Electrochimica Acta 246 (2017) 544–552

Contents lists available at ScienceDirect

Electrochimica Acta

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

Eco-friendly synthesis and morphology-dependent superior electrocatalytic properties of CuS nanostructures

A. Venkadesh, S. Radhakrishnan*, J. Mathiyarasu

Electrodics and Electrocatalysis Division, CSIR-Central Electrochemical Research Institute, Karaikudi-630003, Tamilnadu, India

ARTICLE INFO

Article history:
Received 13 April 2017
Accepted 14 June 2017
Available online 15 June 2017

Keywords:
copper sulphide
nanostructures
electrocatalyst
biosensor
glucose detection

ABSTRACT

Copper sulfide with desired structure is of special interest for electrocatalytical application due to their unique physicochemical properties, simple synthesis and less toxic in nature. In this study, simple and eco-friendly (without using any template or surfactant) route for the fabrication of copper sulfide nanostructure morphologies were tuned from cauliflower, microflower to nanoparticles inter-connected network-like structures by changing the polarity of solvent medium during solvothermal synthesis. However, to the best of our knowledge, no such kinds of special three types of CuS nanostructure with excellent electro-catalytic properties using only H_2O and C_2H_5OH as the solvents have been reported in the literature. The as-prepared different CuS nanostructure was characterized using FE-SEM, HR-TEM, XRD, XPS and cyclic voltammetry. This morphological alteration able to produce several precise nanostructures with improved electrocatalytic properties that led to an excellent performance towards enzymeless glucose oxidation. The CuS inter-connected nanoparticles modified electrode displayed a synergistic effect towards the oxidation of glucose (i_{pa}: 103 ± 5 μA) when compared to that of cauliflower (i_{pa}: 68 ± 3.7 μA) and microflower (i_{pa}: 60 ± 2.4 μA) modified electrode surfaces. Further, the CuS inter-connected nanoparticles modified electrode showed a wide linear range (2.0×10^{-5}–2.5×10^{-3} M), high sensitivity (1085 μA mM^{-1} cm^{-2}), low detection limit (2 μM), rapid response time (< 3s), good stability, selectivity and reproducibility. The obtained sensing parameters based on CuS inter-connected nanoparticles modified electrode were superior with many reports and also comparable with few reports in the available literatures.

1. Introduction

The development of simple and efficient glucose biosensor is considerable importance in clinical diagnostics, food industry, biotechnology and environmental protection [1]. Different methodologies were applied for the investigation of various glucose sensors. Electrochemical detection of glucose is more popular and huge interest because of its simplicity, inexpensive, reliable and real-time analysis [2–4]. Previous investigations on this area involve the use of glucose oxidase (GOx) enzyme, which effectively catalyses conversion of glucose into gluconolactone and enzyme based electrodes showed excellent sensitivity and stability [5]. However, the main shortcoming arises with the enzyme method is the loss of enzyme activity due to the adsorption of proteins from blood sample, high cost, complicated process for enzyme immobilization and susceptibility to temperature, pH, humidity etc. [6,7]. Therefore, enzymeless detection is more promising due to their simplicity, low cost, reproducible, higher stability in different environment and durability [8,9]. In recent years, many efforts have been made to develop enzymeless detection of glucose on noble metals, transition metal oxides/sulfides, carbon nanostructures and composites of these materials [10–16]. Among the various nanomaterials, copper based nanomaterials such as metallic copper (Cu), cupric oxide (CuO), cuprous oxide (Cu_2O) and copper sulfide (CuS) etc. has been deeply investigated for the non-enzymatic glucose detection due to their simple synthesis, low cost and excellent electrochemical and electro-catalytic properties [12,17–22]. In the recent past, CuS has been extensively used and studied for different potential applications including electrochemical biosensor, gas sensors, batteries, optical filter, solar cell and energy storage applications [23–25]. However, its performance in electrochemical application is mainly depends on its unique and special morphologies with huge electrolyte accessible area [26]. In this context, several researchers have been made considerable efforts for the fabrication of CuS nanomaterials with diverse morphologies including nanoflakes, microflower,

* Corresponding author.
E-mail address: s.rkn168@gmail.com (S. Radhakrishnan).

http://dx.doi.org/10.1016/j.electacta.2017.06.077
0013-4686/

hollow sphere, nanorods, nanotubes, etc. [23–39]. However, these morphologies were usually obtained with the support of surfactants/templates and expensive/hazardous chemicals. Hence, it is highly necessary to develop an efficient and eco-friendly protocol for the preparation of CuS nanostructures for practical applications.

Interestingly, the morphology of CuS can be simply controlled by changing the nature of the solvent [30]. The physicochemical property of the solvent strongly influences the reaction system by controlling the structure and morphology of the resulting product. However, there is very few studies are reported in the literature regarding the preparation of CuS by solvent-assisted synthesis [31,32]. Hence, it is highly desirable to fabricate CuS nanostructure for sensor applications by a simple and eco-friendly route with improved electrochemical performance.

