

Supplementary Material for:

Low-loss, centimeter-scale plasmonic metasurface for ultrafast optoelectronics

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Plasmonic Nanopatch Antenna Architecture Fabrication and Optimization

As shown in Figure 1(a) of the main text, the basic structure of the plasmonic nanocavity is comprised of a silver nanocube (60 nm) situated over an ultra-smooth silver film (75 nm), which is separated by a well-controlled nanoscale spacer (7 nm). This structure is fabricated by starting with a 75-nm-thick template stripped silver substrate. Immediately after separation from the template, the silver-coated sample is immersed in a cationic solution of 3 mM poly(allylamine) hydrochloride (PAH) and 1 M NaCl for 5 min, followed by rinsing in clean deionized (DI) water and drying in nitrogen gas. The PAH-coated sample is then immersed for 20 min in a 75 μ M aqueous solution of the photostable fluorescent dye, Atto 532 (90% QE; Sigma-Aldrich: 06699), followed by a thorough rinse in DI water. Next, the sample is immersed in an anionic solution of 3 mM poly(styrenesulphonate) (PSS) and 1 M NaCl for 5 min, followed by immersion in the solution of 3 mM PAH and 1 M NaCl for 5 min. The sample is rinsed with a 1 M NaCl solution between the PSS and PAH layers. After rinsing in DI water and drying in nitrogen gas, the sample is again immersed in the dye solution for 20 min. The above steps are repeated until a 7-nm-thick spacer layer (as measured by spectroscopic ellipsometry) is obtained from seven polymer layers (terminating with PAH). Four layers of Atto 532 dye are sandwiched between each PAH and PSS layers to increase the dye concentration in the gap. This dip coating method allows precise control of the spacer layer thickness over wafer-scale areas using a simple solution-based process. The control sample used for the fluorescence and time-resolved fluorescence measurements is fabricated using the above procedure, but on a glass substrate.

The silver nanocubes are obtained from NanoComposix, Inc. (San Diego). The average size of the nanocubes is 60 nm, including a \sim 3-nm-thick coating of polyvinylpyrrolidone (PVP), which is a result of the synthesis procedure. The nanocubes are stored in ethanol and re-suspended in DI water using centrifugation to a concentration of 3 mg mL⁻¹. An 8 μ L droplet of the nanocube solution is deposited onto a 12-mm round cover glass, which is then inverted onto the polymer-coated sample. The negatively charged nanocubes are electrostatically bound to the positively charged top polymer layer (PAH). The nanocube incubation time is determined according to previous reports to achieve a nearly perfect absorber [1]. After an hour, the non-adhered nanocubes are removed with a water rinse and the sample is dried with nitrogen gas. The sample is measured within a week of fabrication to avoid silver oxidation

and is stored in a nitrogen purge box when not measured.

The concentration for a single layer of the fluorescent dye between the silver ground plane and the nanocubes was varied to optimize the fluorescence intensity. The fluorescence spectra at different dye concentrations is shown in Figure S1. As can be seen, at a dye concentration of 75 μM , the fluorescence intensity was the highest. For dye concentrations higher than 75 μM , the fluorescence intensity decreased due to self-quenching⁵.

Figure S1: Effect of dye concentration on the fluorescence intensity. (a) Measured fluorescence spectra at varying dye concentrations under the excitation of a 532 nm continuous wave laser at a power of 10 nW. (b) Peak fluorescence intensity extracted from (a), as a function of the dye concentration.

Next, this optimized single layer concentration was extended to four layers interspersed between the polyelectrolyte layers. Fluorescence spectra were measured from samples with a single layer and four separate layers of fluorescent dye coupled to the plasmonic nanocavity, as shown in Figure S2. The schematic for each sample is also depicted. As can be seen, the sample with four layers of dye exhibited 1.5-times higher fluorescence intensity than the sample with a single layer of dye. Given the 2-nm space between each dye layer, we do not expect the optimized single layer concentration to be altered when extended to four layers.

