BNL- 112653-2016-JA

***Single Atom Doping Alters the Ultrafast Electron
Dynamics of $M_1Au_{24}(SR)_{18}$ ($M=Pd, Pt$) Nanoclusters***

**Meng Zhou, Huifeng Qian, Matthew Y. Sfeir,
Katsuyuki Nobusada and Rongchao Jin**

Submitted to Nanoscale

February 2016

Center for Functional Nanomaterials

Brookhaven National Laboratory

**U.S. Department of Energy
USDOE Office of Science (SC),
Basic Energy Sciences (SC-22)**

Notice: This manuscript has been authored by employees of Brookhaven Science Associates, LLC under Contract No. DE- SC0012704 with the U.S. Department of Energy. The publisher by accepting the manuscript for publication acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or any third party's use or the results of such use of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Single Atom Doping Alters the Ultrafast Electron Dynamics of $M_1Au_{24}(SR)_{18}$ (M=Pd, Pt) Nanoclusters

Meng Zhou,¹ Huifeng Qian,^{1†} Matthew Y. Sfeir,² Katsuyuki Nobusada,^{3*} Rongchao Jin^{1*}

¹Department of Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213, USA

²Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York 11973, United States

³Department of Theoretical and Computational Molecular Science, Institute for Molecular Science, Myodaiji, Okazaki, 444-8585, Japan, and Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University Katsura, Kyoto 615-8520, Japan

ABSTRACT: Atomically precise, doped metal clusters are receiving wide research interest due to their synergistic properties dependent on the metal composition. To understand the electronic properties of doped clusters, it is highly desirable to probe the excited state behavior. Here, we report the ultrafast relaxation dynamics of doped $M_1@Au_{24}(SR)_{18}$ (M=Pd, Pt; R=CH₂CH₂Ph) clusters using femtosecond visible and near infrared transient absorption spectroscopy. Three relaxation components are identified for both mono-doped clusters: (1) sub-picosecond relaxation within the M_1Au_{12} core states; (2) core to shell relaxation in a few picoseconds; (3) relaxation back to the ground state in more than one nanosecond. Despite similar relaxation pathways for the two doped nanoclusters, the coupling between metal core and surface ligands is accelerated by over 30% in the case of Pt dopant compared with the Pd dopant. Compared to Pd doping, the case of Pt doping leads to much more drastic changes in the steady state and transient absorption of the clusters, which indicates that the 5d orbitals of Pt atom are more strongly mixed with Au 5d and 6s orbitals than do the 4d orbitals of Pd dopant. These results demonstrate that a single foreign atom can lead to entirely different excited state spectral features of the whole cluster compared to the parent $Au_{25}(SR)_{18}$ cluster. The detailed excited state dynamics of atomically precise Pd/Pt doped gold clusters help further understand their properties and benefit the development of energy-related applications.

KEYWORDS: *Doped nanoclusters, electronic properties, excited state dynamics, transient absorption*

Introduction

Understanding the electron and phonon dynamics in nanostructures is of major importance for many applications ranging from chemical sensing, energy conversion, to catalysis.¹⁻⁵ Thiolate-protected gold nanoclusters have attracted considerable research attention due to their structure diversity and a wide range of potential applications.⁶⁻¹³ Recently, doping one or more atoms of foreign metal elements (e.g. Pd, Pt, Ag, Cu, etc) into the gold clusters has been pursued in order to further understand the structure stability, electronic and optical properties as well as to explore luminescence and catalytic reactivity.¹⁴⁻¹⁷ By comparing the electronic structures of doped gold nanoclusters and the homo-gold counterparts, it is possible to unravel the perturbation of doping atoms to the electronic and optical properties.

Among all the gold clusters with known crystal structures, $\text{Au}_{25}(\text{SR})_{18}$ has received the most research interest due to its high stability and attractive applications. In the past few years substitution of gold in $\text{Au}_{25}(\text{SR})_{18}$ with heteroatoms has been attempted to further probe its properties.¹⁴⁻¹⁸ Negishi and Qian obtained pure $\text{Pd}_1\text{Au}_{24}(\text{SR})_{18}$ using different methods.^{19,20} On the other hand, pure monoplatinum-doped $\text{Pt}_1\text{Au}_{24}(\text{SR})_{18}$ cluster was obtained by Qian et. al. using a one-phase method.²¹ The structure of homogold $\text{Au}_{25}(\text{SR})_{18}$ cluster consists of a centered icosahedral Au_{13} core and a surface shell of six $\text{Au}_2(\text{SR})_3$ staples as protecting motifs.⁶ Experimental and theoretical investigations have indicated that both Pd and Pt atoms selectively occupy the central position of Au_{13} to form a M@Au_{12} ($\text{M}=\text{Pd}, \text{Pt}$) core (Scheme 1).^{19, 21-26} Unlike Au_{25} which is negatively charged, both doped clusters are neutral. Compared with the undoped $\text{Au}_{25}(\text{SR})_{18}$, Pd and Pt doped clusters exhibit much higher catalytic activity and structure stability.^{21,27} Herein we are motivated to investigate the electronic structure perturbation by the Pd and Pt dopants in hope of gaining insight into the electronic behavior.

