Nanostructures

DOI: 10.1002/anie.200701554

Metal Nanoparticles: From “Artificial Atoms” to “Artificial Molecules”**

Dmitrii F. Perepichka and Federico Rosei**

Keywords:
gold · ligand exchange · nanostructures · self-assembly

Nanostructured materials often exhibit properties which are unusual for bulk materials of the same composition.[1] When the size of nanostructures shrinks below a certain threshold, for example, they may behave as quantum dots, that is, as zero-dimensional systems in which the charge carriers are confined in atomic-like potentials.[2] To harness nanoscale properties for applications, one must be able to control the size of the nanostructures as well as their assembly into macroscopic structures (such as arrays or films).[3–5]

Noble-metal nanoparticles exhibit unique electronic and optical properties that are critically related to their size and shape.[6] Solution-based syntheses of metal nanoparticles exploit the chemical reduction of metal salts in the presence of functional surfactant molecules, which wrap a full monolayer around the nanoparticle core, preventing coalescence.[7] This molecular monolayer has a protecting function and determines the nature of the interactions between the particles and their environment, hence controlling their solubility in different media, for example.[8] Long-chain thiols are the most widely used surfactant molecules, particularly for gold nanoparticles. Their self-assembly on metal surfaces is based on the formation of a covalent metal–sulfur bond (ca. 50 $\mathrm{kcal\,mol^{-1}}$) and of attractive van der Waals interactions between the hydrocarbon chains, the strength of which scales with the length of the chain (ca. 1.5 $\mathrm{kcal\,mol^{-1}}$ per methylene group).[9] On flat metallic surfaces, these interactions lead to the formation of highly ordered self-assembled monolayers (SAMs),[10] which were first observed, and most extensively studied, on gold surfaces (predominantly Au(111)).

A very similar architecture is generally presumed for SAMs on gold nanoparticles, although conventional wisdom and experimental observations suggest that molecule–surface interactions, which depend on the crystallographic orientation of the surface facets, will be particularly weak at the vertices of the nanoparticle polyhedron.[9,11–13]

The functionality of the molecules composing the SAM at the nanoparticle surface is the key factor defining almost every application of metal nanoparticles. Although the strongly reductive conditions used for the synthesis of nanoparticles set stringent limitations on the insertion of functional groups in the thiol ligands, practically any functionality can be introduced into the nanoparticle by subsequent ligand-exchange reactions.[14]

Covalent and strong noncovalent interactions between molecules attached to nanoparticles have been used to engineer various nanostructures, including mono- and multilayers, and nanocomposites with conducting polymers or oligomers.[8,15] Also, gold nanoparticles have been used as “multivalent” cores to build organic dendritic structures.[8] However, the isotropic character of such binding poses a problem for the bottom-up fabrication of more complex nanoparticle-based architectures.

Several groups have investigated monofunctionalized nanoparticles linked to multidentate molecules with established directional interactions that control the assembly of the nanoparticles. The required monofunctionalized nanoparticles have been prepared through reaction with a functional thiol bound to a solid support.[16] This approach is commonly used in the application of gold nanoparticles as electrode interfaces in molecular junctions. Using the high-fidelity interaction between DNA strands employed as ligands, linear, cyclic, and discrete branched arrays of monofunctionalized gold nanoparticles have been fabricated.[17–19] However, the “monovalent” nature of monofunctionalized nanoparticles renders them spectator pendant groups, rather than building blocks in these nanoengineering endeavors.

Recent work by Stellacci’s group showing that surface curvature plays a key role in molecular self-assembly[20–22] opened new perspectives in this field. This group performed detailed scanning tunneling microscopy (STM) investigations, which suggested that, below certain nanoparticle dimensions, surface

---

[*] Prof. D. F. Perepichka
Department of Chemistry
McGill University
801 Sherbrooke Street West
Montréal, QC H3A 2K6 (Canada)
Fax: (+1) 514-398-3797
E-mail: dmitrii.perepichka@mcgill.ca

Prof. Dr. F. Rosei
INRS-Énergie, Matériaux et Télécommunications
Université du Québec
Varennes, QC J3X 1S2 (Canada)
Fax: (+1) 450-929-8102
E-mail: rosei@emt.inrs.ca

[**] Our work is supported by the Natural Sciences and Engineering Research Council (NSERC) of Canada. We are grateful to the Petroleum Research Fund (AC-type grant) and to the Air Force Office of Scientific Research. D.F.P. acknowledges the support of a DuPont Young Investigator Award. F.R. acknowledges salary support from the FQRNT (programme stratégique nouveaux professeurs-chercheurs) and the Canada Research Chairs Program.

