Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2014, 6(7):2827-2831

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Highly selective glassy carbon electrode based on modified imprinting TS-1 zeolite

Alfa Akustia Widati*, Miratul Khasanah and Muji Harsini

Department of Chemistry, Faculty of Science and Technology, Universitas Airlangga, Surabaya, Indonesia

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ABSTRACT

A new modified electrode is constructed based on uric acid shape selectivity of TS-1 zeolite modified glassy carbon electrode. Fourier Transform Infrared, X-ray Diffraction, and stripping voltammetry were used to characterize material. The imprinting TS-1 zeolite modified glassy carbon electrode exposes Gaussian Graphic and also responses high selectivity, reproducibility and current for determination of uric acid.

Key words: imprinting TS-1 zeolite, glassy carbon, sensor, uric acid, voltammetry.

INTRODUCTION

Zeolites are microporous crystalline aluminosilicates, composed of TO_4 tetrahedra, with O atom connecting neighboring tetrahedral. Zeolites can be exploited as a electrochemical sensor because of (a) the size and shape selectivity due to the rigid structure made of pores and channels of molecular dimensions; (b) the cation exchange capacity arising from the change compensation of negatively charged aluminosilicate lattice by mobile extraframework cations; and (c) the catalytic properties of both intrinsic and extrinsic sites of the zeolite [1]. Many papers have reported the synthesis, design, and application of zeolite modified electrode electrochemistry [2-6].

The development of newer modified zeolite with high selectivity is warranted always. There is a challenging to select shape selective material similarly sized molecules near 1 nm, which are often too large for zeolite pores and too small for size selection in most mesostructured oxides [7]. Shape selectivity of material can be obtained by utilizing chemical vapour deposition (CVD) techniques using tetra(methoxy)silane [8], tetraethylorthosilicate [9] to decrease pore diameter of zeolite; catalytic cracking of silane which is burned a coke in an air stream, leaving mono SiO_2 unit on pore thereby the size of the pores are reduced [10]; providing a metal-exchanged, treating the zeolite on alkali silicate solution, calcining, and reacting calcined zeolite with an ammonium compound [11]; depositing a template onto an material than treating the material in O_3 to remove the templates.

Meanwhile, uric acid is the end product of purine metabolism. Normally, uric acid is present in the blood on concentration range 0.15-0.45 mmol/L and excreted in urine in 1.19-2.98 mmol/day [12].. Abnormal levels of uric acid can causes hyperuricemia, kidney stones, and lead to increase the risk of cardiovascular disease. Therefore, monitoring uric acid is important because it can be used as preventive and investigations of disease diagnosis. In this paper, we report the new design of uric acid sensor through imprinting TS-1 zeolite modified glassy carbon electrode using stripping voltammetry.

EXPERIMENTAL SECTION

2.1 Material preparation

TS-1 zeolite was prepared by using tetraethylorthosilicates (TEOS) as a silicon source, tetrabuthylorthotitanate (TBOT) as a titanium source, tetrapropylammonium hydroxide (TPAOH) as a structure directing agent and provides the alkalinity in the synthesis of TS-1, while uric acid as a molecular template. All reagents were purchased from Merck, analytical grade and used as received without further purification.

TEOS and TBOT were mixed under stirring for 30 min at room temperature. TPAOH was added to the mixture. The resulting clear solution, with a molar composition : 1 TEOS : 0.017 TiO_2 : 0.24 TPAOH : 21.2 H_2O, was aged at 80ºC for 48 hours. In order to create the template of uric acid molecule, uric with molar ratio of uric acid/Si = 0,306 was slowly added to the precursor solution under stirring at room temperature. This final mixture, was aged for 3 h at room temperature. The resulting solid was collected by filtration, extraction of uric acid using hot water, and dried at 60ºC overnight. The resulting material was called imprinting TS-1 zeolite (IZ).

For comparison, we also prepared non imprinting TS-1 zeolite (NIZ) and TS-1 zeolite (Z) using similar procedure to synthesis IZ. The material of Z was synthesized without uric acid addition. In the other hand, the material NIZ was synthesized with addition of uric acid, but the uric acid did not extracted from the zeolite.

