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Strong Plasmon–Exciton Coupling Tuned by Corner Etching of Gold Nanocubes and Nanotriangles

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ABSTRACT

Strong plasmon–exciton coupling occurs when a quantum emitter coherently interacts with the confined field of a plasmonic cavity, forming hybrid polariton states. Here, we investigate how nanoparticle curvature affects this strong coupling by assembling gold nanocubes (AuNCs) and nanotriangles (AuNTs) with cyanine dye J-aggregates. Controlled cysteamine etching systematically modifies nanoparticle curvature, enabling direct evaluation of morphology-dependent coupling. Spectral analyses yield vacuum Rabi splittings of 115 meV for AuNCs and 189 meV for AuNTs. As corners round, coupling strength decreases for AuNCs but remains unaffected for AuNTs, mirroring their plasmonic electric field distributions. Comparing coupling strengths with damping rates reveals that AuNCs operate in the intermediate coupling regime due to large plasmon damping, while AuNTs robustly achieve deep strong coupling across all curvatures. Evaluations of mode volume, quality factor, and figure of merit (FOM) further establish AuNTs as superior cavities. While the FOMs for both geometries are relatively insensitive to local curvature, AuNTs consistently exhibit FOMs nearly twice those of AuNCs. These results demonstrate that overall particle shape, rather than corner sharpness, dictates plasmon–exciton strong-coupling efficiency. This study advances the design of plasmonic cavities for enhanced light–matter interactions by identifying key structural and optical parameters.

1 | Introduction

Strong light–matter coupling has emerged as a central concept in modern photonics and quantum science because it enables phenomena inaccessible in the weak-coupling regime [1, 2]. By hybridizing photons and excitons into polaritons, strong coupling allows coherent control of chemical reactions, manipulation of energy-transfer pathways, and tailoring of emission dynamics [3–6]. It underpins key developments in quantum information processing, polariton lasers, Bose–Einstein condensation of exciton–polaritons, and polaritonic photochemistry [6–11].

When a quantum emitter is placed in the electromagnetic field of an optical cavity, the rapid and reversible exchange of energy

creates two polariton states with mixed light–matter character (Figure 1). A classical coupled-oscillator model describes this interaction: two oscillators, representing the cavity (ω_c) and the emitter (ω_e), generate two normal modes, $\omega_{\pm}$, whose splitting is set by the coupling [12]. In the quantum picture, the Jaynes–Cummings Hamiltonian, including cavity and emitter damping rates (γ_c and γ_e , respectively), yields the complex eigenfrequencies upon diagonalization: [12, 13]

$$\omega_{\pm} = \frac{1}{2} (\omega_c + \omega_e) - \frac{i}{2} (\gamma_c + \gamma_e) \pm \sqrt{g^2 + \left(\frac{\delta}{2} - i \frac{\gamma_c - \gamma_e}{2} \right)^2} \quad (1)$$

where g is the coupling strength and $\delta \equiv \omega_c - \omega_e$ is the detuning. In the absence of damping ($\gamma = 0$), this simplifies to:

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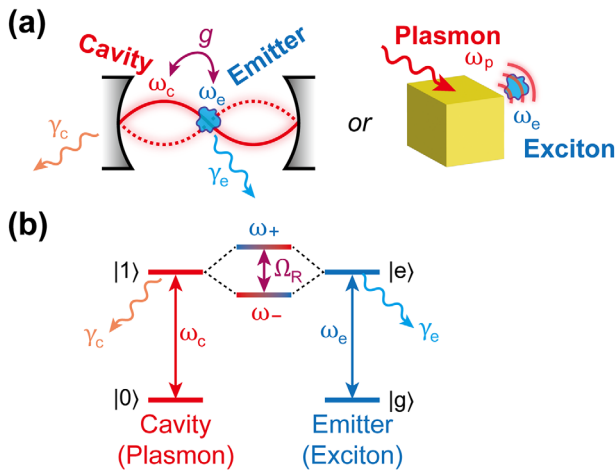


FIGURE 1 | Schematic illustration of strong coupling. (a) Strong coupling between a quantum emitter with angular frequency ω_e and damping rate γ_e , and an optical cavity of frequency ω_c and damping rate γ_c . The coupling strength is denoted by g . Analogously, excitons couple to localized surface plasmons in a plasmonic cavity with frequency ω_p and damping rate γ_p . (b) Energy-level diagram of strong coupling. Hybridization of the cavity (or plasmon) mode with the emitter (or exciton) creates upper (ω_+) and lower (ω_-) polariton states containing mixed light and matter character. The two polariton states are separated by the Rabi splitting energy ($\Omega_R = 2g$). For strong coupling to occur, the coupling strength must exceed the loss rates of the cavity and emitter, i.e., $g > \sqrt{\gamma_c \gamma_e}$.

$$\omega_{\pm} = \frac{1}{2} (\omega_c + \omega_e) \pm \sqrt{g^2 + \frac{\delta^2}{4}} \quad (2)$$

The two polariton branches exhibit anticrossing behavior as a function of detuning, with a minimum energy separation at resonance corresponding to the vacuum Rabi splitting (Ω_R). At resonance ($\delta = 0$), the peak separation is:

$$\omega_+ - \omega_- = \Omega_R = 2\sqrt{g^2 - \left(\frac{\gamma_c - \gamma_e}{2}\right)^2} \quad (3)$$

Without damping, the energy separation as a function of detuning becomes:

$$\omega_+ - \omega_- = 2\sqrt{g^2 + \frac{\delta^2}{4}} \quad (4)$$

Equation 3 shows that distinct eigenfrequencies emerge at resonance when the coupling strength exceeds the differential loss ($g > |\gamma_c - \gamma_e|/2$).

