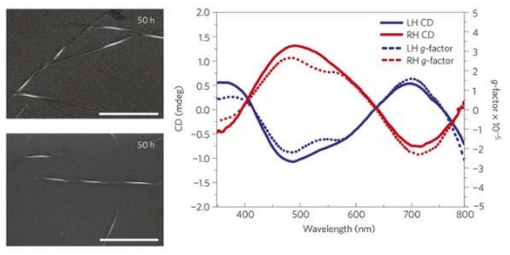
2017 International Bionic Innovation Competition

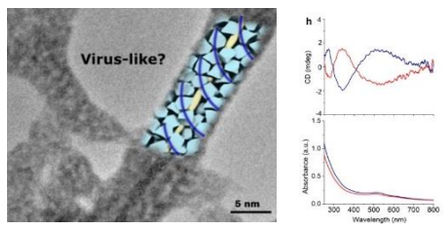
Near-Quantitative Synthesis and Plasmonic Metal Modification of Chiral Semiconductor Helices

MICHIGAN ENGINEERING
UNIVERSITY OF MICHIGAN

1. Introduction



Nature Materials, 2015, **14**, 66–72.



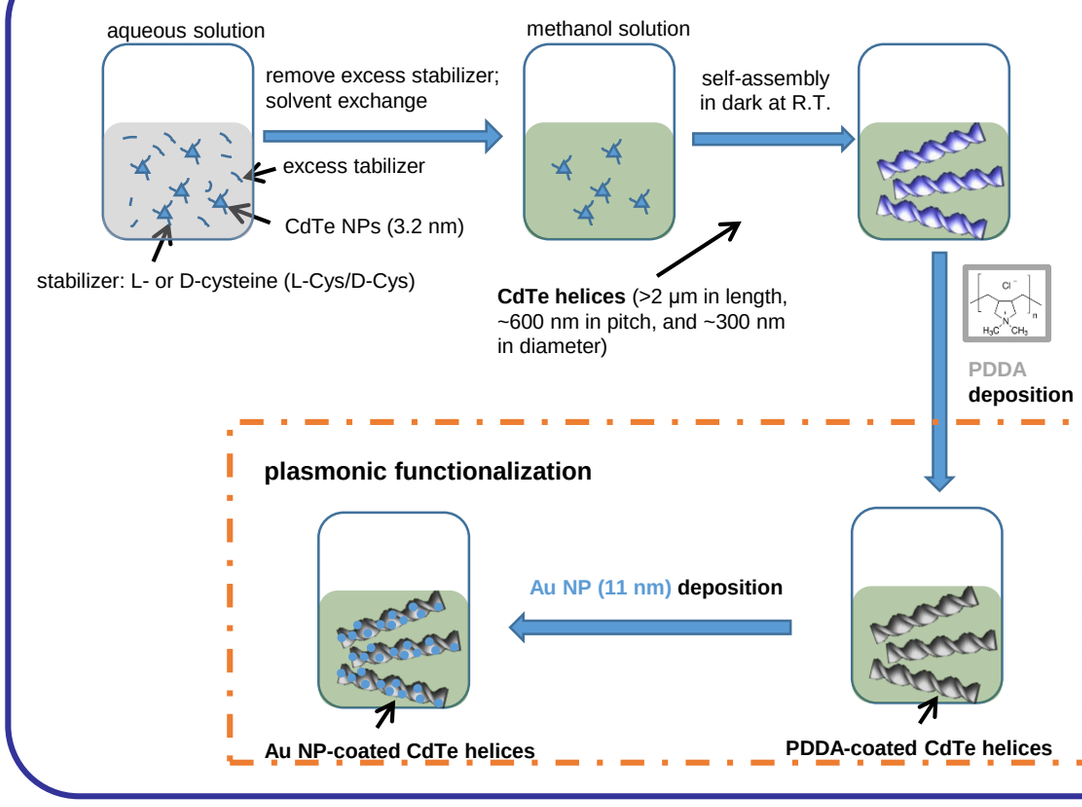
ACS Nano, 2016, **10**, 3248–3256

Semiconductors with chiral geometries at nano- and mesoscale provide a rich materials platform for polarization optics, photocatalysis, and biomimetics.

Unlike metallic and organic optical materials, the relationship between the geometry of chiral semiconductors and their chiroptical properties remains, however, vague.

Homochiral ensembles of semiconductor helices with defined geometries may open the road to understanding complex relationships between geometrical parameters and chiroptical properties of semiconductor materials.

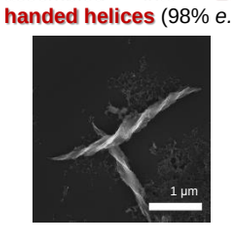
2. Experimental Procedure



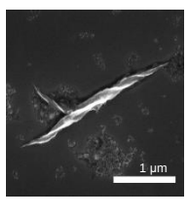
3. Formation Mechanism

Chiral Assemblies

L-Cysteine CdTe NPs assembled into **Left-handed helices** (98% *e.e.*)



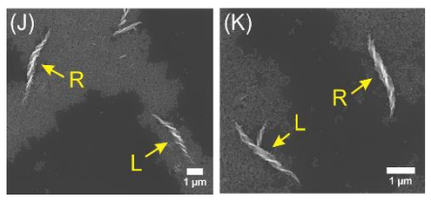
D-Cysteine CdTe NPs assembled into **Right-handed helices** (100% *e.e.*)



Chiral Racemic Assembly

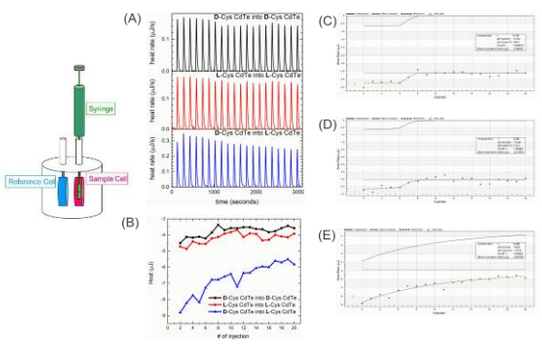
by synthesis → **D,L-Cys CdTe NP** assembly (3% *e.e.*)

by mixing → **D-Cys/L-Cys CdTe NP** assembly (6% e.e.)



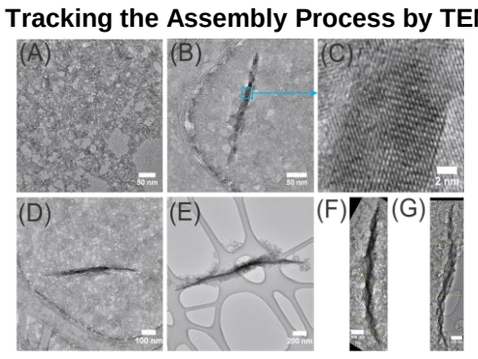
Power of **chiral self-sorting**: Preferential interaction between NPs with the same handedness. NPs with opposite handedness tend not to interact strongly.

Isothermal Titration Calorimetry (ITC): Energetics of NP-NP interaction



ITC results indicate that D-NP and L-NP interaction is less spontaneous than D-NP and D-NP or L-NP and L-NP.

