ORIGINAL RESEARCH



Kelp-Derived Activated Porous Carbon for the Detection of Heavy Metal Ions via Square Wave Anodic Stripping Voltammetry

Jibiao Guan¹ • Yini Fang¹ • Ting Zhang¹ • Lina Wang¹ • Han Zhu² • Mingliang Du² • Ming Zhang¹

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Abstract

Biomass-derived porous carbon materials with environmental adaptability and superior specific surface area have become one of the most promising materials in 21st era, especially in the electrochemical application. Herein, we proposed a kelp-derived carbon material (KPC) with a unique highly disordered graphite layer structure as an outstanding sensor via facile KOH activation method. The BET adsorption-desorption isotherm of KPC shows a typical IUPAC I type, and KPC possesses a high specific surface area with 2064 m² g⁻¹. Morphology observation and pore size analysis indicate that its porous-rich structure comprises countless micropores and mesopores. This unique structure of KPC not only provides massive active sites but exhibits high sensitivity in the detection of heavy metal by square wave anodic stripping voltammetry (SWASV), with Pb²⁺ at 53.4 μ A μ M⁻¹ and Cd²⁺ at 26.5 μ A μ M⁻¹ in simultaneous detection. This study reports a new strategy for the detection of heavy metal ions using porous metal-free carbon materials.

Keywords Kelp · Porous carbon · Heavy metal ions · Square wave anodic stripping voltammetry (SWASV)

Introduction

Heavy metal ions (HMIs) can cause serious damage to human beings due to their refractory degradation and high toxicity [1]. Besides, HMIs is hard to biodegraded by human body, and most of HMIs can even be enriched hundreds of times in food chain and accumulate within human inners eventually. HMIs interact strongly with proteins and enzymes [2], while as a result, functional groups becoming inactivated lead to irreparable damage, such as chronic poisoning [3].

Many spectrophotometric methods, for example, atomic absorption spectrometry (AAS), atomic fluorescence spectrometry (AFS), and inductively coupled plasma mass spectroscopy (ICP-MS), have been applied to detect trace amount of HMIs [4–9]. Although these methods are highly sensitive and accurate with low limits of detection, attendant problems such as high cost and tedious operation, still exist and hinder their application industrially. Another crucial that impeded their development is that these methods are not suitable for on-site and on-time detection, on account of elaborate procedure needed. Therefore, it is becoming increasingly urgent to develop new methods to ensure the sensitive, ecofriendly, and low-cost detection of HMIs. In order to achieve it, electrochemical techniques, especially anodic stripping voltammetry (ASV) determination, are emerging as a promising method to trace HMIs among various detection methods [10–14]. Compared with other spectrophotometric measurements, electrochemical techniques can offer low limits of detection, high sensitivity, while only need short analytical time and facile operation, which make electrochemical techniques suitable for the on-site and on-time detection of HMIs. In electrochemical techniques, electrode material plays a crucial role in the accurate and fast detection of HMIs.

So far, numerous electrode materials have been studied for detection of HMIs by SWASV. For example, Xu et al. used nanostructured magnesium silicate hollow spheres to monitor HMIs, offering sensitivity of 3.28 μ A μ M⁻¹ for Cd²⁺ and 6.25 μ A μ M⁻¹ for Pb²⁺ in simultaneous analysis [15]. 3D honeycomb-like bismuth nanoparticles-decorated N-doped carbon nanosheet frameworks were synthesized for the detection of Pb²⁺ and Cd²⁺ at a limit from 0.5 to 100 μ g L⁻¹ by Lu et al [16]. Dong et al. reported a 3D hierarchical porous wool-

Ming Zhang zhangming@zstu.edu.cn

¹ School of Materials Science and Engineering, Zhejiang Sci-Tech University, Hangzhou 310018, China

² School of Chemical and Material Engineering, Jiangnan University, Wuxi 214000, China

ball-like AlOOH with big accessible surface area and rich pores, and in order to achieve stronger conductivity, they deposited NiO NPs in the surface, which turning electrode out to be more electroactive with more favorable paths for targets transport [17]. These studies prove that porous materials are ideal material of electrodes in electrochemical detection of HMIs [18–20]. Owing to its high specific surface area, porous material provides more space for HMIs deposition. With the better conductivity of carbon-based porous materials, researchers recently are seeking more facile alternatives to produce electrochemical sensors for HMIs detection [21–25].