Spectrally resolving the two polariton peaks, however, requires the Rabi splitting to exceed the combined linewidths of the cavity and the emitter ($\Omega_R > \gamma_c + \gamma_e$) [12, 13]. The damping rates γ_c and γ_e represent the half-width at half-maximum (HWHM) of the cavity and emitter resonance spectra, respectively. When an oscillator's amplitude decays as $e^{-\gamma t}$, its Fourier-transformed spectrum exhibits a Lorentzian lineshape with an HWHM of γ and a full-width at half-maximum (FWHM) of 2γ . Since $\Omega_R = 2g$ at resonance, the spectral resolution criterion ($2g > \gamma_c$

+ γ_e) effectively requires the coupling strength g to exceed the arithmetic mean of the damping rates ($g > (\gamma_c + \gamma_e)/2$).

In quantum optics, the cooperativity C provides a more general criterion for strong coupling: [11, 14, 15]

$$C \equiv \frac{g}{\sqrt{\gamma_c \gamma_e}} \quad (5)$$

The cooperativity compares the coupling strength directly to the geometric mean of the damping rates ($\sqrt{\gamma_c \gamma_e}$). The strong-coupling regime requires $C > 1$, ensuring that coherent energy exchange outpaces dissipative losses. A complete mixing of cavity and emitter modes creates two distinct polariton eigenstates. By contrast, when dissipative losses approach the coupling rate, the cooperativity drops to near unity ($C \approx 1$), restricting the system to the intermediate coupling regime. In systems with a large linewidth mismatch ($\gamma_c \gg \gamma_e$), such as plasmonic cavities, destructive interference in this intermediate regime carves a Fano-like transparency dip into the broad cavity band. This interference yields an apparent peak splitting even before the system achieves genuine polaritonic hybridization [12, 16].

The coupling strength reflects both emitter and cavity properties, scaling with the transition dipole moment (μ) and the electric field amplitude (E): [17, 18]

$$g = \sqrt{N_{\text{eff}}} \mu E = \sqrt{N_{\text{eff}}} \mu \sqrt{\frac{\hbar \omega_c}{2\epsilon_0 \epsilon_r V}} \quad (6)$$

where N_{eff} is the effective number of emitters actively coupled to the cavity mode, ϵ_0 the vacuum permittivity, ϵ_r the relative permittivity, and V the mode volume. Thus, $g \propto \mu$ and $g \propto E \propto V^{-1/2}$.

The intrinsic capability of a cavity to support strong coupling is often assessed by its quality factor (Q) and figure of merit (FOM) [19–23]. The quality factor is defined as:

$$Q \equiv \frac{\omega_c}{\Delta\omega_c} = \frac{\omega_c}{2\gamma_c} \quad (7)$$

where $\Delta\omega_c$ is the FWHM. A higher- Q cavity promotes stronger coupling because photons circulate longer, enabling repeated interactions before dissipation. The FOM is defined as:

$$FOM \equiv \frac{Q}{\sqrt{V}} \quad (8)$$

This metric captures both damping and field confinement. The larger the FOM—that is, the larger Q and the smaller V (or equivalently the smaller γ_c and larger field amplitude E)—the more readily a cavity can drive strong coupling, provided the emitter properties are also favorable. Importantly, FOM reflects only the cavity's potential; realizing strong coupling requires additional conditions such as resonance with the emitter transition, proper dipole–field alignment, and sufficient oscillator strength.

Since the first experimental observation in 1975 [24], following foundational theoretical work [25], strong coupling has been demonstrated with Rydberg atoms, molecules, J-aggregates, and quantum dots. Early studies relied on dielectric microcavities

with Q typically ranging from 10^3 to 10^6 [26]. More recently, plasmonic nanostructures have emerged as alternative cavities [27]. In these systems, the localized surface plasmon resonance (LSPR) directly serves as the cavity mode (i.e., $\omega_c \rightarrow \omega_p$ and $\gamma_c \rightarrow \gamma_p$). These plasmons in gold nanoparticles (AuNPs) produce intense fields concentrated at sharp features and nanogaps (Figure 1a, right). Although plasmonic cavities are intrinsically lossy ($Q \approx 10$ –100), their ultrasmall mode volumes make strong coupling feasible at room temperature [13, 26].

