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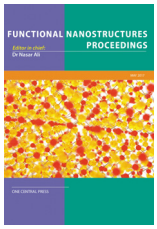

The Effect of Citric Acid Concentration to Functionalize Iron Oxide Nanoparticles for Electrochemical Performance in Glucose Detection

NOORHASHIMAH Mohamad Nor[1], KHAIRUNISAK Abdul Razak[1,2], ZAINOVIA Lockman[1]*

[1]School of Materials and Mineral Resources Engineering Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia.
[2]NanoBiotechnology Research & Innovation (NanoBRI), INFORMM, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia.
[*]corresponding author

ABSTRACT

In this study, iron oxide nanoparticles (IONPs) were synthesized using a precipitation technique and surface functionalized with varying citric acid (CA) concentrations (0.10, 0.25, 0.50 and 0.70 g/ml) to produce colloidal stable IONPs in water. Citric acid provides additional functionality and prevents agglomeration and oxidation of IONPs. The effects of varying CA concentration to the crystallinity, morphology and stability of the IONPs-CA in water were studied using X-ray diffraction (XRD) and transmission electron microscopy (TEM). Colloidal stable IONPs in water were obtained for CA concentration of 0.25-0.70 g/ml but unstable IONPs in water was obtained for 0.10 g/ml CA concentration. This happen because 0.10 g/ml CA contains insufficientcarboxylic group to prevent agglomeration of IONPs. From XRD patterns, high crystallinity of spinel cubic lattice of maghemite (γ-Fe_2O_3) was obtained and from the TEM images, the size of IONPs-CA obtained was in range of 18-22 nm. Then the colloidal stable IONPs-CA in water was drop casted on indium tin oxide (ITO) glass electrode to modify the electrode together with glucose oxidase (GOx) enzyme and Nafion for glucose detection. The bioelectrode designated as Nafion/GOx/IONPs-CA/ITO shows good electrochemical performance for glucose detection for linear range of 1.0-12.0 mM. The effects of varying CA concentration to the electrochemical performance of the modified electrode in glucose sensing were observed. Increasing the concentration of CA decreases the electrochemical performance of the modified electrode. The optimum CA concentration to functionalize and stabilize IONPs was 0.25 g/ml.

I. INTRODUCTION

Increasing the number of diabetic patients every year made the direct monitoring of glucose levels in the bloods is very crucial. High accuracy and high sensitivity glucose biosensor using modified electrode based on enzymes and iron oxide nanoparticles (IONPs) was successfully developed recently [1-3]. However, the main barrier in commercializing the enzymatic glucose biosensor is controlling the morphology and distribution of IONPs on the biosensors to ensure the consistency of the glucose biosensor performance. Therefore, stable dispersion of IONPs is important to obtain in order to control the morphology of IONPs on the glucose biosensor, ensure efficient enzyme immobilization on the matrix as well as reducing matrix interference. Stable IONPs in water can be obtained by surface functionalization of the IONPs with organic, inorganic and biopolymeric material such as chitosan, silica, polymers and carbon [4, 5]. Among them, surface functionalization of IONPs with citric acid (CA) is of interest to explore since the CA is a small molecule that has three carboxyl and one hydroxyl groups and is known to chemisorb to the IONPs by forming a carboxylate group with the Fe−OH molecules presence on the nanoparticle surface, leaving one or two carboxyl groups negatively charged that can be used for further surface modification. In this work, IONPs were initially synthesized and functionalized with varying CA concentration. Then the CA-IONPs were drop casted on the ITO glass electrode to develope enzymatic glucose biosensor. Here IONPs-CA acts as the matrix for GOx enzyme immobilization and increase the electron mobility between analyte and bioelectrode. The effect of citric acid concentration on the morphology and colloidal stability of IONPs in water was observed together with their electrochemical and electrocatlytic performance to glucose sensing. To the best of our knowledge, there is few work explored on using CA-IONPs for modification of electrode in glucose sensing.

II. METHODOLOGY

IONPs were prepared by precipitation method and surface functionalized with varying citric acid concentration. Citric acid was introduced in post-synthesis process at room temperature. Before modification,

the ITO glasses were cleaned using alkaline Radio Corporation America (RCA) to improve the wettability. Then, IONPs was dropped on the ITO glass and dried in an oven at 150 ºC for 2 hours. After that, glucose oxidase enzyme (GOx) was immobilized overnight and Nafion was dropped on the biosensor to protect the enzyme layer and to provide good electrical conductivity.

III. RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of as synthesized IONPs (Fig. 1 (a)) and IONPs functionalized with varying CA concentration (Fig. 1 (b-e)) that corresponds to spinel cubic lattice of maghemite, Fe_2O_3 (ICDD No. 00-039-1346). From the XRD pattern, well-resolved diffraction peaks show pure, highly crystalline, and single-phase IONPs were synthesized. The crystallinity of the as synthesized IONPs and IONPs functionalized with varying CA concentration was similar.

