First Principle Modeling of Catalyst Nanoparticle Synthesis

Giannis Mpourmpakis[1,2] and Dionisios G. Vlachos[1,]*

*[1] Center for Catalytic Science and Technology, Department of Chemical Engineering,
University of Delaware, Newark, Delaware 19716, (USA)*
[2] Institute of Electronic Structure and Laser, FORTH, Heraklion 71110, Crete, (Greece)

[*vlachos@udel.edu](mailto:vlachos@udel.edu) (corresponding author)

Introduction

Metal nanoparticles find numerous nanotechnological applications. For instance, nanoparticles are used as catalysts [1], as well as in environmental and energy related applications [2]. The catalytic selectivity of reactions depends strongly on the nanoparticle facets [3]. By controlling the nanoparticles' structural characteristics during synthesis, such as their shape, size and dispersity, we can fine-tune their catalytic properties. However, their mechanism of growth affecting their size and shape still remains elusive.

In this work, we shed light to the growth mechanisms of silver and gold nanoparticles. We investigate the silver nanoparticle growth in the presence of citrate [4, 5] and the gold nanoparticle growth in the presence of MBAs (para-MercaptoBenzoic Acid) [6]. In both cases, we also accounted for the solvent (water).

Methods

We used the BP86 and BLYP methods within the Density Functional Theory combined with various basis sets, such as the sv(p), TZVP and TZVPP as implemented in the Turbomole 5.9.0 program package [7], in order to describe different interactions (eg. Metal-Metal, Metal-organic and organic-organic interactions). Our calculations were accelerated with the use of the RI (Resolution of the Identities) approximation. We also used the hybrid B3LYP method as implemented in the Gaussian 03 program package [8], combined with the LANL2DZ basis set. In every case, appropriate ECPs were used (in the Au case the ECPs include relativistic corrections).

Results and Discussion

For the silver nanoparticle growth, our work was motivated by the experimental synthesis of silver nanorods or nanoparticles depending on the solution pH, in the presence of citrate [9]. We investigated the carboxyl group interactions with surface atoms of silver nanoparticles exhibiting various symmetries. Our results rationalize anisotropic growth and demonstrate a possible mechanism to stabilize nanoparticles of decahedral symmetry during reduction, in the presence of citrate. We revealed a multifunctional action of citrate depending on pH (see Figure 1A for citrate-Ag nanoparticle interaction). Under certain conditions it can block nanoparticle growth via an electrostatic or a van der Waals stabilization mechanism, and under others, it can act as a "molecular grab" inducing nanoparticle growth. Our results explain why silver nanowires [9] are preferentially synthesized in a window of pH values. Importantly, we show that it may be possible to control particle size by a suitable choice of capping agents.

Regarding the gold nanoparticle growth, our work was motivated by the recent totally structural determination of the monodispersed $Au_{102}MBA_{44}$ [10] nanoparticles. We investigated the structural and electronic characteristics of Au_nMBA_n (n=1-12) complexes (clustering of the capping agents). We revealed magic numbers on their stability, which was attributed to very stable electronic configurations (large HOMO-LUMO gaps). These very stable complexes self-assemble in pairs via hydrogen bonds occurring between COOH groups (Figure 1B). We found a unique action of water being the initial driving force for this stabilization. Water acts as a 'molecular locker' preventing the formation of different conformers in solution. Our study elucidates the overall mechanism of nanoparticle growth that can guide experimentalists to control rational synthesis of monodispersed nanoparticles.

Significance

This -first of its kind- theoretical work introduces first principle calculations into the investigation of nanoparticle growth mechanisms, taking into account solvent effects, experimental conditions and the presence of capping agents. More importantly, it provides possible pathways to control the nanoparticle characteristics, such as size, shape and dispersity during growth.

(A)   (B)
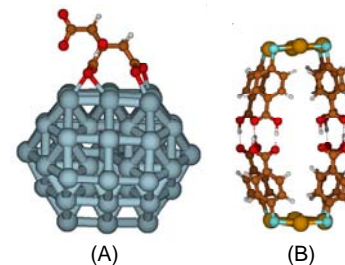
Figure 1. A) Ag_{55} nanoparticle interacting with citrate molecule; B) a Au_4MBA_4 dimmer.

References

1. Bell, A. T., *Science* 299, 1688-1691 (2003).
2. Valden, M., Lai, X. and Goodman, D. W, *Science* 281, 1647-1650 (1998).
3. Bratlie, K. M., Lee, H., Komvopoulos, K., Yang, P. and Somorjai, G. A., Nano Lett. 7, 3097-3101 (2007).
4. Mpourmpakis, G. and Vlachos, D. G. submitted (2008).
5. Mpourmpakis, G. and Vlachos, D. G. *Langmuir* 24, 7465-7473 (2008).
6. Mpourmpakis, G. and Vlachos, D. G. submitted (2008).
7. Ahlrichs R., Bär M., Häser M., Horn H. and Kölmel C., *Chem. Phys. Lett.*, 162, 165 (1989)
8. *Gaussian 03*, Revision C.02; Gaussian, Inc., Wallingford CT: 2004.
9. Caswell, K. K., Bender, C. M. and Murphy, C. J. *Nano Letters* 3, 667-669 (2003).
10. Jadzinsky, P. D., Calero, G., Ackerson, C. J., Bushnell, D. A. and Kornberg, R. D. *Science* 318, 430-433 (2007).