Freeform 3D Plasmonic Superstructures

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Abstract

Plasmonic nanoparticle clusters promise to support various, unique artificial electromagnetisms at optical frequencies, realizing new concept devices for diverse nanophotonic applications. However, the technological challenges associated with the fabrication of plasmonic clusters with programmed geometry and composition remain unresolved. Here, we present a freeform fabrication of hierarchical plasmonic clusters (HPCs) based on omnidirectional guiding of evaporative self-assembly of gold nanoparticles (AuNPs) with the aid of 3D printing. Our method offers a facile, universal route to shape the multiscale features of HPCs in three-dimensions, leading to versatile manipulation of both far-field and near-field characteristics. Various functional nanomaterials can be effectively coupled to plasmonic modes of the HPCs by simply mixing with AuNP ink. We demonstrate in particular an ultracompact surface-enhanced Raman spectroscopy (SERS) platform to detect M13 viruses and their mutations from femtolitre volume, sub-100pM analytes. This SERS microplatform could pave the way towards simple, innovative detection methods of diverse pathogens, which is in high demand for handling pandemic situations. We expect our method to freely design and realize nanophotonic structures beyond the restrictions of traditional fabrication processes.

Plasmonic nanoparticle clusters have attracted great attention due to the unique capability to manipulate electromagnetic fields at the sub-wavelength scale^{1–5}. Ensembles of metallic nanoparticles generate various electromagnetisms at optical frequencies such as artificial magnetism^{6–10} and Fano-like interference^{11–13} and a strong field localization in the structure^{14–16}. These unique properties are geometry-dependent and lead to a broad range of applications in sensing^{16,17}, surface-enhanced spectroscopies^{18–22}, nonlinear integrated photonics^{23,24}, and light harvesting^{25,26}.

Traditionally, plasmonic clusters with tailored size and geometry are fabricated on substrates by top-down processes such as electron-beam lithography^{4,5} or focused-ion beam milling^{27,28}. These approaches suffer from low throughput and are generally limited to in-plane fabrication. Alternatively, the self-assembly of colloids has been proposed as a versatile, high-throughput, and cost-effective route. A number of clever methods based on chemical linking (e.g., DNA origami)^{29–30} and/or convective assembly on lithographically structured templates^{25,26,31} have been devised to construct 2D or 3D plasmonic clusters. The shape formation, however, is mostly constrained by the thermodynamic impetus and/or template geometry. A significant challenge would be overcome these restrictions and expand structural design freedom in the fabrication of plasmonic cluster architectures with symmetry-breaking geometries.

In this work, we develop a freeform, programmable 3D assembly of hierarchical plasmonic clusters (HPCs). By exploiting micronozzle 3D printing, we demonstrate highly localized, omnidirectional meniscus-guided assembly of metallic nanoparticles, constructing a freestanding HPC with a tailored geometry that can control the far-field character. Our approach also allows versatile manipulation and exploitation of the near-field interaction in the HPC by a facile heterogeneous nanoparticle mixing. We demonstrate that 3D-printed HPCs can be utilized as an ultracompact surface-enhanced Raman

spectroscopy (SERS) platform to detect M13 viruses and their mutations from femtolitre volume, sub-100pM analytes.

Background

Plasmonic nanoparticle clusters have attracted great attention due to the unique capability to manipulate electromagnetic fields at the sub-wavelength scale¹⁻⁵. Ensembles of metallic nanoparticles generate various electromagnetisms at optical frequencies such as artificial magnetism⁶⁻¹⁰ and Fano-like interference¹¹⁻¹³ and a strong field localization in the structure¹⁴⁻¹⁶. These unique properties are geometry-dependent and lead to a broad range of applications in sensing^{16,17}, surface-enhanced spectroscopies¹⁸⁻²², nonlinear integrated photonics^{23,24}, and light harvesting^{25,26}.

Traditionally, plasmonic clusters with tailored size and geometry are fabricated on substrates by top-down processes such as electron-beam lithography^{4,5} or focused-ion beam milling^{27,28}. These approaches suffer from low throughput and are generally limited to in-plane fabrication. Alternatively, the self-assembly of colloids has been proposed as a versatile, high-throughput, and cost-effective route. A number of clever methods based on chemical linking (e.g., DNA origami)²⁹⁻³⁰ and/or convective assembly on lithographically structured templates^{25,26,31} have been devised to construct 2D or 3D plasmonic clusters. The shape formation, however, is mostly constrained by the thermodynamic impetus and/or template geometry. A significant challenge would be overcome these restrictions and expand structural design freedom in the fabrication of plasmonic cluster architectures with symmetry-breaking geometries.

