Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information for

Comprehensive Study of Catalytic, Morphological and Electronic Properties of Ligand-protected Gold Nanoclusters by XPS, STM, XAFS and TPD Techniques

Qiyuan Wu,[a] Jiajie Cen,[a] Yue Zhao,[b] Xiao Tong,[c] Yuanyuan Li,[a] Anatoly Frenkel,[a] Shen Zhao,[d] and Alexander Orlov[a]

a. Department of Material Science and Chemical Engineering, Stony Brook University, Stony Brook, NY 11794, USA.

b. Chemistry Department, Stony Brook University, Stony Brook, NY 11794, USA

c. Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY 11973, USA.

d. Energy and Environment Research, Southern Research, Durham, NC 27712, USA

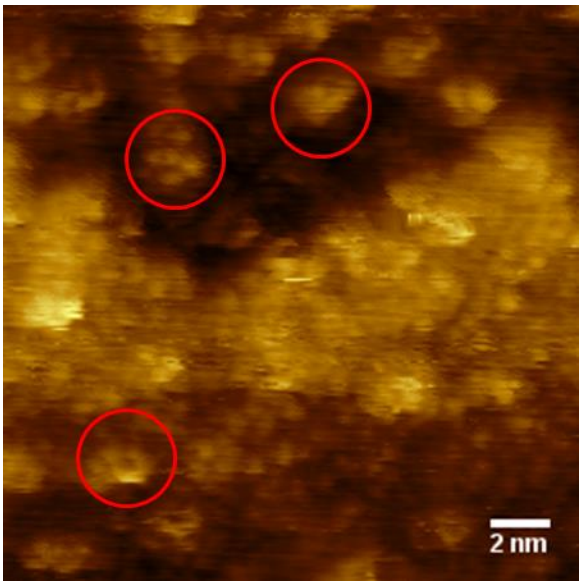

Figure S1: STM image of as-deposited Au NCs. The red circles highlight that those ~ 2 nm particles seen in figure 2a are in fact agglomerate of small An NCs.

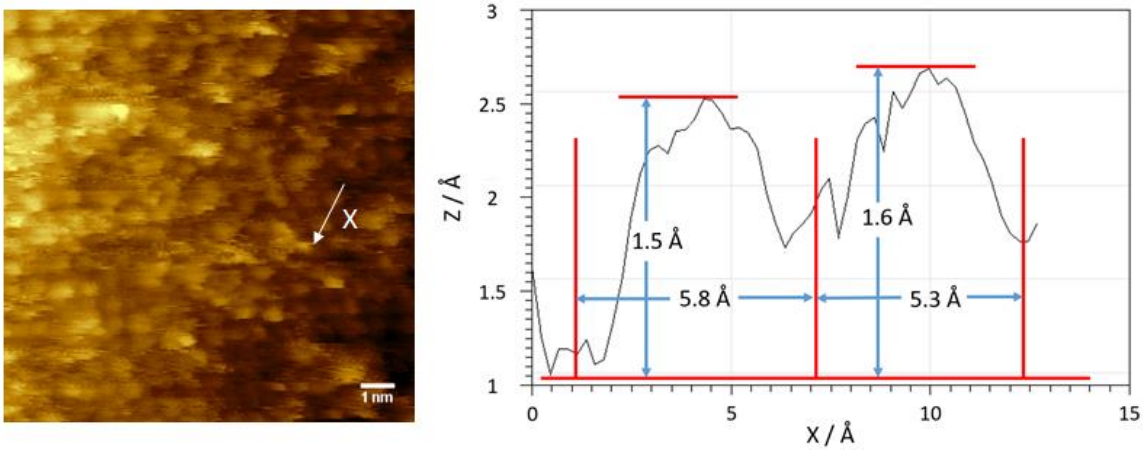

Figure S2: Representative STM line scan profile of two Au NCs. The line is indicated as the arrow in the STM image (left panel) and the profile is presented in the right panel.

