

**Project Title: Atomically Precise Metal Nanoclusters for Catalytic Application**

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**Abstract:**

The central goal of our project is to explore the catalytic application of atomically precise gold nanoclusters. By solving the total structures of ligand-protected nanoclusters, we aim to correlate the catalytic properties of metal nanoclusters with their atomic/electronic structures. Such correlation unravels some fundamental aspects of nanocatalysis, such as the nature of particle size effect, origin of catalytic selectivity, particle-support interactions, the identification of catalytically active centers, etc. The well-defined nanocluster catalysts mediate the knowledge gap between single crystal model catalysts and real-world conventional nanocatalysts. These nanoclusters also hold great promise in catalyzing certain types of reactions with extraordinarily high selectivity. These aims fall within the overall goals of the catalytic science and technology of DOE. Our research is designed to advance the BES mission “to support fundamental research to understand, predict, and ultimately control matter and energy at the level of electrons, atoms, and molecules”.

Our group has successfully prepared different sized, robust gold nanoclusters protected by thiolates, such as  $\text{Au}_{25}(\text{SR})_{18}$ ,  $\text{Au}_{28}(\text{SR})_{20}$ ,  $\text{Au}_{38}(\text{SR})_{24}$ ,  $\text{Au}_{99}(\text{SR})_{42}$ ,  $\text{Au}_{144}(\text{SR})_{60}$ , etc. Some of these nanoclusters have been crystallographically characterized through X-ray crystallography. These ultrasmall nanoclusters (< 2 nm diameter) exhibit *discrete* electronic structures due to quantum size effect, as opposed to *quasicontinuous* band structure of conventional metal nanoparticles or bulk metals. The available atomic structures (metal core plus surface ligands) of nanoclusters serve as the basis for structure-property correlations. We have investigated the unique catalytic properties of nanoclusters (i.e. not observed in conventional nanogold catalysts) and revealed the structure-selectivity relationships.

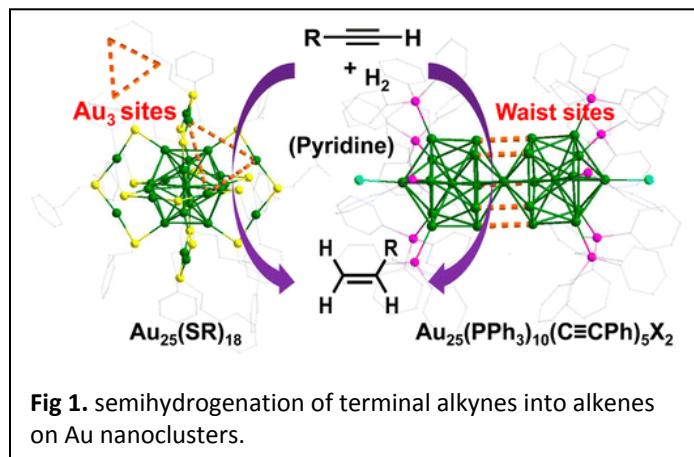
Highlights of our works include: i) Effects of ligand, cluster charge state, and size on the catalytic reactivity in CO oxidation, semihydrogenation of alkynes; ii) Size-controlled synthesis of  $\text{Au}_n$  clusters and structural elucidation; iii) Catalytic mechanisms and correlation with structures of cluster catalyst; iv) Catalytic properties of Au nanorods in chemoselective hydrogenation of nitrobenzaldehyde and visible light driven photocatalytic reactions.

## Detailed Description:

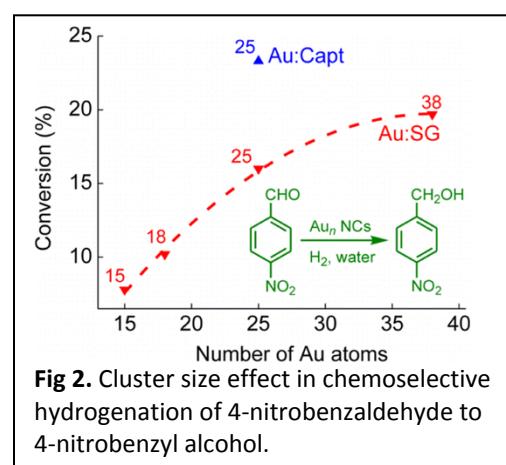
### 1) Cluster synthesis and effects of ligand, cluster charge state, and size on the catalytic reactivity (works published in JACS, Chem. Sci., Nano Lett., Angew. Chem. and ACS Catal.)<sup>1-7</sup>

