

Formation and its mechanism of phosphine-protected gold cluster cations by magnetron sputtering method

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We prepared gold clusters by magnetron sputtering of a gold target onto a polyethylene glycol (PEG) solution of 1,3-bis(diphenylphosphino)propane (dppp). The products were characterized by electrospray ionization (ESI) mass spectrometry and UV-vis absorption spectroscopy as a function of the dppp concentration ([dppp]). The ESI mass spectra in Figures 1a and 1b indicate formation of known magic clusters and their growth in the sequence of $[\text{Au}(\text{dppp})_n]^+$ ($n = 1, 2$) \rightarrow $[\text{Au}_2(\text{dppp})_n]^+$ ($n = 2 - 4$) \rightarrow $[\text{Au}_6(\text{dppp})_n]^+$ ($n = 3, 4$) \rightarrow $[\text{Au}_{11}(\text{dppp})_5]^{3+}$ with decrease in [dppp]. The optical spectrum at the high [dppp] (= 20 mM) is dominated by the peak at ~ 580 nm due to $[\text{Au}_6(\text{dppp})_4]^+$ and that at <350 nm due to $[\text{Au}(\text{dppp})_n]^+$ and $[\text{Au}_2(\text{dppp})_n]^+$.¹⁾ With the reduction of [dppp], a new peak at ~ 430 nm due to $[\text{Au}_{11}(\text{dppp})_5]^{3+}$ was developed,²⁾ followed by the emergence of continuous band that increases toward the short wavelength due to larger, neutral Au clusters. These results demonstrate that atomically-defined magic Au clusters such as $[\text{Au}_6(\text{dppp})_4]^{2+}$ and $[\text{Au}_{11}(\text{dppp})_5]^{3+}$ could be synthesized using the magnetron sputtering onto the ligand solution with controlled concentration.

Interestingly, cationic complex $[\text{Au}(\text{dppp})_2]^+$ was detected as major species although neutral Au atoms are mainly deposited onto the PEG solution. Density functional theory (DFT) calculation showed that the ionization energy of $\text{Au}(\text{dppp})_2$ is smaller than those of alkali metals. Thus, we speculated that $[\text{Au}(\text{dppp})_2]^+$ spontaneously ionized undergo the growth with Au(0) atoms to form $[\text{Au}_6(\text{dppp})_4]^{2+}$ and $[\text{Au}_{11}(\text{dppp})_5]^{3+}$.

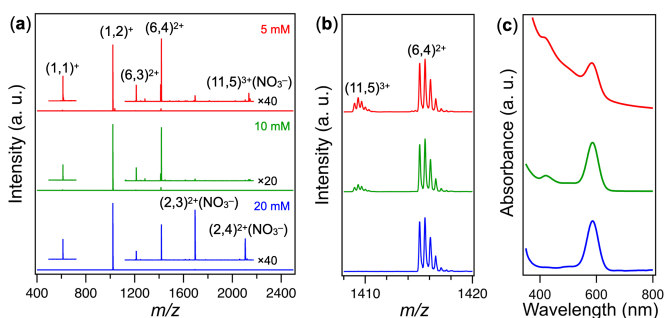


Figure 1. (a) Positive-mode ESI-mass spectra of the products with defined [dppp] and (b) enlarged view of panel (a). (c) UV-vis absorption spectra. Notation (a, b)^{q+} in (a) and (b) represents $[\text{Au}_a(\text{dppp})_b]^{q+}$.

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