J|A|C|S
COMMUNICATIONS

Novel Spherical Assembly of Gold Nanoparticles Mediated by a Tetradentate Thioether

Mathew M. Maye, Sandra C. Chun, Li Han, Daniel Rabinovich,† and Chuan-Jian Zhong*

Department of Chemistry, State University of New York at Binghamton, Binghamton, New York 13902,
and Department of Chemistry, The University of North Carolina at Charlotte,
9201 University City Boulevard, Charlotte, North Carolina 28223

Received January 27, 2002

The synthesis and processing of nanoparticles consisting of metallic nanocrystal cores and organic monolayer shells promise interesting technological applications in sensors, catalysis, drug delivery, microelectronics, and medical diagnostics.[1−2] However, the ability to assemble them with controllable dimensions and spatial properties is still very limited. Most existing approaches to the preparation of capped nanoparticles (e.g., two-phase synthesis[3,4] and place-exchanging[5]) explore the strong affinity of thiol groups to gold or silver surfaces. Recent reports have begun to demonstrate the capability of disulfide[6] and thioether[7] monolayer encapsulation on gold nanoparticles. While the thiol- or disulfide-based chemistry is often exploited in approaches toward nanoparticle assembly (e.g., stepwise assembling,[8−10] place-exchanging,[5] and exchanging-cross-linking[11]), the exploration of thioether-based coordination chemistry for similar purposes is, to our knowledge, unprecedented. There is a difference in metal-binding strength between thiols and thioethers, and the design of molecular assemblies containing multidentate thioethers could lead to unique morphologies while providing chemical reversibility. The ability to tailor framework dimension, binding strength, and assembly reversibility or processibility may be highly desirable in many applications such as controlled drug release, catalysis, and electron or energy storage.

We present herein a novel route toward the spherical assembly of gold nanoparticles using a tetradentate thioether, the tetra-[(methylthio)methyl]silane $Si(CH_2SCH_3)_4$ (TTE), as an interparticle linking agent. We note that the formation of other thin film and spherical assemblies of nanoparticles has been observed using thiol-based methodologies.[12−14] The novelty of our approach compared to existing strategies[8−14] is the viability of multidentate thioethers to link nanoparticles and produce spherical assemblies that can be readily assembled and disassembled.

Gold nanoparticles capped with a tetraoctylammonium bromide monolayer (3.7 ± 1.4 nm, TOA^+Br^--Au_{nm}) and with a decanethiolate monolayer (5.3 ± 0.3 nm, DT-Au_{nm}) were synthesized by the two-phased protocol[3−4,15] and the thermally activated processing route,[16] respectively. The particles were all thoroughly cleaned and stored in toluene solution. $Si(CH_2SMe)_4$ was prepared similarly to the synthesis of $MeSi(CH_2SMe)_3$,[17a] but starting from $SiCl_4$ and $LiCH_2SMe$. The binding ability of $MeSi(CH_2SMe)_3$ and $Si(CH_2SMe)_4$ to other metal ions has recently been demonstrated.[17b]

Upon addition of TTE to a TOA^+Br^--Au_{nm} solution, we detected an evolution of the SP resonance band, which is related to size, shape, and aggregation properties.[1−2] Figure 1A shows a typical set of UV−vis spectra. The decrease in absorbance of the SP band at 520 nm and a new band (shoulder) growing at ~650 nm were evident. The gradual spectral evolution was accompanied by a color change from red to purple. This colorimetric feature was characteristic of nanoparticle aggregation in the solution. The solution was stable for 1−2 days before precipitation of black powders was observable, indicating that the nanoparticle aggregates eventually became too large to remain in solution. Curve c in Figure 1B shows a representative spectrum for the solution of TTE-Au_{nm} after addition of DT. It is evident that both absorbance and wavelength are largely reversed, demonstrating that the TTE-linked assembly can be disassembled via replacement of TTE by DT.

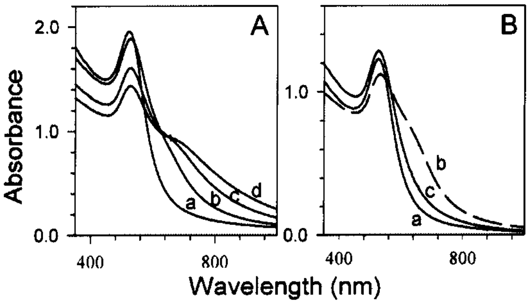


Figure 1. UV−vis spectra. (A) Temporal evolution upon addition of TTE to TOA-Au_{nm}/toluene after (a) 0, (b) 5, (c) 20, and (d) 40 min. TTE/Au_{nm} ratio: ~50 ([TTE] = 29 μM, [Au_{nm}] = 0.6 μM). (B) Spectral changes of a TOA-Au_{nm}/toluene solution (a) after addition of TTE (10 min, b), and followed by addition of DT (~1 h, c). TTE/Au_{nm}: ~50. [DT] = 7 μM.

