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Carbon functionalized metal organic framework/Nafion composites as novel electrode materials for ultrasensitive determination of dopamine

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Carbon functionalized metal organic frameworks (C/Al-MIL-53-$(OH)_2$) were successfully prepared for the first time by a solvothermal technique and characterized by Fourier transform infrared spectroscopy, X-ray diffraction spectrometry, and scanning electron microscopy. This composite was coated with a Nafion film so as to form a Nafion/C/Al-MIL-53-$(OH)_2$ modified glassy carbon electrode. The modified electrode was then used as a novel electrocatalyst for dopamine (DA) oxidation in phosphate buffer solution. Due to the synergistic effects of the different materials, including the high conductivity of carbon, the large surface area of Al-MIL-53-$(OH)_2$, and the film-forming ability of a cation-exchange polymer, the modified electrode exhibited a remarkable enhancement effect on voltammetric response of DA. Under the optimal conditions, the response peak currents had a linear relationship with the DA concentration in the range from 3.0×10^{-8} to 1.0×10^{-5} mol L^{-1}. The limits of detection and quantitation for DA were found to be 0.8×10^{-8} mol L^{-1} and 2.6×10^{-8} mol L^{-1}, respectively. The analytical utilities of the proposed biosensor were achieved by analyzing the content of DA in biological fluids.

1. Introduction

Neurotransmitters have received considerable interest due to their key role in our central nervous system. Dopamine (DA) is one of the most significant and representative catecholamine neurotransmitters existing in the central nervous system of mammals and humans. It plays an important role in the functioning of central nervous, cardiovascular, renal, and hormonal systems. The trace level measurement of DA has been a long-standing goal since the concentration change has been related to various diseases and compulsive behaviors.[1,2] Therefore, it is preferable to develop a sensitive, fast and practical method which provides the determination of DA in different real samples.

Electrochemical approaches have been considered to be superior to other techniques in view of its high accuracy, fast response, and bulk modification with simple instruments.[3–5] Nevertheless, the bare glassy carbon electrode (GCE) has poor sensitivity and selectivity towards the determination of DA. In order to overcome these shortcomings, various materials have been utilized to construct and modify the electrodes, such as self-assembled monolayers,[6] polymers,[7] metal oxides,[8] and nanoparticles.[9,10] As far as we know, some disadvantages such as relatively limited surface areas, their limitation in structural design, and the limited possibility for surface modification are encountered.

Metal–organic frameworks (MOFs) are a new class of structured hybrid materials that consist of inorganic connectors and organic linker molecules. MOFs possess various pore sizes and surface areas, and their surface properties can be manipulated using postsynthetic modification, providing broader access to functional groups within MOFs.[11–13] Although these remarkable characteristics hold great promise in many technological fields such as gas adsorption, separation, and catalysis,[14–16] only a few literatures have fabricated bare MOF materials for electrochemical biosensors due to their poor conductivity and unstable nature in aqueous solution.[17,18] Recently, different MOF based hybrid materials have been constructed to enhance the electrochemical properties and electrocatalytic activities of target analytes by a combination of MOFs with highly conductive and mechanically durable materials. For example, Wang *et al.* prepared Cu–MOF–graphene oxide composite modified electrodes for dopamine detection.[19] Hosseini *et al.* fabricated Au–SH–SiO_2 nanoparticles supported on Cu–MOFs for electrocatalytic oxidation of hydrazine and L-cysteine.[20,21]

Al-based MOFs are nontoxic, and most of these materials are stable against hydrolysis. As a subclass of Al-based MOFs, Al-MIL-53-$(OH)_2$ has pendent hydroxy groups at the organic linker, which could be utilized for postsynthetic modification reactions.[22,23] In this study, we introduced carbon spheres onto the surface of metal organic frameworks (C/Al-MIL-53-$(OH)_2$)

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for the first time and further immobilized C/Al-MIL-53-$(OH)_2$ at the glassy carbon electrode with the Nafion polymer. The fabricated Nafion/C/Al-MIL-53-$(OH)_2$/GCE biosensor was evaluated for the DA biosensor, and this electrode showed a detection limit down to nano-molar levels, favorable stability and reproducibility, and excellent selectivity. The analytical applicability of the developed biosensor was achieved by analyzing the content of DA in urine and serum samples.

