Bismuth Nanoclusters/Porous Carbon Composite: A Facile Ratiometric Electrochemical Sensing Platform for Pb²⁺ Detection with High Sensitivity and Selectivity

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ABSTRACT: In this work, a ratiometric electrochemical sensor was constructed for the detection of Pb²⁺ based on a bismuth nanocluster-anchored porous activated biochar (BiNCs@AB) composite. BiNCs with loose structure and AB with abundant oxygen-containing functional groups are favorable for Pb²⁺ adsorption and preconcentration; meanwhile, porous AB provides more mass transfer pathways and increases electronic and ion diffusion coefficients, realizing high sensitivity for Pb²⁺ detection. At the same time, BiNCs were proposed as an inner reference for ratiometric electrochemical detection, which could greatly enhance the determination accuracy. Under optimized experimental conditions, the anodic peak current ratio between Pb²⁺ and BiNCs exhibited a good linear relationship with the concentration from 3.0 ng/L to 1.0 mg/L. The detection limit can be detected down to 1.0 ng/L. Furthermore, the proposed sensor demonstrated good reproducibility, stability, and interference resistance, as well as satisfactory recoveries for the detection of Pb²⁺ in real samples.

INTRODUCTION

Heavy metal ions, especially lead ions (Pb²⁺), have been rated as the most hazardous environmental pollutants because of their highly toxic and nonbiodegradable nature. The excessive exposure to Pb²⁺ even at trace levels can trigger serious damage to the nervous system, kidneys, liver, reproductive system, and brain. At the same time, nonbiodegradability means it can be concentrated in living tissues throughout the food chain, posing a serious threat to natural ecosystems and public health. Therefore, it is extremely significant to develop Pb²⁺ detection technology with high sensitivity and reliability for human health and environmental monitoring.

Until now, some analytical techniques, such as surface-enhanced Raman spectrometry, atomic absorption spectroscopy, UV−vis spectrophotometry, and X-ray fluorescence spectrometry, have been employed for Pb²⁺ detection. However, these techniques require expensive equipment and time-consuming pretreatment steps. By contrast, the electrochemical sensing strategy possesses significant superiority in terms of portable instruments, low cost, simple operation, fast response, high sensitivity, and excellent selectivity. Typically, electrochemical sensors track the content of analytes by recording single response signal. Nevertheless, the response signal is susceptible to environmental factors and instrument efficiency, resulting in poor stability and low reproducibility.

In contrast, the ratiometric electrochemical sensor with two electrochemical signals is a superior alternative to the
conventional single signal sensing because of its superior built-in self-calibration ability. For the ratiometric sensing strategy, the ratio of two current signals at different potentials is employed as the detected signal in which the peak current signals usually derive from the analyte itself and the internal reference probe, respectively. The current ratio can provide an intrinsic correction factor to eliminate the contribution from nonspecific interferences, thus greatly improving the detection accuracy and sensitivity. At present, several electroactive materials, such as ferrocene, MOFs, paracetamol, and AuNPs, have been exploited as inner references for ratiometric heavy metal ion (HMI) electrochemical sensors. By comparison, metal nanoparticles are attractive since they can provide strong electrochemical signals. Bismuth (Bi) particles are one of the most commonly used nanomaterials in sensing of HMIs due to their low toxicity, easy formation of alloy with HMIs, and insensitivity to the dissolved oxygen in a solution. In addition, good resolution of adjacent peaks from heavy metals and Bi was observed in these studies. These characteristics enable Bi particles to be a promising internal reference probe. However, as far as I am concerned, a Bi-based dual-signal HMII electrochemical sensor has not been reported.

Considering the low electrical conductivity and easy agglomeration of Bi particles, porous activated biochar (AB) with the merits of high electrical conductivity, large surface area, and good chemical stability was chosen as the support material. Additionally, in comparison to other forms of nanomaterials, nanoclusters (NCs) have higher electrocatalytic activity due to a larger number of available electroactive sites to detect analytes. Given these features, herein, through a simple solvothermal method, AB-supported BiNCs (BiNCs@AB) has been synthesized, which was employed as a ratiometric electrochemical sensor for Pb detection (shown in Scheme 1). BiNCs can not only form alloy with Pb to promote the adsorption of Pb on the electrode surface but also provide reference signals for the ratiometric electrochemical detection. Moreover, AB with excellent properties of porous structure, good conductivity, and abundant oxygen-containing functional groups could provide more pathways for the rapid electrical/ionic transport and enrichment of Pb on the electrode surface. Benefiting from the synergistic effect of these advantages, the fabricated sensor showed excellent electrocatalytic performances to Pb with the satisfactory linear range and detection limit. The method was also used for the determination of Pb in the paddy water sample.

