

Detection of trace Cd^{2+} , Pb^{2+} and Cu^{2+} ions via porous activated carbon supported palladium nanoparticles modified electrodes using SWASV

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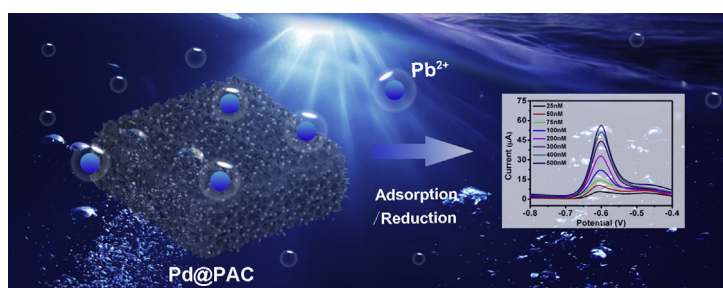
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HIGHLIGHTS

- Pd NPs decorated porous activated carbon materials (Pd@PAC) were synthesized.
- The PAC were derived from pomelo peels via a facile thermal reduction method.
- The Pd@PAC were utilized for the individual detection of heavy metal ions.
- The Pd@PAC were utilized for the simultaneous detection of heavy metal ions.
- The Pd@PAC/GCE exhibits high sensitivity and low detection limit.

GRAPHICAL ABSTRACT



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ABSTRACT

It is still of great challenge to develop green and efficient electrochemical sensors for detection of trace heavy metal ions. In this work, an efficient method was demonstrated for fabricating Palladium nanoparticles (Pd NPs) uniformly decorated porous activated carbon (PAC). The Pd NPs were *in-situ* reduced on PAC (Pd@PAC) via a KOH activation and thermal reduction method. The morphology investigation suggests that the Pd@PAC possess typical interconnected micropores and mesopores architecture with Pd NPs evenly dispersed on the surface of PAC. The Pd@PAC modified glassy carbon electrode (Pd@PAC/GCE) was used for the detection of trace Cd^{2+} , Pb^{2+} and Cu^{2+} ions by square wave anodic stripping voltammetry (SWASV). It exhibited excellent sensitive and selective detection of heavy metal ions simultaneously and individually, together with good anti-interference, reproducibility, repeatability and stability under the same experimental conditions. Moreover, the Pd@PAC/GCE was utilized to detect heavy metal ions in real sample species, indicating potential application in real environment detection. Porous structure and Pd NPs make Pd@PAC excellent electrochemical activity, its interconnected micropores and mesopores architecture accelerate the mass diffusion and facilitate the deposition-stripping process of heavy metal ions. Pd NPs provide more active sites and improved conductivity significantly. The present investigation provides a green and feasible method to assemble efficient electrochemical sensors and electrocatalytic devices.

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1. Introduction

Various heavy metals all have potential harm and toxic. Cadmium (Cd), lead (Pb) and copper (Cu) are widely distributed in the natural water environment, so they would threaten the life of people and ecosystem in high doses [1,2]. Generally, these elements both found II compounds in natural water that have enhanced toxicity and greater mobility [3]. The wide spread of these ions will affect human health and ecosystem stability, so the sensitive and selective detection of cadmium (Cd), lead (Pb) and copper (Cu) becomes more and more urgent and necessary [4]. As reported, various analytical methods have been adopted to detect trace metal ions, such as atomic fluorescence spectrometry (AFS), inductively coupled plasma mass spectrometry (ICP-MS), atomic absorption spectroscopy (AAS), X-ray fluorescence spectrometry (XRF) and square-wave anodic stripping voltammetry (SWASV). However, the applicability of most methods excepted SWASV is often limited by the achievable lowest concentration of measurements and the waste for time and researchers. So it is still a huge challenge about how to improve the selectivity and sensitivity of sensing ions by electrochemical method [5–10].

As one of electrochemical methods, SWASV is an emerging fast and sensitive measurement system for the detection of trace heavy metal ions. Compared with other methods, there are many advantages for SWASV, such as simple instrumentation, excellent sensitivity, low detection limit, high selectivity, short analysis time, and portability [11–14]. But above all, it offers the ability to analyze several trace metal ions simultaneously and select certain metals individually. This is mainly due to the fact that after a long period of pre-electrolysis, the test substance is enriched and concentrated [15]. In the research of electrochemical analytical systems for the trace metal ions detection, the working electrodes are often modified with suitable materials to achieve desired enhancements in sensitivity, selectivity, alternatively, reproducibility and stability [16]. So, the design fantasy electrode material is the most important step in SWASV method.

Over the decades, various materials have been explored, ranging from carbon materials as metal carriers to biological receptors such as DNA or proteins [17]. As electrode materials for SWASV, it needs to offer large specific surface area, fast electron transfer and mass transportation and provide countless active sites for nanoparticles (NPs) loading or deposition. It seems that carbon nanomaterials-based sensors would fit well with boosted electrocatalytic activity, such as carbon nanofibers, mesoporous carbon, carbon nanotubes and graphene [18–22]. Due to higher catalytic properties, some metal oxides have been widely applied in the heavy metal detection. Wei et al. reported SnO_2 /graphene nanocomposites can solve the aggregating problem when used in an electrochemical sensor for the simultaneous analysis of Cd^{2+} , Pb^{2+} , Cu^{2+} , and Hg^{2+} [23]. Zhang et al. prepared three different morphologies (nanoparticles, nanobowls and nanotubes) of MnO_2 , which were developed as sensing materials for the investigation of the mutual interference of Cd^{2+} , Pb^{2+} and Zn^{2+} [24]. Meanwhile, recent reports concluded that noble metal NPs modified carbon materials as electrochemical sensor can provide the obvious advantages for the individual and simultaneous detection of heavy metal ions, such as accelerating mass transfer, lower resistance and better electrical conductivity [25]. Kaur et al. fabricated Ag-Nano-ZSM-5-modified glassy carbon electrode and investigated as electrochemical sensors in the detection of toxic heavy metal ions (Cd^{2+} , Pb^{2+} , As^{3+} , and Hg^{2+}) [26]. In our previous work, we also developed Au NPs modified carbon nanofibers for high active electrochemical sensor and highly sensitive detector for trace Cd^{2+} , Pb^{2+} and Cu^{2+} ions using SWASV [27,28]. Recently, porous materials were developed and employed for the detection of trace metal ions [9]. Zhou et al. prepared the L-cysteine modified mesoporous MnFe_2O_4 nanocrystal clusters as a sensing material for electrochemical detection of Pb^{2+} , Hg^{2+} , Cu^{2+} and Cd^{2+} based on SWASV technique [29]. For sensor technologies by surface functionalization methods, it is well recognized that there are still some

troubles such as long accumulation time, complicated and harsh experimental conditions, expensive and scarce suitable organic precursors [30]. Pitchaimani et al. reported that Pd NP-embedded PAC nanocomposites for application as electrochemical sensors for detection of toxic Cd^{2+} , Pb^{2+} , Hg^{2+} , and Cu^{2+} ions using DPV. The results suggest that the method is efficient and, however, its detection limit was only 500 nM [31]. Therefore, it is necessary to develop a biomass-derived material with excellent sensitivity and low detection limits in detecting heavy metal ions.

