Published in final edited form as:

Nanoscale. 2020 January 02; 12(2): 832–842. doi:10.1039/c9nr08515g.

Optical Properties of Symmetry-breaking Tetrahedral Nanoparticle

Peng Zheng^a, Debadrita Paria^a, Haitao Wang^b, Ming Li^b, Ishan Barman^{*,a,c,d}

^aDepartment of Mechanical Engineering, Johns Hopkins University, Baltimore, MD 21218, United States

^bSchool of Materials Science and Engineering, Central South University, Changsha, Hunan 410083, China

^cDepartment of Oncology, Johns Hopkins University School of Medicine, Baltimore, MD 21287, United States

^dThe Russell H. Morgan Department of Radiology and Radiological Science, Johns Hopkins University School of Medicine, Baltimore, MD 21287, United States

Abstract

Spectrally rich but geometrically simple plasmonic metallic nanoparticles are highly favored in nanophotonics. Yet, they remain elusive owing to the symmetry-induced mode degeneracy and interband transitions-induced plasmonic damping. Hence, most nanoparticles display a single major extinction peak originating from the lowest-order dipole resonance. In this study, we uncover that even a simple tetrahedral nanoparticle supports rich spectral features due to symmetry breaking. This discovery runs counter to the reported gold tetrahedral nanoparticles where only a single extinction peak was observed¹. We find, in the case of a tetrahedral nanoparticle, the plasmonic quadrupole vertex mode becomes a bright mode and hybridizes with the dipole vertex mode, which splits the extinction peak and contributes to the spectral diversity and tunability. The peak splitting is also found to be sensitively dependent on the roundness of vertices and edges. Furthermore, the tetrahedral depolarization factors are determined using the previously generalized absorption coefficient. We envision that this work will not only help fill the gap in understanding optical properties enriched by symmetry breaking but also guide superior probe design by combining spectral tunability with geometric simplicity of the nanoparticle.

Keywords

Tetrahedron; Nanoparticle; Optical Properties; Surface Plasmon; Depolarization Factor

Metallic particles at the single-nanoparticle level support exquisite optical properties, which are highly favored in nanophotonics.^{2–3} They also serve as powerful tools for ultrasensitive biosensing based on surface-enhanced spectroscopies as well as an emerging agent for

*To whom the correspondence should be addressed. ibarman@jhu.edu; Tel: +1-410-516-0656.

The authors declare no competing financial interest.

Supporting Information: Sections S1–S4 and Figures S1–S6.

treating malignant cancer cells in photothermal therapy.^{3–6} Such nanoparticles also provide promising routes for efficient photocatalysis and solar energy conversion by concentrating sunlight beyond the diffraction limit, accelerating kinetics, extending spectral range, or facilitating energy transfer.^{7–8} Advances in self-assembly and nanofabrication techniques permits the production of lattices, superlattices, and even metasurfaces with unique scattering and/or absorption properties that can be leveraged for numerous fascinating optical phenomena, which further extend the functionalities and realm of applications.^{9–13}

A number of prominent optical properties of metallic nanoparticles can be ascribed to the excitation of localized surface plasmon resonances (LSPR) on a single-nanoparticle level in the subwavelength regime.⁴ The LSPR peaks are observed either optically in the extinction spectrum or electronically with electron energy loss spectroscopy, and originate from the plasmonic eigenstates of coherent surface polarization charge oscillations.¹⁴ Given the freedom of surface polarization charge oscillation in response to an incident illumination, the plasmonic eigenstates are expected to be many, which could enormously diversify the LSPR spectral features. Yet, the observed LSPR peaks on a single-nanoparticle level in the subwavelength regime are not as rich as expected from the plasmonic eigenstates.^{15–20}

The discrepancy can be ascribed to the following reasons. First, for a highly symmetric spherical nanoparticle, higher order plasmonic eigenstates are either degenerate or feature dark modes with a net zero moment. Only the lowest-order dipole resonance exhibits a bright mode with a non-vanishing moment and couples with free-space light displaying a single optical resonance peak.^{4, 19} The spectral tunability of the spherical dipole resonance is severely restrained by the shape depolarization factor. Second, although the degeneracy is partially lifted for a cubic nanoparticle, previous studies have suggested that higher-order plasmonic resonances close to or above the energy threshold of interband transitions are subject to plasmonic damping.¹⁶ The extinction spectrum virtually displays only the lowest-order dipole resonance in the subwavelength regime, as observed by several research groups.^{21–23} Except for silver which has a much higher energy threshold for interband transitions, both gold and copper cubic nanoparticles exhibit only a single dipole extinction peak.^{16, 24–27} Despite the double extinction peaks observed on a nanorod featuring the longitudinal and transverse modes, they are essentially the lowest-order dipole resonances under two orthogonal polarizations.²⁸ The double extinction peaks observed on a star-shaped gold nanoparticle can be similarly understood as the longitudinal dipole mode of the rod-like tips and the spherical dipole resonance of the gold core, which hybridize with each other.²⁹ While higher order plasmonic modes have been observed for nanorods with higher aspect ratio,³⁰ the observed LSPR peaks on a single-nanoparticle level in the subwavelength regime under quasistatic approximation fall short of expectations from the plasmonic eigenstates owing to the restraints imposed by the symmetry-imposed selection rules and plasmonic damping from interband transition.

Admittedly, fascinating optical spectral features such as Fano resonance could be introduced by forming nanoparticle dimers or coupling nanoparticles with an underlying substrate but they are generated at the expense of compromising the geometric simplicity of a single nanoparticle.^{24, 31–32} Furthermore, it is challenging to develop nanoprobe and nanodevices using those complex nanostructures in optical biosensing and in photothermal therapy. The

dilemma for a single nanoparticle to simultaneously possess both the geometric simplicity and spectral diversity seemed to be somewhat alleviated when a single palladium nanodisk was found to display an intrinsic Fano resonance.³³ That is made possible due to the disk geometry, which enables the LSPR to be spectrally overlapped with the interband transitions ultimately leading to Fano resonance. Nevertheless, the success of nanoprobe and nanodevices for biomedical applications hinge not only on sensitivity and selectivity, but also on the practicality as determined by the geometrical simplicity to ensure nanoprobe reproducibility and minimal disturbance to the investigated environment. Thus, design of a single nanoparticle that combines these coveted features remains highly desirable.

