

Shape and Size dependent Catalysis by Gold Nano-Particles

B.Viswanathan

National Centre for Catalysis Research,
Indian Institute of Technology Madras, Chennai 600 036

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Abstract

The present article addresses to the questions why gold nano-particles have been receiving considerable attention? Secondly why gold nano-particles with low number of gold atoms (say less than 55) or small size (in the range of few nm) alone are active? This has to be associated with the effective hybridisation of the frontier orbitals of gold which provide effective overlap with the substrate molecules altering their bond order. The possible proof for this postulate is the Au-Au distance in these nano-particles is lower than that found for bulk gold. This type of effective hybridisation of the frontier wave functions of gold is possibly accounts for the unusual surface Plasmon resonance (SPR) most often considered for gold nano-particles. It is hoped that this article will ultimately lead to some clarity for the unusual surface and catalytic properties observed with specific size, shape and number of gold atoms in nano-particles.

Introduction

It is known that metal nano-particles especially that of gold nano-particles exhibit remarkable catalytic properties even for oxidation reactions under ambient conditions[1,2]. This has given rise to a new awakening since bulk gold has been always considered to be inactive for catalysis due to various reasons including its high value of ionization potential. The reasons for this observed unusual reactivity of nano-gold have given rise to a branch of science called 'gold catalysis' as revealed from the numerous publications in this area in recent times. Number of reviews have appeared and the somewhat comprehensive reviews are given in refs.3 to 11. There can be various reasons

for this interest in the catalysis by gold nano-particles, including the possibility of its relevance to fuel cell applications especially, the selective oxidation of carbon monoxide in presence of hydrogen, a reaction of relevance for the development of energy conversion devices. The central theme in these studies is to establish that gold clusters of specific sizes and shapes alone are active for the low temperature oxidation of CO. The necessity of additives and promoters which tend to keep the particle sizes of these clusters in addition as acting as supports for the active phase, in which capacity the additives have other roles like exposing the active component and also act as a heat sink has been emphasized in various publications.

Why gold nano-particles?

It is known in catalysis ever since the specificity of ammonia synthesis on iron(111) surfaces is shown to be nearly 600 times as active as other low index planes, that there can be some specificity of the surface planes exposed in catalysis. This has also been manifested in the concept of demanding and facile reactions, or structure sensitive or structure insensitive reactions a concept that has been routinely used in this field to classify reactions[12]. In fact all known catalytic reactions have also been classified as structure sensitive or structure insensitive reactions. Behind this background of studies, it is not surprising that gold nano particles exhibit size and shape specificity in catalysis. If this is so, why are we so concerned with the shape and size specificity of gold for catalysis if this were to be natural consequence of any catalytic system? At this time, this kind of philosophical issues have not been addressed extensively, but the focus has been on the exploitation of these gold nano particles for a variety of reactions and one simple compilation of the reactions catalyzed by gold nano particles is given in Table 1.

From a DFT study of the clusters of gold, Sankaran and Viswanathan [13] have postulated that in the case of gold, only a particular sized nanoparticles possess spatial orientation and symmetry allowed orbitals and the corresponding eigen values are appropriate for interaction with the incoming adsorbate molecules that undergo surface transformations. For other sized nano particles the frontier wave functions have predominant 's' character and hence there is no spatial orientation or eigen values matching with that of the substrate molecule and hence these other nano particles are not that much reactive. Due to these spatially oriented eigen functions, these gold clusters interacted with support and the reactant system exhibits altered activity. It has been argued by them that only certain sized clusters have the wave functions suitable for interaction with the substrate molecules. In this con-

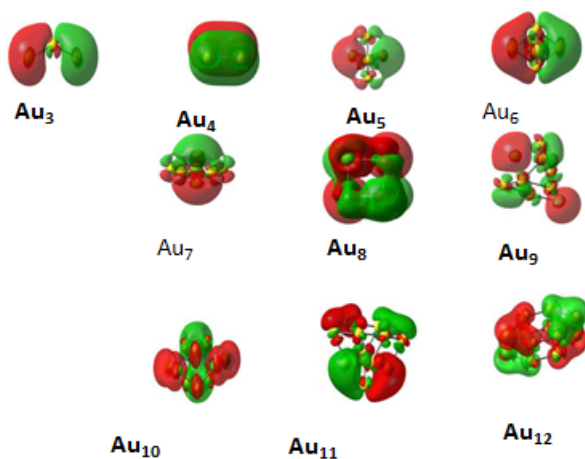


Figure 1: The frontier wave function contours for various gold clusters $(\text{Au})_n$ with $n = 2-12$ (From Ref.13)

nection they quote Au_8 system as one of the active clusters. Their data on the nature of frontier wave functions are reproduced in Fig.1.