2.2 Characterizations

The X-ray diffraction (XRD) analysis was performed on the JEOL JDX-3530 using Cu Kα radiation of wavelength 0.15418 nm. Diffraction data were recorded between 5-50º. Fourier Transform Infra Red (FTIR) spectrum was recorded on the Shimadzu instrument spectrum one 8400S. The electrochemical performance of modified electrode was studied by 797 Voltammetry Computrace (MVA system-1). All the voltammetric measurements was carried out using glassy carbon (GC) electrode as a working electrode, Ag/AgCl as a reference electrode, and Pt wire as a auxiliary electrode.

2.3 The electrochemical performance of material using GC electrode

An IZ in water were placed into the voltammetric cell. Subsequently, IZ was coated at GC electrode by electrocoating on -0.6 volt for 150 seconds. IZ modified GC (GC-IZ) electrode was applied to analysis uric acid with concentration was 3.0 x 10^{-8} M, deposition time was 150 s, solution pH was 7, and scan rate was 59 mV/seconds.

RESULTS AND DISCUSSION

The synthesis procedure used in this work is similar to that reported by Eimer et al. [13]. At the synthesis process, TBOT must be dissolved at isopropanol before TEOS was mixed with TBOT. This is important step to avoid hydrolyzation of TBOT. When TBOT is hydrolyzed, titanium will arrange its structure become TiO_2 that has stable structure [14]. It is disadvantages structure because to build TS-1 frame, titanium has to arrange a sequence with silicone. Then, TPAOH was mixed, the mixture was aged to hold crystallization hydrothemal at 4 days. After that, uric acid as a template was added in the mixture, filtered, washed, and dried. The function of template is make the pore size of material adapted with molecule size of template. In this case, zeolite was interacted with uric acid as a template resulted the pore size of zeolite was closed with uric acid molecule.

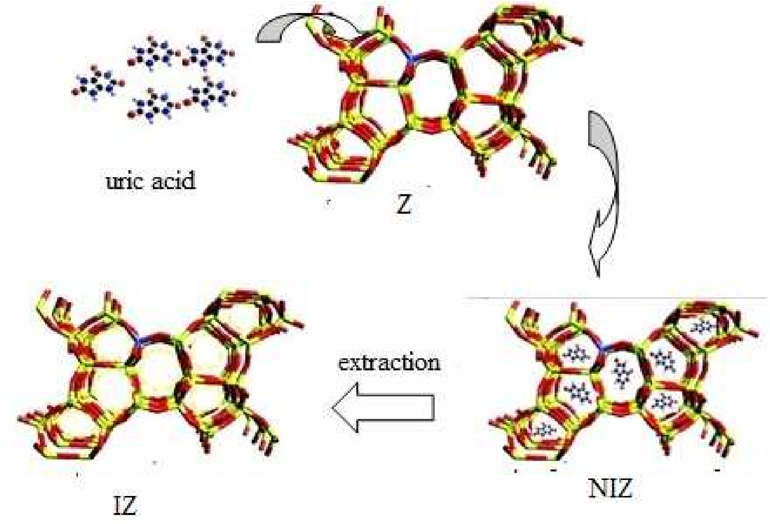

Fig.1. Diagrammatic representation of the steps in the formation of IZ

The XRD patterns of pure Z and IZ are shown in Fig. 2a-b, respectively. The characteristic peaks at 2θ 7,9; 8,9; 23,2; 23,7; 24,1; and 24,9° were observed from diffractogram that show a good agreement with data of TS-1 zeolite [15]. Peak about 23 – 24° show a single diffraction, indicate a change of crystal symmetry from monoclinic symmetry (silicalite structure) become orthorombic symmetry (TS-1 structure) [16]. No other phases were detected in IZ patterns. Therefore, this method have been successfully extracted uric acid from NIZ.

