

Electrocatalysis and Detection of Nitrite on a Polyaniline-Cu Nanocomposite-Modified Glassy Carbon Electrode

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ABSTRACT: A polyaniline (PANI)-Cu nanocomposite-modified electrode was fabricated by the electrochemical polymerization of aniline and the electrodeposition of copper under constant potentials on a glassy carbon electrode (GCE), respectively. Scanning electron microscope result shows that the PANI-Cu composite on the surface of the GCE displays the nanofibers having an average diameter of about 80 nm with lengths varying from 1.1 to 1.2 μm . The electrode exhibits enhanced electrocatalytic behavior to the reduction of nitrite compared to the PANI-modified GCE. The effects of applied potential, pH value of the detection solution, electropolymerization charge, temperature, and nitrite concentration on the current response of the composite-modified GCE were investigated and discussed. Under optimal conditions, the PANI-Cu composite-modified GCE can be used to determine nitrite concentration in a wide linear range ($n = 18$) of 0.049 and 70.0 μM and a limit of detection of 0.025 μM . The sensitivity of the electrode was 0.312 $\mu\text{A } \mu\text{M}^{-1} \text{ cm}^{-2}$. The PANI-Cu composite-modified GCE had the good storage stability. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Nitrite is widely used as food additive and corrosion inhibitor. It is ubiquitous in soil, water, food, and physiological systems.^{1,2} Excessive nitrite in the body can lead to hemoglobin oxidation,³ furthermore, nitrite can react with amine to form a nitrosamine, resulting in cancer and hypertension.⁴ The maximum permitted level of nitrite established by the European Drinking Water Directive is 0.02 mg L^{-1} . Therefore, its determination is of great urgent for both environmental and public health reasons. Many methods for nitrite detection, including spectrophotometry,⁵ chromatography,⁶ chemiluminescence,⁷ and capillary electrophoresis,⁸ have been reported. However, these determination methods usually require expensive instruments and have tedious detection procedures. In recent years, the development and application of electrochemical detection of nitrite is receiving increased attention because of its advantages such as cost effectiveness, safety, selectivity, and fast response.^{9–11} Moreover, the electrochemical approach is considered to be an environmentally friendly method, because no additional chemical loading is required.

Usually, the electrochemical behavior of nitrite is poor at the conventional solid electrode surfaces, and the electrodes tend to be poisoned by the species formed during the electrochemical process.

A good way of solving this problem is using modified electrodes. Therefore, it is very important to select suitable supporting material. Recently, various modified electrodes have been reported, including Au nanoparticles on choline chloride-modified glassy carbon electrode (GCE),¹² thionine-modified aligned carbon nanotubes,¹³ functionalized thiazazole-modified GCE,¹⁴ carbon nanotube/polyvanillin composite microelectrode,¹⁵ carbon nanotube powder microelectrodes,¹⁶ poly(3,4-ethylenedioxythiophene)-modified screen-printed carbon electrodes,¹⁷ alternating layers of iron(III) *tetra*-(*N*-methyl-4-pyridyl)-porphyrin and cobalt(II) tetrasulfonated phthalocyanine,¹⁸ and gold nanoparticles/poly(3-methylthiophene) composite-coated GCE.¹⁹ Although many methods have been developed to determine nitrite, an electrochemical sensor with better properties, such as easy manufacture, low price, wider operational potential window, renewable surface, and environmentally friendly, is still a challenge.

