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PREPARATION OF ELECTROCHEMICALLY IMMOBILIZED IRON ON THIN FILM FAUJASITE-NANOZEOLITE MODIFIED GLASSY CARBON

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ABSTRACT

PREPARATION OF ELECTROCHEMICALLY IMMOBILIZED IRON ON THIN FILM FAUJASITE-NANOZEOLITE MODIFIED GLASSY CARBON. Metal iron that electrochemically immobilized on thin film faujasite type of nanozeolite (FAU-nanozeolite) grown on polyelectrolyte (PDDA, PSS, PDDA layers) modified glassy carbon has been prepared. Thin film of FAU-type nanozeolite was synthesized using seeding method. The seeded modified-glassy carbon then was immersed in FAU colloidal suspension at 100 ^{o}C for certain period. XRD patterns of the seed and as-synthesized zeolite powder have similarity with the patterns from standard NaY zeolite. SEM images of thin film nanozeolite also show the appearance of crystals with homogeneous size of about < 1 μm. The best spread thin film was obtained when using 3 ml seed and immersion in colloidal FAU solution for 20 hours. The thin film then was utilized for metal iron synthesis, in which Fe(III) from $FeNO_3$ solution containing Na-citrate of that adsorbed on the surface of thin film was electrochemically reduced to (Fe^0). SEM image shows some aggregates (size > 100 nm) of the nanozeolite thin film. However, it can also be seen that the crystals actually consist of smaller particles with size < 100 nm. The EDS mapping of the surface indicates that after electrochemical treatment, the surface of thin film consists of about 0.30% (w/w) iron that spread evently both on the surface covered by nanozeolite thin film and that from modified glassy carbon.

Key words : Nanozeolite, Faujasite (FAU), Seeding, Glassy carbon, Iron, Electrochemistry

ABSTRAK

PREPARASI BESI TERIMOBILISASI ELEKTROKIMIA PADA KARBON GELAS TERMODIFIKASI LAPISAN TIPIS *FAUJASITE-NANOZEOLITE*. Telah dipreparasi logam besi yang diimobilisasi secara elektrokimia pada lapisan tipis nanozeolit tipe *faujasite* (*FAU*) yang ditumbuhkan pada karbon gelas termodifikasi dengan polielektrolit (lapisan *PDDA, PSS, PDDA*). Lapisan tipis nanozeolit tipe *FAU* disintesis menggunakan metode *seeding*. Karbon gelas termodifikasi dalam bentuk *seed* dicelupkan ke dalam suspensi koloid *FAU* pada 100 ^{o}C selama waktu tertentu. Pola *XRD* dari *seed* dan serbuk zeolit awal memiliki kemiripan dengan zeolit NaY standar. Gambar *SEM* dari nanozeolit lapisan tipis juga menunjukkan keberadaan kristal dengan ukuran homogen sekitar < 1 μm. Penyebaran lapisan tipis terbaik diperoleh apabila menggunakan *seed* 3 mL dan dicelupkan ke dalam koloid *FAU* selama 20 jam. Lapisan tipis kemudian digunakan untuk mensintesis logam besi, dimana Fe(III) dari larutan $FeNO_3$ mengandung Na sitrat yang terabsorsi pada permukaan lapisan tipis tereduksi secara elektrokimia menjadi Fe(0). Gambar *SEM* menunjukkan beberapa agregat lapisan tipis nanozeolit (ukuran > 100 nm). Tetapi, terlihat juga bahwa kristal tersebut mengandung partikel kecil berukuran < 100 nm. *Mapping EDS* terhadap permukaan menunjukkan bahwa setelah penanganan elektrokimia, permukaan lapisan tipis mengandung sekitar 0,30 % (w/w) besi yang tersebar rata pada kedua sisi, yakni permukaan yang tertutup lapisan tipis nanozeolit dan permukaan dari karbon gelas termodifikasi.

