Supplementary Information (SI) for Journal of Materials Chemistry C.

Supporting Information

Silicon Meta-atoms Enabled Self-powered Selectively Patterned Black Silicon Photodetector for Real-time Monitoring of Sunlight.

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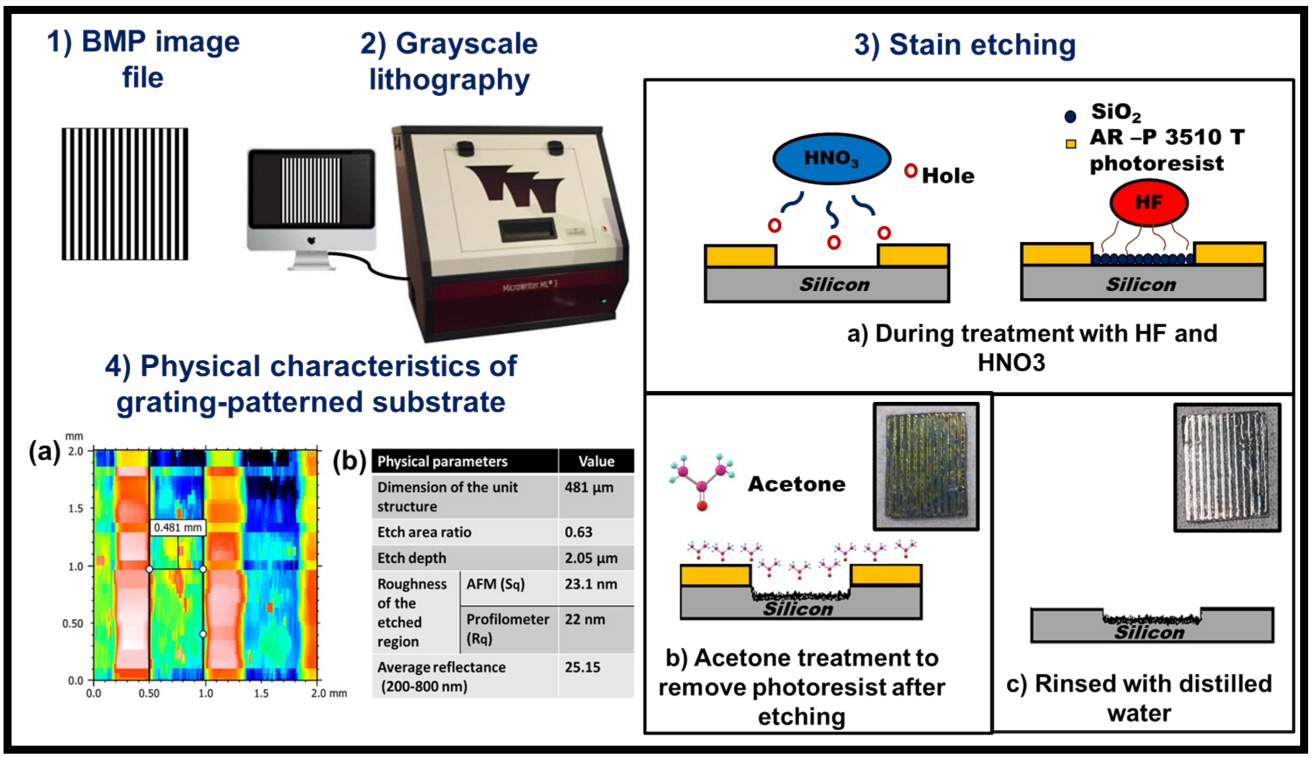


Figure S1. Steps involved in fabrication of grating-patterned black silicon (1-3) and physical characteristics of the grating-patterned substrate (4).

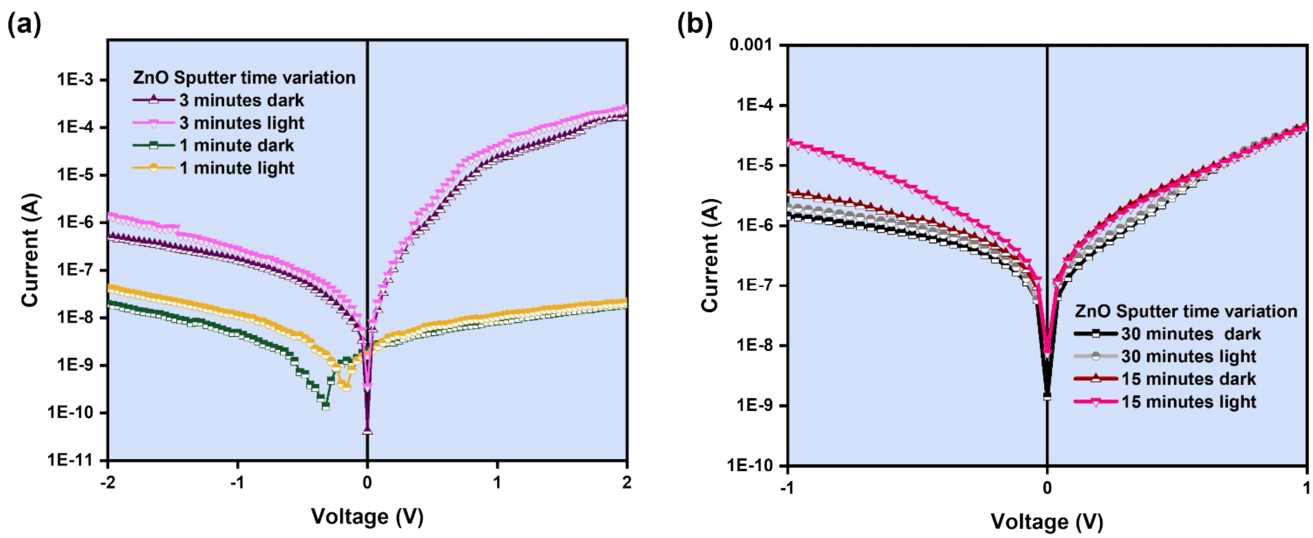


Figure S2. (a & b) Voltage vs current characteristics of the photodetector devices fabricated with ZnO layer deposited under different time durations.

