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Tổng hợp Co_3O_4 từ tiền chất ZIF-67 và ứng dụng biến tính điện cực phát hiện acid ascorbic

TÓM TẮT

Trong nghiên cứu này, Co_3O_4 dạng tinh thể có cấu trúc xốp 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 Co_3O_4 Porous Crystalline Material for The Electrochemical Detection of Ascorbic Acid

ABSTRACT

The Co_3O_4 porous crystalline material was synthesized through the calcination of ZIF-67 sample in air atmosphere. The Co_3O_4 material was characterized by XRD, BET, SEM, and EDS. The electrode modified with Co_3O_4 was used for the determination of ascorbic acid. The proposed Co_3O_4-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_3O_4, ZIF-67, ascorbic acid.*

1. INTRODUCTION

Vitamin C, also known as ascorbic acid (AA), is a common ingredient in multivitamins and is found naturally in many 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.

Numerous analytical methodologies have been reported for the determination of 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 utilizing modified electrodes have attracted considerable interest due to their inherent simplicity, high sensitivity, and cost-effectiveness.

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 Co_3O_4; however, its potential use in electrode modification for pharmaceutical analysis remains relatively underexplored. To date, various porous nanostructures of Co_3O_4 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 (Co_3O_4) while still inheriting the structural characteristics of ZIF-67 and improving its catalytic activity.

In this work, an electrode modified with the Co_3O_4 porous crystalline material derived from ZIF-67 is demonstrated. The obtained electrode was used for the electrochemical determination of AA.

2. EXPERIMENT

2.1. Chemicals

2-methylimidazol (2-H_{mim}, 98.0%), ascorbic acid, graphite powder and parafin oil were received from Sigma Aldrich. Cobalt nitrate hexahydrate [$Co(NO_3)_2{\cdot}6H_2O$, 99%] was purchased from Macklin (China). Phosphoric acid (H_3PO_4, 85%), potassium dihydrogen phosphate (KH_2PO_4, 99%), boric acid (H_3BO_3, 99%) and potassium hydroxide (KOH) were purchased from Guangdong- Guanghua Sci-Tech 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. And

all aqueous solution were prepared with distilled water.

The Britton–Robinson (B-R) buffer solutions were prepared from 0.5 M H_3BO_3, 0.5 M H_3PO_4, and 0.5 M CH_3COOH solutions. The desired pH of the B–R buffer was adjusted using 1 M KOH or 1 M H_3PO_4 solutions.

2.2. Apparatus

All electrochemical measurements (cyclic voltammetry and square wave voltammetry) were carried out at the DY2321 potentiostat made by Digi-Ivy, Inc. Austin. A conventional three-electrodes cell equipped with a working electrode (Co_3O_4-GPE modified electrode or GPE unmodified electrode, with a geometrical area of 0.07 cm^2), a counter electrode (Pt wire), and a reference electrode (Ag/AgCl, KCl_{sat}) was used.

2.3 Synthesis of Co_3O_4 porous crystalline material from ZIF-67

ZIF-67 was synthesized according to the previously reported method[26]

1.455 g of $Co(NO_3)_2{\cdot}6H_2O$ was dissolved in 50 mL of ethanol and 1.64 g of 2-methylimidazole (H_{mim}) was dissolved in 50mL of ethanol. Mole ratio of Co^{2+}: H_{mim} was 1 : 4. The H_{mim} solution was poured slowly into $Co(NO_3)_2{\cdot}6H_2O$ solution under stirring condition for 30 min at room temperature. The obtained solution was kept at room temperature for 6 hours without stirring. The colloidal dispersion was observed, and the product was collected by centrifugation (4000 rpm, 30 min) and washed with ethanol three times, then dried at 80 °C, 12 hours.

Co_3O_4 was obtained through the calcination of ZIF-67 in air atmosphere with a heating rate of 1 °C·min−1.

