

# Three-orders-of-magnitude variation of carrier lifetimes with crystal phase of gold nanoclusters

by Meng Zhou, Tatsuya Higaki, Guoxiang Hu, Matthew Y. Sfeir, Yuxiang Chen, De-en Jiang, and Rongchao Jin

> *Science Volume 364(6437):279-282 April 19, 2019*

> > Esma Khatun 08/06/2019



- They have reported a three-orders-of-magnitude variation of carrier lifetimes in exotic crystalline phases of gold nanoclusters (NCs) in addition to the well-known face-centered cubic structure, including hexagonal close-packed (hcp) Au<sub>30</sub> and body-centered cubic (bcc) Au<sub>38</sub> NCs protected by the same type of capping ligand.
- □ The bcc Au<sub>38</sub> NC had an exceptionally long carrier lifetime (4.7 microseconds) comparable to that of bulk silicon, whereas the hcp Au<sub>30</sub> NC had a very short lifetime (1 nanosecond).
- □ Although the presence of ligands may, in general, affect carrier lifetimes, experimental and theoretical results showed that the drastically different recombination lifetimes originate in the different overlaps of wave functions between the tetrahedral Au<sub>4</sub> building blocks in the hierarchical structures of these NCs.

## Significance of the paper

- □ Understanding the carrier dynamics in ultrasmall (<2-nm) gold nanoclusters is fundamentally important for their applications in solar energy storage and conversion.
- □ This work showed that like semiconductors, small metallic clusters can absorb light and create excitons (electron-hole pairs). In ligand-capped gold clusters of 30 to 40 atoms that adopt the usual face-centered cubic packing, the lifetime of these excitons is ~100 nanoseconds. Despite having similar bandgaps to those of face-centered cubic clusters, a hexagonal close-packed cluster had a much shorter lifetime and a body-centered cubic cluster had a longer lifetime comparable to the bulk silicon.
- □ Hence the report first show that atomic packing can controls exciton lifetime.

## Relevance to the group

- □ In our group many are working in Au and Ag NCs. We are synthesising some new stable nanoclusters. So, ultrafast spectroscopy can be effective study to understand the photophysical properties of these NCs which can explore the application of them.
- □ Also, we have found polymorphic NCs, such as Ag<sub>29</sub>, Ag<sub>14</sub>. One can study the difference in carrier dynamics of two polymorphic NCs.

## **Background reports**

J. Phys. Chem. C 2010, 114, 19935-19940

19935

#### Ultrafast Relaxation Dynamics of [Au<sub>25</sub>(SR)<sub>18</sub>]<sup>q</sup> Nanoclusters: Effects of Charge State

Huifeng Qian,<sup>†</sup> Matthew Y. Sfeir,<sup>\*,‡</sup> and Rongchao Jin<sup>\*,†</sup>

Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213, United States, and Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York 11973, United States

Received: August 20, 2010; Revised Manuscript Received: October 10, 2010





Received:June 22, 2017pubs.acs.org/JPCLAccepted:August 10, 2017Published:August 10, 2017

## Evolution of Excited-State Dynamics in Periodic $Au_{28}$ , $Au_{36}$ , $Au_{44}$ , and $Au_{52}$ Nanoclusters

Meng Zhou,<sup>†</sup><sup>©</sup> Chenjie Zeng,<sup>†</sup><sup>©</sup> Matthew Y. Sfeir,<sup>‡</sup><sup>©</sup> Mircea Cotlet,<sup>‡</sup> Kenji Iida,<sup>§,||</sup> Katsuyuki Nobusada,<sup>§,||</sup><sup>©</sup> and Rongchao Jin<sup>\*,†</sup><sup>©</sup>



Letter



Received:July 23, 2017pubs.acs.org/JPCLAccepted:September 21, 2017Published:September 21, 2017

### Energy Gap Law for Exciton Dynamics in Gold Cluster Molecules

Kyuju Kwak,<sup>†</sup> Viraj Dhanushka Thanthirige,<sup>‡</sup> Kyunglim Pyo,<sup>†</sup> Dongil Lee,<sup>\*,†</sup> and Guda Ramakrishna<sup>\*,‡</sup>



Energy Gap Law for Exciton Dynamics in Gold Cluster Molecules

Letter

## Introduction

- □ Metal nanoclusters (NCs) hold promise in a variety of applications owing to their versatile functionalities that can be tailored by size, structure, and composition.
- □ Unlike plasmonic gold nanoparticles (Au NPs), ultrasmall Au NCs (<2 nm in diameter) show discrete electronic energy levels and multiple peaks in their ultraviolet-visible (UV-vis) absorption spectra.
- □ Achieving a fundamental understanding of the optical properties and photophysics of metal NCs (including the electron and phonon dynamics) is of great importance to the exploration of their applications.
- □ Here, they reported unusual carrier dynamics of Au NCs with hcp and bcc crystalline phases. Specifically, the carrier dynamics of hcp Au<sub>30</sub>(S-Adm)<sub>18</sub> and bcc Au<sub>38</sub>S<sub>2</sub>(S-Adm)<sub>20</sub> NCs exhibited drastic differences compared with the icosahedral Au<sub>25</sub> and fcc Au<sub>36</sub>/Au<sub>44</sub>/Au<sub>52</sub> NCs, although all six NCs possess comparable band gaps (1.3 to 1.77 eV).



