

# Tổng hợp vật liệu $\text{Co}_3\text{O}_4$ có nguồn gốc từ ZIF-67 và ứng dụng trong biến tính điện cực phát hiện acid ascorbic

## TÓM TẮT

Trong nghiên cứu này,  $\text{Co}_3\text{O}_4$  dạng tinh thể có cấu trúc xếp được tổng hợp bằng cách nung ZIF-67 trong môi trường không khí. Đặc trưng vật liệu  $\text{Co}_3\text{O}_4$  được nghiên cứu bằng XRD, BET, SEM và EDS. Điện cực biến tính  $\text{Co}_3\text{O}_4$ -GPE dùng phát hiện điện hóa acid ascorbic thể hiện khoảng tuyến tính từ 2  $\mu\text{M}$  đến 15  $\mu\text{M}$  với giới hạn phát hiện là 0,48  $\mu\text{M}$ . Kết quả độ thu hồi dao động từ 97,82% đến 99,5% đối với acid ascorbic xác định trong viên thuốc thương mại.

**Từ khoá:**  $\text{Co}_3\text{O}_4$ , ZIF-67, acid ascorbic.

# ZIF-67-derived Co<sub>3</sub>O<sub>4</sub> Porous Crystalline Material for Electrochemical Ascorbic Acid Detection

## ABSTRACT

The Co<sub>3</sub>O<sub>4</sub> porous crystalline material was synthesized by calcining ZIF-67 sample in air. The Co<sub>3</sub>O<sub>4</sub> material was characterized by XRD, BET, SEM, and EDS. The electrode modified with Co<sub>3</sub>O<sub>4</sub> was used to determine ascorbic acid. The proposed Co<sub>3</sub>O<sub>4</sub>-GPE electrode exhibited a linear range of 2 μM to 15 μM with a detection limit of 0.48 μM. Recovery results, ranging from 97.82% to 99.5% for ascorbic acid in pharmaceutical tablet.

**Keywords:** Co<sub>3</sub>O<sub>4</sub>, ZIF-67, ascorbic acid.

## 1. INTRODUCTION

Ascorbic acid (AA), the common name for Vitamin C, is a common multivitamin component and occurs naturally in various foods. It is important for a healthy diet and acts as an antioxidant. However, an overdose of vitamin C can lead to side effects such as stomach upset, headache, difficulty sleeping, and skin flushing.<sup>1,2</sup> Therefore, the rapid and accurate determination of AA has attracted scientific attention.

Many analytical methods exist for determining ascorbic acid (AA), including techniques such as spectrofluorometry,<sup>3,4</sup> chromatography,<sup>5,6</sup> spectrophotometry,<sup>7,8</sup> capillary zone electrophoresis,<sup>9,10</sup> and electrochemistry<sup>11,12</sup>. Among these, electrochemical methods employing modified electrodes have received considerable interest owing to their inherent simplicity, high sensitivity, and economic viability.

Cobalt oxide is a semiconductor with wide applications in many fields, including catalysis, electrode materials, gas sensing, and drug delivery.<sup>13-15</sup> Numerous studies have explored the diverse applications of Co<sub>3</sub>O<sub>4</sub>; however, its potential use in electrode modification for pharmaceutical analysis remains relatively underexplored. To date, various porous nanostructures of Co<sub>3</sub>O<sub>4</sub> have been synthesized, including spherical, tubular, rod-like, and flower-like morphologies. Most synthesis methods

utilize cobalt carbonate or hydroxide salts as precursors, often yielding materials with relatively low surface areas.<sup>16,17</sup>

Recent, the application of metal-organic frameworks (MOFs; ZIFs) as precursors in the synthesis of inorganic materials is a growing area of research.<sup>18-25</sup> Studies show that heat treatment of ZIF-67 can pyrolyze their ligands and lead to the formation of metal oxide nanoparticles. Therefore, the metal-centered organic framework material Co (ZIF-67) has appeared as a potential precursor to synthesize cobalt oxide (Co<sub>3</sub>O<sub>4</sub>) while still inheriting the structural characteristics of ZIF-67 and improving its catalytic activity.

In this work, an electrode modified with the Co<sub>3</sub>O<sub>4</sub> porous crystalline material derived from ZIF-67 is investigated. The obtained electrode was used for the electrochemical determination of AA.