Kata kunci : Nanozeolit, *Faujasite*, *Seeding*, Karbon gelas, Besi, Elektrokimia

INTRODUCTION

Nanosized metals have drawn many attention as their catalytic properties increase significantly as well as many other potential application in microelectronic research and optic and magnetic device [1]. So far, several methods in nanometal synthesis have been developed, such as reduction by chemical reaction, photoreduction, thermal decomposition, and electrochemical reduction [2]. The important factor in all above methods

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is the prevention of nanoparticle agglomeration during and after synthesis [3]. Organic compounds such as ligands, polymers or surfactants are usually used as protecting agent to maintain the stability of nanoparticle so that they are separated from each other [4].

However, the use of organic compounds as dispersing agent sometimes limit the applications of metal nanoparticles, e.g. as catalysts and electrodes. Zeolite is an inorganic aluminosilicate material having orderded and homogeneous pores and/or nanochannels that can trap nano metal into its structure. Preparation of Ag nanoparticle have been done using FAU type zeolite as template [1]. The zeolite was grown on Pt-electrode having surface modified by some layers of polyelectrolytes in order to give positive charge to its surface. In our previous work, mordenite type of zeolite was synthesized on the surface of modified glassy carbon electrode, then was used to immobilize Fe(III) cations. The application of this Fe(III)-immobilized glassy carbon electrode as arsen sensor is promising. The detection limit achieved for arsen, so far, is 6.75 ppb [5].

In this work, iron nanoparticle was synthesized by electrochemical reduction method from iron nitrate solution containing sodium citrate, dispersed inside the pores of FAU nanozeolite modified glassy carbon surface (ZGC). Thus, the electrochemical reduction of iron(III) to iron(0) is expected to occur inside the pores. To the best of our knowledge the use of FAU nanozeolite as dispersing agent and glassy carbon electrode as support for iron nanoparticle preparation has not yet been reported.

Modification on preparation of nanozeolite and the process of electrochemical reduction of Fe(III) to Fe(0) are discussed in this paper.

EXPERIMENTAL METHOD

Synthesis of FAU Nanozeolite

Colloidal nanocrystal FAU type zeolites was synthesized following procedure reported by Lassinati et.al [6] with some modification [7]. Seeds was prepared in homogeneous solution with molar composition of 2.46 $(TMA)_2O$, 0.032 Na_2O, Al_2O_3, 3.40 SiO_2, 400 H_2O, by pouring aluminium isopropoxide solution (in ethanol/ water = 1 : 10), TMAOH and 0,1 M NaOH into TEOS solution (in water) with vigorous stirring. After aging overnight, the mixture then was refluxed at 100 °C for 7 days. The seed formed then was washed three times and redispersed in 0.1 M ammonia solution.

FAU nanozeolite then was prepared by adding certain amount of seed into homogeneous mixture with molar composition of Na_2O, Al_2O_3, 10 SiO_2, 798 H_2O, $3Na_2SO_4$ followed by hydrothermal treatment at 80 °C for 24 hours. The product was then washed with solution of 0.1 N NH_3 and aquadest and redispersed in aqueous suspension.

Nanozeolite Immobilization [5, 7]

Glassy carbon was modified with nanozeolite using self assembly method through electrostatic interaction as thin films of three layers of polyelectrolyte PDDA/PSS/PDDA applied giving positive charge to the final layer. Then the nanozeolite seed was added into the surface of modified glassy carbon in solution of 01 M NaCl at pH 9.5 for 20 minutes. Afterward, the modified glassy carbon was immersed in the colloidal FAU nanozeolite suspension for certain period at 100 °C. The FAU nanozeolite modifed glassy carbon was then labelled ZGC.

Synthesis of Iron Nanoparticle

Fe(III) solution 2 x 10^{-3} M containing Na-citrate 5 x 10^{-2} M was prepared from $FeNO_3.9H_2O$. Na-citrate is a capping agent to avoid coagulation and precipitation of Fe(III) cations [8]. Thin film nanozeolite on modified glassy carbon was immersed in $FeNO_3$ solution of 2 x 10^{-3} M, and dried at room temperature. The modified glassy carbon then immersed in Fe(III) solution 1 x 10^{-3} M containing Na-citrate 5 x 10^{-2} M at pH 8.7 and then electrochemically reduced under condition of potential = 2000 mV to -2000 mV, reference electrode = Ag/AgCl, counter electrode = Pt. The result was then called Fe-ZGC.