Two control experiments provide additional insight into the correlation of spectral evolution and reactivity. First, the colorimetic change was not detectable in the reaction of DT-Au_{nm} with TTE, an observation that suggests the stronger binding of thiolates relative to thioethers that precludes the exchange between DT and TTE. Second, the colorimetric change was not detectable using a monodentate thioether (e.g., butyrylsulfide, BS) for the reaction with TOA-Au_{nm}, except for a slight decrease in the 520 nm absorbance, a result that implies that while monothioether binding may occur, sites for cross-linking are not available.

The TTE-mediated exchanging and cross-linking of the nanoparticles and the resulting aggregate morphology were characterized by transmission electron microscopy (TEM). The reaction product was collected by casting a drop of the solution onto a carbon-coated Cu-grid, or onto a flat substrate such as mica or HOPG. Figure 2 shows a representative TEM micrograph. The morphology of the TTE-assembled nanoparticles is remarkable in terms of the shape. The nanoparticles form a 3D assembly with a spherical outline. The individually isolated character for the nanoparticles is evident (see enlarged view). The measured diameter of the spheres based on four samples is in the range of 30−80 nm. Both isolated and chainlike connected spherical assemblies were observed.

---

* Address correspondence to this author at the State University of New York at Binghamton. E-mail: *cjzhong@binghamton.edu.
† The University of North Carolina at Charlotte.

10.1021/ja025724k CCC: $22.00

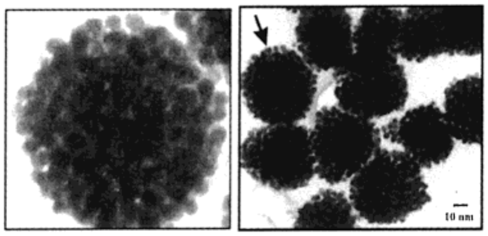


Figure 2. TEM micrograph for a sample of TTE-Au$_{nm}$ nanoparticles cast on carbon-coated Cu-grid. Left: A magnified view of the indicated sphere.

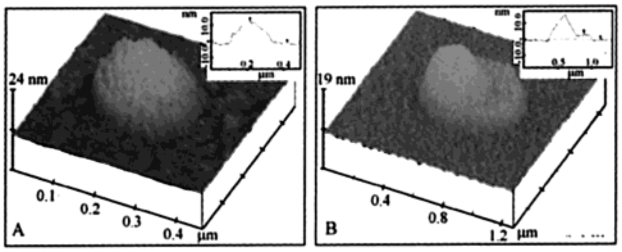
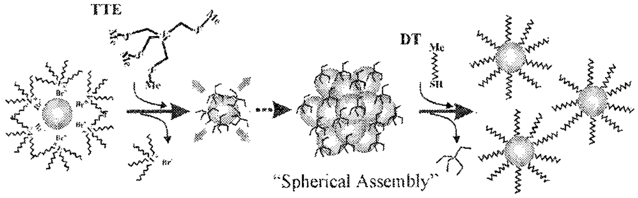


Figure 3. AFM images of TTE-Au$_{nm}$ nanoparticles cast on mica (A) and HOPG (B). Inset: Cross-section line of the feature shown.

Figure 3 shows a typical set of AFM images of an assembly cast on mica (A) and on HOPG (B). On mica (A), the topographical feature is characterized by the presence of spherical islands of various sizes. Since the *xy* data are affected by tip−sample convolution,[18] the spherical sizes appear larger than the TEM-determined actual sizes. However, the corresponding *z*-scale data (i.e., height) of 30−80 nm reflect more closely the true sizes determined by TEM. Interestingly, the spherical islands seem to be partially melted over the substrate surface on HOPG, forming a monolayer of nanoparticles surrounding the spheres, which in many cases leads to merging between two or three spherical islands. The average height of the monolayer, ∼3.5 nm, closely matches the nanoparticle size. We believe that this interesting feature is due to differences of substrate surfaces and their interaction with the hydrophobic spheres. Mica does not wet the sphere that thus forms a spherical island. HOPG wets the sphere and has the propensity of increasing the contact area. The unusual partial spreading of nanoparticles over the contacted surface is indicative of the soft nature of the outmost layer around the spherical assembly, which could form the basis of a new pathway for manipulating nanoscale linkage between individual assemblies of nanoparticles.

