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Fabrication of chiral-molecular@ nanoparticle complex materials with great chiroptical effect in visible region

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ABSTRACT

Chirality plays a key role in biochemical reaction and the self-assembled mechanism of life. The detection of chiral molecules is one crucial issue in biology, clinic, pharmacy and food security fields, which usually refers to the detectable chiroptical effect, i.e. circular dichroism (CD) and optical rotatory dispersion (ORD) Gansel et al. (2009), Quake and Scherer (2000), Pendry (2004), Zhang et al. (2009), Kastel et al. (2007) [1–5]. However, the chiroptical effect from chiral molecules in nature (such as proteins and DNAs) is usually very small and located in ultraviolet spectral region. This limits the detection sensitivity of chiral molecules and their ability to control electromagnetic wave. In this paper, we report a scalable fabrication of a new kind of chiral molecule@ nanoparticle complex materials, which are composed of an achiral nano-cup array and a pair of chiral molecules (L-/D-cysteine). The nano-cup array with localized surface plasmonic response peak of 630 nm is obtained with the micro-sphere assembly technique, which is a kind of scalable, low-cost and material-independent fabrication method. After coating a layer of chiral molecules on the surface of the nano-cup array, a clear induced-CD peak in visible region is demonstrated from the L/D-cysteine@nano-cups complex materials, the intensity of which can be much greater than the existing results [9–16]. Full-wave electromagnetic simulation method has been performed to get insight into the mechanism of the induced chiroptical effect. The simulation results indicate that this giant induced CD signal should be attributed to the electromagnetic interaction between chiral molecules and plasmonic nanostructures, especially for the wave at the plasmonic resonance peak. These results indicate the potential application prospect of these newly-fabricated complex chiral materials.

1. Introduction

Chirality is a common phenomenon in nature and has great impacts on biology, medicine and pharmaceutical sciences. A molecule with structure that cannot be superposed on its mirror image is called as chiral molecule. In general, chiral molecules can interact differently with chiral electromagnetic field (i.e. left- and right-hand circular polarization light, LCP and RCP), resulting in chiroptical effect (including circular dichroism (CD) and optical activity (OA), which refer to the absorbance and phase delay difference respectively). This chiroptical effect paves a way for the detection of chiral molecules and the manipulation of electromagnetic field, and has been widely used in optics, communications, biology, clinic, pharmacy and food security fields. However, the chiroptical effect from nature chiral molecules usually is very weak and located in the ultraviolet region (150–250 nm). This greatly limits the related applications [1–5]. To obtain high chiroptical effect, great efforts have been made to enhance the interaction of chiral molecules with circular polarization light [6]. One typical way is to design molecules with large optical dissymmetry at particular wavelengths. These treatments focus on the molecular aspects of CD, relying on circularly polarized light as the excited source; another way is to achieve highly-twisted chiral electromagnetic field, which will enhance the chiroptical effect of chiral molecules located in this field. In 2011, Yiqiao Tang and Adam E. Cohen demonstrated experimentally an 11-fold enhancement over CPL in discrimination of the enantiomers of a biperylene derivative by precisely placing the detected molecules at the node of a standing wave formed by two circular polarized light. But the internal disadvantages limit the application of these methods [7,8]. The first method is only suitable for the designed molecules, while the second method usually requires other complicated control technique.

Recently, metal nanoparticles are found to own the power to modulate the chiroptical effect from nature chiral molecules. Through placing chiral molecules near or on the surface of metal nanoparticles, the chiroptical effect from chiral molecules can be greatly enhanced and the chiroptical resonance peak can be also adjusted to desired

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region, for example, visible region. There are two basic physical mechanisms in the interaction between chiral molecules and metal nanoparticles [9–17]. One is near-field coupling interaction, where the Coulombic interaction predominates the coupling between chiral molecules and nanomaterials. In fact, the electric dipole from chiral molecules can induce chiral currents inside the metal nanoparticle when a molecule is placed on the metal nanoparticle surface, and produce a new CD signal at the desired frequency; the other is far-field coupling interaction. In this case, a layer of chiral molecules is placed near the surface of metal nanoparticles. And the evanescent field and the scattering field from metal nanoparticles can effectively couple with the chiral molecule layer, and induce a large chiroptical resonance in the desired region where the localized surface plasmon resonance is located. Based on these two mechanisms, some simple nanoparticles have been successfully used to modulate the chiroptical effect from chiral molecules in experiment or theory, such as triangle nanoparticles, nano-spheres and nano-shells. However, the induced chiroptical effect is still very weak, and more efforts should be payed to obtain better results, especially for the metal nanoparticles with high asymmetry, which have been predicted theoretically with better power to enhance the chiroptical effect from chiral molecules.

In this paper, we report the scalable fabrication of a new kind of chiral molecule@nanoparticle complex materials with great chiroptical effect in visible region. The complex materials are composed of chiral molecules (L-/D-cysteine) and achiral nanostructures (nano-cups) with high asymmetry. Micro-sphere self-assembly technology has been used to fabricate the nano-cup array, which is a low-cost, high efficiency and material-independent fabrication method. After placing a layer of L-/D-cysteine near the surface of the nano-cup array, an obviously induced-chiroptical signal can be observed in the visible region with a great enhanced factor. The far-field coupling theory has been used to get insight into the physical mechanism of the induced chiroptical resonance. These results indicate the potential application prospect of these newly-fabricated complex materials in many fields, such as chiral biosensor.