2. Experimental section

2.1. Reagents and materials

Stock solution of dopamine (0.01 mol L^{-1}) was prepared by dissolving dopamine (0.1531 g) in 100 mL deionized water. The phosphate buffer solution (PBS, 0.1 mol L^{-1}), which was prepared by mixing Na_2HPO_4 and NaH_2PO_4 stock solution and adjusted to the pH value of 5.0 with 0.1 mol L^{-1} H_3PO_4 or NaOH solution, was used as the supporting electrolyte during all measurements. Nafion (0.5 wt%) solution was prepared by diluting 5 wt% Nafion in ethanol. All reagents were of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd unless indicated otherwise. Double deionized water (18 MΩ cm) was used throughout the experiments.

2.2. Apparatus

A CHI852C electrochemical workstation (Chenhua Instrument, Shanghai, China) was used for voltammetric measurements with a three-electrode system. A Tensor 27 spectrometer (Bruker Co., Germany) was used to obtain Fourier transform infrared (FTIR) spectra. Field emission scanning electron micrographs (SEM) were obtained using a Hitachi S-4800 microscope (Japan) at an acceleration voltage of 15 kV. X-ray diffraction (XRD) patterns were recorded on a D8 Advance X-ray diffractometer (Bruker Co., Germany) at room temperature. Elemental analyses were performed on a Vario EL cube element analyser (Elementar Co., Germany).

2.3. Synthesis and activation of Al-MIL-53-$(OH)_2$

Al-MIL-53-$(OH)_2$ was synthesized according to the previous reports.[24,25] Briefly, 0.33 g H_2BDC–$(OH)_2$ and 0.2 g $Al(ClO_4)_3{\cdot}9H_2O$ were added rapidly to 7.5 mL *N*,*N*-dimethyl formamide (DMF) with ultrasonic agitation for 30 min. The mixture was quickly transferred to a 25 mL Teflon liner, and the resulting mixture was heated in an oven at 200 °C for 48 h. After the reaction, the vial was cooled to room temperature naturally. Al-MIL-53-$(OH)_2$ was activated *via* Soxhlet extraction with 100 mL ethanol for 48 h. The yellow product was collected by filtration, followed by washing three times with deionized water (15 mL) and ethanol (15 mL), and then dried at 130 °C for 12 h in an oven.

2.4. Synthesis of C/Al-MIL-53-$(OH)_2$

C/Al-MIL-53-$(OH)_2$ was synthesized by a simple hydrothermal reaction: 0.15 g of synthesized Al-MIL-53-$(OH)_2$ was dispersed in 5 mL of deionized water by ultrasonication to form a suspension. Then, 0.5 g of glucose dissolved in 15 mL of deionized water and 10 mL of ethanol were added to the above suspension under gentle stirring. The resulting suspension was transferred into autoclaves at 180 °C for 12 h. The carbon functionalized metal organic compounds were obtained by centrifugation and washed with deionized water and ethanol several times, and then dried at 60 °C in an oven.

2.5. Preparation of the Nafion/C/Al-MIL-53-$(OH)_2$ modified electrode

1 mg of C/Al-MIL-53-$(OH)_2$ was dispersed in 1 mL of DMF and the mixture was agitated in an ultrasonic bath for one hour to achieve a well-dispersed suspension. Prior to use, the bare GCE was polished to a mirror-like surface with 0.5 μm and 0.05 μm of α-Al_2O_3, and then rinsed ultrasonically with water and absolute ethanol and sonicated in de-ionized water. After the solvent was evaporated, the electrode was coated successively with 5 μL of 0.5% Nafion solution. The Nafion/C/MIL-53-$(OH)_2$ composite modified electrode was obtained after it was dried in air for approximately 4 h.

2.6. Operating procedure

In order to get the high sensitivity of detection, the anodic stripping voltammetric technique was used. A 10 mL solution containing an appropriate amount of dopamine and 0.1 mol L^{-1} phosphate buffer solution (PBS, pH 5.0) was transferred into a voltammetric cell. The voltammogram in differential pulse mode was recorded with an anodic scan (step potential, 10 mV; pulse period, 0.5 s; pulse width, 0.25 s; scan ranges from −0.2 to 0.4 V). The calibration curve was obtained by plotting the peak current *versus* the dopamine concentration. All the experiments were performed at room temperature.

