Structural patterns at all scales in a nonmetallic chiral Au$_{133}$(SR)$_{52}$ nanoparticle

Chenjie Zeng,† Yuxiang Chen,† Kristin Kirschbaum,‡ Kannatassen Appavoo,§ Matthew Y. Sfeir,∥ Rongchao Jin*†

Structural ordering is widely present in molecules and materials. However, the organization of molecules on the curved surface of nanoparticles is still the least understood owing to the major limitations of the current surface characterization tools. By the merits of x-ray crystallography, we reveal the structural ordering at all scales in a super robust 133–gold atom nanoparticle protected by 52 thiolate ligands, which is manifested in self-assembled hierarchical patterns starting from the metal core to the interfacial –S–Au–S– ladder-like helical “stripes” and further to the “swirls” of carbon tails. These complex surface patterns have not been observed in the smaller nanoparticles. We further demonstrate that the Au$_{133}$(SR)$_{52}$ nanoparticle exhibits nonmetallic features in optical and electron dynamics measurements. Our work uncovers the elegant self-organization strategies in assembling a highly robust nanoparticle and provides a conceptual advance in scientific understanding of pattern structures.

INTRODUCTION

The atomic structure of nanoparticles is of paramount importance because many applications (such as catalysis and biomedicine) and fundamental studies of quantum size effect in ultrasmall nanoparticles require structural details at the atomic level (1–3). Thus, significant research efforts have been put forth to uncover the structure of nanoparticles (4–7). Among the different types of nanoparticles, gold nanoparticles protected by thiolate ligands (–SR) serve as a paradigm system and constitute an important platform for nanotechnology. Novel nanomaterials with different functionalities are created through manipulating the surface structure of gold nanoparticles (8–11). In recent years, great advances have been made in controlling the quality of thiolate-protected gold nanoparticles (5, 6, 12, 13), and the syntheses of such nanoparticles have reached atomic precision, with a series of reported magic sizes ranging from tens to hundreds of gold atoms (7, 14–16). Such advances have led to total structure determination of a few magic-sized nanoparticles by x-ray crystallography (3, 6, 17–19). The crystal structures provide valuable information on the structural construction and evolution rules in the gold nanoparticles with dozens of gold atoms, and also shed light on the structure of the gold-thiolate interface, which had been sought for decades (20). However, since the first report of the Au$_{102}$(p-MBA)$_{44}$ structure (where p-MBA = SPb-p-COOH) (6), it still remains a daunting task to elucidate even larger structures of gold nanoparticles—which are critically important to understand the growth pattern, surface structural ordering, and the emergence of metallic properties.

Here, we report the hitherto largest crystallographic structure of a chiral gold nanoparticle having 133 gold atoms and 52 surface-protecting thiolate ligands. The Au$_{133}$(SR)$_{52}$ nanoparticle (where R = SPb-p-Bu$^1$ and the same hereafter) exhibits aesthetic orderings from the gold kernel to the Au–S interface to the carbon tails of thiolates, with a kaleidoscope of patterns at the atomic, molecular, and ensemble scales: (i) the gold kernel follows a shell-by-shell growth pattern, forming a quasi-spherical Au$_{107}$ kernel comprising a Au$_{55}$ two-shelled icosahedron and a third Au$_{52}$ transition shell; (ii) the gold-thiolate interface exhibits a helical “stripe” pattern in which the S–Au–S motifs stack into ladders in the curved space; (iii) the carbon tails of thiolates further form “swirl” patterns that are different from the underlying S–Au–S stripe patterns; (iv) the ensemble packing of nanoparticles gives rise to a triclinic single crystal.

The icosahedron-based gold kernel illustrates shell-by-shell growth at the atomic scale and constitutes a smaller counterpart of the 20-fold twinned icosahedral gold nanoparticle observed under an electron microscope (21). The resolved –S–Au–S– helical stripes provide the first crystallographic proof for the formation of self-assembled monolayer (SAM) structures on the curved surface of nanoparticles (10) and offer clues to the SAMs on flat surfaces (22). The –S–Au–S– helical stripes, together with carbon-tail swirls on the spherical gold kernel, also illustrate the unique patterning in the curved space, reminiscent of the twist of ropes, capsids of viruses, and the “hairy ball theorem” (10, 23–25). These self-assembled hierarchical patterns in the chiral Au$_{133}$(SR)$_{52}$ nanoparticle have not been observed in the previously reported gold nanoparticle structures, which were not large enough to support the extended patterning structures. The observed structural features in Au$_{133}$(SR)$_{52}$ demonstrate nature’s patterning strategies in fabricating large and robust nanostructures. The Au$_{133}$(SR)$_{52}$ nanoparticle can be viewed as a transitional state in geometric structure from small nanoclusters toward large nanoparticles.

