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Enhanced photocatalysis and biomolecular sensing with field-activated nanotube-nanoparticle templates

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The development of new catalysts for oxidation reactions is of central importance for many industrial processes. Plasmonic catalysis involves photoexcitation of templates/chips to drive and enhance oxidation of target molecules. Raman-based sensing of target molecules can also be enhanced by these templates. This provides motivation for the rational design, characterization, and experimental demonstration of effective template nanostructures. In this paper, we report on a template comprising silver nanoparticles on aligned peptide nanotubes, contacted with a microfabricated chip in a dry environment. Efficient plasmonic catalysis for oxidation of molecules such as p-aminothiophenol results from facile trans-template charge transfer, activated and controlled by application of an electric field. Raman detection of biomolecules such as glucose and nucleobases are also dramatically enhanced by the template. A reduced quantum mechanical model is formulated, comprising a minimum description of key components. Calculated nanotube-metal-molecule charge transfer is used to understand the catalytic mechanism and shows this system is well-optimized.

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Many industrial processes require efficient catalysis of redox reactions^{1–4}. A seemingly different problem is the sensing of biomolecules, which can pose its own challenges^{4–6}. In fact, these scientific problems are related—both catalytic activity and sensing can be dramatically enhanced by the use of nanostructured templates/chips. In the field of plasmon catalysis, a major goal of current research is to design such templates to facilitate charge transfer to target molecules, thereby enhancing plasmonic photocatalytic activity^{1–4} and enhancing the Raman signal intensity of otherwise spectroscopically dark molecules^{4–6}.

Nanomaterials that exhibit elevated catalytic performance play a significant role in high value industrial processes such as the reduction of carbon dioxide or nitroaromatics^{1–4}. Catalytic processes augmented by plasmon active nanomaterials for example gold (Au) or silver (Ag) offer significant potential to enhance heterogeneous catalytic processes^{4–6}. The catalytic enhancement associated with metal nanoparticles (NPs) results from optical excitation of localized surface plasmon resonances (LSPRs) that act as the energy input to drive chemical transformations in redox reactions, and may also be facilitated by the intense local electric field and local heat generated^{1–4}. The specific mechanisms of LSPR-mediated photocatalytic processes are not fully understood, but are investigated in detail in this paper. It is widely believed that hot electron processes play a significant role in the transfer of chemical, photon, and electrical energies during plasmon-mediated catalysis^{2–4}. The correlation between hot electron flow and the rates of photocatalytic reactions has been reported in several studies revealing that hot electrons strongly influence heterogeneous photocatalysis^{2–6}. Through setting the wavelength of incident radiation to match the HOMO–LUMO gap of attached molecules, charge transfer to the molecule can occur, giving rise to oxidation reactions in certain molecules or enhanced Raman scattering cross section for sensing in other molecules.

Nanocomposites combining semiconductor materials with metal NPs bring additional benefits to plasmonic photocatalysis^{6–9}. The contact potential difference between metal NPs and a semiconductor can separate photogenerated electrons and holes^{6–9}, thereby reducing electron-hole pair diffusion lengths and leading to more efficient photogenerated charge separation and transfer, which in turn enhances photocatalytic activity^{2–5}.

Here, we show an increase in probability and efficiency of both chemical reactions and SERS detection through electro-optical synergy, using a microfabricated chip design (in air rather than electrochemical)^{2–4}. This is achieved through the use of a plasmonic-semiconductor system based on aligned diphenylalanine peptide nanotube (FF-PNTs) wide band gap semiconductors^{10–15}. Diphenylalanine (FF), a peptide consisting of a naturally occurring amino acid phenylalanine, can self-assemble into micro and nanosized tubular structures^{10–17}. The resulting organic self-assembled nanotubes are the FF-PNTs, which are stable/robust, rigid, and also biocompatible. They can be used in applications requiring the use of a wide bandgap semiconductor^{10–17}. FF-PNTs have been reported to have high thermal and chemical stability^{10–15} in addition to piezoelectric^{16,17} and pyroelectric¹⁵ properties. We show experimentally and theoretically that applying a longitudinal electric field allows the FF-PNT density of states to be tuned from a semiconductor to a metal, enabling effective charge transfer from the nanotube to the metal nanoparticles. This results in an enhancement in the state density of hot electrons^{18–20}. The effect is optimized through the physical alignment of the FF-PNTs, since the inherent electric dipoles of the FF-PNTs are then aligned and maximally responsive to the applied longitudinal electric field (a cooperative effect). We demonstrate that this optoelectrical device enhances photocatalytic conversion for model oxidation reactions

(exemplified here by p-aminothiophenol (PATP) oxidized to p-nitrothiophenol (PNTP), and 2-aminophenol (2-AMP) oxidized to 2-nitrophenol (2-NIP)), exploiting the facile field-activated trans-template charge transfer. We also demonstrate that this same approach can be used to enhance the strength of Raman scattering from molecules with small Raman cross-sections for example glucose and DNA-based molecules, establishing the potential of our template design for sensitive detection and analytics. This approach is versatile and can be applied to a range of plasmonic metal nanoparticle and semiconductor combinations.

Results

Photocatalysis studies. The template comprises microfabricated gold electrodes on an Si substrate, with a 0.1 mm opening size between electrodes. FF-PNTs are aligned during self-assembly on an optically-thick insulating layer of SiO₂ 1 mm wide, exploiting Si/SiO₂ wettability differences^{21,22}, and Ag NPs deposited (Fig. 1a, Supplementary Fig. 1). Experiments are undertaken in a dry environment (not electrochemical). Scanning electron microscopy (SEM) images (Fig. 1b–d and Supplementary Fig. 2) show the alignment of the FF-PNT and the topology/morphology of deposited Ag NPs, which aggregate around the FF-PNTs due to functional-group interactions^{21,22}. An external electric field is produced by applying a voltage across the electrodes. The current measured through the FF-PNT/Ag NPs template due to the applied voltage reveals Ohmic behavior (Supplementary Fig. 3), with a resistance ($658 \pm 0.77 \Omega$) lower than for Ag NPs ($1583 \pm 0.92 \Omega$) or for FF-PNTs ($930 \pm 1.03 \Omega$) alone, consistent with previous studies²³. These results further demonstrate the feasibility of using FF-PNTs in electronic devices, and provide a platform to explore the influence on SERS of an applied electric field.

We first investigate the impact of applying an electric field on the oxidation reaction $\text{PATP} \rightarrow \text{PNTP}$ using the FF-PNT/Ag NP template, as monitored by SERS using an excitation wavelength fixed at 532 nm. The Raman and SERS spectra for PATP (Supplementary Fig. 4) is well characterized and is known to undergo photochemical changes in the presence of plasmonic metals^{24–27}. The electric field is generated by applying a voltage across the gold nanoelectrodes (see Methods). For an offset bias of <100 mV, a seven-fold increase in SERS signal intensity was observed, but with no change in the relative positions of the SERS spectral peaks (Supplementary Fig. 5). However, with an offset bias >100 mV, the eight-fold increase in SERS signal strength was accompanied with differences in the vibrational mode

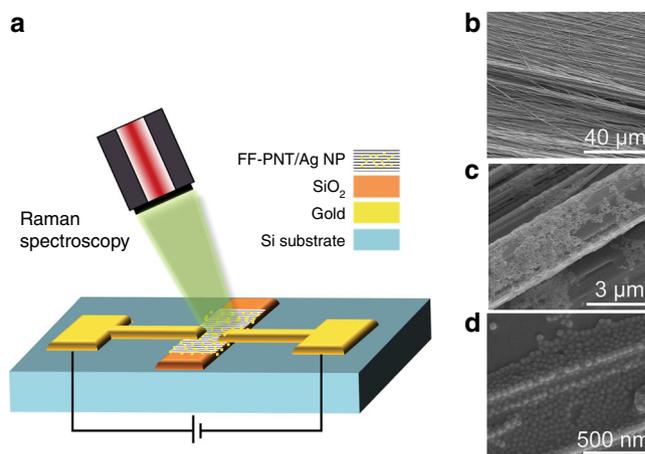


Fig. 1 Substrate fabrication and characterization. **a** Schematic sketch of the template design that is used in the study. **b–d** Scanning electron microscopy images of the aligned FF-PNT/Ag NP structures located between the gold electrodes

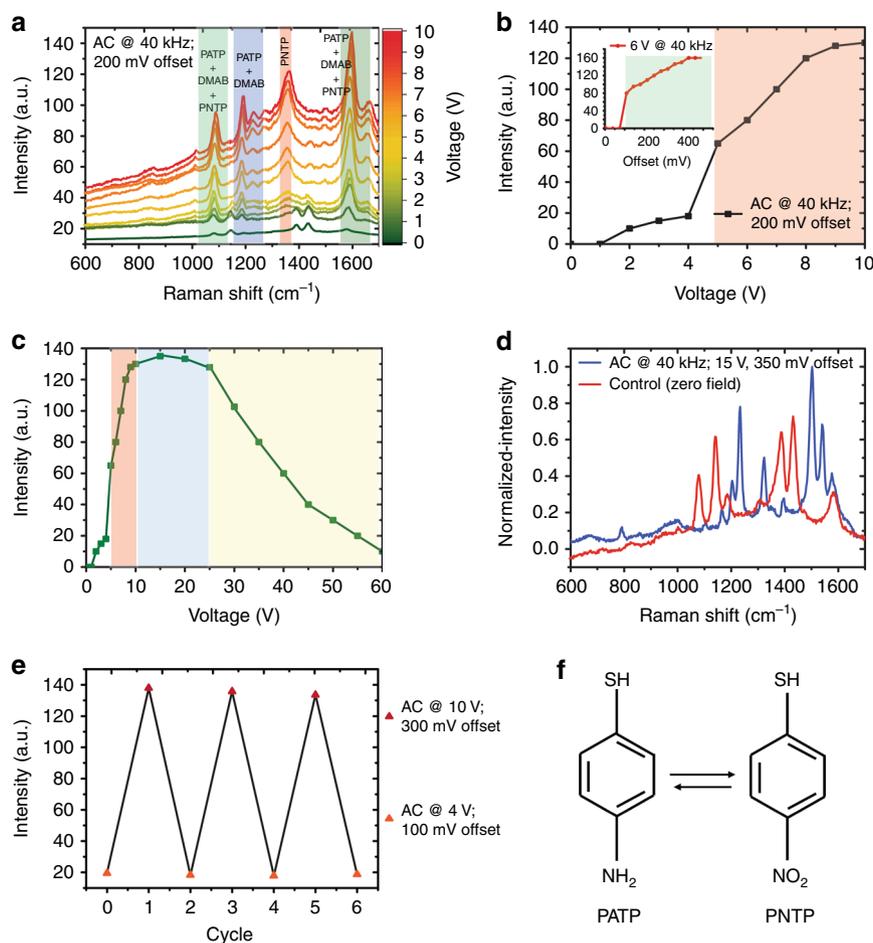


Fig. 2 Influence of applied electric field on the SERS spectra of PATP on the template. **a** SERS measurements of PATP on the FF-PNT/Ag NP template at different electric field strengths, applying voltages from 0–10 V at 40 kHz AC with offset DC bias of 200 mV. **b, c** Corresponding Raman band intensity at 1334 cm^{-1} (assigned to PNTP) as a function of voltage. **b** Critical threshold voltage $\sim 4\text{ V}$ required for the formation of PNTP. Inset illustrates SERS intensity with offset DC bias. **c** The window of 10–20 V is optimal for PNTP product yield via photocatalysis, with SERS intensity reducing above $\sim 25\text{ V}$. **d** Normalized SERS spectra, comparing a fully relaxed control sample at zero field (red) to the spectrum recorded with applied field (blue). **e** Plot of SERS signal strength intensity vs. AC electric field, showing manipulation of the product yield achieved by utilizing an electric field with a voltage of 10 V and an offset DC bias of 300 mV (conditions that yield PNTP) vs. a weaker electric field formed using a voltage of 4 V and an offset DC bias of 100 mV (conditions that yield PATP). **f** Schematic illustration of the transformation and switch of the product formation of PATP to PNTP

distribution (Fig. 2a). In particular, new vibrational modes at 1334 and 1376 cm^{-1} were assigned to symmetric NO_2 stretching vibrations of the oxidation product PNTP^{24–26}. Formation of PNTP can therefore be monitored using SERS through the intensity of the 1334 cm^{-1} Raman band. The inset to Fig. 2b shows that the oxidation reaction is abruptly switched on at a threshold offset bias around 100 mV. We also find that the yield of the oxidized product PNTP increases with an AC voltage applied in addition to the offset bias, allowing to optimize reaction conditions. Figure 2b, c show the band intensity at 1334 cm^{-1} for 200 mV offset bias as a function of AC voltage, demonstrating abrupt threshold behavior at around 4–6 V AC, while very large voltages $>25\text{ V}$ see a decrease in band intensity (and hence product yield). Optimal conditions are found to be 100–200 mV offset bias, combined with 10–25 V AC at 40 kHz (Supplementary Fig. 5–7). Comparing the SERS spectra recorded before and following application of the electric field (Fig. 2d) shows that Raman bands associated with the starting material (PATP) are entirely replaced by Raman bands associated with the product (PNTP). Switching off the electric field results in relaxation of the SERS spectrum of PNTP back to that of PATP (Supplementary Fig. 8). The transformation of PATP to/from

PNTP can in fact be finely controlled using the applied electric field, and is fully reversible. Reactant and product can be interconverted by switching on and off the field over many cycles (with no apparent degradation), Fig. 2e. We note that applying a pure AC voltage (with zero offset bias) does not result in the oxidation of PATP to PNTP (Supplementary Fig. 7), although SERS intensity of the PATP bands is enhanced.

To additionally assess the properties of the FF-PNT/Ag NP template with respect to plasmonic catalysis, we studied the impact of broadband super bandgap irradiation (λ_{ex} centered at 255 nm). Photoexciting the nanotubes directly increases the photocatalytic reaction processes, as well as the SERS signal intensity (Supplementary Fig. 9). The increase in SERS signal strength occurred with transformations in the spectral profile, which included the appearance of a vibrational mode at 1334 cm^{-1} assigned to the occurrence of PNTP^{24–26}. It is known that super bandgap excitation of a Au NPs/ TiO_2 composite enhances the plasmonic photocatalytic oxidation of PATP to PNTP through charge transfer processes, where electrons from UV excited TiO_2 transfer to the Au NPs and then to PATP^{24–27}. The UV-excited electrons from TiO_2 and the hot electrons from the Au NPs take part in the O_2 activation step to yield PNTP^{24–27}. The formation of PNTP from PATP using our

FF-PNT/Ag NP template might be expected to result from a similar mechanism, where fermi level alteration of Ag NPs occurs via charge transfer of photo-generated electrons from FF-PNTs following super band gap irradiation. This creates conditions for a photocatalyzed oxidation reaction of PATP to PNTP²⁸. We find that either an external electric field or UV irradiation treatment of the FF-PNT/Ag NP template catalyzes the oxidation reaction—and in fact that the combination of both electric field and UV irradiation further enhances product yield (Supplementary Fig. 9).

As a control study, PATP attached to Ag NPs on a simple Si substrate (in the absence of FF-PNTs) were studied. The resulting SERS spectra show no changes in the band positions with applied external electric field, although intensity fluctuations were observed (Supplementary Fig. 10). By contrast, SERS measurements on the FF-PNT/Ag NP template in the absence of the probe molecule (Supplementary Figs. 11 and 12) show a ~four-fold intensification in SERS signal intensity, together with strong spectral blinking. This indicates that charging of the FF-PNT/Ag NP complex results from applying an electric field. Previous studies suggest that an external electric field can additionally enhance the localized electric field produced by Ag NP as the electrons are disturbed from their equilibrium positions, resulting in Raman intensity fluctuations^{18–20}. Another possible reason for the appearance of fluctuations in FF-PNT spectra is that the oscillating electric field may induce synchronous FF-PNT molecular vibrations for high voltage and offset bias that can change their dipole moment^{16,17,29,30}.

Raman control studies of a probe molecules on FF-PNTs in the absence of Ag NPs show a modest increase in signal intensity (possibly indicating partial charge redistribution), but no changes in band positions, establishing the need for the LSPRs from the Ag NPs for oxidation reactions.

We also performed extensive tests to establish the high stability of the template. SEM imaging of the sample showed spherical features assigned to Ag NPs. These Ag NPs occur in clusters predominately situated above and amid the FF-PNTs (Fig. 1, Supplementary Fig. 13). We note that following the addition of the probe molecule, these structural characteristics remain unaltered. Following application of the electric field, recorded SEM images also showed no signs of changes in geometrical topologies and morphologies of the Ag NPs or FF-PNT/Ag NP template.

Optical absorption spectroscopy measurements were performed to investigate changes in Ag NP electron density on the FF-PNT template using an applied electric field (Supplementary Fig. 15). Monitoring the LSPR absorption band with increasing electric field showed a broadening and a red shift in the LSPR band ($\Delta\lambda_{\text{shift}} \sim 20$ nm). Noting that no change in the LSPR band was seen for an applied field on the Ag NPs only (Supplementary Fig. 14), this demonstrates that the FF-PNTs influence how the electric field interacts with the LSPR of the Ag NPs^{17,21,22}. The broadening in the LSPR band of the Ag NPs may result from aggregation of the NPs on the tubes (Fig. 1, Supplementary Fig. 3), while the red shift can be accounted for a buildup in Ag NP electron density during irradiation that alters the NP refractive index. The modification of the Ag NPs electron density ($\Delta N/N$) was estimated to be 9%, following an applied electric field resulting in a 20 nm red shift (where $\Delta N/N = 2\Delta\lambda/\lambda_0$, $\Delta\lambda$ being the measured wavelength modification, and λ_0 is the original Ag NPs plasmon peak location)³¹. This is equivalent to the density reported for a FF-PNT/Ag NP template under UV wavelength irradiation, which was assigned to photogenerated electrons being relocated from the FF-PNTs to the Ag NPs as they reach charge equilibration²⁸. These effects were reproducible for different metal nanoparticle sizes.

Finally, we explored the effect of NP size (Supplementary Fig. 16). Although smaller NP size is known to favor hot-electron production and hence catalytic activity, SERS sensitivity is

enhanced by larger NP size. Therefore, in the present work we use 60 nm NPs, which produce significant hot-electron yield while retaining good SERS sensitivity.