3. Results and discussion

3.1. Characterization of C/Al-MIL-53-$(OH)_2$

FTIR spectra of Al-MIL-53-$(OH)_2$ (a), and C/Al-MIL-53-$(OH)_2$ (b) in the range of 400–4000 cm^{-1} are shown in Fig. 1. As for Al-MIL-53-$(OH)_2$, the characteristic peaks at 1462 and 1602 cm^{-1} are attributed to asymmetric and symmetric stretching of the carboxylate group in the coordinated BDC–$(OH)_2$ linker. The broad absorption band due to stretching vibration of the –OH group appended to the BDC–$(OH)_2$ linker is located in the region of 3308–3388 cm^{-1}.[24,26] After carbon incorporation, the surface redox reactions increased the number of reducing organic functional groups, and the –OH stretching band center was enhanced and broadened.[27] The four major peaks of Al-MIL-53-$(OH)_2$ at 2θ = 9.2°, 10.5°, 15.2°, and 18.1° are consistent with the well-defined Al-MIL-53-$(OH)_2$ crystals,[24] suggesting that the current material has the expected structure. Compared with Al-MIL-53-$(OH)_2$, the similar peak positions of C/Al-MIL-53-$(OH)_2$ evidenced the structure of C/Al-MIL-53-$(OH)_2$ was preserved though the peak intensities decreased. The decrease in the peak intensities can be attributed to the decrease in the crystallinity. In order to better explain the panoramic morphologies of the product structure, the SEM images of Al-MIL-53-$(OH)_2$, and C/Al-MIL-53-$(OH)_2$ composite materials are shown in Fig. 1(c) and (d).

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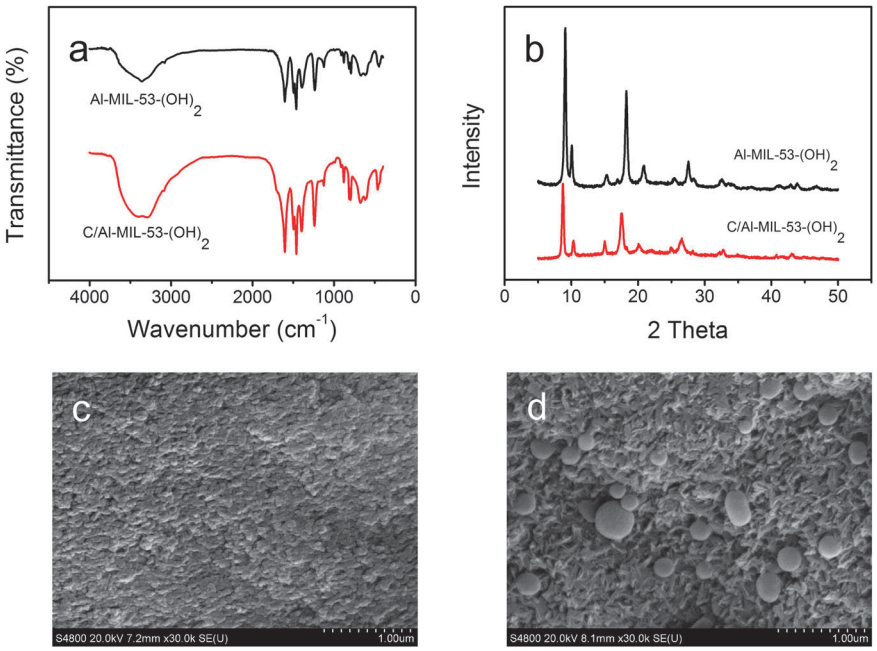

Fig. 1 FTIR transmission spectra (a), XRD patterns (b), and SEM images (c) and (d) of Al-MIL-53-$(OH)_2$ and C/Al-MIL-53-$(OH)_2$.

After the carbon was functionalized on the outer surface of Al-MIL-53-$(OH)_2$, small carbon spheres occurred due to the pyrolysis of glucose under hydrothermal conditions and carbonation. However, due to the high amount of carbon in Al-MIL-53-$(OH)_2$ itself, we cannot reveal the distribution of carbon spheres on the surface of Al-MIL-53-$(OH)_2$ using field emission scanning electron microscope-mapping or other available tools. Elemental analysis shows that the contents of C, H, and O in Al-MIL-53-$(OH)_2$ were 38.2%, 3.65%, and 38.09%. After Al-MIL-53-$(OH)_2$ was mixed with glucose under hydrothermal conditions at 180 °C, the contents of C, H, and O were changed to 39.61%, 3.75%, and 39.35%, suggesting that the carbon spheres are not hydrogen and oxygen free. However, it difficult to determine the exact structure of decomposition products, because various chemical reactions of glucose can take place under hydrothermal conditions and result in a complex mixture of organic compounds.[27,28]

