

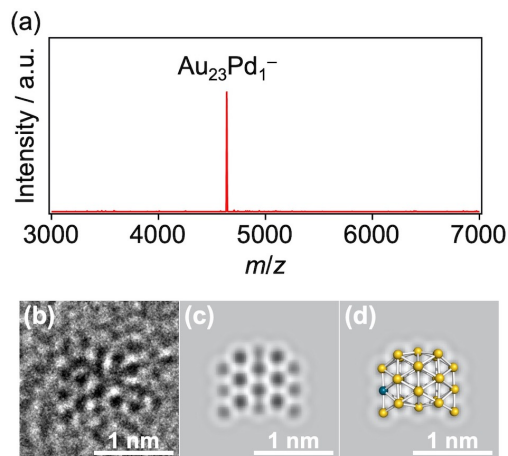
## Single Pd Atom Doping into Au<sub>24</sub> Cluster Stabilized by PVP: Synthesis, Structural Analysis, and Catalysis

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Gold clusters smaller than a critical dimension of ~2 nm exhibit size-specific catalysis for oxidation reactions.<sup>1</sup> Control of the size with atomic precision is essential for elucidating the origin and optimizing the catalysis. Recently, we have achieved atomically precise synthesis of an unprecedented magic number cluster, Au<sub>24</sub> stabilized by polyvinylpyrrolidone (Au<sub>24</sub>:PVP), by the kinetic control of cluster formation process.<sup>2</sup> In this study, we have successfully synthesized Au<sub>23</sub>Pd<sub>1</sub>:PVP by co-reduction method and revealed the geometrical structure of Au<sub>23</sub>Pd<sub>1</sub> and single Pd atom doping effect on catalysis.

Au<sub>23</sub>Pd<sub>1</sub>:PVP was prepared by mixing an aqueous solution of HAuCl<sub>4</sub> and Na<sub>2</sub>PdCl<sub>4</sub> (Au : Pd = 23 : 1) with that of NaBH<sub>4</sub> in the presence of PVP using a micromixer. Selective formation of Au<sub>23</sub>Pd<sub>1</sub> cluster was confirmed by MALDI mass spectrometry (**Figure 1a**). Curve fitting analysis of Pd K-edge EXAFS revealed that the coordination number of Pd–Au bond was  $6.1 \pm 0.7$ , indicating that the doped Pd atom was exposed on the cluster surface. As a result of structural search of bare Au<sub>23</sub>Pd<sub>1</sub> cluster by DFT calculations, several stable isomers with 6-coordinated Pd atoms were obtained and reproduced some of TEM images of Au<sub>23</sub>Pd<sub>1</sub>:PVP (**Figures 1b–d**). Au<sub>23</sub>Pd<sub>1</sub>:PVP exhibited significantly higher activity than undoped Au<sub>24</sub>:PVP for benzyl alcohol oxidation: the apparent activation energy was estimated to be  $45 \pm 2$  and  $56 \pm 3$  kJ mol<sup>-1</sup> for Au<sub>23</sub>Pd<sub>1</sub>:PVP and Au<sub>24</sub>:PVP, respectively. Kinetic isotope effect indicated that hydride elimination from the  $\alpha$ -carbon by cluster surface was rate-determining step for both catalysts. It was proposed that the Pd dopant located on the cluster surface acts as a reaction site for hydride elimination with reduced activation energy.



**Figure 1** (a) MALDI mass spectrum and (b) a representative TEM image of Au<sub>23</sub>Pd<sub>1</sub>:PVP. (c) Simulated TEM image and (d) model structure of Au<sub>23</sub>Pd<sub>1</sub>.

1) S. Yamazoe, K. Koyasu, T. Tsukuda, *Acc. Chem. Res.* **2014**, 47, 816. 2) S. Hasegawa, S. Takano, K. Harano, T. Tsukuda, *JACS Au* **2021**, 1, 660.