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Simple and Cost-effective Synthesis of Co_3O_4 Modified GCE Electrode for C_6H_6O Detection with Unique Lamellar Structure

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Herein, we present a simple and cost-effective strategy to prepare Co_3O_4 modified glassy carbon electrode (Co_3O_4/GCE). The unique lamellar structure of Co_3O_4 is prepared by a hydrothermal process and characterized by XRD and SEM. Then, the as-prepared Co_3O_4/GCE is utilized for C_6H_6O detection and electrochemical performance is measured by cyclic voltammetry and electrochemical impedance spectroscopy. The electrochemical measurements are used to characterize the electron transport at the solution-electrode interface. Through the use of square wave voltammetry, the electrochemical response of C_6H_6O on Co_3O_4 modified was significantly increased in 0.1 M phosphate buffer solution (pH 5.8). The proposed electrode has shown a linear relationship in the concentration range of 3.3 μM to 33 μM, with a C_6H_6O detection limit of 2.03×10^{-6} M and sensitivity of 0.67 μA μM^{-1}. Moreover, the as-prepared Co_3O_4 has shown excellent repeatability and stability, which make it an ideal choice for the replacement of other costly electrode systems.

Keywords: Lamellar stacking structure; Co_3O_4; Electrochemical determination; C_6H_6O

1. INTRODUCTION

C_6H_6O is an important base material and extensively used in chemical fabrications processes, such as antioxidants in food additives [1,2], compost [3], hindered phenolic antioxidants one of emissions from vehicle [4], dyes, textiles, metal coatings, petroleum refining and pharmaceuticals [5,6,7]. Furthermore, C_6H_6O high bane and inferior degradability in the natural environment due to several side effects on animal, plants [8] and humans because it's easily breathable.

Several strategies are used for C_6H_6O detection, such as high performance liquid chromatography [9,10,11] and Fenton reaction-triggered colorimetric spectroscopy [12,13]. Moreover, photocatalysis degradation [14] and detection of hydroquinone and corresponding isomers are carried out by electrochemical methods [15,16]. Electrochemical methods have attracted significant research attention due to their low cost, excellent accuracy and fast response to substances [17,18,19,20]. However, the application of electro-analytical methods is hindered by the low sensitivity caused by the interference of the real samples [21,22]. Therefore, the development of an electrochemical sensor, with the specific analytical method, for C_6H_6O detection is of utmost importance.

Glassy carbon electrode(GCE) has become an ideal choice due to low cost, renewability and excellent sensitivity. Meanwhile, various materials have been used to modify the GCE surface and a variety of GCE based sensors have been developed to investigate the inherent material's behavior. For instance, Quynh et al. [23] have fabricated nanoporous gold (NPG) thin films, and used them for real and accurate sensing of C_6H_6O and catechol. The developed sensor has exhibited a detection limit of was 2 μM for C_6H_6O. Mei et al. [24] have synthesized palladium-copper alloyed nanocages on reduced graphene oxide (RGO-PdCu NCs) by a simple one-pot solvothermal method and utilized for rapid detection of C_6H_6O. Based on the above methods, the biosensor has shown two linear ranges from 0.005 mM to 1.155 mM and 1.655 mM to 5.155 mM for detection. Jović-Jovičić et al. [25] have prepared smectite-chitosan bionanocomposite (SM-C) and used to modify GCE. The modified electrode (SM-C/GCE) was used to detect C_6H_6O and its derivatives. The study has shown that electro-oxidation can be used to detect and differentiate C_6H_6O and nitro derivatives from aqueous solution. Apart from the high cost of raw materials, the synthesis of these modifying materials is a challenging task and always a combination of various materials is selected to modify GCE electrode.

Co_3O_4 is an intriguing p-type semiconductor and extensively used as a modifying material in electrochemical sensing. In addition, the synthesis of Co_3O_4 is relatively easy, cost-effective and environmentally friendly [26]. Yu et al. [27] have revealed that the (111) facet of Co_3O_4 nanoplates has higher electrochemical sensing properties than (001) facet of Co_3O_4 nanocubes towards Pb(II). Liu et al. [28] have investigated the porous Co_3O_4 and layered Co_3O_4 sheets for Pb(II) sensing with different adsorption capacities and porous nafion/Co_3O_4 electrode has shown better sensitivity and lower detection limit than layered nafion/Co_3O_4 electrode. However, to the best of our knowledge, Co_3O_4 has not been used for electrochemical detection of C_6H_6O.

