Medium-sized $\text{Au}_{40}(\text{SR})_{24}$ and $\text{Au}_{52}(\text{SR})_{32}$ nanoclusters with distinct gold-kernel structures and spectroscopic features

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A communication is presented on the study of medium-sized Au40(SR)24 and Au52(SR)32 nanoclusters. The authors analyze the structures of these clusters and identify distinct gold-kernel structures and spectroscopic features. The study uses CO oxidation as a probe to examine the catalytic activities of the nanoclusters. The authors also discuss the potential applications of these nanoclusters in catalysis, nanotechnology, and biomedicine. The communication is published in the journal Nanoscale.
Vibrations, and is set to be 0.03 nm². The corresponding experimental setup and are set to be 0.1051967 nm and 1.01, respectively.

The calculated optical absorption spectra of Au₄₀(SR)₂₄ and Au₅₂(SR)₃₂ are found to be consistent with experimental measurements. Lastly, the catalytic properties of both clusters are examined by using CO oxidation as a probe.

Results and discussion

To understand the structure formation of Au₄₀(SR)₂₄ and Au₅₂(SR)₃₂, their kernel structures are analyzed first. The formation of the Au₃₄ kernel of Au₄₀(SR)₂₄ can be divided into two steps, with the Au₁₃ cuboctahedra as building blocks, as shown in Fig. 1. In step 1, the two Au₁₃ cuboctahedra interpenetrate each other to form a Au₂₀ structure by sharing six Au atoms. This rod-like Au₂₀ geometry has been found as a kernel in the structures of Au₃₆(SR)₂₄ and Au₅₂(SR)₃₂. In step 1 three Au₂₀ geometries interpenetrate each other to form an Au₃₄ structure. Next, the Au₅₂ structure interpenetrates with another Au₁₃ cuboctahedra to form a Au₂₅ geometry, a kernel found in the structure of Au₃₆(SR)₂₄. In step 3, the Au₄₄ kernel with fcc-like symmetry can be formed through two interpenetrating Au₂₅ geometries. The above structure analysis on the kernels of Au₄₀(SR)₂₄ and Au₅₂(SR)₃₂, as well as Au₃₄(SR)₂₀, Au₃₆(SR)₁₈, and Au₃₆(SR)₂₄ (ESI Fig. S1†), shows that the Au kernels of all these clusters with energy. The linear and quadratic synchronous transit (LST/QST) method is used to locate the transition state of CO oxidation on the Au₄₀(o-MBT)₂₄ and Au₅₂(TBBT)₃₂. In all calculations, the o-MBT in Au₄₀(o-MBT)₂₄, TBBT in Au₅₂(TBBT)₃₂, and the ligands of other RS-AuNPs are simplified by methyl groups to lower computation cost.

Computational methods

The theoretical powder X-ray diffraction (XRD) curve is calculated using the Debye formula:

\[ I(s) = \sum_i \sum_{j \neq i} \frac{\cos \theta}{\left(1 + \alpha \cos(2\theta)\right)} \exp \left(-\frac{B s^2}{2}\right) \frac{f_i f_j \sin(2\pi d_{ij})}{2\pi d_{ij}}, \]

where \( s \) is the diffraction vector length and \( \theta \) is the scattering angle, satisfying \( s = 2\sin \theta/\lambda \). \( \lambda \) and \( \alpha \) are determined by the experimental setup and are set to be 0.1051967 nm and 1.01, respectively. \( B \) is the damping factor, which reflects thermal vibrations, and is set to be 0.03 nm². The corresponding atomic numbers are used for the scattering factors \( f_i \). \( d_{ij} \) is the distance between atoms \( i \) and \( j \). The atomic distance \( d_{ij} \) is taken from the optimized structure of clusters based on the density functional theory (DFT) code DMol³ (version 7.0). The generalized gradient approximation with the Perdew–Burke–Ernzerhof (PBE)⁴¹ functional and the double numeric polarized (DNP) basis set coupled with semi-core pseudopotential are employed. Self-consistent calculations are done with a convergence criterion of \( 10^{-5} \) hartree for the total

Fig. 1. The formation of Au₃₄ kernel in Au₄₀(SR)₂₄. The Au atoms marked with the same number and color can be fused together.
fcc-like symmetry are comprised of several interpenetrating cuboctahedra.

Besides Au_{28}(SR)_{20}, Au_{30}S(SR)_{18}, Au_{36}(SR)_{24}, Au_{40}(SR)_{24}, and Au_{52}(SR)_{32}, structure analysis for the kernels of other RS-AuNPs such as Au_{25}(SR)_{18}, Au_{38}(SR)_{24}, Au_{102}(SR)_{44}, Au_{130}(SR)_{50}, and Au_{133}(SR)_{52} are presented in ESI Fig. S2 and S3.† Interestingly, according to different types of kernel structures, those crystallized RS-AuNPs larger than Au_{25}(SR)_{18} can be classified into three categories, as shown in Fig. 3: the first category includes Au_{28}(SR)_{20}, Au_{30}S(SR)_{18}, Au_{36}(SR)_{24}, Au_{40}(SR)_{24}, and Au_{52}(SR)_{32}, whose Au kernels possess fcc-like symmetry, are comprised of several interpenetrating cuboctahedra. The Au_{102}(SR)_{44} and Au_{130}(SR)_{50} nanoclusters in which the Au kernels possess Ino-decahedral (D_{5h}) symmetry can be grouped into the second category. The last category includes the remaining RS-AuNPs such as Au_{25}(SR)_{18} and Au_{133}(SR)_{52} with icosahedral Au kernels, and Au_{38}(SR)_{24} with a fused bicicosahedral kernel.

