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Tartaric acid assisted in-situ growth of CuO nanostructures over ITO substrate for the electrocatalytic detection of Sudan I

Mawada Mohamed Tunesi[a], Nazar Hussain Kalwar[b], Razium Ali Soomro[c,*], Selcan Karakus[a], Sana Jawaid[c], Muhammad Ishaq Abro[d]

[a] Department of Chemistry, Istanbul University, Istanbul 34320, Turkey
[b] Department of Mechanical Engineering, Faculty of Engineering, University of Selcuk, Campus, 42079 Konya, Turkey
[c] National Centre of Excellence in Analytical Chemistry, University of Sindh, Jamshoro 76080, Pakistan
[d] Department of Metallurgy and Materials Engineering, Mehran University of Engineering & Technology, Jamshoro 76080, Pakistan

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ABSTRACT

The study explores the potential of newly developed ITO based electrode for the electro-catalytic detection of Sudan I. The ITO based electrode utilizes a dense layer of 2D CuO nanostructures as an effective electron-transfer facilitator which promotes the electro-catalytic sensing of Sudan I in aqueous solution. The in-situ growth of CuO nanostructures was achieved using simple hydrothermal route with the assistance of tartaric acid utilized as an effective template. The in-situ grown layer comprises of 2D CuO nanostructures with morphological features similar to flowers composed of sharp-flake like features. The electro-catalytic oxidation of Sudan I over the described electrode system demonstrated low-over potential value and excellent working stability with good analytical linearity in the range of 0.001–1.56 μM. The ITO based electrode was found highly selective and sensitive towards Sudan I with limit of detection determined to be 1.2×10^{-4} μM (S/N = 3).

1. Introduction

The integration of nanomaterials with the conventional electrochemical system has drastically enhanced the capabilities of the electrode based sensors. The synergetic platform offers much greater analytical sensitivity and reliability with the potential to meet the market for low-cost, higher throughput devices. The superior characteristics of the nanomaterial based electrode are often attributed to the shape and size of the nanomaterial. This morphological dependency of the electrochemical signal has recently gained substantial research attention [1]. In particular copper oxide (CuO) nanostructures, a versatile semi conducting material with its well-known p-type nature and distinguished catalytic characteristics is highly considered in electro-catalytic applications. Unlike, the other metal oxides (Co_3O_4, NiO and Fe_3O_4), CuO can easily be synthesized without any high degree calcination step. This ease of fabrication allows CuO to be functionalized with any desired chemical moiety that can alter the chemistry at electrode-solution interface. Moreover, the morphology of CuO plays an eminent role in facilitating the electron-transfer kinetics at the electrode surface. In this regard, Cao et al. [2] demonstrated the capability of CuO nanostructures (microsphere, doughnut-like and multi-layered microsphere) for the arsenic (III) removal from aqueous system. The author claimed that the doughnut-like CuO structure possessed higher As (III) removal capacity based on its morphological characteristics. In a recent effort, [3] our group discussed the shape effect of CuO nanostructures on the electrochemical quantification of organophosphate pesticides. Similarly, the variation in electro-catalytic signal for the oxidation of N-acetyl-L-cysteine (NAC) using CuO nanostructures possessing distinct morphological features has also been reported [4]. Despite the wider range of applications, the capability of copper oxide nanostructures in the area of food toxins detection is less explored. In this regard, the identification and quantification of food adulterants such as Sudan I, chemically known as (1-[(2,4-dimethylphenyl)azo]-2-naphthalenol) is an important issue. Sudan I is extensively used as a coloring agent in waxes, textile colorants, shoe polishes and food additives. The azo dye is classified as category III carcinogen, responsible for liver and bladder tumors [5]. Despite its detrimental effects, Sudan I has been reported to be illicitly abused as food adulterant in products such poultry feed, paprika, ketchup and sausage due to its low cost, bright color and stability. The conventional methods for the quantification of Sudan I includes techniques such as high performance liquid chromatography (HPLC) [6], gas chromatography (GC) [7], capillary electrophoresis [8], immunoanalysis [9], chemiluminescence flow injection analysis [10], and plasmon resonance light scattering (PRLS)

* Corresponding author.
E-mail address: raziumsoomro@gmail.com (R.A. Soomro).

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Table 1
Analysis of Sudan I in food samples.

Sample	Added (μM)	Found (μM)	Recovery (%)	RSD (%)
Paprika powder	0	Not detected	–	–
	0.005	0.00482	96.4	3.3
	0.035	0.0341	97.4	2.9
Chilli sauce	0	Not detected	–	–
	0.005	0.00492	98.4	3.1
	0.035	0.0342	97.7	3.7
Ketchup	0	Not detected	–	–
	0.005	0.00478	95.6	3.3
	0.035	0.0339	96.86	2.9

[11]. Although, these techniques are considered highly sensitive. However, the associated complexity, time consumption and costliness makes them an unsuitable candidate for the rapid and efficient detection of Sudan I. Contrary to these, the electrochemical approach enables rapid detection with simple and inexpensiveness instrumentation [12,13]. The quantification of Sudan I using conventional electrodes such as glassy carbon (GCE) and carbon paste (CPE) is highly ineffective, due to the requirement of high over voltage which results in sluggish and non-reproducible electrode response. This issue has been addressed using various modified electrodes where carbon nanotubes, multi wall carbon nanotubes, and nanocomposite materials are considered promising [14] (Table 1).