© 2007 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

curvature drives a crystallization process in which *ordered* alternating domains of two different thiols can form. An STM image of an individual nanoparticle with evident ripples, presumably due to alternating domains of longer molecules (1-octanethiol (OT)) and of shorter molecules (3-mercaptopropionic acid (MPA)) is shown in Figure 1. Although the phase separation of dissimilar ligands in SAMs is a well-known phenomenon, such a high degree of ordering of thiols in parallel rings (resembling the latitude lines on a globe; Scheme 1 a,b) has not been seen on flat surfaces.

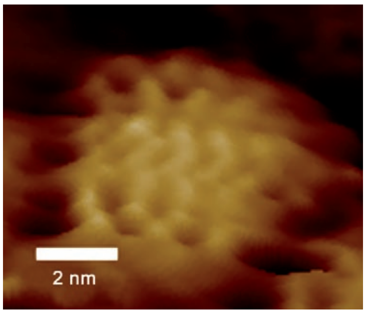
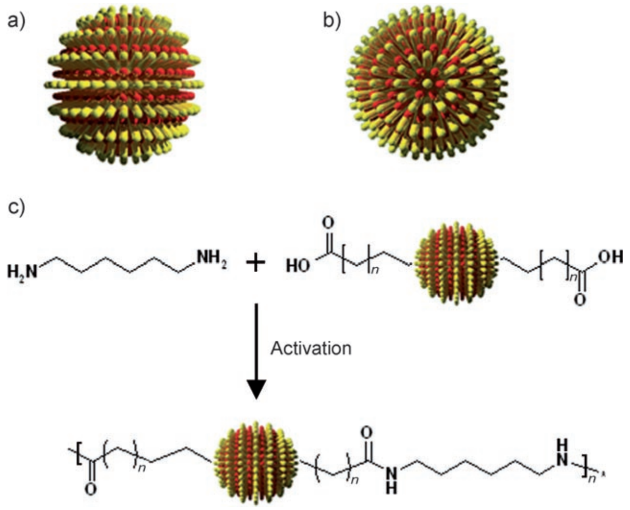


Figure 1. STM topographic image of a gold nanoparticle coated with a 2:1 molar ratio of OT and MPA (on a gold foil). The ripples that run vertically result from the ordered-phase separation of the two ligands. Raised domains of OT alternate with domains of MPA. Reproduced from reference [21] with permission.



Scheme 1. a) Side view and b) top view of a rippled gold nanoparticle. Two polar defects allow the alternation of parallel rings of the two thiol ligands OT (yellow) and MPA (red). c) Polymerization of the carboxy-functionalized nanoparticles with DAH. See text for details. Reproduced from reference [25] with permission.

The unexpected behavior was then topologically described in terms of the hairy-ball theorem: on a sphere covered in fur, it is not possible to brush all the hairs flat without creating two diametrically opposed singularities, known as poles.[23] In other words, the formation of a two-dimensional ordering is topologically possible only if two "poles" or defects are present at opposite ends of the nanoparticle. The singularities appear as single thiol molecules that stick out. Unlike the molecules in the rings, the molecules at the poles are weakly stabilized by their neighbors, as recently suggested by molecular-dynamics simulations,[24] and are easier to displace by ligand-exchange reactions.

The latest report from Stellacci's team builds elegantly on this concept,[25] as they succeeded in replacing the thiol molecules at the poles with longer-chain "handles" carrying carboxylic acid groups at their outer ends. The poles are, thus, exploited as reactive sites to bind a functional ligand, which acts as a "thread" that can bind the gold clusters with strong covalent bonds, as shown in Scheme 1 c.

This procedure adds a new functionality to the nanoparticles, which now behave as divalent molecules and can be bound to other molecules or particles in two distinct directions. The nanoparticles are effectively transformed into molecular building blocks. The carboxy-functionalized nanoparticles were polymerized through classical amide-bond formation with either 1,6-diaminohexane (DAH) or *O*,*O*′-bis(2-aminoethyl)octadeca(ethylene glycol) (EG-DA), yielding chains of varying lengths. In essence, by functionalizing the nanoparticles with suitable chemical handles, Stellacci and co-workers were able to polymerize "nanoparticle monomers" into chains of more than a dozen units. The resulting "strings-of-pearls" were thoroughly characterized by transmission electron microscopy (TEM). The statistical distribution of distances between the particles was found to be relatively broad because of the polydispersity of the nanoparticles, the conformational flexibility of the linkers, and the geometrical arrangement of the linked nanoparticles (Figure 2).