2. Experiment

As mentioned before, the new kind of chiral molecule@nanoparticle complex materials with great chiroptical effect in visible region are composed of chiral molecules (L-/D-cysteine) and achiral nanostructures (nano-cups). The detail fabrication process is shown in Fig. 1, which is the preparation of glass substrate, self-assembly of PSs monolayer on glass substrate, materials deposition, the transferring PSs from glass substrate to PDMS stamping, wet chemical etching PSs and placing a layer of chiral molecules near the nano-cup surface [18,19]. The detail fabrication process is as follows:

Firstly, surface modification of glass substrate is done by wet chemical treatment: the glass substrates are immersed in 1:3 hydrogen peroxide (H_2O_2)\ sulfuric acid (H_2SO_4) mixed solution at 80 °C for 1 h. Then, the substrates are thoroughly rinsed with deionized water. For hydrophilic treatment, the substrates are immersed in the 1:1:5 hydrogen peroxide (H_2O_2)\ammonia (NH_3)\deionized water mixed solution under ultrasound for 1 h. After this treatment, the as-obtained glass substrates are stored in deionized water till they are used, as shown in Fig. 1(a).

Secondly, an ordered monolayer of spheres is formed by microsphere self-assembly technique. The monodispersed polystyrene (PS) sphere suspensions with concentration of 10% are purchased from Duke Company, and the diameter used in experiment is 500 nm. In the PS sphere assembled process, two or three drops of the PS sphere suspensions are dropped onto the surface of the silicon substrate. After holding the substrate stationary for 1 min to obtain good dispersion of the suspension, the silicon substrate is then slowly immersed into deionized water. Once the suspension contacted the water's surface, a mono-layer of PS spheres is observed to immediately form, both on the surface of the water and on the surface of the silicon substrate. To prevent any further addition PS spheres to the substrate, a few drops of 2% dodecylsodiumsulfate solution are added to the water to change the surface tension. As a result, the monolayer of PS spheres that remained suspended on the surface of the water is pushed aside due to the change in the surface tension. The substrate can then be removed through the clear area; thus, no additional PS spheres were deposited on the monolayer during its removal from the water. Then, a glass substrate is put into deionized water. After the water sucking, a monolayer of PSs array with hexagonal symmetry is assembled on glass substrate, as shown in Fig. 1(b).

Thirdly, the gold deposition on the closely packed PSs array monolayer from the top side is performed inside a vacuum thermal evaporation system. The base pressure, deposition rate and temperature are $4 \times 10^{-4} Pa$, 0.1 nm/s and 30 °C, respectively. We just need to control the deposition time to obtain appropriate gold deposition thickness (around 100 nm), as shown in Fig. 1(c).

Fourthly, a polydimethylsiloxane (PDMS) stamp is placed on the top surface of the gold coated PSs array monolayer with a uniform pressure

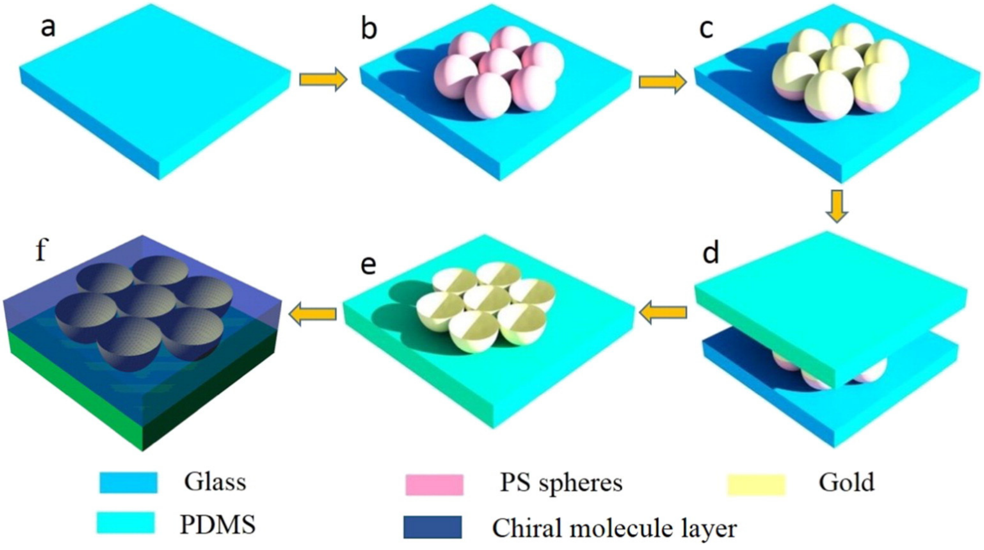

Fig. 1. The fabrication process: (a) preparation of glass substrate; (b) self-assembly of PSs monolayer on glass substrate; (c) materials deposition; (d) the transferring PSs from glass substrate to PDMS stamping; (e) wet chemical etching PSs; (f) placing a layer of chiral molecules near the nano-cup surface.