We have investigated the effect of ligand on catalytic reactions using  $\text{Au}_{25}$  and  $\text{Au}_{144}$  nanoclusters. In CO oxidation, we found that both the nanoclusters and the oxide support ( $\text{CeO}_2$ ) play major roles in the catalytic reaction. With relatively surface inert  $\text{CeO}_2$ , the intact nanocluster itself cannot initiate the reaction. Only when the ligands are partially desorbed at  $>150$  °C, can the adsorption of CO be observed by IR.<sup>1</sup> The cationic gold (surface sites) was found to play critical role for low temperature CO oxidation.<sup>1</sup> Using  $\text{Au}_{144}(\text{SR})_{60}$  nanoclusters and surface-active  $\text{CeO}_2$ , we found that the catalytic reaction can be initiated at very mild conditions,<sup>2</sup> and that the activation of the catalyst is closely related to the production of active oxygen species on  $\text{CeO}_2$ , rather than ligand removal of the  $\text{Au}_{144}(\text{SR})_{60}$  clusters. A redox cycle is devised for catalyst activation, in which CO reduces the surface of  $\text{CeO}_2$  to produce oxygen vacancies—which then adsorb and activate  $\text{O}_2$  to produce more active oxygen species. The  $\text{CO}/\text{O}_2$  pulse experiments confirm that CO is adsorbed on the cluster catalyst even with ligand-on, and active oxygen species present on the surface of the pretreated catalyst reacts with CO pulses to generate  $\text{CO}_2$ .<sup>2</sup> The above studies clearly reveal that both the gold cluster and the surface lattice-oxygen of the support participate in the oxidation of CO with  $\text{O}_2$ .<sup>1,2</sup>

We have explored spherical  $\text{Au}_{25}$  and rod-shaped  $\text{Au}_{25}$  nanoclusters for the semihydrogenation of alkynes into alkenes with  $>99\%$  conversion of alkynes and  $\sim 100\%$  selectivity for alkenes (Fig 1).<sup>3</sup> A distinct ligand effect was found, i.e., internal alkynes cannot be catalyzed by “ligand-on”  $\text{Au}_{25}$  catalysts; however, with “ligand-off”  $\text{Au}_{25}$  catalysts both the internal and terminal alkynes undergo semihydrogenation to yield Z-alkenes. On the basis of the results, a unique activation pathway of terminal alkynes by “ligand-on” gold nanoclusters is identified.<sup>3</sup> This new activation mode is supported by results of IR spectroscopy.



Toward cluster size control, we have developed a new synthetic method based upon the ligand structure, which permitted tunability of a wide size range.<sup>4</sup> The structure of  $\text{Au}_{18}$  was determined by X-ray crystallography.<sup>5</sup> The cluster size effect was investigated in the chemoselective hydrogenation of 4-nitrobenzaldehyde ( $4\text{-NO}_2\text{PhCHO}$ ) to 4-nitrobenzyl alcohol ( $4\text{-NO}_2\text{PhCH}_2\text{OH}$ ), Fig. 2. A  $\sim 100\%$  selectivity of product was obtained in water using  $\text{H}_2$  gas (20 bar) as the hydrogen source.<sup>6</sup> We observed a drastic size dependence and steric effect of protecting ligands on the gold nanocluster catalysts in the hydrogenation reaction. Density functional theory (DFT) modeling of the 4-nitrobenzaldehyde adsorption shows that both the -CHO and -NO<sub>2</sub> groups closely interact with the S-Au-S staples on the gold nanocluster surface.<sup>6</sup>

