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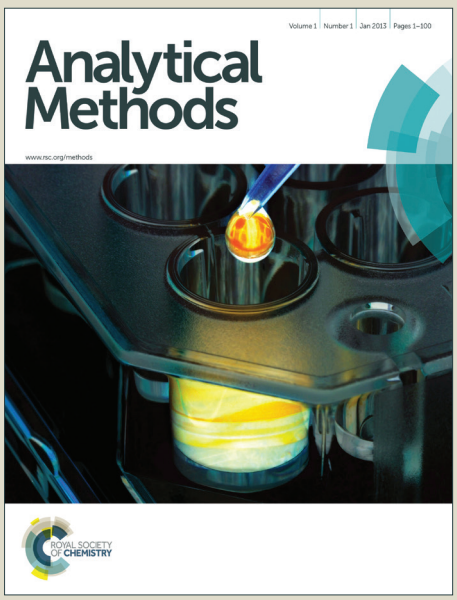

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Interface structure and electrochemical sensing properties of nitrogen-doped diamond like carbon film electrode modified with platinum nanoparticles and 4-aminobenzoic acid

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Abstract

Platinum nanoparticles (PtNPs) and 4-aminobenzoic acid (4-ABA) were applied to modify nitrogen-doped diamond like carbon (N:DLC) film electrode by electrodeposition and cyclic voltammetry. The bare, PtNPs-, 4-ABA-, 4-ABA/PtNPs alternately-modified N:DLC film electrodes were obtained, respectively. Various analysis technologies, such as atomic force microscopy, X-ray photoelectron spectroscopy and micro-Raman spectroscopy, have been used to study surface morphology, chemical composition and bonding structure of the film electrodes. Linear sweep voltammetry and electrochemical impedance spectroscopy were performed to study the relationship between interface structure of chemically modified N:DLC film electrodes and electrochemical sensing properties toward hydrazine sulfate. Acquired results indicate that the different outermost layer modified by 4-ABA or PtNPs behaved differently.

Keywords: Interface structure; electrochemical sensing properties; nitrogen-doped diamond like carbon film; platinum nanoparticles; 4-aminobenzoic acid

1. Introduction

Over the years, detection of biological molecules and improvement of electrochemical sensing interface exert a tremendous fascination on researchers in analytical chemistry filed. Hydrazine sulfate is a sort of cancerogenic compound,[1–3] not only do it harm the health of people who touch it directly or indirectly, but also pollute the environment. When hydrazine sulfate is mixed with air to a certain proportion, it even can trigger explosion. Therefore it is crucial to seek an appropriate method to determine its content accurately. Analytical techniques include ion

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chromatograph, gas chromatography-mass spectrometry, high performance liquid chromatography, fluorescence detection, colorimetric, capillary electrophoresis and electrochemical methods.[4–15] Among them, electrochemical method is favored by a host of researchers due to its fast response, low cost, high sensitivity, simple operation and excellent reproducibility.

As we all know, pure diamond itself is nonconductive. Electric insulativity makes its application being limited in electrochemistry. As always, researchers mainly tried to optimize existing method to produce a sort of amorphous carbon with significant sp^3 bonding, which was firstly named diamond like carbon (DLC) by Aisenberg and Chabot.[16] DLC films not only inherit the excellent properties of diamond, but also own a series of advantages such as favorable optical performance, good chemical resistance, and biological compatibility.[17–20] However, DLC is a semiconductor which has a band gap. In order to develop the electrical conductivity of DLC, the concept of doping metals or nonmetals was investigated quite intensively in recent years. Nitrogen-doped DLC (N:DLC) is one of the nonmetal-doped DLC films. Due to its admirable quality, N:DLC films have been applied in a wide field of mechanical, optical, electronics and electroanalysis.[21–25] As the electrode material, N:DLC films possess quite a few quintessential virtues with a wide electrochemical potential window, low background current and good electrochemical sensing behavior.[26–28] What's more, its production condition is comparably mild comparing to those of highly boron-doped diamond (BDD).[30,31]

In this work, the PtNPs, 4-aminobenzoic acid (4-ABA) and 4-ABA/PtNPs alternately-modified N:DLC film electrodes were employed to detect hydrazine sulfate, respectively. The physical and chemical properties related to the surface of bare and modified N:DLC films were characterized by atomic force microscopy (AFM), electrochemical impedance spectroscopy (EIS), X-ray photoelectron spectroscopy (XPS), micro-Raman spectroscopy and electrochemical measurements.

2. Experimental

2.1 Materials

4-ABA, $H_2PtCl_6 \cdot 6H_2O$ and hydrazine sulfate were obtained from Sigma-Aldrich

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and used as received. N:DLC was obtained from RiteDia Corporation. All solutions were made from analytical grade chemicals and Milli-Q ultrapure water (18.25 MΩ cm). The buffer solution of pH 7.0 was prepared from Na_2HPO_4 and NaH_2PO_4 containing 0.1 M KCl as supporting electrolytes.

