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Article

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Composites of Multiwalled Carbon Nanotubes and Molecularly Imprinted Polymers for Dopamine Recognition

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A novel composite of multiwalled carbon nanotubes (MWNTs) and molecularly imprinted polymers (MIPs) was prepared by using dopamine (DA) as a template molecule. Selective copolymerization of methacrylic acid and trimethylolpropane trimethacrylate (copoly(MAA-*co*-TRIM)) in the presence of DA was achieved at the vinyl group functionalized MWNT surface. Vinyl groups modified on MWNTs surface are a key factor for the formation the composite of MWNTs-MIPs. Attenuated total reflection Fourier transform infrared spectroscopy, transmission electron microscopy, scanning electron microscopy, and thermogravimetric analysis were used to characterize the composite structure and determine the grafted MIPs quantities in the composite. The properties such as adsorption dynamics, special binding, and selective recognition capacity were evaluated. The results demonstrated that MWNTs-MIPs not only possessed a rapid dynamic adsorption but also exhibited a high selectivity toward DA, compared to epinephrine. The electrochemical sensor fabricated by modifying MWNTs-MIPs on the glassy carbon electrode could recognize DA from ascorbic acids (AA), indicating DA could be detected in the presence of AA. And the modified electrode was used to detect the concentration of DA with a linear range of 5.0×10^{-7} to 2.0×10^{-4} mol/L.

Introduction

Multiwalled carbon nanotubes (MWNTs) have enjoyed widespread attention for their high electrical and thermal conductivity properties.[1] In recent years, unique mechanical properties and extremely large surface area endow MWNTs with more applications. For example, MWNTs could serve as the reinforcing element in a polymer or metal matrix in fabricating new advanced materials.[2−3] In the preparation of these materials, the effective utilization of MWNTs depends strongly on the ability to disperse nanotubes homogeneously throughout the matrix and to achieve strong interfacial bonding between MWNTs and the matrix in order to ensure load translation.[4] In reverse, this combination between MWNTs and polymers or metal matrix right offers an attractive route not only to reinforce polymer layer but also to introduce some new properties.[5] Some groups have already functionalized MWNTs with various polymers to assemble the composites with the desired properties, mainly focusing on the effective dispersibility of the composites in a wide range of solvents,[6−7] improvement of the thermal conductivity,[8] thermal stability, and flammability.[9] However, to the best of our knowledge, few reports involved the preparation of composite based on MWNTs and high cross-linked polymers as the molecularly recognized element.

Enzymes, antibodies, or receptors are typical molecularly recognized elements in a biological system. Most of these recognition materials are biomacromolecules; many difficulties in application exist due to their sensibility to various conditions, such as instability against high temperature, organic solvents, and pH. To overcome the above limitations, a molecular imprinting technique, the design and construction of biomimetic receptor system with predetermined recognition for target molecule, has been proposed[10−11] and developed rapidly.[12−14] With the significant advantages in easy preparation, low cost, predictable specific recognition, and high stability, the synthesized molecularly imprinted polymers (MIPs) have the capability of specific adsorption and recognition of the template molecule. Although the bulk MIPs prepared by conventional methods exhibit high selectivity, some disadvantages were suffered, such as the heterogeneous distribution of the binding sites, embedding of most binding sites, and poor site accessibility for template molecule. To resolve these problems, scientists have made efforts to prepare core−shell structural MIPs.[15−18] The thin layer of MIPs was polymerized onto the surface of some solid supports, such as monodispersed polystyrene seeds and silica spheres. The binding cavities in the outer thin MIPs layer can effectively improve the accessibility capacity for template molecules. And the prepared core−shell MIPs also exhibited excellent recognizing, separating, catalyzing, and biosensing properties. MWNTs, with unique mechanical properties and extremely large surface area, should be an excellent candidate as the supported material, which would endow MIPs with large surface area if the MIPs were prepared onto the surface of MWNTs. Thus, the binding sites in the outer layer of the composite would improve the accessibility of template molecule and reduce the binding time.