Ultrafast spectroscopy has been applied to unravel the excited state relaxation dynamics of a series of ligand-protected metal clusters.²⁸⁻³⁶ For Au_{25} clusters, Miller et. al. identified a Au_{13} core state and a core-shell charge transfer state using a transient grating technique.³⁷ Qian et. al. investigated the charge effect on the transient absorption dynamics of Au_{25} with different charge states and established a split HOMO-LUMO transition model to explain the dynamics.³⁸ Moreover, pump/NIR-probe transient absorption measurements have also been used to probe the relaxation dynamics of Au_{25} clusters.³⁹ Based on detailed interpretation on excited state dynamics

of gold clusters, researchers have investigated the mechanism of luminescence^{31,40,41} as well as the photocatalytic behavior⁴². However, the excited state dynamics of precisely doped gold clusters remains largely unexplored.

In this work we report a detailed investigation on the ultrafast visible and near infrared transient absorption dynamics of neutral $[M_1@Au_{24}(SR)_{18}]^0$ ($M=Pt, Pd$) ($R=CH_2CH_2Ph$) clusters (1 nm metal core). The metal atoms in the doped $M_1Au_{24}(SR)_{18}$ cluster exhibit three types of environments, dopant Pd or Pt atom being in the central site (Scheme 1, green), twelve gold atoms in the icosahedral shell (yellow), and twelve gold atoms in the surface layer (cyan). The excited state population first experiences ultrafast relaxation within the core states, followed by several picoseconds core to shell relaxation and eventually very slow decay back to the ground state. By comparison of the excited state dynamics of Pd and Pt doped as well as the undoped Au_{25} clusters, we found that a single foreign atom can give rise to different excited state spectral features and relaxation dynamics of the clusters. These results pave the way to better understand the electronic structure of doped gold clusters.

Scheme 1. Structure of $Au_{25}(SR)_{18}$ and doped $M_1Au_{24}(SR)_{18}$ ($M=Pt, Pd$) clusters (left) and the $M_1@Au_{12}$ metal kernel (right).

Materials and Methods

Synthesis of $Pd_1Au_{24}(SR)_{18}$ clusters and $Pt_1Au_{24}(SR)_{18}$ clusters Detailed syntheses and characterization of $Pd_1Au_{24}(SR)_{18}$ and $Pt_1Au_{24}(SR)_{18}$ ($R=CH_2CH_2Ph$) followed the literature approaches.¹⁹⁻²¹

Femtosecond Transient Absorption Measurements The visible and near infrared broadband transient spectra (TA) of the clusters were performed using an amplified Ti:Sapphire-based

ultrafast laser system. Briefly, ~ 100 fs laser pulses in the ultraviolet and near-infrared regions of the spectrum were generated by a 3.5 mJ regenerative amplifier system (Spitfire, Spectra-Physics) and optical parametric amplifier (OPA, TOPAS). A small portion of the laser fundamental was focused into a sapphire plate to produce supercontinuum both in the visible and NIR range, which overlapped in time and space with the pump. Multiwavelength transient spectra were recorded using dual spectrometers (signal and reference) equipped with array detectors whose data rates exceed the repetition rate of the laser (1 kHz). Solutions of both clusters in 1 mm path length cuvettes were excited by the tunable output of the OPA (pump). All the measurements were performed in toluene and the optical density of the solutions was adjusted to be about 0.3 OD at the excitation wavelength. The polarization of pump and probe pulse was set to magic angle (54.7°) to measure the isotropy signal. During the measurement, the pump fluence was kept as low as 100 nJ/pulse to avoid photodegradation.

Data analysis The spectral chirp was corrected for the transient absorption spectra before the global fitting. We applied the graphical interface Glotaran and TIMP⁴³ to analyze the population dynamics based on the method reviewed by van Stokkum *et. al.*⁴⁴ Before the global analysis, singular value decomposition (SVD) was applied to estimate the time constants needed to fit the data. Subsequently, the transient absorption map was global fitted with a parallel model to give decay associated difference spectra (DADS) and a sequential model to give evolution associated difference spectra (EADS). In a sequential model, the change of concentration can be described as $c_i^{seq}(t) = \sum_{j=1}^i b_{ji} \exp(-t/\tau_j)$, define $b_{11}=1$ and for $j < i$, $b_{ji} = \prod_{m=1}^{j-1} k_m / \prod_{n=1, n \neq j}^i (k_n - k_j)$. In a parallel model, the change of concentration can be described as $c_i^{para}(t) = \exp(-t/\tau_i)$. EADS provide an overview of the spectral dynamics while DADS focus on a specific relaxation process relating to one decaying time constant.⁴⁵ Both EADS and DADS are helpful to determine the exact relaxation pathway of a system.

