

Combination of Microporous Hollow Carbon Spheres and Nafion for the Individual Metal-free Stripping Detection of Pb²⁺ and Cd²⁺

Xiangheng NIU,^{*,**†} Hongwei ZHANG,^{***} Meihua YU,^{***} Hongli ZHAO,^{*} Minbo LAN,^{*,†} and Chengzhong YU^{***}

^{*}Shanghai Key Laboratory of Functional Materials Chemistry, East China University of Science and Technology, Shanghai 200237, China

^{**}Institute of Green Chemistry and Chemical Technology, School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, China

^{***}Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, Brisbane QLD 4072, Australia

Here, the combination of Nafion with microporous hollow carbon spheres (MHCS) is first proposed to fabricate a disposable metal-free electrode for heavy metal stripping sensing. The MHCS-Nafion composite film electrode is prepared by drop-casting a mixture of MHCS and Nafion onto the lab-made screen-printed carbon electrode (SPCE*). Results demonstrate that the interfusion of MHCS into Nafion offers enhanced performance for the electro-enrichment and stripping of lead and cadmium over the only Nafion film: 1) abundant MHCS immobilized on the electrode surface serve as effective nucleation sites for metal ion reduction; 2) the mixing of MHCS into Nafion enlarges the active surface of negative-charged Nafion for the electrostatic adsorption of metal cations. The proposed MHCS-Nafion/SPCE* provides linear responses for Pb²⁺ and Cd²⁺ in the range of 2 - 200 µg/L, with a detection limit of 1.37 and 1.63 µg/L, respectively. Practical applications of the sensor in water sample detection with good accuracy have also been confirmed.

Keywords Microporous hollow carbon spheres, Nafion, metal cations, electro-enrichment, stripping analysis

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Introduction

With the increasingly severe water, soil, agriculture, and food pollutions resulting from heavy metals and their harmfulness to living organisms, the sensing of these heavy metals with reliable results and convenient operations turns out to be of great significance.¹⁻⁴ Among all well-established methods for trace metal determination, including inductively coupled plasma-atomic emission spectrometry (ICP-AES), atomic absorption spectroscopy (AAS), and inductively coupled plasma-mass spectrometry (ICP-MS), electrochemical stripping analysis is always recognized as an efficient detection tool.⁵ Especially, the superiorities of miniaturized equipment, low cost, and test rapidity endow this approach with wide applications in in-field/on-site monitoring. Early stripping measurements of heavy metals are performed with mercury-based electrodes.⁶⁻⁸ Considering its hypertoxicity, replacing mercury with other "green" metals, such as gold,^{9,10} bismuth,¹¹⁻¹⁵ antimony,¹⁶⁻¹⁸ tin,¹⁹ and copper,²⁰ has been recommended for heavy metal sensing. In stripping analysis with metal electrodes as the sensing platform, high-concentration metal precursors (up to mg/L) are usually utilized for the *in-situ* preconcentration, and a post-

treatment is also required to clear off the metal residues. During these processes, secondary pollution from these metals possibly occurs. In this context, developing metal-free electrodes, instead of metal-based electrodes, seems to be more attractive, from the perspective of "green analysis", for the anodic stripping determination of trace heavy metal ions.

Carbon-based materials, especially porous carbon, are extensively used in the adsorption, separation and purification, catalysis, and energy-storage fields.²¹⁻²³ They can provide large specific surface area, excellent chemical and mechanical stabilities, and versatile structures with low production cost. With these properties, nanoscale carbon-based materials are also adopted as an active component for heavy metal sensing.²⁴ Up to date, multi-wall carbon nanotubes,²⁵⁻²⁷ graphene,^{28,29} carbon nanotube-graphene hybrids,³⁰ AIOOH-reduced graphene oxide,³¹ mesoporous carbon,³² SiC,³³ and nitrogen-doped porous carbon³⁴ have been reported for the stripping detection of heavy metal ions. In the present work, we introduced a new carbon-based material, microporous hollow carbon spheres (MHCS), to the stripping analysis application.

Nafion, a perfluorinated ion exchange polymer or ionomer, is commonly used as a binder to immobilize active materials onto electrode substrates. With the easy film-formation and its hydrophobic fluorocarbon network, the Nafion film is highly stable in aqueous solution both thermodynamically and chemically. In addition to the inert binder role, Nafion can act as an active material as well. The hydrophilic charged sulfonate

[†] To whom correspondence should be addressed.