RESULTS AND DISCUSSION

Synthesis of Seeds and Immobilization of FAU Nanozeolite on Modified Glassy Carbon

Modification in seed synthesis (using mixed solvent ethanol/water (1 : 10) was applied in order to slow down the hydrolisis of Al-isopropoxide to $Al(OH)_3$ so that it was easier to form tetrahedral network with SiO_4^- in zeolite framework.

XRD pattern of as-synthesised nanozeolite is similar to that of nanozeolite prepared using commercial NaY as seed (Figure 1), and resemble to nanozeolite reported by Holmberg et.al [9]. Observation with EDAX gives Si/Al ratio within 2.5-2.8 range, which falls into Si/Al ratio for FAU zeolite type Y.

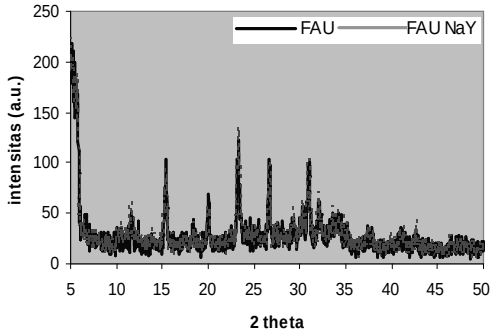

Figure 1. XRD pattern of nanozeolite

Morphology of the as-prepared FAU-nanozeolite, both seeds and bulk are shown by Figure 2. It can be seen that the size and shape of seeds and NaY added-seeds, shown by Figure 2(a) and Figure 2(c), are quite similar. While the shape of bulk powder is rather poor compared to that of NaY-added bulk powder.

Thin films of nanozeolite immobilized on polyelectrolyte modified glassy carbon were then prepared as summarized in Table 1. Only one layer or seed applied to every sample as based on our previous

Table 1. Thin films of nanozeolite grown on modified glassy carbon

No.	Sample name	Details
1	ZGC1-20	Nanozeolite on glassy carbon: 1 mL seed immersion time 20 hours
2	ZGC3-20	Nanozeolite on glassy carbon: 3 mL seed immersion time 20 hours
3	ZGC1-40	Nanozeolite on glassy carbon: 1 mL seed immersion time 40 hours
4	ZGC3-40	Nanozeolite on glassy carbon: 3 mL seed immersion time 40 hours

