Supplemental Information for

Interfacial Engineering of Plasmonic Nanoparticle Metasurfaces

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METHODS

Fabrication of Cu nanoparticle (NP) lattices. Cu NP lattices on quartz were fabricated with a soft nanofabrication process known as PEEL (a combination of phase-shifting photolithography, etching, electron-beam deposition, and lift-off of the film). (1, 2) Briefly, periodic photoresist (PR) posts on Si wafers were generated by SANE (solvent-assisted nanoscale embossing) with controlled post sizes and periodicities. The patterns of PR lattices were then transferred into free-standing Au nanohole films after PR residue removal, Cr deposition, removal of PR posts, etching through the Si nanoholes, Cr etching, lift-off, and transfer of Au film to quartz substrates. A 3-nm Cr layer was deposited before Cu deposition for high adhesion between Cu NP and quartz. Finally, we deposited Cu with 130 nm thickness through the hole-array mask to create Cu NP lattices on quartz and then removed the mask by Scotch tape peeling.

Chemical vapor deposition for graphene encapsulated Cu (Cu@G) NP lattices. As-fabricated Cu NP lattices on quartz were placed inside the standard 1-inch quartz tube of the home-build low-pressure chemical vapor deposition (LP-CVD) MTI system. The reaction chamber was evacuated to ~ 1.5 mTorr and flushed with 100 sccm of H\(_2\) (99.9999% purity, Praxair) at a total pressure of 1.5 Torr for 10 minutes. The temperature was then increased to 900 °C with 100 sccm H\(_2\) in 25 min followed by annealing of Cu NP lattices at 900 °C for 1 min in 100 sccm H\(_2\). Subsequently, 75 sccm of CH\(_4\) (99.999% purity, Praxair) at a partial pressure of 1 Torr with 25 sccm H\(_2\) was introduced into the tube for 5 min. With both gases supplied at same flow rates, the reaction chamber was cooled down to room temperature in about 45 min (~ 20 °C/min).

Annealing treatment for Cu NP lattices. The annealing process was performed in an MTI tube furnace system. As-fabricated Cu NP lattices on quartz were placed on a 1-inch quartz tube. The heating chamber was flushed with H\(_2\) (99.9999% purity, Praxair) at a total pressure of 1.5 Torr for
5 min. The temperature was then increased to 900 °C in 25 min, followed by annealing of Cu NP lattices at 900 °C for 5 min at the pressure of 1 Torr. Subsequently, the heating chamber was cooled down to room temperature over 45 min (~ 20 °C/min).

**Fluoropolymer layer coating on Cu NP lattices.** Annealed Cu NP lattices were treated with CHF$_3$ plasma in a reactive ion etching (RIE) system (Samco RIE-10NR) for a targeted time at a flow rate of 25 sccm under 20 Pa at a power of 70 W. The CF$_x$ layer formed on the surface at a rate of ~0.5 nm/s. Therefore, CF$_x$ layers are about 3 nm with a coating time of 6 s, 10 nm with a coating time of 20 s, and 25 nm with a coating time of 50 s, respectively.

**Alumina layer coating on Cu NP lattices.** Annealed Cu NP lattices were placed in an atomic layer deposition (ALD) system (Arradiance GEMStar XT-P) for the growth of alumina layers. The alumina layer formed on the surface at a rate of 0.12 Å cycle. The thicknesses of the grown alumina coating layer were set to be 3 nm, 10 nm, and 25 nm.

**Lasing measurements.** The NP lattice/IR-140 DMSO dye solution lasing devices were pumped at room temperature with a mode-locked Ti:sapphire laser with a regenerative amplifier (TE-polarized, 800-nm wavelength, 1 kHz operation rate, and 90 fs pulse width). The pump spot was 1 mm in diameter. The incident angle of the pump laser was 45° to the lattice plane; the lasing emission was collected at the direction normal to the lattice plane and analyzed by a charge-coupled device (CCD) spectrometer with a spectral resolution of 0.3 nm (Ocean Insight). For lasing measurements with DCM dye, the pump laser goes through a BBO crystal to convert 800 nm to 400 nm light.

Three to five samples were prepared for each NP lattice compared (Cu@G, annealed bare Cu, and different thickness of dielectric-coated annealed Cu). Samples showed high uniformity over different areas because the NPs are uniform in size and shape after CVD or annealing treatments.
A single lasing measurement ranges from a few seconds with 0.1 mM dye solutions to tens of seconds with 0.4 mM dye solutions. The lasing emission can be restored by refreshing the devices with new dye solutions or moving the pump spot to a different area on the NP lattice.

