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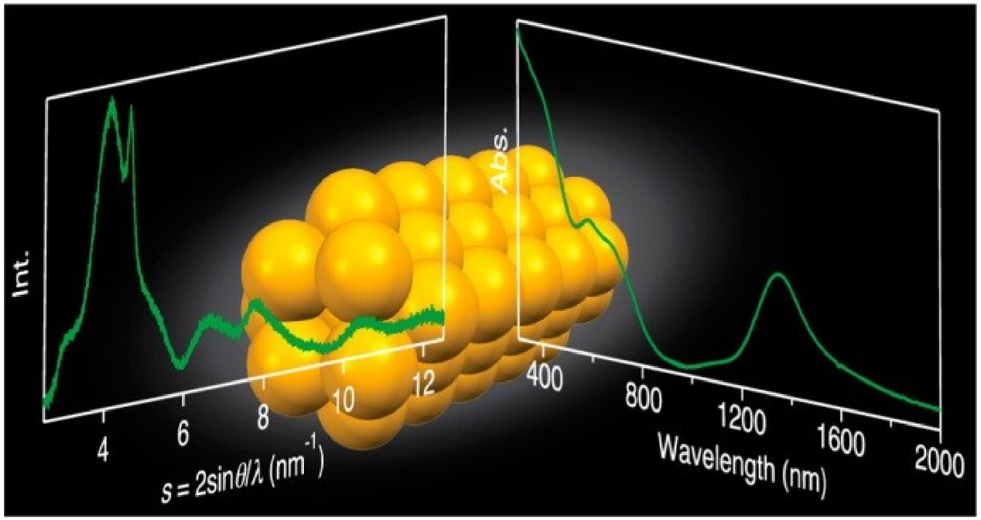
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Slow-Reduction Synthesis of a Thiolate Protected One-Dimensional Gold Cluster Showing an Intense Near-Infrared Absorption

Shinjiro Takano,[†] Seiji Yamazoe,[†,‡] Kiichirou Koyasu,[†,‡] and Tatsuya Tsukuda*,[†,‡]

[†]Department of Chemistry, School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan
[‡]Elements Strategy Initiative for Catalysis and Batteries (ESICB), Kyoto University, Katsura, Kyoto 615-8520, Japan



Received: March 28, 2015

Abhijit Nag
13.06.2015

Introduction

- Gold nanostructures exhibit unique optical properties that depend on their dimensions and morphology.
- It is well established that isotropic gold nanoparticles (AuNPs) with diameters of >2 nm exhibit localized surface plasmon (LSP) bands centered at ∼520 nm.
- If the diameter of the AuNPs is less than 2 nm, the LSP band disappears and the clusters begin to evolve an optical onset, corresponding to electronic transitions between the HOMO and LUMO.
- Optical absorption spectra of ultrathin Au nanowires and nanorods (Au UNWs and Au UNRs) with diameters of ∼1.6 nm have recently been reported. These do not show an LSP band at ∼520 nm because of their very low diameters, but they do show a strong LSP band in the near infrared (NIR)−IR region.
- Theoretical studies predict that linear assemblies of icosahedral Au_{13} units and ultrasmall Au nanorods should exhibit distinct absorption peaks in the NIR region.