2.2 Instrumentation

Electrochemical workstation (CHI852C, Shanghai CH Instruments, China) equipped with a personal computer was used for electrochemical measurements and treating data. The surface morphology of the bare and modified N:DLC films was investigated by AFM (Digital InstrumentsS-3000, Veeco, USA). The EIS was performed with an advanced electrochemical system (PARSTAT 2273, Ametek, America) at room temperature. The bonding structure and chemical composition of the films were measured by XPS (Kratos Axis Ultra, England) with a monochromatic Al Kα X-ray radiation (hυ 1486.71 eV). The bond structure of the films was also detected through micro-Raman spectroscopy (RW1000, Renishaw, England) with a He-Ne (632 nm) laser over the range of 800–2000 cm^{-1}. The conventional three-electrode system was used throughout. A bare or a modified N:DLC film was served as the working electrode, a twisted platinum wire as the auxiliary electrode and an Ag/AgCl electrode (KCl saturated) as the reference electrode. All electrode potentials were reported with respected to Ag/AgCl electrode in this paper.

2.3 Electrodes preparation

A variety of deposition methods (chemical or physical deposition, ion-sputtering, cathodic arc et al) were used to produce N:DLC films.[17, 33] The preparation process of N:DLC thin films used in this work can be described as the following. Employing a pure graphite target (99.95% C) as the carbon source, N:DLC thin films were deposited on conductive n-Si (100) substrates (0.001–0.0035 Ω cm) through a filtered cathodic vacuum arc deposition process. To remove oxide layers and impurities of surface, the Si substrates were etched by pure Ar plasma when the pressure of the vacuum chamber was lowered to ca 2×10^{-6} Torr. During deposition, 10-sccm nitrogen (99.999%) was continuously introduced into the vacuum chamber and an arc was ignited by contacting the graphite anode against the graphite target (cathode), thus

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producing mixed plasma of carbon and nitrogen passing through a double-bend off-plane filter and leading to a N:DLC film deposited on the substrate. A fixed-pulse voltage of 800 V was performed throughout all the depositions. By means of controlling the deposition time, the N:DLC films with a thickness of 100 nm were obtained.[32–35]

PtNPs-, 4-ABA- and 4-ABA/PtNPs alternately-modified N:DLC film electrodes were obtained by electrochemical deposition and cyclic voltammetry. PtNPs was electrodeposited on GCE by a potentiostatic process at –0.2 V for 360 s in 0.1 M H_2SO_4 aqueous solution containing 1 mM H_2PtCl_6. 4-ABA/N:DLC film electrode was produced in 0.1 M KCl aqueous solution containing 5 mM 4-ABA via cyclic voltammetry. The potential was set from 0.5 to 1.2 V at 100 mV s^{-1} for 5 cycles.

2.4 Procedure for electrochemical detecting hydrazine sulfate

The bare or modified N:DLC film electrodes were used to sense hydrazine sulfate. A 0.1 M Na_2HPO_4-NaH_2PO_4 aqueous solution (4 mL) containing a specific amount of hydrazine sulfate of 10 mM was added to the electrochemical cell. The linear sweep voltammograms of hydrazine sulfate on the electrodes were recorded in the potential from 0.0 to 1.0 V at a scan rate of 100 mV s^{-1}.

3. Results and discussion

3.1 Electrode modification and characterization

Fig. 1 shows modification process of PtNPs and 4-ABA on N:DLC films. In Fig. 1A, when the deposition time is about 100 s, the current almost maintains steady, this indicates the formation of PtNPs layer on GCE. The deposition time of 360 s is enough to get a stable PtNPs/N:DLC film electrode. The cyclic voltammograms of 4-ABA on N:DLC film was shown in Fig. 1B. There is an irreversible oxidation peak at about 1.05 V in the first cycle; this oxidation peak disappears with the increasing of scan cycles. This manifests that the surface of N:DLC has been modified by the 4-ABA layer.[36] Combing electrochemical deposition with cyclic voltammetry, the 4-ABA/PtNPs alternately-modified N:DLC film electrode also can be prepared successfully.

