

Tổng hợp vật liệu Co_3O_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, Co_3O_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 Co_3O_4 được nghiên cứu bằng XRD, BET, SEM và EDS. Điện cực biến tính Co_3O_4 -GPE dùng phát hiện điện hóa acid ascorbic thể hiện khoảng tuyến tính từ 2 μM đến 15 μM với giới hạn phát hiện là 0,48 μM . 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: Co_3O_4 , ZIF-67, acid ascorbic.

ZIF-67-derived Co₃O₄ Porous Crystalline Material for Electrochemical Ascorbic Acid Detection

ABSTRACT

The Co₃O₄ porous crystalline material was synthesized by calcining ZIF-67 sample in air. The Co₃O₄ material was characterized by XRD, BET, SEM, and EDS. The electrode modified with Co₃O₄ was used to determine ascorbic acid. The proposed Co₃O₄-GPE electrode exhibited a linear range of 2 μ M to 15 μ M with a detection limit of 0.48 μ M. Recovery results, ranging from 97.82% to 99.5%, for ascorbic acid in pharmaceutical tablet.

Keywords: Co₃O₄, 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.^{1,2} 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,^{3,4} chromatography,^{5,6} spectrophotometry,^{7,8} capillary zone electrophoresis,^{9,10} and electrochemistry^{11,12}. 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.¹³⁻¹⁵ Numerous studies have explored the diverse applications of Co₃O₄; however, its potential use in electrode modification for pharmaceutical analysis remains relatively underexplored. To date, various porous nanostructures of Co₃O₄ 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.^{16,17}

Recent, the application of metal-organic frameworks (MOFs; ZIFs) as precursors in the synthesis of inorganic materials is a growing area of research.¹⁸⁻²⁵ 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 (Co₃O₄) while still inheriting the structural characteristics of ZIF-67 and improving its catalytic activity.

In this work, an electrode modified with the Co₃O₄ 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_{min}, 98%), ascorbic acid, graphite powder and paraffin oil were received from Sigma Aldrich. Cobalt nitrate hexahydrate [Co(NO₃)₂·6H₂O, 99%] was purchased from Macklin (China). Phosphoric acid (H₃PO₄, 85%), potassium dihydrogen phosphate (KH₂PO₄, 99%), boric acid (H₃BO₃, 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 H_3BO_3 , H_3PO_4 , and CH_3COOH . The pH of the B-R buffer was adjusted to the desired value with 1 M KOH or 1M H_3PO_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 (Co_3O_4 -GPE or bare GPE, 0.07 cm^2), a counter electrode (Pt wire), and a reference electrode (Ag/AgCl , KCl_{sat}).

2.3 Synthesis of Co_3O_4 porous crystalline material from ZIF-67

The synthesis of ZIF-67 was conducted according to a previously established method²⁶.

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 (H_{mim}) was dissolved in 50mL of ethanol, resulting in a $\text{Co}^{2+} : \text{H}_{\text{mim}}$ molar ratio of 1 : 4. The H_{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.

Co_3O_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 Co_3O_4 -GPE modified electrode

To prepare the Co_3O_4 -GPE modified electrode, 40 mg of graphite powder and 5 mg of Co_3O_4 powder were thoroughly mixed with 10 μL 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 Co_3O_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 Co_3O_4 material

The XRD diffraction pattern of Co_3O_4 sample are shown in Fig. 1. X-ray diffraction pattern exhibited reflections at 2θ values of approximately 31.5° , 36.8° , 38.0° , 44.6° , 55.8° , 59.4° , 65.3° and 77.5° , corresponding to the (220), (311), (222), (400), (422), (511), (440) and (533) crystalline planes of the Co_3O_4 cubic structure (JCPDS No. 04-043-1003)²⁵.