In this study, efforts are devoted to shedding light on the optical properties of a promising tetrahedral nanoparticle featuring both geometric simplicity and spectral diversity. Although colloidal gold tetrahedral nanoparticles have been previously reported, our findings using finite difference time domain (FDTD) simulations unveil a new landscape for symmetry-breaking behavior of such nanoparticles that runs counter to the prevailing paradigm outlined in the literature¹. While a single prominent extinction peak was reported for gold tetrahedral nanoparticles in the literature¹, we observed two split extinction peaks in the current study. Interestingly, the split extinction peaks are found to be sensitive to the roundness of the vertices and edges of a tetrahedral nanoparticle. They ultimately merge into a single extinction peak consistent with the experimental measurement at a rounded radius of 2 nm or above. Given the reduced symmetry of a tetrahedral nanoparticle and the sensitive spectral dependence on the roundness of the vertices and edges, it is hypothesized that the intriguing optical behaviors results from the symmetry breaking-induced optical hybridization among various plasmonic vertex modes. Furthermore, the tetrahedral depolarization factors can be identified from the FDTD-calculated extinction spectrum in combination with a generalized model for calculation of absorption coefficient we developed based on Fuchs' seminal work.^{16, 34} We envision that this work will help fill the gap in understanding the optical properties, particularly for symmetry breaking behavior on a single-nanoparticle level.

RESULTS AND DISCUSSION

Symmetry breaking of a tetrahedral nanoparticle.

A tetrahedron is formed by rotating the top edge of a rectangle along the cylindrical axis till opposite edges become perpendicular, as shown in Scheme 1. The purpose for the tetrahedron to be constructed in this way is to make the extinction spectra independent of the selected three orthogonal polarizations in a Cartesian coordinate. The obtained polarization-independent extinction spectra thus facilitate identifying the normal modes on a tetrahedral nanoparticle, as will be shown in Figure 1. Detailed description and coordinates for the formation of tetrahedron and the rounding process in Lumerical FDTD software can be found in Section 1 and Figures S1–S3 in the Supporting Information. For a rectangle, only the dipole vertex mode couples with light in free space and displays an observable spectral feature, the so-called bright mode. Because of the symmetry of a rectangle, the quadrupole vertex mode is essentially a dark mode with a net zero moment. Interestingly, the quadrupole vertex mode becomes a bright mode on a single tetrahedral nanoparticle where the

symmetry is naturally broken, leaving behind a nonzero net moment equal to that of a dipole vertex mode. In this study, symmetry breaking refers to the scenario in which the moment of an optical quadrupole mode remains nonzero due to the geometric asymmetry. On the symmetry-breaking tetrahedral nanoparticle, the surface polarization charge distributions for both the quadrupole and dipole vertex modes are expected to be identical and indistinguishable, as shown in Scheme 1. But given that they respectively originate from dipole and quadrupole resonances, we reason that they may potentially interfere with each other, and produce rich and profound optical spectral features even on a single tetrahedral nanoparticle level.

In comparison, the quadrupole vertex mode of a single cubic nanoparticle remains a dark mode unless the symmetry is broken by forming cubic nanodimer or film-coupled cubic nanostructures, which, however, complicates the nanostructure design.^{24, 31}

Optical properties of a gold tetrahedral nanoparticle.

The extinction spectrum provides a unique glimpse of the rich optical properties of a nanoparticle. Herein, the extinction spectra of a gold tetrahedral nanoparticle with an edge length of 30 nm were calculated by FDTD under three orthogonal polarizations, as shown in Figure 1(a). The calculated extinction spectra were found to be independent of the three selected orthogonal polarizations despite the reduced symmetry on a tetrahedron, as shown in Figure 1(b). The polarization independence is typical of highly symmetric objects such as spheres and cubes. In contrast, for a single nanoparticle with reduced symmetry, all three orthogonal polarizations often need to be studied in order to reveal a full picture of the normal modes. For the tetrahedral nanoparticle of interest in this study, the lack of dependence on the three selected orthogonal polarizations suggests that a complete picture of its normal modes is on full display in the extinction spectrum in Figure 1(b), given that any arbitrary polarization can always be decomposed into the three selected orthogonal polarizations. It is noted that the lack of dependence of extinction spectra on the incident polarization has been observed on nanoparticle clusters with reduced symmetry,³⁵ although such a construct is fundamentally different from this study where a single tetrahedral nanoparticle is investigated.

In the extinction spectra for a gold tetrahedral nanoparticle, two prominent peaks at around 622 nm and 704 nm are observed, as shown in Figures 1(b) and S5(a). Interestingly, their origin can both be traced back to the plasmonic vertex modes as evidenced by the surface polarization charge distributions in Figure 1(c) and electric field distributions in Figure 1(d). It is noteworthy that the observed surface polarization charge distribution and electric field distribution for either vertex mode is polarization-dependent despite the polarization-independent extinction spectrum. This indicates that either vertex mode could originate from more than one type of surface polarization charge distributions as shown in Figure 1(c). It is also observed that the surface polarization charge distributions for the two vertex modes under the same polarization are identical, except that their phases are reversed.