The development of such regioselective chemistry on nanomaterials can open the door to a large variety of structures, which can be accessed through classical approaches of supramolecular chemistry. Although there are examples of the regioselective functionalization of one-dimensional nanomaterials,[26] including the asymmetric functionalization of carbon nanotubes,[27] the selective functionalization of zero-dimensional nanomaterials (nanoparticles) is more surprising. The gold nanoparticles are rendered the equivalent of divalent molecules, although the extent of the regioselectivity of the functionalization as well as the "regiochemical" stability of the disubstituted nanoparticles should be the subject of future studies. Using more rigid linkers and ligands (for example, aromatic molecules) to connect the nanoparticles may allow complex and well-defined nanostructures with tailored architectures to be constructed from these building blocks. These findings are of great interest to the broad community of scientists who work on the self-assembly and functionalization of nanoparticles. For them, the ability to control such structures is critical. As the concept presented herein relates to surface curvature and topology in general, it is also likely to influence the future develop-

© 2007 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

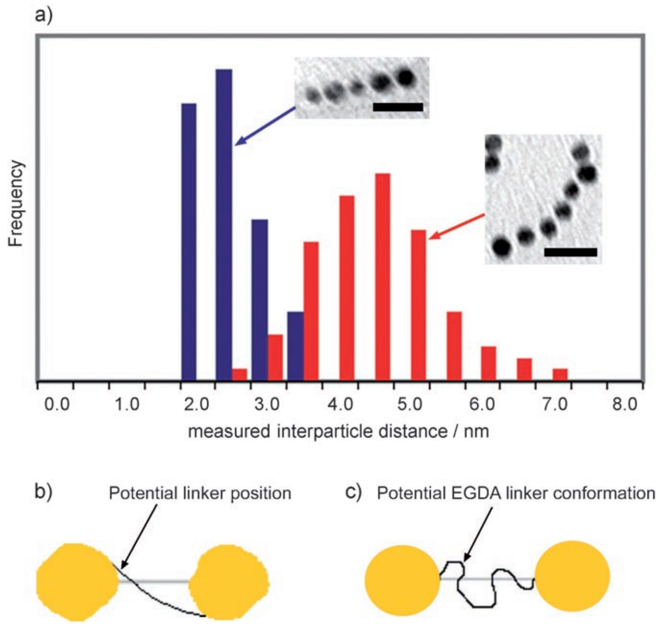


Figure 2. a) Distribution of interparticle distances in nanoparticle chains with DAH (blue) or EGDA (red) linkers. The interparticle distance is clearly correlated to the type of linker. Insets: TEM images of the corresponding nanoparticle chains (scale bars: 20 nm). b) A possible geometrical arrangement of linked nanoparticles that could result in the measured interparticle distance (gray line) being smaller than the linker length. c) The conformational freedom of EGDA that results in the broad distribution of interparticle distances observed for this type of linker. Reproduced from reference [25] with permission.

ment of the chemistry of other types of nanoparticles.

Published online: July 6, 2007

---

[1] F. Rosei, *J. Phys. Condens. Matter* **2004**, *16*, S1373.

[2] a) H. Weller, *Angew. Chem.* **1993**, *105*, 43; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 41; b) A. P. Alivisatos, *Science* **1996**, *271*, 933.

[3] F. Stellacci, C. A. Bauer, T. Meyer-Friedrichsen, W. Wenseleers, V. Alain, S. M. Kuebler, S. J. K. Pond, Y. Zhang, S. R. Marder, J. W. Perry, *Adv. Mater.* **2002**, *14*, 194.

[4] C. J. Kiely, J. Fink, M. Brust, D. Bethell, D. J. Schiffrin, *Nature* **1998**, *396*, 444.

[5] C. V. Cojocaru, C. Harnagea, F. Rosei, A. Pignolet, M. A. F. van den Boogaart, J. Brugger, *Appl. Phys. Lett.* **2005**, *86*, 183107.

