Tunable self-assembled Casimir microcavities and polaritons

Spontaneous formation of ordered structures—self-assembly—is ubiquitous in nature and observed on different length scales, ranging from atomic and molecular systems to micrometre-scale objects and living matter. Self-ordering in molecular and biological systems typically involves short-range hydrophobic and van der Waals interactions. Here we introduce an approach to micrometre-scale self-assembly based on the joint action of attractive Casimir and repulsive electrostatic forces arising between charged metallic nanoflakes in an aqueous solution. This system forms a self-assembled optical Fabry–Pérot microcavity with a fundamental mode in the visible range (long-range separation distance about 100–200 nanometres) and a tunable equilibrium configuration. Furthermore, by placing an excitonic material in the microcavity region, we are able to realize hybrid light–matter states (polaritons), whose properties, such as coupling strength and eigenstate composition, can be controlled in real time by the concentration of ligand molecules in the solution and light pressure. These Casimir microcavities could find future use as sensitive and tunable platforms for a variety of applications, including opto-mechanics, nanomachinery and cavity-induced polaritonic chemistry.

In 1948, Casimir elucidated the nature of attractive forces between two parallel and uncharged plates of a perfect electric conductor in a vacuum, and these forces were later named after him. These forces exist even in the absence of any external impact, and appear even at zero temperature as a consequence of zero-point field fluctuations. In parallel with Casimir’s work, a related theory of colloidal stability—the so-called DLVO theory (after Derjaguin, Landau, Verwey and Overbeek)—was developed. The main ingredients of this theory are attractive van der Waals (vdW) and repulsive electrostatic forces. In aqueous solutions, the latter are characterized by the double layer potential and the Debye–Hückel screening length ($\kappa^{-1}$). Later, Lifshitz and colleagues demonstrated a deep intrinsic relationship between Casimir and vdW forces, and extended their applicability to real media. As opposed to the usual short-range vdW forces, the long-range Casimir interactions require accurate inclusion of retardation effects, which, together with the suitable geometrical parameters of the nanoplates (thickness much smaller than lateral extent), lead to the appearance of stable equilibria in our systems at long separation distances and the emergence of optical Fabry–Pérot resonances in the visible spectral range.

Nanoflake dimers

Figure 1a illustrates the basic mechanisms enabling self-assembled microcavities. When two nanoflakes in an aqueous solution of a ligand approach each other, two types of interactions between them emerge—the attractive Casimir interactions and the repulsive electrostatic interactions (due to the formation of double layers around the flakes, see Methods). The joint action of the two may result in the existence of a stable equilibrium (Fig. 1b, Supplementary Note 1).

We first show this theoretically by calculating the total potential of the system per unit area $U_0$ as a function of the separation $L$ between two charged metallic nanoflakes with a fixed net surface charge density, $\sigma$, and for a series of ligand concentrations, $C$ (Fig. 1b, Methods). For a relatively low ligand concentration $C = 0.35$ mM the electrostatic repulsion dominates, leading to no stable equilibrium at short distances. Next, for $C = 0.7$ mM, a local potential minimum appears at a long-range separation of about 105 nm, giving rise to an optical cavity with a resonance in...
the self-assembled microcavity system and the physical mechanism behind its operation. a. Sketch of the system: two parallel gold nanoflakes floating in an aqueous solution of a ligand (CTAB). The two nanoflakes are in metastable equilibrium at a distance $L_{eq}$ from each other, thanks to the joint action of the attractive Casimir force and the repulsive electrostatic force. b. Calculated total potential (sum of the Casimir and electrostatic potentials) $V_t$ per unit area of the system of two 30-nm-thick gold nanoflakes in an aqueous solution of CTAB with a fixed surface charge density $\sigma = 1 \text{mC m}^{-1}$ and different ligand concentrations, namely, 0.35 mM (left), 0.7 mM (middle) and 1.4 mM (right). Total, electrostatic and Casimir potentials are plotted as dashed, red and green lines, respectively. c. Left, quasi-normal-incidence reflection spectra collected from five representative self-assembled nanoflake dimer cavities (D1–D5) with $L_{eq} = 84$ nm (purple), 100 nm (blue-green), 110 nm (blue), 139 nm (orange) and 160 nm (red), respectively. Right, bottom, key. Different cavity thicknesses are obtained by varying the CTAB concentrations, $C_{\text{CTAB}} = 1.425$ mM (D1), 0.75 mM (D2), 0.35 mM (D3), 0.175 mM (D4) and 0.116 mM (D5), correspondingly. Right top, angle-resolved reflection of an exemplary self-assembled microcavity with $L_{eq} = 139$ nm, exhibiting a characteristic parabolic behaviour. d. Bright-field (BF) image of a self-assembled dimer formed from flake I (triangular) and flake II (hexagonal). Inset, SEM image of an exemplary gold nanoflake. e. Relative displacement between top and bottom nanoflakes within the dimer shown in a along x (top) and y (bottom) directions as a function of time. Note that while flakes can move with respect to each other, their relative displacement (shown as open circles) is always small in comparison to their lateral sizes (shown as pale pink and blue diagrams).