Although the two polarization-independent extinction peaks at 622 nm and 704 nm could come from any of the three surface polarization charge distributions, the density of surface polarization charges are different. This is reflected on the different amplitudes of the electric

fields in Figure 1(d). It is observed that under an incident excitation with $\mathbf{E}_1$ polarization where all four vertices are accumulated with surface polarization charges, the electric field amplitude is lower than under an incident excitation with $\mathbf{E}_2$ or $\mathbf{E}_3$ polarization where only two vertices parallel to the polarization directions are accumulated with surface polarization charges. This suggests that the incident polarization direction has an influence on the electric field amplitude by affecting the distribution and density of surface polarization charges. The electric field amplitude of an optical mode can be maximized by directing the incident polarization along the geometric direction of the mode of interest. In this study, a maximum electric field enhancement ($|\mathbf{E}|/|\mathbf{E}_0|$) of 718 was obtained at the vertices under $\mathbf{E}_3$ polarization, which would produce an estimated SERS enhancement ($|\mathbf{E}|^4/|\mathbf{E}_0|^4$) of $\sim 2.7 \times 10^{11}$ in air. The Stokes shift was ignored in the calculation. Given the sensitivity of the SERS enhancement factor on the vertex sharpness, the lower limit was estimated to be 1.1×10^7 at a roundness of 2 nm. To put such estimated values in the range of 10^7 to 10^{11} in a broad context, we note that a widely recognized threshold for single-molecule SERS is $\sim 10^7$.^{36–39}

More interestingly, while a gold tetrahedral nanoparticle displays two prominent extinction peaks, a gold cubic nanoparticle with the same edge length exhibits only one, as shown in Figure 2. By making the vertices and edges gradually rounded by a radius r , the two prominent extinction peaks on a tetrahedral nanoparticle gradually merge into a single prominent peak, as shown in Figures 2(a)–(f) and S5(b). This newly merged peak undergoes a blue shift with an increasing roundness, which is comparable to the behavior of a cubic nanoparticle with the same rounded radius. While the extinction peak splitting is evidently confirmed on an ideally sharp gold tetrahedral nanoparticle, care needs to be taken in interpretation of the spectral transition from single to double extinction peaks when the rounded radius changes from 0.3 nm to 0.15 nm. At such sub-nanometer length scale, the FDTD simulation may be unable to capture all the plasmonic coupling behaviors, since quantum effects may gradually dominate owing to the non-locality and spill-out of electrons.⁴⁰ As this study is conducted purely based on classical electrodynamics, the quantum effects are beyond the scope of this work.

In comparison, the single extinction peak on the cubic nanoparticle only undergoes a small blue shift while the overall spectral features remain unmodified, as shown in Figures 2(g)–(l). Considering that the quadrupole mode becomes a bright mode on a symmetry-breaking tetrahedral nanoparticle but remains a dark mode on the highly symmetric cubic nanoparticle, it is reasoned that the bright quadrupole mode plays an important role in reshaping the extinction spectral features of a single tetrahedral nanoparticle.

The roundness-induced extinction spectral change has substantial implications. Since experimentally synthesized metallic nanoparticles are almost always rounded to a certain extent, such as nanocubes,^{25, 27, 31} nanorods,^{15, 28} and nanostars,²⁹ it is likely that some (theoretically predicted) spectral features of geometrically special nanoparticles are absent in the experimentally measured extinction spectrum as a result of the roundness, although nanocubes, nanorods, and nanostars only undergo extinction spectral peak shift. It is also noted that experimentally synthesized colloidal gold tetrahedral nanoparticles with an average edge length of 30 nm display a single extinction peak, consistent with the calculated

extinction spectrum in Figure 2(f), suggesting that they are likely naturally rounded by a radius of at least 2 nm.¹

The above intriguing behaviors occurring on a single tetrahedral nanoparticle imply that tetrahedron may possess fundamentally unique optical properties driven by its naturally symmetry-breaking shape that enables a bright quadrupole mode. Its uniqueness further manifests itself as the observed double extinction peaks with identical surface polarization charge distribution but reversed phases under the same polarization, the sensitive dependence of the peak splitting on the roundness of the vertices and edges, and the polarization dependence of either vertex mode on the surface polarization charge distribution – none of which are observed on a single cubic nanoparticle. It is reasoned that the tetrahedral shape commands the interaction between the indistinguishable bright quadrupole and dipole vertex modes, and is thus ultimately responsible for the rich optical spectral behaviors observed above, as will be discussed further in the ensuing sections using the optical hybridization model.

Optical hybridization model.

On a tetrahedral nanoparticle, the indistinguishable quadrupole and dipole vertex modes create a non-deterministic surface polarization charge distribution pattern. The plasmonic eigenstates of the surface polarization charges for the vertex modes primarily include modes ①, ②, and ③ as specified in Figure 3. Although the three modes are phenomenally identical, each one of the modes can hybridize with itself (Figure 3(a)), the inverse of itself (Figure 3(b)) as well as with each other (Figure 3(c) and (d)) in a quadrupole-dipole hybridization manner.²⁴ The hybridization among these eigenstates leads to the formation of antibonding modes at a shorter wavelength and bonding modes at a longer wavelength, producing peak splitting observed in Figure 1(b). The dependence of the peak splitting on the roundness of the vertices and edges for a gold tetrahedral nanoparticle, observed in Figure 2, can thus be understood as a weakened hybridization among the three eigenstates owing to the reduced surface polarization charge density at the vertices.

In essence, the degree of peak splitting is dependent on the dipole-quadrupole coupling strength, which further depends on the strength of the dipole and quadrupole modes (which are essentially the same modes) as well as the intensity of the local field. When the roundness is introduced, although the global surface polarization charge distribution remains largely similar, the local surface polarization charge density changes significantly, especially on the sharp edges and vertices of a gold tetrahedral nanoparticle. In particular, the local re-distribution of surface polarization charges on even only slightly rounded vertices can significantly perturb the surface charge states, and lead to the reduction of the mode strength as well as the local field intensity. This is the reason for the dependence of the extinction spectral peak splitting on the roundness of the vertices, keeping in mind that the extinction spectra for both the dipole and quadrupole vertex modes can trace back to the surface polarization charge accumulations at the vertices.

The roundness of the vertices and edges essentially serves as a new tuning parameter, which controls the hybridization strength and ultimately determines the phenomenally observed extinction peak wavelengths. In comparison, a gold cubic nanoparticle exhibits only a single

prominent extinction peak originating from the bright dipole vertex mode without any involvement of the dark quadrupole mode. Its sole extinction peak only undergoes a mild (often imperceptible) blue shift when the vertices and edges are gradually rounded.

From the optical hybridization picture in Figure 3, the newly formed modes include a dark mode and three bright modes. The dark mode does not exhibit any spectral features and is not discussed further. The three bright modes identified in Figure 3 have also been revealed in Figure 1(c) as distinguishable surface polarization charge distributions. However, due to the mode degeneracy among two of the three bright modes, only two prominent extinction peaks are observed in the polarization-independent extinction spectrum in Figure 1(b). The degenerate modes are substantiated later while studying the tetrahedral depolarization factors.

While the extinction spectral features for a generalized tetrahedral nanoparticle may be explained alternatively, in this study, driven by the construction of a tetrahedron from the geometric evolution of a rectangle, one can reasonably infer that these two seemingly indistinguishable modes with the same surface charge distributions can trace back to the quadrupole and dipole resonances respectively. Thus, the extinction spectral splitting can be reasonably understood as a result of the quadrupole-dipole hybridization.

The hybridization picture implies that the shape nature of a tetrahedral nanoparticle encodes unique optical properties, otherwise not possible on highly symmetric spherical and cubic nanoparticles. The resulting rich and profound optical spectral features unveiled above further demonstrate the necessity to identify the important yet elusive tetrahedral depolarization factors for both fundamental understanding and transformative nanophotonics applications.

Absorption coefficient of normal modes.

Fuchs laid out a fundamental framework to calculate normal modes for nanoparticles of arbitrary shape composed of homogeneous isotropic material.³⁴ For an arbitrary nanoparticle in the subwavelength regime, its susceptibility $\chi(\omega)$ can be calculated by summing over all normal modes:¹⁶

$$\chi(\omega) = \frac{1}{4\pi} \sum_m \frac{C(m)}{\left(\frac{\epsilon}{\epsilon_h} - 1\right)^{-1} + n_m}, \quad \sum_m C(m) = 1 \quad (1)$$

In Equation (1), the resonance behavior for all m normal modes at ω frequency are determined by the nanoparticle depolarization factor n_m , the dielectric function of the host environment ϵ_h and the nanoparticle ϵ , and the oscillation strength $C(m)$. The absorption coefficient $\alpha(\omega)$ for an arbitrary nanoparticle can be calculated by:

$$\alpha(\omega) = 4\pi \frac{\omega}{c} \sqrt{\epsilon_h} V \text{Im} \langle \chi(\omega) \rangle \quad (2)$$

where c and V are the speed of light in vacuum and the volume of the nanoparticle, respectively.

For shapes with known depolarization factors, the absorption coefficient can be readily calculated using Equation (2), and the resonance condition established by Equation (1). For example, the depolarization factor for a sphere is $1/3$, where the resonance conditions can be established at $\frac{\epsilon}{\epsilon_h} = -2$.

In our previous work on studying copper nanocubes, we extended Fuchs' approach by parameterizing all the terms, and obtained a generalized formula for calculation of the absorption coefficient $\alpha(\omega)$ for an arbitrarily-shaped nanoparticle:¹⁶

$$\alpha(\omega) = \sum_m C(m) \frac{A_{m1}\omega^5 + A_{m2}\omega^4 + A_{m3}\omega^3 + A_{m4}\omega^2}{(\omega^2 - B_{m1}^2)^2 + (B_{m2}\omega)^2} \quad (3)$$

where the resonance frequency, linewidth, and oscillation strength of the m normal modes for an arbitrary nanoparticle are encoded into the parameters B_{m1} , B_{m2} , and $C(m)$, respectively. Coefficients of higher-order polynomials of ω are represented by A_{ms} ($s = 1, 2, 3, 4$), where A_{ms} indicates the influence of interband transitions.

Therefore, Equation (3) can be applied to extract the resonance frequency, linewidth, and oscillation strength of the normal modes for a nanoparticle with an arbitrary shape. It follows that the shape-dependent depolarization factors can then be calculated by Equation (1).

Tetrahedral depolarization factors.

Although the calculated extinction spectra for a gold tetrahedral nanoparticle in Figure 1(b) encodes information needed to obtain the material-independent depolarization factors, previous studies have suggested that gold nanoparticles are subject to interband transitions-induced plasmonic damping, which could make many normal modes indiscernible above the energy threshold of interband transitions. To avoid issues related to interband transitions, a Drude Model is used to model the dielectric function of gold:

$$\epsilon(\omega) = \epsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} \quad (4)$$

The high-frequency permittivity ϵ_∞ , the plasma frequency ω_p , and the damping constant γ used are 9.7, 8.89 eV, and 0.07088 eV, respectively.^{24, 42–43} The calculated extinction spectrum in Figure 4(a) reveals more than the two previously observed prominent peaks in Figure 1(b). For instance, two peaks could be resolved in Figure 4(a) at around 621 nm (the main peak) and 604 nm (a bump on the left side of the 621 nm peak) whereas only one peak was observed in Figure 1(b). This is consistent with the prediction in the optical hybridization picture that there is a mode degeneracy among two of the three bright modes in Figure 3. A close examination of the calculated extinction spectrum in Figure 4(a) unveils eleven normal modes in the studied spectral range from 400 to 900 nm. The calculated extinction spectrum was then fitted by Equation (3) and is shown as the solid blue curve in Figure 4(a). The obtained fitting parameters were further combined with Equation (1) to

calculate the eleven depolarization factors and finally summarized in Table 1 together with the oscillating strength, resonance frequency, and linewidth of a gold tetrahedral nanoparticle modeled by Drude Model. The surface polarization charge distributions for the eleven normal modes on the gold tetrahedral nanoparticle based on Drude Model are shown in Figure S6. To the best of our knowledge, this is the first time the tetrahedral depolarization factors are presented.

