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Simultaneous determination of epinephrene and paracetamol at copper-cobalt oxide spinel decorated nanocrystalline zeolite modified electrodes

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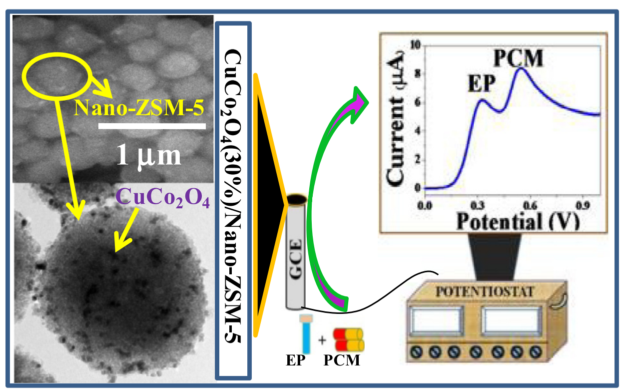
HIGHLIGHTS

- Nanocrystalline MCo_2O_4 materials were prepared.
- $CuCo_2O_4$/nanocrystalline ZSM-5 nanocomposite was prepared.
- Electrochemical sensors based on these materials were fabricated.
- Simultaneous nanomolar detection of epinephrine and paracetamol was achieved.
- Commercial pharmaceutical samples were investigated.

GRAPHICAL ABSTRACT

Nanocrystalline zeolite supported cobalt oxide spinels based efficient electrochemical sensor for the simultaneous determination of epinephrene and paracetamol.



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ABSTRACT

In this study, $CuCo_2O_4$ and $CuCo_2O_4$ decorated nanocrystalline ZSM-5 materials were prepared. For comparative study, a series of MCo_2O_4 spinels were also prepared. Materials were characterized by the complementary combination of X-ray diffraction, N_2-adsorption, UV–visible, and electron microscopic techniques. A simple and rapid method for the simultaneous determination of paracetamol and epinephrine at MCo_2O_4 spinels modified electrodes is presented in this manuscript. Among the materials investigated in this study, $CuCo_2O_4$ decorated nanocrystalline ZSM-5 exhibited the highest electrocatalytic activity with excellent stability, sensitivity, and selectivity. Analytical performance of the sensor was demonstrated in the determination of epinephrine and paracetamol in the commercial pharmaceutical samples.

1. Introduction

Rich valance states and unique electronic structures enable transition metal oxide based smart materials to offer wide range of technological applications in interdisciplinary research areas such as catalysis and electrocatalysis [1–6]. Mixed metal oxides (spinels) have capability to enhance the applications of metal

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oxides due to their tunable electronic structures [7–10]. Depending on the structural motif and the nature of the transition metal atoms in the spinels structure, their catalytic activity, selectivity, and other physico-chemical properties can be altered for the appointed applications. Cobalt oxide (Co_3O_4) is an important p-type semiconductor with normal spinel structure. Literature review suggests that MCo_2O_4 (where M = transition metals) materials have received considerable attention due to their potential applications in many technological areas such as heterogeneous catalysis [11], electrode materials in Li-ion rechargeable batteries [12], electrochemical sensors [13,14], photocatalysis [15], and magnetic materials [16]. Development of spinels based materials is one of the important research areas of our group [17–20]. $NiCo_2O_4$ based electrode materials have been developed for the electrochemical detection of water contaminants and biomolecules [17,18]. Electrochemical oxidation of methanol for fuel cell application at $NiCo_2O_4$ modified electrodes has also been investigated [19,20]. In this study, efforts have been made to develop cobalt oxide based spinels for the electrochemical determination of epinephrine and paracetamol.

Epinephrine (EP) is an important catecholamine neurotransmitter that boosts the supply of oxygen and glucose to the brain and muscles and prepares body for major physical exertion [21]. Abnormal concentration of EP is indicative of possible neurological disorders such as HIV infection [22] and Parkinson's disease [23]. N-acetyl-p-aminophenol or paracetamol (PCM) is used worldwide as antipyretic and analgesic drug [24]. It is an effective and safe analgesic agent used for the relief of mild/moderate pain. It is highly recommended by the doctor for the reduction of fever of any origin. Generally, PCM does not exhibit any harmful side effect. However, abnormal level of PCM is believed to be associated with the formation of some liver and nephrotoxic metabolites, which in some cases is associated with renal failure [25]. Furthermore, the excess dose of PCM in children (<1 year) may cause an increase in asthma, eczema, and rhinoconjunctivitis [26]. Therefore, rapid, selective, and sensitive determination of EP and PCM in biological samples and quality control in pharmaceuticals is very important considering their enormous therapeutic uses. Efforts have been made for the single and simultaneous determination of these analytes using chemically modified electrodes. Most of these electrode materials have been prepared using complex synthesis procedure [25]. Metal oxide based electrodes have been developed for the single detection of these analytes [27–29]. Therefore, it is important to design electrode materials for the simultaneous determination of these analytes with distinguishable voltammetric response, high sensitivity, and low limit of detection. To the best of our knowledge, no report is available for the simultaneous electrochemical determination of EP and PCM using spinels.