Herein, a novel composite with molecular recognition capacity was fabricated by using MWNTs as the reinforcement material in the MIPs matrix. Vinyl group functionalized MWNTs directed selective polymerization of MIPs by covalent bonds on the MWNTs surface. Every MWNT was coated with a layer of MIPs of certain thickness, and the thickness of MIPs layer could be controlled by changing the concentration of

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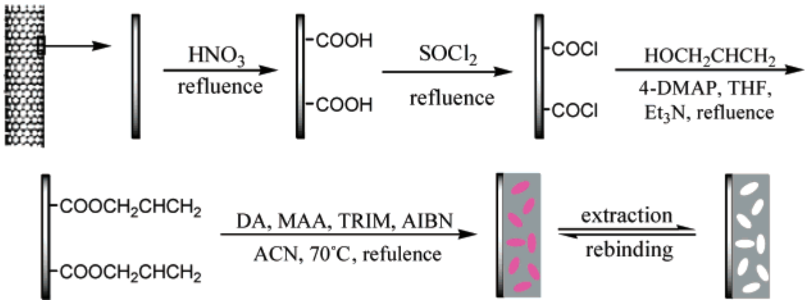
TABLE 1: Preparation of MWNTs-MIPs

polymer	MWNT-C$=$CH$_2$/g	DA/mmol	MAA/mmol	TRIM/mmol	AIBN/mg
MWNTs-MIPs1	0.08	0.2	1	2	30
MWNTs-MIPs2	0.08	0.8	4	8	30
MWNTs-NIPs	0.08		1	2	30

SCHEME 1: Synthesis Route of MWNTs-MIPs



prepolymerization monomers. The adsorption dynamics, special adsorption, and selective recognition of MWNTs-MIPs were investigated. An electrochemical sensor fabricated by modifying the MWNTs-MIPs on the glassy carbon electrode surface was employed to recognize DA from AA and detect the concentration of DA.

Experimental Methods

Chemicals. MWNTs were obtained from Shenzhen Carbon Nanotechnologies Co. Ltd. Trimethylolpropane trimethacrylate (TRIM), (4-dimethylamine) pyridine (4-DMAP), dopamine (DA), and epinephrine (EP) were purchased from Sigma. Methacrylic acid (MAA) was distilled under reduced pressure to remove inhibitors. All other reagents used were of analytical grade and used as received without further purification. Phosphate buffer solution (PBS, 0.1 M) prepared in mixed solvent of doubly distilled water and methanol (9:1 v/v) at pH 7.0 was used as the supporting electrolyte.

Instruments. The morphology of MWNTs-MIPs was observed by transmission electron microscopy (TEM, JEOL IEM-200CX) and scanning electron microscopy (SEM, S4800). All attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopic measurements were performed on a BRUKER IFS 66/S Fourier Transform spectrometer. Ultraviolet visible (UV−vis) absorption spectra of DA and EP were recorded by a UV-2401PC spectrometer. Thermal gravimetric analysis (TGA) was conducted on a Shimadzu TGA-50 instrument from room temperature to 600 °C with a heating rate of 20 °C/min in the nitrogen flow (10 mL/min). Electrochemical measurements were performed with a CHI 660B electrochemical workstation (Shanghai Chenhua Instrument) in a glass vial containing 10 mL of electrolytic solution at room temperature. Cyclic voltammetry (CV) and chronoamperometry were carried out with a typical three-electrode system. A platinum wire was used as an auxiliary electrode, a saturated calomel electrode (SCE) as a reference electrode, and a glassy carbon electrode modified by MWNTs-MIPs1, which was prepared by copolymerizing with 0.08 g of vinyl groups functionalized MWNTs, 0.2 mmol DA, 1 mmol MAA, and 2 mmol TRIM, as a working electrode.

Synthesis of MWNTs-CH$=$CH$_2$. Crude MWNTs (0.5 g) were added to 60 mL of HNO$_3$ under sonication for 10 min. Then the mixture was stirred under 85 °C for 16 h. After cooling to room temperature, the mixture was filtered through a 0.22-μm polycarbonate membrane and washed thoroughly with distilled water for several times until the pH value of the filtrate was neutral. The filtered solid was dried under vacuum, obtaining carboxylic acid-functionalized MWNTs (MWNTs-COOH).