In this work, we develop a freeform, programmable 3D assembly of hierarchical plasmonic clusters (HPCs). By exploiting micronozzle 3D printing, we demonstrate highly localized, omnidirectional meniscus-guided assembly of metallic nanoparticles, constructing a freestanding HPC with a tailored geometry that can control the far-field character. Our approach also allows versatile manipulation and exploitation of the near-field interaction in the HPC by a facile heterogeneous nanoparticle mixing. We demonstrate that 3D-printed HPCs can be utilized as an ultracompact surface-enhanced Raman spectroscopy (SERS) platform to detect M13 viruses and their mutations from femtolitre volume, sub-100pM analytes.

3D printing of HPCs

A key approach that enables the fabrication of freeform hierarchical plasmonic clusters (HPCs) is the exploitation of a femtolitre (fL) liquid meniscus^{32,33} to confine and guide the self-assembly of functionalized nanoparticles in three dimensions, i.e., the meniscus-guided 3D nanoassembly process. **Figure 1** depicts the core of our experimental arrangement. Gold nanoparticles (AuNPs) having 100 nm diameters and functionalized with 50 kDa polystyrene (PS) were suspended in toluene and used as the primary building blocks to promote strong localized surface plasmon resonance (LSPR). The role of PS was to ensure an interparticle distance of tens of nanometres among the AuNPs after the self-assembly.

A glass micropipette (having an aperture diameter of 3 μm , **Supplementary Fig. S1**) was filled with the AuNP suspension and used to 3D print HPCs. As depicted in **Fig. 1a**, a fL-volume, AuNP-laden solution meniscus is formed at a localized area by the micropipette. The continuous supply and assembly of AuNPs are driven by fast evaporation of the toluene solvent at the meniscus surface. We note that this highly localized AuNP assembly can omnidirectionally grow with the guidance of pipette movement, resulting in a freestanding, freeform AuNP cluster with controlled interparticle spacing. This approach can also be used to print freeform heterogeneous clusters, as shown in **Figure 1b**. Various hybrid inks prepared by mixing AuNPs and functional nanomaterials (e.g., dielectric particles, quantum emitters, or biomolecules) can be directly used to fabricate plasmonic-based heterogeneous 3D architectures. The series of optical micrographs in **Fig. 1c** show the printing process consisting of (i) micropipette approach toward a silicon (Si) substrate, (ii) meniscus formation by pipette-substrate contact, (iii, iv) continuous 3D assembly of the HPC by meniscus guiding, and (v) termination. Continuous HPC assembly results from maintaining an adequate pipette moving speed; a speed of 3 $\mu\text{m/s}$ was used herein. Termination of the assembly process is conducted by abruptly and sufficiently increasing the speed so as to disrupt the meniscus. **Figure 1d** schematically depicts the multiscale features of an HPC. At the tens of nm scale, near-field coupling among the AuNPs, which have an interparticle spacing controlled by PS, determines the plasmonic characteristics of the HPC. At the μm scale, the 3D structure, consisting of thousands of assembled AuNPs, confers its far-field characteristics and allows the HPC itself to act as a free-space optical system. **Figure 1e** shows field-emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) images for a resulting 3D-printed HPC with controlled geometry and interparticle spacing. The result shows that the meniscus-guided nanoassembly approach provides unprecedented simplicity and structural design freedom in construction of 3D HPCs.

Plasmonic characteristics of HPCs: experimental and theoretical studies

A notable feature of the 3D printed HPC is that its plasmonic characteristics are highly consistent and uniform throughout the entire structure. To examine the AuNP distributions and corresponding LSPR spectra, we fabricated a straight HPC micropillar that was $\sim 2\text{ }\mu\text{m}$ in diameter and $\sim 20\text{ }\mu\text{m}$ in height (aspect ratio: 10) as a model specimen (**Fig. 2a**). A FE-SEM image taken after focused ion beam (FIB) milling (inset of **Fig. 2a**) clearly shows that the AuNPs are uniformly distributed, having a 20-30 nm interparticle spacing, within the fabricated micropillar. The LSPR of the micropillar was investigated with dark-field spectroscopy. The LSPR spectrum is composed of a superradiant bright mode with a broad peak and a subradiant dark mode with a narrow dip (**Fig. 2b**). The LSPR is consistent along the vertical pillar axis. The spectra obtained from the bottom (i) and the top (v) of the micropillar do not exhibit noticeable differences. No significant shift is observed in the broad peak, and the subradiant dip wavelength ($\lambda_{\text{sub,exp}} = 729 \pm 7\text{ nm}$) is maintained. The LSPR spectra of the HPC depend on the quantity of AuNPs in the measured region. To investigate this, LSPR spectra for AuNP clusters with different particle numbers (N) were simulated by the finite-difference time-domain (FDTD) method. A detailed description of the simulation is provided in the Methods and Supplementary Information (**Supplementary Fig. S2** and