Fig. 1 | The self-assembled microcavity system and the physical mechanism behind its operation. a. Sketch of the system: two parallel gold nanoflakes floating in an aqueous solution of a ligand (CTAB). The two nanoflakes are in metastable equilibrium at a distance $L_{eq}$ from each other, thanks to the joint action of the attractive Casimir force and the repulsive electrostatic force. b. Calculated total potential (sum of the Casimir and electrostatic potentials) $V_t$ per unit area of the system of two 30-nm-thick gold nanoflakes in an aqueous solution of CTAB with a fixed surface charge density $\sigma = 1 \text{mC m}^{-1}$ and different ligand concentrations, namely, 0.35 mM (left), 0.7 mM (middle) and 1.4 mM (right). Total, electrostatic and Casimir potentials are plotted as dashed, red and green lines, respectively. c. Left, quasi-normal-incidence reflection spectra collected from five representative self-assembled nanoflake dimer cavities (D1–D5) with $L_{eq} = 84$ nm (purple), 100 nm (blue-green), 110 nm (blue), 139 nm (orange) and 160 nm (red), respectively. Right, bottom, key. Different cavity thicknesses are obtained by varying the CTAB concentrations, $C_{\text{CTAB}} = 1.425$ mM (D1), 0.75 mM (D2), 0.35 mM (D3), 0.175 mM (D4) and 0.116 mM (D5), correspondingly. Right top, angle-resolved reflection of an exemplary self-assembled microcavity with $L_{eq} = 139$ nm, exhibiting a characteristic parabolic behaviour. d. Bright-field (BF) image of a self-assembled dimer formed from flake I (triangular) and flake II (hexagonal). Inset, SEM image of an exemplary gold nanoflake. e. Relative displacement between top and bottom nanoflakes within the dimer shown in a along x (top) and y (bottom) directions as a function of time. Note that while flakes can move with respect to each other, their relative displacement (shown as open circles) is always small in comparison to their lateral sizes (shown as pale pink and blue diagrams).

the visible range. This long-range equilibrium separation can be shown to obey $L_{eq} > n\kappa$, where $3 < n < 4$ is a material-dependent factor limited by non-retarded vdW and fully retarded Casimir cases (Supplementary Note 1). Finally, for even higher ligand concentration $C = 1.4 \text{mM}$, the local potential minimum disappears, leaving only a trivial minimum at $L = 0$.

To realize a stable Casimir microcavity experimentally, we chemically synthesized gold nanoflakes in an aqueous solution of CTAB (cetyltrimethylammonium bromide), which served as a ligand. The average thicknesses of the nanoflakes was about 34 ± 10 nm, and the lateral dimensions were a few micrometres (Methods)22. In the simplest scenario, two isolated nanoflakes diffuse close to one another at a distance where the attraction becomes relevant and form a stable nanoflake pair (Fig. 1d, Supplementary Video 1). Figure 1c shows reflection spectra collected from five representative self-assembled nanoflake dimers (D1–D5) obtained at different concentrations of CTAB ligand, $C_{\text{CTAB}} = 1.425$, 0.75, 0.35, 0.175 and 0.116 mM. The spectra reveal reflection dips corresponding to Fabry–Pérot modes of the self-assembled microcavities. Fitting the data with the transfer-matrix method yields the equilibrium cavity thickness, $L_{eq}$. Values of $L_{eq}$ (in nm) of about 84, 100, 110, 139 and 160 are found for dimers D1–D5, respectively (see Supplementary Fig. 7). The uncertainties in $L_{eq}$ are within ±5 nm around the stated values as estimated from the transfer-matrix fits. To ensure reproducibility, we recorded reflection spectra from dozens of samples in the solution (data available upon request from the corresponding author). The angle-resolved reflection measurements exhibit a characteristic parabolic dispersion (Fig. 1c, top right), which confirm the formation of a Fabry–Pérot microcavity by two parallel nanoflakes (additional dispersion data are shown in Supplementary Fig. 11).

