

# Resonance photoemission observation and DFT study of s-d hybridization in catalytically active gold clusters on ceria nanorods



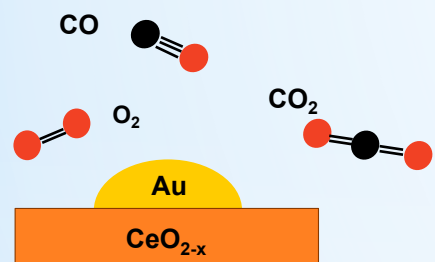
Yunyun Zhou,<sup>1</sup> Neil J. Lawrence,<sup>1</sup> Lu Wang,<sup>2</sup> Lingmei Kong,<sup>1</sup> Tai-Sing Wu,<sup>3</sup> Jing Liu,<sup>1</sup> Yi Gao,<sup>1</sup> Joseph R. Brewer,<sup>1</sup> Viviana K. Lawrence,<sup>1</sup> Renat F. Sabirianov,<sup>2</sup> Yun-Liang Soo,<sup>3</sup> Xiao Cheng Zeng,<sup>1</sup> Peter A. Dowben,<sup>1</sup> Wai Ning Mei<sup>2</sup> and Chin Li Cheung\*,<sup>1</sup>

<sup>1</sup>University of Nebraska-Lincoln; <sup>2</sup>University of Nebraska at Omaha; <sup>3</sup>National Tsinghua University

\*E-mail: clcheung2@unl.edu

## Introduction

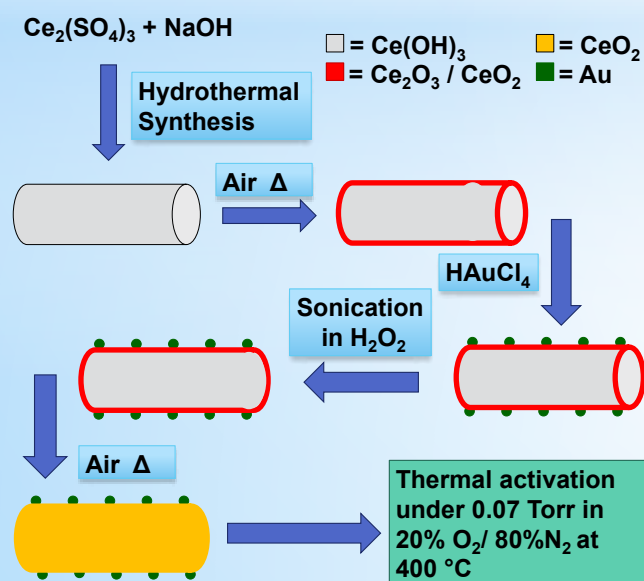
Gold clusters have garnered intense interest because of their unusual catalytic activities towards chemical reactions of industrial importance. Electronic structures of oxide supported gold clusters can provide critical clues to the mechanisms for their catalytic activity. Gold atoms possess an electronic configuration of [Xe] 4f<sup>14</sup>5d<sup>10</sup>6s<sup>1</sup>. However, both relativistic effects and 5d band upshift of gold clusters result in a theoretically expected hybridization of the 5d and 6s orbitals. These s-d hybridized orbitals are expected to, essentially, increase the number of free d states (or d holes) available for bonding with incoming reactant molecules, thus lowering the transition state energy and promoting the reactions.



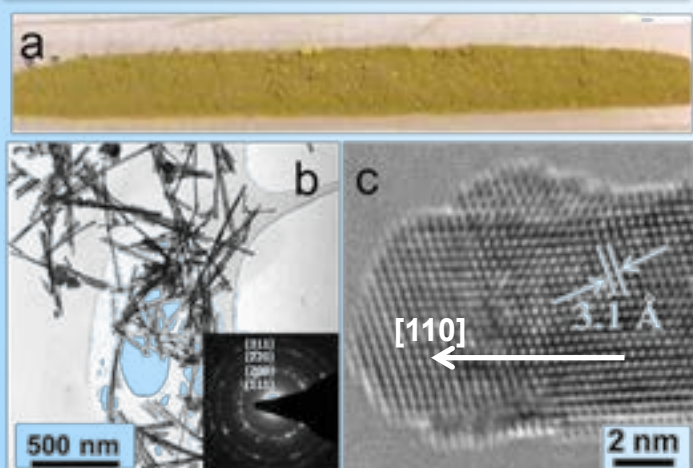
## Objectives

- Investigate s-d hybridization in catalytically active 0.01 at.% Au:CeO<sub>2-x</sub> using resonance photoemission spectroscopy
- Elucidate the detailed 5d and 6s weighted band structure using density functional theory (DFT) calculations, and provide theoretical support to the origin of the hybridization between these bands in low gold concentration Au:CeO<sub>2-x</sub> catalysts.