Fig. S3). In this study, the particle diameter and interparticle spacing were set to 100 nm and 32 nm, respectively. The designated geometries of AuNP clusters with N from 2 to 5 for the simulation are depicted in **Fig. 2c**. **Figure 2d** clearly shows the LSPR dependence on N . Specifically, as N increases from 2 to 5, the simulated LSPR spectra sequentially redshift and broaden due to the enhancement of the superradiant mode with increasing radiative damping⁵. A further 3D model was obtained by vertically stacking $N = 5$ clusters. The simulated LSPR spectrum for $N = 25$ (solid line in grey, **Fig. 2d**) exhibits a broad superradiant peak with a subradiant dip at $\lambda_{\text{sub,cal}} = 730$ nm, consistent with the experimental data ($\lambda_{\text{sub,exp}} = 729$ nm). The surface charge maps clearly show characteristic surface charge distribution for the superradiant mode and the subradiant mode^{5,13}. (**Supplementary Fig. S4**) The peak in the absorbance spectrum for the $N = 25$ cluster ($\lambda_{\text{abs,cal}} = 741$ nm; solid line in blue) is also located near $\lambda_{\text{sub,cal}}$ and $\lambda_{\text{sub,exp}}$, consistent with the existence of a subradiant mode. These results show that the simulation performed for the $N = 25$ cluster well predicts the plasmonic characteristics of a printed HPC pillar.

Freestanding, freeform HPCs

The meniscus-guided method enables omnidirectional printing of HPCs with tailored geometries, providing a facile platform for manipulating light propagation at the nanoscale. In other words, the far-field properties of an HPC can be controlled by its 3D geometry. **Figs. 2e-2h** show the array of 3D shapes that were prepared using our method. These 3D HPC structures were readily fabricated by guiding the meniscus, with control of the printing direction being rapid and programmable. **Figs. 2e, 2f, and 2g** show 2-fold, 3-fold and 4-fold freestanding HPC pillars, respectively. A top-view SEM image of the 4-fold freestanding HPC pillar is shown in **Fig. 2h**. Additional model 3D structures are provided in **Supplementary Fig. S5**. We compared the light guiding direction in the 2-fold HPC pillar (having a folding angle of 90° ; **Fig. 2i**) to that in the straight pillar previously discussed (**Fig. 2j**). **Fig. 2k** shows the directional dependences of the scattering signals from these two HPC pillars, collected by an objective lens located above the samples under side light illumination. Note that the scattering signal generated by LSPR is partially guided along the pillar direction. As a result, the 2-fold HPC pillar, for which the guided mode is excluded from the objective lens (**Fig. 2i**), shows a smaller collected scattering intensity than that of the straight HPC pillar. The scattering signal for the 2-fold HPC pillar has directionality according to the light illumination; the intensity is greater when the incident light is perpendicular to the length direction of the structure (90° and 270°)³⁴.

Heterogeneous HPCs

In addition to the control over the far-field properties by tailoring 3D geometry, the use of hybrid printing ink provides a versatile route to tune and exploit the near-field optical properties of heterogeneous HPCs. The interparticle spacing of AuNPs in the HPC can be precisely controlled by adding secondary spacer

particles such as 20 nm silica (SiO_2) (**Fig. 3a**). This approach does not require a complicated lithography process or rigorous chemical synthesis. The interparticle spacing was controlled in this study by adjusting the ratio of the SiO_2 NPs to AuNPs from $N_{\text{SiO}_2}/N_{\text{Au}} = 0$ to $N_{\text{SiO}_2}/N_{\text{Au}} = 0.005$ or $N_{\text{SiO}_2}/N_{\text{Au}} = 0.01$. The FDTD model was also utilized to predict the dependence of the LSPR spectrum on the interparticle spacing within the HPC. As shown in **Fig. 3b**, when $N_{\text{SiO}_2}/N_{\text{Au}} = 0$, the subradiant mode of the HPC is observed at $\lambda_{\text{sub,exp}} = 733$ nm, which matches well with the simulated spectrum for a 32 nm interparticle spacing (**Fig. 3c**). Upon increasing $N_{\text{SiO}_2}/N_{\text{Au}}$ from 0.005 to 0.01, the LSPR spectrum is shifted from $\lambda = 684$ nm to 632 nm (**Fig. 3b**), consistent with the simulated spectra obtained for 52 nm and 72 nm interparticle spacings (**Fig. 3c**). The change in the interparticle spacing with the $N_{\text{SiO}_2}/N_{\text{Au}}$ ratio was confirmed experimentally by the FE-SEM images in **Supplementary Fig. S6**.

A quantum dot (QD)-embedded HPC was also prepared and demonstrated outstanding near-field fluorescence enhancement and far-field radiation. As schematically depicted in **Fig. 3d**, a 3D QD-embedded HPC was fabricated by mixing AuNPs and cadmium selenide (CdSe) QDs in an ink solution. This approach offers a simpler strategy to embed QDs within AuNP clusters than other existing methods³⁵⁻³⁷. Time-resolved (TR) photoluminescence (PL) measurements were performed to confirm the enhancement of the QD fluorescence. **Figure 3e** compares the TRPL spectra for CdSe QDs on a glass substrate and CdSe QDs within the HPC. The decay time for QD fluorescence coupled to the HPC is 3 ns, which is shorter than the observed 14 ns for QDs on glass. This drastic decrease in decay time is evidence of the strong near-field enhancement of the HPC.