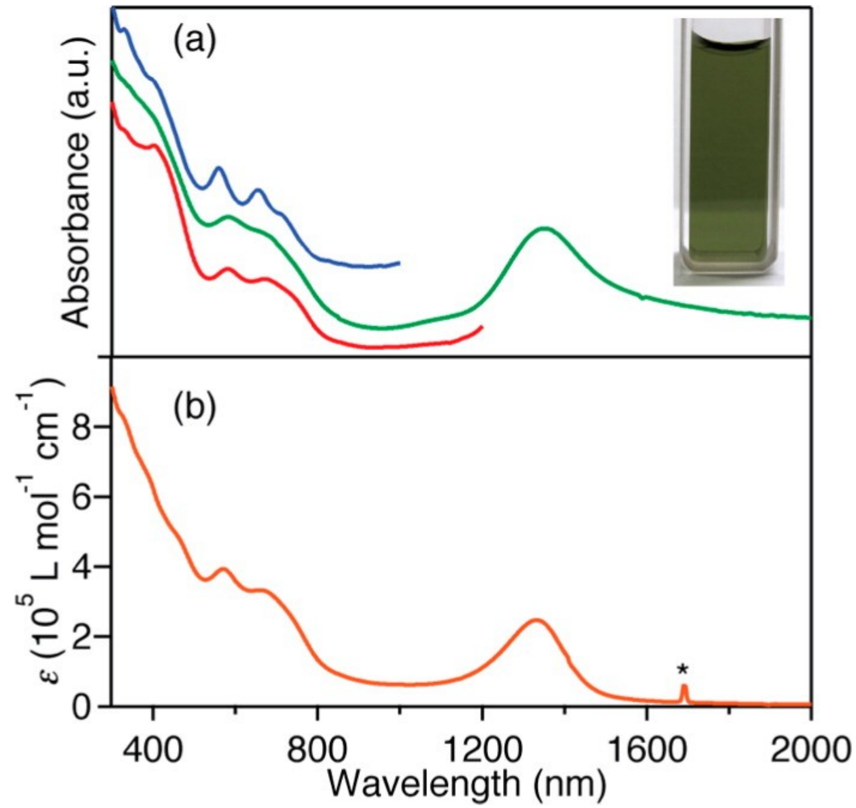
LSP (Localised Surface Plasmon)

- Localized surface plasmon resonance (LSPR) is an optical phenomena generated by a light wave trapped within conductive nanoparticles (NPs) smaller than the wavelength of light.
- The phenomenon is a result of the interactions between the incident light and surface electrons in a conduction band. This interaction produces coherent localized plasmon oscillations with a resonant frequency that strongly depends on the composition, size, geometry, dielectric environment and particle–particle separation distance of NPs.
- Common materials used for NP production are noble metals such as Ag and Au, which due to the energy levels of d–d transitions exhibit LSPR in the visible range of the spectrum. Although, Ag exhibits the sharpest and strongest bands among all metals.

