

Simple one step electrochemical preparation of copper nanostructures



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ARTICLE INFO

Article history:

Received 28 August 2013

Received in revised form 28 October 2013

Accepted 30 October 2013

Available online 12 November 2013

Keywords:

Cu nanoparticles

Electrosynthesis

Electrocatalysis

Dendrite

L-tyrosine

ABSTRACT

Nanostructures based on copper (Cu_{NSS}) are promising materials in different fields of application. To this end, in this work we have studied a simple one-step electrosynthesis of Cu_{NSS} directly onto ITO electrode surface starting from an aqueous solution of copper sulphate. We have investigated the effects of the presence of electrolyte salts such as K₂SO₄, Na₂SO₄ and (NH₄)₂SO₄ and we have found that they gave rise to the formation of a number of remarkably different forms of nanostructures. In particular, when the electrodeposition was conducted in presence of K₂SO₄ fractal-like or dendritic structures consisting of a long central backbone and sharp side branches were observed. The resulting Cu_{NSS} were characterized by SEM, XRD and by electrochemical techniques. Studies on the electrocatalytic behaviour of dendritic Cu_{NSS} modified electrodes towards the oxidation of L-tyrosine in 0.05 M NaOH solution showed a 1.0 10⁻⁶ ÷ 7.0 10⁻⁵ M linear range and a detection limit of ca. 6.0 10⁻⁷ M.

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1. Introduction

Recently, copper due to its high stability, excellent electrical conductivity, catalytic properties and low cost as compared to silver and gold [1–3] has attracted a great interest as an ideal alternative material. Copper nanostructures have great applications as heat transfer systems [4], antimicrobial materials [5,6], super strong materials [7,8], sensors [9–11] and catalysts [12–14].

The synthesis of copper nanostructures with various shapes like cubic [15], prism, wires [16–19] and dendritic [20–23] has been reported by a variety of preparation techniques. The morphology and crystallographic orientation of nanostructures can be controlled in several ways including for example the choice of the underlying substrate and the co-adsorption of some additives. A large number of synthetic methodologies by reduction with hydrazine in ethylene glycol under microwave irradiation [24], seed-mediated growth [25], pulsed electrodeposition [26,27], electrochemical deposition [28–31] have been reported. Among the different shapes, dendritic structures have recently attracted considerable attention, in particular for electrode modification purposes, due to their fascinating hierarchical morphology, the open porous structure and the high aspect ratio. These characteristics significantly affect the electrochemical reactions allowing potential

applications in catalysis and other outcoming technological fields [32–38].

In the present study, we report the synthesis of well-defined assembly of uniform copper nanostructures (Cu_{NSS}) through an easy-to-use and low cost electrochemical deposition on ITO coated glass substrate in no acidic media. The electrodeposition experiments were carried out via chronoamperometry, at a fixed potential, in an aqueous solution of copper sulphate (CuSO₄·5H₂O). The electrodepositions have been conducted in the same experimental conditions with or without electrolyte addition. Different electrolytes such as of K₂SO₄, Na₂SO₄ and (NH₄)₂SO₄ have been studied. The morphology and crystalline structure of the prepared Cu_{NSS} have been investigated via SEM and XRD measurements. The effect on the morphology and crystal size of deposition time and electrolyte concentration has been studied when K₂SO₄ was used as electrolyte. The electrochemical properties of the Cu_{NSS} were analyzed by Cyclic Voltammetry (CV) and electrocatalytic measurements towards L-tyrosine have been also reported. L-tyrosine (tyr) is one of the most important amino acid essential for human as it stabilizes and maintains nutritional balance; for this reason, recently many analytic methods, in particular electrochemical ones, have been investigated in order to detect it in food in a simple, sensitive and selective way [39–42].

2. Experimental

A potentiostat/galvanostat electrochemical workstation (Autolab PGSTAT20 (Ecochemie, Utrecht, The Netherlands))

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interfaced with a personal computer to a three electrode cell: a Ag/AgCl (3.0 M KCl_{inner filling solution}/sat. KNO₃_{outer filling solution}) as reference electrode, a platinum wire as counter electrode, and ITO slide as working electrode was used for the electrodeposition experiments. ITO glasses were purchased from Optical Filters Ltd., England (surface resistivity: 12 Ω cm). ITO exposed area was equal to 0.98 cm². Before modification, the ITO electrode was polished by ultrasounds alternate treatments for 15 min in soapy water, acetone, ethanol solution and then dried at room temperature. Cu nanostructures were deposited on the ITO surface at room temperature in an aqueous Cu electrolyte solution (without stirring) for a preselected deposition time by chronoamperometric experiments stepping the potential from the open-circuit value to -0.60 V. The Cu electrolyte solution consisted of a preselected concentration of CuSO₄·5H₂O with or without a chosen concentration of different supporting electrolytes. The electrolyte solution was appropriately deoxygenated by nitrogen bubbling for at least 20 min prior to use. Three deposition parameters were used to produce NSs with different shapes and sizes. In particular, Cu electrolyte concentrations [CuSO₄·5H₂O] of 50, 100 mM; deposition times of 5, 10, 60, 120 s, and nature (i.e. K₂SO₄, Na₂SO₄ or (NH₄)₂SO₄) and in some cases concentration (100 mM) of the supporting electrolyte were varied in a systematic fashion. The resulting Cu_{NSS} deposited ITO substrates were thoroughly rinsed with Millipore water (resistivity of 18 MΩ cm) and dried under nitrogen-purged current prior to characterization.

