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Observation of Cluster Size Growth in CO-Directed Synthesis of $Au_{25}(SR)_{18}$ Nanoclusters

Yong Yu; Zhentao Luo; Yue Yu; Jim Yang Lee; Jianping Xie

Department of Chemical and Biomolecular Engineering, National University of Singapore

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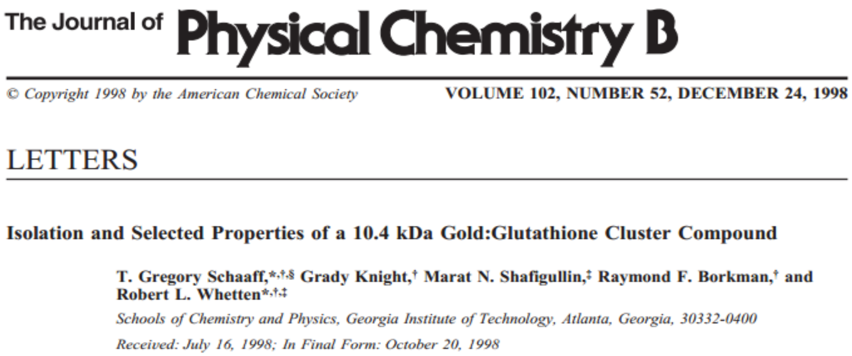
Background



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LETTERS

Isolation and Selected Properties of a 10.4 kDa Gold:Glutathione Cluster Compound

T. Gregory Schaaff,[*,†,§] Grady Knight,[†] Marat N. Shafigullin,[‡] Raymond F. Borkman,[†] and Robert L. Whetten[*,†,‡]

Schools of Chemistry and Physics, Georgia Institute of Technology, Atlanta, Georgia, 30332-0400

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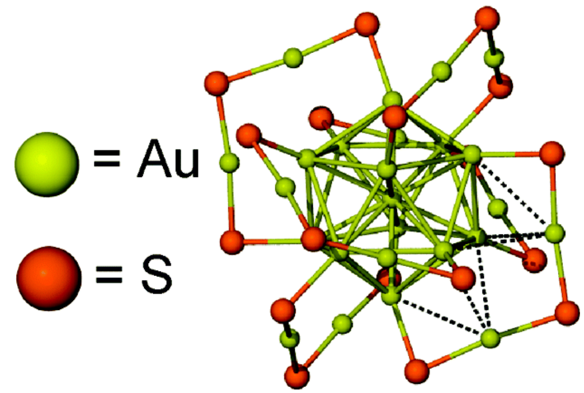
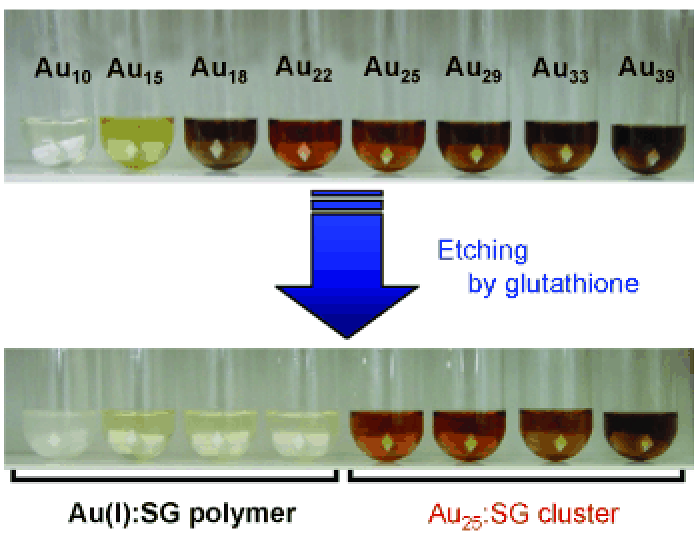
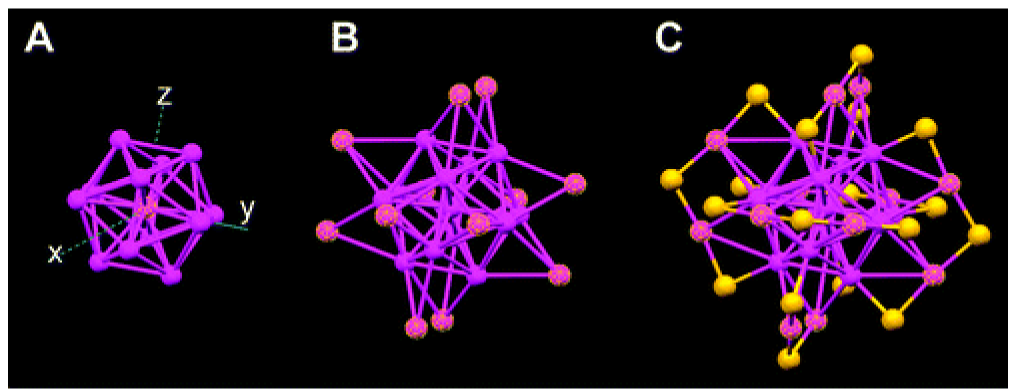