Compared to the other devices, the device fabricated with sputtered ZnO for 1 minute duration showed a negative shift in the open-circuit voltage. This condition represents the deterioration of p-n junction, formed as a result of incomplete ZnO growth, as predicted from XRD results. Instead of charge extraction at the electrodes, charges have been accumulated, indicating the capacitance nature of the device.

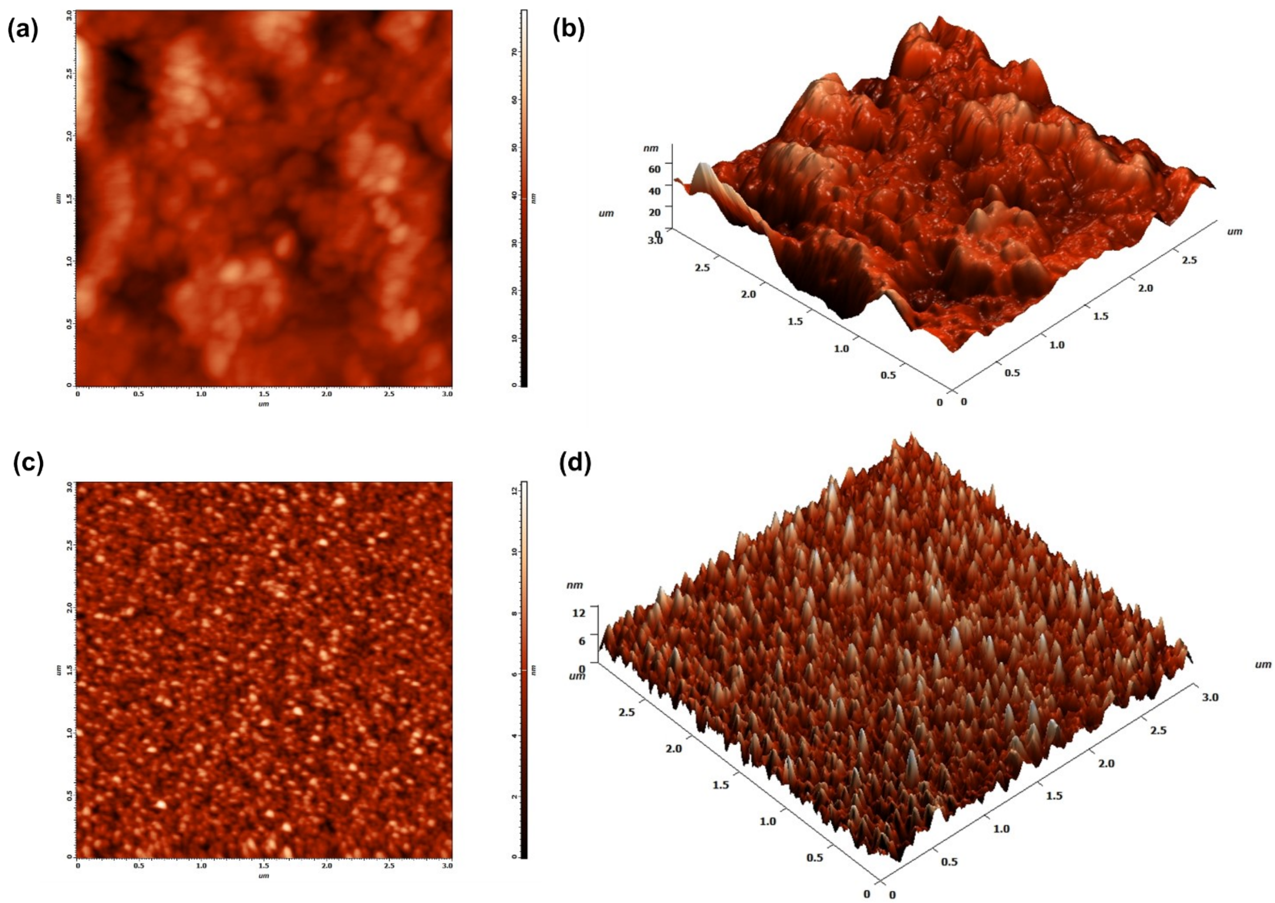
AFM analysis of ZnO thin films

a) Morphological study

The morphology of ZnO thin films deposited at 1 minute and 30 minutes duration were compared, and pictured in panels a-d of Figure S3. The duration of deposition has less significant effects on modification of heights of nanospikes, but the density of nanospikes has been increased with the increase in duration of deposition.

b) Step-height calculation by AFM

From AFM step-height calculation, the thickness of the ZnO thin films deposited at different time durations were calculated, and provided in Table S1. Step-height profiles of the optimized layer (5 minutes duration) were provided in panels e-h of Figure S3. Mean step-height of the optimized layer was calculated as 49 nm with an average deviation of 7 nm, calculated for n=4 profiles. Non-uniformity in the dimensions of the nanospikes is the reason for the deviations, and the distribution of nanospikes can be visualized in Figure 2c. The approach of the AFM tip at these nanospikes resulted in a non-uniform profile, and this pattern was repeated in profiles of different scanning lengths, which can be visualized in panels f and h of Figure S3.