## Synthetic Scheme for Au:CeO<sub>2-x</sub>

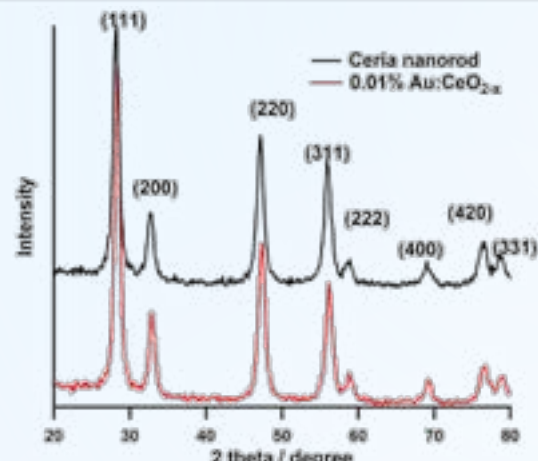


## Morphology Characterization



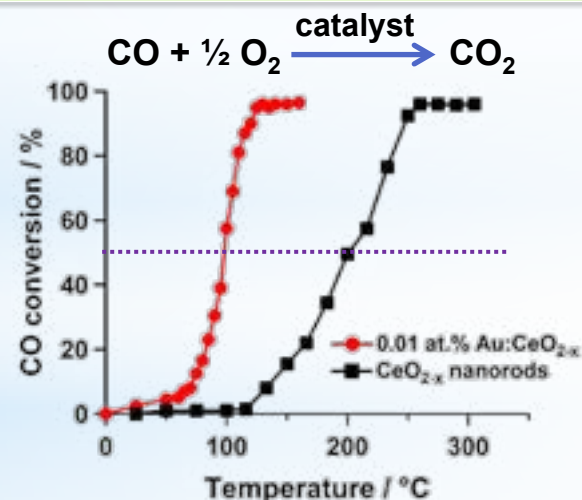
The color of 0.01 at.% Au:CeO<sub>2-x</sub> nanorods is greenish (Figure a), which is different from the pure CeO<sub>2-x</sub> nanorods (pale yellow, not shown). HRTEM image showing lattice fringes with spacing of 3.1 Å, corresponding to the (111) plane spacing of cerium(IV) oxide.

## X-Ray Diffraction Patterns

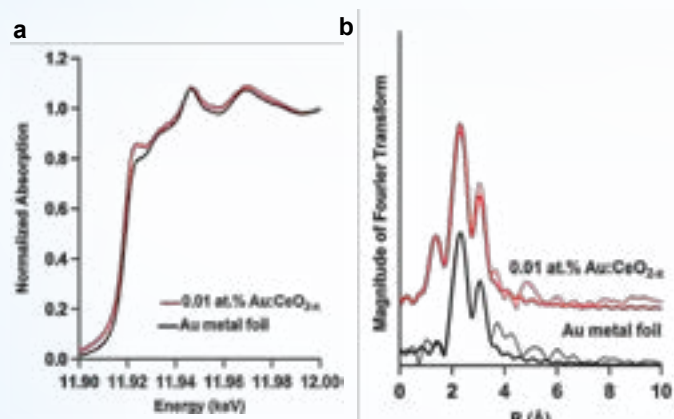


All peaks are indexed with respect to the cubic *Fm* $\bar{3}$ *m* structure of cerium(IV) oxide (CeO<sub>2</sub>). No peaks corresponding to Au, AuO<sub>x</sub>, nor Au(OH)<sub>x</sub> were observed in the XRD patterns.

## Catalytic CO oxidation



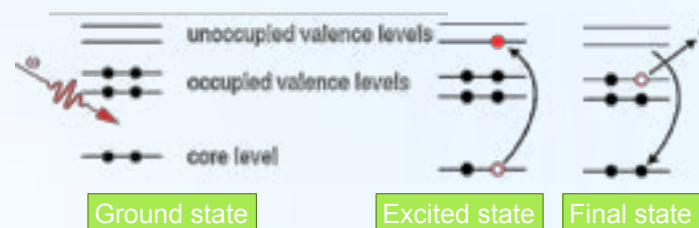
## Electronic Structure Analysis



Sample	Bond	N	R (Å)	$\sigma$ (10 <sup>-3</sup> Å <sup>2</sup> )	$\Delta E$ (eV)
0.01 at.% Au:CeO <sub>2-x</sub>	Au-O	0.6 ± 0.3	2.02	4.1 ± 9.9*	-15 ± 5
	Au-Au	8.9 ± 1.3	2.83 ± 0.01	3.8 ± 1.3	4.0 ± 0.8
Au metal foil	Au-Au	12	2.86 ± 0.01	8.1 ± 1.1	5.2 ± 0.6

An Au-O bond with an average distance of 2.02 Å indicates a strong interaction between the gold clusters and their ceria supports. A slightly shorter Au-Au atomic distance (2.83 Å) and lower coordination number (CN = 8.9) were observed in the catalyst than those of gold foil.

