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One-step electrosynthesis of cadmium/aluminum layered double hydroxides composite as electrochemical probe for voltammetric detection of anthracene

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ABSTRACT

A green and facile electrochemical approach to synthesize novel cadmium/aluminum layered double hydroxides on a glassy carbon electrode (Cd/Al-LDHs/GCE) was proposed. The morphology and structure of Cd/Al-LDHs were characterized by scanning electron microscopy, energy dispersive spectrometer, powder X-ray diffraction. The results indicated that Cd/Al-LDHs were successfully prepared. Cyclic voltammetry and electrochemical impedance spectroscopy were employed to investigate the electrochemical behaviors of Cd/Al-LDHs/GCE. The Cd/Al-LDHs was served as an electrochemical probe in the detection of anthracene. And the Cd/Al-LDHs electrochemical response was greatly suppressed in presence of anthracene. A sensitive and convenient electrochemical method was developed for the determination of anthracene. The linear range and detection limit were 0.1–100.0 pM and 0.5 fM respectively. The method was successfully applied to determine anthracene in cloud-rain water samples of Mount-Taishan. This work provides a promising strategy for polycyclic aromatic hydrocarbons analysis at a very low concentration.

1. Introduction

Layered double hydroxides (LDHs), a typical class of two-dimensional nanostructured anionic clays, have attracted growing interest for their desirable properties [1]. As is known to all, nanomaterials are widely used in the field of analysis and sensing [2,3]. Hence, researchers have explored the applications of LDHs in extensive fields [4–6]. Particularly, some LDHs show electrochemical activity, such as Ni-based, Co-based, Zn-based LDHs, and so on [7–10], which extremely enlarge the applications of LDHs in electrochemical fields. Besides, electrodeposition, which allowed innovations of various electrodes and catalysts [7,11], has been demonstrated to be superior over many other approaches used for the synthesis of LDHs due to its outstanding advantages [12–15], such as less toxic organic solvents used in the synthesis process, time saving, easy to operate and the mild condition of synthesis [7,16]. Cadmium (Cd), a kind of transition element, shows close electronegativity with zinc, cobalt and so on. The nature property of Cd is similar to nickel, cobalt, *etc.* To the best of our knowledge, there had been many reports of LDHs based on nickel, cobalt, zinc and so on [7–9,15,17], while no one reported the synthesis of layered double hydroxides based on cadmium.

It is well known that polycyclic aromatic hydrocarbons (PAHs) are globally distributed environmental contaminants and they have attracted considerable concern because of their high toxicity and bioaccumulative properties [18]. Their qualitative and quantitative analyses are urgently needed. In the past decades, electrochemical method has been applied to develop chemical and biological sensors widely on account of its excellent selectivity and sensitivity [19–23]. However, the direct electrochemical determination of most PAHs is very difficult, because they are non-electrochemical active species in aqueous solutions. Therefore, more and more researches have been focused on the indirect electrochemical determination of PAHs by using electrochemical probe. Anthraquinone derivatives with redox activity, such as alizarin red S, benz[*a*]anthracene-7,12-dione, anthraquinone sulfonate which have a polycyclic structure, can be used as indicators in constructing electrochemical sensor for the detection of PAHs based on π-π interaction [20–22]. Compared with other electrochemical methods, such as electrochemiluminescence (ECL) [24] and electrochemical oxidation [25], this method offers great advantages because it provides more sensitive and lower detection limit. However, these indicators need to be grafted to the electrode material in advance. Besides, the synthetic process is relatively complex.

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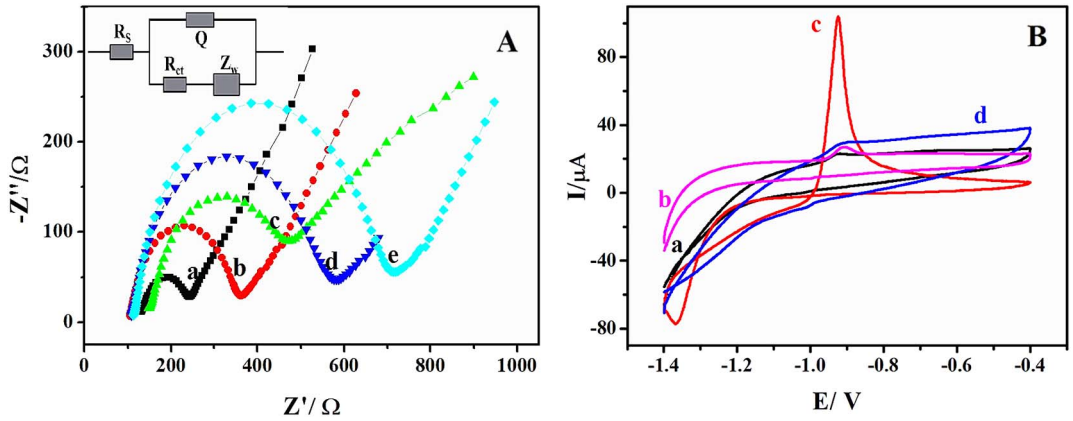

Fig. 1. (A) EIS of GCE(a) and Cd/Al-LDHs/GCE in 0.1 M KCl solution containing 5.0 mM $[Fe(CN)6]^{3-/4-}$ with different electrodeposition time (from b to e: 50, 100, 200 and 300 s).The frequency range is from 0.1 Hz to 100 kHz. Inset is the Randles circuit model for the modified electrodes in the cell. (B) Cyclic voltammograms of GCE (a) and Cd/Al-LDHs/GCE in 1.0 M KOH with different electrodeposition time (from a to d: 50, 100, 200 and 300 s).

