

Ligands Exchange Process on Gold Nanoparticles in Acetone Solution

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Abstract. The ligands exchange process on gold nanoparticles (GNPs) was proceeded by using hydrophobic group (PPh₃) and hydrophilic group (THPO) in acetone solution. The FTIR and XPS results demonstrated that part of THPO was replaced by PPh₃ which was dissolved in polar solution (acetone); the results were in accordance with the electrochemical analysis where the differential capacity decreased with increasing exchange time. After 12 h, the exchange process terminated and the final ratio of PPh₃ and THPO was about 1.4: 1. This ratio remained unchanged although the PPh₃ and THPO modified GNPs re-dispersed in the PPh₃ acetone solution demonstrating the stable adsorption of both ligands after exchanging for 12 h. The TEM images showed that the gold nanoparticles were self-assembled from scattered to arranged morphology due to the existence of hydrophilic and hydrophobic ligands and led to Janus gold nanoparticles.

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. Self-assembling monolayers (SAMs) to modified gold substrates is a powerful method with high orderliness, orientation, thermodynamic stability and low defect. Gold nanoparticles are obtained by using single ligands. However, Janus gold particle need the existence of hydrophilic and hydrophobic ligands on gold particle simultaneously, which possess distinct surface patchiness and exhibit at least two physicochemical properties within a single nanoparticle^[10-11], and result in unique building blocks to prepare advanced ordered structures



based upon their anisotropic attributes^[12-13]. Janus particles have the widespread application prospect in sensing device^[14], imaging probes^[15-16], catalysis^[17-18], optoelectronics device^[19], photoelectric biosensor^[20], drug delivery^[21], functional surface active agent^[22], etc.

Thiol modified gold is widely applied in fundamental and practical issue due to the strong interaction between gold and sulfur^[23-24]. Phosphorus ligands can also adsorb onto gold surfaces due to their electrostatic interactions although which is weaker than that of thiol ligands. However, the replacement of phosphorus ligands on gold substrate is feasible and we infer that Janus gold particles with THPO and PPh₃ ligands can be obtained. In this paper, the ligands exchange process of THPO and PPh₃ is investigated by using electrochemical method, FTIR and XPS. The morphology, Janus gold nanoparticles formation and the ratio of PPh₃ and THPO on the surface of gold was studied in details.

2 Experimental

2.1 Chemicals

Chloroauric acid (HAuCl₄, 47.8%, AR) was purchased from Shanghai Billiton Co.Ltd., China. Triphenylphosphine (PPh₃, CP) was bought from Sinopharm Chemical Reagent Co. Ltd., China. tetrakis(hydroxymethyl)phosphonium chloride (THPC, 80%, CP) was obtained from Tokyo Chemical Industry Co. Ltd., Japan. Sodium hydroxide (NaOH, 96 %,AR), sulfuric acid (H₂SO₄, AR, 95-99%) and hydroxylamine hydrochloride (96%, AR) were purchased from Shantou Xilong Chemical Co. Ltd., China. Trisphosphine oxide (THPO, 95.5%) was bought from Wuhan Jinlin Chemical Technology Co. Ltd., China. Deionized water was used in all experiments.

2.2 Preparation of gold nanoparticles (GNPs) with single ligand

NaOH (1 M, 300 μ L), THPC (50 mM, 1 mL) and HAuCl₄ (25 mM, 2 mL) were added to a conical flask contained 47 mL deionized water under ultrasonic stirring, leading to the formation of a GNPs colloid in palm red color, which were removed in a dialysis bag (with intercept molecular weight of 3500) immersed in deionized water to remove soluble reaction products. The operation lasted for 6~7 days accompanied with the refreshment of deionized water periodically, resulted in the THPO protected nano-gold colloid (THPO-Au).

2.3 Study of exchange process on GNPs

Exchange process of the GNPs in the as-prepared colloids was carried out at the acetone/water solution by ligand exchange reaction. 5 mL as-prepared THPO-protected GNPs colloid were added into a vials contained 5 mL of 50 mM PPh₃ acetone solutions, stirred for 30 min, 4 h, 12 h and 24 h, and then washed by centrifuging and dried with high pure Ar to obtain THPO- PPh₃ modified GNPs (THPO- PPh₃-Au). The THPO- PPh₃ modified GNPs (THPO- PPh₃-Au) were dispersed into DMF solution with the concentration of 0.033 mg mL⁻¹.

