Controllable Synthesis of a Porous PEI-Functionalized Co$_3$O$_4$/rGO Nanocomposite as an Electrochemical Sensor for Simultaneous as Well as Individual Detection of Heavy Metal Ions

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ABSTRACT: The present study focuses on the strategy of employing an electrochemical sensor with a porous polyethylenimine (PEI)-functionalized Co$_3$O$_4$/reduced graphene oxide (rGO) nanocomposite (NCP) to detect heavy metal ions (HMIs: Cd$^{2+}$, Pb$^{2+}$, Cu$^{2+}$, and Hg$^{2+}$). The porous PEI-functionalized Co$_3$O$_4$/rGO NCP (rGO·Co$_3$O$_4$·PEI) was prepared via a hydrothermal method. The synthesized NCP was based on a conducting polymer PEI, rGO, nanoribbons of Co$_3$O$_4$, and highly dispersed Co$_3$O$_4$ nanoparticles (NPs), which have shown excellent performance in the detection of HMIs. The as-prepared PEI-functionalized rGO·Co$_3$O$_4$·PEI NCP-modified electrode was used for the sensing/detection of HMIs by means of both square wave anodic stripping voltammetry (SWV) and differential normal pulse voltammetry (DNPV) methods for the first time. Both methods were employed for the simultaneous detection of HMIs, whereas SWV was employed for the individual analysis as well. The limits of detection (LOD; 3σ method) for Cd$^{2+}$, Pb$^{2+}$, Cu$^{2+}$, and Hg$^{2+}$ determined using the rGO·Co$_3$O$_4$·PEI NCP-modified electrode were 0.285, 1.132, 1.194, and 1.293 nM for SWV, respectively. Similarly, LODs of Cd$^{2+}$, Pb$^{2+}$, Cu$^{2+}$, and Hg$^{2+}$ were 1.069, 0.285, 2.398, and 1.115 nM, respectively, by DNPV during simultaneous analysis, whereas they were 0.484, 0.878, 0.462, and 0.477 nM, respectively, by SWV in individual analysis.

1. INTRODUCTION

Over the past several decades, heavy metal ions (HMIs) have been attracting great attention as they are extremely injurious to the biosphere, and even their minute aggregates are of much threat to human health.$^{1-3}$ In order to prevent this, the most sensitive and rapid removal method of trace HMIs is the need of today. Until now, technologically advanced approaches such as electrochemical exploration, anodic stripping voltammetry (ASV), and differential pulse ASV (DPASV) methods have been employed due to their fast response, convenience, and low cost.$^{4-6}$

So far, a stronger electrochemical sensing interaction in an aqueous solution for Pb$^{2+}$ and Hg$^{2+}$ has also been practiced on the modified carbon electrode (GCE) for DPASV by using an amine functionalized graphene oxide.7 Similarly, DPASV has also been performed for the simultaneous recognition of Cd$^{2+}$, Pb$^{2+}$, Cu$^{2+}$, and Hg$^{2+}$ by using gold nanoparticles (NPs) on the surface of GCE. Here, differential normal pulse voltammetry (DNPV) was used only for the simultaneous sensing/detection of HMIs because the simultaneous detection of HMIs using the DNPV technique results in strong intermetallic interaction; therefore, this method was not used in individual analysis.

Recently, for highly sensitive and selective recognition of HMIs, nanomaterials with various functionalities and accumulating abilities to adjust electrochemical electrodes for specific target HMIs have been reported.$^{9-15}$ Among them, Co$_3$O$_4$ is an important semiconductor oxide that has scientific application in energy storage and redox catalysis.16 However, the concrete use of Co$_3$O$_4$ has been unfulfilled yet, mostly owing to particle aggregation, expansion−contraction in volume, poor cycling stability, and capacity loss.$^{17,18}$

To enhance the electronic conductivity and to avoid aggregation, Co$_3$O$_4$ NPs have been used with carbon-based materials, such as amorphous carbon,$^{19}$ carbon nanofibers,$^{20}$ carbon nanotubes,$^{21,22}$ and graphene/reduced graphene oxide (rGO).23−25 In particular, it has been verified that graphene/rGO not only improves the electronic conductivity but also
prevents the aggregation of Co$_3$O$_4$ NPs. Thus, the design of the Co$_3$O$_4$/graphene composite is the most competent selection for progress of the electrochemical activity of Co$_3$O$_4$.\textsuperscript{26,27}

As reported earlier,\textsuperscript{28} the described N-doped PC-Co$_3$O$_4$ nanocomposite (NCP) that possesses numerous N functional groups deliver additional binding sites and improved electrochemical performance. The N-doped PC-Co$_3$O$_4$ NCPs have efficiently relieved the aggregation of Co$_3$O$_4$ and exhibited excellent cycle performance capacity. Similarly, graphene-based Co$_3$O$_4$ composites have obtainable stability, sustainability, high specific capacity, and excellent electrochemical performance.\textsuperscript{29−31}

