Evolutionary Plasmonic Properties of Single Truncated Ag Nanowire-on-Au Film Nanocavity

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Noble metal nanocavities have been widely demonstrated to possess great potential applications in nano-optics and nanophotonics due to their extraordinary localized surface plasmon resonance. However, most metal nanocrystals synthesized by chemical methods often suffer from truncation with different degrees due to oxidation and dissolution of metal atoms at corner and edges. We investigate the influence of shape truncation on the plasmonic properties of single Ag nanowire on Au film nanocavity using the finite difference time domain method. When the Ag nanowire (the circumradius $R_2 = 50\,\text{nm}$) is gradually truncated from pentagonal to circular geometry, the scattering peak position of the nanocavity shows prominent blue shift from 962 nm to 608 nm, suggesting a nonnegligible role of truncation on plasmonic properties. The electric field strength and charge distribution of the structure reveal the evolution from dipole mode to quadrupole mode. It is also found that the plasmon resonance wavelength is linearly dependent on the truncation ratio R_1/R_2 (R_1 is the inradius) and the modulation slope is also reliable to the size of Ag nanowire. Our observations could shed light on developing high-performance tunable optical nano-devices in future.

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Noble metal nanocavities are attracting increasing attention in nano-optics and nanophotonics due to their extraordinary localized surface plasmon resonance (LSPR).[1–3] Such plasmonic properties can dramatically amplify light-matter interactions as shown in surface enhanced Raman spectroscopy[4,5] and confine light into the sub-wavelength level as displayed in super-resolution imaging[6,7] and plasmonic nanolaser.[8,9] The noble metal nanoparticle-on-film nanocavities are widely considered as a promising platform for tunable plasmonic applications because of their easy fabrication and thickness-controllable nanogap.[3,10,11] Besides the thickness of the insulator layer, the nanocavity plasmonic properties can be effectively adjusted through the size and geometry of metal nanoparticles.[12] Thanks to the development of advanced chemical synthesis, various noble metal nanoparticles with controllable shapes and sizes could be easily obtained, providing great flexibility for the desired plasmonic properties[13–15] and the strong interactions between plasmon exciton.[16–18] Russell *et al.*[17] successfully demonstrated 1000-fold spontaneous emission enhancement from quantum dots within the gap of Ag nanowire on Ag film nanocavity.

It is a common issue that most metal nanocrystals synthesized by chemical methods often suffer truncation with different degrees due to oxidation and dissolution of metal atoms at corner and edges.[19,20] The slight change on geometry of metal nanoparticles can result in the modulation of their plasmon resonance wavelength and the local field enhancement.[21–25] Yao *et al.* observed tunable Fano resonances on scattering spectrum from the nanocavity with a truncated Ag nanocube on Ag film and demonstrated red-shifted spectra as the size of the Ag nanocube increases and its distance from the silver film decreases.[26] However, the truncation effect of Ag nanocube on the plasmonic nanocavity was not taken into account. Fang *et al.*[27] found progressive red shifts and intensity decrease of the dipole plasmon modes during the sulfidation of Ag/Ag_2S hybrid nanostructures using single particle scattering measurements. It is well-known that the plasmonic properties of the nanoparticle-on-film nanocavities are quite sensitive with the change of gap between particle and film.[11,28] Those experimental works mentioned above tried to chemically control the truncation degree via sulfurization or surfactant concentrations. In fact, it is still a big challenge to precisely control the truncation ratio. Moreover, the influence of truncation on plasmonic properties was investigated randomly in theoretical simulations. Therefore, it is essential to have comprehensive understanding on the exact truncation effect on the plasmonic nanocavity, providing direct theoretical evidence for experimental plasmonic research. To our best knowledge, there is lack of systematic investigation on the evolution of plasmonic properties in the metal nanoparticle-on-film nanocavities

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with gradual truncation.

In this work, we mainly focus on the nanocavity based on Ag nanowire due to their exceptional plasmon properties.[17,28] We propose the truncation ratio of R_1/R_2 to quantify the truncation process. We perform a systematic calculation on the evolution of plasmonic properties of single truncated Ag nanowire on Au film nanocavity via the finite difference time domain (FDTD) method. A structural model was established to quantify the truncation degree of Ag nanowire from perfect pentagon to circle. With the increase of truncation ratio R_1/R_2 between nanowire inradius and circumradius, the plasmon resonance wavelength shows continuous and dramatic blue shift. The correlative electric field strength and charge distribution of the structure are found to change from dipole mode to quadrupole mode. The plasmon resonance wavelength is linearly dependent upon the truncation ratio and the modulation slope is also reliable to the size of Ag nanowire. These findings provide a straightforward understanding on the truncation effect on plasmon modulation of metal nanostructure-on-film nanocavity, which is helpful to advance the studies of plasmon-enhanced light-matter interactions.