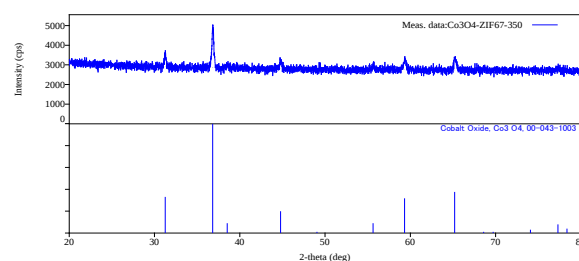


Figure 1. XRD pattern of the Co_3O_4 porous crystalline material.

Nitrogen adsorption-desorption isotherms were employed to characterize the specific surface area and pore morphology of the Co_3O_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.

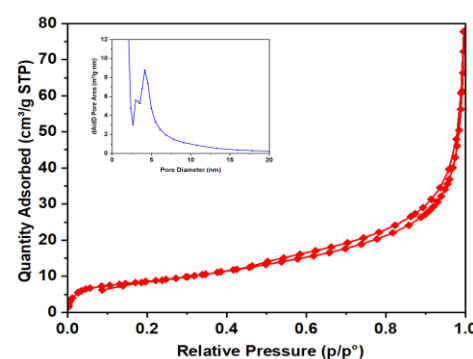


Figure 2. Nitrogen adsorption-desorption isotherms (A) and pore size distribution (B) of the Co_3O_4 porous crystalline material.

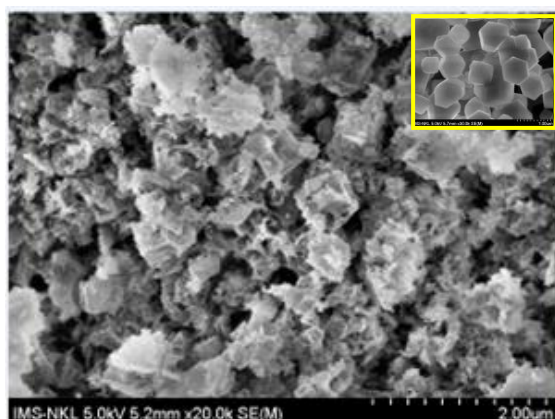


Figure 3. SEM image of the Co_3O_4 porous crystalline material, Inset: SEM image of ZIF-67 material.

SEM images of Co_3O_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.

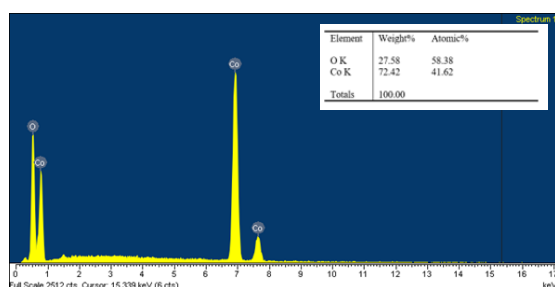


Figure 4. EDS spectra of the Co_3O_4 porous crystalline material.

EDS analysis was conducted on the Co_3O_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 Co_3O_4 yielded 41.62% cobalt and 58.38% oxygen.

A comprehensive morpho-structural analysis of the Co_3O_4 material, utilizing results of XRD, SEM, EDS and BET, validated the successful synthesis of the Co_3O_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).

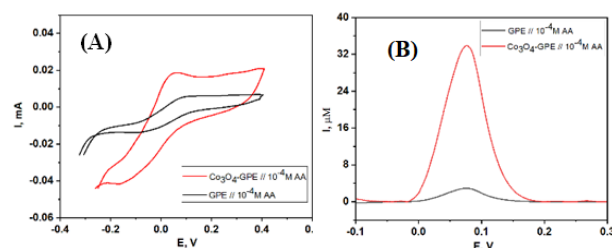


Figure 5. Cyclic voltammograms (A) and square wave voltammograms (B) at GPE and Co_3O_4 -GPE modified electrode in 0.2 M B-R buffer solution pH = 4 containing of 10^{-4} M AA.