MWNTs-COOH (0.4 g) was suspended in the mixture of 10 mL of sulfoxide chloride (SOCl$_2$) and 30 mL chloroform at 60 °C for 24 h under reflux. The solid was washed by anhydrous tetrahydrofuran (THF) for several times to remove the excess SOCl$_2$ and dried under vacuum to give MWNTs-COCl. Then 0.2 g MWNTs-COCl in 30 mL of anhydrous THF was added with 1.16 g allyl alcohol, 0.244 g 4-DMAP and 6.06 g triethylamine. The mixture was stirred at 50 °C for 24 h and then collected by centrifugation and washed with anhydrous THF. After washing and centrifugation, the resulting solid was dried overnight in a vacuum desiccator, obtaining vinyl group functionalized MWNTs (MWNTs-CH$=$CH$_2$).

Synthesis of MWNTs-MIPs. MWNTs-MIPs with DA as a template molecule were prepared by selective polymerizing MIPs onto the vinyl group functionalized MWNT surface. The molar amounts of DA, MAA, TRIM, and 2, 2′-azobisisobutyronitrile (AIBN) and the procedure of preparation of the MWNTs-MIPs are described in Table 1 and Scheme 1, respectively. In brief, MWNTs-CH$=$CH$_2$ was added to the mixture solvent of 30 mL of acetonitrile and 5 mL of toluene in a 250-mL round-bottom flask and purged with N$_2$ under magnetic stirring. DA and MAA dissolved by 5 mL of *N*,*N*-dimethylformamide were added to the reactor and mixed for 30 min to form a complex of template molecule and functional monomer. Then TRIM and AIBN were also added. The temperature was increased to 70 °C, and the reaction was allowed to proceed for 12 h. The resulting product was collected by centrifugation and washing thoroughly with ethanol to discard the reagents. Then the composite was eluted by the mixture solvent of methanol and acetic acid (9:1, v/v) for several times to extract the template molecules until no DA could be detected by UV−vis (at 284 nm) in the eluent. The obtained polymers were finally rinsed with ethanol to remove the remaining acetic acid and dried in the vacuum desiccator for 24 h before use. For comparison, blank polymers (MWNTs-NIPs) were prepared by the same procedure, only without using the template molecule in the polymerization process.

Binding Experiments. MWNTs-MIPs (5 mg) was added into a 5-mL tube and suspended in 2.0 mL of mixing H$_2$O/acetonitrile (1:9, v/v) solutions with specific initial concentrations of DA ranging from 0.04 to 0.4 mmol/L. After shaking at 25 °C for 2 h, the mixture was centrifuged at 15 000 rpm for 2 min. The concentration of free DA in the supernate was

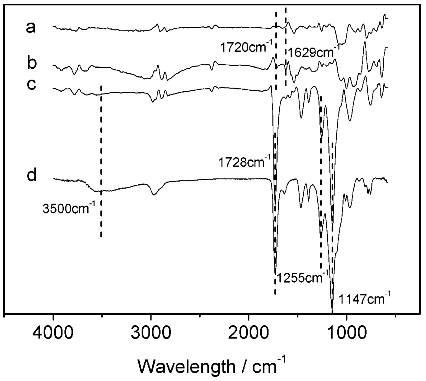


Figure 1. ATR-FTIR spectra of crude MWNTs (a), MWNTs-CH═CH$_2$ (b), MWNTs-MIPs (c), and pure MIPs (d).

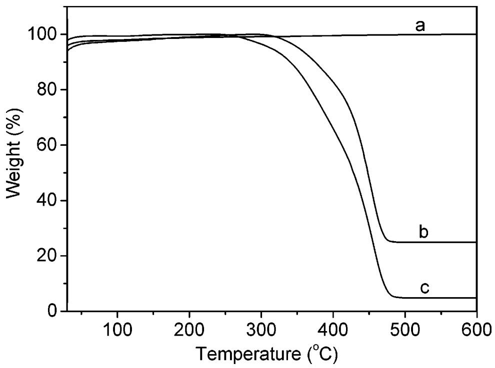


Figure 2. TGA at a heating rate of 20°C min^{-1} from room temperature to 600 °C under a N$_2$ atmosphere for crude MWNTs (a), MWNTs-MIPs1 (b), and pure MIPs (c).

measured by UV−vis at 284 nm. The amount of DA bound to the MWNTs-MIPs was calculated by subtracting the amount of free DA in the supernate from the amount of DA initially added. Similarly, the adsorption dynamics of the MWNTs-MIPs was performed by detecting the free DA concentration in the supernate at the different adsorption time intervals. The selectivity of the MWNTs-MIPs was investigated using EP as the structurally related compound.