Application of microporous zeolites as electrochemical sensor is less explored due to their low conductivity, small pore size, and small external surface area. Development of nanocrystalline zeolites (having intra/inter-crystalline mesoporosity and large external surface area) opens up a new opportunity in the fabrication of zeolite based electrochemical sensors. In recent time, efforts have been made for the development of nanocrystalline zeolite based electrode materials for the selective and sensitive determination of organic/inorganic pollutants and bio-molecules [17,30–35]. Nanocrystalline zeolite can also be used as an effective support material because of its mesoporosity, large surface area, and surface silanol groups [18]. In this study, $CuCo_2O_4$ has been supported on the external surface of nanocrystalline zeolite to enhance the limit of detection.

This work aims to synthesize a nanocomposite material consisting of $CuCo_2O_4$ and nanocrystalline ZSM-5 zeolite for the simultaneous determination of EP and PCM. In this manuscript, MCo_2O_4 (M = Mn^{2+}, Fe^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}) based spinels have been synthesized and used in the fabrication of electrochemical sensors. Beside this, its single components (i.e.; CuO and Co_3O_4 with respect to $CuCo_2O_4$) have also been synthesized for the comparative investigation. In order to achieve high electrocatalytic activity with low limit of detection, different amounts of $CuCo_2O_4$ have been supported on the surface of nanocrystalline zeolite ZSM-5 (hereafter referred as Nano-ZSM-5).

2. Experimental

2.1. Materials

All chemicals were of AR grade and used as received without further purification. Tetraethylorthosilicate (TEOS, 98%), tetrapropylammonium hydroxide (TPAOH), propyltriethoxy silane (PrTES, 97%), Nafion 117 solution (a 5% mixture of lower aliphatic alcohols and water), ammonium fluoride (NH_4F) and paracetamol were purchased from Sigma Aldrich, India. $Cu(NO_3)_2{\cdot}3H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}9H_2O$, were obtained from Loba Chemie Pvt. Ltd. India. Epinephrine was purchased from S.D. Fine Chemical Limited, India. $Mn(NO_3)_2{\cdot}6H_2O$ was purchased from Alfa Aesar, India. Deionized (DI) 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 solutions (for the preparation of 0.1 M 100 mL phosphate buffer solutions (PBS), 30 mL of 0.1 M Na_2HPO_4, 20 mL of 0.1 M NaH_2PO_4 and 50 mL DI H_2O were mixed). The standard PBS with different pH values (lower or higher) were prepared by the addition of 0.1 M aqueous H_3PO_4 or 0.1 M aqueous NaOH solution to 0.1 M aqueous PBS. All electrochemical experiments were performed in 0.1 M PBS at pH 7, unless specified otherwise.

2.2. Synthesis of MCo_2O_4, Co_3O_4, CuO, Nano-ZSM-5 and $CuCo_2O_4$/Nano-ZSM-5

$CuCo_2O_4$ was prepared by following the reported hydrothermal synthesis route with a little modification [19]. In a typical synthesis, 1 mmol of $Cu(NO_3)_2$, 2 mmol of $Co(NO_3)_2$, 6 mmol of NH_4F, and 15 mmol of urea were mixed in 70 mL of distilled water. Reaction mixture was magnetically stirred for 30 min in open vessel under ambient condition. During this period, the reaction mixture became glazy viscous. It was transferred into a 125 mL Teflon-lined stainless steel autoclave and maintained at 413 K for 7 h. After the hydrothermal treatment, autoclave was cooled to ambient temperature, and the obtained copper cobalt hydroxide precursor was washed thoroughly with distilled water. Finally, the material was calcined at 723 K for 3 h to obtain $CuCo_2O_4$. For comparative study, various other spinels such as $MnCo_2O_4$, $FeCo_2O_4$, $NiCo_2O_4$, and $ZnCo_2O_4$ were synthesized by following the method described above just by changing Cu precursor with desired metal precursor. Furthermore, Co_3O_4 was also prepared by the procedure described above but in the absence of Cu precursor. For comparative study, CuO was prepared by following the reported procedure [36].

Nano-ZSM-5 was prepared by following the reported procedure [37]. In a typical synthesis, sodium aluminate (53 wt% Al_2O_3, 43 wt % Na_2O) was dissolved in distilled water to obtain solution A. PrTES was mixed with TPAOH (1 M aq. solution) to obtain solution B. Solution A and solution B were mixed and the resultant solution was stirred at ambient temperature until it formed a clear solution. TEOS was added to the resulting solution to obtain the molar composition of $90TEOS/10PrTES/1Al_2O_3/3.3Na_2O/25TPAOH/2500H_2O$. Synthesis gel was hydrothermally treated at 443 K for 3 days in