E-mail: niuxiangheng@126.com (X. N.); minbolan@ecust.edu.cn (M. L.)

group in Nafion enables it to preconcentrate cations selectively *via* electrostatic interaction.³⁵⁻³⁷ Therefore, Nafion is also supposed to be in favor of the stripping sensing of heavy metal ions, in which it serves as not only an effective binder but also a beneficial active modifier.

With the above considerations, here we suggest a combination of Nafion with microporous hollow carbon spheres (MHCS) for the metal-free stripping determination of trace Pb²⁺ and Cd²⁺. A uniform mixture of MHCS and Nafion drop-cast on the home-made screen-printed carbon electrode (SPCE*) surface result in the disposable “green” sensing platform. The interdiffusion of MHCS into Nafion not only offers abundant sites for the nucleation of metal ion reduction within short time during preconcentration, but also increases the active area of the negative-charged Nafion film for electrostatic adsorption of metal cations. The two effects contribute to the much improved performance of MHCS-Nafion/SPCE* in the electro-enrichment and stripping of lead and cadmium over the only Nafion modified electrode, as demonstrated by the following results.

Experimental

Chemicals

Tetraethyl orthosilicate (TEOS), resorcinol, formalin (37 wt%), and Nafion® 117 solution (5%, v/v) were provided by Sigma-Aldrich; Pb and Cd standard solutions (1.000 mg/L) available from Shanghai Institute of Measurement and Testing Technology (SIMTT) were diluted into stock solutions with different concentrations; acetate buffer solutions with pH 4.5 were prepared with sodium acetate and acetic acid (Sinopharm Chemical Reagent Co., Ltd.); Other chemicals were of analytical grade and used without further purification; Ultrapure water (18.2 MΩ·cm) prepared by a laboratory water purification system (Shanghai Hitech Instruments Co.) was used in the whole study.

Synthesis of MHCS

MHCS were synthesized according to a previously reported method with slight modifications.³⁸ Firstly, a monodispersed SiO₂@resorcinol-formaldehyde (RF) composite was synthesized *via* a one-pot sol-gel process under alkaline conditions in an alcohol-water system. In detail, TEOS (2.8 mL), resorcinol (0.4 g), and formalin (0.56 mL) were added into a mixture composed of an ammonia aqueous solution (3.0 mL, 28 wt%), deionized water (10 mL), and ethanol (70 mL). After a vigorous stirring for 24 h, the product was collected by centrifugation and washing with ethanol three times and dried at 50°C overnight. Then, MHCS were obtained after carbonization of the collected product at 700°C under a N₂ atmosphere and the removal of silica templates by HF (5%, v/v) etching.

Fabrication of bare or modified electrodes

In the present study, the lab-made SPCE* with a working area of 0.126 cm² was used as a disposable electrode substrate for material modification, and its printing procedures had been described in our previous work.¹⁸ In order to enhance its electrical conductivity and electron transfer ability,³⁹ the newly-printed SPCE* was anodized in 0.5 M H₂SO₄ by cyclic voltammetry in 1.5 - 2.0 V *vs.* Ag/AgCl for 40 segments. For the fabrication of MHCS-Nafion/SPCE*, 5 mg of MHCS were first added into 5 mL of Nafion solution (0.2%, v/v, in ethanol) and treated ultrasonically for 30 min for sufficient dispersion; 10 μL of the MHCS-Nafion mixture was then drop-cast onto the SPCE* surface; after drying in air at room temperature, the

electrode was used for further characterization and electrochemical measurements. For a comparison, SPCE* modified with only Nafion (Nafion/SPCE*) was also fabricated in a similar way. The bare SPCE* without any modification was compared as well in this work. What should be noted here is that the SPCE* modified with MHCS only is not compared, because the synthesized carbon spheres can not be fixed firmly onto the electrode surface without other binders like Nafion. When the MHCS suspension was drop-cast onto the SPCE* surface and dried in air at room temperature, it was found that the carbon material easily fell off, which was not desired.

Characterization

The morphology and structure of the synthesized MHCS were investigated by a field emission scanning electron microscope (FESEM, 7800, JEOL) operated at 15 kV and a transmission electron microscope (TEM, 1010, JEOL) operated at 100 kV. Nitrogen adsorption/desorption isotherms were measured at 77 K using a Micromeritic ASAP TriStarII 3020 system, and the sample was degassed under a vacuum for 6 h at 180°C before analysis. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface area, the pore size distribution curve was derived from the adsorption branch of the isotherm using the Barrett-Joyner-Halanda (BJH) method, and the total pore volume was calculated from the amount adsorbed at a maximum relative pressure (P/P_0). The topography of Nafion/SPCE* and MHCS-Nafion/SPCE* was observed by a scanning electron microscope (SEM, S-3400, JEOL) operated at 15 kV. Inductively coupled plasma-mass spectrometry (ICP-MS) was performed on a NexIon 300× spectrometer (PerkinElmer, USA).