The most important characteristic of Co$_3$O$_4$ nanocrystals is their unsaturated surface atoms bound with supplementary atoms. These atoms have strong chemical activities to efficiently adsorb metal ions. Generally, Co$^{3+}$ ions on the exterior are unimpregnated and bonded with several dangling bonds, which can produce catalytic active sites. Also, it is reported that the surface with extra dangling bonds possesses additional active sites and therefore has strong chemical activities.\textsuperscript{32−34} This means that the direct nucleation, growth, and attachment of Co$_3$O$_4$ nanocrystals with a suitable support are responsible features in determining the catalytic behavior. Therefore, the exposed crystal facets of nanocrystals are believed to play a significant role in adjusting the overpotential for the reaction in different contexts. The present study focuses on the detection of HMIIs and the effect of increased potential on voltammetry methods.\textsuperscript{35} For Co$_3$O$_4$ nanocrystals, the facet-dependent electrochemical activities toward HMIIs have also been reported. For example, the (111) facet of Co$_3$O$_4$ nanoplates is considered to be better than the (001) facet of Co$_3$O$_4$ nanocubes in electrochemical sensing.\textsuperscript{36} Few studies have investigated HMI incorporation on active facets of Co$_3$O$_4$ nanoribbons to explore their stripping behavior by electrochemical methods.

In this work, we have tried to combine a conductive polymer polyethylenimine (PEI) with Co$_3$O$_4$ and rGO (from expandable graphite (EG)) to formulate an electrochemical platform for individual as well as simultaneous analysis of
HMs (Cd²⁺, Pb²⁺, Cu²⁺, and Hg²⁺) in solution by applying stripping voltammetry (SWV) and DNPV methods, respectively. During the formation of rGO-Co₃O₄-PEI NCP, Co₃O₄ from EG was simultaneously reduced to rGO along with the precipitation of dense Co₃O₄ with good electron transport property. Meanwhile, PEI was fabricated hydrothermally with less active site Co²⁺ to enhance the interaction between Co₃O₄ and rGO. Moreover, the conductive polymer PEI possesses a lot of N functional groups that provide more binding sites to detect HMIs. Most importantly, we designed a thin Co₃O₄ nanoribbon structure with active planes of (110) and (220) to enhance the activity as well as the stability of Co₃O₄. The design strategy for the formation of a porous rGO-Co₃O₄-PEI NCP is given in Scheme 1. This porous rGO-Co₃O₄-PEI NCP with thin Co₃O₄ nanoribbons was found to be a favorable material for the electrochemical detection of HMIs.

2. RESULTS AND DISCUSSION

2.1. Characterization of the Porous rGO-Co₃O₄-PEI NCP. 2.1.1. Structure and Morphology of the rGO-Co₃O₄-PEI NCP. The methods for the preparation of rGO-Co₃O₄-PEI-1, rGO-Co₃O₄-PEI-2 NCP, and rGO-PEI NCP are summarized in the Supporting Information. The morphology of rGO-PEI, rGO-Co₃O₄-PEI-1, rGO-Co₃O₄-PEI-2, and rGO-Co₃O₄-PEI NCP was analyzed by transmission electron microscopy (TEM) (Figures 1, 2 and S1–S6), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDS).

TEM images in Figure 1a illustrate a porous rGO-Co₃O₄-PEI NCP structure with both nanoribbons and Co₃O₄ NPs covered by the conducting layer of PEI. Both NPs and nanoribbons can be easily seen in Figure 1a.d. The dense Co₃O₄ NPs ranging from 18 to 47 nm covering the rGO layer can be seen in Figure S3. As shown in Figure 1c,e–h, the EDS mapping elucidates the occurrence of all elements C, O, Co, and N in the rGO-Co₃O₄-PEI NCP. The well-bonded N atom of the conducting polymer PEI in porous rGO-Co₃O₄-PEI NCP provides more active sites due to the heterojunction among rGO and Co₃O₄. Thus, it is expected to be used as an electrochemical sensor.

For rGO-Co₃O₄-PEI NCP, the graphene layers acting as a substrate, Co₃O₄, and the conducting layer of PEI in the porous rGO-Co₃O₄-PEI NCP are clearly seen in Figures 1, 2, S3, and S4. The Co₃O₄ NPs and thin nanoribbons are confirmed by TEM and high-resolution TEM (HRTEM) on the surface of rGO and can be clearly seen in Figures 2a–e and S3e,f. The pores in the rGO-Co₃O₄-PEI NCP can be clearly seen in Figure S3d,e. The EDS spectrum (Figure S3g) further confirms the formation of the porous rGO-Co₃O₄-PEI NCP with weight (%) for Co, O, C, and N of 68, 27, 3, and 1%, respectively. This indicates that rGO-Co₃O₄ is covered by a thin conducting layer of PEI, as presented in Figures S1–S4.