Computational Details We performed density functional theory (DFT) calculations to analyze the electronic structure of $M_1Au_{24}(SR)_{18}$ ($M=$ Pd, Pt) in which the SCH_2CH_2Ph ligand was approximated as SCH_3 . First, we carried out geometry optimizations for the doped clusters within a C_i molecular symmetry and then calculated electronic structures of the optimized clusters. The geometry optimizations were performed at the level of Kohn-Sham density functional theory (KS-DFT) employing the Becke three-parameter hybrid exchange functional

with the Lee-Yang-Parr correlation functional (B3LYP).^{46,47} The double- ζ valence-quality plus polarization basis was employed in all calculations along with a 60-electron relativistic effective core potential⁴⁸ for both the gold and platinum atoms. All the calculations were performed by using the TURBOMOLE package of *ab initio* quantum chemistry programs.⁴⁹

Results and Discussions

Absorption spectra and DFT analysis. The UV-Vis spectra of Pt and Pd doped Au_{25} clusters exhibit distinctly different features compared to that of Au_{25} (Figure 1A). The absorption around 680 nm for the homogold Au_{25} cluster (Figure 1A, blue profile) was attributed to HOMO to LUMO transition.⁵⁰

Figure 1. UV-Vis spectra of $\text{Au}_{25}(\text{SR})_{18}$, $\text{Pd}_1\text{Au}_{24}(\text{SR})_{18}$ and $\text{Pt}_1\text{Au}_{24}(\text{SR})_{18}$ clusters. The spectra are slightly shifted vertically for the ease of comparison.

To model the electronic structures of the two doped clusters, we calculated the Kohn-Sham orbitals and contributions of atomic orbitals of each element in the doped clusters using density function theory (Figure 2). For $\text{Pd}_1\text{Au}_{24}$ (Figure 2A), all of the HOMO-1, HOMO and LUMO are dominated by Pd 5p atomic orbitals. LUMO+1 and upper orbitals are mainly composed of 6sp of gold atoms while HOMO-2 and lower orbitals are contributed by 5d¹⁰ orbitals of gold atoms and 4d¹⁰ orbitals of palladium atom as well as 3p orbitals of S atoms. Therefore, HOMO-1 and upper orbitals constitute the quantized sp band while HOMO-2 and lower orbitals constitute the d-

band. For $\text{Pt}_1\text{Au}_{24}$ (Figure 2B), the distribution of orbitals is similar to $\text{Pd}_1\text{Au}_{24}$ except that the HOMO-1, HOMO and LUMO orbitals are mixture of Pt 6p, Au 5d and S 3p orbitals.

Figure 2. Kohn-Sham orbital and contribution of each orbital of (A) $\text{Pd}_1\text{Au}_{24}(\text{SR})_{18}$ and (B) $\text{Pt}_1\text{Au}_{24}(\text{SR})_{18}$.

To identify the origins of electronic transitions contributing to the absorption peaks at 390 nm (i.e. the excitation wavelength in fs experiments), 650 nm for PdAu_{24} , 590 nm for $\text{Pt}_1\text{Au}_{24}$ and 1100 nm for $\text{Pt}_1\text{Au}_{24}$, we performed time dependent density functional theory (TD-DFT) calculations. Based on the calculation results, it is concluded that, for both clusters, the absorption peaks in the visible region are mainly contributed by the intraband ($\text{sp} \leftarrow \text{sp}$) transitions within the $\text{M}@\text{Au}_{12}$ kernel while absorption peaks in the ultraviolet region (>3.0 eV) are contributed by both intraband ($\text{sp} \leftarrow \text{sp}$) transitions in the kernel and the interband ($\text{sp} \leftarrow \text{d}$) transitions in six $\text{Au}_2(\text{SR})_3$ surface staples.

Specifically, the faint hump peak at 1100 nm (experiment) for $\text{Pt}_1\text{Au}_{24}$ corresponds to the transition at 935 nm (theory, note: there is a systematic deviation from DFT) from HOMO-2/HOMO-3 to LUMO, assigned to the Pt 5d to Pt 6p transition (i.e., the transition occurs locally in the centered Pt atom), Figure 2B. Similarly, the computed absorption spectrum of $\text{Pd}_1\text{Au}_{24}$ has a very small hump at 840 nm (but not clearly seen in the experimental spectrum) and it is assigned to the Pd 4d (HOMO-2/HOMO-3) to Pd 5p (LUMO) transition, Figure 2A. For $\text{Pd}_1\text{Au}_{24}$, the broad absorption around 650 nm (Figure 1A, red) was attributed to the HOMO to

LUMO+1 transition and lower MOs to LUMO transitions. While for $\text{Pt}_1\text{Au}_{24}$, the most prominent peak around 590 nm originates from multiple orbital transitions. The absorption peak at ~ 390 nm for both clusters involves multiple transitions within the $\text{M}_1\text{@Au}_{24}$ entire clusters.

