

S1 – Fabrication of nanostructured Silicon/(Polystyrene bead monolayer) template

a) Template fabrication

Polystyrene beads of diameter 400 nm were obtained in the form of an aqueous from Sigma Aldrich. Equal quantities of the suspension and the mixture of MeOH+Triton-X100 (methyl alcohol+surfactant, 100:1 by volume) are mixed and are further diluted with equal volumes of DI water and the MeOH:Triton-X100 mixture [1]. To be precise, 75 μL of the nanosphere suspension was mixed with 75 μL of the MeOH:Triton-X100 mixture, followed by dilution with 30 μL (40% of the initial volume of the suspension drawn) of DI water and 30 μL of MeOH:Triton-X100. Silicon substrates which were cut in the form of 1'' $\times$ 1'' squares, were initially rinsed in acetone, isopropanol and DI water in sequence. Then the substrates were cleaned in a Piranha solution (1:1 (vol) mixture of sulphuric acid and hydrogen peroxide) at 80°C. After piranha cleaning, wafers were thoroughly washed with DI water and treated with 2% HF for 2 min to get the desired oxide free and hydride terminated Si wafer. On freshly prepared Si-H wafer, the polystyrene solution was spin coated at 3000 rpm for 60 seconds, to get uniform monolayer. The nano-sphere monolayer was removed from one half of the substrate by wiping with a dry cotton swab. This way the master template can be used to obtain planar and structured devices on the same substrate. Immediately after spin-coating, nanostructured (Si/polystyrene) template were transferred to nitrogen atmosphere and annealed for at 70°C for an optimal duration, discussed in the next section.

S2 – Optimization of annealing time for Si/nanosphere adhesion

If the annealing time t_a is insufficient, the spheres could be dislodged during the preparation of the inverse PDMS template, sticking to the PDMS while peeling off. Hence, the annealing time was varied to study its effect of the retention of the nano-spheres on the silicon substrate. This data is shown in Figure SF1 (a)-(g) for progressively increasing annealing time t_a . It is seen that there is significant peeling off of the nano-spheres for small annealing times ($t_a < 6$ hours), and a residual deposit of PDMS sticking to the silicon substrate. The dislodging of nano-spheres decreases for $t_a > 12$ hours, and shows almost no dislodging for $t_a = 48$ hours. This was used as an optimal annealing time. In particular, for $t_a = 0$ hr corresponding to no annealing, the SEM image in Figure SF1(a) shows that all spheres have been dislodged. For $t_a = 2$ hr and 6 hr, it is seen that only small islands of spheres are retained on the silicon. However for $t_a = 12$ hr, 24hr and 30 hr, it is seen that the spheres have been removed from relatively smaller areas (roughly within the highlighted rectangles in Figures SF1(d)-(f)), compared to the initial covered area. However for the case of $t_a = 48$ hr, the large area SEM image in Figure SF1(g) shows that there is virtually no dislodging of the nano-spheres. Hence with this optimal anneal time, the Si/Nanosphere templates can be used as permanent master templates.

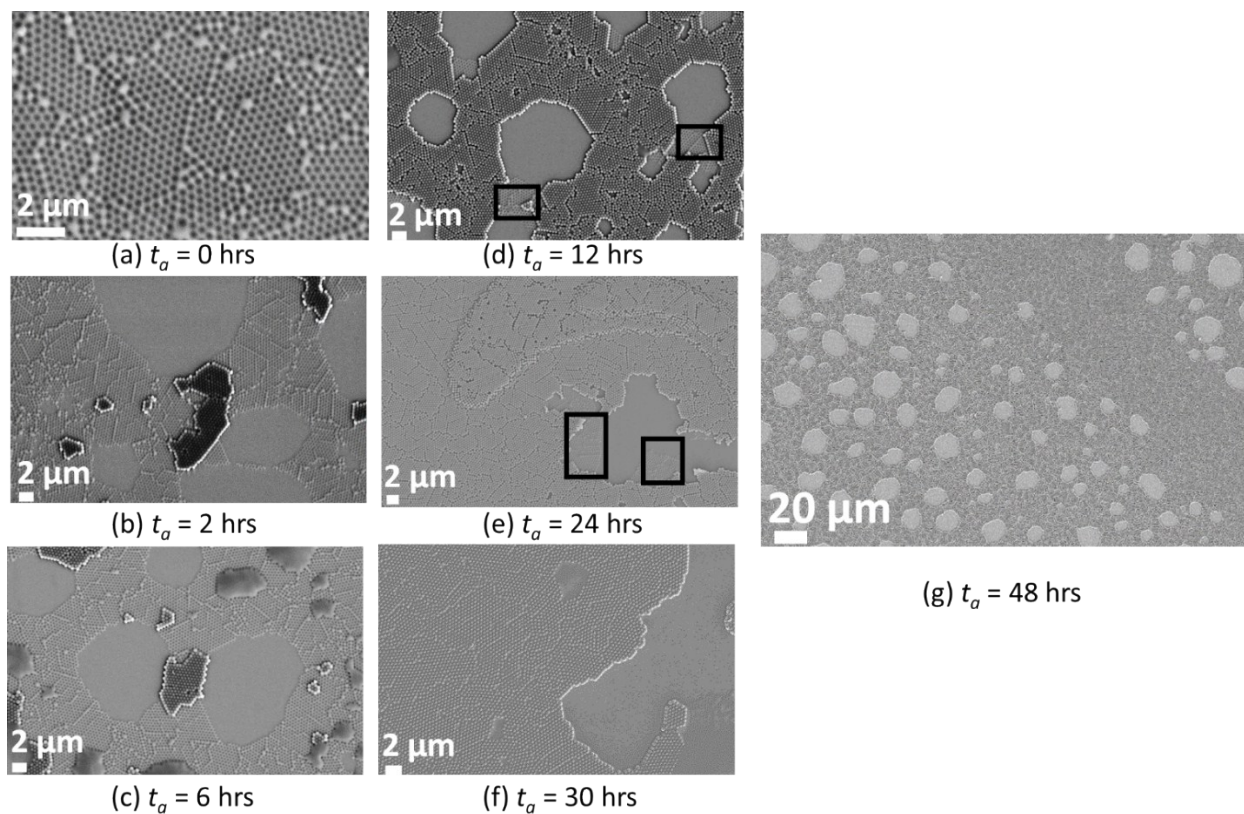


Figure SF1 – The Si/Nanosphere surface morphology after peeling off the PDMS inverse template after different annealing times t_a .