The joint Casimir–electrostatic potential (sum of the Casimir and the electrostatic ones) can be used to analyse the observed equilibrium configurations. To that end, for each known CTAB concentration we varied the surface charge density $\sigma$ until the equilibrium separation predicted by the theory matched the one extracted from the measured reflection spectra (Supplementary Fig. 7). This analysis suggests that $\sigma = 0.1–2 \text{mC m}^{-1}$ and grows linearly with CTAB concentration (Supplementary Fig. 8), which is in line with the previously reported linear dependence of the $\xi$ potential of gold colloids on CTAB concentration below the critical micelle point26,37.

Finally, we tracked the lateral trajectories of the top and bottom nanoflakes within a dimer over time (Fig. 1e). While the cavity as a whole is diffusing in the solution owing to Brownian motion, the flakes also move with respect to each other, translationally and rotationally. However, their trajectories feature submicrometre centre-to-centre displacements, which are small compared to the lateral size (several micrometres) of the flakes (Fig. 1e, Supplementary Video 2). The lateral stability of the dimers is probably ensured by the lateral Casimir force28–30, a rough estimation of which is given in Supplementary Note 3. The self-assembled microcavities are remarkably stable both vertically and laterally, as they showed no signs of degradation for as long as they have been monitored (multiple weeks).
To illustrate this mechanism, we calculated normal incidence reflection spectra of a trimer with the middle mirror thickness gradually reducing from 70 nm down to 0 (Fig. 2c). For an optically thick middle mirror, the interaction vanishes and the reflection spectrum exhibits a single dip associated with the Fabry–Pérot eigenmode of the half-cavity. Reducing the middle mirror thickness allows interaction and opens the splitting between the two hybrid modes, which monotonically increases until the lower-energy branch approaches the first order, while the higher-energy branch approaches the second-order Fabry–Pérot mode of the full cavity formed by top and bottom mirrors.

Experimental data in Fig. 2b show several splitting values, indicating variations in the middle mirror thickness. By fitting the measured spectra with the transfer-matrix method, we extracted the thickness of the middle mirrors and apparent Rabi splittings (Supplementary Tables 2, 3, and Supplementary Figs. 16, 17). The range of extracted thicknesses agrees well with the typical values measured by atomic force microscopy, about 20–30 nm (Supplementary Fig. 18).

**Nanoflake trimers**

The process of self-assembly does not stop at the point of dimer formation, but can proceed to trimers (Fig. 2a) and higher-order aggregates (Supplementary Fig. 14). Moreover, the relative population of dimers, trimers and higher-order aggregates can be controlled by the concentration of nanoflakes and inter-flake interactions, in a manner similar to self-limiting aggregation of silver nanoparticle colloids. Just as for dimers, trimers form a stable aggregate both vertically and laterally (see Supplementary Videos 3, 4 and Supplementary Fig. 15).

The reflection spectra from several exemplary trimers exhibited characteristic double-dip behaviour (Fig. 2b; higher-order aggregates are shown in Supplementary Fig. 14). The origin of this double-dip behaviour lies in the interaction of Fabry–Pérot modes hosted by each half-cavity separated by the semi-transparent middle mirror. This results in symmetric and antisymmetric hybrid eigenmodes with the splitting between the two determined by the thickness of the middle mirror, similarly to the formation of symmetric and anti-symmetric polaritonic states in a Rabi-like problem.

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**Nanoflake on static mirror**

We now examine an alternative microcavity configuration consisting of a nanoflake on a static gold mirror (Fig. 3a). This configuration offers several means of additional control over the self-assembled microcavities, including incorporation of a dielectric (SiO$_2$) or excitonic (WSe$_2$) spacer with controllable thickness above the bottom mirror (Fig. 3c), the adjustable thickness of the bottom mirror, the usage of silver nanoflakes as movable mirrors (Supplementary Fig. 19), and the assessment of the gravity contribution to the self-assembly mechanism.