**Finite-difference time-domain (FDTD) simulations.** Commercial software (FDTD solution, Lumerical Inc., Vancouver, Canada) was used to simulate the optical properties of Cu NP lattices and lasing action. The optical constants of Cu were taken from Palik measurements (400 – 1000 nm). (3) The core-shell configuration was simulated by setting different orders of the Cu, graphene (or CFₓ or AlₓOᵧ) layer, and the dye solutions. Refractive indices of quartz substrates and DMSO are 1.45 (400 – 1000 nm). For the graphene, we used the refractive index in the out-of-plane direction (nₓ and kₓ) in the simulations (4) since the surface plasmon resonance fields are excited perpendicular to the Cu/graphene interface (out of plane). The thickness of the graphene was set to be 3 nm. A uniform mesh size of 2 nm (x, y, and z) was used to ensure the accuracy of electric and magnetic field calculations within the metal NPs. For the simulation with the surface-dye layer model, the thickness of the layer was set at 2 nm, and dye concentration was 2.5 times the bulk concentration. The CFₓ layer was simulated with a refractive index of 1.379 from 400 to 1000 nm based on ellipsometry measurement in a previous study. (5) The optical constants of AlₓOᵧ from 1.787 to 1.756 in the wavelength range 400 to 1000 nm were from Palik measurements in the Lumerical database. (3)

Lasing was simulated with a four-level, one-electron model in FDTD. Notably, this model can be used to investigate the trends in the lasing response from parameters such as dye concentration and pump power but not quantitative values. The calculated thresholds tend to be lower than the experimental thresholds because non-radiative losses are not considered. In the model, the dye concentration is defined by a number density (N) which represents the electron population density.
(unit is number/meter$^3$). Thus, dye solution concentration ($C$) with the unit of mM was set as $N = C \times N_A$ ($N_A = 6.022 \times 10^{23}$ mol$^{-1}$) in the four-level one-electron model. $C$ was varied by changing the $N$ in the model. The electric field amplitude of the incident laser was used to define the pump power intensity in FDTD simulations and can be converted to light intensity with units of $\mu$J/cm$^2$ through the equation (SI unit) $I = 6n\epsilon_0 E_0^2 c t_w$, where the $n$ is the refractive index, $\epsilon_0$ is the permittivity of free space, $E_0$ is the electric field amplitude, $c$ is the speed of light, and $t_w$ is the temporal bandwidth.

**Density function theory (DFT) simulations.** The geometries of the molecule/graphene structures and the electronic couplings were calculated using the Amsterdam Density Functional (ADF) software(6) with density functional theory and with the long-range dispersion correction approach by Grimme (DFT-D3)(7). The double $\zeta$ polarization functions (DZP) basis set and the BP86 exchange-correlation functional(8, 9) were chosen. The conductor like screening model (COSMO)(10-12) was applied to simulate the dielectric response of DMSO as the solvent. A dielectric constant of 46.7 and a solvent cavity radius of 3.04 were used. The electron couplings were calculated from the integral matrix elements. Fock and overlap integral matrix elements were calculated using the TRANSFERINTEGRALS key with the fragment orbital approach as implemented in ADF.(13-15) The effective electronic coupling between orbitals $i$ and $f$, $V_{if}$, was calculated using the following equation:

$$V_{if} = \frac{J_{if} - S_{if}(e_i + e_f)}{1 - S_{if}^2}$$

where $J_{if}$ is the Fock matrix element between a pair of monomers, $S_{if}$ is the overlap integral, $e_i$ and $e_f$ are the Fock matrix elements within a monomer. The adsorption energies were defined as the energy released during the adsorption process as follows:
Surface + Adsorbate $\rightarrow$ Complex \hspace{2cm} $\Delta E = -\Delta E_{ads}$
Figure S1. SEM images of NP lattices ($a_0 = 600$ nm). SEM characterization of (A) as-fabricated Cu NP lattices, (B) annealed Cu NP lattices, and (C) Cu@G NP lattices. Diameters of as-fabricated, annealed, and graphene coated Cu NP are about 160 nm, 125 nm, and 120 nm, respectively.
Height characterization of as-fabricated Cu NPs in lattices