Nowadays, researchers are motivated to utilize ocean resources as raw materials to prepare it. For example, degradable fibers, a rich raw material in the ocean, are derived from chitin. In this work, kelp is used as the raw material to fabricate porous carbon material as electrode for the detection of HMIs (Scheme 1). As an abundant seaweed resource in the ocean, kelp has a certain porosity judging from volume change before and after water absorption [26–28]. KOH as a typical activating agent is introduced to kelp cell and prevent adjacent kelp cell wall aggregation during carbonation process [29]. Kelp-derived activated porosity has a high specific surface area up to 2064 m² g⁻¹. During the electrochemical detection of Pb²⁺ and Cd²⁺, the KPC-modified electrode shows high sensitivity and good linear relationship between concentration and current from 0.01 to 0.5 μ M.

Experimental

Reagents

The original kelp was bought from Qingdao Haihengda Commerce. Co., Ltd. (Qingdao, China). Potassium hydroxide (KOH) and hydrochloric acid were bought from Shanghai Reagents Company (Shanghai, China). Acetic acid sodium acetate buffer (NaAc-HAc, pH = 4.8) was bought from Xiamen Science and Technology Co., Ltd. Standard. (Xiamen, China). Pb(NO₃)₂, Cd(NO₃)₂, and K₃[Fe(CN)₆] were bought from Aladdin Industrial Corporation (Shanghai, China). Pb(NO₃)₂, Cd(NO₃)₂, and K₃[Fe(CN)₆] were dissolved in deionized water to prepare standard metal ion



solution (5.0 mmol/L), which were stored in refrigerator when not in use.

Apparatus

The morphology of KPC was obtained by the field emission scanning electron microscope (JSM-6700F, FESEM, JEOL, Japan) at an accelerating voltage of 3 kV and transmission electron microscopy (JSM-2100, TEM, JEOL, Japan) at an acceleration voltage of 200 kV. 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. XRD patterns of the samples were characterized with a Cu-Ka radiation ($\lambda = 0.1548$ nm), at scan rate of 5°/min in the 20 range of 10-80°. X-ray photoelectron spectra of all the samples were recorded on a Kratos Axis Ultra DLD with an aluminum (mono) K α source (1486.6 eV). The specific surface area was calculated using the Brunauer-Emmett-Teller (BET, 3H-2000PSI). The Raman spectra were measured by a micro-Raman system (Thermo Fisher Scientific DXR laser Raman microscope) operating with a 532-nm wavelength laser under ambient conditions.

Synthesis of KPC and Inactivated Kelp-Derived Carbon (UKC)

Two grams of kelp was dipped in 0.5 M KOH for 20 min. Then redundant solution on the surface of kelp with filter paper was removed and freeze-dried for 48 h. Then the samples were carbonized at 900 $^{\circ}$ C maintaining 3 h in tube furnace with heating rate at 5 $^{\circ}$ C min⁻¹ under Ar (99.999%) flow. After cooling to room temperature, the products were washed by HCl and water, then dried at 60 $^{\circ}$ C for 12 h in oven. The obtained product then was denoted as KPC. As contrast sample, outcomes without KOH activation were also prepared using the same process, named as UKC.

Electrodes Modification with KPC

The bare glassy carbon electrode (GCE), diameter of 3 mm, was polished using 0.3 μ m and 50 nm alumina power slurries



in order, then sonicated by water and absolute ethanol twice for 5 min to remove surface impurity. Three milligrams of KPC was dispersed in 1 mL mixed solvent, composed of 3:1 (v/v) isopropanol/distilled water, then the mix solution was sonicated for 30 min. Followed that, 25 μ L 5% Nafion was dropped into the suspension above and sonicated for 30 min. Finally, pipetting 5 μ L above suspension onto the surface of GCE, then drying it in the air for 24 h to obtain the KPC/GCE electrode. As control, the UKC/GCE electrode was prepared by the same process.

Electrochemical Characterizations

Electrochemical workstation (CHI600E, Chenhua Instrument Co, Shanghai, China) was used for all electrochemical measurements with a three-electrode system. In this three electrode system, Kelp/GCE (or UKC/GCE) was used as the working electrode, platinum net as the counter electrode, and calomel electrode with saturated KCl as the reference electrode. Cyclic voltammetry was performed in 5 mM K_3 [Fe(CN)₆] containing 0.1 M KCl at the potential range from – 0.2 to 0.6 V with scan rate at 0.1 V s⁻¹. SWASV was performed in electrolyte containing NaAc-HAc solution (pH = 4.8) with HMIs at different deposition potentials from – 0.8 to – 1.4 V and different deposition time from 30 to 360 s. In all SWASV tests, the amplitude and the frequency are 0.025 V and 25 Hz with an increment potential of 4 mV. All the quiet potential was at – 1.5 V, quiet time was at 180 s unless otherwise stated, and all electrochemical tests are performed at room temperature.