Electrochemical measurements

Unless otherwise stated, all electrochemical experiments were carried out on a CHI440A electrochemical workstation (CH Instruments Inc., USA) with a conventional three-electrode system composed of a bare or modified SPCE* as the working electrode, a platinum wire as the counter electrode, and a saturated Ag/AgCl electrode as the reference electrode. All potentials reported here were referred to the saturated Ag/AgCl electrode. Square-wave anodic stripping voltammetry (SWASV) was employed for the determination of Pb and Cd, with 0.1 M acetate buffer (pH 4.5) as the supporting electrolyte, a frequency of 5 Hz, an amplitude of 25 mV, and an increment potential of 1 mV.

Results and Discussion

First, the synthesized MHCS were characterized by FESEM, TEM, and nitrogen adsorption-desorption isotherms. As shown in Fig. 1(a), the FESEM image suggests that the collected MHCS had a uniform particle size of ~200 nm. A FESEM image with a higher magnification reveals a slightly rough surface of MHCS (b). Based on the TEM observation, the prepared MHCS consist of a uniform carbon layer of around 12 nm and a hollow cavity of ~170 nm in diameter (c). Nitrogen adsorption-desorption isotherm analysis indicates that MHCS have a BET surface area of as high as 976 m²/g, with a pore volume of 1.7 cm³/g (d). The pore size distribution plot (inset of (d)) shows that the synthesized MHCS are microporous, with the pore size below 1 nm.

Considering the large surface area of MHCS and the negative-charged nature of Nafion, a combination of the two materials is proposed here for possible applications in the anodic stripping

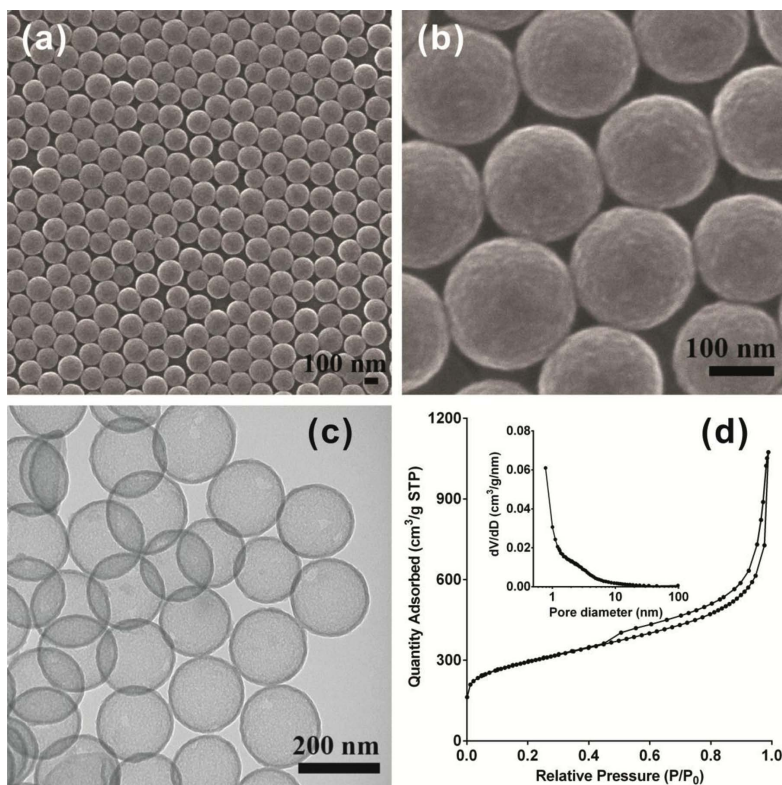


Fig. 1 (a, b) FESEM and (c) TEM images of the synthesized MHCS; (d) shows the nitrogen adsorption-desorption isotherms of MHCS, and the inset in (d) is the corresponding pore size distribution plot.

detection of metal ions. Figure 2 compares the surface topography of the fabricated Nafion/SPCE* (a) and MHCS-Nafion/SPCE* (b). After the drop-casting of Nafion solution, a relatively smooth film is formed, completely covering the SPCE* substrate surface (a). For MHCS-Nafion/SPCE*, spherical particles of MHCS can be seen on the electrode surface, demonstrating the stable immobilization of MHCS with the aid of Nafion as an effective binder. Besides, the participation of MHCS results in a rough electrode surface, as shown in (b).