The lattice fringe spacings of ~0.29 and 0.46–0.54 nm (Figures 2c–e, 3b, 3d–f, S3, and S4) correspond to (110) and (110) planes of the Co₃O₄ nanoribbon and 0.24 and 0.32 nm for (111) and (311) planes of cubic Co₃O₄ respectively. The thin nanoribbon Co₃O₄ of 6.5–11 nm width (Figure 2b,d) and cubic Co₃O₄ crystals of 24–56 nm size can be clearly indicated in Figures 2a,b, S3, and S4.

The TEM images of the porous rGO-Co₃O₄-PEI NCP illustrate that when the Co(NO₃)₂ solution concentration was turned down to half, less nanoribbon/nanorod structures were obtained compared to rGO-Co₃O₄-PEI (Figure S4). TEM images also show a porous structure (Figure S4d). As shown in Figure S6f, the Co₃O₄ nanoribbon or nanorod shows a (220) plane. Therefore, it can be deduced that the Co₃O₄ nanoribbon primarily grows along the {110} or {220} direction and favorably displays the (110) or (220) planes (Figures 3 and S6). Co₃O₄ has a spinel structure with Co³⁺ attached with six oxygen atoms in an octahedral relationship (Figure S6b) and Co²⁺ in a tetrahedral coordination (Figure S6c). The previous Co³⁺ is considered as the active site, while the last is nearly inactive. The compact planes are (220), (111), and (110) with their surface atomic arrangements as presented in Figure 3a–c. It has been proved that the (111) plane comprises Co²⁺ cations, whereas the (220) and (110) planes are mainly imperturbable Co³⁺ cations. Actually, the surface differential diffraction research has proved that Co³⁺ cations exist merely on the (110)/(220) plane. Further information about the nanoribbon Co₃O₄ flat top, atomic plane, and side plane can be found in Co₃O₄ nanorod formation. The planar density for the (111) plane is 0.185 × 10²⁰ atoms nm⁻² (Figure S7), and for the (110) and (220) planes, it is 0.113 × 10²⁰ and 0.113 × 10²⁰ atoms nm⁻², respectively.

The TEM results illustrated in Figures 2, 3, S3, and S4 are in accordance with X-ray diffraction (XRD) spectra. Figure 2f displays the SAED configuration of the porous rGO-Co₃O₄-PEI NCP. The diffraction rings of (220) are in agreement with the Co₃O₄ nanoribbon, and the (111), (311), (400), (422), (511), and (440) planes correspond to Co₃O₄ NPs, demonstrating the presence of Co₃O₄ crystals (JCPDS. no 42-1467) in the rGO-Co₃O₄-PEI NCP.

Figure 2. TEM and HRTEM images of the porous rGO-Co₃O₄-PEI NCP. (a–c) TEM images of rGO-Co₃O₄-PEI, (d,e) HRTEM images of rGO-Co₃O₄-PEI, and (f) selected-area electron diffraction (SAED) pattern of rGO-Co₃O₄-PEI.
2.1.2. Characterization of the rGO-Co3O4·PEI NCP. The crystal structures of rGO, Co3O4, and rGO-Co3O4·PEI were characterized by XRD (Figure 4a). The characteristic curving peaks appear at 26.59 and 44.86° attributed to the (002) and (101) planes of rGO and the peaks at 19.6, 31.24, 36.63, 44.86, 59.14, and 65.17° confirm the (111), (220), (311), (400), (511), and (440) crystalline planes of Co3O4, respectively (JCPDS no. 42-1467).49−51 The broad curve in the XRD pattern at 23.59° is recognized as the construction of layers in the rGO-Co3O4·PEI NCP, which is in accordance with HRTEM and TEM images (Figures 1 and 2).52,53 N2 adsorption/desorption was performed to study the pore size distribution and surface areas of the porous rGO-Co3O4·PEI NCP (Figure 4b,c). The porous rGO-Co3O4·PEI NCPs...
possess a BET surface area of 261.15 cm\(^2\) g\(^{-1}\) with a total pore volume of 0.612 cm\(^3\) g\(^{-1}\). As illustrated in Figure 4c, the average pore size of the porous rGO-Co\(_3\)O\(_4\)-PEI NCP was 9.4 nm, in close resemblance with the reports of t N-doped macroporous and mesoporous graphene-based metal oxides.