Electrochemical Measurements. MWNTs-MIPs1 (20 mg) was dispersed in 1 mL of methanol with ultrasonic for 20 min. The above suspension (4 μL) was dropped on the clean glassy carbon electrode surface and dried at room temperature. And then 10 μL of 1% (w/v) agarose aqueous solution was overlapped on the above electrode surface till the gelling of agarose. The modified electrode was incubated in 1.0 × 10^{-4} mol/L analyte solution. After rinsing with distilled water carefully, the modified electrode was transferred into fresh PBS solution for further electrochemical determination. Cyclic voltammograms were recorded from −0.2 V to +0.8 V for DA and AA with a scan rate of 100 mV/s. The chronoamperometry was employed to detect the concentration of DA.

Results and Discussion

Preparation of MWNTs-MIPs. As to the preparation of the MWNT composites, the good interfacial bonding and interactions between MWNTs and polymers are very important.[4] In the present study, prior to polymerization, the vinyl group was introduced onto the MWNTs surface, which has been previously discovered to interact with acrylate on the surface of solid supports by the covalent bonding.[19] Therefore, vinyl groups on the MWNTs surface could direct selective copolymerization with functional monomers and cross-linkers in the presence of template molecules by radical polymerization[20] and then led to the formation of MIPs on the surface of MWNTs.

The synthetic route of introducing vinyl group and further grafting MIPs onto the MWNTs surface was illustrated in Scheme 1. The crude MWNTs, MWNTs-CH═CH$_2$, MWNTs-MIPs, and pure MIPs were characterized by ATR-FTIR, as shown in Figure 1. The C═O stretch vibration (1720 cm^{-1}), the characteristic carbonyl peak introduced by SOCl$_2$, obviously appeared in the spectrum of MWNT−CH═CH$_2$.[21] The absorbance at 1629 cm^{-1} was assigned to C═C stretch vibration.[22] The results clearly indicated that the vinyl group was successfully introduced onto the MWNTs surface. Besides the characteristic peaks of MWNT−CH═CH$_2$, the pure MIPs characteristic peaks (Figure 1d) also appeared in the spectrum of MWNTs-MIPs, as shown in Figure 1c. The main absorption bands of pure MIPs situating around 3500 cm^{-1}, and 1728, 1255, and 1147 cm^{-1} are assigned to the following vibrations: O−H stretching and C═O stretching vibration of carboxylic, C−O stretching vibration of symmetric and asymmetric ester, respectively.[23] All these adsorption bands suggested the synthesis of MWNTs-MIPs.

On the basis of the different thermal stability between the polymers and MWNTs, the TGA measurements were used to provide evidence regarding the content of grafted MIPs on the surface of MWNTs. Figure 2 showed TGA weight loss curves of crude MWNTs, MWNTs-MIPs1 composites, and pure MIPs, respectively. As shown in Figure 2a, the crude MWNTs are steady without evident weight loss below 600 °C.[6] However, the TGA curve of pure MIPs showed that the polymer was stable to 280 °C, upon which the product degraded, but it became stable above 480 °C. Similarly, the MWNTs-MIPs1 appeared to have a weight loss between 280 °C and 480 °C. The difference in the weight loss in this range between MWNTs-MIPs1 and crude MWNTs indicated that the MIPs grafted to about 75% amount of the total weight of the synthesized MWNTs-MIPs1.

The morphological structure of MWNTs-MIPs was detected by TEM and SEM as shown in Figure 3. The average thickness of wall and length of the crude MWNTs were about 20 nm and several micrometers, respectively. The MWNTs were coated drastically with homogeneous even polymer (Figure 3 B). The average thickness of the MIPs layer of MWNTs-MIPs1 was about 15−20 nm. The thickness of polymer layer increased with the increase in the concentration of the prepolymerization monomers. When the concentration of the monomer and cross linker were increased to four times, the thickness of the polymers layer increased to about 30 nm, as illustrated in Figure 3C. Ungrafted white polymers were also produced during the polymerization and were thoroughly washed out with ethanol. Meanwhile, we also found that MWNTs-MIPs2 became grayer than MWNTs-MIPs1 due to the incrassation of polymer layer. For comparison, the polymerization was carried out by replacing functionalized MWNTs with crude MWNTs. As a result, no polymer shell coating on the MWNTs surface was found, which indicated that the unfunctionalized MWNTs could not be grafted with polymers.[6] When comparing the SEM images of crude MWNTs (Figure 3D), MWNTs-MIPs1 (Figure 3E), and MWNTs-MIPs2 (Figure 3F), there was an increase in the diameter of MWNTs-MIPs1 or MWNTs-MIPs2 as the result of composites formation. It was obvious that an elongated nanotube-like core structures stuck out of the outer polymers shell as illustrated in the insert of Figure 3F.