Compared to the pure Nafion film with a smooth and dense structure, the dispersion of a large number of carbon nanoparticles in the MHCS-Nafion composite film leads to a loosely packed structure (the origin of surface roughness) and thus enhanced active surface area. To confirm this hypothesis, the electrochemical active areas of the proposed MHCS-Nafion/SPCE* and Nafion/SPCE* were compared. The effective surface area, A , of the modified electrode can be calculated by chronocoulometry in the ferricyanide system,⁴⁰ based on the following Anson equation⁴¹:

$$Q = Q_{dl} + Q_{ads} + 2nFAc(Dt/\pi)^{1/2}$$

where Q is the collected charge, Q_{dl} is the double layer charge that can be eliminated by background subtraction, Q_{ads} is the Faradaic charge, n is the transferred electron number, F is the Faraday constant, c is the electrolyte concentration, D is the diffusion coefficient, and t is the elapsed time. Figure S1(a) (Supporting Information) shows the $Q-t$ plots of the bare SPCE*, Nafion/SPCE*, and MHCS-Nafion/SPCE*. According to the slope of $Q-t^{1/2}$ (b), the A value of SPCE* is determined to be 0.689 cm². With respect to Nafion/SPCE*, its active surface

area decreases to 0.413 cm², due to the reduced intrinsic active sites of substrates covered by the thick Nafion film as well as the repulsion between the negative-charged Nafion and the [Fe(CN)₆]³⁻ anion. When the MHCS-Nafion composite is modified, it is found that the effective surface area rebounds to as large as 2.314 cm². Correspondingly, the electrode roughness, defined as the ratio of the effective surface area to the geometric area, decreases in the order of MHCS-Nafion/SPCE* > SPCE* > Nafion/SPCE*.

With the increased active surface area, the proposed MHCS-Nafion/SPCE* is expected to be in favor of the stripping sensing of heavy metals. This assumption is verified by the electro-enrichment and stripping measurements of Pb²⁺ and Cd²⁺. Here, Pb²⁺ and Cd²⁺ are selected as the typical heavy metal analytes because: 1) the two species are amongst the most common metal pollutants, and they widely exist in various environmental (ground water, soil, etc.), food (rice), agriculture (vegetable, fruit, etc.) and biological (blood) samples; 2) both of the metal ions can lead to serious harm to living organisms, and their upper limit in drinking water permitted by the World Health Organization (WHO) is very low (10 and 3 μg/L, respectively), and such that highly sensitive detection platforms should be established for the determination of the two heavy metal ions; 3) the stripping potential of the both species is in the potential window where water can not be decomposed, and this makes it possible to detect trace targets without other interferences. Figure 2(c) depicts the SWASV of the bare SPCE*, Nafion/SPCE*, and MHCS-Nafion/SPCE* in 0.1 M acetate buffer (pH 4.5) containing 100 μg/L Pb²⁺ and Cd²⁺. It is found that the SPCE* substrate exhibits no observable stripping response of the two targets. With the hydrophilic charged sulfonate group