2.4. Preparation of Co_3O_4-GPE modified electrode

The Co_3O_4-GPE modified electrode was prepared by thoroughly mixing 40 mg of graphite powder and 5 mg Co_3O_4 powder with 10 µL of paraffin oil. The obtained paste was put into the cavity of a Teflon holder. The obtained electrode surface was smoothed using paper. When necessary, a new electrode surface was obtained by removing 2 mm of the outer paste layer and adding freshly modified paste.

2.5. Characterization of the Co_3O_4 porous crystalline material

The powder X-ray diffraction (XRD) data was performed on Bruker-AxsD8 diffractometer under 40kV and 40mA. Textural characteristics of sample was determined from the adsorption – desorption isotherms of nitrogen at -196 °C using a Gemini VII 2390 V1.2 Micromeritics automated instrument. Scanning electron microscope (SEM) was performed on a JEOL JSM-6700F field emission SEM, which was operated at the accelerating voltage of 15 kV and the detector current of 10 mA. EDS analysis was recorded by using 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].

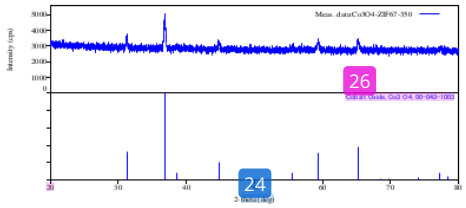


Figure 1. XRD pattern of the Co_3O_4 porous crystalline material.

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 m^2/g, and the pore size distribution was at 3 nm.

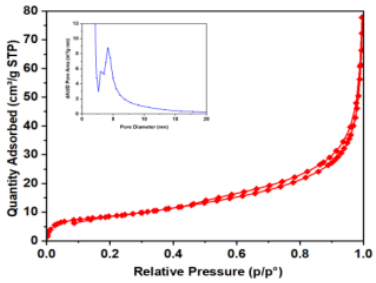


Figure 2. Nitrogen adsorption−desorption isotherms (A) and pore size distribution (B) of the Co_3O_4 porous crystalline material.

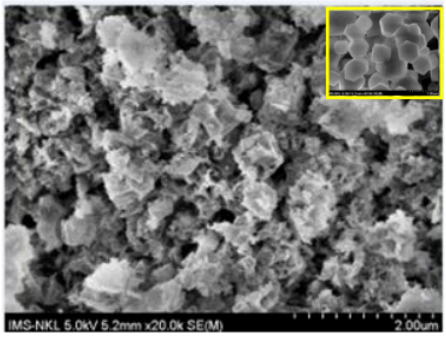


Figure 3. SEM image of the Co_3O_4 porous crystalline material, Inset: SEM image of ZIF-67 material.

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.

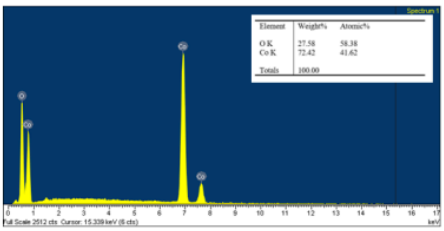


Figure 4. EDS spectra of the Co_3O_4 porous crystalline material.

EDS analysis was conducted on the Co_3O_4 sample (Figure 4). The results confirmed the presence of cobalt (Co) and oxygen (O) elements on the sample's surface. 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 X-ray diffraction (XRD), scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDS) and nitrogen adsorption-desorption isotherm, 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).

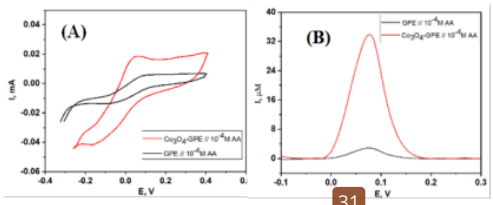


Figure 5. Cyclic voltammograms (A) and square wave voltammograms (B) at GPE and Co_3O_4-GPE modified electrode in 0.2 M B-R buffer solution pH = 4 containing an concentration of 10^{-4} M AA.