Dispersion of crude MWNTs in water or other organic solvent is difficult. After 10 mg of crude MWNTs or MWNTs-MIPs1

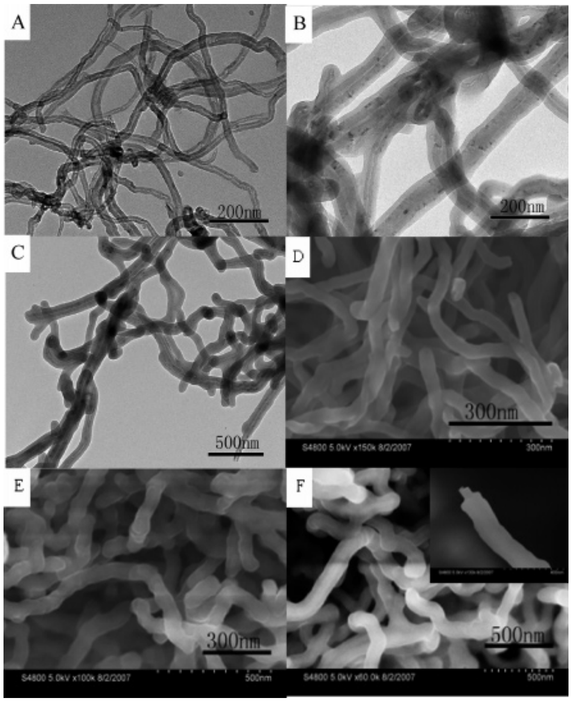


Figure 3. TEM of MWNTs (A), MWNTs-MIPs1 (B), and MWNTs-MIPs2 (C); SEM of MWNTs (D), MWNTs-MIPs1 (E), and MWNTs-MIPs2 (F).

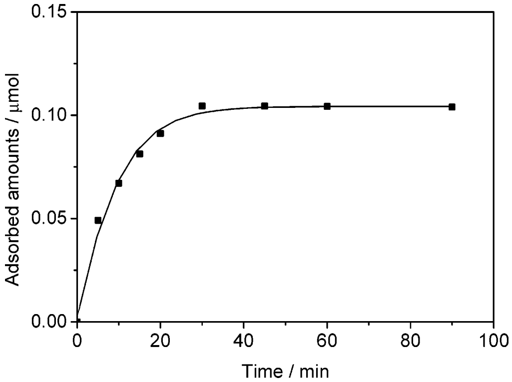


Figure 4. Curve of adsorption dynamics of DA to MWNTs-MIPs1. Amount of polymer, 5 mg; volume, 2.0 mL; initial concentration of DA, 0.2 mmol/L.

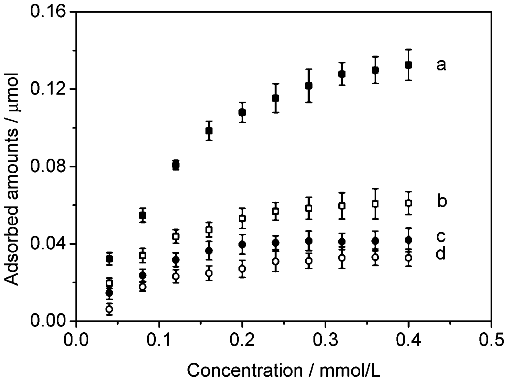


Figure 5. Adsorption isotherms of DA on MWNTs-MIPs1 (a), DA on MWNTs-NIPs (b), EP on MWNTs-MIPs1 (c), and EP on MWNTs-NIPs (d). Amount of polymer, 5 mg; volume, 2.0 mL; binding time, 1.5 h.

with 5 mL of water or acetonitrile as solvent was sonicated for 30 min, the obtained suspension was subsided for 48 h. The crude MWNTs were insoluble in water or acetonitrile due to much sedimentation of MWNTs at the bottom of the vial. On the contrary, MWNTs-MIPs1 was soluble in either water or acetonitrile, forming a homogeneous suspension without observed sedimentation. The result indicated that the modification of MIPs onto MWNTs surface could improve the solubility of MWNTs in water or acetonitrile.