S3 – Fabrication of PDMS inverse templates

PDMS (Sylgard 184 Silicone elastomer) was mixed with the curing agent in the ratio 10:1 by weight, and degassed for 2 hours. The degassed mixture is then cast over the Si/PSS templates which are placed inside a petri-dish. These samples are then annealed at 70°C for 3 hours. The samples are allowed to cool down and are left undisturbed for roughly 12 hours. The cured PDMS films are then peeled off from the Si/PSS template to obtain the inverse template consisting of cup-shaped nanostructured arrays as seen in the SEM image in Figure SF2(a) and (b) in different magnifications.

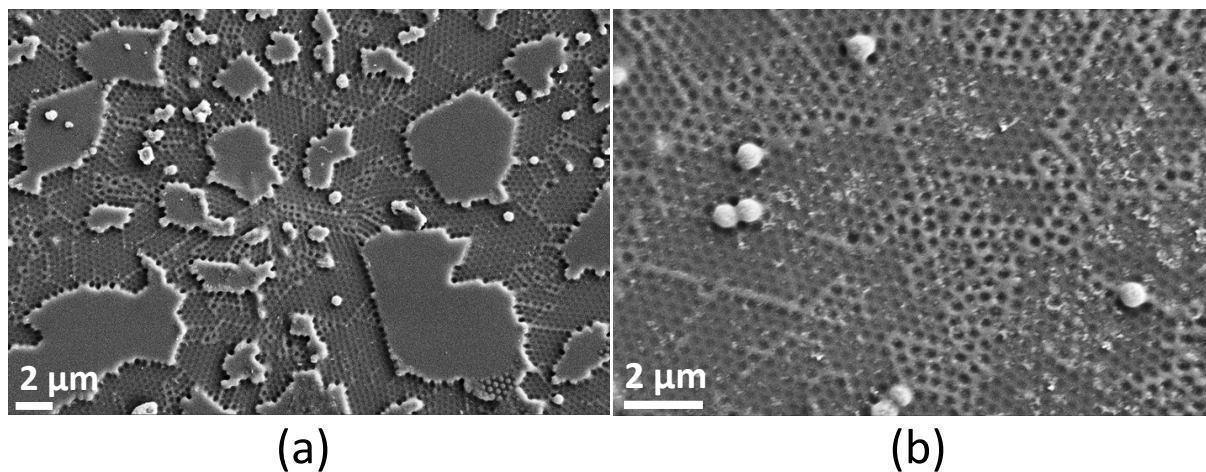


Figure SF2 - PDMS inverse templates carrying cup shaped nano-structured arrays. The image with lower magnification in (a) shows some islands which are flat. These are due to the incomplete coverage of PS beads over the Si surface, and represent the regions which are not covered by the spheres.

S3 – Preparation of patterned epoxy substrates

The transparent epoxy system Araldite LY-5052 (low viscosity epoxy resin) + Aradur 5052 (curing agent), used in our experiment was procured from Huntsman corporation. The epoxy and the curing agent were mixed in the ratio 1:0.38 by weight as specified in the datasheets, and degassed for 30 min. The degassed mixture is then poured over the PDMS inverse templates. The samples are then allowed to cure at room temperature for 24 hours, after which the cured epoxies are peeled off from the PDMS. This transparent epoxies with excellent surface morphologies. For example a planar epoxy (obtained from a planar silicon master) shows a very small RMS roughness of 2.88 nm as against the structured substrates which showed an RMS roughness of 19.1 nm (Figure SF3).

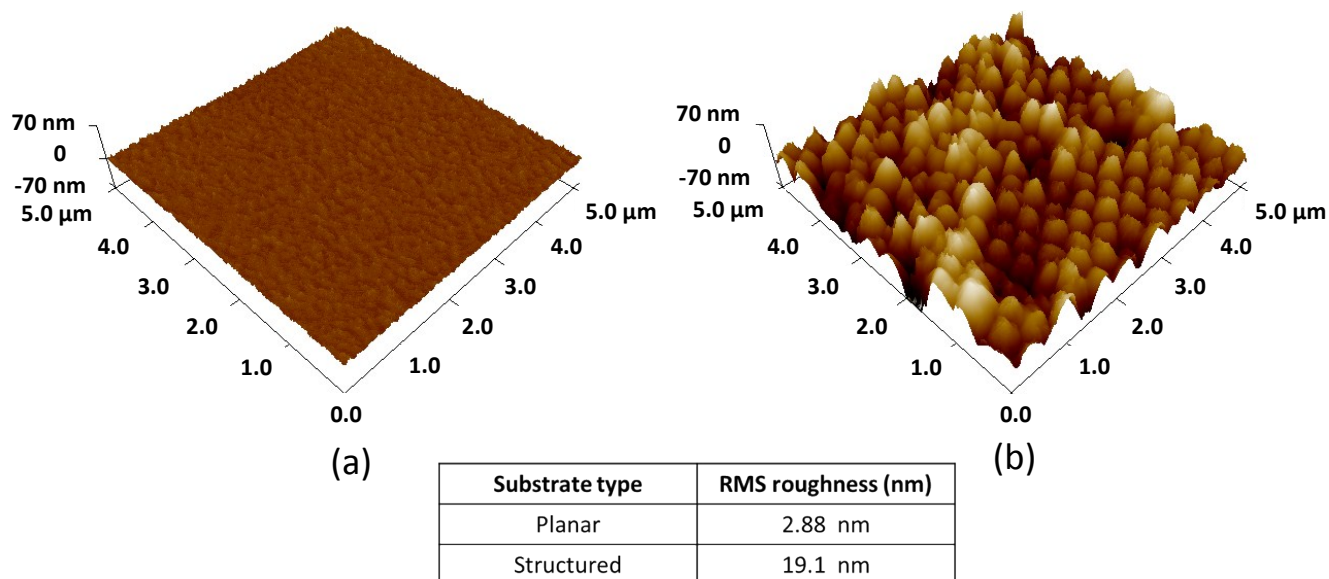


Figure SF3 - (a) and (b) show the Atomic force micrographs of the planar and the structured epoxy substrates over a $5\ \mu\text{m} \times 5\ \mu\text{m}$ projected surface area. The table shows the RMS roughness values for these substrates measured over the same area.

S4 – Reproducibility of patterned epoxy substrates on repeated use of the Si/PSS master template

It is shown here that the repeated use of the Si/PSS master yields nanostructured epoxies without any degradation in the feature sizes. For two consecutive moldings using the same master, the surface morphology of the patterned epoxies (Figures SF4(a) and (b) for batch 1 and batch 2) and line profiles (Figures SF4(c)) remain unchanged.

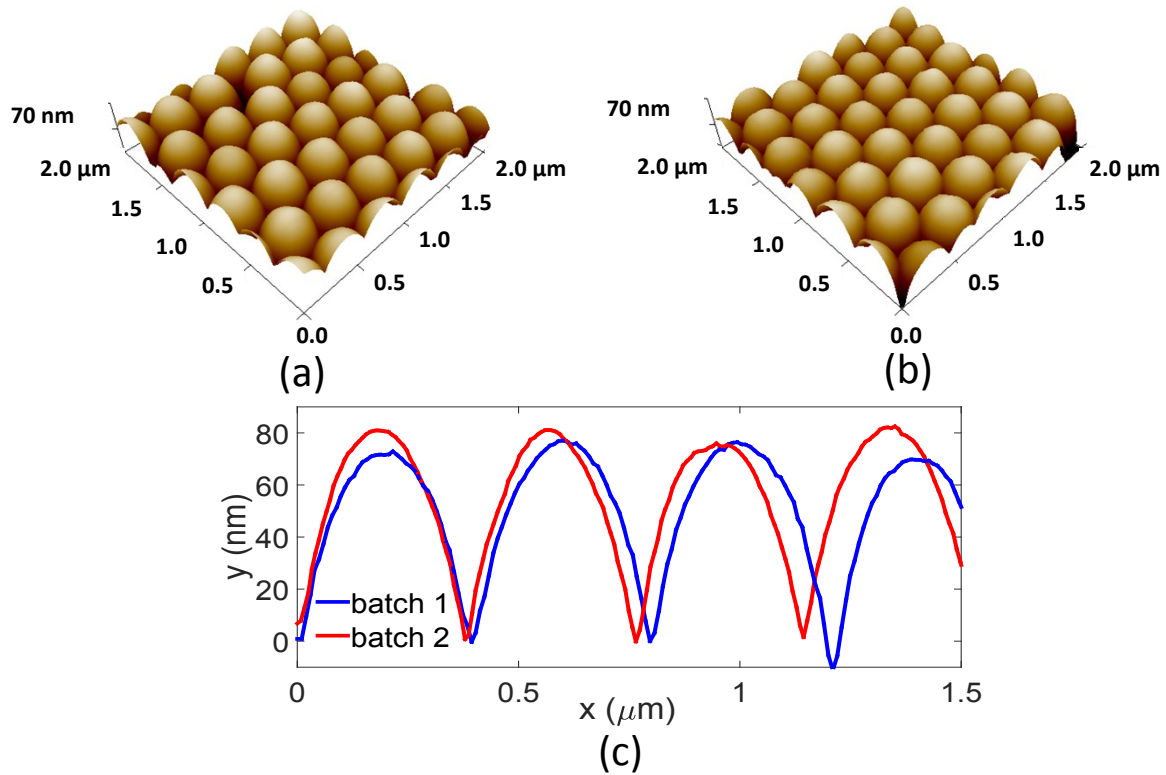


Figure SF4 - (a) and (b) show surface morphologies of nano-structured epoxies obtained by repeated use of the same Si/PSS master. (c) shows the corresponding line profiles for the two batches, revealing similar feature sizes

S5 – Reproducibility of patterned epoxy substrates on repeated use of the PDMS inverse template

It is also seen that a PDMS inverse template can be used multiple times to obtain nanostructures which retain their feature size (Figure SF5), hence not requiring the fabrication of a fresh inverse template for each epoxy substrate. This makes the process more scalable.

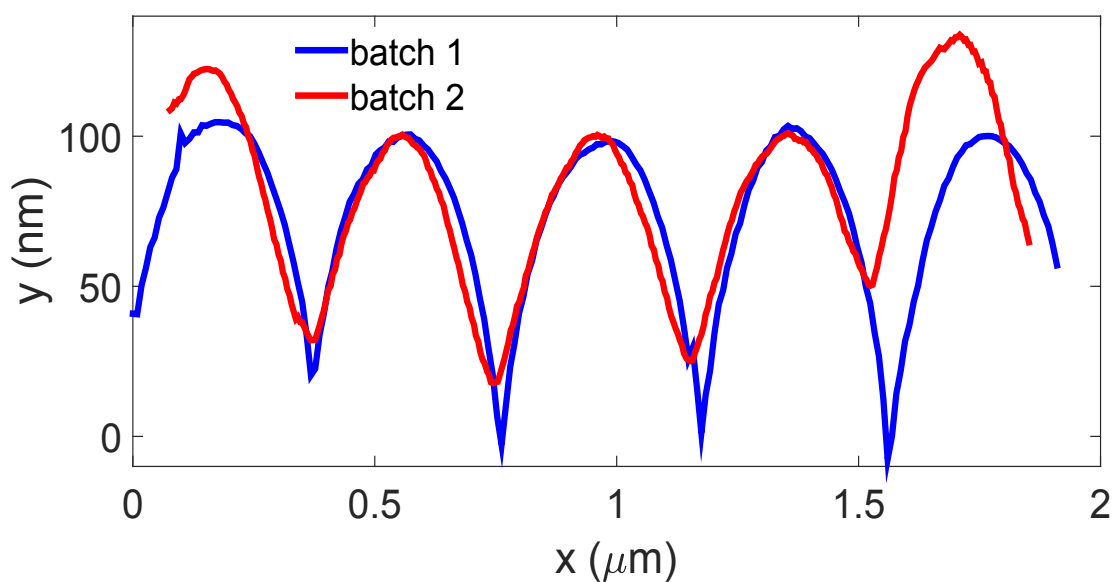
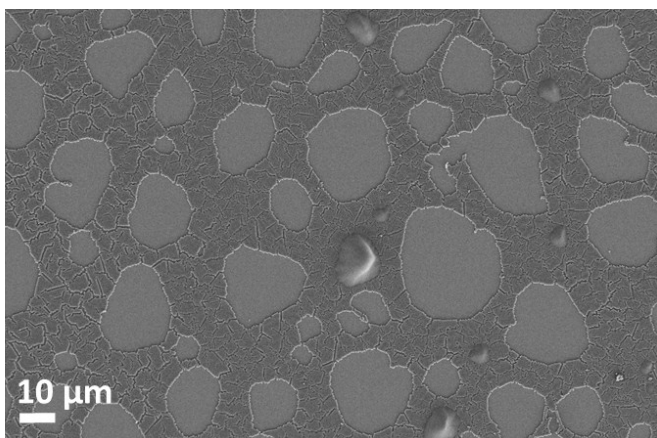


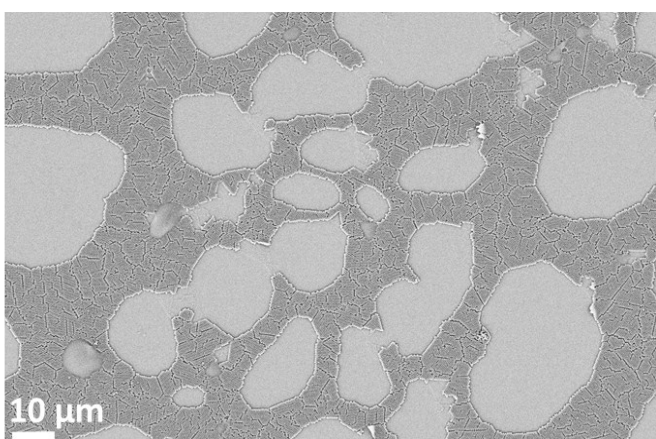
Figure SF5 – Line profiles of epoxy substrates obtained from successive usage of a PDMS inverse template, showing similar feature sizes.

S6 – Modulation the domain sizes of the multiscale pattern

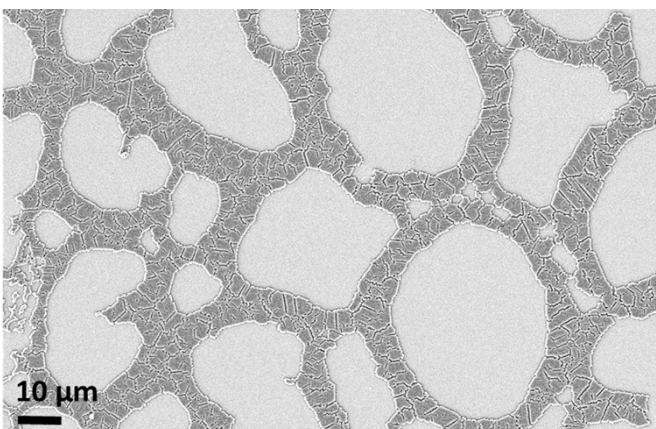
It is seen that domain sizes of the planar and the nanostructured microdomains in the multiscale pattern can be controlled by varying the solution processing parameters during the fabrication of the initial Si/PSS template. Figures SF6 (a) – (c) show that the domain size of the nanostructured region can be reduced by diluting the PSS suspension with equal quantities of DI water and methanol.



PSS suspension:MeOH (1:1)



PSS suspension:MeOH (1:1)
+ 20% (vol) Di water + MeOH



PSS suspension:MeOH (1:1)
+ 40% (vol) Di water + MeOH

Figure SF6 – Modulation of the planar and structured micro-domain sizes by varying solution parameters

S7 – Device fabrication

- 1) **Dielectric spacer** - A 20 nm thick high refractive index TiO_2 layer is sputtered by RF sputtering on the epoxy substrate, to provide a refractive index contrast when sandwiched between the low index substrate and the low index PH1000 hole collecting electrode.
- 2) **Hole collecting electrode** - A PH1000 layer is spin coated at 4000 or 5000 rpm on the TiO_2 layer for 60 seconds and annealed at 90°C for 30 minutes.
- 3) **Active layer** – 200 μL of the P3HT:PC₆₀BM polymer blend solution (1:0.85 by wt, 20 mg/mL of P3HT in 1,2-dichlorobenzene, heated on a stirrer at 60°C for 24 hours) is spin coated on the active layer at 700 rpm for 60 seconds. This is annealed at 100°C for 30 minutes.
- 4) **Electron collecting electrode** - A 100 nm thick Al layer is evaporated on the active layer to complete the device.

Process steps 3 and 4 are carried out inside a N_2 filled glove box (Jacomex). Characterization (J-V measurement and EQE measurement) is also carried out inside the glove box.

S8 – Film thicknesses

The thickness of the active layer, t_{act} , and the thickness of the anode (PH1000), t_{anode} , as measured using a stylus surface profiler are shown in Figure SF7(a) and (b) for a device and (c) and (d) for a second device. It is seen that the PH1000 layer is around 50-60 nm thick and the P3HT:PCBM layer is around 116-160 nm thick.

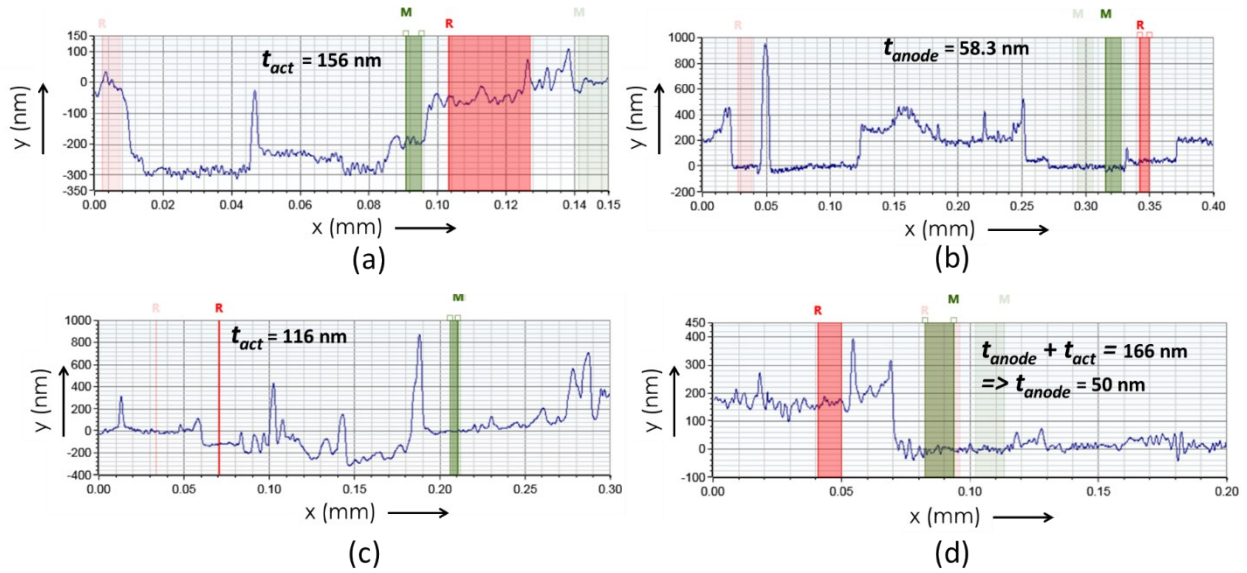


Figure SF7 – Line profiles used to measure the thickness of the PH1000 and the P3HT:PCBM layers. (a), (b) and (c), (d) are pairs of measurements carried out on two different devices.

S9 – AFM images of film interfaces

The AFM images of the surfaces of the epoxy substrate, the TiO_2 layer, the PH1000 layer and the active layer, all carrying periodic the nano-structure are shown in Figure SF8 (a)-(d) in sequence. The line profiles in the main paper are taken from these images, and serve as inputs to simulations.

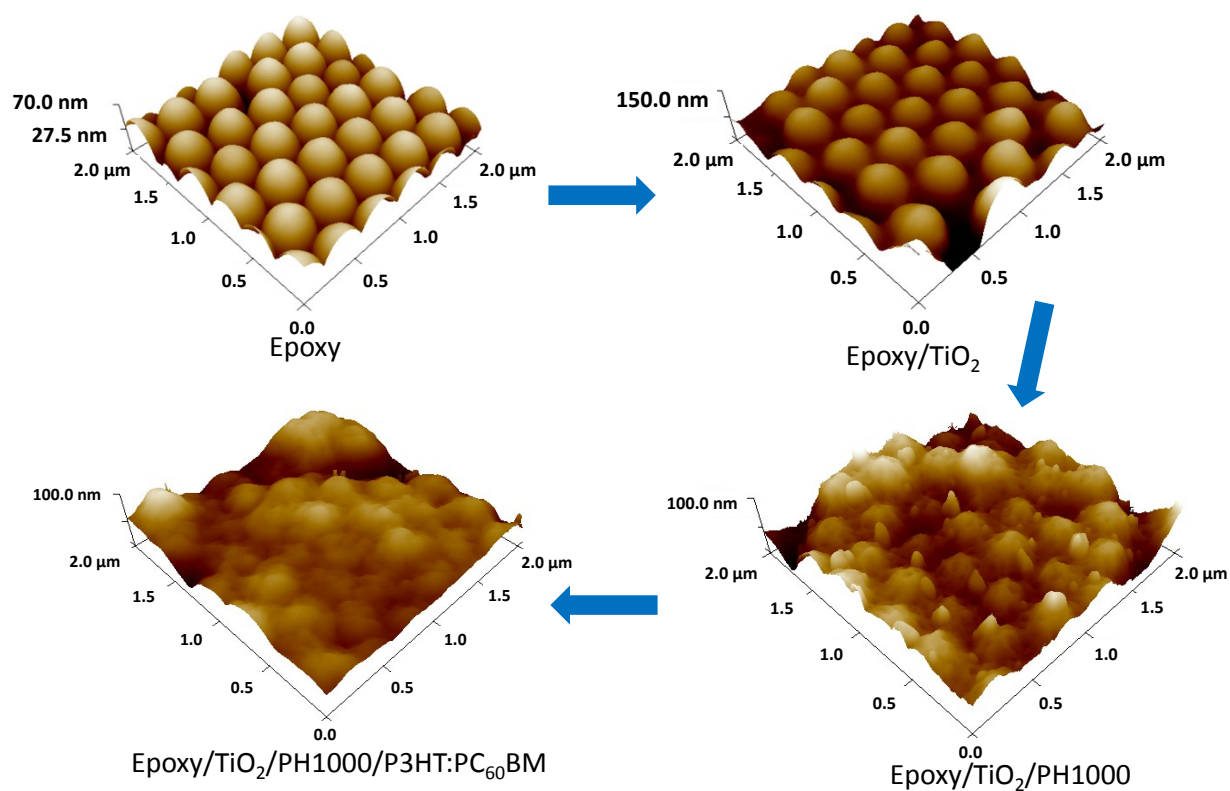


Figure SF8 - The AFM images of successive interfaces in the structured device architecture

