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# Experimental Evidence of Chiral Gold Nanowires with Boerdijk-Coxeter-Bernal Structure by Atomic-Resolution Imaging

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The assembly of chiral crystals from highly symmetric atoms, i.e., the origin of chirality, is of fundamental importance. Bulk crystals with chiral point groups are known, but they rarely exhibit overall chiral morphology or asymmetric surface chemistry.[1] As the size of crystal domains decrease to nanoscale, however, chiral morphology can sometimes arise (often in nanowires).[2] In contrast to the packing of chiral molecules, the atomic packing in metal is always highly symmetric and thus, more interesting when forming chiral structures. To date, there are only a few cases of chiral metal nanocrystals, all in the form of nanowires (NWs),[2] whereas most of the metallic NWs reported in the literature are achiral, as dictated by their intrinsic lattice symmetry.

Here, we report ultrathin Au NWs with an atomic packing mode that is different from all known literature examples. The Au atoms are densely packed in these NWs, forming a straight but overall chiral structure. The NWs are the close representation of single-strand *Boerdijk-Coxeter-Bernal* (BCB) *tetrahelix* in atomic packing.[3] Their chiral atomic structure and morphology are characterized in detail. Combining in-situ electron microscopy with theoretical simulations, we show that the surface ligands play a key role in stabilizing the unusual nanocrystals. Such a structure establishes a direct relationship between dense packing and chirality, and represents an excellent example for the rich variety of unusual lattices at the nanoscale.

As a mathematic model of 1D chiral structure, *tetrahelix* is constructed by linear stacking of regular tetrahedra (Figure. 1c). The orientations of the tetrahedral units vary continuously along the helix, without following any strict periodicity. Specifically, each tetrahedron has a $(1/\sqrt{l}0)L$ advance ($\Delta x$) and a 131.81° rotation angle with respect to the adjacent tetrahedron along the screw axis (Figure 1d). Thus, eleven successive tetrahedra constitute one approximate helical turn, but the orientation of the twelfth tetrahedron has a sizeable redundant angle of 9.9° ($\theta = 131.81° \times 11 - 8\pi$) relative to the first. In our constructed BCB Au NW model, each tetrahedron is made of about 12 layers of densely packed Au atoms. Depending on the stacking orientation, *tetrahelix* appears as either a left-handed spiral or a right-handed one. Experimentally, we synthesized ultrathin (d = 3-7 nm) Au NWs using a seed-mediated substrate growth method. These NWs were typically polycrystalline with different lattice orientations. To our great interest, a radical change of morphology occurred when we pushed for the thinnest NWs with a lowest diameter limit of ~ 3 nm. When this size was reached, the Au NWs became chiral with the BCB-type structure. Briefly, ligand-stabilized Au seeds (d = 3-5 nm) were anchored on a pre-functionalized $Si/SiO_2$ wafer substrate. The Au NWs were further grown *via* chemical reduction.

High-resolution transmission electron microscopy (HRTEM) was employed to investigate the structure of the NWs. Figure 1a shows an HRTEM image of a single Au NW. Successive edge-sharing triangular domains with lattice fringes are observed at the right part of the image (the highlighted area), which resemble the projection of 1D stacked tetrahedra with gradually twisted orientations. To compare with a possible BCB helical structure, we constructed a model BCB helix by stacking {111} faceted Au tetrahedra with an edge length ($L$) of 3.2 nm (i.e., each tetrahedron is composed of 12 layers of Au atoms with a face-centered cubic (f.c.c.) arrangement), and simulated its HRTEM images of different orientations with different defocus conditions. When the model helix was oriented as illustrated in Figure 1c with the long axis having a small deviation angle of 5° from the horizontal and a defocus value of -35 nm was applied, the simulated image showed lattice fringes closely resembling the observed ones (Figure 1b). The similarity is further confirmed by comparing their corresponding fast Fourier transforms (FFTs, insets of Figures 1a and 1b). The left part of the HRTEM image seems slightly out of focus, likely due to the bending of the ultra-thin NWs. The above observations demonstrate that the structural features of our Au NWs essentially match the model of the BCB helix.

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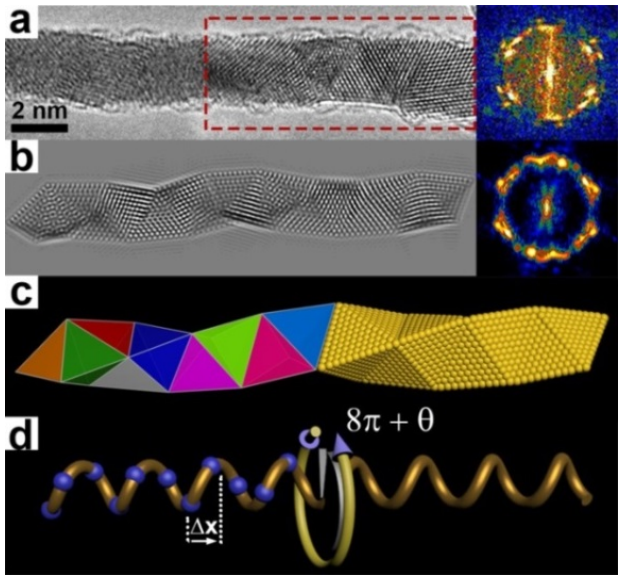


**Figure 1.** a) Experimental and b) simulated HRTEM image of a single BCB-structured Au NW (Δf = -35 nm). In the right are the corresponding FFTs. c) Topological (left) and atomic (right) models of a BCB helix. d) Schematic illustration of the pseudo periodicity of BCB helix. Blue dots represent the mass centers of the tetrahedral units, illustrating their position and orientation relationship. Δx is the advance of each tetrahedron along the screw axis with respect to its neighbor; $8\pi + \theta$ is the total rotation angle of eleven successive tetrahedra that constitute one approximate helical turn (θ refers to the orientation difference between the twelfth tetrahedron and the first).

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