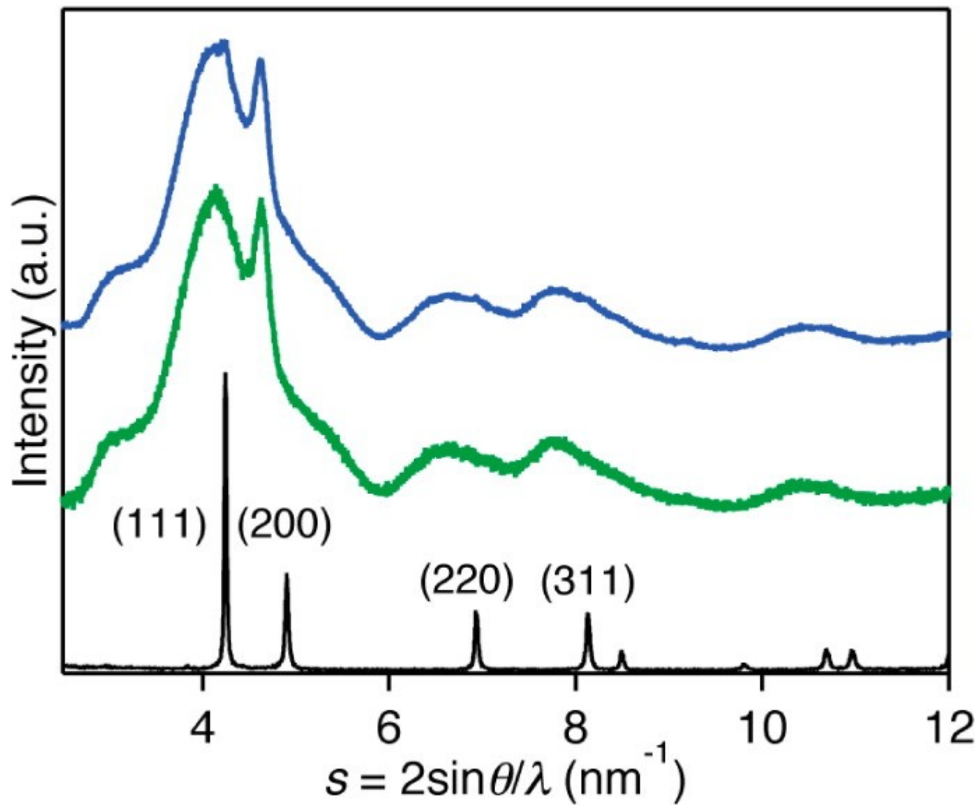
In This Paper

- They have synthesised an one-dimensional gold cluster $Au_{76}SR_{44}$ by slow-reduction.
- They have got an intense absorption near- Infrared region and found out the reason for the intense peak.

- By powder XRD they have solved cluster structure.



(a) UV–vis–NIR absorption spectra of **1** in water (red), as a thin film at room temperature (green) and at 20 K (blue). The blue curve is offset vertically for clarity. The inset photograph shows a dispersion of **1** in water. (b) UV–vis–NIR absorption spectrum of **2** dispersed in $CHCl_3$. The asterisk indicates the absorption of the $CHCl_3$ solvent.



Powder XRD patterns of **1** (green), **2** (blue), and bulk gold (black) recorded under the same experimental setup.

The ESI mass spectrum of 1 measured in the negative-ion mode was dominated by a series of multiply charged anions formed by deprotonation of the carboxylic acid group of the 4-MEBA ligand(S3). The molecular weight (MW) of cluster 1 was determined to be 22.9 kDa. However, because of the limited accuracy of this mass determination, they could not determine the chemical composition unambiguously, as there were several possible candidates, including Au_{73}(4-MEBA)$_{47}$, Au_{74}(4-MEBA)$_{46}$, Au_{75}(4-MEBA)$_{45}$,

or Au_{76}(4-M

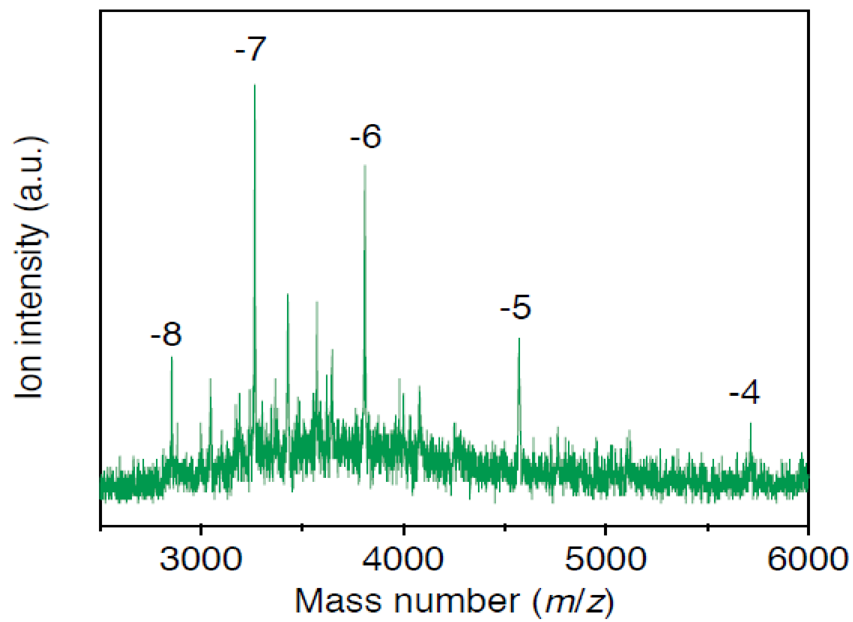
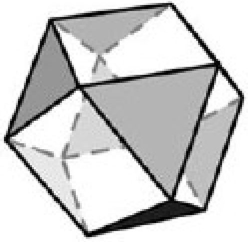


Figure S3. ESI-MS spectrum of **1** in the negative-ion mode. The numbers in the spectrum correspond to a charge state of $[\mathbf{1} - n\mathrm{H}^+]^{n-}$.