In this paper, a new LDHs-based electrochemical sensing protocol which involves a simple one-step electrosynthesis of Cd/Al-LDHs film on a glassy carbon electrode surface was proposed. The Cd/Al-LDHs modified electrode performed excellent electrochemical activity in the KOH solution, and could direct work as an indicator. The influence of PAHs on the electrochemical behaviors of Cd/Al-LDHs/GCE was investigated. The results indicated that the Cd/Al-LDHs electrochemical sensor not only exhibited excellent analytical performance, but also made contributions for simple, low-cost, rapid and sensitive PAHs detection strategy.

2. Experimental section

2.1. Reagents and apparatus

The Cd/Al-LDHs were electrosynthesised starting from freshly prepared solutions of Cd and Al nitrates and KNO_3. Anthracene and other PAHs were obtained from Aladdin Reagent Co., Ltd. and diluted with ethanol. Each PAH standard solution was diluted by ethanol into a stock solution containing 1.0 mM. An appropriate quantity of the PAH stock solution was diluted with ultrapure water and kept in the dark at 4 °C for use. All other reagents were of analytical grade and ultrapure water was used in the experimental process.

The morphology of the prepared Cd/Al-LDHs was measured by a S-4800 field-emission scanning electron microscope for obtaining the scanning electron microscopy (SEM) image. Powder X-ray diffraction (XRD) pattern was collected on a Philips PW1710 instrument (Cu Kα radiation, 1.5418 Å). Electrochemical impedance spectroscopy (EIS) was performed on an IM6ex electrochemical workstation (ZAHNER Co., Germany). Electrochemical measurements were performed on a CHI760E electrochemical workstation (Chenhua Instrumental Co., Shanghai China) with a conventional three-electrode system comprising a platinum wire as an auxiliary electrode, an Ag/AgCl electrode (3.0 M KCl) as reference, and the modified or unmodified glass carbon electrode (GCE) as a working electrode. All experiments were carried out at ambient temperature and prior to each electrochemical experiment; high purity nitrogen was used to purge solutions for at least 10 min.

2.2. Preparation of the modified electrode(Cd/Al-LDHs/GCE)

Prior to modification, the basal GCE was polished with 1.0 and 0.05 μm alumina slurries. After each polishing, the electrode was sonicated in ethanol and ultrapure water for about 5 min, successively. A Cd/Al-LDHs film was electrodeposited on the cleaned GCE at a constant potential of − 0.9 V *vs.* Ag/AgCl for 200 s in an aqueous solution containing 0.0225 M Cd $(NO_3)_2$, 0.0075 M Al $(NO_3)_3$ and 0.3 M KNO_3 [6,15]. The as-prepared Cd/Al-LDHs/GCE was rinsed with water and dried at room temperature for further experiments.

3. Results and discussion

3.1. Characterization of Cd/Al-LDHs/GCE

Electrochemical Impedance Spectroscopy (EIS) is an effective method for monitoring the changes in the surface features of the modified electrodes in the electrodeposition processes. The semicircle diameter of EIS indicates the conductivity of electrode or the electron transfer resistance, Ret, which controls the electron transfer kinetics of the redox-probe at the electrode interface. The results of EIS of the electrodes with different deposition time are shown in Fig. 1A. It can be seen that all the electrodes show a semicircle and a straight line. The bare GCE electrode exhibited a very small semicircle domain (Fig. 1A curve a). Nevertheless, as deposition time (t_d) increased, the semicircle diameter increased dramatically (Fig. 1A curve b–e), indicating an increase of Ret, which could be ascribed to the formation of LDHs film which hindered the electron transfer.

The electrochemical behavior of Cd/Al-LDHs modified electrodes was further studied by cyclic voltammetry (CV). Fig. 1B showed the cyclic voltammograms of modified electrodes with different electrodeposition time in 1.0 M KOH. The oxidation peak of the modified electrode increased with the increase of deposition time and then reached to the maximum at 200 s (Fig. 1B curve a–c). Furthermore, there was crossover of the CV traces in their forward and backward scans (curve c). Also, a peak was observed at − 0.9 V, suggested that Cd was being intercalated and stripped off during reduction and oxidation respectively, indicating the formation of LDHs film on the electrode surface. However, when the deposition time exceeded 300 s, the current response decreased distinctly (Fig. 1B curve d). This is owing to that LDHs are semiconductor materials, long electrodeposition time would make a mass of LDHs accumulate on the surface of electrode hindering the transfer of electron. Therefore, 200 s was chosen as the optimal electrodeposition time based on EIS and CV results.

Meanwhile, the typical morphology of the Cd/Al-LDHs film on GCE was shown in Fig. 2A–B. The image revealed that the LDHs exhibited regular and small sheet structure. Energy dispersive spectrometer (EDS) characterization was employed to confirm the elements in the LDHs in Fig. 2C. The characteristic peaks of Cd, Al and O were simultaneously observed for LDHs. X-ray diffraction (XRD) spectrum was also used to further characterize the structure of Cd/Al-LDHs. Fig. 2D showed the XRD pattern of the Cd/Al-LDHs. Its peaks at 2θ = 11.51°, 23.24°, 35.03° and 67.2° assigned to the (003), (006), (009) and (110) planes could be clearly distinguished. This was considered the typical