Anti-Galvanic Reduction of Thiolate-Protected Gold and Silver Nanoparticles

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Introduction:

- ✓ Among the many techniques to engineer the compositions, structures, and properties of metal nanostructures, galvanic reduction (GR) received particular interest owing to its high tunability and feasibility, in particular the possibility to mechanistically study the properties of nanostructures.
- ✓ Galvanic reaction involves reduction of less reactive (or more noble) metal ions in solution by metals.
- ✓ This simple reaction can be used with a wide variety of metal templates and salt precursors, thus providing a straightforward and versatile route to access a broad range of nanostructures (including simple and complex nanostructures).
- ✓ However, the opposite of GR (anti-galvanic reduction, AGR), that is, metal ions are reduced by less reactive (or more noble) metals, is not recognized.
- ✓ Recently, Murray and co-workers revealed that a well-studied gold nanocluster, $[Au_{25}(SC_2H_4Ph)_{18}]$, can react with silver ions, thus suggesting that AGR could occur.
- ✓ It is well-known that Au_{25} has multiple charge states, even the anionic and neutral species were unambiguously confirmed by single-crystal X-ray diffraction analyses.

In this paper,

- ✓ The reaction of neutral [$Au_{25}(SC_2H_4Ph)_{18}$] with silver ions was tried to exclude the possibility that anionic [$Au_{25}(SC_2H_4Ph)_{18}$] has a particular reducing ability.
- ✓ Furthermore, such replacement on several gold and silver nanoparticles of different sizes was also investigated.
- ✓ Reactions of Au_{25} clusters with other metal ions Fe^{2+}, Ni^{2+} and Pb^{2+} were also studied.

