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Electrostatic assembly of polyaniline and platinum-poly(amidoamine) dendrimers hybrid nanocomposite multilayer, and its electrocatalysis towards CO and O₂

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Abstract
The electrostatic layer-by-layer assembly method was successfully used in a multilayer buildup of polyaniline (PANI) and platinum nanocrystals encapsulated in the carboxyl-terminated poly(amidoamine) dendrimers (generation 4.5 G₄.5COOH) (Pt-G₄.5COOH NPs) on solid substrates. Multilayer growth was monitored by ultraviolet–visible (UV–vis) absorption spectroscopy. The AFM observation revealed a molecularly smooth (PANI/Pt-G₄.5COOH NPs)m multilayer film which is rougher and thicker than the multilayer of PANI and G₄.5COOH (G₄.5COOH/PANI)m. The PANI/Pt-G₄.5COOH NPs multilayers show a fast surface-confined electron-exchange process at the Au electrode in an acid solution, and remains stable, reversible and electroactive, even in neutral solution. Furthermore, the multilayers show a strong electrocatalytic response towards CO oxidation and O₂ reduction, and the catalytic capability can be easily tuned by the control of multilayer thickness.

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1. Introduction
Polyaniline (PANI), as one of the most important conducting polymers, has been intensively investigated for many years. It is derived mainly from its promising applications in sensors [1–5], electrochromic materials [6,7], photovoltaic devices [8], rechargeable battery [9], etc. In general, electropolymerization [10] and spinning/dip-casting methods [11,12] are used to fabricate PANI films. Recently, an alternative and innovative approach is the electrostatic layer-by-layer (LbL) assembly technique, which has been originally introduced by Decher [13] and applied widely in the preparation of controlled and defined multilayers. Based upon this method, PANI multilayers can be prepared by the alternative deposition of PANI and anionic polymers [14–18], or anionized nanostructures [17–22,7]. These PANI films are normally quite stable, and show a good redox activity, even in neutral solution [18–20].

Poly(amidoamine) (PAMAM) dendrimer is a three-dimensional and highly branched polymer with a well-defined size and shape. It has been utilized as a nanoscale template/stabilizer/container in the synthesis and stabilization of inorganic clusters including zero-valent metal clusters by reacting pre-organized reactants in the dendrimer interior [23,24]. On the other hand, PAMAM dendrimer has a great deal of surface groups with tunable charges. It has been widely used in the preparation of PAMAM...
monolayers and multilayers based upon the electrostatic interaction [25–35].

To date, there are few reports concerning the preparation of conducting polymer multilayers with PAMAM dendrimer [25]. In this work, we reported a novel electroactive conducting polymer multilayer deposited by the electrostatic layer-by-layer assembly. Herein, PANI served as the polycation and 4.5 generation carboxyl-terminated poly(amidoamine) (G4.5COOH), which had encapsulated platinum nanoparticles (Pt-G4.5COOH NPs, as illustrated in Scheme 1), as the polyanion. The growth was monitored by Ultraviolet–visible absorption spectroscopy (UV–vis) and cyclic voltammetry. The surface morphology of the multilayer has been examined by atomic force microscopy (AFM). Moreover, the multilayer film shows a good electroactive property in the broad pH range and a high electrocatalytic activity towards CO and O2.

2. Experimental section

2.1. Materials

Unless otherwise stated, chemicals were purchased from Sigma–Aldrich. Aniline was redistilled before use, and purified water was obtained by passing distilled water through a Millipore system.

The chemical structure of the polymer and nanocomposites employed in this experiment is shown in Scheme 1. The synthesis of PANI follows a traditional procedure process reported by MacDiarmid et al. [36]. The initially synthesized emeraldine hydrochloride was converted into emeraldine base by reacting with ammonium hydroxide (NH4OH) for 24 h. The polymer can be obtained in a water-soluble solution according to a previous report by Rubner et al. [37]. A dilute solution of PANI can be obtained by dissolving PANI in dimethylacetamide (DMAc, 20 mg/mL) and subsequently diluting it 1:10 with water (pH 3.0–3.3). The pH was then adjusted finally to 2.6.