We first check the role of gravity in the formation of stable cavities. Figure 3b shows reflection spectra of a single cavity collected in upright and upside-down configurations. The reflection spectra in both cases exhibit dips at around 600 nm, implying that gravity plays no role in the formation of these microcavities, and the equilibrium distance is determined by the interplay of the Casimir attraction and the electrostatic repulsion.

Next we characterized self-assembled cavities in the nanoflake-on-static-mirror configuration as the thickness of the SiO$_2$ spacer was varied (Fig. 3c). The measured spectra indicate that the reflection dip gradually shifts to longer wavelengths with increasing spacer thickness. Transfer-matrix analysis reveals that the equilibrium thickness of the water layer between the SiO$_2$ spacer and the nanoflake in this parameter range increases almost linearly with the SiO$_2$ thickness (Supplementary Fig. 20). This behaviour suggests that the equilibrium water thickness is not a universal constant but rather a parameter governed by more complicated physics, which is expected to include the influence of Casimir attraction and electrostatic repulsion.

To quantify the stability of self-assembled microcavities in the Brownian regime, we studied time-dependent equilibrium cavity thickness, Fig. 4c, extracted by the transfer-matrix method from time-resolved reflection spectra. In this case, the uncertainties in determination of $L_{eq}$ are within ±2 nm for each time frame. The resulting distribution exhibits a standard deviation of only about 1.6 nm around the mean value of $L_{eq}$ = 177 nm, which is a remarkable stability for a micrometre-sized system at room temperature in an aqueous solution. The measured deviation agrees with the characteristic deviation of the mirror displacement obtained in stochastic simulations of the dimer dynamics (Methods and Supplementary Fig. 10). Such small deviations probably stem from the high stiffness of the Casimir-electrostatic potential (Supplementary Note 4).

By introducing an excitonic layer between the bottom mirror and the Au flake, a configuration is obtained that allows proof-of-principle realization of tunable polaritonic states—mixtures of Fabry–Pérot cavity photons and excitons of the material. To realize such a scenario...
Fig. 3 | Self-assembled cavities in nanoflake-on-static-mirror configuration and the formation of polaritons. a, Sketch of a self-assembled Fabry–Pérot microcavity in nanoflake-on-static-mirror configuration, showing the upright and the upside-down configurations. b, Quasi-normal-incidence reflection spectra for the microcavities with upright (blue) and upside-down (red) configurations, respectively. c, Tuning the resonance of microcavities with various SiO$_2$ spacers thickness in the range of 30–300 nm, leading to appearance of the first-order (for 30–110 nm thick spacers), the second-order (for 200 nm thick spacer), and the third-order (for 300 nm thick spacer) Fabry–Pérot resonances in the reflection spectra. d, Sketch of a self-assembled microcavity coupled to a transition metal dichalcogenide (TMD), here WSe$_2$, a few layers thick. e, Quasi-normal-incidence reflection spectra of the cavity coupled to various thicknesses of few-layer WSe$_2$, showing pronounced Rabi splitting and correspondingly microcavity-exciton polariton formation. Red, blue and orange curves correspond to red-detuned, blue-detuned, and nearly resonantly tuned microcavities with respect to the exciton resonance of WSe$_2$. Grey curve shows reflection of an empty cavity. f, Angle-resolved reflection of a WSe$_2$-loaded self-assembled microcavity versus incident angle $\theta$, exhibiting a pronounced mode anti-crossing. Dashed lines are guides for the eye.

experimentally, we choose WSe$_2$ because of its high oscillator strength and the appropriate resonant wavelength of the A exciton. A few-layer WSe$_2$ flake was transferred onto the SiO$_2$ spacer covering the gold film (Methods), and subsequently covered by the nanoflake floating in an aqueous solution (lateral trapping of the gold nanoflake was enabled by a focused laser beam, which acted as an optical tweezer). The reflection spectra measured from several systems reveal pronounced Rabi splitting (Fig. 3e). The corresponding dispersion measurement for the polaritonic microcavity, loaded with a few-layer WSe$_2$ flake, exhibits a pronounced anti-crossing with the Rabi splitting of $\Omega_0 \approx 110$ meV, which proves the system is in the strong coupling regime (Fig. 3f).