Likewise, the calculated extinction spectrum in Figure 1(b) for a gold tetrahedral nanoparticle with the dielectric function from CRC⁴¹ was fitted using Equation (3), as shown in Figure 4(b). In this way, the resonance frequency and linewidth of the eleven normal modes, which would have otherwise been damped due to interband transitions, are obtained and are also summarized in Table 1 for comparison. It is observed that the first five modes ($m = 1, 2, 3, 4, 5$) are well below the energy threshold of interband transition at approximately 500 nm. Therefore, the interband transition has limited influence on these normal modes. This is evidenced by the small differences in the resonance frequency and linewidth of the gold tetrahedral nanoparticle, whose dielectric function is either based on Drude Model or directly extracted from CRC⁴¹. However, the difference becomes increasingly significant for normal modes $m > 5$, as demonstrated by a shifted resonance frequency and broadened linewidth in the grey-shaded rows in Table 1 due to interband transition-induced plasmonic damping.

To further validate the obtained tetrahedral depolarization factors, the extinction spectrum for a copper tetrahedral nanoparticle with an edge length of 30 nm was calculated by Fuchs' approach using the obtained depolarization factors in Table 1, shown as the solid blue curve in Figure 4(c). It was then compared with the extinction spectrum calculated by FDTD. The consistency of the resonant peak position and spectral lineshape confirms the accuracy of the obtained tetrahedral depolarization factors. The variation of the peak magnitude is likely caused by the imperfect fitting of the dielectric function in FDTD and the imperfectly interpolated data points from the calculation using Fuchs' approach. Similarly, a silver tetrahedral nanoparticle of the same size was also used as an independent sample to validate the obtained tetrahedral depolarization factors as shown in Figure 4(d). Despite a certain variation in the peak magnitude, all the major resonance peak positions were correctly captured, further confirming the obtained tetrahedral depolarization factors.

CONCLUSIONS

In summary, tetrahedron proves a naturally symmetry-breaking structure harboring profound optical spectral features not possible on highly symmetric spherical and cubic nanoparticles. The tetrahedron shape makes it possible for the quadrupole vertex mode to become a bright mode with a nonzero net moment equal to that of a dipole vertex mode, which opens the possibility for hybridizations among the bright quadrupole and dipole vertex modes and ultimately contributes to the rich spectral features observed using FDTD simulations. The unveiled eleven normal modes in the considered wavelength range further demonstrates the spectral diversity of a geometrically simple tetrahedral nanoparticle.

Admittedly, the predicted rich extinction spectral features in this study, particularly the dipole-quadrupole hybridization-induced peak splitting, has not yet been experimentally observed, owing to the difficulty in obtaining gold or silver tetrahedral nanoparticles with a rounded radius of less than 0.5 nm. It is noted that palladium and platinum tetrahedral nanocrystals of a few nanometers rounded by a radius of ~0.5 nm have been synthesized.^{44–46} Since both palladium and platinum nanoparticles display very weak plasmonic responses, they are rarely exploited for plasmonic applications. Nevertheless, it is possible to extend their synthesis methods to make high-quality gold or silver tetrahedral nanoparticles with sharp vertices, given that the synthesis of gold and silver tetrahedral nanoparticles has proved successful.^{1, 47–48}

It is also worth noting that the tetrahedron shape not only mediates the interplay between the dipole and quadrupole modes on a single nanoparticle as explained in this study, such a configuration is also found to mediate optical properties of self-assembled tetramer nanoparticles in a similar manner, where both the polarization independence and the peak splitting are observed.⁴⁹ Indeed, the special nature of tetrahedron has more manifestations than the rich extinction spectral features observed on a single tetrahedral nanoparticle. The optical hybridization model used and the tetrahedral depolarization factors obtained in this study can also be extended to guide the design and study of other nanophotonic systems, either on a single nanoparticle level or for self-assembled nanoparticles and others.

METHODS

Finite-difference time-domain (FDTD) simulation.

Lumerical 2019b FDTD Solver Version 8.22.2072 was extensively used throughout the manuscript to calculate optical properties. A total-field scattered-field (TFSF) was used as the input light source. A mesh size of 0.2 nm was used for calculation of extinction spectra, surface polarization charge distribution, and electric fields with an exception: a mesh size of 0.15 nm was used for calculation of extinction spectra for a gold tetrahedral and cubic nanoparticle rounded by a radius of 0.15 nm. The dielectric functions of gold, copper, and silver were extracted from CRC.⁴¹ The background refractive index was fixed at 1.0 except for the rounded gold tetrahedron nanoparticle in water where a background refractive index of 1.33 was used. PML boundary conditions were imposed on all directions. Details on the modelling process in Lumerical FDTD software can be found in the Supporting Information.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

ACKNOWLEDGMENT

This work was supported by the National Institute of Biomedical Imaging and Bioengineering (2-P41-EB015871–31), the National Institute of General Medical Sciences (DP2GM128198), and the Johns Hopkins University Catalyst Award.