The Pt-G4.5COOH NPs was synthesized as in a previous report [38]. 75 μM Pt-G4.5COOH NP was dispersed in aqueous solution and the pH of the solution was adjusted from 9.0 to ca. 3.0 by 1 M HCl. The solution was used directly for multilayer deposition and TEM observation. In the control experiment, a 75 μM G4.5COOH was dissolved in aqueous solution (pH 3.0).

2.2. Layer-by-layer assembly

Multilayers can be deposited on polycrystalline gold substrates, quartz slides and silicon slides, respectively. The gold electrode was polished and functionalized by
immersing it overnight in a 0.1 mM 3-mercaptopropionic acid (MPC)/ethanol solution [39]. The modified gold surface was sonicated and washed with ethanol and water to remove unbonded MPC molecules, then dried under N₂ to obtain resulting multilayers. The quartz slides and the silicon slides were immersed individually in a fresh piranha solution (v/v = 1:3, 30% H₂O₂/98% H₂SO₄) at 80 °C for 1 h to enhance the hydrophilicity of the substrates (Caution: piranha solution must be handled with extreme care). These slides were washed with water and ethanol, and then dried by using N₂. The pretreated slides were grafted with a 5% 3-aminopropyl-trimethoxysilane (APS) toluene solution overnight. The modified slides were sonicated and washed with ethanol and water to desorb unbonded APS molecules. The slides were then heated at 105 °C for 1 h to allow the condensation of siloxane onto the substrates. The slides were stored in pure water prior to use [25]. At this time, the APS layer was positively charged in dilute HCl solution.

Layer-by-layer deposition followed the method introduced previously by Decher. Briefly, a substrate was immersed in PANI solution or in Pt-G₄.₅COOH NPs solution for 15 min, subsequently sonicated in the dilute HCl solution (pH 3.0) and dried by using N₂ for the next adsorption.

2.3. Characterization

UV–vis absorption spectra were recorded on a CARY500 UV/vis/near-IR spectrometer. Voltammetric experiments were performed in a one compartment, three-electrode electrochemical cell using a CHI 660 workstation. The working electrode was the PANI/Pt-G₄.₅COOH NPs-covered multilayer polycrystalline Au electrode, and a Pt wire was used as the counter-electrode. All potentials were referred to a KCl-saturated Ag/AgCl electrode.

TEM images were obtained by JEOL 2000 transmission electron microscope (operating at 200 kV), the samples was prepared by air-drying a drop of dilute Pt-PAMAM NPs solution.

AFM observations were performed in the tapping mode on an AFM Nanoscope III. A crystalline silicon tip on a cantilever was used.

Analysis of the X-ray photoelectron spectra (XPS) was performed on an ESCLAB MKII using Mg as the exciting source.

3. Results and discussion

3.1. Synthesis of Pt-G₄.₅COOH nanocomposites

Chemical synthesis of PAMAM G₄.₅COOH encapsulated platinum ions will yield stable, fairly monodisperse, and water-soluble Pt-G₄.₅COOH nanocomposites [38]. It was found that the resulting nanocomposites remain stable for several months, and even the pH value of the solution was changed from 9.0 to 3.0. As shown in Fig. 1, TEM images show that the Pt-G₄.₅COOH NPs dispersed well in solution (pH 3.0). The average diameter of platinum nanocrystals is 2.1 nm with a 0.5 nm size distribution. From the electron diffraction pattern, the cell unit of the encapsulated platinum crystal is calculated to be 4 Å, which is greatly consistent with that of platinum metal crystals.

