Preparation, characterization and electrochemical application of CuNiO nanoparticles supported on graphite for potentiometric determination of copper ions in spiked water samples

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ABSTRACT

A simple chemical precipitation route was developed to synthesize CuNiO nanoparticles on graphite sheets [CuNiO/Gt] by forming both copper and nickel hydroxide species followed by their calcination at 400 °C for 3 h. X-ray diffraction and transmission electron microscopy were employed to characterize the crystallinity and morphology of fabricated CuNiO/Gt nanocomposite. The ability of this prepared powder to act as an active component inside modified carbon paste electrode (MCPE) for potentiometric determination of copper(II) ions in spiked water samples was investigated. The electrochemical performance of this MCPE was optimized by studying the effect of altering CuNiO content, response time and pH on the measured emf value. The prepared electrode exhibited a divalent Nernstian slope of $30.2 \pm 1.80 \, \text{mV decade}^{-1}$ over Cu(II) ions concentration ranging from 1.0×10^{-6} up to $5.0 \times 10^{-2} \, \text{mol L}^{-1}$. The optimum mass percent ratio of CuNiO:graphite:plasticizer in the prepared MCPE was found to be 0.424:0.279:0.297. A detection limit value of $1.0 \times 10^{-6} \, \text{mol L}^{-1}$ was calculated. Cu(II) ions concentration in real water samples could be efficiently estimated using this synthesized MCPE with recovery values of $102 - 103\%$.

1. Introduction

Copper is widely spread in biological systems [1] in more than 30 important enzymes [2]. It is also an essential element in many agricultural, industrial and domestic purposes. However, it is toxic at higher concentration levels. Its increased dosage results in Wilson disease, gastrointestinal, hypoglycemia, catarrh and dyslexia. Based on these severe human health effects, copper ion determination in water [3] and soil [4] samples becomes a must. Many methods have been examined to determine copper including atomic absorption spectrometry, flame atomic absorption spectrometry-electrothermal atomization [5,6], chromatography [7], gravimetric detection [8], anodic stripping voltammetry [9] and photometry [10,11]. Many difficulties may be observed during the employment of these methods as they need complicated sample pre-treatment protocols that hinder their application for analyzing increased numbers of environmental samples. Most of these problems can be solved when ion selective electrodes are employed. Online analysis can be carried out and the pre-treatment steps of tested samples are time and effort saving. In addition, more sensitive and selective results can be easily attained. In this respect, many attempts have been employed to develop efficient sensors for copper

determination. Electrochemical methods could also offer another platform for sensitive, selective and reproducible assaying of copper ions [2,12–14]. A copper selective electrode with a polyvinyl chloride membrane containing *o*-xylylenebis(*N,N*-diisobutyldithiocarbamate) as ionophore was constructed. It displayed fast response ($< 10 \, \text{s}$) and near-Nernstian behavior during the potentiometric determination of Cu (II) ions using EDTA. A linear calibration plot was shown in Cu(II) ions concentration range of $10^{-6} - 0.1 \, \text{M}$ within the pH range of $4 - 6$ [14]. The coating composition of polyvinyl chloride membrane electrode based on bis[(2-(hydroxyethylimino)phenolato]copper(II) complex was found to affect its capability for Cu(II) ions sensing. The best response was shown at the electrode membrane containing ionophore:2-nitrophenyloctyl ether:polyvinyl chloride:potassium tetrakis(*p*-chlorophenyl)borate ratio of 4:65:30:1 (w/w, mg). No divergence in the potential value was recorded at this proposed electrode even after 3 months [13]. Differential pulse anodic stripping voltammetry was employed to study the effect of adding different interfering ions including Bi^{3+}, Cd^{2+}, Fe^{3+}, Hg_2^{2+}, Pb^{2+}, Sb^{3+} and Zn^{2+} on the electrochemical response of chemically unmodified screen-printed carbon electrodes towards the measurement of trace levels of Cu(II) ions. Hg_2^{2+} ions were the only species that efficiently affected the electrode
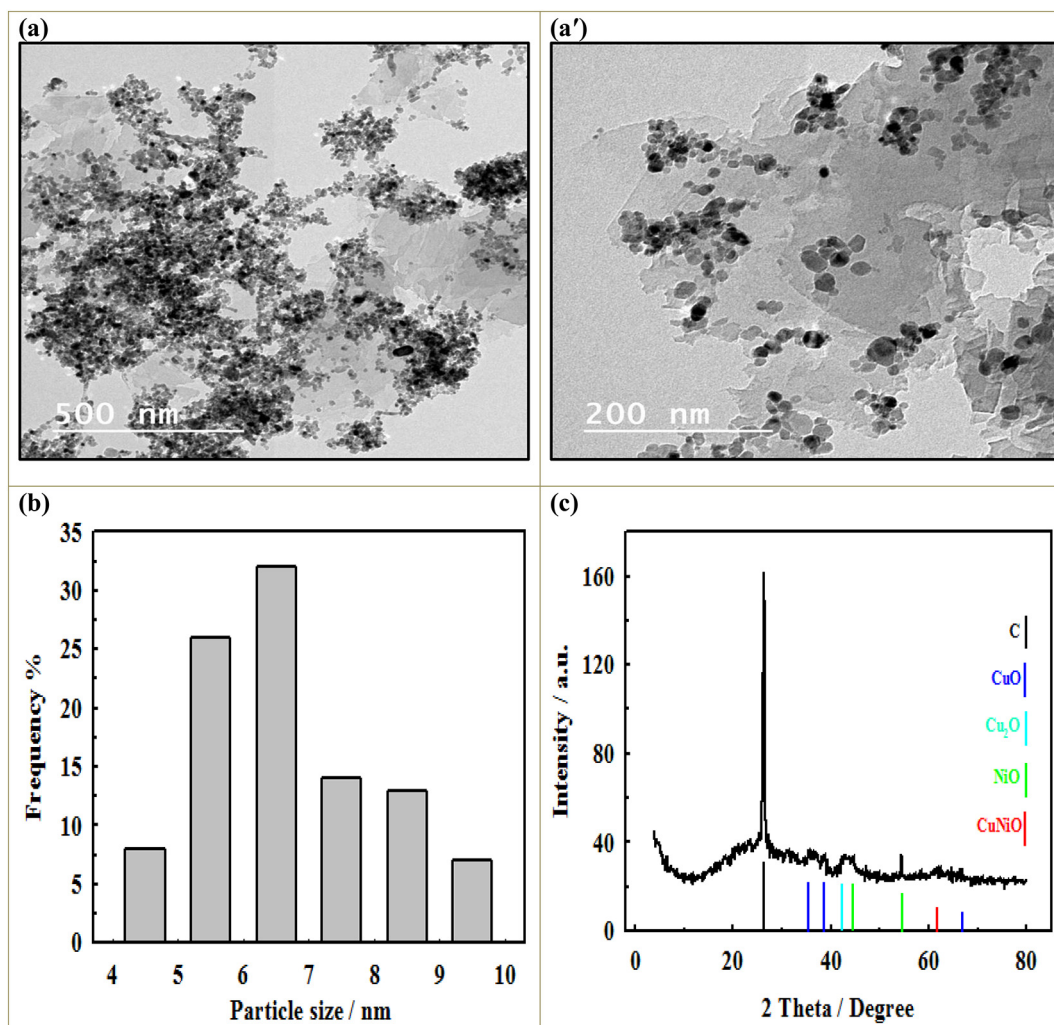