Figure S2: Fluorescence spectra from samples with single layer and four layers of dye sandwiched in the plasmonic cavity. The sample with four layers of dyes sandwiched in the gap exhibits higher fluorescence intensity than the sample with a single layer of dye. The polymer layer thickness and the nanocube size is kept the same for the two samples. A 10 nW, 532 nm continuous wave laser is used for the measurements.

Optical Properties of the Nanopatch Architecture

The small volume between the nanocube and the ground plane introduces a strong, highly localized gap-plasmon mode parallel to the ground plane with the dominant electric field oriented vertically. In this volume, especially at the edges, the electric and magnetic fields are greatly enhanced by over an order of magnitude (Figure S3). Furthermore, this small volume acts as a Fabry-Perot cavity with multiple reflections at the edges providing spectral selectivity by changing either the cube size or gap thickness.

Figure S3: Simulations of the electric and magnetic field enhancements. The simulation, performed with COMSOL Multiphysics, demonstrate an 80 and 40-fold enhancement in the electric and magnetic field, respectively.

The cavity-like behavior and electric field enhancement induce some appealing effects when resonant dipole emitters are placed in the gap. Assuming a spontaneous emission rate for a dipole is given as the sum of the radiative and nonradiative decay rates

where the radiative decay can be expressed as

and where μ is the transition dipole moment, \mathbf{r} is the position, ω is the emission frequency, and $\rho(\omega)$ is the local density of states, which for free space is equivalent to $\rho(\omega) = \frac{\omega^2}{\pi^2 c^3}$ with n being the index of refraction of the environment. Due to the dipole's proximity to the metallic surfaces as well as

the optical cavity formed by the nanocube and ground plane, the density of states is greatly enhanced because¹

where \hat{d} is the dipole orientation and \hat{G} is the dyadic Green's function which describes the electric field of the dipole interacting with its own radiation. This increase in the final density of states is known as the Purcell effect and causes an enhancement in the dipole's spontaneous emission rate. The level of Purcell enhancement depends on the attributes of the surrounding cavity, namely the mode volume, V , and the quality factor, Q , which is a measure of how well the cavity retains light. Thus, the Purcell factor, F_P , can be described as²

where λ is the wavelength of the electric field in the cavity. Given the dimensions of the plasmonic nanopatch antenna, the effective mode volume is V_{eff} , whereas the quality factor is Q where $\Delta\omega$ is the cavity bandwidth, estimated from the metasurface's absorption resonance and bandwidth (Fig. 1c of the main text). Thus, our estimated Purcell enhancement is F_P . While we were only able to experimentally measure a Purcell enhancement of 133-fold, this is likely due to being at the detector resolution limit. In actuality, the Purcell enhancement is likely somewhere between the estimated value of 1000 and the detector-limited enhancement of 133. Also, it should be noted that nonradiative processes can contribute to the reduction in the emitter's lifetime, but it should not be the dominant source of lifetime reduction given the overall efficiency (28.6%) especially when compared to the control sample. While there are likely some contributing within the nanocavity, the predominant source

In addition to the increased spontaneous emission rate, the NPA should also greatly enhance the fluorescence. The excitation rate, R_{exc} , scales as a function of the exciting electric field, E , and the effective dipole orientation, \hat{d} , such that $R_{exc} \propto |E \cdot \hat{d}|^2$. Given the electric field enhancement from the plasmonic cavity, the excitation rate enhancement can be described as³

where the superscript "0" indicates the parameters for the control. Using this in conjunction with the quantum yield, defined as η , as well as the collection efficiency, Ω , the overall fluorescence enhancement can be defined as

Specifically, for the 0.9 NA 100 \times objective used in this experiment, the collection efficiencies for the metasurface and control as estimated by simulations are Ω_{ms} and Ω_{ctrl} , respectively (see Fig. 2a of the main text for radiation pattern simulation). The fluorescence was experimentally found to be enhanced 910-fold.

