Adsorption and Exchange Kinetics of Hydrophilic and Hydrophobic Phosphorus Ligands on Gold Surface

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Abstract. The adsorption kinetics process of hydrophobic ligand (triphenylphosphine, PPh3) and hydrophilic ligand (tris(hydroxymethyl)phosphine oxide, THPO) on the surface of gold electrode were estimated by using electrical double layer capacitance (EDLC). Results showed that the adsorption process of both ligands included fast and slow adsorption processes, and the fast adsorption process could fit the first order kinetic equation of Langmuir adsorption isotherm. During the slow adsorption process, the surface coverage (θ) of PPh3 was higher than that of THPO due to the larger adsorption kinetic constant of PPh3 than that of THPO, which implied that PPh3 could replace THPO on the gold electrode. The exchange process of both ligands on the surface of gold electrode proved that PPh3 take the place of THPO by testing the variation of EDLC which promote the preparation of Janus gold, and the theoretic simulation explained the reason of ligands exchange from the respect of energy.

1. Introduction

Surface modified gold is the most frequently used in the fields of sensors [1-4], corrosion protection [5-7], molecular electronic devices [8-9], and other nanoscale devices. During which, using self-assembling monolayers (SAMs) to modified gold substrates was a powerful method with high orderliness, orientation, thermodynamic stability and low defect. Thiol modified gold is widely applied in fundamental and practical issue due to the strong interaction between gold and sulfur[10-13]. The adsorption kinetics of organic molecules on the surface of gold electrode was investigated by quartz crystal microbalance (QCM)[14-16], atomic force microscopy (AMF)[17], electrochemical methods[18,19] and surface plasmon resonance (SPR). The results showed that adsorption kinetics had two process, the first process was a fast adsorption finished in a short time, the second was a slow adsorption or reorganizing process needed 10 h to 20 h[20]. Compared to thiol, phosphorus ligands can also adsorb onto gold surfaces due to their electrostatic interactions. However, few reports investigated the adsorption process of phosphorus ligands.

For the preparation of modified nanoparticles, ligand exchange reaction is an approach to produce amphiphilic nanoparticles[21]. Recently, various techniques have been applied to investigate the
process of the ligand exchange reaction. The previous reports considered that the electrostatic interaction between phosphorus ligands and gold substrate was weak, however, the replacement of phosphorus ligands on gold substrate was feasible. We inferred that Janus gold particles with THPO and PPh₃ ligands can be obtained. In this work, we studied the adsorption process of two kinds of ligands (PPh₃ and THPO) on the surface of gold electrode by using EDLC, as well as the adsorption kinetics. And the ligand exchange process of THPO with PPh₃ was investigated by means of XPS and contact angle measurement, theoretical simulation was used to describe the possibility of Janus gold formation.

2. EXPERIMENTAL

2.1 Chemicals

Tris(hydroxymethyl)phosphine oxide (THPO, AR, 95.5%) was purchased from Wuhan Jinlin Chemical Technology Co., Ltd. (China). Triphenylphosphine (C₁₈H₁₅P, PPh₃, CP), toluene (AR, 99.5%), acetone (AR, 99.5%), sulfuric acid (H₂SO₄, AR, 95-99%), cupric sulfate (AR, 99%) ethanol (AR, 99.7%) and hydrogen peroxide (H₂O₂, AR, 30%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Deionized water was used in all experiments.

2.2 Adsorption and exchange process of ligands on gold electrodes

A gold disk electrode (2 mm in diameter) was employed as working electrode, which was carefully polished by alumina powder (0.05 μm). After rinsing in deionized water, the electrode was immersed in a “pirhana” solution (H₂SO₄/30% H₂O₂, v/v, 3:1) at 50 °C for 3 min, followed by ultrasonic in ethanol and deionized water for 5 min, respectively. To cleaning the gold electrode further, cyclic voltammetry was carried out for 20 times in 0.5 M H₂SO₄ solution with a scan rate of 100 mV/s and the potential range from -0.6 to 1.1 V, during which Hg/Hg₂SO₄ was used as reference electrode. Then, the gold electrode was rinsed subsequently with acetone, ethanol and deionized water, and dried in ambient temperature.

The surface modification of gold by THPO molecule followed a method described in previous literature [20], typically the gold electrode was immersed in 20 μM THPO aqueous solution of at 25 °C, at the different time intervals (from 0 s to 24 h), as-modified gold electrode was measured by cyclic voltammetry after rinsing with acetone, ethanol and deionized water in sequence. The adsorption process of PPh₃ was the same as THPO except by using 20 M PPh₃ toluene solution. To investigate the ligand exchange reaction, the THPO-modified gold electrode (adsorbed in THPO solution for 24 h) was used, which was soaked and sampled at different intervals in 20 M PPh₃ toluene solution for further characterizations.

