Structural stability originating from hierarchy of bond stiffness in thiolate-protected gold clusters

Metal nanoparticles (NPs) exhibit specific thermal properties and phase transition behaviors that are considerably different from the corresponding bulk metal [1]. For example, the melting point of a metal NP is significantly less than that of the bulk metal [2]. A crucial factor that governs thermal behaviors is the hierarchy of the bonding within NPs; metal–metal bonds on the surface are generally softer than those within the core. However, an atomic-level understanding of the effect of a variety of structural parameters on bond stiffnesses has not yet been attained because of the experimental difficulties in defining the atomic packing of a metal NP and the interfacial structure with the surrounding environment.

Recently, thiolate (RS)-protected gold clusters $Au_n(SR)_m$ with well-defined compositions have gained much attention as ideal platforms for studying the structure-property correlation and the size-dependent evolution of properties [3]. Among them, $Au_{25}(SR)_{18}$, $Au_{38}(SR)_{24}$, and $Au_{144}(SR)_{60}$ are representative systems that have been studied extensively. Single-crystal X-ray diffraction analysis and theoretical calculations showed that these clusters have an icosahedral-based gold core protected by $-SR-(Au-SR)_x-$ (x = 1 or 2) oligomers (Fig. 1). In addition, it has been identified that there are two classes of Au–Au bonds with different lengths (radial and lateral bonds) within the icosahedral cores (Fig. 1). The $Au_n(SR)_m$ clusters (n = 25, 38, 144) provide an ideal opportunity to study the hierarchy of the bond stiffness within Au clusters with well-defined atomic structures and surface modification.

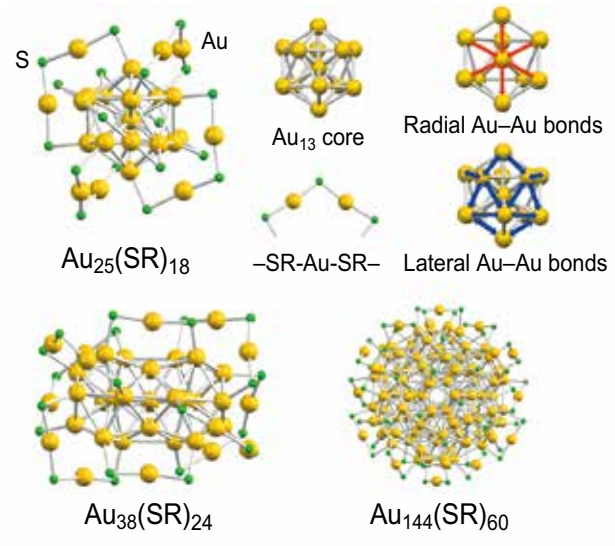

Fig. 1. Structures of $Au_{25}(SR)_{18}$, $Au_{38}(SR)_{24}$, and $Au_{144}(SR)_{60}$.

The stiffnesses of the Au–S and Au–Au bonds within $Au_{25}(PET)_{18}$, $Au_{38}(PET)_{24}$, and $Au_{144}(PET)_{60}$ (PET = PhC_2H_4S) were investigated by analyzing the temperature dependence of Au L_3-edge EXAFS (Extended X-ray Absorption Fine Structure) spectra recorded at SPring-8 **BL01B1** [4]. The temperature dependences of Debye-Waller (DW) factors for individual bonds were analyzed in the framework of the Einstein model, in which a metal cluster is treated as an ensemble of quantum harmonic oscillators. Figure 2(A) shows the Fourier-transformed (FT) EXAFS spectra of $Au_{25}(PET)_{18}$ measured at 300 and 8 K. The spectrum at 8 K exhibits a peak for the Au–Au bonds in the range of 2.1–3.0 Å together with a peak for Au–S bonds at 1.5–2.0 Å, whereas the peak for the Au–Au bonds is not discernible at 300 K. This temperature dependence suggests that the thermal fluctuation of the Au–Au bonds is larger that of the Au–S bonds. The curve fitting analysis of the FT-EXAFS spectrum at 8 K revealed that the Au–Au peak was composed of two components, corresponding to the radial and lateral Au–Au bonds in the icosahedral core. As shown in Fig. 2(A), the FT-EXAFS spectrum of $Au_{25}(PET)_{18}$ at 8 K was reproduced by a simulation using single crystal data.