Adsorption Characterizations of MWNTs-MIPs. The adsorption kinetics of DA was investigated by changing the adsorption time from 5 to 90 min, and the initial concentration of DA was kept constant at 0.2 mmol/L. A fitted curve using a sigmoid curve of the dynamic adsorption was presented in Figure 4. This is the typical kinetic curve for most rebinding processes. In the early 10 min, the adsorption capacity increased quickly, but after 30 min, the adsorption almost reached equilibrium, revealing a rapid dynamic adsorption of DA molecules to the MWNTs-MIPs1. The fast adsorption can be attributed to most of the imprinted cavities situated in the surface and approximately to the surface of outer MIPs shell, which make the recognition sites accessible for the template molecules and thus take shorter time to gain adsorption equilibrium.

As one of the artificial receipted materials, the key property of the MIPs is its capability of special adsorption and selective recognition for template molecule, which is based on the imprinted cavities in complement to the size, shape, and functionality of the template molecule. The binding of DA to MWNTs-MIPs1 was compared with MWNTs-NIPs of DA concentration in the range of 0.04−0.4 mmol/L. The higher binding capacity of the MWNTs-MIPs1 (Figure 5a) over the MWNTs-NIPs (Figure 5b) indicated that the MWNTs-MIPs1 have a specific binding capacity for the template molecule.

The selectivity experiments were carried out by using EP as the similar compound of DA in the binding process. Parts c and d of Figure 5 showed the binding isotherms of EP to MWNTs-MIPs1 and MWNTs-NIPs. The binding capacity toward EP was also much lower than that of DA, which confirmed that the MWNTs-MIPs1 have a good selectivity for recognition of DA. The selective recognition for DA of MWNTs-MIPs1 may be attributed to the shape selective fitting of DA into complementary cavities created in the MWNTs-MIPs1 during the imprinting procedure.

Electrochemical Measurements. Determination of DA has received considerable interests in a wide range, especially in electrochemistry because it plays a very important role in the function of the central nervous, hormonal, and cardiovascular systems. It was widely admitted that a major problem encountered with the electrochemical detection of DA is the interference from AA, which largely coexists with DA in brain tissue. Both of them have an overlapping oxidation potential on the solid electrodes.[24] In our experiments, an electrochemical sensor was fabricated by modifying the prepared MWNTs-MIPs1 on the glassy carbon electrode surface. The modified electrode was used to record the redox curves by CV in fresh PBS solution after the modified electrode was incubated in 1.0×10^{-4} mol/L AA or 1.0×10^{-4} mol/L DA or mixed solution of 1.0×10^{-4} mol/L DA and 1.0×10^{-4} mol/L AA, as shown in parts a−c of Figure 6. The modified electrode showed the negligible current for AA. In contrast, a typical redox peak for DA was found, indicating DA could be detected in the present of AA. pKa of AA is 4.10, and ζ-potential of MWNTs-MIPs1 was determined to be −30.63 mV in pure aqueous, which means that the MWNTs-MIPs1 and AA are both negatively charged in pH 7.0 PBS solution. As a result, electrostatic exclusion exists between MWNTs-MIPs and AA, which may be the main reason

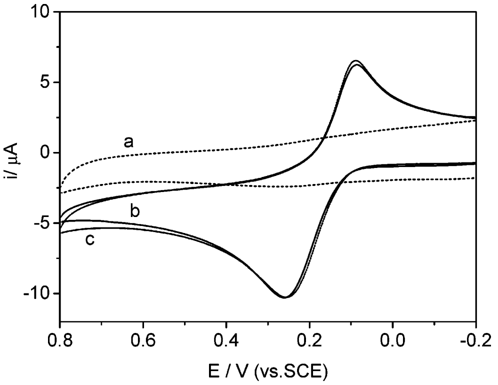


Figure 6. Cyclic voltammograms of modified electrode in fresh PBS buffer solution after the modified electrodes were incubated in 1.0 × 10^{-4} mol/L AA (a), 1.0 × 10^{-4} mol/L DA (b), and mixed solution of 1.0 × 10^{-4} mol/L DA and 1.0 × 10^{-4} mol/L AA (c) for 10 min.

