



# Sensitive determination of caffeine by copper sulphide nanoparticles modified carbon paste electrode



Mallappa Mahanthappa<sup>a,b,c</sup>, Shivaraj Yellappa<sup>a,\*</sup>, Nagaraju Kottam<sup>b</sup>,  
Chiranjeevi Srinivasa Rao Vusa<sup>d</sup>

<sup>a</sup> Department of Chemistry, Government Science College, Bangalore 560 001, India

<sup>b</sup> Department of Chemistry, M.S. Ramaiah Institute of Technology, Bangalore 560 054, India

<sup>c</sup> Visvesvarayya Technological University, Research Resource Centre, Belgaum 590 018, India

<sup>d</sup> Bio-sensors division, CSIR-Central Electrochemical Research Institute, Karaikudi-630003, India

## ARTICLE INFO

### Article history:

Received 18 February 2016

Received in revised form 7 July 2016

Accepted 14 July 2016

Available online 15 July 2016

### Keywords:

CuS NPs

Co-precipitation method

CuS NPs MCPE

Electrocatalytic activity

## ABSTRACT

Copper sulphide nanoparticles (CuS NPs) were synthesized by simple co-precipitation method in aqueous media using starch as a biopolymer. The obtained product was characterized by XRD, SEM, EDX, TEM, FTIR and UV–vis techniques. The particle size was determined by TEM analysis and found to be in the range 20–50 nm. CuS NPs modified carbon paste electrode (CuS NPs MCPE) was employed to determine caffeine (CAF) by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) methods. The CuS NPs MCPE showed better electrocatalytic activity towards the oxidation of CAF, which was confirmed by enhance in the oxidation peak current and decrease in oxidation peak potential. Furthermore, in electrochemical impedance (EI) studies, the charge transfer resistance ( $R_{CT}$ ) at CuS NPs MCPE (12.1 k $\Omega$ ) decreases as compared to bare CPE (42.6 k $\Omega$ ), which suggests that CuS NPs improves the charge transfer capacity of CPE. Electron transfer kinetic parameters, sensitivity and surface active area of the electrode were determined. Under experimental conditions, the oxidation current of CAF was proportional to its concentration from 2  $\mu$ M to 120  $\mu$ M. The detection limit was found to be  $18 \times 10^{-9}$  M. The developed method was successfully applied to determine CAF content in food samples with appreciable results.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

In recent scenario, there is a growing interest in the development of the semiconductor nanostructure materials owing to their distinctive physical and chemical properties. Among the chalcogenides, copper sulphide ( $\text{Cu}_x\text{S}$ ) has attracted extensive attention due to its unique optical and electrical properties [1]. The attractiveness is also arises due to its low synthetic cost, solution processing ability and the dependence of optoelectronic properties as a function of size, shape, doping and surface chemistry. Copper sulphide exists in various stoichiometric compositions, morphology and exhibits non-linear optical property [1,2]. In particular, the band gap of  $\text{Cu}_x\text{S}$  can be varied in a wider range (1.2–2.5 eV) with different stoichiometric compositions ( $x=1-2$ ), making it a highly desirable material for solar cells, non-volatile memory devices and gas sensing applications. Furthermore,  $\text{Cu}_x\text{S}$  is a potentially interesting material for cold cathodes and lithium ion batteries [3,4].

Several methods have been reported for the synthesis of CuS NPs such as sonochemical, sol-gel, hydrothermal method *etc* [4–6].

Caffeine (CAF) is a natural alkaloid which belongs to a class of xanthenes derivatives and found in various food and beverages such as coffee, tea, coca-cola, cocoa beans, yerbamate, guarana berries and chocolates; and even in various drugs. CAF acts as a natural pesticide in plants since it paralyzes and kills certain insects which destroy the plants. CAF has several physiological effects in humans such as stimulation of central nervous system, gastric acid secretion, diuresis and cardiovascular systems [7–9]. Thus, the development of sensitive, fast and cost effective method for the evolution and quantification of CAF is a significant field of research.

Several methods have reported for detection of CAF such as chromatographic and spectroscopic techniques [10,11] but they have their own disadvantages such as low range of detection and low selectivity, complexity in techniques, expensive instrumentation, requires highly skilled technicians *etc*. Whereas electrochemical method is simple, shows high sensitivity, good stability, less expensive *etc* [12] which makes it more promising technique for the detection of CAF. The electrochemical detection of CAF at bare electrode is less effective due to oxidation which occurs

\* Corresponding author.

E-mail address: [shivaraj.y@rediffmail.com](mailto:shivaraj.y@rediffmail.com) (S. Yellappa).

at high positive potential range and may overlap with the electrochemical reactions, limiting potential window from the anodic side and often gives low reproducible analysis [13]. Therefore, these limitations can be overcome by using electrodes such as boron doped diamond electrode (BDDE), pencil graphite electrode (PGE) and chemically modified electrodes [14–22].

In the present work, CuS NPs were synthesized by simple co-precipitation method at low temperature. Electrochemical study of CAF at CuS NPs MCPE was investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). CuS NPs MCPE shows better electrocatalytic activity towards CAF oxidation. Electron transfer kinetics, sensitivity, linear range, detection limit and interfacial properties of CuS NPs MCPE have been discussed.

## 2. Experimental

### 2.1. Materials

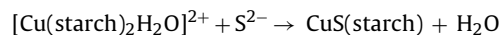
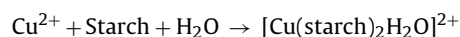
CAF was purchased from Sigma-Aldrich. Cupric chloride, biopolymer starch and other reagents were purchased from Merck and Sdfine chemicals. 0.1 M acetate buffer solution (ABS) was used as a supporting electrolyte throughout the experiment and different pH was adjusted by adding acetic acid and sodium hydroxide in 0.1 M sodium acetate. All the reagents were prepared using doubly distilled water.