## 2. EXPERIMENT

### 2.1. Chemicals

2-methylimidazol (2-H<sub>im</sub>, 98%), ascorbic acid, graphite powder and paraffin oil were received from Sigma Aldrich. Cobalt nitrate hexahydrate [Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 99%] was purchased from Macklin (China). Phosphoric acid (H<sub>3</sub>PO<sub>4</sub>, 85%), potassium dihydrogen phosphate (KH<sub>2</sub>PO<sub>4</sub>, 99%), boric acid (H<sub>3</sub>BO<sub>3</sub>, 99%) and potassium hydroxide (KOH) were received from Guangdong-Guanghua Co. Ltd (China).

Vitamin C tablet (Vitamin C, 500 mg AA, from Pharimexco Viet Nam) was purchased from a local pharmacy. All chemical reagents were used as received without any further purification.

Britton-Robinson (B-R) buffer solutions were made using 0.5 M solutions of  $\text{H}_3\text{BO}_3$ ,  $\text{H}_3\text{PO}_4$ , and  $\text{CH}_3\text{COOH}$ . The pH of the B-R buffer was adjusted to the desired value with 1 M KOH or 1M  $\text{H}_3\text{PO}_4$  solutions.

## 2.2. Apparatus

All electrochemical analyses, including cyclic voltammetry and square wave voltammetry, were conducted using a DY2322 potentiostat, Digi-Ivy, Inc. Austin. A standard three-electrode cell was employed, consisting of a working electrode ( $\text{Co}_3\text{O}_4$ -GPE or bare GPE,  $0.07\text{ cm}^2$ ), a counter electrode (Pt wire), and a reference electrode ( $\text{Ag}/\text{AgCl}$ ,  $\text{KCl}_{\text{sat}}$ ).

## 2.3 Synthesis of $\text{Co}_3\text{O}_4$ porous crystalline material from ZIF-67

The synthesis of ZIF-67 was conducted according to a previously established method<sup>26</sup>.

1.455 g of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was dissolved in 50 mL of ethanol, and 1.64 g of 2-methylimidazole ( $\text{H}_{\text{mim}}$ ) was dissolved in 50mL of ethanol, resulting in a  $\text{Co}^{2+} : \text{H}_{\text{mim}}$  molar ratio of 1 : 4. The  $\text{H}_{\text{mim}}$  solution was slowly added to  $\text{Co}(\text{NO}_3)_2$  solution under continuous stirring for 30 minutes at room temperature. The obtained mixture was allowed to stand at room temperature for 6 hours without stirring, leading to the formation of a colloidal dispersion. The solid product was collected by centrifugation (4000 rpm, 30 minnutes), washed three times with ethanol, and dried at  $80\text{ }^\circ\text{C}$ , 12 hours.

$\text{Co}_3\text{O}_4$  was obtained by calcining ZIF-67 in air at a heating rate of  $1\text{ }^\circ\text{C} \cdot \text{min}^{-1}$ .

## 2.4. Preparation of $\text{Co}_3\text{O}_4$ -GPE modified electrode

To prepare the  $\text{Co}_3\text{O}_4$ -GPE modified electrode, 40 mg of graphite powder and 5 mg of  $\text{Co}_3\text{O}_4$  powder were thoroughly mixed with  $10\text{ }\mu\text{L}$  of paraffin oil. The resulting paste was then packed into a Teflon holder, and its surface was smoothed using paper. To renew the electrode surface, the outer 2 mm of paste was removed and replaced with freshly prepared paste

## 2.5. Characterization of the $\text{Co}_3\text{O}_4$ porous crystalline material

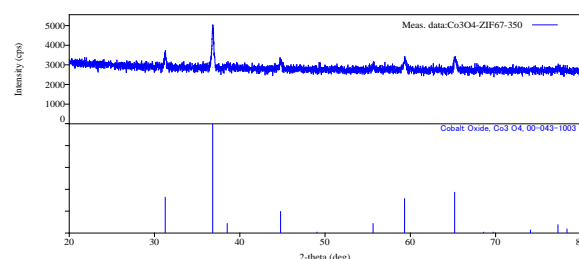
A Bruker-Axs D8 diffractometer (40 kV, 40 mA) was used for powder XRD analysis. Textural properties were determined from nitrogen

adsorption-desorption isotherms at  $-196\text{ }^\circ\text{C}$  with a Micromeritics Gemini VII 2390 V1.02. Sample morphology was examined by scanning electron microscopy (JEOL JSM-6700F, 15 kV, 10 mA), and elemental composition was analyzed using EDS with a JSM-5700 LV.