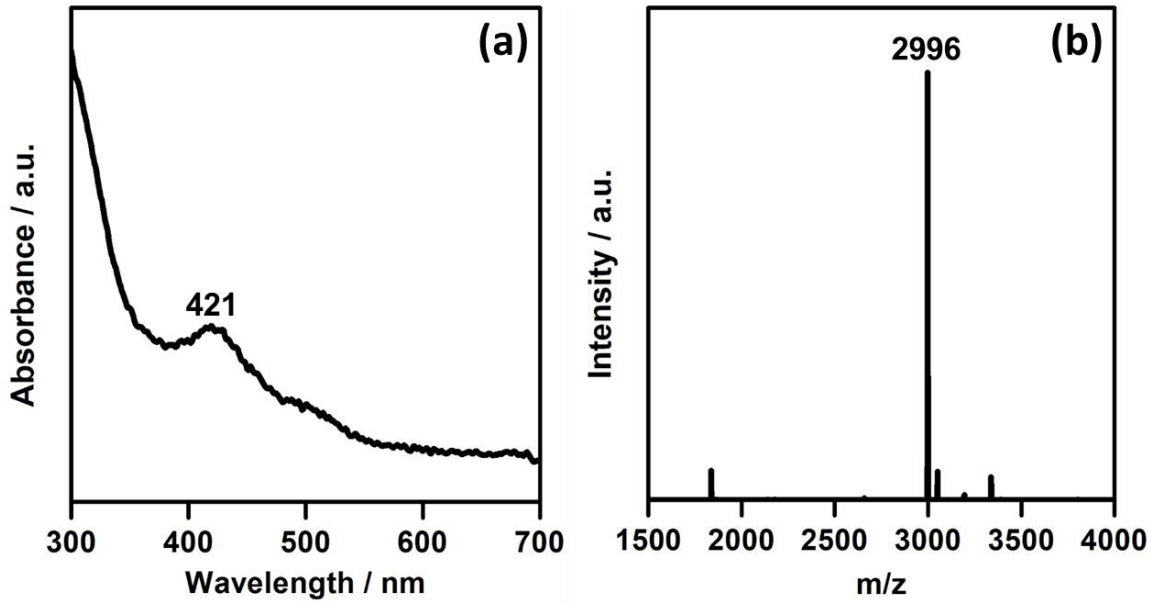

Figure S3: General characterization of synthesized Au NCs suspension before deposition. (a) UV-Visible spectrum of synthesized Au NCs suspension and (b) MALDI-TOF mass spectrum of synthesized Au NCs suspension. Results of both UV-Visible spectroscopy (shown only one absorption peak at ~420nm corresponding to the interband electronic transitions in Au clusters [1]) and mass spectroscopy (shown only one high-intensity peak positioned at m/z = 2996 corresponding to $[Au_{10}L_2Cl_5]^+$ cluster where L represents the diphosphine ligand.) indicated the dispersion of synthesized Au NCs was relatively narrow