A more comprehensive study has been carried out by Visikovskiy et al[14] with cluster sizes $11 < n_A < 1600$. They have shown that the d-band parameters as well as the binding energy of Au 4f core levels undergo drastic changes for nano particles of sizes 2.6 nm or $n_A < 150$ atoms. The smaller number of wave functions of valence electrons undergo effective hybridisation (like in molecular systems) and hence result in narrowing the d band width. These effects can be reflected in the shift of the d band centre with respect to the Fermi level (the concept of the position of d band centre has some consequence in catalysis has been recognized in earlier literature). Even though the authors recognize certain limitations in their calculations of the parameters, they believe that the results provide "prominent insight into dramatic changes of the d band parameters of gold nano-clusters" and they believe that the d band parameters like the width and the spin-orbit splitting possibly scale almost linearly with the average coordination number of the clusters. Another DFT calculations by Fenger et al [15] has shown the molecule to gold cluster adsorption is accompanied by a significant charge transfer from the surface to the nitrogen atom of the reactant nitro-phenol molecule for its reduction to amino-phenol. It may be presumed that the message from this

study is that gold clusters possibly behave more like molecular systems rather than bulk surface properties. This point has not yet come out explicitly in the literature but one can hope that this will be the ultimate destination of the research efforts.

In another detailed study Landman et al[16] have claimed that through combined experimental and first principles quantum mechanical calculations and simulations a detailed mechanism and showed that the barrier for the various steps especially for the interaction of adsorbed CO and adsorbed oxygen and that for the desorption of product carbon dioxide are considerably reduced for a 20 atom gold cluster on MgO surface. However once again they also claim that the cluster size, cluster support interaction, defects in support, charge state of the cluster, the dimensionality of the active cluster, and many other parameters are responsible for the reactivity of the cluster.

Catalysis by gold nano-particles

It is generally believed that the catalytic reactions experience a reduced energy barrier route for the transformations and these alternate routes in the potential energy surfaces could have arisen due to the nano state of the catalytic particles. The reactivity of nano state has been realized at least a century before in practical systems though it might have known for many centuries in living beings. This realization has not been explicitly stated in literature of that period even though it has been in the minds of catalysts scientists all through, since they did not have direct experimental proof for want of resolutions possible with the microscopes available then. This situation has given rise to so many issues in the minds of the interested readers. They are:

1. If shape and size selectivity in catalysis is already known, then why is this importance for catalysis for gold nano particles?
2. Small nano-particles of metals like Au bind strongly to supports like titania and iron oxide which are generally observed to be effective in making Au nano-particles active in catalysis than to supports like MgO which are considered less effective. What is the specific reason for this observation?
3. The thermodynamic stability of adsorbed intermediates for catalytic reactions can either increase or decrease with decreasing metal nano-particle size below 8 nm, depending on the reactant system. Why is this limit of 8 nm?
4. There is a scaling region above which the particle size is linearly related to

Table 1: Typical reactions catalyzed by gold nano-particles

S.No	Reaction	Ref
1	alcohol oxidation	23-26
2	oxidation of glucose and hexoses	27-30
3	oxidation of CO	31-32
4	oxidation of glycerol	33-34
5	Oxidation of styrene, ethylbenzene, allylic oxidation	35-36
6	Reduction of nitrophenols	37-39
7	Hydrochlorination of ethylene	40
8	hydrogenation of alkyne	41
9	gluconic acid from glucose	30
10	methyl glycolate from ethylene glycol	42
11	vinyl acetate monomer from ethylene, acetic acid and oxygen	32
12	CO electrooxidation	43
13	Fine chemicals synthesis	44
14	oxidation of propylene to propylene oxide	5
15	alkene and arene hydrogenation	45

reactivity and also there is a certain range where scaling is not obeyed. The reasons for these two regions of reactivity have not been explicitly known though these two regions have been identified as shown in the hypothetical plot given in Fig.2.

