Reduced Graphene Oxide-Conjugated Urchin-Like NiCo₂O₄ Nanostructures for Individual Detection of o-Nitro and p-Amino Phenol

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ABSTRACT: This work introduced a facile synthesis method of reduced graphene oxide-conjugated urchin-like NiCo₂O₄ nanostructures via a simple, cost-effective, and environmental-friendly one-pot hydrothermal method. The as-prepared rGO-NiCo₂O₄ nanocomposites were used to fabricate 3-aminopropytriethoxysilane-modified glassy carbon electrode (GCE/APTES/rGO-NiCo₂O₄) for ultrasensitive electrochemical detection of o-nitro (o-NP) and p-amino (p-AP) phenols. The structure and morphology of the nanocomposite were characterized by X-ray diffraction, Fourier-transform infrared spectroscopy, scanning electron microscopy, and transmission electron microscopy. Electrochemical experiments revealed that the nanocomposite exhibited remarkable electrochemical performances. A linear relationship is observed with the differential pulse voltammetry experiment between the peak currents and the concentrations in the ranges of 5.0 × 10⁻⁹ to 5.0 × 10⁻⁷ M (R² = 0.996) and 1.0 × 10⁻⁶ to 2.5 × 10⁻⁵ M (R² = 0.992) for o-NP and of 1.0 × 10⁻⁸ to 5.0 × 10⁻⁷ M (R² = 0.996) and 1.0 × 10⁻⁶ to 1.0 × 10⁻⁵ M (R² = 0.987) for p-AP. The calculated detection limits (S/N = 3) are 5.0 × 10⁻⁹ M and 1.0 × 10⁻⁵ M for o-NP and p-AP, respectively. Furthermore, a very high recovery percentage is obtained with the proposed sensor after successful application in the determination of target analytes in tap water samples.

1. INTRODUCTION

In last decades, the synthesis of new nanostructures of metal oxides with attractive morphology is of high interest because of their potential use in different fields.¹⁻² The development of nanostructured materials provides propitious elucidation to enhance catalytic activity toward electrochemical reactions because of their high surface area, improved electron and ion transport pathways, and excellent mechanical strength.³ Recently, ternary metal oxides have received much attention because of their promising characteristics.⁴⁻¹⁰ Among them, NiCo₂O₄ is one of the most promising transition metal oxides for electrochemistry on account of its high specific surface area, low cost, and unique electronic conductivity. Up to now, a number of NiCo₂O₄-based nanostructures such as Co₃O₄/NiCo₂O₄,⁵⁻⁸ Fe₂O₃@NiCo₂O₄,⁹ MnO₂/NiCo₂O₄,¹⁰ NiCo₂O₄/graphene,¹¹ and so forth have been developed and exploited to enhance the electron transfer rate between electrodes and targets. To date, various shape and morphologies of NiCo₂O₄ nanostructures have been observed including nanotubes,⁷ nanosheets,⁸ nanoparticle,⁹ nanorods.¹⁰ However, most NiCo₂O₄-based nanostructures still suffer from some disadvantages, such as undesirably electronic conduction, volume expansion, and instability during redox reactions, structural fragility, agglomeration, and so forth which limit their application in practical devices.⁶⁻¹⁰ Therefore, further explorations are still needed to overcome the abovementioned problems.

Several researchers combined conductive materials like graphene into the NiCo₂O₄ moiety as the composite and reported an improved electrochemical performance.⁸⁻¹⁰ Compared with other carbon materials, reduced graphene oxide (rGO)/nanoparticle composites have attracted increasing attention for electrochemical applications in terms of conductivity, inner architecture, superior electrochemical stability, and dispersibility.¹²,¹³ Therefore, it seems interesting to develop rGO-conjugated NiCo₂O₄ nanostructure with superior performance in practical applications.