Results and Discussion

By activation of KOH, kelp-derived carbon got disordered porous carbon structure. Figure 1 a and b show images of kelp



Fig. 1 a Original dry kelp. b Kelp after dipped in deionized water. c SEM image of KPC. d–e HAADF-STEM and f–h STEM-EDS mapping images of KPC. i–l HRTEM images of KPC

before and after dipped in deionized water. As exhibited clearly, the size of kelp after dipped in deionized water expands to 3–5 times than that of original one. This sponge-like property makes it possible to be based biomaterials to fabricate porous carbon materials. In addition, ions like K⁺ and OH⁻ are easy to go inside the kelp cell, which effectively inhibit the aggregation among cell walls during the active process. Thus, intact porous-rich structure can be produced via carbonization method. Previous studies have pointed out that KOH can react with C to form K₂CO₃ during high-temperature carbonization process. After K₂CO₃ that is remaining in the material is washed away with acid and deionized water, abundant micropores and mesopores emerge [30]. In the present investigations, kelp was firstly activated by KOH and then carbonized. It is expected to obtain porous carbon materials with abundant pores and high specific surface area. The SEM image of KPC in Fig.

1(c) indicates that there are massive honeycomb structures in KPC, which are in accordance to our expectation. Figure 1 d reveals the TEM image of KPC, from which the hierarchical porous structure can be observed obviously. The mapping images of the KPC (Fig. 1e–f) also certify the uniform distribution of C, N, and O elements. And from the TEM images with different magnification (Fig. 1i–l), the highly disordered porous carbon structure can be further illustrated.

To further study the structural characteristics of both KPC and UKC, their XRD patterns were obtained, as shown in Fig. 2a. There were, both for KPC and UKC, two diffraction peaks at 24.3° and 43.1° corresponding to (002) and (100) planes of graphite carbon structure, respectively. Besides, the sharper peak of (100) plane in KPC, compared with that in UKC, demonstrated a higher graphitization of KPC after activation treatment. Figure 2 b shows the differences of the Raman

Fig. 2 a XRD patterns of KPC and UKC. b Raman spectra of KPC and UKC. c XPS survey spectra of KPC. d The highresolution C 1 s spectra of KPC. e N_2 adsorption/desorption isotherm of KPC and UKC. f The distribution curve of pore size calculated with the BJH method from the adsorption branch of the nitrogen sorption measurements



spectra obtained from two samples. The peaks at 1360 cm⁻¹ and 1595 cm⁻¹ are assigned to the D and G band of carbon substance, respectively. It is acknowledged that the D band is an indicator representing the disordered graphitized carbon structure, while the G band is corresponding to the sp² hybridized graphite carbon species. And the ratio between the intensity of the D to G band (I_D/I_G) indicates the degree of disorder in structures. In this work, the I_D/I_G of KPC and UKC were calculated to be 0.88 and 0.93, respectively, which reveals that the order degree of KPC decreases after being activated by KOH, while the level of disorder increases in accordance with the consequence in other studies of this work. This result is related to the coexistence of plentiful micropore and mesopore structures in the carbon material, which can be further explained from BET analysis. The XPS spectra of KPC in Fig. 2c indicates that the C and O are the main elements in the surface of KPC. Further analysis in C 1-s high-resolution spectrum can be seen that there are four major peaks at 284.4, 285.4, 286.5, and 289.1 eV, corresponding to C-C, C = C, O–C = O, and C = O, respectively.

In order to further study characteristics of porous structure and specific surface area, nitrogen sorption isotherms of KPC and UKC were obtained and the results are shown in Fig. 2e-f. The specific surface area of UKC was calculated to be only 295 m² g⁻¹ while the figure for KPC is up to 2064 m² g⁻¹, which is pretty higher than that of almost porous carbon materials previously reported in Table 1. The IUPAC IV type isotherm exhibited in UKC mainly comes from its original mesoporous structure. And the N2 adsorption-desorption curve of KPC shows the IUPAC I type isotherm, manifesting that there are numerous microporous and mesoporous structures in the KPC. Additionally, the BJH model was used to calculate the distribution of pore size, and the result in Fig. 2f illustrates that the pore size of UKC is mainly at 4 nm with an average pore diameter of 3.66 nm, meanwhile pore size of KPC is between 2 and 10 nm with an average pore diameter of 2.10 nm, which further demonstrates the coexistence of micro and mesopores. The large number of micropores and mesopores of 1-5 nm inside the material leads the reduction of

