Effect of Fluoride on the Morphology and Electrochemical Property of Co$_3$O$_4$ Nanostructures for Hydrazine Detection

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Abstract: In this paper, we systematically investigated the influence of fluoride on the morphology and electrochemical property of Co$_3$O$_4$ nanostructures for hydrazine detection. The results showed that with the introduction of NH$_4$F during the synthesis process of Co$_3$O$_4$, both Co(CO$_3$)$_{0.5}$(OH)$_{0.11}$H$_2$O and Co(OH)F precursors would be generated. To understand the influence of F on the morphology and electrochemical property of Co$_3$O$_4$, three Co$_3$O$_4$ nanostructures that were respectively obtained from bare Co(CO$_3$)$_{0.5}$(OH)$_{0.11}$H$_2$O, Co(OH)F and Co(CO$_3$)$_{0.5}$(OH)$_{0.11}$H$_2$O mixtures and bare Co(OH)F were successfully synthesized. The electrochemical tests revealed the sensing performance of prepared Co$_3$O$_4$ nanostructures decreased with the increase in the fluoride contents of precursors. The more that dosages of NH$_4$F were used, the higher crystallinity and smaller specific surface area of Co$_3$O$_4$ was gained. Among these three Co$_3$O$_4$ nanostructures, the Co$_3$O$_4$ that was obtained from bare Co(CO$_3$)$_{0.5}$(OH)$_{0.11}$H$_2$O-based hydrazine sensor displayed the best performances, which exhibited a great sensitivity (32.42 $\mu$A·mM$^{-1}$), a low detection limit (9.7 $\mu$M), and a wide linear range (0.010–2.380 mM), together with good selectivity, great reproducibility and longtime stability. To the best of our knowledge, it was revealed for the first time that the sensing performance of prepared Co$_3$O$_4$ nanostructures decreased with the increase in fluoride contents of precursors.

Keywords: cobaltosic oxide; fluoride; precursor; crystallinity; electrochemical activity

1. Introduction

Hydrazine and based chemicals are water soluble volatile colorless liquids, and the simplest unique diamine in its class has aroused wide concern for its large number of applications in many spheres, for instance, corrosive inhibitors, fuel cells and so on [1–4]. The laboratory research and commercial application of hydrazine as a reducing agent and catalyst are commonly implemented. However, hydrazine and its derivatives do great harm to the body through the digestive system along with skin permeation [5]. Consequently, it is highly imperative to propose a sensitive, original and analytically credible tool for the effective detection of hydrazine. Recently, electroanalytical techniques have developed as a desirable method for detection of many chemicals, such as hydroquinone [6], acetone [7], herbicides [8], etc. due to their great sensitivity, better efficiency and low cost. It is promising to develop electrochemical methods for hydrazine detection. Nowadays, lots of semiconductor metal oxides have been used for hydrazine electrochemical sensing. Ahmad et al. have fabricated a ZnO nanorods-based hydrazine sensor and showed a low detection limit [9]. Wu et al.
used MnO2 nanoflowers for hydrazine detection and exhibited a high sensitivity [10]. However, the study on Co3O4 utilized for hydrazine is rare to report.

Cobaltosic oxide (Co2O4), a kind of vital transition-metal oxide semiconductor with direct optical band gaps at 2.19 eV [11], has undergone extensive exploration recently for its wide-ranging potential applications as a gas sensor [12–14], catalyst [15–18], magnetic material [19], solar-energy absorber [20], supercapacitors and rechargeable lithium-ion-battery materials [21–24]. More significantly, because of its high catalytic performance, nanostructured Co3O4 is widely considered to be an attractive modified electrode material that can enhance the rate of electron transfer and minimize its over potential [25]. Up to now, various synthetic protocols have been developed for the synthesis of Co3O4 with diverse morphologies and designed nanostructures. Among them, a two-step approach, where co-based intermediates, such as Co(OH)2 and (Co(CO3)0.5(OH)-0.11H2O), are first fabricated by thermal annealing exposed to air, as the control on the morphologies of these intermediates has been widely used. However, for certain synthesis procedures, NH4F was normally used during the synthesis step, because F is a good complexing ligand for Co2+. In the presence of F−, CoF2 complex can firstly be formed to prevent Co(OH)2 generation, which would make the morphology controllable [26,27]. Meanwhile, F may also lead to the formation of (Co(OH)F), which may cause the generation of impurities in the products. Up to now, the influence of F content on the formation and electrochemical performance of Co3O4 has not been clarified.