## 3. RESULTS AND DISCUSSION

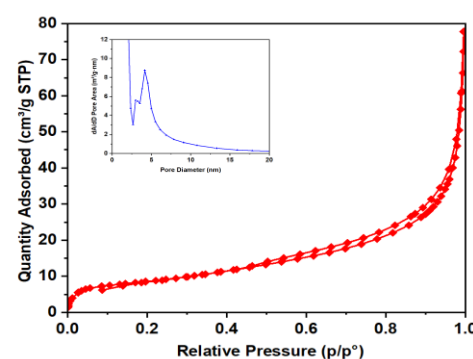
### 3.1. Characterization of the synthesized $\text{Co}_3\text{O}_4$ material

The XRD diffraction pattern of  $\text{Co}_3\text{O}_4$  sample are shown in Fig. 1. X-ray diffraction pattern exhibited reflections at  $2\theta$  values of approximately  $31.5^\circ$ ,  $36.8^\circ$ ,  $38.0^\circ$ ,  $44.6^\circ$ ,  $55.8^\circ$ ,  $59.4^\circ$ ,  $65.3^\circ$  and  $77.5^\circ$ , corresponding to the (220), (311), (222), (400), (422), (511), (440) and (533) crystalline planes of the  $\text{Co}_3\text{O}_4$  cubic structure (JCPDS No. 04-043-1003)<sup>25</sup>.

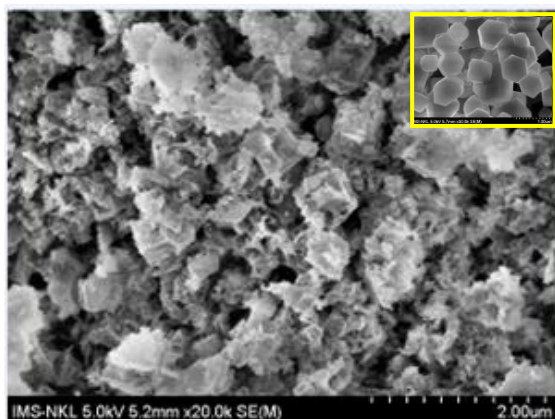


**Figure 1.** XRD pattern of the  $\text{Co}_3\text{O}_4$  porous crystalline material.

Nitrogen adsorption-desorption isotherms were employed to characterize the specific surface area and pore morphology of the  $\text{Co}_3\text{O}_4$  sample. As depicted in Figure 2, the sample presented a Type IV isotherm, accompanied by an H3 hysteresis loop, suggesting a mesoporous structure. The BET surface area was determined to be  $30.43\text{ m}^2/\text{g}$ , and the pore size distribution was at 3 nm.

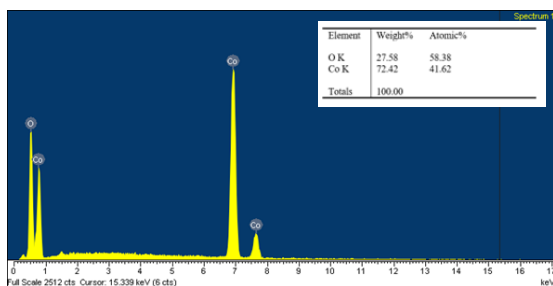


**Figure 2.** Nitrogen adsorption-desorption isotherms (A) and pore size distribution (B) of the  $\text{Co}_3\text{O}_4$  porous crystalline material.



**Figure 3.** SEM image of the  $\text{Co}_3\text{O}_4$  porous crystalline material, Inset: SEM image of ZIF-67 material.

SEM images of  $\text{Co}_3\text{O}_4$  (Figure 3) revealed that the calcined particles retained a cubic morphology, consistent with the original ZIF-67 crystal template, characterized by an internal hollow structure and a surface exhibiting porosity. However, thermal treatment resulted in the observation of some collapsed hollow structures.