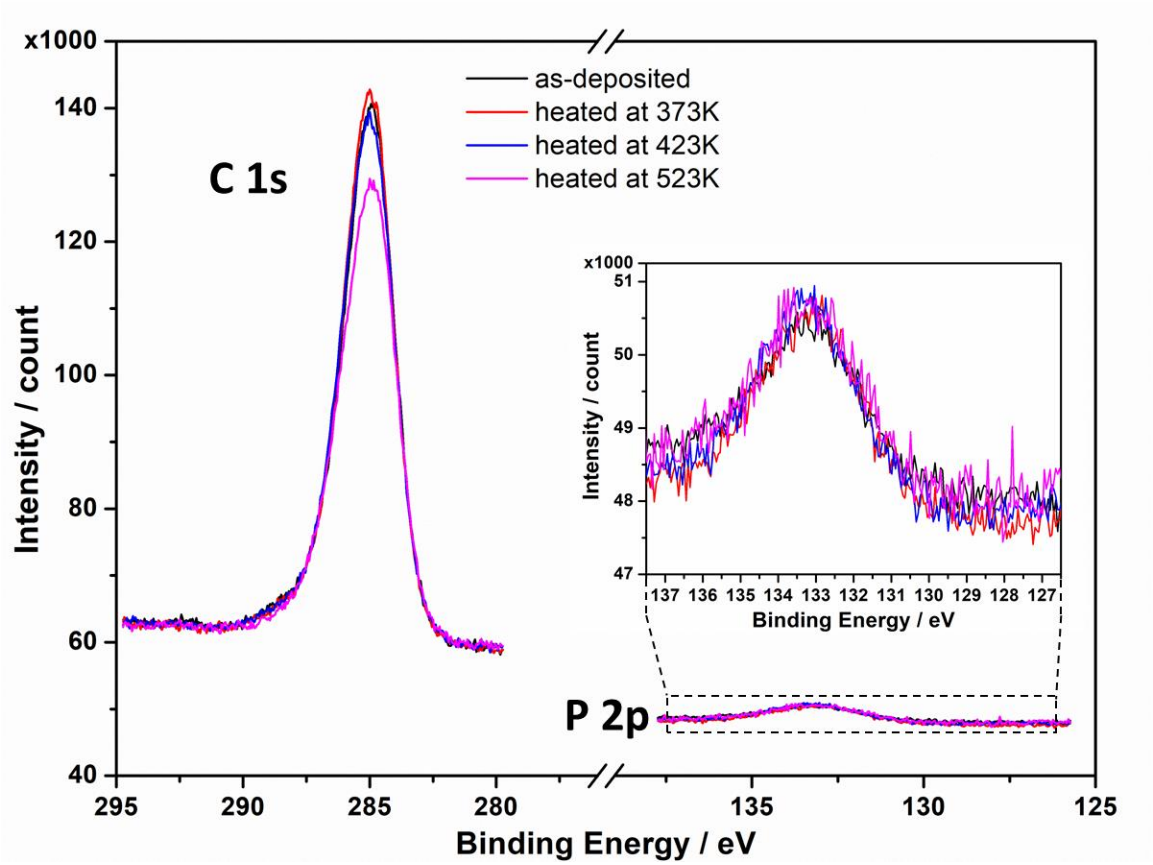

Figure S4: XPS spectra for C 1s and P 2p electrons of samples upon different heating treatment. Insert shows the magnified spectra for P 2p electron. Since the XPS relative sensitivity factors of C 1s electron (1.00) and P 2p electron (1.18) are quite closed, the very weak signal of P 2p electron indicates that the amount of P species is very small. Upon heating up to 523 K, no significant change (neither amount nor chemical state) in P species was observed. However, the XPS spectra for Au $4f_{7/2}$ clearly indicated significant change in chemical state of Au species. Such phenomena are consistent with published study that while diphosphine ligand could be removed by heating treatment start from 423 K, it required higher temperature (>573 K) to vaporize the ligand from the surface of the sample.[2] Nevertheless, our results highlighted the importance of ligand removal for activation of Au NCs where almost all Au atoms were coordinated to ligands.

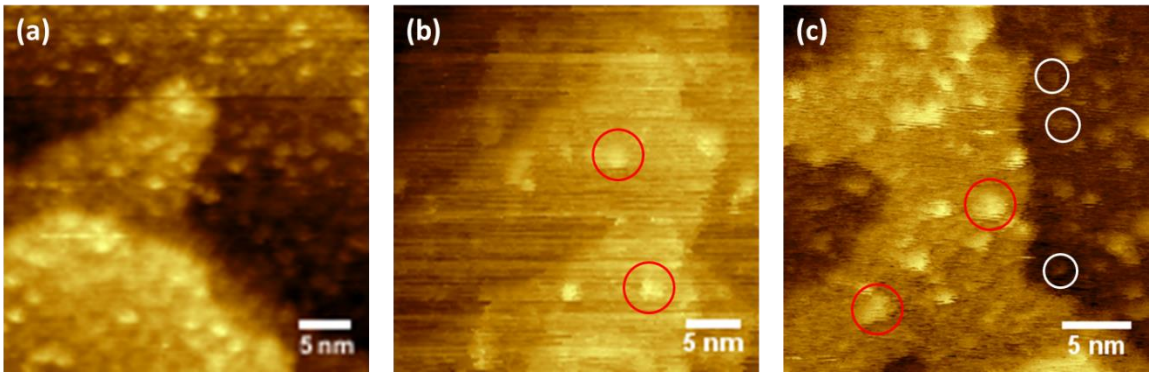

Figure S5: STM image of (a) as-deposited Au NCs samples, and samples subjected to heat treatment at 373 K (b) and 423 K (c). For comparison, (a) is part of Figure 2a The red circles in (b) and (c) highlight the ~ 2nm features seen in Figure 2a and Figure S1, while the white circles highlight Au NCs with dimensions shown in Figure 2d. The Au NCs in ~ 2nm features cannot be clearly resolved due the removal of ligands causing reduction of contrast in STM images.