Fig. 1. (a, a′) TEM images of CuNiO/Gt nanocomposite at two magnifications and its corresponding particle size distribution curve in (b) and XRD pattern in (c).

Table 1

List of the linear range, slope and correlation coefficient values of the potentiometric calibration curves of CuO/Gt, NiO/Gt and CuNiO/Gt nanocomposites, containing 150 mg of the modifier, towards Cu(II) ions determination in acetate buffer solution (pH 5).

Modifier	Linear range/mol L^{-1}	Slope/mV decade^{-1}	Correlation coefficient (r^2)
CuO/Gt	$1.0 \times 10^{-4} - 5.0 \times 10^{-2}$	53.3 ± 1.20	0.9762
NiO/Gt	$1.0 \times 10^{-4} - 5.0 \times 10^{-2}$	20.1 ± 3.30	0.9889
CuNiO/Gt	$1.0 \times 10^{-6} - 5.0 \times 10^{-2}$	30.2 ± 1.80	0.9998

response. A mean recovery value greater than 90% was recorded during the estimation of Cu(II) ions concentration in spiked and unspiked serum and water samples [2]. Naphthol-derivative Schiff's base (2,2′-[1,2-ethanediylbis(nitriloethylidyne)]bis(1-naphthalene))

complex showed linear response to Cu(II) ions concentration in the range of $2.3 - 50.8$ ng/mL. Low accumulation time of 90 s and RSD value of $(3.2 - 3.5)$% were measured [12].

Nanocomposites of active metal nanoparticles have been widely studied in recent years as a result of their important applications in sensors, catalysis and electronics [15–17]. They have superior electronic, catalytic and optical characteristics based on their shape, size and structure [18,19]. Many protocols have been explored to fabricate shape- and size-controlled metallic nanoparticles. These approaches generally require capping agents such as polymers, surfactants or dendrimers to result in the formation of particles in nanometer range. Transition metal oxides are applied in heterogeneous catalysis due to their tunable morphological, chemical and textural properties in addition to their intrinsic redox characteristics [20–23]. Bimetallic and multi-metallic transition metal based nanocomposites displayed synergistic enhancement with respect to chemical activity, stability and

Table 2

List of the linear range, slope and correlation coefficient values of the potentiometric calibration curves of CuNiO/Gt nanocomposite, containing variable mass percent ratios of CuNiO: graphite: plasticizer, towards Cu(II) ions determination in acetate buffer solution (pH 5).

Nanocomposite no.	CuNiO: graphite: plasticizer (mass percent ratio)	Linear range/mol L^{-1}	Slope/mV decade^{-1}	Correlation coefficient (r^2)
1	0.141: 0.562: 0.297	$1.0 \times 10^{-6} - 1.0 \times 10^{-2}$	34.4 ± 1.60	0.9991
2	0.282: 0.421: 0.297	$1.0 \times 10^{-6} - 1.0 \times 10^{-2}$	33.0 ± 2.05	0.9693
3	0.424: 0.279: 0.297	$1.0 \times 10^{-6} - 5.0 \times 10^{-2}$	30.2 ± 1.80	0.9998
4	0.703: 0: 0.297	$1.0 \times 10^{-6} - 1.0 \times 10^{-2}$	30.8 ± 2.35	0.9808