5 mL of THPO-Au mixed with 5 mL of PPh₃ acetone solution and stirred 24 h, and then centrifuged to remove the remained ligands, the solid was re-dispersed in 5 mL acetone to form THPO- PPh₃-Au acetone dispersion, and then 5 mL of 1 mM PPh₃ acetone solution was added into the dispersion and stirred for 24 h. The obtained samples were named as THPO- PPh₃-Au-2nd.

2.4 Characterization

UV-vis absorption spectrum (Beijing Purkinje General Instrument Co. Ltd.) was used to describe the formation of GNPs. FTIR (Thermo Nexus 470 FT-IR) and XPS (AXIS ULTRA XPS, KRATOS) were employed to determine the capping molecules of the as-prepared GNPs. TEM (JEM-2010, JEOL) was applied to measure the morphology of gold nanoparticles.

For electrochemical measurements, 5 μ L of the THPO- PPh₃-Au solution was dropped onto the pre-polished grassy carbon electrode for 6 times, and dried under vacuum at 80°C for 12 h. The electrode was used as working electrode for CV test with Pt and Hg/Hg₂SO₄ as counter and reference

electrode, respectively, 0.5 M H_2SO_4 was used as electrolyte. The voltage window scanned from -0.05 V- 0.05 V with 10 mV s^{-1} .

3. Results and discussion

The morphologies of the samples before and after ligands exchange are showed in Fig.1. The THPO-Au particles (the left image) are scattered with the average size of 2.1 nm. After stirring for 24 h in the 1 mM PPh_3 acetone solution, the obtained THPO- PPh_3 -Au (the right image) aggregate by self-assembling.

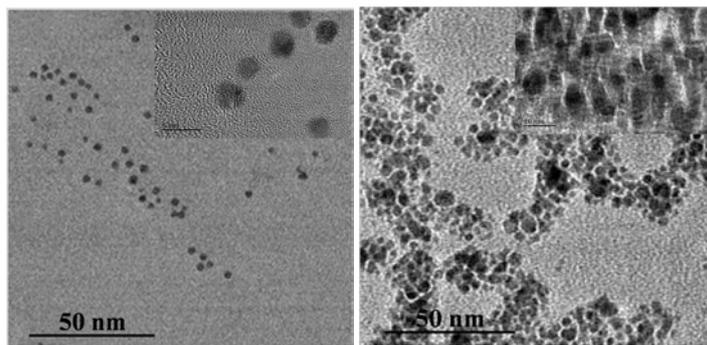


Fig.1, TEM images of THPO-Au (left) and THPO- PPh_3 -Au (right)

The FTIR spectra of THPO- PPh_3 -Au and THPO- PPh_3 -Au-2nd are showed in Fig.2, the high intensity band at 3447 cm^{-1} belongs to the adsorbed H_2O , and the peaks at 1633 cm^{-1} , 626 cm^{-1} represent the vibration of C-H of benzene, which demonstrate the existence of PPh_3 . The peaks located at 1397 cm^{-1} , 1108 cm^{-1} belong to the vibration of C-OH indicating the existence of THPO and THP.

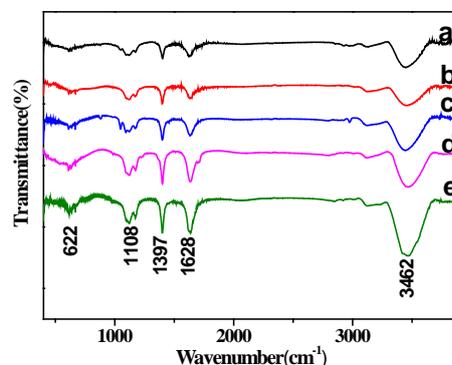


Fig.2 FTIR spectra of THPO- PPh_3 -Au obtained after stirring for 30 min (a), 4 h (b), 12 h (c), 24 h (d) and THPO- PPh_3 -Au-2nd (e).