Simulated powder X-ray diffraction (XRD) curves of these crystallized RS-AuNPs exhibit different characteristic peaks for nanoclusters with different Au kernel structures. First, we confirm the reliability of the theoretical formula for computing the XRD curves by comparing the simulated XRD curves and the measured XRD curves of Au_{25}(SR)_{18} and Au_{38}(SR)_{24}, as shown in ESI Fig. S4.† Next, the XRD spectra of the RS-AuNPs in all three categories are presented in Fig. 4. From Fig. 4(a), one can see that the Au_{28}(SR)_{20}, Au_{30}S(SR)_{18}, Au_{36}(SR)_{24}, Au_{40}(SR)_{24}, and Au_{52}(SR)_{32} nanoclusters exhibit similar diffraction patterns, where a main peak is located at about 4.0 nm\(^{-1}\), and the two weaker peaks are located at 6.5 nm\(^{-1}\) and 7.5 nm\(^{-1}\), respectively. In the second category (Fig. 4(b)), the consistent XRD curves of Au_{102}(SR)_{44} and Au_{130}(SR)_{50} nanoclusters, where only one less pronounced peak is located at 7.7 nm\(^{-1}\), are significantly different from those in the first category. For the last category, as shown in Fig. 4(c), the diffraction pattern of the Au_{133}(SR)_{52} nanocluster, where four weaker peaks are located in the range 5–9 nm\(^{-1}\), differ from those of Au_{25}(SR)_{18} and Au_{38}(SR)_{24}. The multi-peak diffraction
pattern can be attributed to the multi-shell structure of the Au$_{133}$(SR)$_{52}$ nanocluster. The analysis above shows that the diffraction pattern is closely related to the structure of the Au kernel in RS-AuNP, which can offer clues to theoretical prediction of the structure of RS-AuNP even when the single crystal is lacking.

Fig. 5 presents the simulated UV/Vis optical absorption spectra of Au$_{40}$(SR)$_{24}$ and Au$_{52}$(SR)$_{32}$ based on the time-dependent DFT (TD-DFT) computation. In addition, the atomic orbital (AO) component of Kohn–Sham molecular orbitals is displayed. As shown in Fig. 5(a), the extrapolated optical band-edge of Au$_{40}$(SR)$_{24}$ is 1.1 eV, consistent with the measured optical gap. The extrapolated optical band-edge of Au$_{52}$(SR)$_{32}$ is 1.25 eV (Fig. 5(c)). The population analysis of Kohn–Sham (KS) molecular orbitals, as shown in Fig. 5(b) and (d), demonstrates that the occupied frontier molecular orbitals are mainly contributed from the Au(5d), denoted as the d band, while the Au(6sp) atomic orbitals show dominant contributions to the unoccupied orbitals (sp band). The feature absorption peaks can therefore be assigned to the d $\rightarrow$ sp interband transition.

Finally, the catalytic properties of Au$_{40}$(SR)$_{24}$ and Au$_{52}$(SR)$_{32}$ are examined by using CO oxidation as a probe. To this end, a few surface staple motifs on the clusters are removed to allow for the catalytic reaction. The computed catalytic reaction pathway for CO oxidation on the Au$_{40}$(SR)$_{24}$ cluster is shown in Fig. 6(a). CO and O$_2$ are coadsorbed initially with a binding energy of $-1.76$ eV. Then the O$_2$ molecule moves toward the adsorbed CO molecule to form a bridge-like metastable intermediate state characterized by the O–C–O–O species with the
Conclusions

We have performed a systematic structure analysis of two medium-sized \( \text{Au}_{40}(\text{SR})_{24} \) and \( \text{Au}_{52}(\text{SR})_{32} \) nanoclusters. We find that the kernel structures of both nanoclusters can be viewed as several interpenetrating cuboctahedra. Based on this observation, we suggest classification of the crystallized RS-AuNPs into three groups according to their kernel structures. In the first group, Au kernels of RS-AuNPs such as \( \text{Au}_{28}(\text{SR})_{20} \), \( \text{Au}_{10}S-\text{SR}_{18} \), \( \text{Au}_{16}(\text{SR})_{24} \), \( \text{Au}_{40}(\text{SR})_{24} \), and \( \text{Au}_{52}(\text{SR})_{32} \) exhibit fcc-like symmetry, comprising several interpenetrating cuboctahedra. In the second group, Au kernels of RS-AuNPs such as \( \text{Au}_{102}(\text{SR})_{44} \) and \( \text{Au}_{130}(\text{SR})_{50} \) possess icosahedral \( (I_{h}) \) symmetry. The third group includes \( \text{Au}_{25}(\text{SR})_{18} \), \( \text{Au}_{133}(\text{SR})_{52} \) with icosahedral Au kernels, or \( \text{Au}_{16}(\text{SR})_{24} \) with a fused icosahedral Au kernel. Clusters in each group give rise to distinct diffraction patterns, thereby providing important clues for the theoretical prediction of the structure of RS-AuNPs as long as the XRD data are known. We have also computed the UV/Vis absorption spectra and Kohn–Sham orbital energy level diagrams for \( \text{Au}_{40}(\text{SR})_{24} \) and \( \text{Au}_{52}(\text{SR})_{32} \). Our calculation indicates that the first absorption peak can be assigned to the \( d \rightarrow sp \) interband transition. Examination of the catalytic properties of \( \text{Au}_{40}(\text{SR})_{24} \) and \( \text{Au}_{52}(\text{SR})_{32} \) suggests that both clusters can be stand-alone nanoscale catalysts for CO oxidation.

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References