Theoretical Method and Computational Model. We investigate the evolution of plasmonic properties of single Ag nanowire-on-Au-film nanocavity with different truncations. Two-dimensional (2D) FDTD simulation was applied since the Ag nanowire synthesized by chemical method often has the length of tens of micrometers and can be assumed to be infinitely long.

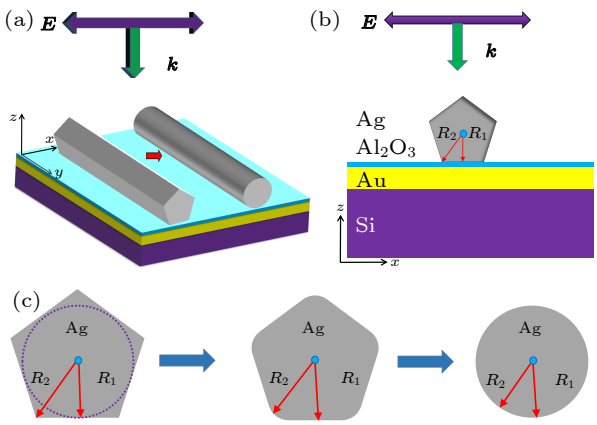

Fig. 1. (a) The structural model of Ag nanowire on Au film nanocavity, i.e., 3D structure of the nanocavity in which Ag nanowire is placed on Al_2O_3 while the electric field is along x-axis. (b) The cross section of the nanocavity prepared on a silicon substrate with an Al_2O_3 spacer layer in between. (c) The truncation evolution of Ag nanowire from perfect pentagon to circle, with R_1 and R_2 being the inradius and circumradius.

The length of Ag nanowire is set as 50 µm. In this nanocavity, a 5-nm-thick Al_2O_3 film is introduced as an insulator layer with Palik permittivity constant.[29] The electric permittivities of Ag, Au and Si are adopted from the data provided by Johnson and Christy,[30] and Palik,[29] respectively. For x and z directions, the boundary conditions are set to a perfectly matched layer. The Ag nanowire and surrounding medium are divided into meshes of 0.5 nm. The mesh size is set as 0.5 nm near the Ag nanowire for x and z directions, 0.25 nm for z direction in the Al_2O_3 layer and 1 nm for z direction in Au film.

The 3D structural model and cross section of single Ag nanowire-on-Au-film nanocavity are shown in Figs. 1(a) and 1(b). The Ag nanowire was closely placed on Au film (50 nm in thickness) with Al_2O_3 (5 nm in thickness) as the insulator layer. The nanocavity was under normal illumination along z-axis and the electric field was polarized along x-axis. The truncation evolution of Ag nanowire is precisely regulated by the truncation ratio (R_1/R_2) of Ag nanowire ranging from 0.81 (perfect pentagon) to 1.00 (circle), as listed in Table 1.

Table 1. Truncation ratio (R_1/R_2) of Ag nanowire.

R_1(nm)	R_2(nm)	R_1/R_2
40.45	50.50	0.81
	48.82	0.83
	47.64	0.85
	46.46	0.87
	45.28	0.89
	44.10	0.92
	42.92	0.94
	41.74	0.97
	40.45	1.00