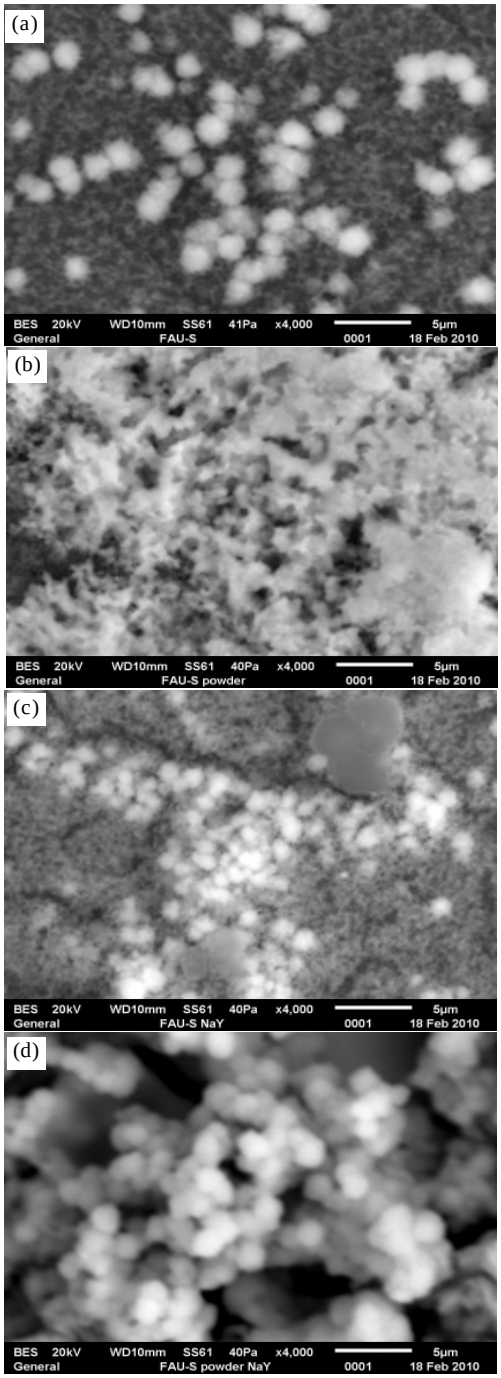

Figure 2. SEM of as-prepared FAU nanozeolite (a). seeds, (b). bulk powder, (c). NaY added seeds and (d). NaY added bulk powder at 4 kx magnification

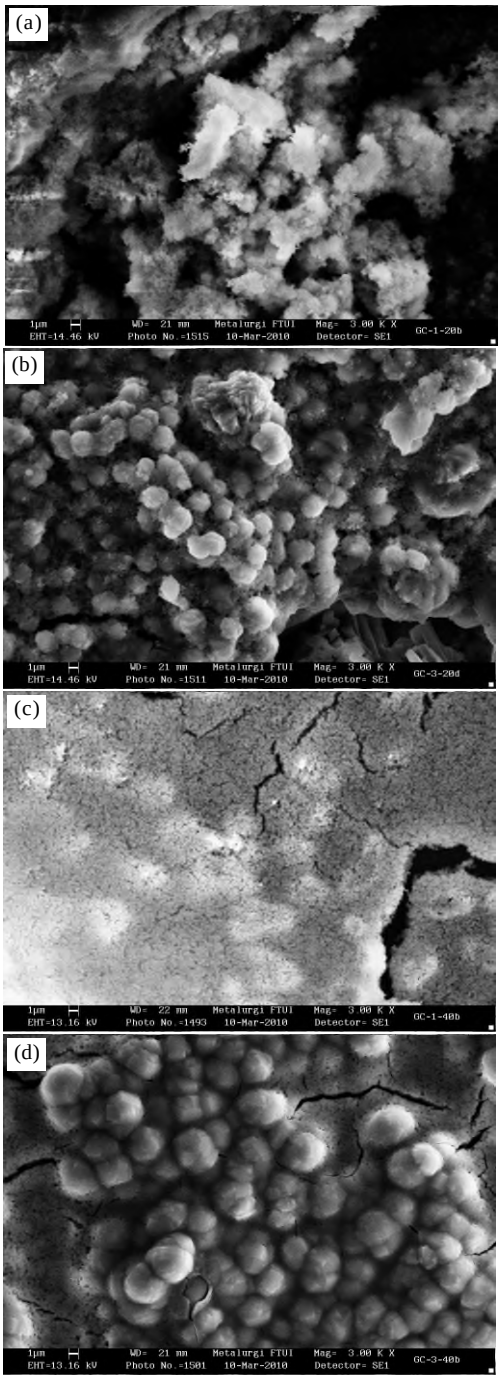

Figure 3. SEM images of (a). ZGC1-20, (b). ZGC3-20, (c). ZGC1-40 and (d). ZGC3-40 with 3 kx magnification

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work [10] the morphology of nanozeolite grown is poorer when more than one layer of seed applied.

SEM images of ZGC1-20, ZGC3-20, ZGC1-40 and ZGC3-40 are shown in Figure 3. It can be seen in Figure 3 that size and morphology of zeolite crystals are influenced by the amount of seeds immobilized on the modified glassy carbon, in which 3 mL of seeds gave more cuboid shape crystals with size about 1 μm. On the other hand, immersion for 40 hours in colloidal nanozeolite at 100 °C has caused cracks on the thin films which do not appear when the immersion time is 20 hours. Therefore the best prepared sample is ZGC3-20, which was used further for iron deposition.