### 2.2. Synthesis of CuS nanomaterials

CuS NPs were prepared in solution phase by co-precipitation method. 0.1 M solution of cupric chloride was taken in a beaker, to which 3% starch solution (act as stabilizing as well as capping agent, which controls the particle size) was added drop wise by constant stirring. Then, 0.1 M Na<sub>2</sub>S solution was added drop wise to the above mixture until a black coloured precipitate of CuS was obtained. Stirring was continued for another 1 h by maintaining the temperature at 60 °C. The resulting precipitate was filtered, washed with distilled water, 1:1 mixture of water-ethanol and dried at 170 °C for about 3 h. The obtained product was characterized by various techniques.

### 2.3. Reaction mechanism

Starch is a natural biopolymer made up of two components amylose and amylopectin which consists of α-glucose units in the carbon <sup>1</sup>C<sup>4</sup> conformation. The semicrystalline structure of starch is lost when starch becomes soluble in water at 75 °C. The copper cations are attracted to the O–H group of starch after the addition of starch to Cu (II) salt solution to form Cu(OH)<sub>2</sub>. To this solution sodium sulphide is added to form a black precipitate of CuS. On heating small amylose molecules forms a network that holds the water molecules and increases the mixture viscosity. The obtained product forms covellite phase of CuS NPs [23]. The morphology and phase transformation in the present system could be described according to XRD, SEM and other techniques.



The overall chemical reactions involved can be described as given below

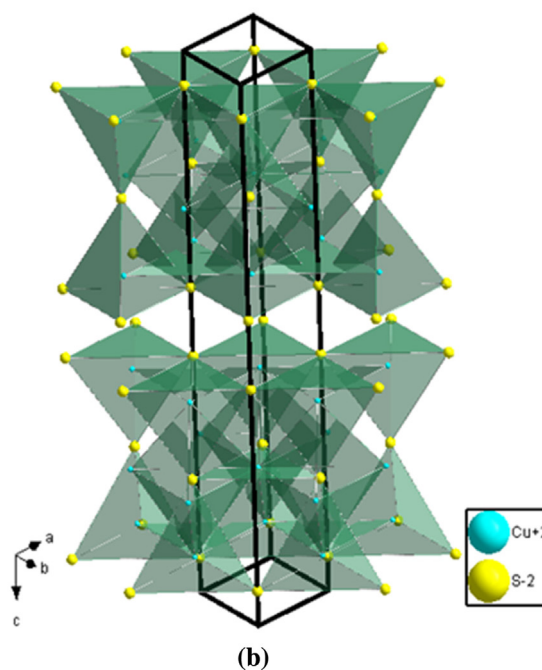
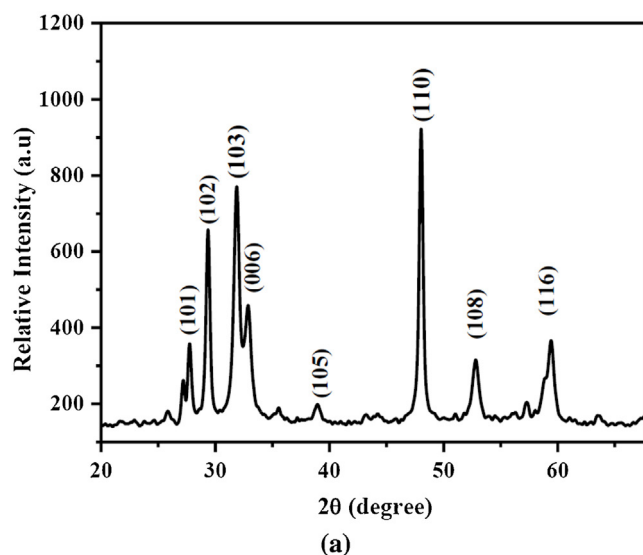
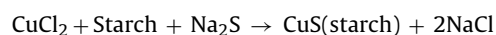


Fig. 1. (a) Powder XRD pattern and (b) Crystal structure (covellite hexagonal) of CuS NPs.

### 2.4. Characterization of copper sulphide nanoparticles

Powder XRD of CuS NPs were recorded on Philips X'pert PRO X-ray diffractometer with graphite monochromatized CuKα radiation ( $k = 1.541 \text{ \AA}$ ) in the range of 10°–80° with 2°/min scanning rate. The morphology of the CuS NPs were examined by JEOL-JSM-6490 LV scanning electron microscope and CM12 Philips transmission electron microscope equipped with EDX (Kevex Sigma TM Quasar, USA). FT-IR spectra of pure starch and CuS NPs in starch matrix were recorded using Agilent carry-630 FT-IR spectrophotometer (Australia) over the range 400–4000  $\text{cm}^{-1}$ . In addition, the optical properties of CuS NPs were analyzed by UV-1800 UV–vis absorption spectrophotometer (Shimadzu, Japan).

Cyclic voltammetry (CV), differential pulse voltammetry (DPV) and electrochemical impedance (EI) measurements were performed using a CH-Electrochemical analyzer (CHI 6039E, USA) connected with a three-electrode cell. A bare carbon paste electrode (BCPE) and modified CPE were used as working electrode. A plat-

Download English Version:

<https://daneshyari.com/en/article/736479>

Download Persian Version:

<https://daneshyari.com/article/736479>

[Daneshyari.com](https://daneshyari.com)