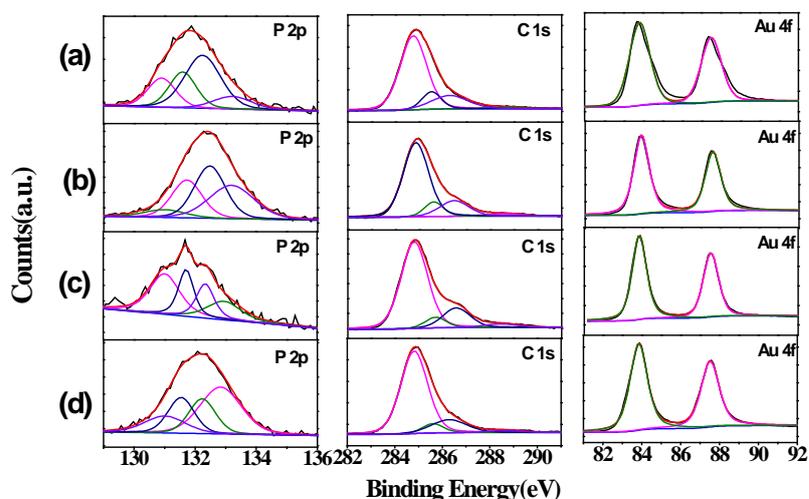


Fig.3 P 2p (left), C 1s (middle) and Au 4f (right) of THPO-PPh₃-Au obtained after stirring for 30 min (a), 4 h (b), 24 h (c) and THPO-PPh₃-Au-2nd (d).

The deconvolution of the corresponding P, C and Au XPS signals are showed in Fig.3. Two fitted peaks at 83.8 eV and 87.5 eV in Fig.3 can be assigned to the Au4f_{5/2} and Au4f_{7/2}[25], indicative of metallic gold. Four fitted peaks for the C1s signal at 284.8 eV, 285.3 eV, 286.4 eV and 288.4 eV were belong to -C-H [26], C-OH, C-P and O-C=O [27] groups, respectively. The fitting of the P2p curve (Fig.3) show four peaks at 131.3 eV and 132.1 eV, 131.0 eV, 131.6 eV corresponding to THP and THPO, PPh₃ and PPh₃O[28-29], respectively. The content of the above mentioned groups, according to P 2p of sample a, b, c, and d, the ratio of PPh₃, PPh₃O and THP, THPO is 0.45:1, 0.66:1, 1.38:1, 1.40:1. According to C1s, the content of C-OH came from THPO and THP and the content of C-P came from PPh₃ and PPh₃O leading to that the ratio of PPh₃, PPh₃O and THP, THPO was 0.47:1, 0.69:1, 1.37:1, 1.42:1, demonstrating of the content of hydrophobic groups of increase with increasing the mixing time. After exchanging for 12 h, the ratio of PPh₃, PPh₃O and THP, THPO almost keep constant, even the sample c re-dispersed in 1 mM PPh₃ solution, the ratio of hydrophobic groups (PPh₃, PPh₃O) and hydrophilic groups (THP, THPO) is unchanged.

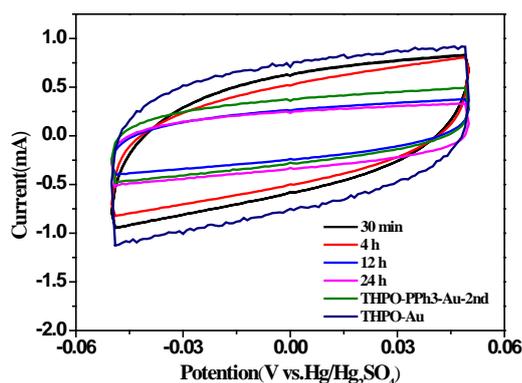
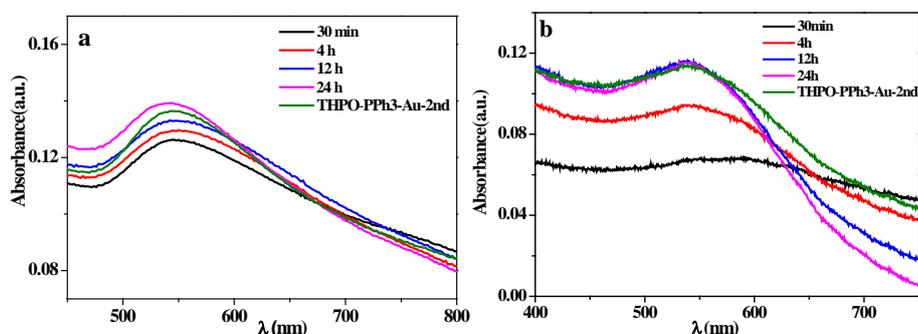