**Active tuning**

Self-assembled microcavities in this study represent damped optomechanical resonators with the restoring force provided by the joint Casimir–electrostatic potential and the friction provided by the hydrodynamic drag. As in any optomechanical system, these microcavities can be tuned by applying external stimuli. Here we use modulated laser light to exert a pressure on the nanoflakes (Fig. 4a).

We start by modulating an empty self-assembled cavity in a nanoflake-on-static-mirror configuration. Figure 4b shows the map of 5-Hz modulated reflection spectra, revealing a dip oscillating between about 1.7 eV and 1.9 eV with time. This corresponds to a vertical displacement of the nanoflake by about ±20 nm. The time-dependent vertical displacements for various laser powers are shown in Fig. 4c (see also Supplementary Note 5 and Supplementary Figs. 22, 23).

We now turn to modulation of the polaritonic system containing a WSe$_2$ multilayer between the mirrors. Variation of the cavity thickness in this scenario has a twofold effect: not only does it enable modulation of the bare Fabry–Pérot resonance, but it also modifies the vacuum field of the cavity, thus affecting the cavity–exciton coupling strength and the composition of polaritonic eigenstates. Positions of the two reflection minima, corresponding to upper and lower polaritons, vary in time (Fig. 4d). The reflection minima red-shift by about 0.2 eV compared to the empty cavity, which is due to the high background index $n = 4$ of WSe$_2$ (ref. 14).

The time-resolved reflection map allows the extraction of parameters of the coupled system as it is modulated. To that end, we fitted the spectral positions of reflection minima with the eigenvalues of a periodically modulated Jaynes–Cummings Hamiltonian (Methods). Figure 4f compares the resulting coupling strength $g(t)$ with the cavity–exciton detuning $\delta(t) = \omega_{\text{exc}}(t) - \omega_{\text{cav}}(t)$. The Jaynes–Cummings description of any polaritonic system predicts that once the detuning substantially exceeds the coupling strength, $|\delta(t)| > g(t)$, the system can be tuned out of the strong coupling regime. Such behaviour is clearly visualized in
the time-dependent Hopfield coefficients of the system showing nearly 100% photonic or excitonic character of the eigenstates at times corresponding to the minima of $g(t)$. Conversely, at time instances near the maxima of $g(t)$, the eigenstates of the system are polaritonic with nearly equal fractions of the photonic and excitonic components (Fig. 4e).

**Conclusions**

We have presented a platform for self-assembly of optical microcavities and polaritons enabled by the joint action of attractive Casimir and repulsive electrostatic interactions. The tunable microcavities studied here are highly stable in both vertical and lateral directions, and exhibit pronounced optical resonances in the visible spectral range. The long-term cavity stability is also remarkable, as the resonances remain unchanged for as long as they have been monitored (multiple weeks).

Our platform enables not only ordinary Fabry–Pérot microcavities, but also vertical multi-mirror aggregates with complicated modal structure, as well as proof-of-principle realization of polaritonic states when the cavities interact with excitonic material (such as WSe$_2$). By modulating the system with a periodically varied laser light, we can actively control the polaritonic eigenstates and tune the system in and out of the strong coupling regime. These findings open possibilities for exploring self-assembled Casimir microcavities as sensitive and tunable platforms in opto-mechanics, nanomachinery, polaritonic chemistry and other promising cavity-induced applications. More generally, our approach expands the toolbox of available self-assembly methods.

**Online content**

Any methods, additional references, Nature Research reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at https://doi.org/10.1038/s41586-021-03826-3.

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Methods

Materials
Gold(III) chloride trihydrate (HAuCl₄, 3H₂O), l-ascorbic acid (AA) and cetyltrimethylammonium bromide (CTAB) were purchased from Sigma-Aldrich for the synthesis of gold nanoflakes. For the synthesis of silver nanoflakes, silver nitrate (AgNO₃), sodium chloride (NaCl), polyvinyl pyrrolidone (PVP), ammonium hydroxide solution (NH₄OH, 25% w/w) and hydrogen peroxide solution (H₂O₂, 30% w/w) were purchased from Sigma-Aldrich. All glassware and stir bars were thoroughly pre-cleaned and dried before use. Ultra-pure deionized water (Millipore, 18 MΩ cm) was used in all preparations.