Femtosecond transient absorption results. To reveal the excited state dynamics, we performed broad band femtosecond transient absorption (TA) measurements on both doped clusters. For $\text{Pd}_1\text{Au}_{24}$ cluster, after excitation at 390 nm, the TA spectrum exhibits positive broad excited state absorption (ESA) around 500 nm and 750 nm overlapped with negative ground state bleaching (GSB) at 650 nm (Figure 3A), which is a typical spectral feature for gold clusters. During the next 1 picosecond, the ESA around 500 nm experiences an ultrafast decay, which gives rise to the negative GSB blueshifted to 620 nm. Subsequently, the TA signal around 620 nm rises in less than 10 ps to form a new net positive ESA. From the kinetic traces in Figure 3B, we can further observe that the rise of TA signal around 620 nm agrees well with the decay of kinetic traces at 500 nm and 740 nm.

Figure 3. (A) Transient absorption spectra for Pd₁Au₂₄ as a function of time delay excited at 390 nm. (B) Transient kinetic traces at selected wavelengths and the fitting. (C) Evolution associated difference spectra (EADS) and (D) Decay associated difference spectra (DADS) obtained from global fitting. The third component is scaled by 5× for clarity in C and D.

To further visualize the excited state dynamics, a global fitting procedure combined with SVD has been utilized to analyze the femtosecond TA data. Both a sequential and a parallel model have been applied to fit the TA data, which yield evolution associated difference spectra (EADS) and decay associated difference spectra (DADS) in Figure 3C and D, respectively. Three time constants (680 fs, 5 ps, and >100 ps) are required for a satisfying fitting (see black traces in Figure 3B which gives an excellent fitting quality) and the temporal evolution of the TA spectra can be seen clearly. The GSB of the second EADS is blueshifted by 30 nm compared with the first one due to the ultrafast decay of ESA. Moreover, another ESA around 650 nm emerged in the third long lived EADS component, probably representing a core-shell charge transfer state which has been reported previously in Au₂₅(SR)₁₈. Unlike EADS, DADS focuses on wavelength distribution of one time constant decay, which patterns the structural change of the spectral features. The first DADS component sees ESA around 600 nm, GSB around 460 nm and stimulated emission (SE) around 700 nm, which decay in 680 fs. The second and third DADS components have almost the identical spectral features with that of EADS.

To probe the pump wavelength dependence, we have also measured the TA spectra pumped at 785 nm. The TA spectra with excitation at 785 nm exhibit two decaying components of 8 ps and >600 ps (see Figure S1 in SI). The absence of ultrafast decay suggests that no excess excited state energy is dissipated through ultrafast relaxation with 785 nm excitation. Since absorption around 785 nm can be solely attributed to the metal core, it suggests that 390 nm (3.1 eV) and 785 nm (1.57 eV) can excite the metal core in the Pd₁Au₂₄(SR)₁₈ to higher and lower excited state, respectively. Therefore, the ultrafast decay (680 fs) with excitation of 390 nm can be safely assigned to the relaxation within the metal kernel's excited states. Moreover, the few-picosecond components under both 390 nm and 785 nm excitation can be attributed to the kernel to shell energy transfer. It should be noted that the excited behavior of Pd₁Au₂₄(SR)₁₈ are different from what was reported by Miller et al in 2010.⁵¹ This is probably due to the less purity of Pd₁Au₂₄ clusters synthesized at that time.

Despite the same doping position of Pd and Pt, the transient absorption spectra of $\text{Pt}_1\text{Au}_{24}(\text{SR})_{18}$ are entirely different from those of $\text{Pd}_1\text{Au}_{24}$. The UV-pump/Vis-probe transient absorption spectra of $\text{Pt}_1\text{Au}_{24}$ excited at 390 nm consist of broad ESA all over the probed window overlapped with GSB at 590 nm (Figure 4A). During the first 10 ps, the negative signal around 580 nm rises quickly to form a new ESA which is accompanied by decay of ESA at other wavelengths (Figure 4B). Global fitting also requires three time constants of 650 fs, 3.8 ps, >1 ns to fit the TA data. From EADS and DADS, the rise of the GSB around 590 nm (much slower than the instrument response of 100 fs) at initial time delay is ascribed to the ultrafast decay of ESA at the same wavelength. The ultrafast decay of ESA in the first DADS component (Figure 4D) also accounts for the blueshift in the GSB at 590 nm (Figure 4A). It is worth noting that the last component (both EADS and DADS) for $\text{Pt}_1\text{Au}_{24}(\text{SR})_{18}$ has a similar spectral shape as that of $\text{Pd}_1\text{Au}_{24}$. As these two clusters have the same ligand structure of S-Au-S-Au-S motifs, the last long-lived component in both doped clusters should originate from the $\text{Au}_2(\text{SR})_3$ staple states which are independent from the metal kernel.

