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Sunlight assisted synthesis of silver nanoparticles in zeolite matrix and study of its application on electrochemical detection of dopamine and uric acid in urine samples

S. Meenakshi [a], S. Devi [a], K. Pandian [a,*], R. Devendiran [b], M. Selvaraj [b]

[a] Department of Inorganic Chemistry, University of Madras, Guindy Campus, Chennai 600 025, India
[b] Department of Chemistry, Guru Nanak College, Velachery, Chennai 600 042, India

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ABSTRACT

Sunlight assisted reduction of silver ions were accomplished for the synthesis of silver nanoparticles incorporated within the mesoporous silicate framework of zeolite Y. The zeolite-Y and AgNP/Zeo-Y were characterized by field emission scanning electron microscopy, transmission electron microscopy, N_2 adsorption-desorption BET isotherm and X–ray diffraction techniques. The incorporation of silver nanoparticles within the porous framework was further confirmed by cyclic voltammetry and electrochemical impedance spectroscopy. An enhanced electrocatalytic oxidation of biologically important molecules like dopamine and uric acid using AgNP/Zeo-Y modified glassy carbon electrode has been developed. A simultaneous oxidation of DA and UA peaks were obtained at +0.31 V and +0.43 V (vs. Ag/AgCl) using AgNP/Zeo-Y/GCE under the optimum experimental condition. A well-resolved peak potential window (~120 mV) for the oxidation of both DA and UA were observed at AgNP/Zeo-Y/GCE system. The calibration curves for DA and UA were obtained within the dynamic linear range of 0.02×10^{-6} to 0.18×10^{-6} M ($R^2 = 0.9899$) and 0.05×10^{-6} to 0.7×10^{-6} M ($R^2 = 0.9996$) and the detection limits were found to be 1.6×10^{-8} M and 2.51×10^{-8} M by using differential pulse voltammetry (DPV) method. The proposed method was successfully applied for the determination of both DA and UA in human urine samples with a related standard deviation was <3%, and n = 5 using the standard addition method.

1. Introduction

Zeolite is a mesoporous alumina silicate based solid materials and its contain well defined open-pore structure, with often the tunable pore size and they are very attractive host materials for developing nanocomposites because of their ability to selectively exchange and integrate transition metal cations within their cages and interconnecting channels [1]. The metal modified porous materials have been used for the wide range of applications like catalysis [2,3], anti-bacterial materials [4], fuels [5], water treatment [6,7], and biosensors [8–12]. Recently, zeolite modified electrodes (ZMEs) have continued to be a major concern because of its surface area, porous nature, surface functionalization and chemical inertness [13–15]. ZMEs are widely used in ion-exchange [16], electrocatalysis and electroanalytical devices with better sensitivity [17], high thermal and chemical stability [18]. Nowadays, the ZMEs were accomplished in various routes through copper doped zeolite expanded graphite epoxy electrode [19], iron-ion doped natrolite zeolite-MWCNT modified GCE [20], Ag-doped zeolite expanded graphite-epoxy composite electrode [21], methylviologen supported on zeolite Y modified electrode [22], graphite-zeolite modified electrode [23], mesoporous carbon [24], cytochrome c immobilized on NaY zeolite [25], methylene blue incorporated into mordenite zeolite [26] bismuth modified zeolite doped CPE [27], $NiCo_2/O_4$/nano-ZSM-5 nanocomposite [28] and Ru-red incorporated zeolite modified CPE [29].

Dopamine (DA) is usually coexisting with uric acid (UA) in biological fluids which are playing an important role in human metabolism [30]. The abnormal concentration level of these molecules will lead to certain diseases such as schizophrenia, Parkinson's disease, hyperuricemia, gout and Pneumonia [31,32]. Therefore, the development of selective and sensitive method is important to determine the concentration level of DA and UA accurately. The electrochemical methods are accessible for sensing and quantification of DA and UA due to simple, more accurate with lower detection limits, high electrocatalytic activity and large potential window [33]. However, the oxidation of DA and UA are occurring in the same potential region at conventional electrodes. To overcome this problem, various kinds of chemically modified electrodes were utilized to resolve well-defined peak separation between DA and UA system. For example, copper nanoparticles incorporated polypyrrole

* Corresponding author at: Department of Inorganic Chemistry, University of Madras, Chennai 600 025, India.
E-mail address: jeevapandian@yahoo.co.uk (K. Pandian).

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film [34] and gold nanoparticles/choline modified electrodes [35] were used for the assay of DA and UA. Lin et al., demonstrated the PtNPs deposited polydopamine coating on MWCNT for simultaneous detection of DA and UA [36]. Recently self-assembled monolayer of cysteamine functionalized MWCNT on gold have shown for the enhanced simultaneous detection of both DA and UA [37].

Silver nanoparticles have been concerned worldwide research interest due to their unique physical and chemical properties which lead to plentiful potential applications like catalysis [38], optics [39], biosensors [40], electronics [41] and antimicrobial agents [42] etc. Several methods have been reported for synthesis of silver nanoparticles for instant thermal method [43], photochemical [44], microwave irradiation [45], green synthesis [46] and microemulsion [47]. In this present work, we proposed a sunlight assisted reduction method to incorporate silver nanoparticles into the mesoporous zeolite matrix. Various analytical methods were used for characterization of silver nanoparticles incorporated zeolite to understand the optical and electrochemical behavior of the system. The electrocatalytic oxidation behavior of AgNP/Zeo-Y modified glassy carbon electrode (GCE) was tested against the electrochemical oxidation of DA and UA in phosphate buffer solution (PBS) medium. Enhanced oxidation peak current values were observed at modified electrodes in both analytes with greater sensitivity. Thus, the present method can be considered as an efficient for simultaneous detection of DA and UA in human urine samples. The electrode stability and interference of other biological important molecules were also tested.