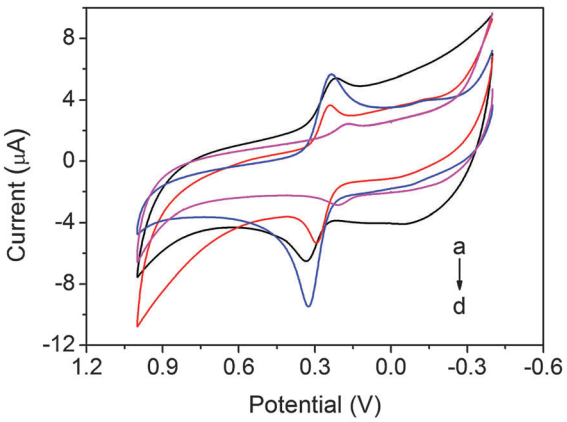

Fig. 2 Cyclic voltammograms at the bare GCE (a), Al-MIL-53-$(OH)_2$ modified GCE (b), C/Al-MIL-53-$(OH)_2$ modified GCE (c), Nafion/C/Al-MIL-53-$(OH)_2$ modified GCE (d) in the presence of DA in pH 5.0 PBS. DA concentration: 0.1 mmol L^{-1}, and scan rate: 100 mV s^{-1}.

3.2. Voltammetric behavior of DA at the Nafion/C/Al-MIL-53-$(OH)_2$/GCE

Fig. 2 shows CVs of DA on the bare GCE (Fig. 2a), the Al-MIL-53-$(OH)_2$/GCE (Fig. 2b), the C/Al-MIL-53-$(OH)_2$/GCE (Fig. 2c), and the Nafion/C/Al-MIL-53-$(OH)_2$/GCE (Fig. 2d). On the bare GCE, DA exhibits a reversible electrochemical behavior with a weak oxidation peak current of 1.89 μA. The small current indicated that the direct oxidation of DA at the bare electrode was inefficient. At the Al-MIL-53-$(OH)_2$/GCE, a couple of broad redox peaks appeared and the peak currents increased significantly. The notable enhancements in the oxidation peak current of DA could be ascribed to the fact that the relative large surface area of the electrode increased after immobilization of Al-MIL-53-$(OH)_2$ on it. However, in the case of the C/Al-MIL-53-$(OH)_2$/GCE, the anodic peak current was increased strikingly up to 3.78 μA with a well-defined peak shape. The significant increase in the current response of the C/Al-MIL-53-$(OH)_2$ electrode can be ascribed to the excellent electric conductivity of carbon which facilitate the electron transfer between DA and the modified electrode. After a drop of Nafion solution was successively coated on the C/Al-MIL-53-$(OH)_2$/GCE, the peak potentials of DA almost did not shift, and the peak currents increased continuously. The reason for the improved performance may be that when the C/Al-MIL-53-$(OH)_2$ modified GCE was coated with a negative-charged Nafion film, they could attract and accumulate cationic DA to some degree *via* an ion-exchange model, which could result in increasing peak currents and selectivity towards DA. These results suggest that the Nafion/C/Al-MIL-53-$(OH)_2$/GCE shows a good electrocatalytic response towards DA.

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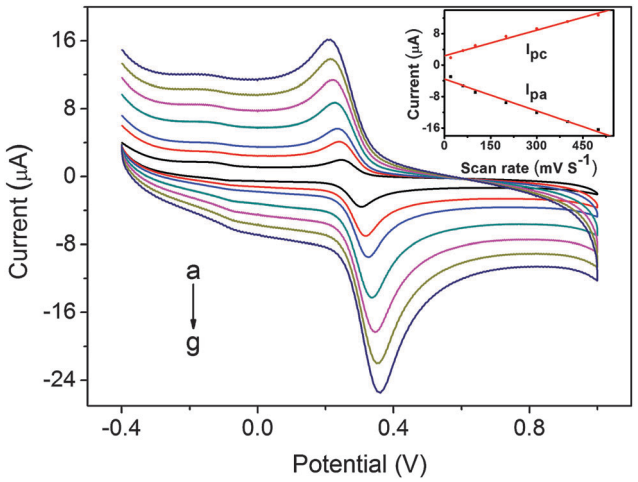

Fig. 3 Cyclic voltammograms of 0.1 mmol L^{-1} DA in 0.1 mol L^{-1} PBS at the Nafion/C/Al-MIL-53-$(OH)_2$/GCE at scan rates of (a) 20, (b) 60, (c) 100, (d) 200, (e) 300, (f) 400 and (g) 500 mV s^{-1}. Inset: dependence of the redox peak current on the scan rate.