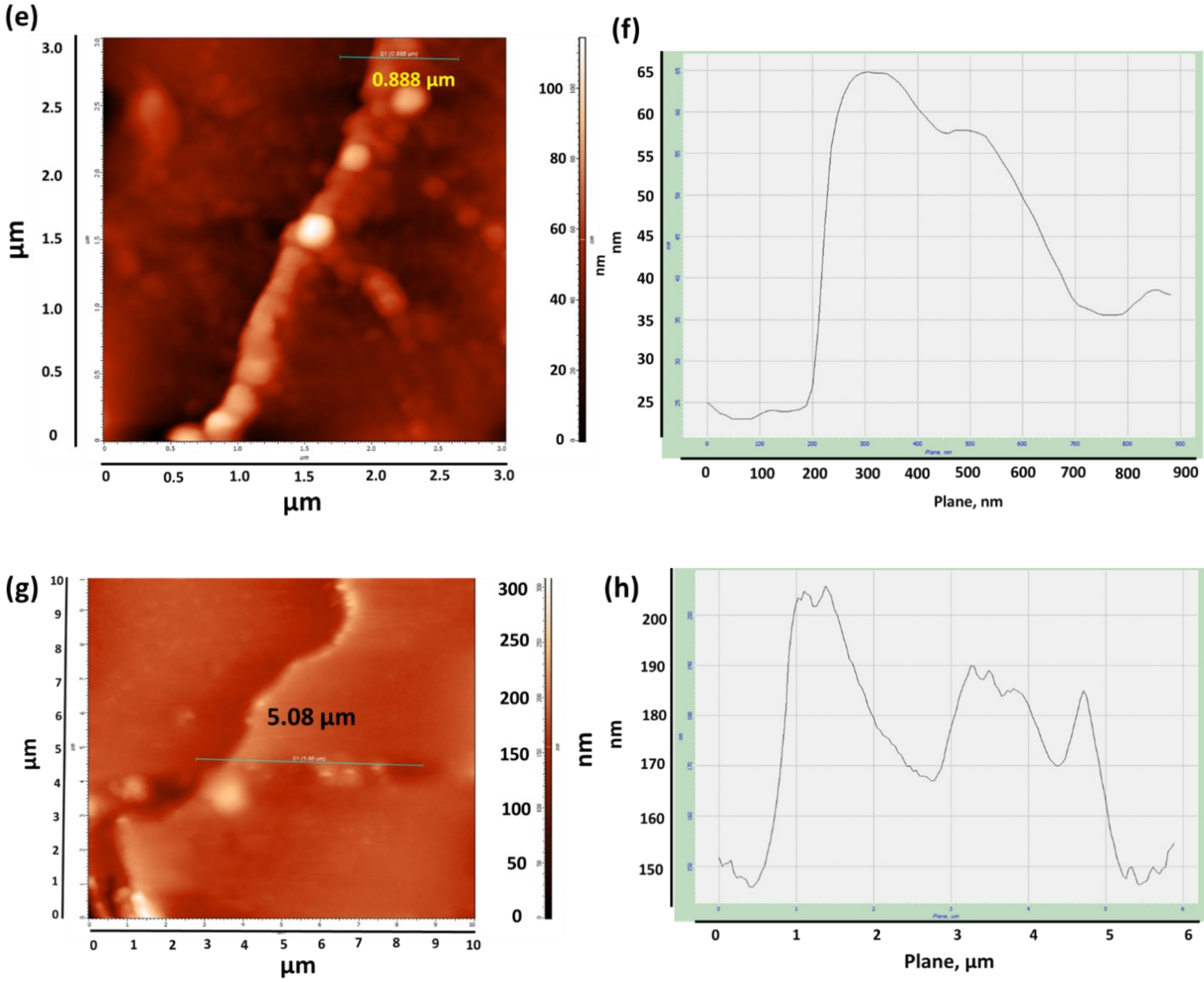


Figure S3. Morphology analysis of ZnO thin films: (a) 2 D and (b) 3D AFM images of thin film deposited at 1 minute duration, (c) 2 D and (d) 3D AFM images of thin film deposited at 30 minutes duration. Step-height calculation of the optimized ZnO layer: (e) & (f) Obtained profile for a scanning length of 0.888 µm, and (g) & (h) Obtained profile for a scanning length of 5.08 µm.

Table S1. Thickness of ZnO thin films deposited under different time durations

S.No.	Duration of deposition of ZnO (minutes)	Thickness of thin film measured by AFM analysis ~(nm)
1	1	5
2	3	20
3	5	49
4	15	120
5	30	280

Raman analysis of ZnO thin film

Raman analysis was carried out on ZnO thin film having higher thickness of 280 nm, since a thickness of greater than ~100 nm is required for the analysis. From the Raman spectrum pictured in Figure S4, the appearance of two peaks at 441 cm^{-1} and 579 cm^{-1} corresponding to E_2^{high} and A_1(LO) modes were observed, which signifies the parallel incidence of light to the c-axis growth of ZnO nanospikes. According to Raman selection rules, the E_1(TO) and A_1(TO) modes were forbidden and the presence of A_1(LO) and E_2^{high} mode indicates the good crystallinity of wurtzite ZnO.