Transition metals, such as Pd, Co, Ni, Rh, and Pt, have proven to have excellent properties in electrocatalysis.²⁰ Cobalt nanoparticle and SWNT composite have been reported to catalyze and detect nitrite.²¹ The catalytic rate constant (K) obtained at the EPPGE-SWCNT-Co for nitrite at pH 7.4 and 3.0 was approximately the same (about $3 \times 10^4 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$), while the limits of detection ($\text{LoD} = 3.3 \delta/m$) were in the

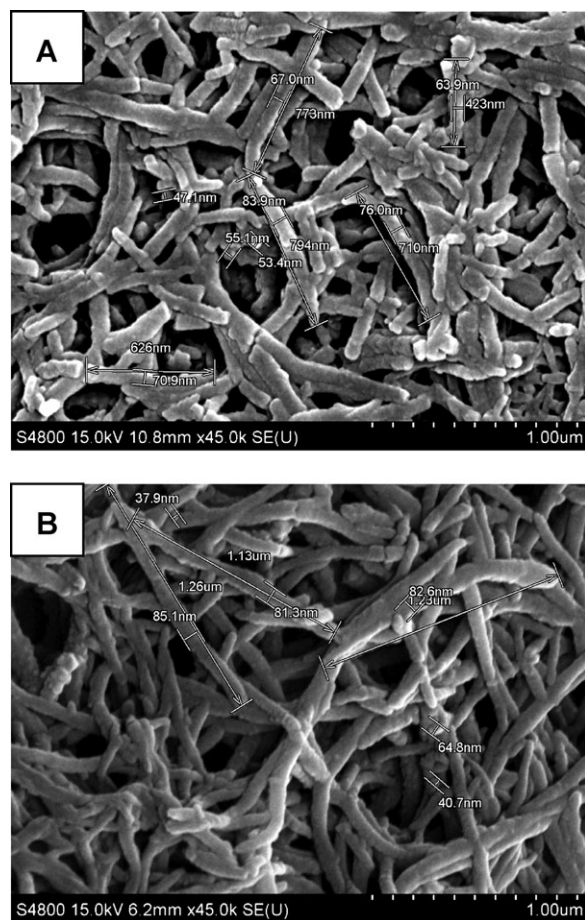


Figure 1. Scanning electron microscope images of (A) PANI/GCE and (B) PANI-Cu/GCE.

micromorality order. Zeng and coworkers²² have reported ultrasonic-electrodeposition of gold-platinum alloy nanoparticles on multiwalled carbon nanotubes-ionic liquid composite film and their electrocatalysis toward the oxidation of nitrite. Under the optimized conditions, the oxidation current of nitrite was linear to its concentration in the range of 5–200 nM, and the detection limit was down to 1.0 nM ($S/N = 3$). Lin and coworkers²³ deposited the Pt nanoparticles and Fe(III) on GCE to detect nitrite. The Pt-Fe(III)-modified electrode had a nitrite detection limit of $4.7 \times 10^{-7} M$ ($S/N = 3$). Different kinds of nitrite sensors have been fabricated, but there is still an expanding demand for the development of more reliable and efficient sensors for sensitive detection of nitrite.

The aim of the work was to (1) develop a simple PANI-Cu modified nanocomposite electrode, (2) use the prepared electrode to determine nitrite in the solution, (3) study the factors affecting the determination, and (4) present the possible mechanism of the electrocatalytic process.

EXPERIMENTAL

Chemicals and Instrument

Sodium nitrite (NaNO_2) and other chemicals were of analytical reagent grade obtained from Shanghai Chemical Company.

Aniline was distilled under reduced pressure before use. All solutions were prepared with doubly distilled water.

All electrochemical experiments were performed in the electrolytic cell consisted of a GC working electrode (3 mm diameter, CHI), a platinum foil counter electrode, and a saturated calomel reference electrode (SCE) on a Model CHI 407 electrochemical workstation. All potentials were referred to a SCE. The pH values of the solutions were determined with a PXD-12 pH meter. The morphologies of PANI and PANI-Cu were observed by using a Hitachi S-4800 scanning electron microscope.

Preparation of PANI-Cu Nanocomposite-Modified Electrode

Before modification, a GCE was polished with alumina slurry of 0.5 μm on polishing cloth with water and then thoroughly rinsed with water and sonicated in a doubly distilled water bath for 10 min before use.