Even though In Fig 2 the variation is shown in one pattern with a particular type of gradient change, this gradient changes can have both types of slopes though only one of them is depicted. The trend can be either upward or downward as the particle size increases.

5. The reaction to insert O_2 into the Au-H bond of adsorbed H on the Au(111) surface to make Au-OOH($O_{2,g} + H_{ad} \rightarrow OOH_{ad}$) is exothermic by -80 kJ mol^{-1} . This adsorbed hydroperoxy species is thought to be a key intermediate in selective oxidation reactions over Au nanoparticle catalysts, but its production by this reaction may also provide a route for O_2 evolution in possible electro-chemical cells.

6. Gold nano particles appear to exhibit strong interactions with the support and hence their reactivity in the supported state is noticeably different from that of the unsupported state. This aspect has not received required attention in literature, though this has been repeatedly observed and recorded in the literature. See also point 2 for specific cases.

7. There are a variety of other aspects of gold nano particles which deserve attention like the plasmon resonance and its dependence on size and shape of nano-particles. These aspects will not be considered in this presentation

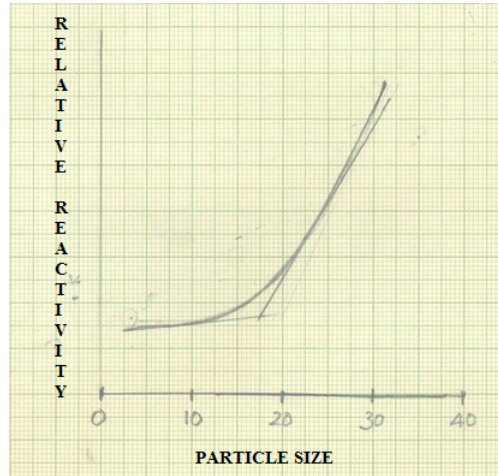


Figure 2: The dependence of reactivity for scaling and non-scaling regions of particle size

except quoting some essential points from literature for reference. Haiss et al [17] have shown that the peak position of plasmon resonance is a function of particle size (see Fig.3) and also the linear dependence of the absorption ratio (A_{spr}/A_{650}) as the function of the logarithm particle size (Refer to Fig.4.)[17].

Even though this type of straight forward relationships between the behaviour of gold nano-particles on the particle size have been indicated in some of the published literature, it should be emphasized that these relationships are not as straight forward as they appear to be.

A possibly comprehensive study on cluster sizes ranging from 11 to 1600 gold atoms has been reported by Visikovskiy as stated earlier [14]. They have employed photo-emission technique to monitor the changes of the d-band width, $5d_{3/2}-5d_{5/2}$ separation and the d-band center. They have also recorded step changes in these parameters when the cluster size decreases from 150 atoms owing to the band narrowing caused by the hybridization of fewer wave functions of the valence electrons That is when the system tends towards molecular systems. Eliminating the final state effects from the raw data and only considering the initial state parameters for their photo-emission measurements, they concluded that the average Au-Au distance is shorter in clusters compared to the bulk gold. This shortening could have arisen due to effective overlap of the wave functions while in bulk this type of directional overlap may not be possible and hence Au-Au distance can be higher in bulk systems. It has been recognized that the localized surface

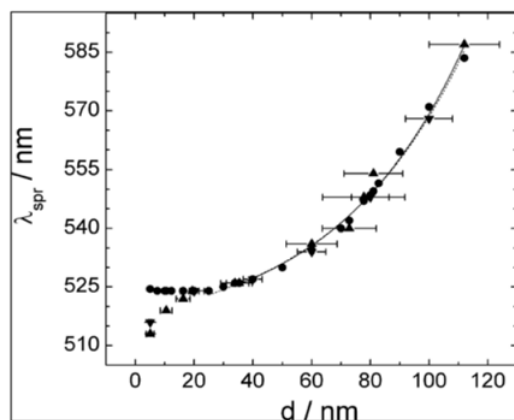


Figure 3: Relationship between particle size and surface plasmon resonance (SPR) both in scaling and non-scaling regions of size; data points triangles synthesized, inverted triangles commercial gold nano-particles, dashed-line-theoretical data and circles is for calculated particles. Reproduced from W.Haiss, N.T.K.Thanh, J.Aveyard and D.G.Fernig, *Analytical Chemistry*, 79,4215 (2007)

plasmon resonances are central for specific behaviour of nano particles and this has been shown to be size dependent and this indirectly means that the surface properties which is essential for catalysis can also depend on the surface plasmon resonance.[18].

