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Short Communication

Experimental and Theoretical Study on the Redox Reaction of Noradrenaline on the Gold Electrode Surface

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Noradrenaline (NA) can be oxidated and become into noradrenaline quinone (NAquinone). We studied the electron transfer properties of NA in a phosphate buffer solution at various pH values with cyclic voltammetry (CV) method. The results indicate that the redox reaction is diffusion-controlled under our experimental environment. To study the microcosmic nature of the oxidation reaction of NA, we also select gold electrode as the probe to study the electron-transfer properties of NA on the electrode surface by employing theoretical methods. Our calculated results suggest that the rate-limited step is the dehydrogenation reaction of first hydrogen.

Keywords: noradrenaline; Au(111) surface; adsorption; cyclic voltammetry; theoretical study

1. INTRODUCTION

Catecholamine, as one of the most important neurotransmitters in mammals, plays an important role in the bodies [1-4]. It includes dopamine, adrenaline, and noradrenalin (NA). As the electron-transfer reaction is important in NA's reaction, redox potentials determine NA biological actions [5]. To study the electrochemical behaviors of NA will facilitate us to understand diagnose certain diseases in clinical medicine and its physiological functions. NA cannot be dissolved in water and organic solvent, but can be dissolved in proton-donor solvents. NA (Figure 1) is unstable and can be oxidized to form protonated NAquinone (Figure 1). NA has important biological functions and can form supra-molecular complexes with many biological molecules in the human body through hydrogen bond [6].

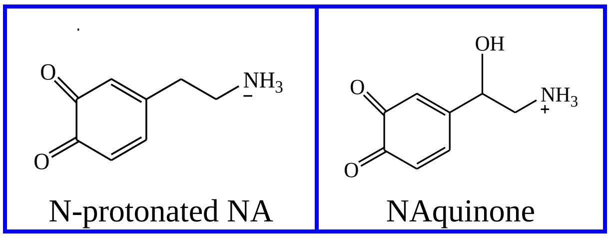


Figure 1. The structures of N-protonated NA and NAquinone.

Recently, the experimental and theoretical studies of catecholamine increases obviously [7-11]. Among of them, cyclic voltammetry (CV) is widely applied in the researches [12-16]. However, though there are lots of studies on the catecholamine, the microcosmic electron-transfer property of NA is still unclear. Therefore, in the present article, we will select gold electrode as the probe to investigate the electron-transfer properties of NA on the electrode surface by employing experimental and theoretical methods. We would expect that the accurate calculation results for the model systems will be useful for the experimental researchers working in this field.

2. EXPERIMENTAL SECTION

The three-electrode electrochemical cell was employed for all the electrochemical measurements. A gold electrode was served as a working electrode. The counter electrode was platinum wire electrode, and reference electrode was saturated calomel reference electrode. All potentials we obtained directly from cyclic voltammograms were relative to saturated calomel reference electrode. The solutions were prepared with analytic grade reagents and doubly distilled water. The supporting electrolyte was 0.1 mol L^{-1} KCl solution. Electrochemical measurements were carried out using a CHI 660C electrochemical station.