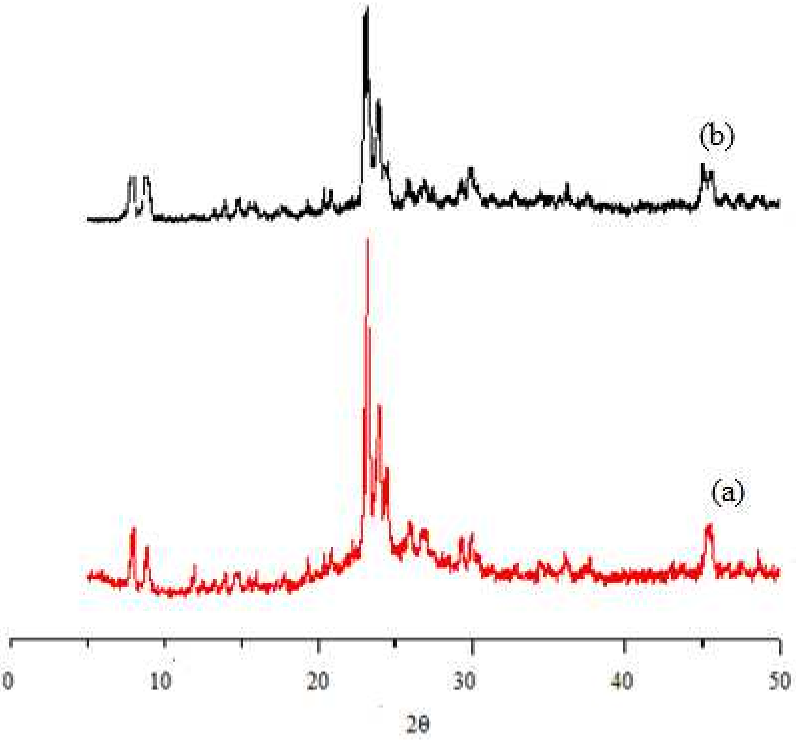

Fig.2. XRD patterns of a (a) Z and (b) IZ

FTIR spectra of Z, NIZ, and IZ are shown in Fig. 3a-c. An absorption peak was found at 960 cm^{-1} in all samples, which is considered that titanium has been incorporated into the framework of zeolite [17,18]. An adsorption at 960 cm^{-1} could not be detected in silicalite-1, because this adsorption is specific for tetrahedrally coordinated Ti^{4+} framework incorporated into the silicalite framework [19]. TS-1 zeolite also have characteristic spectra at about 1230 and 550 cm^{-1}, specific bands for tetrahedral structure at MFI zeolite frame.

FTIR spectra of NIZ also revealed peaks at about 840, 1450, 1650, and 3450 cm^{-1}, indicating presence of uric acid as a template. No peaks corresponding to chemical interaction between TS-1 skeleton and uric acid molecule. Meanwhile, similar spectra was observed at Z and IZ, which is supported XRD analysis that uric acid has been removed from NIZ, Electrochemical performance of IZ was studied using stripping voltammetric studies. Table 1 represents the anodic current which is contributed from electrodes response. GC electrode showed a high current but low selectivity. In the comparison of all modified electrodes, GC-NIZ had highest current, due to the contribution of zeolite and uric acid conductivity. It was considered that GC-NIZ had limited analyte diffusion because the electrode surface of glassy carbon fully covered by uric acid as molecule template. The best electrode response was performed by GC-IZ. It had Gaussian graphic, high current and selectivity. GC-IZ had a better diffusion than GC-NIZ and had a highest selectivity than others because of the pore template preparation using uric acid.

Table 1: Voltammetric performance of GC; GC-NIZ; GC-IZ; and GC-Z to analyse uric acid

Sensor	Annodic Current (nA)	RSD (%) (n=3)
GC	3082.00	4.28
GC-NIZ	3643.67	10.17
GC-IZ	619.90	1.89
GC-Z	489.63	13.44

