Sensors and Actuators B 137 (2009) 437–441

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Highly electrocatalytic reduction of nitrite ions on a copper nanoparticles thin film

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ARTICLE INFO

Article history:
Received 7 June 2008
Received in revised form 12 December 2008
Accepted 9 January 2009
Available online 22 January 2009

Keywords:
Copper nanoparticles
Electrocatalysis
Nitrite
Nitric oxide

ABSTRACT

High dense Cu nanoparticles thin films, with the average size of 25.1 nm, were prepared by electrodeposition Cu nanoparticles on Au electrodes pre-coated 1-decanethiol layers (Cu NPs/thiol/Au). It shows high electrocatalytic capability for the reduction of nitrite ion (NO_2^-) and exhibits a good reproducibility, which can be utilized as efficient electrochemical sensors. The detection limit of NO_2^- approaches $\sim 10^{-7}$ mM and the response time is fast with the average time of 2 s.

1. Introduction

Nitrite ion (NO_2^-), a health-hazard chemical which extensively exists in the environment and uses for food preservation, has been proved that the excess of which would cause carcinogens because it can be recognized as a precursor to form *N*-nitrosamines [1,2]. In addition, their derivatives are the major components in low-level radioactive waste solution [3]. Nitric oxide (NO), a neuronal signal in the central and peripheral nervous system, can be produced by mammalian cells and acts as a vasodilatory messenger and cytotoxic agent [4]. Thus, sensitive sensing for NO_2^- and NO has been taken into consideration increasingly. At present, metal nanoparticles (NPs) have been attracted extensive interest for detecting NO_2^- and NO species by various methods due to their relative high surface area-to-volume ratio, such as Au, Pt, Cu, Pd, and Pt–Cu [5–11]. Specifically, voltammetric sensing, in which electrode was fabricated with metallic nanoparticles films, has become one of the most promising technologies because it not only offers a faster, cheaper and safer analysis but also could be applied in vivo [7–9]. But their detection limit is only up to approximately 10^{-4} mM due to the fact that the surface coverage of metal nanoparticles is regularly low, almost less than 30%. Therefore, with the hope of improving the efficiency of the catalyst, the integration of high-density metallic nanoparticles onto thin film served as the electrodes is the primary work. A number of methods, such as laser ablation [12], electroadsorption [13], and dispersion of metal nanoparticles solution onto substrates [14], have been developed for the preparation of the metal nanoparticles thin films.

In recent year, using additional linker molecules to bind metal nanoparticles on substrates has received considerable attention for their capabilities of modifying the surface in such a way to create well-defined thin films and increasing the nanoparticles loading on substrates [15–18]. For instance, alkanethiols are known to form well-ordered nanostructures on Au substrate, on which modified electrode is thermally stable due to the robust chemical nature of S–Au bonding [19,20]. On the other hand, metallic Cu nanoparticles are favored as electrochemical catalysts for the detection of NO_2^- and NO molecules because of its high electrical conductivity and excellent catalytic properties [6,21]. However, it is very difficult to obtain freestanding Cu nanoparticles because they can be easily converted into oxides, which will adversely affect catalytic reactivity of the nanoparticles [21–25]. Thus, it is an important feature of Cu NPs/thiol/Au system, whereby metallic film was comprised of a dense packing of Cu nanoparticles deposited thiol-modified Au substrate, with regard to catalysis applications. In this paper, we reported that high dense Cu nanoparticles electrodes, fabricated by Cu nanoparticles on Au substrate covered by 1-decanethiol, have been achieved by using electrodeposition process and exhibited high electrocatalytic capability for the reduction of NO_2^- species up to $\sim 10^{-7}$ mM within 2 s.

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doi:10.1016/j.snb.2009.01.014

2. Experimental

2.1. Chemicals

Milli-Q water (18 MΩ resistivity; Millipore System) was used for all experiments. Copper(II) tetrafluorobrorate hydrate ($Cu(BF_4)_2{\cdot}xH_2O$), dodecylbenzene sulfonic acid sodium salt (DBSA), 1-dodecanethiol (98.5%) and sodium nitrite ($NaNO_2$) were purchased from commercial suppliers (Aldrich, Fluka, Acros, SHOWA, respectively). All chemicals were used as received without further purification.

2.2. Instrumentation

Electrochemical experiments were performed on a CH Instruments 672A electrochemical system with a three-electrode system at room temperature. It consisted of a bare Au substrate with a surface area of 0.8 cm^2 pre-coated by thiol was used as the working electrode (99.999%), a platinum wire as the counter electrode, an Ag/AgCl (immersed in a 3 M KCl filling solution saturated with AgCl) as reference electrode. All potentials are measured versus the Ag/AgCl. The field-emission scanning electron microscopic (FESEM) images were obtained using GEMINI-URTRA 55 field-emission microscope. UV–vis spectrum was recorded at room temperature by UV/VIS/NIR spectrophotometer (PerkinElmer Lambda 990). The high-resolution transition electron microscopy (HRTEM) images was obtained by JEOL-2010 electron microscope operated at 200 kV. Samples for TEM were prepared by scraping Cu NPs from Au substrate and stamping onto a Ni grid covered with a carbon film. Particle size analysis of FESEM images was performed with SigmaScan Pro 5 software, by measuring ~1000 particles. The X-ray diffraction patterns (XRD patterns) was recorded from SWLS—X-ray powder diffraction with 01C beamline at the National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan. The angle of incidence and the wavelength of X-rays were 0.5 and 0.77490 Å, respectively.

