NMR Spectroelectrochemistry in Studies of Dopamine Oxidation

Xiao-Ping ZHANG, Wei SUN, Shuo-Hui CAO, Wen-Long JIANG, Hao PENG, Shu-Hui CAI, and Zhong CHEN

Key Laboratory of Laser Technology and Optoelectronic Functional Materials of Hainan Province, Key Laboratory of Functional Materials and Photoelectrochemistry of Haikou, College of Chemistry and Chemical Engineering, Hainan Normal University, Haikou 571158, P. R. China

Department of Electronic Science, Fujian Provincial Key Laboratory of Plasma and Magnetic Resonance, State Key Laboratory for Physical Chemistry of Solid Surfaces, Xiamen University, Xiamen 361005, China

Corresponding authors: shuohuicao@xmu.edu.cn, chenz@xmu.edu.cn

ABSTRACT

In this paper, the electrochemical oxidation of dopamine was studied by using gold nanoparticles modified nano-polyaniline film as the catalyst. Electrochemistry and nuclear magnetic resonance spectroscopy (EC-NMR) were used to explore the electrocatalytic mechanism and evaluate the electro-catalytic capacity. The influence of various pH values and voltages in the electrocatalytic process was studied. The oxidation mechanism of dopamine can be proposed: (1) at pH 1 and 600 mV, the main oxidation product is dopamine quinone (DQ). Only a small amount of DQ occurs cyclization reaction to form quinone aminochrome (AC); (2) at pH 1 and 800 mV, the oxidation products are DQ and 5,6-dihydroxyindole (DHI). (3) With the pH value increases, the oxidation of dopamine steps over DQ and AC, and directly produces DHI. DHI is aggregated to form melanin sediment. Our results indicate that the gold nanoparticles modified electrode displays high catalytic performance toward dopamine electrochemical oxidation.

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1. Introduction

The coupling of electrochemistry and NMR spectroscopy presents an interesting approach on monitoring and understanding electrochemical and electrocatalysis processes at a molecular level, which has received considerable attention recently. Conducting polymers are often considered to be useful matrices for the immobilization of the dispersed noble metal nanoparticles. The use of conducting polymer including polyaniline (PAn), polyvinylpyrrolidone, poly (3,4-ethylene-dioxythiophene) as a stabilizer for the preparation of noble metal nanoparticles can reduce nanoparticles reunion, and effectively regulate the size of nanoparticles. Being one of the most commonly used conducting polymers, due to its facile synthesis, low price tag, high conductivity, good redox reversibility and environmental stability, PAn has been extensively studied as an ideal carrier for the preparation of nanosized noble metal catalyst. The porous structure of PAn allows dispersing the metal particles into the polymer matrix and generates additional electrocatalytic sites.

Noble metal nanoparticles modified PAn such as Pd/PAn, Au/PAn, Pt/PAn, Ag/PAn has been reported, Gold nanoparticles (AuNPs) are well acknowledged to possess remarkable electrocatalytic properties, high conductivity, high stability, and good biocompatibility. AuNPs modified electrodes exhibit excellent electrocatalytic effect on DA, which can effectively promote the electron transfer and enhance the reversibility of the reaction. Boisselier developed a functionalizing commercially available electrode contain gold nanoparticles to successfully detect dopamine, the selectivity for dopamine was considerably improved versus ascorbic acid. DA is a chemical messenger and a neurotransmitter in the mammalian central nervous system that controls many biological functions such as cognition, emotion, endocrine regulation, motivation, locomotion, and so on. Furthermore, some pathologies such as parkinson disease or schizophrenia and the use of some types of drugs are linked to a dysregulation of dopaminergic transmission.

2. Experimental

2.1 Chemicals

All reagents including DA, potassium chloride, sulfuric acid,
perchloric acid, potassium nitrate, ethanol, hydrochloric acid and aniline were of analytical reagent grade, purchased from Sinopharm Chemical Reagent Co., Ltd., and used without further treatment. Indium tin oxide conducting glass plates (ITO glass, purchased from Xiang Cheng Glass Co., China) were used as substrates for preparing AuNPs modified nano-PAn films.