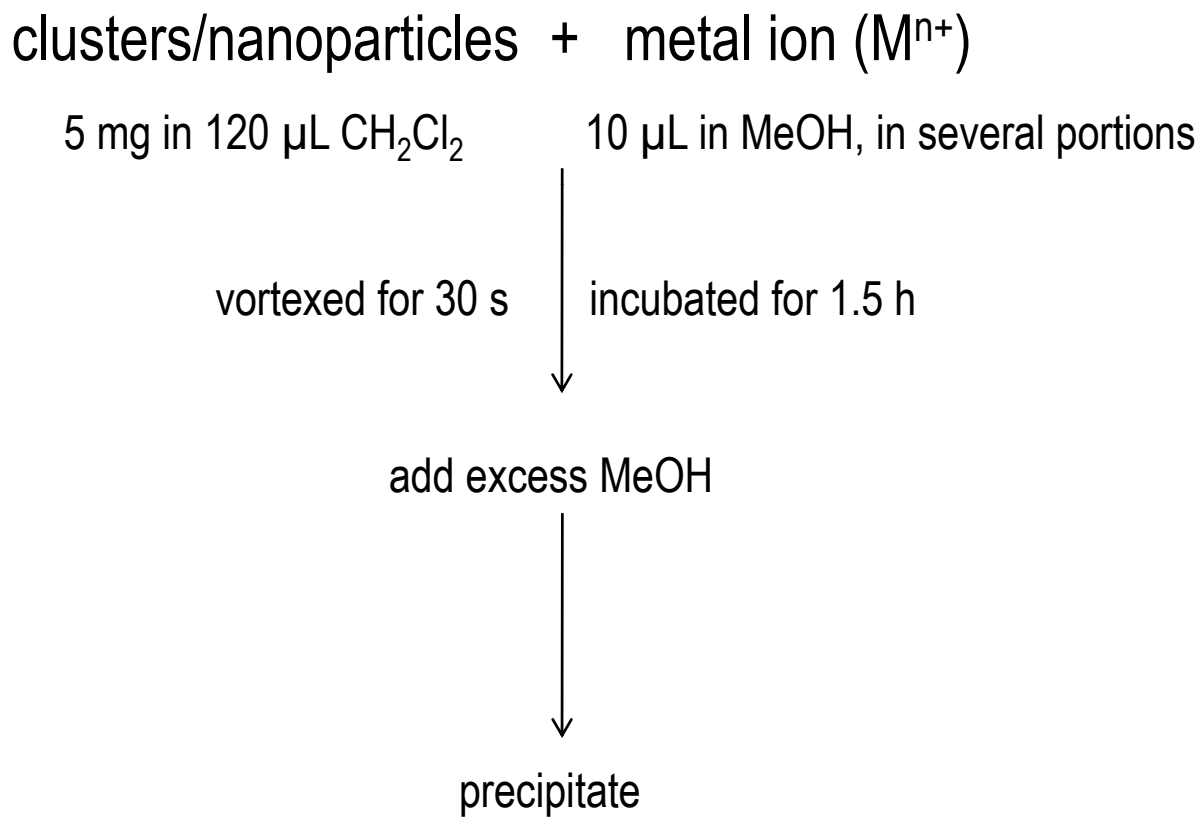
Experimental Section

Synthesis of $Au_{25}(SC_2H_4Ph)_{18}$ and 2 nm sized gold nanoparticles:

$$\underset{\text{in THF at } 0\ ^0C}{TOABr + HAuCl_4 \cdot 4H_2O} \xrightarrow[PhCH_2CH_2SH]{\text{after 30 min.}} \text{colorless solution after 2.5 h} \xrightarrow[\text{stir for 1.0 h}]{\text{aq. } NaBH_4} \text{clusters + nanoparticles}$$

- Clusters are extracted into CH_3CN; nanoparticles are extracted into toluene.
- For neutralization, clusters were stirred overnight in CH_2Cl_2.

Reactions with metal ions:



