Preparation of Janus Ag nanoparticles by liquid/liquid interfacial reaction

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Abstract. Janus silver (Ag) nanoparticles have been successfully synthesized by intense agitation at the interface of toluene and water which contains Ag (PPh₃)₂NO₃ and THPC. Contact angle of the film prepared by L-B technology is measured which indicates that the Ag nanoparticle is amphipathicity because they have hydrophobic region and hydrophilic region separately. TEM image showed the assembled morphology of Ag instead of monodispersed particles. After purification, analysis of FT-IR and XPS showed the Janus Ag nanoparticles are protected by ligands of THPC and PPh₃ with a ratio of 1:1.

1. Introduction

In 1978, Lehn came up with “supermolecular chemistry”, which investigate the self-assembled molecular based on the interaction of molecular including hydrogen bond, electrostatic force, Van der Waals’ force, hydrophilic and hydrophobic interaction. By using these interactions, various supermolecular are prepared. Janus particles is a typical structure of these supermolecular, which attracted intensive interest in the fields of self-assembling and molecular recognition[1], catalysts[2], optical biosensor[3] and etc[4,5] due to their anisotropy.

Synthesis of amphiphilic Janus nanoparticles requires creating two distinct compartments on the surface in a cost-effective and reliable way. Masking was one of the techniques initially applied on larger Janus particles and scaled down to the nanoscale involving the protection of one side and modification of another, followed with the removal of the protection. However, the use of gas/liquid, liquid/liquid, and liquid/solid interfaces that trap homogeneous nanoparticles is much more popular[6].

Previous researches have reported the preparation of Janus metal nanoparticles or Janus alloy nanoparticles by using metallo-organic compound as precursor, THPC as reductant, and the reaction mechanism and application were investigated. In this paper, we prepared ligands modified Ag by using ultrasonic, which is a rapid method. Janus Ag particles were prepared by using liquid/liquid interfacial reaction. The structure, morphology and the distribution of ligands on the surface of Janus Ag particles were measured.

2. Experimental

2.1 Chemicals

Triphenylphosphine (PPh₃), Tetramethylolphosphonium chloride (THPC), Sinopharm Chemical Reagent Co., Ltd. (China). Other chemical agents were purchased from Wuhan Jinlin Chemical
Technology Co., Ltd. (China). Deionized water was used in all experiments.

2.2 Preparation of Ag (PPh₃)ₓNO₃

0.1065 g AgNO₃ and 0.6560 g PPh₃ was dissolved in 1 mL H₂O and 10 mL toluene, respectively. The obtained solutions were mixed under ultrasonic for 10 min and the white precipitate was obtained in water phase, which was washed with ethyl ether three times and dried at 65°C for 1 h. 3 mL CH₂Cl₂ was added to dissolve the precipitate and then the solution was placed in refrigerate at -15°C for 15 min. 18 mL n-pentane was added into the above solution to separate crystal out, which was washed by n-pentane for 3 times, and dried at 65°C for 1 h to obtain white powder for FTIR and XRD measurement.

2.3 Preparation of Janus Ag nanoparticles

AgNO₃ solution (0.6 mL, 25 mM) and PPh₃ solution (1.2 mL, 50 mM) were mixed under ultrasonic for 10 min to obtain white precipitate for use. NaOH (0.09 mL, 1M), 14.01 mL H₂O and 13.8 mL toluene were mixed by emulsifier under 4000 r/min, and then THPC solution (0.3 mL, 50 mM) and the obtained white precipitate was added in sequence, the mixture was kept stirring for another 2 h to obtain self-assembled Janus Ag film. The assembled Janus Ag film on quartz was prepared in Langmiuir film balance (JML04C1-P).

2.4 Characterization

Janus Ag film was characterized by a contact angle goniometer (JWA-360, Xiamen Chongda Intelligent Technology Co., Ltd., China), an XPS (ESCALAB250Xi, ThermoFisher Scientific), FTIR (Thermo Nexus 470), XRD (Xpert-Pro), TEM (JEM-2100F) and ICP-OES (Optima 8000, PerkinElmer).

3. Results and discussions

3.1 Characterization of Ag (PPh₃)ₓNO₃

The structure of Ag (PPh₃)ₓNO₃ was measured by FTIR and XRD. In Fig.1a, the band at 3055 cm⁻¹ is assigned to vibration of C-H, as well as the peaks at 745 cm⁻¹ and 694 cm⁻¹. The peaks at 1435 cm⁻¹ and 513 cm⁻¹ are attributed to vibration of benzene. The peaks at 1385 cm⁻¹ and 1310 cm⁻¹ belong to the vibration of −NO₂. These vibrations prove the existence of PPh₃.

Fig.1b shows the XRD pattern of Ag (PPh₃)ₓNO₃. The red line is the measured XRD pattern which is similar to the simulated results. The sharp XRD peaks indicate high crystallinity. According to the XRD pattern, the obtained Ag (PPh₃)ₓNO₃ belongs to orthorhombic system (Aba2, a=14.846Å, b=25.440Å, c=10.318Å). These results indicate that Ag (PPh₃)ₓNO₃ can be prepared by ultrasonic.