REFERENCES

1. Zheng Y; Liu W; Lv T; Luo M; Hu H; Lu P; Choi S-I; Zhang C; Tao J; Zhu Y; Li Z-Y; Xia Y, Seed-Mediated Synthesis of Gold Tetrahedra in High Purity and with Tunable, Well-Controlled Sizes. *Chemistry – An Asian Journal* 2014, 9 (9), 2635–2640.
2. Alekseeva S; Nedrygailov II; Langhammer C, Single Particle Plasmonics for Materials Science and Single Particle Catalysis. *ACS Photonics* 2019.
3. Lenzi E; Jimenez de Aberasturi D; Liz-Marzán LM, Surface-Enhanced Raman Scattering Tags for Three-Dimensional Bioimaging and Biomarker Detection. *ACS Sensors* 2019.
4. Willets KA; Van Duyne RP, Localized Surface Plasmon Resonance Spectroscopy and Sensing. *Annual Review of Physical Chemistry* 2007, 58 (1), 267–297.
5. Li JF; Huang YF; Ding Y; Yang ZL; Li SB; Zhou XS; Fan FR; Zhang W; Zhou ZY; Wu DY; Ren B; Wang ZL; Tian ZQ, Shell-isolated nanoparticle-enhanced Raman spectroscopy. *Nature* 2010, 464, 392. [PubMed: 20237566]
6. Jaque D; Martínez Maestro L; del Rosal B; Haro-Gonzalez P; Benayas A; Plaza JL; Martín Rodríguez E; García Solé J, Nanoparticles for photothermal therapies. *Nanoscale* 2014, 6 (16), 9494–9530. [PubMed: 25030381]
7. Li J; Cushing SK; Meng F; Senty TR; Bristow AD; Wu N, Plasmon-induced resonance energy transfer for solar energy conversion. *Nature Photonics* 2015, 9, 601.
8. Cushing SK; Wu N, Progress and Perspectives of Plasmon-Enhanced Solar Energy Conversion. *The Journal of Physical Chemistry Letters* 2016, 7 (4), 666–675. [PubMed: 26817500]
9. Volk K; Fitzgerald JPS; Karg M, In-Plane Surface Lattice and Higher Order Resonances in Self-Assembled Plasmonic Monolayers: From Substrate-Supported to Free-Standing Thin Films. *ACS Applied Materials & Interfaces* 2019, 11 (17), 16096–16106. [PubMed: 30945839]
10. Kravets VG; Kabashin AV; Barnes WL; Grigorenko AN, Plasmonic Surface Lattice Resonances: A Review of Properties and Applications. *Chemical Reviews* 2018, 118 (12), 5912–5951. [PubMed: 29863344]
11. Matricardi C; Hanske C; Garcia-Pomar JL; Langer J; Mihi A; Liz-Marzán LM, Gold Nanoparticle Plasmonic Superlattices as Surface-Enhanced Raman Spectroscopy Substrates. *ACS Nano* 2018, 12 (8), 8531–8539. [PubMed: 30106555]
12. Czaplicki R; Kiviniemi A; Huttunen MJ; Zang X; Stolt T; Vartiainen I; Butet J; Kuittinen M; Martin OJF; Kauranen M, Less Is More: Enhancement of Second-Harmonic Generation from Metasurfaces by Reduced Nanoparticle Density. *Nano Letters* 2018, 18 (12), 7709–7714. [PubMed: 30423245]
13. Monticone F; Alù A, Metamaterials and plasmonics: From nanoparticles to nanoantenna arrays, metasurfaces, and metamaterials. *Chinese Physics B* 2014, 23 (4), 047809.
14. Koh AL; Bao K; Khan I; Smith WE; Kothleitner G; Nordlander P; Maier SA; McComb DW, Electron Energy-Loss Spectroscopy (EELS) of Surface Plasmons in Single Silver Nanoparticles and Dimers: Influence of Beam Damage and Mapping of Dark Modes. *ACS Nano* 2009, 3 (10), 3015–3022. [PubMed: 19772292]
15. Li M; Cushing SK; Zhang J; Lankford J; Aguilar ZP; Ma D; Wu N, Shape-dependent surface-enhanced Raman scattering in gold–Raman-probe–silica sandwiched nanoparticles for biocompatible applications. *Nanotechnology* 2012, 23 (11), 115501. [PubMed: 22383452]
16. Zheng P; Tang H; Liu B; Kasani S; Huang L; Wu N, Origin of strong and narrow localized surface plasmon resonance of copper nanocubes. *Nano Research* 2019, 12 (1), 63–68.
17. Gawande MB; Goswami A; Felpin F-X; Asefa T; Huang X; Silva R; Zou X; Zboril R; Varma RS, Cu and Cu-Based Nanoparticles: Synthesis and Applications in Catalysis. *Chemical Reviews* 2016, 116 (6), 3722–3811. [PubMed: 26935812]
18. Knight MW; King NS; Liu L; Everitt HO; Nordlander P; Halas NJ, Aluminum for Plasmonics. *ACS Nano* 2014, 8 (1), 834–840. [PubMed: 24274662]
19. Mogensen KB; Kneipp K, Size-Dependent Shifts of Plasmon Resonance in Silver Nanoparticle Films Using Controlled Dissolution: Monitoring the Onset of Surface Screening Effects. *The Journal of Physical Chemistry C* 2014, 118 (48), 28075–28083.

