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Plasmonic characteristics of rhodium dual broken nanorings in UV–visible regime

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Abstract
This work reports on the plasmonic properties of a symmetry-breaking system consisting of rhodium dual broken nanorings, in the ultraviolet–visible regime. In the structure, two rhodium broken rings are located with a separation on the scale of nanometers. As the separation, the light polarization, and the relative orientation of the broken angles are, respectively, varied, the plasmonic scattering efficiency of the system is investigated, using the finite difference time domain method. Multiple plasmonic resonances are revealed, and the associated asymmetry-induced Fano-like lineshapes are fitted to a model that employs multiple Fano lineshape functions. The resonance wavelengths, the spectral widths, and the characteristic \( q \) values are determined from the best fit parameters, and the plasmonic characteristics of the system are quantitatively probed. The results in this work may be beneficial in designs of plasmonic devices that operate at ultraviolet–visible wavelengths.

1 Introduction

The plasmonic properties of noble metal-based nanostructures are mainly determined by the oscillations of their free electrons that are excited by the irradiation of incident light [1]. Surface plasmons have attracted much attention due to their ability to alter photon interactions at nanoscale and their various applications, such as optical waveguides, nonlinear optics, as well as surface-enhanced spectroscopy, etc. [2–4] The influence of the shape and surface morphology of plasmonic nanoparticles on the near-field enhancement performance has been revealed [5]. The plasmonic mode hybridization induced by the substrate of silver nanocylinder has been investigated experimentally and numerically [6]. The effects of several nanocavities formed by a truncated spherical nanoparticle and a rhombicuboctahedron nanoparticle on the patterns of plasmonic nanocavities have been shown, which lays a foundation for various applications utilizing these nanocavities [7]. Besides, the nonlocal effects of propagating gap surface plasmon modes in ultrathin metal–dielectric–metal planar waveguides have been studied [8]. Compared with structures with certain symmetry, symmetry-breaking systems provide us with great plasmonic tunability, thanks to its non-uniform electromagnetic fields, and the induced multiple plasmonic modes [9]. To date, symmetry-breaking structures have been shown to have useful optical properties and a wide range of applications [10, 11].

