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PAPER

Layer-by-layer assembly of layered double hydroxide/cobalt phthalocyanine ultrathin film and its application for sensors[†]

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This paper reports the preparation of cobalt phthalocyanine/layered double hydroxide ultrathin films (UTFs) through an electrostatic layer-by-layer (LBL) technique as well as its application in electrocatalysis for dopamine oxidation. UV-vis absorption and electrochemical impedance spectra indicate the uniform deposition of the LBL films. XRD measurements demonstrate the long-range ordered structure of organic/inorganic UTFs, with an average repeating distance of 1.89 nm. SEM images show that the film surface displays a continuous and uniform morphology, with the root-mean-square (rms) roughness of ~6.4 nm revealed by AFM. The UTF modified ITO electrode exhibits significant electrocatalytic performance for the oxidation of dopamine which is related to the Co(II)/Co(III) couple in the (LDH/CoPcTs)_n UTF. The dopamine biosensor shows rather high sensitivity, low detection limit and excellent anti-interference properties in the presence of ascorbic acid. Furthermore, compared with pristine organic multilayer (PDDA/CoPcTs)_n modified electrodes, the (LDH/CoPcTs)_n electrodes show superior repeatability and long-term stability, due to the immobilization and dispersion of electroactive CoPcTs molecules by LDH nanosheets. Therefore, this work demonstrates a successful paradigm for the fabrication of electroactive species in an inorganic 2D matrix, which can be potentially used for practical applications in bioanalysis and biodetection.

Introduction

Dopamine (DA) is an important neurotransmitter¹ in mammalian central nervous systems and the loss of DA-containing neurons may result in serious diseases including schizophrenia, Huntington's and Parkinson's diseases. Detection of DA has therefore been a subject of considerable interest.² The electrochemical methods exhibit many advantages over other detection approaches because of their convenience to sense neurotransmitters in living organisms. The major problem in the detection of DA by electrochemical methods is the presence of a high concentration of ascorbic acid (AA), which is oxidized at almost the same potential as DA on bare electrodes. One effective solution for this problem is the use of modified electrodes,³ which can induce selective oxidation of AA or DA and thus distinguish the single signal for each species.

Cobalt phthalocyanine (CoPc), and its derivatives modified electrodes are widely used for the detection of DA due to the electrocatalytic effect towards oxidation of DA.⁴ The catalytic behavior of CoPc is related to the Co(II)/Co(II) or Co(II)/Co(I)couples in CoPc complexes.⁵ However, one major problem of CoPc modified electrodes is that the desquamation of electroactive species from the electrode surface under biological conditions generally results in the loss of electrochemical activity and/or bioactivity. Therefore, it is highly essential to select a host matrix which can both provide a suitable microenvironment for electroactive molecules and enhance direct electron transfer between the electroactive species and underlying electrodes.

Layered double hydroxides (LDH) are available as both naturally occurring minerals and synthetic materials,⁶ and have been widely used as host matrixes for the storage and release of biomolecules and drug molecules.⁷ Metallophthalocyanine intercalated LDHs as biomimetic oxidation catalysts have been reported.⁸ Some electrochemical biosensors based on LDH composites have also been successfully developed normally *via* the dip-coating method.⁹

Recently, the delamination of LDHs into single nanosheets as building blocks and the preparation of inorganic/organic ultrathin films (UTFs) have been reported by Sasaki's and our groups.¹⁰ This inspired us to challenge the goal of fabricating

State Key Laboratory of Chemical Resource Engineering, Beiing University of Chemical Technology, Beijing, 100029, China. E-mail. weimin@mail.buct.edu.cn; Fax: +86-10-64425385; Tel: +86-10-64412131 † Electronic supplementary information (ESI) available: Powder XRD patterns of the MgAl-CO₃ and MgAl-NO₃ LDH samples (Fig. S1), SEM image of the MgAl-NO3 LDH precursor (Fig. S2), tapping-mode AFM image for the exfoliated MgAl-LDH nanosheets deposited on a Si wafer substrate (Fig. S3), voltammetric responses at different scan rates (Fig. S4), the measurement stability of (LDH/CoPcTs)₄ and (PDDA/CoPcTs)4 modified electrodes (Fig. S5), the long-term stability of (LDH/CoPcTs)₄ and (PDDA/CoPcTs)₄ modified electrodes (Fig. S6), UV-vis absorption spectra of (LDH/CoPcTs)₄ and (PDDA/CoPcTs)₄ film before and after dipping into PBS (pH 7.4) for 6 days (Fig. S7), XRD patterns of (LDH/CoPcTs)₄ film before and after dipping into PBS (pH 7.4) for 6 days (Fig. S8). See DOI: 10.1039/c0jm02430a