Mechanism for catalysis and SERS enhancement. The plasmonic photocatalytic pathway without an external electric field may result from the formation of hot electrons following the excitation of the Ag NPs LSPR by the Raman excitation laser. These hot electrons are reallocated to adsorbed O₂ molecules, generating triplet diradical ³O₂ formed in degenerate antibonding π_{2px} and π_{2py} orbitals, that subsequently is involved in the oxidation of PATP to DMAB (Fig. 3)^{24–27}. Studies have reported that based on the spectral similarity of PATP and DMAB, the non-a₁-type peaks can be ascribed to N–N stretching of DMAB generated from PATP via a photocatalytic coupling reaction^{24–26}. Additional electron(s) added to the π^* level (LUMO) of the PATP molecule from the Ag NPs may weaken the resonance structure, reducing the bond order. This can result in downshifts in the vibrational modes that are sensitive to this resonance structure. Specifically, these are the C=C stretching 1575 and the C–S stretching 1082 cm⁻¹ peaks for PATP, which shift to 1580 cm⁻¹ and 1077 cm⁻¹, respectively (Fig. 2a). The frequency shifts can be understood as resulting from the strong interaction between the adsorbate molecule and substrate. Similar behavior of such interaction between PATP and a substrate, as well as the downshifts in the vibrations was previously reported when using TiO₂ with metal NPs^{24–26}. The application of a sufficiently strong electric field to the FF-PNT/Ag NP template thus forms PNTP from

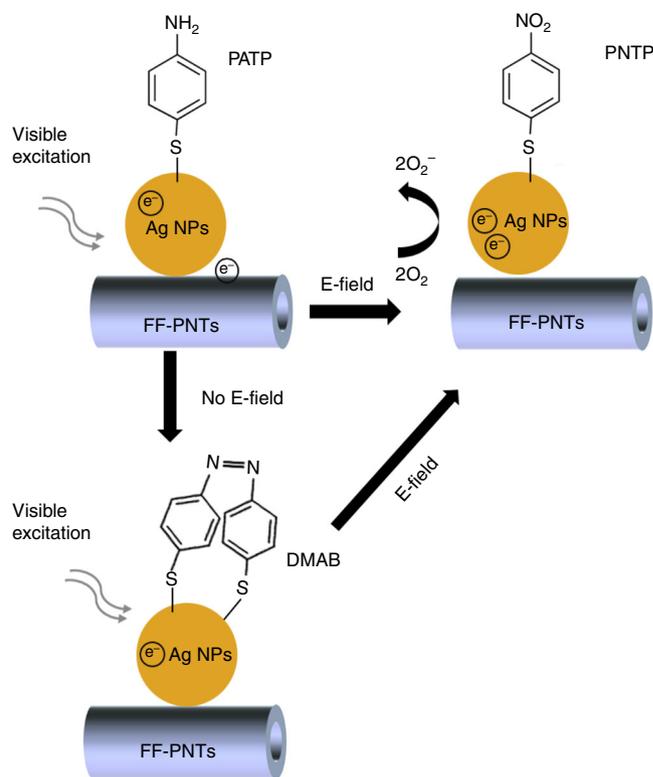


Fig. 3 Mechanism for oxidation of PATP to PNTP on the FF-PNT/Ag NP template. When the FF-PNT/Ag NP template was excited by the Raman laser in the presence of an electric field, LSPR-excited hot electrons and additionally electrons relocated from FF-PNTs to Ag NPs contribute to the O₂ activation step, resulting in the creation of PNTP rather than DMAB. Also shown also is the formation of DMAB on the FF-PNT/Ag NP template, which occurs at zero field. The DMAB dimer may subsequently convert to PNTP upon application of an electric field, together with optical excitation of the Ag NPs LSPR

PATP rather than oxidizing PATP to DMAB (Fig. 3). We note that there is an alternative reaction pathway, in which a DMAP dimer converts directly to PNTP with sufficiently strong applied electric field via optical excitation of the Ag NPs LSPR (Fig. 3).

To better understand the mechanism for template-mediated photocatalysis of PATP oxidation, and for optimization of the template for future rational design, we turn now to the theory of NT-NP-molecule charge transport. Photoexcitation of the Ag NPs produces hot electrons; the wavelength of the incident radiation is tuned so the excitation energy of these hot electrons matches the HOMO–LUMO gap of the attached target molecule, thereby promoting an oxidation reaction. However, this process alone cannot be catalytically sustained without replenishing the lost electrons from the Ag NPs. The choice of substrate for the Ag NPs is therefore critical to the design of an effective template for photocatalysis. While a metallic substrate is an ideal source for NP charge replacement, the plasmonic properties of the NP would be drastically changed and any hot electrons produced would be quickly lost to the thermal conduction electron reservoir. An insulating substrate preserves the photoexcitation-oxidation mechanism, but obviously hinders template charge redistribution. In principle, however, semiconductors allow for a separation of time scales for the NP-molecule oxidation reaction, and the substrate-NP charge equilibration.

We argue that the optimal setup involves careful matching of the substrate semiconductor band-gap to the metallic NP band-width. On one hand, we aim to preserve an efficient NP-molecule plasmon-driven oxidation, while on the other hand allowing for a catalytic cycle through subsequent redistribution of charge across the semiconductor and NPs. Low-energy (non-excited) electrons of the semiconductor substrate transferred to the metallic NPs quickly relax. In general, a small finite conduction band overlap and weak coupling is required.

In this work, we use FF-PNTs as the semiconducting substrate, whose band-gap of ~ 4.6 eV matches approximately the Ag NP bandwidth, and so are rather well decoupled electronically at experimentally relevant temperatures. However, as was shown in Fig. 2, use of an electric field along the length of the FF-PNTs activates and dramatically enhances photocatalysis of PATP oxidation. As shown below, this is due to a field-induced coupling of low-energy electrons in the FF-PNT with the Ag NPs, opening a channel for facile charge transport across the template. The in-situ controllability of the product yield using a tunable electric field has obvious practical utility, and also opens the possibility to suppress unwanted side-reactions.

In the following, we develop a theory of charge transport across the template, to substantiate the general principles discussed above. Our philosophy here is not to undertake a realistic simulation of the full system. Even if exact first-principles calculations for such a system was possible, the significant structural and chemical complexity of the FF-PNT alone obfuscates the underlying mechanisms, largely limiting use to a case-by-case basis. Rather, we seek to develop the simplest possible quantum-mechanical model that encapsulates the vital physics of the constituents, which can then be solved exactly by quantum many-body techniques to understand in detail the key ingredients for template-enhanced plasmonic catalysis. Our model will comprise physically-motivated reduced descriptions of the FF-PNT, the Ag NPs, and the PATP molecule.

Figure 4 outlines schematically the justification for our reduced model. Figure 4a illustrates the self-assembled FF-PNT superstructure³²: a tube-like hexagonal array of individual PNTs shown in Fig. 4a, b. FF units (Fig. 4c) are stacked to form a tube held together by CO...HN hydrogen bonds (and other non-bonded interactions)³², as illustrated in Fig. 4d–f. The tubes can therefore

be regarded as (coupled) 1d chains of alternating strong bonds (C=O) and weak bonds (O...H) running longitudinally. Our reduced model of the FF-PNT (e) is highly simplified, consisting of a single infinite 1d quantum tight-binding chain with alternating couplings. The NT Hamiltonian in second-quantized notation reads,

$$H_{\text{NT}} = \sum_{n=-\infty}^{\infty} [(t + \Delta)c_{n,a}^\dagger c_{n,b} + (t - \Delta)c_{n,b}^\dagger c_{n+1,a} + \text{H.c.}] + \sum_{n=-\infty}^{\infty} \sum_{\alpha} n \delta V c_{n,\alpha}^\dagger c_{n,\alpha}, \quad (1)$$

where $c_{n,\alpha}^\dagger$ creates an electron on sublattice $\alpha = a, b$ in unit cell n , and $c_{n,\alpha}$ is the corresponding annihilation operator. Electron interactions³³ are neglected. The effect of an aligned static electric field is taken into account via a potential gradient in the last term of Eq. 1. The NT model is a semiconductor at zero field, as required, with a spectral gap of 4Δ . In the following, we set $4\Delta = 4.6$ eV to match experiment, and $t = 2.5$ eV. The gapped NT local density of states (see Methods) is shown in Fig. 5a for zero field. Figure 5b–d show spectral weight redistribution into the gap when an electric field is applied.

The model for the Ag NP is taken to be a finite 3d tight-binding lattice with typical experimental dimensions (approximately $N = 75$ Ag atoms in diameter). The NPs are large enough to be metallic, but their finite size is a critical feature that must be retained in the model to understand charge transfer across it from NT to molecule. Specifically,

$$H_{\text{NP}} = t' \sum_{\langle \vec{r}, \vec{r}' \rangle} [d_{\vec{r}}^\dagger d_{\vec{r}'} + \text{H.c.}], \quad (2)$$

where $d_{\vec{r}}^\dagger$ creates a NP electron at site $\vec{r} \equiv (x, y, z)$, with $\{x, y, z\} = 1, 2, \dots, N$. Here $\langle \dots \rangle$ indicates nearest neighbors, taken to be on a cubic lattice for simplicity. The NP bandwidth $12t' \simeq 4$ eV is again fit to experiment. Finally, we use a standard tight-binding model for the target molecule backbone, H_{mol} , with parameters chosen to reproduce the HOMO–LUMO gap. These three components are coupled in the sequence NT–NP–molecule, via local hopping matrix elements $V_{\text{NT-NP}}$ and $V_{\text{NP-mol}}$ (for further details, see Methods). Despite its simplicity, we show below that this quantum model describes the physics controlling the functionality of the template.

The central quantity of interest for our theoretical analysis is the differential conductance $G = dI/dV$ for quantum transport of electrons from the NT to the molecule. A high conductance indicates facile charge transport across the template, which is necessary for its catalytic function in oxidation reactions. We do not simulate the plasmonic physics directly per se, but focus instead on the charge redistribution following photoexcitation, encoded in the conductance. We employ the Landauer–Büttiker^{34–36} formalism within linear response to calculate the conductance from NT to molecule across the NP,

$$G = \frac{2e^2}{h} \int dE \left(-\frac{df}{dE} \right) T(E), \quad (3)$$

where f represents the Fermi function and $T(E)$ the transmission function at energy E . In the following we are interested in temperatures $T \ll t$. In terms of Green's functions, the transmission function can be expressed exactly as^{34–36},

$$T(E) = 4\pi\Gamma V_{\text{NT-NP}}^2 A_{\text{NT}}^0 \times |\mathcal{G}_{\text{NT-mol}}|^2, \quad (4)$$

where $A_{\text{NT}}^0 = -\frac{1}{\pi} \text{Im}[\mathcal{G}_{\text{NT}}^0]$ is the free NT density of states at the NP as shown in Fig. 5(a–d), and $\mathcal{G}_{\text{NT-mol}}$ is the electronic propagator across the template, from NT to molecule, in the

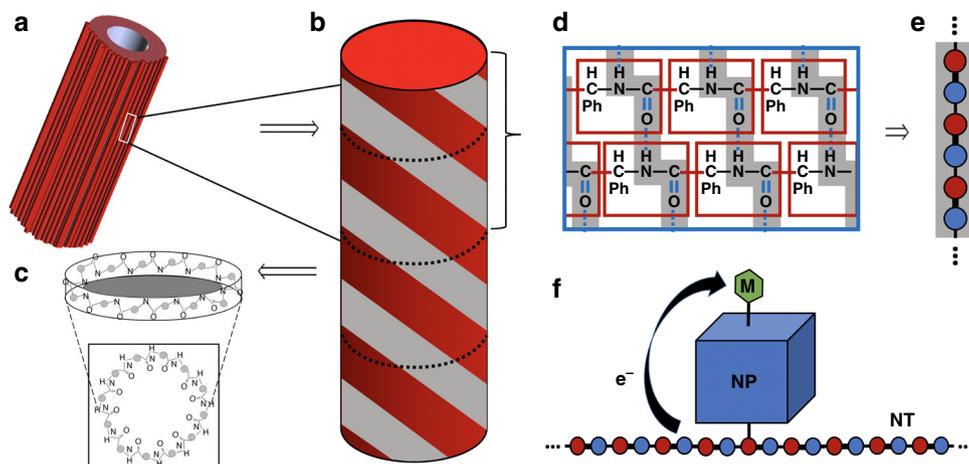


Fig. 4 Schematic formulation of reduced theoretical model. **a** Self-assembled FF-PNT superstructure of **(b)** individual tubes, each of which is built up from **(c)** stacked six-fold macrocycles (FF comprises a ring of 6 diphenylalanine units). **d** The FF units in adjacent layers are hydrogen bonded, resulting in **(d)** the corkscrew structure and longitudinal chains with alternating strong (C=O) and weak (O...H) bonds. **e** Reduced model for the FF-PNT consisting of a single 1d chain with alternating couplings. **f** Model for the entire system, with the target molecule attached to a metallic NP, which itself is coupled to the NT chain

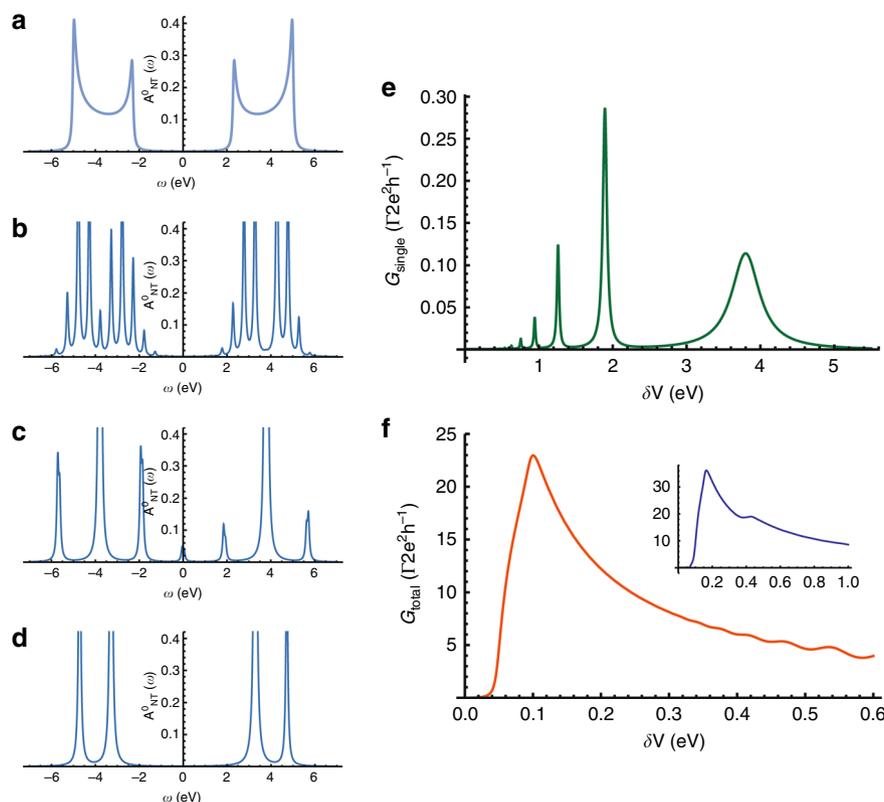


Fig. 5 Theoretical results obtained from reduced model. **a–d** Local density of states of the NT model, Eq. 1, at the point of attachment to a NP. No electric field is applied in **a**; it is a perfect semiconductor with spectral gap 4.6 eV. Potential difference $\delta V = 0.5, 2.0, 8.0$ eV in **b, c, d**, respectively, due to an applied field. Spectral weight redistribution upon increasing field strength first yields conducting, then insulating, behavior. **e** Conductance for electron transport from the NT to the molecule across a single NP, as a function of applied field. **f** Collective conductance due to a dense array of NPs along the NT, showing threshold activation and significant enhancement of charge transport at moderate field strengths, then attenuation upon further increasing the field strength. Inset: qualitatively similar behavior for a more realistic model of the FF-PNT taking into account the six-fold macrocycle FF unit cell and inter-layer hydrogen bonding

fully coupled model. These Green's functions are calculated exactly^{37,38}, as described in Methods. $\Gamma \ll 1$ is the hybridization to a fictitious probe electrode which we introduce only to define a conductance (results for conductance in Fig. 5 are given in units of Γ).

The conductance across the template as a function of applied potential difference δV (and hence longitudinal NT electric field) when a single NP is attached to the NT, is presented in Fig. 5e. It shows a series of conductance resonances as the field is tuned, indicating that there are specific values of the field strength that strongly enhance catalytic activity of the template. Closer analysis

also reveals that there is an threshold field, with $\delta V/t \sim 0.1$, below which charge transfer is blocked.

To understand the experimental results in Fig. 2c, we must also take into account the cooperative effect of dense NP coverings (see Fig. 1d). Also, note that the experimental SERS intensity results from the combined scattering from target molecules on all NPs. Accounting for this in the theoretical modeling, we assume a NP is coupled to each NT unit cell and calculate the total conductance from the NT to the molecules (Methods). The result is shown in Fig. 5f, and demonstrates the same features as the experimental data (Fig. 2b, c)—a sharp electric-field threshold to catalytic activation, strongly enhanced intensity over a window of applied voltage, and then subsequent intensity decay on further increasing the voltage. To confirm this, we also implemented a more realistic model of the FF-PNT, taking into account the stacked layers of six-fold macrocycles (Fig. 4c and Methods), and very similar results are obtained—see inset to Fig. 5f. We again emphasize that the reduced quantum model is designed to capture the essential physics of the problem, not to provide quantitative agreement with experiment. Our theoretical results do demonstrate that spectral weight redistribution in the FF-PNT induced by an applied electric field does activate a facile charge-transport channel across the template, which in turn we argue is responsible for enhanced catalytic function for oxidation reactions of target molecules.

Heating effects and temperature-gradient sensing. The local heat generated from metal NPs due to LSPR excitation during laser illumination can enhance photocatalytic activity¹¹. Heat generated from the FF-PNT/Ag NPs template with PATP was measured during the use of an electric field (Supplementary Fig. 17); we find that the temperature increases linearly with field strength. FF-PNTs are known to have piezo and pyroelectric characteristics that can be affected by temperature^{10,11,15–17,29}. The increased temperature arising from an applied electric field may therefore lead to an enhanced pyroelectric effect for the FF-PNTs, where charge excited during heating can be transferred to Ag NPs^{10,11,15–17,29,39,40}. It should be noted that the pyroelectric effect of FF-PNT decreases as the temperature increases above $\sim 60^\circ\text{C}$ ¹⁵. This is keeping with our measurements which show that SERS intensity decreases for voltages $> \sim 25\text{ V}$ (Fig. 2c), as the temperature reached $\sim 70^\circ\text{C}$.

Thermally-induced water loss and corresponding changes in the chemical and hydrogen bonds that hold the FF-PNT structure together may also play a role. The applied electric field introduces local heating that leads the water molecules present in the PNTs to evaporate¹⁵. Studies have shown that the increase in temperature could possibly effect the organization of water molecules in the nanochannel of individual nanotubes^{15–17}. Reduction in SERS intensity observed after heating above 50°C (Supplementary Fig. 18) can be as a result of the hydrophilic temperature-dependent binding of water with COO^- tails, and the disturbance of dipole ordering in the tubes interior. The dipolar organization of water molecules positioned near carboxyl groups in the nanocavities cannot convalesce at these temperatures due to their high mobility, resulting in a measured decrease of pyroelectric current and hence reduction in SERS signal^{15–17}. Such temperature-dependence can be applied as a nanoscale thermometer amenable with a biological environment. An advantage of such pyroelectric thermometers based on FF-PNTs ($2\ \mu\text{C}/(\text{m}^2\text{K})$ pyroelectric coefficient) is their sensitivity to the temperature gradient. This would be useful, for example, in monitoring fast thermal properties in cells. A second proposed use is in thermal energy harvesting, which may participate with piezoelectric harvesting when abrupt differences of temperature occur, such as in living human systems^{15–17}.