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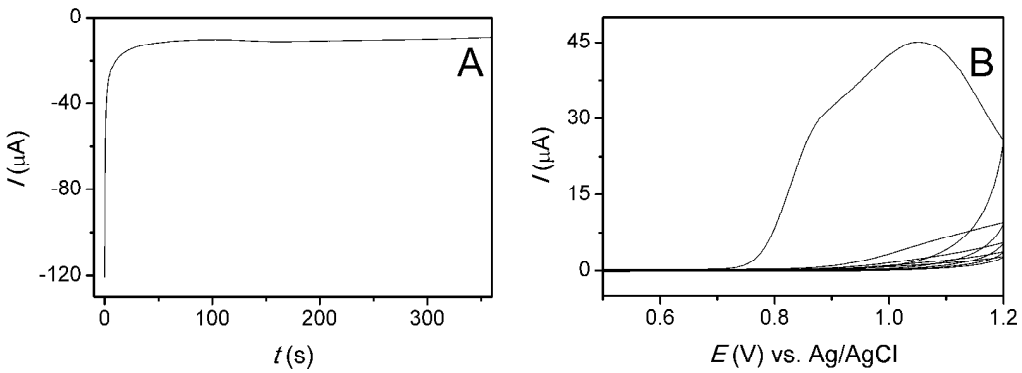

Fig. 1. The modification process of PtNPs (A) and 4-ABA (B) on N:DLC films.

The surface morphology of the bare and modified N:DLC films were investigated by AFM using a Si_3N_4 cantilever which was operated in a tapping mode with a scan size of 5 μm × 5 μm. An average surface roughness value was taken by measuring five times on each sample. The root-mean-square (RMS) roughness of the bare (A), 4-ABA- (B), PtNPs- (C), 4-ABA/PtNPs (D) alternately-modified N:DLC films are 0.68, 1.71, 87.34 and 59.61 nm, respectively. Fig. 2A shows that the AFM images of the bare N:DLC film, which is presented as a woolen carpet.[37] After 4-ABA was decorated, the woolen carpet was transformed to ice falls, as revealed in Fig. 2B. Fig. 2C displays that the N:DLC coated by PtNPs, which looks like the stone forests. Discovered through comparative analysis, the surface coverage of PtNPs-modified N:DLC film is not as compact as the N:DLC film modified by 4-ABA. The last one showed in Fig. 2D seems like a cauliflower. It was modified by 4-ABA and PtNPs alternately and possessed the surface property of the both.[38]

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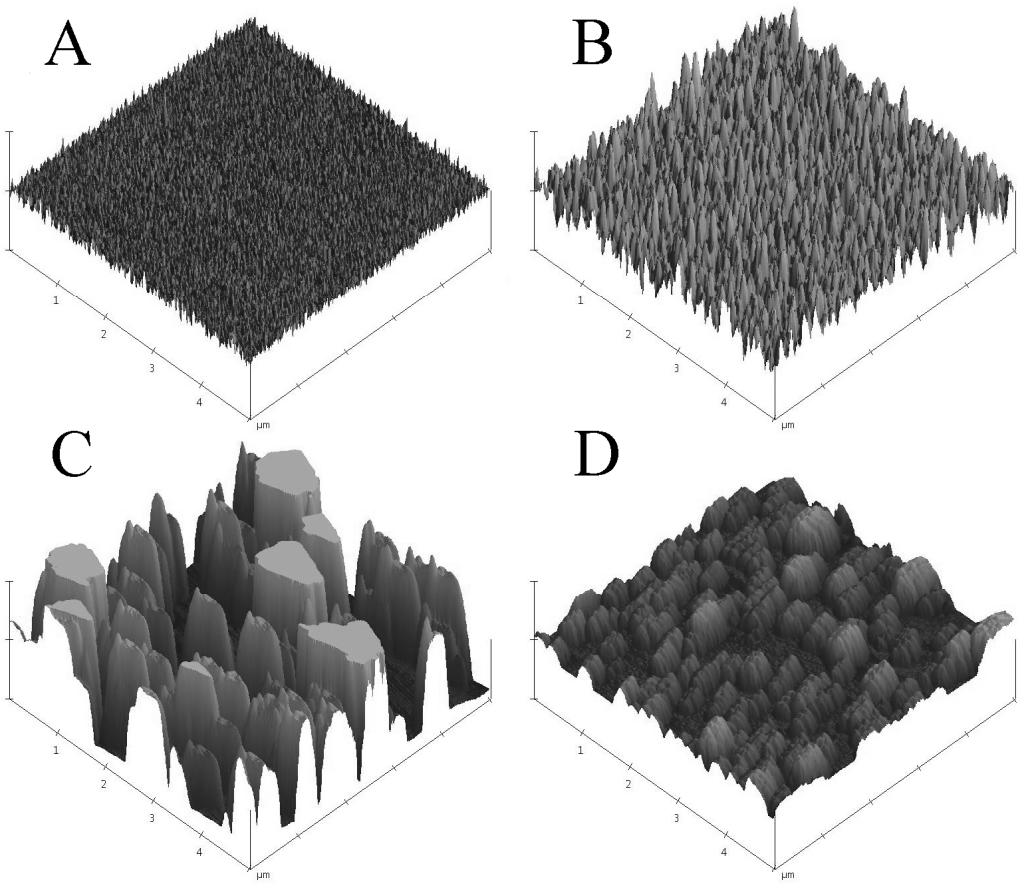

Fig. 2. AFM images of the bare N:DLC (A), 4-ABA-modified N:DLC (B), PtNPs-modified N:DLC (C), 4-ABA/PtNPs alternately-modified N:DLC (D).