Phenols and substituted phenolic compounds have been included in environmental legislations because of their existence in normal water and effluents from a broad range of human performances.¹⁴ These phenolic derivatives have the potential to provoke mutagenesis and carcinogenesis in a grade that is considered to be priority toxic pollutants by European
Union and Environmental Protection Agency.\textsuperscript{15} 2-Nitrophenol (p-NP) and 4-aminophenol (p-AP) are amongst the highly hazardous and toxic phenols which are extensively used in industrial production of pesticides, dyes, and pharmaceuticals.\textsuperscript{16} These two compounds are well known and widely studied because of their toxicity and serious impact on the metabolic activities and growth of the organism.\textsuperscript{17,18}

Therefore, it is highly desirable to develop an efficient, sensitive, and selective device for phenolic compound detection for environmental monitoring and diagnostic research. Till date, many analytical methods are routinely utilized for the determination of phenol derivatives such as high-performance liquid chromatography,\textsuperscript{19} fluorescence spectrocopies,\textsuperscript{20} liquid chromatography,\textsuperscript{21} capillary electrophoresis,\textsuperscript{22} and electrochemical sensors.\textsuperscript{23–27} Among all these techniques, electrochemical methods have received more considerable attention because of low-cost, simple operation, fast response, and higher sensitivity. However, because of their very low concentration existence in real samples and too close peak potentials with similar electroactive isomers, it is still a challenge to develop highly selective and sensitive electrochemical sensors.

Herein, we synthesized rGO-conjugated NiCo\textsubscript{2}O\textsubscript{4} nanomaterials with a space group of Fd\textsubscript{m} m (JCPDS no. 15-0804) and deposited onto the silane-modified glassy carbon electrode. The surface physiochemical properties of the resulted materials were characterized by different microscopic and spectroscopic methods. The electrochemical behavior of two phenolic compounds at the modified electrode is investigated and their electrochemical reaction mechanism is also discussed. The proposed method was further applied to determine trace amounts of target analytes in real water samples.

2. MATERIALS AND METHODS

2.1. Reagents. All chemicals used in this experiment were of analytical grade and used as received unless otherwise specified. 3-Aminopropyltriethoxysilane (APTES), NiCl\textsubscript{2}-6H\textsubscript{2}O, CoCl\textsubscript{2}-6H\textsubscript{2}O, l-ascorbic acid were purchased from Aladdins Reagent, Shanghai, China. Modified Hummers’ method was used to synthesize graphene oxide nanosheets, and it was kindly supplied by Yuta, Japan, the preparation method of which was described in the previous report.\textsuperscript{13}

During electrochemical experiments, all the analyte solutions were prepared in 0.1 M PBS (pH 7.0). KCl (0.1 mol L\textsuperscript{-1}) containing 5.0 mmol L\textsuperscript{-1} Fe (CN)\textsubscript{6}\textsuperscript{3–} and 5.0 mmol L\textsuperscript{-1} Fe (CN)\textsubscript{6}\textsuperscript{4–} was used as redox probe solution. Throughout the experiments, deionized water of 18.2 M\textsubscript{Ω} was used.

2.2. Synthesis of rGO-NiCo\textsubscript{2}O\textsubscript{4} Nanostructures. At first, freshly prepared GO was uniformly dispersed in water by ultrasonication (30 mL, 1 mg mL\textsuperscript{-1}) for 1 h. Then, the resultant solution was mixed with 200 mg of NiCl\textsubscript{2}-6H\textsubscript{2}O, 200 mg of CoCl\textsubscript{2}-6H\textsubscript{2}O (1:1 molar ratio), and 30 mg of ascorbic acid under vigorous stirring and ultrasonication for 30 min each. Subsequently, the resulting suspension was transferred into a 100 mL Teflon-lined autoclave and heated to 150 °C for 24 h. As the autoclave cooled down to room temperature, the precipitate was cleaned with deionized water and ethanol several times and dried at 60 °C for 6 h. The urchin-like rGO-conjugated NiCo\textsubscript{2}O\textsubscript{4} nanocomposites were thus obtained and referred to as rGO-NiCo\textsubscript{2}O\textsubscript{4}. Other nanocomposites were also prepared by the same procedure in the absence of either Ni, Co, or rGO and used as reference materials.