3. THEORETICAL SECTION

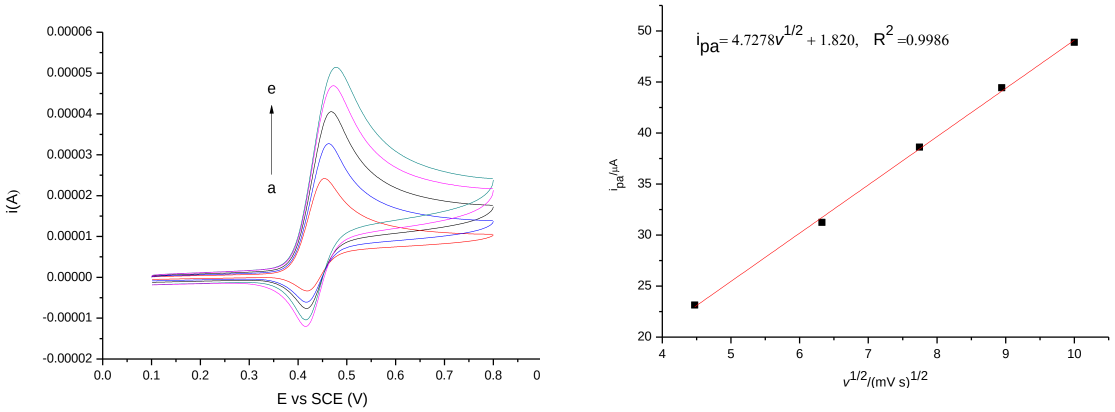
Based on plane-wave pseudopotential density functional theory (DFT) [17,18] by using generalized gradient approximation with the Perdew−Burke−Ernzerhof (PBE) exchangecorrelation functional [19,20], as implemented in the Cambridge sequential total energy package (CASTEP) code [21,22]. A 2×2×l Monkhorst-Pack k-point grid was used by integrations in reciprocal space. The criteria for energy and maximum force convergence used were 2.0×10^{-5} eV/atom and 0.05 eV/Å. The transition states (TSs) were searched for with the linear and quadratic synchronous transit (LST/QST) complete search.[23]

Au(111) surface is stable thermodynamically, so we select it to study the catalytic oxidation of noradrenaline on the electrode surface. A periodic three-layer slab with a (3 × 3) unit cell was used in our calculations. In the three-layer slab, the atoms in the two bottom layers were fixed and the ones in the top layer were allowed to be fully relaxed. As previous report [24,25], the vacuum region between slabs was selected as 15 Å.

4. RESULTS AND DISCUSSION

4.1. The electrochemical behaviors of NA

The electrochemical behaviors of NA are investigated by CV in a phosphate buffer solution containing 6.0×10^{-4} mol L^{-1} NA at various pH values ranging from 2.2 to 6.0. Fig. 2A shows that both the anodic peak current (i_{pa}) and cathodic peak (i_{pc}) increase with increase of the scan rate (v).



A B

Figure 2. (A) The CV behaviors of 6.0×10^{-4}mol L^{-1} NA at gold electrode in phosphate buffer solution of pH 2.2 with various scan rates (curves a to e: scan rate (v) =20, 40, 60, 80, 100 mV/s). (B) The plot of i_{pa} vs $v^{1/2}$.

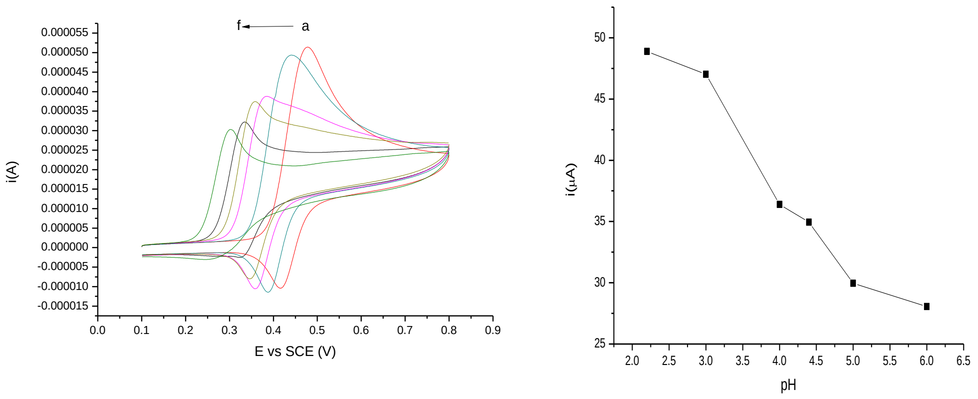


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Figure 3. (A) the CV behaviors of 6.0×10^{-4} mol L^{-1} NA at gold electrode in phosphate buffer solution with different pH values at a scan rate of 100 mV/s (curves a to f: pH=2.2, 3, 4, 4.4, 5, 6). (B) The plot of anodic peak current i_{pa} vs pH.

