Supplementary Information

Total Electrification of Large-Scale Nanophotonic Arrays by Frictional Charges

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Emission spectra of light source

Figure S1 below shows the emission spectra of the white light used in our work.

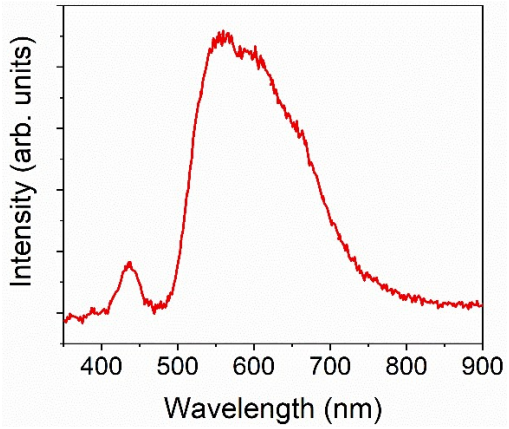

Figure S1. The emission spectra of the white-light LED used for KPFM experiments.

LSPR correlation to KPFM surface potential

The variation of the surface potential (SP) as a function of the illumination percentage in KPFM experiments can be explained in terms of the number density ($N_{hot\text{-}electrons}$) of generated hot electrons, which is dependent on its generation rate (R) and electronic relaxation time (T_e), as $N_{hot-electrons} \sim T_e \times R_{hot-electrons}$ [1], [2]. By assuming T_e is a constant in the steady-state, the generation rate of high-energy hot-electrons in spherical nanoparticles, which can overcome the barrier height, E_b, and are different from the low-energy carriers (Drude response), can be estimated as following:

$$R_{hot-electrons} = \frac{2}{\pi^2} \times \frac{e^2 E_F^2}{\hbar\omega} \frac{1}{(\hbar\omega)^3} \frac{4\pi}{3} R_0^2 \left| \frac{3\varepsilon_0}{2\varepsilon_0 + \varepsilon_{metal}} \right| \frac{2\pi}{c_0\sqrt{\varepsilon_0}} I_0 \qquad (1)$$

where I_0 is the intensity of the incident light, R_0 is the radius of the Au nanoparticles and ε_0 and ε_{metal} are the dielectric constants of air and metal, respectively [1], [2]. As can be observed in the above equation, an increase in the intensity of the light will invariably lead to an increase in the rate of generation of of high-energy electronic charge carriers *i.e.*, hot electrons. Given that the SP of the Au/ITO rises upon illumination whilst that of PDMS remains constant, an increasing difference in work functions should invariably lead to an increase in the electrical output [3] of the Au/PDMS TENG as observed in Figure 2(a-e) in the main manuscript. We also plot the relative (normalized by the rate of smallest particle size) amount of hot electron

ejection rates upon increase in size of the Au nanoisland in Figure S2. Note that the chosen size range corresponds to the radius of the nanoislands in our LSPR substrate as shown by the statistics in Figure 1 of the main manuscript.

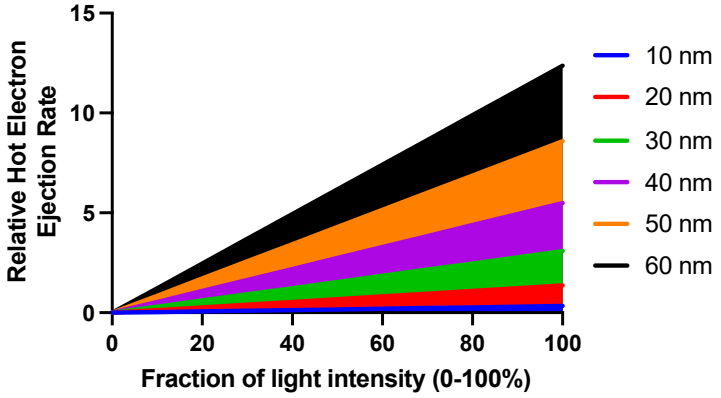

Figure S2. Relative rate of hot electron ejection in the LSPR substrate of our experimental setup

Kelvin probe force microscopy (KPFM)

Figure S3 below shows the KPFM characterisation of the Au/ITO substrate by varying the intensity of the light source.

