



CuO nanostructures for highly sensitive shape dependent electrocatalytic oxidation of *N*-acetyl-L-cysteine



Mawada Mohamed Tunesi^a, Razium Ali Soomro^{b,c}, Ramazan Ozturk^{c,*}

^a Department of Chemistry, Fatih University, Istanbul 34500, Turkey

^b National Centre of Excellence in Analytical Chemistry, University of Sindh, Jamshoro 76080, Pakistan

^c Genetic and Bioengineering Department, Fatih University, Istanbul 34500, Turkey

ARTICLE INFO

Article history:

Received 17 May 2016

Received in revised form 1 July 2016

Accepted 25 July 2016

Available online 26 July 2016

Keywords:

CuO

Citric acid

Adipic acid

Cyclic voltammetry

ABSTRACT

The study describes the application of CuO nanostructures as an effective electrode modifying material for the direct electrocatalytic oxidation of *N*-acetyl-L-cysteine (NAC). The CuO nanostructures were synthesized using hydrothermal growth method with the assistance of NAC, adipic acid (AS) and citric acid (CA) utilized as effective growth modifiers. The morphological characterization of the as-synthesized nanostructures revealed formation of highly distinct and attractive structural features signifying the efficient growth controlling and directing capabilities of the used modifiers. Although, all the fabricated nanostructures were known to possess electrocatalytic potential for the oxidation of NAC. However, the CA modified CuO nanostructures were noted to demonstrate greater sensitivity compared to its other competitors. The developed sensor system relies on the relatively high electro-active area and charged moieties associated with the surface of CA assisted CuO, thus creating a favorable environment for the faster diffusion of analyte towards catalyst surface. The developed sensor exhibited excellent working linearity in the selected concentration range of 0.1 to 5.0 μM with estimated LOD value of 0.01 μM .

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1. Introduction

The combination of nanomaterials with electrochemistry has offered researchers a diverse platform for the interdisciplinary nano-electroanalytical investigations. The higher surface to volume ratio with structurally unique shaped nanostructures have enabled production of sensitive and selective sensor systems for various molecules of interest [1]. Unlike homogeneous catalyst in the solution phase, electrocatalysis is largely influenced by the shape of the utilized nanomaterials. Such shape dependency based on its complex nature can either facilitate or impede the reaction of interest [2].

The excellent sensitivity of the nanomaterials based electrochemical sensors have empowered pharmaceutical companies to embrace highly innovative protocols in a bid to meet the strict regulations and quality control requirement at each stage of the drug formulation. In this context, quantitative analysis of *N*-Acetyl-L-cysteine (NAC) is considered clinically important based on its usage as an effective mucolytic agent anti-oxidant and antidote against acetaminophen poisoning. Although, the conventional techniques such as chromatography [3], titrimetry [4], spectrophotometry [5], chemiluminescence [6], fluorimetry [7] and turbidimetry [8] are considered sensitive. However, the associated complexity, time consumption and costliness makes them an unsuitable

candidate for the rapid and efficient analysis of NAC. Contrary to this, the electrochemical approach provides greater analytical privileges with additional advantage of device miniaturization which can enable development of lab to field sensor system. In regard to NAC determination, various reports have been published describing the numerous electrochemical strategies previously adopted for the selective quantification. The direct oxidation of NAC using bare glassy carbon electrode (GCE) is usually hindered by the poor voltammetric response at the solid surface electrodes. Whereas, the application of gold, mercury and platinum electrodes does not only increase the costliness of the protocols but are also associated with certain complexities [9]. Recently, the usage of modified electrodes have proven to be effective against the said restrains. Beitollahi, H., et al. (2013) [10] discussed the suitability of a benzoylferrocene (BF) modified carbon nanotube paste electrode (BFCNPE) as an effective electrode system for the determination of NAC. Similarly, Heli, H., et al. (2010) [11] described the application of iron(III) oxide core-cobalt hexacyanoferrate shell ($\text{Fe}_2\text{O}_3@\text{CoHCF}$) with carbon paste as a transducer for the effective determination of NAC. Furthermore, the usage of 1-benzyl-4-ferrocenyl-1H-[1,2,3]-triazole (BFT)/carbon nanotube modified glassy carbon electrode (BFT-CNT-GCE) has also been suggested by Salmanipour, A., et al. (2013) [12]. Lately, Beitollahi, H. and S. Nekooei (2016) [13] reported the capability of 1-[2-hydroxynaphthylazo]-6-nitro-2-naphthol-4-sulfonate/CuO nanoparticles modified carbon paste electrode (HNNSCCPE) for the determination of NAC. The report suggested CuO NPs as an effective

* Corresponding author.

E-mail address: rozturko@gmail.com (R. Ozturk).

electron facilitating materials for the oxidation of NAC. The application of metal oxide nanostructures with high surface area can provide greater active site density for the electrochemical oxidation of interest. In particular, CuO with its well-known p-type nature and distinguished catalytic characteristics has gained significant attention in regard to its usage as an alternate electrode material. Unlike other metal oxides (Co_3O_4 , NiO and Fe_3O_4), CuO can be synthesized easily without performing the high degree calcination step. This allows easy functionalisation of CuO nanomaterial with any desired functional moiety.

Since it's widely accepted that the presence of certain functional moiety at electrode/solution interface can significantly alter the observed electro-chemical response whereas, the shape of nanomaterial can largely influence electrocatalysis. This study discusses the fabrication of functionalized CuO using NAC, adipic acid (AS) and citric acid (CA) as effective growth modifiers. The functionalized nanostructures were then studied for their electrocatalytic potential towards the oxidation of *N*-acetyl-L-cysteine in aqueous buffer solution.

