Triphenylmethanethiol: a novel rigid capping agent for gold nanoclusters

Di Li and Jinghong Li*

State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China. E-mail: lijingh@ciac.jl.cn; Fax: +86 431 526 2243

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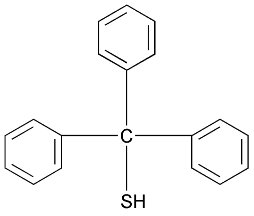
In this article, we employed triphenylmethanethiol (TPMT) as a novel rigid agent for capping gold nanoparticles and the TPMT monolayer-protected gold nanoparticles were characterized by various analytical techniques. High-resolution transmission electron microscopy showed a narrow dispersed gold core with an average core diameter of *ca.* 3.6 nm. The UV/vis spectrum revealed the surface plasmon absorbance at 528 nm. The p-π conjugated structure of the TPMT ligand was confirmed by nuclear magnetic resonance. Differential scanning calorimetry and Fourier transform infrared spectroscopy revealed the rigid nature of the TPMT chains.

Introduction

Au colloids have, to date, been the focus of the majority of the research on metal colloid-based nanostructures and nanostructured materials.[1] Brust *et al.* developed a two-phase approach to synthesize thiol-derivatized Au nanoparticles (monolayer-protected clusters, MPCs).[2] They combined techniques based on the self-assembly of alkanethiol monolayers on flat Au surfaces with the reduction of $AuCl_4^-$ by sodium borohydride to produce 1–3 nm Au particles bearing a stabilizing thiol coating.

MPCs have smaller sizes and narrower size distributions compared with those of their classical sodium citrate reduced counterparts[3] and are particularly attractive owing to their air-stability, tunable solubility and ease of functionalization. However, as the coatings are mainly flexible alkyl derivatives, the thermal disorder resulting from surface-gauche is hard to avoid. Therefore, a preferred system will be one in which conformational disorder has been eliminated. This can be achieved by using rigid molecules,[4,5] where surface functional groups have no conformational freedom and are "stuck" at the surface.[6] Phenyl derivatives are such coating materials that could satisfy the above requirements.

Brust,[7] Chen[8] and their coworkers have reported phenyl derivatives as a capping agent for MPCs, but the rigid nature of the coatings was not specially emphasized. Herein, we aim to employ triphenylmethanethiol (TPMT) as a novel capping agent to synthesize triphenylmethanethiol monolayer-protected gold nanoparticles (TPMT-MPCs). The advantage of rigidity, besides the peculiar p-π conjugation structure, makes TPMT the best agent to study rigid monolayer-protected metal nanoclusters.



TPMT

Experimental

Reagents and materials

Triphenylmethanethiol and tetraoctylammonium bromide were purchased from Aldrich. $HAuCl_4 \cdot 4H_2O$ (99%), $NaBH_4$ (A.R), toluene (A.R, distilled), ethanol (A.R), acetone (A.R) were used as received. Water was purified with a Milli-Q (18.3 MΩ) water system.

Synthesis of TPMT-MPCs. TPMT-MPCs were synthesized following a two-phase reaction.[2] Tetrachloroauic acid (aq., 0.5 mM) was phase-exchanged into the toluene phase in the presence of 1 mM tetraoctylammonium bromide as the phase transfer catalyst. The aqueous phase was quickly cleared and the organic phase became orange-brown in color, indicating that the $AuCl_4^-$ had transferred into it. A 1 mM toluene solution of TPMT was added into the isolated organic phase. The resulting solution was then stirred for another 15 min until the addition of 5 mM sodium borohydride. The organic solution turned dark immediately, indicating the presence of gold nanoclusters. The mixture was stirred overnight and the organic phase was isolated. Toluene solvent was removed on a rotatory evaporator and the crude product was washed consecutively with excess amount of water, ethanol and acetone to remove excess TPMT, disulfide and tetraoctylammonium bromide.

