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Tuning the plasmon shift and local electric field distribution of gold nanodumbbell: The effect of surface curvature transition from positive to negative

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ABSTRACT

The localized surface plasmon resonance (LSPR) properties and local electric field distributions of the gold nanodumbbell are theoretically studied by using the finite-difference time-domain (FDTD) calculation. The decrease of both positive curvature radius in the spherical end and the negative curvature radius in the midsection results in the absorption peak corresponding to longitudinal plasmon mode red shifts distinctly. However, the transverse plasmonic absorption peak is not sensitive to the change of the curvature radii. The physical mechanism has been illuminated by studying the shape transformation dependent local field distribution between nanorod and nanodimer. It has been found that the decrease of the radii of curvature leads to the dumbbell-shaped particle transforming to a dimer-like structure, while the change in inter-particle plasmon coupling results in the "hot spots" of the local field migrating from the spherical ends to the midsection of the particle. There is an associated red shift of longitudinal LSPR. These results indicate that the transition of surface curvature between positive and negative greatly affects the surface charge distribution, local field enhancement and plasmon coupling.

1. Introduction

The optical properties resulted from localized surface plasmon resonance (LSPR) of noble metal nanoparticles have generated enormous scientific interest [1,2]. Because both the wavelength position of LSPR and the enhancement of plasmon induced local electric field are sensitive to the particle shape, tailoring LSPR through the morphology and structure of metallic nanoparticles becomes very important for us to enlarge the application of plasmonic optics [3–7]. It is well known that the spherical gold nanoparticles exhibit only one LSPR band at about 520 nm, and the intense light absorption at this frequency results in the wine red color of gold colloid [8]. When the spherical gold nanoparticle has been elongated into rod-like nanoparticles, the LSPR splits into two bands corresponding to transverse and longitudinal resonance, respectively, and the longitudinal LSPR could be tuned from visible to infrared region by increasing the aspect ratio [9,10]. It has been found that both the band number and wavelength shifting of LSPR become more tunable as the particle symmetry is decreased. For example, the absorption spectra of triangular silver nanoprisms usually exhibit three LSPR bands corresponding to the in-plane dipolar resonance, in-plane quadrupolar resonance and out-of-plane resonance [11,12]. Husu et al. reported an experimental and theoretical investigation of the LSPR of L-shaped gold nanoparticles [13]. They have observed more higher-order plasmon resonances. What's more, because of the asymmetry of the L-shape, a volume plasmon has been excited although it should be forbidden. LSPR and local field enhancement in #-shaped gold nanowires have been studied by Hu et al. [14]. It has been found that the #-shaped nanostructure has two pronounced LSPRs that are insensitive to the incident polarization. Furthermore, the electromagnetic Raman enhancement factors of about 10^6 could be achieved on the symmetrically distributed field hotspots of this nanostructure.

Core–shell type metallic nanoparticle is another kind of plasmonic nanostructure which has well tunable LSPR. Because of the interaction between sphere plasmon on the outer surface and the cavity plasmon on the inner surface, there are two LSPR bands corresponding to anti-symmetric and symmetric coupling, respectively, [15]. And a strong dependence of the symmetric LSPR band at longer wavelength on the shell thickness has been observed [16]. In order to create more abundant and tunable LSPR bands,

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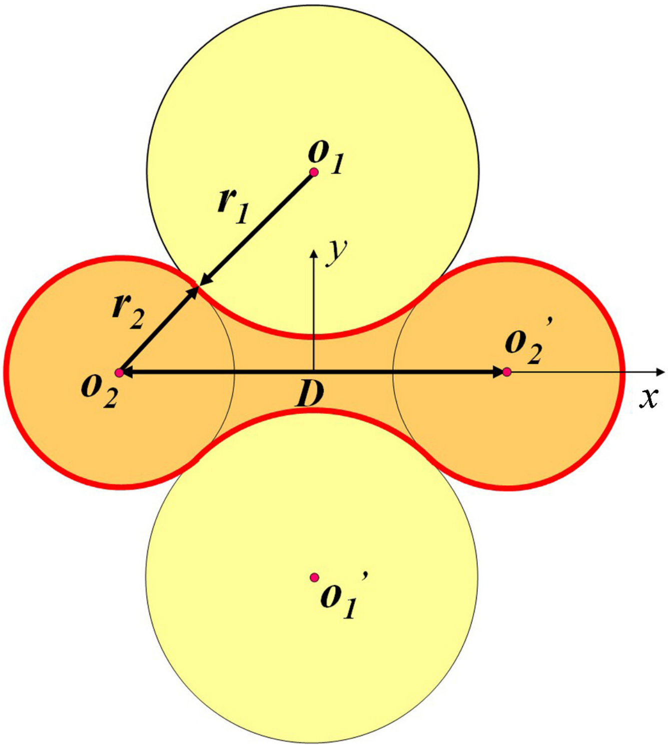

Fig. 1. Geometry of the gold nanodumbbell.

a metal sphere/wire or a metal shell/tube has been inserted into another metallic nanoshell/tube to fabricate multilayered nanostructure [17–20]. In these multilayered core–shell nanostructures, more dielectric–metal interfaces result in more plasmon coupling and more tunable LSPR.