As well known, bio-sources materials can be successfully converted into activated carbon by chemical activation method, physical activation method or template method [32–35]. Among them, chemical activation method is crucial for the formation of pore architectures to enhance the surface area of the electrode materials and then facilitate the electrochemical detection of heavy metal ions. Moreover, KOH activation is also efficient for generating micropores and mesopores into the framework of various carbon architectures [36]. In the present investigation, sustainable pomelo peels were employed to synthesis porous activated carbon (PAC) via a chemical activation method and a high temperature calcination process. Palladium NPs decorated PAC was prepared via one step thermal reduction method for the electrochemical detection of trace heavy metal ions using SWASV technique. Both the porous architecture and the homogeneously dispersion of Pd NPs on PAC assist in accumulating the target heavy metal ions and generating strong current response on the electrode surface. Pd@PAC/GCE could not only adsorb different heavy metal ions, but also ensure a fast and high sensitivity current response thanks to the high electron transfer speed between the electrode and solution. The present investigation provides a green and feasible method to prepare PAC with evenly dispersed metal NPs for electrochemical analysis and electrocatalytic applications.

2. Experiment

2.1. Preparation of Pd NPs embedded PAC (Pd@PAC)

PAC from the waste pomelo peels was synthesized by a KOH activation method as followed. First the pomelo peels were cut into small pieces and dried at 80 °C for 12 h. Then, soaked in 1 M KOH for 24 h and dried at 80 °C for 12 h. The dried pieces were carbonized in a tube furnace at 700 °C for 3 h with a heating rate of 5 °C min⁻¹ under an argon (Ar) atmosphere, following by washing with 1 M HCl and dried at 80 °C for 4 h and the KOH was successfully removed finally (Fig. S1). The resulting material was denoted as PAC in the subsequent discussions. Pd@PAC was prepared via a simple one step thermal reduction method. The PdCl_2 (5 mg) and PAC (100 mg) was dispersed in ethanol (5 mL), following by the 2 h ultrasonic to homogenize, then dried at 80 °C for 12 h. The dried ultrasound samples were carbonized in a tube furnace at 900 °C for 3 h with a heating rate of 5 °C min⁻¹ under an Ar atmosphere and then cooled down to room temperature to obtain Pd NPs decorated on the porous activated carbon. The load content of Pd NPs in the Pd@PAC is about 5.06 wt% (Fig. S3). And the detailed synthesis process of the Pd@PAC and the detection mechanism of trace metal ions are illustrated in Fig. S4.

2.2. Characterizations

The morphology of the Pd@PAC was characterized by field-emission scanning electron microscopy (JSM-6700 F, FESEM, JEOL, Japan) and field emission transmission electron microscopy (JSM-2100, TEM, JEOL, Japan). High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images and STEM mappings were acquired using a STEM (Tecnai G2 F30S-Twin, HAADF-STEM, Philips-FEI) at an acceleration voltage of 300 KV. X-ray diffraction (XRD) patterns of the Pd@PAC were acquired on a Bruker AXS D8 Advance with Cu K α radiation (wavelength of 1.5406 Å). X-ray photoelectron

spectroscopy (XPS) analyses of the samples were conducted on a Kratos Axis Ultra DLD with an Al (mono) K α source (1486.6 eV). Raman spectra was collected on a Thermo Fisher Scientific DXR laser Raman microscope with 532 nm laser lines under ambient conditions. The specific surface area was performed using the Brunauer-Emmett-Teller (BET, 3H-2000PSI) method.

2.3. Electrochemical characterizations

To remove the impurity on the surface of the bare glassy carbon electrode (GCE), the bare GCE was ultrasonically cleaned in ethanol and distilled water for 20 min and then polished carefully by using 0.5 nm alumina slurry. The polished GCE was washed with ethanol and distilled water for 5 min and then dried at room temperature. Then, 3 mg of Pd@PAC powder was dispersed in 1 mL of a solvent, composed of 3:1 (v/v) isopropanol/distilled water and 25 μ L Nafion solution. To create a homogeneous suspension, 1 mL of the solvent mixture was ultrasonically stirred for 30 min. Subsequently, 5 μ L of the homogeneous suspension was added onto the GCE surface and dried at room temperature. Hence, the modified electrode was composed of Pd@PAC/GCE. To facilitate comparison, other samples were prepared using the same process.

Electrochemical experiments were recorded using a CHI660E electrochemical workstation (Chenhua Instruments Co., Shanghai, China) with a standard three-electrode system. A bare GCE, or modified GCE served as a working electrode; a platinum net was used as a counter electrode and a saturated calomel electrode as a reference electrode. Cyclic voltammograms (CV) was carried out in a 5 mM K₃[Fe(CN)₆] solution with steps from -0.2 – 0.6 V vs SCE with the scanning rate of 100 mV s^{-1} . Square-wave anodic stripping voltammetry (SWASV) curves were deposited at the potential of -2.1 V for 210 s in 0.1 M NaAc-HAc (pH 4.8) buffer solution and performed in the potential range of -1.2 to 0.4 V at the following optimized parameters: the amplitude was 50 mV, the increment potential was 4 mV and the frequency was 15 Hz. All the experiments were conducted at room temperature in air atmosphere.

3. Results and discussion

3.1. Morphology of the Pd@PAC materials

From Fig. 1a it can be observed that the pomelo peels derived PAC exhibits typical honeycomb-like porous architecture structure. Moreover, the PAC has a typical three-dimensional interconnected structure and thin nanosheet (as shown in Fig. 1b), suggesting the large specific surface area and abundant porous structure. These networks were employed as a well-suited support frame and reaction vessel to load the Pd NPs [37]. Through the thermal reduction, the Pd NPs successfully loaded into PAC and well dispersed throughout the whole porous material (Fig. 1c). Compared with pure PAC, the Pd@PAC still has a typical 3D network structure and Pd NPs were uniformly immobilized on the surface of the PAC (Fig. 1d). Thus, it confirmed the successful synthesis of the Pd@PAC.