The Fourier-transform infrared (FTIR) spectra of rGO and rGO-Co\(_3\)O\(_4\)-PEI NCP (Figure 4d,e) were recorded to additionally explore the property of the porous rGO-Co\(_3\)O\(_4\)-PEI NCP. The widespread absorption peaks at 3000–3700 cm\(^{-1}\) are ascribed to the –NH and –OH groups in the rGO-Co\(_3\)O\(_4\)-PEI NCP. Similarly, the peak at 1625 cm\(^{-1}\) is assigned to the –OH bending vibration of absorbed water molecules, and the involvement of aromatic C=C (1218 and 1225 cm\(^{-1}\)) further confirms the successful reduction of GO. The peaks at 567 and 661 cm\(^{-1}\) are allotted to Co–O vibrations. The FTIR study additionally confirms that Co\(_3\)O\(_4\) NPs are effectively deposited on the surfaces of rGO.

Figure 5. CV curves (a), EIS curves (b,c), and MS plots (d) of rGO-Co\(_3\)O\(_4\)-PEI NCP (5 mM Fe(CN)\(_6\)^{3-}/4-, 1 M KCl, 1 M NaAc–HAc, pH 5 ± 0.2, 0.1 mV s\(^{-1}\)).

As shown in Figure S11a, both the anodic (0.27 V) and cathodic (0.18 V) peaks of GO are less compressed than those of rGO, rGO-PEI, and rGO-Co\(_3\)O\(_4\)-modified electrodes. The electrochemical gaps are adjusted to the spots of the redox couples. It can be sensed that at the anodic current curve of the rGO-Co\(_3\)O\(_4\)-modified electrode, there are two redox couples from 0.2 to 0.6 V/s. They are situated at 0.27/0.56 V/s and 0.63/0.45 V/s, respectively. As presented in Figure 5a, both the anodic (0.41 V) and cathodic (0.02 V) peak of GCE are less thick/broad than those of the rGO-Co\(_3\)O\(_4\)-PEI-modified electrode. The peaks around 0.29 (I) and 0.57 V (III) in the first cycle are ascribed to the decline of Co\(_3\)O\(_4\) to Co along with the construction of a solid electrolyte edge as well as the development of a solid electrolyte connection reaction on the exterior of the rGO-Co\(_3\)O\(_4\)-PEI NCP (same as that reported\(^{63,64}\) for the Co\(_3\)O\(_4\) nanowall in Li-ion batteries). At the anodic current curve, two redox couples are detected from 0.2 to 0.6 V/s. They are positioned at 0.22/0.47 V and 0.57/0.647 V, respectively, arising due to the reversible conversion attributed to Co\(_3\)O\(_4\) and CoOOH(II/III) and similar reversible conversions between CoOOH and CoO\(_2\)(III/IV).\(^{57,62,65}\) The peaks at 0.72 (V) and 0.29 V (I) in the first cycle are ascribed to the depletion of Co\(_3\)O\(_4\) to Co along with the development of a solid electrolyte edge on the exterior of rGO-Co\(_3\)O\(_4\)-PEI, with 0.65 μA current greater than GCE, as shown in Figure 5a.

The porous PEI-functionalized Co\(_3\)O\(_4\)/rGO NCPs were characterized by X-ray photoelectron spectroscopy (XPS) spectrum as shown in Figure S13. The strong peaks at 287.9, 400, 538.2, and 783.2 eV analogous to the distinct peaks of C...
1s, N 1s, O 1s, and Co 2p indicate the presence of C, N, O, and Co elements, respectively, in the sample. The Co 2p$_{1/2}$ and Co 2p$_{3/2}$ spectra can be deconvoluted into four peaks at 794.8 and 793.2 eV for Co 2p$_{1/2}$, 782.7 and 781.4 eV for Co 2p$_{3/2}$, showing the characteristic of the Co$_3$O$_4$ phase (Figure S13b). Similarly, for co-doping of graphene with Co$_3$O$_4$ and PEI O 1s and N 1s spectrum linkage and interaction with graphene and Co$_3$O$_4$ shown in Figure S13c,d confirm rGO·Co$_3$O$_4$·PEI NCP.

The EIS experiments were performed between −0.2 and 0.6 V at room temperature, as illustrated in Figure 5b,c. Figure 5b shows Nyquist plots of GCE and rGO·Co$_3$O$_4$·PEI (Figure 5c). It might be perceived that the rGO·Co$_3$O$_4$·PEI electrode has the smallest diameter (825 Ω), compared to GO (2868 Ω), GCE (1271 Ω), and rGO·Co$_3$O$_4$ (1849 Ω) (Figure S11b), signifying that the rGO·Co$_3$O$_4$·PEI-modified electrode possesses a smaller $R_{ct}$ value than GCE (Table S1). The results show that the electrochemical reaction on the surface of anode/electrolyte for rGO·Co$_3$O$_4$·PEI is more prominent than that on the GCE electrode, which is almost the same as reported by ref 57 for the Co$_3$O$_4$/rGO-0.50 electrode. Meanwhile, the film resistance and resistance of charge transfer (Rs and Rct) of the rGO·Co$_3$O$_4$·PEI electrode are lower than those of GCE (Table S1). Further suitable results are displayed in Table S1, indicating that the Rs (135.6 Ω) and Rct (419.7 Ω) of the rGO·Co$_3$O$_4$·PEI NCP-modified electrode are lesser in comparison with those of the pure GCE electrode (193 and 1070 Ω, respectively).