RESULTS AND DISCUSSION

Characterization. The structures and morphologies of AB and BiNCs@AB nanomaterials were evaluated using SEM. KOH activation brought a remarkable change in the material morphology. Focused on the surface of AB derived from Litsea cubeba, lots of dense pores with irregular size could be seen (Figure 1A). Such a porous structure provides a larger surface area and accelerates mass transfer on the surface of samples. At the same time, it is a substantial platform for the loading of BiNCs due to the presence of abundant functional groups (e.g., carboxyl and amine groups). Through using a reducing agent, the BiNCs were successfully loaded on AB. As can be seen from Figure 1B,C, a large number of BiNCs are anchored on the AB surface, which confirms the successful synthesis of the BiNCs@AB. The TEM image of BiNCs@AB is shown in Figure 1C. It could be distinctly seen that BiNCs (dark dots) are well dispersed and anchored on the surface of AB. Figure 1D displays the particle size distribution of BiNCs on AB. From the bar chart, it is observed that the BiNC size distribution conforms to normal distribution with a mean diameter of 59.6 ± 23.5 nm. Figure 1E shows the EDS spectrum and corresponding composition information of the BiNCs@AB composite. As listed, the wt % values of C, O, and Bi are 68.46, 20.74, and 10.80%, respectively.

X-ray diffraction (XRD) patterns of AB, BiNCs, and BiNCs@AB are shown in Figure 2A. For the AB sample, two distinct diffraction peaks at around 21.1° and 42.7° are observed, which are attributed to (002) and (101) reflections of graphite. In the case of BiNCs, five diffraction peaks are observed at 28.1°, 37.9°, 39.6°, 46.3°, and 51.9°, which agree well with the data for metallic Bi present in the JCPDS card (no. 44-1246). The crystallite size of BiNCs can be calculated from the obtained XRD results by using the Scherer equation (D = Kλ/βcosθ). The achieved crystallite size is 38 nm. In the spectrum of the BiNCs@AB composite, both the characteristic peaks of BiNCs and AB appear, suggesting the successful doping of BiNCs in the porous carbon matrix.

XPS was carried out to further analyze the element composition and valence electronic conurbation of the BiNCs@AB composite. In Figure 2B, the XPS survey spectrum demonstrates the presence of C, Bi, and O elements in the BiNCs@AB. The high-resolution C 1s spectrum of BiNCs@AB depicts four apparent peaks at 284.6, 286.0, 287.4, and 289.1 eV, corresponding to C−C, C−O, C=O, and O−C−
Figure 2. (A) XRD patterns of BiNCs, AB, and BiNCs@AB; (B) survey scan spectrum, high-resolution spectra of (C) C 1s and (D) Bi 4 f.

For the XPS spectra of Bi 4 f (Figure 2D), two distinct peaks appeared at 164.9 and 159.6 eV are associated with the binding energies of Bi 4 f5/2 and Bi 4 f7/2, respectively. The peak separation between the two peaks is 5.3 eV, indicating the chemical state of Bi 3+,23 which demonstrates that the surface of BiNCs is covered by an oxide layer. The absence of Bi2O3 reflections in the XRD patterns suggests that the Bi2O3 shell is amorphous, probably originating from the spontaneous surface passivation on contact with air.24

Figure 3 exhibits the Nyquist diagrams of different modified electrodes in a solution of 0.1 M KCl containing 5.0 mM Fe(CN)6 3−/4−. Inset in Figure 3: the corresponding equivalent Randles circuit. The Nyquist plots of different modified electrodes in 0.1 M KCl solution containing 1.0 mM [Fe(CN)6]3−/4−. Inset in Figure 3: the corresponding equivalent Randles circuit.