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 enhancement is attributed to the increased surface area, porous morphology, and functional properties of the Co_3O_4 modification compared to the bare GPE.

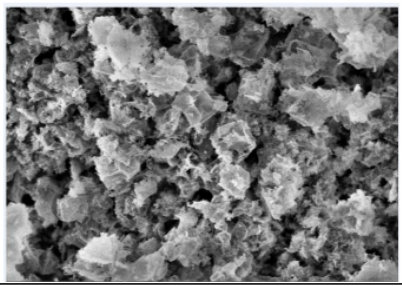
3.3. The effect of pH

The effect of pH on the voltammetric signals of AA was studied in the pH range of 3 to 6 using square wave voltammetry (SWV). 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. Accommulation

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 solution (pH 4) containing 10^{-4} M AA (Figure 7).



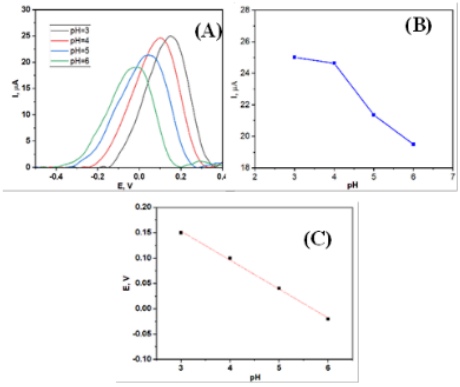


Figure 7. Square wave voltammograms of Co_3O_4-GPE in 0.2 M B-R buffer solution pH 4 containing 3×10^{-4} M AA (A); Influence of pH on peak current (B); linear plot of E_p vs. pH (C).

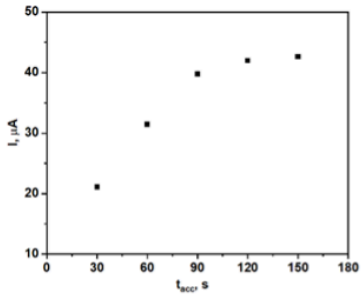


Figure 7. Dependence of I_p for AA in 0.2M B-R buffer solution pH 4 on accummulation time.

3.5. Calibration

The calibration curves for the AA detection with varying concentration 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.

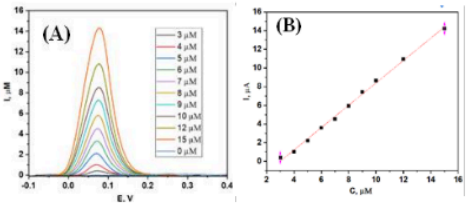


Figure 8. Square wave voltammograms recorded at Co_3O_4-GPE increasing concentration of AA (A) and the corresponding calibration curve (B).

The linear regression equation was as follow:

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

The Co_3O_4-GPE electrode achieved a detection limit of 0.48 μM and a sensitivity of 1.19 for ascorbic acid (AA) determination. The obtained results are lower comparatively with some reported in the literature 1.52 μM at CL-TiN/GCE,[27] 0.5 μM atNiCoO$_2$/C,[28] 0.83 μM at AgNP-Psi[29].

4. REAL SAMPLE ANALYSIS

To evaluate the applicability of the Co_3O_4-GPE for real sample analysis, the Co_3O_4-GPE was employed for the analysis of ascorbic acid in Vitamin C tablet (Pharimexco Viet Nam) using the standard addition method. The results, summarized in Table 1, confirm the electrode's efficacy for AA determination in pharmaceutical formulations. The measured mean AA concentration demonstrated agreement with the labeled value, and recovery rates ranged from 97.82% to 99.5%.

Table 1. Results of real sample analysis

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 Co_3O_4-GPE porous crystalline material were used to develop a modified electrode, which demonstrates promise for AA detection due to its high sensitivity, and low detection limit. The Co_3O_4-GPE was successfully used for the determination of ascorbic acid in real samples.

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