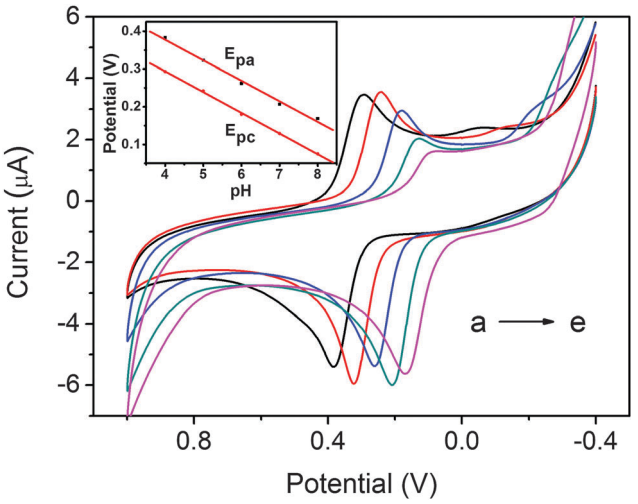

Fig. 4 Cyclic voltammograms of 0.1 mmol L^{-1} DA in 0.1 mol L^{-1} PBS at the Nafion/C/Al-MIL-53-$(OH)_2$/GCE with solution pH values of (a) 4.0, (b) 5.0, (c) 6.0, (d) 7.0, and (e) 8.0. Inset: dependence of redox peak potentials on solution pH.

The influence of the scan rate (v) on the oxidation current of 0.1 mmol L^{-1} DA was examined using the proposed modified electrode. Fig. 3 shows that both the values of the anodic peak current (I_{pa}) and the cathodic peak current (I_{pc}) exhibit a linear relationship with a scan rate over the range of 20–500 mV s^{-1}. The linear regression equation for the anodic peak current was I_{pa} (μA) = −3.5805–0.02681v (mV s^{-1}), with a correlation coefficient of r = 0.9910, and for the cathodic current was I_{pc} (μA) = 2.3604 + 0.02183v (mV s^{-1}), with a correlation coefficient of r = 0.9903. This result implies that the electrochemical oxidation is an absorption-controlled process for DA at the Nafion/C/Al-MIL-53-$(OH)_2$/GCE surface. This was consistent with the previous reports.[28,29] In addition, with the increase of scan rate, the anodic peak potential (E_{pa}) shifted more positively and the cathodic peak potential (E_{pc}) shifted more negatively, indicating that the electron-transfer rate decreased and the electrochemical reaction of dopamine tended to be less reversible.

3.3. Optimization of experimental parameters

The effect of pH of the supporting electrolyte on the peak currents of 0.1 mmol L^{-1} DA in 0.1 mol L^{-1} PBS is shown in Fig. 4. Both the reduction and oxidation peak potentials of dopamine shifted negatively with the increase in the solution pH values, and varied linearly in the range of pH values from 4.0 to 8.0 with the slope of 54 and 55 mV pH^{-1} (E_{pa} = −0.05440 pH + 0.5952, r = 0.9965; E_{pc} = −0.05490 pH + 0.5132, r = 0.9996), which was close to the theoretical value of 59 mV pH^{-1}. This means that the electrocatalytic oxidation of DA at the Nafion/C/Al-MIL-53-$(OH)_2$ modified GCE is an equal electron and proton process. The results were in agreement with the literature that two protons and two electrons are estimated to be involved in the electrochemical oxidation of DA.[30]

Moreover, the peak currents also changed with the solution pH. The anodic current increased with the increase of pH values in the range of 4.0–5.0 (Fig. 5a), however, it decreased when the solution pH was higher than 5.0. The reason may be due to the competitive function of DA and the proton with the Nafion film. On the one hand, the Nafion film could combine with the protons in the solution when the pH value is lower, which would decrease its ability to attract DA *via* electrostatic repulsion. On the other hand, DA may become deprotonated and gain a negative charge with increasing pH, which would also result in the decrease of its ability to combine with the Nafion film. Therefore, pH 5.0 was selected in the following experiments.

An accumulation step is usually a simple and effective way to enhance the sensitivity of the voltammetric determination. The effect of accumulation potential on the stripping peak currents of DA over the potential range from −0.2 to 0.3 V was explored (Fig. 5b). The oxidation peak current increased gradually and the maximum was obtained at 0.0 V. After that, the peak current decreased with the further positive shift of accumulation potential. Therefore, for further study, an accumulation potential of 0.0 V was recommended. The effect of the accumulation time on the stripping current of DA was changed from 100 to 600 s (Fig. 5c). The peak current increased with the accumulation time increasing up to 400 s. It was probably owing to the interaction between the DA and the active sites of the modified electrode. When the accumulation time exceeded 400 s, the peak current almost remain the same. Taking into account both the sensitivity and the efficiency, an accumulation period of 400 s was employed in the experiments.