Thus, in this paper, the influence of fluoride (F) on the morphological and electrochemical performance of Co3O4 for hydrazine sensing was systematically investigated for the first time. Three types of Co3O4 samples were synthesized by thermal treatment of their precursors, which contain different amounts of F. The physical and chemical compositions of all constructed materials were systematically investigated. The electrochemical activity of these Co3O4 were comprehensively compared using cyclic voltammetry and amperometric response analysis.

2. Results and Discussion

2.1. Structural and Morphological Studies

The composition of the prepared precursors was first examined by XRD characterization. As shown in Figure 1a, all of the diffraction peaks could be well indexed to Co(CO3)0.5(OH)-0.11H2O (JCPDS card No. 48-0083) and Co(OH)F (JCPDS card No. 50-0827), respectively, and no other peak could be found from the XRD patterns. Figure 1b verifies that the precursor powders are the mixture of Co(CO3)0.5(OH)-0.11H2O and Co(OH)F. Furthermore, the characteristic peaks at 17.5°, 24.2°, 26.8°, 28.8°, 35.5°, 59.9°, and 62.2° can be indexed to the reflections of (020), (111), (220), (121), (040), (340), (412), and (450) planes of Co(CO3)0.5(OH)-0.11H2O; while the characteristic peaks at 20.8°, 32.3°, 33.5°, 38.8°, 51.9°, 52.8°, and 57.0° can be indexed to the reflections of (110), (310), (201), (211), (221), (420), (511) planes of Co(OH)F. For the synthesis of Co3O4, all these three precursors were thermally annealed at 400 °C for 5 h in air. Figure 1d–f clearly indicate that all the diffraction peaks are well-assigned to the standard diffraction pattern of Co3O4 (JCPDS card No. 43-1003), which indicates that the precursors had been thoroughly converted to Co3O4 phase and there were no other impurities that could be detected. The crystallinity of the prepared products was evaluated via the Formula (1).

\[
X_c = \frac{I_c}{(I_c + K I_a)} \times 100\%
\]  

(1)

In Formula (1), Xc represents the crystallinity measured by X-ray diffractometry; Ic is the integral intensity of the crystal diffraction peak; and Ia is the integral intensity of the amorphous diffuse peak; K is the elative scattering factor.

The crystallinity of prepared Co3O4 samples is calculated and shown in Table 1. It is obvious that Co3O4-1 possesses the lowest crystallinity (73.87%) and Co3O4-3 has the highest crystallinity 91.62%). To explore the influence of F on the crystallinity of Co3O4, different dosages of NH4F (from 0 to 20 mmol) had been added during the synthesis process of Co3O4. As shown in Table 1, the crystallinity...
of Co$_3$O$_4$ presents an increase trend with increasing the amount of NH$_4$F during the synthesis process of precursors, which indicates that the strong interaction between Co$^{2+}$ and F$^-$ can make the particles grow regularly.

The formation of the precursors and annealed products can be illustrated with the following steps. When CO(NH$_2$)$_2$ is used as a hydrolysis reagent, the formation process of Co(CO$_3$)$_{0.5}$(OH)$\cdot$0.11H$_2$O can be depicted as Equations (2)–(4). While when HMT is used as a hydrolysis reagent, with the existence of F$^-$, the formation of Co(OH)F can be possibly expressed by Equations (5)–(8). After calcination, both of the precursors can be converted into cobaltosic oxide by Equations (9) and (10).

\[
\begin{align*}
H_2O + CO(NH_2)_2 &\rightarrow CO_2 + 2NH_3 \quad (2) \\
H_2O + CO_2 &\rightarrow 2H^+ + CO_3^{2-} \quad (3) \\
0.11H_2O + Co^{2+} + OH^- + 0.5CO_3^{2-} &\rightarrow Co(CO_3)_{0.5}(OH)\cdot0.11H_2O \quad (4) \\
Co^{2+} + F^- &\rightarrow CoF^+ \quad (5) \\
6H_2O + (CH_2)6N_4 &\rightarrow 6HCHO + 4NH_3 \quad (6) \\
H_2O + NH_3 &\rightarrow OH^- + NH_4^+ \quad (7) \\
CoF^+ + OH^- &\rightarrow Co(OH)F \quad (8) \\
6Co(OH)F + O_2 &\rightarrow 2Co_3O_4 + 6HF \quad (9) \\
6[Co(CO_3)_{0.5}(OH)\cdot0.11H_2O] + O_2 &\rightarrow 3CO_2 + 3.66H_2O + 2Co_3O_4 \quad (10)
\end{align*}
\]