3.2. Layer-by-layer deposition

Fig. 2 shows the UV–vis absorption spectra of Pt-G₄.₅COOH NPs/PANI multilayers on a quartz substrate with 1–10 layers. A band at 350 nm arises from the π–π⁺ transition while the bands at 420 nm and 800 nm originate from the charged cationic species known as polarons [12]. The presence of UV–vis absorbance at 350, 420 and 800 nm is indicative of the doped emeraldine salt state of PANI, which is similar to that in a previous report [40]. The number of (Pt-G₄.₅COOH NPs/PANI)ₙₙ multilayers as used in this figure represents that PANI is the
outmost layer, i.e. the multilayers are always terminated with PANI layer. The absorption at 800 nm was used to monitor the multilayer growth. It is clear from the inset of Fig. 2 that the growth of the multilayers is linear with sequential deposition of the Pt-G4.5COOH NPs and PANI over the range of PANI concentrations in our study, suggesting that a successful film deposition was achieved by the electrostatic layer-by-layer assembly. As indicated by the slopes of these two lines (upper and lower), the amount of PANI deposited on the substrate initially increases with the increasing solution concentration of PANI.

### 3.3. Surface morphology of Pt-G4.5COOH NPs/PANI multilayers

AFM image reveals the subtle surface morphology of the (Pt-G4.5COOH NPs/PANI)$_2$ multilayer. As shown in Fig. 3A, the (Pt-G4.5COOH NPs/PANI)$_2$ multilayer film is a molecularly flat and smooth with a 0.8 nm root-mean-squared (RMS) surface roughness and a 2.05 nm height variation from the cross-sectional AFM analysis. Comparatively, the (G4.5COOH/PANI)$_2$ multilayer film is much smoother and thinner with a 0.3 nm root-mean-squared (RMS) surface roughness and a 1.15 nm height variation from the cross-sectional AFM analysis (as seen in Fig. 3B).

The chemical nature of the two-bilayers, (Pt-G4.5COOH NPs/PANI)$_2$ and (G4.5COOH/PANI)$_2$, were further confirmed by XPS (Fig. 4). The (Pt-G4.5COOH NPs/PANI)$_2$ multilayer showed a Pt 4f peak in the range of 70–85 eV, while the (G4.5COOH/PANI)$_2$ multilayer did not, which reveals that the platinum nanoparticles exist in the (Pt-G4.5COOH NPs/PANI)$_2$ multilayer. The results of XPS on the two bilayers, (Pt-G4.5COOH NPs/PANI)$_2$ and (G4.5COOH/PANI)$_2$, are consistent with their AFM observation. Thus, the encapsulation of platinum nanocrystals by PAMAM will result in an increment for the feature height of PAMAM on the AFM observation [41], which, we believe, is the cause of the micro-structural discrepancy between the multilayers, (Pt-G4.5COOH NPs/PANI)$_2$ and (G4.5COOH/PANI)$_2$, as shown in Scheme 1.

### 3.4. Redox property of PANI/Pt-G4.5COOH NPs multilayers

Fig. 5A shows the cyclic voltammograms of PANI/(Pt-G4.5COOH NPs/PANI)$_m$ multilayers on the modified gold
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Electrode recorded in the PANI-free 0.5 M H₂SO₄ (saturated with N₂), for m = 0 to 7, respectively. The CV curves are similar to the PANI electrochemically prepared in the acid solution, which shows two pairs of typically reversible redox peaks of PANI. The first wave at ca. 0.20 V is assigned to the transition between leucoemeraldine and emeraldine forms, and the second at ca. 0.80 V is due to the transition between emeraldine and pernigraniline states [12]. The two peak currents linearly increase with the bilayer numbers of PANI/(Pt-G4.5COOH NPs/PANI)ₘ multilayers, which confirmed such a linear growth.

Fig. 5 B depicts the cyclic voltammograms of the PANI/(Pt-G4.5COOH NPs/PANI)₄₈ multilayer on the gold electrode in 0.5 M H₂SO₄ (saturated with N₂), for m = 0 to 7, (B) cyclic voltammograms of PANI/(Pt-G4.5COOH NPs/PANI)₇₈ multilayer on the gold electrode in 0.5 M H₂SO₄ saturated with N₂ at various scan rates (10 < V < 800 mV), the inset shows the dependence of the first oxidation current on the scan rates.