electrochemical sensors through alternating assembly of positively charged LDH nanosheets and negatively charged phthalocyanine *via* the layer-by-layer (LBL) technique, which would exhibit the following advantages: the LDH nanosheets can provide a confined and stable microenvironment for the immobilization of phthalocyanine; the nanometre scale control of the assembly will result in a high dispersion of electroactive species with uniform orientation, facilitating the electron transfer. Moreover, the film components and thickness can be precisely controlled with simple manipulation and versatility.

In this work, UTFs were fabricated by alternating assembly of cobalt(II) phthalocyanine tetrasulfonate (CoPcTs) and nonelectroactive Mg–Al LDH nanosheets on ITO substrates using the LBL deposition technique. The modified electrode displays excellent electrochemical catalytic properties towards oxidation of DA with high sensitivity, low detection limit as well as high stability for long-term applications. The results demonstrated that LDH nanosheets can serve as one promising material for fabrication of nanostructured electrochemical sensors.

Experimental section

Materials

Dopamine, ascorbic acid and poly(dimethyldiallylammonium chloride) (PDDA) were purchased from Sigma-Aldrich Company. Analytical grade chemicals including $Mg(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, NaOH, Na_2HPO_4 , and NaH_2PO_4 were used without further purification. Deionized and decarbonated water was used in the preparation process.

Synthesis and exfoliation of Mg-Al LDH

MgAl-CO₃ LDH was synthesized according to a previous report.^{10e} MgAl-NO₃ LDH was prepared by the so-called saltacid method.^{6b} Typically, 0.5 g of MgAl-CO₃ LDH was treated with 500 cm³ of an aqueous salt-acid solution containing NaNO₃ (0.75 mol) and HNO₃ (0.0025 mol) in a three-neck flask under nitrogen flow and continuous stirring at ambient temperature for 24 h. The resulting product were filtered, washed and vacuumdried. Subsequently, formamide was used as solvent to swell and exfoliate the MgAl-NO₃ LDH particles. A colloidal suspension of LDH nanosheets was obtained by vigorously agitating 0.1 g of MgAl-NO₃ LDH in 100 cm³ of formamide at room temperature under a N₂ gas flow for 2 days.

Fabrication of (LDH/CoPcTs)_n and (PDDA/CoPcTs)_n multilayer films

ITO glass substrates (1×3 cm, 10Ω per square) were cleaned in an ultrasonic bath using the following reagents in sequence: water, acetone, ethanol and water for 10 min. After the cleaning procedure, the surface of substrates was hydrophilic and negatively charged. The substrates were stored in deionized water before use.

The multilayer films composed of LDH nanosheets and CoPcTs were fabricated on pretreated ITO glass electrode through the LBL technique. The substrate was dipped into a colloidal suspension of LDH nanosheets (0.5 g L^{-1}) for 15 min and washed thoroughly with deionized water. Then it was

immersed into an aqueous solution of CoPcTs (1.0 g L⁻¹) for another 10 min and rinsed with water. Subsequently, the deposition operation for LDH nanosheets and CoPcTs was repeated *n* times to obtain a multilayer film of $(LDH/CoPcTs)_n$. The resulting organic–inorganic UTFs on ITO substrates were dried in a vacuum oven at ambient temperature.

For comparison study, poly(dimethyldiallylammonium chloride) (PDDA) was chosen as the polycation to alternatively assemble with CoPcTs. The (PDDA/CoPcTs)_n films were prepared by a similar method to that of (LDH/CoPcTs)_n films described above. The concentration of PDDA (Mw = *ca*. 100 000–200 000) was 1.0 g L⁻¹.

Techniques of characterization

UV-vis absorption measurements were performed on a Shimadzu UV-2501PC spectrometer. The morphology of the LDH samples was investigated by using a Hitachi S-4700 scanning electron microscope (SEM) and a NanoScope IIIa atomic force microscope (AFM) from Veeco Instruments. X-Ray diffraction data were recorded using a Shimadzu XRD-6000 X-ray diffractometer using Cu-K α radiation ($\lambda = 0.154$ nm) at 40 kV, 30 mA, a scanning rate of 1° min⁻¹, and a 2 θ angle ranging from 3° to 20°.