Figure 1. XRD patterns of (a) Co(CO$_3$)$_{0.5}$(OH)$\cdot$0.11H$_2$O; (b) Co(CO$_3$)$_{0.5}$(OH)$\cdot$0.11H$_2$O and Co(OH)F mixture; (c) Co(OH)F; (d) Co$_3$O$_4$-1; (e) Co$_3$O$_4$-2 and (f) Co$_3$O$_4$-3.
XPS analysis was then performed. Figure 3a shows the Co 2p peaks of Co3O4. The intensity of the peaks shows downward course from Co3O4-1 to Co3O4-3, respectively. The curve of Co 2p shows two spin-orbit doublets of Co 2p1/2 at 779.96 and 794.94 eV attributed to Co3+, and two spin-orbit doublets of Co 2p3/2 at 781.46 and 796.46 eV belonging to Co3+. The intensity of the peaks shows downward course from Co3O4-1 to Co3O4-3. Figure 3b depicts the O1s spectra of the prepared Co3O4 samples, the large O 1s peak at 530.12 eV is attributed to the lattice oxygen (LO) in Co3O4 crystals and the small O 1s peak at 531.47 eV represents the oxygen vacancies (OV) on the surface of Co3O4 [32–34]. The intensity of the oxygen vacancy also shows a decreased trend from Co3O4-1 to Co3O4-3 (Table 2). The more oxygen vacancies indicate a higher possibility for the exposure of active sites [35].

The general morphology of the precursors and the obtained Co3O4 products was further explored using FE-SEM, as shown in Figure 4. The Co(CO3)0.5(OH)-0.11H2O precursor exhibited a nanorod structure, with a smooth surface (Figure 4a). The average length of the nanorods is in

| Sample     | Amount of Oxygen Species | Oxygen Vacancy (OV) | Lattice Oxygen (LO) |
|------------|--------------------------|--------------------|---------------------|
|            |                          | at. %              | BE (eV)             | at. %               | BE (eV)     |
| Co3O4-1    |                          | 44.9               | 530.12              | 55.1                | 531.47      |
| Co3O4-2    |                          | 43.8               | 530.12              | 56.2                | 531.47      |
| Co3O4-3    |                          | 41.8               | 530.12              | 58.2                | 531.47      |
the range of 3–5 μm. The Co(OH)F precursor showed gear-like nanosheets, with an uneven surface (Figure 4e). The average thickness of Co(OH)F nanosheets is about 0.025 μm and the typical diameter of the nanosheets is in the range of 8–12 μm. Figure 4b depicts the SEM image of the mixture of Co(CO$_3$)$_{0.5}$(OH)·0.11H$_2$O nanorods and Co(OH)F nanosheets. When CO(NH$_2$)$_2$ was used as the hydrolysis reagent, both Co(CO$_3$)$_{0.5}$(OH)·0.11H$_2$O and Co(OH)F precursors were generated in the same time with the existence of F. However, from Figure 4c, it is noteworthy that the quantity of nanorods is far more than nanosheets, which indicates that the growth rate of Co(CO$_3$)$_{0.5}$(OH)·0.11H$_2$O is faster than the growth rate of Co(OH)F. The elemental mapping analysis in the selected area of Figure 4c further confirmed the generation of Co(OH)F. Figure 5 suggests that the F element was evenly dispersed within the Co(OH)F sample, with a calculated atomic amount of ca. 5.8%. After annealing the precursors, the morphology of obtained Co$_3$O$_4$-1, Co$_3$O$_4$-2, and Co$_3$O$_4$-3 samples were also characterized using FE-SEM, as shown in Figure 4b,d,f. It was worthwhile mentioning that the products still maintained the similar morphology with their precursors after the annealing treatment. Contrary to the precursors, the Co$_3$O$_4$ displayed rough and porous surfaces, which might be due to the abscission of attached OH ions during the calcination process. The difference of morphology may lead to the difference of specific surface area of Co$_3$O$_4$. Based on the BET data, it could be found that the rod-like Co$_3$O$_4$ possessed larger specific surface area than sheet-like Co$_3$O$_4$. The relatively large specific surface area of rod-like structure may be beneficial to the exposure of active sites and in the meantime facilitate the contact of Co$_3$O$_4$ to the targeted chemicals.

Figure 2. Typical FTIR spectra of the (a) precursors and (b) obtained Co$_3$O$_4$ products.
Figure 3. XPS analyses of (a) Co 2p and (b) O 1s for Co$_3$O$_4$-1, Co$_3$O$_4$-2 and Co$_3$O$_4$-3 nanocrystals.

