

Communication

pubs.acs.org/JACS

# Bulky Surface Ligands Promote Surface Reactivities of $[Ag_{141}X_{12}(S-Adm)_{40}]^{3+}$ (X = Cl, Br, I) Nanoclusters: Models for Multiple-Twinned Nanoparticles

Liting Ren,<sup>†,§</sup> Peng Yuan,<sup>†,§</sup> Haifeng Su,<sup>†</sup> Sami Malola,<sup>‡</sup> Shuichao Lin,<sup>†</sup> Zichao Tang,<sup>†</sup> Boon K. Teo,<sup>\*,†</sup> Hannu Häkkinen,<sup>\*,‡</sup> Lansun Zheng,<sup>†</sup> and Nanfeng Zheng<sup>\*,†</sup>

<sup>†</sup>Collaborative Innovation Center of Chemistry for Energy Materials, State Key Laboratory for Physical Chemistry of Solid Surfaces, and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China <sup>‡</sup>Departments of Physics and Chemistry, Nanoscience Center, University of Jyväskylä, FI-40014 Jyväskylä, Finland

Supporting Information



**ABSTRACT:** Surface ligands play important roles in controlling the size and shape of metal nanoparticles and their surface properties. In this work, we demonstrate that the use of bulky thiolate ligands, along with halides, as the surface capping agent promotes the formation of plasmonic multiple-twinned Ag nanoparticles with high surface reactivities. The title nanocluster [Ag141X12(S- $Adm)_{40}$ ]<sup>3+</sup> (where X = Cl, Br, I; S-Adm = 1adamantanethiolate) has a multiple-shell structure with an Ag<sub>71</sub> core protected by a shell of  $Ag_{70}X_{12}(S-Adm)_{40}$ . The Ag<sub>71</sub> core can be considered as 20 frequency-two Ag<sub>10</sub> tetrahedra fused together with a dislocation that resembles multiple-twinning in nanoparticles. The nanocluster has a strong plasmonic absorption band at 460 nm. Because of the bulkiness of S-Adm, the nanocluster has a low surface thiolate coverage and thus unusually high surface reactivities toward exchange reactions with different ligands, including halides, phenylacetylene and thiols. The cluster can be made water-soluble by metathesis with water-soluble thiols, thereby creating new functionalities for potential bioapplications.

## **INTRODUCTION**

- Surface-capping agents stabilizes metal nanoparticles from aggregation and also controls their size, shape, and morphology.
- Bulky thiolates facilitate the formation of multiple-twinned Ag nanoparticles with enhanced surface reactivity.
- > Multiple-twinned  $Ag_{71}$  core is protected by a shell of  $Ag_{70}X_{12}(S-Adm)_{40}$
- ► Low surface coverage of thiolates on  $[Ag_{141}X_{12}(S-Adm)_{40}]^{3+}$  is caused by the sterically demanding S-Adm creating a high surface reactivity toward exchange reactions with halides, phenylacetylene and thiols.
- Such NPs can be easily converted into water-soluble Ag nanoparticles.
- Synthesis : a polymeric silver 1-adamantanethiolate was used as the metal precursor and reduced with  $NaBH_4$  in the presence of  $PPh_4Br$  and triethylamine.



**Figure 1.** (a) UV–vis spectrum of **1** in CH<sub>2</sub>Cl<sub>2</sub>. (b) ESI-MS spectra of the crude product of **1**,  $[Ag_{141}Br_{12-n}Cl_n(S-Adm)_{40}]^{3+}$  (n = 0-12) (top, experimental; bottom, simulated).

#### > Soluble in DCM

High-quality dark green crystals having orthorhombic space group Pbcn

#### Multiple-twinned Ag<sub>71</sub> core terminated by a Ag-thiolate shell of Ag<sub>70</sub>(S-Adm)<sub>40</sub> and 12 halides



Ag

Ag

Ag

Br

S

С

Figure 2. Overall structure of  $[Ag_{141}Br_{12}(S-Adm)_{40}]^{3+}$  (characterized by X-ray crystallography) is viewed approximately along the 5-fold (a) and 2-fold (b) symmetry axes. Green, blue, orange: silver; claret-red: bromide; yellow: sulfur; gray: carbon. All hydrogen atoms are omitted for clarity.

#### **STRUCTURAL DETAILS**

The ellipsoidal-shaped core consists of a two-shell Ag<sub>19</sub>@Ag<sub>52</sub> structure

> Innermost shell interpenetrating biicosahedra (*IBI*) of  $Ag_{19}$  with 2 icosahedral centers bonded at 2.678 Å.

This IBI is twisted about the 5-fold axis by 7.3 degrees.