2.3 Characterizations

The adsorption of phosphorus molecules on gold surface was mainly investigated by electrochemical analysis, which was performed on a potentiostat (CHI 660, Shanghai Chenhua Instruments Co., Ltd. China) by a three-electrode system, including gold disk (2 mm in diameter), platinum plate and Hg/Hg₂SO₄ electrode as working electrode, counter electrode and reference electrode, respectively. The surface property of the gold electrode was characterized by a contact angle goniometer (JWA-360, Xiamen Chongda Intelligent Technology Co., Ltd., China) and an X-ray photoelectron spectroscopy (ESCALAB250Xi, Thermo Fisher Scientific).

2.4 Theoretic calculation

Using Discover of Materials Studio package, molecular dynamics was employed to calculate the adsorption of phosphorus ligands on the Au (111), (110) and (100). The dynamics was performed in NVT ensemble, with the time step of 0.1 fs, and the total dynamics time is 100 ps.

3. Results and Discussion

3.1 Adsorption process of ligands on gold surface

The adsorption of the THPO and PPh₃ was accompanied by the decrease of the real surface area of the gold electrode, and the reduction degree of the surface area was related to the adsorption capacity which can be measured by cyclic voltammogram. Fig.1 showed the CV plots of the gold electrode in 0.5 M H₂SO₄ solution after 20 times scanning at a rate of 100 mV/s, in which the bands in the area B were assigned to the formation of AuO monolayer according to previous reports [37], and the peak A is the reduction of AuO monolayer with a charge of 31.11 μC (integral area of peak A). So, the real area of gold is determined as 0.085 cm², calculated by the ratio of the reduction charge (31.11 μC) to the
theoretical value (400 μC/cm²). The roughness factor \( R_f \) (2.72) was then obtained according to ratio of the real area (0.085 cm²) to the geometrical area (0.0314 cm²).

\[ Cd = \frac{\Delta i}{2 \nu A} \]  

Where \( \nu \) was scanning rate (V/s), \( A \) was the real area of the electrode (cm²). Fig. 3 showed that trend of \( C_d \) varying with adsorption time. The differential capacitance was inversely proportional to the surface coverage, with the time increasing \( C_d \) obtained from PPh₃ adsorbed gold decreased at the earlier stage (t < 1800 s) and then reached its final value (ca. 16.72 μF/cm²). \( C_d \) obtained from THPO adsorbed gold needed at least 7200 s to reach a constant value (ca. 18.87μF/cm²). It was obvious that the final value of \( C_d \) in THPO solution was lower than that of PPh₃, which indicated that the film formed by PPh₃ on the gold electrode surface is compact and less defects.
According to $C_d$, the value of surface coverage ($\theta$) during the adsorption process could be calculated by the following formula,

$$\theta_t = \frac{C_d(0) - C_d(t)}{C_d(0) - C_d(\text{film})}$$

(2)

Where $C_d(0)$ and $C_d(t)$ was the differential capacitance of the ligand adsorbed gold electrode at the time of 0, t, respectively. $C_d(\text{film})$ was the differential capacitance at equilibrium adsorption.

The $\theta$ was presented in Fig. 4 obtained from the gold electrode after soaking in PPh$_3$ and THPO solution, respectively. For PPh$_3$, at the initial adsorption step, the surface coverage ($\theta$) was increased from 0.226 to 0.908 as the adsorption time increasing from 5 s to 20 min, which approached to 1 finally. While for THPO, when deposition time t was 5 s, the surface coverage ($\theta$) was only 0.062, $\theta$ approached to 0.9 needed at least 2 h, and the final value of $\theta$ was 0.958. This indicated that adsorption rate of PPh$_3$ was faster than that of THPO. At the fast increasing range of $\theta$, the time dependence of coverage could be described with Langmuir adsorption model:

$$\ln(1 - \theta) = -k_{ad}ct$$

(3)

Where $k_{ad}$ was the adsorption rate constant, $c$ was the concentration of ligands.
As showed in Fig.5a, plot of ln(1-θ) versus t showed good linearity in the initial adsorption process ranging from 0 to 60 s due to the formation of PPh₃ film on the gold electrode surface. And the fitting coefficient r was 0.97451. The adsorption rate constant (k_ad) calculated by formula (3) was 625 M⁻¹s⁻¹. The k_ad of THPO was 319 M⁻¹s⁻¹. It was obvious that k_ad of PPh₃ was much higher than that of THPO indicating that the adsorption of PPh₃ was much easier than THPO.

### 3.3 Ligands exchange processes on gold surface

To investigate the exchange possibility of PPh₃ and THPO, gold electrode was immersed in the both ligand solution successively. As showed in Fig.6, curve A showed the C_d of the THPO modified Au electrode soaked in 20 μM PPh₃ toluene solution for the different time to investigate the kinetic of PPh₃ replacing THPO. As the dipping time increasing, variation of C_d can be dividing into four stages: fast increasing stage (t < 300 s), fast decreasing stage (300 ≤ t < 1 h), slow decreasing stage (1 h ≤ t < 5 h), and equilibrium stage (t ≥ 5 h).