2.3. Fabrication of GCE/APTES/rGO-NiCo\textsubscript{2}O\textsubscript{4}. Typically, GCE (3 mm diameter) was polished consecutively by using 0.05 μm alumina powder and subsequently cleaned ultrasonically with nitric acid/water (1:1), ethanol, and deionized water and finally rinsed with ultra-pure water and dried under N\textsubscript{2}. The polished GCE was then dipped in 1% APTES anhydrous ethanol solution for 1.5 h at 70 °C to form a self-assembled monolayer of APTES. The functionalized alkyllsian was usually used to prepare amine-functionalized monolayers on the electrode surface. As we have reported earlier, the negatively charged NH\textsubscript{2}-terminated monolayer created through the protonation of the amino group on the electrode surface is very effective to attach with graphene.\textsuperscript{13} Finally, 10 μL of rGO-NiCo\textsubscript{2}O\textsubscript{4} solution (0.1 mg/mL dispersed in deionized water under ultrasonic agitation to form a suspension) was dropped onto the APTES-modified GCE and kept for 30 min, and then washed with deionized water and dried with N\textsubscript{2} to obtain the GCE/APTES/rGO-NiCo\textsubscript{2}O\textsubscript{4}-modified electrode.

2.4. Apparatus. CHI electrochemical workstation (Shanghai CH Instruments) with a conventional three electrode system was used for electrochemical measurements. GCE with a surface area of 3 mm was used as the working electrode, platinum wire as the counter electrode, and the Ag/AgCl electrode as the reference electrode. The morphology of nanomaterials was characterized by transmission electron microscopy (TEM) (Tecnai G2 20, USA) and Hitachi S-3000H model scanning electron microscopy (SEM) instruments. X-ray diffractometer (Bruker D8 ADVANCE, Germany) was used to study the crystallographic information of samples, while Fourier transform infrared spectrometer (12 Nicolet 170, USA) was used to obtain infrared spectra. Impedance analyzer EIM656 ZAHNER (Kroach, Germany) was used to study electrochemical impedance spectroscopy (EIS).

3. RESULTS AND DISCUSSION

3.1. Structural and Morphology Analysis. X-ray diffraction (XRD) was used to study the phase structure of the as-synthesized samples and is shown in Figure 1a. The observed major diffraction peaks at 65.2, 59.3, 44.8, 36.5, 31.2, and 19.0° corresponded to (440), (511), (400), (311), (220), and (111) reflection planes, respectively. All the diffraction peaks were in absolute agreement with face-centered cubic-structured NiCo\textsubscript{2}O\textsubscript{4} with a space group of Fd\textsubscript{3}m (JCPDS no. 73-1702; red line). The diffraction peak at 24.9° corresponding to the (002) reflection plane is due to the GO reduction in the presence of ascorbic acid, which is an agreement with our previous report. No other impurity peaks were observed, indicating the pure phase of NiCo\textsubscript{2}O\textsubscript{4}. Figure 1b is the Fourier transform infrared (FT-IR) spectra of the as-prepared samples, in which the broad peaks centering at 3500 and 1630 cm\textsuperscript{-1} verifies the presence of a hydroxyl group and are attributed to the stretching of carboxyl (–COOH and/or H\textsubscript{2}O).\textsuperscript{28} The absorption peaks appeared at 1777, 1378, 567, and 1630 support the presence of epoxy C–O, C–OH, C=C=O, and O–H bond stretching in GO. After complete reduction, those peak intensities are decreased with a new peak at ~1548 cm\textsuperscript{-1} that is observed for rGO.\textsuperscript{29} In the spectrum of rGO-NiCo\textsubscript{2}O\textsubscript{4} nanocomposites, the two bands at around 571 and 654 cm\textsuperscript{-1} along with the other bands at lower frequencies can be
assigned to the stretching vibrations of the Ni–O and Co–O bonds.29