Support effect on the activity of gold Nano particles

This is one aspect of gold catalysis which has been given considerable attention with no single postulate emerging as the reason for the reactivity of supported gold nano particles. It is generally conceived that there can be two kinds of interactions between the active metallic species and the support namely electronic effect where charge transfer to or from gold nano-particles is envisaged as a possible reason for the altered activity observed with supported nano-particles. The same postulate has also been seen with variance like creation of oxygen vacancies in the support with geometrical disposition or geometrical regularity. In addition the phase composition of the support like brookite or anatase in the case of TiO_2 has also been shown to have an influence on the observed catalytic behaviour of nano-particles. The supports

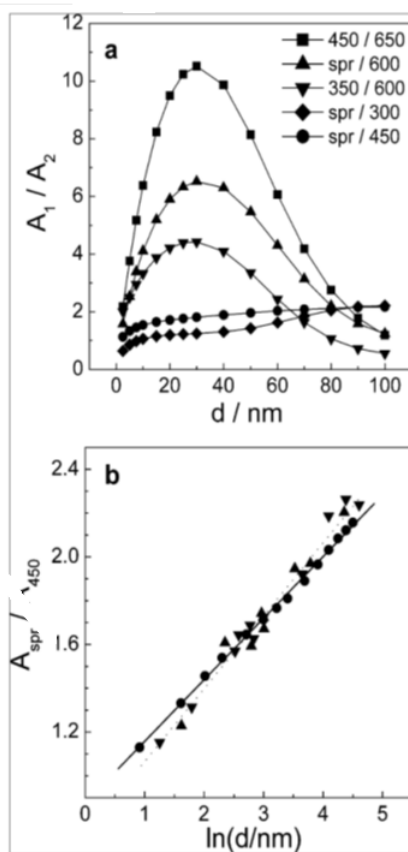


Figure 4: (a) Calculated ratios of absorbance values of gold particles in relation to their diameter; (b) Ratio of absorbance of Gold nano-particles the surface plasma resonance peak (A_{SPR}) to the absorbance at 450 nm (A_{450}) as a function of the logarithm of the particle diameter. Reproduced from ref, Anal.chem., 79,4219 (2007)

can also facilitate the shape and geometry of the nano-particles formed on it which goes with the terminology decoration of the active phase in the field of catalysis. Even though the electronic or geometric factor as responsible for metal support interaction is known in literature for several decades now it is still not clear which one is really responsible for the supported system to exhibit altered normalized activity. However, it is necessary that one considers additional aspects for the reactivity of supported gold nano particles.

(i) Does the support sustain the integrity of the nano-particles without allowing them to agglomerate?

(ii) Does the support facilitate the formation of specific shapes of the nano-particles of gold?

(iii) Does the support partially cover the nano-particles and thus stabilize the hemi-spherical geometry of the nano-particle?

(iv) Does the support active phase interaction induce the generation and sustaining of the active sites that are responsible for the observed catalytic activity?

(v) The support/nano-particle interface may be facilitating some catalytic reactions for example in the oxidation reactions, these interface sites may facilitate the oxygen release which is involved in the partial oxidation reaction. This aspect has not so far been addressed adequately to in the literature.

(vi) The interface sites between the support and the active nano-particle can be facilitating the activation of the substrate molecules and also it is possible that the transformation or required rearrangement in the reactant molecule (the so called intermediates) may be formed on these interface sites in a facile manner.

(vii) Even though the nature of the support (oxides, carbides, nitrides) has always been considered, there is no concerted view emerged if the surface group's functionality or the bulk electronic behaviour is responsible for the support metal interaction in these systems?

Beatriz Roldan Cuenya [19] has expressed this concern by stating that "by now one cannot simply neglect Nano-particle support interaction especially when a thorough understanding of the origin of the catalytic reactivity of the supported nano-particles is desired".