As shown in Fig. 2a, the TEM image further confirms the 3D interconnected porous structure and existence of Pd NPs on the PAC. It also can be observed that the Pd NPs uniformly dispersed on the PAC with the size distribution of approximately 20 nm–30 nm (Fig. 2b). The HRTEM image of Pd NPs displays the clear lattice fringes with an average value of 0.22 nm, which can demonstrate the crystalline nature of Pd crystal, corresponding to the Pd (111) crystal plane [38]. Fig. 2c shows the HAADF-STEM images of the Pd@PAC. All C, N and O signals were well distributed on the porous materials, and the Pd signals are mainly centered at the bright spots area and further indicate that formation of Pd NPs. Meanwhile the line-scan EDX spectra of all the elements in the selected region are shown in Fig. 2d. The C, N and O signals demonstrated the existence of these elements again, the Pd signals only have strong signals in the position of the bright spots particularly, which agree well with by the SEM and TEM observations. All above results indicate the successful synthesis of Pd@PAC materials.

Fig. 3a shows the X-ray diffraction (XRD) patterns of PAC and Pd@PAC materials. As shown in Fig. 3a, those materials both have a strong and a broad peak at around 23° , which is assigned to the graphitic carbon (002) plane. Owing to the high-temperature carbonization process, PAC exhibits a sharp peak at around 44° , corresponding to the (100) planes of graphitic carbon (Fig. 3a, black line, PDF#12-0212), which can demonstrate the high graphitization of the porous carbon materials after KOH activation. After a thermal-reduction process,

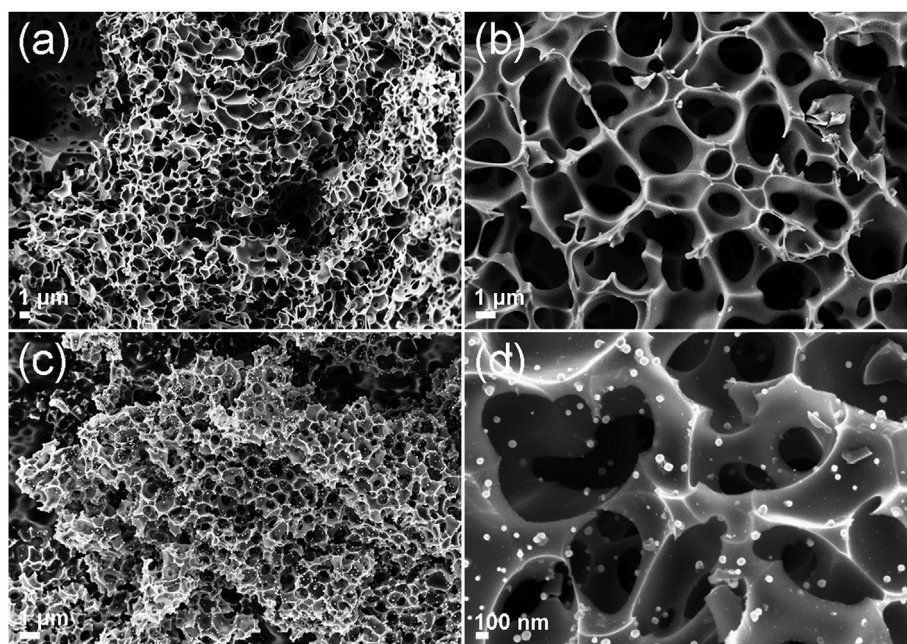


Fig. 1. SEM images of the PAC (a, b) and Pd@PAC (c, d).

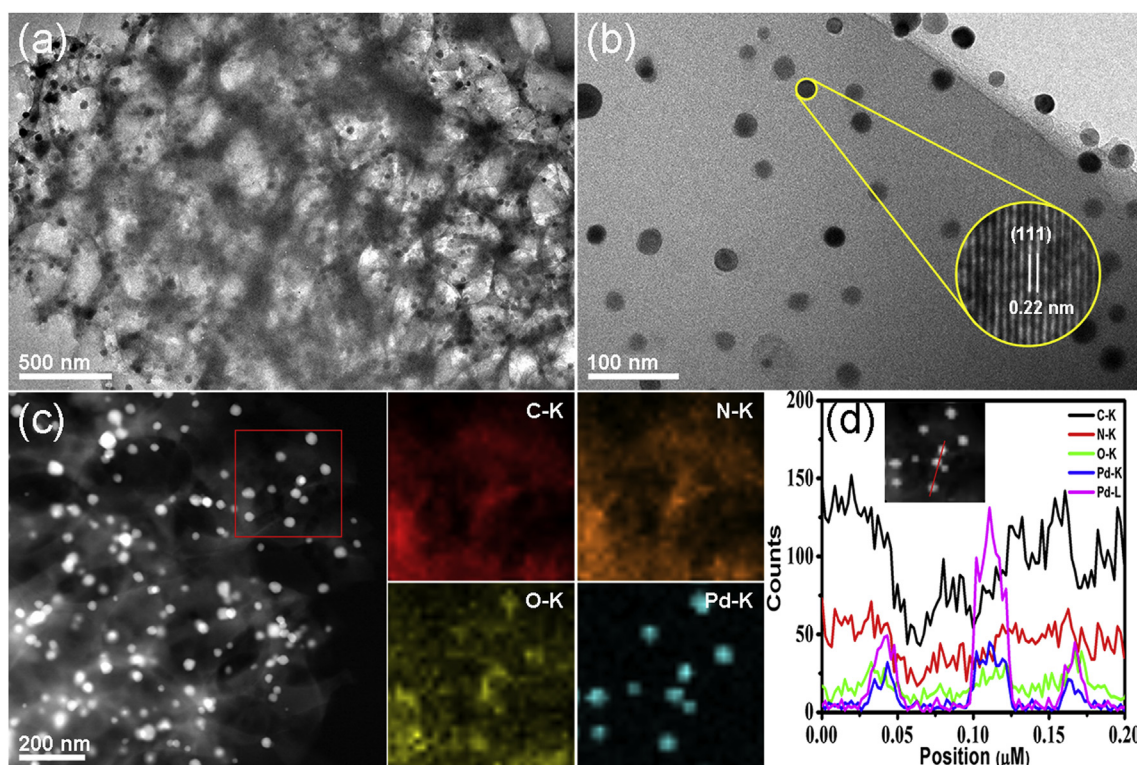


Fig. 2. TEM and HR-TEM images (a, b), the HAADF-STEM and corresponding elemental mapping images of C, N, O, and Pd (c) and the line-scan EDX spectra (d) of the Pd@PAC.

typical diffraction peaks at 40.1, 46.5, 67.9, 81.8 and 86.3° appeared, corresponding to (111), (200), (220), (311) and (222) planes of a face centered cubic (fcc) crystal of Pd NPs, respectively (Fig. 3a, red line, PDF#88-2355). Furthermore, the X-ray photoelectron spectroscopy (XPS) spectra of Pd@PAC are shown in Fig. 3b, which exhibited two characteristic signals for Pd. The shape peaks appeared at 334.65 and 340.1 eV, which are associated with the binding energies of Pd 3d_{3/2}

and Pd 3d_{5/2}, respectively. All the peaks of the Pd 3d are in accordance with the peaks of metallic Pd, namely the PdCl₂ was totally decomposed into Pd nanoparticles, which are a good correspondence with previous literature reports [39–41]. All those typical peaks demonstrated the formation of single crystal Pd NPs, which is beneficial to providing more active sites and responsible for high sensitivity and low detection limits. It is well known that Raman spectroscopy is one of the most