The rGO·Co$_3$O$_4$·PEI NCP exhibited a negative (adverse) slope for the MS plot and hence exhibit a p-type semiconducting performance, as illustrated in Figure 5d and Table S2; the carrier density ($N_d$) of rGO·Co$_3$O$_4$·PEI NCP was calculated as $1.56 \times 10^{18}$ (with a quiet time of 2 s, an amplitude of 0.005 V, and an increased potential of 0.05 V).

2.2.2. SWV and DNPV Voltammetry Analyses Intended for the Sensing/Detection of Cd$^{2+}$, Pb$^{2+}$, Cu$^{2+}$, and Hg$^{2+}$ by Means of the rGO·Co$_3$O$_4$·PEI-Modified Electrode. SWV and DNPV electrochemical analyses were used to detect the four HMIs (Cd$^{2+}$, Pb$^{2+}$, Cu$^{2+}$, and Hg$^{2+}$). Figure 6a,b illustrates the SWV and DNPV peaks from 1 to 10 μM concentration of Cd$^{2+}$, Pb$^{2+}$, Cu$^{2+}$, and Hg$^{2+}$ (Figure 6a,b) are assigned to the occurrence of inter-metallic interactions.66,67 Figure 6c shows the increased potential from 0.001 to 0.007 V for SWV analysis at 10 μM concentrations of four HMIs (Cd$^{2+}$, Pb$^{2+}$, Cu$^{2+}$, and Hg$^{2+}$). Similarly, Figure 6d illustrates the increased potential of 0.001 to 0.007 V for SWV at 7 μM concentration. The peaks at an increased potential of 0.007 V (7 mV) are recommended to be the best for the 1–10 μM concentration of Cd$^{2+}$, Pb$^{2+}$, Cu$^{2+}$, and Hg$^{2+}$ for both individual (Figure S9) and simultaneous analyses of SWV (Figure 6c,d). Figure S9 illustrates the individual analysis of the
Figure 7. Voltammetric curves (a,b) for the increased potential of 0.001−0.007 V for DNPV at 10 μM and 5 μM concentrations, respectively, for simultaneous analysis, (c) for the increased potential of 0.004−0.007 V for SWV at 5 μM concentration, and (d) for the increased potential of 0.001 V (1 mV) and 0.003 V (3 mV) carried out on SWV at 3 μM concentration.

Figure 8. SWV response of the rGO-Co$_3$O$_4$·PEI NCP-modified electrode and calibration curves for the individual investigation of (a) Cu$^{2+}$, (b) Hg$^{2+}$, (c) Pb$^{2+}$, and (d) Cd$^{2+}$ in the 1−10 μM concentration range, while other parameters were the same as in Figure 6 in acetate buffer (0.1 M).
However, two stronger intermetallic interactions between Co$_3$O$_4$ with the increase in potential from 1 to 7 mV (Figure 7c,d). The intensity of voltammetric peaks increases with an increased potential from 0.007 (7 mV) to 0.049 V, demonstrating that 7 mV potential is the best for the individual measurement of Cd$^{2+}$, Pb$^{2+}$, Cu$^{2+}$, and Hg$^{2+}$. The sensing performance of rGO, rGO-PEI, and rGO-Co$_3$O$_4$ NCPs was satisfactory but not strong enough as that of the rGO-Co$_3$O$_4$·PEI NCP (Figure S12).

To check the increased potential effect on voltammetric peaks, the potential was varied from 1 to 7 mV; when the potential was increased from 1 to 5 mV, the intensity of voltammetry peaks increased a little. However, the voltammetry spectrum becomes better than before at an increased potential of 7 mV. Therefore, an increased potential of 7 mV is recommended to be the best for the simultaneous sensing/detection of Cd$^{2+}$, Pb$^{2+}$, Cu$^{2+}$, and Hg$^{2+}$ on SWV, as shown in Figure 6c,d. As shown in Figure S10, the corresponding calibration curves for the four HMIs (inset in Figure S10) are shown in Figure S10 and Table S5. For Cd$^{2+}$, Pb$^{2+}$, Cu$^{2+}$, and Hg$^{2+}$, the inevitable LODs were 0.285, 1.13, 1.19, and 1.29 nM for SWV (Table S3); similarly, they were 1.07, 0.285, 2.40, and 1.12 nM for DNPV (Table S4) for simultaneous detection, whereas they were 0.484, 0.878, 0.462, and 0.477 nM for SWV (Table S5) for individual analysis of Cd$^{2+}$, Pb$^{2+}$, Cu$^{2+}$, and Hg$^{2+}$. The linearization equation and the calculation of the corresponding coefficients for concurrent determination of Cd$^{2+}$, Pb$^{2+}$, Cu$^{2+}$, and Hg$^{2+}$ are enumerated in Tables S6 and S7.