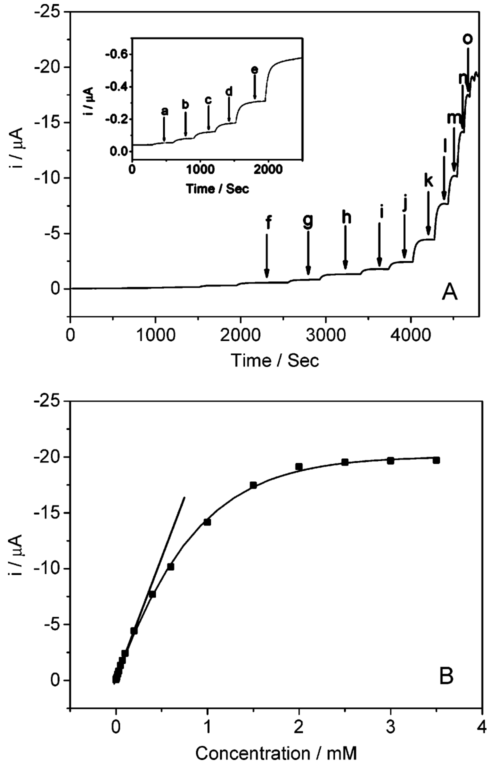


Figure 7. Typical current response curve at MWNTs-MIPs1 modified glassy carbon electrode with addition of increasing concentration of DA in PBS. Applied potential: +0.3V (A) and valibration curve for DA obtained by $I-T$ curve (B). Concentration of DA: 5.0 × 10^{-7} (a), 1.5 × 10^{-6} (b), 3.0 × 10^{-6} (c), 5.0 × 10^{-6} (d), 1.0 × 10^{-5} (e), 2.0 × 10^{-5} (f), 3.0 × 10^{-5} (g), 5.0 × 10^{-5} (h), 7.0 × 10^{-5} (i), 1.0 × 10^{-4} (j), 2.0 × 10^{-4} (k), 4.0 × 10^{-4} (l), 6.0 × 10^{-4} (m), 1.0 × 10^{-3} (n), and 1.5 × 10^{-3} mol/ L (o).

that the MWNTs-MIPs1 modified electrode could detect DA in the presence of AA.[25] The negligible change of current intensity between curves b and c further confirmed this result. To a certain degree, this discrimination is important in bioanalytical applications, which provide another feasible approach for determining DA in the presence of a large excess of AA.[26]

Compared to a bare glassy carbon electrode, the remarkable enrichment of DA at MWNTs-MIPs1 modified electrode was obviously observed. The current obtained by the differential pulse voltammetry method was 1.765, 3.474, 5.109, and 5.085 × 10^{-6} A, which was detected in fresh PBS solution after the modified electrode was incubated in 1.0 × 10^{-4} mol/L DA solution for 2, 5, 10, and 20 min, respectively. To the contrary, the current was only 0.109 × 10^{-6} A after the bare electrode was incubated in DA solution for 20 min. The results indicated that DA could be enriched onto the modified electrode compared to bare electrode.

Chronoamperometry was employed to determine DA. An amperometric response was shown in Figure 7A. Figure 7B illustrated the corresponding plot showing a linear relation between current response and DA concentration in the range of 5.0 × 10^{-7} to 2.0 × 10^{-4} mol/L with a correlation coefficient $r = 0.998$. The result also showed that DA could be enriched by the MWNTs-MIPs1 on the modified electrode surface, thus increasing the sensitivity of the modified electrode.[27]

Conclusions

A novel MWNT composite with homogeneous MIP outer layer about 15−20 nm for selective recognition of DA was synthesized. For grafting MIPs on MWNTs, the vinyl group was first introduced on the surface of MWNTs, which directed the selective polymerization of functional monomers and cross linkers in the presence of DA on the MWNTs surface. The thickness of the MIPs can be adjusted by changing the concentration of prepolymerization monomers. The resulting MWNTs-MIPs possessed a faster adsorption dynamics, higher selectivity for DA. The modified electrode fabricated by modifying the MWNTs-MIPs on the glassy carbon electrode can recognize DA in presence of AA. Furthermore, the modified electrode can also be used to determinate the concentration of DA with a linear range from 5.0 × 10^{-7} to 2.0 × 10^{-4} mol/L.

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