ZnCr2-xFexO4 Nanoparticles-Modified Electrochemical Sensors: A Comparative Study

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$ZnCr_{2-x}Fe_xO_4$ Nanoparticles-modified electrochemical sensors: A comparative study

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***Abstract*— This work presents the $ZnCr_{2-x}Fe_xO_4$ (x = 1, 1.25, 1.5, 1.75, 2) nanomaterials modified screen-printed carbon-based electrochemical sensors. The electrochemical sensor's performance was studied towards paracetamol sensing. The sensitivity and kinetic rate constant were evaluated for each sensor and compared. Found that the sensitivity and kinetic rate constant decreased as the amount of Cr decreased from x = 1 to 1.75. The best sensitivity and kinetic rate constant were observed for the pure ferrite sensor (x = 2).**

Keywords*— *Nanoparticles, spinel, sensors, sensitivity, rate constant, paracetamol

I. INTRODUCTION

Paracetamol is the most widely used antipyretic drug to treat fever, headache, cold, migraine, and chronic pain in the world [1-3]. Paracetamol is also known as acetaminophen, N-acetyl-p-aminophenol, this is a very safe and effective agent when used within the limits; limited usage can avoid toxic metabolite accumulation and liver or kidney damage [4]. To avoid problems concerning paracetamol overdose or to understand the usage within the limits it is very important to have a reliable, low-cost, user-friendly sensing system. Among all the approaches, electrochemical sensing is a very simple, low-cost technique, easily employable in on-site applications [2, 5]. Developing new electrode materials to improve the sensing performance of electrochemical sensors is a wide research topic. For this purpose, several research studies used different nanomaterials to tailor the screen-printed carbon electrodes (SPCE) [6-8].

In this work, we focused on spinel-based ferrite nanomaterials as an electrochemical sensing platform. A spinel crystal structure is a face-centered cubic system with O anions forming tetrahedral and octahedral voids. Metallic cations have the tendency to occupy these voids depending on their oxidation states. Based on the occupancy of cations the spinel can be normal or inverse spinel [9-10]. In normal spinel ferrites, M(II) occupies the tetrahedral void and M(III) occupies the octahedral void [9]. Inverse spinel has octahedral voids occupied by M(II) and M(III) whereas tetrahedral voids are occupied by only M(III) [10]. There is not much research has been carried out on the application of spinel nanomaterials as electrochemical sensing species. In our previous work, we studied how the chemical composition and transition from normal spinel ($ZnFe_2O_4$) to inverse spinel ($NiFe_2O_4$) affect the electrochemical sensing performance [11]. How the electrochemical sensing be affected by replacing Fe(III) with Cr(III) and Bi(III) in the octahedral void of the $ZnFe_2O_4$ structure? was also partly studied [12].

The present paper presents the application of the Zn(II) based normal spinel nanomaterials as electrochemical sensing materials. We present the electrochemical sensing capability of $ZnCr_{2-x}Fe_xO_4$ (x = 1, 1.25, 1.5, 1.75, 2) nanomaterials by comparing the sensitivity and kinetic rate constant. Commercially available SPCEs were modified by synthesized spinel nanomaterials. The electrochemical sensing ability of the surface modified SPCEs was studied towards paracetamol. The sensitivity, and kinetic rate constant of different sensors are reported and discussed.

II. MATERIALS AND METHODS

A. Chemicals

$Zn(NO_3)_2{\cdot}6H_2O$, $Cr(NO_3)_3{\cdot}9H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, $C(NH_2)_2O$ (Urea), $C_4H_{10}O$ (Butanol), and paracetamol powder were purchased from Sigma Aldrich and used without further modification.

B. Material synthesis

The auto-combustion method as described in the literature [13] was used to synthesize nanomaterials. $Zn(NO_3)_2{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, $Cr(NO_3)_3{\cdot}9H_2O$, were acted as oxidizing agents, and $C(NH_2)_2O$ (Urea) as a reducing agent. A redox mixture of 1:1 mole ratio was prepared in a crucible, inserted inside a graphite reactor, and heated up to 600 ºC within a furnace. The resulting product was annealed at 600 ºC for 1hr and cooled down at normal conditions until the material reached room temperature. The final material was grounded to obtain fine powders of $ZnCr_{2-x}Fe_xO_4$ (x = 1, 1.25, 1.5, 1.75, 2).

C. Electrodes modification

Commercially available screen-printed carbon working electrode (0.12 cm^2) (WE), carbon counter electrode (CE), and Ag/AgCl reference electrode (RE) were used as three electrodes in the electrochemical system. Nanomaterial suspension was prepared (3:1 material to solvent ratio) in

Table 2. Electrochemical parameters of $ZnCr_{2-x}Fe_xO_4$ and bare sensors.