Figure 4. Cont.
The electrocatalytic activity of Co(II) peak at 0.46 V during the reverse sweep. Among them, Co3O4 possesses when it was tested. However, for Co3O4 differences among them. For Co3O4 activity of bare GCE. However, for these three kinds of Co3O4 modified electrodes, there are significant differences among them. For Co3O4-3 (obtained from Co(OH)F) modified electrode, no peak could be observed when it was tested. However, for Co3O4-2 (obtained from the mixture) and Co3O4-1 (obtained from Co(CO3)0.5(OH)-0.11H2O) modified electrodes, an oxidation peak (I) apparently emerged at around 0.50 V. The observed CV response also exhibited reversible nature as it showed a reduction peak (II) at 0.46 V during the reverse sweep. Among them, Co3O4-1 possesses the best electrochemical activity towards hydrazine oxidation while Co3O4-3 has the poorest electrochemical activity towards hydrazine. This result suggests that F has a negative effect on the performance of Co3O4. We believe that F introduction decreases the electrocatalytic properties of Co3O4. The electrocatalytic activity of Co3O4 nanomaterials towards hydrazine was firstly investigated by cyclic voltammetry technique. Figure 6a shows the cyclic voltammogram (CV) of bare GCE in the presence of 1 mM hydrazine in 0.1 M NaOH electrolyte at a scan rate of 0.02 V·s−1.

It is apparent that no matter whether hydrazine exists, the bare GCE does not exhibit any redox peak in 0 to 0.6 V, just the current elevated when hydrazine added. This result indicates the low catalytic activity of bare GCE. However, for these three kinds of Co3O4 modified electrodes, there are significant differences among them. For Co3O4-3 (obtained from Co(OH)F) modified electrode, no peak could be observed when it was tested. However, for Co3O4-2 (obtained from the mixture) and Co3O4-1 (obtained from Co(CO3)0.5(OH)-0.11H2O) modified electrodes, an oxidation peak (I) apparently emerged at around 0.50 V. The observed CV response also exhibited reversible nature as it showed a reduction peak (II) at 0.46 V during the reverse sweep. Among them, Co3O4-1 possesses the best electrochemical activity towards hydrazine oxidation while Co3O4-3 has the poorest electrochemical activity towards hydrazine. This result suggests that F has a negative effect on the performance of Co3O4. We believe that F introduction decreases the electrocatalytic properties of Co3O4.

**Figure 4.** Typical FE-SEM images of (a) Co(CO3)0.5(OH)-0.11H2O precursor; (b) Co3O4-1; (c) the mixture of Co(CO3)0.5(OH)-0.11H2O and Co(OH)F; (d) Co3O4-2; (e) Co(OH)F precursor; and (f) Co3O4-3.

**Figure 5.** SEM-EDS elemental mapping (C, O, F, and Co) of the precursor of Co3O4-2.

2.2. Hydrazine Chemical Sensor Studies of Co3O4 Modified Electrodes

To prepare the hydrazine sensor, Co3O4 nanomaterials were coated on the surface of GCE. The electrocatalytic activity of Co3O4 nanomaterials towards hydrazine was firstly investigated by cyclic voltammetry technique. Figure 6a shows the cyclic voltammogram (CV) of bare GCE and Co3O4/GCE in the presence of 1 mM hydrazine in 0.1 M NaOH electrolyte at a scan rate of 0.02 V·s−1. It is apparent that no matter whether hydrazine exists, the bare GCE does not exhibit any redox peak in 0 to 0.6 V, just the current elevated when hydrazine added. This result indicates the low catalytic activity of bare GCE. However, for these three kinds of Co3O4 modified electrodes, there are significant differences among them. For Co3O4-3 (obtained from Co(OH)F) modified electrode, no peak could be observed when it was tested. However, for Co3O4-2 (obtained from the mixture) and Co3O4-1 (obtained from Co(CO3)0.5(OH)-0.11H2O) modified electrodes, an oxidation peak (I) apparently emerged at around 0.50 V. The observed CV response also exhibited reversible nature as it showed a reduction peak (II) at 0.46 V during the reverse sweep. Among them, Co3O4-1 possesses the best electrochemical activity towards hydrazine oxidation while Co3O4-3 has the poorest electrochemical activity towards hydrazine. This result suggests that F has a negative effect on the performance of Co3O4.