XPS is an effective and non-destructive technique to investigate the chemical composition and structure of carbon materials. In this work, a wide scan range from 0 eV to 1200 eV was employed. An overview of all elements was provided by the binding energy of bare and modified N:DLC film. Fig. 3 exhibits the determination signals deprived from the elements of O, C, N and Pt. From Fig. 3A it can be seen that the peak of O 1s is at around 531.3 eV which was attributed to the oxidation of the N:DLC film surface.[39] Fig. 3B demonstrates that the peaks of C 1s, N–N sp^2 and sp^3 approximately appeared at 284.6 eV, 284.5 eV and 286.2 eV, respectively. The peak at about 287.3 eV certificated the formation of C–N bonding. Fig. 3C reveals that the N 1s, N–N sp^2 and sp^3, and N–O peaks are separately at 390.4 eV, 390.2 eV, 400.0 eV and 402.2 eV.[40] In Fig. 3D, the characteristic peaks at about 75.9 eV and 72.3 eV manifest the presence of Pt $4f_{5/2}$ and Pt $4f_{7/2}$. It also can be seen that the Pt^0 and Pt^{4+} of

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Pt 4f components were located at cal 72.1 eV and 73.7 eV, respectively. The existence of such elements characterize the structure of the bare N:DLC and N:DLC modified by PtNPs.

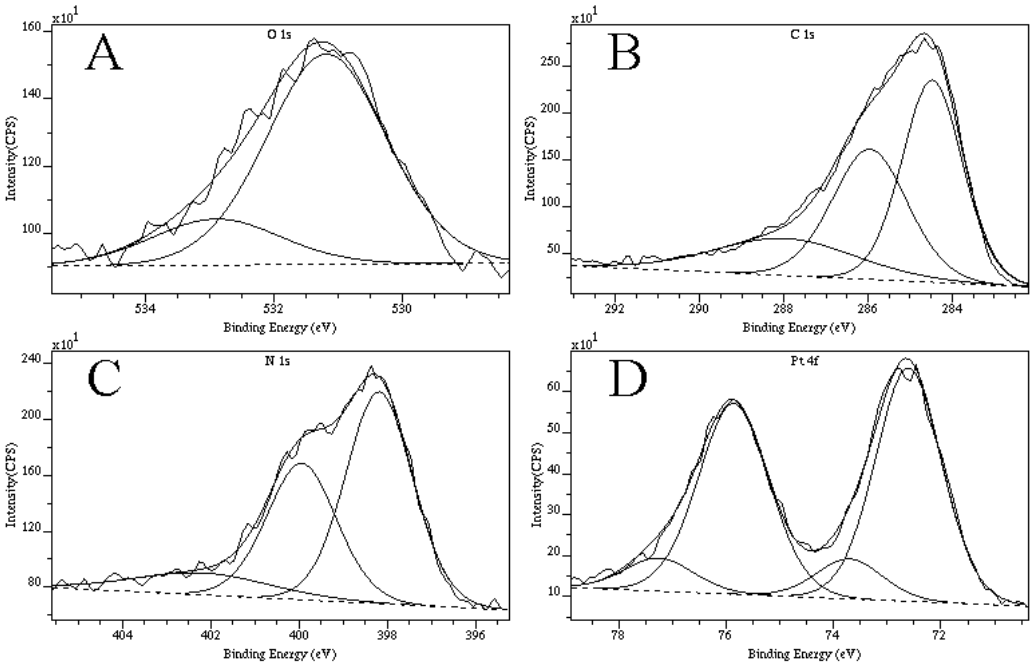

Fig. 3. XPS results of O 1s (A), C 1s (B) and N 1s (C) peaks of the N:DLC film, Pt 4f (D) peak of Pt_{400}/N:DLC films.