Electrochemical impedance spectra (EIS) were recorded on a potentiostat (CHI 660C) by using a three-electrode cell with modified ITO glass as the working electrode, platinum wire as the counter electrode, and Ag/AgCl (saturated KCl) as the reference electrode. The measurements were performed with the frequency range from 0.1 Hz to 100 kHz in the presence of a 2.5×10^{-3} mol L^{-1} K₃[Fe(CN)₆]/K₄[Fe(CN)₆] (1 : 1) mixture in 0.1 mol L^{-1} KCl. The above mentioned three-electrode system was also employed for the cyclic voltammograms measurement, and 0.1 mol L^{-1} phosphate buffer solution (PBS) with pH = 7.4 was used as supporting electrolyte. The solutions were prepared with Milli-Q water (>18 MΩ cm) and purged with highly purified nitrogen. All measurements were performed at room temperature.

Results and discussion

Synthesis and characterization of exfoliated LDH nanosheets

The characterization of LDH precursor (Mg : Al = 2 : 1, molar ratio) and exfoliated nanosheets is described in ESI† (Fig. S1–S3).

UV-visible absorption of the (LDH/CoPcTs)_n UTFs

The film fabrication process was monitored by UV-vis absorption spectra of ITO glass substrates coated with (MgAl-LDH/ CoPcTs)_n UTFs (Fig. 1: *n* varies from 2 to 20). The peaks at 631 and 676 nm are due to the π - π * transition centered on the macrocycle of CoPcTs molecule, which are the Q bands of dimer and monomer of CoPcTs respectively.¹¹ A red-shift of the monomer band was observed compared with its counterpart in aqueous solution (661 nm, dashed line in Fig. 1), as a result of the electrostatic affinity between CoTsPc⁴⁻ and LDH nanosheets. The inset in Fig. 1 shows a linear increase of the absorbance at 631 and 676 nm as a function of the bilayer number of (LDH/ CoPcTs)_n, indicating a uniform growth process for the LBL films.



Fig. 1 UV-vis absorption spectra of the $(LDH/CoPcTs)_n$ UTFs assembled on ITO substrates ("*n*" denotes the number of bilayers; n = 2-20). The dashed line shows the absorption of CoPcTs in aqueous solution. The absorbance of the UTFs at 631 and 676 nm is plotted against the bilayer number in the inset.

Electrochemical impedance spectra (EIS) of the (LDH/CoPcTs)_n UTFs

Electrochemical impedance spectroscopy (EIS) is an effective tool for probing the interface properties of surface-modified electrodes. The complex impedance can be presented as the sum of the real (Z_{re}) and imaginary (Z_{im}) components that originate mainly from the resistance and capacitance of the cell. The semicircle diameter of EIS equals the electron transfer resistance (R_{et}), which controls the electron transfer kinetics of the redox probe at the electrode interface. In this work, R_{et} reflects the restricted diffusion of the redox probe through the multilayer system, and relates directly to the accessibility of the underlying electrode or the film permeability. Fig. 2 shows the typical EIS for the (LDH/CoPcTs)_n film modified electrodes in 0.1 mol L⁻¹ KCl solution containing the redox probe Fe[(CN)₆]^{4-/3-}. A

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Fig. 2 Electrochemical impedance spectra of the $(LDH/CoPcTs)_n$ multilayer film (n = 2-20) modified electrodes in the presence of 2.5×10^{-3} mol L⁻¹ Fe[(CN)₆]^{4-/3-} in 0.1 mol L⁻¹ KCl solution.

semicircle portion was observed at higher frequencies, corresponding to the kinetic control of the charge-transfer process; a linear correlation followed by a semicircle at lower frequencies was attributed to the diffusion process. The diameter of the semicircle parts increased significantly as the bilayer number increased, resulting from the hindrance effect on the redox couples along with the stepwise deposition of LDH/CoPcTs multilayers. The EIS results further confirmed the effective assembly of (LDH/CoPcTs)_n UTF on ITO substrates.