>Overall,  $Ag_{71}$  core can be described as 20 frequency-two (v<sub>2</sub>) tetrahedra interlaced together to form a multiple-twinned prolate metal core with 10 slightly concave butterfly "defects"

> 141 silver atoms in the three shells form a prolate ellipsoidal metal framework with  $D_5$  symmetry.

> The metal framework is further protected by 40 S-Adms and 12 bromides, giving rise to the formulation of  $[Ag_{141}Br_{12}(SAdm)_{40}]^{3+}$ 

➢ S-Adm is a rigid and bulky ligand with ~57% surface S-Adm coverage.

Low coverage of S-Adm on Ag NPs leaves surface sites accessible to small-sized molecules (e.g., halides).



**Figure 3.** Detailed structure of  $[Ag_{141}Br_{12}(S-Adm)_{40}]^{3+}$ . (a) The inner shell of  $Ag_{19}$ . (b) The two-shell  $Ag_{19}@Ag_{52}$  of the nanoparticle. (c) The three-shell  $Ag_{19}@Ag_{52}@Ag_{70}$ . (d) Decoration of  $Ag_{141}$  with 12 Br (Claret-red) and 40 S (yellow) atoms. (e) Structural details (bond lengths in Å) of the Br and S ligands.

#### ATOMIC AND ELECTRONIC STRUCTURE

- > Jelliumatic electron count is 86 electrons, charge state of +3.
- Not a shell closing in a spherical electron system (e.g. 2, 8, 18, 20, 34, 40, 58, 68, 70, 92) is due to the overall prolate shape of the particle, which splits the degeneracies of angular momentum symmetries with an additional splitting is due to the D<sub>5</sub> symmetry.
- Strong splitting of the states below and above the HOMO level (Figure S10) in the charge state of +3 has an empty orbital (2-electron hole) virtually at the HOMO level and an energy gap of ~ 0.3 eV to two upper levels that complete the electron filling to the spherical magic number of 92.
- Electron holes close to the HOMO suggests that the stability mainly due to structural packing of the metal core and bulky ligand shell, instead of electron shell closing.
- Plasmonic peak is due to transitions over a large number of single-electron/single-hole states.



Figure S10. Level scheme of the electronic states close to the HOMO energy (E=0) of the  $[Ag_{141}Br_{12}(S-Adm)_{40}]^{3+}$ cluster. The numbers in the scheme indicate the free-electron counts after each level. On the right, the two almost-degenerate levels are magnified and electron occupancies for 1+ and 3+ states of the cluster are shown.

#### **Surface Exchange Reactions**

- Substitution of  $Br^-$  by  $Cl^-$  and  $Cl^-$  by  $I^-$  (from solvent) under ESI-MS condition.
- Weakest Ag–I bonds are not so easily replaced by Ag–Cl bonds owing to the large size of the iodides that fit snugly in the cavities created by the S-Adm ligands.
- ➤ When phenylacetylene (PA) is used as the exchange ligand, two [PA]<sup>-</sup> replace two [S-Adm]<sup>-</sup> ligands (Figure 4a) instead of substituting halides.
- Successful transformation of  $Ag_{141}$  NP into water-soluble in the molar ratio of MSA:  $Ag_{141}$  NP is low as 4:1 while the same ligand exchange process failed to solubilize TBBT-capped  $[Ag_{136}(SR)_{64}Cl_3]^-$  in water, even with a MSA:  $Ag_{136}$  molar ratio of 12:1.
- Results the  $Ag_{141}$  exhibits enhanced surface reactivity toward ligand exchange due to its low surface thiolate coverage.



**Figure 4.** (a) ESI-MS spectra of **1** after ligand-exchange with phenylacetylene (PAH), yielding  $[Ag_{141}Br_{12-n}Cl_n(S-Adm)_{38}PA_2]^{3+}$  (n = 0-12). (b) Photographs of the solution of  $[Ag_{141}Br_{12}(S-Adm)_{40}]^{3+}$  before and after ligand-exchange with mercaptosuccinic acid, followed by dissolving in a mixture of dichloromethane and water.

### CONCLUSION

- ➤ Using bulky 1-adamantanethiolate facilitated the formation of a heavily twinned metal nanoparticle,  $[Ag_{141}Br_{12}(S-Adm)_{40}]^{3+}$ , with a prolate  $Ag_{71}$  core protected by a shell of  $Ag_{70}Br_{12}(S-Adm)_{40}$ .
- Even with 20  $v_2$  tetrahedral domains, the Ag<sub>71</sub> core adopts a non-perfect spherical geometry instead of icosahedron, serving as a molecular structure model for multiple-twinned nanostructures of face-center cubic metals.
- Low surface thiolate coverage yields high surface reactivities toward ligand exchange.
- The chemistry behind the controlled formation of heavily twinned metal nanoparticles with high surface reactivity using bulky ligands is expected to be useful in creating atomically precise metal nanoparticles with desirable surface and/or unusual properties for specific applications.