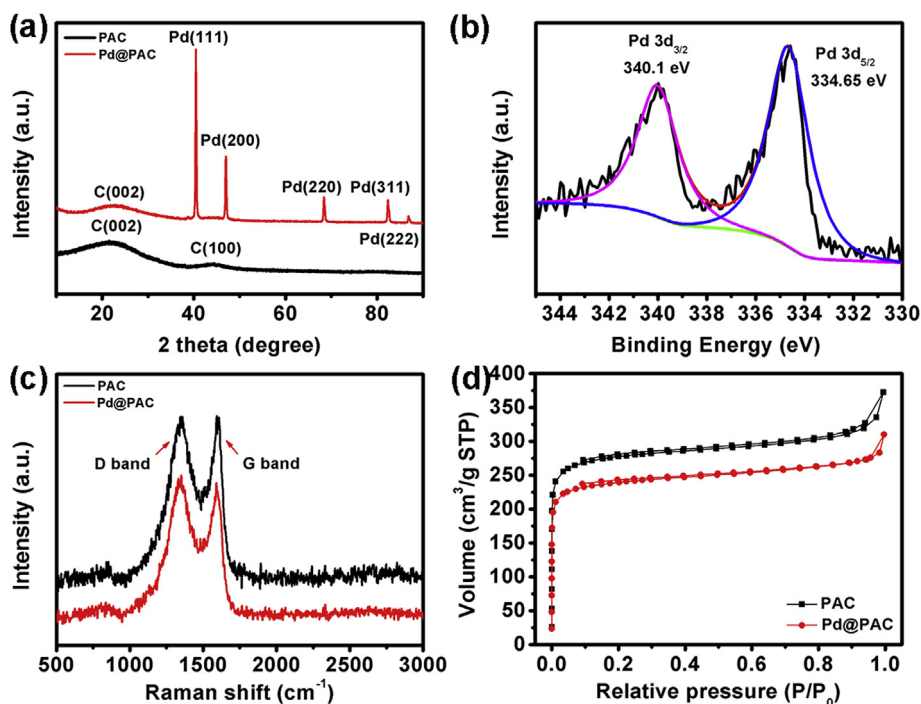


Fig. 3. The XRD patterns (a), XPS spectra (b), Raman spectra (c) and N₂ adsorption/desorption isotherms (d) of Pd@PAC and PAC.

effective ways to analyze and characterize regular and irregular carbon materials. As shown in Fig. 3c, both PAC and Pd@PAC have two noticeable peaks at 1348 and 1597 cm^{-1} , which was ascribed to D band (known as the disorder, defects or diamond band) and G band (known as the graphite or tangential band). These suggest that both PAC and Pd@PAC have high graphitization degree, which would facilitate the electron transfer during the electrochemical detection process. Fig. 3d shows the N_2 adsorption/desorption isotherms of the samples, in which the emblematic type IV isotherm and huge specific surface area (PAC: 953.38 $\text{m}^2 \text{g}^{-1}$ and Pd@PAC: 881.79 $\text{m}^2 \text{g}^{-1}$, respectively) both emerged. It can be observed that the PAC with Pd NPs loading still preserves the porous structure. The N_2 adsorption/desorption isotherm results suggest that KOH activation is an efficient method to produce porous architecture and increase the specific surface area (SSA) in the preparations of sustainable carbon materials.

3.2. Growth mechanism of Pd@PAC

PAC was prepared via KOH activation and high temperature carbonization using waste pomelo peels. KOH activation plays a key role in the formation of porous carbon. During the high temperature carbonization process, KOH reacts with the carbon groups in the flocculent layer of the pomelo peels to form a K_2CO_3 . Then the K_2CO_3 is decomposed to produce a large amount of CO_2 , which runs out to form a porous structure, and the carbon structure is partially graphitized [36]. PAC was chosen as a suitable carbon vessel due to its 3D network structure, high specific surface area and micro- and mesoporous structures, which contribute to the load of metal nanoparticles.

The prepared PAC and PdCl_2 were dispersed in an ethanol solution and dried in an oven to prepare Pd@PAC for *in-situ* thermal reduction methods. The SEM shows that there was no change in the porous structure between the PAC and Pd@PAC, so the formation of Pd NPs is fully dependent on the thermal carbonization process. We here argue that the formation of small and well-dispersed PdCl_2 in PAC is ascribed to the *in situ* nuclear and growth during the thermal carbonization synthesis. As the FTIR (Fig. S2) shown, PAC has O-H and C-O bands. C-O band would break easily and combine with hydrogen to form hydroxyl groups [42,43]. Pd^{2+} would chelate with the hydroxyl group and form Pd-OH chelates. Due to the chelation between Pd^{2+} and hydroxyl group, the nuclei are not easily touched or agglomerated [44,45]. Pd-OH chelate are thermal reduced to Pd NPs by carbon. Meanwhile, Pd^{2+} can catalyze carbon to reconstruct on the surface of Pd NPs to form a layer of amorphous carbon, which play a certain protective role on Pd NPs.

3.3. Electrochemical performance of the GCE, PAC/GCE and Pd@PAC/GCE

To explore the detection performance of Pd@PAC/GCE, we first investigated the electrochemical activity, using cyclic voltammetry in a 5 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ solution with steps from -0.2 – 0.6 V vs SCE with the scanning rate of 100 mV s^{-1} . As shown in Fig. 4a, all samples have

clearly redox peaks and huge anodic-cathodic peak current. As everyone knows, the metal NPs and electrical conductivity are the most critical factor affecting peak current. Compared with bare GCE and PAC/GCE, the cathodic peak current of Pd@PAC/GCE is supreme, which may offer prefer electrochemical detecting behavior. Fig. 4b displays the electrochemical detecting behavior of bare GCE, PAC/GCE, and Pd@PAC/GCE using SWASV in a solution containing 500 nM Pb^{2+} in 0.1 M acetate buffer solution under the optimized experimental conditions. The results indicate that the sensitivity for PAC/GCE is obviously higher in comparison with GCE, due to honeycomb-like porous structure is beneficial to the heavy ions adsorption as well as rapid diffusion, resulting in an improved detection performance. And the sensitivity for Pd@PAC/GCE is the highest in three GCE, thanks to Pd NPs played an important role in the testing process because of their excellent electrocatalytic activity, good intrinsic conductivity, and electronic property and robust sensitivity [46]. The promotion of electron transfer process and strong electrochemical response results in the large stripping peak current of Pd@PAC. Therefore, the combination of porous structure and Pd NPs will be a huge breakthrough.