The far-field characteristics of the QD-embedded HPC can be manipulated by its 3D geometry at the microscale. **Figure 3f** compares the PL spectra of a vertical QD-embedded HPC pillar and a collapsed pillar (**Supplementary Fig. S7**) having the same QD concentration. The PL signals were collected by an objective lens located above the sample. The PL signal collected from the vertical pillar is 19 times brighter than that from the collapsed sample. These results show the ability of the freestanding HPC pillar to confine and guide the propagation of an electromagnetic wave along a specific direction. The far-field property of the QD-embedded freestanding HPC pillar was simulated by the finite element method using a symmetric $N = 95$ cluster model schematically illustrated in **Fig. 3g**. The results show more directed, confined radiation characteristics than the QD on a dielectric film (**Fig. 3h** and **Supplementary Fig. S8**), resulting in increased QD emission collection efficiency. We expect that this heterogeneous HPC approach will offer a facile strategy to design the far-field radiation of quantum emitters in three-dimensions.

HPC-based SERS platform for virus detection

Our heterogeneous HPC approach allows for the placement of small molecule analytes at plasmonic hot spots during the self-assembly process by simple mixing, directly printing an ultracompact surface-enhanced Raman spectroscopy (SERS) platform, as depicted in **Fig. 4a**. The 3D-printed SERS

microplatform enables high-sensitivity diagnosis of diseases or pathogens from a femtolitre-volume analyte), which can be easily collected from blood, tear, or urine samples. For this study, AuNPs having 75 nm diameter and functionalized with polyvinylpyrrolidone (PVP) were used. The PVP-coated AuNPs had smaller interparticle spacing than the PS-coated one, leading to increased electromagnetic field enhancement. The performance of the 3D-printed SERS microplatform (HPC) was tested first using a thiophenol analyte, which showed a clear Raman signal enhancement over that embedded in the control PS pillar (**Supplementary Fig. S9**). To demonstrate the practical use of this microplatform for bio-sensing, we performed SERS detection of M13 bacteriophages, which are filamentous viruses (width: ~ 6.6 nm, length: ~ 880 nm) that have a well-established mutagenesis protocol³⁸. M13 bacteriophages were effectively placed in the nanogaps between AuNPs during 3D printing of the HPC due to their nanometre-width. The printed HPC can be used as a SERS microplatform to detect M13 functional peptides. To prove the detection capability, we tested the wild-type M13 bacteriophage (WT phage) and three types of mutant M13 bacteriophage – 4E phage (Glu-Glu-Glu-Glu), 3H phage (His-His-His), and 3Q phage (Gln-Gln-Gln) – prepared by site-directed mutagenesis polymerase chain reaction (PCR) at the +81 nucleotide sequence position of the N-terminus of the major coat protein (pVIII), as illustrated in **Fig. 4b**. Each M13s were simply mixed with the AuNPs and used to produce an array of M13-embedded HPC micropillars, as shown in the top-view dark-field scattering images of **Fig. 4c**. **Figure 4d** shows the SERS spectra for WT-phage-embedded HPC pillars, having WT phage concentrations ranging from 0 to 300 pM, under 633 nm laser illumination. The obtained Raman spectra arising from the capsid protein enabled WT phage M13 sensing at tens of picomolar concentration. **Figures 4e-h** show SERS spectra for the WT-phage, 4E-phage, 3H-phage and 3Q-phage-embedded HPCs, which clearly exhibit their characteristic SERS spectra. **Figure 4i-l** show the fingerprint patterns by selected Raman responses for each mutant phage. The differentiated intensity of SERS spectra was used for the fingerprint patterns to prevent distortion due to baseline differences. The fingerprint patterns clearly visualize differences in the SERS peak positions for different phage genetic types. Principal component analysis was also able to discriminate the various SERS spectra (**Supplementary Fig. S10**). The SERS spectra obtained from different HPC locations showed high consistency, suggesting that reliable diagnostic results may be obtained. The results of this study indicate the potential for HPCs to not only diagnose specific viruses, but also detect their mutations in a facile and flexible manner. We expect that the application of HPCs will be extended to the diagnosis of pathogens and diseases in the near future.

Conclusion

In this work, we present the construction of freeform 3D HPCs with programmed shape and composition by 3D printing. The 3D printing method is based on a meniscus-guided self-assembly process, which offers unprecedented simplicity and structural design freedom in the fabrication of freeform 3D plasmonic components. This study sets the groundwork for future research endeavours utilizing 3D plasmonic architectures. In particular, the ease of tuning the geometry of HPCs using this method allows on-demand control of optical properties at scales ranging from the near- to the far-field. Additionally, we show that HPCs have great potential to be used as a SERS platform to diagnose viruses and their

mutations. We expect 3D printing to pave the way for customized manufacturing of plasmonic-based nanophotonic architectures if full-scale development and characterization of the printing process are achieved.