Following the first observation in silver films [28], numerous nanoparticle shapes and assemblies have been investigated at both ensemble [23, 29–40] and single-particle levels [20, 23, 41–43]. Nanogap architectures, such as dimers and nanoparticle-on-mirror constructs, provide the strongest field confinement [44–49]. Most previous studies tuned coupling by varying nanoparticle size or shell thickness, with additional control achieved through molecular orientation or excitation polarization.

In this work, we investigate the effect of a subtler structural parameter—curvature. Gold nanocubes (AuNCs) and nanotriangles (AuNTs) concentrate electric fields at their sharp edges and corners. By gradually etching these features with cysteamine, we systematically round the corners to track how plasmon–exciton coupling evolves. We assemble these etched nanoparticles with TDBC J-aggregates and measure their extinction spectra, observing distinct peak splittings that depend on the etching stage. By extracting coupling strengths (g) and damping rates (γ) from these spectral features, we determine the cooperativity (C), quality factors (Q), and FOMs. These quantitative metrics, combined with mode volume analyses, allow us to explicitly distinguish genuine polaritonic hybridization from intermediate Fano interference. Ultimately, we demonstrate that the global macroscopic architecture of the cavity—specifically the triangular geometry of AuNTs—dictates strong-coupling efficiency far more decisively than local corner sharpness.

2 | Results and Discussion

We synthesized AuNCs and AuNTs following the protocols established by the Nam and Liz-Marzán groups [50, 51]. The AuNCs have an edge length of 94 nm and a corner curvature radius of 11 nm (Figure 2a; Figure S1). The AuNTs exhibit more complex morphologies (Figure 2b). Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images reveal that they are truncated triangular pyramids rather than triangular prisms, with top and bottom edge lengths of 47 and 77 nm and a height of 34 nm (Figure S2). Their corner curvature radius is ~ 5 nm (Figure S1).

The AuNCs and AuNTs display LSPR bands at 611 nm (2.03 eV) and 650 nm (1.91 eV), respectively (Figure 2a,b). After subtracting the interband transition (IBT) baselines (dashed lines), Lorentzian fitting (dotted lines) yields bandwidths of 457 meV for AuNCs and 189 meV for AuNTs. The corresponding plasmon damping rates are $\gamma_p = 228$ meV (AuNCs) and $\gamma_p = 95$ meV (AuNTs). The broad LSPR bands reflect ultrafast plasmon damping, consistent with the lossy character of plasmonic nanoparticles. While inhomogeneity in size and shape also contributes, comparison with the calculated linewidth of

a single AuNC indicates that intrinsic damping is dominant (Figure S3).

As quantum emitters, we employed J-aggregates of a cyanine dye, 5,5',6,6'-tetrachloro-1,1'-diethyl-3,3'-di(4-sulfobutyl)-benzimidazolocarboxyanine (TDBC). At concentrations above ~ 50 μM , TDBC molecules self-assemble into J-aggregates in a slipped head-to-tail geometry [52, 53]. This arrangement produces constructive dipole–dipole coupling at the bottom of the exciton band, lowering its energy relative to the monomer and yielding a redshifted absorption maximum ($\lambda = 586$ nm, 2.12 eV; Figure 2c). Exciton delocalization across many molecules further enhances the transition dipole and concentrates oscillator strength into the lowest-energy bright state, resulting in an intense and narrow absorption peak ($\gamma_e = 17$ meV). These combined features—the redshifted resonance, large oscillator strength, and sharp linewidth—make TDBC J-aggregates ideal quantum emitters for strong coupling.

For assembly, AuNCs or AuNTs were immobilized on glass substrates (12.5 mm $\times$ 9 mm; Figure 2d). Thoroughly cleaned substrates were aminated with (3-aminopropyl) trimethoxysilane (APTMS). AuNCs or AuNTs, stabilized by cetyltrimethylammonium chloride (CTAC) bilayers, were centrifuged and redispersed in 90% (v/v) aqueous acetonitrile, which reversed the particle ζ -potential from positive to negative [54]. Immersing the amine-coated glass in this dispersion electrostatically immobilized the nanoparticles on the substrates. After rinsing, an air-plasma treatment (0.8 Torr, 18 W, 1 min) was conducted to (i) remove CTAC from the nanoparticle surfaces and (ii) strip APTMS from the exposed glass regions [55]. This step prevented the anionic TDBC J-aggregates from binding to the substrate in the subsequent coupling step, ensuring that they attached selectively to the nanoparticle surfaces after cysteamine treatment [55].

We then incubated the plasma-treated AuNCs or AuNTs on glass substrates in cysteamine solution ($\text{SH}(\text{CH}_2)_2\text{NH}_2$, 2–3 mM) to functionalize the nanoparticle surfaces with amine groups. During this step, we unexpectedly observed that the extinction spectra changed markedly depending on the solvent used for cysteamine. When cysteamine was dissolved in ethanol, the UV–vis extinction spectra of AuNCs remained essentially unchanged for up to 6 h (Figure 2e). By contrast, cysteamine in water induced a progressive blueshift of the LSPR band (Figure 2f). Methanol produced similar behavior, whereas acetonitrile and dimethyl sulfoxide (DMSO) had negligible effects (Figure 2g). SEM confirmed that cysteamine in water or methanol progressively rounded nanoparticle corners and edges. Prolonged exposure eventually transformed both AuNCs and AuNTs into spheres. This effect is consistent with previous reports that cysteamine generates H_2O_2 in water under aerobic conditions, which oxidizes Au^0 preferentially at high-surface-energy sites [56]. The observed blueshift with increasing curvature radius was fully reproduced by calculations (Figure S3).