Characterization methods

Transmission electron microscopy (TEM). The initial micrographs were taken with a JEOL-JEM-2010 transmission electron microscope operating at 200 kV (JEOL, Japan). Samples for TEM were prepared by casting one drop of the cluster solution (*ca.* 1 mg per 10 ml) onto a standard carbon-coated (200–300 Å) formvar film on a copper grid (230 mesh). The core size distribution for at least 100 individual clusters was obtained using Scion Image Beta 4.02 (download from www.scioncorp.com).

UV/vis spectroscopy. The UV/vis spectrum of the TPMT-MPCs was acquired with a Cary-500 UV-Vis-NIR

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spectrophotometer (Varian, USA) over the wavelength range from 400 to 800 nm.

Fourier transform infrared spectroscopy. Fourier transform infrared spectroscopy (FT-IR) was conducted using a FTS135 infrared spectroscope (BIO-RAD, USA). The transmission spectrum of the sample was obtained by forming a thin transparent KBr pellet containing *ca.* 2 mg of the material.

Nuclear magnetic resonance (NMR). The ^{1}H NMR spectra of TPMT and the TPMT-MPCs in deuterium DMSO solution were collected on a 400 MHz NMR spectrometer (Bruker, Swiss) and the chemical shifts were internally referenced to the 2.5 ppm signal of the deuterium DMSO.

Differential scanning calorimetry (DSC). The DSC measurement was performed with a 7 Series Thermal Analysis System (Perkin–Elmer, USA) with 2.2 mg TPMT-MPCs. The thermogram was run on a TPMT-MPCs sample in a sealed aluminum pan under a purging atmosphere of nitrogen at a heat-cool rate of 10 °C min^{-1} and the temperature range was varied from −70 to 100 °C.

Results and discussion

TEM

TEM is a potent tool to determine the core size and the shape of metal nanoparticles. The core shape of MPCs is a truncated octahedral. The number of gold atoms in each cluster tends to be 225, 314, 459, *etc.*, which are called "magic numbers".[9] The closest core–core spacing is approximately equal to the length of one ligand, which can be interpreted by the intercalation of ligand chains.[10]

Fig. 1 shows the high-resolution TEM image of TPMT-MPCs and their core size distribution. The TEM image displayed a representative selection of the unfractionated TPMT-MPCs. Individual nanoparticles and loosely packed aggregations can be seen and the average core diameter was calculated as 3.6 nm. The core diameter of TPMT-MPCs was larger than that of dodecanethiol capped gold MPCs formed under the same synthetic conditions,[11] which may be interpreted by the large steric hindrance of TPMT decreasing its diffusion velocity from the solution to the core surface; the growth process of the gold core was prolonged accordingly.

UV/vis

Fig. 2 shows the UV/vis spectrum of TPMT-MPCs with the absorbance peak appearing at 528 nm. Metal nanoparticles exhibit strong UV/vis absorbance, which is absent for bulk metal. This is attributed to a resonance in the collective motion of the conduction electrons in response to optical excitation, the so-called localized surface plasmon resonance (SPR).[12] The classical surface plasma wavelength is proportional to $(Ne^2/Km\varepsilon_0)^{-1/2}$, where N is the density of free electrons, e and m are the charge and mass of the electron, respectively, K is the dielectric constant and ε_0 is the permittivity constant.[13]

Alkanethiolate-MPCs exhibit the surface plasmon absorbance around 520 nm.[10] Compared with alkanethiolate-MPCs, the red shift in the present study may be interpreted as follows: the p-πconjugated structure of TPMT decreases its electron density and free electrons hop from gold to the TPMT ligands, therefore decreasing the free electron density of gold core, resulting in a red shift of the SPR band.

