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Octupole plasmon resonance improves light enhancement by a metal nanodimer

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Metal nanoparticles are extensively used in science and technology to resonantly confine and enhance optical fields. Highest enhancement factors are achieved in nanosized gaps of metal dimers. It is commonly assumed that higher-order plasmon resonances, such as electric quadrupole and octupole, are in nanoparticles much weaker than a dipole resonance. Indeed, in the classical multipole expansion that deals with the scattered fields, these “dark” multipoles can be invisible. In this work, we show that an octupole resonance in a metal nanodimer can lead to a substantially larger field enhancement than a dipole resonance. The effect is explained by the fact that the near-field enhancement provided by the excited electric currents can be strong when the excitation is dark. This finding extends the design principles of a plasmonic nanostructure toward higher-order multipoles that, being naturally narrowband, can be useful for a variety of applications, especially in plasmonic sensing and detection.

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Localized surface plasmon resonances in metal nanoparticles are widely used in optics and photonics due to their ability to confine and enhance optical fields at the nanoscale [1]. The applications of plasmon resonances range from optical sensors and detectors to nanostructured light sources, optical nano-waveguides, and nanomaterials [2–4]. As an example, metal nanoparticles are ideal building blocks for optical metasurfaces and metamaterials, in which individual plasmon excitations lead to a desired optical response of the system [5,6]. Another important field of applications of plasmon resonances is surface-enhanced fluorescence and Raman spectroscopy [7–9], in which locally enhanced optical fields induce electronic and vibrational transitions in atoms and molecules, making it possible to detect them even with a portable spectroscopic device [10,11].

A particularly high enhancement of light intensity is achieved at the locations of abrupt and small-volume inhomogeneities and discontinuities of the used nanostructures, e.g., in a nanometer-scale gap between two metal nanoparticles [12–17]. It has been shown that the dipole–dipole interaction between the particles can shift the resonance frequency and further increase the field intensity in the gap [18–20]. Plasmonic nanoparticles can also show higher-order multipole excitations, such as electric quadrupoles, but they are often neglected because their scattering cross sections are much smaller than those of electric dipoles [21]. We have recently shown, however, that multipole resonances in metal nanoparticles interacting with other particles can hybridize and exhibit simultaneously bright and narrowband scattering [21,22]. In such cases, multipoles of different orders enhance each other at the same spectral location, which can be used to create spectral sensors [23] or magneto-electric optical metamaterials [24,25].

In this work, we show that higher-order plasmon resonances in interacting nanoparticles can lead to exceptionally high local enhancement of light intensity. As an example, an octupole resonance in a pair of two silver nanospheres is shown to result in a higher enhancement factor in the interparticle gap than the dipole resonance. Since octupoles are usually neglected in such small structures, we consider the discovered effect remarkable. We explain it as follows. The higher the order of a multipole resonance, the smaller its contribution to the scattered field. However, if the scattered field is dark, the photons must be trapped in the near-field. This can lead to a significant enhancement of both the electric current density in the particles and the near-field intensity, even though the multipole is nearly invisible in the far-field [26–31]. We prove that this is the case by calculations and show that not all higher-order multipoles can result in an improved enhancement, but only those that have co-directed current densities around the enhancement region.

Consider a metal nanodimer composed of two silver nanospheres of radius $R = 40$ nm separated by distance $g = 7$ nm. Such dimers are frequently used to enhance light intensity in the gap. The smaller the gap, the higher the intensity. In our dimer, the gap size is chosen to be sufficiently small for a significant enhancement and still large enough for being obtainable in nanofabricated samples. The intensity enhancement is calculated at the origin of the coordinate system shown in Fig. 1. The optical constants of silver are taken from [32]. For the medium surrounding the dimer, we consider three options: glass, water, and air. The dimer is assumed to be illuminated by an x-polarized optical plane wave propagating in the z-direction.

