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Plasmonic refractive index sensitivity of ellipsoidal Al nanoshell: Tuning the wavelength position and width of spectral dip



Jian Zhu^{a,*}, Shu-min Zhao^b

^a The Key Laboratory of Biomedical Information Engineering of Ministry of Education, School of Life Science and Technology, Xi'an Jiaotong University, Xi'an 710049, China

^b Non-equilibrium Condensed Matter and Quantum Engineering Laboratory, the Key Laboratory of Ministry of Education, School of Science, Xi'an Jiaotong University, Xi'an 710049, China

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ABSTRACT

The absorption spectra of ellipsoidal Al nanoshell show a distinct dip due to the two adjacent localized surface plasmon resonance (LSPR) peaks corresponding to the longitudinal resonance from the inner and outer surfaces of the Al shell. Both the dip position and its linewidth are sensitive to the refractive index of the outer surrounding. And the sensitivity could be well tuned by the shell thickness, aspect ratio, shell nonuniformity and the dielectric environment. By comparing with the dip wavelength, the dip width is more sensitive to the geometry of the Al nanoshell. It has been found that the widening speed of the spectrum dip as a function of environmental dielectric could be greatly enlarged by increasing the aspect ratio and longitudinal shell thickness. It has also been interesting to note that the dip width changes non-monotonously when the Al nanoshell has a large dielectric constant of the inner core and a thick transverse shell thickness. The physical mechanism has been attributed to the different shift speeds between symmetric and antisymmetric LSPR along the longitudinal direction. This dielectric environment dependent-spectrum dip presents a new sensing picture based on tuning the dip width and position.

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1. Introduction

In recent years, the tunable plasmonic spectrum properties of metal nanoparticles have attracted extensive investigations and displayed well potential applications in analytical chemistry to biology [1–4]. The intense light absorption from localized surface plasmon resonance (LSPR) is very sensitive to the tiny change of the environmental dielectric constant, thus the metal nanostructurebased spectroscopic analysis could be used in the detection of the concentration induced ultra small refractive index changes [5,6]. Because of the LSPR induced polarized field in the environmental dielectric medium, the plasmon energy could be reduced. Thus resonance wavelength of LSPR red shifts as the refractive index of environment medium increases [7]. Therefore, the wavelength shift per refractive index unit (nm/RIU) is used to denote the sensitivity. On the other hand, the line width (full width half maxima, FWHM) of the plasmonic absorption peak also depends on the particle shape, dielectric environment and the wavelength position of

E-mail address: nanoptzj@163.com (J. Zhu).

LSPR [8–10]. However, too broad line width of the LSPR absorption has been deemed to reduce the detectivity. Thus the FWHM of the plasmonic absorption band is usually regarded as a negative factor in refractive index sensing. To combine these two effects on the refractive index sensing, the figure of merit (FOM) defined as the ratio of sensitivity and FWHM was introduced [11].

Recently, many efforts have been investigated to improve the sensitivity and FOM of the refractive index sensing. By using the finite-difference time-domain method, Lin et al. investigated the LSPR properties and refractive index sensitivity of Ag elliptical nano-ring arranged in rectangle lattice [2]. They found that high sensitivity can be achieved by small particle distance arrays composed of metal elliptical nano-rings with big inner size and small ring-width. Raza et al. reported the refractive index sensing of ultrathin Au nanotubes [11]. Their analytical expression results indicated how the sensitivity are affected by the shape and size of the nanotubes. By using the plasmonic coupling between spherical Au nanoparticles, the enhancement of the refractive index sensitivity has been investigated [12]. It has been found that the coupled plasmon bands exhibit higher refractive index sensitivity compared to well-separated nanoparticles. In the report of Sekhon et al., the refractive index sensitivity of Ag, Au, and Cu nanoparticles have been compared [7]. They found that Ag exhibits a better

^{*} Corresponding author at: School of Life Science and Technology, Xi'an Jiaotong University, Xian Ning West road 28#, Xi'an 710049, China.

sensing behavior than Au and Cu over the entire visible to infrared region of the plasmonic spectrum. The effects of multipolar plasmon resonances on the refractive index sensitivity has been studied by Lee et al. [13]. Their results show that the dipolar resonance has the highest sensitivity, while the quadrupolar resonance has the largest FOM. Katyal et al. reported the refractive index sensitivity of metal-dielectric-metal multilayered nanostructures [14]. This three-layered metal-dielectric nanostructure not only exhibits good refractive index sensitivity but also cover a wide wavelength region from ultraviolet to near-infrared.