Synthesis of gold nanoflakes
Single crystalline gold nanoflakes were synthesized using the rapid and seedless wet chemical method. In brief, 100 μl of 100 mM HAuCl₄ was added to 3 ml of 20 mM CTAB aqueous solution in a glass vial, and the mixture was gently mixed and left undisturbed for several minutes. Then, 100 μl of 100 mM AA was added to the mixture, followed by a rapid inversion for 10 s. The resulting solution was immediately placed in a water bath at 85 °C and kept undisturbed for about an hour. The products were washed by centrifugation at 4,000 r.p.m. for 10 min and finally redispersed in the deionized water for further experiments.

Synthesis of silver nanoflakes
Single crystalline silver nanoflakes were selectively synthesized using the reduction of colourless silver ammine complex [Ag(NH₃)₂]+ in the presence of Cl⁻ using H₂O₂ as a reducing agent. Briefly, a colloidal AgCl nanoparticle solution was prepared by a rapid injection of 4 ml of 100 mM NaCl into a solution of 1 ml of 1 M AgNO₃ and 10 ml of PVP (5% w/v) under vigorous stirring. A milky white colloidal AgCl nanoparticle spontaneously developed. The total volume was adjusted to 96 ml with deionized water. The colloid was further stirred for 5 min before an additional 1.7 ml of 5.3 M NH₄OH solution. The colloidal solution became opaque due to partial dissolution of AgCl nanoparticles upon formation of a water-soluble Ag(NH₃)₂⁺ complex. To induce the formation of silver nanoflakes, 2.3 ml of H₂O₂ (30% w/w) was quickly injected into the colloid. The milky white colloid turned into sparkling glitter within 2 min, indicating the formation of silver nanoflakes. The colloid was further stirred for an hour to complete the reaction. The shiny silver precipitate was collected and washed 5 times with deionized water.

Sample preparation
All samples were prepared on thin (170 μm) microscope glass coverslips. The coverslips were cleaned in acetone and isopropanol at 60 °C in an ultrasonicator, then dried with compressed nitrogen, followed by oxygen plasma cleaning. For the nanoflake dimer configuration, self-assembled Fabry–Pérot microcavities were formed between freely floating Au nanoflakes by drop-casting an aqueous solution containing the Au nanoflakes onto a glass coverslip. The droplet was encapsulated by another coverslip using a thin polydimethylsiloxane (PDMS) spacer, to prevent evaporation of the liquid. After drop-casting, the non-aggregated nanoflakes slowly sediment towards the glass substrate, where they diffuse laterally owing to Brownian motion until eventually colliding with another individual flake to form a stable dimer. The trimmer samples were prepared from a diluted mixture solution of stock batch and deionized water with a volume ratio of 1:1.

For nanoflake-on-static-mirror configuration, various thicknesses (10, 30 and 50 nm) of gold mirrors were prepared by e-beam evaporation. Chromium (2 nm) was used as an adhesion layer. Various thicknesses of SiO₂ layer for half-cavities were sputtered on top of a freshly prepared bottom gold mirror, in order to tune the resonance of the cavity.
To fabricate polaritonic systems, few-layer WSe₂ flakes were mechanically exfoliated from a crystal (HQ Graphene) and transferred on top of freshly-prepared half-cavities using a dry-transfer technique. Subsequently, an aqueous solution containing Au nanoflakes was drop-cast and liquid was sealed by a PDMS O-ring with a cover glass. The floating Au nanoflakes over the half-cavities with a bottom Au mirror form Fabry–Pérot cavities, which strongly couple to excitons in WSe₂.

Optical measurements
Reflection spectra at quasi-normal incidence (NA = 0.5) were collected using an inverted microscope (Nikon Eclipse TE2000-E) equipped with an oil-immersion 100× objective (switchable NA = 0.5–1.3, Nikon), directed to a fibre-coupled spectrometer (Andor Shamrock SR-303i, equipped with a CCD detector Andor iDus 420). Dispersion relations in reflection were measured using NA = 1.3 in the Fourier plane. Spectra at various angles were obtained simultaneously with a fibre bundle (Andor SR-OPT-8002). All reflection experiments were conducted using a laser-driven white light source (LCLS, EQ-99FC, high-brightness, flat-broadband spectrum).