Fe(CN)6 3−/4−. A typical Nyquist plot consists of a semicircle at higher frequencies and a linear part at lower frequencies, which are related to the electron-transfer-limited and diffusion-limited process, respectively.25 The Randle equivalent circuit (the inset in Figure 3) was employed to fit the impedance data, where Rct and Rsh represent the solution resistance and charge transfer resistance, respectively. Cdl and Zw serve as the double layer capacitance and Warburg constant, respectively. Fitting results reveal that bare GCE displays an Rct value of about 506 Ω. By contrast, AB/GCE exhibits a low Rct value (158.8 Ω). This is because AB with excellent conductivity accelerates the electron transport of [Fe(CN)6]3−/4− on the electrode surface.27 However, the BiNCs@AB/GCE shows a higher Rct value (276 Ω), which is due to the fact that the introduction of BiNCs reduces the conductivity of the composite electrode.

Electrochemical Behaviors of the Modified GCEs. Electrochemical performances of bare GCE, AB/GCE, and BiNCs@AB/GCE were investigated by DPASV in HAc-NaAc buffer (0.1 M, pH 5.0) containing 100 ng L−1 Pb2+. As shown in Figure 4, bare GCE (curve a) presents a weak Pb2+ stripping peak at −0.54 V, while, at AB/GCE, an increased stripping peak for Pb2+ is observed at AB/GCE (curve b). The functional groups and porous structure of AB facilitate the preconcentration of Pb2+ on the electrode surface. Furthermore, a sharper peak with a remarkably increased current is achieved at BiNCs@AB/GCE (curve c), which is 3.0 and 1.5 times higher than those at bare GCE and AB/GCE, respectively. This is because BiNCs@AB produces a synergistic effect, demonstrating large specific surface area, abundant active sites, and high electrical conductivity, which are beneficial to the loading of Pb2+ and the electron transfer. In addition, BiNCs can form a “fusion alloy” with trace metal ions, further increasing the Pb2+ adsorption capability. In addition, it is worth noting that another anodic peak appears at around −0.17 V originating from the oxidation peak of BiNCs, which makes the construction of the ratiometric Pb2+ electrochemical sensor feasible.

Optimization of Experimental Conditions for Electrochemical Detection. To gain the best performance of the sensing platform, experimental parameters including the amount of modifier (different volumes of the homogenized 1 mg/mL BiNCs@AB suspension), pH, deposition potential, and deposition time were optimized. The influence of the amount of the BiNCs@AB suspension volume on the current ratio of Pb2+ and BiNCs (Ipb2+/IbiNCs) was investigated from 1.0 to 9.0 μL (Figure 5A). As shown, Ipb2+/IbiNCs increases as the modifier volume changes from 1.0 to 5.0 μL. The possible reason is that the content of BiNCs on the modified electrode is enhanced with the increase of the volume of modified materials, which is favorable for the adsorption of Pb2+.28 However, a decrease in Ipb2+/IbiNCs is noticed with a further increase in suspension volume. This might be because a high amount of BiNCs@AB on the electrode surface causes considerable resistance against electron transfer.
The concentrations of Pb²⁺ is found, which is expressed as concentrations of Pb²⁺ on the BiNCs@AB/GCE. The peak examined in the range of 180−290 s owing to the increasing amount of Pb²⁺ resulted from the saturation of Pb²⁺ at the BiNCs@AB/GCE surface.30 Considering the balance between the detection sensitivity and measurement efficiency, a deposition time of 270 s is applied in the study.

The effect of deposition time on stripping signal was examined in the range of 180−360 s (Figure 5C). As shown, a significantly enhanced trend of the deposition time is observed between 180 and 270 s owing to the increasing amount of Pb²⁺ accumulated on the surface of BiNCs@AB/GCE. Nevertheless, the deposition time of 270 s, which resulted from the saturation of Pb²⁺ at the BiNCs@AB/GCE surface,30 considering the balance between the detection sensitivity and measurement efficiency, a deposition time of 270 s is applied in the study.

The result of deposition potential optimization is shown in Figure 5D. When the deposition potential is shifted from −0.3 to −0.7 V, the deposition potential of Pb²⁺/BiNCs increases remarkably with the complete reduction of Pb²⁺. However, with the continuous negative shift of deposition potential (−0.7 to −1.0 V), the deposition potential of Pb²⁺/BiNCs increases slowly and even decreases, which is caused by the increase of hydrogen evolution interference.31 Thus, −0.7 V is selected for detection of Pb²⁺.

**Determination of Pb²⁺ at BiNCs@AB/GCE.** Under the optimized conditions, the superior properties of the as-prepared ratiometric electrochemical sensor were evaluated by DPASV. Figure 6A shows the DPASV responses of different concentrations of Pb²⁺ on the BiNCs@AB/GCE. The peak current of Pb²⁺ gradually increases with the increase of Pb²⁺ concentration, while the current intensity of BiNCs is nearly unchanged. Within the concentration range of 3.0 ng/L to 1.0 mg/L, an excellent linear relationship between Iₚb²⁺/BiNCs and the concentration of Pb²⁺ is found, which is expressed as

\[
I_{\text{Pb}^{2+}/\text{BiNCs}} (\mu A) = 0.0091 + 0.0015c (\mu g/L) (R^2 = 0.9917)
\]

Based on the equation of LOD = 3σ/q, the limit of detection (LOD) is estimated to be 1.0 ng/L, which is comparable to or even lower than those reported in other studies (Table 1). The porous structure and good electrical conductivity of AB and the highly close active sites provided by BiNCs make BiNCs@AB become an ideal material for constructing high-efficiency electrochemical sensors to detect Pb²⁺.

**Reproducibility, Repeatability, Stability, and Selectivity of the BiNCs@AB/GCE.** Five different BiNCs@AB electrodes were fabricated to monitor 100 μg/L Pb²⁺ with the same procedure to analyze the reproducibility of the sensor. As depicted in Figure 7A, the relative standard deviation (RSD) of Iₚb²⁺/BiNCs is 2.26%. In addition, the repeatability of BiNCs@AB/GCE was explored by using the same electrode toward the detection of 100 μg/L Pb²⁺ 15 times, and the corresponding RSD value is 3.90% (Figure 7B). These results confirm that the electrode has good reproducibility and repeatability.

The electrochemical sensor was stored at room temperature, and the electrode stability during storage was tested every other day. According to Figure 7C, even after the sensor was stored for 30 days, the deposition potential of Pb²⁺/BiNCs still retains 97.53% of the initial value, which suggests that BiNCs@AB/GCE has excellent storage stability.

To explore the selectivity of the BiNCs@AB/GCE, the DPV response of Pb²⁺ was measured in the presence of interfering substances and without interfering substances. Under the selected optimal experimental conditions, 50 fold concentrations of Hg²⁺, Na⁺, Zn²⁺, NO₃⁻, K⁺, Cl⁻, Al³⁺, Cu²⁺, SO₄²⁻, CO₃⁻, and Cd²⁺ were added into 0.1 M HAc-NaAc buffer containing 100 μg/L Pb²⁺. As presented in Figure 7D, the signal of Iₚb²⁺/BiNCs change does not exceed 5%, which demonstrates that the synthesized sensor has high selectivity for the determination of Pb²⁺.

**Table 1. Comparison of the Performance of the Present Sensor with the Reported Bi-Based Sensors for Pb²⁺ Determination**

| electrode material | measurement technique | linear range (μg L⁻¹) | LOD (μg L⁻¹) | reference |
|--------------------|------------------------|-----------------------|--------------|-----------|
| Bi/Au-GN-Cys/GCE   | SWASV                  | 0.50−40               | 0.05         | 32        |
| Hg-Bi-SWNTs/GCE    | ASV                    | 0.5−130               | 0.18         | 33        |
| BiNPs@Ti₃C₂Tₓ/GCE  | SWASV                  | 12.43−124.3           | 2.24         | 34        |
| Bi-BiOCl@C/GCE     | SWASV                  | 1−60                  | 0.2          | 35        |
| BiNCs@AB/GCE       | DPASV                  | 0.003−1000            | 0.001        | this work |

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Practical Feasibility. To further illustrate the potential application of the proposed ratiometric electrochemical sensor, DPASV technology was applied to detect the Pb²⁺ in real paddy water. The filtered water samples (by the 0.45 μm membrane) were diluted with a 0.1 M NaAc-HAc buffer (pH = 5.0). Prior to the addition of Pb²⁺, no obvious current signal is found in diluted paddy water samples, indicating that the concentration of Pb²⁺ in paddy water samples is less than 1.0 ng/L or there were no target heavy metal ions. A recovery test was performed by adding Pb²⁺ with the concentrations of 5.0, 50.0, and 100.0 ng/L to diluted water samples. As listed in Table 2, the detected values of Pb²⁺ are close to spiked ones, with recovery values of 99.75–101.6% and RSDs of 2.20–2.40%. These results show that this ratiometric strategy-based sensor can efficiently determine Pb²⁺ in actual water samples, showing admirable reliability and good practicability.