2.2 Preparation of gold modified PAN deposited ITO (Au/PAN/ITO)

PAN films were prepared through electro-polymerization. ITO glass was dipped into 1 M polycarboxylic aqueous media containing 0.5 M aniline, and voltammetric sweep was performed between -0.2 V and 0.9 V (vs. saturated Ag-AgCl electrode) at a scanning rate of 50 mV s⁻¹. After 16 cycles, the sweep was stopped at 0.4 V vs. Ag/AgCl. The PAN film covered working electrode (WE) was removed from the monomer solution and washed thoroughly with distilled water. Then AuNPs were electrodeposited on the PAN film, and PAN deposited ITO electrode was immersed into a 6 mmol L⁻¹ hydrogen tetrachloroaurate (HAuCl₄) solution containing 0.1 mol L⁻¹ KNO₃ (prepared in doubly distilled water and deaerated by bubbling with nitrogen). A constant potential of negative 0.4 V vs. Ag/AgCl was applied for 400 s. Then, the modified electrode was washed with distilled water and dried in the oven of 323 K for 10 min before being used.

2.3 Measurements

DA was dissolved in water with 0.1 M potassium chloride as the supporting electrolyte, and H₂SO₄ for the adjustment of the pH in all NMR experiments. These electrochemical experiments were performed with a CHI760C electrochemical workstation (CH Instruments, China) using the three-electrode system with Au/ PAN/ITO as the working electrode, the platinum wires as counter electrode, and the silver wire as the quasi-reference electrode.

One-dimensional ¹H NMR spectra were acquired at 298 K on a Bruker 600 MHz NMR system (Bruker AVANCE HD III, Germany) equipped with a 5 mm indirect detection probe. And a standard 1D pulse sequence was used. The chemical shifts of ¹H NMR spectra were calibrated by the signal of 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt (DSS). The spectral width was set as 10 ppm to cover the chemical shift range of protons. Each spectrum was recorded with 32 scans and an experimental time of ~2 s (delay time of 1 s and acquisition time of 1 s). The morphology of the nanoelectrodes were obtained on a HITACHI S-4800 SEM.

3. Results and Discussion

The morphologies of the nano-PAn film and the nano-gold modified nano-polyaniline film are shown in Fig. 1(a) and (b). It is seen that the synthesized PAN material has nanobelt structure. A porous film is obtained after PAN has been dried. The well connected network of PAN nanobelts in the film is beneficial for transporting holes. Figure 1(c) and (d) show the morphology of gold modified PAN film. The gold film deposited on the PAN nanobelts also has nanobelt structure, and gold particles with size of about 100 nm disperse on the PAN nanobelts. The porous network structure of the PAN nanobelts ensures that AuNPs are stored. Due to the small particle sizes and large specific surface areas, the gold film would have high catalytic activity for DA oxidation.

To investigate the electrocatalytic behavior of DA (0.02 M) at bare ITO electrode, PAN/ITO electrode, and Au/PAN/ITO electrode, cyclic voltammograms were obtained at pH value of 1.0 in aqueous solution (Fig. 2). The current at the Au/PAN/ITO electrode is the highest, with the lowest one at bare ITO electrode, implying that Au/PAN/ITO electrode would present highest catalytic performance toward DA electrochemical oxidation.

EC-NMR was used to evaluate electrocatalyst capacity of Au/PAN/ITO toward DA oxidation. At pH value of 1.0, ¹H NMR spectra and amperometric i-t curve of DA at different electrodes (ITO, PAN/ITO, Au/PAN/ITO) in aqueous solution were obtained during electrolysis process at 600 mV respectively (Fig. 3). As shown in Fig. 3(a), the oxidation currents from high to low are at Au/PAN/ITO, PAN/ITO, ITO electrodes. The results indicate that the AuNPs loading on the porous network structure of PAN show highest catalytic activity for DA.

As shown in Fig. 3(b), when the electrolysis is carried out using ITO as WE in aqueous solution, no new signal is observed. Nevertheless, from Figs. 3(c) and (d) it can be seen that PAN/ITO or Au/PAN/ITO as WE, gave new signals at 2.8 ppm, 6.36 ppm, and 6.9 ppm and increase with the electrolysis time. These peaks are assigned to the protons of DQ. Meanwhile, two signals arisen from the protons of AC appear at 6.2 ppm and 6.8 ppm and increase with the electrolysis time. The DA electro-oxidation rate at Au/PAN/ITO electrode is significantly larger than that at PAN/ITO at measured potentials. The quantitative analysis of the oxidized products over the electrolysis is shown in Fig. 4. It is observed that...
Au/PAn/ITO electrode displays higher catalytic performance toward DA electrochemical oxidation. EC-NMR experiments on DA electrolysis at Au/PAn/ITO electrode were also executed at 800 mV. Figure 5(a) shows the 1H NMR spectra during the oxidation process. Signals also appear at 2.8 ppm, 6.36 ppm, and 6.9 ppm from DA quinine and increase during electrolysis time, the same as at 600 mV. However, different from the electrolysis process at 600 mV, no AC signal is observed, while three new singles appear in the range of 7.0 ppm and 7.2 ppm, which are assigned to the protons of DHI.30,31 Figure 5(b) shows the quantitative analysis of the DHI and DQ during the electrolysis, it is observed that the production of DQ at 800 mV is lower than that at 600 mV, meanwhile, the production of DHI increases with the electrolysis. Different reaction pathway between 600 mV and 800 mV probably because the changes of DA oxidation rate at different voltage. At 800 mV, the reaction is become faster, so some intermediates were not detected by in situ EC-NMR. EC-NMR experiments on the electrochemical oxidation of dopamine were carried out under varied pH values. Figure 6 shows the 1H NMR spectra during the oxidation process at Au/PAn/ITO