It should be noted that we tailored our metasurface such that both the excitation and emission of our fluorescent dye is resonant with the fundamental resonance of the plasmonic nanocavity. This design choice was to maximize the spontaneous emission rate enhancement (i.e. the Purcell factor) as well as to maximize the fluorescent enhancement. As is evident by the above the equations, the emission rate enhancement is solely dependent on the cavity parameters, which are maximized when the emission is on resonant with the cavity. Similarly, the total fluorescent enhancement originates from both the excitation rate enhancement, which is maximized when the excitation is resonant with the cavity, and the emission rate enhancement. Thus, by designing both excitation and emission to be resonant with the nanocavity, we are maximizing the fluorescent yield and rate for this nanocavity design.

Lastly, as is mentioned in the main text, the above enhancement effects arise from the individual nanocavity geometry. In general, the primary ensemble effect from the cube density is the total absorption of the metasurface, where there is an optimized cube spacing

for maximal absorption at a particular wavelength. This does have a minor effect on the total excitation rate, but would more heavily influence the saturation intensity limit (i.e. the more nanocavity-coupled fluorescent molecules, the more energy can be absorbed). Minor density fluctuations below the intensity saturation limit should not have much effect on the emission intensity as long as there are more cube-coupled dye remaining to exciting. At too high of cube density, cross coupling occurs which should lower the overall efficiency within each nanocavity, but the cube deposition itself is a self-limiting process due to the charge repulsion from the polymer layer (PVP) on the cube surfaces.

Details of experimental setup for intensity and lifetime measurements

All of the optical measurements are performed using a custom-built bright-field/dark-field confocal microscope unless mentioned otherwise. The light source for the reflectance measurement at near normal incidence is a spectrally broad lamp with emission from the visible to the near-infrared. White light is coupled into the collar of a 20 \times , 0.45 NA dark-field objective, and the reflected or scattered light from the sample is collected by the same objective and spectrally resolved on an imaging spectrograph (HR 550 Horiba Jobin Yvon) with a charge coupled device (CCD) camera. A pinhole aperture (150 μm in diameter) is placed at the intermediate image plane to select light only from the area of interest.

The excitation source for the two-dimensional (2D) fluorescence measurements is a 532-nm cw laser, which is defocused to a ~ 100 μm diameter laser spot and imaged on the sample plane through the 20 \times objective. The 2D fluorescence image, shown as an inset of Figure 1d in the main text, is collected using the same objective and imaged on an electron multiplying digital camera (Hamamatsu EM-CCD, model C9100). A 550 nm long-pass filter (Omega Optics) is used to reject scattered laser light. For the measurements of fluorescence enhancement, the defocusing lens is removed and the laser is focused on the sample plane to a diffraction-limited spot with a diameter of ~ 3 μm . The fluorescence is collected by the 20 \times objective, passed through a 532 nm long-pass filter (Semrock) and detected by the imaging spectrograph. For the absolute fluorescence intensity measurements and calibration, the 20 \times objective was replaced with a 100 \times objective, 0.9 NA to increase the collection efficiency.

Time-resolved fluorescence measurements are performed using a 532 nm pulsed laser from a frequency-doubled optical parametric oscillator (OPO), which is synchronously pumped by a Ti:Sapphire pulsed laser with an 80 MHz repetition rate and a nominal pulse length of 150 fs. The OPO laser is coupled to a single-mode optical fiber and collimated at the output, producing a Gaussian beam. The laser is directed into the objective lens and is imaged onto the sample plane, resulting in a laser spot with a diameter of ~ 3 μm . The fluorescence emission from the sample is collected by the same objective, passed through two 550 nm long-pass filters to remove the scattered laser, and detected by a single-photon counting avalanche photodiode (APD, 50 μm active area, Micro Photon Devices). The APD is connected to a time-correlated single-photon counting module (TCSPC, Picoharp 300, Picoquant Inc.), which assembles a histogram of photon arrival times.