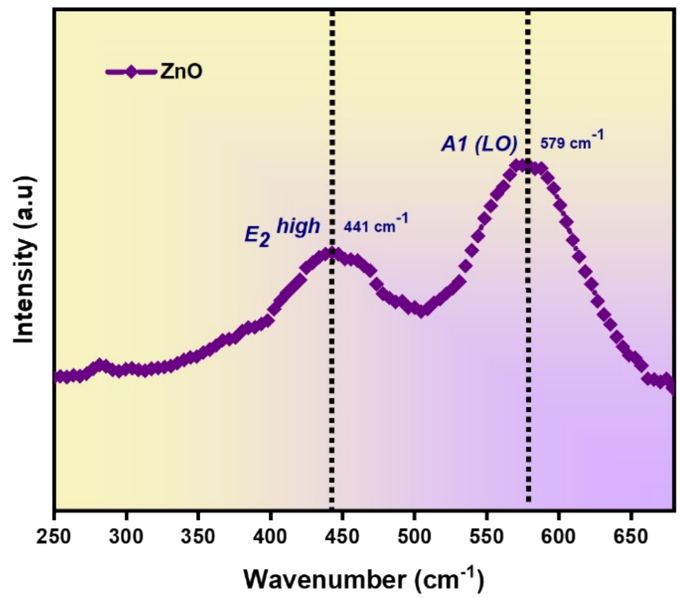


Figure S4. Raman analysis of ZnO thin film.

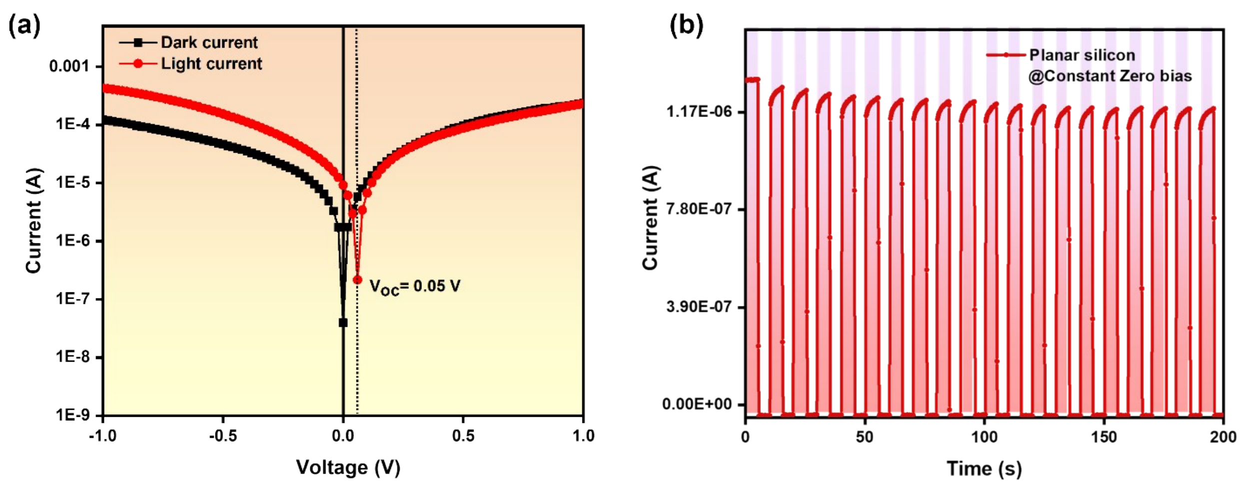


Figure S5. (a) Voltage vs current characteristics of the planar photodetector device and (b) Temporal response of the planar device measured under constant zero bias.

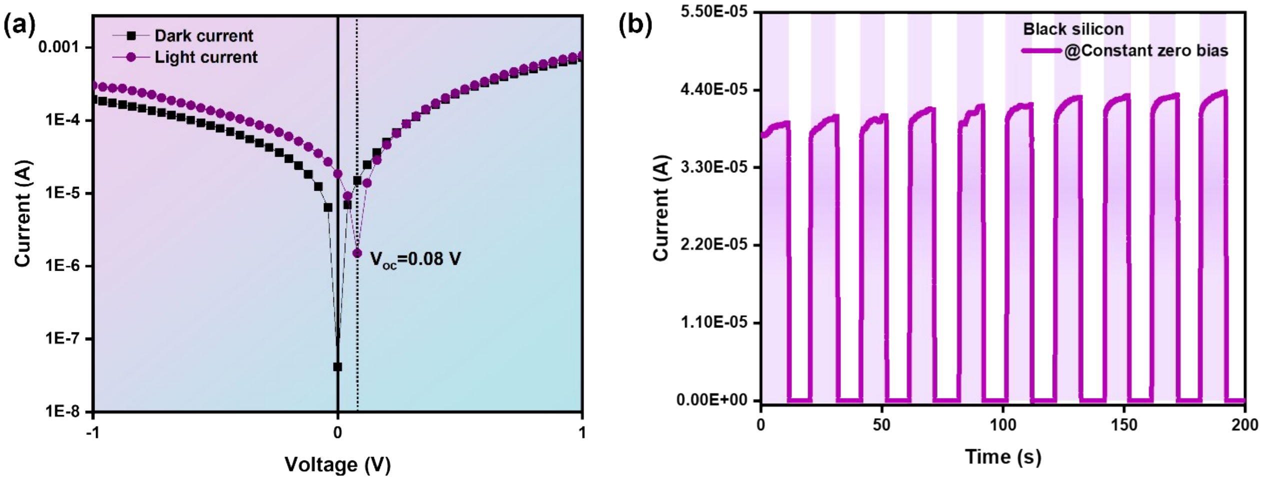


Figure S6. (a) Voltage vs current characteristics of the black silicon photodetector device and (b) Temporal response of the black silicon device measured under constant zero bias.