One of the characteristics in symmetry-breaking systems is the generation of asymmetric lineshapes once the resonance condition is met, which is known as Fano resonance. The asymmetric mechanism in Fano resonance was first addressed by Ugo Fano from the perspective of quantum mechanics in 1961 [12]. In general quantum systems, Fano resonance may occur when there is interference between discrete and continuous quantum states. In plasmonic nanostructures, Fano resonance may arise from the strong coupling between the discrete and the continuous mode, which manifests itself into an asymmetric lineshape in the spectrum [13–15]. Fano lineshapes can thus be adjusted by changing the parameters in plasmonic nanostructures, through affecting the coupling of the plasmonic modes [16]. For example, multiple Fano resonances were generated due to the interference of the dimer plasmonic modes in a split nanoring dimer [17]. In addition, it was also found that the symmetry breaking in a concentric ring/disk cavity enabled the coupling between plasmonic modes of differing multipolar order, which could result in a tunable Fano resonance [18, 19].
Nowadays, most plasmonic studies have been focused on metals of gold, silver and copper, etc., which respond mainly in the visible and near-infrared wavelength region [20]. However, as the investigations of novel materials keep going, the plasmonic devices and structures that operate in the ultraviolet (UV) spectrum are also in demand [21]. The optoelectronic devices operating in the ultraviolet region are characterized by high sensitivity, fast response, and stable operation. The third harmonic generation of deep UV light in an indium tin oxide (ITO) film, which can be substantially enhanced by a metasurface consisting of metallic toroidal meta-atoms covered with an alumina layer for protection against laser-induced damage, has been demonstrated [22]. Strategies for enhancing the intensity of nonlinear ultraviolet signals were summarized, and the performance of deep ultraviolet and vacuum ultraviolet super sources were also studied, paving the way for the design of more efficient luminous tools [23]. A metal–semiconductor–metal structured photodetector decorated with Al NPs has been fabricated. It was found that the response rate of the ZnO UV detector decorated with Al NPs had been improved greatly [24]. The effect of the chemical synthesis of gold nanoparticles on the performance of GaN nanostructured ultraviolet detectors was analyzed. GaN detectors prepared by Au NPs significantly responded to UV in both self-powered and photoconductive modes, and showed a fast and stable time-dependent light response, with significantly enhanced performance parameters [25]. Therefore, it is necessary to find new metals that can be used in UV plasmonics. An aluminum nitride single nanowire self-powered flexible UV photodetector was reported, showing an extremely high responsivity, response speed, and excellent detective upon exposure to 254 nm UV light [26]. Chiral magnesium nanoparticles showed remarkable plasmonic extinction- and chiroptical-effects in the ultraviolet region and could be used as plasmonic sensors for molecular detection [27]. Among many promising UV plasmonic metals including aluminium, titanium, indium, tin, magnesium, lead, and thallium, etc., aluminum is a promising plasmonic material in the UV range, however, aluminum presents a high oxidation tendency, which significantly affects plasmonic properties. Rhodium has recently been shown to possess good UV plasmonic properties by both experiments and theories [28, 29]. Experimentally, it was reported that the surface plasmon resonances in the UV region could be tuned by controlling the size and morphology of rhodium nanoparticles [30]. Tunable optical features at UV wavelengths were also addressed in self-organized rhodium nanostructures [31]. In theory, the UV plasmonic behavior and surface charge distribution of rhodium tetrahedra were studied, and the applications in surface-enhanced spectroscopies and photocatalysis were discussed [32]. In addition, rhodium nanoparticles of planar tripods were investigated and the potential use in plasmonically enhanced UV photocatalysis was also demonstrated [33].

In this work, a symmetry-breaking system comprised of rhodium dual broken nanorings was proposed, and the associated plasmonic characteristics in the UV–visible regime were investigated. Multiple asymmetric lineshapes were revealed in the frequency dependent scattering efficiency curve, correlating to multiple Fano resonances. The electric field distributions at resonance wavelengths were presented, and detailed quantitative studies were also carried out.

### 2 Structure and method

The structure of rhodium dual broken nanorings is illustrated in Fig. 1. In this work, the centers of both rings were placed along the x-axis, and their y and z coordinates were always kept the same, respectively. For simplicity, the sizes of the rings were set the same, i.e., the outer radius was \( R = 10 \) nm, the inner radius was \( r = 8 \) nm, the thickness was \( h = 10 \) nm, and the broken angle was \( \theta = 30^\circ \). Referring to the structure in Ref. [34], where the radii of the inner and outer silver rings were \( r = 80 \) nm and \( R = 100 \) nm, respectively, a smaller size of the ring (i.e., \( r = 8 \) nm and \( R = 10 \) nm) was studied in this work, since the effects were found to be more pronounced under the condition of a smaller size. The

**Fig. 1** Schematic of the structure of rhodium dual broken nanorings. The sizes of two rings are the same. The outer radius of the ring is labeled ‘\( R \)’, the inner radius is indicated in ‘\( r \)’, the thickness is denoted ‘\( h \)’, and the broken angle is labeled ‘\( \theta \)’. The centers of both rings are along the x-axis, and the y and z coordinates are the same, respectively. The separation is indicated in ‘\( d \)’, which is the distance between the centers of the rings. **a** A mirror-image like geometry along the x-axis, where the positions of the broken parts are faced each other. The polarization of the incident light is denoted by the angle ‘\( \psi_r \)’, which is the angle between the electric vector and the x-axis. **b** The left ring is fixed, while the right ring is rotated about the z-axis, and the rotation angle is labeled ‘\( \psi_y \)’, which represents the clockwise-rotating angle starting from its original position.

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separation (labeled ‘d’) was defined as the distance between the centers of the rings, and the value of d was chosen to be greater than 20 nm, to make sure the two rings were separate from each other. Two scenarios were studied in this work: as indicated in Fig. 1a, the positions of the broken parts were placed in a way that they faced each other, and it formed a mirror-image like geometry along the x-axis. In Fig. 1b, the left rhodium broken ring was fixed, while the ring on the right hand side was rotated about the z-axis, and the rotation angle (labeled ‘\(\psi_r\)’) represents the clockwise-rotating angle, with respect to its original position.

In this work, numerical simulations were carried out by employing the finite difference time domain (FDTD) method [35].

3 Simulation settings

A total-field scattered-field light was incident along the z-axis, in the UV–visible wavelength range of 130–600 nm. The calculated region was 0.8 μm on the x, y, and z axes. To avoid the possible artifacts that might be induced by the simulation method, the mesh size was always kept smaller than 1/10 of the shortest wavelength studied in the simulation region of non-plasmon-carrying media. The polarization of the light was denoted by the angle that was away from the x-axis, that is, \(\varphi_p = 0^\circ\) indicates the x-polarized light, and it becomes y-polarized when \(\varphi_p = 90^\circ\). In the simulation, perfect matching layer (PML) boundary conditions were used in all directions. The optical constants of rhodium were from Palik’s experimental data [36]. Material fitting data according to the Drude model by the FDTD software was used, and is given as following:

\[
\varepsilon_{\text{total}}(f) = \varepsilon - \frac{(\omega_p^2)}{2\pi f(i\nu_c + 2\pi f)}
\]  

where \(\varepsilon\) is permittivity, \(\omega_p\) is plasmonic resonance in units of rad/s, and \(\nu_c\) is plasmonic collision in units of rad/s. The fit tolerance was 0.1, and the max coefficients was 6 [35].

4 Results and discussions

According to the structure shown in Fig. 1a, the scattering efficiency was first computed, and two exemplary results are presented in Fig. 2. In Fig. 2a the separation was as great as 40 nm, whereas in Fig. 2b the separation was small, that is, \(d = 21\) nm. In both figures, all other parameters were kept the same, and their values were mentioned to Eq. (2), and the one in (b) is a best fit to Eq. (3). Dashed curves are individual components in each fit.

![Fig. 2](image-url)
above. As shown in Fig. 2a, two distinguishable peaks are observed in the scattering efficiency curve, indicating two plasmonic resonances. One occurs at the UV-visible wavelength of about 355 nm, and the other appears at the much shorter UV wavelength of about 140 nm. Both resonances display asymmetric lineshapes, and this is due to the symmetry-breaking structure of the rhodium broken rings.

As known to the community, Fano resonance may take place in symmetry-breaking systems, when the interference between a continuum and a discrete state of a quantum system is established, and the asymmetric lineshape may quantitatively be described by the Fano function, in which the degree of the asymmetry can be characterized by its $q$ factor [12].

$$\frac{(\xi + q)^2}{\varepsilon^2 + 1}$$  \hspace{1cm} (2)

In Eq. (2) the reduced energy variable may be written as $\xi = (f - f_0)/f$, where $f$ is the frequency of the incident light, $f_0$ is the resonance frequency, and $f$ denotes the spectral width of the discrete state. The characteristic parameter, $q$, depends on both the continuum and the discrete states of the quantum system.