Finally, TDBC J-aggregates were electrostatically attached to the amine-terminated AuNP surfaces, yielding AuNP@J-aggregates (AuNP = AuNC or AuNT) (Figure 2d). Immobilizing the AuNPs on glass facilitated surface modification without aggregation and allowed thorough rinsing after each step. Wide-area SEM

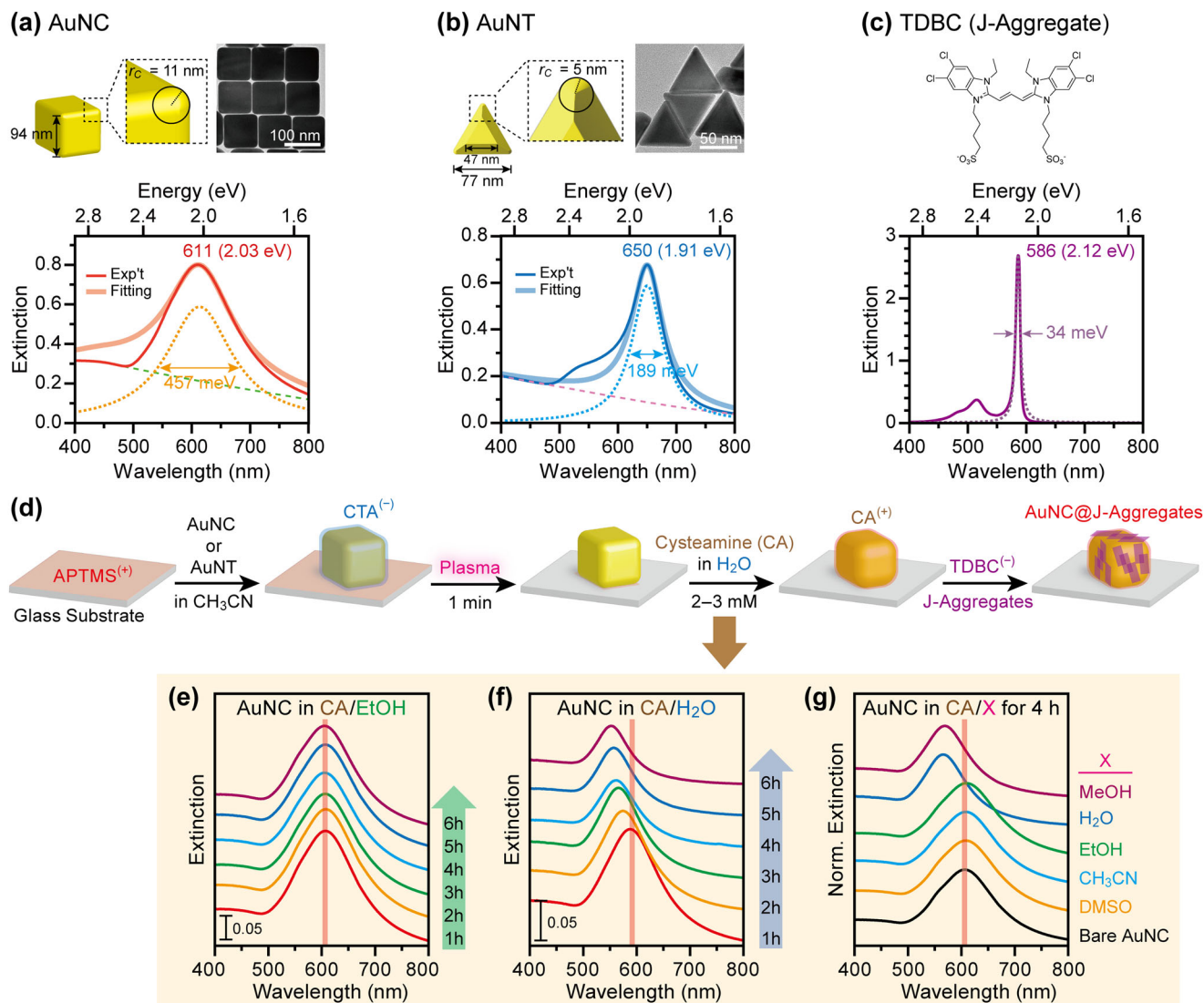


FIGURE 2 | Preparation and characterization of AuNCs, AuNTs, TDBC J-aggregates, and their assemblies. (a) Dimensions, TEM images, and UV-vis extinction spectrum (red line) of AuNCs. The spectrum is fitted with a Lorentzian function (orange dotted line) after subtracting the interband-transition (IBT) background (green dashed line), yielding a peak at $\lambda = 611$ nm ($\omega_p = 2.03$ eV) and a bandwidth of 457 meV. The thick faint red line shows the total fitted spectrum. (b) Dimensions, TEM images, and extinction spectrum (blue line) of AuNTs. (c) Chemical structure of TDBC and its UV-vis absorption spectrum (purple line). (d) Schematic illustration of the preparation of AuNC@J-aggregates and AuNT@J-aggregates: amine-coated glass substrates immobilize AuNCs or AuNTs, which are then plasma-cleaned, etched with cysteamine, and coupled with TDBC J-aggregates. (e–g) UV-vis spectra of AuNCs on glass after incubation in cysteamine dissolved in ethanol (e), water (f), or other solvents (g). Vertical red lines mark the LSPR peak position of the initial spectra, serving as visual references for peak shifts.

confirmed uniform distributions of AuNT@J-aggregates across the substrates (Figure S4).

With the nanoparticles and J-aggregates prepared and characterized, we next examined how nanoparticle curvature influences plasmon–exciton coupling. Systematic etching of AuNCs and AuNTs enabled direct correlation between structural evolution, optical spectra, and coupling parameters.

