Supplementary Figure S1 | X-ray diffraction pattern of the Ag nanowires shown in Fig. 1a dispersed in their original solution. The wavelength of the x-ray beam was 0.1771 Å. The saturated broad peak and the sloped background were due to the solvent and the quartz cuvette in which the dispersion of Ag nanowires was stored. As highlighted in the inset, the relative intensities between the (220) and (202)/(022) reflections are different from that shown in Fig. 1. The discrepancy is due to the high morphological anisotropy of the Ag nanowires. The longitudinal axis of each nanowire is along the [011] crystalline direction. When the dry Ag nanowires are deposited on a substrate, the orientations of all the {110} planes cannot be equally distributed due to the high aspect ratios of the nanowires. As a result, the relative diffraction intensities of the (220), (202), (022) reflections exhibit variations in comparison with the standard powder diffraction pattern. On the other hand, the Ag nanowires dispersed in a liquid solution randomly orient along different directions, leading to a diffraction pattern consistent with the standard pattern (red curve in Fig. 1d).
Supplementary Figure S2 | X-ray diffraction patterns of Ag nanowires synthesized via different methods. (a) Fivefold multiply-twinned (MT) Ag nanowires with diameter of ~50 nm that were synthesized through the same method used for the nanowires shown in Fig. 1 except for a lower concentration of AgNO₃. (b) Fivefold MT Ag nanowires with diameter of ~110 nm that were synthesized through the same method used for the nanowires shown in Fig. 1 except that Fe(acac)₃ was replaced with Fe(NO₃)₃. (c) Fivefold MT Ag nanowires with diameter of ~60 nm that were synthesized through the reduction of AgNO₃ with glycerol in the absence of iron species [see the reference: Adv. Mater. 23, 3052-3056 (2011)]. All the Ag nanowires exhibit the face-centered tetragonal (f.c.t.) phase. The splitting degree of the (200)/(020) and (002) reflections is dependent on the diameter of the nanowires and the synthetic methods.
Supplementary Figure S3 | Transmission electron microscopy (TEM) images of Ag nanocubes with an average size of 35 nm. The high-resolution TEM image in b clearly shows the single crystallinity of the nanocubes and defect-free lattice. According to the square symmetry of the lattice fringes, their surfaces can be determined to be bounded with \{100\} crystalline faces.
Supplementary Figure S4 | X-ray diffraction patterns of Ag nanocubes with different sizes. (a) Nanocubes with an average size of 35 nm as shown in Supplementary Figure S3. (b) Nanocubes with an average size of 120 nm. The wavelength of the x-ray beam was 0.42460 Å. The blue curves are the fitted results on the basis of the standard face-centered cubic (f.c.c.) phase with a correction of size-dependent broadening. The perfect matching between the fitting results and the measurement x-ray diffraction patterns indicates that defect-free Ag nanocubes are crystallized in f.c.c. phase regardless of their sizes. The peak indices correspond to the f.c.c phase of Ag.
Supplementary Figure S5 | Crystalline unit cells of face-centered cubic (f.c.c.), face-centered tetragonal (f.c.t.), and body-centered tetragonal (b.c.t.) phases and their relationship.
Supplementary Figure S6 | Transmission electron microscopy (TEM) and electron diffraction (ED) characterization of Ag nanowires shown in Fig. 1a. (a) TEM image of randomly assembled Ag nanowires on a TEM grid. (b) ED pattern of a nanowire corresponding to the superposition of $<110>$ (highlighted with yellow lines) and $<111>$ (highlighted with red lines) zone axes. (c) ED pattern of a nanowire corresponding to the superposition of $<100>$ (highlighted with green lines) and $<112>$ (highlighted with blue lines) zone axes.
Supplementary Figure S7 | Scanning electron microscopy image of the back side (i.e., the copper mesh side) of a transmission electron microscopy grid with Ag nanowires after the cross-sectional samples were prepared with the assistance of focused ion beam. The red arrows highlight the nanowires that were cut along the surfaces at 45° with respect to the longitudinal axes of the nanowires.
Supplementary Figure S8 | Enlarged electron diffraction pattern of the one shown in Fig. 3e. All the (111) reflection spots between the two red circles exhibit clear splitting although the splitting levels for different spots are different.
Supplementary Figure S9 | Transmission electron microscopy image and electron nanodiffraction patterns at different positions along the twin planes. The numbers represent the positions where the electron beam was located. The intensity profiles of the 222 reflection spots show their splitting degrees displayed in reciprocal space (nm⁻¹). The difference between the two diffraction patterns along the same twin plane at different positions shows that the 222 reflect spot recorded from the core region exhibits larger splitting in comparison with the spot recorded from the surface region, indicating that the core of the nanowire has higher strain than its surface region.
Supplementary Figure S9 (continued) | Comparison of electron diffraction patterns (left) and intensity profile of the 222 reflection spots along the straight lines shown in the electron diffraction patterns (right) at positions #1 and #2.
**Supplementary Figure S9 (continued)** | Comparison of electron diffraction patterns (left) and intensity profile of the 222 reflection spots along the straight lines shown in the electron diffraction patterns (right) at positions #3 and #4.
Supplementary Figure S9 (continued) | Comparison of electron diffraction patterns (left) and intensity profile of the 222 reflection spots along the straight lines shown in the electron diffraction patterns (right) at positions #5 and #6. The existence of more than 2 peaks in the intensity profile curve of position #6 indicates that there are more than two crystalline domains at position #6.
Supplementary Figure S9 (continued) | Comparison of electron diffraction patterns (left) and intensity profile of the 222 reflection spots along the straight lines shown in the electron diffraction patterns (right) at positions #7 and #8.
Supplementary Figure S9 (continued) | Comparison of electron diffraction patterns (left) and intensity profile of the 222 reflection spots along the straight lines shown in the electron diffraction patterns (right) at positions #9 and #10.
Supplementary Figure S10 | Scanning electron microscopy images of the cross-sectional samples prepared by focused ion beam.
Supplementary Figure S11 | Transmission electron microscopy (TEM) image of cross-sections of different nanowires shown in Supplementary Figure S10 and their corresponding electron diffraction (ED) patterns. The cross sections shown in different images were made from different nanowires. The variation of the profiles of the cross sections is due to the difference between different nanowires. All the ED patterns show the splitting of the (111) reflection spots which are between the red circles. This figure corresponds to the wire #1 shown in Supplementary Figure S10.
Supplementary Figure S11 (continued) | This figure corresponds to the wire #2 shown in Supplementary Figure S10.
Supplementary Figure S11 (continued) | This figure corresponds to the wire #3 shown in Supplementary Figure S10.
Supplementary Figure S11 (continued) | This figure corresponds to the wire #4 shown in Supplementary Figure S10.
Supplementary Figure S12 | Characterization of Ag-Au alloy nanotubes that were synthesized through the galvanic replacement reaction between the Ag nanowires shown in Fig. 1a and an aqueous solution of HAuCl₄ at 100 °C. (a) Scanning electron microscopy (SEM) image of the nanotubes. The open nanotubes clearly show the fivefold symmetry as same as that of the Ag nanowires. The small dots on the surfaces of the nanotubes correspond to AgCl nanoparticles and the Ag nanoparticles derived from the AgCl nanoparticles due to illumination of electron beam in SEM chamber. The inset in a is the schematic illustration to highlight the pentagonal cross section of the nanotubes and the existence of five twin planes in each nanotube. (b) Electron diffraction (ED) pattern of an individual nanotube obtained by aligning the electron beam perpendicular to one of the side surfaces of the nanotube as shown by the blue arrow in a. The ED pattern is essentially same as that obtained from a Ag nanowire as shown in Supplementary Figure S6c. The ED pattern corresponds to the superposition of <100> (highlighted with green lines) and <112> (highlighted with blue lines) zone axes.
Supplementary Figure S13 | Time-dependent x-ray diffraction patterns of the Ag nanowires during the replacement reaction. The strong background from the solvent was not subtracted. As the reaction proceeded, the face-centered tetragonal (f.c.t.) Ag nanowires were transformed to face-centered cubic (f.c.c.) Ag-Au alloy nanotubes and f.c.c AgCl solids were also formed due to the low solubility of AgCl. The wavelength of the x-ray beam was 0.1771 Å.
Supplementary Figure S14 | Schematic drawing of a Ag nanowire with a highly strained core and a less strained (or unstrained) sheath. The core/shell structure expose strained lattices only at the ends of the nanowire to the surrounding environment. Due to the high reactivity of the strain surfaces and stability of the less strained side surfaces, the short nanowire formed at the early stage tend to grow longer by preferentially adding more Ag atoms to the strained surfaces.