Sensors and Actuators B 211 (2015) 476–488

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

Simultaneous determination of epinephrine, paracetamol, and folic acid using transition metal ion-exchanged polyaniline–zeolite organic–inorganic hybrid materials

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ARTICLE INFO

Article history:
Received 4 December 2014
Received in revised form 18 January 2015
Accepted 21 January 2015
Available online 30 January 2015

Keywords:
Nanocrystalline zeolite
Polyaniline
Electro-catalytic oxidation
Bio-molecules
Simultaneous determination

ABSTRACT

Transition metal ion-exchanged polyaniline–zeolite (M^{2+}-PANI-Nano-ZSM-5, where $M^{2+} = Cu^{2+}$, Ni^{2+}, Co^{2+}, Fe^{2+}, and Mn^{2+}) organic-inorganic hybrid materials were synthesized and characterized by the complementary combination of X-ray diffraction, N_2-adsorption, scanning electron microscopy, FT-IR and thermo gravimetric techniques. Electrochemical sensors based on M^{2+}-PANI-Nano-ZSM-5 was developed for the simultaneous determination of epinephrine, paracetamol, and folic acid. Among the materials investigated in this study, Cu^{2+}-PANI-Nano-ZSM-5 modified glassy carbon electrode exhibited the highest electro-catalytic activity with excellent stability, sensitivity, and selectivity. Under the optimum conditions, a wide linear range was obtained from 10 nM–600 μM for epinephrine, 15 nM–800 μM for paracetamol, and 13 nM–700 μM for folic acid. The detection limit was found to be 4, 8, and 5 nM for epinephrine, paracetamol, and folic acid, respectively. The analytical performance of the developed sensor was demonstrated in the determination of epinephrine, paracetamol, and folic acid in the commercial pharmaceutical preparations (epinephrine injection, paracetamol, and folic acid tablets) with satisfactory recovery. The proposed methodology provides promising application in drug analysis.

1. Introduction

Organic-inorganic hybrid nanocomposite materials have attracted significant attention due to their remarkable physico-chemical properties [1–3]. Nanocomposite materials have shown promising applications in the interdisciplinary research areas with significantly improved activity because of the synergistic contribution provided by the constituent components of the nanocomposite material. In general, conducting polymers exhibit potential applications in electronics, photonics, and electrochemical sensors [4]. Similarly, inorganic porous materials exhibit important applications in catalysis and electro-catalysis [5,6]. Our research group is interested in developing polyaniline based conducting polymers, zeolites, and metal oxides [7–16].

Zeolites play an important role in catalysis due to its microporous nature and shape selectivity. However, its application as electrochemical sensor in the detection of large molecules is limited due to the low surface area and microporous nature. To overcome this limitation, zeolites with interconnected intra or inter-crystalline mesoporosity have been developed [17,18]. Several attempts have been made for the preparation of nano-sized zeolites using soft and hard templates [5,19,20]. Our group has developed several soft-template based synthesis methodologies to prepare nanocrystalline/mesoporous zeolites of different framework structure [10,11,21,22]. We have recently reported that nanocrystalline zeolite exhibits improved sensing capability when compared to bulk zeolite materials [12,15].

Polyaniline (PANI) with different morphology can be prepared without template. Morphology of the polyaniline can be tailored by varying the pH and organic additive [9]. However, these methods do not produce nanoporous polyaniline. We have reported the dual surfactant based synthesis strategy for the preparation of mesoporous polyaniline [7]. Mesoporous polyaniline exhibited better sensing capability than conventional polyaniline for glucose and various other bio-molecules [7,9].

Polyaniline exhibits good conductivity but its application as electrochemical sensor is limited because it does not contain any redox site. We recently reported that redox site in the polyaniline can be incorporated by metal ion-exchange or coating a uniform layer of metal oxide on polyaniline matrix [7,23]. Transition metal ion-exchanged materials have shown redox capability in many

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http://dx.doi.org/10.1016/j.snb.2015.01.081
0925-4005/

catalytic applications [24]. Transition metal ion-exchanged zeolites can play an important role in the electrochemical sensing of bio-molecules [12,25].