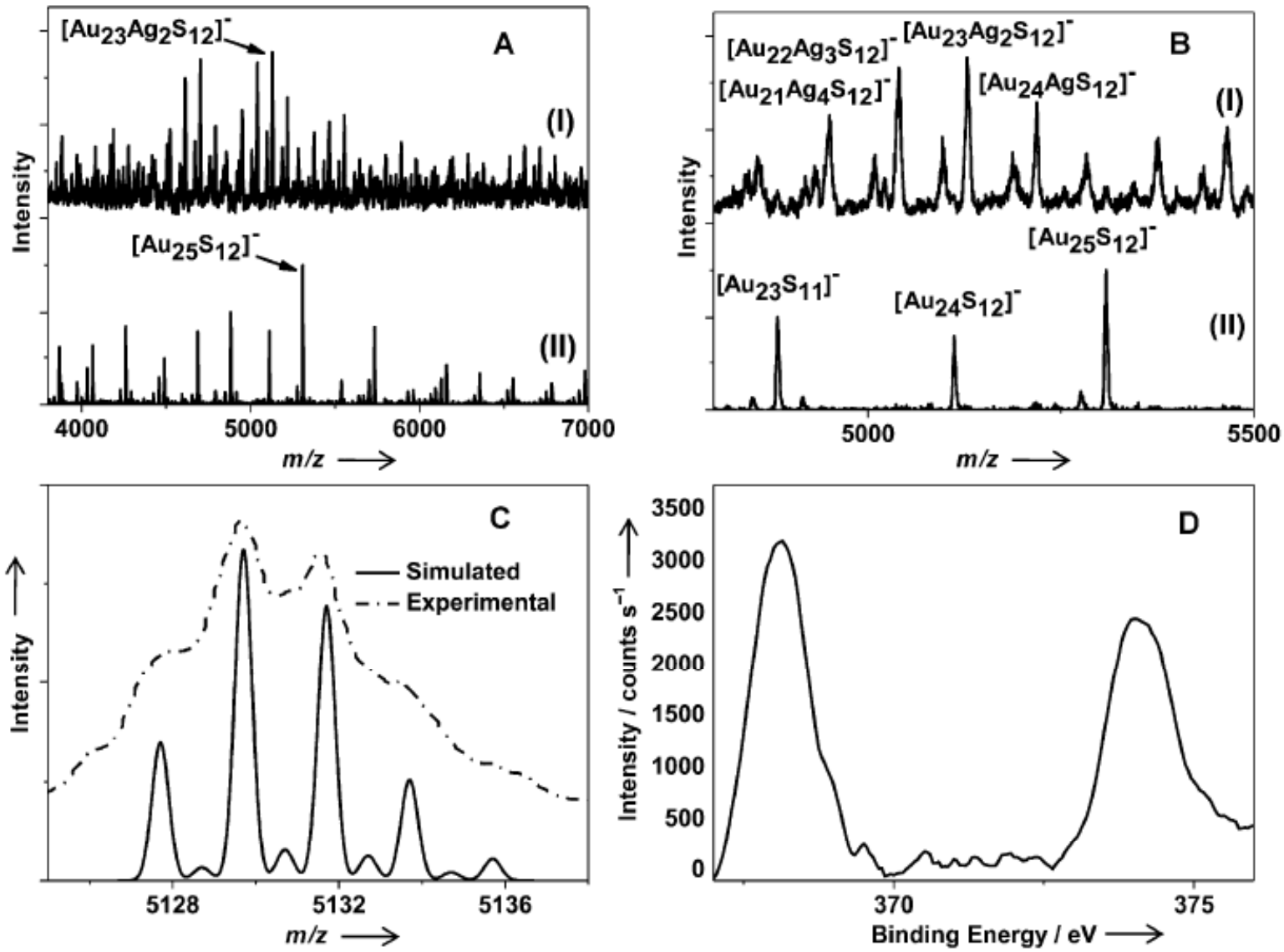


Figure 1. A) Comparison of mass spectra of compounds I and II, and B) magnification of a region of these spectra. C) Comparison of experimental and theoretical isotopic patterns of $[Au_{23}Ag_2S_{12}]^{-}$. D) Ag3d XPS spectrum of compound II. Note: compound I: $[Au_{25}(SC_2H_4Ph)_{18}]^0$ treated with 9.0 equiv Ag^+; compound II: $[Au_{25}(SC_2H_4Ph)_{18}]^0$.