Our theoretical studies show that a necessary condition for photocatalysis is facile charge transfer across the template, activated at a critical threshold electric field. Hot electrons produced by photoexcitation of NPs and lost in the oxidation reaction of the molecule can thus be replaced, permitting a sustainable catalytic cycle. The plasmonic particles can generate new and alternate reaction conduits by the creation and injection of hot electrons and via charge transfer based processes between FF-PNTs and Ag NPs. However, we have also shown experimentally that heating effects are important, due to the known piezoelectric and pyroelectric properties of the FF-PNTs^{15–17}. These likely contribute to the dramatic enhancement of catalytic activity in this FF-PNT/Ag NP template system.

Oxidation of 2-AMP. To demonstrate the versatility and robust functionality of the FF-PNT/Ag NP template, we now turn to the oxidation reaction, $2\text{-AMP} \rightarrow 2\text{-NIP}$. The Raman and SERS spectra for 2-AMP are well-characterized and are known to undergo photochemical change on oxidation to 2-NIP in the presence of plasmonic metals^{25,27,41–44}. SERS measurements of 2-AMP on the FF-PNT/Ag NP template were recorded under the same conditions as for PATP. The applied electric field is shown to influence the spectral behavior of the analyte molecule—as well as SERS intensity (Fig. 6a–d and Supplementary Fig. 19), similar to the PATP case discussed above (Fig. 2).

Applying a voltage to produce an electric field, but keeping the offset bias at $\leq 100\text{ mV}$, resulted in a (six-fold) increase in SERS signal intensity with no change in the SERS spectral relative band intensities (as for PATP). However, when the offset bias was raised above 100 mV the (eight-fold) SERS intensity increase was accompanied by significant changes in spectral relative band intensity. The strong appearance of bands at 1285 cm^{-1} (C–N stretching mode) and 1334 cm^{-1} (amine scissoring mode) cm^{-1} signifies the transformation from 2-AMP to 2-NIP^{41–44}. A lowering of the SERS Raman band frequency to 1334 cm^{-1} from 1342 cm^{-1} , as well as intensity increases for bands at 1285 and 1334 cm^{-1} implies transformation from 2-AMP to 2-NIP through a strong chemical interaction of 2-AMP with the substrate through the nitro group^{41–44}. In the absence of FF-PNTs, Ag NPs alone do not result in changes to the 2-AMP spectral features with an applied electric field (Supplementary Fig. 20). A plot of Raman band intensities (Fig. 6b) associated with 2-NIP (at 1258 and 1334 cm^{-1}) with electric field shows that a threshold field strength is required for the formation of these two bands to in the SERS spectra. Note, however that further increasing the field causes the SERS signal associated with 2-NIP to decrease (Fig. 6c). Similar behavior was observed for PATP in Fig. 2. Removal of the electric field causes the relaxation of the SERS intensity and results in the back reaction $2\text{-NIP} \rightarrow 2\text{-AMP}$ (Supplementary Fig. 21).

Combining both electric field with super band irradiation of the FF-PNT at $\lambda = 254\text{ nm}$ (Supplementary Fig. 22) resulted in the rapid transformation of 2-AMP to 2-NIP with a nine-fold increase in SERS intensity. This result provides further evidence that combining both electric field and UV irradiation significantly enhances such photocatalytic processes.

Enhancing SERS sensing. Finally, we investigate the alternative application of this FF-PNT/Ag NP template for enhanced SERS sensing of biomolecules such as glucose and other nucleobases (Fig. 7). Such biomolecules have a low Raman cross-section and are therefore challenging to observe directly. Below, we demonstrate that the template dramatically enhances sensing when an electric field is applied. SERS measurements of glucose (Fig. 7a, and Supplementary Fig. 23) on the FF-PNT/Ag NP template

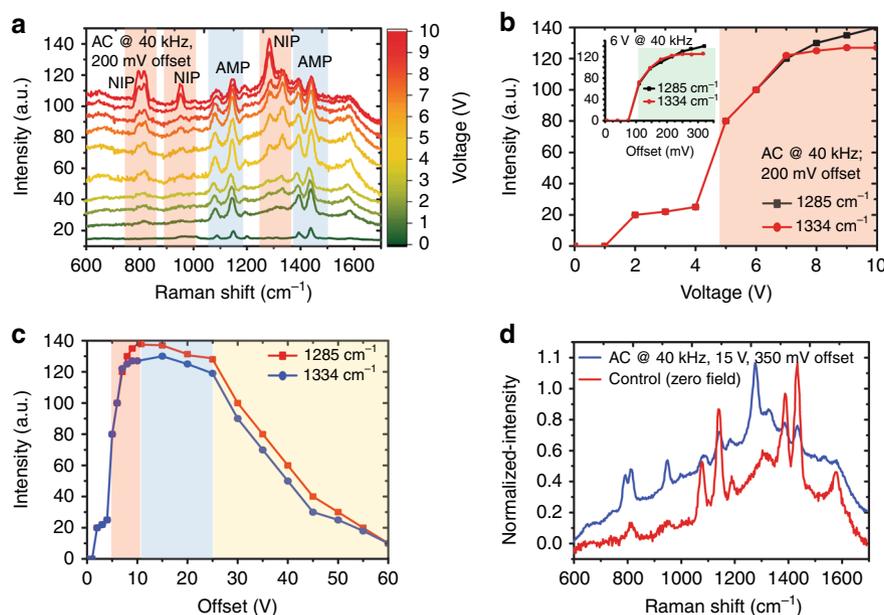


Fig. 6 SERS study of 2-AMP on the template in an applied electric field. **a** SERS measurements of 2-AMP on the FF-PNT/Ag NP template at different electric fields strengths, applying voltages from 0–10 V at 40 kHz AC with offset bias of 200 mV. **b, c** Corresponding Raman band intensity of bands associated with 2-NIP as a function of voltage. **b** Critical threshold voltage ~4 V required for the formation of 2-NIP. Inset shows the SERS signal strength as a function of offset bias. **c** The window of 10–20 V is optimal for 2-NIP product yield via photocatalysis, with SERS intensity reducing above ~25 V. **d** Normalized SERS spectra, comparing a fully relaxed control sample at zero field (red) to the spectrum recorded with applied field (blue). The similarity with Fig. 2 demonstrates robust and versatile template functionality

showed Raman bands in good agreement with other reports^{45,46}. With increasing electric field, strong and clear appearance of all glucose bands combined with an eight-fold increase in SERS intensity was seen. Relaxation of the Raman signal (Supplementary Fig. 23) occurred following removal of the electric field, as with previous probe molecules (PATP and 2-AMP). Uniformity and reproducibility tests were performed on the sample at different spots or different samples, with only a 5% change observed (Supplementary Fig. 23)

To further future demonstrate the applicability of FF-PNT/Ag NP templates with applied electric field, the nucleobases uracil and thymine were investigated, as well as the proteins bovine serum albumin (BSA) and albumin (Lys-egg and Lys-human)—see Fig. 7 (b–f) and Supplementary Fig. 23. In optimized conditions (300 mV offset bias, 10 V AC at 40 kHz) a seven to eight-fold intensification in SERS signal was observed (compared with zero-field measurements). The Raman bands recorded in our study are in line with previous reports^{47–50} (Supplementary Tables 1 and 2). For all molecules, a return to the original Raman signal level occurred when turning off the electric field, as with previous probe molecules (PATP, 2-AMP, and glucose). Supplementary Fig. 24 further establishes the high degree of reproducibility of our results, taking BSA and Lys target molecules as examples. We tested with and without field, over different samples at different spot positions, finding only a 5–6% variability in signal intensity.

Since DNA-based molecules are notoriously difficult to detect due to their small Raman cross-sections^{47–50}, our results demonstrate the power and utility of employing the FF-PNT/Ag NP template with an applied field to enhance sensing. We note that SERS sensing of guanine, adenine, and cytosine target molecules was similarly enhanced. However, these molecules were also oxidized by the template in applied field (Supplementary Fig. 25).

Discussion

Our results show that the FF-PNT/Ag NP template controls and greatly enhances product formation and selectivity in

plasmon-activated catalytic reactions. Applying an external electric field of sufficient strength to the FF-PNT/Ag NP template, together with LSPR excitation, resulted in the catalyzed oxidation of PATP to PNTP. Interestingly, the reaction is fully reversible, with PNTP molecules reduced back to PATP after switching off the field. Similar results were obtained in a second probe molecule, 2-AMP. The FF-PNT/Ag NP template affects the plasmonic photocatalyst reaction by creating different reaction pathways through the formation and injection of LSPR-excited hot electrons and through charge transfer processes involving FF-PNTs and Ag NPs. Our detailed theoretical analysis, based on full quantum transport calculations, demonstrates that the key ingredient necessary for template functionality is a channel for facile charge redistribution across the template, here activated by electric field application. Both the pyroelectric and piezoelectric properties of FF-PNTs with an applied electric field may play a part in the improvement of the catalyst activity, by facilitating charge transfer processes across the template. In addition, heat generated from both Ag NPs and the FF-PNTs because of the absorbed Raman excitation photons or applied voltage may also change the reaction conditions. Furthermore, we have successfully detected a number of biomolecules such as glucose, thymine, and uracil, without any further chemical treatment or binder molecule, using the highly stable FF-PNT/Ag NP template with electric field, resulting in eight-fold increase in SERS intensity. Our results may enable a new platform technology for monitoring catalytic activity and surface-enhanced Raman scattering of biomolecules with low Raman cross-sections, utilizing the strength and frequency of the applied field. In addition, the capacity to dynamically control SERS spectra of specific bond types in situ adds an extra dimension to the collection of SERS measurements in nanocomposite structures based on biological materials such as FF-PNTs. We finally note that our approach is versatile. By matching the electronic bandwidth of plasmonic metal nanoparticles to the bandgap of 1D semiconductors, other material composites can be formed which are similarly expected to

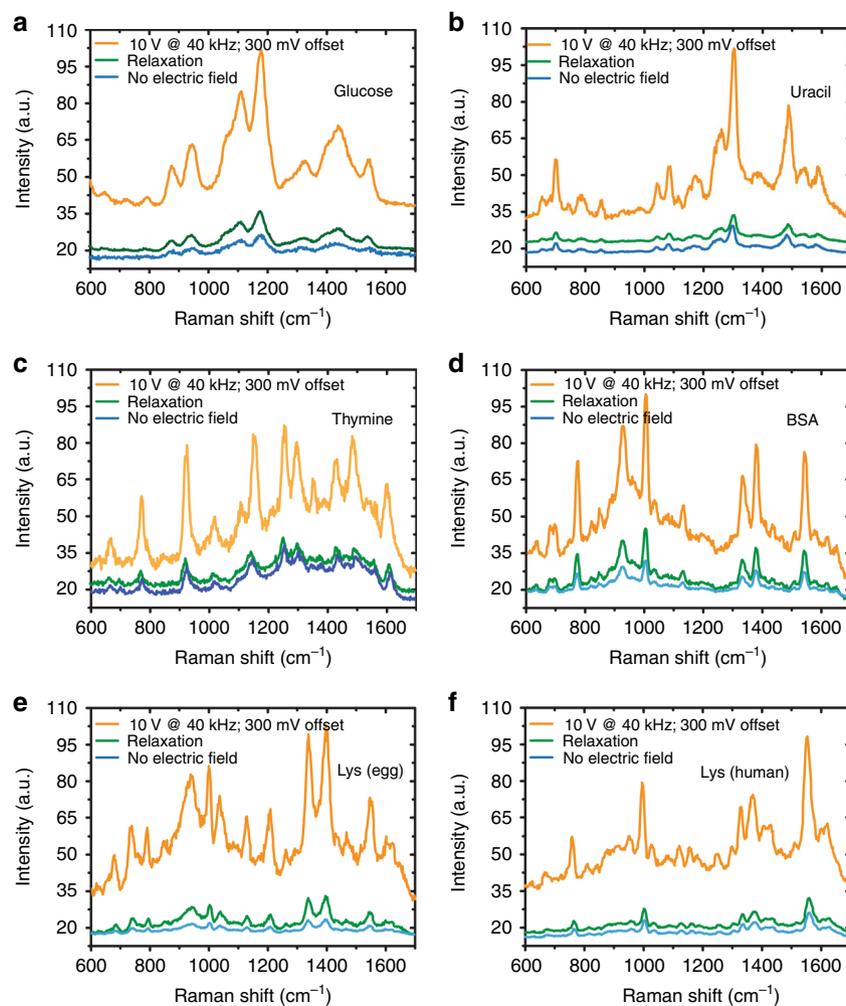


Fig. 7 SERS sensing of biomolecules on the template using an externally applied electric field. SERS measurements of (a) glucose, (b, c) DNA based molecules uracil and thymine, (d) BSA, (e) Lys-egg and (f) Lys-human, demonstrating field-enhanced sensing using the FF-PNT/Ag NP template

enhance plasmonic catalysis and SERS sensing on application of an external electric field.

Methods

Preparation of the Si substrate with gold electrode pair. Si wafers (Si Mat) were cut as 2×1 cm samples. The Si wafer surfaces were first cleaned by immersing in acetone for 2 min, followed by washing with ethanol and isopropanol. De-ionized water was then used to rinse the substrates, followed by the application of nitrogen gas to blow dry the silicon's surface of any residue solvent. To make the gold electrode pair on the Si substrate, a 3D printed mask with dimensions of 2×1 cm and opening 0.1 mm was used. Gold was sputtered through mask openings forming the electrode pair. The process is illustrated in Supplementary Fig. 1.

Preparation of FF-PNT/Ag NP template. The FF-PNTs were made by dissolving L-diphenylalanine peptide (Bachem) in the solvent 1,1,1,3,3,3-hexafluoro-2-propanol (Sigma-Aldrich). Using a starting concentration of 100 mg/ml, this was diluted in deionized water to a concentration of 2 mg/ml. The FF-PNT/Ag NP templates were prepared using 2 mg/ml of this solution heated at 100 °C for 2 min. Twenty microliters of Ag NP solution presenting a concentration of 0.02 mg/ml in water was added to 60 μ l of the heated FF solution and stirred for 3 min. Following this 30 μ l of the mixed solution was then placed on the gold electrode patterned Si substrate to create the aligned FF-PNT/Ag NP template. For the control sample; Ag NPs on a Si substrate. This sample was made using 20 μ l of Ag NPs (0.02 mg/ml) which was diluted in 60 μ l of water then 30 μ l of the solution was deposited on the Si substrate. SEM images show the alignment of the FF-PNT/Ag NP template in the gap between the gold electrodes (Supplementary Fig. 13). The diameter of the FF-PNTs, determined from SEM images, was 3.2 ± 1.3 μ m from $n = 30$ FF-PNTs.

Probe molecule solutions. 4-aminothiophenol (PATP) (New Star Chemical) and 2-aminothiophenol (2-AMP) (Sigma-Aldrich, Ireland) solutions were prepared in

methanol to a concentration of 10^{-4} M. These solutions were then diluted with deionized water to a final concentration of 10^{-5} or 10^{-6} M. Thymine cytosine, uracil, adenine, and guanine (all nucleotides sourced from Sigma-Aldrich) solutions were prepared in deionized water to a final concentration range of 10^{-5} M. Similarly, with glucose, TMPyP (5,10,15,20-Tetrakis(1-methyl-4-pyridinio)porphyrin tetra(p-toluenesulfonate), BSA (Bovine Serum Albumin), Lys-egg and Lys-human (Albumin from chicken egg white and humans, respectively) all sourced from Sigma-Aldrich Ireland.

Spectral characterization. Optical absorbance measurements (V-650, JASCO, Inc.) were performed using the following settings of a 1 nm step size, with a 1 nm bandwidth, and a 400 nm/min scan speed. Recording spectra over a 190–900 nm wavelength range. Optical absorbance measurements were then performed on the FF-PNT/Ag NP template that was aligned on cover slip with electrodes during electric field application with different AC voltages between 0 V and 10 V, frequency of 40 kHz, and offset bias of 5 to 60 V.

Fourier Transform Infrared Spectroscopy (FTIR) was undertaken using an Alpha Platinum Bruker system. To record FTIR spectra FF-PNT/Ag NP solution (10 μ l) was deposited onto the ATR interface. Spectra were collected using transmission mode scanning from 1400–4000 nm.

A Scanning Electron Microscopy (SEM) (JSM-7600F) system was employed to characterize the samples. To obtain SEM images a thin (~8 nm) layer of gold was sputtered on the samples before SEM imaging (Hummer IV, Anatech USA).

To record SERS spectra a bespoke Raman system was used. This system comprised of an inverted optical microscope (IX71) with a SP-2300i spectrograph (Princeton Instruments), and a EMCCD camera (IXON). The 532 nm Raman excitation laser was fixed at a 5 mW incident power. SERS measurements were performed using an arbitrary waveform generator (Tektronix 3390) with different AC voltage (0 to 10 V) and frequency (from 0 to 100 kHz) and offsets of 0 to 500 mV. Offsets in the range of 5 to 60 V were applied using a DC power supply (TENNA, 72–2015). UV irradiation was applied using a UV pencil lamp with a

wavelength of 254 nm possessing an output power of 4.5 mW/cm² (Edmond Optics) when located at a distance of 2 cm from the sample.

Application of applied electric field. During SERS measurements, an electric field was applied. This was generated by applying a voltage across the electrode pair on either side of the FF-PNT/Ag NP template, at 0–10 V and 1–105 kHz, resulting in electric fields upto 10 V/mm. An Offset was also applied, ranging between 0 and 355 mV. AC frequency was fixed at 40 KHz which was found to produce the maximum enhancement on SERS enhancement and plasmonic catalysis (Supplementary Fig. 7). In contrast the applied voltage and also the applied offset bias both impacted the photochemical reaction yield and rate (as shown in Fig. 2, Supplementary Fig. 6).

Theoretical calculations. For the theoretical modeling described in this paper, we formulated and analyzed the following fully quantum mechanical Hamiltonian, $H = H_{\text{NT}} + H_{\text{NP}} + H_{\text{mol}} + H_{\text{NT-NP}} + H_{\text{NP-mol}} + H_{\text{probe}}$. Here, H_{NT} and H_{NP} describe the isolated NT (given by Eq. 1) and the isolated NP (Eq. 2), respectively. The isolated PATP molecule is likewise described by a minimal tight-binding model of the molecular backbone, with parameters chosen to reproduce the HOMO–LUMO gap extracted from the experiment. These three basic elements of the full system are coupled together by,

$$H_{\text{NT-NP}} = V_{\text{NT-NP}} \left(c_{0,a}^\dagger d_{r_1} + \text{H.c.} \right),$$

$$H_{\text{NP-mol}} = V_{\text{NP-mol}} \left(d_{r_2}^\dagger a_{\text{FO}} + \text{H.c.} \right), \quad (5)$$

which describe local electronic tunneling between the NT, NP and molecule. Here, we assume the NP is attached to the middle of the NT (at unit cell $n = 0$). For NPs with $N = 75$ atoms across the diameter, we use $\vec{r}_1 = (38, 38, 1)$ and $\vec{r}_2 = (38, 38, 75)$, corresponding to NT and molecule attachment at the center of opposite NP faces. a_{FO} is an operator for the molecule frontier orbital coupling to the NP. We set $V_{\text{NT-NP}} = V_{\text{NP-mol}} = 1$ for simplicity. To quantify the charge flow across the template into the molecule, we also introduce into the model a term H_{probe} describing a metallic probe electrode contacting the molecule, which acts as a reservoir into which charge is absorbed (physically equivalent to an STM tip). The current I into this probe electrode, due to an infinitesimal test bias, defines the calculated conductance $G = dI/dV|_{V \rightarrow 0}$ in linear response. The probe electrode and its coupling to the molecule are characterized by the hybridization Γ featuring in Eq. 4. The coupling of the probe electrode to the molecule is assumed to be very weak so that properties of the system itself are not perturbed by it, $\Gamma \ll 1$ (the STM limit). Results for the conductance are presented in units of Γ .