The electrochemical polymerization was carried out in a solution containing 0.20 M aniline and 0.60 M H_2SO_4 , under a constant potential of 0.75 V. The thickness of the PANI film was controlled by adjusting polymerization charge. The charge consumed in the copolymerization was monitored and controlled

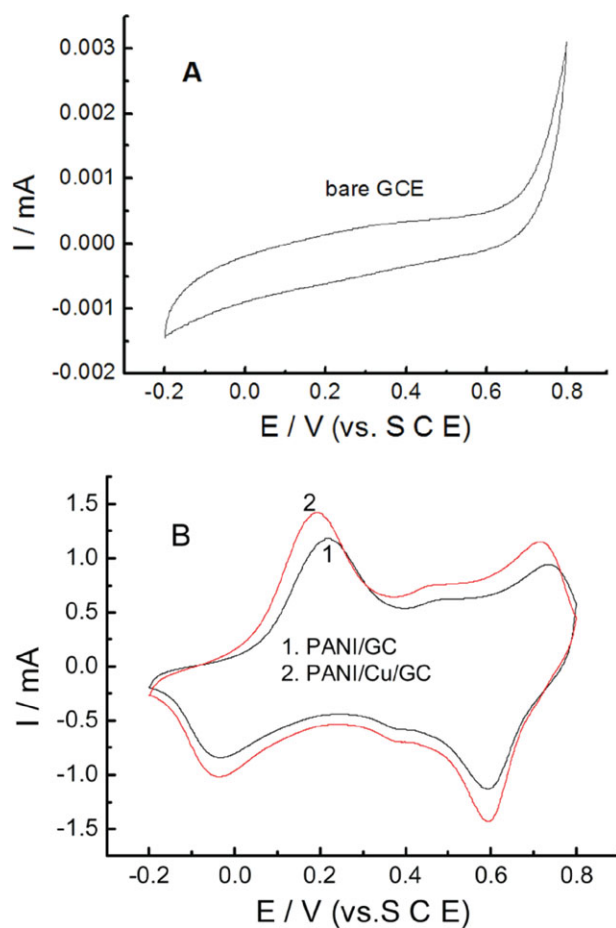


Figure 2. Cyclic voltammograms of (A) bare GCE, (B) PANI-modified GCE (curve 1) and PANI-Cu composite-modified GCE (curve 2) in a 0.10 M H_2SO_4 solution containing 0.50 mM nitrite, at a scan rate of 50 mV s^{-1} . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

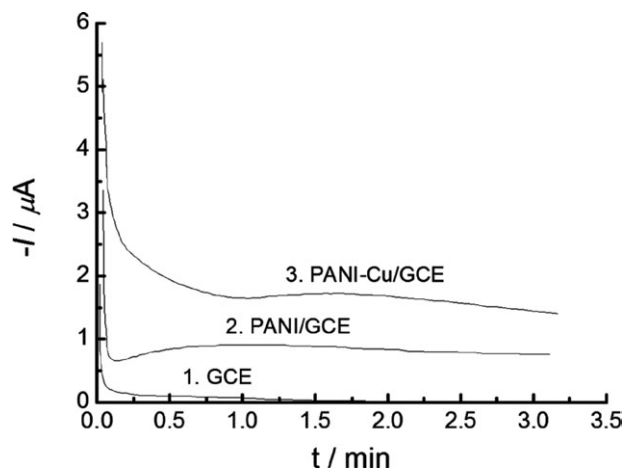


Figure 3. The $I - t$ plots of bare GCE (curve 1), the PANI-modified GCE (curve 2), and the PANI-Cu composite-modified GCE (curve 3).

to 0.05 C except stated otherwise. After synthesis, all samples were washed with 0.10 M H_2SO_4 solution to remove unreacted reactants, rinsed with doubly distilled water and finally dried.

The copper nanoparticles were electrochemically deposited on the PANI/GCE by applying -0.2 V for 120 s in a 0.50 mM CuSO_4 solution. The obtained modified electrode is denoted as PANI-Cu composite-modified GCE.

RESULTS AND DISCUSSION

Characterization of PANI-Cu Composite-Modified GCE

The surface morphologies of PANI and PANI-Cu composite-modified GCE are shown in Figure 1(A,B), respectively. Figure 1(A) shows that the film is constructed of nanofibers with diameters of 50–60 nm and lengths varying from 600 to 700 nm. Figure 1(B) shows the nanofibers having an average diameter of about 80 nm with lengths varying from 1.1 to 1.2 μm . It can be seen clearly in Figure 1 that the morphology in A is different from that of in B. The Cu-deposited GCE surface presents the larger diameter and length. This difference is caused by the deposited Cu, which may complex with the N atoms in PANI chains.

Electrocatalytic Reduction of Nitrite at PANI-Cu Composite-Modified GCE

Figure 2(A) shows cyclic voltammogram of the GCE in a 0.10 M H_2SO_4 solution with 0.50 mM nitrite. As shown in Figure 2(A), no redox peak is observed, indicating that nitrite is electrochemically inactive at the bare GCE. Curves 1 and 2 in Figure 2(B) show the cyclic voltammograms of PANI and PANI-Cu composite-modified GCE in a 0.10 M H_2SO_4 solutions with 0.50 mM nitrite, respectively. It can be seen in Figure 2(B) that the two curves show the similar shape, indicating that both substrates have redox activities in the 0.10 M H_2SO_4 solution with 0.50 mM nitrite. However, the redox currents of curve 2 are higher than that of curve 1, which gives us a hint that the presence of copper could improve the efficiency of nitrite reduction.

The $I - t$ plots of bare GCE (curve 1), the PANI-modified GCE (curve 2), and the PANI-Cu composite-modified GCE (curve 3) are recorded in Figure 3. The experiment was carried out in a

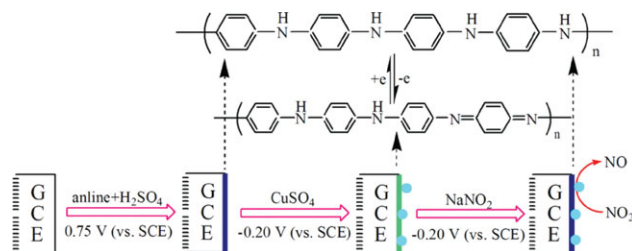


Figure 4. Electrocatalytic mechanism of PANI-Cu composite to the reduction of nitrite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

0.10 M H_2SO_4 solution containing 0.50 mM nitrite, at -0.20 V (vs. SCE). As expected, the bare GCE shows no current response, and both PANI-modified GCE and PANI-Cu composite-modified GCE have response currents. Compared to curve 2, curve 3 has a larger peak response current (1.63 μA), which is almost twice that of curve 2 (0.85 μA). This result indicates that the presence of copper can improve the nitrite reduction efficiency, which is in agreement with the result of cyclic voltammograms.

The electrocatalytic mechanism can be expressed in Figure 4. Polyaniline (PANI) at -0.20 V is at its reduced state, which is immediately oxidized by nitrite when the PANI is in contact with the solution containing nitrite, and then PANI is reduced again by the applied potential of -0.20 V. It is clearly that the PANI in the composite plays a role in charge transfer during the catalytic reduction process, while the copper accelerates the catalytic reduction.

Factors Influencing the Response Current of Nitrite

It is known that different factors such as pH, temperature of electrolytic medium and electrolysis parameters (applied current or potential) can affect the nitrite determination. In this part, the effects of the factors on the current response of the modified electrode to nitrite have been investigated and discussed.

Effect of Potential. The effect of potential on the response current was examined in a 0.1 M H_2SO_4 solution containing 0.50

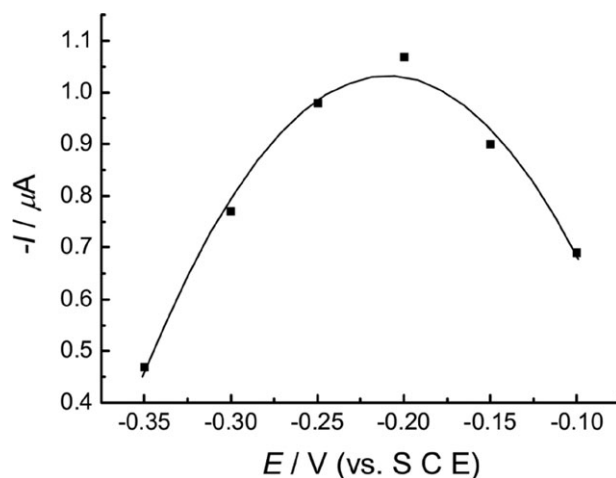


Figure 5. The relationship between response current and potential.

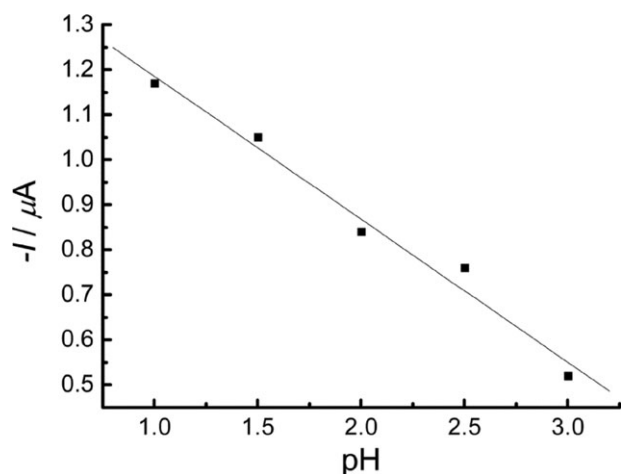


Figure 6. The relationship between response current and solution pH.

mM NaNO_2 . Figure 5 shows the changes in the response current of the PANI-Cu composite-modified GCE with applied potentials. As expected, the response current increases as the applied potential decreases from -0.10 to -0.20 V, which means the reduction of nitrite. However, the response current decreases as the applied potential decreases (from -0.20 to -0.35 V). This may be caused by the decrease in the electrochemical activity of PANI-Cu composite-modified GCE. Therefore, -0.20 V was selected as the working potential in the following experiments.

Effect of Solution pH. The effect of solution pH on the response current of the sensor was also considered and shown in Figure 6. A 0.10 M Na_2SO_4 solution with 0.50 mM nitrite was used in this experiment. The potential of the sensor was set at -0.20 V. As illustrated in Figure 6, response current of the sensor was greatly influenced by the solution pH. In the pH range of 1.0 – 3.0 , with the increase of solution pH, the response current decreased sharply. The response current at pH 3.0 was half that of at pH 1.0 . It is important to point out that when pH was higher than 3.0 , only small response was obtained. This result is similar to that of reported in literature.²⁴ The decrease in current response with pH

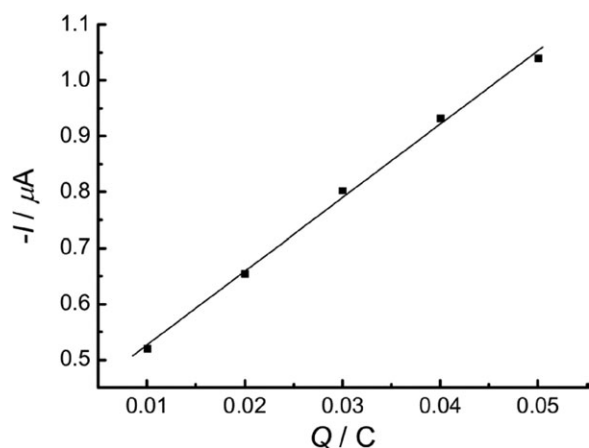


Figure 7. The relationship between response current and charge consumed.