Herein, we aimed to synthesize Co_3O_4 with simple hydrothermal and annealing processes and utilized it to modify GCE for C_6H_6O detection. The Co_3O_4 modified electrode exhibited excellent electrocatalytic performance towards C_6H_6O due to the presence of active sites and efficient electron transportation route. In addition, we have also investigated the reproducibility and stability of GCE. Therefore, the present study provides a simple synthesis route for Co_3O_4 and excellent electrochemical performance for C_6H_6O sensing.

2. EXPERIMENTAL METHODS

2.1 Reagents

Cobalt nitrate ($CoNO_3 \cdot 6H_2O$), ammonium fluoride (NH_4F) and urea ($CO(NH_2)_2$) were purchased from Tianjin, China. Hydroquinone was purchased from Tianjin Kermel. 0.1 M phosphate buffer solution (PBS) with pH 5.8 was prepared by mixing stock solutions of 0.1 M sodium hydrogen phosphate ($Na_2HPO_4{\cdot}12H_2O$) and 0.1 M sodium dihydrogen phosphate ($NaH_2PO_4{\cdot}2H_2O$). The deionized water (18.2 $M\Omega cm^{-1}$) were prepared with the ultrapure water system. All reagents were of analytical grade and used without further purification.

2.2 Co_3O_4 Synthesis

The Co_3O_4 was prepared by hydrothermal method. Briefly, 2 mmol of $CoNO_3{\cdot}6H_2O$, 8 mmol of NH_4F and 15 mmol of $CO(NH_2)_2$ were dissolved in 40 mL of ultrapure water and mixed for 30 min to form a homogeneous solution. Then, the homogeneous solution was poured into a 50 mL Teflon-lined stainless steel autoclave, followed by hydrothermal treatment at 130℃ for 8 h and cooled down to room temperature. The as-prepared materials was collected through vacuum filtration and washed with deionized water and absolute ethanol for four times, followed by drying in an oven at 60 ℃ for 4 h. Finally, the as-prepared material was annealed at 400 ℃ in the air, for 3 h, to obtain Co_3O_4.

2.3 Preparation of modified electrode(Co_3O_4/GCE)

Before the modification, bare GCE was repeatedly polished by using 0.05 μm of alumina slurry and rinsed to get a mirror-like surface. Then, the polished-GCE was immersed in an ultrasonic bath with 1:1 (*v*/*v*) HNO_3, alcohol and ultrapure water to remove surface impurities from the electrode. After being dried by nitrogen, 10 μL of Co_3O_4 suspension in H_2O was dropped on the electrode surface and dried at a room temperature in air. The concentration of Co_3O_4 suspension was 1 g/L.

2.4 Physical properties of materials

The crystal structure of the as-prepared and annealed Co_3O_4 was investigated by using a Bruker D8 Avance X-ray diffractometer(XRD), equipped with Cu Kα radiations, at a scan rate of 5 ^{o}/min. The morphology of the as-prepared electrode was observed by a scanning electron microscope (SEM, Hitachi SU-3500).

2.5 Electrochemical characterization

The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were carried out on an Electrochemical Workstation (CHI660E, Chenhua Company, Shanghai, China) with a three-electrode single-cell system. The modified GCE served as the working electrode, a saturated calomel electrode (SCE, 232 model) worked as the reference electrode and a platinum sheet played the role of the counter electrode. CV and EIS were carried in ferricyanide (5 mM $K_3[Fe(CN)_6]$) containing 0.1 M KCl solution. All electrochemical measurements were carried out at room temperature. In order to remove the effect of dissolved oxygen, the electrolyte was purged with N_2 for 5 min prior to electrochemical measurements.

The electrochemical measurement was carried out in square wave stripping voltammograms (SWASV) mode for C_6H_6O detection in 0.1 M PBS (pH 5.8). A deposition potential of -0.5 V was applied for 120 s to the working electrode under stirring. The SWASV responses were recorded between -0.4 V to 0.4 V with step potential of 5 mV, amplitude of 20 mV and frequency of 25 Hz. A desorption potential of 0.35 V was applied for 270 s was performed to remove the residual metals under continuous stirring.