Murray et al.



Tsukuda et al.



Jin et al.

Introduction

- Thiolated Au nanoclusters (NCs) are a family of ultra small (<2 nm) particles stabilized by thiol ligands.
- Due to the strong quantum confinement effect in this size regime, the physical and chemical properties of NCs are mainly governed by the particle size.

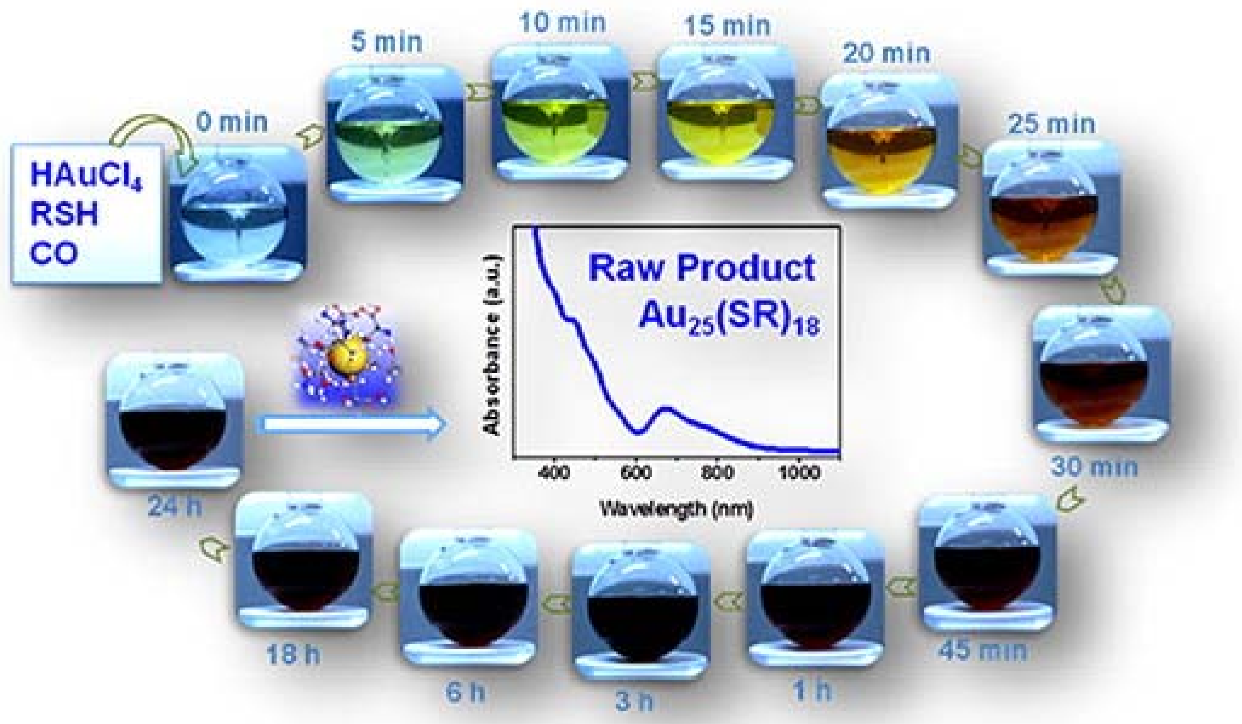
Common dialog for all cluster papers

- The large scale production of thiolated Au NCs in well controlled sizes (or atomically precise NCs) is therefore a most pivotal step toward utilizing their size-tunable properties.
- Thiolated Au NCs are generally synthesized via the reductive decomposition of thiolate-Au(I) complexes by a strong reducing agent…
- The fast reduction kinetics often leads to the formation of a mixture of thiolated Au NCs in different sizes.