Figure 2(B) shows the temperature dependence of the DW factor for each bond of $Au_{25}(PET)_{18}$. The DW values for both the radial and lateral Au–Au bonds increase monotonically with the temperature, whereas those of the Au–S bonds remain almost constant in the temperature range of 8–300 K. The Einstein temperature, θ_E, which is a measure of bond stiffness, was evaluated by fitting the temperature dependence of the DW factors (Fig. 2(B)). The θ_E values estimated for the Au–S and the radial and lateral Au–Au bonds were 429 ± 38, 137 ± 10, and 101 ± 4 K, respectively. This result indicates that the Au–S bond is the stiffest among them and that the radial Au–Au bonds are stiffer than the lateral ones in the gold core. Similar analysis was conducted for $Au_{38}(PET)_{24}$ and $Au_{144}(PET)_{60}$. The θ_E values of the Au–S and the radial and lateral Au–Au bonds were 416 ± 57, 153 ± 11, and 106 ± 15 K for $Au_{38}(PET)_{24}$, and 381 ± 45, 148 ± 11, and 128 ± 9 K for $Au_{144}(PET)_{60}$, respectively.

To the best of our knowledge, these results are the first experimental evidence of the hierarchy of the Au–Au bond stiffnesses in thiolate-protected Au clusters. The data indicate that thiolate-protected Au clusters can be viewed as “soft” icosahedral Au cores capped by “rigid” $-SR-(Au-S)_x-$ oligomers

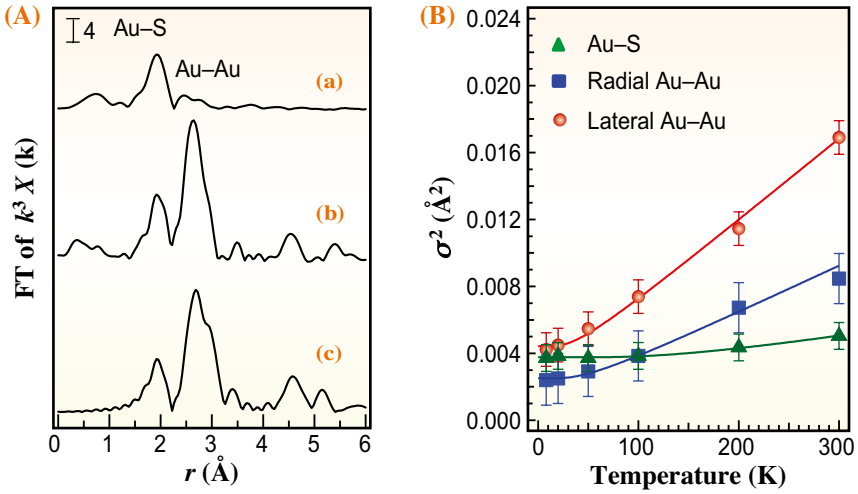

Fig. 2. **(A)** Au L_3-edge FT-EXAFS spectra of $Au_{25}(PET)_{18}$ measured at (a) 300 and (b) 8 K and (c) obtained by simulation. **(B)** Temperature dependences of the DW values for Au–S and radial and lateral Au–Au bonds of $Au_{25}(PET)_{18}$.

(Fig. 3(A)). Interestingly, the radial Au–Au bonds in the icosahedral core are stiffer than those of bulk gold (θ_E = 135 K) [5]. Similar inspection of the distribution of the stiff Au–Au bonds revealed that they are distributed not only in the center of the core but also on the surface of the core. The rigid ring structures are formed by bridging the stiff Au–Au bonds on the surface and the Au–S bonds (Fig. 3(B)). These rigid ring structures may act as frameworks to enhance the thermal stability of the thiolate-protected gold clusters.

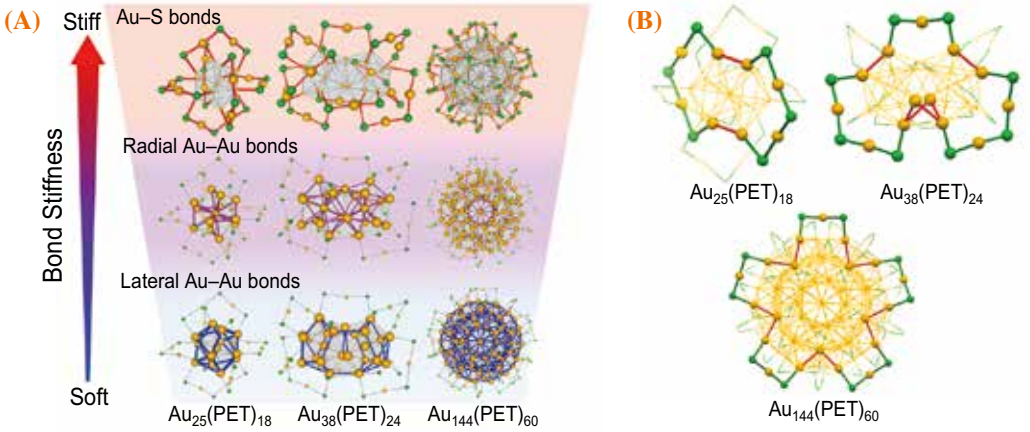

Fig. 3. **(A)** Hierarchy of bond stiffnesses and **(B)** rigid ring network structures in $Au_{25}(PET)_{18}$, $Au_{38}(PET)_{24}$, and $Au_{144}(PET)_{60}$.

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