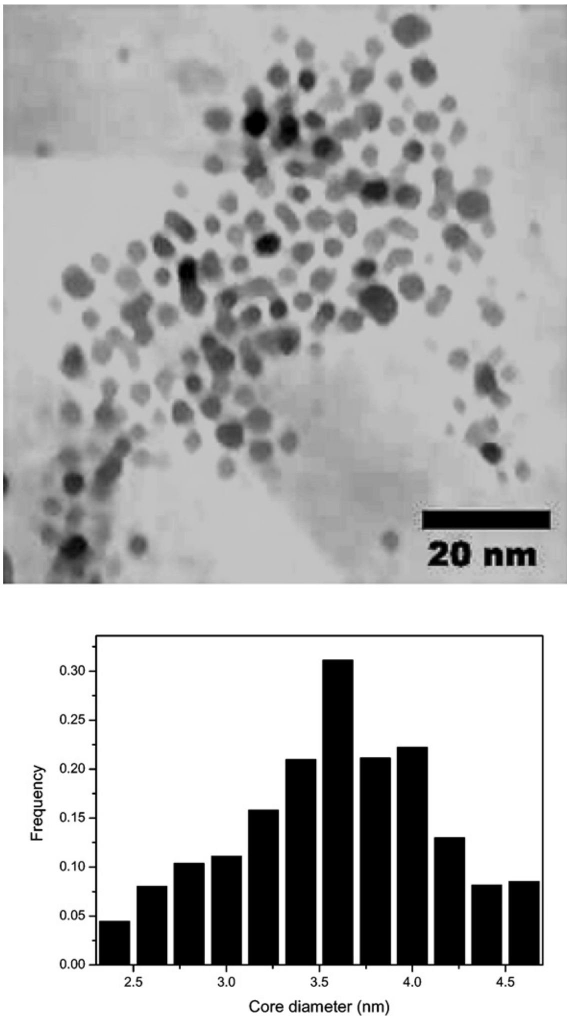

Fig. 1 TEM image of TPMT-MPCs and core size distribution.

FT-IR

FT-IR has been used to probe the structure of alkanethiolate monolayers adsorbed onto gold nanoparticles.[14] Fig. 3 shows the FT-IR spectra of the TPMT monomer and TPMT-MPCs. The peak at 2574 cm^{-1} in Fig. 3(a) was attributed to the S–H stretching vibration of free TPMT. It is absent in Fig. 3(b), indicating that TPMT has assembled onto the gold core *via* the SH group. X-Ray photoelectron spectroscopy (XPS, not

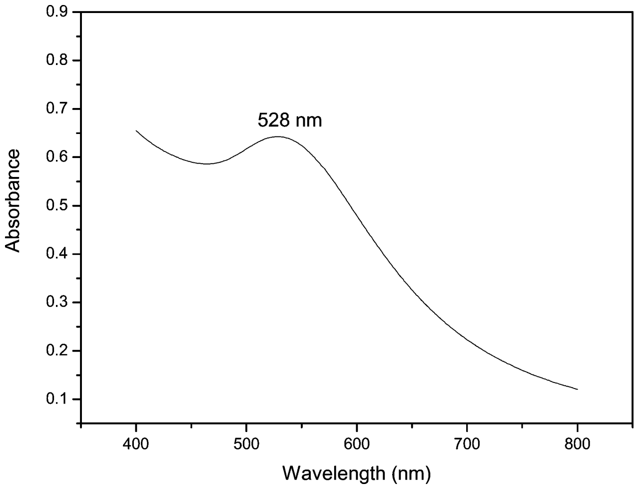

Fig. 2 UV/vis spectrum of TPMT-MPCs showing the SPR absorbance at 528 nm.

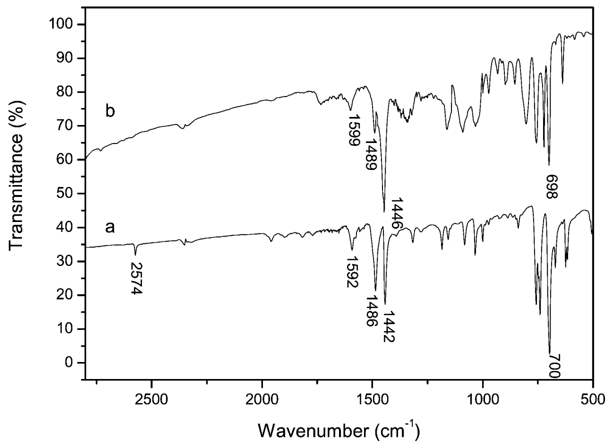

Fig. 3 FT-IR spectra of TPMT monomer (a) and TPMT-MPCs (b); several characteristic peaks are labeled.