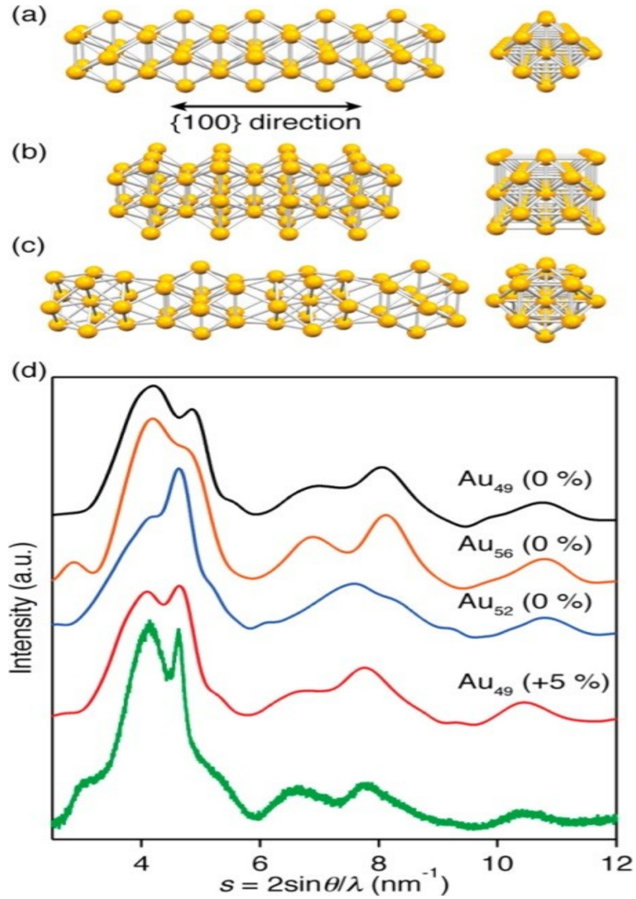
Table 1. Chemical Compositions of 1 and 2

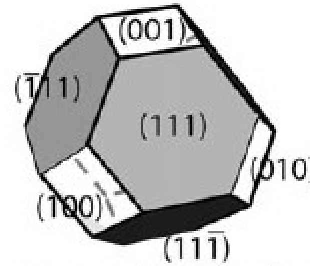
	cluster 1		cluster 2
composition[a]	MW[b] (Da)	mass loss (%)[c]	mass loss (%)[c]
73, 47	22896	37.2	48.1
74, 46	22912	36.4	47.3
75, 45	22928	35.5	46.4
76, 44	22944	34.7	45.5
experiment	22.9×10^3	35.1	45.3

[a]The numbers of Au atoms and thiolate moieties, respectively. [b]Calculated molecular weight for each composition. [c]Calculated mass loss for each composition.



cuboctahedron





truncated octahedron

Side and front views of model structures of (a) Au_{49}, (b) Au_{56}, and (c) Au_{52} cores of $Au_{76}(SR)_{44}$ and (d) their simulated XRD patterns. The green plot corresponds to the experimental pattern for **1**.

Summary

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- In summary, They report the synthesis of Au_{76}(4-MEBA)$_{44}$ which exhibits a strong NIR absorption band.

- The powder XRD pattern of the material was reproduced by assuming the existence of a Au_{49} core consisting of five Au_{13} cuboctahedra sharing their (100) facets.

Future Plan

- Generally we take optical spectra in UV-Visible range for cluster. We have also many clusters which do not show any UV-Visible absorption features. We can take near Infrared spectra for these clusters. We may get some interesting data.

- Now we have new mass spectrometry machine through which we can get good mass spec. and structure of the cluster in gas phase through ion mobility.

Thank You