Landman et al [16] have considered the oxidation of CO on gold in the non-scalable regime and concluded the factors responsible for the altered activity are "the role of the metal oxide support and the defects in them, the charge state of the cluster, structural fluxionality of the cluster, electronic size effects the chemical reactivity of the metal clusters adsorbed on the support". It is therefore to assume that not one single factor appears to be responsible for the altered activity of gold nano-particles. Possibly that the present available information restricts one from outlining the one single reason for this

altered activity of gold nano-particles. Turner et al.,[20] have reported that nano-particles of gold with sizes less than 2 nm (or a cluster of 55 atoms) alone are active for the selective oxidation of styrene with dioxygen which has been attributed to the altered electronic structure intrinsic to small nano particles.

Insights into catalysis by gold nanoparticles and their support effects through surface science studies of model catalysts. The search for reactivity differences with cluster size of gold nano-particles has not yet led to a fixed value or a narrow range of values at which the reactivity shows a maximum. Choudhary and Goodman [5] show that the cluster sizes in the range 3-4 nm shows maximum activity for CO oxidation. Fenger et al [15] have shown that particles sizes in the range 10-15 nm exhibit highest rates for borohydride reduction of p-nitrophenol to p-aminophenol. Geng and Lu [21] showed that gold nano-particles of sizes 2-6 nm were more active compared to the large sized particles(12-41 nm) for the oxidation of CO in alkaline medium. Landmann et al (16) have considered the reactivity differences between various sized nano-particles from the correlation diagram of Local Density of States (LDoS) and showed that the wave functions of Au₄ (narrow d-band) cluster give rise to weak binding with oxygen on top mode due to lack of overlap between d-states of the cluster and molecular states of Oxygen. Their results are shown in Fig.5. It can be seen from this figure how the frontier orbitals of CO namely 5 σ , 1 π and 2 π orbitals are perturbed on adsorption on gold (Au₈) cluster and the oxygen also is capable of interacting with the same cluster which is shown in the right side of the figure. Goodman[22] has carried out surface science studies on model systems to understand the enhanced catalytic activities of nano-sized metal clusters. He has observed a correlation among cluster size, morphology and electronic properties with catalytic activity. Emilie Ringe et al [18] have studied the size dependent plasmonic properties of nano particles and concluded that the distance along which the oscillation occurs is important for the plasmonic resonance and not the intrinsic shape of the nano-particle. However, it is not clear if this postulate can be extended to the catalytic activity also. The catalytic behaviour of nano-particles is dependent on the nature of active sites generated and these can be different for different shaped nano-particles especially due to the fact the coordinative unsaturation of the sites may be depend on the shape of the particle. The size and shape of nano-particles are not the thermo-dynamically stable state and hence they can undergo reconstruction under the influence of process parameters or interaction with the reacting molecules. This situation may be particularly applicable to gold nano-particles. The effect of the size of gold nanoparticles on the observed catalytic reactivity can still be considered to be an open question. The essential observations leading to this

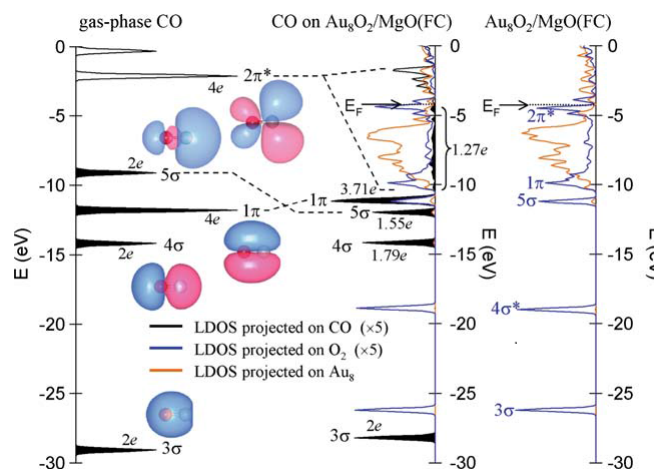


Figure 5: Local Density of states Projected on the orbitals of CO, Oxygen and Au_8 together that of free CO to indicate how these clusters are specific in activating the wave functions of the reactant molecule

state of affairs are:

- (1) The quantum size effects generated by the electrons confined in a small volume
- (2) The changes in conducting behaviour especially the transition from semi-conducting to metallic behaviour as function of particle size
- (3) The changes to higher binding energy (nearly 0.8 eV for gold nanoparticles of 1.9 nm size) with respect to pure gold ($4f_{7/2}$) due possibly to initial state effects as well as the positive charge left in the system after photo-ionization (final state effects)
- (4) The specificity of special planes for reactivity has been established and has been identified as roughness of the surface
- (5) The possibility of existence of energetically favourable isomers which could also be associated with the phenomenon of reconstruction
- (6) The underlying support can interact with the active phase and thus can induce generation of so called active sites
- (7) $1/d^3$ scaling law (where 'd' stands for the size of nano-particle) for activity has also been proposed in literature

It is therefore clear that the reactivity of gold nano-particles cannot be associated to a single governing parameter, while in the case of other metallic nano-particles a single or consistent group of parameters could be assigned for the activity alterations observed.

shape effects

One could expect that the shapes of nano-particles can have influence on the observed catalytic properties. However in the case of gold nano-particles the only established observation is that the hemispherical particles are better performing for CO oxidation as compared to spherical particles. The dependence of shape of nano-particles on reactivity has possibly been shown for silver and Pt nano-particles and not to the same extent on gold nano-particles.

Perception

The motivation to present this article is not to summarize all the results reported in literature. In fact the omission is far more than the selection. It is also not claimed the ones selected are the most appropriate ones. However, the sole aim in this presentation is to point out that there is some speciality of the wave functions of gold nano particles of particular size and shape and these features are not simply altering as the number of gold atoms found in gold nano-particles. Only certain number of gold atoms provide specific geometry and active sites possibly because of the participation of 4f and 5d orbitals of gold atoms. It is hoped that the speciality of these wave functions with respect to gold nano clusters will be soon identified and the speciality of catalysis by gold nano-particles will be rationalized.

References

- 1a.D.Y.Cha and GParravano, *J.Catalysis*, 18,200 (1970).
- 1b.G.C.Bond, P.A.Sermon, G.Webb,D.A.Buchanan and P.B.Wells, *J.Chem.Soc., Chem.Comm.*,444 (1973).
- 1c.M.Haruta, N.Yamado, T.Kobayashi and S.Iijima, *J.Catal.*,115,301 (1989).
- 1d.M.Haruta, T.Kobayashi, H.Sano and N.Yamada, *Chem.lett.*,16,405 (1987).
- 2.G.J.Hutchings, *J.Catal.*,96,292 (1985);*Gold Bull.*,29,123 (1996).
3. Yan Zhang,Xinjiang Cui, Feng Shi,and Youquan Deng, *Chem.Revs.*, 112,2467 (2012)
4. Marie-Christine Daniel and Didier Astruc, *Chem. Rev.*104, 293-346 (2004).
5. T.V.Choudhary and D.W.Goodman,*Topics in Catalysis*, 21, 25-34 (2002).
- 6.M. Haruta and M. Date, *Appl. Catal. A*, 2001, 222, 427
7. Manolis Stratakis and Hermenegildo Garcia,*Chem Rev.*, 112,4469-4506