Results and Discussion. The truncation effect on the plasmonic properties of Ag nanowire-on-Au film nanocavity is investigated. In Fig. 2(a), the scattering spectrum shows a clear plasmon resonance with peak at 962 nm of the nanocavity without any truncation. The simulated scattering and absorption spectra are almost identical as displayed in Fig. S1 in the Support Information, and thus only the scattering spectra are discussed in the following. When the pentagonal Ag nanowire is truncated gradually to be circular, the plasmon resonance of the nanocavity in scattering spectra shows a prominent blue shift towards 608 nm ($\Delta\lambda$ = 354 nm), as illustrated in Fig. 2(a). The evolution and dependence of plasmonics on truncation degree are completely opposite to the observation of single Ag nanocube by Fang *et al.*,[27] showing gradual red shift mainly due to the change of local refractive index besides the decrease of nanoparticle diameter. To further verify the origin of such a phenomenon, we calculate the plasmonic properties of pure Ag nanowire (without substrate) and circular Ag nanowire-on-Au film nanocavity for comparison, as displayed in Figs. 2(b) and 2(c), respectively. With the identical truncation ratio, it can be easily found that the scattering peak of pure Ag nanowire slightly shifts from 371 to 353 nm (∼ 18 nm) due to size effect, which is in good agreement with Hamans' observation,[21] and we also indicate that the truncation has almost negligible influences on plasmonic property of Ag nanowire. In the latter case, with the decrease of nanowire radius from 50 to 40.45 nm, the resonance peak gradually reduces from 660 to 608 nm (∼ 52 nm), comparable to the observation in single Au nanoparticle with different diameters placed on Au film by Benz *et al.*[31] The direct comparison can be referred to the plot of the plasmon peak wavelength of all these three models in Fig. 2(d). The most dramatic

changes on plasmonic properties are realized in the case of truncated Ag nanowire on Au film, indicating the important roles of both the substrate and truncation effects.

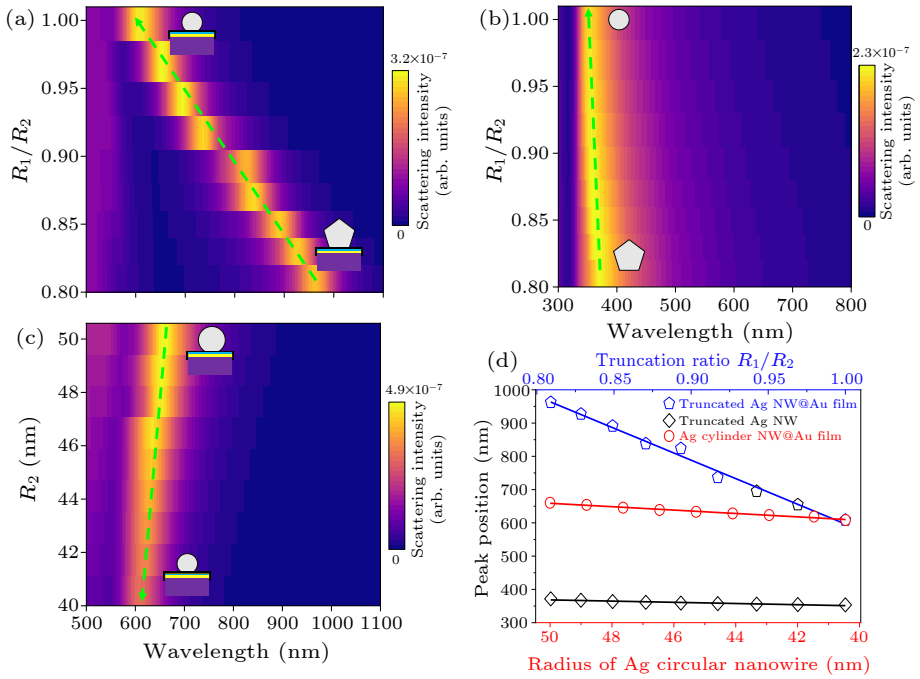

Fig. 2. The plasmonic properties of single Ag nanowire-on-Au film nanocavity with different truncation ratios and sizes. (a) Scattering spectra of single Ag nanowire-on-Au film nanocavity with different truncation ratios. (b) Scattering spectra of pure Ag nanowire without substrate as a function of truncation ratio. (c) Scattering spectra of single circular Ag nanowire-on-Au film nanocavity as a function of nanowire radius R_2. (d) Scattering peak positions as a function of the truncation ratio (blue and black symbols) and the Ag nanowire radius (red symbols), respectively.