Methods

Preparation of NPs. PS-coated 100 nm diameter AuNPs dispersed in toluene (5mg/ml) and PVP-coated 75 nm diameter AuNPs dispersed in water (5mg/ml) (Nanocomposix, San Diego, CA 92111, USA) were used as the primary building blocks in the self-assembly process. Twenty nanometre-diameter SiO₂ NPs dispersed in water (5mg/ml) (Nanocomposix, San Diego, CA 92111, USA) were re-dispersed in toluene by means of a centrifuge-based solvent exchange. Colloidal CdSe QDs with an emission peak at 620 nm were utilized in this work (Zeus Inc., Hwaseong, 18363, South Korea). A hybrid solution for fabricating heterogenous HPCs was also prepared and consisted of 1 mg/ml AuNPs and 0.05 mg/ml CdSe QDs.

3D printing of NPs. An in-house 3D printing setup was utilized and consisted of three main parts: an x-y-z motorized stage (M-VP-25XA-XYZR, Newport, Irvine, CA 92606, USA) operated by a controller (XPS-D4, Newport, Irvine, CA 92606, USA), an x-y-z manual stage (PT3A/M, Thorlabs, Newton, NJ 07860, USA) and an optical system consisting of a halogen fibre illuminator (OSL2, Thorlabs, Newton, NJ 07860, USA), an objective lens (MY20X-804, Mitutoyo, Kanagawa, 213-8533, Japan) and a charge-coupled device (CCD) camera. To prepare the micropipette (an aperture diameter = $\sim 3 \mu\text{m}$), a glass capillary (1B100F-6, World Precision Instruments, Sarasoto, FL 34240, USA) and a commercial glass pipette puller (P-97, Sutter Instruments, Novato, CA 94949, USA) was used. A silicon wafer was placed on the x-y-z motorized stage, and the micropipette was installed in the home-built micropipette holder attached to the x-y-z manual stage. Using a syringe, the NPs were injected into the micropipette. To observe the printing process in real time, the micropipette was aligned to the CCD camera by adjusting the x-y-z manual stage. Contact between the micropipette and the substrate during the printing process was maintained by adjusting the position of the x-y-z motorized stage. The pull-up process was carefully controlled at a speed of $3 \mu\text{m/s}$.

SEM analysis of the plasmonic nanostructures. SEM images were taken using a field-emission scanning electron microscope (S-4700, Hitachi, Tokyo, 105-6409, Japan and S-4800, Hitachi, Tokyo, 105-6409, Japan). Additionally, FIB milling (Helios NanoLabTM, Thermo Fisher Scientific, Waltham, MA 02451, USA and LYRA 1 XMH, Tescan, Brno-Kohoutovice, 623 00, Czech Republic) was conducted to prepare nanopillar cross-sections.

Optical measurements of the plasmonic nanostructures. PL measurements were performed using a custom-built micro-PL setup with a Mitutoyo 100x 0.55 NA infinity corrected long working distance objective lens. A continuous wave diode laser (402 nm) was used as an excitation source. Dark-field (DF) images and spectra were obtained using an Olympus bright-field/dark-field microscope with a 100x 0.9 NA objective. An unpolarized halogen light source was used to illuminate the sample. The PL and DF spectra were characterized using an Ocean Optics Flame spectrometer.

TRPL measurements of the plasmonic nanostructures. The TRPL study was carried out using a confocal microscope (MicroTime-200, Picoquant, Berlin, 12489, Germany) with a 40x objective. A single-mode pulsed diode laser (470 nm with a pulse width of ~30 ps) was used as an excitation source. An avalanche photodiode detector (MPD, Picoquant, Berlin, 12489, Germany) was used to collect emission photons from the samples. Exponential fitting of the obtained PL decays was accomplished using analysis software (Symphotime-64 software Ver. 2.2, Picoquant, Berlin, 12489, Germany).