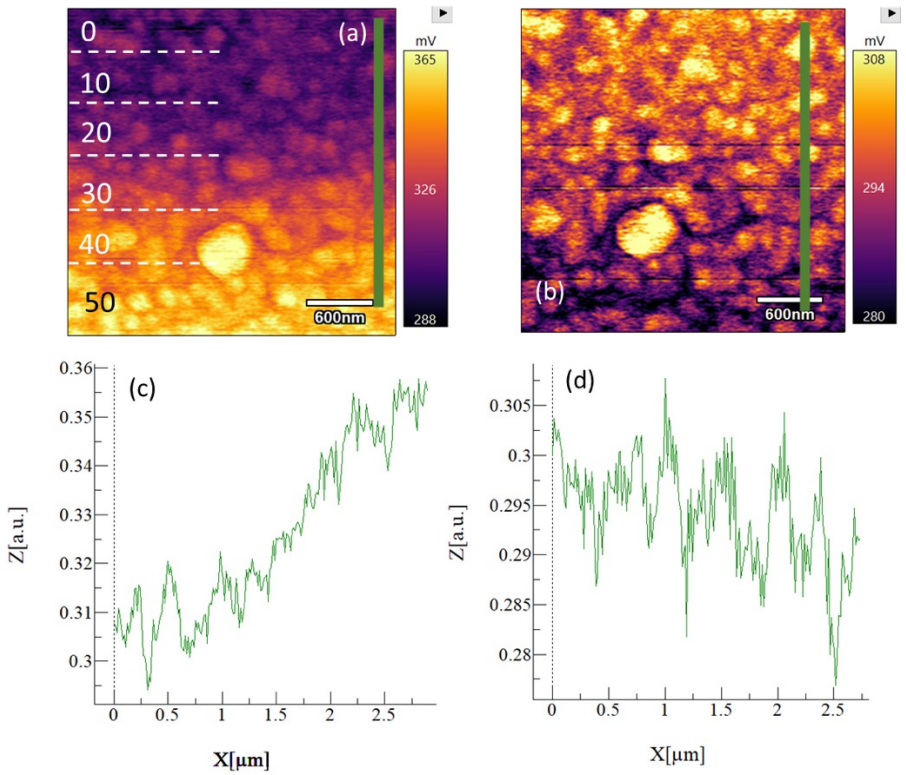

Figure S3. (a) KPFM images of Au/ITO sample at varying light intensity (the numbers correspond to the applied percentage of the full intensity) (c) with the corresponding line

profile. (c) KPFM scan of the same area after 1 hour showing the return of SP to the original (in dark) values and (d) the corresponding line profile.
Considering the KPFM measurement shown in Fig. 1(e), where the illumination was switched to the maximum value during the scan, the rise time can be calculated using the scan rate and pixels per line information. The image was acquired at 0.69754 Hz with 224 pixels/line and 224 lines, thus providing 3.2 ms/pixel temporal resolution for the image. As can be seen from the data extracted across the vertical line profile, the initial rise in the surface potential is quick, however, the maximum surface potential is reached in nearly 40 seconds after illumination.

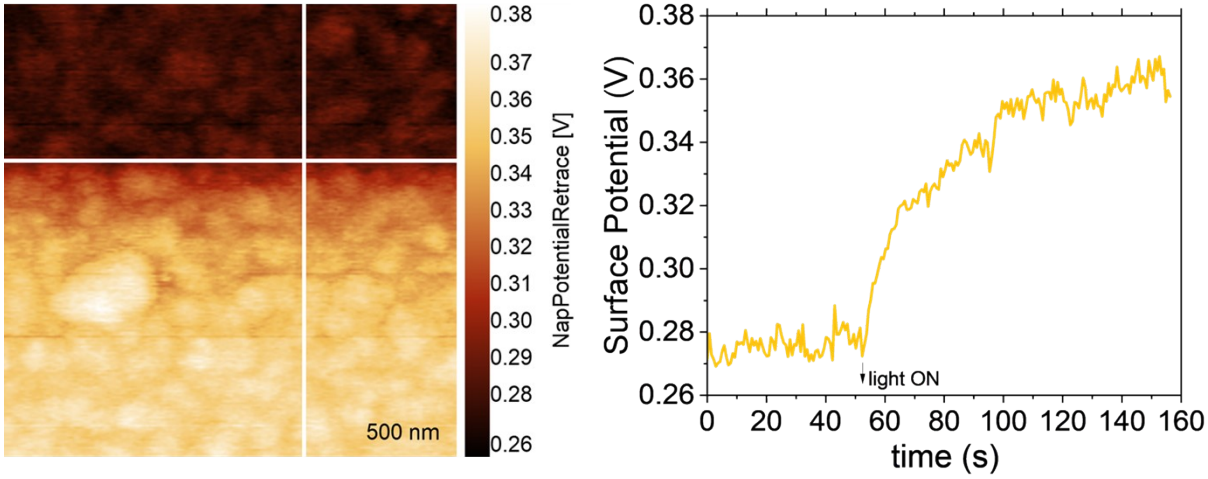

Figure S4. KPFM measurements on the Au/ITO substrates under dark and illuminated conditions. The vertical line profile upon conversion into temporal scale provides information about the rise time of the surface potential.