As shown in Figure S10, the corresponding calibration curves for the four HMIs (inset in Figure 8a and Table S6) represent the linearization equations with comparable correlation coefficients of 0.99, 0.97, 0.99, and 0.98 for individual analysis by SWV when the rGO-Co$_3$O$_4$·PEI NCP was employed. The LODs for simultaneous sensing/detection of Cd$^{2+}$, Pb$^{2+}$, Cu$^{2+}$, and Hg$^{2+}$ with the use of the rGO-Co$_3$O$_4$·PEI-modified electrode were estimated to be 0.285, 1.13, 1.19, and 1.29 nM for SWV (Table S3); similarly, they were 1.07, 0.285, 2.40, and 1.12 nM for DNPV (Tables S4 and S7) during simultaneous detection (3σ method), respectively. The benefits acquired by the use of the rGO-Co$_3$O$_4$·PEI NCP for LOD in both DNPV and SWV voltammetry analyses were found to be inferior to the values of the peak-to-peak width for Cd$^{2+}$, Pb$^{2+}$, Cu$^{2+}$, and Hg$^{2+}$ at 0.02 V for SWV and –0.35 V for DNPV between Cu$^{2+}$ and Hg$^{2+}$ (Figure 6a,b), which are due to the presence of inter-metallic interactions.69 Due to stronger intermetallic interactions, the DNPV voltammetry method was not proceeded further. However, at an increased potential of 1 mV for simultaneous DNPV analysis, the limit of detection (LOD) and sensitivity were found to be good (Table S4).

### 2.3. Stripping Analysis of Pb$^{2+}$, Cd$^{2+}$, Hg$^{2+}$, and Cu$^{2+}$.

#### 2.3.1. Individual Depriving Performance Analysis for Cd$^{2+}$, Cu$^{2+}$, Hg$^{2+}$, and Pb$^{2+}$ Using SWV.

The SWV response of the rGO-Co$_3$O$_4$·PEI-modified electrode (GCE), linearization equations, and calibration curves for the individual voltammetry examination of Cd$^{2+}$, Pb$^{2+}$, Cu$^{2+}$, and Hg$^{2+}$ from 1 to 10 μM concentration are presented in Figure 8a and Table S5.

The respective calibration curves of rGO-Co$_3$O$_4$·PEI for the simultaneous sensing/detection of Cd$^{2+}$, Pb$^{2+}$, Cu$^{2+}$, and Hg$^{2+}$ corresponding to Figure 6a are shown in Figure S10 and Table S3. For Cd$^{2+}$, Pb$^{2+}$, Cu$^{2+}$, and Hg$^{2+}$, the inevitable LODs were 0.285, 1.13, 1.19, and 1.29 nM for SWV (Table S3); similarly, they were 1.07, 0.285, 2.40, and 1.12 nM for DNPV (Table S4) for simultaneous detection, whereas they were 0.484, 0.878, 0.462, and 0.477 nM for SWV (Table S5) for individual analysis of Cd$^{2+}$, Pb$^{2+}$, Cu$^{2+}$, and Hg$^{2+}$. The linearization equation and the calculation of the corresponding coefficients for concurrent determination of Cd$^{2+}$, Pb$^{2+}$, Cu$^{2+}$, and Hg$^{2+}$ are enumerated in Tables S6 and S7.