The desired conductance is calculated exactly^{34–36} via Eqs. 3 and 4, and requires a knowledge of the free NT Green's function $[G_{\text{NT}}^0]_{ij} \equiv \langle \langle c_{0,i}^\dagger; c_{0,j} \rangle \rangle$ computed from H_{NT} , and the trans-template propagator

$G_{\text{NT-mol}} = \langle \langle d_{r_1}^\dagger; a_{\text{FO}} \rangle \rangle$ of the full system, H . We first obtain G_{NT}^0 using (recursive) equations of motion³⁷, whose exact solution is a generalized matrix continued fraction,

$$[G_{\text{NT}}^0]^{-1} = E_0 - \mathbf{M}[\mathbf{E}_1 - \mathbf{M}[\mathbf{E}_2 - \mathbf{M}[\dots]^{-1} \tilde{\mathbf{M}}]^{-1} \tilde{\mathbf{M}}]^{-1} \tilde{\mathbf{M}}$$

$$\tilde{\mathbf{M}} - \tilde{\mathbf{M}}[\mathbf{E}_{-1} - \tilde{\mathbf{M}}[\mathbf{E}_{-2} - \tilde{\mathbf{M}}[\dots]^{-1} \mathbf{M}]^{-1} \mathbf{M}]^{-1} \mathbf{M} \quad (6)$$

where in this case $[\mathbf{M}]_{ij} = \delta_{ia} \delta_{jb} (t - \Delta)$, and $[\mathbf{E}]_{aa} = [\mathbf{E}]_{bb} = \omega + i0^+ - n\delta V$, and $[\mathbf{E}]_{ab} = [\mathbf{E}]_{ba} = t + \Delta$. All matrices are 2×2 since there are two orbitals in the NT model unit cell. To further substantiate our results, we also implemented a more sophisticated model of the real FF-PNT, comprising stacked FF macrocycle rings (Fig. 4). The FF unit consists of 6 diphenylalanine units coupled in a ring. We took into account the 48 backbone C, N, O atoms in the FF macrocycle (at the level of one active orbital involved in transport per atom), with the structural information and coupling strengths encoded in \mathbf{E}_n . Stacked FF rings forming a quasi-1d tube are coupled together by C=O...H–N hydrogen bonds, as encoded in \mathbf{M} . FF-PNT Green's functions for this model are obtained using the above equation, Eq. 6, apart from using these new 48 \times 48 matrices \mathbf{E}_n and \mathbf{M} . In this model, to reproduce the experimental semiconductor bandgap of 4.6 eV, we took all C–C and C–N single bonds to have equal coupling strengths $t_{\text{cb}} = 4$, while the C=O double bond was taken to be $t_{\text{db}} = 8$, and the hydrogen bonds $t_{\text{hb}} = 0.6$. The final results using the two NT models are compared in Fig. 2f and are qualitatively equivalent.

The full $G_{\text{NT-mol}}$ is obtained by coupling together the isolated NT, NP, and molecule. This can be done efficiently using the T-matrix formalism in real space³³,

$$G_{xy} = G_{xy}^0 + \sum_{p,q} G_{sp}^0 T_{pq} G_{qy}^0,$$

$$\mathbf{T} = [\mathbf{I} - \mathbf{H}_1 \mathbf{G}^0]^{-1} \mathbf{H}_1, \quad (7)$$

where the 0 superscript indicates Green's functions of the uncoupled system as before, $[\mathbf{T}]_{pq} \equiv T_{pq}$ is the T-matrix describing electronic scattering between sites p and q , which are the specific sites coupled by \mathbf{H}_1 . Here, \mathbf{H}_1 is the matrix representation of $H_{\text{NT-NP}}$ or $H_{\text{NP-mol}}$ in the full Hilbert space of H . Eq. 7 is an exact

non-perturbative expression, and can be used successively to couple the molecule to the NP, and then to couple this system to the NP. To do this, we require electronic propagators across the NP, $\langle \langle d_{r_1}^\dagger; d_{r_2}^\dagger \rangle \rangle^0$. In practice, this can be done accurately and efficiently using the convolution method introduced in ref. 38.

Finally, we discuss a straightforward modification to the above protocol to make better connection with the experiment. Instead of considering a single NP located at the middle of the NT, we now generalize to a dense covering of NPs. Specifically, we take one NP per unit cell of the NT (clearly an approximation, but one which recovers the essential physics of the problem). The effect of the hybridization between NT and NP at each unit cell can be simply incorporated on the level of the NT Green's functions by modifying \mathbf{E}_n . The dense NP coverage has a cooperative effect on the NT density of states, and therefore the conductance through each NP. Denoting the conductance between the NT and a target molecule attached to a NP at site n as G_n , we now compute the total conductance as $G_{\text{total}} = \sum_n G_n$. This is plotted in Fig. 5f, and captures the basic features of the experiment, including the field-activated enhancement and threshold behavior.

Data availability

All the data are available from the authors.

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Author contributions

S.A. carried out the experiments and processed data. S.A., B.R., and J.R. designed the experiments and developed the experimental setup. S.A. carried out sample preparation, Raman measurements, FTIR, UV-vis measurements, SEM, and optical imaging. S.T.B. performed IV measurements. A.K.M. carried out all the theoretical work and calculations. S.A., B.R., J.R., and A.K.M. wrote the manuscript. All authors discussed results and reviewed the manuscript.

Additional information

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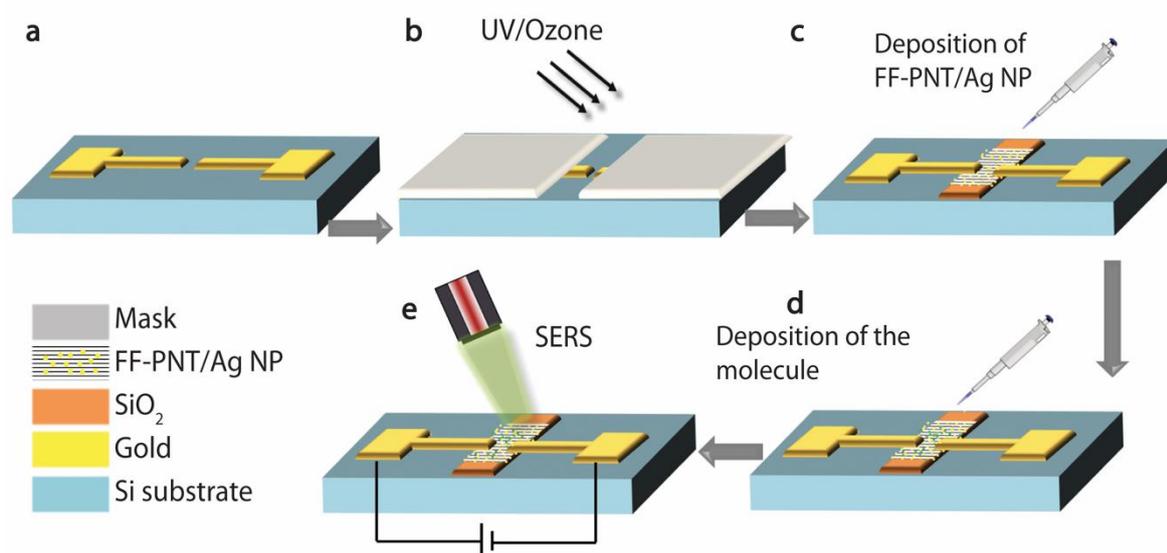
Supplementary Information for

Enhanced photocatalysis and biomolecular sensing with field-activated nanotube-nanoparticle templates

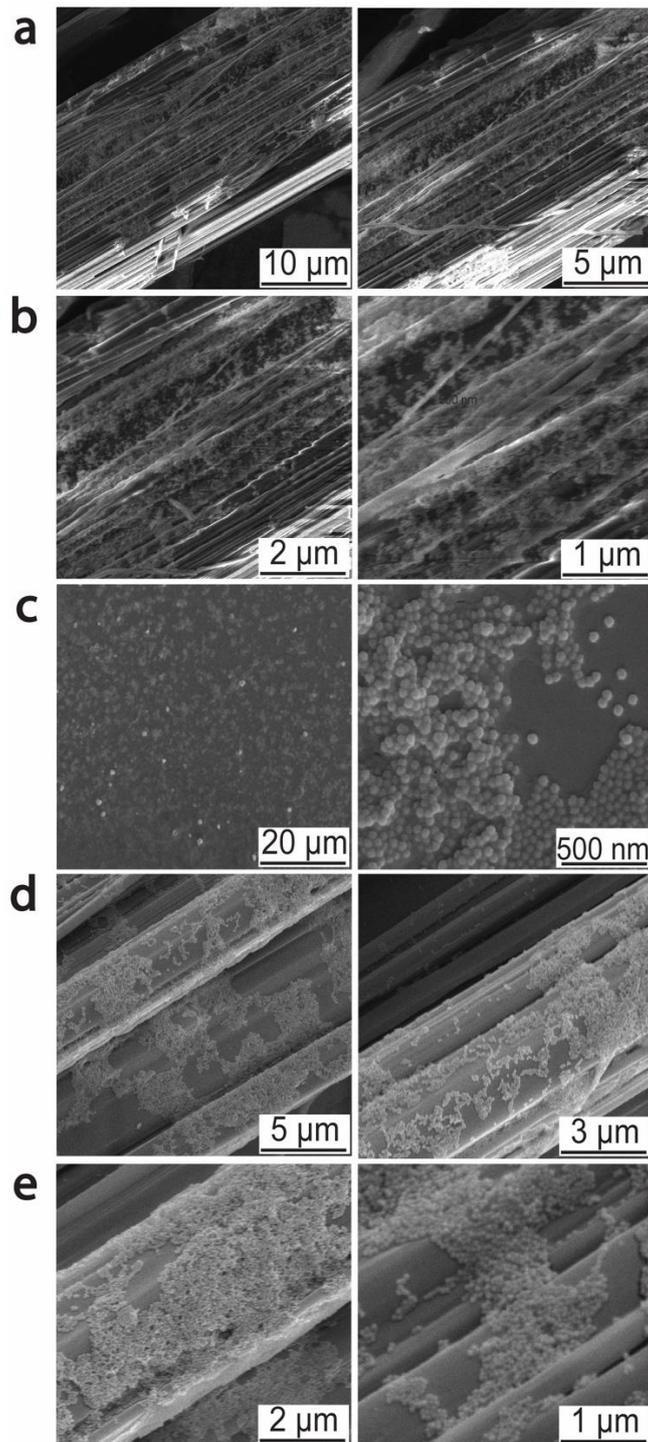
Sawsan Almohammed ^[a, b], Sebastian Tade Barwich ^[c], Andrew K. Mitchell * ^[a], Brian J. Rodriguez * ^[a, b], and James H. Rice * ^[a]

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brian.rodriguez@ucd.ie

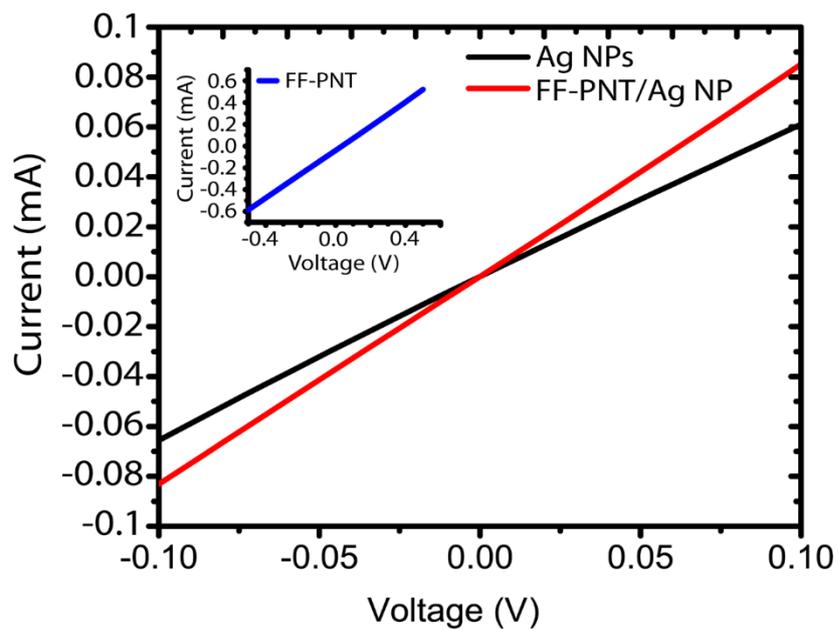
Substrate fabrication and characterization



Supplementary Figure 1. Process to align FF-PNT/Ag NP template on the microfabricated gold electrode device. (a) Gold coating through 3d printed mask with ~ 0.1 mm opening size between electrodes. **(b)** Exposure to UV/ozone through physical mask with 1 mm gap to produce the insulating SiO_2 layer. **(c)** Deposition of FF-PNT/Ag NP solution onto the SiO_2 substrate (only) and drying. FF-PNTs are aligned on the SiO_2 substrate. **(d)** Deposition of the probe molecules on the aligned dried template. **(e)** SERS measurements on FF-PNT/Ag NP template with applied electric field.

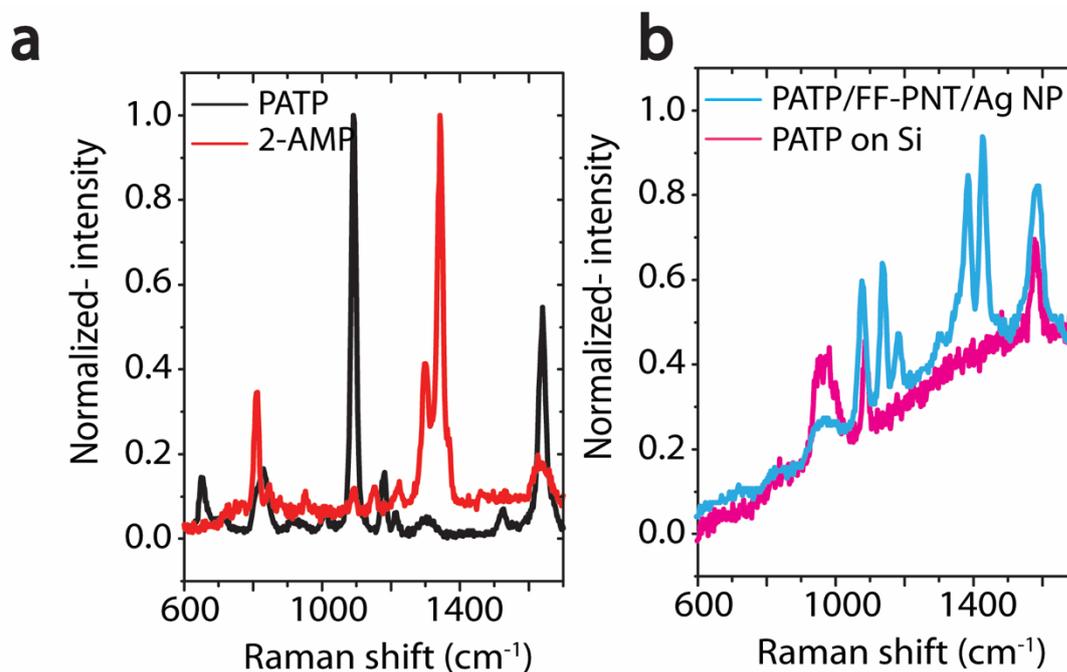


Supplementary Figure 2. Characterization of FF-PNT/Ag NP template. (a, b) Scanning electron microscopy (SEM) images for the FF-PNT/Ag NP template without gold coating, showing spherical features assigned as Ag NPs, with clustering predominately above and between the FF-PNTs. **(c)** SEM images of Ag NPs on Si without FF-PNT, with gold coating. **(d, e)** SEM images of the template FF-PNT/Ag NP with gold coating. Note that there is no observed change in topology or morphology before and after application of the electric field.



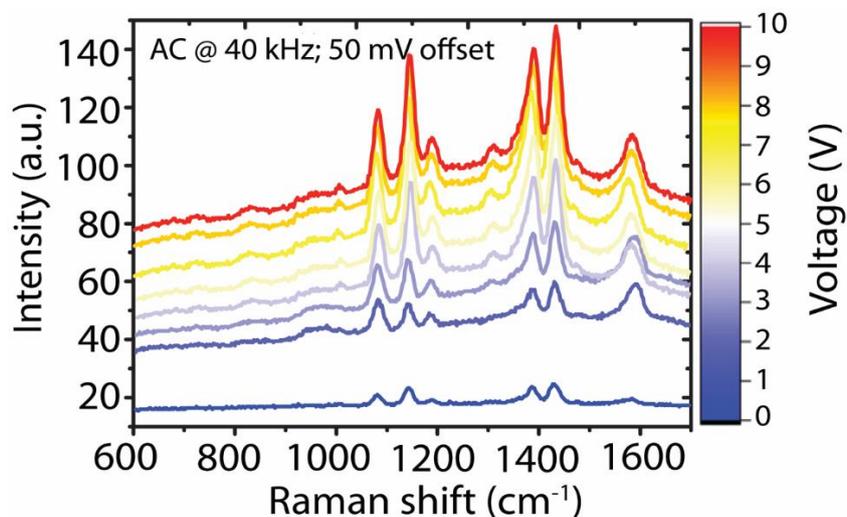
Supplementary Figure 3. Electrical conductivity studies on the template. IV (current and voltage) measurements of FF-PNT/Ag NP template (red), FF-PNT only (blue; inset), Ag NPs only (black). Data recorded using a Keithley device and a bespoke electrode substrate with dimensions 2 cm x 1 cm and gap of ~ 1 mm.