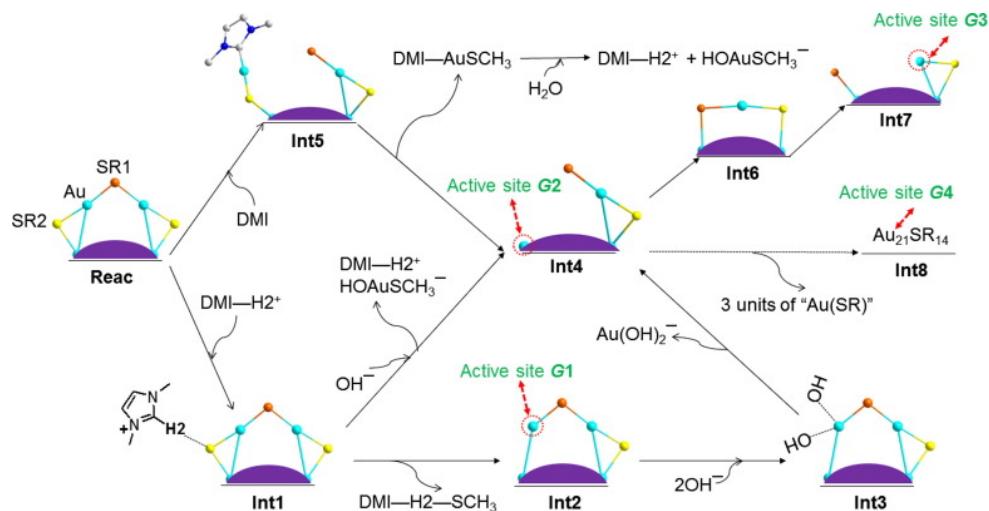


Overall, this work offers molecular insight into the hydrogenation of 4-nitrobenzaldehyde and the catalytically active site structure on gold nanocluster catalysts.

By electrochemical means, we created  $\text{Au}_{25}^-$ ,  $\text{Au}_{25}^0$  and  $\text{Au}_{25}^+$  and found charge state-dependent electrocatalytic activity for  $\text{CO}_2$  reduction, CO oxidation and  $\text{O}_2$  reduction reactions in aqueous media.<sup>7</sup> Our results mapped out a clear relationship between the  $\text{Au}_{25}^q$  charge state, the stability of adsorbed reactants or products, and the catalytic reaction rate. Specifically, anionic  $\text{Au}_{25}^-$  promoted  $\text{CO}_2$  reduction by stabilizing coadsorbed  $\text{CO}_2$  and  $\text{H}^+$  reactants. Cationic  $\text{Au}_{25}^+$  promoted CO oxidation by stabilizing coadsorbed CO and  $\text{OH}^-$  reactants. Stronger product adsorption at  $\text{Au}_{25}^+$  inhibited  $\text{O}_2$  reduction rates.<sup>7</sup>

## 2) Catalytic mechanisms and correlation with structures of cluster catalyst (works published in J. Catal., JACS, Nanoscale, and Nat. Commun.)<sup>8-12</sup>

Based on the cluster structures, we have achieved structure-reactivity correlations and molecular-level understanding of catalytic mechanisms. Here a case study is that the full structure of the  $\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}$  nanocluster catalyst allows detailed mechanistic insight into the Suzuki cross coupling reaction pathways at the atomic/molecular level (Fig 3)—in particular, the promotional effect of imidazolium-based ionic liquids (ILs) on the coupling reaction between phenylboronic acid and p-iodoanisole.<sup>8</sup> The catalytic mechanisms are studied using UV-vis spectroscopy, MALDI mass spectrometry, density functional theory (DFT) calculations, and classical molecular dynamics (MD) simulations. Partial removal of thiolate ligands ( $-\text{SR}$ ) and “ $\text{Au}-\text{SR}$ ” units from the protected  $\text{Au}_{25}$  cluster through interactions with imidazolium cations is deemed the promotion mechanism in the cross-coupling reaction. Both the experiment and DFT calculation indicate that the acidic proton at position 2 of the imidazolium ions plays an important role in the detachment of SR ligands and Au atoms from the nanocluster surface, which in turn allows the cross-coupling reaction to occur at a much milder temperature than in the absence of the IL promoter. Results suggest that oxidation of the active gold species not only prevents further fragmentation of the nanoparticles by the ILs but also increases the interaction of reactants with the catalysts, thereby improving the conversion rate.



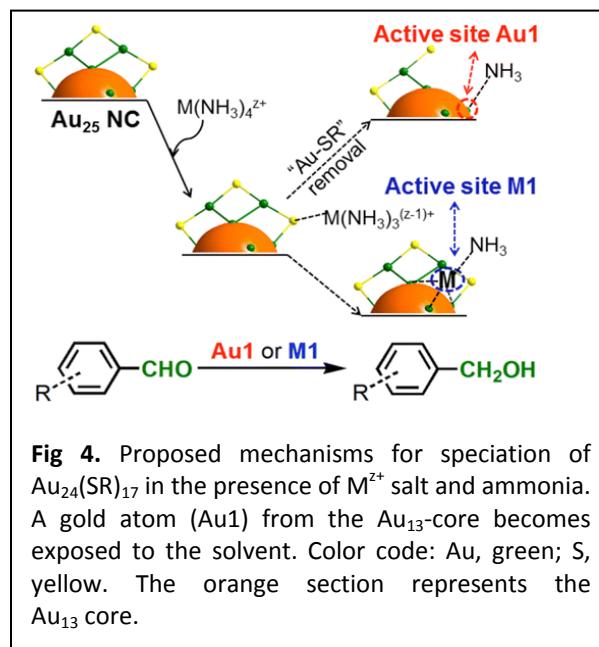
**Fig 3.** Reaction Mechanism 1 for the formation of catalytically active sites on the  $\text{Au}_{25}$  cluster promoted by imidazolium-based ionic liquids. Color code: Au, cyan; SR2, yellow; SR1, orange. The purple section represents the icosahedral  $\text{Au}_{13}$  core. The thiolate carbon tails are omitted for clarity.

