of nitrobenzene reduction keeps almost unchangeable after 30 s, indicating the stability of nitrobenzene reduction on the NiCu0.04 electrode. The linear relationship between the reduction current and the concentration of nitrobenzene is shown in the inset of Figure 5.
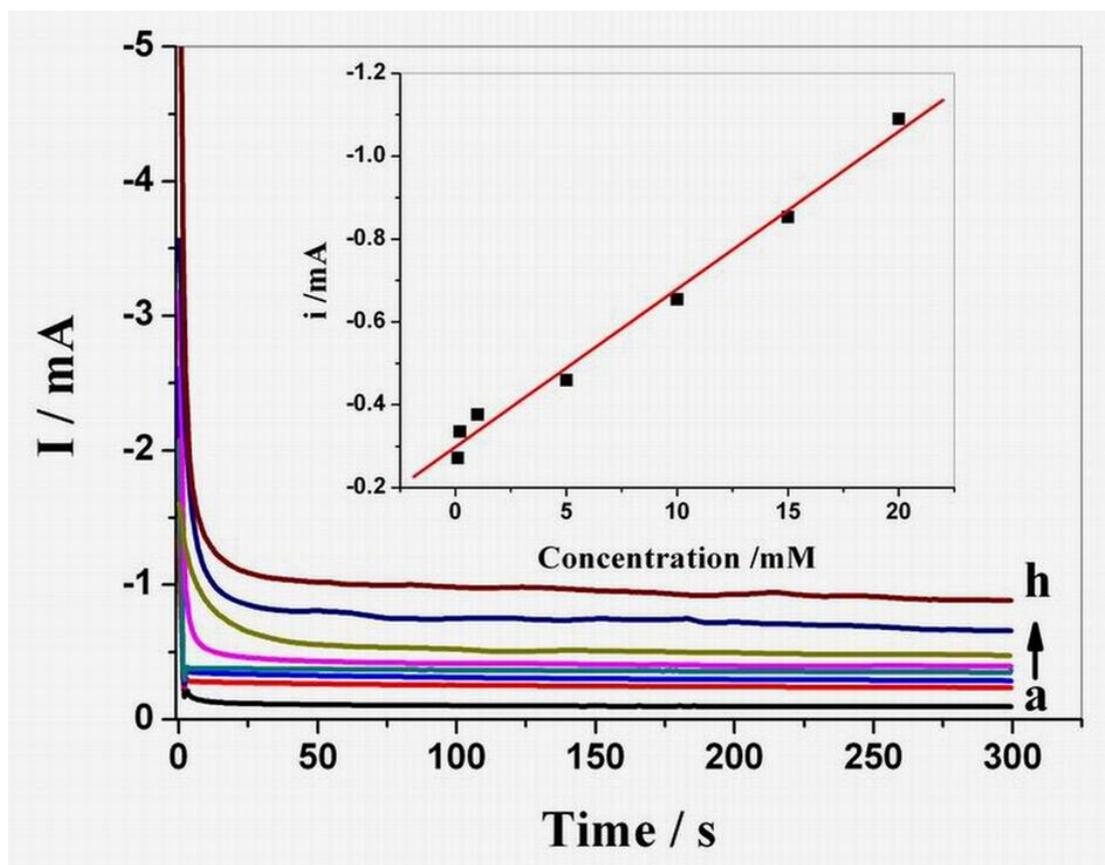
Figure 5. Current-time curves of NiCu0.04 in water-ethanol (3:1, v/v) solution containing 0.1 M NaOH and nitrobenzene with successive concentration at −1.05 V (a →h: 0, 0.1, 0.5, 1, 5, 10, 15 and 20 mM, respectively). Inset: the linear relationship between the reduction current and the concentration.

The NiCu0.04 electrode exhibits an expanded linear response range of 0.1 to 20 mM with correlation coefficient of 0.995, indicating a good linear relationship between the nitrobenzene concentration and its electroreduction current. The detection limit on the NiCu0.04 electrode is 4×10^{-5} M at a signal-to-noise ratio of three and the sensitivity is 298 µA/mM. The relative standard deviation (RSD) of 5 successive determination of 10 mmol nitrobenzene is 4.1%, suggesting good reproducibility of the NiCu0.04 electrode for the detection of nitrobenzene. The result suggests that the NiCu0.04 electrode may be successfully used as an amperometric sensor for nitrobenzene detection.

4. CONCLUSION

NiCux (x=0, 0.01, 0.02, 0.04 and 0.1) electrodes have been successfully prepared by a simple electrodeposition method. The electrochemical investigation showed that NiCux electrodes exhibited an excellent electrocatalytic activity toward the reduction of nitrobenzene. Particularly, the NiCu0.04 electrode showed a more sensitive response to nitrobenzene electroreduction possibly due to its more Cu content and larger surface area. The detection limit of the NiCu0.04 sensor for nitrobenzene detection was 4×10^{-5} M (S/N= 3) with a correlation coefficient of 0.995. This provides a new apportunity to develop a simple and novel sensor for fast detection of nitroaromatic compounds in the environment.

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