20. Chan GH; Zhao J; Hicks EM; Schatz GC; Van Duyne RP, Plasmonic Properties of Copper Nanoparticles Fabricated by Nanosphere Lithography. *Nano Letters* 2007, 7 (7), 1947–1952.
21. Crane CC; Wang F; Li J; Tao J; Zhu Y; Chen J, Synthesis of Copper–Silica Core–Shell Nanostructures with Sharp and Stable Localized Surface Plasmon Resonance. *The Journal of Physical Chemistry C* 2017, 121 (10), 5684–5692.
22. Yang H-J; He S-Y; Chen H-L; Tuan H-Y, Monodisperse Copper Nanocubes: Synthesis, Self-Assembly, and Large-Area Dense-Packed Films. *Chemistry of Materials* 2014, 26 (5), 1785–1793.
23. Pinchuk A; Plessen G. v.; Kreibig U, Influence of interband electronic transitions on the optical absorption in metallic nanoparticles. *Journal of Physics D: Applied Physics* 2004, 37 (22), 3133–3139.
24. Zhang S; Bao K; Halas NJ; Xu H; Nordlander P, Substrate-Induced Fano Resonances of a Plasmonic Nanocube: A Route to Increased-Sensitivity Localized Surface Plasmon Resonance Sensors Revealed. *Nano Letters* 2011, 11 (4), 1657–1663. [PubMed: 21410217]
25. Nicoletti O; de la Peña F; Leary RK; Holland DJ; Ducati C; Midgley PA, Three-dimensional imaging of localized surface plasmon resonances of metal nanoparticles. *Nature* 2013, 502, 80. [PubMed: 24091976]
26. Zhang KJ; Da B; Ding ZJ, LSP modes of Ag nanocube and dimer studied by DDA simulation. *Surface and Interface Analysis* 2016, 48 (11), 1256–1262.
27. Wu H-L; Tsai H-R; Hung Y-T; Lao K-U; Liao C-W; Chung P-J; Huang J-S; Chen IC; Huang MH, A Comparative Study of Gold Nanocubes, Octahedra, and Rhombic Dodecahedra as Highly Sensitive SERS Substrates. *Inorganic Chemistry* 2011, 50 (17), 8106–8111. [PubMed: 21797229]
28. Chen H; Shao L; Li Q; Wang J, Gold nanorods and their plasmonic properties. *Chemical Society Reviews* 2013, 42 (7), 2679–2724. [PubMed: 23128995]
29. Hao F; Nehl CL; Hafner JH; Nordlander P, Plasmon Resonances of a Gold Nanostar. *Nano Letters* 2007, 7 (3), 729–732. [PubMed: 17279802]
30. Guiton BS; Iberi V; Li S; Leonard DN; Parish CM; Kotula PG; Varela M; Schatz GC; Pennycook SJ; Camden JP, Correlated Optical Measurements and Plasmon Mapping of Silver Nanorods. *Nano Letters* 2011, 11 (8), 3482–3488. [PubMed: 21732618]
31. Pellarin M; Ramade J; Rye JM; Bonnet C; Broyer M; Lebeault M-A; Lermé J; Marguet S; Navarro JRG; Cottancin E, Fano Transparency in Rounded Nanocube Dimers Induced by Gap Plasmon Coupling. *ACS Nano* 2016, 10 (12), 11266–11279. [PubMed: 28024347]
32. Zhang S; Xu H, Tunable dark plasmons in a metallic nanocube dimer: toward ultimate sensitivity nanoplasmonic sensors. *Nanoscale* 2016, 8 (28), 13722–13729. [PubMed: 27412788]
33. Pakizeh T; Langhammer C; Zori I; Apell P; Käll M, Intrinsic Fano Interference of Localized Plasmons in Pd Nanoparticles. *Nano Letters* 2009, 9 (2), 882–886. [PubMed: 19175307]
34. Fuchs R, Theory of the optical properties of ionic crystal cubes. *Physical Review B* 1975, 11 (4), 1732–1740.
35. Liu L; Ge L; Hu P; Xiang H; Yang W; Liu Q; Han D, Toroidal dipolar response in plasmonic nanoparticle clusters. *Journal of Physics D: Applied Physics* 2018, 51 (3), 035106.
36. Lim D-K; Jeon K-S; Kim HM; Nam J-M; Suh YD, Nanogap-engineerable Raman-active nanodumbbells for single-molecule detection. *Nature Materials* 2010, 9 (1), 60–67. [PubMed: 20010829]
37. Sonntag MD; Klingsporn JM; Garibay LK; Roberts JM; Dieringer JA; Seideman T; Scheidt KA; Jensen L; Schatz GC; Van Duyne RP, Single-Molecule Tip-Enhanced Raman Spectroscopy. *The Journal of Physical Chemistry C* 2012, 116 (1), 478–483.
38. Lee HM; Jin SM; Kim HM; Suh YD, Single-molecule surface-enhanced Raman spectroscopy: a perspective on the current status. *Physical Chemistry Chemical Physics* 2013, 15 (15), 5276–5287. [PubMed: 23525118]
39. Le Ru EC; Blackie E; Meyer M; Etchegoin PG, Surface Enhanced Raman Scattering Enhancement Factors: A Comprehensive Study. *The Journal of Physical Chemistry C* 2007, 111 (37), 13794–13803.
40. Esteban R; Borisov AG; Nordlander P; Aizpurua J, Bridging quantum and classical plasmonics with a quantum-corrected model. *Nature Communications* 2012, 3 (1), 825.
41. Haynes WM, *CRC Handbook of Chemistry and Physics*. CRC Press: 2011.

42. Zeman EJ; Schatz GC, An accurate electromagnetic theory study of surface enhancement factors for silver, gold, copper, lithium, sodium, aluminum, gallium, indium, zinc, and cadmium. *The Journal of Physical Chemistry* 1987, 91 (3), 634–643.
43. Ehrenreich H; Philipp HR, Optical Properties of Ag and Cu. *Physical Review* 1962, 128 (4), 1622–1629.
44. Chiu C-Y; Li Y; Ruan L; Ye X; Murray CB; Huang Y, Platinum nanocrystals selectively shaped using facet-specific peptide sequences. *Nature Chemistry* 2011, 3, 393.
45. Wang Y; Xie S; Liu J; Park J; Huang CZ; Xia Y, Shape-Controlled Synthesis of Palladium Nanocrystals: A Mechanistic Understanding of the Evolution from Octahedrons to Tetrahedrons. *Nano Letters* 2013, 13 (5), 2276–2281. [PubMed: 23570582]
46. Narayanan R; El-Sayed MA, Effect of Nanocatalysis in Colloidal Solution on the Tetrahedral and Cubic Nanoparticle SHAPE: Electron-Transfer Reaction Catalyzed by Platinum Nanoparticles. *The Journal of Physical Chemistry B* 2004, 108 (18), 5726–5733.
47. Langille MR; Zhang J; Personick ML; Li S; Mirkin CA, Stepwise Evolution of Spherical Seeds into 20-Fold Twinned Icosahedra. *Science* 2012, 337 (6097), 954. [PubMed: 22923578]
48. Mariscal MM; Velázquez-Salazar JJ; Yacaman MJ, Growth mechanism of nanoparticles: theoretical calculations and experimental results. *CrystEngComm* 2012, 14 (2), 544–549.
49. Barrow SJ; Wei X; Baldauf JS; Funston AM; Mulvaney P, The surface plasmon modes of self-assembled gold nanocrystals. *Nature Communications* 2012, 3 (1), 1275.