We obtained UV-vis extinction spectra for AuNC@J-aggregates and AuNT@J-aggregates on glass substrates. Representative TEM images (Figure 3a,b) shows that corners and edges become progressively smoother with etching in cysteamine in water, and extended treatment ultimately converts both AuNCs and

AuNTs into nanospheres (AuNSs). The overall particle size also decreases gradually for AuNTs. The corresponding extinction spectra (faint lines) reveal a continuous blueshift of the plasmon resonance (ω_p) with etching, consistent with calculations (Figure S3).

Coupling the nanoparticles to TDBC J-aggregates drastically alters their spectra (bold lines). Two distinct peaks (ω_+ and ω_-) emerge near the J-aggregate transition line ($\lambda = 586$ nm or $\omega_e = 2.12$ eV; vertical dashed line). When the plasmon is red-detuned relative to the exciton ($\delta = \omega_p - \omega_e < 0$), the long-wavelength branch carries more oscillator strength; as etching blueshifts ω_p across ω_e (δ passes through zero), spectral weight shifts to the short-wavelength branch. Near resonance, the splitting is nearly

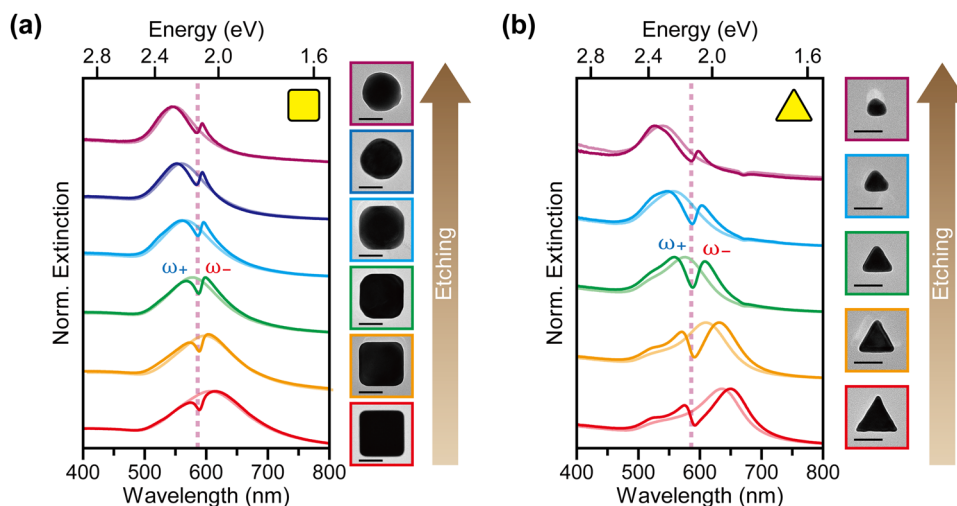


FIGURE 3 | Strong coupling modulated by the curvature of (a) AuNCs and (b) AuNTs. AuNCs and AuNTs with various curvatures were obtained by progressively etching the initial nanoparticles (bottom images) with cysteamine in water. Their TEM morphologies and corresponding UV-vis spectra (faint lines) are shown with matching colors for direct comparison. Nanoparticles of each curvature were combined with J-aggregates as in Figure 2d, and their UV-vis spectra showing mode splitting are presented in bold lines. The vertical dashed line indicates the resonance peak of the TDBC J-aggregates ($\lambda = 586$ nm, $\omega_e = 2.12$ eV). The split peaks are assigned to the upper (ω_+) and lower (ω_-) polariton states. Scale bars in all TEM images are 50 nm.

symmetric (green traces). More importantly, the peak splitting is significantly larger for AuNTs than for AuNCs.