Reference SERS and Raman spectra for molecule PATP

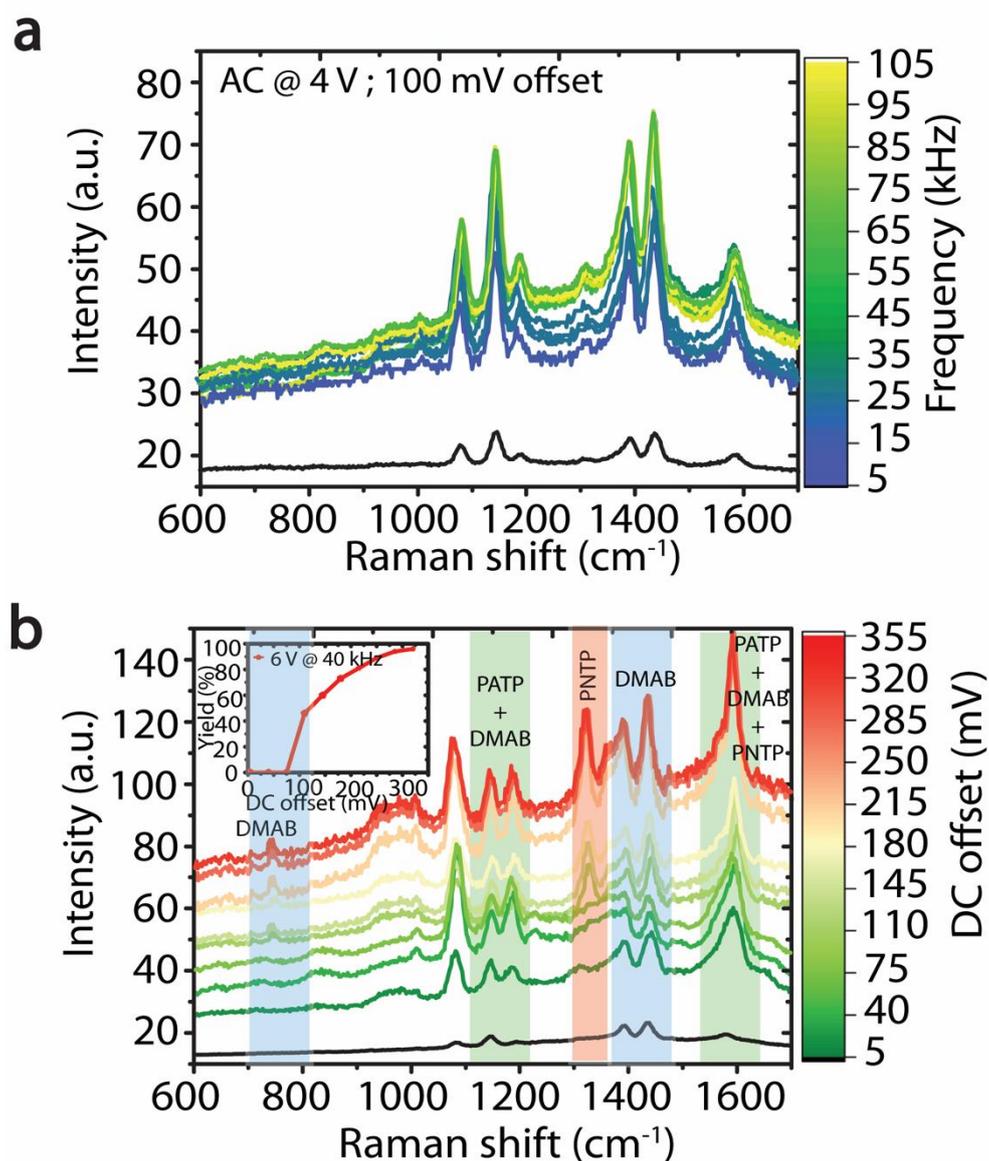


Supplementary Figure 4. Raman spectra of PATP. (a) Raman spectra of PATP and 2-AMP in powder form. (b) SERS spectra of PATP on the FF-PNT/Ag NP template (blue) vs on Si substrate only (pink). The SERS spectra for PATP is assigned to a combination of a- and b-type vibrational bands. Assignments of four of the five most intense bands (at 1142, 1390, 1433, and 1575 cm^{-1}) can be attributed to b_2 modes. The band at 1082 cm^{-1} can be assigned to an a_1 mode. In contrast, the Raman spectrum for PATP in powder form shows peaks at 1081, 1182, 1489, and 1593 cm^{-1} that are assigned to a_1 type vibrations^{1,2}. The observed b-type bands are intrinsic to PATP and are associated with a chemical enhancement mechanism^{1,2}. The four non-totally symmetric b_2 modes are known to be selectively enhanced in SERS through Herzberg-Teller vibronic coupling³. However, spectral differences may also originate from a photochemical reaction of PATP to form p,p'-dimercaptoazobenzene (DMAB)⁴⁻⁶ with the b_2 vibrations of N=N at 1433 and 1390 cm^{-1} and the 1142 cm^{-1} peak assigned as a C-N vibrational mode⁴⁻⁶.

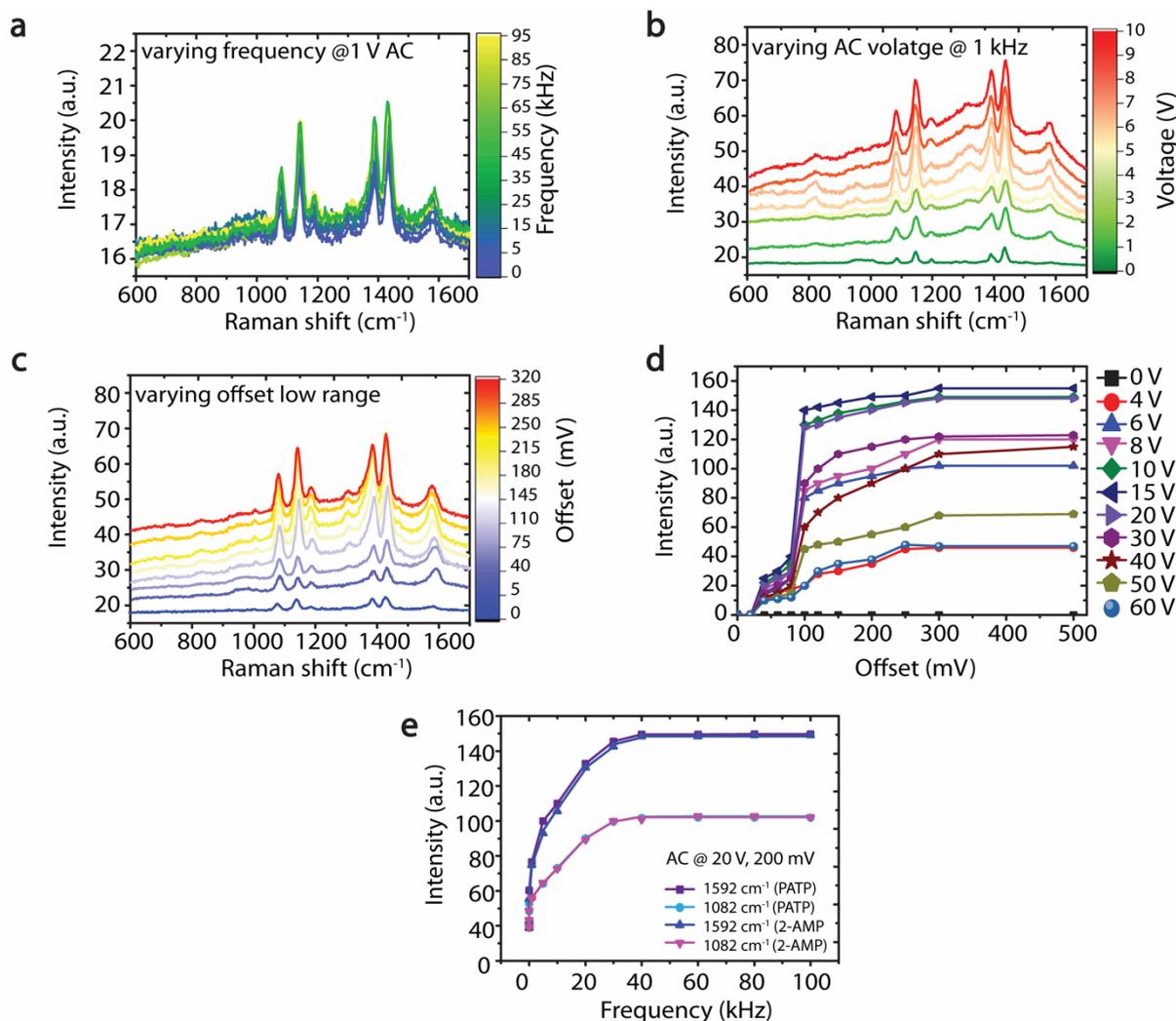
SERS with applied electric field for molecule PATP



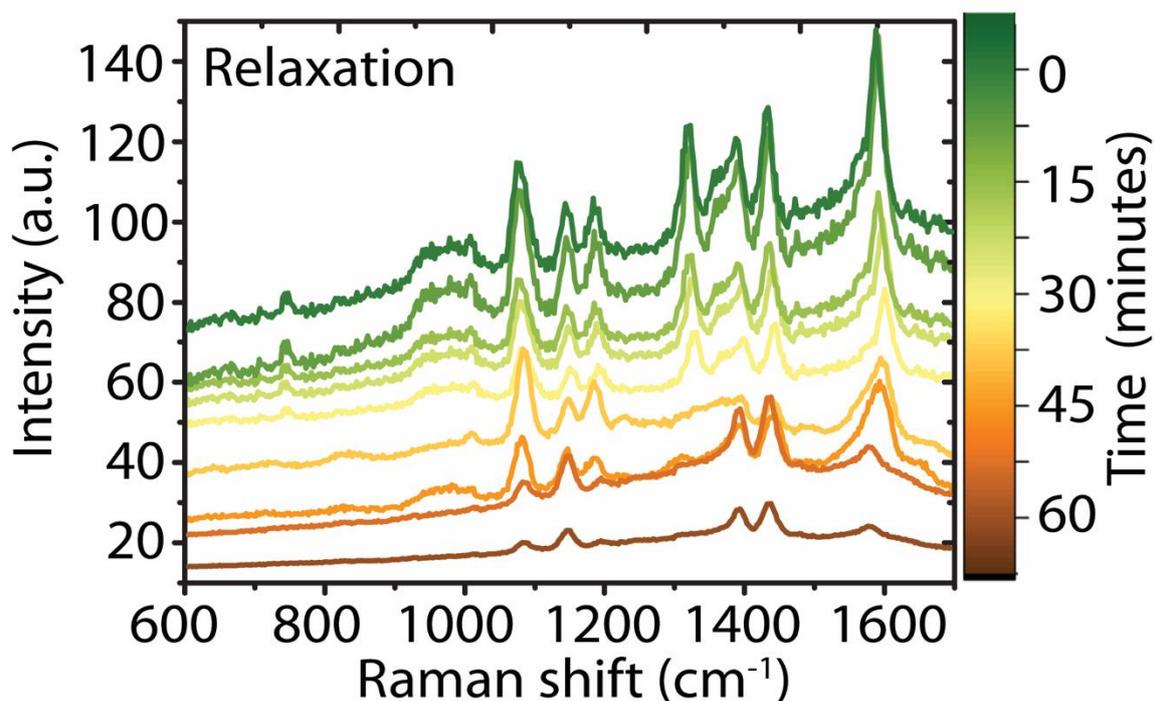
Supplementary Figure 5. SERS measurements of PATP on the FF-PNT/Ag NP template. SERS spectra are shown for PATP on the FF-PNT/Ag NP template at various voltages from 0 to 10 V at 40 kHz AC, with an offset DC bias of 50 mV. Increasing the voltage, while keeping the offset bias fixed at 50 mV, results in an increase in SERS signal intensity (up to ~7 fold at 10 V) with no change in the SERS spectral relative band intensities, indicating no oxidation product PNTP is produced.



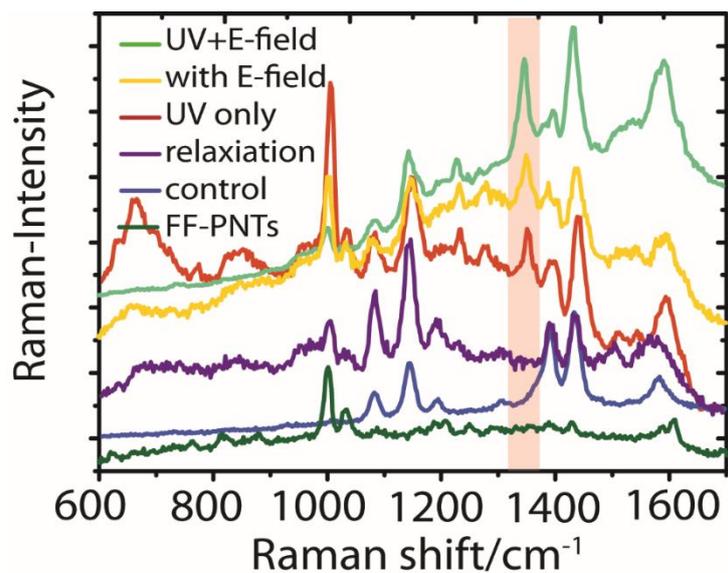
Supplementary Figure 6. SERS measurements of PATP on the FF-PNT/Ag NP template. **(a)** Data obtained at constant 4V and 100mV bias offset, varying AC frequency in the range 5-105 kHz. For reference, the black line corresponds to 0V. A ~7 fold increase in SERS intensity is observed, compared with the result at 0V (no electric field). We find that varying the frequency results in slight fluctuations in SERS intensity at high voltage and offset, which stabilizes at around ~40 kHz. Data presented in the main paper is therefore at 40 kHz. **(b)** SERS spectra recorded at different offset DC bias from 0-355 mV at a fixed 6V and 40 kHz AC. Inset shows the yield (formation of PNTP measured through the relative band intensity of the Raman mode at 1334 cm^{-1}) as a function of offset bias. Increasing the offset bias up to 355 mV resulted in an ~8 fold increase in SERS intensity. The SERS vibrational mode distribution also changes, with new vibrational modes at 1334 and 1376 cm^{-1} . These modes are assigned to symmetric NO_2 stretching vibrations of the product PNTP⁴⁻⁶, created from PATP through a photochemical plasmonic-assisted catalytic oxidation reaction⁴⁻⁷.



Supplementary Figure 7. SERS measurements of PATP on the FF-PNT/Ag NP template. (a) SERS spectra recorded for 1V AC (zero offset) with varying frequency, demonstrating an increase in SERS intensity up to around 40 kHz, after which no further intensity increase is observed. (b) SERS spectra at 1 kHz AC, varying voltage (zero offset). (c) SERS spectra for varying DC offset bias (0V AC). (d) SERS intensity of PNTP band at 1334 cm⁻¹ as a function of offset bias at different voltages (40 kHz AC). (e) SERS intensity of various bands of PATP and 2-AMP at 20V AC and 200 mV offset bias, as a function of frequency. (a, b) demonstrate that at zero offset, no change in relative band intensities is observed, and no new Raman bands appear, indicating that the oxidation product PNTP is not generated, independent of AC voltage and frequency. (c) demonstrates, through the appearance of new Raman bands, that a threshold offset bias is required for plasmonic catalysis of PATP → PNTP. (d) indicates that the optimum combination of AC voltage and offset is ~15-25 V and >200 mV respectively, while (e) shows that >40 kHz AC frequency is required for optimal results (as measured through product yield indicated by product band intensities). Increasing the voltage above ~30V causes a rapid decrease in SERS intensity and catalytic deactivation of the template (the origins of which are both electronic and pyroelectric, as discussed in the main paper). Note that increasing the offset bias >30 V also results in a sharp reduction in SERS intensity (not shown).

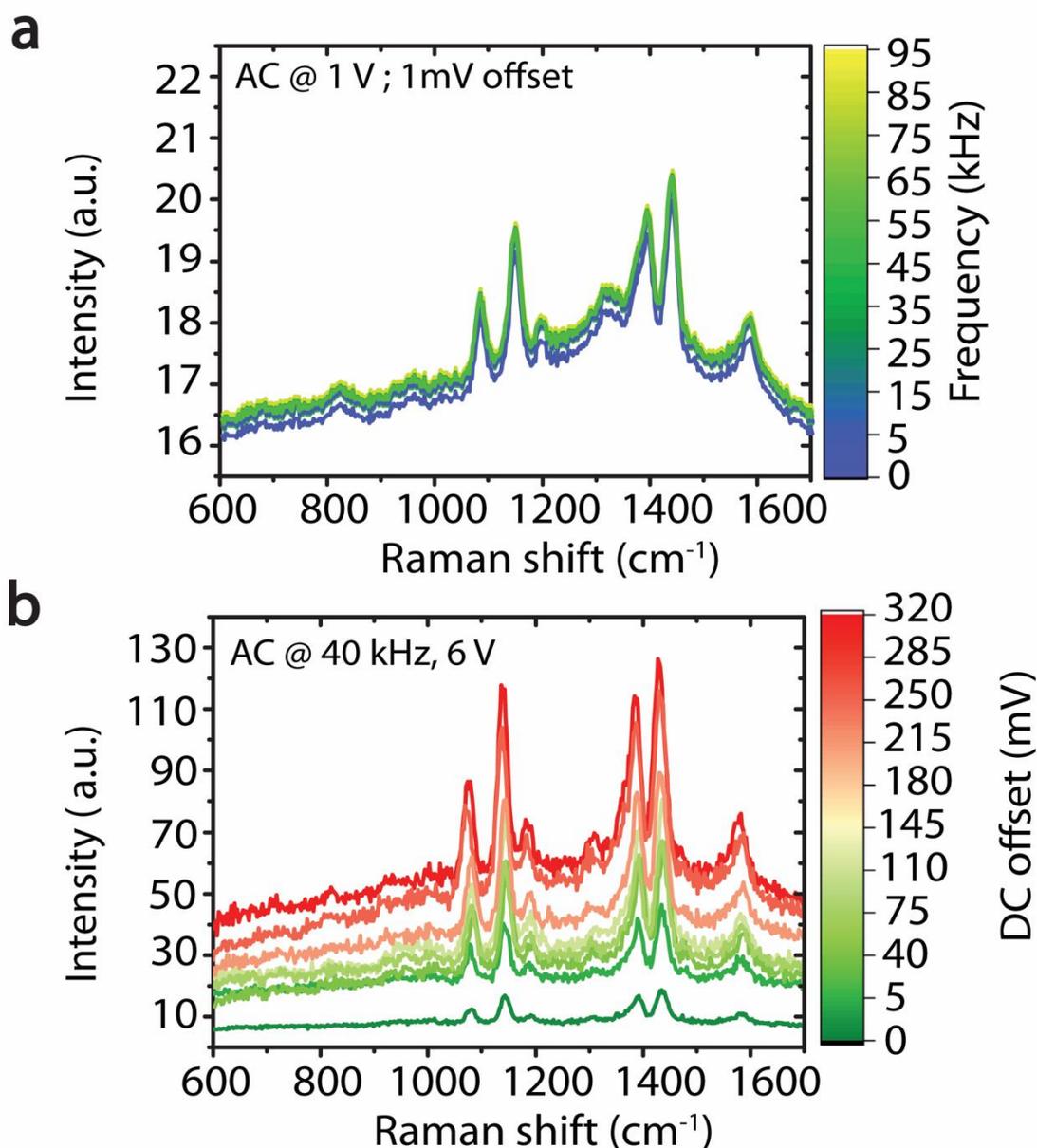


Supplementary Figure 8. SERS spectra of PATP on the FF-PNT/Ag NP template, showing relaxation after removing the electric field. The equilibrated spectrum at $t < 0$ minutes (dark green) is obtained for 10 V AC at 40 kHz with 350 mV offset bias; the electric field is then removed by turning off the electric field (0 V AC and 0 mV offset) at $t = 0$. Spectra are then recorded after t minutes, and demonstrate how the product yield can be controlled. In particular, at long times $t > 60$ minutes, the original spectral features of PATP are recovered. We note also that switching to e.g. 4 V AC with 100 mV offset at $t = 0$ produces very similar results, since these conditions are below the threshold for PNTP generation by template-mediated plasmonic catalysis.