In this study, the potential of a new type of electrode has been evaluated against the sensitive determination of Sudan I in aqueous buffer solution. The newly discussed electrode is based on in-situ growth of CuO nanostructures over ITO substrate using simple hydrothermal process. The growth process was assisted by tartaric acid which acts as a template. The in-situ growth allowed complete coverage, high density and assembly of nanostructures over ITO substrate which enabled stable signal response and high sensitivity of the electrode towards Sudan I.

2. Experimental

2.1. Reagent and materials

All chemical utilized were analytical reagent grade and used directly without further purification. Copper chloride ($CuCl_2{\cdot}2H_2O$), ammonia solution (NH_3) 32%, tartaric acid ($C_4H_6O_6$), Sudan I ($C_{16}H_{12}N_2O$) and phosphate buffered saline (PBS) were purchased from Sigma Aldrich. Sudan I stock solution, 1.0×10^{-3} mol L^{-1}, was prepared by dissolving 0.028 g of the reagent in a 100 mL volumetric flask (ethanol/water (1:1) solution) and stored at 4 °C in the dark. The Phosphate buffer solution (PBS) 0.1 M (pH 6) was used as active electrolyte. 1.0% nafion solution in isopropanol solvent (C_3H_8O) (Merck) was utilized as electro active polymer. Where all the other solution were prepared using de-ionized water.

2.2. In-situ growth of CuO nanostructures

The CuO nanostructures were grown in-situ over ITO substrate using hydrothermal route. 1.67 g of $CuCl_2{\cdot}5H_2O$ was allowed to vortex with 0.6 g of tartaric acid in 100 mL of de-ionized water. A set of pre-clean ITO glasses (1×1 cm^2) with conductive side facing upside were then introduced into the homogenized mixture followed by 4 mL of NH_3 (35%). It must be noted that, a portion of ITO substrate was covered with paper tape to inhabit growth on that section which was later used for electrical connection. The mixture was then subjected to hydrothermal treatment for 4 h at 85 °C in a pre-heated electric oven. At the completion of growth, the ITO glasses were carefully removed and thoroughly rinsed with de-ionized water and methanol to remove any surface adhered impurities.

2.3. The characterisation and electrochemical assessment of ITO based electrode

High resolution scanning electron microscopy (HR-SEM) (JEOL JSM-7001F), X-ray diffraction (XRD) (Bruker D-8) and AT-IR analysis (Thermo Scientific™ Nicolet 5700 FTIR Spectrometer) was carried to completely characterize the in-situ grown CuO nanostructure. The electrochemical assessment of the newly formed ITO electrode was assessed using a bipotentiostat model E-760 (CH Instruments) Texas, USA. The electrochemical cell housed a conventional three electrode system with standard calomel electrode as reference and a platinum wire as auxiliary electrode. The ITO based electrode (CuO-ITO) was utilized as working electrode. To ensure versatility of the developed electrode. The electrochemical assessment was carried in reference to glassy carbon electrode (GCE), modified with CuO nanostructures synthesized exactly as quoted for CuO-ITO. The GCE was modified using a pre-formed suspension (0.5 mg into 1 mL of methanol) of CuO nanostructures which were surface deposited over pre-polished GCE. The modified GCE was then dried under ambient air condition followed by deposition of 2 μL of Nafion® to inhabit surface removal of nanostructures. GCE modified electrode has been denoted as GCE-CuO throughout the manuscript.

3. Results and discussion

3.1. Characterisation of in-situ grown CuO over ITO substrate

Fig. 1 shows the representative SEM images of CuO nanostructures in-situ grown over ITO substrate. Fig. 1(a) is indicative of dense population of synthesized nanostructures with shape similar to flowers composed of sharp and thin flake-like features. The average thickness of the flakes were estimated in rage of 15–45 nm ± 2.4 nm. The Fig. 1(c) shows layer formation over ITO substrate where complete coverage of CuO nanostructure is evident. Unlike the slurry- driven modification where discrete nanostructures are adhered to the surface, this proposed method provides greater contact points between electrode and nanostructure. Moreover, the in-situ growth exempts the use of polymer binder which in other cases affects the availability of active sites on the nanostructures. The XRD pattern for pure ITO and CuO-ITO is shown in Fig. 2. The sharp peaks in XRD pattern for CuO were indexed to (110), (111), (−111), (−202) plane of monoclinic CuO as referenced against ICCD Card No. 80-0076 [15]. The peaks indexed to (211), (222), (004) and (044) were observed for pure ITO glass [16].

Fig. 3 represents the AT-IR characteristics of the as-synthesized CuO nanostructures. The IR evaluation was carried in reference to the spectra recorded for the pure tartaric acid. The major bands were found near 2825 and 2927 cm^{-1} which were associated with asymmetric stretching of CH_2 group of the hydrophobic tail of the TA. The symmetric stretching of C=O and C-O from the COOH group of TA were identified near 1760 and 1250 cm^{-1}. The spectra of final product (CuO-ITO) demonstrate a significant shift in the recorded frequencies of these groups in addition to the decline in the peak intensities. This variation in the spectral features of the CuO confirms the surface binding of the TA with the CuO nanostructures. The appearance of M-O band near 500 cm^{-1} further indicates the presence CuO as supported by relevant studies [17].

The in-situ growth of CuO over ITO electrode is governed by slow and controlled precipitation of growth nuclei where the used template acts as a controller and modifier of growth. In this case, the steady nucleation is achieved by the use of ammonium hydroxide where the generated hydroxyl radical (OH^-) react with copper ions to form Cu $(OH)_2$ nuclei as a result of metal-ammonia complex dissociation. The provided temperature than facilitates the conversion of hydroxide phase to oxide phase. The utilized template (tartaric acid) not only contributes in directing the growth process but also slows down the process of precipitation leading to the growth of regular nanostructures