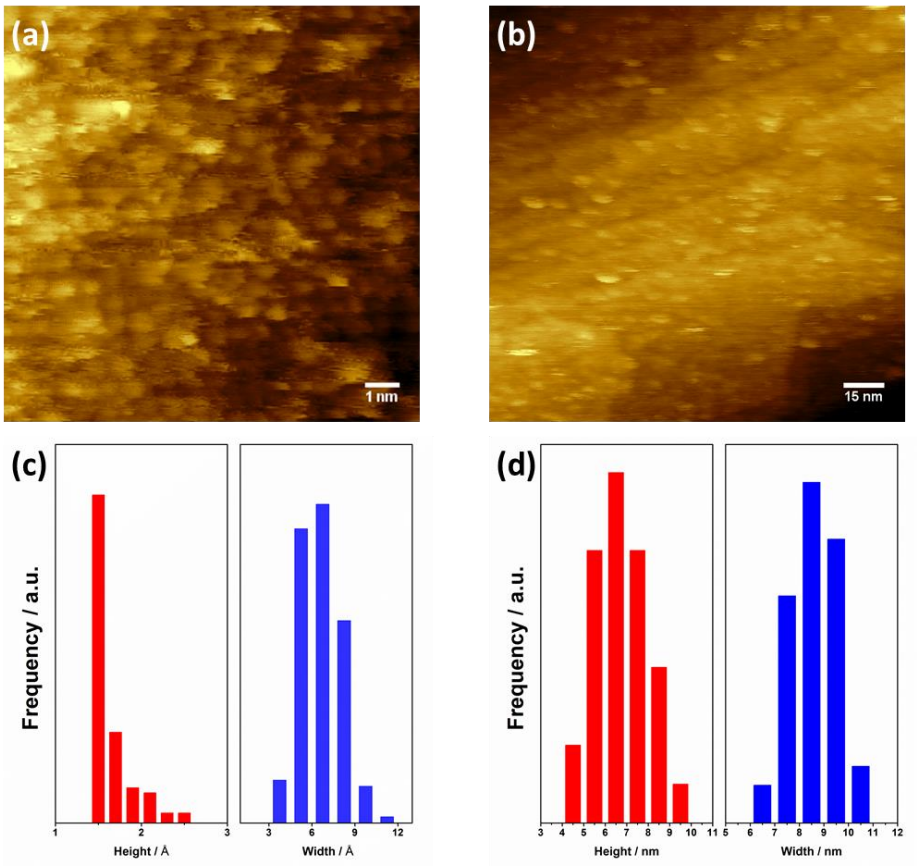

Figure S6: STM images of (a) as-deposited Au NCs samples and (b) samples subjected to heat treatment at 523 K. (b) shows the formation of Au particles with diameter of ~ 8.6 nm. For comparison, size distribution of as-deposited Au NCs samples and samples heated at 523 K are shown in (c) and (d).

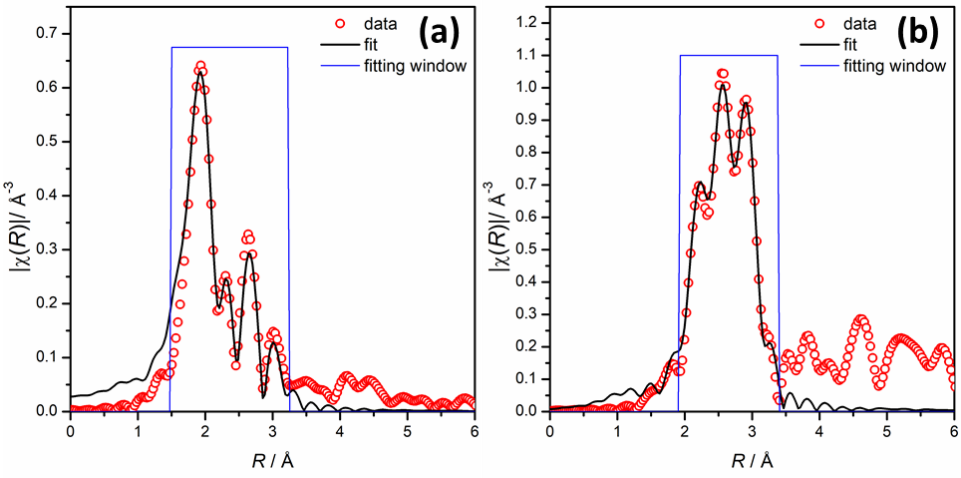

Figure S7: *In-situ* EXAFS results and STM images. (a) and (b): *in-situ* EXAFS data (empty red circle) and corresponding theoretical fittings (solid black lines) of Au L_3 edge of as-deposited Au NCs (a) and Au NCs after heating treatment at 523K (b). Data are presented in R space. The fitting windows (solid blue lines) are also included.