There is an excellent liner relation between i_{pa} and $v^{1/2}$ as shown in Fig. 2B, indicating that the electrochemical reaction of NA is controlled by diffusion under our experimental environment. Figure 3A shows the cyclic voltammograms of NA in phosphate buffer solution with different pH values at room temperature. It is very evident that both anodic peak potential and cathodic potential shift to negative potential with the increase of pH. As shown in Figure 3B, anodic peak current responses decrease with the increase of pH. The increasing number of $H_2PO_4^-$ is responsible for the current decrease.

4.2. The theoretical study on the oxidation reaction of NA on the Au surface

In many previous report [26-28], the electrochemical properties of various chemical species have been studied DFT calculations. In addition, Tugsuz [28] performed an extensive DFT study of studied the standard electrode potentials of hydrogen bonded complexes by employing 10 hybrid density functions. While, in this article we select Au(111) surface to study the catalytic oxidation of noradrenaline on the electrode surface by using DFT calculation.

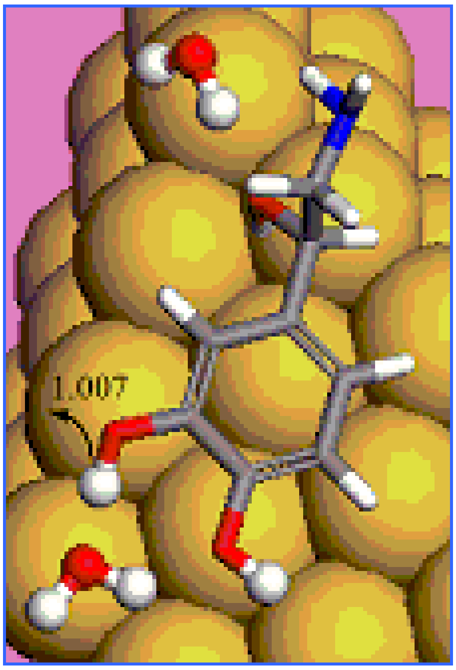

Figure 4. The length of N-H bond of NA on Au(111) surface.

To investigate the microcosmic nature of the oxidation reaction of NA, we also study the adsorption of NA on the Au surface. We firstly study the adsorption of NA on the Au(111) surface in the vacuum environment without water. We select the following formula to calculate the adsorption energy of noradrenaline. In the equation, $E_{tot}(NA)$, $E_{tot}(Au)$, and $E_{tot}(NA/Au)$ denote the energy of free NA, the energy of Au(111) surface without adsorption, and the total energy of NA/Au adsorption system. The calculated adsorption energy of NA is 0.057 eV, which suggests that the surface interaction is very weak.

$$E_{ad}(NA) = E_{tot}(NA) + E_{tot}(Au) – E_{tot}(NA/Au) \qquad (1)$$

Then, we select water as the solvent to investigate the catalytic oxidation reaction of NA. The oxidation reaction of NA on the Au(111) surface is NA → NAquinone + H_2. As shown in Figure 4, the N-H bond length of free NA is 1.007 Å on the Au(111) surface (the corresponding value of free NA is 0.978 Å). The calculated results show that there exists adsorption of NA at the Au(111) surface. The calculated adsorption energy in aqueous solution is 0.29 eV by using energy of Au(111) surface with two water molecules, which indicates that the adsorption interaction become stronger with the participation of water. Therefore, we will only discuss the reaction in the aqueous solution in the following sections.

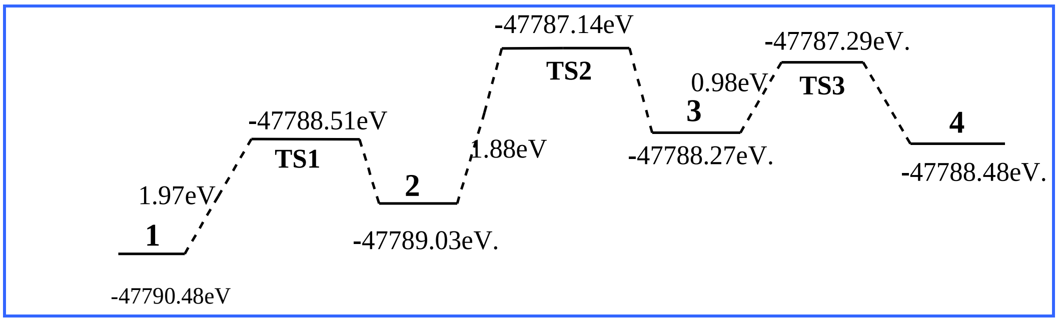

Figure 5. The potential energy diagram of the reaction.