Table 2. Recoveries of Trace Pb²⁺ in the Local Paddy Water Sample (n = 3)

| sample          | added (μg·L⁻¹) | found (μg·L⁻¹) | RSD (%; n = 3) | recovery (%) |
|-----------------|----------------|---------------|----------------|--------------|
| paddy water     | 5              | 5.03 ± 0.12   | 2.4            | 100.7        |
|                 | 50             | 50.80 ± 1.15  | 2.27           | 101.6        |
|                 | 100            | 99.75 ± 2.20  | 2.27           | 99.75        |

In summary, a ratiometric electrochemical platform based on the BiNCs@AB-modified electrode was constructed for the analysis of Pb²⁺. For design of the sensing material, hierarchical porous AB was employed as the substrate material for in situ growth of BiNCs. The prepared BiNCs@AB composite possesses large active area, fast electron transfer ability, high mass transfer efficiency, and strong enrichment capacity for Pb²⁺. Additionally, the oxidation signal of BiNCs served as the internal reference, which greatly raises the reproducibility and reliability of the sensor. Benefiting from the synergy of BiNCs and AB, the proposed sensor exhibits excellent sensitivity, good selectivity, and high stability for the detection of Pb²⁺ and was successfully applied for monitoring Pb²⁺ in real water samples.

CONCLUSIONS

In summary, a ratiometric electrochemical platform based on the BiNCs@AB-modified electrode was constructed for the analysis of Pb²⁺. For design of the sensing material, hierarchical porous AB was employed as the substrate material for in situ growth of BiNCs. The prepared BiNCs@AB composite possesses large active area, fast electron transfer ability, high mass transfer efficiency, and strong enrichment capacity for Pb²⁺. Additionally, the oxidation signal of BiNCs served as the internal reference, which greatly raises the reproducibility and reliability of the sensor. Benefiting from the synergy of BiNCs and AB, the proposed sensor exhibits excellent sensitivity, good selectivity, and high stability for the detection of Pb²⁺ and was successfully applied for monitoring Pb²⁺ in real water samples.
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All authors have given approval to the final version of the manuscript.

