Chiral Transformation: from Single Nanowire to Double Helix

Yong Wang,† Qingxiao Wang,‡ Hang Sun,† Weiqing Zhang,§ Gang Chen,† Yawen Wang,† Xiaoshuang Shen,† Yu Han,‡ Xianmao Lu,§ and Hongyu Chen*,†

†Division of Chemistry and Biological Chemistry, Nanyang Technological University, Singapore 637371, ‡Advanced Membranes and Porous Materials Center & Core Lab of Imaging and Characterization, King Abdullah University of Science and Technology, Saudi Arabia 23955-6900 and §Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore 117576.

AUTHOR EMAIL ADDRESS: hongyuchen@ntu.edu.sg

Experiment section

Materials: All chemical reagents were used as purchased without further purification. Hydrogen tetrachloroaurate(III) hydrate (HAuCl₄·3H₂O), 99.9% (metal basis Au 49%), pyrrole (98%), aniline (99%), sodium dodecylsulfate (SDS, 99%), and ammonium persulfate (APS, (NH₄)₂S₂O₈, 98%) were purchased from Alfa Aesar; silver nitrate (99+%) and polyvinylpyrrolidone (PVP, M_w: 40,000) were purchased from Sigma Aldrich; 2-propanol (HPLC grade) and ethanol (analytical grade) were purchased from Fisher Scientific; all other chemicals were purchased from Aldrich. Deionized water (resistance > 18 MΩ·cm⁻¹) was used in all reactions. Copper specimen grids (300 meshes) with formvar/carbon support film (referred to as TEM grids in the text) were purchased from Beijing XXBR Technology Co, Ltd.
**Characterization Methods:** TEM images were collected from a JEM-1400 transmission electron microscope (JEOL) operated at 100 kV. High-resolution TEM was performed on an FEI Titan Cubed S-Twin transmission electron microscopy operated at 80 kV with image Cs corrector applied. High-resolution scanning transmission electron microscopy (STEM) and energy-dispersive X-ray spectroscopy (EDS) were performed on an FEI aberration-corrected Titan Cubed S-Twin transmission electron microscope operated at 200 kV. Probe Cs corrector was applied to get better spatial resolution. In a typical experiment, high-resolution STEM imaging was conducted at a 2-us/pixel scanning rate with 70 μm C2 aperture, spot size 9, a high-angle annular dark-filed (HAADF) detector, and 146 mm camera length. Under such conditions, a spatial resolution of ~1.0 Å was obtained. EDS spectra were collected with 150 μm C2 aperture, spot size 6, and 240 s collection time. SEM images were collected from a JEOL-6700F Scanning Electron Microscopy operated at 10/15 kV. UV–Visible spectra were collected on a Cary 100 UV-Vis spectrophotometer.

**Preparation of TEM samples:** TEM grids were treated with oxygen plasma in a Harrick plasma cleaner/sterilizer for 1 min to improve the surface hydrophilicity. The grid was placed face-down on a droplet of as-synthesized sample laid on a plastic Petri dish. A filter paper was used to wick off the excess solution on the TEM grid, which was then dried in air for 5 min. (NH₄)₆Mo₇O₂₄ was used as the negative stain in the TEM images of polypyrrole and polyaniline encapsulated double helices samples, so that the polymer shells appear white against the stained background.

**Preparation of ultrathin Au-Ag alloy NWs:** In 800 μL DMF solution, 100 μL PVP (500 mM in DMF), 20 μL HAuCl₄ (50 mM in DMF), 20 μL AgNO₃ (50 mM in H₂O) were added in the order given. Then, 100 μL ascorbic acid (400 mM in H₂O) was added into the mixture by vortex mixing. The total volume of the final mixture was 1040 μL (V_{DMF}/V_{water}: 7.7:1), where [PVP] = 48.1 mM, [HAuCl₄] = 0.962 mM, [AgNO₃] = 0.962 mM and [ascorbic acid] = 38.5 mM. Finally, the solution was left undisturbed at room temperature for 10 days (the long incubation is necessary). The ultrathin Au-Ag
nanowires could be precipitated out by acetone, washed by \( \text{H}_2\text{O} \) to remove the DMF and PVP, and isolated by centrifugation. The product can be re-dispersed in 1 mL \( \text{H}_2\text{O} \) without aggregation.

**Deposition of metal (Pd, Au, Pt, or Ag) on the Au-Ag NWs:** Metallic double helices could be obtained by growing a thin metal layer on the surface of the Au-AgNWs. Taking Pd layer growth for instance, typically, into 640 \( \mu\text{L} \) of aqueous ascorbic acid solution (1.875 mM), 50 \( \mu\text{L} \) of as-synthesized Au-Ag NWs solution was added. The mixture was gently shaken, followed by addition of 60 \( \mu\text{L} \) of aqueous \( \text{H}_2\text{PdCl}_4 \) solution (1 mM). The final mixture was left undisturbed at room temperature for 2 h to complete the Pd growth reaction. The color of the solution changed from brown red to dark brown, indicating the reduction of \( \text{Pd}^{2+} \).

**Preparation of (Au-Ag)@Pd double helices with NaBH\textsubscript{4} as the reducing agent:** The conditions used were similar to the above method using ascorbic acid, except that NaBH\textsubscript{4} (with a same concentration) dissolved in ice/water mixture was used to replace ascorbic acid.

**Preparation of (Au-Ag)@M (M = Pd, Au, Pt, or Ag) double helices using pyrrole as the reducing agent:** Taking Pd layer growth for instance, typically, into 500 \( \mu\text{L} \) aqueous pyrrole solution (10 mM), 50 \( \mu\text{L} \) aqueous SDS solution (40 mM), and 50 \( \mu\text{L} \) of the as-synthesized Au-Ag NWs solution were added in the order given. The solution was gently shaken, followed by addition of 60 \( \mu\text{L} \) of aqueous \( \text{H}_2\text{PdCl}_4 \) solution (1 mM). The mixture was left undisturbed at room temperature overnight (about 10 h) to complete the Pd growth reaction.

**Preparation of ultrathin (Au-Ag)@M (M = Pd, Au, Pt, or Ag) double helices using aniline as the reducing agent:** The conditions used were similar to the pyrrole reduction method above, except that aniline of the same concentration was used as the reducing agent to replace pyrrole.
Polypyrrole encapsulation of the Au-Ag NWs: Typically, to 200 μL of aqueous pyrrole solution (20 mM), 50 μL of aqueous SDS solution (40 mM), and 50 μL of the as-synthesized Au-Ag nanowires solution were added in the order given. The solution was vortexed for 5 s, followed by addition of 200 μL acidic APS solution (the final concentration of [APS]: 5 mM; [HCl]: 7.5 mM). After vortexing for 10 s, the reaction mixture was incubated at room temperature overnight.

Determining the yields reported in the main text: The yields of different samples were determined from the surveys of figures in the supporting information, as well as additional TEM images of different samples. As shown in Table S1, different samples were labelled by the reducing agents and the metal precursors.

<table>
<thead>
<tr>
<th></th>
<th>Double helices</th>
<th>Unwound NWs</th>
<th>Total</th>
<th>Yield</th>
</tr>
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<tbody>
<tr>
<td>Ascorbic acid-H₂PdCl₄ᵃ</td>
<td>230</td>
<td>16</td>
<td>246</td>
<td>93.5%</td>
</tr>
<tr>
<td>Ascorbic acid-H₂PdCl₄ᵇ</td>
<td>98</td>
<td>30</td>
<td>128</td>
<td>76.6%</td>
</tr>
<tr>
<td>Ascorbic acid-H₂PdCl₄ᶜ</td>
<td>100</td>
<td>11</td>
<td>111</td>
<td>90.1%</td>
</tr>
<tr>
<td>Ascorbic acid-HAuCl₄</td>
<td>9</td>
<td>76</td>
<td>85</td>
<td>10.6%</td>
</tr>
<tr>
<td>Ascorbic acid-K₂PtCl₄</td>
<td>129</td>
<td>27</td>
<td>156</td>
<td>82.7%</td>
</tr>
<tr>
<td>Pyrrole-HAuCl₄</td>
<td>91</td>
<td>12</td>
<td>103</td>
<td>88.3%</td>
</tr>
<tr>
<td>Aniline-HAuCl₄</td>
<td>88</td>
<td>10</td>
<td>98</td>
<td>89.8%</td>
</tr>
<tr>
<td>Pyrrole-H₂PdCl₄</td>
<td>104</td>
<td>10</td>
<td>114</td>
<td>91.2%</td>
</tr>
</tbody>
</table>

ᵃAs-synthesized Au-AgNWs were used for the Pd layer growth; ᵇPurified Au-AgNWs were dispersed in pure water, and used for the Pd layer growth; ᶜPurified Au-AgNWs were dispersed in DMF/water mixture (v/v 1:13.7, or 0.88 M DMF), and used for the Pd layer growth;

Kinetic UV-Vis spectra study: The UV-Vis spectra of the as-synthesized Au-AgNWs and (Au-Ag)@Pd double helices (Figure S1a) showed that after the metal layer growth, the absorbance increased over the whole spectrum and the characteristic peaks around 400 nm and 500 nm disappeared. Nevertheless, the trend in the increase of absorbance was similar at different wavelengths, showing a
plateau after initial increase in absorbance. The rates of metal deposition were reflected by the rates of
increase in absorbance. In Figure S1b, the deposition reactions were studied by following the
absorbance change at 510 nm. In the case of HAuCl₄ reduction in water, the reaction was too fast for us
to move the cuvette into the UV-vis spectrometer. All reactions reached a plateau within 8 min (for Au,
less than 1 min).

Figure S1. (a) UV-Vis spectra of the purified Au-Ag NWs, and [Au-Ag]@Pd double helices in aqueous solutions; (b) the
normalized absorbance increase at 510 nm wavelength of Pd and Au growth in pure water or 0.88 M DMF aqueous
solution.

References

(3) (a) Stober, W.; Fink, A.; Bohn, E. J. Colloid Interface Sci. 1968, 26, 62; (b) Chen, T.; Chen, G.;
(4) Xing, S. X.; Tan, L. H.; Yang, M. X.; Pan, M.; Lv, Y. B.; Tang, Q. H.; Yang, Y. H.; Chen, H. Y. J.
Figure S2. A large-area TEM image of the as-synthesized Au-Ag NWs.
Figure S3. A large-area TEM image of the as-synthesized Au-Ag NWs at slightly higher magnification (inset: one typical thick tail of the Au-Ag NW).
Figure S4. HRTEM images of the as-synthesized Au-Ag NWs; the “fan”-like contrast is highlighted in brackets.
The EDS analyses of the central thin sections of the as-synthesized Au-Ag nanowires: (a-d) the (S)TEM images with the selected area marked (d: the rectangle area); (e-h) the corresponding EDS spectra of the selected areas in a-d. The EDS analyses (atomic ratio) have been summarized in the above table.

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag (L)</td>
<td>50.40%</td>
<td>60.51%</td>
<td>50.28%</td>
<td>35.76%</td>
<td>49.2%</td>
</tr>
<tr>
<td>Au (L)</td>
<td>49.59%</td>
<td>39.48%</td>
<td>49.71%</td>
<td>64.23%</td>
<td>50.8%</td>
</tr>
</tbody>
</table>
The EDS analyses of the tails of the as-synthesized Au-Ag nanowires: (i-l) STEM images with the selected areas marked (l: the circle area); (m-p) the corresponding EDS spectra of the selected areas in i-l. The EDS analyses (atomic ratio) have been summarized in the above table.

**Figure S5.** EDS analysis of the as-synthesized Au-AgNWs.
Figure S6. HAADF-STEM images of the Au-Ag NWs, and the corresponding element mapping of gold and silver. These two elements show homogeneously distribution, although the NWs were broken under the electron beam.
Figure S7. Large-area TEM images of typical (Au-Ag)@Pd double helices obtained by ascorbic acid reducing H$_2$PdCl$_4$ (final concentration of H$_2$PdCl$_4$ is 80 $\mu$M).
Figure S8. Magnified HAADF-STEM image of one typical (Au-Ag)@Pd double helix (same as Figure 1d) and the selected area EDS analyses at the bracketed regions.
**Figure S9.** Large-area HAADF-STEM images of the typical (Au-Ag)@Pd double helices.
Figure S10. TEM images of the (Au-Ag)@Pd double helices obtained by ascorbic acid reducing H$_2$PdCl$_4$ (final concentration of H$_2$PdCl$_4$ is 270 µM).

Figure S11. TEM images of the (Au-Ag)@Pd double helices obtained by ascorbic acid reducing H$_2$PdCl$_4$ (final concentration of H$_2$PdCl$_4$ is 540 µM).
Figure S12. Complete images of Figure 2f and 2g, respectively.
Figure S13. Large-area TEM image of the NWs incubated in the absence of H$_2$PdCl$_4$, with all other conditions unchanged. No obvious change was observed.
Figure S14. TEM images of the (Au-Ag)@Pd double helices obtained by ascorbic acid reducing \( \text{H}_2\text{PdCl}_4 \), in which the purified Au-Ag NWs were dispersed in water, leading to faster reaction. In a similar control experiment, purified Au-Ag NWs were dispersed in \textit{DMF/water mixture} (v/v = 1:13.7), the result was the same as Figure 1c and S7 (thus not shown).

Figure S15. TEM images of the (Au-Ag)@Pt double helices obtained by ascorbic acid reducing \( \text{K}_2\text{PtCl}_4 \).
Figure S16. TEM images of the (Au-Ag)@Au double helices obtained by ascorbic acid reducing HAuCl₄.

Figure S17. TEM images of the (Au-Ag)@Ag obtained by ascorbic acid reducing AgNO₃.
**Figure S18.** TEM images of NWs after the incubation of purified Au-Ag NWs with aq. H$_2$PdCl$_4$ solution for 20 min (left) and 24 h (right).

**Figure S19.** The selected-area EDS analyses of H$_2$PdCl$_4$ treated Au-Ag NWs in the absence of ascorbic acid: (a-c) the TEM images with the selected areas marked; (d-f) the corresponding EDS analyses of the selected areas. The EDS analyses are summarized in the above table.
Figure S20. TEM images of the H2PdCl4 treated Au-Ag NWs sample (same as above) after addition of ascorbic acid. DMF was added back to follow the typical Pd growth condition.

Figure S21. TEM images of the (Au-Ag)@Pd double helices obtained by NaBH4 reducing H2PdCl4.
Figure S22. TEM images of the (Au-Ag)@Pt double helices obtained by NaBH$_4$ reducing K$_2$PtCl$_4$.

Figure S23. TEM images of the (Au-Ag)@Au double helices obtained by pyrrole reducing HAuCl$_4$. The contrast of the polymer shells depended on the presence of stain solution at the different locations after the drying of solution.
Figure S24. TEM images of the (Au-Ag)@Au double helices obtained by aniline reducing HAuCl₄.

Figure S25. TEM images of the (Au-Ag)@Pd double helices obtained by pyrrole reducing H₂PdCl₄.
Figure S26. TEM images of the polypyrrole encapsulated Au-Ag NWs by oxidizing pyrrole with (NH₄)₂S₂O₈.