As shown in Figure S10, the corresponding calibration curves for the four HMIs (inset in Figure 8a) represent the linearization equations with comparable correlation coefficients of 0.99, 0.97, 0.99, and 0.98 for individual analysis by SWV when the rGO-Co$_3$O$_4$·PEI NCP was employed. The LODs for simultaneous sensing/detection of Cd$^{2+}$, Pb$^{2+}$, Cu$^{2+}$, and Hg$^{2+}$ with the use of the rGO-Co$_3$O$_4$·PEI-modified electrode were estimated to be 0.285, 1.13, 1.19, and 1.29 nM for SWV (Table S3); similarly, they were 1.07, 0.285, 2.40, and 1.12 nM for DNPV (Tables S4 and S7) during simultaneous detection (3σ method), respectively. The benefits acquired by the use of the rGO-Co$_3$O$_4$·PEI NCP for LOD in both DNPV and SWV voltammetry analyses were found to be inferior to the values of the peak-to-peak width for Cd$^{2+}$, Pb$^{2+}$, Cu$^{2+}$, and Hg$^{2+}$ at 0.02 V for SWV and –0.35 V for DNPV between Cu$^{2+}$ and Hg$^{2+}$ (Figure 6a,b), which are due to the presence of inter-metallic interactions.69
the disturbance initiated by structural and volume variations of Cu\(^{2+}\), and Hg\(^{2+}\) in Pb\(^{2+}\), Cu\(^{2+}\), and Hg\(^{2+}\) are 1.20, 1.20, 2.90, and 2.60 respectively. Similarly, for simultaneous analysis by SWV, the sensitivities of the rGO-Cu\(_2\)O\(_4\)-PEI-modified electrode calculated for Cd\(^{2+}\), Pb\(^{2+}\), Cu\(^{2+}\), and Hg\(^{2+}\) are 3.50, 9.60, 13.9, and 14.6 \(\mu A/\mu M\) respectively. The Co\(_3\)O\(_4\) nanoribbons and NPs well dispersed on thin-layer rGO nanosheets can effectively relieve or prevent Co\(_3\)O\(_4\) NPs from aggregation. Thus, the design of the objective HMIs and hence improve the electrochemical performances. Also, the Co\(_3\)O\(_4\) nanoribbons with active (110) and (220) planes retain the chemical sensitivity and adsorb HMIs. The approach developed in the present work provides a novel route for low-cost and comprehensive porous rGO-Cu\(_2\)O\(_4\)-PEI with highly promising applications in heavy metal detection.

4. EXPERIMENTAL SECTION

4.1. Chemicals. All the chemicals used in this study were of analytical grade and used without further purification. Cobalt nitrate hexahydrate \([\text{Co(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}\text{, }99\%]\) and sodium hydroxide (NaOH, 96\%) were provided by Xilong Chemical Co., Ltd. Hydrochloric acid (HCl, 37\%) was obtained from Beijing Chemical Works. Branched PEI (M\(_n\) = 600, 99\%) was bought from Alfa Aesar Chemical Co. Ltd. (Tianjin, China). Lead nitrate [Pb(NO\(_3\))\(_2\)], cadmium nitrate tetrahydrate [Cd(NO\(_3\))\(_2\cdot4\text{H}_2\text{O}\)], copper nitrate trihydrate [Cu(NO\(_3\))\(_2\cdot3\text{H}_2\text{O}\)], mercury nitrate [Hg(NO\(_3\))\(_2\)], acetic acid, and sodium acetate were provided by Tianjin Chemical Works. EG of 300 mesh used in the preparation of rGO-PEI and rGO-Cu\(_2\)O\(_4\)-PEI NCP was obtained from Qingdao Tianyuan Chemical Co., Ltd. Concentrated sulfuric acid (H\(_2\)SO\(_4\), 98\%) was purchased from Yaohua Chemical Reagent Co. Ltd. (Tianjin, China).

4.2. Synthesis of the rGO-Cu\(_2\)O\(_4\)-PEI NCP. The thin-sheet-like structure of EG was attained by heating expandable graphite in a microwave oven. Graphite oxide was prepared by the Hummers method.\(^{39}\) Then, 20 mL of PEI (2 g/L) and 80 mL of EG solution (0.03 g/L) were mixed with deionized (DI) water (100 mL) under magnetic stirring, the pH was adjusted (9.0 ± 0.2), and the solution was allowed to stand for 1 h; then it was sonicated for 0.5 h, and 20 mL of Co(NO\(_3\))\(_2\) solution (2 g/L) was added dropwise to the solution. During the mixing process, the pH of the solution was kept at 9.0 ± 0.2. The flow rate of air was maintained as 50 mL/min for 20 min. Then, the pH of the solution (12.0 ± 0.2) was balanced by the gradual addition of NaOH solution and the air flow was maintained for 2 h. After the completion of aeration, the solution was further sonicated for 0.5 h followed by pH adjustment (12 ± 0.2). Finally, the mixed precursor solution was placed for 24 h at room temperature (RT), the precipitate was filtered and washed with DI water; the pH was adjusted to about 7. The obtained precipitates were dispersed in DI water and transferred to a 100 mL Teflon-lined stainless steel autoclave. The hydrothermal method was done at 190 °C for 5 h. The obtained rGO-Cu\(_2\)O\(_4\)-PEI NCP was named rGO-Cu\(_2\)O\(_4\)-PEI. When the Co(NO\(_3\))\(_2\) solution concentration was 30 and 40 mL, the obtained NCPs were named rGO-Cu\(_2\)O\(_4\)-PEI-1 and rGO-Cu\(_2\)O\(_4\)-PEI-2, respectively.

