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Synthesis of ionic liquids coated nanocrystalline zeolite materials and their application in the simultaneous determination of adenine, cytosine, guanine, and thymine

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ABSTRACT

In this study, ionic liquids coated nanocrystalline zeolite based inorganic-organic hybrid materials were synthesized. Nanocrystalline ZSM-5 zeolite was prepared under hydrothermal condition in the presence of propyltriethoxysilane as an additive in the synthesis composition of conventional ZSM-5. Ionic liquids (methylimidazolium chloride and 1-butyl-3-methylimidazolium chloride) were coated on the surface of nanocrystalline ZSM-5 by the post synthesis method. For comparative study, ionic liquids coated conventional ZSM-5 based inorganic-organic hybrid materials were also prepared. Ionic liquids coated nanocrystalline ZSM-5/ZSM-5 modified electrodes were constructed for the simultaneous determination of all four DNA bases such as adenine, cytosine, guanine, and thymine. Difference in the electro-catalytic activity of the modified electrode is explained with the help of textural properties, conductivity, and density functional theory. The analytical performance of the proposed method was demonstrated in the simultaneous determination of all four DNA bases in calf thymus DNA sample.

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1. Introduction

Nanocrystalline materials are used to separate or selectively adsorb guest molecules according to their pore size and architecture. Among a variety of nanocrystalline materials, zeolites have molecular-sized cages and channels, which provide excellent steric control in reaction pathways [1–3]. Zeolites act as an acid catalyst, cation-exchange materials, and high surface area support for the uniform dispersion of metal nanoparticles because of the high thermal, hydrothermal, and mechanical stability. The superior performance of zeolites in catalysis is attributed to the existence of a well-defined system of micropores (size below 1.5 nm in diameter) with uniform shape and size, typically of molecular dimensions. The presence of micropores restricts their potential applicability in biomedical applications (owing to the involvement of large organic molecules) [1]. To overcome this limitation, zeolites with interconnected intra- or inter-crystalline mesoporosity have attracted much attention [2,4]. Several attempts have been made for the preparation of nanosized zeolites [5–10]. Zeolite modified electrodes have been developed for the detection of inorganic and organic analytes [11–14]. Compounds, as diverse as herbicides, surfactants, and pharmaceuticals were detected using zeolite modified electrodes [16–19]. Zeolite modified electrodes have also been used for the electrochemical detection of biological compounds [12–14].

Deoxyribonucleic acid (DNA) plays major role in the life process. DNA carries heritage information and instructs the biological synthesis of proteins and enzymes through the process of replication and transcription of genetic information. DNA is a natural polymer, which consist of a phosphate acid group, a basic group (guanine (G), adenine (A), thymine (T), and cytosine (C)), and a sugar unit [15]. The direct electrochemistry of nucleic bases (G, A, T, and C) has attracted much attention because of its important significance in bio-analytical chemistry and life sciences [16–19]. DNA exhibits widespread effect on coronary and cerebral circulation, control of blood flow, prevention of cardiac arrhythmias, control of neurotransmitter release, and modulation of adenylate cyclase activity [20]. Changes in the concentration of DNA bases affect the activity of catabolic, anabolic, and inter-conversion of enzymes and cause various diseases, which alter the normal purine and pyrimidine metabolic pathways [21]. The abnormal changes in the DNA bases lead to the deficiency and mutation of the immunity system, which are responsible for various diseases. Concentration levels of DNA basses are considered to be an important parameter for the diagnosis of cancer, AIDS, myocardial cellular energy status, disease progress, and therapy responses [22]. Hence, determination

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of the individual concentrations of G, A, T, C, and their ratio in DNA is important. DNA bases can be classified in two categories: purine (G, A) and pyrimidine (T, C). These bases exhibit low sensitivity due to slow electron transfer at the bare electrode. Therefore, a variety of chemically modified electrodes were fabricated to investigate the direct electrochemistry of nucleic bases and its related nucleosides [23–26]. The electro-catalytic oxidation of purine bases has been extensively investigated in the literature [27–30]. However, there are only a few reports available for the electro-catalytic oxidation of pyrimidine bases [31]. It is difficult to obtain accurate oxidation signals for pyrimidine bases because of their high positive oxidation potentials and slow electron transfer. In order to overcome these limitations, modified electrodes with a wide potential window, high electro-catalytic activity, and excellent antifouling property are highly required. Only a few electrochemical methods are reported for the simultaneous determination of all four DNA bases [32–37].

Our research is focused on the synthesis of mesoporous/nanocrystalline zeolites and finds their catalytic & electro-catalytic applications (in the single or simultaneous detection of various physiologically important bio-molecules) [38,39]. Our research group is actively engaged in the synthesis of ionic liquids and their applications in catalysis and zeolite synthesis [40–43]. Consequently, an attempt was made to design and synthesize electrode materials based on nanocrystalline zeolites & ionic liquids. In this study, we report a novel synthesis of ionic liquids (ILs) coated nanocrystalline ZSM-5 (Nano-ZSM-5/ILs) based inorganic-organic hybrid materials. Electrochemical sensors based on Nano-ZSM-5/ILs were fabricated for the simultaneous detection of all four DNA bases. To the best of our knowledge this is first report, which deals with the design and construction of Nano-ZSM-5 coated ILs for the simultaneous determination of all four DNA bases. Nano-ZSM-5 with high surface area enables the coating of economical ILs on the large external surface of Nano-ZSM-5 to obtain materials with good electro catalytic activity. Structure activity relation is established using electro-catalytic activity, textural properties of the materials, and density functional theory (DFT).