 Table 1
 Comparison of several different carbon sources-derived porous carbon

Carbon sources	$\begin{array}{c} S_{\rm BET} \\ (m^2 g^{-1}) \end{array}$	Average pore size (nm)	Pore volume $(cm^3 g^{-1})$	Ref
Corn husk	867	4.97	0.51	[20]
Rice straw	2399	1.78	1.59	[24]
Coconut shells	209	3.03	0.88	[26]
Water hyacinth	950.6	6.33	1.49	[28]
Fungus	1103	4	0.54	[<mark>30</mark>]
This work	2064	2.10	1.07	

the spacing between the pores of the carbon material. The molecular fragments, which are more favorable for the graphite layer structure, are randomly stacked together to form a disordered layer structure, which is consistent with the result obtained from Raman spectroscopy.

The electrochemical properties of KPC/GCE electrode were tested by cyclic voltammetry and electrochemical impedance spectra in 5 mM $[Fe(CN)_6]^{3-/4-}$ containing 0.1 M KCl. Figure 3 a shows that there was a separately pair of redox peaks for the GCE, Nafion, UKC/GCE, and KPC/GCE electrodes, while the redox peaks for the KPC/GCE electrode are more significant than others, which indicated good charge transfer kinetics evaluated with ferricyanide/ferrocyanide redox. This is caused by abundant porous structures in KPC, which gives faster electron transfer rate in the surface of the electrode. The following HMIs tests further proved that abundant porous structures in KPC also enhanced HMIs redox in SWASV tests. The electrochemical impedance spectra of four electrodes were tested, shown in Fig. 3b. Compared with larger resistance of bare GCE, when modified with KPC, the resistance is much smaller. It demonstrates that KPC/GCE has a better electrical conductivity and gives less resistance during electron transfer process. Double-layer capacitance is related to effective surface area. The bigger double-layer capacitance of KPC/GCE could indicate a relatively higher effective surface area. By CV tests of different scan rate, the double-layer capacitance was calculated to be 0.28, 0.036, 0.55, and 3.13 mF cm^{-2} for GCE, Nafion, UKC/GCE, and KPC/GCE, respectively. Compared with UKC/GCE, the double-layer capacitance of KPC/GCE was about 5-7 times greater than that of UKC/GCE, indicating that KPC/GCE have bigger electrode effective surface area and could further enhanced the detection sensitivity. The results of electrochemical test by SWASV in NaAc-HAc containing 0.5 µM Cd²⁺ and Pb^{2+} with deposition potential at -1.1 V and deposition time at 180 s are shown in Fig. 3c. For different electrodes, the response peaks for Cd²⁺ and Pb²⁺ also appeared at different potentials. And the KPC/GCE electrode exhibits the best discrimination that response peaks of Cd²⁺ and Pb²⁺, emerging at around - 0.82 V and - 0.55 V, respectively. Because the porous structure in KPC gives the way to enhance electrochemical reaction, the peak currents of Cd²⁺ and Pb²⁺ in the KPC/ GCE electrode significantly increase, compared with the weaker peak currents in other electrodes.

Deposition potential and deposition time also make enormous difference in the electrochemical test of SWASV. Therefore, we further explored the optimal experimental conditions for the detection ability of KPC/GCE electrode. The most effective deposition potential and deposition time of Cd^{2+} and Pb^{2+} are determined by changing the deposition potential or deposition time while detecting Cd^{2+} and Pb^{2+} under the same conditions. As shown in Fig. 4a, as the voltage gradually decreases, the peak current increases firstly and then Fig. 3 Cyclic voltammetry (a) and electrochemical impedance spectra (b) of bare GCE, Nafion, UKC/GCE, and KPC/GCE in 5 mM [Fe(CN)₆]^{3-/4-} containing 0.1 M KCl. c Double-layer capacitance derived from CVs of different scan rate. d SWASV of bare GCE, Nafion, UKC/GCE, and KPC/GCE at 0.5 μ M Cd²⁺ and Pb²⁺