Fig. 4 CV plots of THPO-Au, THPO-PPh₃-Au obtained after stirring for 30 min, 4 h, 12 h, 24 h and THPO-PPh₃-Au-2nd.

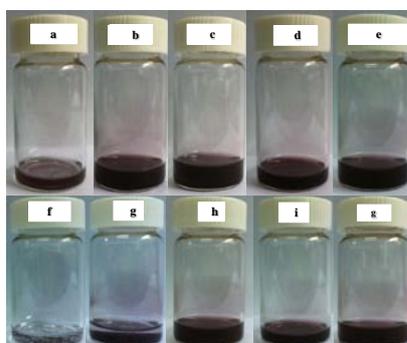
Table 1, Differential capacity of THPO-Au, THPO-PPh₃-Au obtained after stirring for 30 min, 4 h, 12 h, 24 h and THPO-PPh₃-Au-2nd.

Echange time	30mi n	4h	12h	24h	THPO-PPh ₃ -Au-2n d
C _d (mF/mg)	61.23	51.9	28.0	28.8	29.90
		1	2	2	

The CV plots with the potential ranged from -0.05 to 0.05 V represent the differential capacity of the electrode which is calculated through the following equation: $C_d = \Delta i / 2vm$, the variation of Δi indicates the adsorption of ligands. The C_d of THPO-Au is 75.45 mF/mg, Δi decrease with increasing of stirring time. The variation of C_d is showed in Table 1, with the time increasing, the value of C_d decrease, after 12 h, the C_d maintain unchanged, after exchange for the second time, the C_d increase slightly indicating that after stirring for 12 h, the ligands exchange process is completely finished that even fresh PPh₃ solution can't exchange further.

Fig.5 UV-vis spectra of THPO-PPh₃-Au obtained after stirring for 30 min, 4 h, 12 h, 24 h and THPO-PPh₃-Au-2nd in DMF (a) and acetone (b).

THPO-PPh₃-Au obtained after stirring for 30 min, 4 h, 12 h, 24 h and THPO-PPh₃-Au-2nd are re-dispersed in DMF and acetone, the UV-vis spectra are showed in Fig.5. The adsorption peak (Fig. 5a) at 540 nm demonstrate the existence of Au nanoparticles, with increasing the stirring time, the absorbance increase demonstrating the increase of Au content, and the variation trend of the absorbance of THPO-PPh₃-Au in acetone is the same as that in DMF (Fig.5b).

Fig.6 Images of THPO-PPh₃-Au after stirring for 30 min (a, f), 4h (b, g), 12 h (c, h), 24 h (d, i) and THPO-PPh₃-Au-2nd (e, g) before (a, b, c, d, e) and after (f, g, h, i, g) standing for 24 h in acetone solution.

The dispersibility and stability of the THPO-PPh₃-Au and THPO-PPh₃-Au-2nd are measured by re-dispersing in acetone and standing for 24 h. As showed in Fig.6, the color darkens by increasing the stirring time, possibly due to the content of Au increases, which is in accordance with the UV-vis

results. After standing for 24 h, the samples obtained by stirring 30 min and 4 h settle, and the samples obtained by stirring for more than 12 h is stable possibly due to the high content of PPh₃ which is demonstrated by XPS results.

