Synthesis and Catalytic Performance Evaluation of New Magic-numbered Au_{69} Cluster Stabilized by Polyvinylpyrrolidone

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Gold nanoparticles stabilized by polyvinylpyrrolidone (Au:PVP) exhibit size-specific catalytic activity in alcohol oxidation. Activity appears as the diameter decreases below approximately 5 nm and increases as the diameter decreases to approximately 2 nm.[1] To reveal the size effects on catalysis in sub-2 nm region, our group has recently synthesized Au_{24}:PVP and Au_{38}:PVP with atomically precision by controlling reduction kinetics of Au(III) precursor.[2,3] We herein found that the size distribution could be tuned by the amount of base added to the Au(III) solution and discovered Au_{69}:PVP as a new magic-numbered cluster. The structures and oxidation catalysis of Au_{69}:PVP were compared with those of Au_{24}:PVP, Au_{38}:PVP, and Au nanoparticles.

A series of Au:PVP-*x* was prepared by mixing aqueous solutions of $NaAuCl_4$ containing *x* equivalent of NaOH (*x* = 0, 1.0, 1.5, 1.75, 2.0 or 3.0) and $NaBH_4$ in the presence of PVP using a micromixer. UV-vis absorption spectra of Au:PVP-*x* show a gradual increase in the intensity of the localized surface plasmon resonance band with increasing *x* (**Figure 1**), indicating that the particle size increases with *x*. Matrix-assisted laser desorption/ionization (MALDI) mass spectra of Au:PVP-*x* (**Figure 2**) indicated that the Au_{38} cluster was the main component for *x* = 1.0, whereas unprecedented Au_{69} cluster was obtained as the main product for *x* = 1.5 and 1.75. The gradual increase in the size of Au:PVP was also supported by the powder X-ray diffraction analysis and transmission electron microscopy. The size dependency of the catalytic activity for the benzyl alcohol oxidation will be discussed in the presentation.

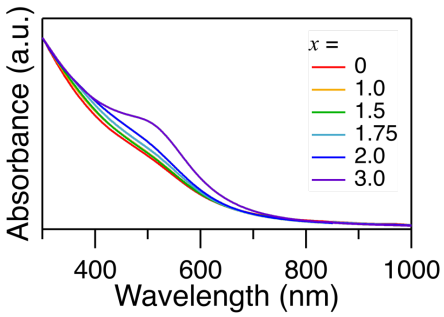

Figure 1. UV-vis spectra of Au:PVP-*x* in water.

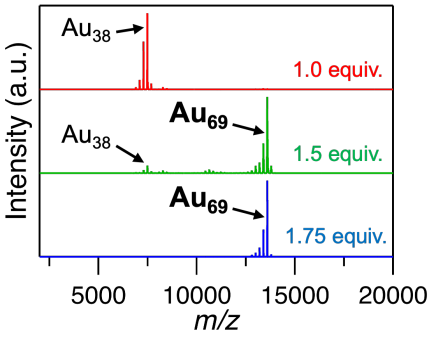

Figure 2. Negative-mode MALDI mass spectra of Au:PVP-*x* with *x* = 1.0, 1.5, and 1.75.

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