decreases, with a maximum peak current appearing at -1.1 V. When the deposition potential overtops -1.1 V, the decrease of peak current is mainly due to the interference by the generation of H₂ through water splitting. H₂ bubbles occupy the active sites which are initially for Cd and Pb ions, resulting in the decrease in peak currents of Cd²⁺ and Pb²⁺. Therefore, -1.1 V is optimal deposition potential in this work. The effect of deposition time on the current response was demonstrated in Fig. 4b. With time increasing, the peak currents of Cd²⁺ and Pb²⁺ rise gradually, when deposition time reaches at 180 s, the values peak at maximum and then decrease. In the further increase in deposition time, the decreasing peak currents may be since the active sites of KPC were saturated. As a result, 180 s is the optimum deposition time. Simultaneous detection with different concentrations of Cd²⁺ and Pb²⁺ was carried out under the optimal experimental parameters. Figure 4 a shows electrochemical response from 0.010 to 0.5 μ M Cd²⁺ and Pb²⁺ by SWASV, which indicated that as the concentration increases, the peak current rise simultaneously. The linear fit between the peak current and the concentration of Cd²⁺, Pb²⁺in Fig. 4b manifests a good linear relationship between the concentration and the peak current, with linear correlation equations of $Y(Pb^{2+}) = 53.4c + 5.47$ ($R^2 = 0.995$) and $Y(Cd^{2+}) = 26.5c + 3.71$ ($R^2 = 0.997$), while "Y" representing the peak current and "c" presenting the concentration. For Cd²⁺ and Pb²⁺, the sensitivities are 53.4 μ A μ M⁻¹ and 26.5 μ A μ M⁻¹, respectively. The limit of detection (S/N = 3) were calculated to be 11.38 nM and 23.3 nM for Pb²⁺ and Cd²⁺, respectively.

Fig. 4 Influence of a deposition potential and b deposition time at 1 μ M Cd²⁺ and Pb²⁺ at peak currents



Fig. 5 a SWASV responses of KPC/GCE in HAce-NaAc solution containing 0.010–0.500 μ M Cd²⁺ and Pb²⁺. **b** The corresponding calibration for Cd²⁺ and Pb²⁺ respectively. **c** SWASV responses of KPC/GCE in HAce-NaAc solution containing 0.025–0.500 μ M Pb²⁺ and **d** its corresponding calibration. **e** SWASV responses of KPC/GCE in HAce-NaAc solution containing 0.025–0.500 μ M Cd²⁺ and **f** its corresponding calibration. Deposition potential = – 1.1 V; Deposition time = 180 s



To further evaluate the mutual interference and selectivity among HMIs, the SWASV responses of sole Pb^{2+} or Cd^{2+} were tested in HAce-NaAc (pH = 4.8) at the range from 0.025 to 0.500 μ M. Compared with simultaneous detection, the SWASV response curves of sole Pb^{2+} have a little peeling

peak when concentration was high than 0.2 μ M. For the solution of sole Cd²⁺, the SWASV response curves had a strong peeling peak, which makes the individual sensitivity of sole Cd²⁺ lower than the simultaneous sensitivity of Cd²⁺. These phenomena can be summarized as follows: when the

Table 2 Summary of analytical
parameters for simultaneous and
individual detection of Cd^{2+} and
 Pb^{2+} for KPC/GCE

		Linear range (µM)	Sensitivity (µA µM ⁻¹)	Detection limit (nM)	R ²
Simultaneous sensitivity	Pb ²⁺	0.010-0.500	53.4	11.38	0.995
	Cd ²⁺	0.010-0.500	26.5	23.3	0.997
Individual sensitivity	Pb ²⁺	0.025-0.500	63.0	10.12	0.996
	Cd ²⁺	0.025-0.500	20.4	26.7	0.998

 Table 3
 Comparison of current

 sensitivity and LOD of this work
 with other previous researches of

 different electrodes for
 electrochemical detection of

 Pb(II)
 Pb(II)

Electrodes	LOD (nM)	Sensitivity ($\mu A \ \mu M^{-1}$)	Refs
MgSiO ₃ /GCE	0.247	9.44	[15]
MnFe ₂ O ₄ /NC/GCE	54	19.9	[31]
OMC/GCE	4.6	17.4	[32]
Nanoplate-stacked Fe ₃ O ₄ /GCE	15.2	24.6	[33]
OMC-OXI-Fe/GCE	7.57	30.19	[34]
KPC/GCE	11.38	53.4	This work