XPS depth-profiling & UPS

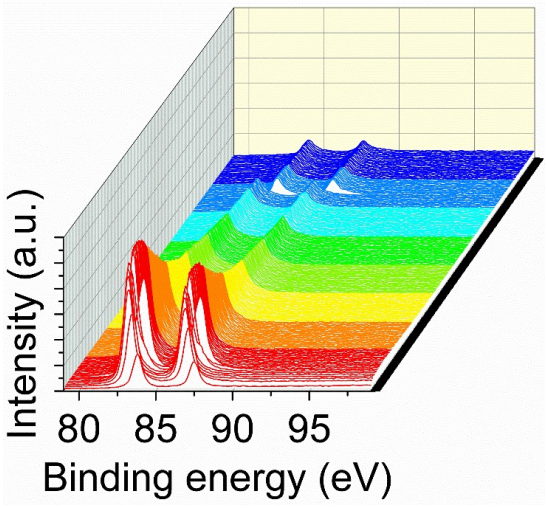

Figure S5. Depth-profile variation of the core-level Au 4f XPS spectra.

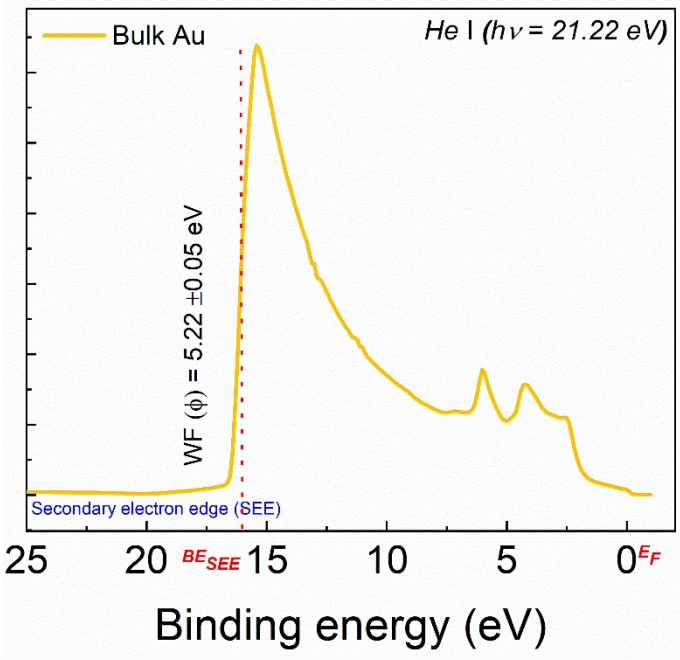

Figure S6. UPS spectrum for the Au reference

Theoretical modelling of Au-ITO interface

To find the thickness of the non-stoichiometric oxide layer between gold islands and ITO, we need to find a relation of the capacitance between Au nanoislands on top of an oxide dielectric covered conductive ITO. First, we approximate the capacitance by taking the semi-analytical equation, Eq.2, which calculates the capacitance between a conductive spherical (nanoisland is considered spherical in shape here) apex on the top of a dielectric covered conductive substrate [4]:

$$C = 2\pi\varepsilon_0 R ln\left(1 + \frac{\varepsilon_r R}{h}\right) + 4\pi\varepsilon_0 R \qquad (2)$$

In this equation, R is the radius of gold NPs (here 30 nm), ε_r is the dielectric constant of oxide formed between gold NPs and ITO (assumed 3.9) and h is the thickness of the oxide layer. As can be seen in this equation, both capacitance and oxide layer thickness is unknown. Therefore, to find the thickness of the oxide layer, we need to have the capacitance value. On the other hand, the approximate equation for the capacitance of a conductive sphere near a conductive wall is given by equation 3 below [4, 5]:

$$C = 4\pi\varepsilon_0\varepsilon_r R\sum_{n=0}^{\infty}\frac{2\sqrt{\frac{h}{R}(2+\frac{h}{R})}}{e^{(1+2n)cosh^{-1}(1+\frac{h}{R})}-1} \quad (3)$$

Moreover, in the sphere-plane model, taking the integral of the gradient of the capacitance [6] of the system the capacitance is calculated by equation 4:

$$C = -2\pi\sigma_{SP}\varepsilon_r\varepsilon_o R ln(h) \quad (4)$$

Where σ_{SP} is a proportionality constant characteristic of the experimental setup and which is assumed as a fitting parameter. To determine the thickness of oxide layer, the dependence of capacitance to the thickness was fitted to the expressions above, and the obtained best fit value is displayed in Table S1.

