Supporting Information

Effect of Hydrophobic Chain Length of Surfactant on Controlling the Morphology of gold crystals

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Chemicals

Hydrogen tetrachloroaurate (III) trihydrate (HAuCl₄·3H₂O, 2 wt % solution in water), ammonium chloride (NH₄Cl, 99 %) and Melamine (99.99%) were purchased from Aldrich and used as received. Bis- (amidoethyl-carbamoylethyl) octadecylamine (C18N3) was synthesized as reported in the literature¹⁷. Ultra-pure water (18 M Ω cm) was used for all aqueous preparations.

Experimental Procedures

Synthesis of CxN3 (x=18, 16, 14, 12)

The synthesis of CXN3 procedures was present with an example of C18N3. A solution of freshly recrystal octadecylamine 8.1g (for C16N3 was hexadecylamine 7.2g, C14N3 was tetradecylamine 6.4g and C12N3 was dodecylamine 5.6g) in methanol (20 ml) at room temperature was added dropwise to a stirred solution of methylacrylate (6ml, 0.12mol) in methanol (20 ml), under nitrogen, over a period of 2 h. The final mixture was stirred for a further 24 h. The solvent was removed under reduced pressure at 40°C using a rotary evaporator and the resulting colourless oil. The residue was dissolve in chloroform and washed with 0.1M NaOH solution twice. The chloroform solution collected and dried with anhydrous calcium chloride. Then the crude product separated by column chromatogram to get colorless oil product, which was measured by NMR and MS. The result was consulted with the reference to be accordant. 1 H-NMR (300MHz, CDCl3): 0.78(t, 3H), 1.16(s, 32H), 2.38(m, 6H), 2.71(t, 4H), 3.57(m, 6H), ESI-MS (m/z): 442.6 [M+H]⁺.

Then the solution of above product 10.9 g (for C16N3 was 10.2g, C14N3 was 9.5g and C12N3 was 8.8g) in methanol (20 ml) was carefully added to a vigorously

stirred solution of 1, 2-diaminoethane (75g, 85ml, 1.2mol) in methanol (100 ml) at room temperature. After complete addition the mixture was stirred for another 24 h at room temperature at which time no ester groups was detectable by NMR spectroscopy. The solvent was removed under reduced pressure maintaining the temperature no higher than 40°C. The excess 1, 2-diaminoethane was removed using an azeotropic mixture of toluene and methanol (9: 1). The remaining toluene removed by azeotropic distillation using methanol. Finally, white powder 10.2 g (for C16N3 was 9.9 g, C14N3 was 9.2 g and C12N3 was 8.6 g) was obtain, which separated by TLC with chloroform: methanol: ammonia=1:1:0.1. The final product was then repeated recrystallization with chloroform and cyclohexane and given a white solid, which was measured by NMR and MS. The result was consulted with the reference to be accordant. 1 H-NMR (300MHz, CDCl3): 0.88(t, 3H), 1.25(s, 32H), 1.84 (s, 4H), 2.38(m, 6H), 2.73(m, 4H), 2.82(m, 4H), 3.29(m, 4H), 7.47(s, 2H), ESI-MS (m/z): 498.6[M+H]⁺.

Synthesis of gold cracked potatochip-like plates

First, 20 ml of water was heated with stirring in a three-neck flask to 80 °C over a heating mantle. Then, 5 ml of 10 mM CxN3 (x=12, 14 and 16) aqueous solution was added. One minute later, 1.6 ml of 5×10^{-2} M 50mM HAuCl₄ was added into the flask, which was sealed and refluxed. The reaction was allowed to proceed for a total of 12 h before the heating mantle was removed from the flask. After the reaction finished, the sample was centrifuged at 9000 × g and washed four times with water. The precipitates were redispersed in water for characterization.

Synthesis of gold nanodesert rose

First, 23 ml of ammonium chloride solution (0.5 M) was heated with stirring in a three-neck flask to 80 °C over a heating mantle. Then, 1 ml of 10 mM C14N3 aqueous solution was added. One minute later, 1.6 ml of 5×10^{-2} M 50mM HAuCl₄ was added to the flask. To prevent loss of water, the solution was refluxed by connecting one neck of the flask to a condenser, and the others were sealed. The reaction was allowed to proceed for a total of 8h before the heating mantle was removed from the flask. The solution was kept at room temperature for 24 h, centrifuged at 8000 × g and washed with water repeated four times. The final products were sand-like golden crystals; the precipitates were redispersed in ethanol for characterization. If the surfactant were C12N3, C16N3 and C18N3, the resulting products from this procedure were gold nanoplates.

Synthesis of gold durian-like microspheres

First, 20 ml of water was heated with stirring in a three-neck flask to 80 °C over a heating mantle. Then, 5 ml of 10 mM C12N3 aqueous solution was added. One minute later, 0.4 ml of 50mM HAuCl₄ was added into the flask, which was sealed and refluxed as already described. The reaction was allowed to proceed for a total of 12 h before the heating mantle was removed from the flask. After the reaction finished, the

sample was centrifuged at $4000 \times g$ and washed four times with water. The precipitates were redispersed in water for characterization.

Characterization.

The products were characterized by scanning electron microscopy (SEM, Hitachi S4300, 15 kV), transmission electron microscopy (TEM, JEOL JEM-1011CX, 100 kV), and X-ray diffraction (XRD, Rigaku Dmax-2000, Ni-filtered Cu K α radiation). For the XRD measurements, the gold product was dispersed in water and several drops of the suspension were dropped onto a clean glass slide, and then left in ambient air to dry. For the TEM and SEM measurements, the suspension was dropped onto a Formvar-covered copper grid and a silicon wafer, respectively, followed by air drying.

Raman measurements were made with a Renishaw System 1000 Raman imaging microscope (Renishaw PLC, U.K) equipped with a 50 mW (641nm) He-Ne laser (model 127-25RP, Spectra-Physics, USA) and a Peltier-cooled CCD detector (576 pixels \times 384 pixels). A 50 \times objective (NA = 0.80) mounted on an Olympus BH-2 microscope was used to focus the laser onto a spot approximately 1µm in diameter and to collect the back-scattered light from the sample.



Salt Effect on Controlling Morphology of Gold Crystals.

Fig. S1 SEM images of gold particles obtained by different CXN3 (Standard conditions were maintained at 80 °C, 1 mM CxN3, 4.5 mM HAuCl₄ and 0.5 M NH₄Cl aqueous solution;); (a) C12N3, (b) C14N3, (c) C16N3; (d) C18N3.



Fig. S2 SEM images of gold particles obtained by C18N3 (Standard conditions were maintained at 80 °C, 1 mM C18N3, 4.5 mM HAuCl₄ and 0.5 M NaCl aqueous solution)

Reducing ability of CxN3.



Fig. S3. UV-vis absorption spectra of gold crystals with different CxN3, obtained when the reaction preceded 3 min. (Standard conditions were maintained at 80 °C, 1 mM CxN3, 1.13 mM HAuCl₄ aqueous solution). It can be seen that the order of reducing ability of CxN3 was as follows: C18N3 > C16N3 > C14N3 > C12N3. According to previous report⁽¹⁾, the probable oxidized products of CXN3 molecules in the reaction were the two organic groups -CH₂-NH₂ oxidized to -CH=NH or further oxidized to -C=N.

Reference

(1) Meng Chen, Yong-Gang Feng, Xia Wang, Ting-Cheng Li, Jun-Yan Zhang, and Dong-Jin Qian. Langmuir 2007, 23, 5296-530.