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that the performance of Co$_3$O$_4$ should be related to their crystallinity and specific surface area. According to the XPS analysis, with increasing the amount of F in the synthesis process, the oxygen vacancy of their final product (Co$_3$O$_4$) shows a decreased trend. The addition of F allows the precursor to grow more regularly but cause the decrease of the specific surface area, resulting in relatively less active sites and worse performance of Co$_3$O$_4$ [36]. The possible reactions on Co$_3$O$_4$ electrode can be expressed as the following Equations (11)–(13).

\[
\begin{align*}
\text{OH}^- + \text{H}_2\text{O} + \text{Co}_3\text{O}_4 &\rightarrow 3\text{CoOOH} + e^- \quad (11) \\
\text{OH}^- + \text{CoOOH} &\rightarrow \text{H}_2\text{O} + \text{CoO}_2 + e^- \quad (12) \\
4\text{CoO}_2 + \text{N}_2\text{H}_4 &\rightarrow 4\text{CoOOH} + \text{N}_2 \quad (13)
\end{align*}
\]

Figure 6. (a) Cyclic voltammograms for different modified electrodes in the presence of 1 mM hydrazine at a scan rate of 0.02 V·s$^{-1}$; (b) Cyclic voltammograms of Co$_3$O$_4$-1/GCE with different hydrazine concentrations at a scan rate of 0.02 V·s$^{-1}$; (c) Cyclic voltammograms of Co$_3$O$_4$-1/GCE with different scan rates (From 0.01 to 0.08), inset shows the anodic peak current vs. the square root of scan rate ($\nu^{1/2}$); and (d) the anodic peak potential (Ep) vs. log $\nu$.

The influence of hydrazine concentration and the scan rates on the performance of modified electrode was then investigated using the Co$_3$O$_4$-1 sample. Figure 6b exhibits the cyclic voltammograms of Co$_3$O$_4$-1 modified GCE with different hydrazine concentrations at a scan rate of 0.02 V·s$^{-1}$. With increasing the hydrazine concentration from 0.5 to 5 mM, the current displays a growth trend. The simultaneous response reveals that the fabricated Co$_3$O$_4$-1-based sensor can be used for the effective determination of hydrazine. Figure 6c depicts the cyclic voltammograms of Co$_3$O$_4$-1 modified GCE with 1 mM hydrazine at different scan rates ranging from 0.01 to 0.08 V·s$^{-1}$. The inset of Figure 6c shows that the peak current (Ip) also increases synchronously with the scan rate. The relationship between Ip and the scan rate was further calculated based on the Randles–Sevcik equation [37]. The equation can be expressed as

\[\text{Ip} = 261.3 \nu^{1/2} - 14.4 \text{ (R}^2 = 0.997)\]

The negative intercept may be due to the adsorption of the N$_2$H$_4$ occurred on the electrode surface, which indicates that the electrode reaction is not a single diffusion-controlled process [38]. Moreover, it is notable that
the peak potential shift towards positive potential with increasing the scan rate. Figure 6d exhibits the linear relation between the peak potential (Ep) and log (ν), implying the irreversible oxidation of hydrazine at the surface of Co$_3$O$_4$-1/GCE.

Figure 7a displays the chronoamperometric response of Co$_3$O$_4$-1/GCE with different concentration of hydrazine. The transient currents decayed with prolonging the time, also revealing the diffusion-controlled process of hydrazine electrooxidation. The peak current exhibited linear relationship with $t^{-1/2}$ (Figure 7b). In addition, the slope of the line increased with increasing the hydrazine concentration (Figure 7c). Thus, the diffusion coefficient of hydrazine ($D$) could be calculated via Cottrell’s equation:

$$I_p = n F A D^{1/2} C \pi^{-1/2} t^{-1/2}$$  \hspace{1cm} (14)

In Equation (14), $n$, $F$ (C·mol$^{-1}$), $A$ (cm$^2$), $C$ (mol·cm$^{-3}$) respectively represents the number of involved electron transfer, the Faraday constant (96,485), the surface area of GCE, and the dosage of hydrazine. The slopes of the obtained linear lines were plotted against the hydrazine concentrations (Figure 7c). Based on this plot, $D$ was determined to be 1.66 × 10$^{-5}$ cm$^2$·s$^{-1}$, which is consistent with the previous report [39].

