Investigation of optical properties of one-dimensional nanostructures with engineerable heliciity and surface modification

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Abstract

In this work, the optical properties of two kinds of one-dimensional (1D) nanomaterials, mesoporous silicon nanowires (mpSiNWs) and plasmonic nanospirals (NSs), were studied. These emerging nanomaterials are of great interest because of their fundamental structure-derived properties and potential practical applications. Four aspects of these materials were analyzed in this work.

First, although the fabrication mechanism of mpSiNWs has been studied previously via metal-assisted chemical etching, the porosification-induced disturbance to the etching direction, which plays a vital role in controlling the surface crystallinity of mpSiNWs, has not been characterized. In Chapter 2, I discuss the porosification etching mechanism of n-Si(111), which proceeds along the intrinsic back bond etching direction of [111] at room temperature. The porosification substantially weakens the back bonds under the sinking particles, resulting in the deviation of etching from [111]. The preferred direction of etching changes to that with a small angle α, because the direction-switching barrier increases with α and intrinsic back-bond etching is thermodynamically preferential.

Second, mpSiNWs typically generate red photoluminescence (PL), but the PL mechanism is still under debate. A laser was used to oxidize the surfaces of mpSiNWs and tune the PL from red to greenish-blue (GB), as described in Chapter 3. The laser oxidation was tuned as a function of laser power, and a complex model of the laser-induced surface modification was proposed to account for the laser-power and post-annealing effect. The laser-induced modification of the PL of mpSiNWs may be useful for data encryption.

Third, the fabrication of plasmonic NSs and the study of their optical activities are in their infancy. In Chapter 4, I describe the use of glancing-angle deposition (GLAD) to fabricate

silver NSs (AgNSs) with controllable helicity and demonstrate that AgNSs have intrinsic optical responses that originate from their structural helicity. The optical activity of an AgNSs dispersion was characterized by circular dichroism (CD), and systematic engineering of the helicity revealed that their UV and visible optical activities have two different origins.

Fourth, physical limits prohibit the sensitive differentiation of enantiomers. In Chapter 5, I describe the grafting of chiral molecules onto AgNSs, which dramatically enhanced the differentiation of L- and D-glutathione (GSH). AgNSs have very strong optical activities that are weakened by GSH adsorption. The severity of the chiroptical weakening effect varies with the absolute configuration of GSH, resulting in enantiomeric differentiation with an anisotropic *g*-factor of approximately 0.5. This chiral nanoplasmon-induced anisotropy *g*-factor is superior by 2 to 4 orders of magnitude to those obtained with other methods and about one-fourth of the theoretical value. This proposed method can be adapted to differentiate chiral drugs, which is highly desirable in the pharmaceutical industry for the production of single-enantiomer drugs.

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