Figure 4. (A) Transient absorption spectra for $\text{Pt}_1\text{Au}_{24}(\text{SR})_{18}$ cluster as a function as a function of time delay excited at 390 nm and probed in the visible region. (B) Transient kinetic traces at selected wavelength and the corresponding fitting. (C) Evolution associated difference spectra (EADS) and (D) Decay associated difference spectra (DADS) obtained from global fitting. The third component is enlarged by 3× for clarity in C and D.

Figure 5. (A) Transient absorption spectra for $\text{Pt}_1\text{Au}_{24}$ cluster as a function of time delay excited at 390 nm and probed in the NIR region. (B) Transient kinetic traces at selected wavelength and the fitting. (C) Evolution associated difference spectra (EADS) and (D) Decay associated difference spectra (DADS) obtained from global fitting.

$\text{Pt}_1\text{Au}_{24}$ shows a steady-state absorption band around 1100 nm in the NIR region (Figure S2), thus we also performed the UV-pump/ NIR-probe TA measurements (probed between 850 nm and 1500 nm, Figure 5). After excitation at 390 nm, the NIR probe TA spectra exhibit broad GSB centered at 1100 nm overlapped with ESA around 850 nm and 1400 nm. As time delay evolves, the ESA gradually decreases to form a flat structure with only one faint ESA peak

around 870 nm in less than 20 ps. Global fitting gives three components (see Figure 5 C and D), which has identical time constants to that of the TA spectra probed in the visible range. To probe the pump wavelength dependent spectra, we have also performed the NIR-probe TA measurement with pump pulse centered at 1300 nm. With NIR excitation at 1300 nm, the ultrafast decay is absent and the TA spectra at initial time delay (0.5 ps) is similar to that obtained with 390 nm excitation at longer time delays (see Figure S3A in SI). Moreover, the kinetic traces around 840 nm and 1300 nm are exactly the same (see Figure S3B), suggesting that they originate from the same excited state species. Since 1300 nm is mainly contributed by the HOMO-2 to LUMO transition, the ESA around both 850 nm and 1400 nm can be assigned to the LUMO to sp transition within the metal kernel. Similar to the case in $\text{Pd}_1\text{Au}_{24}(\text{SR})_{18}$ cluster, the first ultrafast relaxation in $\text{Pt}_1\text{Au}_{24}(\text{SR})_{18}$ with 390 nm excitation can be assigned to relaxation with the $\text{Pt}_1\text{Au}_{12}$ kernel states while the 3.8 ps component stands for kernel to shell relaxation.

Scheme 2. Proposed relaxation schemes of (A) $\text{Pd}_1\text{Au}_{24}(\text{SR})_{18}$ and (B) $\text{Pt}_1\text{Au}_{24}(\text{SR})_{18}$ clusters.

Figure 6. Normalized kinetic traces and the corresponding fitting obtained from the global analysis of $\text{Pd}_1\text{Au}_{24}(\text{SR})_{18}$, $\text{Pt}_1\text{Au}_{24}(\text{SR})_{18}$ and $[\text{Au}_{25}(\text{SR})_{18}]^0$ clusters at the same probed wavelength (550 nm) after 390 nm excitation.

Table 1. Time constants obtained from global analysis of transient absorption spectroscopy of $\text{Pd}_1\text{Au}_{24}(\text{SR})_{18}$, $\text{Pt}_1\text{Au}_{24}(\text{SR})_{18}$ and $[\text{Au}_{25}(\text{SR})_{18}]^0$ (obtained from Ref. 31).

	$[\text{Au}_{25}(\text{SR})_{18}]^0$	$\text{Pd}_1\text{Au}_{24}(\text{SR})_{18}$	$\text{Pt}_1\text{Au}_{24}(\text{SR})_{18}$
τ_1	1.0 ps	0.68 ps	0.65 ps
τ_2	5.0 ps	5.0 ps	3.8 ps
τ_3	> 1 ns	>1 ns	>1 ns