Figure 7. (a) Chronoamperograms obtained at Co$_3$O$_4$-1/GCE with different concentrations of hydrazine in 0.1 M NaOH. Applied potential was 0.50 V; (b) Plot of current versus $t^{-1/2}$; and (c) The plot of slopes obtained from straight lines versus concentration of hydrazine.
2.3. Amperometric Detection of Hydrazine Using Co$_3$O$_4$ Modified Electrodes

The Co$_3$O$_4$-1 and Co$_3$O$_4$-2 modified electrodes were then used as a sensor for detection of hydrazine. The work potential was set at 0.50 V. For comparison, the amperometric responses of Co$_3$O$_4$-1 and Co$_3$O$_4$-2 electrodes are displayed. From Figure 8a,c, it is apparent that with the successive addition of hydrazine to a stirred solution, the anodic current increases gradually. When an aliquot of hydrazine was dropped into the stirred NaOH solution, the amperometric responses of the Co$_3$O$_4$-1 modified electrode achieved a steady state within 2 s, which is faster than the Co$_3$O$_4$-2 modified electrode. On the other hand, the magnitudes of the response current of the Co$_3$O$_4$-1 modified electrode is also larger than the Co$_3$O$_4$-2 modified electrode at the same condition. These results suggest that the Co$_3$O$_4$-1 modified electrode has better electrochemical performance than the Co$_3$O$_4$-2 modified electrode. When the hydrazine concentration exceeds a certain range, the response currents will no longer increase, but turn to be a declining trend. This phenomenon indicates that the hydrazine concentration exceeds the critical value of linear range. In order to further distinguish the difference between the two electrodes, mathematic fitting was utilized to calculate the sensitivity, linear response range and the detection limit. Figure 8b,d exhibit the linear relationship between hydrazine concentration and response current. For the Co$_3$O$_4$-1 modified electrode, the equation can be presented as $I(\mu A) = 32.42C(mM) - 0.69$ ($R^2 = 0.999$), while for the Co$_3$O$_4$-2 modified electrode, the equation can be presented as $I(\mu A) = 25.28C(mM) + 1.160$ ($R^2 = 0.999$). The plots also displayed a linear relationship with the hydrazine concentration in the range of 0.010 to 2.380 mM and 0.027 to 0.890 mM, respectively. For Co$_3$O$_4$-1 and Co$_3$O$_4$-2, the sensitivity that was found to be 32.42 $\mu$A·mM$^{-1}$ and 25.28 $\mu$A·mM$^{-1}$, respectively. The detection limit for the Co$_3$O$_4$-1 and Co$_3$O$_4$-2 fabricated hydrazine sensors were calculated to be 9.73 $\mu$M and 10.74 $\mu$M ($S/N = 3$).

![Figure 8](image-url)  
Figure 8. Amperometric responses of (a) Co$_3$O$_4$-1 and (c) Co$_3$O$_4$-2 modified electrodes with successive addition of hydrazine into 0.1 M NaOH; (b,d) the linear relationships between current vs. hydrazine concentration of Co$_3$O$_4$-1 and Co$_3$O$_4$-2 modified electrodes.
Table 3 summarizes the electrochemical parameters of some reported N$_2$H$_4$ sensors. Compared with them, the Co$_3$O$_4$-1/GCE and Co$_3$O$_4$-2/GCE exhibit rather high sensitivity and wide linear range. The performance of Co$_3$O$_4$-1/GCE is better than Co$_3$O$_4$-2/GCE. These results reveal that the existence of F in the synthesis of Co$_3$O$_4$ has a great impact on its electrochemical performance. To explore the influence of surface area of the obtained Co$_3$O$_4$ samples on their electrochemical performances, the surface area normalized current and sensitivity of Co$_3$O$_4$-1 (obtained bare Co(CO$_3$)$_{0.5}$(OH)-0.11H$_2$O) and Co$_3$O$_4$-2 (obtained the mixture of Co(CO$_3$)$_{0.5}$(OH)-0.11H$_2$O and Co(OH)F) were shown as Table 4. The Co$_3$O$_4$-1/GCE and Co$_3$O$_4$-2/GCE exhibit no significant difference in surface area normalized current and surface area normalized sensitivity, which implies that the specific surface area is one of crucial factors for the electrochemical performances of Co$_3$O$_4$. As above-mentioned, the amount of NH$_4$F is inversely related to the specific surface area. The dosage of NH$_4$F during the hydrothermal process affects the specific surface area of the products directly and therefore causes the difference in their electrochemical performances. To obtain the highly active Co$_3$O$_4$-based modified electrodes for hydrazine detection, F should be avoided, although in many cases the F species cannot be detected by the XRD and FTIR analysis. However, the mechanism on how the remaining F affects the electrochemical activity of Co$_3$O$_4$ is still under investigation.