3.4. Individual detection of the Pd@PAC/GCE

To further investigate the individual detection capability of a specific metal ion, we used the Pd@PAC/GCE to test Cd^{2+} , Pb^{2+} and Cu^{2+} ions under the previous experimental conditions, respectively. As shown in Fig. 5, the currents for Pd@PAC/GCE linearly increase with the continuous addition of specific metal ions solution in a concentration range from 25 to 500 nM and the lowest detectable concentration is 25 nM. The linear regression equation for Cd^{2+} , Pb^{2+} and Cu^{2+} ion detection is determined as y (μA) = 3.5892 + 0.1059x (nM), y (μA) = 6.0926 + 0.1130x (nM) and y (μA) = 16.1101 + 0.0817x (nM), respectively, with correlation coefficient of 0.9997, 0.9954 and 0.9967, respectively, the sensitivities of 0.1059 $\mu\text{A/nM}$, 0.1130 $\mu\text{A/nM}$ and 0.0807 $\mu\text{A/nM}$, respectively. The detection limit of Cd^{2+} , Pb^{2+} and Cu^{2+} ions are calculated by a 3 σ method [15], determined as 13.33 nM, 6.60 nM and 11.92 nM, respectively. Those results indicate the Pd@PAC can use SWASV to detect heavy metal ions successfully. The detection mechanism of trace metal ions is as follows, taking Pb^{2+} for example. Firstly, under stirring, the Pb^{2+} would move rapidly, would be deposited and absorbed on the surface of the Pd@PAC, gradually diffuse into the micro- and mesopores of PAC; stop stirring, at a constant negative potential, Pb^{2+} would be reduced to Pb. Because of Pd NPs, more Pb would accumulate on the surface of the material after a period of time; when the reverse scan potential from positive to negative, Pb would be oxidized to Pb^{2+} again eventually [47]. From the above analysis, we know the higher ion concentration in solution, the higher concentration on the GCE surface, the higher sensitivity in anodic stripping process, thus strengthening the stripping peak response. The Pd@PAC materials exhibit preferred detection sensitivity and low detection limit for separate detection of three ions. Because the well-dispersed Pd NPs not only could provide more active sites in the redox reaction but also can accelerate the electron transfer and improve

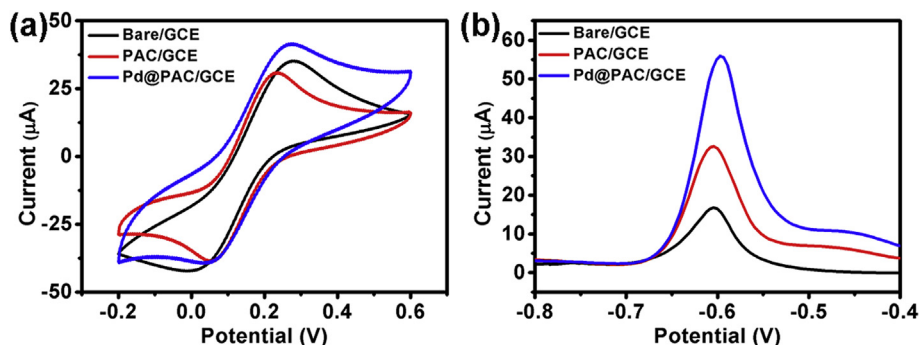


Fig. 4. (a) Cyclic voltammogram curves of the bare, PAC-modified and Pd@PAC-modified GCEs in a solution of 5 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$, with steps from -0.2 – 0.6 V vs SCE. (b) SWASV curves for 500 nM each of Cd^{2+} , Pb^{2+} and Cu^{2+} on the bare, PAC-modified and Pd@PAC-modified GCEs in 0.1 M acetate buffer solution (pH 4.8). Conditions: deposition potential: 2.1 V; deposition time: 210 s; room temperature; amplitude: 50 mV; increment potential: 4 mV; and frequency: 15 Hz.

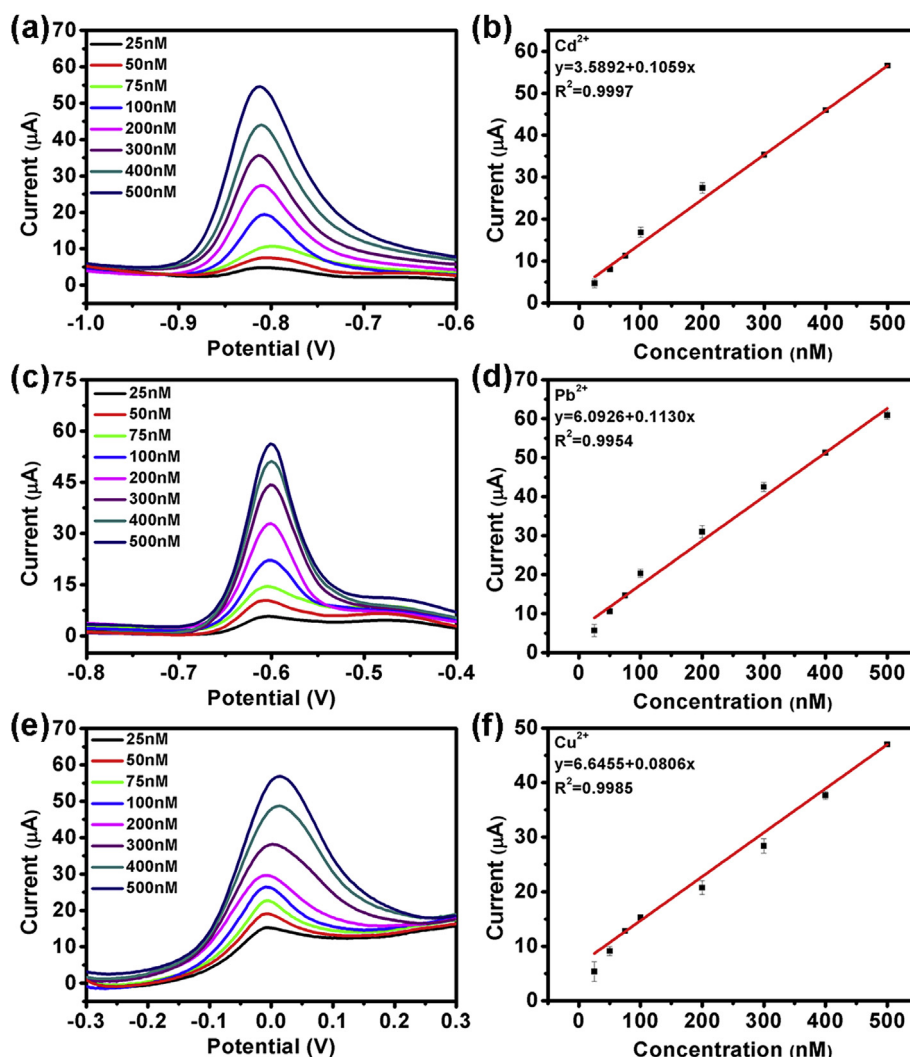


Fig. 5. SWASV curves and the corresponding calibration plots of the Pd@PAC/GCE for the individual analysis of Cd^{2+} (a,b), Pb^{2+} (c,d) and Cu^{2+} (e,f). The experimental conditions are the same as those listed in Fig. 4.

samples conductivity toward the reduction of heavy metal ions [48,49]. Furthermore, it is believed that the interconnected micro- and mesopores architecture could act as efficient ion-transfer channels, which can provide more active surface areas to accelerate mass diffusion and significantly facilitate the deposition-stripping process of detection.