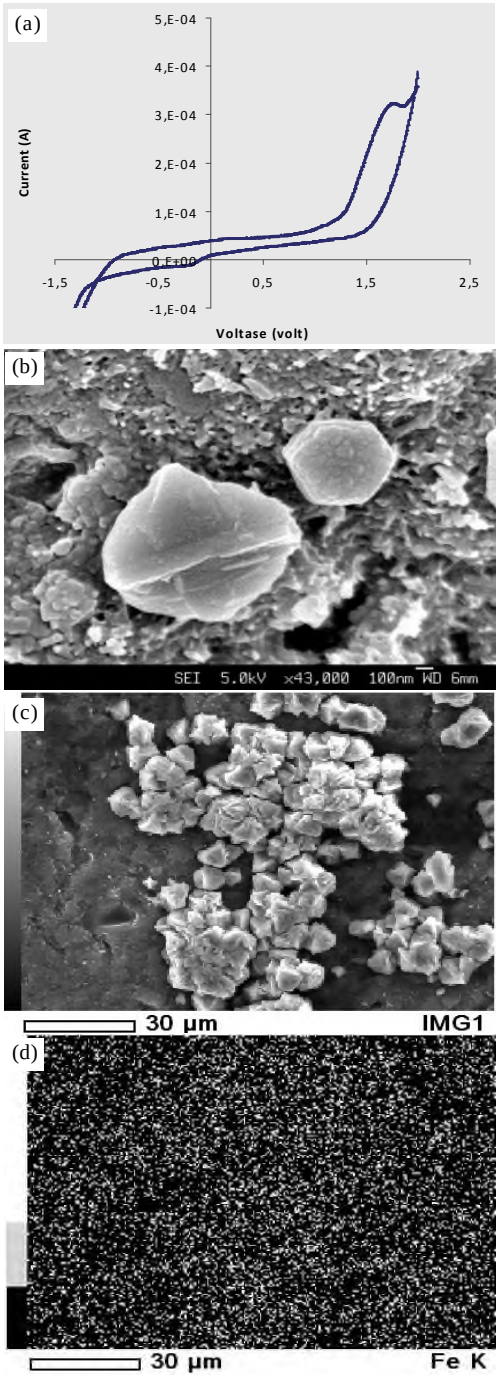

Figure 4. (a). Cyclic voltamogram of Fe(III) solution on ZGC3-20 plate, SEM image of plate Fe-ZGC3-20 (b). 43 kx, (c). 1 kx magnification and (d). EDS mapping for Fe in 1 kx image

Iron Electrochemical-Deposition in Thin Film Nanozeolite Grown on Modified Glassy Carbon

The containing Fe(III) ZGC3-20 plate that treated electrochemically then was labelled Fe-ZGC3-20. Figure 4 a shows the cyclic voltamogram of the electrochemistry experiment. It can be seen the appearance of potential reduction at -0.3 V, indicative of the reduction of $Fe^{2+} \rightarrow Fe^{0}$. Hence, it could be assumed that the reduction process of $Fe^{3+} \rightarrow Fe^{(0)}$ has occured. At +1.5 V, another peak was also observed, that could be assigned to the oxidation of $Fe^{2+} \rightarrow Fe^{3+}$ or/and the oxidation of oxygen ($O^{2-} \rightarrow O_2$).

However, it needs further investigation to understand this process. After electrochemical reduction of Fe(III) → Fe(0), the thin nanozeolite film was covered by white thin layer, which also can be observed by SEM (Figure 4(b)). It can be seen that the shape and size of nanocrystalline zeolite are unchanged after the electrochemical treatment, but some of the crystals combined to become larger aggregates, due to the weakening of the bonding between polyelectrolyte with the nanozeolite.

The EDS mapping of the surface of Fe-ZGC3-20 (Figure 4(d)) indicates that after electrochemical treatment, the surface thin film consists of about 0.30% (w/w) iron that spread evently both on the surface covered by nanozeolite thin film and that from modified glassy carbon.

CONCLUSION

Preparation of iron nanoparticle by electrochemical method has been attempted. The success of this preparation greatly depends on the success of the synthesis of thin film of FAU type nanozeolite grown on modified glassy carbon electrode. There is indication that nanozeolite obtained has particle size < 100 nm. The amount of seed added and the immersion time in FAU colloid influence the overall quality of the thin film. Cyclic voltamogram indicates successful Fe(0) formation, while SEM image shows the formation mostly occur outside the zeolite. It needs further investigation to observe iron nanoparticle formation inside the pores of nanozeolite.

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