Although the LSPR of non-spherical metallic nanoparticles is controlled by the shape anisotropy, and the LSPR of core–shell metallic nanoparticles is tuned by the inter-surface coupling, is there a common geometrical factor that can be used to predict the LSPR of both non-spherical solid nanoparticles and core–shell type nanoparticles? Many previous studies indicated that curvature radius plays an important role in affecting the surface electron distribution, and consequently controlling the LSPR frequency [21–25]. There are two types of curvature of metal surface: positive and negative. For example, the surface of gold nanorods has a positive curvature. Although the aspect ratio greatly affects the LSPR of rod-like metallic nanoparticles, it has been found the end-cap geometry, such as flat, oblate spheroid, and sphere, also has a significant effect on the shift of LSPR bands [26,27]. It has also been found that, although the prolate gold spheroid and oblate gold spheroid have the same aspect ratios, the corresponding LSPR wavelengths are different [21]. Indeed, the ratio of curvature radius corresponding to the climaxes is a more accurate factor in predicting the LSPR wavelength. LSPR properties of metal nanoparticles possessing sharp corners with variable curvature have also been studied [28]. By increasing the corner curvature, the main dipolar plasmonic peak experiences a great red shift. What's more, the resonant frequency is controlled by the apex angle of the corner when

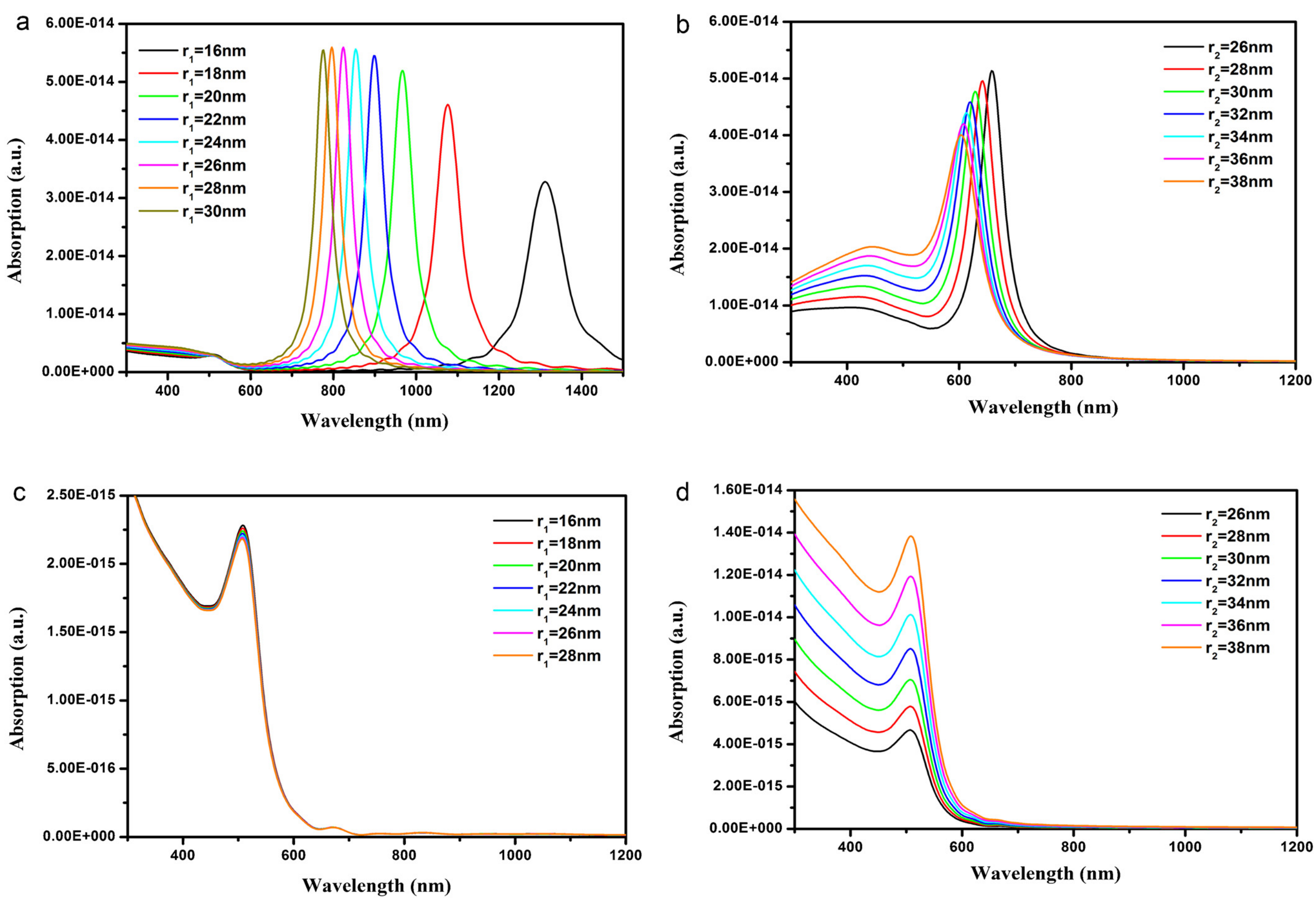

Fig. 2. Absorption spectra properties of gold nanodumbbell with different (a) concave curvature radius, the incident field is polarized in *x* axis direction; (b) convex curvature radius, the incident field is polarized in *x* axis direction; (c) concave curvature radius, the incident field is polarized in *y* axis direction; (d) convex curvature radius, the incident field is polarized in *y* axis direction.