3.5. Simultaneous detection of the Pd@PAC/GCE

It is well known that various heavy metal ions can coexist in the water environment. During the experiments, the interaction between different ions is also a meaning work. So the performance of the simultaneous detection of all metal ions under the presence experiment conditions was also examined (Fig. 6). Fig. 6a shows the SWASV response to metal ions over the metal ion concentration range from 25 to 500 nM in 0.1 M NaAc-HAc buffer solution. It can be observed that the stripping peak currents and the concentrations of metal ions increase synchronously. As one can see, specific peaks and clear stripping performance were observed for every individual trace metal ion when the three types of ions coexist. Furthermore, the peak current of Pb^{2+} is the highest, demonstrating the optimal sensitivity to Pb^{2+} in the simultaneous detecting environment. Meanwhile, it shows individual peaks located at approximately -0.8 , -0.6 and 0.0 V for Cd^{2+} , Pb^{2+} and Cu^{2+} , respectively. The corresponding calibration curves for Cd^{2+} , Pb^{2+} and Cu^{2+} were shown in Fig. 6 (b, c, d), with linearization

equations of y (μA) = $1.642 + 0.015x$ (nM), y (μA) = $2.2284 + 0.1048x$ (nM) and y (μA) = $3.365 + 0.058x$ (nM), with the sensitivities of 0.015, 0.1048 and 0.058 $\mu\text{A}/\text{nM}$, correlation coefficient of 0.9992, 0.9945 and 0.9893, respectively. Those results indicated that the individual or simultaneous detection of the three heavy metal ions all has strong current response, prominent sensitivity and well-separated stripping peaks, suggesting that it can be considered as the ideal sensor for detection. In the present investigations, the excellent electrochemical activity toward the detection of heavy metal ions of the Pd@PAC is attributed as follows: (i) the interconnected micropores and mesopores architecture in the PAC could act as efficient ion-transfer channels and provided more active surface areas. These can accelerate mass diffusion and significantly facilitate the deposition-stripping process of detection to guarantee the heavy ions adsorption as well as rapid diffusion; (ii) the well dispersed Pd NPs on the PAC could provide more active sites in the redox reaction and thus substantially increase the electrochemical activity; (iii) the Pd NPs decoration would significantly accelerate the electron transfer toward the reduction of heavy metal ions; (iv) the Pd NPs has excellent electrocatalytic activity, good intrinsic conductivity, and electronic property and robust sensitivity. This present investigation provides a green and feasible method to prepare porous activated carbon materials for electrochemical analysis and electrocatalytic applications.

To further evaluate the detection capability between the three ions,

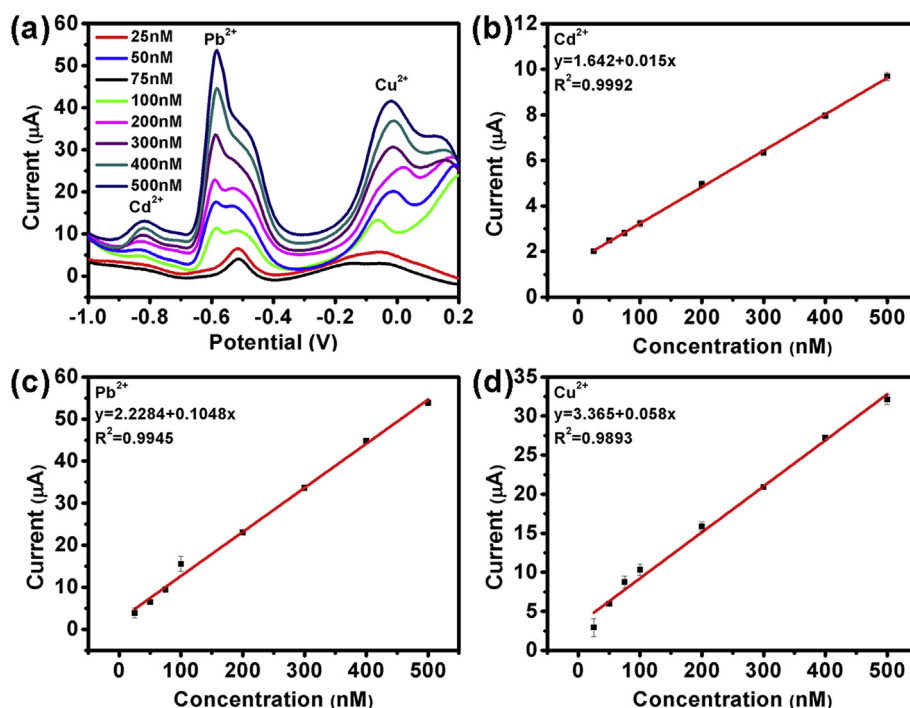


Fig. 6. SWASV curves (a) and the corresponding calibration plots of the Pd@PAC/GCE for the simultaneous analysis of Cd^{2+} (b), Pb^{2+} (c) and Cu^{2+} (d). The experimental conditions are the same as those listed in Fig. 4.

Table 1

Summary of individual and simultaneous detection of Cd^{2+} , Pb^{2+} and Cu^{2+} .