X-ray diffraction (XRD) analysis was carried out by means of a PANalytical X'Pert PRO powder diffractometer equipped with a fast X'Celerator detector. Ni-filtered CuKα radiation was used (40 mA, 40 kV). For phase identification the 2θ range was investigated from 30 to 65 2θ° with a step size of 0.05° and time/step of 200 s. The line broadening of the Cu reflection 111 was used to evaluate crystallite size (τ) using the Scherrer equation [43]. SEM images were recorded using an EVO 50 Series Instrument (LEO ZEISS) operating at an acceleration voltage of 15 keV.

3. Results

3.1. Electrochemical behaviour

In order to find the optimal deposition potential for the preparation of Cu_{NSS}, Cyclic Voltammograms (CV) were preliminary registered on a bare ITO electrode at a scan rate of 0.02 V s⁻¹ in 50 mM CuSO₄ solution in absence and in presence of K₂SO₄ (100 mM). The CV curves are reported in Figure 1; as expected in the presence of only CuSO₄ (curve a) a very broad and resistive voltammogram was obtained whereas in the presence of K₂SO₄ (curve b) two peaks at -0.43 V and +0.47 V were present due to the cathodic deposition and the anodic re-dissolution of Cu. Moreover the crossing-over of the cathodic and anodic branches, which is characteristic of the nucleation process, was also observed [44,45].

As a consequence, the electrochemical synthesis of Cu_{NSS} was potentiostatically conducted at fixed potential of -0.60 V, starting from OCP potential. The following operative conditions were investigated (for the sample labelling see Table 1):

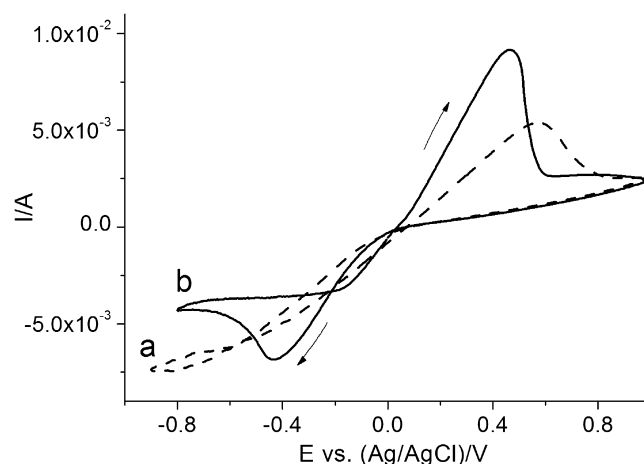


Figure 1. First cyclic scan recorded at ITO electrode in 50 mM CuSO₄ (curve a, dashed line) and in 50 mM CuSO₄ with 100 mM K₂SO₄ (curve b, solid line); scan rate: 0.02 V s⁻¹. Starting potential value: +0.0 V.

- i) electroreduction at two different deposition times d_t in the absence of electrolytes and at a fixed 50 mM CuSO₄ concentration ($d_t = 5$ and 10 s, samples Cu_{NSS}-1 and Cu_{NSS}-2, respectively);
- ii) two CuSO₄ concentrations (50 and 100 mM) in absence of electrolytes keeping d_t fixed at 10 s (samples Cu_{NSS}-2 and Cu_{NSS}-3);
- iii) the addition of K₂SO₄, Na₂SO₄ or (NH₄)₂SO₄ at 100 mM concentration to a 50 mM CuSO₄ solution, at $d_t = 10$ s (samples Cu_{NSS}-K, Cu_{NSS}-Na and Cu_{NSS}-NH₄).

Since SO₄²⁻ ions were already present in the medium before the addition of the electrolytes any observed change can be reasonably assigned as an effect of the used cation.

The current transient for the electrodeposition of all investigated samples presented the same typical feature consisting in the rapid current decrease at very short times which corresponds to the changing of the double layer, followed by a rise of the current due to the growth of the new phase and the increasing number of nuclei on the electrode surface [46] (Supplementary Information (SI), Fig. 1S).

The amount of deposited Cu (m_{Cu}) can be obtained by graphical integration of the charge associated to the deposition process (Q_{Cu}) (similar to Figure 2), according to the following equation (Faraday law):

$$m_{Cu} = \frac{(Q_{Cu} \cdot M)}{(F \cdot z)}$$

where M is the atomic weight of Cu (63.546 g mol⁻¹), F is the Faraday constant (96485 C mol⁻¹) and z is the Cu valence. This equation assumes a 100% current efficiency and takes the consumed charge as due just to the two-electron reduction of Cu²⁺. The values of m_{Cu} are reported in Table 1 as well as the I_{max} , and the time at which the maximum current was observed, t_{max} .

Table 1
Experimental data of the maximal current density (I_{max}), the time at which the maximum current was observed (t_{max}) and the amount of deposited Cu (m_{Cu}).

Sample	[CuSO ₄]/ d_t /[M ₂ SO ₄] (mM/s/mM)	I_{max} (mA cm ⁻²)	t_{max} (s)	m_{Cu} (μg cm ⁻²)
Cu _{NSS} -1	50/5	5.0	0.2	6.5
Cu _{NSS} -2	50/10	5.6	0.4	18.5
Cu _{NSS} -3	100/10	9.1	0.4	30.6
Cu _{NSS} -K	50/10/100	10.7	0.5	14.4
Cu _{NSS} -Na	50/10/100	11.8	0.6	26.2
Cu _{NSS} -NH ₄	50/10/100	7.8	0.6	22.8

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