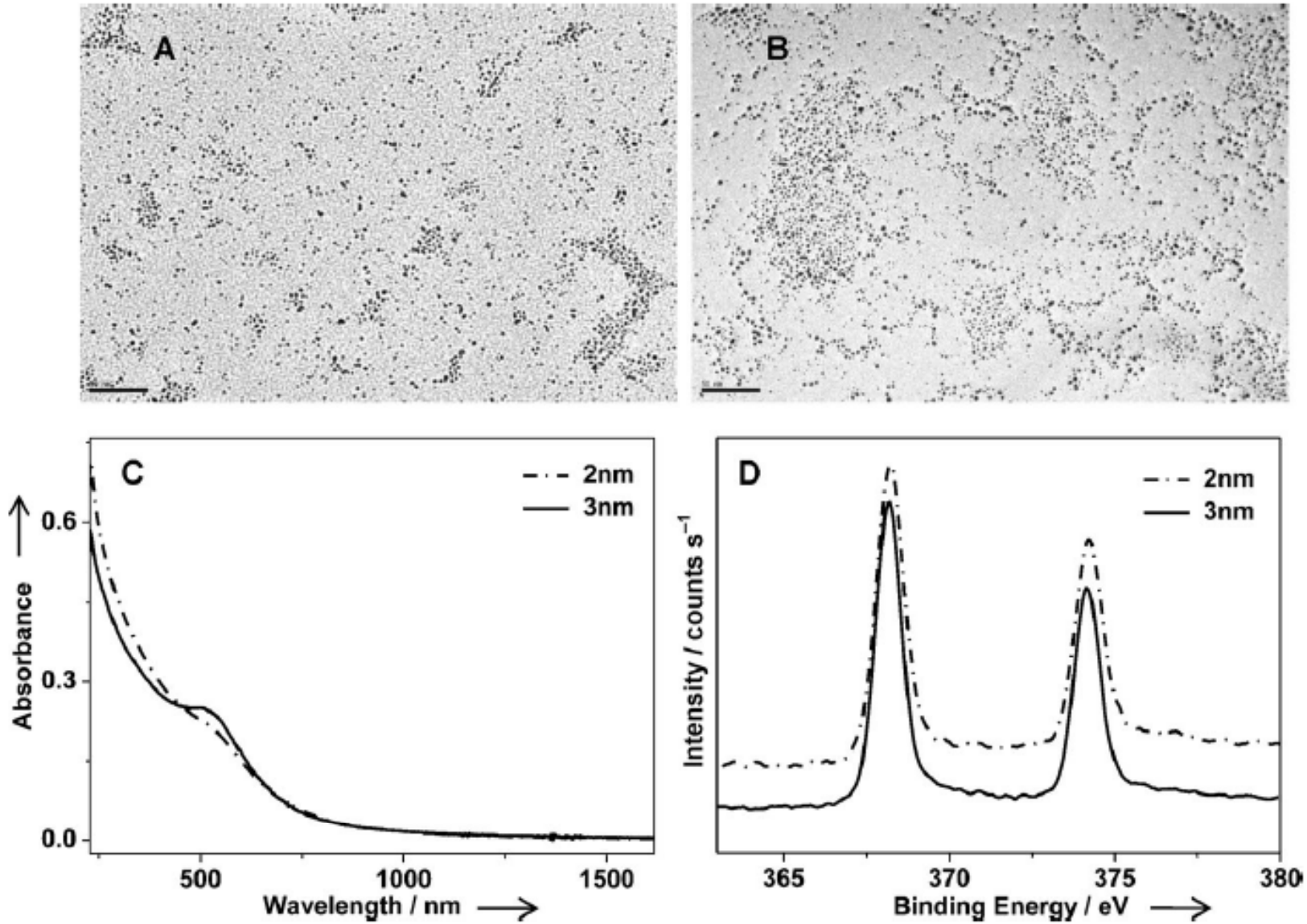


Figure 2. Transmission electron microscopy (TEM) image of A) ca. 2 nm Au nanoparticles and B) ca. 3 nm Au nanoparticles (the scale bar is 50 nm). C) Absorption spectra of ca. 2 and 3 nm sized Au nanoparticles. D) Ag3d XPS spectra of ca. 2 and 3 nm sized Au nanoparticles with incorporated silver(0) (the graphs were shifted and enlarged for clarity).

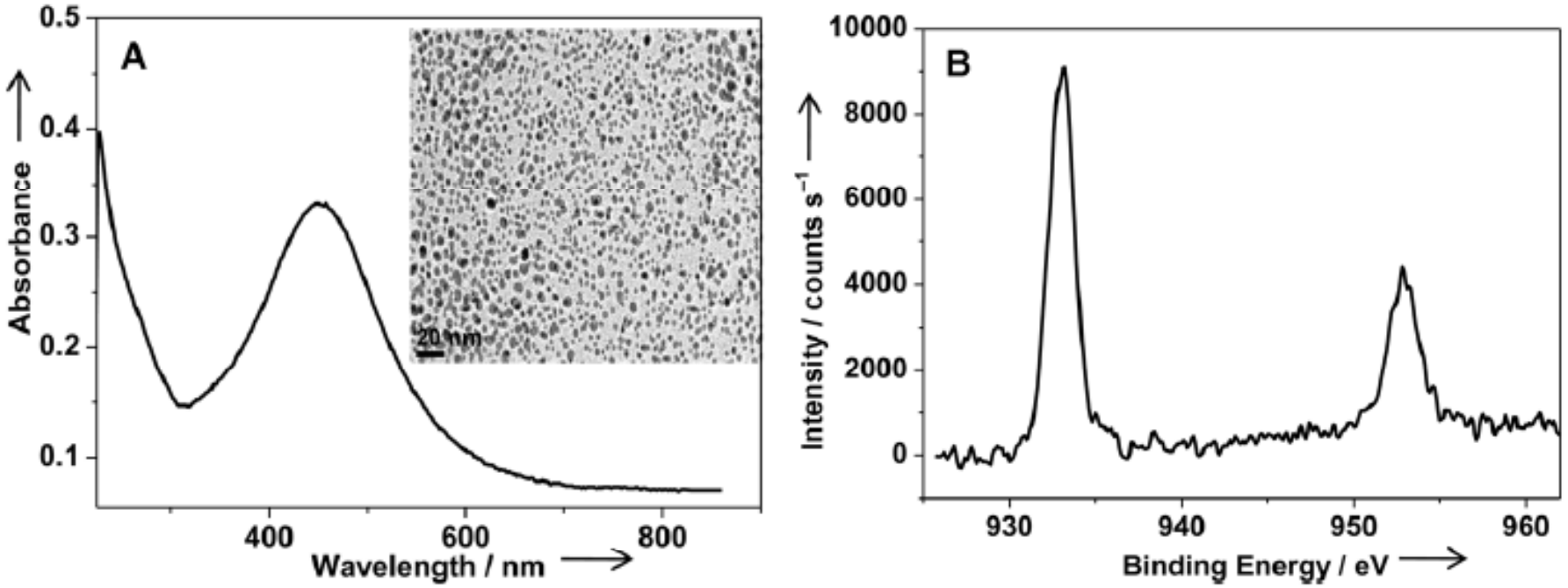


Figure 3. A) Absorption spectrum of ca. 3 nm sized Ag nanoparticles (the inset is a TEM image of Ag nanoparticles, the scale bar is 20 nm). B) Cu2p XPS spectrum of ca. 3 nm sized Ag nanoparticles (treated with $Cu(NO_3)_2$).