The morphologies and structural features of as-synthesized rGO-NiCo2O4, rGO-Ni, and rGO-NiCo2O4 nanostructures with different magnifications were elucidated by SEM and TEM measurements. Figure 2a represents the uniformly spheroidal morphology of the pure Co3O4 nanoball with a diameter of about 100–300 nm wrapped with the rGO nanosheet. The SEM image in Figure 2b shows Ni nanowire with an average diameter size of ca. 7 nm conjugated with rGO. Figure 2c,d displays the as-synthesized urchin-like NiCo2O4 nanostructures with an average diameter of about 0.7 μm. The SEM image of an individual urchin-like NiCo2O4 nanostructure (Figure 2d) shows that numerous Ni nanowires with very high density grow pointing toward the center of the Co3O4 nanosphere. Based on the above observations, a “nanosphere/nanowire to urchin structure” transformation mechanism is presented in Figure 2f to explain the growth of urchin-like NiCo2O4 nanostructures. The observed 3D framework is beneficial for providing efficient electron transport and developing electronic conductivity which leads to improved electrochemical performance.30 The EDX elemental mapping from the region of Figure 2e of the SEM image reveals a uniform distribution of NiCo2O4 nanostructures conjugated with rGO nanosheets via a strong coupling interaction between the GO and metal nanosphere.

To confirm the architectural structure of the as-made rGO-NiCo2O4 nanostructures and to have an insight into the morphology, TEM and high-resolution TEM (HR-TEM) were done and presented in Figure 3. The uniform distribution of Ni nanowire on the graphene surface is shown by the low-magnification image (Figure 3a). The length of the nanowires is ~250 nm, with a diameter of ~7 nm. The TEM image of a single NiCo2O4 nanostructure (Figure 3c) reveals urchin-like spherical structures which size and shape very much consistent with SEM observations. The clear image of rGO nanosheets is distinctly observed all over the surface film. The HR-TEM images (Figure 3e,f) show lattice fringes with an interplanar
spacing of 0.20 and 0.24 nm, corresponding to that of the (400) and (311) lattice planes of the NiCo2O4 nanostructure, respectively. The resultant unique urchin-like 3D nanostructure is assumed to facilitate electron transport during electrochemical reactions.

### 3.2. Electrochemical Performance of GCE/APTES/rGO-NiCo2O4

The electrochemical performance of the rGO-NiCo2O4 nanocomposite-modified GCE is performed via cyclic voltammetry (CV) and EIS in 0.1 M L⁻¹ KCl including 5.0 mM L⁻¹ Fe(CN)₆³⁻/⁴⁻. CVs of the GCE/APTES/rGO-NiCo2O4 electrode in 0.1 M PBS (pH 7.0) solution with 10 μM o-NP measured at different scan rates (20, 30, 50, 60, 70, 80, 90, and 100 mV/s) (c) and the corresponding calibration plots between different scan rate versus anodic and cathodic peak currents (d). CVs of 10 μM p-AP in 0.1 M PBS (pH 7.0) solution with the same electrode at different scan rates (10, 30, 40, 50, 60, 70, 80, 90, and 100 mV/s) (e) and the corresponding calibration plots between different scan rate versus the anodic and cathodic peak currents (f).

The electrochemical active surface area for bare and modified electrodes was calculated by the Randles–Sevcik equation as shown below.³¹

\[ I_p = 2.69 \times 105 A D^{1/2} n^{3/2} γ^{1/2} C \]

where \( A \) is the electroactive surface area, \( C \) is the concentration of the probe molecule in the solution (mol/cm²), \( D \) is the diffusion coefficient of the molecule (equal to 6.70 ± 0.02 × 10⁻⁶ cm²/s), \( γ \) is the scan rate (V/s), and \( n \) is the number of electrons in the redox reaction. The calculated \( A \) value for the GCE, GCE/APTES/rGO, and GCE/APTES/rGO-NiCo₂O₄ were 0.078, 0.287, and 0.272 cm² respectively.