Generally, in plasmonic systems where multiple discrete states exist, multiple Fano resonances may occur. Regarding Fig. 2a, the double-peak feature in the scattering efficiency curve is a manifestation of two Fano resonances, and hence the scattering efficiency (indicated in ‘$S$’) may be fitted to Eq. (3), which consists of two Fano lineshape functions. Note that similar treatments were successfully implemented in previous work [37].

$$S = A_\alpha \frac{(\varepsilon_\alpha + q_\alpha)^2}{\varepsilon_\alpha^2 + 1} + A_\beta \frac{(\varepsilon_\beta + q_\beta)^2}{\varepsilon_\beta^2 + 1} + A_\gamma \frac{(\varepsilon_\gamma + q_\gamma)^2}{\varepsilon_\gamma^2 + 1}$$  \hspace{1cm} (3)

where $A_\alpha$ and $A_\beta$ are coefficients. The best fit result is also shown in Fig. 2a as the solid curve, which is in good agreement with the simulated data. This shows that in the region of 130–600 nm, the plasmonic properties of the system can be decomposed into two individual Fano resonances (labeled $\alpha$ and $\beta$, respectively).

Referring to Fig. 2b, apart from Peaks $\alpha$ and $\beta$, the third peak at about 230 nm becomes non-negligible, as the separation of the nanorings is reduced to a small value of $d = 21$ nm. Note that the data in Fig. 2b was first fitted to Eq. (3), and yet the region around 230 nm could not be well fitted using two Fano lineshapes only (for brevity, that fit is not shown here). The scattering efficiency curve was then fitted to Eq. (4) by considering three Fano lineshape functions, and the best fit result is also given in Fig. 2b. The consistency between the fit and the data infers that a third Fano resonance occurs at the UV wavelength of about 230 nm, and it is labeled $\gamma$ in this work.

$$S = A_\alpha \frac{(\varepsilon_\alpha + q_\alpha)^2}{\varepsilon_\alpha^2 + 1} + A_\beta \frac{(\varepsilon_\beta + q_\beta)^2}{\varepsilon_\beta^2 + 1} + A_\gamma \frac{(\varepsilon_\gamma + q_\gamma)^2}{\varepsilon_\gamma^2 + 1}$$  \hspace{1cm} (4)

To further probe the Fano resonances at different wavelengths, the distributions of the electric fields at the peak wavelengths were calculated, and the results are plotted in Fig. 3. By comparing Fig. 3a, b, it is evident that Peaks $\alpha$ and $\beta$ in Fig. 2a arise from two different electromagnetic modes. By examining Fig. 3a, c, it is shown that as the rhodium rings’ separation is narrowed, the electromagnetic hot spots (i.e., the electric field with great intensity) appear more pronounced in the middle space between the broken rings. This
effect has been observed in many other nanostructures and it can also be utilized as a way to generate practical hot spots. Besides, the similarity between Fig. 3c, d reveals that Peaks $\alpha$ and $\gamma$ in Fig. 2b undergo similar physical mechanisms, albeit the intensities are different.

Systematically, the effects of the separation on the scattering efficiency curve were studied, with changing $d$ from 60 to 21 nm. The results are plotted in Fig. 4. Note that the best fit curves shown in Fig. 4a were obtained by using Eq. (3), while those in Fig. 4b were from Eq. (4). This indicates that once the separation is as large as 30 nm, the lineshape can be decomposed into two separate Fano resonances. However, when the separation is small enough, e.g., 23 nm, the third resonance peak becomes obvious and cannot be neglected. To quantitatively probe the resonance properties, the best fit values for the resonance wavelength, the spectral width, and the characteristic $q$ parameter were extracted, and the corresponding data are given in Fig. 5.

Regarding Fig. 5a, with narrowing the separation from 60 to 21 nm, the resonance wavelength of Peak $\alpha$ keeps almost at 435 nm, Peak $\beta$ is constant at 140 nm, and Peak $\gamma$ is at 225 nm, if any. From Fig. 5b, it is witnessed that as $d$ is decreased, the spectral width of Peak $\alpha$ is raised from 370 to 430 THz, and Peak $\beta$ is broadened from 400 to 550 THz; Peak $\gamma$ oscillates slightly within 230 and 250 THz. Interestingly, different trends are revealed in the $q$ values that are shown in Fig. 5c. With the value of $d$ is decreased, Peak $\alpha$’s $q$ value is raised from 2 to 6, and Peak $\gamma$ from 8 to 10, while Peak $\beta$ is reduced from 28 to 23. This difference in the trends for $q$ values verifies the aforementioned fact that Peaks $\alpha$ and $\beta$ are associated with two different modes.