We have also studied the catalytic mechanism of the aldehyde hydrogenation reaction over  $\text{Au}_{25}(\text{SR})_{18}$  nanoclusters ( $\text{R} = \text{C}_2\text{H}_4\text{Ph}$ ) in the presence of a base, e.g., ammonia or pyridine, and transition-metal ions  $\text{M}^{2+}$ , such as  $\text{Cu}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$ , as a Lewis acid.<sup>9</sup> The addition of a Lewis acid is found to significantly promote the catalytic activity of  $\text{Au}_{25}(\text{SR})_{18}/\text{CeO}_2$  in the hydrogenation of benzaldehyde and a number of its derivatives. Matrix-assisted laser desorption ionization (MALDI) and electrospray ionization (ESI) mass spectrometry in conjunction with UV-vis spectroscopy confirm the generation of new species,  $\text{Au}_{25-n}(\text{SR})_{18-n}$  ( $n = 1-4$ ), in the presence of a Lewis acid. The pathways for the speciation of  $\text{Au}_{24}(\text{SR})_{17}$  from its parent  $\text{Au}_{25}(\text{SR})_{18}$  nanocluster as well as its structure are investigated via the density functional theory (DFT) method. The adsorption of  $\text{M}^{2+}$  onto a thiolate ligand “ $-\text{SR}-$ ” of  $\text{Au}_{25}(\text{SR})_{18}$ , followed by a stepwise detachment of “ $-\text{SR}-$ ” and a gold atom bonded to “ $-\text{SR}-$ ” (thus an “Au-SR” unit) is found to be the most likely mechanism for the  $\text{Au}_{24}(\text{SR})_{17}$  generation (Fig 4). This in turn exposes the  $\text{Au}_{13}$ -core of  $\text{Au}_{24}(\text{SR})_{17}$  to reactants, providing an active site for the catalytic hydrogenation. DFT calculations indicate that  $\text{M}^{2+}$  is also capable of adsorbing onto the  $\text{Au}_{13}$ -core surface, producing a possible active metal site of a different kind to catalyze the aldehyde hydrogenation reaction.<sup>9</sup>

We have also devised an approach to synthesizing a meta-stable  $\text{Au}_{38}(\text{SR})_{24}$  nanocluster and compared its catalytic activity in the reduction of 4-nitrophenol with the thermodynamically stable  $\text{Au}_{38}(\text{SR})_{24}$  structure.<sup>10</sup> The new cluster exhibited much higher catalytic activity, indicating the structural sensitivity of the catalytic reaction.<sup>10</sup>

### 3) Catalytic properties of Au nanorods in chemoselective hydrogenation of nitrobenzaldehyde and visible light driven photocatalytic reactions (works published in JPC-C and Appl. Catal. B).<sup>11,12</sup>

We have also investigated Au nanoparticles ( $\sim 10$  nm) and nanorods ( $\sim 20$  nm) for hydrogenation<sup>11</sup> and photocatalytic reactions.<sup>12</sup> The chemoselective hydrogenation of 4-nitrobenzaldehyde to 4-nitrobenzyl alcohol used the unsupported Au spherical nanoparticle and nanorod catalysts at  $80^\circ\text{C}$  in water. A  $\sim 100\%$  selectivity for the 4-nitrobenzyl alcohol product was obtained when the hydrogenation reaction, and the Au nanorod catalysts exhibited an aspect-ratio dependent reactivity and generally performed much better than the Au spherical nanoparticle catalyst. In addition, the Au nanorod catalysts showed excellent recyclability in the chemoselective hydrogenation ( $>99\%$  conversion and 100% selectivity after 5 cycles).<sup>11</sup>