In this work, we have reported an eco-friendly (without surfactant/templates and with water and/or ethanol as solvent) and simple (solvothermal method) synthesis of CuS with different nanostructures (cauliflower, microflower and nanoparticle interconnected network-like structures) by simply altering the solvent during solvothermal synthesis. The obtained nanostructures of CuS exhibited interesting electrocatalytic properties for enzymeless detection of glucose.

2. Experimental

2.1. Materials and reagents

Copper (II) acetate monohydrate and Nafion (5 wt%) were purchased from Sigma Aldrich. Glucose, thiourea and ethanol were obtained from SRL, India. All the reagents were of analytical grade and used without further purification. All aqueous solutions were prepared with deionized (DI) water (18.2 MΩ.cm, Elix water system).

2.2. Apparatus and measurements

The phase purity and crystalline nature of CuS products was investigated using powder X-ray diffraction technique (Bruker D8 Advance) using CuKα radiation (λ = 1.5418). The surface morphologies of the CuS products were characterized using a field emission-scanning electron microscope (FE-SEM; Carl Zeiss AG, Supra 55VP) with an accelerating voltage of 30 kV and high resolution transmission electron microscopy (HR-TEM) using a Tecnai G2F20S-TWIN at 200 kV (operating voltage). The electronic states of the as-prepared materials were studied by X-ray photoelectron spectroscopy (XPS: ESCA 2000 spectrometer). The electrochemical experiments, including cyclic voltammetry (CV), linear sweep voltammetry (LSV), and chronoamperometry (CA) were performed with a PalmSens electrochemical workstation at room temperature using a conventional three-electrode system composed of CuS modified glassy carbon electrode (GC, 3 mm in diameter) as a working electrode, a Ag/AgCl (3 M KCl) as the reference electrode and a platinum wire as an auxiliary electrode. All electrochemical measurements were carried out in 0.1 M NaOH solution.

2.3. Preparation of CuS nanostructure

Solvothermal method was employed to synthesis copper sulfide material. In a typical synthesis, copper acetate (0.7 mmol) and thiourea (2.1 mmol) were dissolved in 70 mL of solvent (water and/or ethanol). The homogenous reaction mixture was then transferred into a 100 mL Teflon-lined stainless-steel autoclave. The autoclave was tightly closed and kept at 160 °C for 16 h, and then cooled to room temperature. The residues obtained were centrifuged and washed several times sequentially with DI water/isopropanol and dried under vacuum. The as-prepared CuS from water, ethanol and water/ethanol mixture (1:1) were designated as CuS-W, CuS-E and CuS-W/E, respectively (Fig. 1).

2.4. Electrode preparation and modification for glucose electro-oxidation

The glassy carbon (GC) electrode surface modified with CuS products was prepared by simple drop-cast method. Initially, the GC electrode surface for each experiment was mechanically cleaned with alumina powders (0.3 and 0.5 μM, respectively), and rinsed with deionized (DI) water followed by sonication with ethanol-water mixture. Finally, 10 μL aliquot of as-prepared CuS

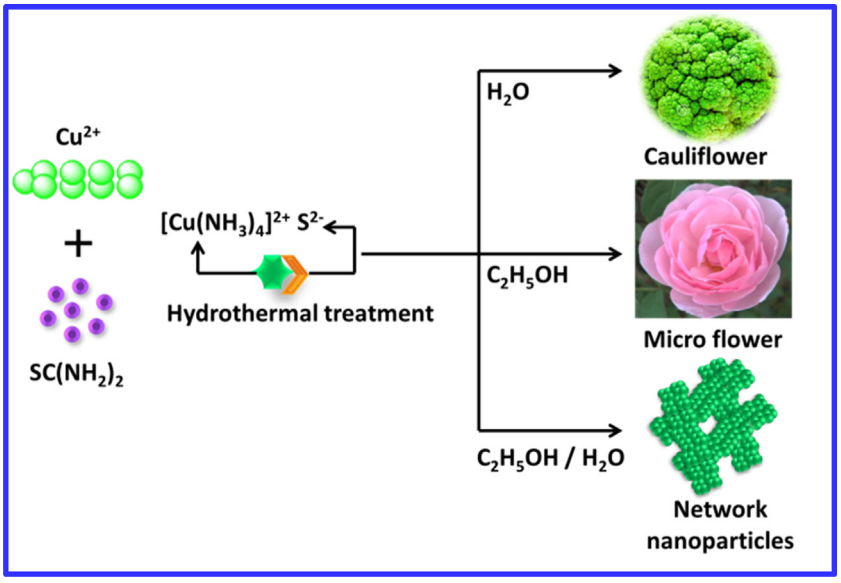

Fig. 1. Schematic illustration of the surface morphological alteration caused by changing the polarity of solvent.