- (2012).
8. Susie Eustis and Mostafa A. El-Sayed, *Chem. Soc. Rev.*, 2006, 35, 209217 (2006).
 9. Sujit Kumar Ghosh and Tarasankar Pal, *Chem. Rev.* 107, 4797-4862 (2007).
 10. M.Chen and D.W.Goodman, *Acc.Chem.Res.*, 39,739 (2006).
 11. Clemens Burda, Xiaobo chen, Radha Narayanan and Mostafa A.El-sayed, *Chem Rev.*, 105, 1025-1102 (2005).
 - 12a. B.C.Gates, *Chemical reviews*, 95 ,511-522 (1995).
 - 12b. Yusuke Mikami, Amarajothi Dhakshinamoorthy, Mercedes Alvaro and Hermenegildo Garca, *Catal. Sci. Technol.*, 3, 58(2013).
 13. M.Sankaran and B.Viswanathan, *Bulletin of the Catalysis Society of India*, 5, 26-32 (2006).
 14. A.Visikovskiy, H.Matsumoto, K.Mitsuhara, T.Nakada, T.Akita and Y.Y.Kido, www.ritsumei.ac.jp/acd/re/src/kankobutsu/vol.13/p89.pdf
 15. R.Fenger, E.Fertitta, H.Kirmse, A.F.Thunemann and K.Rademann, *Phys.Chem.Chem.Phys.*, 1, 9343 (2012).
 16. U.Landman, B.Yoon, C.Zhang, U.Heiz and M.Arez, *Topics in Catalysis*, 44,145 (2007).
 17. W.Haiss, N.T.K.Thanh, J.Aveyard and D.G.Fernig, *Analytical Chemistry*, 79,4215 (2007).
 18. Emilie Ringe, M.R.Langille, K.Sohn, J.Zhang, J.Huang, C.A.Mirkin, R.P.van Duyne and L.D.Marks, *J.Phys.Chem.Lett.*, 3,1479(2012).
 19. Beatriz Roldan Cuenya, *This solid films*, 518,3127 (2010).
 20. M.Turner, V.B.Golovko, O.P.H. Vaughan, P.Abdulhan, A.Berenguer-Murcia, M.S.Tikhov, B.F.G.Johnson and R.M.Lambert, *Nature*, 981 (2008).
 21. D.Geng and G.Lu, *Journal of Nanoparticle Research*, 9,145 (2007).
 22. D.W.Goodman, *Encyclopedia of nano science and nano-technology*, 611 (2004).
 23. H. Tsunoyama, H. Sakurai, Y. Negishi and T. Tsukuda, *J. Am. Chem. Soc.*, 2005, 127, 9374.
 24. H. Tsunoyama, N. Ichikuni, H. Sakurai and T. Tsukuda, *J. Am. Chem. Soc.*, 2009, 131, 7086.
 25. H. Tsunoyama, T. Tsukuda and H. Sakurai, *Chem. Lett.*, 2007, 36, 212.
 26. W. Hou, N. A. Dehm and R. W. J. Scott, *J. Catal.*, 2008, 253, 22.
 27. M.Comotti, C.Della Pina, R.Matarrese and M.Rossi, *Angew.Chem.Int.Ed* 43,5812 (2004).
 28. P.Beltrame, M.Comotti, C.Della Pina and M.Rossi, *Appl.Catal.,A*, 297,1 (2006).
 29. M.Comotti, C.Della Pina, E.Falsetta and M.Rosi, *Adv.Synth.Catal.*, 348,313 (2006).

30. C. Duan, H. Cui, Z. Zhang, B. Liu, J. Guo and W. Wang, *J. Phys. Chem.*, C111, 4561 (2007).
31. K. Hayakawa, T. Yoshimura and K. Esumi, *Langmuir*, 19, 5517 (2003).
32. M. A. Sanchez-castillo, C. Couto, W. B. Kim, and J. A. Dumesic, *Angew. Chem. Int. Ed.*, 43, 1140 (2004).
33. L. Prati, P. Spontoni and A. Galassi, *Top. Catal.*, 52, 288 (2009).
34. A. Villa, D. Wang, D. S. Su and L. Prati, *Chemcat.*, 1, 510 (2000).
35. L. Hu, X. Cao, J. Yang, M. Li, H. Hong, Q. Xu, J. Ge, L. Wang, J. Lu and L. Chen., *Chem. Commun.*, 47, 1 (2011).
36. M. Boualleg, K. Guillois, B. Istria, L. Burel, L. Veyre, J. M. Basset, C. Thieuleux and V. Caps, *Chem. Commun.*, 46, 5361 (2010).
37. M. H. Rashid and T. K. Mandal, *Adv. Funct. Mater.*, 18, 2261 (2008).
38. Z. Chen, C. Dellapina, E. Falletta, M. Lofaro, M. Pasta, M. Rossi and N. Santo, *J. Catal.*, 259, 1 (2008).
39. Yuriy Khalavka, Jan Becker, and Carsten Sonnichsen, *J. Am. Chem. Soc.*, 131, 1871 (2009).
40. M. Haruta, *Cattech*, Vol6 (2002).
41. Yolanda Seguraa, Nria Lpeza, Javier Prez-Ramrez, *J. Catal.*, 247, 383 (2007).
42. D. T. Thompson, *Nano today*, 2, 40 (2007).
43. Yan Zhang, Xinjiang Cui, Feng Shi, and Youquan Deng *Chemical Reviews*, 112, 2467 (2011).
44. G. C. Bond and Thompson, *Catal. Rev. Sci. Engg.*, 41, 319 (1999).