**Publications:**

1. Thiolate Ligands as a Double-Edged Sword for CO Oxidation on CeO<sub>2</sub> Supported Au<sub>25</sub>(SCH<sub>2</sub>CH<sub>2</sub>Ph)<sub>18</sub> Nanoclusters. Zili Wu, De-en Jiang, Amanda K. P. Mann, David R. Mullins, Zhen-An Qiao, Lawrence F. Allard, Chenjie Zeng, Rongchao Jin, and Steven H. Overbury. *J. Am. Chem. Soc.* 2014, **136**, 6111–6122.
2. “Mild activation of CeO<sub>2</sub>-supported gold nanoclusters and insight into the catalytic behavior in CO oxidation”, Weili Li, Qingjie Ge, Xiangang Ma, Yuxiang Chen, Manzhou Zhu, Hengyong Xu, Rongchao Jin, *Nanoscale* 2016, **8**, 2378-2385.
3. Gold Nanocluster-Catalyzed Semihydrogenation: A Unique Activation Pathway for Terminal Alkynes. Gao Li and Rongchao Jin. *J. Am. Chem. Soc.* 2014, **136**, 11347–11354.
4. “Tuning the magic size of atomically precise gold nanoclusters via isomeric methylbenzenethiols”, Yuxiang Chen, Chenjie Zeng, Douglas R. Kauffman and Rongchao Jin. *Nano Lett.* 2015, **15**, 3603-3609.
5. Structure Determination of [Au<sub>18</sub>(SR)<sub>14</sub>]. Anindita Das, Chong Liu, Hee Young Byun, Shuo Zhao, Nathaniel L. Rosi, Rongchao Jin, *Angew. Chem. Int. Ed.* 2015, **54**, 3140-3144.
6. Size Dependence of Atomically Precise Gold Nanoclusters in Chemoselective Hydrogenation and Active Site Structure. Gao Li, De-en Jiang, Santosh Kumar, Yuxiang Chen, and Rongchao Jin. *ACS Catal.* 2014, **4**, 2463–2469.
7. Probing active site chemistry with differently charged Au<sub>25</sub><sup>q</sup> nanoclusters (q = 1, 0, +1). Douglas R. Kauffman, Dominic Alfonso, Christopher Matranga, Paul Ohodnicki, Xingyi Deng, Rajan C. Siva, Chenjie Zeng, and Rongchao Jin. *Chem. Sci.* 2014, **5**, 3151-3157.
8. Molecular Mechanism on the Activation of Au<sub>25</sub>(SCH<sub>2</sub>CH<sub>2</sub>Ph)<sub>18</sub> Nanoclusters by Imidazolium-based Ionic Liquids for Catalysis. Hadi Abroshan, Gao Li, Jizhi Lin, Hyung J. Kim, and Rongchao Jin, *J. Catal.* 2016, **337**, 72-79.
9. Experimental and Mechanistic Understanding of C=O Hydrogenation Using Au<sub>25</sub> Nanoclusters with Lewis-Acids: Unique Sites for Catalytic Reactions. Li, Gao; Abroshan, Hadi; Chen, Yuxiang; Jin, Rongchao; Kim, Hyung. *J. Am. Chem. Soc.* 2015, **137**, 14295-14304.
10. Structural isomerism in gold nanoparticles revealed by X-ray crystallography. S Tian, YZ Li, MB Li, J Yuan, J Yang, Z Wu, R Jin, *Nature Communications* 2015, **6**, 8667.
11. Chemoselective Hydrogenation of Nitrobenzaldehyde to Nitrobenzyl Alcohol with Unsupported Au Nanorod Catalysts in Water. Gao Li, Chenjie Zeng, and Rongchao Jin, *J. Phys. Chem. C*, 2015, **119**, 11143-11147.
12. Integrating plasmonic Au nanorods with dendritic like  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub>/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> heterostructures for superior visible-light-driven photocatalysis. Changlin Yu, Wanqin Zhou, Lihua Zhu, Gao Li, Kai Yang, Rongchao Jin. *Appl. Catal. B: Environ.* 2016, **184**, 1–11.

13. Atomically Precise Metal Nanoclusters: Stable Sizes and Optical Properties. Rongchao Jin, *Nanoscale*, 2015, 7, 1549–1565.

14. Atomically Precise Colloidal Metal Nanoclusters and Nanoparticles: Fundamentals and Opportunities. Rongchao Jin, Chenjie Zeng, Meng Zhou, Yuxiang Chen. *Chem. Rev.* 2016, DOI: 10.1021/acs.chemrev.5b00703.

Book chapters:

15. Yuxiang Chen, Gao Li, Huifeng Qian, and Rongchao Jin. Ch. 8, Catalysis by Atomically Precise Gold Nanoclusters, Pages 239-262, In *Catalysis by Materials with Well-defined structures* (Zili Wu, Steven H. Overbury, Eds.), Elsevier Inc. 2015.

16. Changlin Yu, Wanqin Zhou, Gao Li, and Rongchao Jin. Ch. 8, Some Strategies in Designing Highly Efficient Photocatalysts for Degradation of Organic Pollutants in Water, pp 139–160, In *ACS Symposium Series\_Green Technologies for the Environment* (Eds.), ACS, 2014.