2.3. Preparation of the Cu NPs/thiol/Au modified electrode

The Cu NPs/thiol/Au modified electrode was synthesized by immersing the thiol-modified Au which was steeped in 1 ml 1-dodecanethiol solution for 12 h in copper ion containing solution. The solution was prepared from 0.029 g of $Cu(BF4)_2{\cdot}xH_2O$ and 0.058 g of DBSA used as precursor and capping reagent, respectively. The deposition potential was accordingly controlled in the range of −0.6 to −0.8 V at a scan rate of 0.05 V s^{-1}, and the deposition time was 800 s. After deposition, the electrodes were rinsed with copious amounts of Milli-Q water to remove the residual capping reagent.

3. Results and discussion

3.1. Characterization of the Cu NPs/thiol/Au electrode

The surface morphology of the Cu NPs/thiol/Au modified electrode was investigated by FESEM. In Fig. 1a, it is observed that the Cu nanoparticles with dense density and near-spherical shape are homogeneously distributed on the top of 1-decanethiol layers, in which the size distribution of Cu NPs was in the range of 8–48 nm. A Gaussian fit illustrates that these particles have an average size of 25.1 nm, with the standard deviation of 7.04 nm (Fig. 1b). The UV–vis spectrum of the copper nanoparticles deposited on Au substrate (Fig. 2) displays a peak at 555 nm, which can be attributed to the excitation of plasmon resonance or interband transitions excitation and are characteristic properties of the metallic nature of Cu particles [26]. The detailed structural analysis of the Cu NPs/thiol/Au modified electrode was characterized by XRD, as shown in Fig. 3. The peaks located at 2θ values of about 24.9, 35.7 and 42.0 are assigned to the Cu(2 0 0), Cu(2 2 0), and Cu(3 1 1) facets of the face-centered cubic (*fcc*) Cu, respectively. Crystallographic planes of XRD patterns were indexed using Bragg's law ($2d \sin\theta = n\lambda$) in which the wavelength of X-rays were 0.77490 Å, as well as combined with those of the JCPDS database (Cu file code: 85-1326). The Au peaks come from the gold substrate for deposition of Cu NPs. Furthermore, energy-dispersive X-ray (EDX) analysis

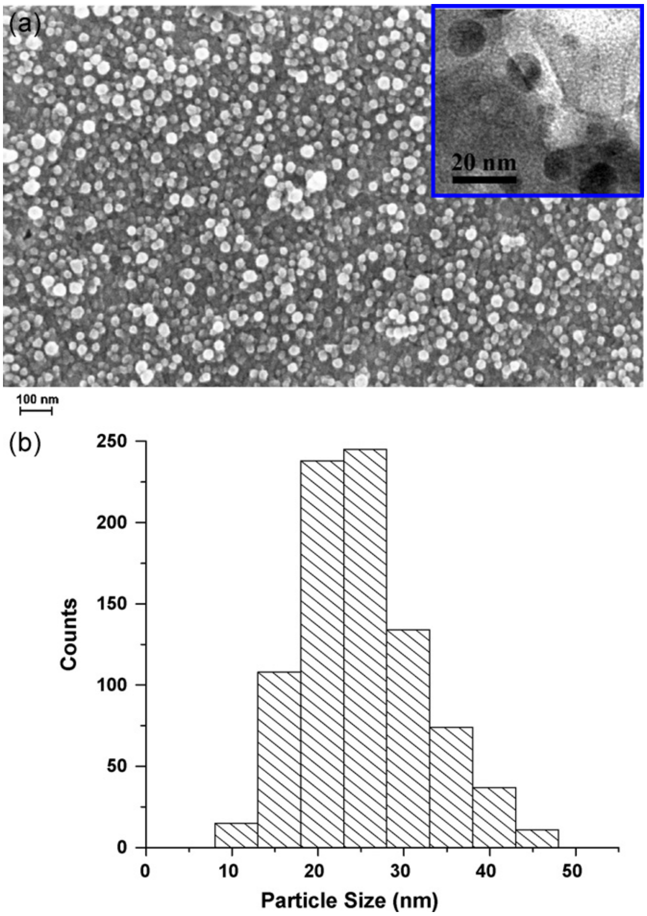

Fig. 1. (a) FESEM images of Cu NPs/thiol/Au modified electrode. The electrodeposited potential was controlled between −0.6 and −0.8 V versus Ag/AgCl at scan rate of 0.05 V s^{-1}. (b) Size distribution of Cu nanoparticles.

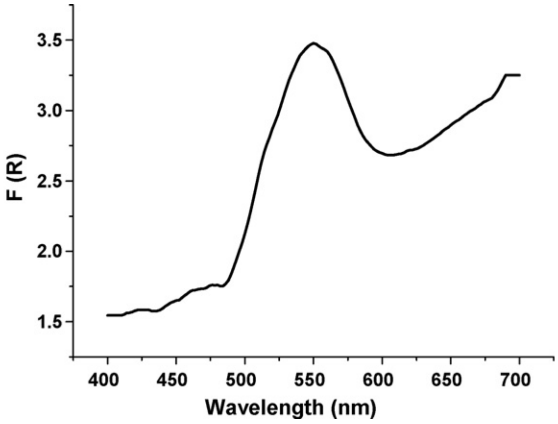

Fig. 2. UV–vis diffuse reflectance spectra of the deposed Cu nanoparticles on gold substrate. The relative reflectance of a film, $F(R)$, is given by the Kubelka–Munk equation [$F(R) = (1 - R)^2/2R$, where R is the ratio of the reflected intensities of the sample and the gold film standard].