Figure S2. Atomic force microscopy (AFM) characterization of as-fabricated Cu NP lattices. (A-B) Two-dimensional height images of as-fabricated Cu NP lattices. (C) Three-dimensional height image of as-fabricated Cu NP lattices.
Height characterization of the Cu@G NPs in lattices

Figure S3. AFM characterization of Cu@G NP lattices. (A) Two-dimensional height images of Cu@G NPs lattices. (B) Three-dimensional height image of Cu@G NPs lattices. (C) Side view of a single Cu@G NP in lattices.
Diameter optimization of lattices with $a_0 = 600$ nm

Figure S4. Transmission spectra for Cu and Cu@G NP lattices in FDTD simulations ($a_0 = 600$ nm). Diameter sweep of (A) Cu and (B) Cu@G NP lattices from 100 to 130 nm. The thickness of the graphene is 3 nm. D is the diameter of Cu NPs in both lattices, and NP lattices with D = 110 and D = 120 nm can support narrow and strong SLRs.
Far-field beam profile of lasing emission above threshold

Figure S5. Far-field pattern of lasing emission with IR-140 as gain media and Cu@G NP lattices. Dye concentration was 0.4 mM IR-140 in DMSO, and pump power was ca. 120 μJ/cm². The TE-polarized pump light was parallel to the one of axes of the square NP lattices, and the off-normal amplified spontaneous emission along this axis direction resulted in the slightly elongated far-field pattern.
Lasing from Cu NP lattices with 0.4 mM IR-140 solutions

Figure S6. Waterfall plot of lasing spectra vs. pump intensity for annealed Cu NP lattices. The gain medium was 0.4 mM IR-140 in DMSO.
Lasing from Cu@G and Cu NP lattices with 0.2 mM IR-140 solutions

Figure S7. Waterfall plot of lasing spectra vs. pump intensity with 0.2 mM IR-140 in DMSO. Lasing from (A) Cu@G NP lattices and (B) annealed Cu NP lattices.
Lasing from Cu@G and Cu NP lattices with 0.15 mM IR-140 solutions

Figure S8. Waterfall plot of spectra vs. pump intensity with 0.15 mM IR-140 in DMSO. Lasing spectra from (A) Cu@G NP lattices and (B) annealed Cu NP lattices.
Lasing from Cu@G and Cu NP lattices with 0.1 mM IR-140 solutions

Figure S9. Waterfall plot of lasing spectra vs. pump intensity with 0.1 mM IR-140 in DMSO. Lasing spectra from (A) Cu@G NP lattices and (B) annealed Cu NP lattices.
Rising slopes of light-light curves for lasing with IR-140 as gain media

**Figure S10. Rising slopes of lasing light-light curves with IR-140 solutions.** The Cu@G NP lattices support higher rising slopes than the Cu NP lattices at high concentrations (0.2 and 0.4 mM). The Cu@G NP lattices can support lasing at low concentrations (0.1 and 0.15 mM), but the Cu NP lattices cannot.
Simulated near fields of NP lattices with $a_0 = 600$ nm

Figure S11. Electromagnetic near-field enhancement around a single Cu and Cu@G NP in lattices. Side view (left) and top view (right) of the simulated near-field enhancement $|E|^2$ a single NP in (A) Cu NP lattices and (B) Cu@G NP lattices.
Diameter optimization of lattices with $a_0 = 450$ nm

Figure S12. Simulated transmission spectra for Cu and Cu@G NP lattices in FDTD simulations ($a_0 = 450$ nm). Diameter sweep of (A) Cu NP and (B) Cu@G NP lattices from 80 to 110 nm. The thickness of the graphene is 3 nm. D is the diameter of Cu NP in both lattices.
SEM images of NP lattices with \( a_0 = 450 \) nm

**Figure S13.** SEM images of NP lattices \( (a_0 = 450 \text{ nm}) \). (A) As-fabricated Cu NP, (B) annealed Cu NP lattices, and (C) Cu@G NP lattices. Diameters of as-fabricated, annealed, and graphene coated Cu NP are about 120 nm, 90 nm, and 80 nm, respectively.
Experimental transmission spectra of NP lattices with $a_0 = 450$ nm