### Table 3. Comparison of electrochemical parameters of various nanomaterials-based hydrazine sensor.

| Electrode Materials               | Sensitivity (µA·µM$^{-1}$) | Detection Limit (µM) | Linear Range (mM) | Ref. |
|-----------------------------------|----------------------------|----------------------|-------------------|------|
| Ru-complex films                  | -                          | 8.5                  | 0.010–10          | [40] |
| Nano-Au/Ti                        | 1.117                      | 42                   | 0.5–4             | [41] |
| Nickel tetrasulfonated phthalocyanine | 0.0079                  | 10                   | 0.1–0.6           | [42] |
| MWCNTs/Chlorogenic                | 41.2 µA·mM$^{-1}$·cm$^{-2}$| 8                    | 0.0025–0.5        | [43] |
| GO/CTS/Pt                         | 104.6 µA·mM$^{-1}$·cm$^{-2}$ | 3.6                | 0.02–1           | [44] |
| Co$_3$O$_4$-1                     | 32.42                      | 9.73                 | 0.010–2.38        | This work |
| Co$_3$O$_4$-2                     | 25.28                      | 10.74                | 0.027–0.890       |      |

### Table 4. The surface area normalized current and sensitivity of the obtained Co$_3$O$_4$ samples.

| Materials      | Current (µA) | Sensitivity (µA·mM$^{-1}$) | SSA (m$^2$·g$^{-1}$) | Surface Area Normalized Current (µA·mM$^{-1}$·g$^{-1}$) | Surface Area Normalized Sensitivity (µA·mM$^{-1}$·m$^{-2}$·g$^{-1}$) |
|----------------|--------------|-----------------------------|----------------------|---------------------------------------------------------|---------------------------------------------------------------------|
| Co$_3$O$_4$-1  | 46.05        | 32.42                       | 25.83                | 1.78                                                     | 1.26                                                            |
| Co$_3$O$_4$-2  | 33.58        | 25.28                       | 18.44                | 1.81                                                     | 1.37                                                            |
| Co$_3$O$_4$-3  | -            | -                           | 10.37                | -                                                       | -                                                              |

### 2.4. Selectivity, Reproducibility and Stability Tests

Selectivity and stability are two of key parameters to evaluate performance of chemical sensors. Thus, the selectivity and stability of the Co$_3$O$_4$-1-based hydrazine sensor were also explored. Figure 9a exhibits the i-t curve response of hydrazine and interferent (Cl$^-$, CO$_3^{2-}$, NO$_3^-$, NO$_2^-$, CH$_3$COO$^-$, K$^+$, Na$^+$, tap water, and humic acid). When 0.1 M N$_2$H$_4$ (10 µL) was injected to the NaOH solution, a quick response can be detected. However, when the same dosage of interfering species is added to the electrolyte, no obvious current response could be observed, suggesting the good selectivity of Co$_3$O$_4$-1/GCE for N$_2$H$_4$ detection. To evaluate the reproducibility, seven different glassy carbon electrodes were prepared via the same modification step. The relative standard deviation value of peak current towards 1 mM hydrazine was found to be 7.23% (Figure 9b). To test the stability, the electrode was stored for five days in ambient conditions. Figure 9c displays the peak current of Co$_3$O$_4$-1/GCE within five days. The value of peak current shows a declining trend with prolonging the time, but the peak current can still reach 86% of its initial response after being stored for five days. The obtained result suggests the long time stability of Co$_3$O$_4$-1/GCE.
Figure 9. (a) The amperometric response to the addition of hydrazine with interfering species including Cl$^-$, CO$_3^{2-}$, NO$_3^-$, NO$_2^-$, CH$_3$COO$^-$, K$^+$, Na$^+$, tap water, and humic acid; (b) Peak currents of seven electrodes evaluated in 1 mM hydrazine; and (c) The peak current of Co$_3$O$_4$-1/GCE after being stored at room temperature for five days.
2.5. Real Sample Test

In order to evaluate the validity of the proposed method, the Co₃O₄-1/GCE was applied for the detection of hydrazine in different water samples which prepared by adding known amounts of hydrazine in water samples, the results are listed in Table 5. When a known amount of hydrazine was added to distilled water, tap water, and river water, quantitative recoveries of 99.77–102.79%, 98.33–101.63%, 98.63–99.30% were obtained respectively. All the results revealed the feasibility of the proposed electrode in the determination of hydrazine in water samples.