RESULTS AND DISCUSSION

The magic-sized Au$_{133}$(SR)$_{52}$ nanoparticle was obtained via a thermal reaction of molecularly pure Au$_{444}$(SCH$_2$CH$_2$Ph)$_{100}$ nanoparticles (26) with excess 4-tert-butylibenzene at 80°C for 4 days (see Supplementary Materials for details). The Au$_{133}$(SR)$_{52}$ nanoparticles crystallized in space group P1; the final anisotropic (Au and S atoms) refinement converged at R$_1$ = 8.65% for the observed data (tables S2 to S4). Figure 1 shows the total structure of an enantiomer of the Au$_{133}$(SR)$_{52}$ nanoparticle and packing of the racemic pair in the crystal. The diameter

1 Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA 15213, USA.
2 College of Natural Sciences and Mathematics, University of Toledo, Toledo, OH 43606, USA.
3 Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY 11973, USA.
*Corresponding author. E-mail: rongchao@andrew.cmu.edu

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of the entire nanoparticle (including the ligand shell) is ~3.0 nm, with the metal core diameter being ~1.7 nm. The Au133(SR)52 nanoparticle is charge-neutral, evidenced by electrospray ionization mass spectrometry analysis; thus, cesium acetate was added to form positively charged cesium adducts of the Au133(SR)52 nanoparticle \((15)\). Two strong peaks at mass/charge ratio \(m/z = 17,528.3\) and 11,729.9 are observed (fig. S1), corresponding to \([\text{Au}_{133}(\text{SR})_{52} + 2\text{Cs}]^{2+}\) (expected \(m/z = 17,528.20\), deviation: 0.1) and \([\text{Au}_{133}(\text{SR})_{52} + 3\text{Cs}]^{3+}\) (expected \(m/z = 11,729.77\), deviation: 0.13); that is, the nanoparticle's intrinsic charge is zero.

The 133 gold atoms in the nanoparticle are distributed in four shells, that is, one central atom with successive shells of 12, 42, 52, and 26 gold atoms (Fig. 2A to D). The central atom and the first shell form a 13-atom icosahedron (Fig. 2A), which is enclosed by a second 42-atom icosahedral shell (Fig. 2B, gray), forming the 55-atom Mackay icosahedron \((\text{Au}_{55}-\text{MI})\) \((27)\). The \(\text{Au}_{55}-\text{MI}\) can be viewed as 20 tetrahedral units joined together with a common vertex (that is, the center) through sharing three adjacent facets. The gold atoms in each tetrahedral unit are assembled in a layered \(a-b-c\) manner (Fig. 2, E and F, green-pink-gray), that is, cubic close-packing. This is indeed the first observation of the icosahedral \(\text{Au}_{55}\) motif, which has long been sought since Schmid et al. reported phosphine-protected \(\text{Au}_{55}\) nanoparticles in 1981 \((28)\).

The third shell serves as a transition layer between the \(\text{Au}_{55}-\text{MI}\) and the surface layer and is largely dictated by the surface. This shell is constructed through capping the 20 exposed triangular (111) facets of \(\text{Au}_{55}-\text{MI}\) (Fig. 2C), with 16 facets each capped by three gold atoms in an \(a-b-c\) manner (Fig. 2E, capping atoms highlighted in cyan) and the remaining four facets each capped by only one gold atom in an \(a-b\) manner (Fig. 2F, capping atom in blue), hence totaling 52 gold atoms in this third shell. The 52 gold atoms actually provide the “foot-holds” for the 52 thiolate ligands. Overall, the 107 gold atoms in the first three shells constitute a nearly perfect sphere with a diameter of 14 Å (atomic-center-to-center distance). The Au-Au bond lengths between successive shells (that is, radial bonds) and within each shell (that is, transverse bonds) are listed in table S1. The radial bonds \((r)\) are shorter than the transverse bonds \((a)\); for example, the average bond length between the central gold atom and the first shell is \(r = 2.760 \pm 0.008\) Å, whereas the bond length within the first icosahedral shell is \(a = 2.920 \pm 0.035\) Å. Their ratio (that is, \(2.760/2.920 = 0.945\)) closely matches the geometry requirement \((r = 0.95a)\) of an icosahedron.

The fourth gold shell contains 26 gold atoms, which combine with 52 thiolate ligands to form the surface of the \(\text{Au}_{133}(\text{SR})_{52}\) nanoparticle (Fig. 2D). The surface gold atoms and thiolates are organized into 26 \(-\text{S+Au-S}\) staple motifs. The 52 thiolates terminate the 52 gold atoms of the third shell in a one-on-one manner (Fig. 2G), that is, \(26 \times 2 = 52\) sites. The surface-protecting monomeric staples require that the underlying foothold Au-Au distance \((4.872 \pm 0.377\) Å) roughly matches with the span of the staple, that is, twice the \(\text{Au}_{55}-\text{MI}\) bond length \((2 \times 2.319 \pm 0.023\) Å). Together, the \(\text{Au}_{133}(\text{SR})_{52}\) nanoparticle can be divided into \([\text{Au}_{117}\text{Au}_{12}\text{Au}_{42}\text{Au}_{52}]^{2+}\).

The monomeric staples \((-\text{S+Au-S}\) ) are self-assembled into aesthetic “helical stripes” on the spherical surface of the \(\text{Au}_{107}\) kernel (Fig. 3). Each stripe comprises six staples that are parallel to each other and form a ladder-like helix with a width of ~4.9 Å (Fig. 3, A and C). The four helices emanate from one pole of the globular
Au$_{107}$ kernel and coil up like a four-stranded rope (24) and converge at the other pole (Fig. 3, B and C). The clockwise and anticlockwise rotations of the four helices give rise to chirality in the Au$_{133}$(SR)$_{52}$ nanoparticle (that is, the left- and right-handed isomer pair in the unit cell; Figs. 1B and 3D). Such a self-organized helical -S–Au–S– stripe pattern on the surface of a nanoparticle is remarkable. It provides the first crystallographic evidence that highly ordered patterns of staple motifs can form on the extended curved surface of nanoparticles. This is in contrast to the smaller Au$_{102}$(p-MBA)$_{44}$ structure (6), in which the -S–Au–S– motifs do not form such an ensemble pattern. It is worth noting that rectangular stripes (rather than helical stripes) were previously observed on flat gold film by scanning tunneling microscopy (STM) (22). Also, Jackson et al. reported ripple-like stripe domains on mixed-thiolate monolayer-protected gold nanoparticles through STM analysis (10, 29).

The crystallographically characterized helical stripe patterns of -S–Au–S– motifs provide more insight into those systems.

Resolving every thiolate ligand by x-ray crystallography allows us to further examine the arrangement of the Ph-p-Bu' carbon tails on the spherical surface. Surprisingly, the carbon tails do not adopt the same helical stripe pattern as that of the underlying -S–Au–S– motifs; that is, the orientation of carbon tails do not follow the all-cis or all-trans conformation in each -S–Au–S– stripe. Instead, the tails tend to self-organize into multiple swirls in accord with the spherical surface of the nanoparticle (Fig. 4A), and each swirl consists of four rotatively arranged phenyl rings (Fig. 4B). Such a twisted arrangement of phenyl rings in Au$_{133}$(SR)$_{52}$ is in contrast with the preferred parallel stacking of phenyl rings of p-MBA (that is, SPH-p-COOH) ligands in Au$_{102}$(p-MBA)$_{44}$ (6). The swirly arrangement of phenyl rings can be attributed to the combined effects of spherical surface and bulky tert-butyl substituents and is a more compact packing mode compared to the parallel stacking of phenyl rings. It is worth noting that self-assembly of carbon tails of the ligands on the Au$_{133}$ surface also induces chirality (Fig. 4A), but the chiral pattern is different from that formed by the -S–Au–S– motifs (that is, swirls versus helices). The surface patterns of both the helical ladders of -S–Au–S– motifs and the swirly distribution of carbon tails destroy the perfect symmetry of the spherical gold kernel and may act as specific reaction sites for functionalization (10, 30).

The extraordinary stability of the Au$_{133}$(SR)$_{52}$ nanoparticle is largely attributed to its highly ordered geometric structure. The hierarchical patterning from the inner gold core to the surface ligand shell minimizes the internal stress of the nanoparticle. Furthermore, the proper arrangement of the staple motifs and carbon tails provides full protection of the Au$_{133}$ nanoparticle’s surface from attack by excess thiols or other chemicals. In terms of the electronic factor, the Au$_{133}$(SR)$_{52}$ nanoparticle has 81 valance electrons (that is, 133 – 52 = 81), which is an odd number and does not match with the superatom series (for example, 2, 8, 18, 58, 92...). As the size of nanoparticles increases and the spacing between the electronic orbitals decreases, the geometric effect will contribute more to the stability of nanoparticles than the electronic effect (7).