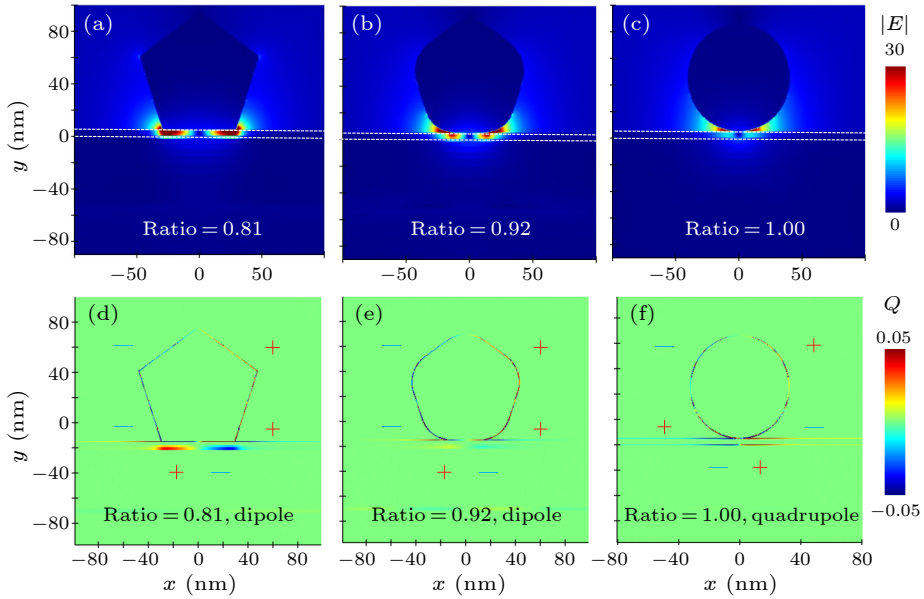

Fig. 3. (a)–(c) The electric field magnitude profiles of the main plasmon resonance peak in the scattering spectra of nanowire-film nanocavity with different truncation ratios. (d)–(f) The correlative charge distribution of nanocavity with different truncation ratios. Note that the corresponding peak positions are 962, 736, and 608 nm, respectively.

To obtain further insight of the plasmonic evolution with truncation, the electric field magnitude of the nanowire-film nanocavity with three selected truncation ratios are given in Figs. 3(a)–3(c). The correlative charge distributions are illustrated in Figs. 3(d)–3(f), respectively. Note that the truncation ratios of 0.81, 0.92, and 1.00 represent the nanowire in nanocavity with perfect pentagonal, partially truncated, and circular geometries, respec-

tively. When the nanowire is free of truncation, there are two types of hotspots with obvious enhancements of field strength, a big volume in the Al_2O_3 insulator layer and a small one in the corners between nanowire and film as shown in Fig. 3(a). With the increase of truncation, the maximum of field strength seems to gradually transforms from the gap layer to the corner as displayed in Fig. 3(c) and Fig. S2. To quantitatively evaluate the filed enhancement, two point monitors were placed at the gap layer and the corner, respectively. As shown in Fig. S3, the maximum electric field enhancement at the corner slightly decreases from 30 to 28.5, while the maximum enhancement in the Al_2O_3 gap significantly reduces from 30 to 11.5. These findings further confirm that the truncation can play important role in both nanocavity plasmonics and field enhancement. The corresponding pattern of charge distribution confirms a dipole mode formed on the surface of Ag pentagonal nanowire, which almost remains similar pattern with the partially truncated Ag nanowire but shows obvious change on the surface of Au film. It eventually converts into a quadrupole mode for a circular nanowire. The plasmonic property of nanowire-film nanocavity is the consequence of the strong coupling between the localized plasmon mode of Ag nanowire and its induced surface plasmon polariton on Au surface. With existence of nanowire truncation, the slight change on geometry can result in redistribution of surface charge as displayed in Fig. 3(e), which is amplified and contributes to prominent modification on the plasmon resonance wavelength and field enhancement of this nanocavity. It is also suggested that the exact geometry of metal nanoparticles for nanoparticle-film cavity is not negligible and should be taken into account when applying for biosensors or plasmon-enhanced spectroscopy.