Optical simulation of the plasmonic nanostructures. Three-dimensional simulations based on the finite element method (FEM, Wave Optics Module, COMSOL Multiphysics 5.5) and finite-difference time-domain (FDTD) method (Lumerical Solutions) were employed to computationally analyse HPCs. A broadband plane wave source was used to excite the HPC structure from the top (+z direction). The scattering spectra were obtained by employing a box-shaped power monitor close to the HPC structure in FDTD simulations. The corresponding near-field enhancement profiles and surface charge maps at significant wavelength positions were obtained using 3D FEM simulations. The averaged near-field enhancement profiles were obtained with the following equation³⁹:

$$\frac{\iiint_V |E/E_0| dV}{V} \quad (1)$$

Here, the modulus of the incident electric field is given as $E_0 = 1 \text{ V m}^{-1}$, the local electric field is described as $E = (E_x, E_y, E_z)$, and V is the volume within a specific distance above the metallic surface. The plasmonic modes are visualized with the help of 3D surface charge maps, which were calculated by integrating Gauss's law and utilizing the skin effect³⁹:

$$\Phi E = \frac{Q}{\epsilon_0} = \oiint_S (\mathbf{n} \cdot \mathbf{E}) dS \quad (2)$$

where Q is the total charge, ϵ_0 is the permittivity of vacuum, $\mathbf{n} = (n_x, n_y, n_z)$ is the outward normal vector of the metallic surface, $\mathbf{E}$ is the local electric field, and ΦE is the electric flux through the metallic surface S . Au is well known for its good electrical conductance; therefore, most of the induced charges will be distributed on the clustered NPs at the HPC surface. This simplifies equation 2 to the following:

$$Q = \oiint_S \rho dS \quad (3)$$

where ρ is the surface density, which can be further expanded as follows:

$$\rho = \frac{\epsilon_0 (n_x \cdot E_x + n_y \cdot E_y + n_z \cdot E_z)}{\delta (1 - e^{-R/\delta})} \quad (4)$$

$$\alpha (n_x \cdot E_x + n_y \cdot E_y + n_z \cdot E_z) \quad (5)$$

For simulations involving QDs, an x-polarized dipole source was chosen to calculate the radiation pattern and far field. The HPC was surrounded by perfectly matched layers. For Au, the Au dielectric functions from the Johnson and Christy database were fitted using the Lorentz-Drude dispersion model^{40,41}.

$$\epsilon(\omega) = 1 - \frac{f_0 \omega_p^2}{\omega(\omega - i\Gamma_0)} + \sum_{j=1}^m \frac{f_j \omega_p^2}{(\omega_j^2 - \omega^2) + i\omega\Gamma_j} \quad (5)$$

In equation 5, the first term is the result of the Drude modification: “ Γ_0 ” is the damping constant and “ ω_p ” is the plasma frequency with oscillator strength “ f_0 ”. The second term in the equation is the result of the Lorentz modification: the number of oscillations is “ m ”, with frequency “ ω_j ”, damping constant “ Γ_j ”, and oscillator strength “ f_j ”. A 5 nm mesh was applied to the entire structure, with a mesh override of 2 nm surrounding the HPC. The structure was surrounded by perfectly matched layers.

Declarations

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Author contributions

W.G.K. prepared the samples. W.G.K., J.M.L. and M.K. performed optical measurements. V.D. performed the optical simulations. H.J., J.Y. and J.M.L. prepared the experimental setups. E.J.C. prepared the M13 bacteriophages. W.G.K., J.M.L. and J.T.K. prepared the manuscript. D.H. L, J.W.O. and J.T.K. designed and managed the research.

Additional information

The authors declare no competing financial interests. Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.Nature.com/reprints. Correspondence and requests for materials should be addressed to J.W.O.

References

1. Barnes, W. L., Dereux, A. & Ebbesen, T. W. Surface plasmon subwavelength optics. *Nature* **424**, 824-830 (2003)
2. Prodan, E., Radloff, C., Halas, N. J. & Nordlander, P. A hybridization model for the plasmon response of complex nanostructures. *Science* **302**, 419-422 (2003)
3. Fan, J. A. *et al.* Self-assembled plasmonic nanoparticle clusters. *Science* **328**, 1135-1138 (2010)
4. Verellen, N. *et al.* Fano resonances in individual coherent plasmonic nanoparticles. *Nano Lett.* **9**, 1663-1667 (2009)
5. Dregely, D., Hentschel, M. & Giessen, H. Excitation and tuning of higher-order fano resonances in plasmonic oligomer clusters. *ACS Nano* **5**, 8202-8211 (2011)
6. Monticone, F. & Alù, A. The quest for optical magnetism: from split-ring resonators to plasmonic nanoparticles and nanoclusters. *J. Mater. Chem.* **2**, 9059-9072 (2014)
7. Papadakis, G. T. *et al.* Optical magnetism in planar metamaterial heterostructures. *Nat. Commun.* **9**, 296 (2018)
8. Alù, A. & Engheta, N. Dynamical theory of artificial optical magnetism produced by rings of plasmonic nanoparticles. *Phy. Rev. B.* **78**, 085112 (2008)
9. Verre, R., Yang, Z. J., Shegai, T. & Kall, M. Optical magnetism and plasmonic fano resonances in metal-insulator-metal oligomers. *Nano Lett.* **15**, 1952-1958 (2015)
10. Maier, S. A. & Atwater, H. A. Plasmonics: Localization and guiding of electromagnetic energy in metal/dielectric structures. *J. Appl. Phys.* **98**, 011101 (2005)
11. Collins, S. M. Excitation dependent Fano-like interference effects in plasmonic silver nanorods. *Pys. Rev. B* **90**, 155419 (2014)
12. Shafiei, F. *et al.* A subwavelength plasmonic metamolecule exhibiting magnetic-based optical Fano resonance. *Nat. Nanotechnol.* **8**, 95-99 (2013)
13. Fan, J. A. *et al.* Fano-like interference in self-assembled plasmonic quadrumer clusters. *Nano Lett.* **10**, 4680-4685 (2010)
14. Hutter, E. & Fendler, J. H. Exploitation of localized surface plasmon resonance. *Adv. Mater.* **16**, 1685-1706 (2004)
15. Maier, S. A. *et al.* Local detection of electromagnetic energy transport below the diffraction limit in metal nanoparticle plasmon waveguides. *Nat. Mater.* **2**, 229-232 (2003)
16. Aćimović, S. S. *et al.* Plasmon near-field coupling in metal dimers as a step toward single-molecule sensing. *ACS Nano* **3**, 1231-1237 (2009).