Based on the results discussed above, the relaxation pathway of both Pd and Pt doped clusters can be summarized in Scheme 2. For both doped clusters, 390 nm excite both the 13-atom metal core and $\text{Au}_2(\text{SR})_3$ surface staples while excitation at lower energy can only excite the metal core. The excited state dynamics obtained so far indicates that a single atom can give rise to different excited state behavior of the whole cluster, which motivates us to compare the excited state dynamics of $\text{M}_1\text{Au}_{24}(\text{SR})_{18}$ ($\text{M}=\text{Pd}, \text{Pt}$) clusters and Au_{25} . In Figure 6, we plotted the normalized kinetic traces from transient absorption of $\text{Pd}_1\text{Au}_{24}(\text{SR})_{18}$, $\text{Pt}_1\text{Au}_{24}(\text{SR})_{18}$ and $[\text{Au}_{25}(\text{SR})_{18}]^0$. The ESA at 550 nm were monitored since all these three clusters only have positive DAS components at this wavelength. The time constants obtained from global fitting for all three clusters are listed in Table 1. Despite similar relaxation mechanism for Pd and Pt doped nanoclusters (Scheme 2), it is found that the core to shell relaxation is accelerated by over 30% from $\text{Pd}_1\text{Au}_{24}(\text{SR})_{18}$ ($2 \times 10^{-13} \text{ s}^{-1}$) to $\text{Pt}_1\text{Au}_{24}(\text{SR})_{18}$ ($2.63 \times 10^{-13} \text{ s}^{-1}$), which also can be seen clearly from Figure 6. It is interesting to see that $\text{Pd}_1\text{Au}_{24}(\text{SR})_{18}$ and neutral $[\text{Au}_{25}(\text{SR})_{18}]^0$ clusters have similar transient spectral features, while $\text{Pt}_1\text{Au}_{24}(\text{SR})_{18}$ has entirely different transient absorption spectra compared with that of $[\text{Au}_{25}(\text{SR})_{18}]^{0,-1}$ clusters.³¹ Moreover, differences are also manifested in the steady state absorption, UV-vis absorption spectrum of $\text{Pt}_1\text{Au}_{24}(\text{SR})_{18}$ is distinctly different from that of $\text{Au}_{25}(\text{SR})_{18}$ while the absorption spectrum of $\text{Pd}_1\text{Au}_{24}(\text{SR})_{18}$ is similar to that of $\text{Au}_{25}(\text{SR})_{18}$. From the Kohn-Sham orbital distribution (Figure 2), the HOMO-n orbitals in both doped clusters contain atomic orbitals from all over the cluster, including the 4d orbitals of Pd in $\text{Pd}_1\text{Au}_{24}(\text{SR})_{18}$ and the 5d orbitals of Pt in $\text{Pt}_1\text{Au}_{24}(\text{SR})_{18}$. Table S1 in the

Supporting Information lists the atomic energy levels of Au, Pd and Pt. The ionization energy of 5d orbital of Pt (18.56 eV) is closer to the 5d orbital of Au (20.2 eV) than 4d orbital of Pd (8.33 eV). Therefore, it is suggested that the 5d of the Pt atom is more strongly mixed with the 5d and 6s orbitals of Au atoms, while the 4d orbital of Pd is less involved. The distinct differences between the excited state features of Pd and Pt doped Au₂₅ nanocluster reported here are in contrast to the cases of plasmonic Au-Pd and Au-Pt double-shell nanocages.⁵² For plasmonic gold nanostructures, the introduction of Pd or Pt alters the elastic modulus rather than the electronic structures of the resultant bimetallic nanostructures; while for gold clusters, single Pd or Pt doping can lead to different electronic structures and thus excited state features.

Conclusion

In summary, we have indentified the excited state behavior of mono Pd and Pt doped M₁Au₂₄(SR)₁₈ clusters (M=Pd, Pt) by both visible and near infrared femtosecond transient absorption spectroscopy. The excited state deactivation of both doped clusters are composed of ultrafast (~0.6 ps) relaxation within the metal core states, several picoseconds core to shell relaxation (3–5 ps) and very slow relaxation (>1 ns) back to the ground state. The excited state behavior of Pd₁Au₂₄ cluster is similar to that of the neutral Au₂₅(SR)₁₈, while the spectral feature and excited state dynamics of Pt₁Au₂₄(SR)₁₈ is largely different from those of the neutral and anionic Au₂₅(SR)₁₈. Compared with Pd doping, Pt doping accelerates the core-shell coupling by over 30%. The distinctly different excited state and ground state behavior between Pd and Pt doped clusters could be attributed to the different hybridization of Pd or Pt atomic orbitals with the 5d and 6s orbitals of Au atoms in the metal core. These results are of great importance for further understanding of electronic structure of foreign metal-doped gold clusters and their optical properties.

ASSOCIATED CONTENT

Supporting Information

The pump dependent transient absorption spectra and the corresponding global analysis results. Supporting Information is available free of charge via the Internet at <http://pubs.rsc.org>.

AUTHOR INFORMATION

Corresponding Author

*Rongchao Jin, E-mail: rongchao@andrew.cmu.edu

*Katsuyuki Nobusada, E-mail: nobusada@ims.ac.jp

[†] (H.Q.) Current address: Dow Chemical Company

Notes

The authors declare no competing financial interest.