S10 – Analysis of devices with thicker anodes

It was seen in the main paper that a thicker anode (PH1000) led to obscuring of the nanoscale enhancement in the photocurrent density. This corresponds to a PH1000 thickness t_{anode} of around 140 nm, and an active layer thickness t_{act} of around 160 nm (Figure SF9 (c) and (d)). The reduced photocurrent is also seen in the J-V characteristics of this device seen in Figure SF9 (c). It is seen that the PH1000 thickness and the PH1000/P3HT:PCBM interface morphology plays a critical role in the nanoscale enhancement. Further investigate of the PH1000 surface as seen from Figure SF9(d) shows that similar RMS roughness in the planar and the structured cases (11.767 nm and 11.068 nm respectively), with absence of nano-scale periodic patterns are seen on the PH1000 films in the structured case. Thus the thick PH1000 film obscures the underlying pattern from the active layer. Thus the presence of the periodic nano-scale interface between the active layer and the anode is seen to be critical to light –scattering induced enhancement in absorptance.

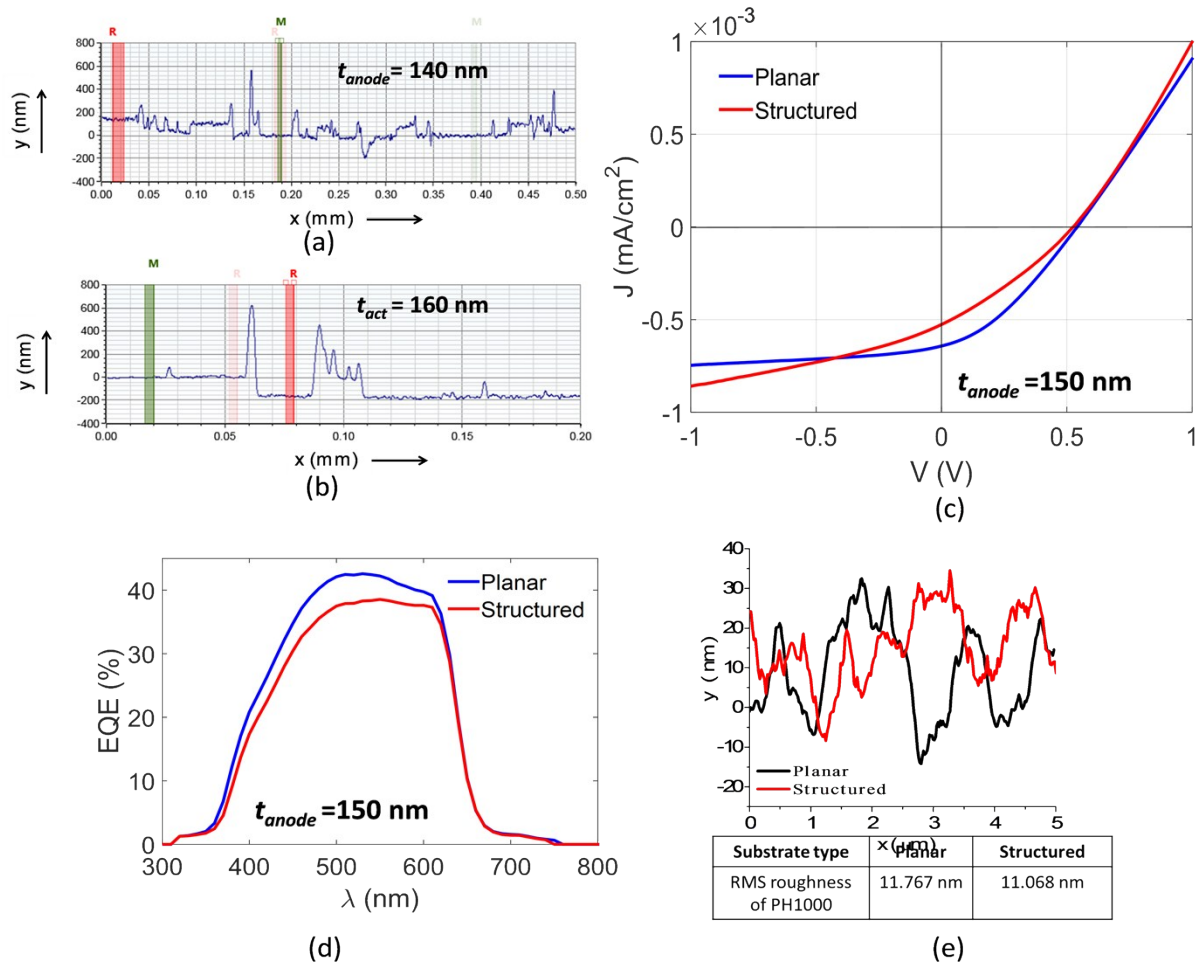


Figure SF9 – (a) and (b) are line profiles to measure the thickness of PH1000 and P3HT:PCBM films respectively in a device in which nano-patterning did not lead to enhancement in photocurrent. (c) shows the J-V curve of this sample, for the planar and structured cases. (d) shows the EQE for the planar and patterned samples, when the anode thickness is around 150 nm (e) shows an atomic force line profile of the PH1000 in this sample, with the accompanying table showing the RMS roughness of the surfaces

S11 – Simulation setup

The simulations consists of two parts – optical transport simulations in which the Maxwell's equations are solved in the nanoscale geometry in the frequency domain, and charge transport simulations which compute the charge transport, carrier continuity and electrical potential distribution in the steady state.