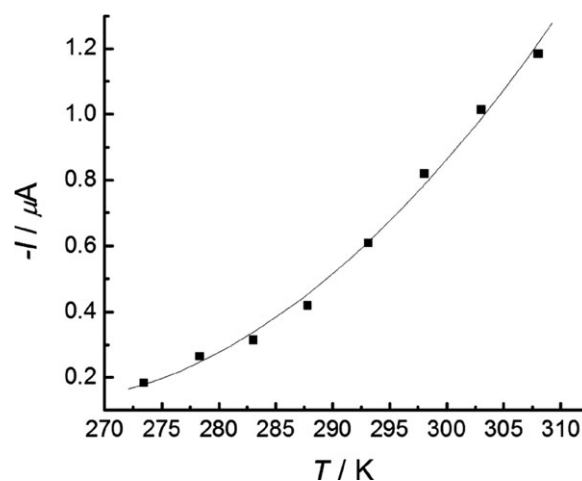


Figure 8. The relationship between response current and temperature.

is probably attributed to the property of PANI.²⁵ Many research works reported that the PANI film possesses higher electronic conductivity in acidic solution and loses electrochemical activity when solution pH is higher than 4.0 .²⁶ Therefore, 0.1M H_2SO_4 solution was used for the determination of nitrite.

Effect of PANI Film Thickness. It was reported that the thickness of the active layer defines the magnitude of the current response.²⁴ Therefore, the effect of film thickness was considered in this part. For chronoamperometry method used in this work, the PANI thickness can be easily controlled by charge consumed during the electropolymerization process. Figure 7 presents the response current for 0.5 mM nitrite as a function of charge consumed. As shown in Figure 7, a straight line is obtained. As expected, the response current increases rapidly with the increment of charge consumed from 0.01 to 0.05 C. Therefore, 0.05 C was selected in the work.

Effect of Temperature. The relationship between temperature and the response current of the sensor in a 0.10 M H_2SO_4 solution containing 0.50 mM nitrite is shown in Figure 8. The potential was set at -0.20 V. The temperature was controlled between

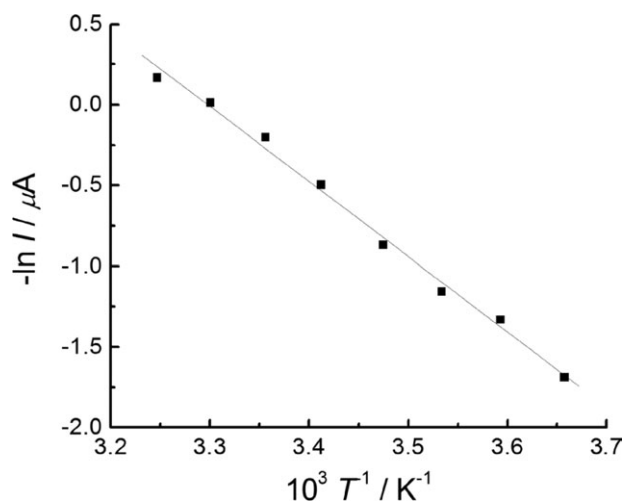


Figure 9. Plot of $\ln I$ versus T^{-1} according to the data in Figure 9.

0 and 35°C. Figure 8 shows that the response current increases with increasing temperature. This result is coincident with that of the copolymer,²⁷ but is different from most of the enzyme-modified electrode, which generally has an optimum temperature.²⁸ Considering the operation simplicity, the experiment was carried out at the ambient temperature (24.8°C ± 0.5°C).

According to the data shown in Figure 8, a plot of $\ln I$ versus T^{-1} was obtained (Figure 9). Based on the slope of the straight line (Figure 9) and Arrhenius equation, the apparent activation energy E_a was calculated. The value of E_a is 38.7 kJ mol⁻¹. This activation energy is low and similar to that of enzyme-catalyzed reactions, which is an additional evidence for the electrocatalytic reduction of nitrite taking place at the PANI-Cu composite-modified GCE. This result implies that the PANI-Cu composite plays an important role in lowering the activation energy of nitrite reduction, which is an essential issue for the electrocatalytic reaction.