Figure S14. Experimental transmission spectra of treated Cu NP lattices. Transmission spectra of Cu@G NP lattices and annealed Cu NP lattice with periodicity $a_0 = 450$ nm.
Lasing of Cu@G and Cu NP lattices at 5 mM DCM solutions

Figure S15. Waterfall plot of lasing spectra vs. pump intensity with 5-mM DCM in DMSO as gain media. Lasing from (A) Cu@G and (B) annealed Cu NP lattices.
Rising slopes of light-light curves for Cu@G and Cu NP lattices with DCM solutions

Figure S16. Rising slopes of lasing light-light curves with DCM as gain media. Cu@G NP lattices support higher rising slopes than the Cu NP lattices at high concentrations (4 and 5 mM). Cu@G NP lattices can support lasing at lower concentration (3 mM). No lasing was observed for either Cu@G or Cu NP lattices at concentration of 2 mM.
Simulated molecules on Cu and Cu@G surfaces

Figure S17. Simulated molecules on graphene coated Cu. DFT simulation of a dye molecule on (A) bare Cu, (B) Cu@ monolayer graphene, (C) Cu@ multilayer graphene, and (D) Cu@ multilayer doped graphene. The dye molecule is modelled by benzene, graphene sheet is simplified by a graphene quantum dot with 20 C atoms, and Cu blocks contain 20 atoms. The adhesion energies between molecule and surface in a, b, and c are 22.07, 23.27, and 22.41 kcal/mol, respectively. The hole and electron transfer couplings in (A) are 0.204 and 0.003 eV. The hole and electron transfer couplings in (B) are 0.052 and 0.041 eV. The hole and electron transfer couplings in (C) are 0.006 and 0.009 eV. The hole and electron transfer couplings in (D) are 0.097 and 0.005 eV.
Simulated trans- and cis- IR-140 molecule on graphene

Figure S18. Simulated trans- and cis- IR-140 molecule on graphene. 3D structure of (A) free trans- and (B) free cis- IR-140 molecules. Top and side view of (C) trans- and (D) cis- IR-140 molecules on graphene. The molecule aligns parallel to graphene with an offset stacking.
Simulated dye molecules on graphene

Figure S19. Simulation of spatial alignment of different dye molecules on graphene. Top view and side view of (A) Pyrromethene 650, (B) Oxazine 750, and (C) LD 700 on graphene. The calculated adhesion energies of Pyrromethene 650, Oxazine 750, and LD 700 on graphene are 83, 113, and 104 kcal/mol, respectively.
Simulated adhesion energies of dye molecules on graphene

![Graph showing simulated adhesion energies of dye molecules on graphene. The x axis indicates the number of aromatic rings that aligns parallel to the graphene plane in the corresponding molecules.]

**Figure S20. Simulated adhesion energies of dye molecules on graphene.** The x axis indicates the number of aromatic rings that aligns parallel to the graphene plane in the corresponding molecules.
Simulated lasing from Cu@G and Cu NP lattices

Figure S21. Simulated lasing with a surface dye layer around Cu@G NPs in lattices. (A) Waterfall plot of lasing spectra vs. pump at concentration of 0.4 mM IR-140 in Cu@G NP lattices. (B) Light-light curves of lasing from Cu NP lattices at different dye concentrations without a surface dye layer. The legends indicate the concentrations in the bulk dye solutions.
Energy diagram of molecules near different surfaces

Figure S22. Energy diagram of molecules near different surfaces. (A) Photoluminescence (PL) quenching when dye molecules are close to NP surface. (B) PL quenching of dye molecules on intrinsic graphene. (C) SLRs inject electron into graphene, and the doped graphene suppress quenching in Cu@G NP lattices. Solid arrow indicates the direction of an electron transition process, and the dashed arrow depicts an energy transfer process. Arrow with cross stands for a quenched or blocked process.
XPS spectra of Cu surface coated with dielectric layers

Figure S23. Surface chemistry characterization of coated Cu surface. XPS survey scans spectra of (A) Cu@CF$_x$ and (B) Cu@Al$_x$O$_y$ surfaces. XPS Cu 2p scans spectra of (C) Cu@CF$_x$ and (D) Cu@Al$_x$O$_y$ surfaces. No satellite peaks or peaks shifts of Cu 2p peaks from CuO$_x$ were observed, which indicated both dielectric-coated lattices were not oxidized.
Lasing from CF\textsubscript{x} and Al\textsubscript{x}O\textsubscript{y} coated Cu NP lattices (3 nm of dielectric)

