Single-atom doping on thiolate-protected gold nanoclusters: a TDDFT study on the excited states

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Abstract
The optical features of thiolate-protected gold nanoclusters can be tuned in different ways to achieve the desired features. One promising approach is doping with a single metallic atom to the gold core to form the 'Atomically Precise Gold Nanoparticle'. However, the tuning mechanism and the changes in the excited states are not discussed thoroughly. In this work, we perform theoretical analyses of Ag, Cu, Pd, and Pt doped gold nanoclusters and focus on the doping induced changes in the excitations. Our results indicate several significant impacts of the platinum family dopings, which are not presented in the gold family dopings: low energy (infrared) excitation features, extra 'in-gap’ energy levels, and significant redistribution of the electrons/holes in response to the external electric field.

Introduction
Thiolate-protected Gold Nanoclusters continuously draw increasing attentions for their fundamental properties and potentials in biological applications, including radiotherapy and imaging [1–6]. A typical thiolate-protected nanocluster is formed of a core of several metal atoms with some ligands attached. Synthesis of the clusters with ligands that can be commonly found in tissues or blood guarantees the biocompatibility [7–9]. The gold clusters are known for decades, but the structure was unclear until one of them is crystalized and scanned in 2008 [10]. The Au25 rod was discovered with its structure soon after that [11, 12]. For the well-known Au125 cluster, it turned out that the low energy features in the spectrum were sensitive to the gold–gold distances in the core [13] or the ligand units attached [14].

To further improve the desired properties of the nanoclusters, atom-level doping is another convincing strategy. The doped atom may initiate the self-assembly [15, 16], change the absorption spectra [17] and the photoluminescence properties [18]. The clusters with introduced doping atoms are 'alloy nanoclusters' [19–21] with different physical and chemical properties. Among all the alloy nanoclusters, doped clusters with a single different metallic atom are special cases. Such doping techniques have been applied to the well-known Au25 clusters by Qian, Negishi, and Gottlieb: they modified the central atom in the Au25 clusters to synthesis a series of alloy clusters, 'Atomically Precise Gold Nanoparticles' [22]. In their original work, the optical properties were briefly summarized. But the correspondence between the optical properties and their heteroatom substitution has not been fully explored yet.

In this work, we extend the study on the ‘atomically precise gold nanoparticles’: systematically compare and analyze the atomically precise Au125 nanoclusters theoretically. We focus on the excited states (density response) and charge redistribution in response to the light absorption. By comparing the doped structures with undoped structures, we aim at finding out the features of dopings, including how the dopings change the excited states in the core region. Our models contain the original Au25 cluster, two platinum family atoms, Pt [23], and Pd [24] doped clusters and two gold family atoms, Cu [25] and Ag [26] doped clusters.

Simulation method
The structure of the gold nanocluster out of XRD experiments is adopted as the beginning point of this work [10]. The well-known Au25 gold cluster contains an icosahedron core of 13 gold atoms and 6 branches of
gold-sulfur chains. For simplicity, the phenyl units in the original structure are removed, i.e. all the ligands of the nanocluster are replaced by \( \text{SCH}_2\text{CH}_3 \). The simplified geometry is shown in figure 1(a). As shown in figure 1(b), 18 ligands are attached to the gold core via \( \text{S–Au–S–Au–S} \) chains. The geometry presents the special roles of \( \text{S} \) atoms in coordinating with the metal and organic parts. Thus, a larger basis set, 6–311++G(3df, 3pd) is chosen for \( \text{S} \) to include such hybridization. We use the 6–31G basis sets for \( \text{C, H} \) and the Lanl2tz(f) basis sets for heavy atoms. We denote the clusters as \( \text{Au, Au(Ag), Au(Cu), Au(Pt), Au(Pd)} \) cluster as shown in figure 1(d).

To exclude the distance effect, the modifications involve only the central atom, and further geometry optimizations for the relaxations of the structures are not performed.

The exchange-correlation potential in the Time-dependent Density Functional Theory (TDDFT) calculation in our model is M06-2x [27]. The systems contain more than 500 electron pairs which cannot be simulated easily with an ordinary PC. So the calculations are done on a computer server using Gaussian 09 [28] in parallel mode. The Casida Equation [29] is the theoretical tool to solve for excitation states including the excitation energy, oscillation mode, and oscillator strength.

\[
A \begin{bmatrix} X \\ Y \end{bmatrix} = \begin{bmatrix} A & B \\ B^* & A^* \end{bmatrix} \begin{bmatrix} X \\ Y \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} X \\ Y \end{bmatrix} \]
\]

The eigenvalues, \( \omega \)'s are the excitation energies while \( X \) and \( Y \) are vectors of the weights of excitations associated to different energy levels. The elements of the matrices \( A \) and \( B \) are given by

\[
A_{\text{ia}, \text{ia}'} = \delta_{\text{ia}, \text{ia}'} \Omega_{\text{ia}} + K_{\text{ia}, \text{ia}'}
\]

\[
B_{\text{ia}, \text{ia}'} = K_{\text{ia}, \text{ia}'}
\]

\[
K_{\text{ia}, \text{ia}'} = \int d\tau \int d\tau' \left[ \psi_i^{(0)}(\tau) \phi_{a}^{(0)}(\tau) \right] \frac{1}{|\tau - \tau'|} + f_{\text{xc}}(\tau, \tau') \left[ \psi_i^{(0)}(\tau') \phi_{a}^{(0)}(\tau') \right]
\]

where \( \Omega_{\text{ia}} \) is the uncorrected excitation energy between occupied level \( \text{i} \) and unoccupied level \( \text{a} \). The correction term \( K \) includes the integral of exchange-correlation kernel \( f_{\text{xc}} \). The predicted excitations can be simple excitations such as the Highest Occupied Molecular Orbital (HOMO) to the Lowest Unoccupied Molecular Orbital (LUMO), but they are ‘collective excitations’ which are superpositions of several simple excitations in general. With the eigenvectors of Casida equation, one can obtain the eigenmode as

\[
\delta \mathbf{n}(\tau) = \sum_{\text{ia}} \left[ X_{\text{ia}}(\omega_{\text{ia}}) \psi_{\text{ia}}(\tau) \right] \left[ X_{\text{ia}}(\omega_{\text{ia}}) \phi_{\text{ia}'}(\tau) \right] + Y_{\text{ia}}(\omega_{\text{ia}}) \left[ Y_{\text{ia}}(\omega_{\text{ia}}) \psi_{\text{ia}}(\tau) \right] \left[ Y_{\text{ia}}(\omega_{\text{ia}}) \phi_{\text{ia}'}(\tau) \right]
\]

Each predicted excitation energy \( \omega_{\text{ia}} \) has its associated eigenvector \( X_{\text{ia}} \) and \( Y_{\text{ia}} \). \( \text{i} \) runs over the occupied levels and \( \text{a} \) runs over the occupied and unoccupied levels. Thus, \( \psi_{\text{ia}}(\tau) \) and \( \phi_{\text{ia}'}(\tau) \) are the occupied and unoccupied Kohn–Sham levels.

In addition, the positive part of the eigenmode can be interpreted as an electron probability distribution. And the negative part is a hole probability distribution. The electron and hole distributions integrate to 0 since the eigenmode integrates to 0. Based on the simulation results of Gaussian, the excitation eigenvectors are also extracted for electron-hole analysis in this work. We also make comparisons based on the electron-hole distribution analysis.

**Figure 1.** (a) Model gold cluster with electron cloud represented as iso-surfaces. (b) 6 branches of gold-sulfur chains in the gold cluster. (c) The icosahedron core of 13 gold atoms. (d) Possible single atoms doping (replacement).
Results

A typical absorption spectrum of the Au_{25} cluster contains a long wavelength feature and a mid-visible ‘shoulder’. The ‘shoulder’ appears to be a significant peak in this work due to the limitation of excitation mode we simulated and a small broadening constant we selected. The simulation results agree with the experimental results summarized by Jin in 2014 [22]. Minor differences may due to the different ligands we used and the geometry is adopted from the crystal image.

The long wavelength feature in the original Au cluster is between 500–700 nm. The Ag and Cu substitutions cause 100 nm redshift of it, while the shoulders do not shift much. In contrast, the Pd and Pt dopings significantly change the spectra. Eigenmodes in the shortwave infrared (SWIR) region emerge which yield a wide band of excitation but in low intensity. Such feature is significant in the spectrum of Au(Pt) cluster (figure 2) which agrees with experimental results in Qian’s work. In addition, the shoulder features are also changed especially in the excitation lines without broadenings. The modes spread between 400–500 nm compared with the concentration of the original cluster and gold family doped clusters.

The gold family doped clusters show regular shifts, such that the overall feature is maintained but redshifted. The platinum family doped clusters have significantly different features in the absorption spectra: eigenmodes in the SWIR region appear and the shoulder feature around 400–500 nm is reduced. Such difference indicates the platinum family doped clusters have much lower fundamental gaps due to the different atoms introduced. We will discuss the Kohn–Sham gap in the following discussion to approach the fundamental gap to some level.

The Kohn–Sham energy levels of the clusters are shown in figure 3. The Kohn–Sham gap, the difference between the Kohn–Sham energy of HOMO and LUMO, is gradually changed by the gold family doping. As the doped atom weight decreases, the Kohn–Sham gap is slowly reduced. In contrast, the platinum family dopings ‘create’ new Kohn–Sham levels in the gaps which significantly reduce the Kohn–Sham gaps.

The lowest excitation energy is plotted by adding its value to the HOMO Kohn–Sham energy. To approximate the electron-hole binding energy, we calculate the difference between the Kohn–Sham gap and the

Figure 2. Simulated absorption spectra: (a) Au cluster, (b) Au(Ag) cluster, (c) Au(Cu) cluster, (d) Au(Pt) cluster and (e) Au(Pd) cluster.
lowest excitation energy. The binding energies are about 1.9 eV for all 3 gold family doping cases. Though the platinum dopings behave differently from the gold family doping, the approximated binding energies do not change much. Thus the lowest excitation energy is very small.

The eigenvectors of the Casida equation reflect that the platinum family doped excitations are much simpler than the gold family doped excitations. The Au(Pd) and Au(Pt) clusters show simple excitations between HOMO and LUMO combined with small fractions of their counterparts (deexcitation) parts. However, the Au(Cu) and Au(Ag) clusters contain 3 simple excitations between pairs of Kohn–Sham levels. Such differences indicate that each platinum family doping (in our models) creates a pair of doping introduced HOMO and LUMO orbitals, thus suppresses the original orbitals of the cluster for excitation.

In order to understand how the doping changes the whole spectrum by changing the orbital mixing, a complete plot of the significant components is a good starting point. As shown in figure 4, all the excitation pairs which contribute the excitation significantly are plotted up to 50th excitation mode. The gold family doping makes a minor shift of the excitation pairs. Ag and Cu atoms change the higher excitation modes by allowing slightly more excitation pairs involved, but the overall patterns are not changed much. In contrast, the platinum dopings include a significant number of occupied levels but exclude many unoccupied levels. In addition, in the gold family doping cases, there are about 30 excitations which are free of HOMO or LUMO. But in the platinum family doping cases, there are more than 30 LUMO free excitations. The extra energy level created by the platinum family makes significant impacts on the whole excitation pattern.

Last, we calculate the excitation modes of the 5 model clusters using the eigenvectors of Casida Equations. To compare excitation modes, we calculate the difference between the modes of doped clusters with respect to the excitation modes of the Au cluster. Thus, the doping effect can be visualized by the iso-surface plotted in figure 5.

We can interpret the results as the redistribution of the electrons and holes caused by the single atom dopings. The Ag and Cu atoms substitutions do not change the electron-hole redistribution much, but only form some extra electrons and holes near the icosahedron core. Due to the similarity of the electron structure of Au, Ag and Cu atoms, we can expect smooth level alignments among the core atoms which lead to some minor changes in the lowest excitation modes. However, the monoplatinum dopings significantly change the excitation patterns. The doped atoms behave like ‘donor’ sites which allow free electrons to move over the entire
metallic network of the cluster. The lower electronegativity of Pt indicates its tendency to donate electrons. The tendency means the electronic density may show a higher concentration around the neighboring Au atoms, which yields a core with more metallic features such as lower band gap. Such analysis agrees with the 1100 nm spectrum feature. Therefore, we observe significant redistributions for the excitations which are very different from the gold family dopings.
Conclusion

In this work, we model an Au$_{25}$ cluster with simplified ligands and 4 variants of the Au clusters with the single atom doping to study the different behaviors in the optical excitations. The gold family dopings and the platinum family dopings show significant differences in 3 aspects. First, the gold family dopings redshift the low energy features, while the platinum family dopings change the spectra significantly: SWIR energy features appear and low energy features disappear. Second, the platinum family dopings add extra Kohn–Sham levels to the Kohn–Sham gaps which reduce excitation energies, while the gold family dopings only reduce the gaps. The components in the lowest excitation are much simpler in platinum family doped clusters. Third, for the whole spectrum structures, the platinum family dopings allow more occupied Kohn–Sham levels involved than the gold family dopings. Last, the differences in the excitation modes (density responses) show that the platinum family atoms introduce electrons with higher mobility in the excitations near the core.

The impact of the single atom doping to the Au cluster is demonstrated. One can use the atoms from the gold family for a slight shift in the excitation. While considering the platinum family doping, one may expect a totally different spectrum. The reason may be linked to the miss alignment of energy levels of different metal atoms. The electron-rich atoms create extra energy levels which behave as electron ‘donors’. In medical applications, the super low energy excitation may be the desired feature to pursue. Unlike the central dopings, we may expect that the non-central dopings do not significantly change the spectra that much as shown by the Cu doping experiments [30]. For other gold clusters, one may expect similar analysis in this paper can be applied. In the Pd doped Au38 cluster, a similar IR feature, which is a good indication of the gap reduction, is verified by experiments [31]. To extend the absorption spectrum to the photoluminescence spectrum, one may also need to consider the molecular dynamics which may be related to the ‘ligand-to-metal–metal charge transfer’ [32] model for the basic essence of luminescence.

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