		Linearization equation y (μA) = $a + bx$ (nM)	Sensitivity ($\mu\text{A}/\text{nM}$)	Detection limit calculated (nM)	Coefficient of detection
Individual detection	Cd^{2+}	$y = 3.5892 + 0.1059x$	0.11	13.33	0.99
	Pb^{2+}	$y = 6.0926 + 0.1130x$	0.11	6.60	0.99
	Cu^{2+}	$y = 16.1101 + 0.0817x$	0.08	11.92	0.99
Simultaneous detection	Cd^{2+}	$y = 1.642 + 0.015x$	0.02	20.9	0.99
	Pb^{2+}	$y = 2.2284 + 0.1048x$	0.10	9.19	0.99
	Cu^{2+}	$y = 3.365 + 0.058x$	0.06	14.78	0.99

we summarized the linearization equations, sensitivities, detection limit and coefficients in the individual and simultaneous detection condition (Table 1). Compared with the simultaneous detections, it could be noticed that the sensitivities of Cd^{2+} , Pb^{2+} and Cu^{2+} are weakened in a specific metal ion. It is probably owed to that there is no competition of the limited activity sites on the surface of electrode for a specific ions. Although the properties of the sensitivity in the individual detection are not the best compared with those in the simultaneous detection, the detection limit are the optimum, which is feasibly attributed to the formation of intermetallic compound among the heavy metal ions. Furthermore, the detection level of the Pd@PAC was compared with other previously reported modified GCEs and summarized in Table S1. It can be indicated that Pd@PAC/GCE exhibit excellent performance in the detection of trace metal ions.

3.6. Reproducibility, repeatability and stability of the Pd@PAC/GCE

The reproducibility, repeatability and stability investigation of the Pd@PAC material is also a critical factor, which can measure the value of the sample and determine whether it can be used in actual water environment. Therefore, repetitive SWASV response for 500 nM Pd^{2+} in 0.1 M NaAc-HAc solution (pH 4.8) under the same condition is shown in Fig. 7a. The peak currents corresponding to the 20 repetitive electrodes show much lower volatility and higher reproducibility with RSD of only 1.21%. Meanwhile, the peak patterns of the same electrode (1st, 10th and 20th time) show complete consistency and perfect

repeatability (Fig. 7a). The operational stability of the electrode was estimated in the presence of 500 nM Pb^{2+} NaAc-HAc solution (pH 4.8) under the same condition for 7 days (Fig. 7b). The two curves around 7 days almost coincided and the peak currents are not significantly reduced, indicating long-time stability of the Pd@PAC/GCE. The above results all indicated that the samples have excellent reproducibility, repeatability and stability for detection of trace heavy ions. It would be applied to the practical application very well, and would be suitable as an electrochemical sensor.

3.7. Interference of the Pd@PAC/GCE

When multiple heavy metal ions co-existing, there is bound to be competition for the adsorption sites on the surface of the modified electrode. Therefore, the performance of the interference of the Pd@PAC/GCE in the detection of other metal ions under the presence experiment conditions was also examined (Fig. 8). Fig. 8a shows the SWASV responses obtained at Pd@PAC/GCE in the different concentrations of Cd^{2+} while keeping the concentrations of Pb^{2+} and Cu^{2+} constant at 500 nM. The peak currents of Cd^{2+} increases with the increase of detection concentration while the responses of the other two co-existing ions are practically unaltered. And no significant interference was observed in the detection of Cd^{2+} under the certain concentrations of Pb^{2+} and Cu^{2+} . Fig. 8c and e also prove that Pd@PAC/GCE has the same anti-interference property for the detection of Pb^{2+} and Cu^{2+} . The corresponding calibration curves for Cd^{2+} , Pb^{2+} and

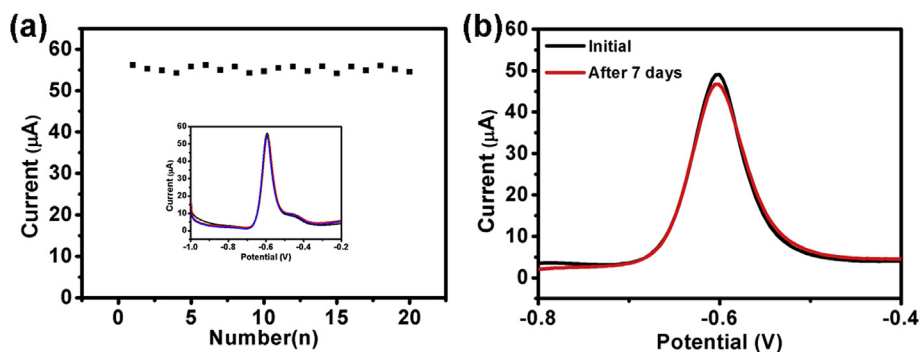


Fig. 7. (a) The reproducibility and repeatability study of the Pd@PAC/GCE in 0.1 M HAC-NaAc containing 500 nM Pb^{2+} . (b) SWASV curves for the simultaneous detection of Pb^{2+} in initial (black line) and after 7 days of storage (red line) at 500 nM. The experimental conditions are the same as those listed in Fig. 4. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Cu^{2+} were shown in Fig. 8 (b, d, f), with linearization equations of y (μA) = $27.9 + 0.036x$ (nM), y (μA) = $21.2 + 0.036x$ (nM) and y (μA) = $15.5 + 0.058x$ (nM), with the sensitivities of 0.036, 0.036 and 0.058 $\mu\text{A}/\text{nM}$, correlation coefficient of 0.9955, 0.9952 and 0.9963, respectively. Those sensitivities and correlation coefficient are slightly smaller than the value of the simultaneous detection. The decrease is might attributed to weaker competition between target ions. The above results all indicated that the samples have excellent anti-interference for detection of trace heavy ions.

3.8. Electrochemical performance in the realistic water of the Pd@PAC/GCE

The level of detection in the actual water environment is one of the vital indicators for evaluating excellent electrochemical sensors. To verify the detecting performance in the real detecting environment, the Pd@PAC/GCE was applied for the simultaneous detection of Cd^{2+} , Pb^{2+} and Cu^{2+} ions into a solution containing 0.1 M NaAc-HAc buffer solution and practical water (ratio 1:1) under the previous experimental conditions. As shown in Fig. 9a, the stripping peak potentials for simultaneous detections of Cd^{2+} , Pb^{2+} and Cu^{2+} ions are about -0.8 ,