17. King, N. S. *et al.* Fano resonant aluminum nanoclusters for plasmonic colorimetric sensing. *ACS Nano* **9**, 10628-10636 (2015)
18. Ferry, V. E., Munday, J. N. & Atwater, H. A. Design considerations for plasmonic photovoltaics. *Adv. Mater.* **22**, 4794-4808 (2010)
19. Willets, K. A. & Duyne, R. P. V. Localized surface plasmon resonance spectroscopy and sensing. *Annu. Rev. Phys. Chem.* **58**, 267-297 (2007)
20. Xie, W. *et al.* Synthesis of bifunctional Au/Pt/Au core/shell nanoraspberries for in situ SERS monitoring of platinum-catalyzed reactions. *J. Am. Chem. Soc.* **133**, 19302-19305 (2011)
21. Wustholz, K. L. *et al.* Structure-activity relationships in gold nanoparticle dimers and trimers for surface-enhanced raman spectroscopy. *J. Am. Chem. Soc.* **132**, 10903-10910 (2010)
22. Orendorff, C. J., Gole, A., Sau, T. K. & Murphy, C. J. Surface-enhanced raman spectroscopy of self-assembled monolayers: Sandwich architecture and nanoparticle shape dependence. *Anal. Chem.* **77**, 3261-3266 (2005)
23. Kauranen, M. & Zayats, A. V. Nonlinear plasmonics. *Nat. Photon.* **6**, 737-748 (2012)
24. Michaeli, L. *et al.* Nonlinear surface lattice resonance in plasmonic nanoparticle arrays. *Phys. Rev. Lett.* **118**, 243904 (2017)
25. Zhou, L. *et al.* Self-assembly of highly efficient, broadband plasmonic absorbers for solar steam generation. *Sci. Adv.* **2**, e1501227 (2016)
26. Stampelcoskie, K. G. & Kamat, P. 3D self-assembly of aluminium nanoparticles for plasmon-enhanced solar desalination. *Nat. Photon.* **10**, 393-398 (2016)
27. Horák, M. *et al.* Comparative study of plasmonic antennas fabricated by electron beam and focused ion beam lithography. *Sci. Rep.* **8**, 9640 (2018)
28. Chen, Y. *et al.* Rapid focused ion beam milling based fabrication of plasmonic nanoparticles and assemblies via “sketch and peel” strategy. *ACS Nano* **10**, 11228-11236 (2016)
29. Kuzyk, A. *et al.* DNA-based self-assembly of chiral plasmonic nanostructures with tailored optical response. *Nature* **483**, 311-314 (2012)
30. Hsu, S. -W. *et al.* Colloidal plasmonic nanocomposites: From fabrication to optical function. *Chem. Rev.* **118**, 3100-3120 (2018)
31. Hanske, C. *et al.* Strongly coupled plasmonic modes on macroscopic areas via template-assisted colloidal self-assembly. *Nano Lett.* **14**, 6863-6871 (2014)
32. Chen, M. *et al.* 3D nanoprinting of perovskites. *Adv. Mater.* **31**, 1904073 (2019)
33. Chen, M. *et al.* Meniscus-on-demand parallel 3D nanoprinting. *ACS Nano* **12**, 4172-4177 (2018)
34. Yang, M. *et al.* Orientation-and polarization-dependent optical properties of the single Ag nanowire/glass substrate system excited by the evanescent wave. *Sci. Rep.* **6**, 25633 (2016)
35. Ureña, E. B. *et al.* Excitation enhancement of a quantum dot coupled to a plasmonic antenna. *Adv. Opt. Mater.* **24**, OP314-OP320 (2012)