Table S1. Parameters of the Best Fit of Spherical Model

Analytical models	ε_r	$h\,(nm)$	$R(nm)$	σ_{SP}
C1-C2	3.9	1.06-1.08	30	----
C1-C3	3.9	1.1-1.2	30	0.082
C2-C3	3.9	1.22-1.24	30	0.082

Scanning electron microscopy

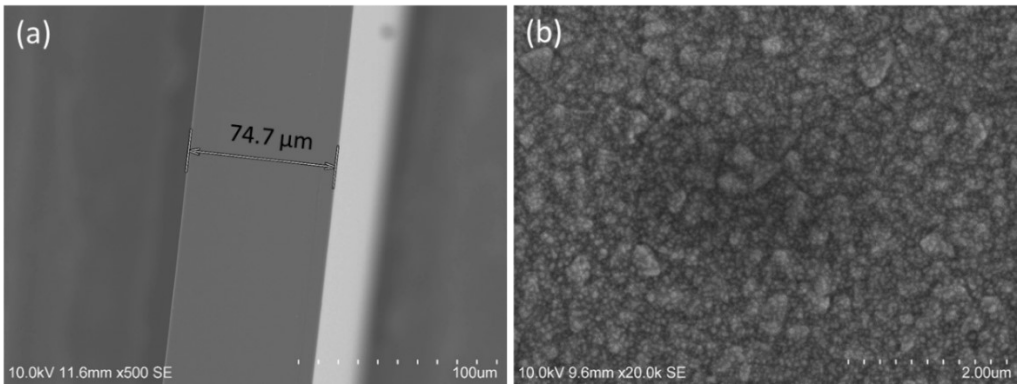

Figure S7. (a) Cross-sectional SEM image highlighting the PDMS film's thickness. (b) Surface morphology of the Au/ITO films, the undulations on the surface arise from the microstructure of the ITO surface itself.

Test bench

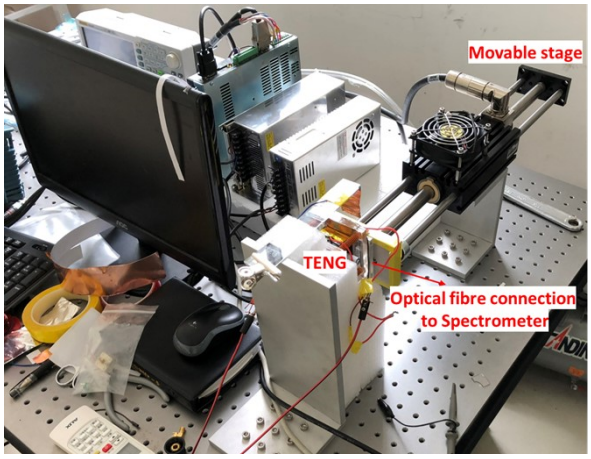

Figure S8. *Photograph of the test bench with the movable stage for TENG measurements clearly visible and marked out. The optical connections for the spectrometric measurements have been labelled.*

References

[1] Han, Gi Hyeon, et al. "Photo-stimulated charge transfer in contact electrification coupled with plasmonic excitations." *Nano Energy* 65 (2019): 104031.

[2] Besteiro, Lucas V., et al. "Understanding hot-electron generation and plasmon relaxation in metal nanocrystals: Quantum and classical mechanisms." *ACS Photonics* 4.11 (2017): 2759-2781.

[3] Yu, Zidong, et al. "Bismuth oxyhalide based photo-enhanced triboelectric nanogenerators." *Nano Energy* 89 (2021): 106419.

[4] Zhang, Yingjie, et al. "Sensing the charge state of single gold nanoparticles via work function measurements." *Nano letters* 15.1 (2015): 51-55.

[5] Crowley, Joseph M. "Simple expressions for force and capacitance for a conductive sphere near a conductive wall." *Proceedings of the ESA Annual Meeting on Electrostatics*. 2008.

[6] Salomão, Francisco C., et al. "Determination of high-frequency dielectric constant and surface potential of graphene oxide and influence of humidity by Kelvin probe force microscopy." *Langmuir* 31.41 (2015): 11339-11343.