Known to the community, the polarization of the electric vector of the incident light may also affect the resonance behaviors associated with plasmonic systems, since the surface plasmons are induced by the incident light with a certain polarization. In this work, the effect of the light’s polarization was also studied, by varying the polarization angle from 0 to 90°. Taking the structure of $d = 40$ nm as an example, the polarization angle dependent scattering efficiency curves were simulated and the results are shown in Fig. 6. To observe the situation under the weak coupling effect, an example of $d = 40$ nm was chosen to probe the physical effects caused by different variables. Based on the data given in Fig. 6, the curves were all fitted to Eq. (3), and the best fit results are presented as solid curves in the figure. It is clear that the resonance peaks $\alpha$ and $\beta$ can both be well fitted for all the polarization angles. In addition, the field distributions at the resonance wavelengths were also computed, and the results are illustrated in Fig. 7.

For both Fig. 7a, b, as $\varphi_p$ is changed, it is obvious that the spatial regions where the hot spots appear strongly depend

![Fig. 4](image-url)  
**Fig. 4** Frequency-dependent scattering efficiency of the structure shown in Fig. 1a. a $d$ was from 60 to 30 nm, and b from 23 to 21 nm. The incident light was $x$-polarized. The solid curves in (a) represent a best fit to Eq. (3), and the ones in (b) are a best fit to Eq. (4). For clarity, the curves are presented with an offset in the $y$-axis: in (a) $d = 40$ nm is offset by 4, the 50 nm the 8, and the 60 nm the 12; in (b) $d = 22$ nm is offset by 4, and the 23 nm the 8.
on the polarization of the incident light. Similar effects were also observed and addressed in previous work [38].

Based on Fig. 6, the best fit parameters for Peaks $\alpha$ and $\beta$ were extracted, and the values are presented in Fig. 8. As indicated in Fig. 8a, with changing the polarization vector from the x-axis to the y-axis (i.e., $\varphi_p$ from 0 to 90°), the resonance wavelength of Peak $\alpha$ is blueshifted from 400 to 350 nm, while Peak $\beta$ remains unchanged at 150 nm. Referring to Fig. 8b, the spectral widths for the two peaks are both reduced, that is, the spectral width of Peak $\alpha$ is decreased from 450 to 410 THz, and Peak $\beta$ from 530 to 430 THz. Referring to Fig. 8c, with increasing the value of $\varphi_p$, the $q$ parameter of Peak $\alpha$ is slightly decreased from 6 to 3, whereas Peak $\beta$ is increased from 20 to 33. Based on the results revealed in this work, it is shown that the properties of Peak $\alpha$ have potential applications in several fields, such as sensing and filtering.

![Fig. 5](image-url)  
**Fig. 5** Best fit values for a resonance frequency/wavelength, $f_0\lambda_0$, b spectral width, $f_s$, and c $q$ parameter, as a function of the separation, $d$, determined by fitting the scattering efficiency curve in Fig. 4

As mentioned above, Fano resonance usually takes place in symmetry-breaking systems, and its plasmonic properties are correlated to the degree of the asymmetry. In this work, the effects of asymmetry on the plasmonic behaviors were also probed, by considering the geometry that is demonstrated in Fig. 1b. According to Fig. 1b, the left rhodium broken ring was fixed, while the ring on the right-hand side was delicately rotated about the z-axis, to vary the degree of the asymmetry by changing the location of the broken part of the ring. Under this scheme, the scattering efficiency curves were calculated, and they are plotted in Fig. 9 as a function of the rotation angle of the right-hand side ring, $\psi_r$. An interesting fashion is witnessed from Fig. 9; the curves of $\psi_r = 0^\circ$ and $180^\circ$ coincide with each other, $\psi_r = 30^\circ$ and $150^\circ$ are very close, and moreover, $\psi_r = 60^\circ$ and $120^\circ$ are very similar. To probe the underlying physics of this observation, the field distributions at resonance wavelengths were further collected and are shown in Fig. 10.