The repeatability of Co_3O_4/GCE was studied by detecting the responses to the mixture of 3.3 μM C_6H_6O in 0.1 M PBS (pH 5.8) for eleven sequential measurements. The stability of Co_3O_4/GCE was investigated after 30 days in 0.1 M phosphate buffered solution (pH 5.8).

3. RESULTS AND DISCUSSION

3.1 Structural and morphological characterization of Co_3O_4

Fig. 1 shows the XRD pattern of the Co_3O_4. All the diffraction peaks can be indexed to a pure face-centered cubic phase of Co_3O_4(JCPDS card no. 42-1467).

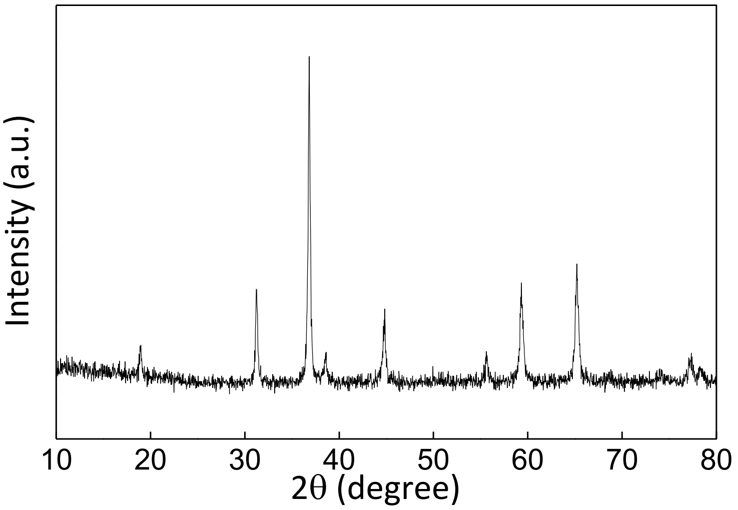

Figure 1. XRD patterns of as-prepared and annealed Co_3O_4.

Fig. 2 presents the typical SEM images of Co_3O_4. Most of the particles have shown an irregular block-like structure (Fig. 2a). In addition, the high-magnification SEM images (Fig. 2b and 2c) exhibit that the microstructure of Co_3O_4 consists of sliced and stacked lamellas. One should note that such structure results in the high specific surface area and renders abundant adsorption sites, which favor efficient diffusion and transportation of electrons and electrolyte ions in the bulk of the Co_3O_4 slices.