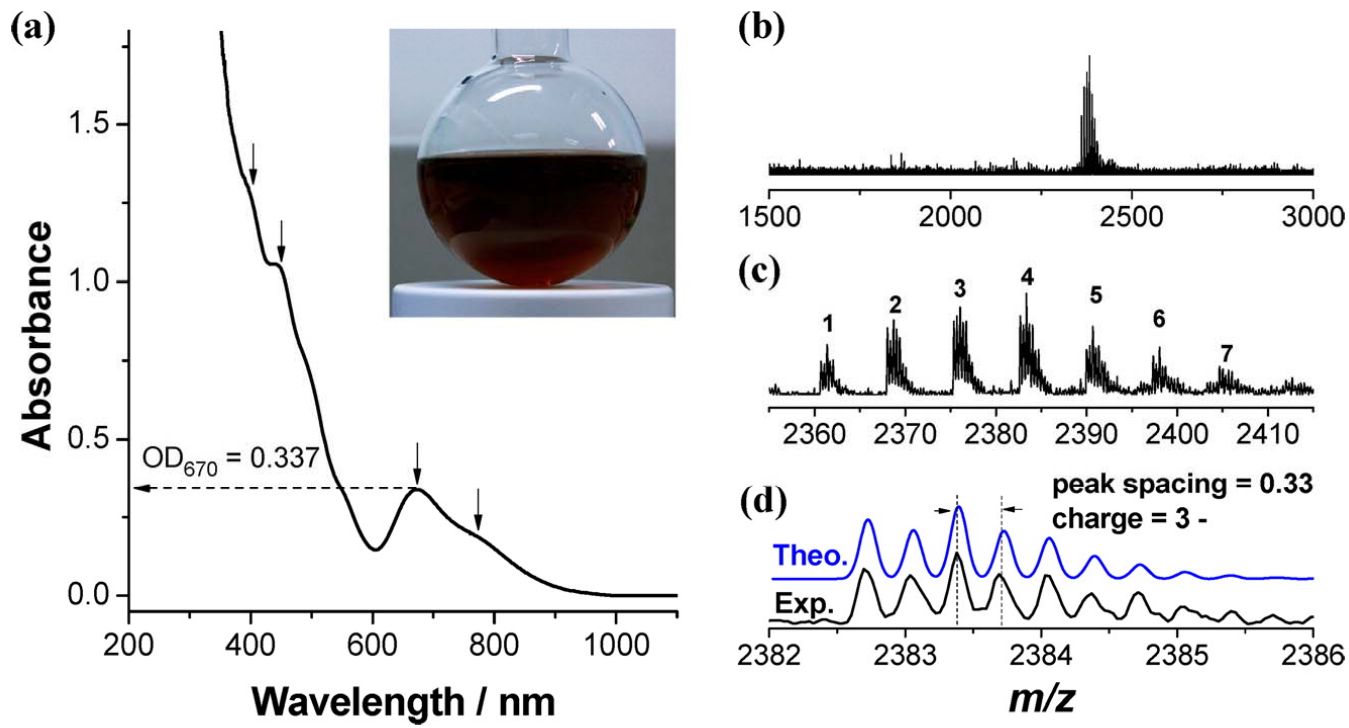
In this paper

A simple and versatile synthetic protocol was used to synthesize Au NCs using a gaseous reducing agent, carbon monoxide (CO), to create a mild reduction environment for the Au ions.

Scheme



Result and Discussion



UV–vis spectrum (a) and ESI spectra (in negative ion mode; b–d) of the as-synthesized Au25(Cys)18 NCs. The blue curve in (d) is the theoretical isotope pattern of peak #4 in (c).