1) Optical transport

The Maxwell's equation for the electric field in the frequency domain is given by

$$\nabla \times (\mu_r^{-1} \nabla \times \mathbf{E}) - k_0^2 \epsilon_r \mathbf{E} = 0 \quad (1)$$

where $\mathbf{E} = \mathbf{E}(X, \omega)$, μ_r and ϵ_r are the relative permeability and relative permittivity of the material. k_0 is the free space wavenumber given by $k_0 = 2\pi / \lambda_0$ and λ_0 is the free space wavelength. For the materials considered here, $\mu_r = 1$. The permittivity is modelled in terms of the refractive index components as $\epsilon_r = (n_r - in_i)^2$, where n_r and n_i are the real and imaginary components of the refractive indices. The variational weak form of Eq. (1) is written as

$$F(\mathbf{E}) = \frac{1}{2} \int_{\Omega} [\nabla \times \mathbf{E} \cdot \mu_r^{-1} \nabla \times \mathbf{E} - k_0^2 \mathbf{E} \cdot \epsilon_r \mathbf{E}] dV - \int_{\Omega} \mathbf{E} \cdot \mathbf{f} dV \quad (2)$$

where Ω is the volume in the device domain shown schematically in Figure 1(a) and $\mathbf{f}$ is the source function given by

$$\mathbf{f} = -j\omega\mu_0\mathbf{J} - \nabla \times (\mu_r^{-1} \mathbf{M}) \quad (3)$$

where ω is the angular frequency, μ_0 is the absolute permeability, $\mathbf{J}$ is the electric current density and $\mathbf{M}$ is the magnetic current density. Finite element discretization based on minimization of the function in Eq. (2) is implemented in COMSOL software package. The problem is simplified to a two-dimensional plane wave problem involving two polarizations s and p . Electromagnetic

power transport across an arbitrary interface is computed by integrating the time averaged Poynting vector over the area of the interface as

$$P = \oint_S \frac{1}{2} \text{Re}(\mathbf{E}_{\text{max}} \times \mathbf{H}_{\text{max}}^*) \cdot \mathbf{n} dS, \quad (4)$$

where $\mathbf{n}$ is the unit vector normal to the interface of area dS . The frequency domain simulations are carried out with maximum element size of 5 nm whereas the minimum wavelength simulated is 330 nm. This equation is used to compute the absorptance in the main paper. The refractive indices are taken from literature for TiO₂ [2], PH1000 [3] and Al [4]. The refractive indices of P3HT:PCBM is measured by ellipsometry. The refractive index of the substrate is taken as 1.5.

2) Steady state charge transport

The semiconducting active layer consists of electrons and holes. We compute the carrier density distribution, and potential distributions in the steady state by using the following equations of charge transport [5].

$$\mathbf{J}_n = qD_n \nabla \cdot n - q\mu_n \nabla \cdot \psi \quad (5)$$

$$\mathbf{J}_p = qD_p \nabla \cdot p - q\mu_p \nabla \cdot \psi \quad (6)$$

$$-\frac{1}{q} \nabla \cdot \mathbf{J}_n = G(x, y) - R(x, y) \quad (7)$$

$$\frac{1}{q} \nabla \cdot \mathbf{J}_p = G(x, y) - R(x, y) \quad (8)$$

$$\nabla^2 \psi = -\frac{q}{\epsilon_0 \epsilon_r} (p - n + N_{\text{eff}}) \quad (9)$$

Equations (5) and (6) represent the drift-diffusion formalism for the electron and hole current densities $\mathbf{J}_n$ and $\mathbf{J}_p$. n and p are electron and hole densities and ψ is the potential distribution. μ_n and μ_p are the electron and hole mobilities and $D_n=(kT/q)\mu_n$ and $D_p=(kT/q)\mu_p$ are the electron and hole diffusivities. q is the electronic charge ($1.6\text{e-}19$ C), k is Boltzmann's constant ($1.38\text{e-}23$ JK⁻¹). N_{eff} is the effective doping concentration in the active layer. T is the operating temperature of the semiconductor device (assumed equal to 300 K). Equation (7) and (8) model electron and hole continuity in the steady state. G and R are the generation and recombination rates of electrons and holes respectively, in the steady state. The generation rate G of excitons is obtained from the optical domain simulations, and is explained in the next section. The recombination rate R is modelled by a Langevin mobility dependent bimolecular recombination given by [6]

$$R(x, y) = \frac{q}{\varepsilon} \min(\mu_n, \mu_p) (np - n_i^2) \quad (10)$$

where ε is the permittivity of the active material and n_i is the intrinsic concentration in the active semiconductor material given by

$$n_i = \sqrt{N_c N_v} e^{-\frac{E_g}{2kT}} \quad (11)$$

where N_c and N_v are relative density of states in the conduction and valence bands. This comes from the simplified picture of the active layer which is treated as a single effective medium with effective density of states N_c and N_v [7].

Dirichlet boundary conditions are applied on the variables n, p and ψ at the hole and electron collection interfaces. This assumes that the interfaces are at thermal equilibrium [7]. If B_e and B_h

are the barrier heights at the electron and hole collection interfaces, we have the following boundary conditions for n and p at the interfaces [7]

$$n_e = N_C e^{-\frac{B_e}{kT}}, \quad p_e = \frac{n_i^2}{n_e}, \quad p_h = N_V e^{-\frac{B_h}{kT}}, \quad n_h = \frac{n_i^2}{p_h} \quad (12)$$

where the subscripts e and h refer to the electron and the hole collecting boundaries respectively.

The values used in the simulations are standard values for P3HT:PCBM [7] and are tabulated in Table 1.