The Q-factors of self-assembled microcavities were evaluated from measured reflection spectra by estimating the linewidth of cavities as the full-width of the reflection dip. For a typical dimer, this analysis yields a Q-factor of the order of 5.6 ± 0.7. The Q-factors were tailored by varying the thickness of the mirrors in the nanoflake-on-static-mirror configuration—10 nm, 30 nm and 50 nm (bottom gold mirror)—resulting in Q-factors of the order of 2, 15 and 26, respectively (Supplementary Fig. 19).

To modulate the system in an active manner, the samples were illuminated from the top using a 100× long-working-distance objective (NA = 0.6) and a mechanically chopped (4 Hz–15 Hz) continuous wave (CW; λ = 455 nm) laser source (see Fig. 4a). Simultaneously, time-resolved reflection spectra were recorded using bottom illumination by an oil-immersion 100× objective (NA = 0.5, Nikon). The reflected light was collected by the same objective and directed to a fibre-coupled spectrometer in a kinetic mode. A long-pass (λ = 500 nm) optical filter was installed in the detection path to block the modulating laser.

Casimir–electrostatic potential
The total ground-state potential per unit area U₀ is the sum of the Casimir and the electrostatic contributions. The Casimir potential Uₐ of two gold mirrors in an aqueous solution was calculated using the Lifshitz framework. The potential per unit area is obtained by integration over the imaginary frequency ω = iξ (with the parameter ξ acquiring real values):

\[ U₀ = \frac{\hbar}{2\pi} \int_0^\infty d\xi \int \frac{d^3k}{(2\pi)^3} \text{Im} \text{det} G \]  

(1)

where kᵢ is the in-plane component of the wave vector in the gap region of thickness L, G = 1 - Rᵢ × Rₑ⁻²ik·d, and

\[ Rᵢ = \begin{pmatrix} rᵢ^x & 0 \\ 0 & rᵢ^y \end{pmatrix} \]  

(2)

is the reflection operator for ith side of the system (i = 1, 2); rᵢ are the Fresnel reflection coefficients for ith subsystem and polarization q evaluated at the imaginary frequency. k₀ = \sqrt{kᵢ² + ξ²/c²} is the z-component of the wave vector in the gap between the two mirrors evaluated at the imaginary frequency.

The permittivity of gold at imaginary frequencies was evaluated with the Drude model εᵦ = 8 − ω_p²/ω(ω + iη) with ω_p = 8.6 eV and η ≅ 70 meV approximating the Johnson and Christy experimental data.

The permittivity of water at imaginary frequencies εᵦ was evaluated by approximating the experimental data from ref. with a series of Lorentzian transitions and a static Debye contribution:
\[ \varepsilon(\omega) = \varepsilon_{\infty} + \frac{\varepsilon_0 - \varepsilon_{\infty}}{1 - i\omega\tau} + \sum_{i=1}^{n} \frac{\omega_i^2}{\omega_i^2 - \omega^2 - i\gamma\omega} \]  

where \( \omega_i \) is the plasma frequency of \( i \)th resonant transition, \( \omega_0 \) and \( \gamma \) are the resonance frequency and linewidth, \( \varepsilon_0 \) is the refraction index of water at the imaginary axis \( n(\omega) \), which takes purely real values and is presented in Supplementary Fig. S5b. The analytical form of this expression allows us to evaluate the refractive index of water at the imaginary axis \( n(\omega) \), which takes purely real values and is presented in Supplementary Fig. S5b. The analytical form of this expression allows us to evaluate the refractive index of water at the imaginary axis \( n(\omega) \), which takes purely real values and is presented in Supplementary Fig. S5b.

Calculating the Casimir potential for two 30-nm-thick Au films in water yields approximately \( L \) distance dependence of the potential with \( n = -2.63 \) (Supplementary Fig. 6). The slope being different from \( n = -3 \) predicted by the exact theory in the original Casimir effect stems from partial transparency of the mirrors.