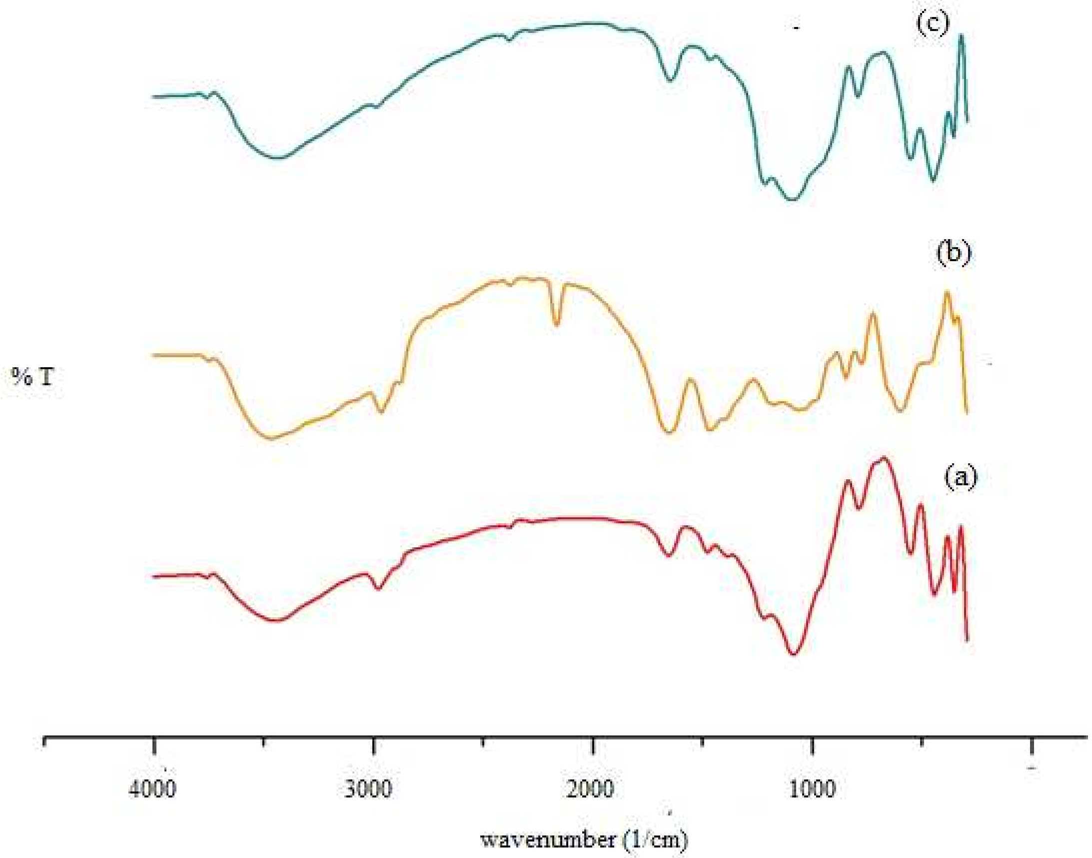

Fig.3. FTIR spectra of (a) Z, (b) NIZ, and (c) IZ

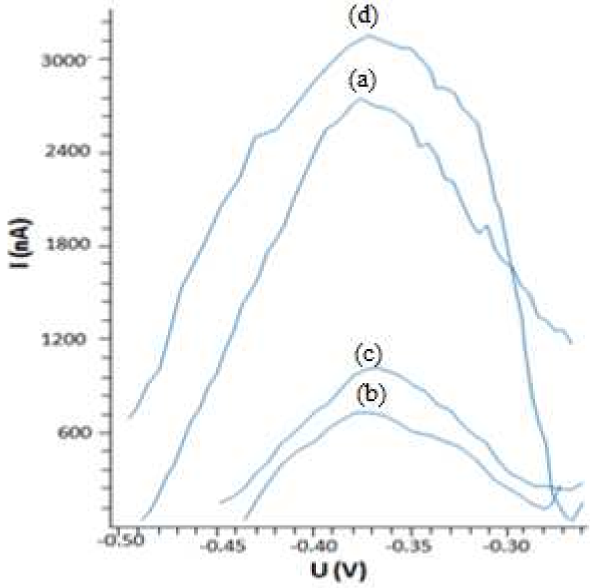

Fig.4. Stripping voltammmogram of uric acid using (a) GC, (b) GC-Z, (c) GC-IZ, and (d) GC-NIZ

CONCLUSION

TS-1 zeolite can be used as a sensor of uric acid by modified pore of zeolite using uric acid molecule as a template. The electrochemical behavior by voltammetric procedures was studied using TS-1 zeolite modified glassy carbon electrode. This analysis resulted high sensitivity and selectivity, good reproducibility, Gaussian graphic and simple methods.

Acknowledgement
The authors thank the Directorate General of Higher Education, Indonesia under RUPT Grants No.: 001/ UN3.6/KU/PPK/2013 for their financial support.

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