Table 5. The real sample analysis of Co₃O₄-1-based hydrazine sensor using recovery method.

| Sample       | Hydrazine Added (µM) | Hydrazine Founded (µM) | Recovery  |
|--------------|-----------------------|------------------------|-----------|
| Distilled Water | 10                    | 10.28                  | 102.79%   |
|              | 20                    | 19.98                  | 99.88%    |
|              | 50                    | 49.88                  | 99.77%    |
| Tap Water    | 10                    | 10.16                  | 101.63%   |
|              | 20                    | 19.63                  | 98.14%    |
|              | 50                    | 49.16                  | 98.33%    |
| River Water  | 10                    | 9.86                   | 98.63%    |
|              | 20                    | 19.51                  | 97.56%    |
|              | 50                    | 49.65                  | 99.30%    |

3. Materials and Methods

3.1. Synthesis of Co₃O₄ Nanostructures

All the precursors were synthesized using a straightforward hydrothermal process. The detailed synthesis procedures were described as follows. 1.455 g (5 mmol) of Co(NO₃)₂·6H₂O and 0.601 g (10 mmol) of CO(NH₂)₂ were mixed in 50 mL DI water and stirred continuously for 10 min. The obtained mixture solution was moved into a 100 mL autoclave and then hydrothermally at 95 °C for 24 h. The attained precipitates were concentrated via centrifugation, and repeatedly rinsed with absolute ethanol and distilled water and subsequently dried at 60 °C. The dried powder was the precursor for Co₃O₄-1, being Co(CO₃)₀.₅(OH)·0.₁₁H₂O. The precursor for Co₃O₄-2 was prepared using the similar way except extra addition 0.370 g (10 mmol) of NH₄F, being Co(CO₃)₀.₅(OH)·0.₁₁H₂O and Co(OH)F mixture. The precursor for Co₃O₄-3 was synthesized similarly to the precursor of Co₃O₄-2 but changing the urea to hexamethylenetetramine (C₆H₁₂N₄, HMT), being pure Co(OH)F. The detailed synthesized conditions are summarized in Table 1. To obtain the Co₃O₄ products, all the precursors were annealed at 400 °C for 4 h. For ease of description, the products obtained from bare Co(CO₃)₀.₅(OH)·0.₁₁H₂O, pure Co(OH)F, and their mixture were designated as Co₃O₄-1, Co₃O₄-3, and Co₃O₄-2, respectively.

3.2. Electrode Modification

Before modification, the prepared glassy carbon electrode (GCE) was respectively polished with 1.0, 0.3, 0.05 µm alumina powder for 10 min, and then rinsed with distilled water followed by drying under ambient conditions. The obtained homogeneous slurries containing 5 mg Co₃O₄, 50 µL of Nafion solution (5 wt.%, DuPont 520, Wilmington, DE, USA), and 1 mL of ethanol was the mixture of all chemical together via sonication for 30 min. The Co₃O₄ modified GCE was produced by transferring 5 µL of the above attained homogeneous slurry on the GCE, and followed dried at ambient temperature.
3.3. Characterization of Samples

XRD spectra were acquired from Shimadzu XRD-7000 (Shimadzu, Kyoto, Japan) diffractometer (2θ = 10°–70°). Molecular speciation of the samples was examined by Bruker VERTEX 70 FT-IR spectrophotometer (Bruker, Billerica, MA, USA) in the range of 4000–400 cm⁻¹. XPS analysis was performed on a Thermo Scientific Escalab 250Xi instrument (Thermo Scientific, Waltham, MA, USA). The specific surface area (SSA) analysis was conducted by using Builder SSA-7000 (Beijing Builder Electronic Technology Co., Ltd, Beijing, China). SEM analysis was performed on a Hitachi SU8010 (Hitachi, Tokyo, Japan) field emission scanning microscope.

4. Conclusions

In summary, three types of Co₃O₄ samples were prepared and utilized as electrode materials for hydrazine detection. XRD analyses demonstrated that the precursors for Co₃O₄-1, Co₃O₄-2, and Co₃O₄-3 were Co(CO)₃0.5(OH)·0.11H₂O, the mixture of Co(OH)F and Co(CO)₃0.5(OH)·0.11H₂O, and Co(OH)F, respectively. SEM analyses showed that these three Co₃O₄ samples possess different morphologies. The existence of F in their precursors was confirmed using SEM-EDS elemental mapping. Cyclic voltammetry results revealed that the electrochemical activity of Co₃O₄ decreased with the increase of F content in precursors. Furthermore, the prepared Co₃O₄-1 and Co₃O₄-2 were used to fabricate hydrazine chemical sensor. The results indicated that the Co₃O₄-1-based hydrazine sensor possessed a high sensitivity of 32.42 µA·mM⁻¹, a low detection limit of 9.7 µM (S/N = 3), and a wide linear range from 0.010 to 2.380 mM. All these observed parameters were much better than those of the Co₃O₄-2 or Co₃O₄-3-based hydrazine sensors. The obtained results show that the fabricated hydrazine sensor also has good selectivity, great reproducibility and longtime stability.

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