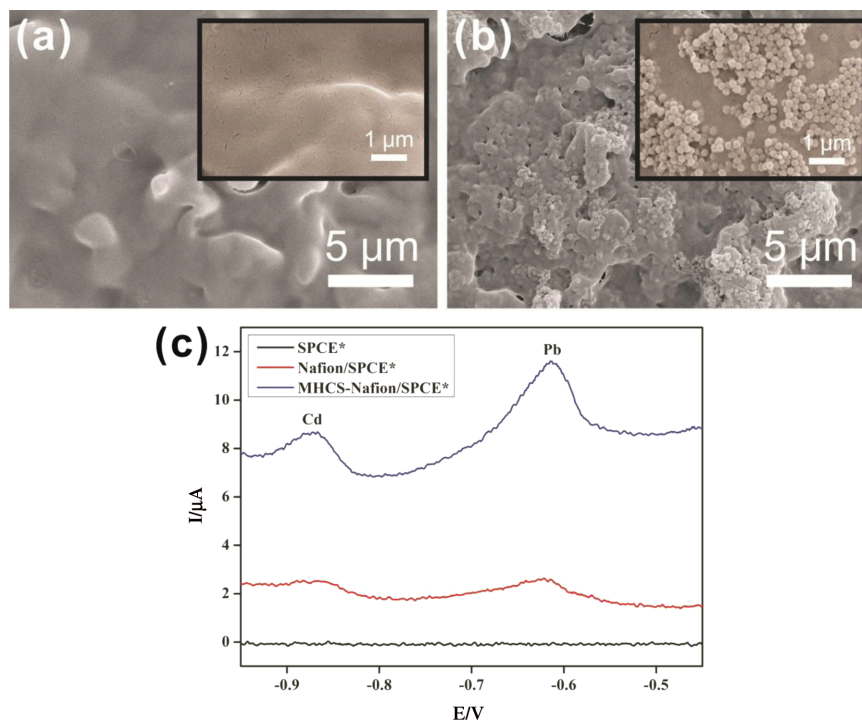


Fig. 2 SEM images of Nafion/SPCE* (a) and MHCS-Nafion/SPCE* (b). In this case, 10 μL Nafion or MHCS-Nafion solution was drop-cast on the anodized SPCE* surface, resulting in Nafion/SPCE* or MHCS-Nafion/SPCE*, respectively. (c) shows SWASV responses of the bare SPCE*, Nafion/SPCE*, and MHCS-Nafion/SPCE* in 0.1 M acetate buffer (pH 4.5) containing 100 $\mu\text{g/L}$ Pb^{2+} and Cd^{2+} . Preconcentration potential, -1.2 V vs. Ag/AgCl; preconcentration time, 120 s; stirring rate, 150 rpm; equilibration time, 10 s; initial potential, -0.95 V vs. Ag/AgCl; final potential, -0.45 V vs. Ag/AgCl.

that can enrich cations *via* the electrostatic interaction, the Nafion modified electrode provides two recognizable, but very weak, signals in the potential window: the peak located at ~ -0.86 V originates from Cd, and Pb contributes to the stripping response of -0.62 V. When the MHCS-Nafion composite is modified, much enhanced stripping signals of the two metals are observed. The peak current of Pb obtained on MHCS-Nafion/SPCE* (~ 3.7 μA) is over three-times that on Nafion/SPCE* (~ 1.0 μA), and the collected Cd response also increases to ~ 1.5 μA when MHCS are mixed into Nafion over the Nafion/SPCE* (~ 0.5 μA). These results demonstrate the improved properties of MHCS-Nafion/SPCE* for heavy metal (Pb and Cd) stripping detection.

The enhanced stripping response of heavy metals is usually considered originating from the favorable preconcentration process.⁵ In this context, the features of the bare SPCE*, Nafion/SPCE*, and MHCS-Nafion/SPCE* for 10 mg/L Pb^{2+} and Cd^{2+} electro-enrichment were probed. Figure S2 (Supporting Information) displays the chronoamperometric plots of the three electrodes in 0.1 M acetate buffer (pH 4.5) with/without 10 mg/L Pb^{2+} and Cd^{2+} . Obviously, the modified electrodes, especially MHCS-Nafion/SPCE*, show larger double layer background currents than the bare SPCE*. After the addition of targets into the buffer, an increase of the current response was observed on all electrodes, due to the participation of Pb^{2+} and Cd^{2+} electrochemical reduction. After background subtraction, the steady current signals of the three electrodes increase in the order of SPCE* < Nafion/SPCE* < MHCS-Nafion/SPCE*, as shown in Fig. 3(a). The enriched metal content was further determined by ICP-MS, as listed in Table S1 (Supporting Information). It was found that the ability for Pb and Cd

electro-enrichment also increases in the order of SPCE* < Nafion/SPCE* < MHCS-Nafion/SPCE*, in good agreement with Fig. 3(a).

The above results verify the improved properties of the MHCS-Nafion/SPCE* for both the stripping and preconcentration of heavy metals over the bare SPCE* and the only Nafion modified SPCE*. Similar phenomena have also been observed in carbon nanotube-Nafion,²⁶ ordered mesoporous carbon/Nafion (OMC/Nafion),³² Nafion-graphene,^{28,42} and carbon nanotube-graphene hybrid/Nafion.³⁰ This enhancement may originate from two contributions of MHCS. On the one hand, MHCS particles immobilized on the electrode surface by Nafion provide abundant effective nucleation sites for metal ion reduction, as illustrated in Fig. 3(b). As the metal nucleation and growth occur preferentially on top of already deposited nuclei,⁴³ these MHCS particles facilitate the preconcentration process of trace targets, as confirmed by Fig. 3(a) and Table S1 (Supporting Information). On the other hand, the mixing of MHCS into Nafion enlarges the active surface of Nafion, as verified by the effective surface area test. With larger active surface of Nafion, it turns to be easier for metal anions adsorbed onto the electrode surface for further preconcentration.