2. Experiments

2.1. Reagents and materials

All the utilized chemicals were analytical grade and used without any prior purification. Analytical grade copper chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), ammonia solution (NH_3) 32%, Adipic acid ($\text{C}_6\text{H}_{10}\text{O}_4$), citric acid ($\text{C}_6\text{H}_8\text{O}_7$), *N*-Acetyl-L-cysteine ($\text{C}_5\text{H}_9\text{NO}_3\text{S}$) and phosphate buffered saline (PBS) were purchased from Sigma Aldrich. Nafion® solution ($\text{C}_7\text{HF}_{13}\text{O}_5\text{S} \cdot \text{C}_2\text{F}_4$) (1.5%) was utilized as an ionic membrane where all the stock solution were prepared using de-ionized water.

2.2. Instrumentation

Morphological and structural characterization was carried using field emission scanning electron microscopy (HR-SEM) (JEOL JSM-7001F) and X-ray diffraction (XRD) (Bruker D-8). The electrochemical measurements were performed using a bipotentiostat model E-760 Texas, USA.

2.3. The growth of functionalized CuO nanostructures

The functionalized CuO nanostructures were grown using low-temperature hydrothermal treatment. In a representative experiment, specific amounts (1.68 g) of $\text{CuCl}_2 \cdot 5\text{H}_2\text{O}$ were homogenized with 1.0 mg of NAC, AS and CA in 100 ml of de-ionized water. The mixtures were then subjected to 5 ml of NH_3 (37%) with a gentle swirl followed by sealing the containers with aluminum foil to avoid any solvent spills. The containers were then placed in a pre-heated electrical oven for hydrothermal treatment under constant temperature of 85 °C for 8 h. After completion of the reaction, the grown materials were thoroughly washed with de-ionized water to remove any unwanted surface bound impurity.

2.4. The electrode modification

The electrode modification was achieved using simple drop casting methodology. Prior to surface modification of glassy carbon electrode (GCE), the representative nanomaterials were transformed into suspensions by sonication of 0.1 mg within 1 ml of methanol. The suspensions were then used for the modification of pre-polished GCE with specific

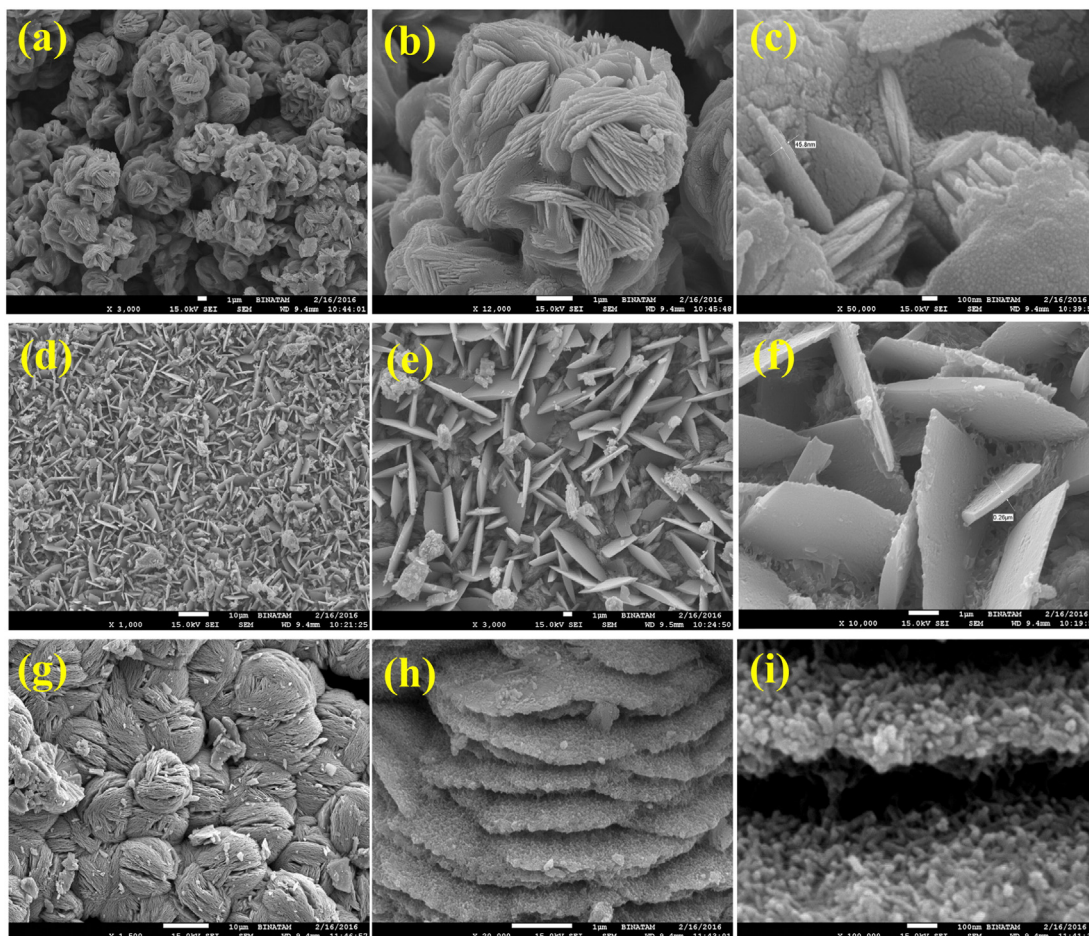


Fig. 1. HR-SEM image of CuO nanostructures synthesized using (a–c) NAC, (d–f) AS and (g–i) CA as effective growth modifiers.

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