Two-dimensional (2D) k-space imaging setup

The 532 nm continuous-wave (CW) laser is used for excitation via the 100 \times , 0.9 NA objective. As shown in Figure S4, the back focal plane of the objective, which is the Fourier plane, is imaged onto an electron multiplying digital camera (Hamamatsu EM-CCD 9100) via a 4f configuration. The angular dependence of the emission can be calculated from the obtained 2D k-space image. Essentially, the 2D k-space image is a spatial map of the fluorescence intensity by angle. For instance, if a slice of the image along the k_x axis is taken, the intensity at zero corresponds to the light that is emitted normal to the surface while the intensities at the edges corresponds to the extreme angle that the objective is able to collect. Given that the NA is 0.9, the objective is capable of collecting light up to approximately 64° from normal incidence. For simulating the emitted radiation pattern in COMSOL

Multiphysics, an electric dipole source with a vertical orientation was placed beneath the edge of a cube and the near-field emission was extracted. The near-to-far-field transformation method based on reciprocity arguments was then used to compute the far-field radiation pattern using a freely available software package⁴.

Figure S4: The experimental setup for the radiation pattern measurement. The back focal plane of the objective lens (Fourier plane) is imaged onto a Hamamatsu camera via a 4f configuration. The angular dependent emission can be obtained from the 2D k-space image.

Angular Excitation Rate Measurements and Simulation

To measure the angular dependence of the excitation rate (Fig. 2a of the main text), an experimental setup was built such that the collimated CW excitation laser at 532 nm could be swept over multiple angles while maintaining incidence with the same region on the metasurface. The emitted light from the metasurface was collected using a 10 cm lens placed a focal distance away from the surface. The emitted light was then coupled to a spectrometer where the intensity was recorded (Figure S5). The emission intensity provides information on the excitation rate as they are directly proportional. Special care was taken to ensure that the region of the metasurface that was probed was much smaller than the beam diameter of the excitation laser. Furthermore, the emission intensity was normalized to the excitation laser irradiance since the excitation irradiance would decrease with increasing angle relative to the normal of the metasurface; i.e. as the excitation laser was swept from 90° to close to parallel with the surface, the laser spot size on the sample would increase thus decreasing the irradiance. While the change in irradiance is easily calculated as a function of incidence angle, the area of the probed region must remain constant to successfully normalize. This is experimentally achieved by constraining the field of view via a 2f telescope and pinhole before the spectrometer such that the probed region is much smaller than the region excited by the excitation laser.

Figure S5: The experimental setup for measuring the angular dependence of the excitation rate. The 532 nm excitation laser swept over multiple angles while the intensity of emission was recorded with a spectrometer. The normal orientation of the metasurface relative to the collection optics remained the same throughout this study.

Simulations were performed using COMSOL multiphysics to confirm the excitation rate's angular dependence. As shown earlier, the excitation rate, Γ , is proportional to E_{eff}^2 and E_{eff} are the effective dipole orientation and the local excitation field, respectively. Thus, in the simulations, Γ can be extracted as a function of the incident angle θ of the electric field, E_0 . Specifically, the incident angle-dependent background field of the dielectric material (i.e. the fluorescent dye in the polyelectrolyte space layers) was computed without a coupled nanocube. The computed angle-dependent background field is then used to compute the total field of the film-coupled cube. The projection of the square of the average electric field in the gap underneath the cube is thus obtained as a function of incident angle.

Fast modulation setup

For the fast modulation measurements, a 50:50 non-polarizing beam-splitter is used to divide the output of the fiber into two different paths, namely the pump and the control pulses as shown in Figure S6. To control the time delay between the arrival of the two pulses, the control pulse is passed through a delay line consisting of a retro-reflector mirror on a linear translation stage. Then, the two pulses are spatially overlapped and focused onto the sample

via the 20× objective. The emission from the sample under the subsequent excitation of the two pulses is collected by the same objective and is detected by the APD in conjunction with the TCSPC module, same as for the single pulse time-resolved fluorescence measurements as described above.

Figure S6: Schematic of fast modulation setup. APD: avalanche photodetector, TCSPC: time-correlated single-photon counting.

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