The development of fast, simple and accurate detection methodologies is required in quality control analysis (in pharmaceutical formulations) and clinical practice (in biological fluids such as urine, blood and plasma) due to the large scale therapeutic use of drugs. Among different methods, electrochemical technique is widely employed because of its high sensitivity, simplicity, and reproducibility [26,27]. Epinephrine (EP) is an important catecholamine neurotransmitter in the mammalian central nervous system with specific physiological functions and pharmacological actions. It prepares the body for an action in perceived emergency situations by boosting the supply of oxygen and glucose to the brain and muscles. Hence, it is also known as flight hormone [28]. It can be used as a doping agent to improve the performance of athletes in sports. But its use is banned in competitive games by World Anti Doping Agency [29,30]. Low levels of EP are found in patients with Parkinsonism disease [30]. EP is also used in the treatment of cardiac arrest, sepsis, severe allergic reactions, asthma and anaphylaxis [31,32]. Paracetamol (PCM) is one of the most extensively employed drugs in the world. It is an antipyretic and analgesic drug commonly used for mild to moderate pain and fever. Overdose ingestions of PCM leads to accumulation of toxic metabolites, which may cause severe and sometimes fatal hepatotoxicity and nephrotoxicity, which in some cases associate with renal failure [33]. Folic acid (FA) is widely distributed as water-soluble vitamin and acts as coenzyme in the transfer and utilization of one-carbon groups and in the regeneration of methionine from homocysteine [34]. Deficiency of FA is a common cause of anaemia and growth weakness in mammals. Though there are a few reports available in the literature for the individual or simultaneous electrochemical determination of these bio-molecules [33,35–38], it is still highly desirable to develop electrode materials for their simultaneous determination with significantly distinguishable voltammeteric response, high sensitivity, and low detection limit. The present study is focused to achieve this objective.

Polyaniline exhibits good conductivity but has low surface area. Conventional zeolites exhibit low conductivity and porosity. It may be noted that nanocrystalline zeolites exhibit large surface area and large mesopore volume but lacks conductivity. To enhance the conductivity of zeolite, highly conductive materials are incorporated to make zeolite applicable for electro-catalytic applications. It is reported in the literature that PANI-zeolite composites exhibit maximum conductivity with weight ratio of one [39]. It may be noted that ion exchange property of zeolite also enhances the conductivity of the materials [12,25]. Nanocrystalline zeolite and polyaniline based hybrid materials can overcome the shortcomings associated with individual components. Therefore, poyaniline-nanocrystalline zeolite nanocomposite was prepared to obtain the desired conductivity for this study. We chose nanocrystalline zeolites for this study because it exhibits large surface area and mesopore volume when compared to conventional zeolite. Intercrystalline mesoporosity of nanocrystalline zeolite provides an efficient transport path for reactant/product molecules because of the short diffusion length and mesoporosity. Furthermore, the high surface area of nanocrystalline zeolite provides highly dispersed redox active metal centers for electrochemical reaction. Therefore, metal ion-exchanged PANI-Nano-ZSM-5 nanocomposite were synthesized and explored in the simultaneous electrochemical detection of EP, PCM, and FA.

In this work, transition metal ion-exchanged PANI-Nano-ZSM-5 nanocomposite materials (hereafter represented as M^{2+}-PANI-Nano-ZSM-5, where $M^{2+} = Cu^{2+}$, Ni^{2+}, Co^{2+}, Fe^{2+} and Mn^{2+}) were prepared. M^{2+}-PANI-Nano-ZSM-5 modified glassy carbon electrodes (GCE) were fabricated for the detection of physiologically important bio-molecules EP, PCM, and FA. Impressive electrocatalytic activity was observed at Cu^{2+}-PANI-Nano-ZSM-5 modified GCE in the determination of EP, PCM, and FA when compared to other materials investigated in this study and bare GCE. To the best of our knowledge, this is the first report, which deals with the simultaneous determination of EP, PCM, and FA using transition metal ion-exchanged PANI-Nano-ZSM-5 nanocomposite as an electrode material.