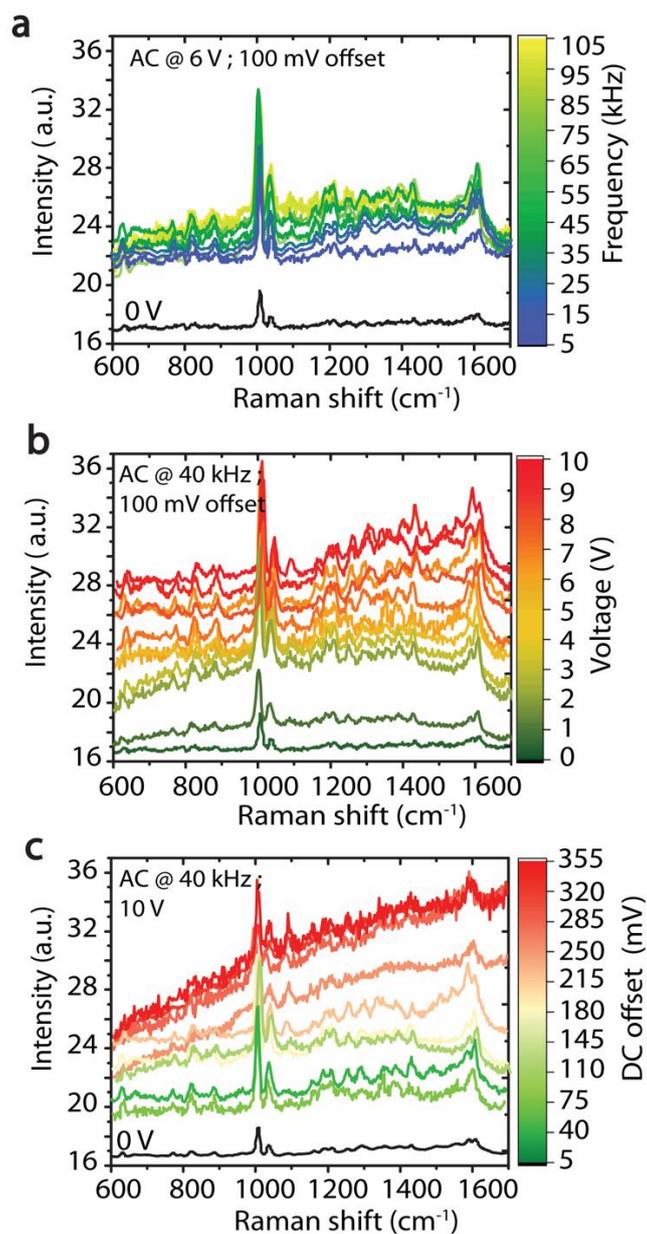


Supplementary Figure 9. SERS spectra of PATP on the FF-PNT/Ag NP template. SERS spectra recorded under different conditions: with electric field (yellow line), with electric field and exposure to UV (light green line), UV exposure only (red line), relaxation after 16 minutes (purple line), control (blue line), and FF-PNTs only (dark green line).

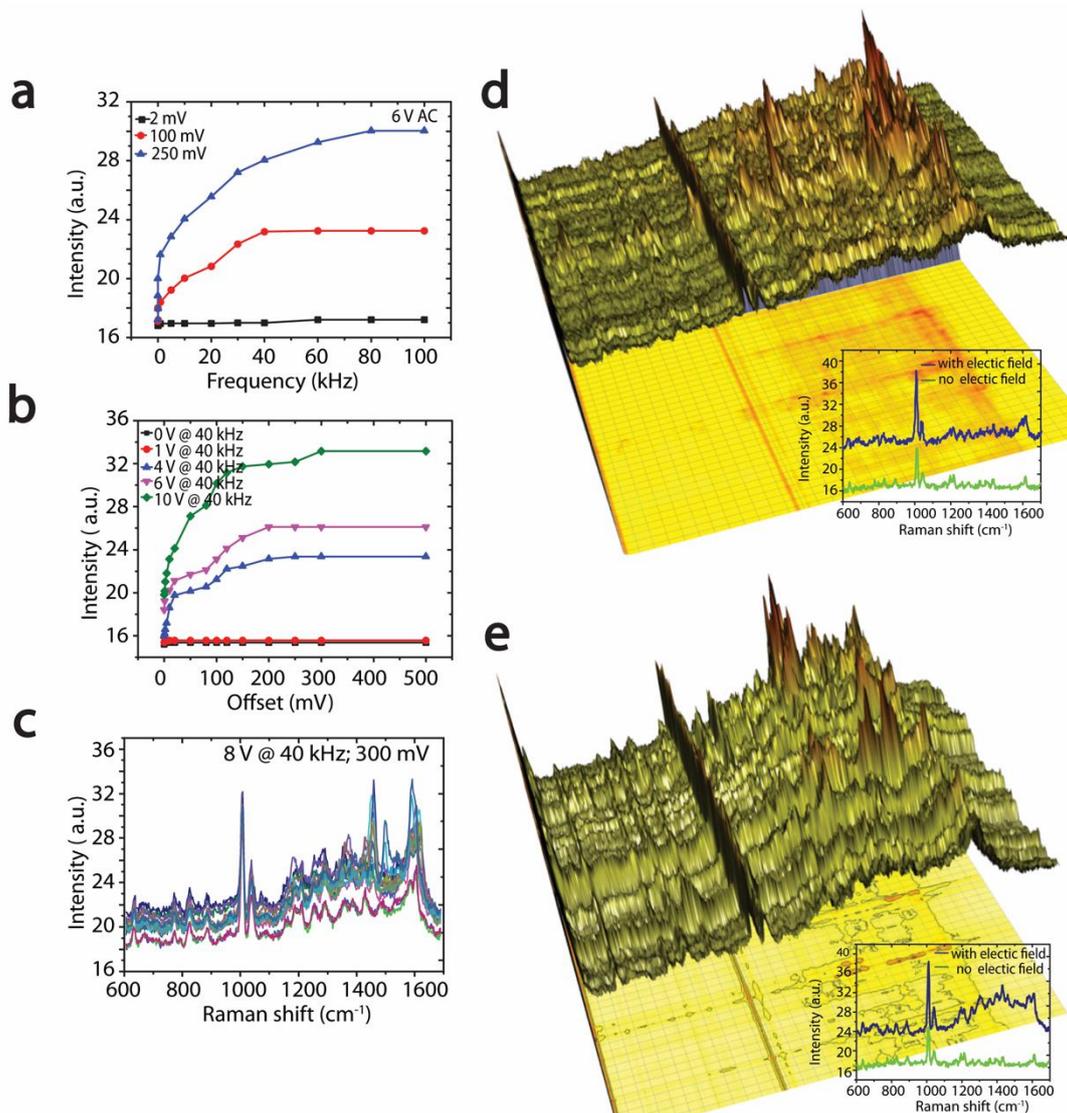
Supporting control studies



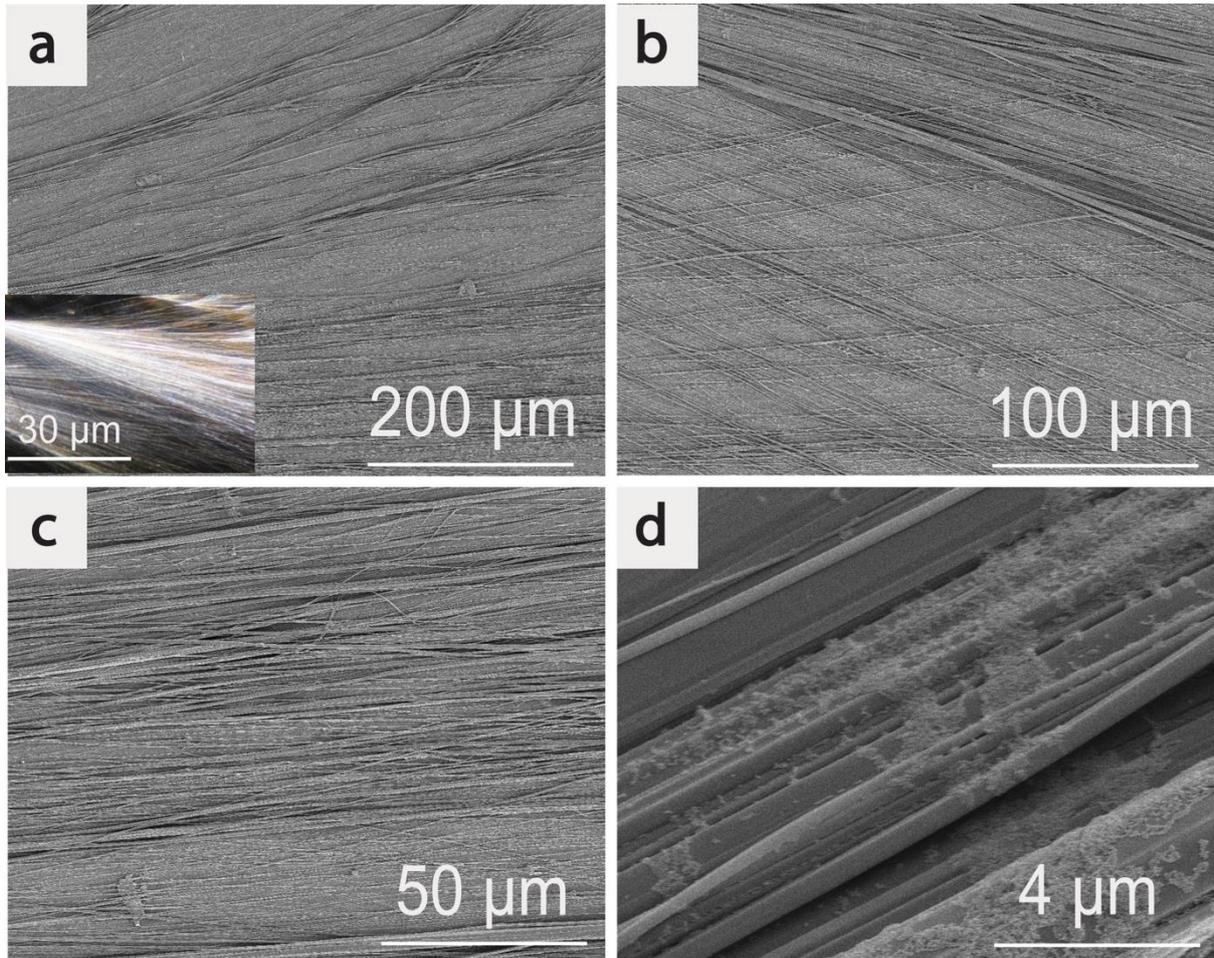
Supplementary Figure 10. SERS spectra of PATP on Ag NPs on a SiO_2 substrate in the absence of FF-PNTs. (a) Constant 1 V AC and 1 mV offset DC bias, varying frequency. Under these conditions, very little change in the SERS spectrum is observed. **(b)** Constant 6 V AC at 40 kHz frequency, varying the DC offset bias. Note that, although the SERS signal intensity increases on increasing the offset bias under these conditions, no new bands are observed. This indicates that PNTP is not generated from PATP when using the Ag NPs alone. The template including FF-PNTs is required for plasmonic catalysis of the oxidation reaction; by contrast to the results presented in here **(b)**, Fig. 2 shows new bands corresponding to PNTP at e.g. 6 V AC at 40 kHz and 200 mV offset. We speculate that the increase in SERS signal observed here is due to aggregation of Ag NPs forming an electrically conductive network.



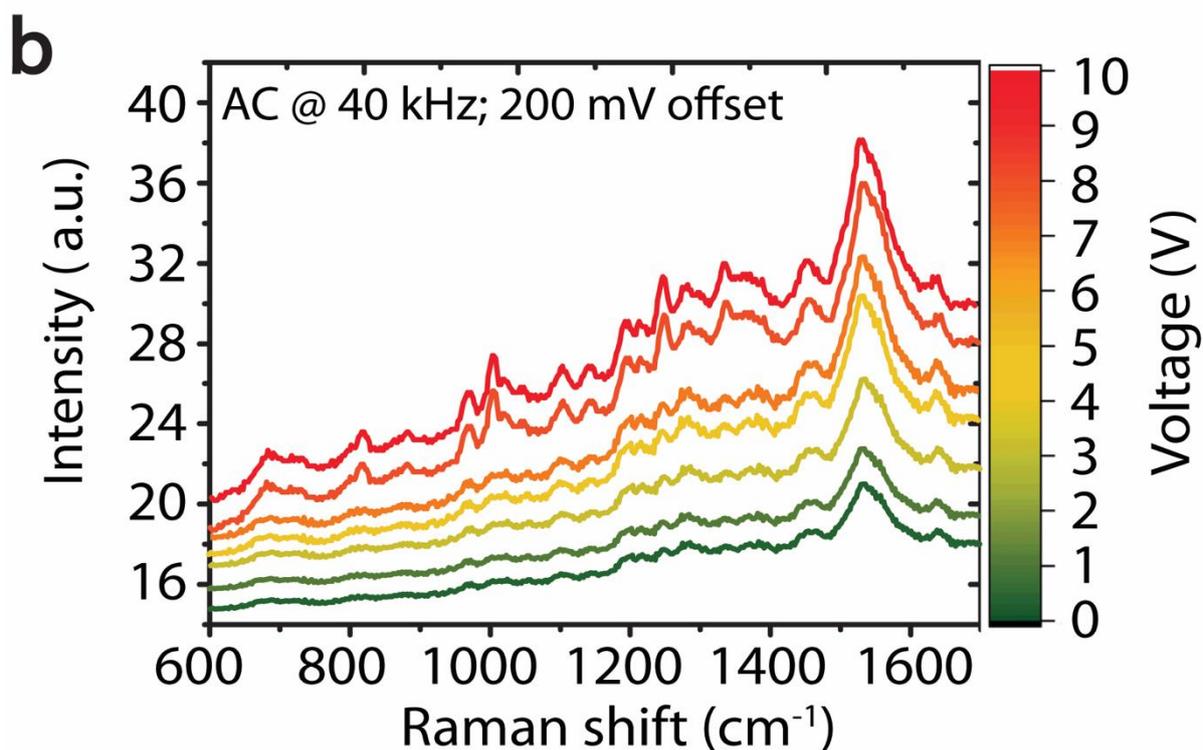
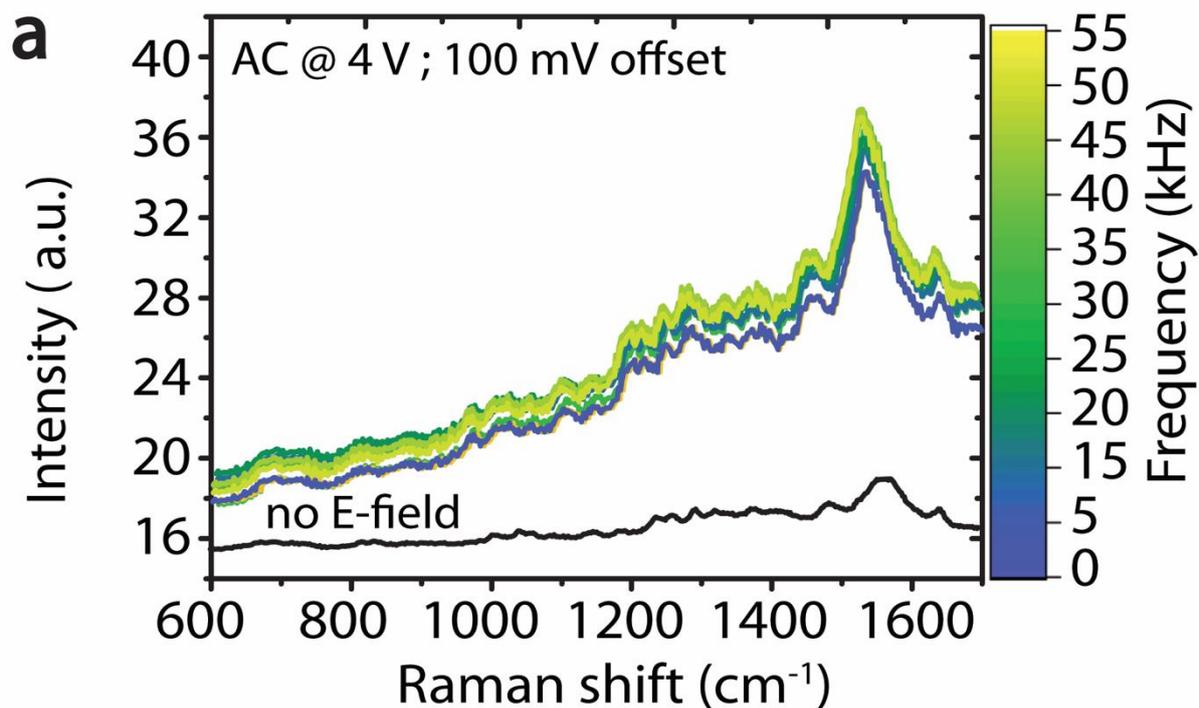
Supplementary Figure 11. SERS measurements of the FF-PNT/Ag NP template (only), in the absence of the probe molecule. (a) Constant 6 V AC with 100 mV bias offset at different frequencies. **(b)** Constant 100 mV bias offset, varying AC voltage (at 40 kHz). **(c)** Constant 10 V AC at 40 kHz, varying DC offset bias. These SERS data, obtained for the template in the absence of the probe molecule, show that all FF-PNTs Raman peaks are clearly visible and detectable under all relevant conditions. In particular, we observe the aromatic ring breathing mode at 1002 cm^{-1} and a phenyl vibrational band at 1603 cm^{-1} . Modes at 1249 cm^{-1} corresponding to amide III vibrations are seen, which indicate a strong coupling between $C_{\alpha}\text{-H}$ and N-H bending vibrations, in agreement with density functional theory calculations reported in the assignment of FF-PNT Raman modes⁸⁻¹¹. The intensity of the amide I mode (1670 cm^{-1}) can be used to determine the orientation of the carbonyl groups in FF-PN with respect to the nanotube axis. The amide I Raman band is mainly attributed to a C=O stretching vibrational mode along with C-N stretching and $\text{C}_{\alpha}\text{-C-N}$ deformation⁸⁻¹¹. The amide I frequency (1670 cm^{-1}) indicates that only N-H is involved in hydrogen bonding^{9,11}. The Raman band at 1418 cm^{-1} (assigned to the symmetric stretching vibration) also showed a strong polarization effect^{9,11}. The intense band located at 1002 cm^{-1} , corresponding to the in-plane breathing mode of the phenylalanine benzene rings, increased linearly with applied electric field. Once both the voltage and offset DC bias are increased sufficiently, as shown in **(b)** and **(c)**, an increase in SERS intensity was observed, combined with intense fluctuation and blinking in the Raman spectral window between $1200 - 1670\text{ cm}^{-1}$.



Supplementary Figure 12. SERS spectra of the FF-PNT/Ag NP template (only), in the absence of probe molecule. (a) SERS intensity of the 1002 cm⁻¹ band as a function of AC frequency at 6 V for different values of the offset bias. **(b)** SERS intensity of the 1002 cm⁻¹ band as a function of offset bias for different voltages, at 40 kHz AC. **(c)** SERS intensity blinking recorded sequentially for 10 V at 40 kHz AC and 300 mV offset. **(d, e)** 3D time series plots for SERS spectra recorded sequentially for 9 V at 40 kHz AC and 100 mV offset. The strong fluctuation in the spectra could be an indication of possible charge transfer process induced by the electric field. When the AC voltage and bias offset are increased above ~6 V and ~100 mV, respectively, a 4 to 5-fold increase in SERS intensity is observed, combined with intense fluctuation and blinking in the Raman spectral window between 1200 – 1670 cm⁻¹. The blinking observed in the spectra potentially arise from an increase in Ag NP electron density, induced by electric field-activated charge transfer between the FF-PNTs and Ag NPs (see theoretical analysis presented in the main paper). We note there are no signs of geometrical, topological, or morphological changes of the FF-PNT/Ag NP template on application of the electric field, as seen in SEM images (Supplementary Fig.13). These results further establish the stability of the template.