Although most of the previous studies are focused in the shift and line shape of the spectrum peak, the appearance of a dip in the spectrum could also been tuned and applied in the spectroscopic analysis [15]. In a complex metal nanoparticle with anisotropic shape and core-shell structure, the plasmon splitting and coupling leads to the LSPR mode becomes abundant, which provides the exist condition of spectrum dip. For example, Fano resonance could be observed as a dip in the plamonic spectrum when a dark plasmon mode interferes with a broad bright plasmon mode [16]. Yang et al. reported the plasmonic Fano resonances in metallic nanorod complexes [17]. In single Au nanorod, Fano resonance could be observed by excitations of higher order plasmon modes. For dimers of Au nanorod, Fano resonance could be induced by the interference of the hybridized plasmon modes. Fano dip has also been observed in the plasmonic spectrum of mismatched Au nanocone dimers [18]. It has been found that the Fano resonances could be attained by using several geometrical configurations. The tunable Fano resonance could also be observed in the plasmonic nanocavities with symmetry breaking [19]. The coupling between plasmon modes of differing multipolar order in the plasmonic ring/disk nanocavity results in a tunable Fano resonance. What's more, the spectra with Fano resonance also display an unusually large LSPR sensitivity. Recently, highly sensitive plasmonic sensor based on Fano resonance has been reported by Chang et al. [20]. A sharp asymmetric

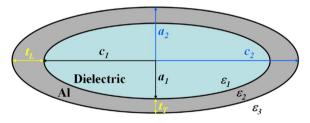


Fig. 1. Geometry of the ellipsoidal Al nanoshell.

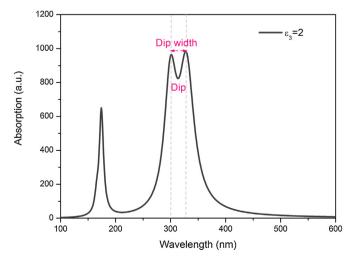


Fig. 2. Absorption spectrum of ellipsoidal Al nanoshell. P=2, $a_1 = 5$ nm, t = 3 nm, $\varepsilon_1 = 4$, $\varepsilon_3 = 2$, uniform coating.

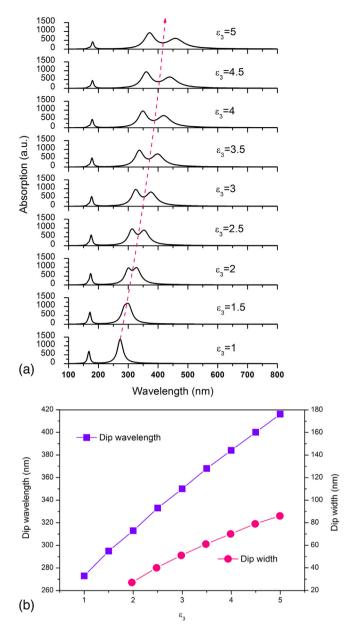


Fig. 3. (a) Environmental dielectric dependent absorption spectrum of ellipsoidal Al nanoshell; (b) Dip wavelength and dip width as a function of environmental dielectric constant. p = 2, $a_1 = 5$ nm, t = 3 nm, $\varepsilon_1 = 4$, uniform coating.

Fano dip resulted from the interference of the localized nanoparticle plasmons and surface plasmon polaritons of metallic film has been obtained in the reflection spectrum, which is highly sensitive to the refractive index of the surrounding host. Lee et al. reported a sensitive biosensors using Fano resonance in single gold nanoslit with periodic grooves [21]. It has been found that the Fano-type biosensor has a sharper resonance which yields a FOM of 48. Compared to conventional plasmonic sensors, this Fano-type sensor is better for chip-based and high-throughput biologic detections. And the sensitivity could be further increased by increasing the period. By using a full-wave finite element method, Zhan et al. studied the plasmonic Fano resonances in nanohole guadrumers for ultra-sensitive refractive index sensing [22]. By fine optimizing the geometric parameters, the nanohole quadrumer supported on a conductive substrate display an overall sensing FOM value of 14.25. The physical origin has been attributed the strong plasmon coupling between either two antiparallel dipolar modes or dipole-quadruple modes in the nanohole quadrumer.

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