Next, the effect of various experimental parameters on the stripping response of Pb^{2+} was investigated. Figure S3 (Supporting Information) depicts the influence of the MHCS-Nafion volume on the stripping peak current of 100 $\mu\text{g/L}$ Pb^{2+} . Similar to the only Nafion modified electrode (Fig. S4, Supporting Information), a “volcano-type” variation of stripping responses upon the modifier loading has been observed. The stripping peak current gradually increases as increasing the MHCS-Nafion volume from 2 to 8 μL . A further increase of

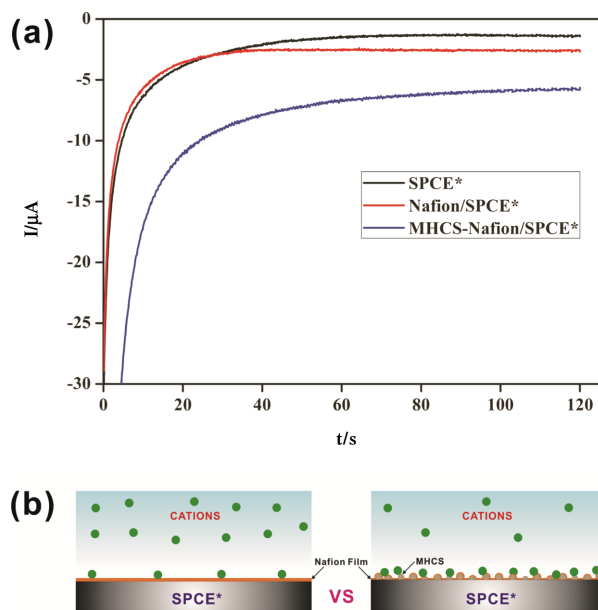


Fig. 3 (a) Chronoamperometric plots of the bare SPCE*, Nafion/SPCE*, and MHCS-Nafion/SPCE* in 0.1 M acetate buffer (pH 4.5) containing 10 mg/L Pb^{2+} and Cd^{2+} after background subtraction. Potential, -1.2 V vs. Ag/AgCl; stirring rate, 150 rpm. (b) shows the illustration of Nafion/SPCE* (left) and MHCS-Nafion/SPCE* (right) for the enrichment of metal anions.

the modifier volume leads to a thicker film, and the mass transport and electron transfer may be conversely reduced,²⁶ finally resulting in a peak-current decline. Thus, the optimized amount of MHCS-Nafion is chosen to be 8 μL . Figure S5 (Supporting Information) shows the influence of the preconcentration potential (a) and time (b) on the stripping response of 100 $\mu\text{g/L}$ Pb^{2+} in 0.1 M acetate buffer (pH 4.5). When the enrichment potential shifts negatively from -0.7 to -1.2 V vs. Ag/AgCl, the stripping peak current of Pb increases and arrives to a maximum of -1.0 V (a). With more negative deposition potentials, the competitive generation of hydrogen starts to occur, thus resulting in the decrease of the stripping peak signal. When the preconcentration time extends, an increase of the Pb stripping response is found, and a gradual saturation is obtained at a preconcentration time of 240 s (b). Therefore, -1.0 V vs. Ag/AgCl and 4 min are selected as the optimal enrichment potential and time, respectively.

Afterwards, the proposed MHCS-Nafion/SPCE* was applied to detect trace Pb^{2+} under the optimized conditions. Figure 4(a) displays the SWASV responses of Pb^{2+} with different concentrations. Obviously, the stripping signal of the target increases proportionally with the increasing Pb^{2+} content. The plot of peak current versus Pb^{2+} concentration, shown in the inset of Fig. 4(a), suggests a linear dependency in the content scope of 2 – 200 $\mu\text{g/L}$. The sensitivity is determined to be as high as 0.11 $\mu\text{A}/(\mu\text{g/L})$. According to the signal-to-noise of three ($S/N = 3$) rule, the limit of detection (LOD) is further calculated to be 1.37 $\mu\text{g/L}$, which is much lower than the limited value of 10 and 15 $\mu\text{g/L}$ in drinking water permitted by the WHO and the US Environmental Protection Agency (EPA), respectively. Compared to other modified electrodes summarized in Table S2 (Supporting Information), the proposed MHCS-Nafion/SPCE* exhibits comparable or even preferable linear range and LOD for Pb^{2+} stripping sensing.