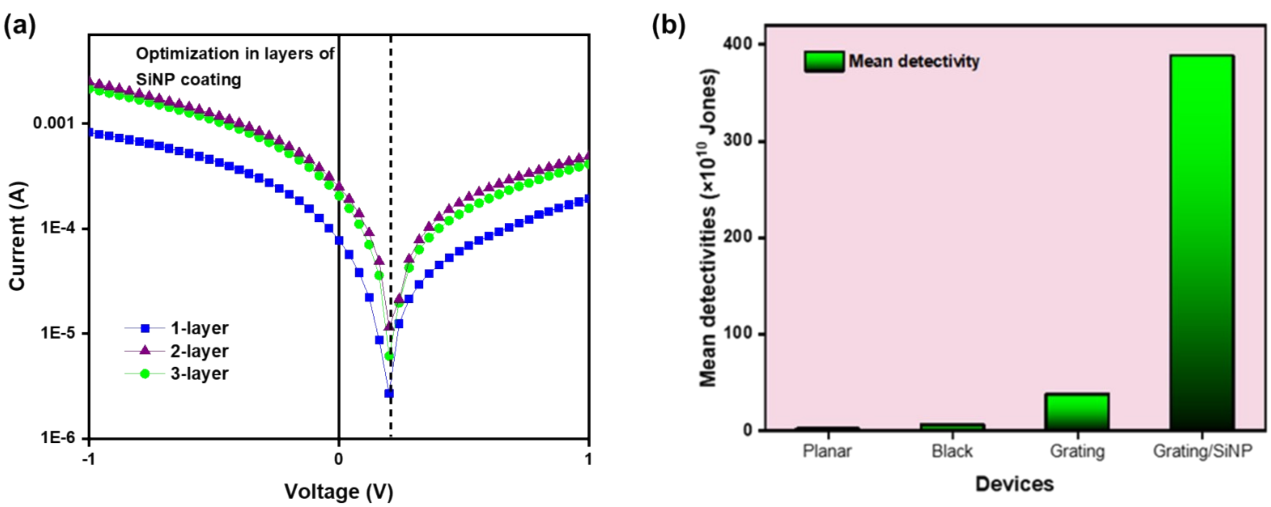


Figure S7. (a) Voltage vs Current characteristics of the grating patterned SiNP coated device with optimization in number of layers for fabrication of device, (b) Mean detectivities of the planar, black, grating-patterned, and grating-patterned SiNP coated devices under 1 sun illumination (calculated for n=3 samples).

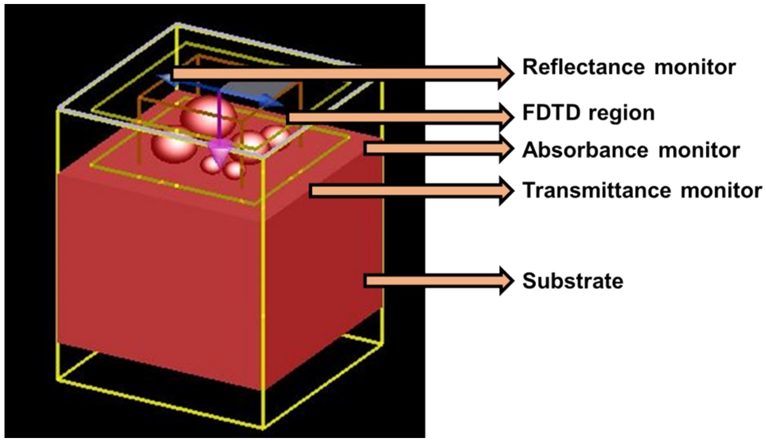


Figure S8. Perspective view of the simulation setup: Silicon substrate with distribution of non-spatially arranged multi-dimensional silicon nanoparticles.

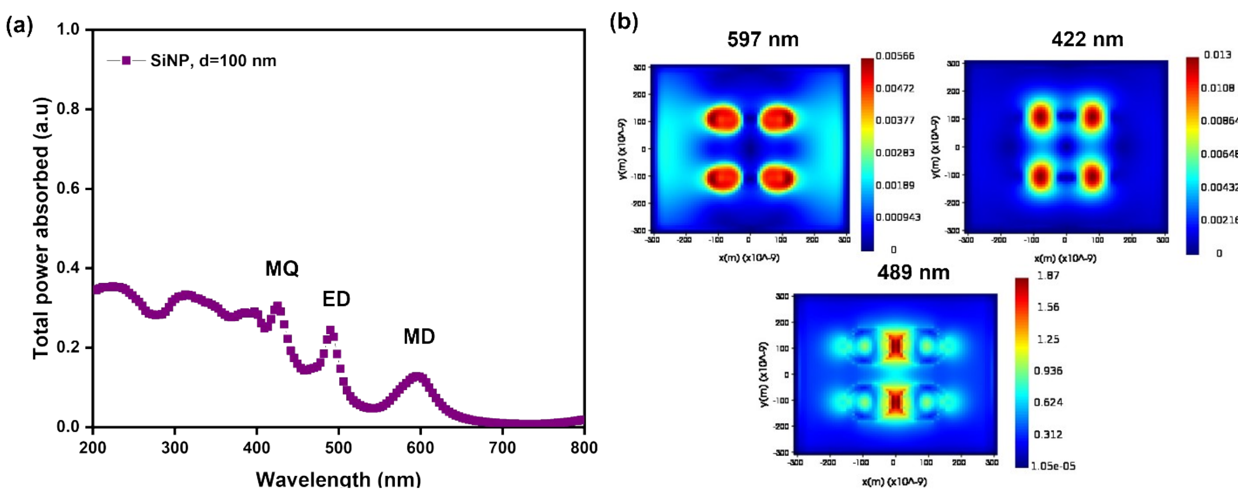


Figure S9. FDTD simulation of silicon nanoparticles with uniform diameter, d= 100 nm. a) Total power absorbed by the silicon nanoparticles showing resonant peaks at 422 nm, 489 nm, and 597 nm due to magnetic quadrupole (MQ), electric dipole (ED), and magnetic dipole (MD) respectively. b) Magnetic field images showing hotspot generation inside the nanoparticles due to MD at 597 nm, and MQ at 422 nm (top row) and Electric field image showing hotspot generation between the particles due to ED at 489 nm (bottom row).