4.3. Characterizations. The morphological and surface compositions for NCPs were studied by SEM (HITACHI S-4800), EDS, and TEM (JEOL-2100) analyses. X-ray powder diffraction (XRD; D/Max-III-B40 kV, Japan, Cu K\(_\alpha\) radiation, \(\lambda = 1.5406\) Å) analysis was used to define the crystalline
structure and the composition of the assembled composites. FTIR measurements (PerkinElmer spectrometer, KBr pellet technique) and Raman spectroscopy (Jobin Yvon HR 800 micro-Raman spectrometer) were also performed. The surface composition study was done by XPS(AXIS ULPRA DLD Shimadzu Corporation). The porous PEI-functionalized Co₃O₄/rGO NCPs were characterized by XPS using an Mg Kα X-ray source (hν = 1.254 MeV) and a 120 mm arched electron energy analyzer, with an energy resolution of ~0.8 eV. Thermogravimetric (TG) quantification was achieved with a Shimadzu TGA-50.

For electrochemical experiments, a traditional three-electrode system electrochemical workstation (Beijing Company CHI660D) was used. The Ag/AgCl electrode (no 218 ± 3 potential) purchased from the Shanghai Branch of the Inst. Eq. Company and platinum (Pt J110, with the snap width below 1 mm) made at Tianjin Ida Heng Sheng Tech. Dev. Co., Ltd. were used as the reference and auxiliary electrodes, respectively. SWV and DNPV electrochemical analyses were conducted to detect the four HMIs (Cd²⁺, Pb²⁺, Cu²⁺, and Hg²⁺). Both SWV and DNPV were performed with a three-electrode cell using a CHI660D electrochemical workstation.

The GCE coated with rGO-Co₃O₄:PEI was used as the working electrode for EIS, CV, MS measurements, and SWV experiments. The CV responses of rGO-Co₃O₄:PEI-modified electrodes were studied in Fe(CN)₆³⁻/⁴⁻ (5 mM) solution comprising KCl (1 M) using the Fe(CN)₆³⁻/⁴⁻ redox couple, and the pH was attuned to 5 ± 02 with acetate buffer solution (CH₃COOH/CH₃COONa). The EIS experiments were carried out between −0.2 and 0.6 V at RT with Ag/AgCl as the reference electrode and a Pt electrode as the counter electrode. EIS experiments were completed with an initial potential of 0.294 V in the frequency range of 1 Hz to 0.1 μHz.shikeying2008@163.com

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c05989.

TEM images of rGO from expanded graphene and rGO:PEI NCP; TEM and HRTEM images of rGO:PEI NCP; TEM image and EDS spectrum of porous rGO-Co₃O₄:PEI NCP; TEM and HRTEM images of porous rGO-Co₃O₄:PEI-1 NCP; TEM images of rGO-Co₃O₄:PEI-1 and rGO-Co₃O₄:PEI-2 NCP; spinel structure of the Co₃O₄ nanoribbon crystal and surface atomic configuration of Co₃O₄; HRTEM images of {220}, {111}, and {110} planes; crystallographic plans and planar density in {111}, {110}, and {220} planes along with the arrangement of atoms; weight lost by VS heat flow; fitted impedance parameters of rGO-Co₃O₄:PEI NCPs; MS results and carrier densities of rGO-Co₃O₄:PEI NCP; individual analysis of rGO-Co₃O₄:PEI NCP; linearization equations, adj. R² response of rGO-Co₃O₄:PEI NCP-modified GCE and calibration curves for the simultaneous voltammetry investigation of Cd²⁺, Pb²⁺, Cu²⁺, and Hg²⁺; CV curves of GO, rGO, rGO:PEI, and rGO-Co₃O₄-modified electrode; EIS curves of GO, rGO, rGO:PEI, and rGO-Co₃O₄-modified electrode; SWV curves of rGO, rGO:PEI, and rGO-Co₃O₄ NCP; SWV analysis at 10 μM concentration and 5 μM concentration of the four HMIs; XPS full spectrum of the PEI-functionalized Co₃O₄:rGO NCP; Co 2p XPS spectrum of the PEI-functionalized Co₃O₄:rGO NCP; statistical calculation data of LOD for simultaneous sensing/detection of the four HMIs using the SWV voltammetry technique; statistical calculation data of LOD for simultaneous degradation of the four HMIs using the DNPV voltammetry technique; statistical calculation data of LOD for individual detection of the four HMIs using the SWV voltammetry technique; results of the porous rGO-Co₃O₄:PEI NCP used for the simultaneous and individual analyses of HMIs by using the SWV electrochemical method; comparison of the LOD (individual analysis via SWV and simultaneous analysis via SWV and DNPV); comparison of simultaneous analysis of HMIs via SWV and WHO; comparison of sensitivity; and comparison study of rGO-Co₃O₄:PEI NCP with previous work used for the sensing/detection of Cd²⁺, Pb²⁺, Cu²⁺, and Hg²⁺ (PDF)

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Notes
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