When the incident light wave interacts with the dimer, it excites electric currents in it, some of which exhibit plasmon resonances. A conventional way to characterize these currents is...
observed in the far-field. This means that all the multipoles scattering are very small (in the figure, they are scaled up to multipole resonances, mainly the electric quadrupole resonance = the origin of the coordinate system. The parameter values used are \( R = 40 \text{ nm}, g = 7 \text{ nm}, \) and \( n = 1 \) (for vacuum or air), \( n = 1.33 \) (for water), and \( n = 1.5 \) (for glass).

Fig. 1. Interaction geometry of a silver nanodimer with an incident optical plane wave polarized along its long axis. The spheres are considered to be embedded in a dielectric medium of refractive index \( n \). The intensity enhancement is calculated in the gap, i.e., in the origin of the coordinate system. The parameter values used are \( R = 40 \text{ nm}, g = 7 \text{ nm}, \) and \( n = 1 \) (for vacuum or air), \( n = 1.33 \) (for water), and \( n = 1.5 \) (for glass).

Let us next calculate the intensity enhancement spectra in the gap for the dimer in the three media (directly with COMSOL Multiphysics). The spectra at \( x = y = z = 0 \) are shown by the black lines in Figs. 3(a)–3(c) for the dimer in glass, water, and air, respectively. The spectra averaged over a small cubic volume in the gap (with the side length of \( 7 \text{ nm} \)) are shown by the yellow lines. The selected media are typical solid, liquid, and gaseous media in experiments dealing with plasmonic enhancement of light. The spectra show a surprisingly strong and narrowband resonance in the region of higher-order multipole excitations and a lower and wider peak corresponding to the electric dipole resonance. Note that, in the expansion presented in Fig. 2, the only considerable higher-order multipole is the electric quadrupole that cannot contribute to the gap enhancement due to its symmetry, producing a field that is dark at the center. The amplitude distributions of the overall field at the wavelength of the narrow peak are shown in the insets.

In order to explain the obtained spectra, we use the fact that the near-field enhancement in the gap is connected to the electric currents of the multipoles rather than to their scattered fields. The complex amplitude of the effective current density associated with each point multipole moment can be accessed using the following equation [33]:

\[
\mathbf{J}(r) = i\omega \sum_{l=1}^{\infty} \sum_{k=0}^{l} \sum_{m=-l}^{l} M^{(l)}(\mathbf{r}, a, b) \hat{\mathbf{r}}
\]

\[
(−1)^{(l−1)!} \frac{d^l}{dl^l} \frac{d^b}{db} \frac{d^{(l+b+1)}}{d^{(l+b+1)}} \delta (r),
\]