2. Experimental

2.1. Materials

All chemicals used in the study were of AR grade and used as received without further purification. Tetraethylorthosilicate (TEOS, 98%), tetrapropylammonium hydroxide (TPAOH), propyltriethoxy silane (PrTES, 97%), and paracetamol were purchased from Sigma Aldrich, India. $CuCl_2{\cdot}2H_2O$, $MnCl_2{\cdot}4H_2O$, $NiCl_2{\cdot}6H_2O$, $CoCl_2{\cdot}6H_2O$, $FeCl_2{\cdot}4H_2O$, aniline, and ammonium peroxydisulphate (APS) were obtained from Spectrochem Pvt. Ltd., India. Epinephrine was purchased from SD Fine Chemical Limited, India. Folic acid was purchased from Central Drug House (CDH) Ltd., India. Deionized water from Millipore Milli-Q system (Resistivity 18 MΩ cm) was used in the electrochemical studies. Electrochemical measurements were performed in 0.1 M phosphate *buffer* (*Sorenson's buffer*) solution, which was prepared by mixing NaH_2PO_4 and Na_2HPO_4. The standard phosphate buffer solutions (PBS) with different pH values (lower or higher) were prepared by adding 0.1 M aqueous H_3PO_4 or NaOH solution to 0.1 M aqueous PBS, while magnetically stirring until the pH of the aqueous solution reached the desired value. All electrochemical experiments were performed in 0.1 M PBS at pH 7, unless specified otherwise.

2.2. Synthesis of transition metal ion-exchanged PANI-Nano-ZSM-5 nanocomposites

Nanocrystalline zeolite Nano-ZSM-5 was prepared using molar composition TEOS/10 PrTES/2.5 Al_2O_3/3.3 Na_2O/25 TPAOH/2500 H_2O by following the reported procedure [12]. Nano-ZSM-5 was then converted into H^+ form by three times ion-exchange using 1 M NH_4Cl aqueous solution. In a typical ion-exchange, 1 g of zeolite was added to 50 mL of 1 M NH_4Cl aqueous solution and stirred at 343 K for 6 h. The resultant product was filtered, washed with distilled water (several times), and dried in oven at 373 K for 4 h. Final product was then calcined at 823 K for 6 h.

In a typical synthesis of PANI-Nano-ZSM-5 nanocomposites, 0.53 g H^+ form of Nano-ZSM-5 was dispersed in 14 mL distilled water. 0.53 g aniline was added drop wise to the reaction mixture. The suspension was stirred for 10 min and then 14 mL aqueous solution containing 1.6 g APS was added drop-wise into the zeolite-aniline suspension with constant stirring. The mixture was further stirred for 2 h at room temperature. The resultant product was filtered, rinsed with 5×10^{-3} M H_2SO_4 and dried at 333 K for 10 h. For comparison, conventional PANI was prepared using the same procedure but without adding zeolite.

PANI-Nano-ZSM-5 (0.2 g) was cation-exchanged into M^{2+}-PANI-Nano-ZSM-5 (where $M = Cu^{2+}$, Ni^{2+}, Co^{2+}, Fe^{2+}, and Mn^{2+}) with 1 M aqueous solution of the metal source (20 mL) at 343 K for 6 h. For comparison, Nano-ZSM-5 and PANI were cation-exchanged in the similar manner as mentioned above.

2.3. Instrumentation

X-ray diffraction (XRD) patterns were recorded in the 2θ range of 5–50° with a scan speed of 2°/min on a PANalytical X'PERT PRO diffractometer, Netherland, using Cu $K\alpha$ radiation