4. Conclusions

The ligands exchange taken place by mixing the THPO modified Au in PPh₃ acetone solution and stirring for different time, with the increasing of adsorption time, the surface of bare Au was decreased as well as the differential capacity. The FTIR results demonstrated the existence of PPh₃ and THPO, and XPS results showed that the content of PPh₃ was increased with the increasing of stirring time, as well as the dispersibility and stability measured by UV-vis and standing experiments.

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Reference

- [1] S. Campuzano, M. Pedrero, *Talanta*, 66(2005), 1310-1319.
- [2] C. Boozer, J. Ladd, *Anal. Chem.*, 76(2004), 6967-6972.
- [3] N.K. Chaki, K. Vijayamohanan, *Biosens. & Bioelectron.*, 17(2002), 1-12.
- [4] K. Motesharei, M.R. Ghadiri, *J. Am. Chem. Soc.*, 119(1987), 11306-11312.
- [5] F.P.Zamborini, J. K.Campbell, R. M.Crooks, *Langmuir*, 14(1998), 640-647.
- [6] G.K.Jennings, P.E. Laibinis, *J. Am. Chem. Soc.*, 119(1997), 5208-5214.
- [7] S. Ramachandran, B-L.Tsai, M. Blanco, *Langmuir*, 12(1996), 6419-6428.
- [8] K. Kitagawa, T. Morita, S.Kimura, *Langmuir*, 21(2005), 10624-10631.
- [9] J. Chen, M.A. Reed, A.M. Rawlett, *Science*, 286(1999), 1550-1552.
- [10] A. Walther, A. H. EMuller, *Application. Chem. Rev.*, 2013, 113, 5194-5261.
- [11] X. Y.Ling, I. Y.Phang, ; C.Acikgoz, *J. Angew. Chem, Int. Ed.*, 2009, 48, 7677-7682.
- [12] S. K.Smoukov, S.Gangwal, M.Marquez, *Soft Matter* 2009, 5, 1285-1292.
- [13] S.Gangwal, O. J.Cayre, O. D.Velev, *Langmuir*, 2008, 24, 13312- 13320.
- [14] J.Lee, J. Kim, *Chem. Mater.*, 2012, 24, 2817-2822.
- [15] G. A.Sotiriou, A. M.Hirt, P. Y.Lozaeh, *Chem.Mater.*, 2011, 23, 1985-1992.
- [16] M.Yoshida, K. H.Roh, J.Lahann, *Biomaterials*, 2007, 28, 2446-2456.
- [17] L.Baraban, D.Makarov, R.Steubel, *ACS Nano.*, 2012, 6, 3383-3389.
- [18] D. J.Cole-Hamilton, *Science*, 2010, 327, 41-42.
- [19] Y. K.Takahara, S.Ikeda, S.Ishino, K.Tachi, *Am. Chem. Soc.*, 2005, 127, 6271-6275.
- [20] P. A.Suci, S.Kang, M.Yong, *Am. Chem. Soc.*, 2009, 1, 1747 - 1754.
- [21] G.Zheng, M.Chen, X. Y.Liu, *Electrochim. Acta*, 2014, 136, 301-309.
- [22] M.Motaghedifard, M.Behpour, S. M.Ghoreishi, *Sens. and Actuator B: Chem.*, 2014, 203, 802-811.
- [23] K. Sunil, M. K.Aryan, Park, *Biosens. & Bioelectron.*, 2014, 61, 260-265.
- [24] X.Du, Z. Y.Miao, D.Zhang, *Biosens. & Bioelectron.*, 2014, 62, 73-78.
- [25] C.J. Powell, *Appl. Surf. Sci.*, 1995, 89: 141- 149.
- [26] D Briggs, G Beamson, *Anal. Chem.*, 1992, 64: 1729-1736.
- [27] G Beamson, D Briggs, *Mol. Phys.*, 1992, 76: 919-936.
- [28] J.K. Kouba, J.L. Pierce, R.A. Walton, *J. Organomet. Chem.*, 1980, 202: C105-107.
- [29] W.J .Stec, W.E. Morgan, R.G. Albridge, et al., *Inorgan. Chem.*, 1972, 11: 219-225.