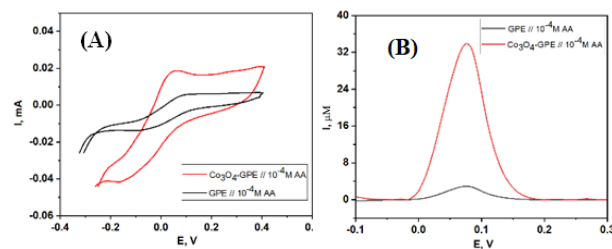
**Figure 4.** EDS spectra of the  $\text{Co}_3\text{O}_4$  porous crystalline material.

EDS analysis was conducted on the  $\text{Co}_3\text{O}_4$  sample (Figure 4). Cobalt (Co) and oxygen (O) were confirmed to be present on the sample's surface based on the results. Elemental analysis of the  $\text{Co}_3\text{O}_4$  yielded 41.62% cobalt and 58.38% oxygen.

A comprehensive morpho-structural analysis of the  $\text{Co}_3\text{O}_4$  material, utilizing results of XRD, SEM, EDS and BET, validated the successful synthesis of the  $\text{Co}_3\text{O}_4$  porous crystalline material.

### 3.2. Electrochemical characterization

The electrochemical behavior of ascorbic acid (AA) was investigated using cyclic voltammetry (CV) and square wave voltammetry (SWV).



**Figure 5.** Cyclic voltammograms (A) and square wave voltammograms (B) at GPE and  $\text{Co}_3\text{O}_4$ -GPE modified electrode in 0.2 M B-R buffer solution pH = 4 containing of  $10^{-4}$  M AA.

A peak of AA at 0.08 V was observed in the CV and SWV curves obtained at both the bare GPE and the  $\text{Co}_3\text{O}_4$ -GPE, as illustrated in Figure 5. The  $\text{Co}_3\text{O}_4$ -GPE exhibited a lower peak potential and higher current. The oxidation peak current for AA at the  $\text{Co}_3\text{O}_4$ -GPE was approximately fifteen-fold greater than that observed at the bare GPE (Figure 5B). This observed enhancement can be attributed to the greater surface area, porous morphology, and functional properties of the  $\text{Co}_3\text{O}_4$  modification compared to the bare GPE.

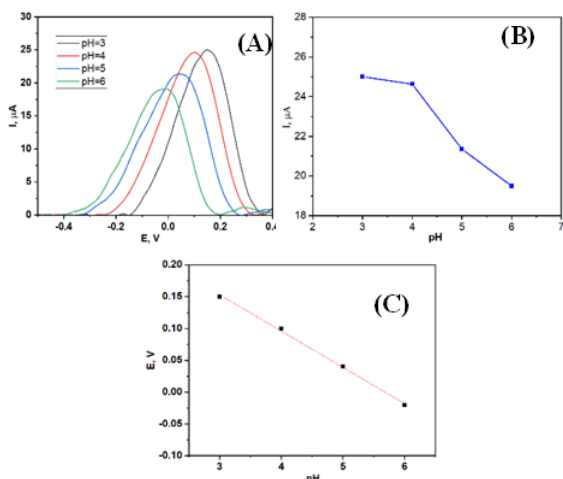
### 3.3. The effect of pH

Square wave voltammetry (SWV) was employed to examine the impact of pH (within the range of 3 to 6) on the voltammetric signals of AA. The pH of the electrolyte significantly affects the AA oxidation on the modified electrode. Figure 6 displays the current responses recorded on the  $\text{Co}_3\text{O}_4$ -GPE under different pH conditions.

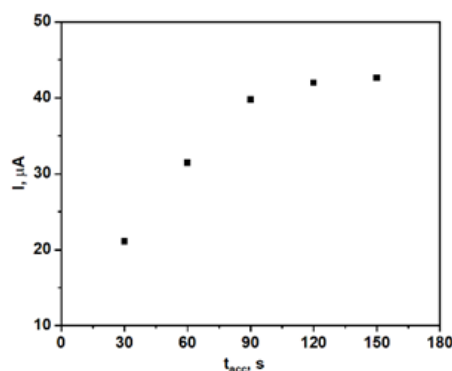
A substantial increase in peak current was observed as  $t_{\text{acc}}$  increased from 0 to 90 seconds, suggesting a corresponding enhancement of AA accumulation at the electrode surface. Beyond 90 seconds, however, the peak current exhibited negligible increase, indicative of the electrode surface approaching adsorption equilibrium. Based on this observation, 90 seconds was selected as the optimal  $t_{\text{acc}}$ .