To probe whether the Au$_{133}$(SR)$_{52}$ nanoparticle is in the metallic state, we performed ultraviolet-visible (UV-vis) absorption and femtosecond transient optical measurements. The Au$_{133}$(SR)$_{52}$ nanoparticles exhibit a highly structured UV-vis spectrum with absorption bands at 336, 421, 503, and 712 nm (Fig. 5A), being distinctly different from the single plasmon band (for example, at ~520 nm) of metallic-state spherical nanoparticles. Thus, Au$_{133}$(SR)$_{52}$ nanoparticles are nonmetallic in nature, which is further supported by femtosecond broadband transient absorption measurements. Upon photoexcitation above the optical gap, we observe three primary transient optical features (Fig. 5B), including a net bleach near 500 nm and two net positive features of excited-state absorption at ~580 and

Fig. 2. The four-shell structure of Au$_{133}$(SR)$_{52}$. (A to D) The first icosahedral shell with 12 Au atoms (pink) (A); second icosahedral shell with 42 Au atoms (gray) (B); third shell with 52 Au atoms (blue and cyan) (C); fourth shell with 26 Au atoms (orange) and 52 sulfur atoms (yellow) (D). (E) Layered a-b-c-b packing of Au atoms in a tetrahedral unit of an icosahedron; total of 16 such units. (F) a-b-c-a packing of atoms; total of four such units. (G) Monomeric –SR–Au–SR– motifs clamping on the third shell gold atoms. Carbon groups are omitted for clarity.
640 nm (Fig. 5B, lower panel). The bleach at 500 nm correlates to the ground-state transition at 503 nm observed in Fig. 5A. The other ground-state transition observed at 712 nm is superimposed on the excited-state absorption features such that no net negative signal can be seen. These overlapping contributions cannot be rigorously separated (for example, using global analysis) because identical kinetics are observed at all wavelengths in our data set. This is illustrated in the right panel of Fig. 5B, where decay kinetics at each wavelength are plotted.

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**Fig. 3.** Self-assembled $-S$-$Au$-$S$– helical stripes on the spherical Au$_{107}$ kernel. (A and B) Side views. (C and D) Top views. The two chiral isomers are shown in (D). Each stripe is composed of six monomeric staples stacked into a ladder-like helical structure. Yellow: sulfur; orange/red/blue/green: gold in the helices; purple: gold in the independent monomeric staples.

**Fig. 4.** Chiral self-assembly of the carbon tails of the SPh-$p$-Bu$^1$ ligands. (A) The rotative arrangement of phenyl rings results in the formation of fourfold swirls. (B) Carbon-tail swirls on the square unit; top: left-handed isomer; bottom: right-handed isomer. Yellow: sulfur.
of the three primary transient features can be globally fit with just two time constants (~2.8 and ~30 ps). The absence of more complex spectral dynamics suggests that a single electronic configuration is responsible for all of the resolvable transient features. This is in contrast with the expected dynamics for a metallic-state nanoparticle (31, 32).

All of the observed relaxation dynamics are independent of laser fluence, in sharp contrast to metallic noble metal nanoparticles (33). Normalized kinetic traces measured at either the bleach (500 nm) or the excited-state absorption features (580 nm, Fig. 5C) can be superimposed over an absorbed fluence range of 12 to 192 μJ/cm². Both the faster (~2.8 ps) and slower components (~30 ps) of the biexponential decay are found to be independent of pump fluence and pump wavelength (Fig. 5D). These results significantly differ from the traditional carrier relaxation processes in metallic-state nanoparticles, where carrier cooling is described by the two-temperature model (31, 33). Within this model, the rate of thermal equilibration between the electronic and lattice subsystems is described by a constant electron-phonon coupling term, such that an increase of the electronic temperature (at high laser fluence) results in a longer relaxation time. Together, our results suggest that despite its relatively large size, the unique structure of the Au_{133}(SR)_{52} nanoparticle delays the onset of metallic behavior.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/1/2/e1500045/DC1

Materials and Methods

Fig. S1. Electrospray ionization mass spectrum of Au_{133}(SR)_{52} nanoparticles.

Table S1. Au-Au bond lengths in the Au_{107} kernel.

Table S2. Sample and crystal data for Au_{133}.

Table S3. Data collection and structure refinement for Au_{133}.

Table S4. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å²) for Au_{133}.

Fig. 5. Optical properties of Au_{133}(SR)_{52} nanoparticles. (A) The dashed lines represent peak positions extracted from fitting to a series of inhomogeneously broadened transitions and a nonresonant scatter background. (B) Image plot of transient absorption data with optical pumping at 420 nm, along with representative kinetics (absolute value) at wavelengths corresponding to the dashed lines in the image plot (right panel) and transient spectra (bottom panel) at 1 ps. (C and D) Normalized decay kinetics as a function of laser fluence with 500-nm pump pulses (C) and extracted values of the rate constant for the faster decay component of a two-exponential fit showing the fluence independence of the carrier dynamics (D).
REFERENCES AND NOTES


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