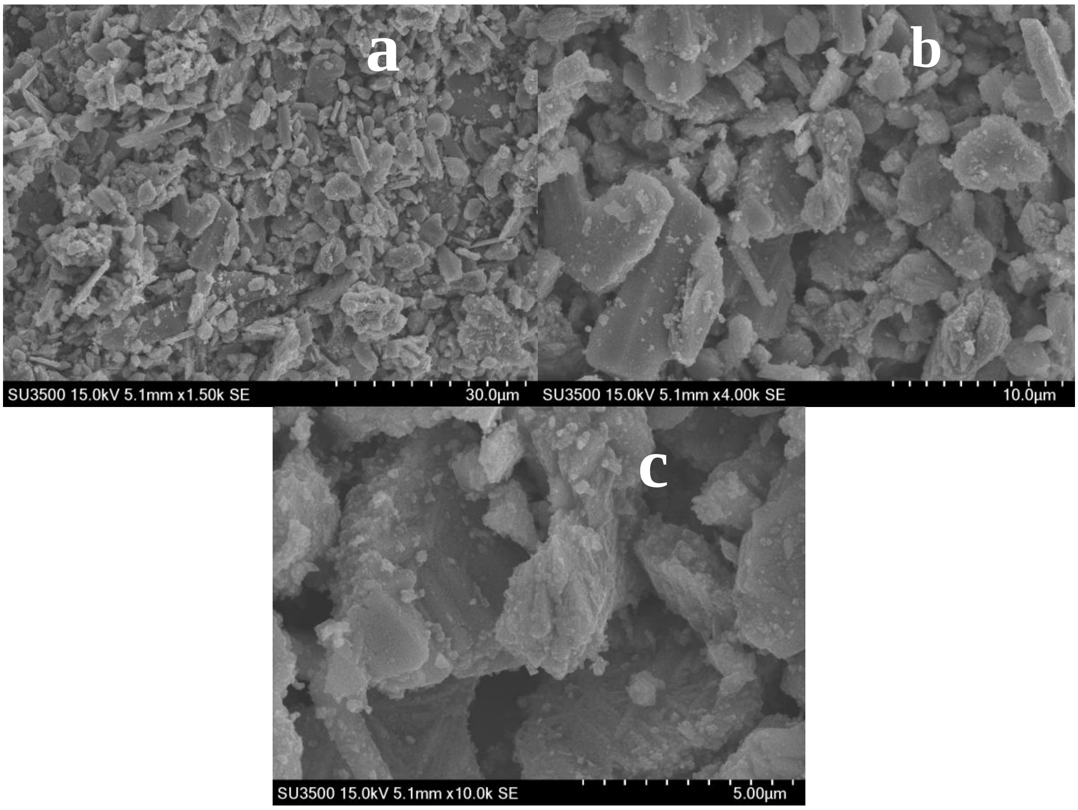

Figure 2. SEM images of Co_3O_4 at different magnifications: (a) 1500x, (b) 4000x and (c) 10000x.

The valid area of different modified electrodes was calculated by using the Randles–Sevcik equation:

$$Ipc=(2.69 \times 10^5)n^{3/2}AD^{1/2}C^{*} v^{1/2}$$

Where i_{pc} represents the maximum current (A), n denotes the number of electrons transferred in the redox event (usually 1), A corresponds to the electrode area (cm^2), D refers to the diffusion coefficient (cm^2/s), C represents the concentration of what (mol/cm^3) and v denotes the scan rate (V/s).

By exploring the redox peak current with the scan rate, the average effective area of the bare GCE and Co_3O_4/GCE was calculated to be 0.0841 cm^2 and 0.1032 cm^2, respectively. Moreover, we have observed that the Co_3O_4 has shown a tremendously enhanced surface area, which resulted in a significantly improved electrochemical response of the modified electrodes.

3.2 Electrochemical behavior of Co_3O_4

CV is often used to characterize the electron transfer kinetics of redox reactions [29,30,31]. As shown in Fig. 3(a), a pair of redox peaks, with a peak-to-peak separation (ΔE_p) of 88 mV, was observed in the CV of bare GCE, whereas the ΔE_p increased to 226 mV for Co_3O_4/GCE electrode and the response current became twice lower than the bare GCE. One should note that the Co_3O_4/GCE has hindered the electron-transfer process, which can be attributed to the presence of Co_3O_4 at the electrode surface. EIS is an important technique to investigate the electron transfer efficiency of the electrode. The size of the semicircle represents the electron-transfer resistance (R_{ct}), whereas the straight line corresponds to the diffusion process [32,33,34]. Fig. 3(b) present the Nyquist plots of the Co_3O_4/GCE and bare GCE in 5 mM $K_3[Fe(CN)_6]$ containing 0.1M KCl aqueous solution. The Nyquist plot consists of the imaginary part of the impedance (Z_{im}) and the real part of impedance (Z_{re}). Fig. 3(b) shows that the Nyquist plot of bare GCE consists of almost a straight line, which indicates that the bare GCE has excellent electron transfer performance. However, the Co_3O_4/GCE has shown a larger semicircular, corresponding to the large charge transfer resistance of the Co_3O_4/GCE electrode. The EIS spectra were measured at open circuit voltage, in the frequency range of 0.01 Hz to 100 kHz, with a sine wave voltage of 5 mV. The diameter of the semicircle reflects the charge transfer resistance (R_{ct}). The higher charge transfer resistance due to the Co_3O_4 coincides well with the CV results.