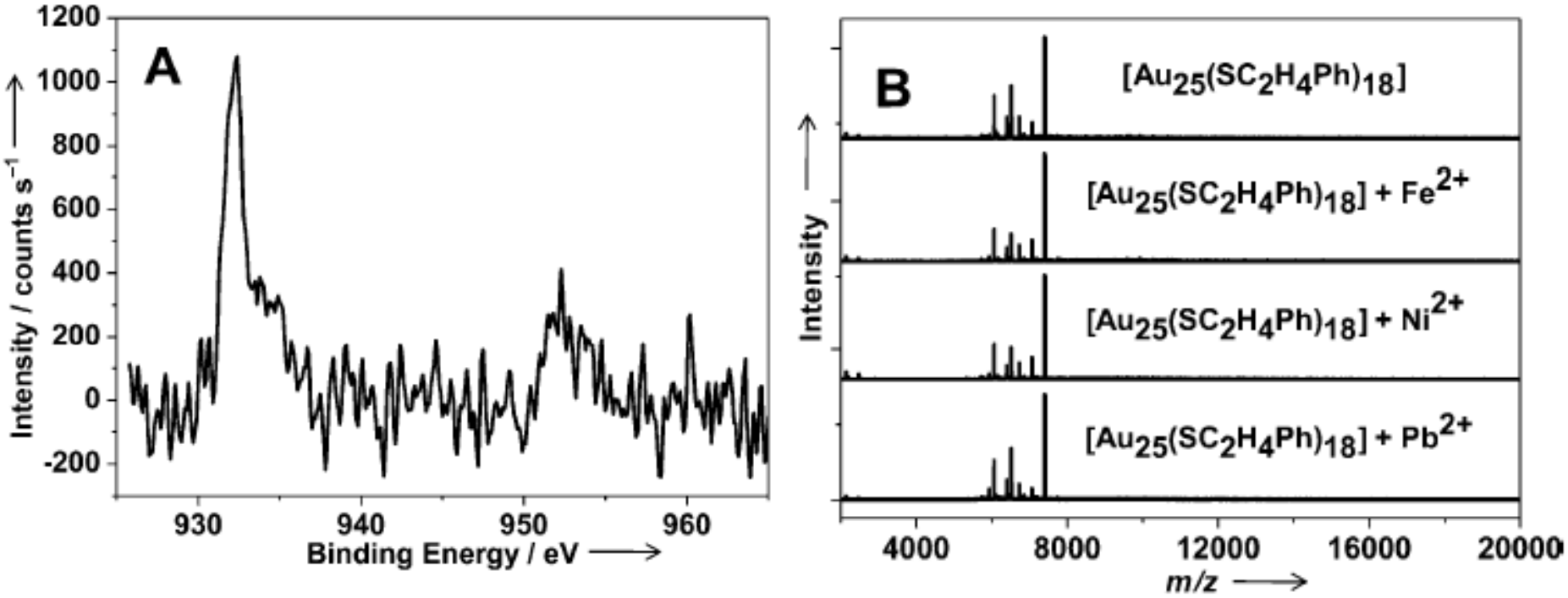


Figure 4. A) Cu2p XPS spectrum of $[Au_{25}(SC_2H_4Ph)_{18}]$ (treated with $Cu(NO_3)_2$). B) MS spectra of pure $[Au_{25}(SC_2H_4Ph)_{18}]$ and $[Au_{25}(SC_2H_4Ph)_{18}]$ treated with different cations (Fe^{2+}, Ni^{2+}, Pb^{2+}; spectra acquired in positive ionization mode).

Summary:

1. Anti-galvanic reduction is possible due to reduction in size of the particles.
2. It could provide a facile and mild method to make alloys on the nanoscale or tune the compositions, structures, and properties of nanostructures.