With regard to the measurement of defects and disordered structures, Raman spectroscopy is the most efficient technology. Fig. 4 presents the micro-Raman spectrum of the N:DLC film, which displays the G band and D band in N:DLC film. The G and D bands represent stretching vibration in-plane of the graphitic sp^2-based carbon and the lattice defects of carbon atom. The peaks of the G and D bands are located at 1563 cm^{-1} and 1380 cm^{-1}, respectively.[41] The intensity of the I_D/I_G ratio is about 1.48, this value indicates that the carbon atom of sp^2 hybridization is higher than that of sp^3 hybridization. And the higher the I_D/I_G ratio is, the more the lattice defects exist.[42]

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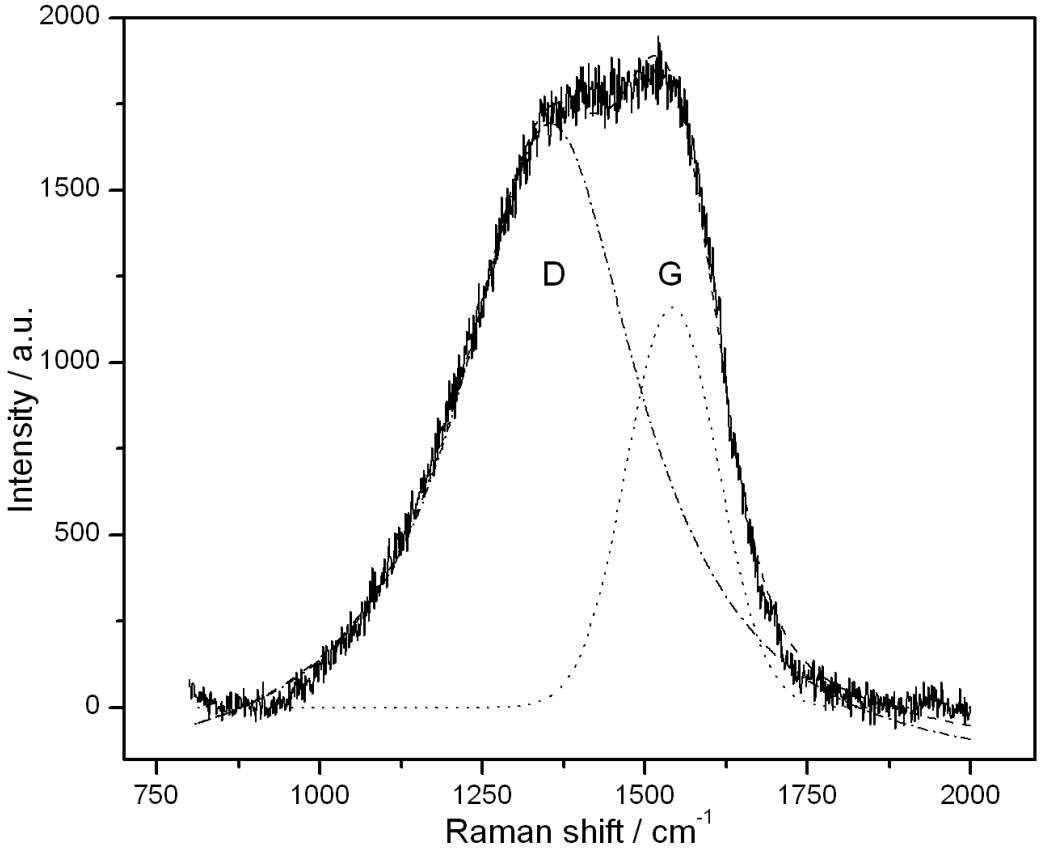

Fig. 4. The micro-Raman spectrum of the N:DLC film

Fig. 5 shows that the impedance diagrams of the bare and modified N:DLC films. The left column of Fig. 5 displays that the PtNPs as outermost layer were modified on N:DLC film, while the right column represents the outermost layer was grafted by 4-ABA. On the whole, the radius of first semicircle is bigger, but the second is smaller with increasing the layer numbers in the left column. The first semicircle is controlled by the polarization resistance, which is also called intramembranous resistance.[43] The second semicircle is attributed to the resistance related to the redox reaction of probes. Fig. 6 shows the relationship between the resistance and layer numbers of 4-ABA/N:DLC (A) and PtNPs/N:DLC (B). With the layer numbers increasing, the intramembranous resistance was growing. The conclusion is also in accordance with the resistance of redox reaction in right column. The variation trend of the resistance is decreasing at first, and then increasing, finally decreasing. The resistance seems unlike owing to its different conductivity. As a sort of metal NPs, PtNPs possess excellent conductivity. The conductivity of N:DLC modified by

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4-ABA is other than that by PtNPs. A conclusion can be made that when the N:DLC was alternately coated by PtNPs and 4-ABA, the impedance performance of the modified N:DLC film was controlled by the outermost layer. This result is also suitable for 4-ABA/N:DLC film electrodes. With the increasing of the layer numbers, the electron-transfer resistance is enlarging. It implies that the solid electrolyte interphase layer is more and more stable.