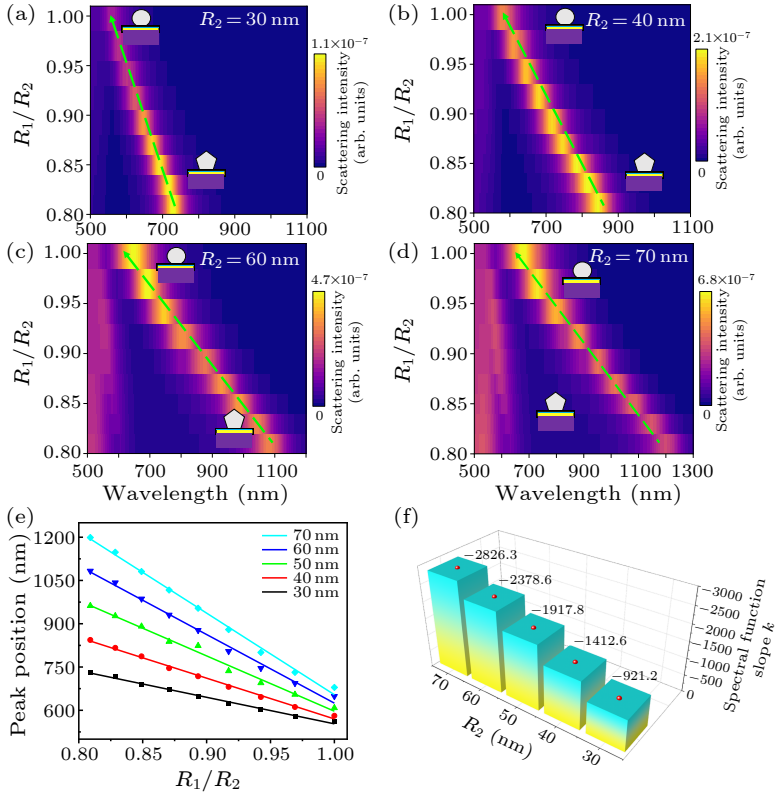

Fig. 4. The truncation evolution of the plasmon resonance of single Ag nanowire on Au film with different nanowire circumradius. (a)–(d) The scattering spectra of nanocavity with R_2 = 30, 40, 60, and 70 nm. Note that the truncation of Ag nanowire is presented by the ratio R_1/R_2 changing from 0.81 (pentagonal shape) to 1 (circle). (e) The plasmon peak positions in the scattering spectra are plotted as a function of the truncation ratio of Ag nanowire. (f) Histogram of each slope k for the corresponding evolution trends via linear fitting.

To get comprehensive understanding on the shape truncation on nanowire-film nanocavity, we evaluate the evolution of the nanocavity plasmonics with different-size Ag pentagonal nanowire, which could also play an important role on the scattering spectra as observed by Hu *et al.*[28] In our case, the circumradius of Ag nanowire is varied from 30 to 70 nm and the calculated corresponding scattering spectra are displayed in Figs. 4(a)–4(d). We find that, with the increasing nanowire size, the plasmon resonance peak in the scattering spectrum shows obvious red shift, even to near-infrared Ⅱ region (60 and 70 nm), which is consistent with the experimental observations on nanowire[28] and nanosphere.[31–33] With the existence of truncation, all nanocavities show similar and consistent blue-shifting on plasmon resonance wavelength. The resonance peak positions in scattering spectra are plotted with the truncation ratio R_1/R_2 changing from 0.81 (pentagonal shape) to 1 (circle), as illustrated in Fig. 4(e). Interestingly, we can clearly see that the influence of truncation on the nanocavity plasmonic property is highly dependent

upon the size of Ag nanowire. The larger the size of the Ag nanowire, the more dramatically the truncation can modify the plasmon resonance. By fitting with a linear relationship $y = kx + b$, where k is the slope, we obtain the slope varying from -921.2 to -2826.3, when the nanowire size increases from 30 to 70 nm. It is also worthy to point out that the spectral width of plasmon mode becomes slightly narrower with the increase of truncation ratio as shown in Fig. S4, indicating that the quality factor of plasmon resonance could be slightly modulated by truncation effect. These data can give a reference value for design and applications of tunable plasmonic devices with high performance.

In summary, we have performed a comprehensive investigation on influences of shape truncation on the plasmonic properties of Ag nanowire-on-Au film nanocavity with FDTD simulation. With the increase of truncation, the nanocavity shows prominent plasmon modulation of $\sim$354 nm blue shift of scattering peak position. The enhanced field strength for different truncation ratios are gradually transformed from the Al_2O_3 insulator layer to the corner between the insulator layer and partially truncated or circular nanowire observed. The correlative charge distribution further confirms the evolution induced by truncation, gradually changing from dipole mode to quadrupole mode, contributing to strong plasmon modulation on the coupling between the LSPR and its induced surface plasmon polariton in the Au film. The truncation effect on nanocavity plasmonics shows obvious dependence upon the size of Ag nanowire, showing linear modulation on the plasmon resonance wavelength as a function of truncation ratio. Our simulation results reveal the influence of shape truncation on nanocavity plasmonic properties and provide the theoretical evidence to design the plasmonic devices via truncation in real measurements. Moreover, similar effects can be expected from other complicated metal plasmonic nanostructures like nanorod and nanooctahedron in applications for enhanced light emission and detections.

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