In our experiments, CTAB plays a role of a colloid stabilizing agent. At \( C_{CTAB} = 0.35 \text{ mM} \), the most appropriate CTAB phase on the nanoflake surface is a double layer. This double layer is responsible for the electrostatic repulsion between the nanoflakes. The electrostatic potential per unit area \( \gamma \) was modelled by the Langevin equation with the noise term:

\[ \frac{\partial z}{\partial t} = \frac{e_0}{\varepsilon_0} \varepsilon(0) k B T \eta(z, t) \quad \text{(5)} \]

where \( \eta(z, t) \) is the effective surface charge density of the plates.

Diffusion modeling

The stochastic dynamics of the vertical displacement \( z \) of a self-assembled cavity near the equilibrium position in a nanoflake dimer configuration was modelled by the Langevin equation with the noise term:

\[ m \ddot{z} = -\gamma z + F_{\text{rest}}(z) + \sqrt{2k_B T f(t)} \quad \text{(5)} \]

where \( z \) is the vertical displacement, \( m \) is the effective mass (twice the mass of a single flake), \( F_{\text{rest}} = -A dU/dz \) is the restoring force, \( A \) is the surface area of the flake, \( \gamma \) is the friction coefficient, \( f(t) \) is the white noise term with the correlator \( \langle f(t)f(t') \rangle = \delta(t - t') \) experienced by the flake during its laminar motion in water can be described by Stokes' law:

\[ \nu = \frac{6\pi \eta R}{viscosity} \]  

where \( \nu \) is the viscosity, and \( R \) is the Stokes’ radius of the flake. The Stokes’ radius of the object is determined by many factors, and it can be further greatly affected by the close presence of the substrate (the boundary). Therefore, to make a reasonable assumption, we take the disk radius as a measure of its Stokes’ radius \( R \).

Analysis of modulated cavities

Empty modulated cavities were analysed by the standard transfer-matrix method. The reflection spectra at each time instance were fitted by reflection coefficient at normal incidence calculated assuming 30-nm-thick gold mirrors, a 53-nm SiO2 spacer with \( n = 1.45 \), and a solution refraction index of \( n = 1.38 \) consistent with other calculations.

Reflection spectra from the modulated coupled structures were analysed with the Hamiltonian approach. Time-dependent positions of reflection dips were fitted with eigenvalues \( \omega_i \) of the Hamiltonian:

\[ \omega_i = \frac{(\omega_{\text{cav}} + \omega_0)/2 - i(\gamma_{\text{cav}} + \gamma_0)/4}{\pm \sqrt{\frac{g^2}{4} + (\omega_{\text{cav}} - \omega_0 + i(\gamma_{\text{cav}} - \gamma_0)/2)^2/4}}, \]

where \( \omega_{\text{cav}} - i\gamma_{\text{cav}}/2 \) is the cavity complex eigenergny, \( \omega_0 - i\gamma_0/2 \) is the exciton complex energy, and \( g \) is the coupling strength. The cavity energy and the coupling strength were assumed to be modulated periodically with the triangular-like function (as suggested by the suggested by the nature cavity reflection spectra dynamics):

\[ \omega_{\text{cav}}(t) = \omega_{\text{cav},0} + \delta\omega_{\text{cav}} f(\Omega t + \phi), \quad \text{where } \Omega = \frac{\omega_{\text{cav}}}{\gamma_{\text{cav}}}, \quad \phi = \frac{\omega_{\text{cav}}}{\gamma_{\text{cav}}}, \quad f(t) = \frac{4}{6} \left[ -\left| t - \left| t + 1/2 \right| \right| - 1 \right], \]

where \( \omega \) is the modulation frequency and \( f(t) \) is the triangle wave.

Data availability

The set of experimental and calculated optical spectra, SEM images, optical images and numerical codes are available through figshare.com with the identifier https://doi.org/10.6084/m9.14883024.v2. Additional data are available from T.O.S. upon request.

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Author contributions

B.M. and T.O.S. conceived the idea. B.M. fabricated the samples. B.M. and T.O.S. performed the optical measurements. B.M. and A.C. performed optical measurements. B.M. and T.O.S. conceived the idea. B.M. fabricated the samples. B.M. and T.O.S. performed the optical measurements. B.M. and T.O.S. conceived the idea. B.M. fabricated the samples. B.M. and T.O.S. performed the optical measurements. B.M. and T.O.S.