Amperometric Determination of Nitrite

On the basis of the earlier results, a solution of 0.10 M H₂SO₄ and an applied potential of -0.20 V were chosen as the optimal conditions for the determination of nitrite. Figure 10 shows the relationship between the responses current of the PANI-Cu composite-modified GCE and the concentration of nitrite. A response was observed under the successive addition of 1.0×10^{-5} , 1.0×10^{-4} , and 1.0×10^{-3} M of nitrite. As shown in Figure 11, the response current at the modified GCE is proportional to the concentration of nitrite in the range of 0.049–0.50, 0.50–8.0, and 8.0–70.0 μM. It is clear that the PANI-Cu composite-modified GCE has a wide linear response range from 0.049 to 70.0 μM nitrite with correlation coefficients higher than 0.995 and a limit of detection of 0.025 μM. The sensitivity of the PANI-Cu composite-modified GCE is 0.312 μA μM⁻¹ cm⁻².

Stability of the PANI-Cu Composite-Modified Electrode

The stability of the PANI-Cu nanocomposite-modified GCE was tested in a 0.10 M H₂SO₄ solution containing 0.50 mM nitrite. The potential and the temperature were controlled at -0.20 V and 25°C, respectively. The response current of the GCE

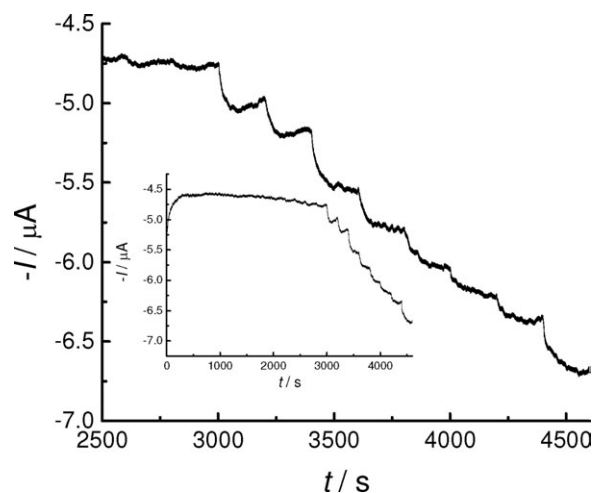


Figure 10. Amperometric response curves of PANI-Cu composite-modified GCE.

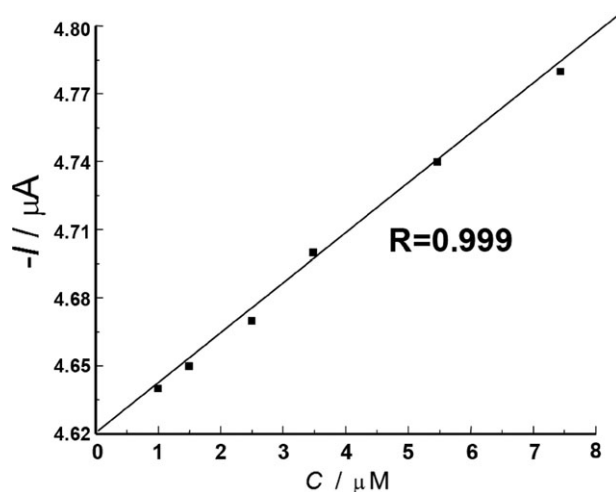


Figure 11. Plot of response currents versus nitrite concentrations.

changes slightly from 0.936 to 0.933, 0.941, and 0.925 μA after 7, 15, and 30 days, respectively. No decay of the electrode activity was observed after 30 days, because PANI has the good stability in an acidic solution and air. This electrode was kept in a solution of 0.05 M H₂SO₄ solution at room temperature when not in use.

CONCLUSION

It was found that the PANI-Cu composite-modified GCE can strongly catalyze the reduction of nitrite in a H₂SO₄ solution, which was proved by the bare GC, PAN/GC, and Cu/PAN/GC electrodes and the determination of activation energy. This composite film modified electrode provides a sensitive method for the amperometric detection of nitrite. This electrode has many advantages such as low cost, simple operation, a less negative operation potential of -0.20 V, and good storage stability.

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