36. Curto, A. G. *et al.* Unidirectional emission of a quantum dot coupled to a nanoantenna. *Science* **329**, 930-933 (2010)
37. Busson, M. P. *et al.* Accelerated single photon emission from dye molecule-driven nanoantennas assembled on DNA. *Nat. Commun.* **3**, 962 (2012)
38. Oh, J. -W. *et al.* Biomimetic virus-based colourimetric sensors. *Nat. Commun.* **5**, 3043 (2014)
39. Devaraj, V. *et al.* Modifying plasmonic-field enhancement and resonance characteristics of spherical nanoparticles on metallic film: effect of faceting spherical nanoparticle morphology. *Coatings* **9**, 387 (2019)
40. Johnson, P. B. & Christy R. W. Optical constants of the noble metals. *Phy. Rev. B* **6**, 4370-4379 (1972)
41. Sehmi, H. S., Langbein, W. & Muljarov, E. A. Optimizing the Drude-Lorentz model for material permittivity: Method, program, and examples for gold, silver, and copper. *Phy. Rev. B* **95**, 115444 (2017)

Figures

Figure 1

3D printing of HPCs. a, Schematic illustrating the 3D printing process to prepare freestanding HPCs based on omnidirectional guiding of a fL AuNP ink meniscus using a micropipette. b, Schematic illustrating 3D printing of a heterogeneous HPC by mixing functional NPs with AuNPs in the ink. c, Series of optical micrographs showing the 3D printing process consisting of (i) micropipette approach, (ii) meniscus formation, (iii, iv) 3D assembly with meniscus guiding and (v) termination (the lower half of the

image shows a reflection of the pipette in the substrate). d, Schematic illustrating the hierarchy of a 3D-printed HPC at multiple scales, and e, corresponding FE-SEM (left, middle) and TEM (right) images.

Figure 2

Plasmonic characterization. a, FE-SEM image of a freestanding HPC pillar and (inset) its cross-sectional FIB image showing the internal AuNP distribution. b, Dark-field scattering spectra obtained at different positions along the HPC pillars. The spectra are consistent from the (i) bottom of the HPC to the (v) top of

the HPC. c, Schematic illustrating NP clusters having different particle numbers (N), which are used in the simplified simulation model. d, Calculated dark-field scattering spectra for NP clusters with $N = 2, 3, 5$ and 25 (grey), measured dark-field scattering spectrum for an HPC (red), and calculated absorbance spectrum for the $N = 25$ NP cluster (blue). (e-h) Freeform fabrication of HPCs. FE-SEM images of e, 2-fold, f, 3-fold and g, 4-fold (h, top-view) freestanding HPC pillars fabricated by the omnidirectional meniscus-guiding self-assembly process. (i, j) Schematics illustrating directional far-field radiation in i, a 2-fold HPC with a folding angle of 90° and j, a straight HPC pillar. The scattering signals were collected by an objective lens under side light illumination along one direction. k, Directional dependence of the scattering signals collected from the 2-fold HPC pillar (blue) and the straight HPC pillar (red) during sample rotation.

Figure 3

Heterogeneous HPCs. (a-c) Nanogap control. a, Schematic illustrating control of the interparticle spacing between AuNPs in an HPC by addition of a secondary spacer particle, SiO₂ NPs. b, Dark-field scattering spectra for HPCs with ratios of SiO₂ NPs to AuNPs ranging from NSiO₂/NAu = 0 (red) to NSiO₂/NAu = 0.005 (green) and NSiO₂/NAu = 0.01 (blue). c, Calculated dark-field scattering spectra for HPCs with interparticle gaps ranging from 32 nm (red) to 52 nm (green) and 72 nm (blue). (d-h) Fluorescence enhancement and far-field radiation. d, Schematic illustrating the fabrication of a QD-embedded HPC. e, TRPL spectra for QDs embedded in an HPC (red) and QDs on glass. f, PL intensities for freestanding (red) and collapsed (blue) QD-embedded HPCs, collected by an objective lens located above the samples. g, Schematic illustrating the simulation model used to predict far-field QD enhancement. h, Comparison of the simulated radiation patterns for a QD embedded HPC and a QD anchored to a dielectric medium.

Figure 4

Plasmonic microplatform for virus detection. a, Schematic illustrating the direct fabrication of an M13 bacteriophage-embedded HPC pillar for SERS sensing. b, The WT phage and three of its mutations (4E, 3H and 3Q) were successfully added into HPC pillars during the meniscus-guided 3D printing process. c, Dark-field scattering top-view images of HPC pillar arrays containing different types of M13 bacteriophages. d, Raman spectra for embedded HPC pillars having WT phage concentrations ranging

from 0 to 300 pM. The Raman spectra for 300 pM WT phage suspended in solution is given in grey. (e-h) Characteristic SERS spectra for e, WT, f, 4E, g, 3H and h, 3Q phages embedded within HPC pillars. Spectra denoted i-v are taken from different sampling locations in the HPC. Fingerprint patterns obtained by differential intensity from the SERS spectra (e-h) of i, WT, j, 4E, k, 3H, and l, 3Q phages.

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