### 3.4. Accumulation

The effect of accumulation time ( $t_{\text{acc}}$ ) on electrode response was investigated across a range of 0 to 150 seconds in a 0.2 M B-R buffer (pH 4) with  $10^{-4}$  M AA (Figure 7).



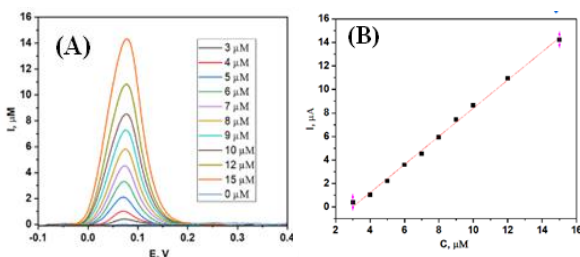
**Figure 6.** Square wave voltammograms of  $\text{Co}_3\text{O}_4$ -GPE in 0.2 M B-R buffer (pH 4) containing  $10^{-4}$  M AA (A); Influence of pH on  $I_p$  (B); Plot of  $E_p$  vs. pH (C).



**Figure 7.** Dependence of  $I_p$  for AA in 0.2M B-R buffer solution pH 4 on accumulation time.

### 3.5. Calibration

The calibration curves for the AA detection with varying concentrations of AA was constructed by recording SWV in 0.2 M B-R buffer solution at pH = 4 (Figure 8A). Accordingly, a calibration curve was shown in Figure 8B. The electrode exhibited a linear response for AA concentrations between 2  $\mu\text{M}$  and 15  $\mu\text{M}$ .



**Figure 8.** Square wave voltammograms recorded at  $\text{Co}_3\text{O}_4$ -GPE increasing concentration of AA (A) and the corresponding calibration curve (B).

The resulting linear regression equation was:

$$I_{pa}/\mu\text{A} = (-3.56335 \pm 0.19192) + (1.19706 \pm 0.02218) [\text{AA}]/\mu\text{M}, \quad (R = 0.99726)$$

For ascorbic acid (AA) detection, the  $\text{Co}_3\text{O}_4$ -GPE electrode exhibited a 0.48  $\mu\text{M}$  detection limit and a sensitivity of 1.19, which are lower compared to some published results 1.52  $\mu\text{M}$  at CL-TiN/GCE,<sup>27</sup> 0.5  $\mu\text{M}$  at NiCoO<sub>2</sub>/C,<sup>28</sup> 0.83  $\mu\text{M}$  at AgNP-Psi<sup>29</sup>.

## 4. REAL SAMPLE ANALYSIS

The  $\text{Co}_3\text{O}_4$ -GPE electrode was used to analyze AA in Vitamin C tablets (Pharimexco Viet Nam) via the standard addition method to assess its applicability. Table 1 summarizes the results, confirming the electrode's effectiveness for AA determination in pharmaceuticals. The measured mean AA concentration demonstrated agreement with the labeled value, and recovery rates ranged from 97.82% to 99.5%.

Table 1. Results from the analysis of AA in a real Vitamin C tablet sample.

| Sample             | Added ( $\mu\text{M}$ ) | Found ( $\mu\text{M}$ ) | Recovery (%)     | RSD (%) |
|--------------------|-------------------------|-------------------------|------------------|---------|
| Vitamin C (500 mg) | 3                       | $2.96 \pm 0.02$         | $98.66 \pm 0.84$ | 0.85    |

## 5. CONCLUSION

The synthesis of  $\text{Co}_3\text{O}_4$  porous crystalline material was performed using the ZIF-67 material as a precursor. The resulting  $\text{Co}_3\text{O}_4$  possesses an internal hollow structure and a surface exhibiting porosity. The modified electrode developed with  $\text{Co}_3\text{O}_4$  porous crystalline material offers high sensitivity and a low detection limit, making it promising for AA detection. It has also been successfully used to determine AA in real samples.

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