Since a large number of studies are related to the individual or

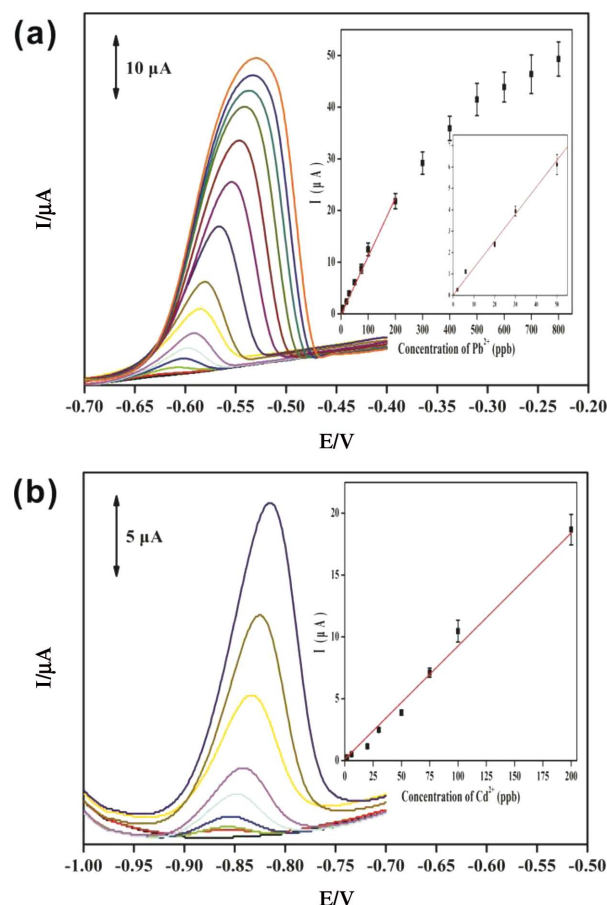


Fig. 4 (a) SWASV responses of Pb^{2+} with different concentrations obtained on the proposed MHCS-Nafion/SPCE*, and the inset shows the relationship between the peak current and the Pb^{2+} content. MHCS-Nafion volume, 8 μL ; preconcentration potential, -1.0 V vs. Ag/AgCl; preconcentration time, 240 s; stirring rate, 150 rpm; equilibration time, 10 s; initial potential, -0.7 V vs. Ag/AgCl; final potential, -0.4 V vs. Ag/AgCl. (b) shows SWASV responses of Cd^{2+} with different concentrations obtained on the proposed MHCS-Nafion/SPCE*, and the inset shows the relationship between the peak current and the Cd^{2+} content. MHCS-Nafion volume, 8 μL ; preconcentration potential, -1.0 V vs. Ag/AgCl; preconcentration time, 240 s; stirring rate, 150 rpm; equilibration time, 10 s; initial potential, -1.0 V vs. Ag/AgCl; final potential, -0.7 V vs. Ag/AgCl.

simultaneous detection of heavy metals, the present work has the following characteristics or superiorities: 1) different from the cases that Bi,^{11,44,45} Sb,¹⁶ or Au⁴⁶ is used as a sensing element, where second pollution from these metals may occur, the MHCS-Nafion/SPCE* avoids the utilization of any metal in stripping analysis, and is a real “green” tool for heavy metal ion detection; 2) with no metal as the sensing element, the proposed carbon-based electrode may expand the number of metals detected individually or simultaneously compared to metal-based sensors, because the background response of MHCS-Nafion/SPCE* is very weak, while metal-based electrodes will exhibit the stripping signal of the sensing element; 3) the analytical performance of the metal-free modified electrode, as demonstrated by the above results, is comparable to or even better in some cases than those metal-based electrodes, and this favorable property makes it possible to monitor trace heavy metal ions in real samples; 4) the SPCE* support, which is well known as a cheap and disposable test strip, is supposed to find

wide applications in the analysis of metals when cooperating with the carbon-based modifier, because the whole sensing component is environmentally-friendly and can be throw away after use; 5) and even compared to the amino-functionalized carbon microspheres as the sensing element,⁴⁷ the interfusion of Nafion into MHCS, on the one hand, may make it easier to immobilize MHCS onto the SPCE* surface stably, because Nafion can service as a good binder; on the other hand, the negative-charged Nafion will be beneficial for the adsorption and further enrichment of heavy metal ions, which has been demonstrated in favor of the stripping analysis.

