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Gold-copper bimetallic nanoparticles supported on nano P zeolite modified carbon paste electrode as an efficient electrocatalyst and sensitive sensor for determination of hydrazine

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ABSTRACT

In this report, a facile, efficient and low cost electrochemical sensor based on bimetallic Au-Cu nanoparticles supported on P nanozeolite modified carbon paste electrode (Au-Cu/NPZ/CPE) was constructed and its efficiency for determination of hydrazine in trace level was studied. For this purpose, agro waste material, stem sweep ash (SSA) was employed as the starting material (silica source) for the synthesis of nano P zeolite (NPZ). After characterization of the synthesized NPZ by analytical instruments (scanning electronic microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and Fourier transform infrared (FT-IR) spectroscopy), construction of Au-Cu/NPZ/CPE was performed by three steps procedure involving preparation of nano P zeolite modified carbon paste electrode (NPZ/CPE), introducing Cu^{+2} ions into nano zeolite structure by ion exchange and electrochemical reduction of Cu^{+2} ions upon applying constant potential. This procedure is followed by partial replacement of Cu by Au due to galvanic replacement reaction (GRR). The electrochemical properties of hydrazine at the surface of Au-Cu/NPZ/CPE was evaluated using cyclic voltammetry (CV), amperometry, and chronoamperometry methods in 0.1 M phosphate buffer solution (PBS). It was found that the prepared sensor has higher electrocatalytic activity at a relatively lower potential compared to other modified electrodes including Au/NPZ/CPE, Cu/NPZ/CPE, Au-Cu/CPE and etc. Moreover, the proposed electrochemical sensor presented the favorable analytical properties for determination of hydrazine such as low detection limit (0.04 μM), rapid response time (3 s), wide linear range (0.01–150 mM), and high sensitivity (99.53 μA mM^{-1}) that are related to the synergic effect of bimetallic of Au-Cu, porous structure and enough surface area of NPZ. In addition, capability of Au-Cu/NPZ/CPE sensor was successfully tested in real samples with good accuracy and precision.

1. Introduction

Hydrazine is an important example of NH_2 containing compounds with high hydrogen storage capability which is extensively used in numerous scopes such as rocket propellant, chemical reactions, industrial factories, corrosive inhibitor and photography chemicals (Yang et al., 2015; Shuang et al., 2016; Devasenathipathy et al., 2014). Notably, it has acquired considerable attention as promising fuel candidate in fuel cells due to high energy, high power density, generation of environmentally friendly nitrogen and water as products and easily availability (Liu et al., 2013a, 2013b; Serov and Kwak, 2010). Nevertheless, it is well known that acute exposure to hydrazine can cause injury to humans such as dermal corrosion to mutagenesis, cancer and as well irreversible deterioration of nervous system once absorbed through the skin (Zhang et al., 2015). Hence, intensive efforts including development of high sensitive analytical methods such as chemiluminescence (Safavi and Karimi, 2002), chromatography (Wang et al., 2016), spectrophotometry (Gu et al., 2016) and fluorescence (Bharath et al., 2015) for monitoring trace amount of hydrazine have been done. It is defined that efficiency of these methods is limited due to high cost, complication and critical operation procedures (Radhakrishnan et al., 2014). Electrochemical sensors are one of the simple, sensitive and selective tools which can be considered as an alternative analytical instrumental to obtain low detection limit, good sensitivity, fast response and large linearity over concentration.

In recent years, noble metals and their bimetallic alloys such as Pd, Pt and Au have been conducted toward the preparation of modified electrodes for the determination of hydrazine (Tamasauskaite-

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Tamasiunaite et al., 2014; Afzal et al., 2017; Ensafi et al., 2016). They have high conductivity and electrocatalytic activity which greatly facilitates the electron transfer reactions of various analytes (Gupta and Ganesan, 2015). Bimetallic Au-Cu catalysts have attracted substantial interest for various important analytes and reactions in recent years compared to their single-metal analogues due to both decrease in the required amount of Au and synergic electrocatalytic effects (Hosseini et al., 2013; Mierczynski et al., 2016; Krasimir et al., 2016).

A suitable catalyst support causes to the high dispersion of catalyst. The profitable catalyst support can prevent the aggregation of nanoparticles and also improve the utilization of active components demonstrating promising high electrocatalytic activity towards the oxidation of hydrazine (Dong et al., 2010). Nanozeolites as porous crystalline aluminosilicates materials with open structures and dimensions less than 100 nm with higher surface area as well as better accessibility to internal micropores than traditional zeolites comprise a promising class of new support and present attractive materials in the electrode surface modification for designing new electrochemical sensors. The driving force for widespread utilization of zeolites is the mobility of cations in zeolite structure achieving unique ion-exchange and the catalytic properties of zeolite. Among zeolites, P zeolite, as one of the oldest synthesized zeolites, possess high exchange ability and adsorption capacity and is easily adapted to the needs of industry without the use of anticoagulation agents (Behin et al., 2016).

Recently, Ahmed et al. (2018) prepared bimetallic and three metallic zeolite-supported catalysts in steam reforming of tar using simulated-toluene as model compound. Also, up to now, zeolite-supported bimetallic electrodes such as Pt-Ru(HY) (Samant and Fernandes, 2004) and Ni(II)Co(II) salen complexes encapsulated in mesoporous zeolite A (Wang et al., 2015) have been used in methanol electrooxidation. Therefore, it seems that zeolite-supported bimetallic modified electrodes can provide interesting electrochemical sensors and biosensors with favorable analytical and electrochemical properties due to the high catalytic activity of bimetallic species and porous architecture endowed by zeolites.