We plotted the upper (ω_+) and lower (ω_-) polariton branches against detuning δ , along with the uncoupled plasmon (ω_p) and exciton (ω_e) resonances, as the nanoparticle shape evolved (Figure 4a,b). The two hybrid polariton branches bend away from each other, creating a gap at resonance. This anticrossing behavior in the dispersion curve provides a classic signature of strong coupling between excitons in TDBC J-aggregates and plasmons in AuNCs or AuNTs.

The experimental data are well fitted by Equation (2), yielding vacuum Rabi splittings (Ω_R) of 115 meV for AuNCs and 189 meV for AuNTs (blue and red dotted curves in Figure 4a,b). Details of the global fitting protocol used to generate these overarching dispersion curves are provided in Section S6 and Figure S5. This larger splitting observed for AuNT@J-aggregates demonstrates that AuNTs couple more strongly to the excitons than do AuNCs.

We next extracted the coupling strength g for each individual AuNP@J-aggregate system from the apparent peak splitting to evaluate the quantitative morphology dependence. Because the experimentally observed peak splitting ($\omega_+ - \omega_-$) inherently depends on both the intrinsic cavity-emitter interaction and the spectral detuning δ , we used the coupled-oscillator model (Equation (4)) to mathematically factor out the contribution of δ . This approach isolates the pure coupling strength g dictated solely by the nanoparticle morphology. Figure 4c,d plot the coupling strength between the excitons in J-aggregates and the plasmons in AuNCs and AuNTs with various curvatures. For AuNCs, g decreases slightly as the corners are rounded (square symbols), whereas AuNTs maintain higher and more stable coupling values (triangle symbols). These trends mirror the simulated electric field distributions (Figure 4e,f): as AuNC corners become smoother, the maximum field intensity diminishes, while AuNTs retain strong localized fields. The electric fields around AuNTs are

also consistently stronger than those around AuNCs. Because the coupling strength scales with the electric field magnitude ($g \propto E$, Equation (6)), these distributions account for both the reduction in coupling strength for rounded AuNCs and the overall larger coupling strength for AuNTs compared to AuNCs.

For severely etched nanoparticles approaching spherical morphology, the coupling strength deviates from the overall trend (open circles). Although nanospheres generate weaker fields than anisotropic particles, their fundamental dipole modes distribute the near field over a significantly larger fraction of the particle surface. Assuming uniform surface coverage, this isotropic broadening geometrically increases the effective interaction area (A_{eff}), allowing a vastly larger number of J-aggregates to couple simultaneously with the plasmonic mode. Because the coupling strength scales with the square root of the effective number of participating emitters ($g \propto \sqrt{N_{\text{eff}}}$), this drastic increase in N_{eff} overcompensates for the weaker local fields, resulting in the unexpectedly elevated g values for the spherical particles.

To evaluate whether the observed interactions satisfy the strong-coupling condition, we calculated the cooperativity C (Equation (5)), which compares the coherent energy exchange rate (g) with the dissipative losses of the plasmonic cavity (γ_c) and the exciton (γ_e). As shown in the lower panels of Figure 4c,d, the cooperativity for AuNC@J-aggregates remains close to unity ($C \approx 1$) across different curvatures. To rigorously assign their coupling regime, we further evaluated these systems against stricter criteria for distinct eigenfrequencies and spectrally resolved polaritons (Section S7 and Table S1). Because the AuNCs fail to satisfy these stricter thresholds, they operate in the intermediate coupling regime, near the strong-coupling boundary. Nevertheless, they exhibit a distinct two-peak spectrum. In plasmonic systems with a large linewidth mismatch ($\gamma_p \gg \gamma_e$), the intense, narrow exciton absorption carves a Fano-like transparency dip into the broad plasmon band, yielding an apparent peak splitting even before reaching deep strong coupling [12, 16]. Notably, sharpening the

