Sensors and Actuators B 155 (2011) 843–847

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Improve the refractive index sensitivity of gold nanotube by reducing the restoring force of localized surface plasmon resonance

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ARTICLE INFO

Article history:
Received 3 August 2009
Received in revised form 24 January 2011
Accepted 29 January 2011
Available online 5 February 2011

PACS:
78.67.Bf
73.20.Mf
36.40.Gk
78.66.Bz
73.20.Mf

Keywords:
Gold nanotube
Refractive index sensors
Localized surface plasmon resonance
Wall thickness

ABSTRACT

The core refractive index sensitivity of a gold nanotube was investigated by calculating the shift of local surface plasmon resonance (LSPR). It was found that the core refractive index sensitivity can be improved by reducing the wall thickness or the surrounding refractive index. The sensitivity increases exponentially with decreasing wall thickness, but increases linearly with decreasing surrounding refractive index. This multi-factor controlled sensitivity of gold nanotube enlarges the ability of optimizing the refractive index sensors. The physical origin of this tunable refractive index sensitivity of gold nanotube was also investigated based on the plasmon hybridization and repulsive effects on the restoring force of plasmon oscillation. This physical mechanism can be used for designing core–shell metallic nanostructures for effective LSPR chemical and biological sensing.

1. Introduction

Localized surface plasmon resonance (LSPR), the collective oscillation of conduction electrons in noble metallic nanoparticles, gives rise to the strong and tunable optical response of gold and silver nanostructures. It is demonstrated that both the intensity and resonance wavelength of LSPR are controlled by the local environment [1–4], which provides possibility for the design and fabrication of ultrasensitive chemical and biological sensors [5–17].

For example, when an Au/TiO_2 film was immersed in various kinds of solutions, a linear relation was clearly observed between the LSPR peak wavelength and the refractive index of the solutions [7]. Furthermore, Ye et al. [8] found that the number of gold nanoparticle deposition cycles has a strong effect on the sensitivity of the sensor and the multilayer structure fabricated from four nanoparticle deposition cycles exhibits maximum sensitivity to the change of the environmental refractive index. By using accurate electrodynamic simulations of gold nanoparticles of significant size parameters, Miller and Lazarides [9] have demonstrated that the sensitivity of a plasmon peak wavelength to a variation in refractive index of the environment is determined by the location of the peak wavelength and the dielectric properties of the material.

In order to improve the sensitivity of these LSPR sensors, many efforts have been developed to control the sensitive response of LSPR to environmental changes. Wang et al. [10] have reported the shape and size dependent refractive index sensitivity of gold nanoparticles. They found that the index sensitivities generally increase as gold nanoparticles become elongated and their apexes become sharper. Lee and El-Sayed [11] investigated the dependence of the sensitivity of the LSPR response to changes in their surrounding environment on the size and shape of nanorods and metal composition. It is observed that the sensitivity does not depend on the type of the metal but depends largely on the aspect ratio of nanorods. The direct dependence of the sensitivity on the aspect ratio becomes more prominent as the size of nanorods becomes larger. Wang et al. [12] also demonstrated the feasibility of using the longitudinal component of gold nanorod's LSPR in biomolecular sensing. Such a biosensor was further modified to demonstrate its effectiveness in quantitative detection for selective binding events through a process in which biotin molecules were chemically attached to the gold nanorods' surface prior to detection measurements. In the studies of Hafner et al. [13], robust gold nanorod substrates were fabricated for refractive index sensing based on LSPR. To monitor biomolecular interactions, the nanorod

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doi:10.1016/j.snb.2011.01.059

surfaces were covered with a self-assembled monolayer and conjugated to antibodies by carbodiimide cross-linking. Interactions with a specific secondary antibody were monitored through shifts in the LSPR spectral extinction peak.

Core–shell metallic nanostructures also possess a tunable LSPR that is a sensitive function of their relative core and shell dimensions. A comparative spectroscopic study on the gold nanoshells and their solid counterparts suggested that the gold nanoshells were more sensitive in detecting changes that might occur on the surfaces of the particle [4]. Compared to solid gold nanospheres, Raschke et al. [14] also found the gold nanoshells show a larger plasmon shift for the same amount of change in refractive index of the surrounding environment. By using Mie scattering theory, Halas et al. [15] have modeled the parameters affecting the LSPR sensitivity of gold nanoshells using. They found the LSPR sensitivity increases dramatically with overall particle size and to a lesser extent with increasing r_1/r_2 (the ratio of inner and outer radius of the shell). Their calculations based on Mie scattering theory indicate that the LSPR sensitivity may be further enhanced by fabricating larger nanoshells with thinner shell thickness [15]. Jain and El-Sayed [16] show using extended Mie theory simulations that the sensitivity of the LSPR of a dielectric core-metal nanoshell increases near-exponentially as the ratio of the shell thickness-to-core radius is decreased. For metallic nanoshells, the sensitivity to external refractive index also depends on the core media. Miller and Lazarides [9] found the metallic nanoshell with a high refractive index core has a lower sensitivity to the external refractive index. On the basis of a quasi-static theory, Cao et al. [17] have reported the sensitivity of LSPR to the refractive index of the surrounding medium for gold nanoboxes with fixed inner edge length. It was found that the refractive index sensitivity increases near-exponentially as the wall thickness is decreased.