concentration of Pb^{2+} or Cd^{2+} increases to a higher level, peeling peak will appear. For Pb²⁺, only a little peeling peak appears, while a strong peeling peak for Cd^{2+} , which makes sensitivity of Cd²⁺ decreases. As shown in Fig. 5c-f, they exhibited good linear relationships between the concentration and the peak current for sole Pb²⁺ and Cd²⁺, and the corresponding linearization equations were $Y(Pb^{2+}) = 63.0c + 2.67$ $(R^2 = 0.996)$ and $Y(Cd^{2+}) = 20.4c + 4.00 (R^2 = 0.998)$, respectively. The sensitivities were 63.0 μ A μ M⁻¹ and 20.4 μ A μ M⁻¹ for Pb²⁺ and Cd²⁺, respectively. The detection limitations (S/N = 3) were 10.12 nM and 26.7 nM for Pb²⁺ and Cd², respectively (Table 2). Compared to simultaneous analysis, the sensitivity of Cd²⁺ was reduced and the sensitivity of Pb²⁺ was increased, which can be explained by the competition between the two metal ions for modifying a limited number of active sites on the surface of the electrode in simultaneous analysis. Besides, the strong peeling peak makes the sensitivity of Cd^{2+} decrease.

These results above indicate that KPC possesses excellent reproducibility in the detection of HMIs. Compared with other reported electrochemical methods for metal ion co-detection (Table 3), KPC/GCE has lower limit of detection (LOD) and higher sensitivity. The comparison shows that the KPC/GCE can be used as a better sensor to the detection of Pb²⁺ and Cd²⁺.

Conclusions

In summary, the KPC with a high specific surface area and a porous-rich structure was synthesized via a facile method. By the treatment of KOH and high temperature carbonization, the KPC possesses multi-stage pore structures and abundant micropores and mesopores, which provided a large number of active sites for the adsorption and desorption of Pb²⁺ and Cd²⁺ in the tests by SWASV. Under optimal experimental conditions, KPC-modified electrodes showed excellent electrochemical activity and high sensitivity for the determination of Pb²⁺ and Cd²⁺. This work proposed a novel strategy to the prepare biomass-based micro and mesoporous-coexisted porous carbon materials. The bio-metal-free materials modified electrodes have the potential application in the rapid and accurate analysis of HMIs.

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Compliance with ethical standards

Conflict of Interest The authors declare that they have no conflict of interest.

References

- G. Aragay, A. Merkoçi, Nanomaterials application in electrochemical detection of heavy metals. Electrochim. Acta 84, 49–61 (2012). https://doi.org/10.1016/j.electacta.2012.04.044
- B. Çeken, M. Kandaz, A. Koca, Electrochemical metal-ion sensor based on a cobalt phthalocyanine complex captured in Nafion® on a glassy carbon electrode. J. Coord. Chem. 65(19), 3383–3394 (2012). https://doi.org/10.1080/00958972.2012.716517
- J. Gong, T. Zhou, D. Song, L. Zhang, Monodispersed Au nanoparticles decorated graphene as an enhanced sensing platform for ultrasensitive stripping voltammetric detection of mercury(II). Sensors Actuators B Chem. 150(2), 491–497 (2010). https://doi. org/10.1016/j.snb.2010.09.014
- A. Simpson, R.R. Pandey, C.C. Chusuei, K. Ghosh, R. Patel, A.K. Wanekaya, Fabrication characterization and potential applications of carbon nanoparticles in the detection of heavy metal ions in aqueous media. Carbon 127, 122–130 (2018). https://doi.org/10. 1016/j.carbon.2017.10.086
- M.B. Gumpu, S. Sethuraman, U.M. Krishnan, J.B.B. Rayappan, A review on detection of heavy metal ions in water – an electrochemical approach. Sensors Actuators B Chem. 213, 515–533 (2015). https://doi.org/10.1016/j.snb.2015.02.122
- O. Karnitz, L.V.A. Gurgel, J.C.P. de Melo, V.R. Botaro, T.M.S. Melo, R.P. de Freitas Gil, L.F. Gil, Adsorption of heavy metal ion from aqueous single metal solution by chemically modified sugarcane bagasse. Bioresour. Technol. 98(6), 1291–1297 (2007). https://doi.org/10.1016/j.biortech.2006.05.013
- G.-J. Lee, H.-M. Lee, C.-K. Rhee, Bismuth nano-powder electrode for trace analysis of heavy metals using anodic stripping voltammetry. Electrochem. Commun. 9(10), 2514–2518 (2007). https://doi. org/10.1016/j.elecom.2007.07.030
- M.R. Knecht, S. Manish, Bio-inspired colorimetric detection of Hg2+ and Pb2+ heavy metal ions using Au nanoparticles. Anal. Bioanal. Chem. **394**(1), 33 (2009). https://doi.org/10.1007/s00216-008-2594-7
- R. Raghunandhan, L.H. Chen, H.Y. Long, L.L. Leam, P.L. So, X. Ning, C.C. Chan, Chitosan/PAA based fiber-optic interferometric sensor for heavy metal ions detection. Sensors Actuators B Chem. 233, 31–38 (2016). https://doi.org/10.1016/j.snb.2016.04.020
- A.L. Suherman, E.E.L. Tanner, S. Kuss, S.V. Sokolov, J. Holter, N.P. Young, R.G. Compton, Voltammetric determination of