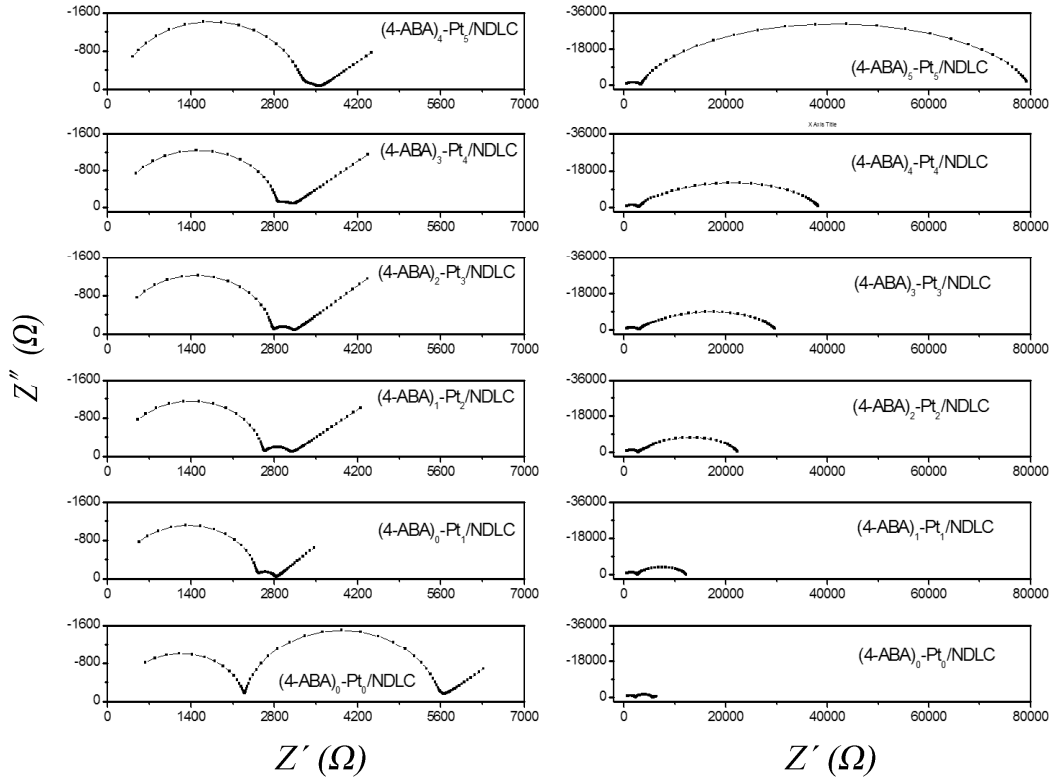

Fig. 5. The Nyquist plots of the bare N:DLC film and N:DLC alternately coated by PtNPs and 4-ABA with different layer numbers (the number in the right bottom corner of modifiers represents the layer numbers) in 0.1 M KCl solution containing 5 mM $Fe(CN)^{3-/4-}$.

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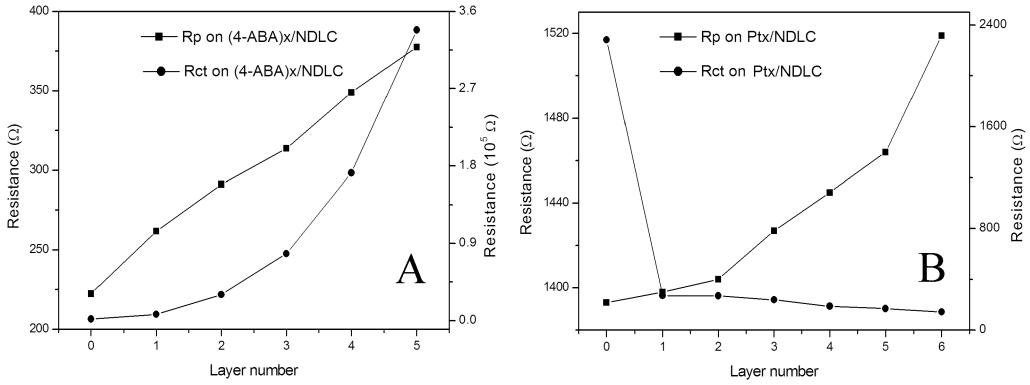

Fig. 6. The relationship between the resistance and layer numbers of 4-ABA/N:DLC (A) and PtNPs/N:DLC (B).