## Resonance Photoemission Spectroscopy



When the photon energy is swept through the binding energy of a core electron, the core electron can be excited into an unoccupied state of a partially filled valence band and decay in a subsequent auto-ionization process. This results in emission of an electron from the occupied part of the valence band. A photoelectron of the same kinetic energy can be excited by direct photoemission from the occupied valence band. These two processes have the same initial and final states and they interfere each other. This gives rise to a resonance, an enhanced photoelectron intensity.

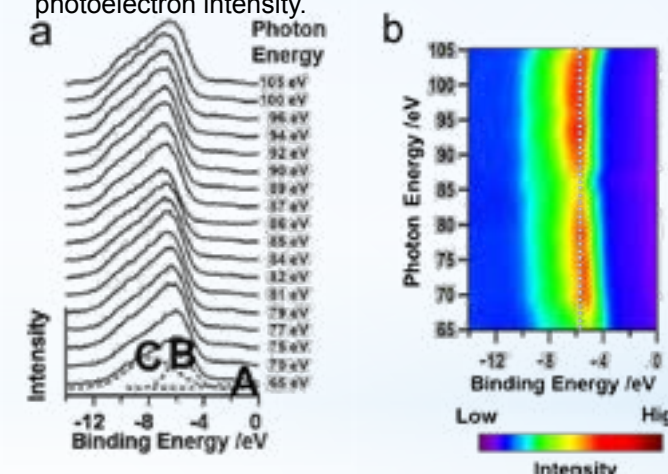
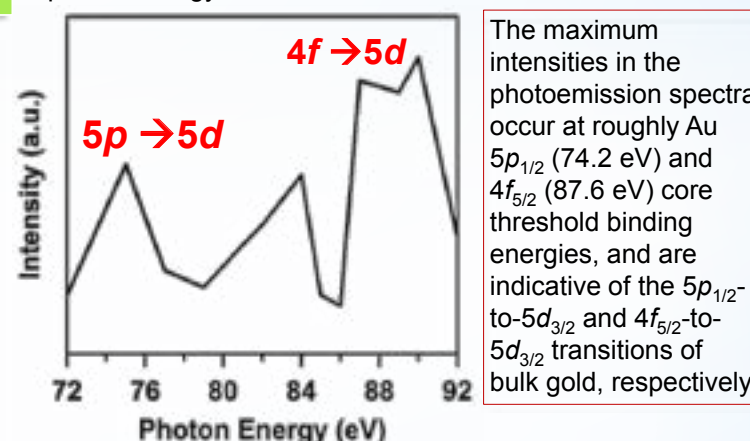


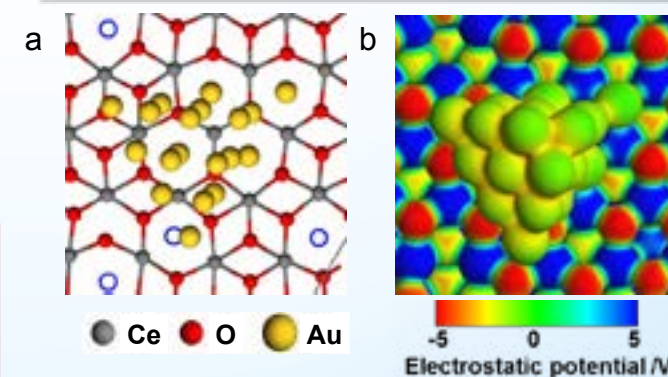
Figure a shows the normalized intensity of the VBS recorded at different incident photon energies. (Binding energies are denoted in terms of  $E - E_F$ ) Peak A is attributed to the emission of electrons from the localized Au 5d state. Peaks B and C in the broad band (-10 eV to -4 eV) arise from the photoemission from the O 2p<sub>x</sub>, O 2p<sub>y</sub> orbitals (-5.7 eV) and O 2p<sub>z</sub> orbital (-7.7 eV), respectively. Figure b demonstrates the intensity change of photoemission corresponding to the photon energy variation in 2D manner.