[6] a) J. F. Hicks, F. P. Zamborini, A. Osisek, R. W. Murray, *J. Am. Chem. Soc.* **2001**, *123*, 7048; b) E. V. Shevchenko, D. V. Talapin, N. A. Kotov, S. O'Brien, C. B. Murray, *Nature* **2006**, *439*, 55; c) C. P. Collier, T. Vossmeyer, J. R. Heath, *Annu. Rev. Phys. Chem.* **1998**, *49*, 371; d) C. C. You, M. De, G. Han, V. M. Rotello, *J. Am. Chem. Soc.* **2005**, *127*, 12873.

[7] a) M. Brust, M. Walker, D. Bethell, D. J. Schiffrin, R. Whyman, *Chem. Commun.* **1994**, 801; b) A. Templeton, M. P. Wuelfing, R. W. Murray, *Acc. Chem. Res.* **2000**, *33*, 27.

[8] M.-C. Daniel, D. Astruc, *Chem. Rev.* **2004**, *104*, 293.

[9] J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo, G. M. Whitesides, *Chem. Rev.* **2005**, *105*, 1103.

[10] F. Schreiber, *Prog. Surf. Sci.* **2000**, *65*, 151.

[11] M. J. Hostetler, A. C. Templeton, R. W. Murray, *Langmuir* **1999**, *15*, 3782.

[12] A. Ulman, *Chem. Rev.* **1996**, *96*, 1533.

[13] F. Rosei, M. Schunack, Y. Naitoh, P. Jiang, A. Gourdon, E. Laegsgaard, I. Stensgaard, C. Joachim, F. Besenbacher, *Prog. Surf. Sci.* **2003**, *71*, 95.

[14] a) Y. Song, T. Huang, R. W. Murray, *J. Am. Chem. Soc.* **2003**, *125*, 11694; b) V. J. Gandubert, R. B. Lennox, *Langmuir* **2005**, *21*, 6532; c) A. Kassam, G. Bremner, B. Clark, G. Ulibarri, R. B. Lennox, *J. Am. Chem. Soc.* **2006**, *128*, 3476.

[15] B. C. Sih, M. O. Wolf, *Chem. Commun.* **2005**, 3375.

[16] a) K.-M. Sung, D. W. Mosley, B. R. Peelle, S. Zhang, J. M. Jacobson, *J. Am. Chem. Soc.* **2004**, *126*, 5064; b) J. G. Worden, A. W. Shaffer, Q. Huo, *Chem. Commun.* **2004**, 518; c) F. Huo, A. K. R. Lytton-Jean, C. A. Mirkin, *Adv. Mater.* **2006**, *18*, 2304.

[17] Z. Deng, Y. Tian, S.-H. Lee, A. E. Ribbe, C. Mao, *Angew. Chem.* **2005**, *117*, 3648; *Angew. Chem. Int. Ed.* **2005**, *44*, 3582.

[18] F. A. Aldaye, H. F. Sleiman, *Angew. Chem.* **2006**, *118*, 2262; *Angew. Chem. Int. Ed.* **2006**, *45*, 2204.

[19] A. Shelley, S. L. Claridge, J. Goh, M. J. Frechet, S. C. Williams, C. M. Micheel, A. P. Alivisatos, *Chem. Mater.* **2005**, *17*, 1628.

[20] A. M. Jackson, J. W. Myerson, F. Stellacci, *Nat. Mater.* **2004**, *3*, 330.

[21] A. M. Jackson, Y. Hu, P. Silva, F. Stellacci, *J. Am. Chem. Soc.* **2006**, *128*, 11135.

[22] A. Centrone, Y. Hu, A. M. Jackson, G. Zerbi, F. Stellacci, *Small* **2007**, *3*, 814.

[23] H. Poincaré, *J. Math. Pure Appl.* **1885**, *1*, 167.

[24] S. Rapino, F. Zerbetto, *Small* **2007**, *3*, 386.

[25] G. A. DeVries, M. Brunnbauer, Y. Hu, A. M. Jackson, B. Long, B. T. Neltner, O. Uzun, B. H. Wunsh, F. Stellacci, *Science* **2007**, *315*, 358.

[26] R. G. S. Goh, N. Motta, J. M. Bell, E. R. Waclawik, *Appl. Phys. Lett.* **2006**, *88*, 053101.

[27] a) K. M. Lee, L. Li, L. Dai, *J. Am. Chem. Soc.* **2005**, *127*, 4122; b) Z. Wei, M. Kondratenko, L. H. Dao, D. F. Perepichka, *J. Am. Chem. Soc.* **2006**, *128*, 3134.

© 2007 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim