

# Real Time Monitoring of the Dynamic Intracluster Diffusion of Single Gold Atoms into Silver Nanoclusters

Kaiyuan Zheng,<sup>†</sup><sup>®</sup> Victor Fung,<sup>§</sup> Xun Yuan,<sup>∗,‡</sup> De-en Jiang,<sup>§</sup><sup>®</sup> and Jianping Xie<sup>∗,†,⊥</sup><sup>®</sup>

<sup>†</sup>Department of Chemical and Biomolecular Engineering, National University of Singapore, 4 Engineering Drive 4, 117585 Singapore

<sup>‡</sup>College of Materials Science and Engineering, Qingdao University of Science and Technology, Qingdao 266042, P. R. China <sup>§</sup>Department of Chemistry, University of California, Riverside, California 92521, United States

<sup>1</sup>Joint School of National University of Singapore and Tianjin University, International Campus of Tianjin University, Binhai New City, Fuzhou 350207, P. R. China

# Swetashree Acharya 14.03.2020

# **Graphical Abstract**



### BACKGROUND



ARTICLE

DOI: 10.1038/s41467-017-01736-5 OPEN

Precise control of alloying sites of bimetallic nanoclusters via surface motif exchange reaction

Qiaofeng Yao <sup>[6]</sup>, Yan Feng<sup>1,2</sup>, Victor Fung<sup>3</sup>, Yong Yu <sup>[6]</sup>, De-en Jiang<sup>3</sup>, Jun Yang<sup>2</sup> & Jianping Xie <sup>[6]</sup>

#### ChemComm

#### FEATURE ARTICLE



View Article Online View Journal | View Issue

### Engineering ultrasmall water-soluble gold and silver nanoclusters for biomedical applications

Cite this: Chem. Commun., 2014, 50, 5143

Zhentao Luo, Kaiyuan Zheng and Jianping Xie\*



#### Synthesis of Water-Soluble $[{\rm Au}_{25}({\rm SR})_{18}]^-$ Using a Stoichiometric Amount of ${\rm NaBH}_4$

Tiankai Chen,<sup>†</sup><sup>©</sup> Victor Fung,<sup>‡</sup> Qiaofeng Yao,<sup>†</sup><sup>©</sup> Zhentao Luo,<sup>†</sup><sup>©</sup> De-en Jiang,<sup>‡</sup><sup>©</sup> and Jianping Xie<sup>\*,†</sup><sup>©</sup>

<sup>†</sup>Department of Chemical and Biomolecular Engineering, National University of Singapore, 4 Engineering Drive 4, Singapore 117585, Singapore

<sup>‡</sup>Department of Chemistry, University of California, Riverside, California 92521, United States

## **Motivation**

1. To resolve the fundamental issues of the alloy systems, such as

- Position of heteroatoms inside the metal alloy NCs
- Heteroatoms replace the parental atoms or occupy vacant sites during the alloying process
- > Why would the heteroatoms locate at a specific position
- How are the heteroatoms diffused dynamically inside the alloy NPs during the alloying process

2. To overcome the technical limitations and challenges in characterization and real-time tracking of reactions.

## Why this paper?

- First to observe the dynamic intracluster heteroatom diffusion during the alloying process.
- Explained with details how atom transfer occur between Au complex and Ag NCs.

## Some alloy nanoclusters



### Methods of alloying:

DopingIntercluster reaction

![](_page_6_Figure_2.jpeg)

# Introduction

- Metal alloy NPs promising class of functional materials, finding increasing acceptance in optical, catalytic, electrochemical, and biomedical applications.
- Alloying is an efficient way to produce metal alloy NCswhere the exact positions and numbers of heteroatoms could be obtained by ESI-MS, single crystal XRD and DFT simulation.
- This alloying process is a stoichiometric reaction.
- The hydrophilic metal NCs could be directly ionized, which makes real-time monitoring of the alloying process of AuAg NCs by ESI-MS possible.

## Results

![](_page_8_Figure_1.jpeg)

**Figure 1.** UV–vis absorption spectra of (a) Ag25(MHA)18 and (c) AuAg24(MHA)18. Insets are photographs of the NC solutions. ESI mass spectra of (b) [Ag25(MHA)18]– and (d) [AuAg24(MHA)18]–. The upper panels are broad ESI mass spectra, and the charges of the ionized NC species are labeled upon each set of peaks. The middle panels are magnified ESI mass spectra of [Ag25(MHA)18 + xNa – (x + 5)H]6– and [AuAg24(MHA)18 + xNa – (x + 5)H]6–. The first peak (marked as 0) represents [Ag25(MHA)18 – 5H]6– and [AuAg24(MHA)18 – 5H]6–, respectively, in (b) and (d); the rest of the peaks are from the successive coordination of [+Na – H] of peak 0. The bottom panels are experimental (black curves) and theoretical (red curves) isotope patterns of [Ag25(MHA)18 – 5H]6– and [AuAg24(MHA)18 – 5H]6. (e) Photograph of the PAGE results of Ag25(MHA)18 and AuAg24(MHA)18NCs, showing only one distinct band for each sample.

![](_page_9_Figure_0.jpeg)

**Figure 2.** Time-course (a) UV-vis absorption and (b) ESI mass spectra of formation of AuAg24(MHA)18 from Ag25(MHA)18. Insets are photographs of the reaction solution at different time points. The dashed red line marks the peak of [Ag25(MHA)18 – 5H]6–, and the dashed blue line marks the peak of [AuAg24(MHA)18 – 5H]6–. The orange arrow marks the peak of [Ag25(MHA)17 – 4H]6–, and the green arrow marks the peak of [AuAg24(MHA)17 – 4H]6–. (c) Time-dependent abundance of Ag25(MHA)18 and AuAg24(MHA)18.

![](_page_10_Figure_0.jpeg)

**Figure 3.** (a) Tandem mass spectra of [Ag25(MHA)18 - 5H]6 - (centered at m/z = 890) obtained at collision energies of 2 and 6 eV. (b) Time course tandem mass spectra of [AuAg24(MHA)18 - 5H]6 - (centered at m/z = 905) obtained at collision energies of 2 and 6 eV. (c) Time dependent abundance of each fragment. The number in front of each molecular formula corresponds to the labeled number of each fragment in (a) and (b).

![](_page_11_Figure_0.jpeg)

**Figure S13**. XPS spectra of Au(I)-MHA complexes and the time-dependent reaction solution of AuAg24(MHA)18 NCs. The spectra are deconvoluted into Au(0) (84 eV, dashed pink line) and Au(I) components (85 eV, dashed black line).

![](_page_12_Figure_0.jpeg)

**Figure S3**. Time-course (a) UV-vis absorption and (b) ESI mass spectra of the reaction solution of Au(I)-MHA complexes and Ag25(MHA)18 NCs with a feeding ratio of Au(I)-MHA complexes to Ag25(MHA)18 = 2 : 1. The dashed red line marks the peak of [Ag25(MHA)18 - 5H]6–, and the dashed blue line marks the peak of [AuAg24(MHA)18 - 5H]6–, while the dashed purple line marks the peak of [Au2Ag23(MHA)18 - 5H]6–. The orange arrow marks the peak of [Ag25(MHA)17 - 4H]6–, whereas the green arrow marks the peak of [AuAg24(MHA)17 - 4H]6–. (c) Experimental (black curve) and theoretical (red curve) isotope patterns of [Au2Ag23(MHA)18 - 5H]6.

![](_page_13_Figure_0.jpeg)

**Figure S14**. (a) Time-course tandem mass spectra of [Au2Ag23(MHA)18 - 5H]6- (centered at m/z = 920) obtained at collision energies of 2 and 6 eV. (b) Time-dependent abundance of each fragment. The number in front of each molecular formula corresponds to the labeled number of each fragment in (a).

# Conclusion

![](_page_14_Figure_1.jpeg)

Figure 4. Proposed intracluster Au heteroatom diffusion mechanism. Color scheme: Ag atoms on the surface staple motifs (gray); Ag atoms on the surface layer of the icosahedral kernel (green); central Ag atom of the icosahedral core (blue); gold atom (yellow); sulfur atoms of the MHA ligand on the surface staple motifs (pink).

![](_page_15_Picture_0.jpeg)