What should be stated here is that the SPCE* used in the present work also has some advantages over other disposable electrodes like pencil graphite electrodes.⁴⁸ The thickness of active layers of SPCE* prepared in lab can be controlled more precisely *via* tailoring the thickness of templates. Besides, various modifications of SPCE* can be easily achieved by simple ink doping. For example, graphene can be doped into commercial inks to increase the electrical conductivity. These characters will make the fabricated MHCS-Nafion/SPCE* find wide applications in the stripping analysis of heavy metals. In this work, ten newly-fabricated MHCS-Nafion/SPCE* are used to evaluate the reproducibility, and the relative standard deviation (RSD) of the stripping peak current of 100 µg/L Pb²⁺ is determined to be 7.3%. This good repeatability reveals that the MHCS-Nafion composite film electrode is suitable for real sample analysis. In respect of detection selectivity, the effect of common metal ions (Na⁺, Mg²⁺, Zn²⁺, Co²⁺, Cu²⁺, Hg²⁺, Fe³⁺, and Al³⁺) and inorganic anions (Cl⁻, NO₃⁻, SO₄²⁻, and PO₄³⁻) at the same concentration on the stripping of 100 µg/L Pb²⁺ is investigated. As listed in Table S3 (Supporting Information), except Cu²⁺ and Hg²⁺, these ions have negligible influence, with deviations of <10%, on the stripping detection of Pb²⁺. With the presence of Hg²⁺, an amalgam consisting of mercury and lead is supposed to be formed, making the target being electrochemically reduced more easily.⁴⁹ Similar results are also observed in nitrogen-doped porous carbon used for the stripping analysis of Cd.³⁴ Conversely, the stripping response of Pb²⁺ is seriously diminished by Cu²⁺. Therefore, ferricyanide is suggested to be used to exclude Cu²⁺ before the stripping detection of Pb²⁺.³⁴

Finally, the practicability of the proposed MHCS-Nafion/SPCE* was demonstrated by sensing the Pb content in polluted river water collected from the Qingchun river in ECUST, with the ICP-MS test as a calibration method. The similar results determined by SWASV and ICP-MS, as listed in Table S4 (Supporting Information), indicate the good accuracy of the proposed MHCS-Nafion/SPCE* for the Pb stripping determination in real samples.

In addition to the sensing of Pb²⁺, the stripping analysis of another trace heavy metal ion, Cd²⁺, is also demonstrated. Figure 4(b) shows the SWASV profiles of Cd²⁺ with different content levels. It is observed that the stripping signal of the target increases proportionally with the increasing Cd²⁺ concentration. The plot of peak current *versus* Cd²⁺ concentration, shown in the inset of Fig. 4(b), suggests a linear dependency in the concentration range of 2 – 200 µg/L. According to the signal-to-noise of three (*S/N* = 3) rule, the LOD of Cd²⁺ detection is further calculated to be 1.63 µg/L, also lower than the limited value of 3 and 5 µg/L in drinking water permitted by the WHO and the EPA, respectively.

These above results confirm that the fabricated MHCS-Nafion/SPCE* can be used for the individual metal-free stripping detection of Pb²⁺ and Cd²⁺. As a matter of fact, the proposed metal-free modified electrode is considered to be capable of determining other heavy metal ions whose stripping signals are

located in the potential window where water is not decomposed, and such that heavy metal ions including common Cu²⁺, Hg²⁺, and Ni²⁺ may be sensitively detected with anodic stripping voltammetry.

Conclusions

The combination of Nafion with MHCS, a new microporous hollow carbon-based material, has been suggested for the stripping sensing of heavy metal ions. With the interfusion of MHCS, abundant nucleation sites provided by MHCS for metal ion reduction and enlarged effective surface of the Nafion film jointly contribute to the improved electro-enrichment of trace Pb²⁺ and Cd²⁺ on MHCS-Nafion/SPCE*, finally resulting in its much enhanced performance for stripping analysis. The proposed MHCS-Nafion/SPCE* exhibits high sensitivity and good accuracy for the sensing of Pb²⁺ and Cd²⁺ in a large linear content scope. These results reveal that the MHCS-Nafion composite, with metal free and low production cost, is a promising electrode modifier for the real “green analysis” and removal of heavy metals.

Acknowledgements

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Supporting Information

Figures S1 – S5 and Tables S1 – S4. This material is available free of charge on the Web at <http://www.jsac.or.jp/analsci/>.

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