ACKNOWLEDGEMENTS

R.J. acknowledges financial support from the Air Force Office of Scientific Research under AFOSR Award No. FA9550-15-1-9999 (FA9550-15-1-0154). K.N. acknowledges a financial support by JSPS KAKENHI Grant Number 25288012, Elements Strategy Initiative for Catalysts & Batteries (ESICB), the Strategic Programs for Innovative Research (SPIRE), MEXT Japan.

REFERENCES

1. G. V. Hartland, *Chem. Rev.*, 2011, **111**, 3858-3887.
2. M. A. Mahmoud, D. O'Neil and M. A. El-Sayed, *Nano Lett.*, 2014, **14**, 743-748.
3. D. Mongin, E. Shaviv, P. Maioli, A. Crut, U. Banin, N. Del Fatti and F. Vallée, *ACS Nano*, 2012, **6**, 7034-7043.
4. S. Park, M. Pelton, M. Liu, P. Guyot-Sionnest and N. F. Scherer, *J. Phys. Chem. C*, 2007, **111**, 116-123.
5. R. J. Newhouse, H. Wang, J. K. Hensel, D. A. Wheeler, S. Zou and J. Z. Zhang, *J. Phys. Chem. Lett.*, 2011, **2**, 228-235.
6. G. Li and R. Jin, *Acc. Chem. Res.*, 2013, **46**, 1749-1758.
7. R. Jin, *Nanoscale*, 2015, **7**, 1549-1565.
8. S. H. Yau, O. Varnavski and T. Goodson, *Acc. Chem. Res.*, 2013, **46**, 1506-1516.
9. S. Raut, R. Chib, R. Rich, D. Shumilov, Z. Gryczynski and I. Gryczynski, *Nanoscale*, 2013, **5**, 3441-3446.
10. S. Raut, R. Rich, R. Fudala, S. Butler, R. Kokate, Z. Gryczynski, R. Luchowski and I. Gryczynski, *Nanoscale*, 2014, **6**, 385-391.
11. I. Russier-Antoine, F. Bertorelle, M. Vojkovic, D. Rayane, E. Salmon, C. Jonin, P. Dugourd, R. Antoine and P.-F. Brevet, *Nanoscale*, 2014, **6**, 13572-13578.
12. L. Polavarapu, M. Manna and Q.-H. Xu, *Nanoscale*, 2011, **3**, 429-434.

13. D. Yang, G. Yang, S. Gai, F. He, G. An, Y. Dai, R. Lv and P. Yang, *Nanoscale*, 2015, **7**, 19568-19578.
14. R. Jin and K. Nobusada, *Nano Res.*, 2014, **7**, 285-300.
15. W. Kurashige, M. Yamaguchi, K. Nobusada and Y. Negishi, *J. Phys. Chem. Lett.*, 2012, **3**, 2649-2652.
16. S. Wang, Y. Song, S. Jin, X. Liu, J. Zhang, Y. Pei, X. Meng, M. Chen, P. Li and M. Zhu, *J. Am. Chem. Soc.*, 2015, **137**, 4018-4021.
17. L. Liao, S. Zhou, Y. Dai, L. Liu, C. Yao, C. Fu, J. Yang and Z. Wu, *J. Am. Chem. Soc.*, 2015, **137**, 9511-9514.
18. Y. Negishi, T. Iwai and M. Ide, *Chem. Commun.*, 2010, **46**, 4713-4715.
19. Y. Negishi, W. Kurashige, Y. Niihori, T. Iwasa and K. Nobusada, *Phys. Chem. Chem. Phys.*, 2010, **12**, 6219-6225.
20. B. E. Qian Huifeng, Zhu Yan, Jin Rongchao, *Acta Phys Chim Sin*, 2011, **27**, 513-519.
21. H. Qian, D.-e. Jiang, G. Li, C. Gayathri, A. Das, R. R. Gil and R. Jin, *J. Am. Chem. Soc.*, 2012, **134**, 16159-16162.
22. D.-e. Jiang and S. Dai, *Inorg. Chem.*, 2009, **48**, 2720-2722.
23. S. L. Christensen, M. A. MacDonald, A. Chatt, P. Zhang, H. Qian and R. Jin, *J. Phys. Chem. C*, 2012, **116**, 26932-26937.
24. M. Walter and M. Moseler, *J. Phys. Chem. C*, 2009, **113**, 15834-15837.
25. Y. Negishi, W. Kurashige, Y. Kobayashi, S. Yamazoe, N. Kojima, M. Seto and T. Tsukuda, *J. Phys. Chem. Lett.*, 2013, **4**, 3579-3583.
26. M. A. Tofanelli, T. W. Ni, B. D. Phillips and C. J. Ackerson, *Inorg. Chem.*, 2016, **55**, 999-1001.
27. S. Xie, H. Tsunoyama, W. Kurashige, Y. Negishi and T. Tsukuda, *ACS Catalysis*, 2012, **2**, 1519-1523.
28. B. A. Smith, J. Z. Zhang, U. Giebel and G. Schmid, *Chem. Phys. Lett.*, 1997, **270**, 139-144.
29. M. Zhou, S. Vdović, S. R. Long, M. Z. Zhu, L. Y. Yan, Y. Y. Wang, Y. L. Niu, X. F. Wang, Q. J. Guo, R. C. Jin and A. D. Xia, *J. Phys. Chem. A*, 2013, **117**, 10294-10303.
30. M. Y. Sfeir, H. Qian, K. Nobusada and R. Jin, *J. Phys. Chem. C*, 2011, **115**, 6200-6207.
31. M. S. Devadas, J. Kim, E. Sinn, D. Lee, T. Goodson, III and G. Ramakrishna, *J. Phys. Chem. C*, 2010, **114**, 22417-22423.