Regarding Fig. 10, for both Peaks $\alpha$ and $\beta$, as the rotation angle, $\psi_r$, is changed from 0 to 180°, the field distributions appear similar once two rotation angles have a summation of 180°. For example, the field of $\psi_r = 0^\circ$ is quite similar to that of $180^\circ$, and $\psi_r = 60^\circ$ has little variations with respect to that of $120^\circ$. To quantitatively verify this, the best fit parameters were determined for Fig. 9, and the values are presented in Fig. 11. It is clear from Fig. 11a that little variations in the resonance wavelength are shown for both peaks, respectively; $\lambda_0$ is almost 390 nm for Peak $\alpha$, and it is around 130 nm for $\beta$. The observations made in Fig. 11b, c also well support the fashion witnessed in Fig. 9. For instance, The spectral width of Peak $\alpha$ for $\psi_r = 30^\circ$ and $150^\circ$ are both
Fig. 7 Electric field distribution in the $x$–$y$ plane for the case shown in Fig. 6. The electric fields were determined at the wavelength of (a)–(d) Peak $\alpha$, and (e)–(h) $\beta$. In the $z$ direction, the $x$–$y$ plane was through the center of the rhodium rings. Note that the maximum intensities of the color bars in (a)–(d) and (e)–(h) are different.

Fig. 7 Electric field distribution in the $x$–$y$ plane for the case shown in Fig. 6. The electric fields were determined at the wavelength of (a)–(d) Peak $\alpha$, and (e)–(h) $\beta$. In the $z$ direction, the $x$–$y$ plane was through the center of the rhodium rings. Note that the maximum intensities of the color bars in (a)–(d) and (e)–(h) are different.

5 Conclusions

In this work, the plasmonic properties of a symmetry-breaking system consisting of rhodium dual broken nanorings have been investigated. The scattering efficiency curves have been calculated in UV–visible wavelength range, using the FDTD method. Multiple resonances have been identified and the data have been well fitted to the equations that employ multiple Fano lineshape functions. With respectively varying the separation between the broken rings, the polarization of the incident light, and the rotation angle of one of the dual rings, the plasmonic properties of the system have been studied. The electric field distributions at resonance wavelengths

Fig. 8 Best fit values for (a) resonance frequency/wavelength, (b) spectral width, and (c) $q$ parameter, as a function of the light polarization, $\varphi_p$, determined by fitting the scattering efficiency curve in Fig. 6.

430 THz, and the $q$ value of Peak $\beta$ for $\psi_r = 60^\circ$ and $120^\circ$ are both 24.

Fig. 9 Frequency-dependent scattering efficiency of the structure shown in Fig. 1b, with $d = 40$ nm. The polarization of the incident light was $x$-polarized. The rotation angle of the right-hand side rhodium broken ring was varied from $\psi_r = 0$ to $180^\circ$. The solid curves are a best fit to Eq. (3).

Fig. 9 Frequency-dependent scattering efficiency of the structure shown in Fig. 1b, with $d = 40$ nm. The polarization of the incident light was $x$-polarized. The rotation angle of the right-hand side rhodium broken ring was varied from $\psi_r = 0$ to $180^\circ$. The solid curves are a best fit to Eq. (3).
have also been simulated, indicating different plasmonic modes occurring at different resonances. The best fit parameters of the resonance wavelength, the spectral width, as well as the $q$ parameter have been determined, and a quantitative analysis of the system has been achieved. According to this work, rhodium-based nanostructures may be implemented in designs of plasmonic devices in the UV–visible regime.

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Data availability All data generated or analysed during this study are included in this published article.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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