The amount of C/Al-MIL-53-$(OH)_2$ suspension has a predominant effect on the voltammetric response of DA. In order to determine the optimal amount of suspension, the amounts of 2, 3, 4, 5, 6 and 7 μL of C/Al-MIL-53-$(OH)_2$ suspension (1 mg mL^{-1}) were investigated. The results showed that the oxidation peak current of DA increased quickly through increasing the volume of C/Al-MIL-53-$(OH)_2$ suspension deposited on the surface of the GCE up to 5 μL (Fig. 5d). A further increase caused

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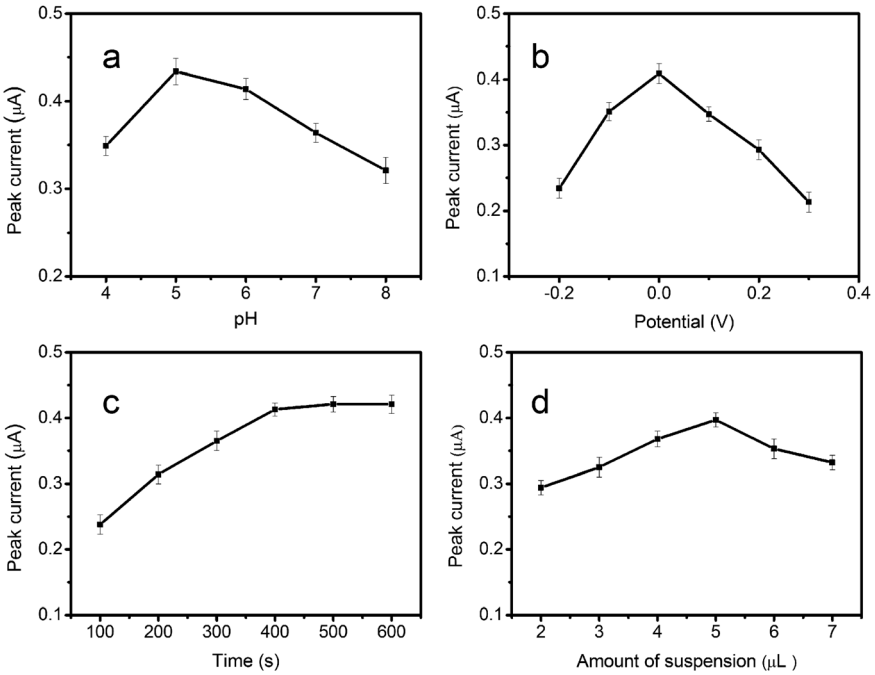

Fig. 5 Effects of pH, accumulation potential, accumulation time, and the amount of Nafion/C/Al-MIL-53-$(OH)_2$ suspension on the current intensity of 5.0×10^{-7} mol L^{-1} DA.

a reduction in the anodic peak current of DA. This can arise from the large film thickness, which caused increasing resistance of the film modifier against the electron transfer and sluggish mass transfer processes for DA. As a result, 5 μL of 1 mg mL^{-1} C/Al-MIL-53-$(OH)_2$ was selected as the optimum volume.

3.4. Interference studies

In order to demonstrate the selectivity of the developed method for the determination of dopamine, various potential organic compounds and inorganic ions in biological fluids were added to the solution containing 5.0×10^{-7} mol L^{-1} DA. The tolerance limit for interfering species was considered as the maximum concentration that gave a relative error of less than ±5.0%. Ascorbic acid and uric acid exist in negatively charged form at pH 7.0 PBS. Thus, they get repelled by Nafion from the electrode surface and thus do not interfere with the analysis of DA. It was found that 800-fold concentration of ascorbic acid; 300-fold concentration of L-tryptophane and L-cysteine; 200-fold concentration of uric acid, citric acid and glucose have no influence on the signals of dopamine. Moreover, some ions such as 1000-fold concentration of Na^+, Fe^{3+}, Zn^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, Mn^{2+}, $Ca^{2+}$and Ba^{2+} have no influences on the determination of DA. These results suggested that the determination of DA in biological samples at the Nafion/C/Al-MIL-53-$(OH)_2$ modified electrode is free from the most common interfering species and thus this method is selective in nature.