A peak of AA at 0.08 V was observed in the CV and SWV curves obtained at both the bare GPE and the Co_3O_4 -GPE, as illustrated in Figure 5. The Co_3O_4 -GPE exhibited a lower peak potential and higher current. The oxidation peak current for AA at the Co_3O_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 Co_3O_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 Co_3O_4 -GPE under different pH conditions.

A substantial increase in peak current was observed as t_{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_{acc} .

3.4. Accumulation

The effect of accumulation time (t_{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).

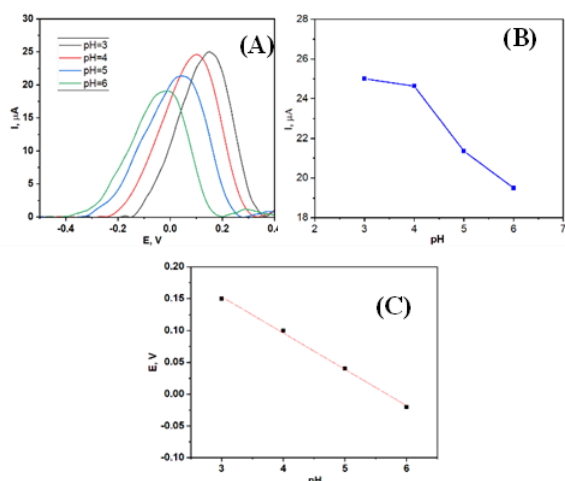


Figure 6. Square wave voltammograms of Co_3O_4 -GPE in 0.2 M B-R buffer (pH 4) containing 10^{-4} M AA (A); Influence of pH on I_p (B); Plot of E_p vs. pH (C).

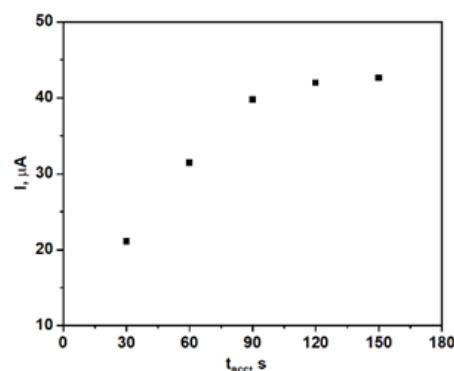


Figure 7. Dependence of I_p for AA in 0.2M B-R buffer solution pH 4 on accumulation time.

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 μM and 15 μM .

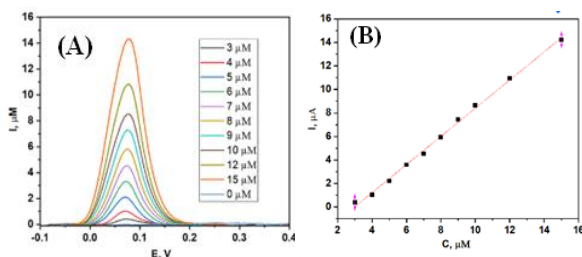


Figure 8. Square wave voltammograms recorded at Co_3O_4 -GPE increasing concentration of AA (A) and the corresponding calibration curve (B).

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 Co_3O_4 -GPE electrode exhibited a 0.48 μM detection limit and a sensitivity of 1.19, which are lower compared to some published results 1.52 μM at CL-TiN/GCE,²⁷ 0.5 μM at NiCoO₂/C,²⁸ 0.83 μM at AgNP-Psi²⁹.

4. REAL SAMPLE ANALYSIS

The Co_3O_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 (μM)	Found (μM)	Recovery (%)	RSD (%)
Vitamin C (500 mg)	3	2.96 ± 0.02	98.66 ± 0.84	0.85

5. CONCLUSION

The synthesis of Co_3O_4 porous crystalline material was performed using the ZIF-67 material as a precursor. The resulting Co_3O_4 possesses an internal hollow structure and a surface exhibiting porosity. The modified electrode developed with Co_3O_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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