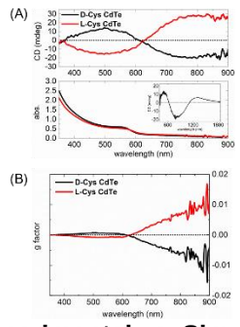
Tracking the Assembly Process by TEM



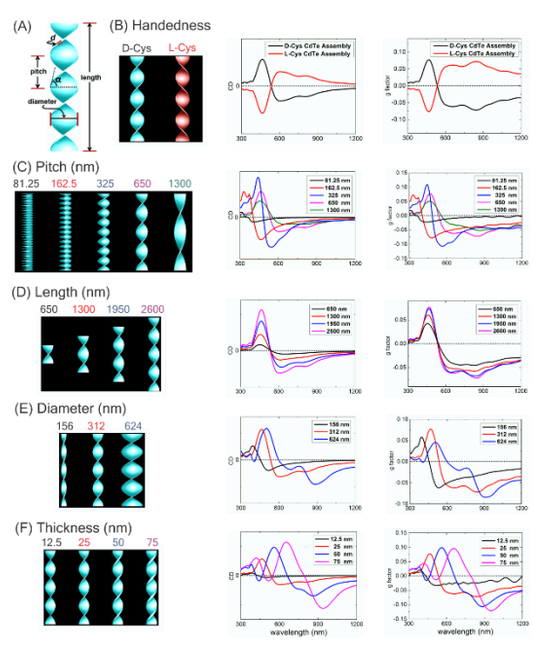
Lattice Fringes (0.40 and 0.59 nm) correspond to ***hexagonal tellurium***

4. Chiroptical Activity

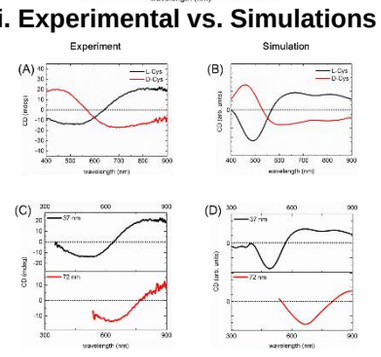
i. Circular Dichroism



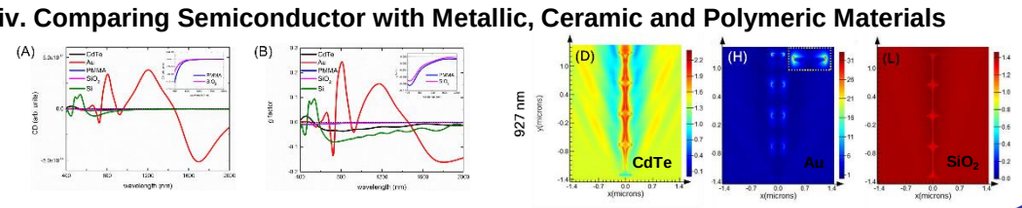
ii. Lumerical Simulations



iii. Experimental vs. Simulations



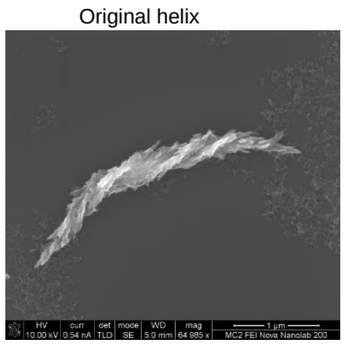
iv. Comparing Semiconductor with Metallic, Ceramic and Polymeric Materials



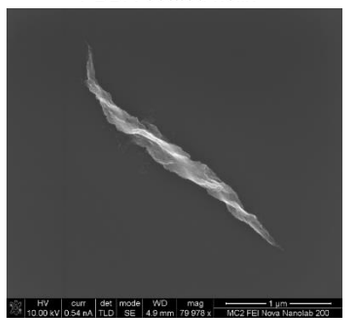
5. Plasmonic Functionalization

i. SEM Analysis

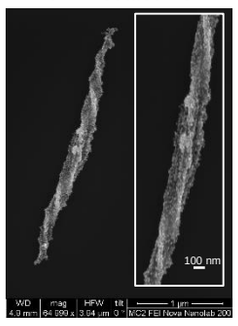
Original helix



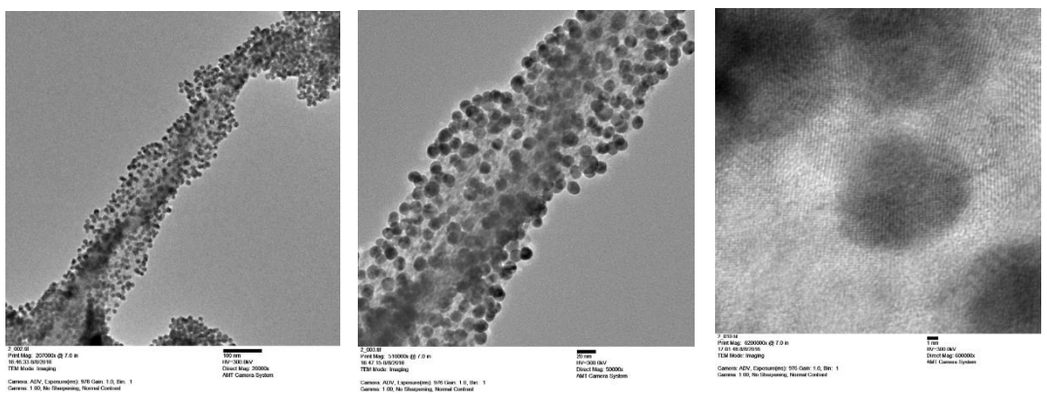
PDDA-coated helix



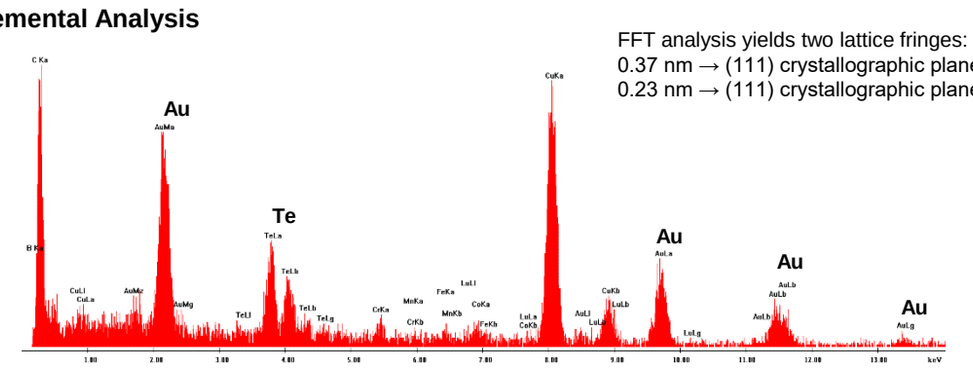
Au NP-coated helix



ii. TEM Analysis (Au NP-coated helix)

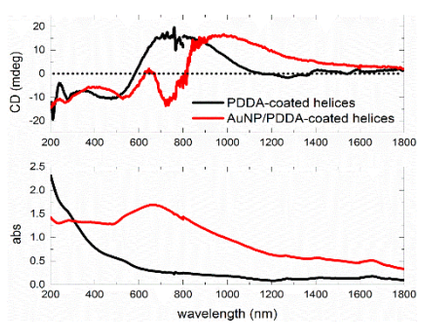


iii. Elemental Analysis



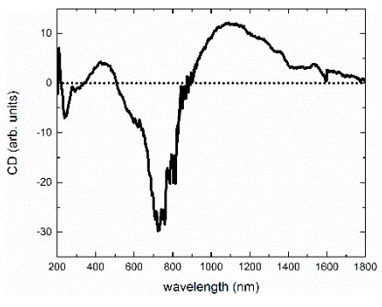
FFT analysis yields two lattice fringes:
0.37 nm → (111) crystallographic plane of **CdTe**
0.23 nm → (111) crystallographic plane of **Au**

iv. Chiroptical Property Modulation after Plasmonic Functionalization



After Au functionalization, the spectral wavelength red-shifted by ~200 nm, with a sharp peak at ~700 nm.

If the chiroptical contribution from Au and CdTe can be assumed to be linearly superimposed, then **the contribution from Au NP alone** can be obtained by subtracting the above two CD spectra: Similar to the original helix, its CD spectrum also has a bisignate spectral shape. This specific spectral shape for Au NP helix has been previously predicted.[2]



Conclusions

- 1. Chiral self-sorting represents an important characteristic for this self-assembly system, ensuring the efficient transfer of chirality from small molecules to mesoscale.
- 2. Chiral semiconductor mesoscale helices demonstrated unique chiroptical properties compared to metallic, ceramic, or polymeric ones.
- 3. Plasmonic functionalization modulated the chiroptical response of the original CdTe helix by a significant spectral shift.
- 4. This study will facilitate the development of chiral semiconductor nanostructures with tunable, geometry-dependent chiroptical activity and broad-band Vis-NIR characteristics.

Acknowledgement

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