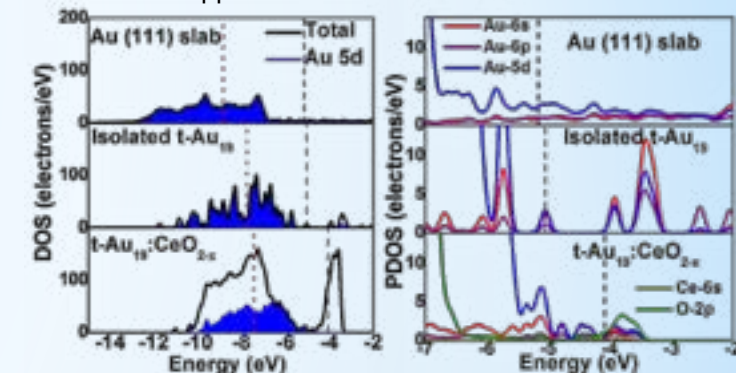
The maximum intensities in the photoemission spectra occur at roughly Au 5p<sub>1/2</sub> (74.2 eV) and 4f<sub>5/2</sub> (87.6 eV) core threshold binding energies, and are indicative of the 5p<sub>1/2</sub>-to-5d<sub>3/2</sub> and 4f<sub>5/2</sub>-to-5d<sub>3/2</sub> transitions of bulk gold, respectively.

## DFT Study

### Tetrahedral Au<sub>19</sub> Cluster on Defective Ceria

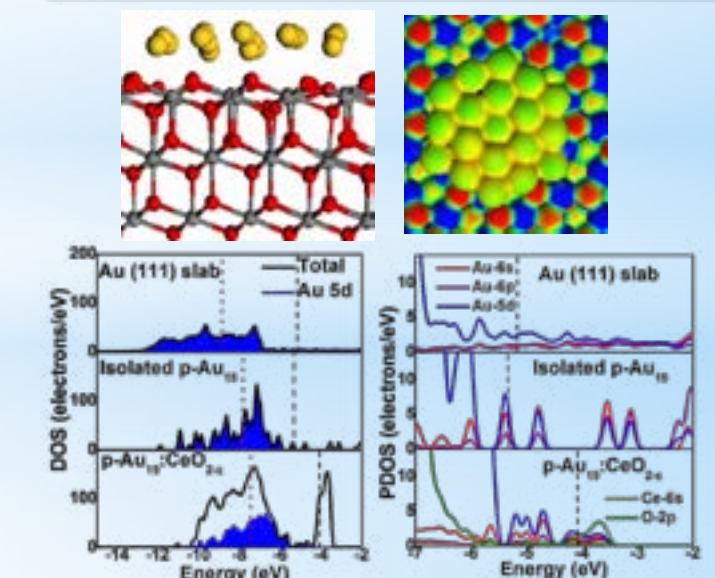


Tetrahedral Au<sub>19</sub> (t-Au<sub>19</sub>) is considered the most stable of the Au<sub>19</sub> clusters (shown in Figure a). The optimized structure of the t-Au<sub>19</sub>:CeO<sub>2-x</sub> model, shown in Figure b, was found to be slightly negatively charged (-0.17 e<sup>-</sup> per Au atom) from Bader charge analysis. The excess charge in the t-Au<sub>19</sub> cluster was likely transferred from the electron density of the oxygen vacancies in the defective ceria slab support



- The interaction of t-Au<sub>19</sub> with the ceria support possibly introduces the pin-in gap state feature (or metal-induced gap states (MIGS) present below the empty Ce 4f states and the Fermi level. These MIGS are mainly composed of Au 5d and 6s states, consistent with our photoemission findings.
- The similarities among the shapes of these 5d and 6s band structures in the MIGS region further confirm the strong s-d hybridization in this supported t-Au<sub>19</sub> cluster

### Planar Au<sub>19</sub> Cluster on Defective Ceria



Planar Au<sub>19</sub> is also investigated because the planar structure is strongly favored by the relativistic effect. The gold cluster is negatively charged as analyzed by Bader charges (-4.33 e<sup>-</sup> or -0.23 e<sup>-</sup> per Au atom). 6s-5d orbitals hybridization was observed in planar Au<sub>19</sub> on ceria support and the 5d band up-shift.

## Conclusion

- The existence of s-d hybridization in the gold clusters of a catalytically active 0.01 at.% Au:CeO<sub>2-x</sub> catalyst was demonstrated using resonance photoemission spectroscopy and model calculations.
- Significant 5p<sub>1/2</sub>-to-5d<sub>3/2</sub> and 4f<sub>5/2</sub>-to-5d<sub>3/2</sub> resonant electronic transitions observed in our Au:CeO<sub>2-x</sub> catalysts indicate the presence of an unfilled 5d subshell (or 5d holes) in the gold clusters of the catalyst and thus provide the evidence for the s-d hybridization in these gold clusters.

## Acknowledgement

This research is supported by Nebraska Center for Energy Sciences, Department of Energy and Army Research Office. We thank the University of Nebraska Holland Computing Center, the University of North Texas, Nebraska Center for Materials and Nanoscience and Center for Advanced Microstructures & Devices for the use of their facilities.