shown here) revealed that the binding energies of Au $4f_{7/2}$ and S 2p are 83.6 and 163.5 eV, respectively, corresponding to Au(0) and S(−2), which is another piece of evidence for self-assembly. Moreover, the sulfur signal in the XPS spectrum was much weaker than that of dodecanethiolate-MPCs, indicating that the packing density of TPMT on gold nanoparticles is rather low,[10] due to the rigidity and large steric hindrance of the TPMT ligands.

The peaks at 1592, 1486 and 1442 cm^{-1} in Fig. 3(a) and at 1599, 1489 and 1446 cm^{-1} in Fig.3(b) could be interpreted as the C=C stretching of phenyl. The peaks at 700 cm^{-1} in Fig. 3(a) and 698 cm^{-1} in Fig. 3(b) are attributed to the C–S stretching vibration. The analogy in Fig. 3(a) and (b) indicates that TPMT does not experience a conformation transformation in the assembly process, again due to the rigid nature of TPMT.

NMR

Unlike most other techniques, NMR can provide information about the dynamics of the MPCs systems in addition to structural information. An excellent review on the use of NMR to characterize self-assembled nanostructured materials has been provided by Liu *et al.*[15]

Fig. 4 gives the ^{1}H NMR spectra of TPMT monomer and TPMT-MPCs (phenyl moiety only). The attribution of the chemical shifts is shown in Table 1. NMR spectra of alkanethiolate-MPCs were characteristically broadened relative to those of free alkanethiol,[10] which was attributed that CH_2 group closed to thiolate/Au surface were the most densely packed and solid-like, thereby experienced fast spin relaxation from dipolar. However, in the present study, the ^{1}H spectrum of TPMT-MPCs did not exhibit the characteristic expansion compared with that of TPMT. This could be interpreted that the phenyl moiety was not directly connected to Au core, which avoided the spin relaxation.

Compared with TPMT, it was amazing that the chemical shifts of *m*- and *p*- H in TPMT-MPCs shifted to higher frequency while those of *o*- H shifted to lower frequency. Perhaps the different electron densities of hydrogen at the three positions could be responsible, that is, the electron density of the *o*- H increased while those of *m*- and *p*- H decreased, caused by the peculiar conjugation structure of TPMT.