Figure 3. (a) Amperometric i-t curve of DA at different electrodes (ITO, PAn/ITO, and Au/PAn/ITO) in aqueous solution. (b, c, d) 1H NMR spectra of DA acquired during electrolysis process at ITO (b), PAn/ITO (c), and Au/PAn/ITO (d) electrodes in aqueous solution at 600mV.

Figure 4. Normalized peak areas of one 1H NMR spectra for DQ at 6.36 ppm during electrolysis process at different electrodes (ITO, PAn/ITO, and Au/PAn/ITO) at 600mV with PAn/ITO as WE.
electrode under various pH values and external voltage of 600 mV.
After 6 hours of electrolysis, it is seen that the signals at 7.01 ppm,
7.08 ppm, and 7.15 ppm from 5,6-dihydroxyindole also appear and
increase with the increase of pH value. Normalized peak areas of 1H
NMR spectra for products under various pH values listed in Table 1,
which corresponds to Fig. 6. It is also observed that the normalized
peak areas of one of 1H NMR spectra for DHI increase with the pH
value increase. Meanwhile, black precipitate is generated in aqueous
solution, which is considered to be melanin since 5,6-dihydroxy-
indole is easily polymerized to produce melanin. Melanin cannot be
described as classic polymers since it does not possess well-defined repeat units, and it cannot even be called polymer. The molecular dynamics simulations suggest that melanin consists of oligomeric proto molecules with intermolecular
stacking interactions, and the amorphous particles are insoluble in
most solvents. Nevertheless, the signals from DQ and AC decrease
with the increase of pH value (Table 1). This illustrates that the
pathway of DA oxidation is related with pH value, which most
likely follows Scheme 1. At low pH, when external voltage is 600 mV,
the main oxidation product is DQ, only a small amount of DQ occurs
cyclization reaction to form AC; when external voltage is 800 mV, the
oxidation products are DQ and DHI. With the pH increases, cyclization reaction of DQ leads to the formation of AC, DHI is formed by tautomerization of AC, and the reaction is fast. We assume that the oxidation of dopamine proceeds over DQ and AC, DHI is generated directly and further oxidized to melanin.

4. Conclusions

We utilized EC-NMR to study the electro-oxidation of dopamine

![Figure 5](image1.png)

Figure 5. (a) 1H NMR spectra of DA acquired during electrolysis process at Au/PAn/ITO electrode in aqueous solution at 800 mV, (b) Normalized peak areas of one of 1H NMR spectra for DQ at 6.36 ppm and one of 1H NMR spectra for DHI at 7.15 ppm.

![Figure 6](image2.png)

Figure 6. 1H NMR spectra of DA acquired during electrolysis process at Au/PAn/ITO electrode in aqueous solution with various pH values.

| pH | Ascription | DHI (7.15 ppm) | DQ (6.36 ppm) | AC (6.8 ppm) |
|----|------------|----------------|----------------|-------------|
| 1  | DHI        | 0              | 1.26           | 0.40        |
| 2  | DHI + DQ   | 0.68           | 0.39           | 0.19        |
| 3  | DHI + DQ   | 0.78           | 0              | 0           |
| 4  | DHI + DQ + AC | 1.14   | 0              | 0           |
at various voltages and pH by using gold modified PAn film as the catalyst. It is found that the gold modified PAn electrode displays highest electrocatalysis activity for oxidation of DA. When at pH 1 and 600 mV, the main oxidation product is DQ. Only a small amount of DQ occurs cyclization reaction to form DHI; at pH 1 and 800 mV, the oxidation products are DQ and DHI. With the pH value increases, black precipitate is generated in aqueous solution. The oxidation of DA steps over DQ and AC, and directly produces DHI with the increase of pH value. DHI is aggregated to form melanin for the oxidation products are DQ and DHI; With the pH value 1, the main oxidation product is DQ. Only a small amount

Scheme 1. Pathway of DA oxidation at various pH values and voltages.

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