where \( M^{(l)}(\mathbf{r}, a, b) \) represents a current multipole tensor of rank \( l \) written in Cartesian coordinates. This Cartesian expansion yields multipole excitations that differ from those of the classical multipole expansion. They are composed of parallel current elements spatially displaced from each other along the three coordinate axes and phase-shifted by \( \pi \). The displacement is set to be infinitesimally small. Unit vector \( \hat{\mathbf{r}} \) defines the orientation of the current elements in the excitation. Integers \( a, b \), and \( l−(a+b+1) \) show how many times the original single current element is split and displaced along the \( x, y, \) and \( z \)-directions, respectively. The multipoles are not divided into electric and magnetic multipoles, but ordered in accordance with integer \( l \). For example, \( M^{(0)}(\mathbf{x}, 0, 0) \) stands for a dipole oriented along the \( x \) axis (moment \( p_x \)), \( M^{(2)}(\mathbf{z}, 1, 0) \) for a quadrupole (moment \( Q_{xz} \)) composed of two mutually displaced along the \( x \)-direction and flipped current elements oriented along \( z \), and \( M^{(3)}(\mathbf{x}, 2, 0) \) for a current octupole \( (Q_{xyz}) \) composed of four current elements displaced and oriented along the \( x \)-direction. These and other multipole configurations are illustrated schematically in Fig. 4, assuming that the scatterer is a dimer. Once the multipole moment is known, the effective current density associated with it can be calculated from Eq. (1). For the multipole moments shown in Fig. 4, we obtain \( \mathbf{J}_{\phi_0}(r) = −i\omega \hat{\mathbf{x}} Q_{xx} \delta (r)/x, \) \( \mathbf{J}_{\phi_0}(r) = −i\omega \hat{\mathbf{y}} Q_{yy} \delta (r)/y, \) \( \mathbf{J}_{\phi_0}(r) = −i\omega \hat{\mathbf{z}} Q_{zz} \delta (r)/z, \) and \( \mathbf{J}_{\phi_0}(r) = −2i\omega \hat{\mathbf{x}} Q_{xy} \delta (r)/x^2 \). Other multipole excitations are either symmetry-forbidden or negligible in the dimer we consider. Since the dimer is not a point scatterer and the current density is distributed smoothly inside it, we can replace the delta function in the above expressions with a finite, but still localized, function \( s(r) \) of radial sizes corresponding to those of the dimer. We recall that the quadrupole currents cannot contribute to the enhancement at the center of the dimer due to expand the field scattered by the system into orthogonal spherical harmonics, each originating from a certain electromagnetic multipole [33]. The electric current excitation in the scatterer is then written as a sum of the obtained multipole moments. We used the COMSOL Multiphysics software to calculate the scattered field and the multipole expansion procedure of [33] to calculate the contributions of the multipole moments to the scattering cross section. In Fig. 2, we show the spectra of the scattering cross section of the dimer, when it is embedded in glass (\( n = 1.5 \)). The total scattering cross section (red curve) exhibits two peaks, at wavelengths \( \lambda = 420 \text{ nm} \) and \( 630 \text{ nm} \). The longer-wavelength peak corresponds to the electric dipole resonance, while the shorter-wavelength peak includes also higher-order multipole resonances, mainly the electric quadrupole resonance hybridized with the electric dipole excitation (see the black and blue lines). The contributions of the electric octupole (EO), magnetic dipole (MD), and magnetic quadrupole (MQ) to the scattering are very small (in the figure, they are scaled up to become visible), and the contributions of all other higher-order multipoles are even smaller. This means that all the multipoles of higher orders than the electric quadrupole are dark, when observed in the far-field.
to their centrosymmetric distributions. For the effective current densities associated with the dipole and octupole excitations in the dimer, we can then write

\[ J_{p}(r_x) = -i\omega p_x s(r_x), \]  
\[ J_{O_{xxx}}(r_x) = -2i\omega O_{xxx} s(r_x)^2, \]

where \( r_x \) is the effective radial extent of the current density in the \( x \)-direction. The complex amplitude of the total current density contributing to the field in the gap is

\[ J(r_x) = A\xi \left( p_x + \frac{2O_{xxx}}{\xi^2} \right), \]

where \( A \) is a constant that is not relevant for our calculations. Since \( \xi \) depends on the shape of the scatterer (through the shape of \( s(r_x) \) that we do not define here), we use it as a fitting parameter to match the spectrum of the current density to the spectrum of the enhanced intensity. The electric current multipole moments that appear in Eqs. (2)–(4) can be calculated using the classical electric and magnetic multipole expansion coefficients \( a_{1l}(l, m) \) and \( a_{3l}(l, m) \) of orders \( l \) and \( m \) (see Eqs. (35)–(48) in Ref. [33]). Excluding the expansion coefficients of all symmetry-forbidden and negligible multipole moments, we obtain

\[ p_x = \frac{1}{C_1} \left( a_{1l}(1, 1) + \frac{7}{3} a_{3l}(3, 1) \right), \]  
\[ O_{xxx} = -\frac{1}{3C_3} a_{3l}(3, 1), \]

where coefficients \( C_1 \) and \( C_1 \) are \( C_1 = -ik^3/(6\pi\varepsilon e_0) \) and \( C_1 = -ik^3/(210\pi\varepsilon e_0) \). Parameter \( k \) is the wavenumber in the surrounding medium of electric permittivity \( \varepsilon \), and \( E_0 \) is the electric field amplitude of the incident wave. The expansion coefficients \( a_{1l}(l, m) \) and \( a_{3l}(l, m) \) are obtained, using Eqs. (15) and (16) in Ref. [33]. The fields are calculated using COMSOL Multiphysics.