![Fig.1. FTIR (a) and XRD(b) spectra of Ag(PPh₃)ₓNO₃](image)

3.2 Characterization of Janus Ag nanoparticles

The morphology of Janus Ag nanoparticles were measured by TEM which are showed in Fig.2a and 2b. No monodispersed Janus Ag nanoparticles are observed, indicating the Janus Ag nanoparticles are
self-assembled to form film. Ag nanoparticles have three major lattice fringe which can be assigned to (111), (200) and (311) with the interplanar spacing of 0.236 nm, 0.204 nm and 0.123 nm, respectively. In Fig.2b, only (200) facet of Ag nanoparticles can be observed.

Fig.2 TEM images of Janus Ag nanoparticles

The structure of Janus Ag nanoparticles were measured by UV-vis and FTIR analysis. Janus Ag nanoparticles were dispersed in DMF for UV-vis analysis (inset of Fig.2a). The absorption peak at about 443 nm manifests the existence of Ag nanoparticles (Fig.2a). Fig.2b shows the FTIR of Janus Ag nanoparticles, the peaks at about 3443 cm⁻¹ and 1400 cm⁻¹ are assigned to the stretch vibration and transformation vibration of –OH. The peaks at about 1629 cm⁻¹ and 611 cm⁻¹ are attributed to the vibrations of benzene and C-H, which indicates the existence of PPh₃.

Fig.3 UV-vis (a) and FTIR (b) spectrum of Janus Ag nanoparticles

The contact angle of H₂O is measured to investigate the amphiphilic property of Janus Ag particles. Before measurement, Janus Ag nanoparticles were deposited onto the hydrophilic and hydrophobic quartz substrate through Langmuir-Blodgett method, respectively. Quartz substrate was treated by piranha solution (98% H₂SO₄:30%H₂O₂=3:1) to introduce hydrophilic property, and then immersed in trimethylchlorosilane/DMF solution for 20 min to introduce hydrophobic property. The contact angles of H₂O on Janus Ag nanoparticles deposited on hydrophilic and hydrophobic quartz substrate are showed in Fig.4.

Fig.4 Contact angles of H₂O on hydrophilic (a) and hydrophobic (c) quartz substrate, on Janus Ag nanoparticles deposited on hydrophilic (b) and hydrophobic (d) quartz substrate.
Before deposition of Janus Ag nanoparticles, the contact angle of H$_2$O on hydrophilic and hydrophobic quartz substrate is 0° and 93.5°. After deposition of Janus Ag nanoparticles, the contact angles increase, the contact angle on Janus Ag nanoparticles is 23.1° and 96.4°, exhibiting hydrophilic and hydrophobic properties.

![Fig.5](image)

**Table 1** XPS data of the C 1s, P 2p, Ag 3d of the sample

| Elements | BE(eV) | Fwhm(eV) | Atomic percentage(%) | Possible chemistry |
|----------|--------|----------|----------------------|-------------------|
| C 1s     | 283.88 | 1.22     | 65.77                | C-C$^7$           |
|          | 284.43 | 1.22     | 10.42                | C-OH$^8$          |
|          | 284.94 | 1.7      | 20.41                | C-P$^9$           |
|          | 286.51 | 1.42     | 3.40                 | C=O$^{10}$        |
| P 2p     | 131.56 | 1.33     | 25.05                | PPh$_3$$^{11}$    |
|          | 132.19 | 1.33     | 41.68                | PPh$_3$O$^{12}$   |
|          | 133.20 | 1.33     | 24.22                | THPO$^{13}$       |
| Ag 3d    | 367.50 | 0.87     | 59.86                | Ag$^0$ 3d$^{5/2}_{3/2}$$^{14}$ |
|          | 373.5  | 0.87     | 40.14                | Ag$^0$ 3d$^{5/2}_{3/2}$$^{15}$ |

Atomic percentage$^a = \frac{A_{peak}}{A_{total}}$ for a selected element

The surface property of Janus Ag nanoparticles are further investigated by XPS analysis, the results are showed in Fig. 5 and Table 1. From Ag 3d spectrum, the ratio of 3d$^{5/2}$ and 3d$^{3/2}$ is about 2:3, indicating the existence of Ag$^0$. The atomic percentage of C-C, C-OH, C-P and C=O is about 65.77 at.%, 10.42 at.%, 20.41 at.% and 3.40 at.% respectively. According to the structure of PPh$_3$/PPh$_3$O (P is connected with three benzene) and THP/THPO (P is connected with three C-OH), the ratio of C-P to C-OH is calculated to be 1.05:1. According to P 2p spectrum, the ratio of PPh$_3$/PPh$_3$O and THP/THPO is about 1.03:1, which is in line with the results obtained from C 1s spectrum. We can conclude that Ag has both hydrophilic and hydrophobic ligands with the ratio about 1:1.

### 4. Conclusions

In conclusion, we find that Ag (PPh$_3$)$_x$NO$_3$ precursor can be prepared by ultrasonic, XRD and FTIR confirm the crystal structure of Ag (PPh$_3$)$_x$NO$_3$ which has the PPh$_3$ ligands. Janus Ag nanoparticles can be prepared by vigorous stirring which exhibits the morphology of self-assembled film. The Janus Ag nanoparticles has hydrophilic and hydrophobic properties due to the existence of THP/THPO and PPh$_3$/PPh$_3$O with the ratio about 1:1.

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