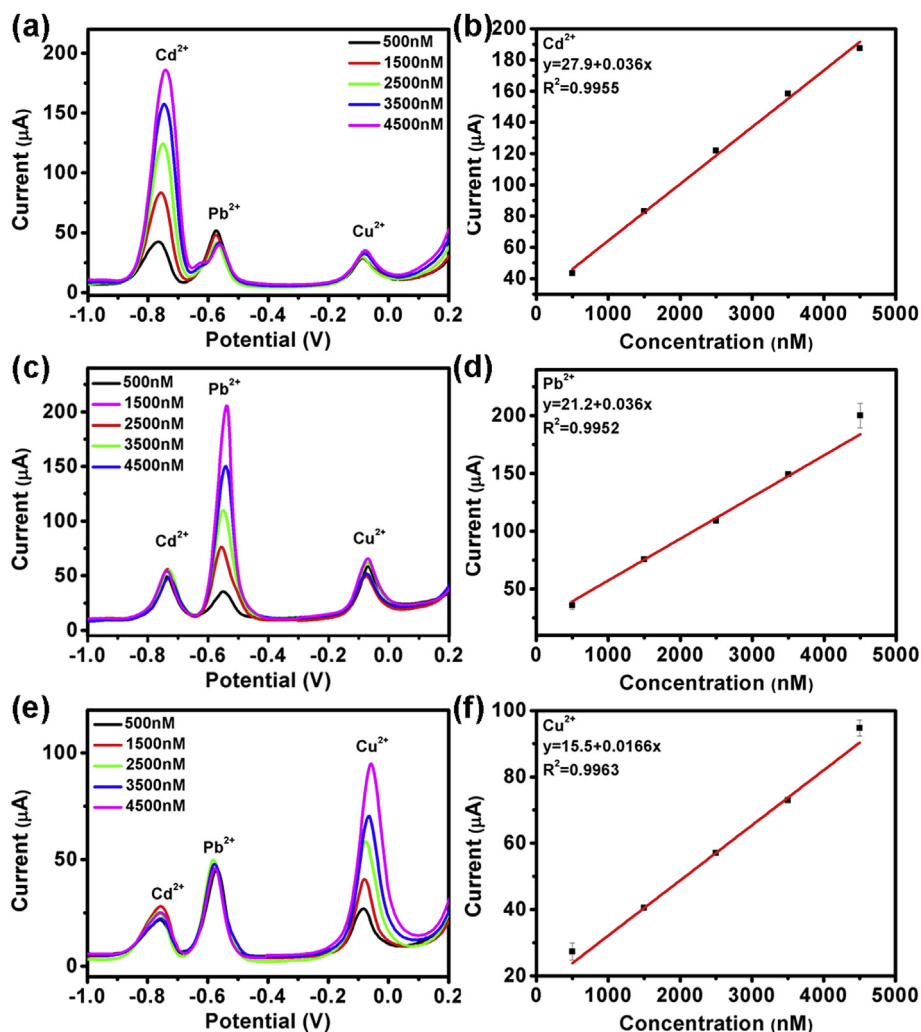


Fig. 8. Anti-interference experiment and the corresponding calibration plots of the Pd@PAC/GCE for Cd^{2+} (b), Pb^{2+} (c) and Cu^{2+} (d) detection. The experimental conditions are the same as those listed in Fig. 4.

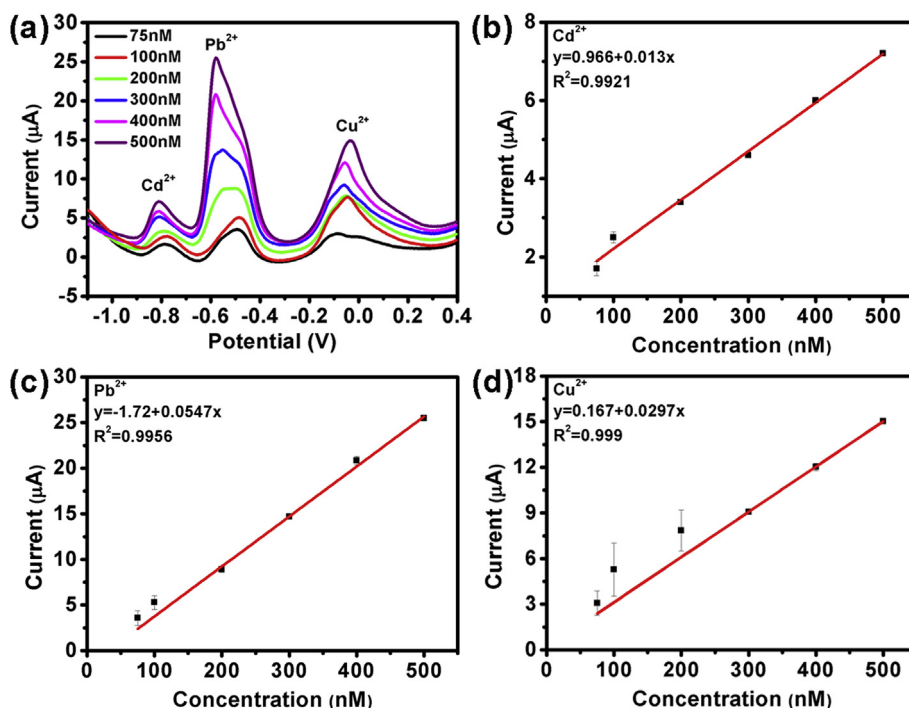


Fig. 9. SWASV curves of the Pd@PAC/GCE for the simultaneous analysis of Cd^{2+} , Pb^{2+} and Cu^{2+} into a real water sample diluted with 0.1 M HAC-NaAc solution (pH = 4.8) in a ratio of 1:1. The experimental conditions are the same as those listed in Fig. 4.

−0.6, and 0.0 V respectively. Moreover, the peak currents increase with the continuous increase of Cd^{2+} , Pb^{2+} and Cu^{2+} concentration and exhibit optimal selectivity toward Pb^{2+} , consisting with the results of previous detection. The corresponding calibration curves for Cd^{2+} , Pb^{2+} and Cu^{2+} were shown in Fig. 9 (b, c, d), with linearization equations of y (μA) = $0.966 + 0.013x$ (nM), y (μA) = $-1.72 + 0.0547x$ (nM) and y (μA) = $0.167 + 0.0297x$ (nM), with the sensitivities of 0.013, 0.0547 and 0.0297 $\mu\text{A}/\text{nM}$, correlation coefficient of 0.9921, 0.9956 and 0.999, respectively. The sensitivities and correlation coefficient are well maintained, which was good agreement among the obtained results. Those results all indicated the potential application in the real environment detection of the present Pd@PAC/GCE.

4. Conclusions

In summary, we demonstrated an efficient method to fabricate Pd NPs decorated PAC materials derived from pomelo peels via a KOH activation and thermal reduction method. The Pd NPs were *in-situ* reduced and evenly dispersed on the surface of the PAC with typical interconnected micropores and mesopores architecture. The as-synthesized Pd@PAC was applied as a sensing material for individual and simultaneous detections of Cd^{2+} , Pb^{2+} and Cu^{2+} and exhibits high sensitivity, low detection limit, good anti-interference, reproducibility, repeatability and stability. Moreover, the Pd@PAC/GCE was utilized to detect heavy metal ions in real sample species, indicating potential application in real environment detection. The excellent electrochemical activity of the Pd@PAC was ascribed to the interconnected micropores and mesopores architecture and Pd NPs. The porous structure accelerates the mass diffusion and facilitates the deposition-stripping process of heavy metal ions and the Pd NPs provide more active sites and have excellent conductivity. The present investigation provides a green and feasible method to synthesis PAC and assembles efficient electrochemical sensors and electrocatalytic devices.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matchemphys.2019.01.010>.

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