3.5. Influence of pH on UV–vis absorption and the electrochemical property of PANI/Pt-G4.5COOH NPs multilayers

As known, the electrical structure of PANI is pH dependent, which was manifested by UV–vis measurements (as shown in Fig. 6A) and cyclic voltammetry (Fig. 6B). With the increase in the pH value, the polaron bands, 400 nm and 800–1200 nm, decrease gradually, and a strong adsorption due to exciton transition of quinoid rings [25] at 500–700 nm grows simultaneously. As mentioned above, the polaron bands at ca. 400 nm and 800–1200 nm is indicative of the emeraldine salt state of doped PANI. The UV–vis spectra around 500–700 nm is typical for the emeraldine base state of PANI [40]. On the basis of UV–vis spectral analysis, it is clear that the polaron units reduce and the quinoid components increase in the electrical structure of PANI with an increase in the pH, demonstrating the transition of emeraldine salt to emeraldine base of PANI.
On the other hand, two separate redox peaks are clearly seen at a low pH (1.0) value. The redox peaks at 0.2 V, as discussed above, is assigned to the leucoemeraldine/emeraldine transition, i.e. doping/dedoping process, and its formal potential is independent of the variation of the pH value in the solution. The redox peaks at 0.8 V is due to the transition of emeraldine/pernigraniline state, i.e. deprotonation/protonation process, and its formal potential was affected by the pH change in the solution. With increase in the pH, the redox peaks at 0.8 V shift quickly towards low potentials with a rate of –100 mV/pH and finally merges with the first redox peak at pH 6.0 to show only a pair of broad peaks. The electrochemical behavior of the PANI/(Pt-G4.5COOH NPs/PANI)$_m$ multilayer film is also similar to that of PANI doped by polyanions or modified Au nanoparticles prepared via the LbL method [18–20].

![Fig. 6](image1.png)

On the other hand, two separate redox peaks are clearly seen at a low pH (1.0) value. The redox peaks at 0.2 V, as discussed above, is assigned to the leucoemeraldine/emeraldine transition, i.e. doping/dedoping process, and its formal potential is independent of the variation of the pH value in the solution. The redox peaks at 0.8 V is due to the transition of emeraldine/pernigraniline state, i.e. deprotonation/protonation process, and its formal potential was affected by the pH change in the solution. With increase in the pH, the redox peaks at 0.8 V shift quickly towards low potentials with a rate of –100 mV/pH and finally merges with the first redox peak at pH 6.0 to show only a pair of broad peaks. The electrochemical behavior of the PANI/(Pt-G4.5COOH NPs/PANI)$_m$ multilayer film is also similar to that of PANI doped by polyanions or modified Au nanoparticles prepared via the LbL method [18–20].

![Fig. 6](image2.png)

![Fig. 7](image3.png)

Fig. 6. The influence of pH change in the solution on (A) UV–vis absorption (Pt-G4.5COOH/PANI)$_8$ and (B) electrochemical property of PANI/(Pt-G4.5COOH/PANI)$_7$ at the scan rate of 100 mV/s ((a) pH 1.0, (b) pH 2.2, (c) pH 3.0, (d) pH 4.0, (e) pH 5.0, (f) pH 6.0, (g) pH 7.0 and (h) pH 8.0).

Fig. 7. Cyclic voltammograms of (A) PANI/(G4.5COOH/PANI)$_5$ multilayer, (B) platinum electrode, in 0.5 M H$_2$SO$_4$ saturated with (a) N$_2$ and (b) CO, and (C) PANI/(Pt-G4.5COOH NPs/PANI)$_m$ multilayer, for $m$ = 0 to 5, in 0.5 M H$_2$SO$_4$ saturated at a scan rate of 50 mV/s.
3.6. Electrocatalysis towards CO and O2

It has been reported that the platinum nanocrystals are highly electrocatalytically active towards CO oxidation and O2 reduction [43,44].

Fig. 7A shows cyclic voltammograms of the PANI/(G4.5COOH/PANI)₅ multilayer films in the 0.5 M H₂SO₄ solution saturated with (a) N₂, (b) air and (c) O₂ at a scan rate of 50 mV/s.