Fig. 1. X-ray structures and steady-state UV-vis absorption spectra of  $Au_{30}(S-Adm)_{18}$  and  $Au_{38}S_2(S-Adm)_{20}$  NCs.



Fig. S1. Absorption spectra of hcp  $Au_{30}$  and bcc  $Au_{38}$  nanoclusters on photon energy scale, the bandgap is determined to be 1.55 eV and 1.45 eV, respectively.



Fig. 2. Comparison of spectral features and carrier dynamics of the two NCs. (A and B) TA spectra (black) of (A) hcp Au<sub>30</sub> and (B) bcc  $Au_{38}$  NCs at a time delay of 10 ps pumped at 360 Steady-state absorption nm. spectra (gray) are also shown for comparison. (C and D) TA data map with excitation of 360 nm and kinetic traces of the hcp Au<sub>30</sub> NC. (E and F) TA data map with excitation of 360 nm and kinetic traces of the bcc Au<sub>38</sub> NC. (G) Data map of ns-TA in bcc Au<sub>38</sub> NCs between 0.01 and 20  $\mu$ s with an excitation of 480 nm. (H) Kinetic traces probed at 620 nm and the corresponding fit. DA, change in absorbance; mOD, milli-optical density units.



Fig. S2. Decay associated spectra (DAS) obtained from global fitting of TA measurements of hcp Au<sub>30</sub> with (A) 360 nm and (B) 560 nm excitation.



**Fig. S3.** (A) Transient absorption data map with excitation at 560 nm and (B) kinetic traces of hcp Au<sub>30</sub>. Scattering due to the pump laser at ~560 nm was cut off.



**Fig. S4.** Decay associated spectra (DAS) obtained from global fitting of TA measurement of bcc Au<sub>38</sub> with (A) 360 nm and (B) 730 nm excitation.



Fig. S5. (A) Transient absorption data map with excitation at 730 nm and (B) kinetic traces of bcc Au<sub>38</sub>. Scattering due to the pump laser at ~730 nm was cut off.

12



Correlation Fig. 3. between structures and excited-state lifetimes of bcc, hcp, and fcc NCs. (A to C) Tetrahedral Au<sub>4</sub> networks in  $Au_{30}$ ,  $Au_{38}$ , and  $Au_{36}$  NCs. (D) Excited-state lifetimes versus Eg of several gold NCs. (E) Excited-state lifetimes versus distance between the  $Au_4$  units in the cores of bcc hcp  $Au_{30}$ ,  $Au_{38}$ , and fcc  $Au_{36}/Au_{44}/Au_{52}$  NCs. (F) Frontier orbitals and HOMO-LUMO centroid distances of  $Au_{30}$ ,  $Au_{38}$ , and  $Au_{36}$  from DFT calculations. Color labels: yellow, S atoms; all other colors indicate Au. Carbon tails are omitted for clarity.



Fig. 4. Oscillations observed in NCs. (A to C) TA data map of hcp  $Au_{30}$ , bcc  $Au_{38}$  (pumped at 360 nm), and  $Au_{246}$  (pumped at 470 nm) NCs between –1 and 16 ps. (D to F) Kinetic traces probed at selected wavelengths. Strong oscillations were observed in  $Au_{30}$  and  $Au_{246}$  but not in  $Au_{38}$ .

## Conclusion

- □ They demonstrated a three-orders-of magnitude variation of carrier dynamics with crystalline phases of hcp Au<sub>30</sub> and bcc Au<sub>38</sub> NCs that relates to the distance between the Au<sub>4</sub> tetrahedral units and their connection modes.
- □ The extraordinarily long lifetime of 4.7  $\mu$ s in bcc Au<sub>38</sub> is comparable to that of bulk silicon and is much longer than that of semiconductor quantum dots, so this NC material may hold promise in boosting the NC solar-cell performance.
- □ The correlation of the structure and photodynamics of these metal NCs may stimulate their future applications in solar energy conversion, photocatalysis, and other optoelectronic processes.