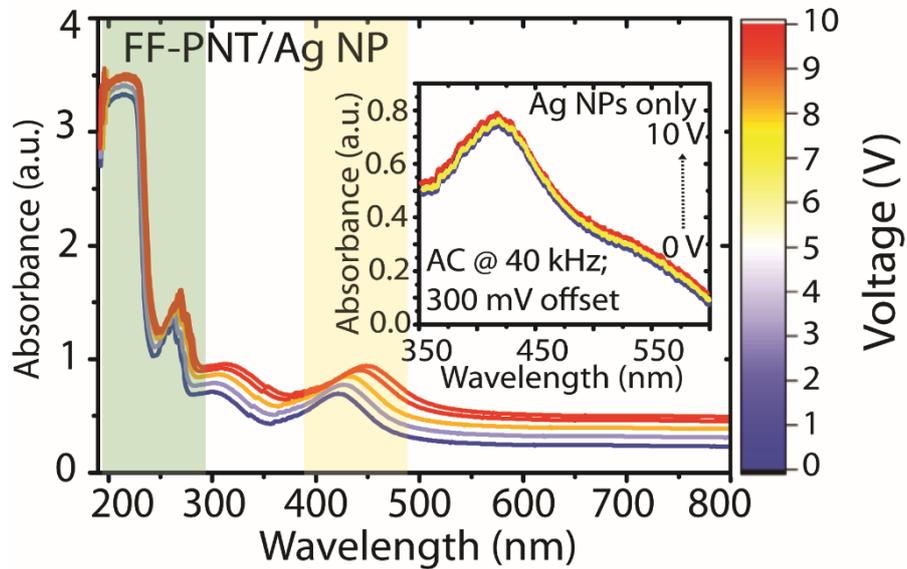


Supplementary Figure 13. Stability of the template after the application of electric field. SEM images of FF-PNTs on the microfabricated device without Ag NPs (a,b) and with Ag NPs (c,d), for 10 V AC at 40 kHz and 300 mV offset. On increasing the voltage to 25 V, no geometrical, topological, or morphological changes are observed, indicating that the template is stable and the structure can withstand application of high voltages, consistent with previous work^{10,12}, which demonstrated template stability under high laser illumination with a power density of ~ 6.25 MW/cm². These results demonstrate that FF-PNT are promising materials that could be used as an alternative to carbon nanomaterials to prevent photobleaching^{10,12}.

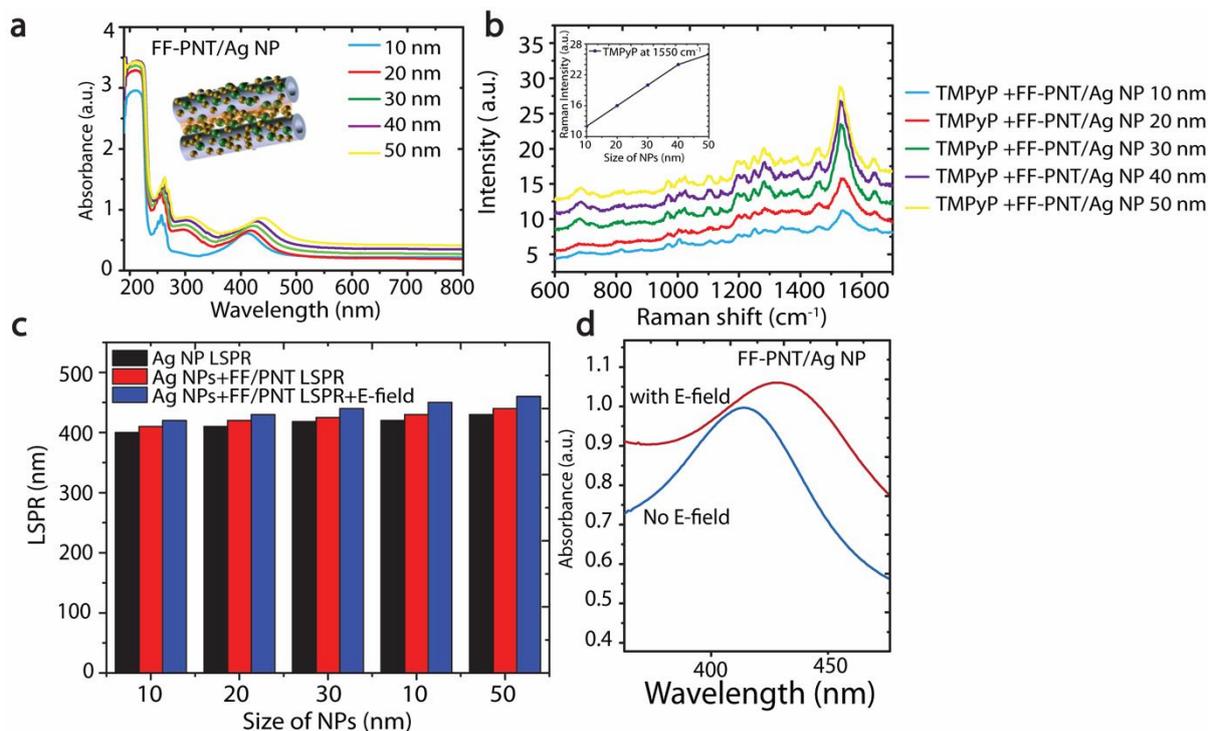


Supplementary Figure 14. SERS measurements of the probe molecule Tetrakis(1-methyl-4-pyridinio) porphyrin (TMPyP) on the FF-PNT template. **(a)** Constant 4 V AC with 100 mV offset bias, varying frequency (black line shows the zero-field spectrum at 0V for reference). **(b)** Varying voltage at 40 kHz AC, with constant 200 mV offset bias. The intense band at 1552 cm^{-1} exhibits a ~ 5 fold increase in SERS intensity on increasing voltage to 10 V AC, but no new bands appear.

Optical absorption measurements (UV vis)



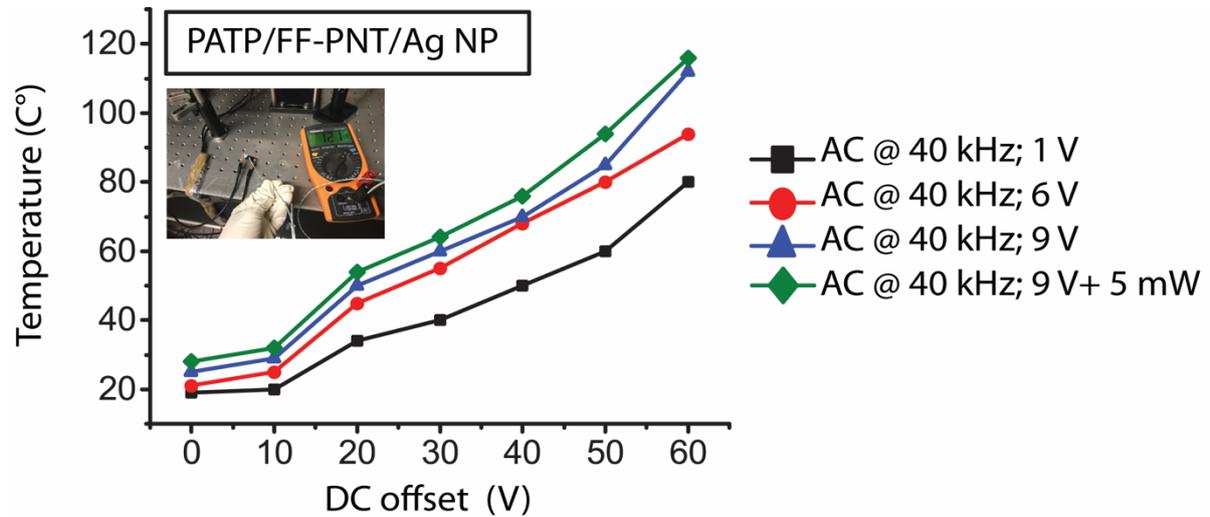
Supplementary Figure 15. UV-vis absorption spectra of the template FF-PNT/Ag NP on glass. UV vis spectra for voltages in the range 1-10 V at 40 kHz AC and 300 mV offset bias. Inset shows for comparison the spectra obtained for Ag NPs only, without the FF-PNTs.



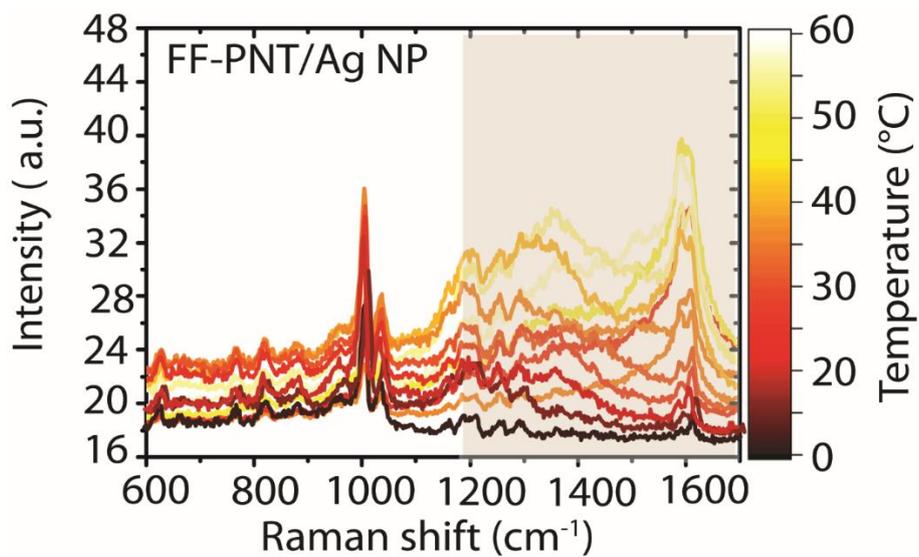
Supplementary Figure 16. UV vis absorption and SERS spectra of the FF-PNT/Ag NP template for different NP size. (a) UV vis absorption spectra recorded for nanoparticles with different sizes. **(b)** SERS spectra recorded for nanoparticles with different sizes. **(c)** Histogram plot for LSPR frequency as a function of nanoparticle size. **(d)** UV vis absorption spectra recorded with and with an applied electric field.

Larger NP size is found to yield higher SERS intensity and therefore improves sensitivity, consistent with results of previous studies¹³. This is likely due to the higher electromagnetic field associated with larger NPs and the fact that larger NPs aggregate more, leading to more hotspots in the substrate.

Heating effects

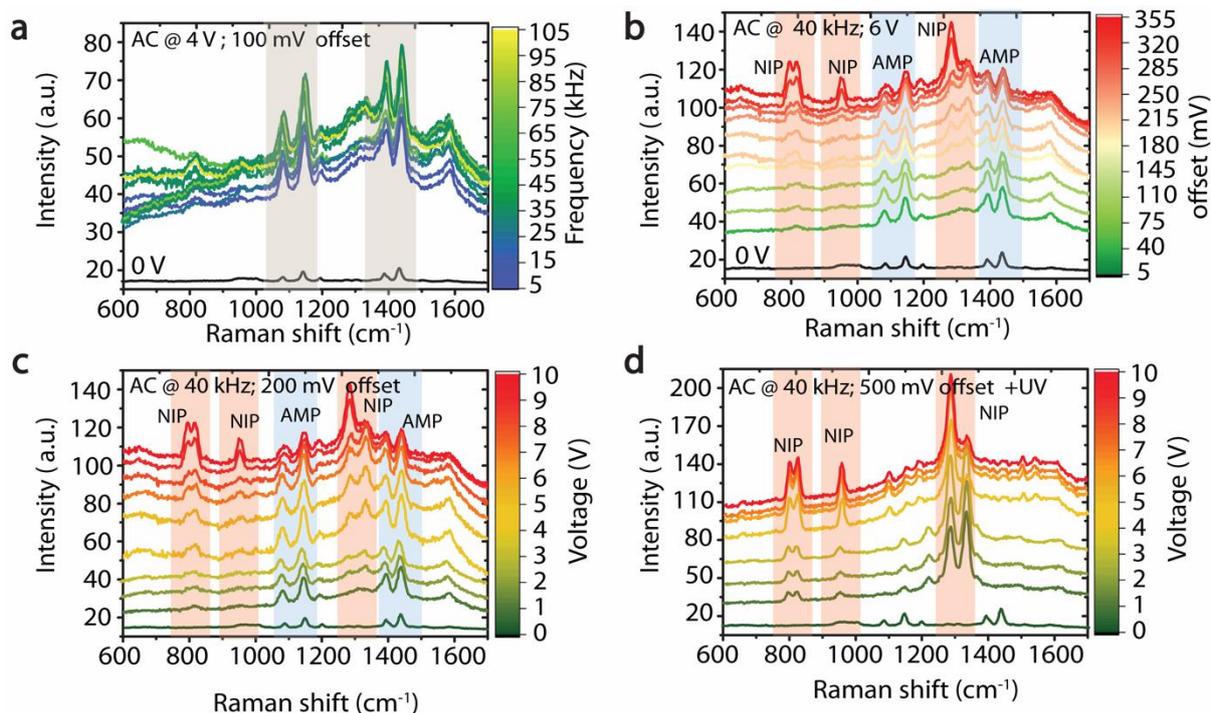


Supplementary Figure 17. Evolution of temperature of the PATP/FF-PNT/Ag NP system on increasing the DC offset bias, for various AC voltages. As expected, the temperature increases with both AC and DC voltages. The green points also include the effects of a photoexcitation laser of 5 mW power ($\lambda_{\text{ex}} = 532 \text{ nm}$).

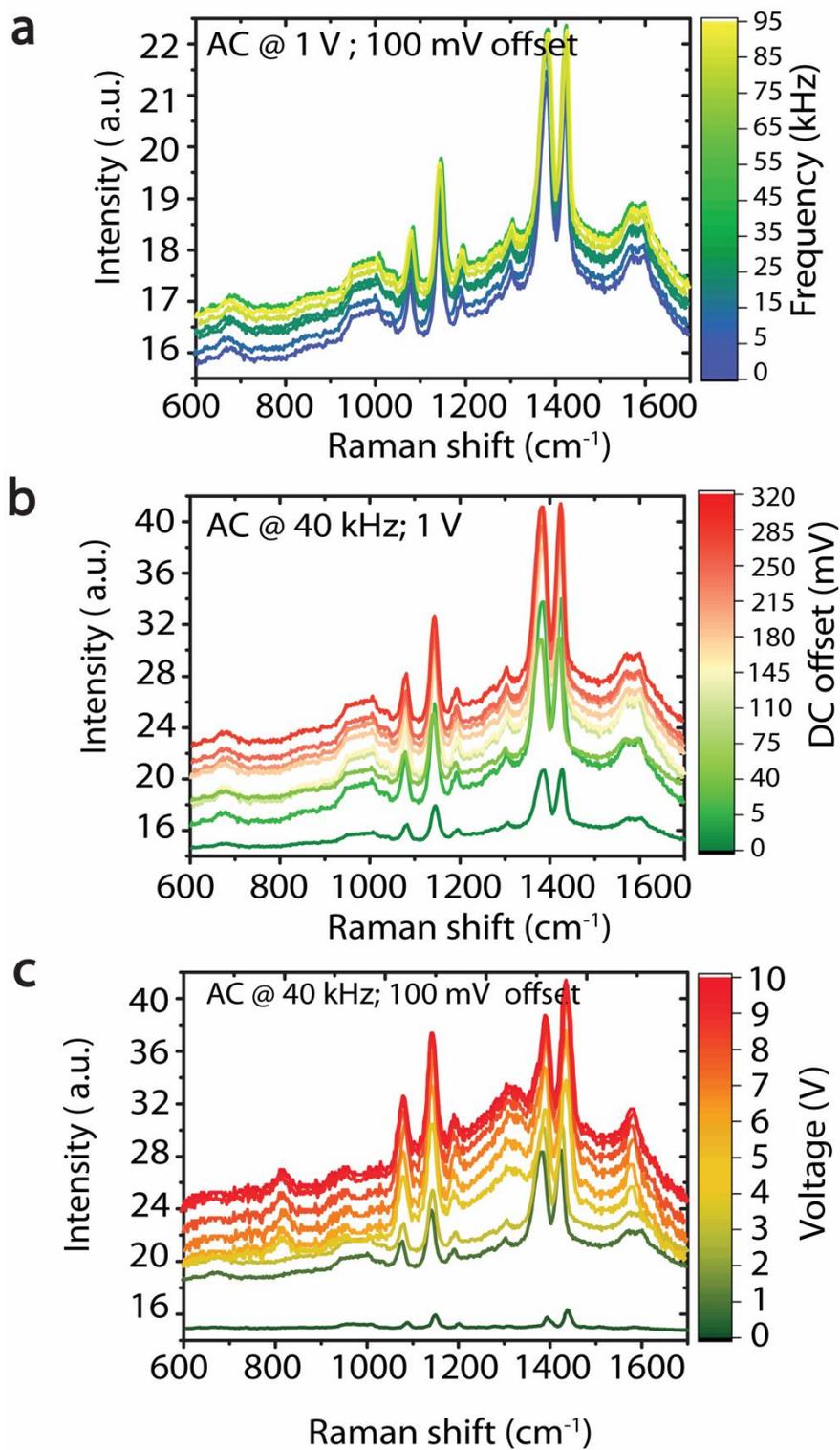


Supplementary Figure 18. SERS spectra of the FF-PNT/Ag NP template at different temperatures. Temperature shown is set and controlled with an electrical hot-plate heater.