aluminium(III) at tannic acid capped-gold nanoparticle modified electrodes. Sensors Actuators B Chem. **265**, 682–690 (2018). https://doi.org/10.1016/j.snb.2018.03.098

- A.R. Thiruppathi, B. Sidhureddy, W. Keeler, A. Chen, Facile onepot synthesis of fluorinated graphene oxide for electrochemical sensing of heavy metal ions. Electrochem. Commun. 76, 42–46 (2017). https://doi.org/10.1016/j.elecom.2017.01.015
- L. Xiao, G.G. Wildgoose, R.G. Compton, Sensitive electrochemical detection of arsenic (III) using gold nanoparticle modified carbon nanotubes via anodic stripping voltammetry. Anal. Chim. Acta 620(1-2), 44–49 (2008). https://doi.org/10.1016/j.aca.2008.05.015
- B.K. Bansod, T. Kumar, R. Thakur, S. Rana, I. Singh, A review on various electrochemical techniques for heavy metal ions detection with different sensing platforms. Biosens. Bioelectron. 94, 443–455 (2017). https://doi.org/10.1016/j.bios.2017.03.031
- E.S. Forzani, Z. Haiqian, C. Wilfred, T. Nongjian, Detection of heavy metal ions in drinking water using a high-resolution differential surface plasmon resonance sensor. Environ. Sci. Technol. 39(5), 1257–1262 (2005). https://doi.org/10.1021/es049234z
- R.X. Xu, X.Y. Yu, C. Gao, Y.J. Jiang, D.D. Han, J.H. Liu, X.J. Huang, Non-conductive nanomaterial enhanced electrochemical response in stripping voltammetry: The use of nanostructured magnesium silicate hollow spheres for heavy metal ions detection. Anal. Chim. Acta **790**, 31–38 (2013). https://doi.org/10.1016/j.aca.2013. 06.040
- Z. Lu, W. Dai, X. Lin, B. Liu, J. Zhang, J. Ye, J. Ye, Facile one-step fabrication of a novel 3D honeycomb-like bismuth nanoparticles decorated N-doped carbon nanosheet frameworks: Ultrasensitive electrochemical sensing of heavy metal ions. Electrochim. Acta 266, 94–102 (2018). https://doi.org/10.1016/j.electacta.2018.01. 188
- Y. Dong, L. Zhang, Constructed 3D hierarchical porous wool-balllike NiO-loaded AlOOH electrode materials for the determination of toxic metal ions. Electrochim. Acta 271, 27–34 (2018). https:// doi.org/10.1016/j.electacta.2018.03.110
- C. Zhu, H. Li, S. Fu, D. Du, Y. Lin, Highly efficient nonprecious metal catalysts towards oxygen reduction reaction based on threedimensional porous carbon nanostructures. Chem. Soc. Rev. 45(3), 517–531 (2016). https://doi.org/10.1039/c5cs00670h
- P. Zhang, Y. Gong, Z. Wei, J. Wang, Z. Zhang, H. Li, S. Dai, Y. Wang, Updating biomass into functional carbon material in ionothermal manner. ACS Appl. Mater. Interfaces 6(15), 12515– 12522 (2014). https://doi.org/10.1021/am5023682
- N. Sudhan, K. Subramani, M. Karnan, N. Ilayaraja, M. Sathish, Biomass-derived activated porous carbon from rice straw for a high-energy symmetric supercapacitor in aqueous and nonaqueous electrolytes. Energy Fuel **31**(1), 977–985 (2016). https:// doi.org/10.1021/acs.energyfuels.6b01829
- M. Lu, Y. Qian, C. Yang, X. Huang, H. Li, X. Xie, L. Huang, W. Huang, Nitrogen-enriched pseudographitic anode derived from silk cocoon with tunable flexibility for microbial fuel cells. Nano Energy 32, 382–388 (2017). https://doi.org/10.1016/j.nanoen. 2016.12.046
- J. Li, K. Liu, X. Gao, B. Yao, K. Huo, Y. Cheng, X. Cheng, D. Chen, B. Wang, W. Sun, D. Ding, M. Liu, L. Huang, Oxygen- and nitrogen-enriched 3D porous carbon for supercapacitors of high volumetric capacity. ACS Appl. Mater. Interfaces 7(44), 24622– 24628 (2015). https://doi.org/10.1021/acsami.5b06698