Figure S24. Waterfall plots of lasing spectra vs. pump intensity from Cu NP lattices with 3 nm of dielectrics. Lasing from (A) Cu@CF\textsubscript{x} and (B) Cu@Al\textsubscript{x}O\textsubscript{y} NP lattices. The gain was 0.4 mM IR-140 in DMSO.
Lasing light-light curves of CF$_x$ and Al$_x$O$_y$ coated Cu NP lattices (3 nm of dielectric)

Figure S25. Lasing light-light curves from Cu NP lattices with different surface layers (3 nm). Input-output light-light curves of Cu@CF$_x$ NP lattices in (A) linear and (B) log-log scales. Input-output light-light curves of Cu@Al$_x$O$_y$ NP lattices in (C) linear and (D) log-log scales.
Simulated transmission spectra of Cu NP lattices with dielectric coatings

Figure S26. Simulated transmission spectra with different thickness of CF$_x$ and Al$_x$O$_y$ layers. Thickness sweeps of coating layers in (A) Cu@CF$_x$ and (B) Cu@Al$_x$O$_y$ NP lattices with periodicity $a_0 = 600$ nm.
Lasing from CF$_x$ and Al$_x$O$_y$ coated Cu NP lattices (10 nm of dielectric)

Figure S27. Waterfall plot of lasing spectra vs. pump intensity from Cu NP lattices with 10 nm of dielectrics. Lasing from (A) Cu@CF$_x$ and (B) Cu@Al$_x$O$_y$ NP lattices. The gain was 0.4 mM IR-140 in DMSO.
Lasing light-light curves of CF<sub>x</sub> and Al<sub>x</sub>O<sub>y</sub> coated Cu NP lattices (10 nm of dielectrics)

Figure S28. Lasing light-light curves from Cu NP lattices with different surface layers (10 nm). Input-output light-light curves of Cu@CF<sub>x</sub> NP lattices in (A) linear and (B) log-log scales. Input-output light-light curves of Cu@Al<sub>x</sub>O<sub>y</sub> NP lattices in (C) linear and (D) log-log scales.
Lasing from CF\textsubscript{x} and Al\textsubscript{x}O\textsubscript{y} coated Cu NP lattices (25 nm of dielectric)

Figure S29. Waterfall plot of lasing spectra vs. pump intensity from Cu NP lattices with 25 nm of dielectrics. Lasing from (A) Cu@CF\textsubscript{x} and (B) Cu@Al\textsubscript{x}O\textsubscript{y} NP lattices. The gain was 0.4 mM IR-140 in DMSO.
Lasing light-light curves of CF\(_x\) and Al\(_x\)O\(_y\) coated Cu NP lattices (25 nm of dielectrics)

**Figure S30.** Lasing light-light curves from Cu NP lattices with different surface coating (25 nm). Input-output light-light curves of Cu@CF\(_x\) NP lattices in (A) linear and (B) log-log scales. Input-output light-light curves of Cu@Al\(_x\)O\(_y\) NP lattices in (C) linear and (D) log-log scales.
Simulated lasing from CF$_x$ and Al$_x$O$_y$ coated Cu NP lattices (3 nm of dielectric)

**Figure 31.** Simulated lasing with 3 nm of CF$_x$ or Al$_x$O$_y$ on Cu NPs lattices. (A) Waterfall plot of lasing spectra vs. pump at concentration of 1mM from Cu@CF$_x$ NP lattices. (B) Waterfall plot of lasing spectra vs. pump at concentration of 1mM from Cu@Al$_x$O$_y$ NP lattices. The right panels are the zoom-in spectra near the threshold in the corresponding left panels.
Simulated light-light curves of NP lattices with dielectric coatings

Figure S32. Simulated lasing of NP lattices with different thickness of CF_x and Al_{x}O_{y} coating layers. Simulated lasing input-output light-light curves of Cu NP lattices coated with (A) CF_x layers and (B) Al_{x}O_{y} layers with different thicknesses.
Simulated light-light curves from NP lattices with thick CF$_x$ layers

**Figure S33.** Simulated lasing light-light curves from Cu NP lattices with thick CF$_x$ coatings. Lasing input-output light-light curves of Cu@CF$_x$ NP lattices in (A) linear and (B) log-log scale with different thicknesses of CF$_x$ layers.
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