Notes

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REFERENCES

(1) Kokab, T.; Shah, A.; Ifikhar, F. J.; Nisar, J.; Akhter, M. S.; Khan, S. B. Amino Acid-Fabricated Glassy Carbon Electrode for Efficient Simultaneous Sensing of Zinc(II), Cadmium(II), Copper(II), and Mercury(II) Ions. ACS Omega 2019, 4, 22057−22068.
(2) El-Shishtawy, R. M.; Al-Ghamdi, H. A.; Alam, M. M.; Alamshany, Z. M.; Asiria, A. M.; Rahman, M. M. Development of Cd²⁺ sensor based on BZNA/Nafion/Glassy carbon electrode by electrochemical approach. Chem. Eng. J. 2018, 352, 225−231.
(3) Jaiswal, A.; Ghosh, S. S.; Chattopadhyay, A. Quantum Dot Impregnated-Chitosan Film for Heavy Metal Ion Sensing and Removal. Langmuir 2012, 28, 15687−15696.
(4) Gao, W.; Nyein, H. Y. Y.; Shahpar, Z.; Fahad, H. M.; Chen, K.; Emaninejad, S.; Gao, Y. J.; Tai, L. C.; Ota, H.; Wu, E.; Bullock, J.; Zeng, Y. P.; Lien, D. H.; Javey, A. Wearable Microsensor Array for Multiplexed Heavy Metal Monitoring of Body Fluids. ACS Sens. 2016, 1, 866−874.
(5) Lee, M. H.; Wu, J. S.; Lee, J. W.; Jung, J. H.; Kim, J. High Y. Sensitive and Selective Chemosensor for Hg²⁺ Based on the Rhodamine Fluorophore. Organ. Lett. 2007, 9, 2501−2504.
(6) Makam, P.; Shilpa, R.; Kandjani, A. E.; Kandjani, A. E.; Periasamy, S. R.; Sabri, Y. M.; Madhu, C.; Bhargava, S. K.; Govindaraju, T. SERS and fluorescence-based ultrasensitive detection of mercury in water. Biosens. Bioelectron. 2018, 100, 556−564.
(7) Hira, S. A.; Nallal, M.; Park, K. H. Fabrication of PdAg nanoparticle infused metal-organic framework for electrochemical and solution-chemical reduction and detection of toxic 4-nitrophenol. Sens. Actuators, B 2019, 298, 126861−126872.
(8) Qiu, X. L.; Lu, L. M.; Leng, J.; Yu, Y. F.; Wang, W. M.; Jiang, M.; Bai, L. An enhanced electrochemical platform based on graphene oxide and multi-walled carbon nanotubes nanocomposite for sensitive determination of Sunset Yellow and Tartrazine. Food Chem. 2016, 190, 889−895.
(9) Luo, J.; Zhao, D.; Yang, M.; Qu, F. Porous Ni₃N nanosheet array as a catalyst for nonenzymatic amperometric determination of glucose. Microchim. Acta 2018, 185, 229−234.
(10) Yang, T.; Yu, R.; Yan, Y.; Zeng, H.; Luo, S.; Liu, N.; Morrin, A.; Luo, X.; Li, W. A review of ratiometric electrochemical sensors: From design schemes to future prospects. Sens. Actuators, B 2018, 274, 501−516.
(11) Wan, J.; Shen, Y.; Xu, L. Q.; Xu, R. X.; Zhang, J. F.; Sun, H. D.; Zhang, C. Y.; Yin, C. X.; Wang, X. X. Ferrocene-functionalized Ni(II)-based metal-organic framework as electrochemical sensing interface for ratiometric analysis of Cu²⁺, Pb²⁺ and Cd²⁺. J. Electroanal. Chem. 2021, 859, 115374−115383.
(12) Zhong, W.; Gao, F.; Zou, J.; Liu, S. W.; Li, M. F.; Gao, Y. S.; Yu, Y. F.; Wang, X. Q.; Lu, L. M. M. Xene@Ag-based ratiometric electrochemical sensing strategy for effective detection of carbendazim in vegetable samples. Food Chem. 2021, 360, 130006−130012.
(13) Cheng, H.; Wang, X.; Wei, H. Ratiometric electrochemical sensor for effective and reliable detection of ascorbic acid in living brains. Anal. Chem. 2015, 87, 8889−8895.
(14) Wang, L.; Gong, C. C.; Shen, Y.; Ye, W. H.; Xu, M. L.; Song, Y. H. A novel ratiometric electrochemical biosensor for sensitive detection of ascorbic acid. Sens. Actuators, B 2017, 242, 625−631.
(15) Wang, X. X.; Qi, Y. X.; Shen, Y.; Yuan, Y.; Zhang, L. D.; Zhang, C. Y.; Sun, Y. H. A ratiometric electrochemical sensor for simultaneous detection of multiple heavy metal ions based on ferrocene-functionalized metal-organic framework. Sens. Actuators, B 2020, 310, 127756−127768.
(16) Cui, L.; Wu, J.; Ju, H. X. Synthesis of bismuth-nanoparticle-enriched nanoporous carbon on graphene for efficient electrochemical analysis of heavy-metal ions. Chem. − Eur. J. 2015, 21, 11525−11530.
(17) Gholivand, M. B.; Solgi, M. Sensitive warfarin sensor based on cobalt oxide nanoparticles electrodeposited at multi-walled carbon nanotubes modified glassy carbon electrode (CoxOy NPs/MWCNTs/GCE). Electrochim. Acta 2017, 246, 689–698.

(18) Shu, J.; Qin, Z. L.; Lv, S. Z.; Zhang, K. Y.; Tang, D. P. Plasmonic enhancement coupling with defect-engineered TiO2-x: a new mode for sensitive photoelectrochemical biosensing. Anal. Chem. 2018, 90, 2425–2429.

(19) Wang, J.; Kaskel, S. KOH activation of carbon-based materials for energy storage. J. Mater. Chem. 2012, 22, 32710.

(20) Gao, C.; Yu, X. Y.; Xu, R. X.; Liu, J. H.; Huang, X. J. ALOOH-reduced graphene oxide nanocomposites: one-pot hydrothermal synthesis and their enhanced electrochemical activity for heavy metal ions. ACS Appl. Mater. Interfaces 2012, 4, 4672–4682.