The surface morphology and structure of the $(LDH/CoPcTs)_n$ UTFs

A top view SEM image for the (LDH/CoPcTs)₂₀ (Fig. 3A) shows that the film surface is continuous and uniform with a thickness of ~38 nm revealed by its side view image (Fig. 3B), corresponding to an average increment of ~1.9 nm per bilayer. The AFM topographical image (Fig. 3C) shows a smooth surface of LDH/CoPcTs film, with a root-mean-square roughness of 6.4 nm. XRD patterns (Fig. 3D) exhibit a Bragg peak at $2\theta = 4.67^{\circ}$ and its intensity increased successively upon increasing the number of deposition cycles, demonstrating the ordered structure of (LDH/CoPcTs)_n UTFs. The average repeating distance is ~1.89 nm, which is consistent with the result obtained from cross-sectional SEM measurements.

(LDH/CoPcTs)_n UTF modified electrode as biosensor

In order to examine the electrocatalysis performance of the $(LDH/CoPcTs)_n$ modified electrode, the electrochemical behavior of DA, AA and a mixture of them at this electrode as well as at various comparative electrodes was studied. The oxidation of DA occurs at ~1.03 V at the bare electrode in phosphate buffer solution (PBS) (Fig. 4, curve a), close to that of AA (1.05 V, curve c); while the $(LDH/CoPcTs)_6$ modified electrode reduces the overvoltage of DA oxidation significantly, shifting the E_p value negatively by 390 mV (curve b). In addition, the oxidation current is enhanced about 1.5 times compared with the bare ITO electrode. However, no obvious electrocatalytic



Fig. 3 (A) Top-view SEM image, (B) cross-sectional view SEM image, (C) tapping-mode AFM image of the $(LDH/CoPcTs)_{20}$ film and (D) XRD patterns for the $(LDH/CoPcTs)_n$ films with n = 5, 15 and 20.



Fig. 4 Cyclic voltammogram curves recorded in 1.0×10^{-3} mol L⁻¹ DA at a bare ITO electrode (curve a) and the modified electrode (curve b), in 1.0×10^{-3} mol L⁻¹ AA at a bare ITO electrode (curve c) and the modified electrode (curve d), in a mixture solution of AA and DA at a bare ITO electrode (curve e) and the modified electrode (curve f). pH: 7.4 PBS; scan rate: 100 mV s⁻¹.

performance was found for AA at the same modified electrode (curve d). Compared with the bare ITO electrode, the peak potentials for DA and AA were well resolved at the (LDH/ CoPcTs)₆ modified electrode (curves e and f), demonstrating that the modified electrode selectively catalyzes the oxidation of DA in the presence of AA. This is possibly related to the selective electrocatalysis of negatively charged CoPcTs for the oxidation of DA, which accelerates the electron transfer. The dependence of electrochemical response on the bilayer number is shown in Fig. 5. It was found that the oxidation current increased and the oxidation potential shifted negatively upon increasing the deposition cycle (n varies from 1 to 6), while both a decrease in oxidation current and positive shift of oxidation potential were observed with further increase of bilayer number. Therefore, the film with n = 6 was chosen as the optimum electrode for voltammetric determination of DA.



Fig. 5 Cyclic voltammograms obtained for the oxidation of DA (1 × 10^{-3} mol L⁻¹) at the (LDH/CoPcTs)_n modified electrodes (n = 2, 4, 6, 8 and 10) in 0.1 mol L⁻¹ phosphate buffer (pH 7.4). Scan rate: 100 mV s⁻¹.

Based on the results in this work and previous reports,¹² the electrocatalytic behavior of the (LDH/CoPcTs)₆ modified electrode for the oxidation of DA can be tentatively expressed as follows:

$$2 \operatorname{Co(II)}\operatorname{PcTs} \to 2 \operatorname{Co(III)}\operatorname{PcTs} + 2e \tag{1}$$

$$2 \operatorname{Co(III)}\operatorname{PcTs} + \operatorname{DA}_{\operatorname{red}}(\operatorname{aq}) \rightarrow 2 \operatorname{Co(II)}\operatorname{PcTs} + \operatorname{DA}_{\operatorname{ox}}(\operatorname{aq})$$
 (2)

The electrooxidation of DA is related to the catalytic circulation of the Co(II)/Co(III) couple in the (LDH/CoPcTs)₆ film. The effect of scan rate on the anodic peak current (i_{pa}) in 1.0×10^{-3} mol L⁻¹ DA was investigated. As shown in Fig. S4,† i_{pa} was proportional to the square root of the scan rate over the range 10–100 mV s⁻¹, indicating that the diffusion process is the ratedetermining step for electrocatalytic oxidation of DA.