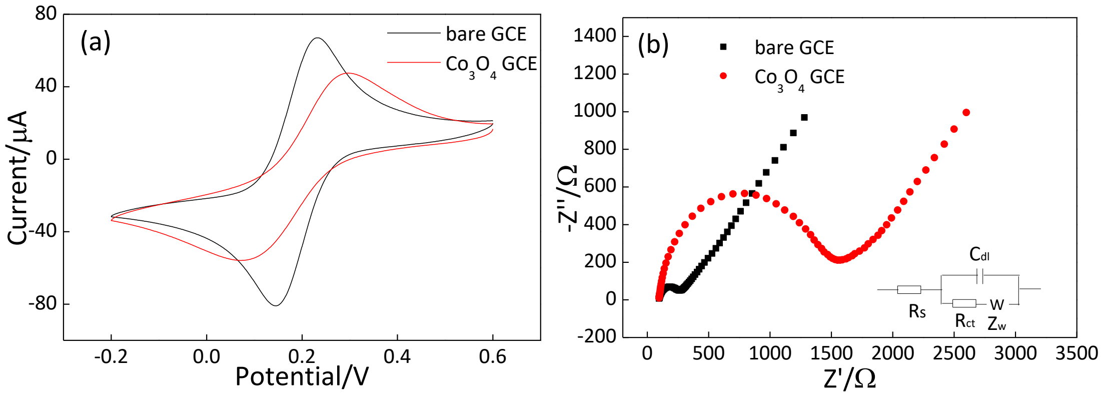

Figure 3. Electrochemical characterization of bare GCE and Co3O4 modified GCE electrodes: (a) CV responses and (b) and Nyquist plots Co_3O_4/GCE.

3.3 Square wave parameter

The square wave stripping voltammograms (SWASV) responses were investigated to find the suitable frequency, the pulse height and the step size in a solution containing phenol. Using SWASV which is strongly affected the outcome signal will get a peak current at high scanspeed with better sensitivity and reduced background noise [35]. Fig. 4a presents the SWASV under the different concentrations of C_6H_6O from 3.3 µM to 33 µM. The peak current has shown a direct relationship with the phenol concentrations. A sensitivity level of 0.067 µA µM^{-1} (inset of Fig. 4(b)) and a detection limit of 2.03 µM (3σ method) have been demonstrated by SWASV analysis. These results reveal that the porous Co_3O_4/GCE exhibits high sensitivity to C_6H_6O concentrations. Moreover, the high sensitivity and low detection limit correspond to the adsorption capacity. In addition, these results confirm that the high adsorption capacity promotes the detection of C_6H_6O.

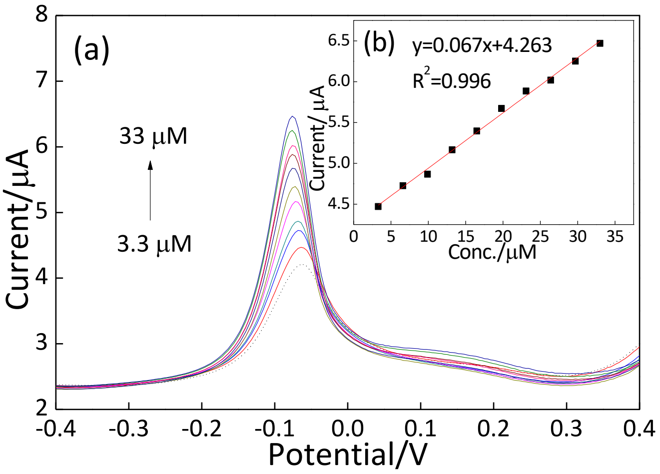

Figure 4. (a) SWASV curves and (b) the calibration curve of Co_3O_4/GCE towards C_6H_6O at various concentrations in 0.1M PBS (pH = 5.8) solution.

Table 1 presents a comparative analysis of the Co_3O_4/GCE with other types of electrodes. Even though the detection limit and linear range of Co3O4/GCE electrode are similar to previously published electrodes, one should note that the Co_3O_4 can be synthesized by a simple and cost-effective hydrothermal method. On the other hand, most of the previously published reports have used either expensive synthesis strategies or materials, such as nano-pore gold thin film, to obtain comparably high performance. Hence, the as-prepared Co_3O_4/GCE is a promising electrode for C_6H_6O detection in the linear range.

Table 1. Comparison of the Co_3O_4/GCE with previously published electrode systems for C_6H_6O detection.