3.5. Analytical performance and applications

Fig. 6 displays the differential pulse voltammograms of DA under the optimal experimental conditions. The peak current increased with the increasing concentration of DA, linearly proportional to the concentration of DA from 3.0×10^{-8} to 1.0×10^{-5} mol L^{-1}. The values of limits of detection (LOD) and quantitation (LOQ) for DA were obtained by utilizing LOD = $3\sigma/s$ and LOQ = $10\sigma/s$, where σ is the standard deviation of the blank signals and s is the slope of the linear calibration graph. And the resulting concentrations at LOD and LOQ levels were 0.8×10^{-8} mol L^{-1} and 2.6×10^{-8} mol L^{-1}, respectively. The linear regression equation for DA is $I_p = 6.4576C + 10.7768$ (I_p: 10^{-8} A, C: 10^{-7} mol L^{-1}) and the correlation coefficient is 0.9989. In order to study the reproducibility of the electrode preparation procedure, five modified electrodes based on the

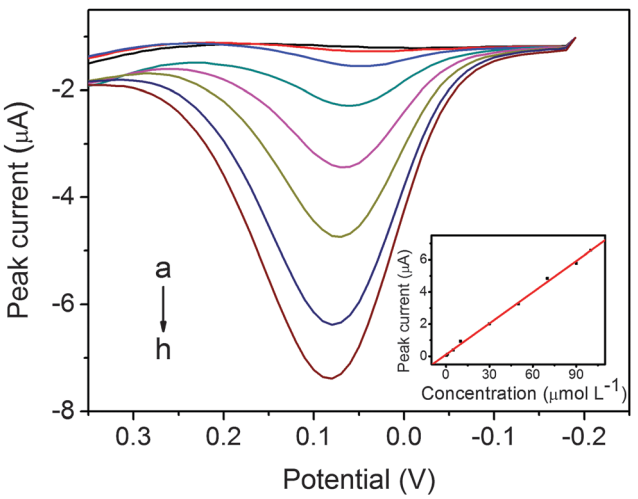

Fig. 6 Differential pulse voltammograms of DA at the Nafion/C/Al-MIL-53-$(OH)_2$ modified electrode in the pH 5.0 PBS. DA concentration (from a to h): 0.3, 5, 10, 30, 50, 70, 90, and 100×10^{-7} mol L^{-1}. The inset shows the relationship between the peak current and the DA concentration.

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Table 1 Comparison of the analytical performance with other methods for the determination of DA at different modified electrodes[a]

Electrode	Linear range (μM)	Detection limit (μM)	Methods	Ref.
PdNPs/GR/CS/GCE	0.5–15, 20–200	0.1	DPV	29
MPEG/GCE	2.0–140	0.047	DPV	30
Pretreated graphite/Nafion/SPCE	0.5–70	0.02	LSV	31
DNA/PAMAM/MWNT-Chit/Au electrode	0.2–10, 10–100	0.03	DPV	32
L-Cys/Au electrode	0.1–12, 40–1100	0.02	CE	33
PA-SWNTs/Pt electrode	0.2–10	0.08	DPV	34
MWNTs-MIPs/GCE	0.5–200	—	DPV	35
GO/SiO_2-MIPs/GCE	0.05–160	0.03	DPV	36
CDP-GS-MWCNTs/GCE	0.15–21.65	0.05	DPV	37
Nafion/Sulfonated-G/GCE	0.2–20	0.02	DPV	38
RGO-MWNTs-PTA/GCE	0.5–20	1.14	DPV	39
Porphyrin-RGO/GCE	1–70	0.0095	DPV	40
Pretreated pencil graphite electrode	0.15–15	0.033	DPV	41
EDTA-GS/Nafion/GCE	0.2–25	0.01	DPV	42
Nafion/C/Al-MIL-53-$(OH)_2$/GCE	0.03–10	0.008	DPV	This work

[a] Abbreviations: PdNPs, palladium nanoparticles; GR, graphene; CS, chitosan; MPEG, methoxypolyethylene glycol; PAMAM, poly(amidoamine); MWNTs, multi-walled carbon-nanotubes; Chit, chitosan; DPV, differential pulse voltammogram; L-Cys, L-cysteine; CE, chronoamperometric method; PA, phytic acid; SWNTs, single-walled carbon nanotubes; MIPs, molecularly imprinted polymers; GO, graphene oxide; CDP, cyclodextrin prepolymer; Sulfonated-G, sulfonated graphene; RGO, reduced graphene oxide; PTA, phosphotungstic acid; GS, graphene sheet.

same fabrication procedure were prepared and used for the determination of 5.0×10^{-7} mol L^{-1} DA solution. The relative standard deviation (R.S.D.) between electrode peak currents (an average of five determinations on each electrode) was calculated to be 4.5%. Moreover, the R.S.D. for 12 replicate measurements on a single electrode in 5.0×10^{-7} DA solution was 3.2%. The results indicate that the modified electrode has high reproducibility and repeatability in both the preparation procedure and the voltammetric determinations.