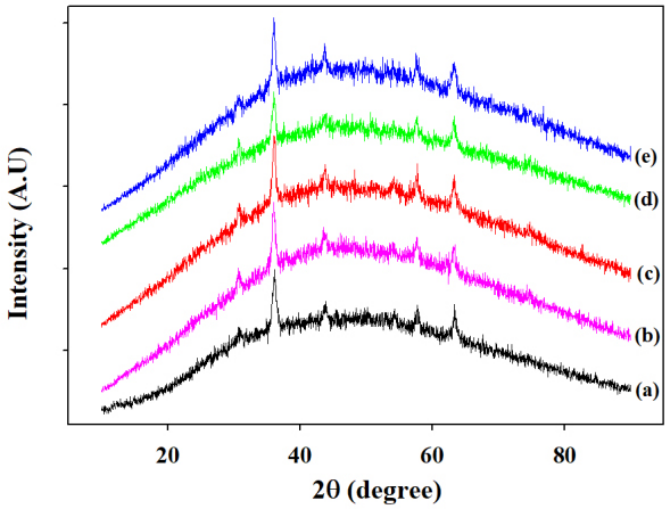

Figure 1 XRD patterns for (a) as synthesized IONPs, (b) IONPs-0.10CA, (c)) IONPs-0.25CA, (d) IONPs-0.50CA and (e) IONPs-0.70CA.

Fig. 2 shows the TEM images of the IONPs functionalized with varied CA concentration with mode particles size of 18-22 nm. With increasing the CA concentration, the particle size tends to decrease. Among all IONPs functionalized with varied CA, IONPs-0.25CA (Fig. 1 (b)) shows well distributed IONPs and less aggregation between IONPs obtained.

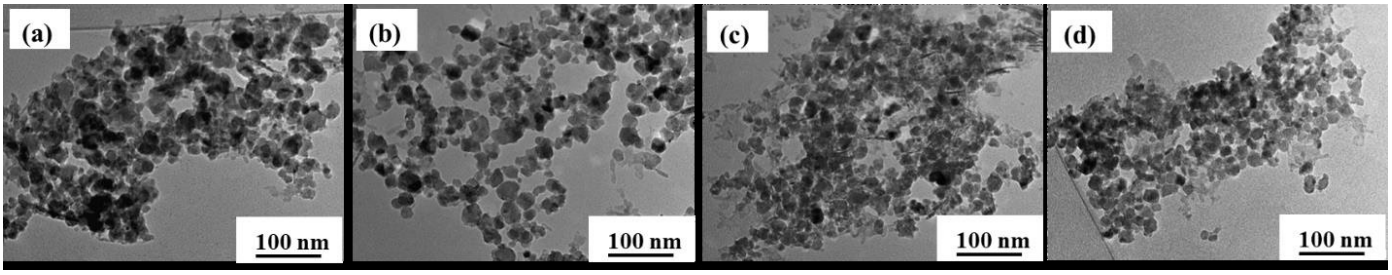

Figure 2 TEM images for (a) IONPs-0.10CA, (b) IONPs-0.25CA, (c) IONPs-0.50CA and (d) IONPs-0.70CA.

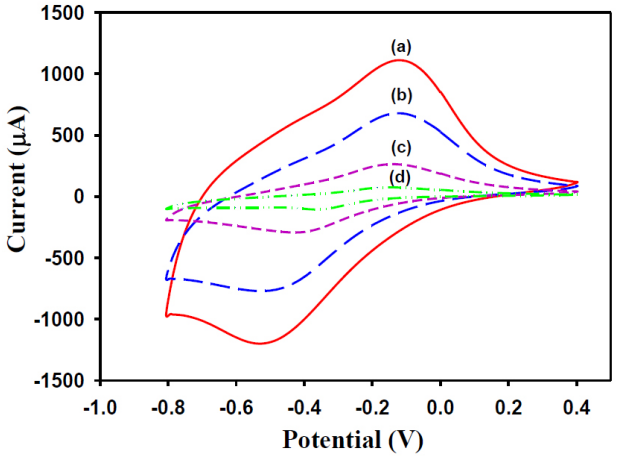

Figure 3 CV response of modify electrode with (a) IONPs-0.10CA, (b) IONPs-0.25CA, (c) IONPs-0.50CA and (d) IONPs-0.70CA in 1mM glucose into PBS (pH 7.0) at scan rate of 100 mV/s.

Fig. 3 shows the cyclic voltammetry (CV) of IONPs functionalized with varied CA together with GOx enzyme and Nafion layer to modify the ITO glass electrode in the presence of 1mM glucose solution. Increasing CA concentration decreased the electrochemical performance of the modified electrode. This is due to increasing coating layer with increased of CA concentration. Optimum CA concentration to functionalize IONPs for glucose sensing was 0.25 g/ml because at this condition, high electrochemical response was obtained together with high colloidal stable of IONPs in water.

IV. CONCLUSION

In this work CA-IONPs, GOx enzyme and Nafion were successfully modified the ITO electrode for glucose sensing applications. Increasing the concentration of CA to functionalize IONPs decreased the electrochemical performance of the modified electrode. The optimum CA concentration to produce high colloidal stable IONPs in water together with high electrochemical response in glucose sensing application was at 0.25 g/ml.

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