2. Experimental details

2.1. Materials

All chemicals used in this study were of A.R. grade. Tetraethylorthosilicate (TEOS), propyltriethoxysilane (PrTES), tetrapropylammonium hydroxide (TPAOH), methylimidazolium chloride [Hmim][Cl], 1-butyl-3-methylimidazolium chloride [Bmim][Cl], and DNA sodium salt of calf thymus were purchased from Sigma Aldrich. Adenine, guanine, thymine, and cytosine were obtained from Spectrochem Pvt. Ltd. Deionized water from Millipore Milli-Q system (Resistivity 18.2 M Ohms cm) was used in the electrochemical studies. Guanine, adenine, thymine, and cytosine stock solutions were prepared by dissolving them into 0.1 M NaOH solution. Electrochemical measurements were performed in **Phosphate Buffer (*Sorenson's buffer*)** solution, which was prepared by mixing NaH_2PO_4 and Na_2HPO_4. All electrochemical experiments were performed in 0.1 M **Phosphate Buffer** at pH = 7.4, unless specified otherwise.

2.2. Sample preparation

Nano-ZSM-5 was synthesized by following the reported procedure [44]. In a typical synthesis, 1.2 g of sodium aluminate (53 wt.% Al_2O_3, 43 wt.% Na_2O) was dissolved in 25 mL of distilled water (Solution A). 2.06 g of PrTES was mixed with 25 mL of TPAOH (1 M aq. solution) (Solution B). Solution A and solution B were mixed, and the resultant solution was stirred for 15 minutes at ambient condition, until it became a clear solution. 18.7 g of TEOS was added into the resultant solution and stirring was continued for 6 h. The molar composition of the gel mixture was 90 TEOS/10 PrTES/2.5 Al_2O_3/3.3 Na_2O/25 TPAOH/2500 H_2O. This mixture was transferred to a Teflon-lined autoclave, and hydrothermally treated at 443 K for 3 days under static conditions. The final product was filtered, washed with distilled water, and dried at 373 K. Material was calcined at 823 K for 4 h under flowing air.

ZSM-5 was synthesized at 443 K using the same synthesis composition as mentioned above for the Nano-ZSM-5, but without PrTES additive.

For the synthesis of ILs coated zeolites (Zeolite/ILs), 0.2 g of zeolite was taken in 20 mL of distilled water. Reaction mixture was sonicated for 5 minutes for uniform dispersion. 0.4 g of ILs (where ILs = [Hmim][Cl] or [Bmim][Cl]) were added into the reaction mixture in one proportion and sonicated for another 30 seconds. pH of reaction mixture was adjusted to 10.0 by the addition of 1 M aqueous NaOH solution. The reaction mixture was further sonicated for 30 min in order to assure the complete dispersion, and then allowed to equilibrate for 10 min. At the end, the reaction mixture was centrifuged, washed with distilled water, and dried to obtain ILs coated zeolite composites. Zeolite/ILs materials obtained using [Hmim][Cl] are represented as Nano-ZSM-5/MIM and ZSM-5/MIM. Material obtained using [Bmim][Cl] is represented as Nano-ZSM-5/BMIM.

2.3. Real sample preparation

The calf thymus DNA sample was hydrolyzed for quantification of G, A, T, and C. 3 mg of calf thymus DNA sample was digested using 1 mL of 1 M HCl in a sealed 10 mL glass tube. After heating in a boiling water bath for 60 min, the pH of the solution was adjusted to pH 7 with 1 mL of 1 M NaOH. Required amount of this solution was added to the electrochemical cell consisting 10 mL of buffer solution (pH 7.4).

2.4. Material characterizations

X-ray diffraction (XRD) patterns were recorded in the 2θ range of 5–60° with a scan speed of 2°/min on a PANalytical X'PERT PRO diffractometer using Cu Kα radiation (λ = 0.1542 nm, 40 kV, 20 mA). Scanning electron microscopy (SEM) measurements were carried out on a JEOL JSM-6610LV to investigate the morphology. During the SEM investigation, energy-dispersive X-ray spectroscopy (EDS) was utilized for the sample characterization and the EDS elemental maps were obtained. Nitrogen adsorption measurement at 77 K was performed by Autosorb-IQ Quantachrome Instruments volumetric adsorption analyzer. Sample was out-gassed at 423 K for 4 h in the degas port. The specific surface area was determined by Brunauer–Emmett–Teller (BET) method using the data points of P/P_0 in the range of about 0.05–0.3. Fourier-transform infrared spectrometer (FT-IR) spectra were recorded on a spectrophotometer model Bruker TENSOR-27 in the wave number range 400–4000 cm^{-1} at a 4 cm^{-1} resolution with KBr as compressed slices. Electrochemical measurements were carried out by using Potentiostat-Galvanostat BASi EPSILON, USA. The conductivity of zeolite materials was measured through plane conductivity cell. Cell design is two copper block electrodes with high quality gold plated in the contact area to ensure good contact. The maximum contact size is 25.4 mm diameter. The pressure applied by electrode is even throughout the experiment due to the mechanical pressure generated by the weight of the electrode. For conductivity measurements, sample (0.1 g) was pelletized using pellet maker

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