However, because of the invariability of the dielectric constant of core medium, the sensitivity of refractive index sensors based on metallic nanoshell can only be tuned by the changing of shell thickness. Furthermore, when we use the metallic nanoshells as the chemical or biological sensor, the nanoshell must be suspended in solutions, which brings the difficulty in device fabrication. In this paper, we report a new refractive index sensor based on gold nanotube. Nowadays, arrays of gold nanotubes can be fabricated by electrodeposition into thin film porous alumina templates [18]. These gold nanotubes can act as conduits for molecule and biological matter transport. These condensed matters can also be stored in the nanotubes, which brings the facilitation in device fabrication. Furthermore, the sensitivity of these gold nanotubes can be tuned by the changing of both wall thickness and surrounding medium, which enlarge the ability of optimizing the refractive index sensors.

2. Model

Localized surface plasmon resonance and local electric field of metallic nanotubes have already been modeled previously by our group [19–21]. In the model, the gold tube is infinitely long and has an inner radius r_1 and an outer radius r_2. In our studies, the incident electric field E_0 is perpendicular to the long gold tube, so we only discuss the transverse LSPR and corresponding local electric field. In this calculation, the tube diameter is less than 50 nm, which is much smaller than the light wavelength, so we can evaluate the absorption cross section of gold nanotube by using the quasi static expressions [22].

In the quasi static treatment, the induced dipole moment P in a gold nanotube resulting from the imposition of an incident field E_0 is given by

$$P = E_{\text{local}} - E_0 = \alpha E_0, \tag{1}$$

where E_{local} is the local electric field at the outer surface of gold tube when $r = r_2$, $\phi = 0$ (here ϕ is the included angle incident field makes with the position vector $\vec{r}$). This local electric field could be derived from Laplace's equation [20]. From Eq. (1), we can get the corresponding polarizability [23],

$$\alpha = 4\pi \frac{(\varepsilon_1 - \varepsilon_{2r} - i\varepsilon_{2i})(\varepsilon_{2r} + i\varepsilon_{2i} + \varepsilon_3)e^2 + (\varepsilon_1 + \varepsilon_{2r} + i\varepsilon_{2i})(\varepsilon_{2r} + i\varepsilon_{2i} - \varepsilon_3)}{(\varepsilon_1 - \varepsilon_{2r} - i\varepsilon_{2i})(\varepsilon_{2r} + i\varepsilon_{2i} - \varepsilon_3)e^2 + (\varepsilon_1 + \varepsilon_{2r} + i\varepsilon_{2i})(\varepsilon_{2r} + i\varepsilon_{2i} + \varepsilon_3)}, \tag{2}$$

where ε_1, $\varepsilon_2 = \varepsilon_{2r} + i\varepsilon_{2i}$ and ε_3 are the dielectric functions of the dielectric core, gold wall, and embedding dielectric medium, respectively. Both ε_{2r} and ε_{2i} are functions of light wavelength [24]. $e = r_1/r_2$ is the radius ratio. Finally, we can obtain the absorption cross section by using the optical scattering theory [25]

$$C_{\text{abs}} = k\,Im(\alpha), \tag{3}$$

where $k = 2\pi/\lambda$ is the wavenumber of the light. Therefore, the absorption cross section of a gold nanotube may be tuned by core dielectric constant ε_1, surrounding dielectric constant ε_3 and radius ratio e.

3. Results and discussion

To investigate the LSPR induced refractive index sensitivity of the gold nanotube, absorption spectra of gold nanotube with different core medium have been plotted in Fig. 1, in this calculation, $r_2 = 25$ nm. In a gold nanotube, there are two metal–dielectric interfaces, so there are two kinds of free plasmon, i.e., wire plasmon and the well plasmon. Well plasmon is similar to the cavity plasmon in metallic nanoshell. In this plasmon mode, the conduction electrons oscillate at the inner surface of the gold nanotube. Wire plasmon is similar to the sphere plasmon in metallic nanoshell. In this plasmon mode, the conduction electrons oscillate at the outer surface of the gold nanotube. Because of the hybridization between the wire plasmon and the well plasmon, there are two absorption peaks in the spectra [26]. The shorter wavelength peak, which is less than 500 nm, corresponds to the higher energy antisymmetric plasmon; the longer wavelength peak, which is greater than 500 nm, corresponds to the lower energy symmetric plasmon [27]. It is obvious that the lower energy plasmon peak is much stronger than the shorter wavelength peak. Furthermore, the shift of this lower energy plasmon peak is more sensitive to the local environment. Therefore, the shift of this lower energy plasmon peak is suitable to probe the changing of the local surrounding refractive index. As shown in Fig. 1(a), when the core medium was changed from water ($\varepsilon_1 = 1.77$) to biomolecule ($\varepsilon_1 = 1.99$ [9]), the lower energy plasmon peak red shifts 8 nm. For a thinner gold nanotube, the lower energy plasmon peak red shifts distinctly. Simultaneously, the sensitivity of the peak wavelengths to the core refractive index also increases greatly. When the wall thickness of gold tube is reduced to 2.5 nm, increasing the core dielectric constant from 1.77 to 1.99 leads to the lower energy plasmon peak red shift 24 nm. From this comparison, it is apparent that the refractive index sensitivity can be improved by reducing the tube thickness. The other important influence factor is surrounding dielectric constant ε_3. The absorption spectra in Fig. 1(b) show that, increasing the surrounding dielectric constant also leads to the lower energy plasmon peak red shift distinctly. However, the sensitivity of the peak wavelengths to the core refractive index decreases unexpectedly. Increasing the core dielectric constant from 1.77 to 1.99 leads to the lower energy plasmon peak red shift 21 nm for $\varepsilon_3 = 1$, but only red shift 15 nm for $\varepsilon_3 = 5.4$. From