32. M. Zhou, S. Long, X. Wan, Y. Li, Y. Niu, Q. Guo, Q.-M. Wang and A. Xia, *Phys. Chem. Chem. Phys.*, 2014, **16**, 18288-18293.
33. C. Yi, M. A. Tofanelli, C. J. Ackerson and K. L. Knappenberger, Jr., *J. Am. Chem. Soc.*, 2013, **135**, 18222-18228.
34. S. Mustalahti, P. Myllyperkiö, T. Lahtinen, K. Salorinne, S. Malola, J. Koivisto, H. Häkkinen and M. Pettersson, *J. Phys. Chem. C*, 2014, **118**, 18233-18239.
35. S. H. Yau, N. Abeyasinghe, M. Orr, L. Upton, O. Varnavski, J. H. Werner, H.-C. Yeh, J. Sharma, A. P. Shreve, J. S. Martinez and T. Goodson, III, *Nanoscale*, 2012, **4**, 4247-4254.
36. S. M. Aly, L. G. AbdulHalim, T. M. D. Besong, G. Soldan, O. M. Bakr and O. F. Mohammed, *Nanoscale*, 2016, DOI: 10.1039/C5NR05328E.
37. S. A. Miller, J. M. Womick, J. F. Parker, R. W. Murray and A. M. Moran, *J. Phys. Chem. C*, 2009, **113**, 9440-9444.
38. H. Qian, M. Y. Sfeir and R. Jin, *J. Phys. Chem. C*, 2010, **114**, 19935-19940.
39. T. D. Green and K. L. Knappenberger, *Nanoscale*, 2012, **4**, 4111-4118.
40. M. S. Devadas, V. D. Thanthirige, S. Bairu, E. Sinn and G. Ramakrishna, *J. Phys. Chem. C*, 2013, **117**, 23155-23161.
41. M. Zhou, J. Zhong, S. Wang, Q. Guo, M. Zhu, Y. Pei and A. Xia, *J. Phys. Chem. C*, 2015, **119**, 18790-18797.
42. K. G. Stampelecoskie and P. V. Kamat, *J. Am. Chem. Soc.*, 2014, **136**, 11093-11099.
43. J. J. Snellenburg, S. P. Laptenok, R. Seger, K. M. Mullen and I. H. M. van Stokkum, *J. Stat. Software*, 2012, **49**, 1-22.
44. I. H. M. van Stokkum, D. S. Larsen and R. van Grondelle, *Biochim. Biophys. Acta, Bioenerg.*, 2004, **1657**, 82-104.
45. M. Kullmann, A. Hipke, P. Nuernberger, T. Bruhn, D. C. G. Gotz, M. Sekita, D. M. Guldi, G. Bringmann and T. Brixner, *Phys. Chem. Chem. Phys.*, 2012, **14**, 8038-8050.
46. C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785-789.
47. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652.
48. D. Andrae, U. Häußermann, M. Dolg, H. Stoll and H. Preuß, *Theor. Chim. Acta*, 1990, **77**, 123-141.
49. Q. C. G. TURBOMOLE; version 5.10, University of Karlsruhe: Germany.

50. M. Zhu, C. M. Aikens, F. J. Hollander, G. C. Schatz and R. Jin, *J. Am. Chem. Soc.*, 2008, **130**, 5883-5885.
51. S. A. Miller, C. A. Fields-Zinna, R. W. Murray and A. M. Moran, *J. Phys. Chem. Lett.*, 2010, **1**, 1383-1387.
52. M. A. Mahmoud, P. Szymanski and M. A. El-Sayed, *J. Phys. Chem. Lett.*, 2012, **3**, 3527-3531.

Table of Contents Graphic: