

DOCTORAL THESIS

Engineering Materials and Structures of Inorganic Nanopillars for Chiral and Optoelectronic Applications

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ABSTRACT

Rapid developments in science and technology have yielded a new form of material, known as nanomaterials. The unique properties of nanomaterials, which differ from those of their bulk counterparts, have attracted great interest from researchers who have applied them to solve prominent societal problems associated with health and energy. The enhanced functionality of nanomaterials relies on the flexible engineering of their constituents, compositions, shapes and sizes.

In this thesis work, I perform glancing angle deposition (GLAD) to reliably produce a close-packed array of inorganic nanopillars containing flexibly controlled material types and structures. These GLAD-fabricated nanopillar arrays (NaPAs) exhibit unique optical activity, chiral plasmonic and optoelectronic properties, resulting in enantiospecific interactions with molecules, the chiropasmonic amplification of the optical chirality of superchiral near-fields and functionality as electron transporting layers (ETLs). In Chapter 2, inorganic NaPAs are deposited on rigid and flexible substrates using GLAD, and the materials and structures of the nanopillars are engineered for purposes such as the specific differentiation of neural stem cells.

In Chapter 3, N3 dyes, which have fluctuating optical activity, are grafted on silver chiral nanoparticles (CNPs) by forming NCS–Ag contacts, leading to the enantiospecific adsorption of N3 dyes. The enantiospecific configurations of the immobilised N3 dyes are primarily determined by the helical handedness of the CNPs. The adsorption enantiospecificity is maximised at a helical pitch of ~15 nm, probably due to the formation of supramolecular chiral complexes and/or the

helical handedness-induced breaking of the mirror symmetry of the adsorption configuration.

In Chapter 4, GLAD is performed to fabricate close-packed NaPAs by replacing metal oxides with metals (e.g. Ti, with $\mu_e \approx 294 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). The Ti NaPAs vertically protrude from a transparent electrode to obtain sufficient optical transmission for light harvesting in perovskite solar cells (PSCs). The rough surfaces of the Ti NaPAs are passivated with 5-nm-thick TiO_2 (i.e. Ti NaPAs@ TiO_2) to suppress exciton recombination. This leads to an extremely high power conversion efficiency (PCE) of 18.89%, which is superior to that of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ PSCs without Ti NaPAs@ TiO_2 or containing TiO_2 NaPAs@ TiO_2 . This performance is mainly attributable to the high surface wettability, high μ_e and relatively low work function of Ti. Furthermore, Ti NaPAs@ TiO_2 effectively prevents the decomposition of $\text{CH}_3\text{NH}_3\text{PbI}_3$ to achieve long-term shelf stability, whereby 50-day ageing causes only 15% PCE degradation.

In Chapter 5, oxygen-assisted GLAD is used to facilitate deposit polycrystalline SnO_2 NaPAs that are free of oxygen deficiencies and vertically protrude on large-area transparent electrodes. Functioning as ETLs, the deposited SnO_2 NaPAs comprehensively lead to the prevention of perovskite decomposition, as well as the enhancement of light harvesting in perovskites, exciton separation, electron extraction and collection, and hole blocking. Large-area (1 cm^2) flexible PSCs containing the SnO_2 NaPAs show the champion PCE of 14.9%, which undergoes only 10% degradation for approximately 800-hr solar illumination and 13% degradation for more than 200 times of manual bending. These photovoltaic performances are remarkably superior to large-area flexible PSCs having the

conventionally used spin-coated SnO₂ thin films that contain oxygen vacancies. These results pave the way toward scale-up fabrication of flexible PSCs containing inorganic NaPAs that simultaneously satisfy the commercial requirements of high photovoltaic efficiency, shelf stability, and mechanic stability.

These results pave the way towards the development of metal CNPs to function as intrinsically chiral catalysts and the design of an alternative method to perform heterogeneous asymmetric catalysis with high enantioselectivity, which is in practical demand for the enantiopure manufacture of important chemicals. Furthermore, the NaPA material spectrum is broadened from semiconductors to metals to generate a wide range of ETLs for producing efficient optoelectronic devices with long-term shelf stability.

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