3.2 Electrochemical sensing properties of the electrodes

Different electrochemical sensing properties were controlled by different geometric and electronic structures of surface.[44–46] Fig. 7 shows linear sweep voltammograms of the bare, PtNPs-, 4-ABA-, 4-ABA/Pt alternately-modified N:DLC films in different concentrations of $N_2H_4 \cdot H_2SO_4$ at a scan rate of 100 mV s^{-1}. From Fig. 7A it can be seen that the currents are increasing with adding $N_2H_4 \cdot H_2SO_4$ successively. While the electrode which was modified by PtNPs behaved differently from the bare N:DLC electrode. Its current response is too little to recognize. That is because the PtNPs-modified N:DLC looks like a stone forest, its effective surface area called active sites is less. Therefore its sensing performance was not satisfied. From Figs. 7C and D we can see that there are two peaks enlarging as the increasing of the $N_2H_4 \cdot H_2SO_4$ concentration. However the heights of the left peak at around 0.72 V and the right at about 0.84 V are diverse. The height of the left peak at around 0.72 V is higher than the right at about 0.84 V, as shown in Fig. 7C, but the phenomenon in Fig. 7D is exactly opposite. Obtained results prove that 4-ABA/PtNPs alternately-modified N:DLC films possess an outstanding property of both the 4-ABA/N:DLC and PtNPs/N:DLC film electrodes for sensing $N_2H_4 \cdot H_2SO_4$, therefore the peak at around 0.84 V was attributed to the mutual detection of the PtNPs and 4-ABA. From Figs. 7C and D it can be seen that there are two background peaks respectively at 0.2 V and 0.8 V without adding $N_2H_4 \cdot H_2SO_4$. The peaks are attributed to the modified layer itself which was oxidized in buffer solution. When a certain concentration of $N_2H_4 \cdot H_2SO_4$

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was added in the electrochemical cell, the environment of detection was also changed. Consequently background current was decreasing and disappeared finally. With a continued addition of $N_2H_4 \cdot H_2SO_4$, the electrochemical signal was enhancing.

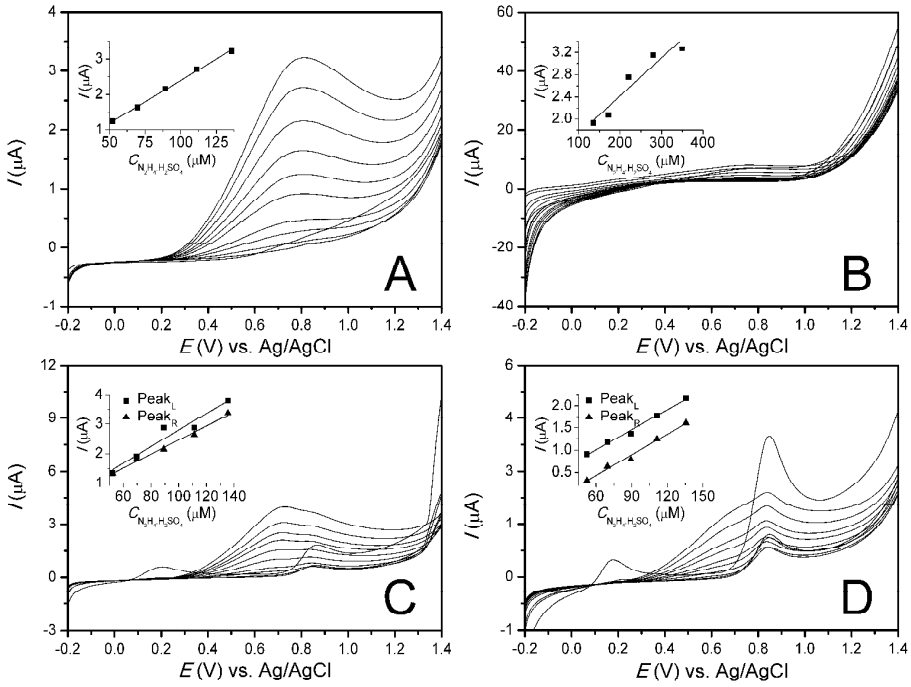

Fig. 7. Linear sweep voltammograms of the bare (A), PtNPs- (B), 4-ABA- (C), 4-ABA/PtNPs (D) alternately-modified N:DLC films in different concentrations of $N_2H_4 \cdot H_2SO_4$ at a scan rate of 100 mV s^{-1}.

Table 1. The parameter of the linear regression equation for the electrodes

Parameters / Electrodes		*k* (μA/μM)	*b* (μA)	*R*	LOD (μM)	Liner range
Bare N:DLC		0.0240	–0.0054	0.9976	7.6636	15μM–0.35mM
PtNPs/N:DLC		0.00682	1.0557	0.8820	125.787	110μM–0.35mM
4-ABA/N:DLC	P_L	0.0278	0.0044	0.9211	4.6064	15μM–0.35mM
	P_R	0.0236	0.1034	0.9891	65.6562	25μM–0.35mM
4-ABA-PtNPs/N:DLC	P_L	0.0151	0.0994	0.9893	16.5554	25μM–0.35mM
	P_R	0.0154	–0.4882	0.9825	39.7442	37μM–0.35mM