Generally, the bare MOF based modifier cannot be used in acidic solution, which are easily washed from the electrode with buffer solution and become unstable during the potential scan. However, once the C/Al-MIL-53-$(OH)_2$ composites were formed, they could be stable in a relatively acid environment. The antiacid ability of the C/Al-MIL-53-$(OH)_2$ composites was investigated and compared to pure Al-MIL-53-$(OH)_2$ composites by ultrasonicating them in 0.1 mol L^{-1} PBS solution at 50 °C for 10 h. After the acid treatment, Al-MIL-53-$(OH)_2$ composites were fully dissolved and their dispersion turned to light yellow which was the color of organic ligands. In contrast, the C/Al-MIL-53-$(OH)_2$ composite spheres did not exhibit much change. The stability of Nafion/C/Al-MIL-53-$(OH)_2$/GCE was further tested by keeping the electrode in pH 5.0 PBS and then the anodic peak currents were recorded after continuous scanning for 50 cycles. Nearly no decrease in the voltammetric response appeared and 98.3% of the initial current response was retained, indicating that the Nafion/C/Al-MIL-53-$(OH)_2$/GCE was stable in the buffer solution. Table 1 shows the comparison between the analytical performance of the present method and previous literature methods for the determination of DA.[28–41] Out of all these electrodes, the limit of detection obtained for DA is the lowest by the proposed method. In addition, the Au–SH–SiO_2@Cu–MOF modified electrode was also prepared according to the literature,[19] and it's linear range and detection limit were found to be 0.1–20 μmol L^{-1} and 0.04 μmol L^{-1}, respectively, which were also lower than the Nafion/C/Al-MIL-53-$(OH)_2$ modified electrode. These results reveal that the proposed Nafion/C/Al-MIL-53-$(OH)_2$/GCE has a large advantage over other reported methods in terms of linear working range, limit of detection and the number of cycles.

Table 2 Determination of dopamine in urine and serum samples using the Nafion/C/Al-MIL-53-$(OH)_2$ modified electrode (n = 5)

Samples	Added (μmol L^{-1})	Found (μmol L^{-1})	RSD (%)	Recovery (%)
Urine 1	—	0.125	2.62	—
	0.200	0.327	2.37	101.6
Urine 2	—	0.271	3.85	—
	0.200	0.469	3.49	99.3
Urine 3	—	0.186	2.91	—
	0.200	0.385	2.14	99.5
Serum 1	—	0.631	3.33	—
	0.500	1.153	2.91	103.5
Serum 2	—	0.907	3.57	—
	1.00	1.932	3.14	102.7
Serum 3	—	0.536	3.54	—
	1.00	1.525	2.86	97.9

To illustrate the feasibility of the Nafion/C/Al-MIL-53-$(OH)_2$/GCE for routine analysis, the electrode was applied to determine the DA concentration in urine and human serum samples. Urine and serum were collected from a local hospital, and all the samples were determined directly or properly diluted with 0.1 mol L^{-1} pH 5.0 PBS to fit the calibration curve and reduce the matrix effect. The analytical results are shown in Table 2. As observed, the recoveries were in the range of 97.9–103.5% with a relative standard derivation (RSD, n = 5) of less than 3.85%. These results indicate that the method is reliable for the quantitative determination of DA in real samples.

4. Conclusion

In this paper, a carbon sphere was functionalized onto Al-MIL-53-$(OH)_2$ by hydrothermal treatment for the first time. XRD results indicated that Al-MIL-53-$(OH)_2$ retained its native structure in the composite materials. By combining the unique properties of the C/Al-MIL-53-$(OH)_2$ composite such as high specific surface area and high conductivity, with the cation

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selectivity of the Nafion film, a Nafion/C/Al-MIL-53-$(OH)_2$ composite film modified glassy carbon electrode was successfully constructed and used to study the catalytic oxidation of DA. The modified electrode shows excellent electrocatalytic activity, significantly lower detection limit, and stability response. The response characteristics of the proposed electrochemical biosensor are significantly improved compared to most of some modified electrodes reported as DA biosensors. We believe that the functional MOF based electrochemical biosensor may offer high application potential for the quantitative determination of biomolecules in real samples.

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