(21) Zhu, X. L.; Liu, B. C.; Li, L.; Wu, L. S.; Chen, S. J.; Huang, L.; Yang, J. K.; Liang, S.; Xiao, K. J.; Hu, J. P.; Hou, H. J. A micromilled microgrid sensor with delaminated MXene-bismuth nanocomposite assembly for simultaneous electrochemical detection of lead(II), cadmium(II) and zinc(II). Microchim. Acta 2019, 186, 776–783.

(22) Shi, S.; Li, Y.; Rong, X.; Wang, Y.; Ding, S. Facile fabrication of a novel 3D graphene framework/Bi nanoparticle film for ultrasensitive electrochemical assays of heavy metal ions. Anal. Chim. Acta 2017, 968, 21–29.

(23) Li, S. Z.; Yang, Y. Z.; Liu, L. J.; Zhao, Q. Electron transfer-induced catalytic enhancement over bismuth nanoparticles supported by N-doped graphene. Chem. Eng. J. 2018, 334, 1691–1698.

(24) Gich, M.; Fernández-Sánchez, C.; Cotet, L. C.; Niu, P. F.; Roig, A. Facile synthesis of porous bismuth-carbon nanocomposites for the sensitive detection of heavy metals. J. Mater. Chem. A 2013, 1, 11410–11418.

(25) Sultan, S.; Shah, A.; Khan, B.; Qureshi, R.; Mutawah, J. I. A.; Shah, M. R.; Shah, A. H. Simultaneous Ultrasensitive Detection of Toxic Heavy Metal Ions Using bis(imidazo [4,5-f][1,10]-phenanthroline) Appended bis-triazolo Calix[4] Arene (8)/Glassy Carbon Electrode. J. Electrochem. Soc. 2019, 166, B1719–B1726.

(26) Peerthika, M.; Sundaramoorthy, A. K. Humic acid/halloysite nanotube/flavin adenine dinucleotide nanocomposite based selective electrochemical biosensor for hydrogen peroxide. Appl. Surf. Sci. 2019, 488, 503–511.

(27) Wang, Q. Z.; Zhang Sun, H.; Zhao, Y. J.; Zhuang, Y. T.; Xu, Z. H.; Bu, T.; Li, R. X.; Wang, L. Macro-meso-microporous carbon composite derived from hydrophilic metal-organic framework as high-performance electrochemical sensor for neonicotinoid determination. J. Hazard. Mater. 2021, 411, 125122–125133.

(28) Huang, Z. H.; Zheng, X.; Lv, W.; Wang, M.; Yang, Q. H.; Kang, F. Adsorption of lead(II) ions from aqueous solution on low-temperature exfoliated graphene nanosheets. Langmuir 2011, 27, 7558–7562.

(29) Zhao, X. Y.; Bai, W. L.; Yan, Y. J.; Wang, Y. F.; Zhang, J. K. Core-Shell Self-Doped Polyaniline Coated Metal-Organic-Framework (SPAN@UIO-66-NH4) Screen Printed Electrochemical Sensor for Cd2+ Ions. J. Electrochem. Soc. 2019, 166, B873–B880.

(30) Gumpu, M. B.; Sethuraman, S.; Krishnan, U. M.; Rayappan, J. B. B. A review on detection of heavy metal ions in water-An electrochemical approach. Sens. Actuators, B 2015, 213, 515–533.

(31) Zhu, L.; Xu, L. L.; Huang, B. Z.; Jia, N. M.; Tao, L.; Yao, S. Z. Simultaneous determination of Cd(II) and Pb(II) using square wave anodic stripping voltammetry at a gold nanoparticle-graphene/cysteine composite modified bismuth film electrode. Electrochim. Acta 2014, 115, 471–477.

(32) Ou Yang, R. Z.; Zhu, Z. Q.; Tatum, C. E.; Chambers, J. Q.; Xu, Z. L. Simultaneous stripping detection of Zn(II), Cd(II) and Pb(II) using a bimetallic Hg-Bi/single-walled carbon nanotubes composite electrode. J. Electroanal. Chem. 2011, 656, 78–84.

(33) He, Y.; Ma, L.; Zhou, L. Y.; Liu, G. H.; Jiang, Y. J.; Gao, J. Preparation and Application of Bismuth/MXene Nano-Composite as Electrochemical Sensor for Heavy Metal Ions Detection. Nanomaterials 2020, 10, 866–876.