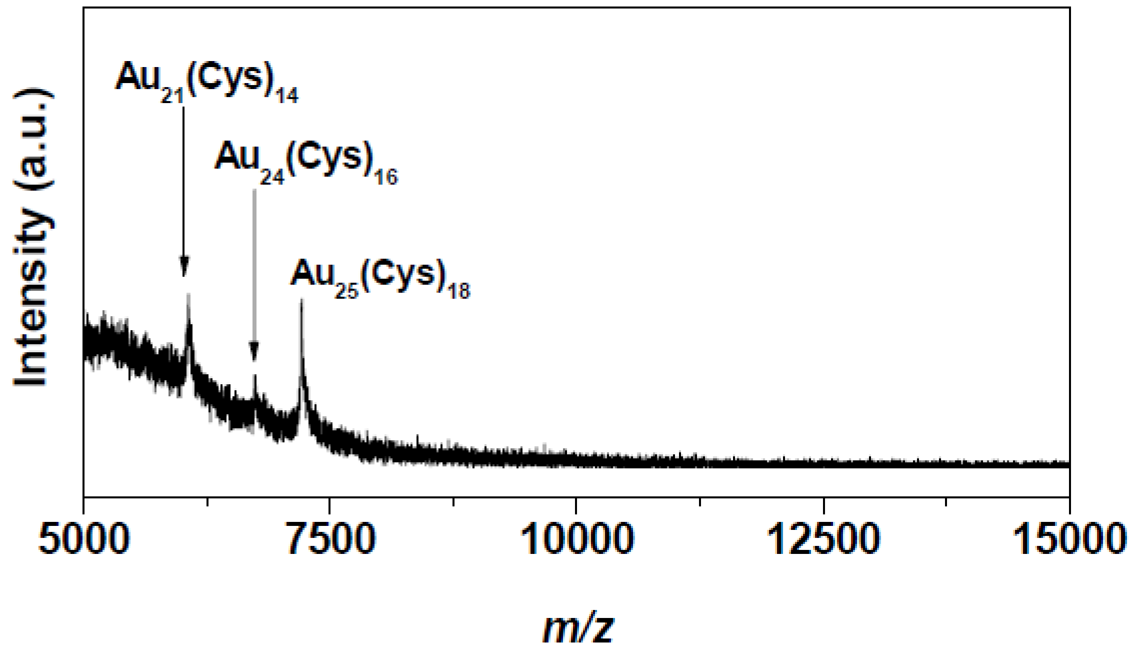
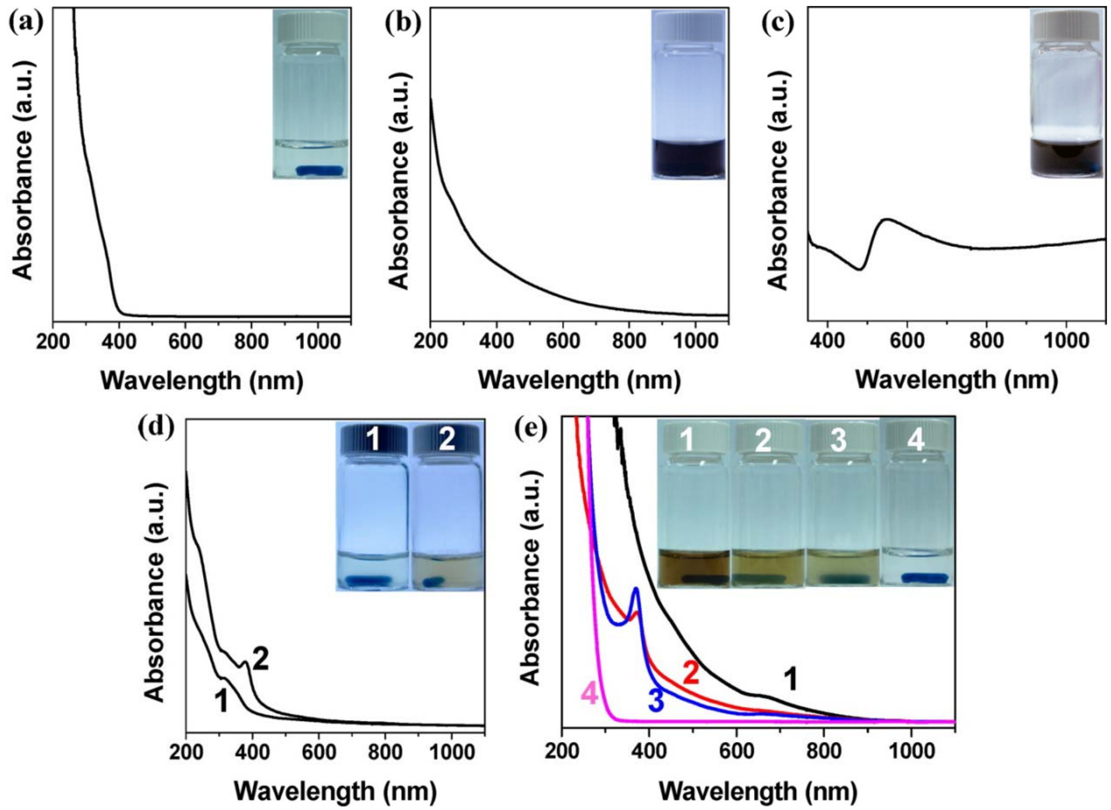