2. Experimental methods

2.1. Chemicals

Dopamine hydrochloride, uric acid and silver nitrate ($AgNO_3$) were received from Sigma Aldrich (Bio Corporals, Chennai, India). Zeolite Y was obtained from Hi-Media (Sri Hari Chemicals Pvt. Ltd., Chennai, India). Potassium hydrogen phosphate (K_2HPO_4), potassium dihydrogen phosphate (KH_2PO_4) and potassium chloride (KCl) were received from SRL Pvt. Ltd. (Vijaya Scientific, Chennai, India). All other chemicals obtained from commercial sources without any further purification processes. Double distilled (DD) water was used for the preparation of all stock solutions.

2.2. 2.2. Synthesis of silver nanoparticles using zeolite Y as a template

0.03 gof silver nitrate was dissolved in 20 mL of distilled water. Then 1% ammonium hydroxide solution was added drop wise, until the color of the solution change from greenish gray to colorless. 1 g of zeolite Y was added into the above reaction mixture and then stirred under sunlight for 1 h. Finally, the product was collected and washed several times with distilled water, centrifuged and then dried at room 40 °C.

2.3. Instrumental methods

Morphological and structural investigations are carried out using field emission scanning electron microscopy (FE-SEM, SU6600, Hitachi, Japan) and transmission electron microscopy (TEM, JEM 2100, 200KeV, JEOL, USA). UV–Visible diffuse reflectance spectrophotometer was carried out using a Perkin-Elmer Lambda 650. Nitrogen adsorption measurements were performed at 77.3 K by a Quantachrome Instruments, Autosorb-IQ volumetric adsorption analyzer. The sample was out gassed at 300 K for 3 h in the degas port of the adsorption apparatus. The specific surface area of each zeolite was calculated from the adsorption data points obtained at P/P_0 using the Brunauer-Emmett-Teller (BET) equation. The pore diameter was estimated using Barret-Joyner-Halenda (BJH) method. The XRD patterns of the powdered samples were recorded using X PERT-PRO diffractometer with a Cu Kα Radiation ($\lambda = 1.5406$ Å). Electrochemical experiments were carried out using Gamry, USA model 330 including PV220 software and a CHI 660A electrochemical instrument, USA. A three electrode system consisting of GCE of 3 mm of the geometrical surface area was purchased from BAS, Pvt. Ltd., USA. The Ag/AgCl with 3 M KCl was used as a reference electrode and platinum wire as a counter electrode. Bioanalytical system (BAS, USA) polishing kit was used to polish GCE surface. The surface of GCE was cleaned first mechanically by polishing with 500 μm alumina powder, washing with DD water and then sonicated for 5 min. GCE substrate was modified with AgNP/Zeo-Y solution (5 μL) by a drop casting method using micro-syringe and dried under room temperature.

Electrochemical impedance spectroscopy (EIS) measurements were performed with the use of CHI-660A electrochemical instrument. The electrolyte was prepared by using 0.1 M KCl containing 10 mM $[Fe(CN)_6]^{3-/4-}$ redox probe. All solutions were purged with high purity nitrogen gas for about 10 min before performing all electrochemical experiments. All experiments were carried out at room temperature.

A buffer solution of pH 7.0 was prepared by mixing of 0.1 M KCl, 0.1 M KH_2PO_4 and 0.1 M K_2HPO_4 in 250 mL standard flask using DD water. The pH of the solution was checked using an Elico-pH meter at room temperature. The stock solution of dopamine (0.1 M) and uric acid (0.1 M) were prepared freshly with deoxygenated DD water and stored in a dark room at 5 °C.

3. Results and discussion

3.1. Synthesis and characterization of AgNP incorporated with zeolite-Y

The sunlight assisted photochemical reduction method was adapted to synthesis AgNP incorporated on zeolite Y system. The photochemical conversion of silver ion into silver nanoparticles is characterized using various instrumental methods like FE-SEM, TEM, XRD, BET and DRS-UV spectroscopy. Fig. 1 depicts the FE-SEM images of zeolite Y (Fig.1

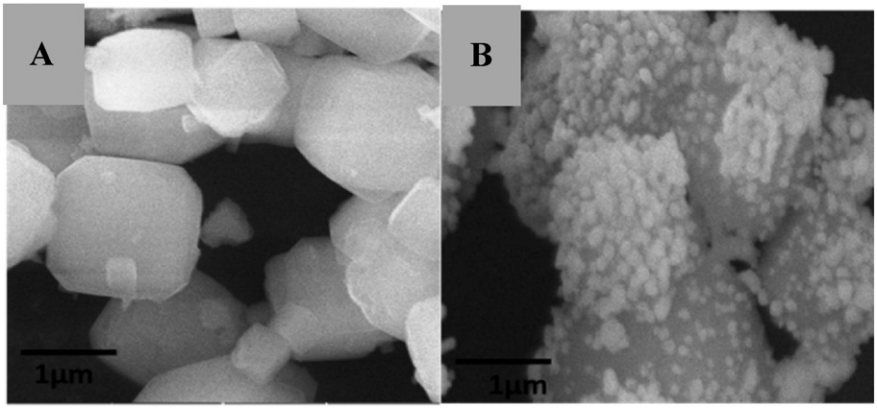

Fig. 1. FE-SEM images for Zeolite-Y (A) and AgNP/Zeo-Y (B).