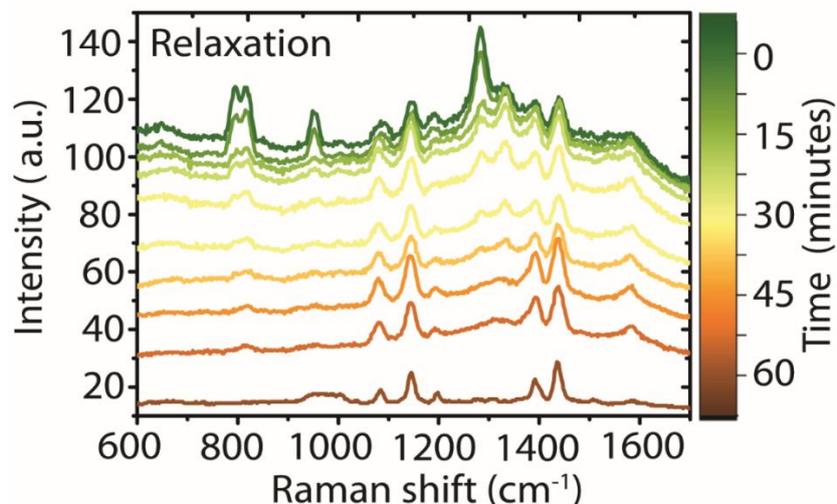
Photocatalysis and field effects for molecule 2-AMP



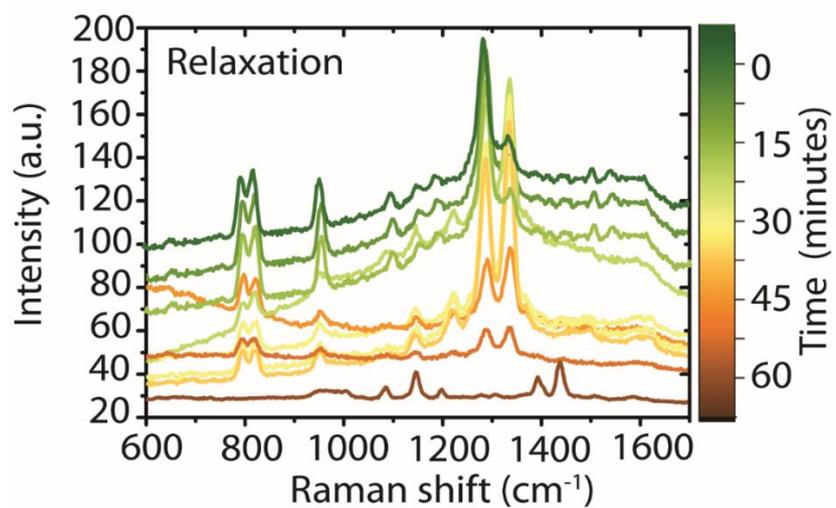
Supplementary Figure 19. SERS spectra of probe molecule 2-AMP on the FF-PNT/Ag NP template under different conditions. (a) Data obtained for constant 4V AC voltage and 100 mV offset bias, varying AC frequency. (b) Constant 6V AC at 40 kHz, varying the offset bias. (c) Constant 200 mV offset bias, varying AC voltage at fixed 40 kHz frequency. (d) As for (c) but with 500 mV offset and with additional super bandgap UV irradiation. Without electric field (0V, black reference lines in a, b), the 2-AMP SERS spectra has peaks located at 1580 (C–C symmetric stretching mode), 1440 (C–H in-plane bending modes), 1390 (C–H in-plane bending modes), 1180 (C–H in-plane bending), 1145 (C–N stretching), and 1098 cm^{-1} (CS stretching)^{6,7,14–17}. Applying a sufficiently strong electric field (voltage >4 V and offset DC bias >100 mV) results in an ~8 fold increase in SERS intensity (panels b, c). Changes in the SERS spectral features with electric field include the strong appearance of bands at 1285 (C–N stretching mode, $\nu(\text{C–N})$) and 1334 (amine scissoring mode, $\delta(\text{NH}_2)$ cm^{-1}), signifying the transformation from 2-AMP to 2-NIP^{14–17}. The appearance of bands at lower wave numbers, such as 920 (SH), 858 (C–S stretching mode), and 820 cm^{-1} (CH bending vibration of the nitro group) are also assigned to the oxidized product 2-NIP. Combining both electric field with UV irradiation ($\lambda = 254$ nm; for ~20 or 40 min) as in panel (d) at different voltages using a high offset DC bias (500 mV) resulted in the rapid transformation of 2-AMP to 2-NIP with a ~10 fold increase in SERS intensity.



Supplementary Figure 20. SERS spectra of 2-AMP on Ag NPs on a SiO_2 substrate, in the absence of FF-PNT. (a) 1V AC, with 1mV DC offset bias, varying AC frequency. **(b)** 1V AC at 40 kHz frequency, varying the DC offset bias. **(c)** AC at 40 kHz frequency, varying voltage with constant offset bias of 100mV.

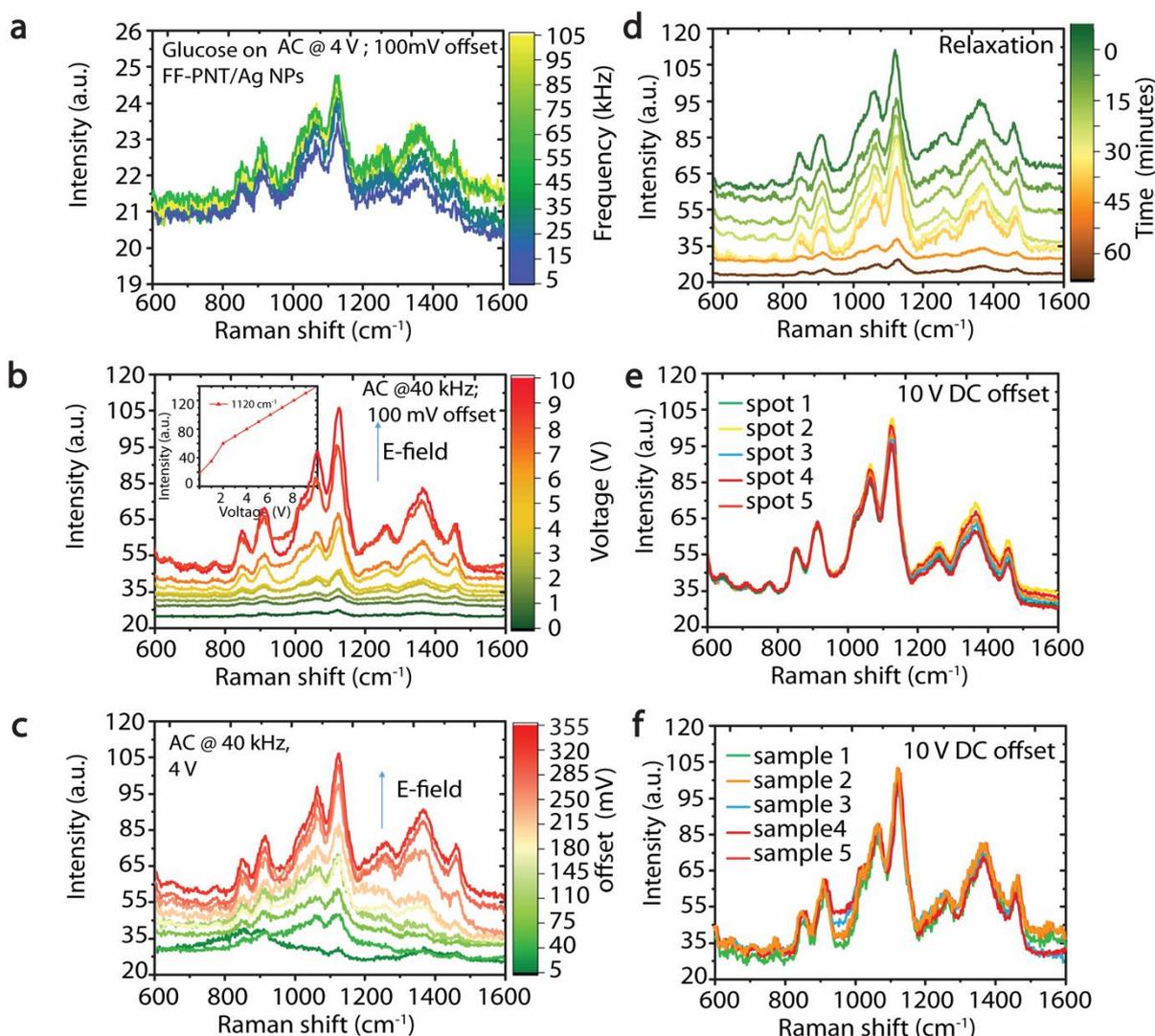


Supplementary Figure 21. SERS spectra of 2-AMP on the FF-PNT/Ag NP template, showing relaxation after removing the electric field. The equilibrated spectrum at $t < 0$ minutes (dark green) is obtained for 10 V AC at 40 kHz with 350 mV offset bias; the electric field is then removed by turning off the electric field (0 V AC and 0 mV offset) at $t = 0$. Spectra are then recorded after t minutes, and demonstrate how the product yield can be controlled. In particular, at long times $t > 60$ minutes, the original spectral features of 2-AMP are recovered. We note also that switching to e.g. 4 V AC with 100 mV offset at $t = 0$ produces very similar results, since these conditions are below the threshold for 2-NIP generation by template-mediated plasmonic catalysis.

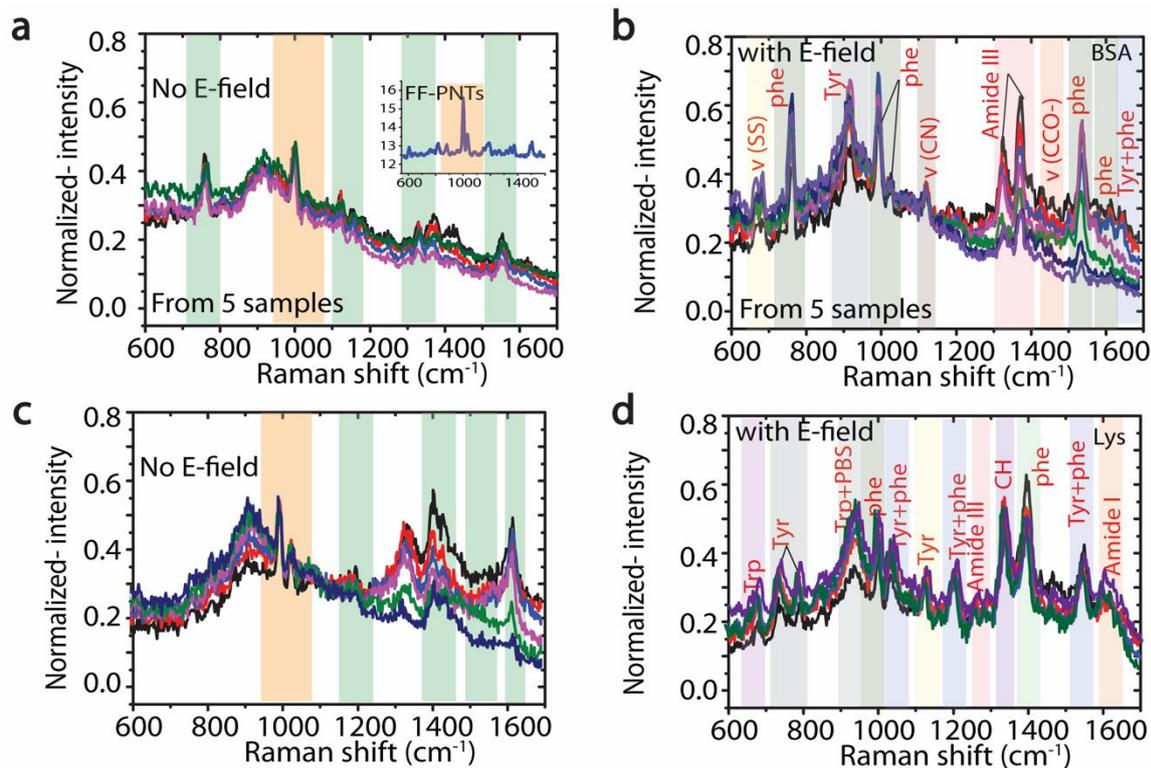


Supplementary Figure 22. SERS spectra of 2-AMP on the FF-PNT/Ag NP template with UV irradiation, showing relaxation. As Supplementary Figure 21, but with additional UV irradiation ($\lambda_{\text{ex}} = 532 \text{ nm}$).

SERS sensing



Supplementary Figure 23. SERS measurements of glucose target molecules on the FF-PNT/Ag NP template under different conditions. (a) Constant 4V AC with 100 mV offset bias, varying frequency. **(b)** Constant 100 mV offset bias with 40 kHz AC, varying voltage. Inset shows Raman intensity of the 1120 cm⁻¹ band associated with glucose as a function of voltage, showing sensing enhancement. **(c)** Constant 4V AC at 40 kHz, varying the offset DC bias, showing sensing enhancement. **(d)** Relaxation after removing electric field, following the protocol of Supplementary Figure 21. **(e)** Uniformity and reproducibility tests on the sample at different physical locations (spot tests), showing a 5% variability in signal intensity. **(f)** As in **(e)** but with using different samples, and showing a 4% variability in signal intensity.



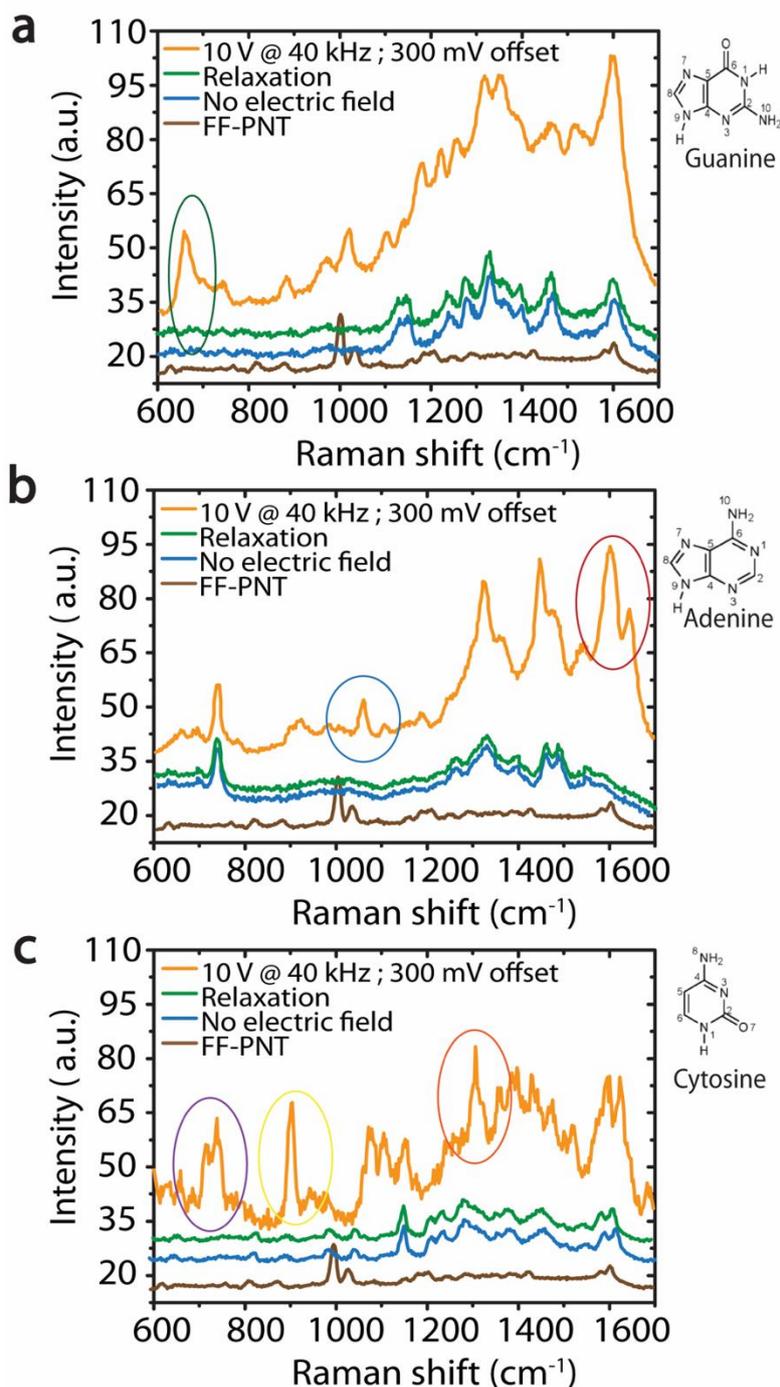
Supplementary Figure 24. Reproducibility tests on the template. SERS measurements of target molecule BSA (**a,b**) and Lys (**c,d**) on the FF-PNT/Ag NP template, without electric field (**a,c**) and with electric field (b,d). The different spectra are for different samples, showing a 5-6% variability in signal intensity, thereby demonstrating the good reproducibility of field-enhanced sensing using the FF-PNT/Ag NP template^{21,22}.

Supplementary Table 1. Raman peak positions in the SERS spectra of thymine with FF-PNT/Ag NP template. Assignment of the bands are shown based on refs^{19,20}. Shown also are band intensities: vs, very strong; s, strong; m, medium; w, weak; vw, very weak, along with conformational assignments: br, broad; bend, bending; breath, breathing; def, deformation; wag, wagging; str, strong.

Wavenumber (cm ⁻¹)	Plane	Assignment
1600 m	in	C ₂ = O, C ₄ = O
1520 m	in	ring str
1477 s	in	bend CH ₃
1397 vs	in	bend N ₁ -H, N ₃ -H
1352 s	in	bend CH ₃ , def C ₆ -H
1279 s	in	ring str
1221 m	in	str C ₅ -C ₉
1198 m	in	bend C ₅ -H, str C ₅ -C ₆ , C ₆ -N ₁
1035 vw	out	wag CH ₃
1000 w, 935 s	out	wag N ₁ -H, N ₃ -H
820 w	out	ring def
785 vs	in	ring breath
630 w	in	C ₂ = O ₂ , C ₄ = O def

Supplementary Table 2. Raman shift values in the SERS spectra of uracil with FF-PNT/Ag NP template. Assignment to vibrations of uracil based on refs^{19,20}. Shown also are band intensities: vs, very strong; s, strong; m, medium; w, weak; vw, very weak, along with conformational assignments: br, broad; bend, bending; breath, breathing; def, deformation; wag, wagging; str, strong.

Wavenumber (cm ⁻¹)	Plane	Assignment
1630 s	in	str C ₂ = O, C ₄ = O, bend N ₁ -H, C ₅ -H
1530 w	in	str C ₅ -C ₆ , C ₆ -N ₁ , bend C ₆ -H
1485 m	in	bend N ₁ -H, C ₆ -H, C ₅ -H
1402 vw	in	bend N ₁ -H, C ₆ -H, C ₅ -H
1375 vw	in	bend N ₃ -H, C ₅ -H, C ₆ -H
1300 s	in	bend N ₃ -H, C ₅ -H, C ₆ -H
1279 m	in	str N ₃ -C ₄ , C ₄ -C ₅ , C ₆ -N ₁ , bend N ₁ -H, C ₅ /6-H
1198 m	in	bend C ₅ -H, str C ₅ -C ₆ , C ₆ -N ₁
1100 m	in	bend C ₅ -H, str C ₅ -C ₆ , C ₆ -N ₁
1020 m	in	ring def
920 vw	out	wag C ₆ -H
802 w	in	ring breath
780 w	out	ring def
700 m		
619 w	in	ring def



Supplementary Figure 25. SERS sensing from DNA based molecules with electric field.

SERS measurements of **(a)** guanine, **(b)** adenine, and **(c)** cytosine, on the FF-PNT/Ag NP template, demonstrating template-mediated field-enhanced sensing. Orange lines correspond to the optimal 10V AC at 40 kHz with 300 mV offset, showing enhancement over the spectra with no electric field (0V, blue lines) or the spectra recorded after relaxation (16 minutes, green lines). The brown lines are for FF-PNT only, without the target molecules, shown for reference. For these molecules, in addition to enhanced sensing, we also observe the appearance of new bands when the electric field is applied, indicating formation of oxidation products from the nucleotides, as highlighted in the figure with colored circles. For example, a new band at 684 cm⁻¹ signifies oxidation of guanine¹⁸ in **(a)**. This provides additional evidence of the effect of the electrical field used in conjunction with the template, and its potential utility for plasmonic catalysis.

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