Evaluating \( p_x \) and \( O_{xxx} \), inserting them into Eq. (4), and properly tuning \( \xi \), we obtain the normalized spectra of the squared amplitude of the current density \( (|J|^2/J_0^2) \) shown in Fig. 3 (see the blue dash-dotted lines). Here, \( J_0 \) is the peak value of the current density in the spectrum. We emphasize that the field intensity is determined by the squared amplitude of the current density. The fitting parameter (distance \( x_0 \)) assumed the values of 47.6 nm, 46.8 nm, and 45.6 nm for the dimer in glass, water, and air, respectively. The spectra of the squared amplitudes of the effective current density associated with the excited moments \( p_x \) (blue line) and \( O_{xxx} \) (red line) are shown in (d)–(f) for the dimer embedded in glass, water, and air, respectively.

Fig. 4. Schematic illustration of electric current configurations excited in the dimer. They correspond to a dipole (moment \( p_x \)), a quadrupole (\( Q_{xx} \), \( Q_{xz} \), and \( Q_{zxx} \)), and an octupole (\( O_{xxx} \)) of the Cartesian electric current multipole expansion.
show that the highest peak in the enhancement spectrum originates primarily from the octupole resonance. There is a certain degree of hybridization of the current multipole resonances in the dimer caused by local sharing of the same electric current densities by different multipoles. We have also found that if the gap size changes, e.g., from 2 to 20 nm, the octupole enhancement factor at its peak gradually decreases from $7.5 \times 10^2$ to $1.7 \times 10^2$ and the dipole enhancement factor from $3.3 \times 10^2$ to $1.3 \times 10^2$.

The electric charge and current density profiles on the surface of the dimer are shown in Fig. 5 by the color and arrow distributions. The length of the arrows is given in a logarithmic scale. Figure 5(a) corresponds to the peak enhancement at $\lambda = 434$ nm for the dimer in glass [see Fig. 3(a)]. It exhibits a clear octupole excitation ($O_{3\alpha}$) slightly mixed with a dipole excitation ($p_x$). Note that the current and surface charge densities are high near the gap. The same excitation, but phase-shifted by $\pi/2$, is shown in Fig. 5(b). This phase-shifted distribution reflects excitation of quadrupole moments $Q_{\alpha}$ and $Q_{\beta}$. In Fig. 5(c), corresponding to $\lambda = 640$ nm, the charge and current profiles exhibit a pure electric dipole excitation ($p_x$). These profiles support our conclusions.

To summarize, we have shown that octupole resonances in metal nanodimers can lead to a local intensity enhancement that exceeds that achieved with other multipole resonances, including the dipole resonance. This discovery can have significant consequences in nano-optics, extending the design principles of plasmonic nanoparticles to those based on higher-order multipoles. We studied the effect using a simple metal dimer consisting of two silver nanospheres as an example. However, we expect that, if the particles are specifically designed to facilitate an octupole or another dark higher-order excitation, much higher enhancement factors can be achieved. For example, the system can be composed of four rods instead of two spheres. Octupole and higher-order excitations in nanoparticles are usually ignored because they do not contribute much to the scattered light. Despite this fact, they can produce high electric current densities, which can lead to a significant near-field enhancement. Hence, the relative darkness of a higher-order plasmon resonance can result in a “hotter” spot in the particle near-field. Furthermore, the local enhancement will have a narrower spectrum, which can be used in near-field sensors and detectors based on spectral shifts of the plasmon resonance wavelength. Hybrid resonances forming electromagnetic anapoles are particularly promising in this regard.

**Disclosures.** The authors declare no conflicts of interest.

**Data availability.** Data underlying the results presented in this paper may be obtained from the authors upon reasonable request.

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