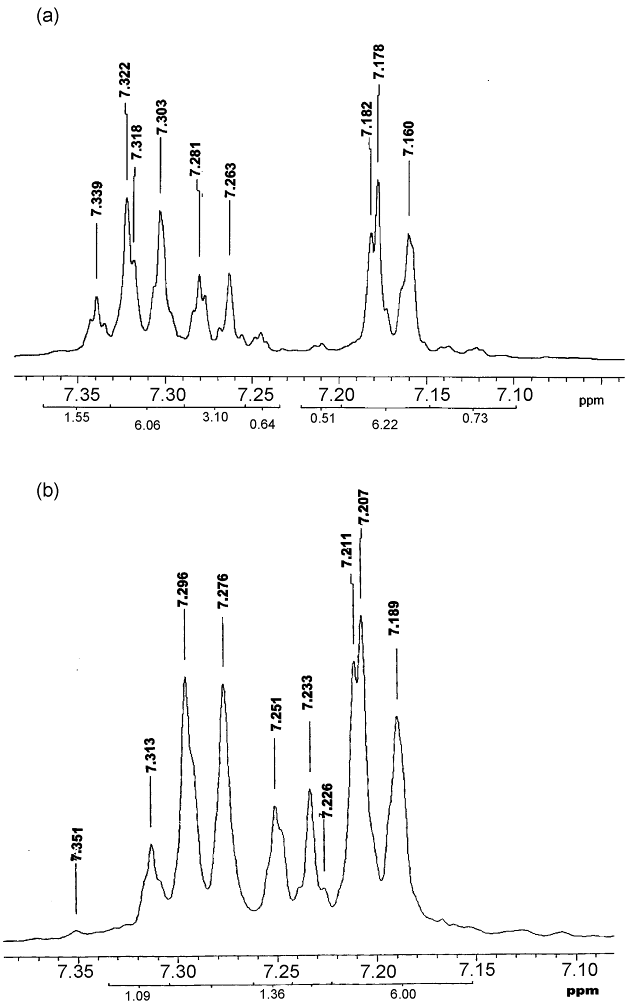

Fig. 4 NMR spectra of TPMT nomomer (a) and TPMT-MPCs (b) in deuterium DMSO solution (phenyl moiety only).

DSC

The phase behavior of alkanethiol-derivatized Au nanoparticles could be characterized by DSC in terms of the temperature and the phase transition. For instance, dodecanethiolate-MPCs underwent a distinct phase transition at *ca.* 0 °C,[10] which could be associated with the reversible disordering of the alkyl chains.[16] Temperature-dependent FT-IR studies revealed that trans-ordering increased in the cooling temperature region where enthalpy transitions were detected.[17]

Fig. 5 shows the DSC spectrum of TPMT-MPCs. In the range of −70–100 °C, a melting transition is absent, indicating that a conformational transition is avoided due to the rigidity

Table 1 Attribution of chemical shifts of benzene moiety of TPMT and TPMT-MPCs

	^{1}H NMR peaks/ppm								
TPMT	7.160	7.178	7.182	7.303	7.318	7.322	7.263	7.281	7.339
TPMT-MPCs	7.189	7.207	7.211	7.276		7.296	7.233	7.251	7.313
Difference	0.03	0.03	0.03	−0.03		−0.03	−0.03	−0.03	−0.03
Attribution	ortho			meta			para		

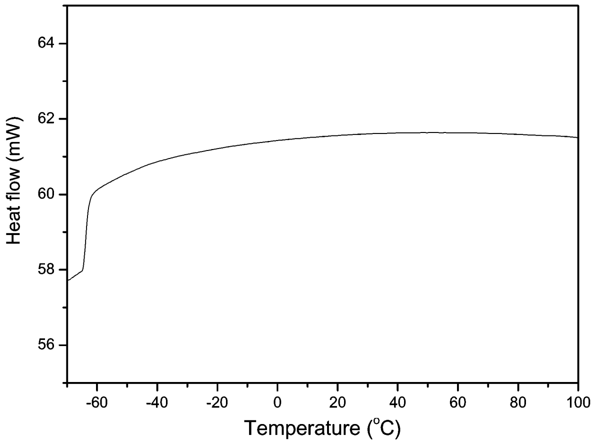

Fig. 5 DSC spectrum of TPMT-MPCs. The temperature range was selected as from −70 °C to 100 °C and the heat-cool rate was set as 10 °C min^{-1}.

of TPMT, which differs from the usual alkyl derivative capping agents.

Conclusion

In the present study, we employed a novel rigid agent, TPMT, as the capping agent to synthesize TPMT monolayer-protected gold nanoparticles. TEM gave an average core diameter of *ca.* 3.6 nm. The conjugation properties of TPMT were observed in the UV/vis and ^{1}H NMR spectra. The conjugated structure caused the SPR absorbance band to shift to 528 nm in the UV/vis spectrum and the chemical shifts of *o*-H shifted to lower frequency while those of *m*- and *p*- H shifted to higher frequency. The rigid nature of TPMT was confirmed by FT-IR and DSC. TPMT-MPCs provide a stable molecularly engineered structure on nanoparticle surfaces, which can be used as a model in studies of molecular recognition, biomaterial interfaces, cell growth, crystallization and many other systems and processes.

Acknowledgements

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