DOCTORAL THESIS

Extension of Compositional Space in Inorganic Chiral Nanoparticles

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ABSTRACT

The origin of life is a fundamental problem that has attracted the attention of several generations of scientists. Useful clues about the origin of life can be gleaned from the homochirality (i.e., uniformity of chirality) of molecules or objects. According to the homochirality phenomenon and the existence of chirality in inorganic compounds before the birth of life, the hypothesis that chirality has been transferred from inorganic compounds to organisms has been come up to the beginning of the study for life's origin. To clarify the mechanisms by which chirality is transferred from inorganic objects to living organisms, various inorganic chiral nanoparticles (CNPs) must be fabricated to recreate the natural environments that induce chirality.

In the research described herein, the glancing angle deposition (GLAD) approach is combined with galvanic replacement reactions (GRRs) to produce a close-packed array of inorganic CNPs, composed of metals, alloys and semiconductors with flexible nanostructures. These inorganic CNPs exhibit unique chiral plasmonic and optical responses and novel chiral surfaces, which can facilitate the induction of chirality in organisms.

Chapter 2 describes the use of unary CNPs serving as sacrificial templates in GRRs to generate alloy CNPs with intrinsic structural chirality. This GRR-mediated chirality transfer is a general phenomenon resulting in the formation of copper–silver (Cu–Ag) CNPs with solid morphologies and mesoporous CNPs composed of silver–gold (Ag–Au), silver–platinum

(Ag–Pt), and silver–palladium (Ag–Pd). The insights obtained from this work enhance our fundamental understanding of the principles of GRRs and help to establish a versatile method to generate mesoporous alloy CNPs for chirality-related applications in asymmetric catalysis, enantiodifferentiation, enantioseparation, biodetection, and bioimaging.

Chapter 3 describes the extension of the compositional space to the ternary scale based on the generation of binary metal CNPs, which are in demand for practical applications and of fundamental interest. Through layer-by-layer GLAD, host Cu CNPs were doped using the galvanic dopant Au to generate binary Cu:Au CNPs. These "inert" dopants serve as a structural scaffold and facilitate the transmission of chirality from a host to a third type of metal (M) that cathodically precipitate on the CNPs, enabling the formation of polycrystalline ternary Cu:Au:M CNPs. The compositions of these CNPs can be tailored by tuning the GRR duration. The introduction of a large number of scaffold Au atoms accelerated the transfer of chirality, and this process follows first-order kinetics and has a reaction rate coefficient of 0.3 h^{-1} at room temperature.

Chapter 4 describes the production of semiconductor (II–VI n-type semiconductor, cadmium selenide or CdSe) nanohelices with controllable sizes and morphology by GLAD. The optical activities and crystallinity of chiral CdSe nanostructures were found to be related to their pitch. Besides, as CdSe is a luminescent material, when they are with the intrinsic chirality, circularly polarized luminescence could be produced by CdSe nanohelices and tuned as a function of the nanohelicity.

These results pave the further way to the development of inorganic chiral nanoparticles to serve as chiral surface to study the chirality transmission from inorganic objects to organism, which is in fundamental demand for the study of symmetry breaking. Moreover, the inorganic chiral nanoparticles, especially semiconductors can generate an enhancement in a wide range of CPL for producing efficient 3D optical devices.