EIS experiments were performed to verify impedance changes during the modification processes and to confirm synergy between various modified electrodes and the results are shown in Figure 4b. Theoretically, the diameter of the semicircular portion represents the electron transfer limited process, which is equivalent to the charge transfer resistance (\( R_t \)). It is observed that the semicircular diameter of the modified electrodes decreased substantially compared with that of bare GCE, indicating the decline of electron transfer resistance. Comparing with the modified electrode, the bare GCE shows the largest semicircle with an \( R_t \) of 202 Ω, showing the lowest transfer rate, whereas for the GCE/
were investigated for GCE/APTES/rGO-NiCo$_2$O$_4$-modified electrode. As shown in Figure 4c–f, the peak currents for both $\alpha$-NP and p-AP increase linearly with the scan rate from 20 to 100 mV s$^{-1}$. These results suggest the electrochemistry of the rGO-NiCo$_2$O$_4$-modified GCE, corresponding to an adsorption-controlled electrochemical process$^{32}$ and consistent with the fast charge propagation with the proposed sensor.

3.3. Individual Voltammetric Responses of $\alpha$-NP and p-AP. The electrochemical behavior of the modified electrode in the presence of different concentration of target analytes and their calibration curves were investigated by differential pulse voltammetry (DPV) in the wide potential range and presented in Figure 5. As shown in Figure 5a, the change of DPVs indicates that the oxidative peak current ($I_{pa}$) increases with the concentration ($C$) of $\alpha$-NP. The calibration curve for $\alpha$-NP exhibits two linear segments in the range from 5.0 × 10$^{-8}$ to 5.0 × 10$^{-7}$ M ($R^2 = 0.996$) and 1.0 × 10$^{-6}$ to 2.5 × 10$^{-5}$ M ($R^2 = 0.992$), with a detection limit (S/N = 3) of 5.0 × 10$^{-9}$ M. On the other hand, a linear relation between the peak current and concentration for p-AP (Figure 5b) is in the range of 1.0 × 10$^{-8}$ to 5.0 × 10$^{-7}$ M ($R^2 = 0.996$) and 1.0 × 10$^{-6}$ to 1.0 × 10$^{-4}$ M ($R^2 = 0.987$), with a detection limit of 1.0 × 10$^{-8}$ M (S/N = 3), which is lower than many reported methods. Table 1 represents the comparison of the analytical findings of this study with several modified electrodes reported in the last few years.

The reproductivity and stability of the GCE/APTES/rGO-NiCo$_2$O$_4$ electrode have also been evaluated at different cycle numbers. The observed RSD value of 2.11 and 1.87% for $\alpha$-NP, and p-AP, respectively, indicate excellent reproducibility. Moreover, the modified electrode is kept at 4°C for three weeks and a slightly decreased oxidation peak current (lower than 7%) is observed which illustrates the good film stability of the proposed sensor.

The feasibility and performance of the proposed sensor were investigated with the detection of target analytes in environmental samples. Several tap water samples were diluted with phosphate-buffered saline (PBS) (0.1 M, pH 7.0) and the obtained recovery results ranged from 98.5 to 101.5%, which reveals the possibility of the proposed sensor for real sample

### Table 1. Comparison of Response Characteristics of Different Modified Electrodes for the Determination of $\alpha$-NP and p-AP$^{41}$