The Self-powering nature of SiNPs

The influence of both optical and electrical characteristics of SiNPs that favored self-driving nature in photodetector devices was identified. The device fabrication procedure was similar to that of the previously reported work.[1] ZnO ink was spin-coated over the p-type planar silicon substrate, followed by the deposition of aluminium over the ZnO layer and at the back side of the silicon substrate. To differentiate the active working of SiNPs, the front metal coverage was chosen to be 100% to facilitate a minimum amount of light passing through it. As expected, the device had more reflection losses and a voltage of 0.3 mV was required to activate the device. SiNPs was spin-coated over 75% of the front aluminium contact and the remaining 25% was left free to collect the charge carriers. The device exhibited photo-voltaic effect which triggered it to operate under self-powered mode. The introduction of SiNPs tuned the electrical characteristics of the device by increasing the electron-hole pair generation, followed by carrier separation and propagation which was formed as a result of built-in electric fields at the junction. The high surface-to-volume ratio of Si nanostructures had the ability to tune the recombination rate, in addition to the light absorption.[2] The photoresponse characteristics were visualized in panel a of Figure S 10 with an increase in open-circuit voltage observed in the case of device coated with SiNPs and the temporal responses of the device were shown in panel b of Figure S10.

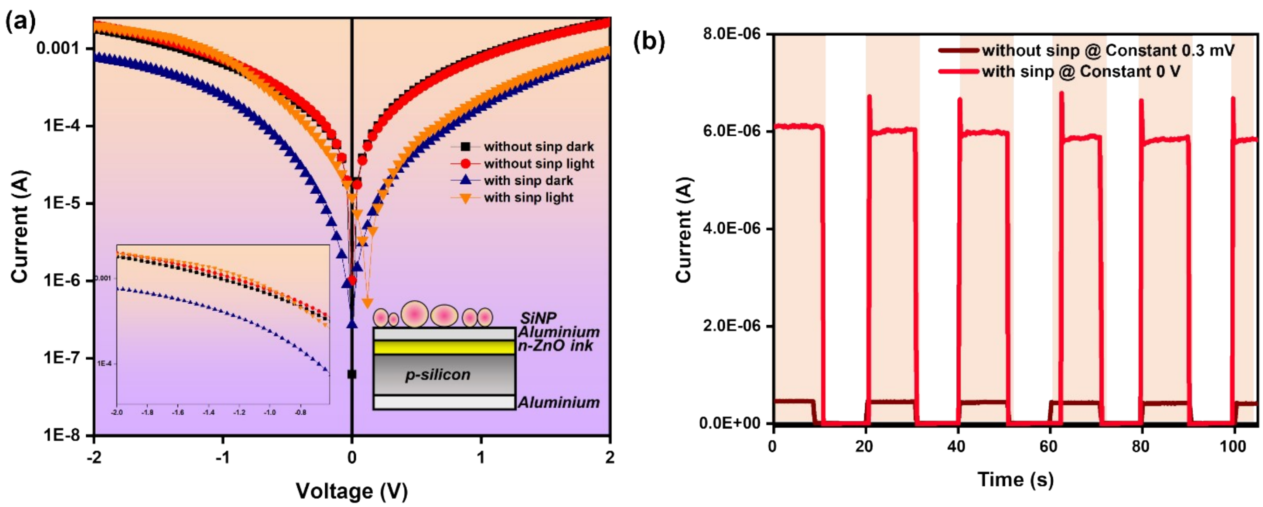


Figure S10. (a) Voltage vs current characteristics of the planar photodetector device with and without SiNP coating. The insets show the IV characteristics under reverse bias and the schematic representation of the device and (b) Comparison of the temporal response of the device with and without SiNPs coating, tested at regular intervals of light on and off.

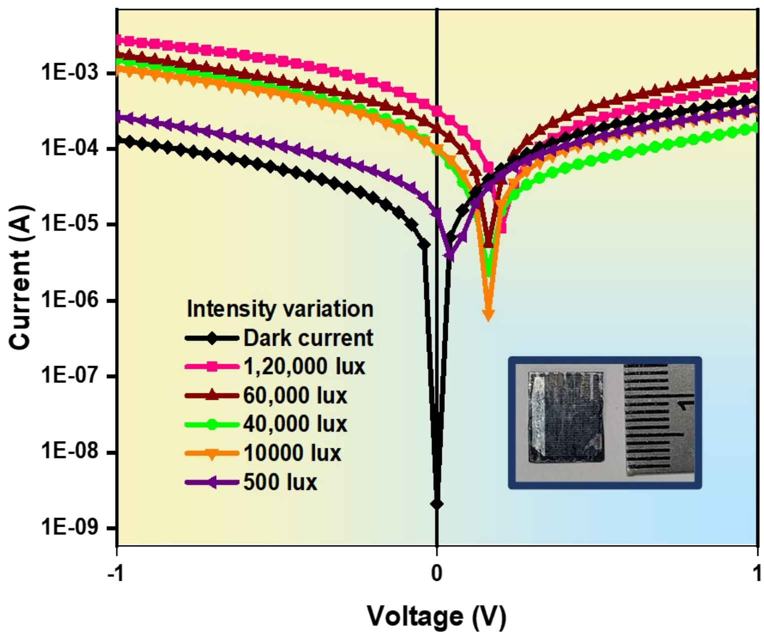


Figure S11. Voltage vs current characteristics of the grating-patterned SiNPs coated photodetector device tested under varied light intensities from solar simulator and the inset shows the photographic image of the fabricated device.