Sensor	Ox. Potential (mV)	Ox. Current (μA)	α	ΔE_p (mV)	k (ms^{-1})	Sensitivity (μA/mM)
Bare	396 ± 2	34.50 ± 0.20	0.543 ± 0.003	746 ± 5	$2.29 \pm 0.27 \cdot 10^{-3}$	16.68 ± 0.93
$ZnCrFeO_4$	285 ± 2	47.68 ± 0.72	0.24 ± 0.01	446 ± 2	4.53 ± 0.54	35.72 ± 0.11
$ZnCr_{0.75}Fe_{1.25}O_4$	282 ± 2	45.88 ± 0.39	0.355 ± 0.003	564 ± 7	0.175 ± 0.028	34.48 ± 0.15
$ZnCr_{0.5}Fe_{1.5}O_4$	285 ± 2	45.92 ± 0.12	0.35 ± 0.01	455 ± 4	1.1 ± 0.06	32.93 ± 0.27
$ZnCr_{0.25}Fe_{1.75}O_4$	280 ± 1	47.81 ± 0.26	0.32 ± 0.01	488 ± 4	0.88 ± 0.16	32.07 ± 0.15
$ZnFe_2O_4$	244 ± 1	52.41 ± 0.56	0.23 ± 0.02	386 ± 2	13.1 ± 2.8	37.75 ± 0.17

constant 'k'. We can see from Table 1 that the $ZnFe_2O_4$ sensor has the lowest ΔEp, and greatest k, indicating a high likelihood of reversibility and quicker response at the interface. All other sensors exhibit greater 'k' values when compared to the bare sensor, demonstrating the interface's decreased reaction time.

By changing the paracetamol concentration, the CV was carried out three times for each sensor. To build the calibration for each type of sensor, linear fitting was done using the average oxidation current at each concentration, as shown in Fig. 5. The sensitivity of each sensor to detect paracetamol was determined by the slope of the linear calibration fit, and this information is presented in Table 1. It is observed that the sensitivity has reduced as the amount of Cr decreased from x = 1 to 1.75 and increased for the $ZnFe_2O_4$ sensor. This demonstrates that the presence of Cr in $ZnFe_2O_4$ is arguably affecting the electrochemical performance.

C. Conclusion

As a result, we were able to effectively develop a variety of zinc-based nanomaterials by inserting Cr into the structure. The sensing performance of the six different normal spinel nanomaterials was demonstrated electrochemically. The change in the amount of Cr in $ZnFe_2O_4$ is appreciably affecting the sensitivity and kinetic rate constant in comparison to the bare carbon sensor.

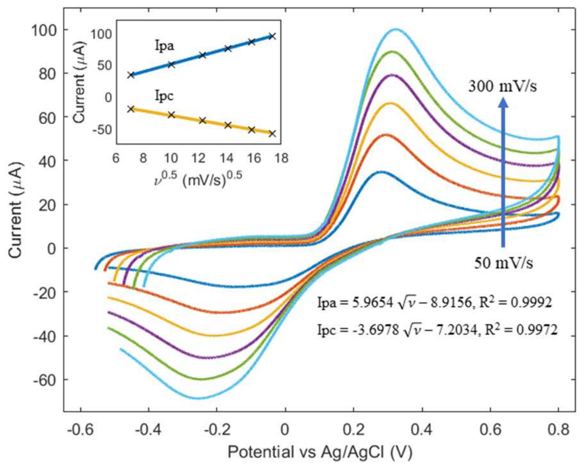

Fig. 3. Cyclic voltammograms of $ZnCrFeO_4$ sensor at different 'ν' with 1mM paracetamol in 0.1M PBS pH 6.9. The inset shows the redox currents with respect to $\nu^{0.5}$.

To understand the effect clearly, further nanomaterial characterization is needed. Nanomaterials bandgap, specific surface area, and electroactive surface area can remarkably affect the electrochemical sensing performance. Ionic radii and the spin of Cr and Fe with O may play a role too in describing their performance in sensing. The outcome of sensors has good electrochemical sensing capability; as a result, it is suggested that they can be utilized in biosensors to monitor additional molecules of biomedical relevance.

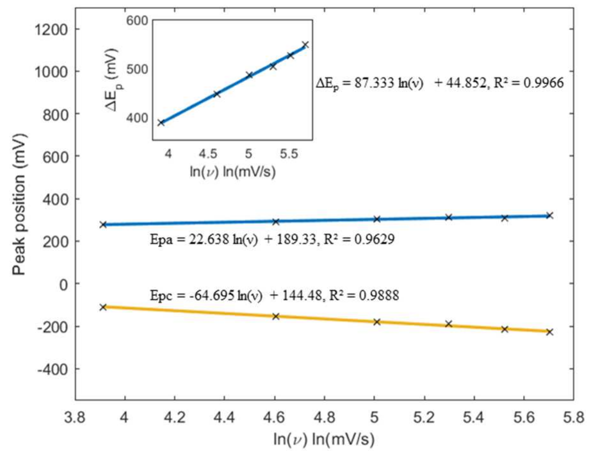

Fig. 4. Linear fitting of E_{pa} and E_{pc} of $ZnCrFeO_4$ sensor with ln(ν), inset: ΔEp vs ln(ν).

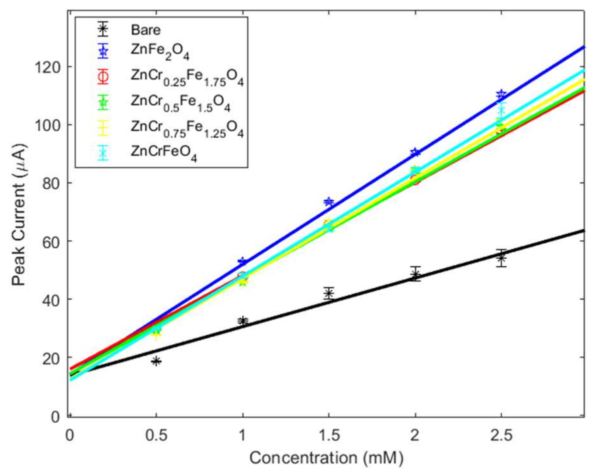

Fig. 5. Calibration of $ZnCr_{2-x}Fe_xO_4$ (x = 1, 1.25, 1.5, 1.75, 2) sensors compared with the bare sensor.

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