The present study presents a simple, economic, fast, selective and precise sensor with remarkable electrocatalytic activity for the detection the trace amount of hydrazine. Previously, we introduced for the first time a facile and effective cost value synthesis of nano P zeolite (NPZ) from stem sweep ash (SSA) as silica source and prepared modified electrode based on Ni doped NPZ to study the oxidation of methanol and formaldehyde (Azizi et al., 2016; Azizi et al., 2014). In the present article to make the process more cost effective, we persuaded to use agro waste as a starting material in zeolite synthesis procedure and then, bimetallic Au-Cu nanoparticles supported on P nanozeolite modified carbon paste electrode (Au-Cu/NPZ/CPE) was prepared via a simple galvanic replacement technique for determination of hydrazine (Tamasauskaite-Tamasiunaite et al., 2013a, 2013b, 2013c). To the best of our knowledge, there is no report on P zeolite loaded with bimetallic Au-Cu as electrode material toward the detection of hydrazine.

2. Experimental

The detailed information about the chemical and reagents, apparatus and procedures, support preparation can be accessed in with in Supporting data Section S1. Construction of the sensor is achieved by immersion of nano P zeolite modified carbon paste electrode (NPZ/CPE) in copper sulfate solution (0.5 M) for 10 min to enter Cu^{+2} into nanozeolite structure through the diffusion of Cu^{2+} into the pores of zeolite during the exchange with Na^{+}. The mechanism of ions exchange was investigated and the following mechanism was suggested (Rolison and Bessel, 2000):

$$Cu^{2+}{}_{(z)} + 2E^{+}{}_{s} \rightarrow Cu^{2+}{}_{(int)} + 2E^{+}{}_{(z)} \quad (1)$$

where the descriptors z, s and int describe for zeolites, solution and zeolite-solution interface, respectively. Also E^{+} is referred to electrolyte cation. The electrode surface was washed with double distilled water several times to acquire surface without any adsorbed species or occluded material. Then, by applying the constant potential (− 0.17 V vs. Ag|AgCl|KCl (3 M)), the reduction of Cu^{+2} was carried out which leads to the formation Cu° (Cu-NPZ/CPE). To create Au -Cu alloy, Cu-NPZ/CPE was immersed into slowly stirring H_2SO_4 (0.5 M) solution containing 5 mM of $HAuCl_4$ at 25° C to perform galvanic replacement reaction (GRR) between Cu species and Au^{+3} ions (Fig. S1). Finally, the prepared Au-Cu/NPZ/CPE was rinsed with double distilled water. According to following GRR, the deposition of Au particles is occurred on the surface of the electrode:

$$2Au^{+3} + 3Cu \rightarrow 2Au + 3Cu^{+2} \quad (2)$$

GRR was occurred at open circuit condition for 2 min via 6 electrons transfer. To evaluate NPZ effect, CPE modified with bimetallic Au-Cu (Au-Cu/CPE) was fabricated with the same approach.

3. Result and discussion

3.1. Characterization

The typical synthesis of silica and nanozeolite as well as the detailed information about the characterization of SSA, silica and NPZ were presented in our previous paper (Azizi et al., 2016; Azizi et al., 2014). Dynamic light scattering (DLS) measurements provide estimation of average hydrodynamic diameter of the majority of the NPZ and the results are reported in Supporting data (Section S.2.1.1 and Fig. S2A, B and C). To more investigate the structural information, TEM images of synthesized zeolite are shown in Fig. 1A and B. They indicate the synthesis of nanoparticles in the range of 30–70 nm.

Fig. 1C and D illustrate FESEM images of NPZ/CPE and Au-Cu/NPZ/CPE, respectively. A dispersion of NPZ in the graphite powder is observed (Fig. 1C). In Fig. 1D the change in morphology of surface and formation of some connected particles, probably Au-Cu nanoparticles, is observed. To present the bulk composition of the prepared electrode, the spectrums and elemental analysis data of electrodes are shown in Fig. 1E and F. The absence of Au and Cu species on the NPZ/CPE (Fig. 1E) and the presence of Au and Cu species on the Au-Cu/NPZ/CPE (Fig. 1F) give evidences for the formation of desired samples. Elemental analysis data obtained from EDS for NPZ/CPE, Cu/NPZ/CPE and Au-Cu/NPZ/CPE are listed in Supporting data Section S.2.1.2 and Table S1. It can be found that 0.98 wt% of Cu exist in Cu/NPZ/CPE, much of them are replaced by Au and only 0.01 wt% of Cu remains on the Au-Cu/NPZ/CPE. It should be pointed out that the high carbon contents in all samples are due to the presence of graphite in carbon paste.

3.2. Electrochemical study

3.2.1. Electrochemical characteristics of modified electrode

The electrochemical study were performed in three electrodes configuration in the electrochemical workstation containing an Ag|AgCl|KCl (3 M) electrode as reference electrode, a platinum wire as an auxiliary electrode and a modified CPE as a working electrode. Fig. 2A shows the successive cyclic voltammograms of Cu-NPZ/CPE in aqueous solution of 0.5 M H_2SO_4 at the scan rate of 50 mV s^{-1}. At the first scan, the appearances of redox peaks with high current densities at 0.3 and −0.13 V describe Cu oxidation and Cu^{+2} reduction, respectively (Zheng et al., 2013). Additionally, along with the increase of scan cycle, both peaks decreased and almost disappeared at the 30th scan which confirm the dissolution of Cu. Based on the first Cu anodic stripping peak and also using atomic ratio between Cu and Au obtained from EDS analysis, the Au loading on the electrode could be estimated. According to Faradic law, the number of Cu moles can be calculated as expressed in Eq. (3):