Modified electrode	Method	Linear range	LOD	Reference
NPG thin film	Amperometric	2 μM–0.5 mM 0.5 mM–10 mM	2 μM	23
RGO-PdCu NCs/GCE	CV	0.005–1.155 mM 1.655–5.155 mM	–	24
GO–ZnO/GCE	SWV	5–155 μM	2.2 nM	36
Bacterium with AuNPs/Gold IDE	Conductometric measurements	10–3187 μM	2 μM	37
Co_3O_4/GCE	SWASV	3.3–33 μM	2.03×10^{-6} M	this work

NPG: Nanoporous gold
RGO**:** Reduced Graphene Oxide
PdCu NCs: Palladium–Copper Alloyed Nanocages
GO: graphene oxide
SWV: Square Wave Voltammetry
IDE: interdigitated electrodes

3.4 The repeatability and stability of Co_3O_4/GCE

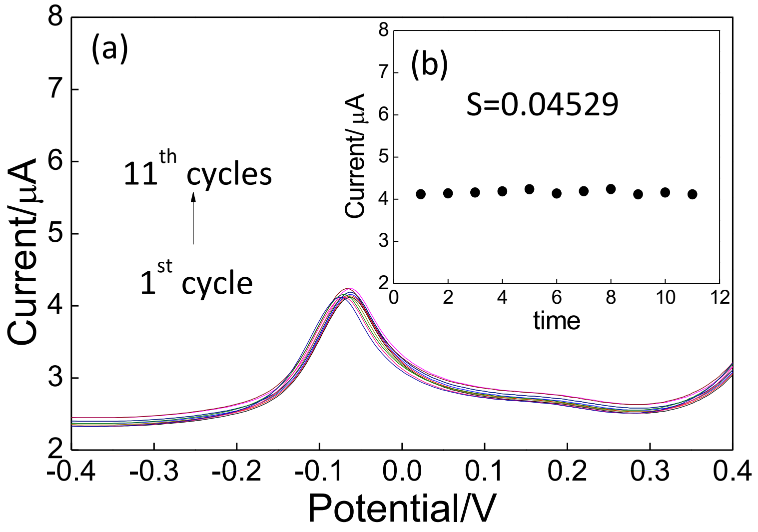

Figure 5. (a) SWASV responses and (b) scatter diagram between measured times and peak current of Co_3O_4/GCE towards C_6H_6O from 1st to 11th cycle.

The repeatability of Co_3O_4/GCE was examined by measuring the response to the mixture of 3.3 μM phenol in 0.1 M PBS (pH = 5.8) for eleven successive measurements. The obtained data have shown a relative standard deviation (RSD) of 1.079%. Moreover, the stability of Co_3O_4/GCE was also investigated by measuring the current response after 30 days. The current response has shown 92.4% of the initial value, which confirmed the excellent stability of the modified electrode. Hence, we can claim that the Co_3O_4/GCE is an ideal choice for C_6H_6O detection with excellent reproducibility and stability.

Table 2. The RSD of peak current value. Co_3O_4/GCE was used to detect C_6H_6O 11 times.

Time	1	2	3	4	5	6	7	8	9	10	11	RSD%
Peak current/μA	4.209	4.212	4.21	4.212	4.238	4.181	4.092	4.24	4.176	4.192	4.126	1.079%

3.5 Analysis of tap water samples

We carried out lab-scale and recycling experiments to determine the C_6H_6O content in local tap water samples. Since the water treatment aims to remove the C_6H_6O, the C_6H_6O content in tap water is extremely low and unknown. Therefore, we have added a small amount of C_6H_6O in tap water for testing purpose. As shown in Table 3, the calculated recycling rate is within a reasonable range, which confirms the excellent detection performance of the Co3O4/GCE electrode.

Table 3. The C_6H_6O detection in tap water samples with modified electrodes

Sample	Content (μM)	Spiked(μM)	Observed(μM)	Recovery (%)
1	5.00	5.00	9.98	99.60%
2	5.50	5.50	11.04	100.7%
3	6.00	6.00	11.96	99.33%

4. CONCLUSIONS

The present study has demonstrated the utilization of Co_3O_4 modified GCE for C_6H_6O detection by SWASV. The structure and morphology of Co_3O_4 have been characterized by XRD and SEM, respectively. The SEM images revealed that C_6H_6O based products are likely to be adsorbed by Co_3O_4 due to its unique lamellar structure. Interestingly, the Co_3O_4 modified electrode did not improve the electron transfer kinetics. However, the overall C_6H_6O detection performance has been improved due to the high specific surface area and unique morphology. The results suggest that Co_3O_4 modified electrodes are promising for C_6H_6O detection due to simple processing, low cost, eco-friendly nature and low operating power. The sensitivity and detection limit of Co_3O_4 modified electrodes are in a workable range and promising to replace the costly alternatives. The enhanced reproducibility and repeatability of the as-prepared electrodes make them promising for C_6H_6O detection.

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