To further probe the effect of toluene on the exchange process of THPO, PPh₃, THPO modified Au electrode soaked in toluene solution for the different time, the variation tendency of C_d (curve B) was similar to that of curve A except the mission of slowly decreasing stage and the variation time: C_d increased fast when t < 120s, then decreased quickly when 120 s < t < 30 min, and then reached equilibrium finally.

### 3.4 XPS analysis

XPS measurements were used to investigate the composition of the capping ligands in the replacement processes on the surface of gold electrode. For the PPh₃ modified gold electrode, the chemical states of phosphorous with the binding energies of 130.7 eV, 132.83 eV and 134.32 eV were attributed to PPh₃, PPh₃O (oxidation form of PPh₃) and the adsorption of phosphorus on the gold surface.

For the C 1s spectrum, the binding energy of 284.85 eV, 286.36 eV and 288.12 eV are attributed to C-C, C-P and -C=O groups.
For the different replacement time (30 min, 2 h, 12 h, 24 h) of the samples, there were not only THPO ligand, but also PPh$_3$ and PPh$_3$O ligands. Considering the data analysis of the P 2p spectrum, the fixed ration of THPO or PPh$_3$ and PPh$_3$O for 30 min, 2 h, 12 h, 24 h samples were about 0.39:1, 0.48:1, 0.93:1, 1:1, respectively. For the C 1s spectrum, the ratio was 0.37:1, 0.46:1, 0.91:1, 0.95:1, respectively. With the increasing of the replacement time, the content of PPh$_3$ and PPh$_3$O molecules were increasing. Finally, the fixed ratio of THPO or PPh$_3$ and PPh$_3$O on the surface of gold was close to 1:1, which showed that the substitution reaction of phosphorus ligands on the surface of gold electrode has occurred, about half the THPO molecules replaced by PPh$_3$ molecules.

3.5 Amphipathic property

Static contact angles were further characterized to investigate the amphipathicity of the self-assembled films. The bare gold electrode surface turned to be a hydrophilic interface after soaking in THPO toluene solution due to the adsorption of THPO (b), and which became a hydrophobic surface after soaking in PPh$_3$ toluene solution (c). It is worthy to noted that the hydrophobic content of THPO-modified gold surface increased after soaking in PPh$_3$ toluene solution for 24 h (d). The contact angle of water on surface of bare (a), THPO-modified (b), PPh$_3$-modified (c) and THPO/PPh$_3$ modified (d) gold were 77.1°, 40.1°, 95.3° and 63.3°, respectively. Which demonstrated that the co-adsorption of THPO and PPh$_3$ contributed to the amphipathicity of the gold surface.

3.6 Theoretic simulation

The optimized structure of PPh$_3$ and THPO on Au (1 1 1), (1 1 0) and (1 0 0) were showed in Fig.9. The adsorption energy ($E_{ad}$) of ligands was calculated through equation (4)

$$E_{ad} = E_{molecule} + E_{surface} - E_{total}$$

(4)
Where $E_{\text{molecule}}$, $E_{\text{surface}}$ and $E_{\text{total}}$ was the energy of ligands, facet of Au and the optimized structure. The adsorption energy of PPh$_3$ on Au (111), (110) and (100) was 108.474 kcal/mol, 55.440 kcal/mol and 70.080 kcal/mol, respectively. As for THPO, the adsorption energy was 43.250 kcal/mol, 26.683 kcal/mol and 25.000 kcal/mol, respectively. It was obvious that the adsorption energy of PPh$_3$ was more than twice of THPO. The bond length between P of PPh$_3$ and Au of (111), (110) and (100) was 3.705 Å, 4.001 Å and 3.769 Å, and the bond length between P of THPO and Au of (111), (110) and (100) was 3.745 Å, 4.012 Å and 3.982 Å, respectively. The higher adsorption energy of PPh$_3$ and shorter bond length between P and Au demonstrated that the adsorption of PPh$_3$ on each facet of Au was much easier than THPO, which explained the exchange process from the respect of theoretic study.

![Fig.9 Side view of optimized structures of PPh$_3$ and THPO on Au (111), (110) and (100).](image)

4. Conclusions
In this study, the adsorption kinetics of THPO and PPh$_3$ on gold electrode was studied by electrical double layer capacitance, which was an effective method to investigated dynamic process of ligand adsorption on the surface of gold electrode. The results showed that the adsorption processes of both ligands included fast and slow adsorption process, and the fast process followed the langmuir adsorption isotherm. The surface coverage ($\theta$) for PPh$_3$ was higher than that of THPO, and the adsorption of PPh$_3$ was quicker compared to THPO due to the larger adsorption kinetic constant of PPh$_3$. In addition, the exchange process of the ligands was studied on the surface of gold electrode by electrical double layer capacitance indicating that the ligand exchange was a complex process, and about half of THPO was replaced by PPh$_3$ on the surface of THPO-Au resulting Janus Au with amphiphilic property.

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