Table 1 – Material properties for the active layer, used in the charge transport simulations

Material property	Value employed in simulation
E_g	1.0 eV
N_C	$3.9 \times 10^{25} \text{ m}^{-3}$
N_V	$3.9 \times 10^{25} \text{ m}^{-3}$
μ_n	$1 \times 10^{-7} \text{ m}^2/\text{V-s}$
μ_p	Varied
ϵ_r	3
N_{eff}	0

3) Point-wise exciton generation rate in the active layer

The relationship between in the optical transport domain and the charge transport domain is explicitly through the term G , which is the point-wise exciton generation rate in the semiconductor. This is obtained by applying photon continuity conditions on the electric and magnetic field distributions obtained from the optical domain simulations. This is explained in the case of a simplified two dimensional architecture. Consider an infinitesimal with sides Δx and Δy . The time-averaged Poynting vector for a particular frequency f , $\mathbf{P}$ has the components P_x and P_y as depicted in Figure SF10. The net power absorbed in the per unit volume assuming a unit outward projection along the outward normal (z-axis), is given by $|\nabla \cdot \mathbf{P}|$. The number of photons absorbed per unit volume is obtained by dividing this quantity by hf where h is the Planck's constant ($=6.626 \times 10^{-34}$ J/s). Using this, the total generation integrates across the electromagnetic spectral band of interest spanning the interval of frequencies $[f_{min}, f_{max}]$ is given by

$$G(x, y) = \int_{f_{min}}^{f_{max}} \frac{1}{hf} |\nabla \cdot \mathbf{P}| df \quad (11)$$

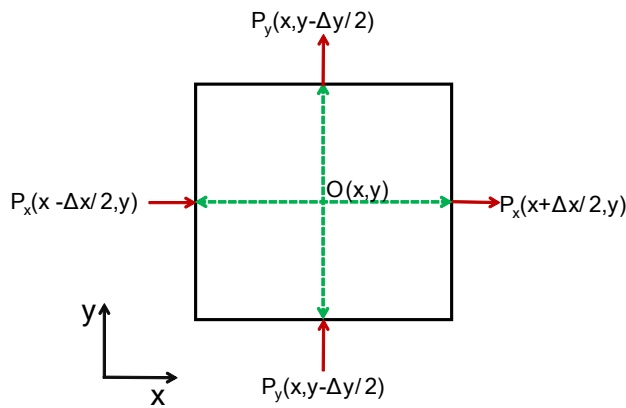


Figure SF10 – Two-dimensional area element schematically depicting the linearized approximation used for photon continuity

S12 – Simulated dependence of photocurrent enhancement on thickness of the anode and the thickness of active layer

Figure SF11 shows the enhancement in the photo-current density obtained from optical frequency domain simulations, as a function of anode thickness (t_{anode}) and thickness of the active layer (t_{active}). It is clear that the enhancement mechanism causes significant enhancement in the photocurrent only if both the anode and active layer are smaller than some critical values. These results are obtained with simulations in which the fading out of the nanostructure with successive layers has been approximately modelled by considering the successive layers are concentric ellipses in two dimensions. This model however overestimates the fading of the nanostructure with film height and the actual behavior would reflect the properties of a more conformal coating model. However this serves as an approximate guide to understand the nanostructured mechanism in our experiments. It clearly says why thick anodes and active layers do not experience nanoscale enhancement.

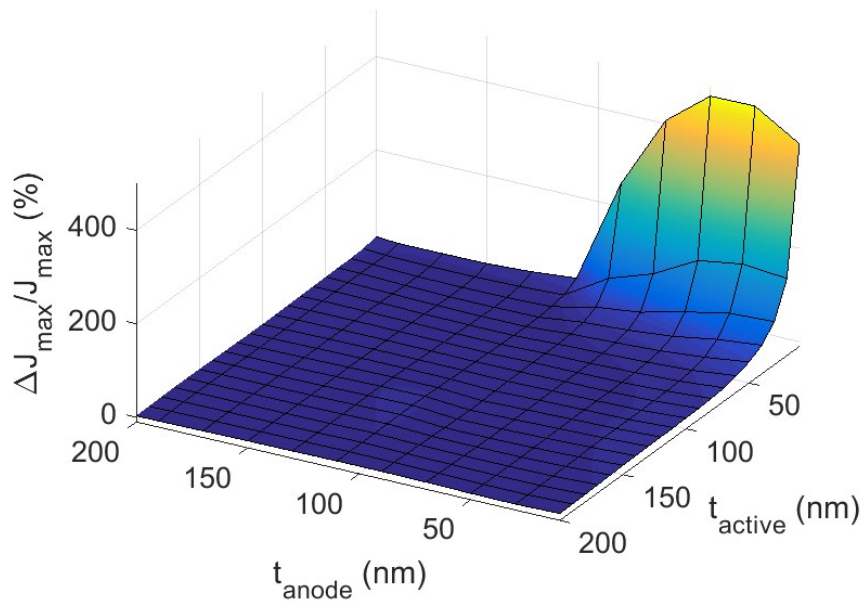


Figure SF11 – Simulated photocurrent enhancement as a function of film thicknesses

S13 – Non-ideal device fabrication conditions and possible optimizations for practical devices

As seen in the main paper, the device behavior is highly non-ideal compared to the reported performance in current literature. We emphasize that this is only a proof of concept to establish the design and fabrication of bio-mimetic patterns over unconventional substrates. The various non-idealities in the devices fabricated here are

- 1) High series resistance – The anode layer PH1000 is very thin (~50 nm) in the devices where enhancement was seen. This creates a high series resistance. However, for the demonstration of the enhancement, the design needs to incorporate a very thin layer. This problem can be overcome by selection of high conductivity electrode materials such as transparent conducting oxides (TCOs). We could not use TCOs here because of the high annealing temperatures (~300°C) which the epoxy substrates cannot withstand.
- 2) Non-ideal processing conditions of the active layer – The active layer was annealed at a sub-optimal temperature (100°C) to keep the temperature within the glass transition of the epoxy. This could contribute to reduction in performance compared to practical reported devices. However, this can be addressed by proper choice of epoxies and absorbers.

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