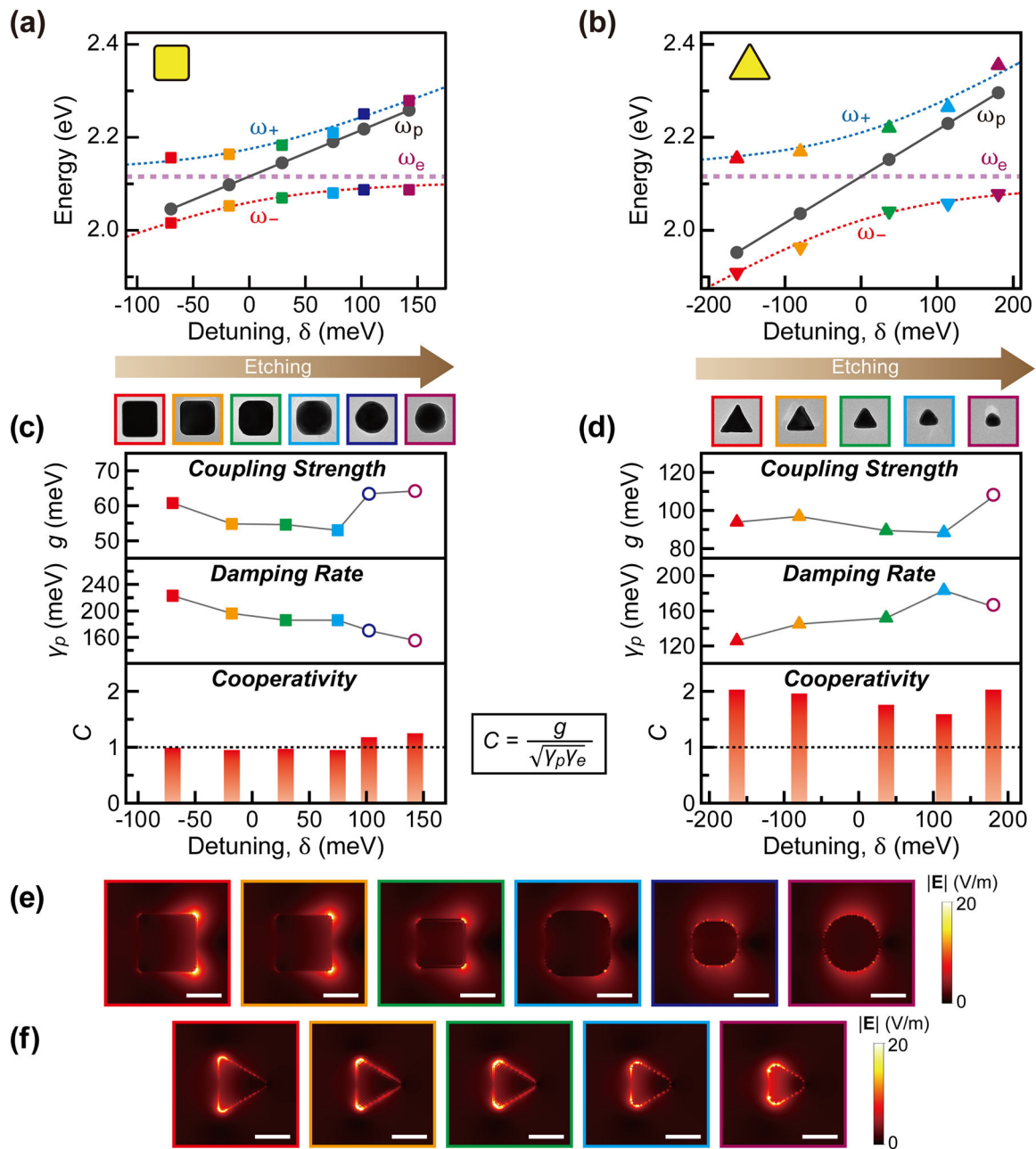


FIGURE 4 | Nanoparticle-curvature-dependent strong coupling. (a) Dispersion curves of AuNC@J-aggregates and (b) AuNT@J-aggregates. Split peak positions for nanoparticles with different curvatures coupled to J-aggregates are plotted as a function of detuning (δ). The upper (ω_+) and lower (ω_-) polariton states exhibit anticrossing. Dotted curves are best fits to Equation (2). (c, d) Coupling strength (g) extracted from dispersion curves, plasmon damping rates (γ_p) obtained from extinction spectra, and cooperativity (C) calculated from g and γ_p (Equation (5)) for each AuNP@J-aggregate structure. The horizontal dotted line at $C = 1$ indicates the criterion for strong coupling. (e, f) Simulated electric field distributions at ω_e for vertically polarized excitation, with light propagating from left to right. Cross-sectional views are shown at the plane of maximum field intensity. Scale bars: 50 nm.

corners of AuNCs does not significantly increase C , demonstrating that their intrinsically large plasmon damping limits their cavity performance.

In contrast, AuNT@J-aggregates robustly satisfy all criteria, yielding cooperativity values well above 1. Although etching slightly increases the damping rate and lowers C , all AuNTs maintain values far exceeding unity, preserving deep strong coupling. Together, these results demonstrate that while high damping losses restrict AuNCs to intermediate coupling, AuNTs

provide a much more favorable balance of field localization and loss, ensuring stable and efficient strong coupling across different curvatures.

To compare the capability of AuNCs and AuNTs with different curvatures to function as plasmonic cavities, we analyzed their mode volumes [57–59], quality factors, and FOMs, as summarized in Figure 5. The mode volume reflects the degree of field confinement, with smaller values corresponding to stronger local fields. To ensure robust evaluation, we parameterized the simulated