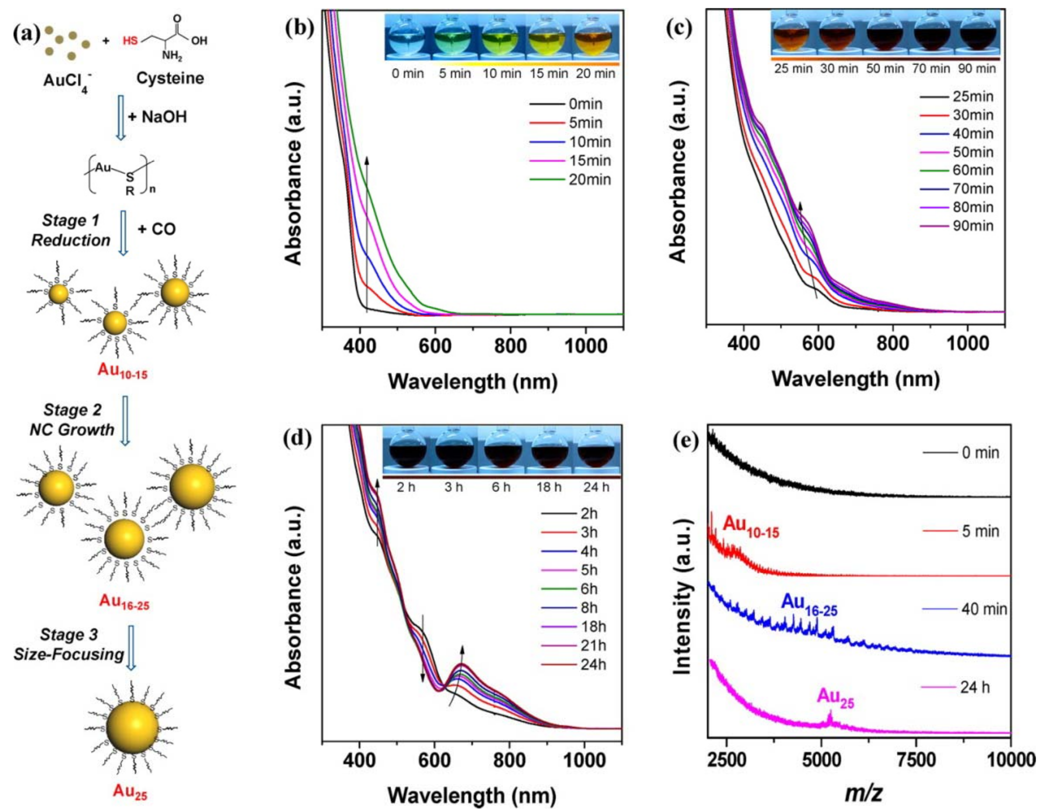
Figure S2. MALDI-TOF mass spectrum (in negative ion mode) of the as-synthesized $Au_{25}(Cys)_{18}$ NCs.

Results and Discussion



UV–vis spectra and digital photographs (inset) of (a) the mixture of HAuCl4 and Cys in the absence of CO after 24 h of reaction (pH = 11); (b) Au NCs synthesized by substitution of CO with NaBH4; (c) Au nanoparticles synthesized by the CO reduction without Cys; (d) Au NCs synthesized under different pHs (pH 4.4 (no. 1) and pH 9.1 (no. 2)); and (e) Au NCs synthesized by different *R*[Cys]/[Au] values at pH 11 (*R*[Cys]/[Au] = 1 (no. 1), *R*[Cys]/[Au] = 2 (no. 2), *R*[Cys]/[Au] = 3 (no. 3), and *R*[Cys]/[Au] = 4 (no. 4)).