Figure 1.

(a) Three orthogonal polarizations (E_1 , E_2 , E_3) where E_1 is perpendicular to the tetrahedral edge AD and BC, E_2 and E_3 are respectively parallel to the edges AD and BC; (b) the corresponding calculated extinction spectra, (c) the surface polarization charges and (d) electric field enhancement for the vertex modes of a gold tetrahedral nanoparticle (edge length: 30 nm). The scale for the electric field color bar is $\log_{10}(E/E_0)$. The maximum electric field enhancement ($|\mathbf{E}|/|\mathbf{E}_0|$) of 718 is obtained at the vertex under E_3 polarization.

Figure 2.

Calculated extinction spectra for (a)-(f) a gold tetrahedral nanoparticle (edge length: 30 nm) and (g)-(l) a gold cubic nanoparticle (with the same edge length as the tetrahedron) with all the edges and vertices gradually rounded by a radius r . Three respective orthogonal polarizations are applied for the tetrahedron consistent with Figure 1; a single polarization is applied along the edge of the cube. All simulations were conducted in air except that the gold tetrahedral nanoparticle with a rounded radius of 2 nm that was also simulated in water, shown as the dashed curves in Figure 2(f), which is consistent with the experimentally synthesized gold tetrahedral nanoparticles.¹

Figure 3.

Hybridizations of vertex modes on a tetrahedron producing a dark mode and three bright modes. (a) Self-coupling of mode ① gives rise to an antibonding dark mode and a bonding bright mode 1; (b) mode ① coupling with the inverse of itself produces an antibonding bright mode 1 and a bonding dark mode; (c) coupling of modes ② and ③ results in an antibonding bright mode 2 and a bonding bright mode 3; (d) coupling of mode ② and the inverse of mode ③ brings about an antibonding bright mode 3 and a bonding bright mode 2. Energy level not to scale.

Figure 4.

Fitting of the extinction spectra of a gold tetrahedral nanoparticle (edge: 30 nm) using the generalized model (Equation (3)) in order to extract the strength and depolarization factor of the normal modes of a tetrahedron. The extinction spectra are calculated using the dielectric data (a) modeled by Drude Model (hollow magenta circle) and (b) taken from CRC⁴¹ (hollow green circle). The fitted curves are shown in blue.

Scheme 1.

Tetrahedron is formed by rotating the top edge of a rectangle $\theta=90^\circ$ counterclockwise around the axis of a cylinder with a radius of R and a height of H where $H = \sqrt{2}R$. Thus, the resulting tetrahedron has an edge length of $a = 2R$. The vertex dipole and quadrupole modes of a rectangle become indistinguishable on a tetrahedron because the vertex quadrupole mode is basically the same as the vertex dipole mode on a tetrahedron with a nonzero net moment due to symmetry breaking. In this study, the symmetry breaking is defined as when the quadrupole mode has a nonzero net moment due to the geometrical asymmetry. The geometric evolution from rectangle to tetrahedron considered in this study helps to illustrate how the symmetry breaking transforms the quadrupole vertex mode from being a dark mode on a rectangle into a bright mode on a tetrahedron.

Table 1.

Values of the strength $C(m)$ and depolarization factor n_m for the eleven normal modes of a tetrahedron. Also shown are the resonance frequency w_0 (corresponding to B_{m1} in Equation (3)) and linewidth γ (corresponding to B_{m2} in Equation (3)) for the eleven plasmon modes of a gold tetrahedron nanoparticle. They are calculated using the dielectric function of gold modeled by Drude Model and taken from CRC⁴¹, respectively. For those plasmon modes in the grey-shaded area, they are strongly damped due to interband transitions of gold, as evidenced by the increased linewidths.

<i>m</i>	<i>C(m)</i>	<i>n_m</i>	Normal modes of a gold tetrahedron nanoparticle (edge length: 30 nm)							
			Gold dielectric by Drude Model				Gold dielectric from CRC			
			<i>w₀(eV)</i>	<i>w₀(nm)</i>	<i>γ(eV)</i>	<i>γ(nm)</i>	<i>w₀(eV)</i>	<i>w₀(nm)</i>	<i>γ(eV)</i>	<i>γ(nm)</i>
1	0.272	0.060	1.763	703	0.071	56	1.761	704	0.045	36
2	0.204	0.090	1.997	621	0.072	45	1.994	622	0.077	48
3	0.175	0.100	2.053	604	0.081	48	2.040	608	0.100	60
4	0.028	0.121	2.157	575	0.080	43	2.131	582	0.127	70
5	0.084	0.165	2.314	536	0.068	31	2.273	546	0.109	52
6	0.025	0.199	2.397	517	0.138	60	2.314	536	0.442	212
7	0.047	0.225	2.449	506	0.099	41	2.476	501	0.376	156
8	0.081	0.272	2.526	491	0.117	45	2.633	471	0.378	138
9	0.072	0.365	2.629	472	0.142	51	2.655	467	0.367	132
10	0.008	0.749	2.807	442	0.164	52	2.818	440	0.450	144
11	0.004	0.775	2.812	441	0.158	50	2.864	433	0.515	161