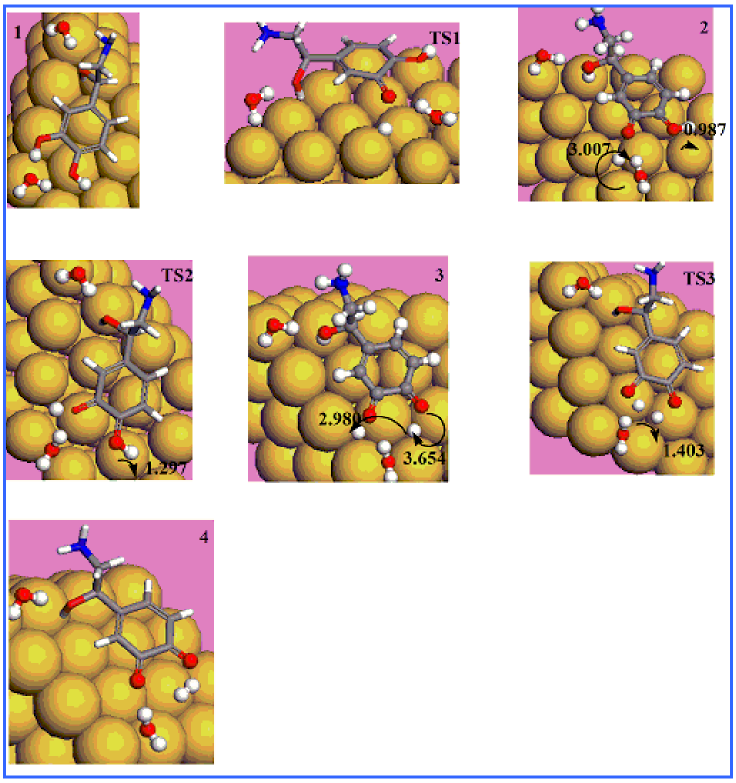

Figure 6. The structures of reactant **1**, intermediates **2** and **3**, transition states **TS1**, **TS2**, **TS3**, and product **4.**

The reaction potential energy diagram is show in Figure 5 and the related structures of reactant, product, intermediates, and transition states are list in Figure 6. Reactant **1** firstly becomes intermediate **2** via the transition state **TS1** with the energy barrier of 1.97 eV. In this step, the H atom of phenolic hydroxy group in NA transfers to the hole activity site of Au surface and causes the distance of H and O to be 3.007 Å. Simultaneously, the O atom in another phenolic hydroxy group gets a negative charge through the electron transfer. Then, another dehydrogenation occurs and forms NAquinone. The energy barrier of this step is 1.88 eV. The calculated distances of H and O, and H and H are 3.654 and 2.980 Å, respectively. Finally, the two H atoms on the Au surface are close to each other to form hydrogen through a energy barrier 0.98 V (**TS3**). As shown in Figure 5, the rate-limited step is the first step (dehydrogenation reaction of first hydrogen).

5. CONCLUSION

N-protonated NA can be oxidated to N-protonated NAquinone. The electron transfer properties of NA in a phosphate buffer solution at various pH values were investigated by CV method. The results indicate that the electrochemical reaction of NA is controlled by diffusion under our experimental environment. By employing theoretical methods, we also study the the electron-transfer properties of NA on the electrode surface using gold electrode as the probe. Our calculated results suggest that the rate-limited step is the dehydrogenation reaction of first hydrogen.

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