| Analyte | Sensor | Method | Linear Range (M) | LOD (M) | Refs |
|---------|--------|--------|------------------|---------|------|
| $\alpha$-NP | CD-SBA/CPE | DPV | 2.0 × 10$^{-7}$ to 1.4 × 10$^{-6}$ | 1.0 × 10$^{-8}$ | 33 |
|         | MWCNT-GCE | DPV | 4.0 × 10$^{-7}$ to 2.0 × 10$^{-5}$ | 5.0 × 10$^{-7}$ | 34 |
|         | HMSC/CPE | DPV | 1.0 × 10$^{-6}$ to 1.5 × 10$^{-6}$ | 3.0 × 10$^{-7}$ | 35 |
|         | Fe$_3$O$_4$–Pt/GCE | DPV | 1.0 × 10$^{-7}$ to 1.5 × 10$^{-6}$ | 3.0 × 10$^{-8}$ | 36 |
|         | Gr–Chit/ABPE | LSV | 4.0 × 10$^{-7}$ to 8.0 × 10$^{-5}$ | 2.0 × 10$^{-7}$ | 37 |
|         | OMCs/GCE | DPV | 5.0 × 10$^{-7}$ to 9.0 × 10$^{-5}$ | 8.0 × 10$^{-8}$ | 38 |
|         | Dual β-CD–SiC/GCE | DPV | 1.0 × 10$^{-7}$ to 1.5 × 10$^{-4}$ | 1.9 × 10$^{-8}$ | 39 |
|         | GCE/APTES/rGO-NiCo$_2$O$_4$ | DPV | 5.0 × 10$^{-7}$ to 0.5 × 10$^{-6}$ | 5.0 × 10$^{-9}$ | this work |
|         | aPcCo/CNT/GC | DPV | 5.0 × 10$^{-7}$ to 3.0 × 10$^{-4}$ | 3.0 × 10$^{-6}$ | 40 |
|         | RGO–TiN/GCE | CV | 5.0 × 10$^{-7}$ to 5.2 × 10$^{-4}$ | 1.3 × 10$^{-8}$ | 41 |
|         | naifen-GCNFE | DPV | 1.0 × 10$^{-7}$ to 1.5 × 10$^{-6}$ | 4.0 × 10$^{-9}$ | 42 |
|         | MIP/HG/GCE | DPV | 3.0 × 10$^{-7}$ to 2.5 × 10$^{-5}$ | 6.0 × 10$^{-8}$ | 43 |
|         | GR–PANI/GCE | DPV | 2.0 × 10$^{-7}$ to 1.0 × 10$^{-4}$ | 6.5 × 10$^{-8}$ | 44 |
|         | poly-Cys/GCE | DPV | 2.0 × 10$^{-7}$ to 2.0 × 10$^{-5}$ | 8.0 × 10$^{-9}$ | 45 |
|         | GCE/APTES/rGO-NiCo$_2$O$_4$ | DPV | 1.0 × 10$^{-7}$ to 5.0 × 10$^{-6}$ | 1.0 × 10$^{-8}$ | this work |

$^{41}$CD-SBA: β-cyclodextrin functionalized SBA-15; HMSC: hexagonal mesoporous silica; Gr–Chit/ABPE: graphene–chitosan-modified acetylene black paste electrode; OMC: ordered mesoporous carbons; β-CD-SiC: β-cyclodextrin-modified silicon carbide; aPcCo: tetra-b-[3-(dimethylamine)phenoxy] phthalocyanine cobalt (II); GR–PANI: graphene–polyaniline; rGO–TiN: rGO–titanium nitride.
analysis. The recovery values were estimated by the standard addition method and the results are summarized in Table S1-1 (Supporting Information).

4. CONCLUSIONS

We have reported a novel strategy for facile synthesis of rGO–conjugated NiCo2O4 architectures by the one-pot hydrothermal method. The detail of urchin-like shape formation was investigated and a growth mechanism was discussed. The experimental results revealed that the rGO-NiCo2O4 nano-composite-modified GCE electrode was attributed to the large specific surface area and multiple oxidation states for the detection of phenol derivatives. In particular, the electrode displays excellent analytical performance for the electrochemical sensing of o-NP and p-NP with broad linear dynamic ranges and a very low detection limit of 5.0 × 10^{-9} and 1.0 × 10^{-8} M for o-NP and p-NP, respectively. Additionally, the modified electrode shows applicability for the detection of these analytes in tap water samples with high recovery values. Hence, the proposed GCE/APTES/rGO-NiCo2O4 sensor could provide a potential platform for recognition and detection of phenol isomers in environmental control and chemical industry.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00804.

Preparation of GO nanosheet, real sample analysis with proposed modified electrode, and reproducibility and stability checking (PDF)

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Notes

The authors declare no competing financial interest.

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