- X. Liu, M. Zhang, D. Yu, T. Li, M. Wan, H. Zhu, M. Du, J. Yao, Functional materials from nature: honeycomb-like carbon nanosheets derived from silk cocoon as excellent electrocatalysts for hydrogen evolution reaction. Electrochim. Acta 215, 223–230 (2016). https://doi.org/10.1016/j.electacta.2016.08.091
- X. He, P. Ling, M. Yu, X. Wang, X. Zhang, M. Zheng, Rice huskderived porous carbons with high capacitance by ZnCl2 activation for supercapacitors. Electrochim. Acta 105, 635–641 (2013). https://doi.org/10.1016/j.electacta.2013.05.050
- D. Jia, W. Huanlei, L. Zhi, K. Alireza, C. Kai, X. Zhanwei, Z. Beniamin, T. Xuehai, L. Elmira Memarzadeh, B.C. Olsen, Carbon nanosheet frameworks derived from peat moss as high performance sodium ion battery anodes. ACS Nano 7(12), 11004 (2013). https:// doi.org/10.1021/nn404640c
- Y. Zhang, H. Jiang, Q. Wang, J. Zheng, C. Meng, Kelp-derived three-dimensional hierarchical porous N, O-doped carbon for flexible solid-state symmetrical supercapacitors with excellent performance. Appl. Surf. Sci. 447, 876–885 (2018). https://doi.org/10. 1016/j.apsusc.2018.04.061
- P. Wang, X. Zhu, Q. Wang, X. Xu, X. Zhou, J. Bao, Kelp-derived hard carbons as advanced anode materials for sodium-ion batteries. J. Mater. Chem. A 5(12), 5761–5769 (2017). https://doi.org/10. 1039/c7ta00639j
- E. Raymundo-Piñero, M. Cadek, F. Béguin, Tuning carbon materials for supercapacitors by direct pyrolysis of seaweeds. Adv. Funct. Mater. 19(7), 1032–1039 (2009). https://doi.org/10.1002/adfm.200801057
- J. Wang, S. Kaskel, KOH activation of carbon-based materials for energy storage. J. Mater. Chem. 22(45), 23710 (2012). https://doi. org/10.1039/c2jm34066f
- C. Long, X. Chen, L. Jiang, L. Zhi, Z. Fan, Porous layer-stacking carbon derived from in-built template in biomass for high volumetric performance supercapacitors. Nano Energy 12, 141–151 (2015). https://doi.org/10.1016/j.nanoen.2014.12.014
- X.-J. Han, S.-F. Zhou, H.-L. Fan, Q.-X. Zhang, Y.-Q. Liu, Mesoporous MnFe2O4 nanocrystal clusters for electrochemistry detection of lead by stripping voltammetry. J. Electrochem. Soc. 755, 203–209 (2015). https://doi.org/10.1016/j.jelechem.2015.07. 054
- L. Zhu, C. Tian, R. Yang, J. Zhai, Anodic stripping voltammetric determination of lead in tap water at an ordered mesoporous carbon/ nafion composite film Electrode. Electroanalysis 20(5), 527–533 (2008). https://doi.org/10.1002/elan.200704088
- W.-J. Li, X.-Z. Yao, Z. Guo, J.-H. Liu, X.-J. Huang, Fe3O4 with novel nanoplate-stacked structure: surfactant-free hydrothermal synthesis and application in detection of heavy metal ions. J. Electrochem. Soc. 749, 75–82 (2015). https://doi.org/10.1016/j. jelechem.2015.04.038
- C.M. Quiroa-Montalván, L.E. Gómez-Pineda, L. Álvarez-Contreras, R. Valdez, N. Arjona, M.T. Oropeza-Guzmán, Ordered mesoporous carbon decorated with magnetite for the detection of heavy metals by square wave anodic stripping voltammetry. J. Electrochem. Soc. 164(6), B304–B313 (2017). https://doi.org/10. 1149/2.0231707jes

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