3.6. Electrocatalysis towards CO and O2

It has been reported that the platinum nanocrystals are highly electrocatalytically active towards CO oxidation and O₂ reduction [43,44].

Fig. 7A shows cyclic voltammograms of the PANI/(G4.5COOH/PANI)₅ multilayer films in the 0.5 M H₂SO₄ solution saturated with CO and N₂; no obvious response to CO oxidation in the investigated potential range was observed. While the solution was saturated with CO, a sharp peak ascribed to CO oxidation is present at 0.8 V for the platinum electrode, and the result is shown in Fig. 7B. This is the same with the PANI/(Pt-G4.5COOH NPs/PANI)₅ (0 < m < 5) multilayer film that all the bilayers exhibit a remarkable cathodic peak due to CO oxidation at 0.8 V in the 0.5 M H₂SO₄ solution saturated with CO (as shown in Fig. 7C). The inset shows the dependence of the anodic peak current on the number of bilayers. It
can be seen clearly that the anodic current of CO oxidation increases linearly with an increase in the bilayer number of PANI/(Pt-G4.5COOH NPs/PANI)₅ multilayers, indicating that the electrocatalytical activity towards CO oxidation can be promoted by increasing the thickness of PANI/(Pt-G4.5COOH NPs/PANI)₅ multilayers. The PANI/(Pt-G4.5COOH NPs/PANI)₅ multilayer can be used as an electrochemical catalyst for the reduction of O₂. As was shown in Fig. 8A, O₂ reduction current cannot be observed entirely in the investigated potential range on the cyclic voltammograms of the PANI/(G4.5COOH/PANI)₃ in the 0.5 M H₂SO₄ solution saturated with air (Fig. 8A), while a reduction peak of O₂ at 0.4 V is present on the cyclic voltammograms at the platinum electrode in the 0.5 M H₂SO₄ solution saturated with air and O₂ (shown in Fig. 8B). Moreover, the reduction peak current of O₂ increases with an increase in the concentration of O₂ in the 0.5 M H₂SO₄ solution. Similarly, O₂ can be reduced in the investigated potential range at the PANI/(Pt-G4.5COOH NPs/PANI)₅ multilayer film in the 0.5 M H₂SO₄ solution saturated with air and O₂, and the reduction peak current of O₂ increases with an increase in the concentration of O₂ in the 0.5 M H₂SO₄ solution. Differently, the peak potential of O₂ reduction shifts negatively by 0.2 V in comparison with that at the platinum electrode.

As discussed above, the PANI/(Pt-G4.5COOH NPs/PANI)₅ multilayers remain great electroactivity in a wide pH range (pH 7.0). A similar catalysis towards O₂ reduction can be observed on such PANI/(Pt-G4.5COOH NPs/PANI)₅ multilayers in the neutral solution (pH 7.0), as shown in Fig. 9B. The O₂ reduction peak mainly occurred at 0.05 V, which shifted negatively by ca. 0.15 V in contrast with that in the 0.5 M H₂SO₄, and 0.05 V with that at the platinum electrode, and results are shown in Fig. 9A, demonstrating that the reduction process was pH dependent. Similarly, the electrocatalytical activity of O₂ reduction can be tuned by controlling the thickness on the PANI/(Pt-G4.5COOH NPs/PANI)₅ multilayer.

4. Conclusion

The electroactive PANI/Pt-G4.5COOH NPs multilayers were successfully deposited onto solid substrates by an electrostatic layer-by-layer assembly. The structure and properties of such multilayers were investigated by various analytical methods such as UV–vis spectra, cyclic voltammetry, XPS, TEM and AFM. The uniform, controllable multilayer films are stable, reversible and electroactive even in neutral solution. Moreover, the platinum nanocrystals encapsulated in the PAMAM dendrimer show a high electrocatalytical activity towards CO oxidation and O₂ reduction, and the catalytic capability can be tunable by tuning the multilayer thickness, which can be used potentially as the chemical sensor in the detection of CO in the air and O₂ dissolved in water.

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