Scheme 1. Schematic Illustrations for the TTE-mediated Assembling of TOA-Au$_{nm}$ Particles into a Spherical Assembly, and the Thiol-Initiated Disassembling Process



Scheme 1 illustrates the above observations by showing the assembling and disassembling processes in an idealized fashion. Since the size of TTE is slightly short for its contact simultaneously with more than two nanoparticles, the particles are linked by TTE mostly at interfacial sites between two neighboring nanoparticles. The spherical assembly process is likely to start with one particle and proceed in a layer-by-layer fashion to grow spherically. While the spherical shape is comparable with those derived by thiol or polymer chemistry,[12−14] the fact that it can be disassembled and partially melted on a hydrophobic surface demonstrates a novel spherical assembly. An in-depth investigation of kinetic factors of the assembling process (e.g., concentrations of Au$_{nm}$ and TTE) and structural effects (e.g., chain length tridentate, thioethers (e.g., MeSi(CH$_2$SMe)$_3$) and steric bulk (e.g., Si(CH$_2$SBu^t)$_4$)) and a survey of potential technological applications are in progress.

Acknowledgment. Financial support of this work from the Petroleum Research Fund administered by the American Chemical Society and the 3M Corporation is gratefully acknowledged. D.R. also thanks Research Corporation for a Cottrell College Science Award.

Supporting Information Available: Additional AFM data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Templeton, A. C.; Wuelfing, W. P.; Murray, R. W. *Acc. Chem. Res*. **2000**, *33*, 27.
(2) Storhoff, J. J.; Mirkin, C. A. *Chem. Rev.* **1999**, *99*, 1849.
(3) Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. *J. Chem. Soc., Chem. Commun.* **1994**, 801.
(4) Hostetler, M. J.; Wingate, J. E.; Zhong, C. J.; Harris, J. E.; Vachet, R. W.; Clark, M. R.; Londono, J. D.; Green, S. J.; Stokes, J. J.; Wignall, G. D.; Glish, G. L.; Porter, M. D.; Evans, N. D.; Murray, R. W. *Langmuir* **1998**, *14*, 17.
(5) Hostetler, M. J.; Templeton, A. C.; Murray, R. W. *Langmuir* **1999**, *15*, 3782.
(6) Shon, Y. S.; Mazzitelli, C.; Murray R. W. *Langmuir* **2001**, *17*, 7735
(7) Li, X. M.; de Jong, M. R.; Inoue, K.; Shinkai, S.; Huskens J.; Reinhoudt, D. N. *J. Mater. Chem.* **2001**, *11*, 1919.
(8) (a) Bethell, D.; Brust, M.; Schiffrin, D. J.; Kiely, C. J. *J. Electroanal. Chem.* **1996**, *409*, 137. (b) Andres, R. P.; Bielefeld, J. D.; Henderson, J. I.; Janes, D. B.; Kolagunta, V. R.; Kubiak, C. P.; Mahoney W. J.; Osifchin, R. G. *Science* **1996**, *273*, 1690.
(9) (a) Musick, M. D.; Pena, D. J.; Botsko, S. L.; McEvoy, T. M.; Richardson, J. N.; Natan, M. J. *Langmuir* **1999**, *15*, 844. (b) Zamborini, F. P.; Hicks, J. F.; Murray, R. W. *J. Am. Chem. Soc.* **2000**, *122*, 4514.
(10) Elghanian, R.; Storhoff, J. J.; Mucic, R. C.; Letsinger, R. L.; Mirkin, C. A. *Science* **1997**, *277*, 1078.
(11) (a) Leibowitz, F. L.; Zheng, W. X.; Maye, M. M.; Zhong, C. J. *Anal. Chem.* 1999, *71*, 5076. (b) Zheng, W. X.; Maye, M. M.; Leibowitz, F. L.; Zhong, C. J. *Anal. Chem.* **2000**, *72*, 2190.
(12) Adachi, E. *Langmuir* **2000**, *16*, 6460.
(13) Boal, A. K.; Ilhan, F.; DeRouchey, J. E.; Thurn-Albrecht, T.; Russell T. P.; Rotello, V. M. *Nature* **2000**, *404*, 746.
(14) Jin, J.; Iyoda, T.; Cao, C.; Song, Y.; Jiang, L.; Li, T. J.; Zhu, D. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 2135.
(15) Fink, J.; Kiely, C. J.; Bethell, D.; Schiffrin. D. J. *Chem. Mater.* **1998**, *10*, 922.
(16) Maye, M. M.; Zheng, W. X.; Leibowitz, F. L.; Ly, N. K.; Zhong, C. J. *Langmuir* **2000**, *16*, 490.
(17) (a) Yim, H. W.; Tran, L. M.; Dobbin, E. D.; Rabinovich, D.; Liable-Sands, L. M.; Incarvito, C. D.; Lam, K.-C.; Rheingold, A. L. *Inorg. Chem.* **1999**, *38*, 2211. (b) Yim, H. W.; Tran, L. M.; Pullen, E. E.; Rabinovich, D.; Liable-Sands, L. M.; Concolino, T. E.; Rheingold, A. L. *Inorg. Chem.* **1999**, *38*, 6234.
(18) Maye, M. M.; Luo, J.; Han, L.; Zhong, C. J. *Nano Lett.* **2001**, *1*, 575.

JA025724K