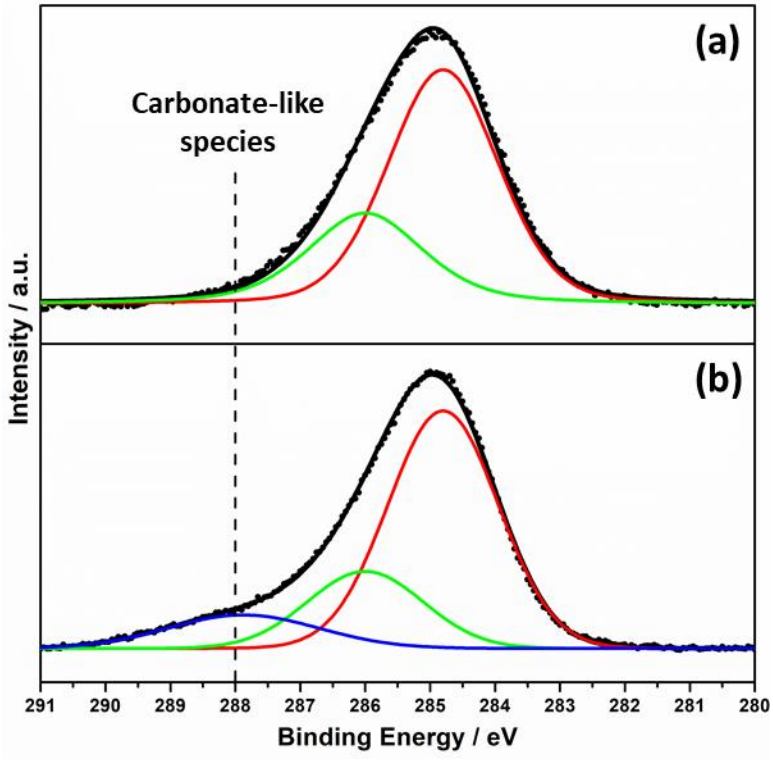

Figure S8: XPS spectra for C 1s electrons of samples upon heating at 523 K (a) before dosing of CO and (b) after dosing of CO. Black dots are experimental data and colored lines are fitted lines. It can be clearly seen that carbonate-like species were formed upon dosing of CO. For proper comparison, two fitting parameters (binding energy and FWHM) for carbon species (represented by green and red lines) that already existed in (a) were fixed during the fitting for (b).

Samples	Average CN	Bond length / Å	σ^2 / Å^2
As-deposited	3.2 ± 0.9 / 2.2 ± 0.9	2.67 ± 0.21 / 2.87 ± 0.01	0.008 / 0.008
After heating	10.6 ± 0.5	2.86 ± 0.03	0.008
Au foil	12	2.86 ± 0.02	0.008

Table S1: Detailed theoretical fitting results of EXAFS data of as-deposited Au NCs and Au NCs after heating treatment at 523 K. Corresponding values for bulk Au foil are also included. In the fitting strategy, the energy shift ΔE_0 and the disorder factor (σ^2) were fixed to be the same for both Au-Au bond while the coordination number (N) and the bond distance (R) for each Au-Au bond were variables. The EXAFS data of as-deposited Au NCs were fitted within the k-range from 2.5 Å^{-1} to 14 Å^{-1}. The EXAFS of Au NCs after heating treatment and Au foil were fitted within the k-range from 2 Å^{-1} to 15 Å^{-1}. For as-deposited Au NCs, two kinds of Au-Au bonds are included in the fitting based on published literature.[3] The total average CN for as-deposited Au NCs is thus: 3.2 + 2.2 = 5.4 as described in the main text.

Reference

1. Y. Yang and S. Chen, *Nano Letters*, 2003, **3**, 75-79.
2. Z. Wu, G. Hu, D.-e. Jiang, D. R. Mullins, Q.-F. Zhang, L. F. Allard, L.-S. Wang and S. H. Overbury, *Nano Letters*, 2016, **16**, 6560-6567.
3. M. J. Calhorda, O. Crespo, M. C. Gimeno, P. G. Jones, A. Laguna, J. M. López-de-Luzuriaga, J. L. Perez, M. A. Ramón and L. F. Veiros, *Inorganic Chemistry*, 2000, **39**, 4280-4285.