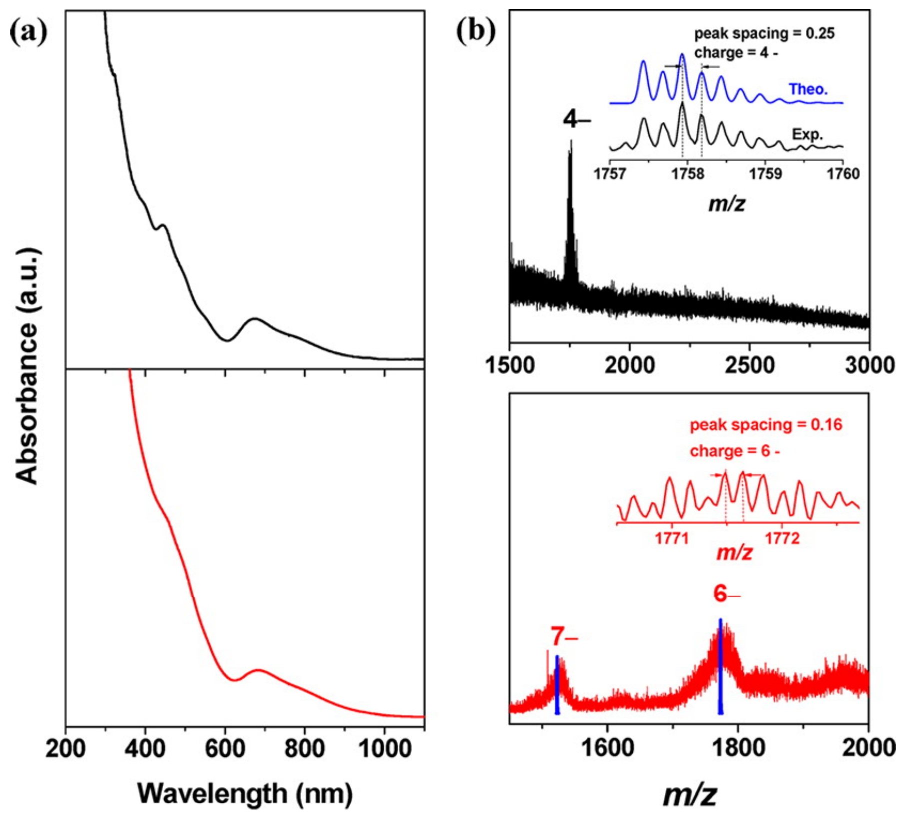
Results and Discussion



(a) Schematic diagram illustrating the postulated formation of Au25(Cys)18 NCs in the presence of CO. UV–vis spectra as a function of reaction time: (b) 0–20 min; (c) 20–90 min; and (d) 90 min to 24 h. Insets are digital photographs of the reaction solution at different times. (e) MALDI-TOF mass spectra (in positive ion mode) of the reaction solution at different reaction times: 0 min (black), 5 min (red), 40 min (blue), and 24 h (magenta).

Possible mechanism

Results and Discussion



UV–vis spectra (a) and ESI mass spectra (in negative ion mode; b) of Au25(SR)18 NCs synthesized by using MPA (black curve) and GSH (red curve) as the protecting agent. The inset in the top panel of (b) is the experimental (black curve) and theoretical (blue curve) isotope pattern of the most abundant species in MPA-Au25 NCs ([Au25(MPA)18 – 14H + 10Na]4–). The inset in the bottom panel of (b) is the isotope pattern analysis of the 6– ion in GSH-Au25 NCs, and the blue curves are the predicted isotope distributions of the two most abundant species ([Au25(GSH)18 – 17H + 10Na]7– and [Au25(GSH)18 – 15H + 9Na]6–).

Conclusion

- They developed a simple one-pot method for the synthesis of high-purity thiolated Au_{25}-$(Cys)_{18}$ NCs (~95% yield) by using gaseous CO as a mild reducing agent.

- Several key intermediates in the growth of $Au_{25}(Cys)_{18}$ NCs (NCs of Au_{10-15}, Au_{16-25}, and Au_{25}) could be identified from the time course measurements of UV/Vis spectroscopy and MALDI-TOF data.

Information that might help !!

Slow reducing agent

- CO
- HCOOH
- $NaBH_3CN$

Intermediate identification

- MALDI
- ESI
- HPLC

Thank you