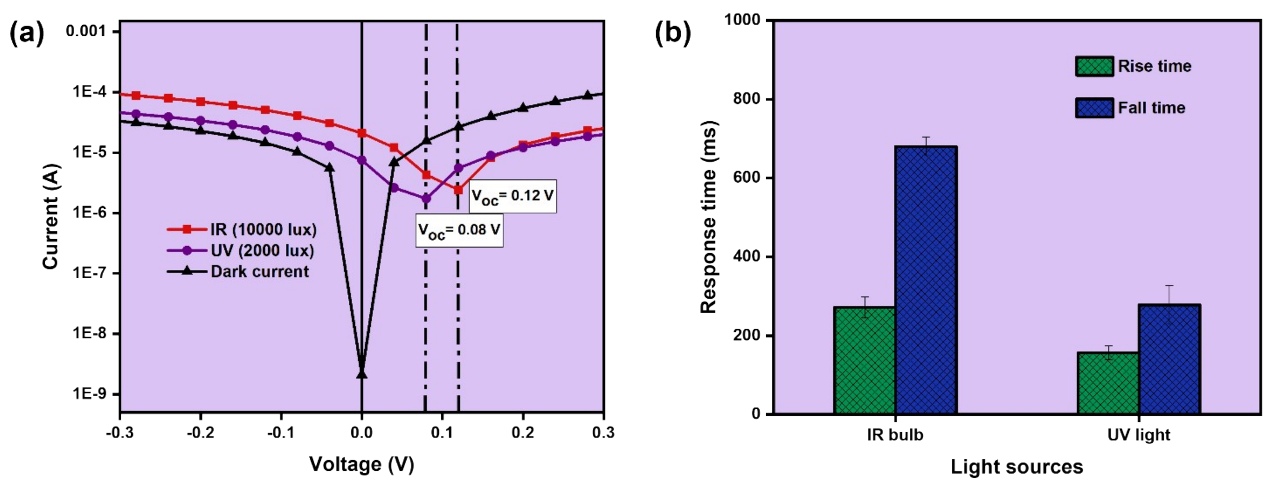


Figure S12. (a) Voltage vs current characteristics of the grating-patterned SiNPs coated photodetector device tested under IR and UV light sources and (b) Bar diagram representing the mean rise and fall time with Standard Error Mean (SEM), calculated for n=5 cycles.

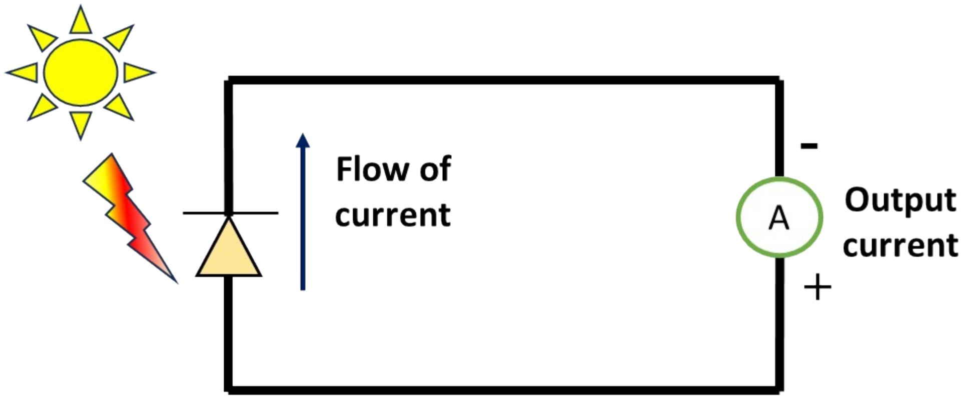


Figure S13. Schematic representation of the circuit diagram for self-powered real-time monitoring of sunlight