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The data shows that the correlations of the linear regression equation related to the bare N:DLC, 4-ABA/N:DLC and 4-ABA/PtNPs alternately-modified N:DLC are very good. This indicates that the 4-ABA/PtNPs alternately-modified N:DLC film is other than PtNPs/N:DLC, which possess very stable electrochemical sensing properties toward $N_2H_4 \cdot H_2SO_4$ in neutral solution. In addition, the limit of detection (LOD) of $N_2H_4 \cdot H_2SO_4$ on the bare and modified N:DLC electrodes was also calculated according to 3σ method[47]

$$\mathrm{LOD} = \frac{3s_{\mathrm{bl}}}{k} = 3\sigma \qquad (1)$$

where s_{bl} is the standard deviation of the peak currents of the blank (n = 5), and k is the slope of the calibration curve as shown in Table 1.

4. Conclusion

In this work, the 4-ABA-, PtNPs- and 4-ABA/PtNPs alternately-modified N:DLC electrodes were successfully prepared via a simple electrochemical deposition and oxidation method. Various characterizations and electrochemical measurements show that different film structure strongly affect the sensing performance for electrooxidizing $N_2H_4 \cdot H_2SO_4$. Consequently, the special property for detecting $N_2H_4 \cdot H_2SO_4$ can be realized through the construction of composite structure. Further optimization of the work will continue to be investigated by our group.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Nos. 21005008 and 51374040); SRF for ROCS, SEM (No. 20111568-2); High-level Innovation and Entrepreneurship Talent Program, Jilin Province of China; and the Scientific and Technical Innovation and Entrepreneurship Project for Returned Overseas Chinese Scholars, Jilin Province of China (No. 201129).

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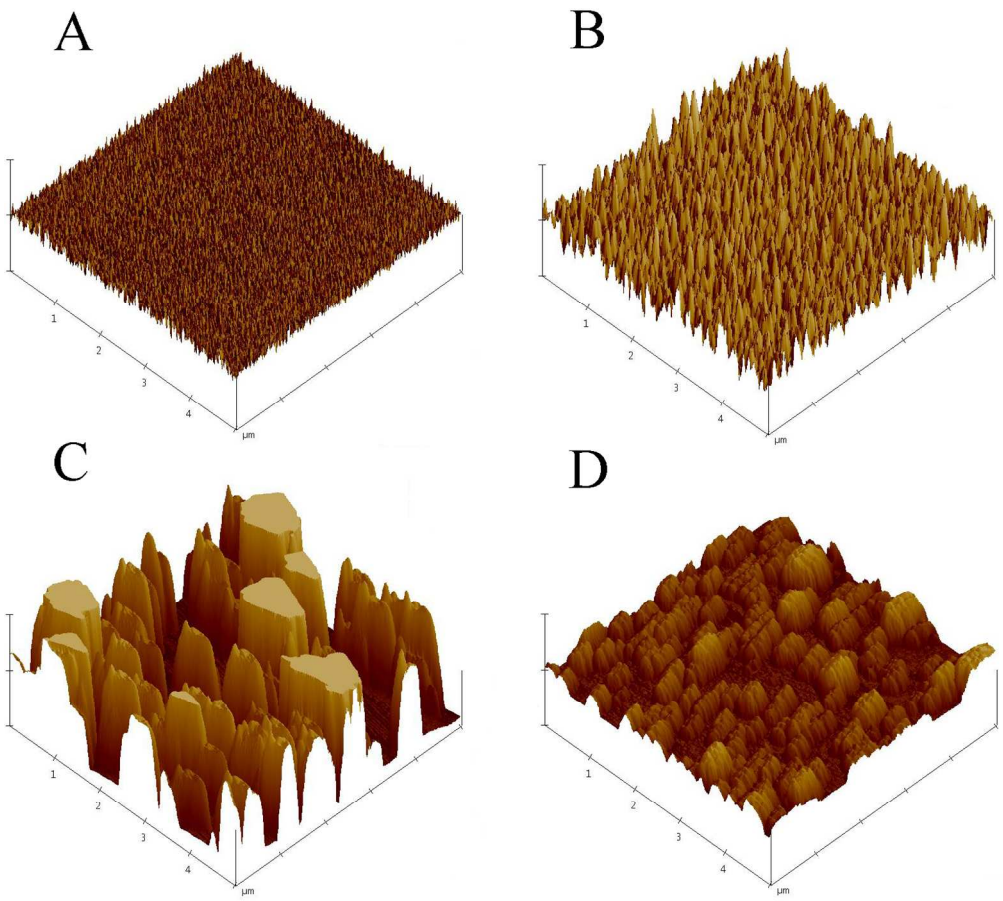

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