The influence of DA concentration on the response of the modified electrode was investigated (Fig. 6A), demonstrating a linear correlation in the range 2.0 \times 10⁻⁵–1.4 \times 10⁻⁴ mol L⁻¹, with a regression equation of $i_{pa}(mA) = -0.29 + 0.133c (10^{-4} \text{ mol})$ L^{-1}), r = 0.998 (Fig. 6B). A plateau of current was observed as the DA concentration went higher, indicative of a mass transport limitation.¹³ In addition, this series of voltammograms shows that the CoPcTs catalytic sites within the film are not poisoned by the oxidation products, which is a serious problem for surface fouling. The limit of detection was 3.2×10^{-7} mol L⁻¹ based on the signal to noise ratio of 3, which is close or equal to previously reported results.^{3c,4b} Chronoamperometric measurement was used to determine the response time of the (LDH/CoPcTs)₆ modified electrode towards electrocatalysis of DA (Fig. 7). Taking into account the time cost to reach 100% of the signal, the response time was found to be 2 s. The results above demonstrate the potential application of (LDH/CoPcTs), UTF modified electrodes for the determination of DA.

The $(LDH/CoPcTs)_n$ modified electrode exhibits good measurement stability from 10 times of test using one electrode with a relative standard deviation (RSD) less than 2.5% (Fig. S5A†). The long-term stability of the electrode was investigated for the measurement of 1.0×10^{-4} mol L⁻¹ DA each day for 6 consecutive days, and the result shows that 93% of its initial current remains (Fig. S6A†), indicating that the LDH matrix effectively stabilizes the electroactive species (CoPcTs). It is instructive to further compare the stability of (LDH/CoPcTs)_n film modified electrodes with other (polycation/CoPcTs)_n systems. Poly(dimethyldiallylammonium chloride) (PDDA) was



Fig. 6 (A) Cyclic voltammograms of the $(LDH/CoPcTs)_6$ modified electrode in 0.1 mol L⁻¹ PBS (pH 7.4) with the presence of different concentrations of DA, scan rate 100 mV s⁻¹. (B) Linear correlation between the amperometric current and the concentration of DA.



Fig. 7 Chronoamperometric measurement for the $(CoPcTs/LDH)_6$ modified electrode with successive additions of 8.0×10^{-5} mol L⁻¹ DA in PBS (pH 7.4) poised at 0.67 V vs. Ag/AgCl.

chosen as the polycation to alternatively assemble with CoPcTs. Although the $(PDDA/CoPcTs)_n$ modified electrode exhibited electrocatalytic activity for DA oxidation, the stability was rather poor (Fig. S5B and Fig. S6B[†]). This is related to the partial desquamation of $(PDDA/CoPcTs)_n$ film from the electrode into PBS during the measurement, which was confirmed by UV-vis absorption spectroscopy (Fig. S7[†]). After dipping the modified electrodes into PBS (pH 7.4) for 6 days, the absorbance of the $(PDDA/CoPcTs)_n$ film decreased dramatically, while the $(LDH/CoPcTs)_n$ film remained almost unchanged. The XRD pattern of the (LDH/CoPcTs), film after storage for 6 days did not show an obvious change compared with the as-prepared sample (Fig. S8[†]), demonstrating that the CoPcTs was not exchanged by the phosphate from PBS. This comparison study illustrates the superiority of using inorganic LDH nanosheets as a matrix for the immobilization of electroactive molecules in sensor applications.

Conclusion

In conclusion, multilayer films containing exfoliated LDH nanosheets and cobalt phthalocyanines were assembled using the LBL technique on ITO substrates, which was confirmed by UV-vis and XRD. The structural and morphological studies show that the surface of UTFs is continuous and uniform with long range stacking order in the normal direction of the substrate. The $(LDH/CoPcTs)_6$ modified electrode exhibits a low detection limit, fast response and excellent long-term stability for the determination of DA. Therefore, this work provides a novel approach to immobilize electroactive species into an inorganic layered matrix with nanoscale level control, for the purpose of technological applications in electroanalysis and biosensors.

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