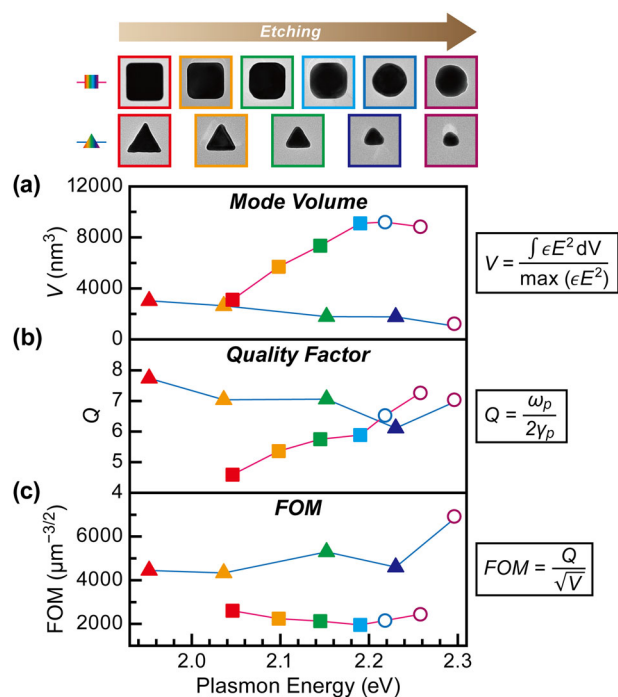


FIGURE 5 | Evaluation of AuNCs and AuNTs with different curvatures as plasmonic cavities for strong coupling. (a) Mode volumes (V) and (b) quality factors (Q) calculated for AuNCs (squares) and AuNTs (triangles). (c) FOM determined from the mode volumes and quality factors. AuNC mode volumes increase as corners are rounded, consistent with weaker field confinement, whereas AuNTs maintain consistently small mode volumes. Both particle types exhibit low Q (<10), reflecting intrinsic plasmonic losses. Overall, FOM values of AuNCs improve with sharper corners, but remain substantially lower than those of AuNTs. AuNTs show FOM values nearly twice those of AuNCs, confirming that overall particle geometry, rather than subtle curvature, dictates strong-coupling performance.

geometries directly from TEM measurements. Furthermore, we calculated the effective mode volumes using a dispersive energy density formulation to account for intrinsic plasmonic losses, and computed the quality factors directly from the resonance linewidths (see Sections S1.7 and S1.8 for full computational details) [20, 60]. As shown in Figure 5a, the calculated mode volume of an AuNC increases progressively as its corners are rounded, consistent with the weakening of localized fields observed in Figure 4e. By contrast, AuNTs maintain comparably small mode volumes across all curvatures, indicating persistent strong field localization during etching. These results reveal that AuNTs not only provide stronger field confinement than AuNCs but also retain it more effectively even if their corners are rounded.

Despite their favorable field confinement, both AuNCs and AuNTs are limited by their intrinsically lossy character, which is reflected in their quality factors. As shown in Figure 5b, the quality factors of both particle types remain below 10—values typical of plasmonic cavities and significantly smaller than those of dielectric microcavities [13]. The low quality factor indicates rapid plasmon damping and sets a fundamental limit on the coherence of light–matter interactions in these systems.

To capture both confinement and damping in a single metric, we evaluated the FOM defined in Equation (8). As shown in Figure 5a,b, sharpening the corners of an AuNC significantly reduces its mode volume but simultaneously lowers its quality factor. Consequently, these two effects offset each other, resulting in a relatively constant FOM across all AuNC curvatures (Figure 5c). The FOM values of AuNTs similarly exhibit little systematic dependence on curvature. However, a stark contrast emerges between the two morphologies: the FOM values of AuNTs are approximately twice those of AuNCs across all etched states, highlighting the superior balance of field localization and damping losses inherent to triangular geometries.

Crucially, this comprehensive analysis reveals why local curvature alone cannot dictate strong-coupling performance. Overall, our results demonstrate that while sharpening the corners of an AuNC improves field confinement, the overall cavity performance remains fundamentally constrained by increased plasmon damping. In contrast, AuNTs consistently provide smaller mode volumes, comparable quality factors, and significantly larger FOM values. These results establish that a nanoparticle's global geometric architecture dictates the fundamental boundaries of its cavity efficiency—rendering local curvature a secondary perturbation—and confirm that AuNTs are more effective plasmonic cavities for robust strong coupling.

3 | Conclusion

In summary, we systematically investigated how nanoparticle curvature and shape influence plasmon–exciton interactions by etching AuNCs and AuNTs with cysteamine in water. Coupling these nanoparticles with TDBC J-aggregates produced distinct peak splittings in the UV–vis spectra and clear anticrossing behavior. However, strict cooperativity evaluation demonstrated that large plasmon damping restricts AuNCs to the intermediate coupling regime ($C \approx 1$), producing Fano-like peak splitting. In contrast, AuNTs robustly exceed the strong-coupling threshold, achieving genuine polaritonic hybridization with significantly larger Rabi splittings. The extracted coupling strengths tracked the simulated electric field distributions: rounding of AuNC corners weakened local fields and reduced g , whereas AuNTs maintained stronger fields and more stable coupling. Finally, analyses of the mode volume, quality factor, and FOM established AuNTs as superior plasmonic cavities, exhibiting FOMs nearly twice those of AuNCs. Taken together, these results demonstrate a broader design principle: the global macroscopic architecture of a plasmonic cavity dictates its strong-coupling efficiency far more decisively than the sharpness of its local morphological features. Exemplified here by the highly confined triangular geometry of AuNTs compared to the symmetric cubic geometry of AuNCs, this principle highlights that overall shape supersedes local curvature in designing robust polaritonic platforms.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Supporting Information

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