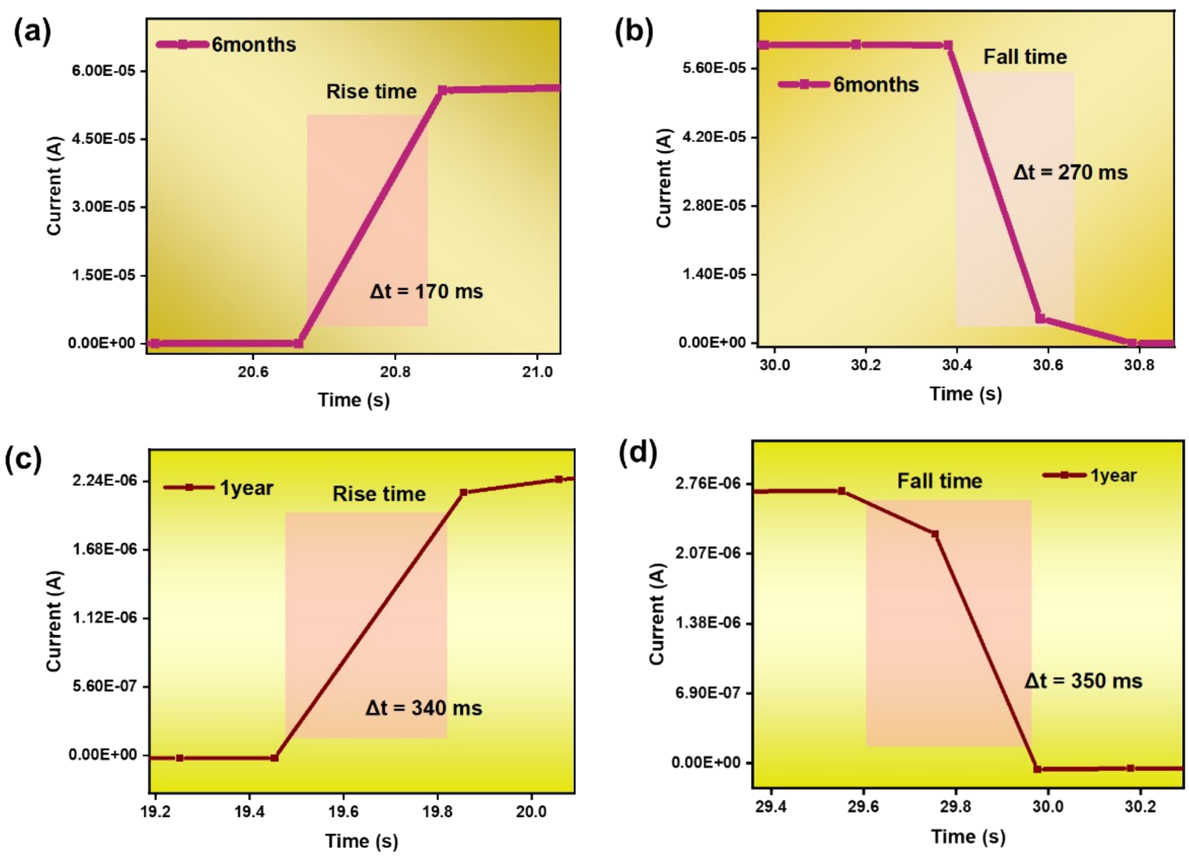


Figure S14. (a) Rise time, and (b) Fall time of the device tested after 6 months. (c) Rise time, and (g) Fall time of the device tested after 1 year.

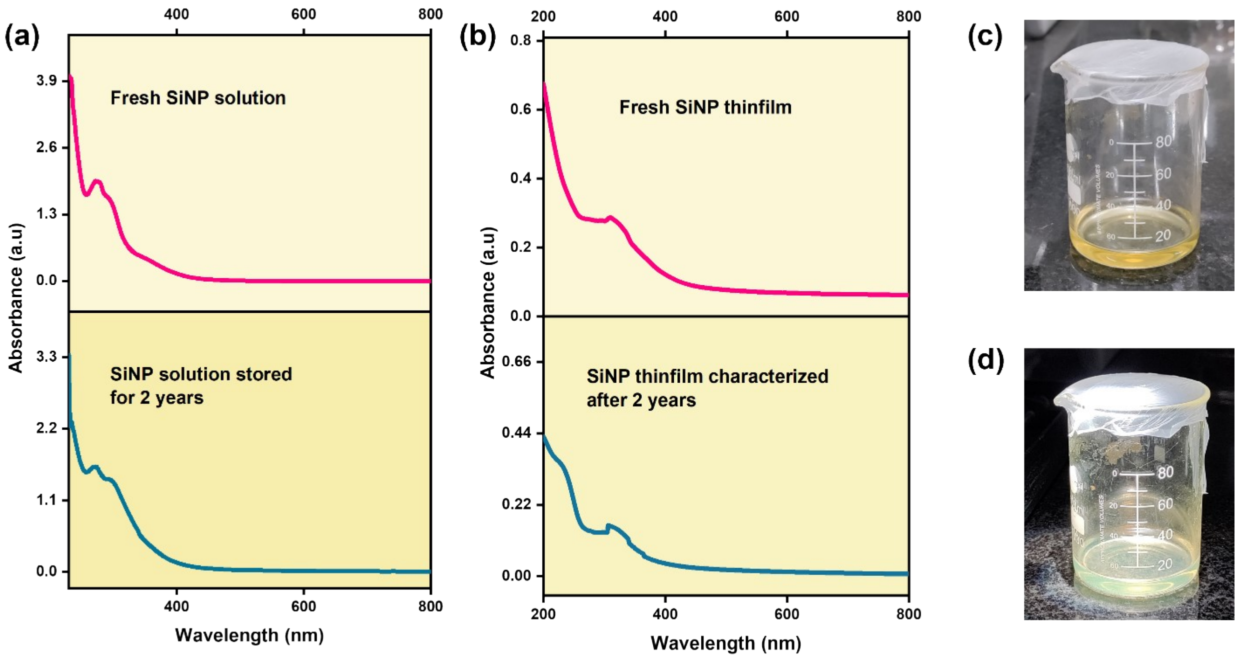


Figure S15. (a) Comparison of absorbance studies of fresh and stock SiNPs solution-stored for 2 years. (b) Comparison of absorbance studies of fresh and stock SiNPs coated quartz substrate-stored for 2 years. (c) Stock SiNPs solution under normal illumination. (d) Stock SiNPs solution under solar simulator.

References

(1) Nataraj, C.; Mohanta, K.; Badhirappan, G. P. Investigations on Optical Absorption and the Pyro-Phototronic Effect with Selectively Patterned Black Silicon for Advanced Photodetection. *ACS Appl. Mater. Interfaces* **2024**. https://doi.org/10.1021/acsami.3c18632.

(2) Priolo, F.; Gregorkiewicz, T.; Galli, M.; Krauss, T. F. Silicon Nanostructures for Photonics and Photovoltaics. *Nat. Nanotechnol.* **2014**, *9* (1), 19–32. https://doi.org/10.1038/nnano.2013.271.