Supporting information for

Fabrication of Broadband Antireflective PEDOT Nanocone Arrays with Unique Electroreflective Properties

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Experimental procedure

Fabrication of PEDOT thin film

The fluorine doped tin oxide coated glass (FTO-glass; ~7 Ω/sq, Sigma-Aldrich) was degreased by sonication in deionized water, acetone and methanol and then dried with a nitrogen jet. Additionally, FTO-glass was treated by oxygen plasma cleaning (PDC-32G, Harrick Plasma) for 3min. Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS, 1.0 wt. % in H_2O, Sigma-Aldrich) was mixed with isopropyl alcohol and ethylene glycol (ratio 85:10:5) to enhance electronic conductivity and improve wetting.[1,2] Uniform and thin PEDOT:PSS layer was coated on FTO by spin coating at 3000rpm for 20s. The sample was dried for 30min on a hot plate at 130°C. Chronoamperometry was used to electrodeposit PEDOT films on the PEDOT:PSS coated FTO surface. The PEDOT electrodeposition were performed with a potentiostat (Autolab) at a constant potential of 1.0V for 75s to make 450nm thick film with a Pt counter electrode, a Ag/AgCl reference electrode, and an aqueous electrolyte consisted with 0.02M 3,4-

ethylenedioxythiophene (EDOT, 97%, Sigma-Aldrich), 0.1M sodium dodecyl sulfate (SDS) and 0.1M lithium perchlorate ($LiClO_4$, 99.5%, Alfa).

Fabrication of PEDOT nanocone arrays

A solution of polystyrene beads with a diameter of 0.2μm (Polybead carboxylate, 2.6 w/v %, Polyscience) were centrifuged and transferred to a mixture containing ethanol and methanol with a 2:1 ration. Surfactant trition-X-100 (TX100, Fischer Scientific) was added to the solution at 7.5mM. The concetration of PS beads was adjusted to about 5 w/v %. The PS beads were spin coated on PEDOT thin film with 650rpm for 20s and allowed to dry at dried at room temperature. The PEDOT film with PS beads sample was etched by oxygen plasma (50W, 200mTorr, South Bay Technology) for 1m 30s. To remove any remaining PS beads the sample was cleaned with tetrahydrofuran (THF, EMD) for 2h.

Characterization

For morphological characterization, a field-emission scanning electron microscope (FEI Magellan 400) was used. For UV-Vis measurements, a Hewlett Packard 8453 UV-Visible spectrophotometer was used. For reflectivity measurements, a halogen ramp was used as a white light source (7V, DC regulated power supply, BK presicion). The emitted light from a halogen light was coupled into an optical fiber (M25L01, Thorlabs), collimated with an achromatic lens (f = 50 mm, AC254-050-A-ML, Thorlabs), then aligned incident to the sample surface. The reflected of transmitted light was coupled into an optical fiber (P1000-2-VIS/NIR, Ocean Optics) with an achromatic lens (f = 30 mm,

AC254-030-A-ML, Thorlabs), then characterized with a UV-Vis spectrometer (USB4000, Ocean Optics). To measure the *ex situ* UV-vis spectra and reflectivity spectra, the samples applied potential for 20 seconds before removing the film from solution.

Figure S1

Current density and charge curves during PEDOT electropolymerzation and electrodeposition at +1.0V on thin PEDOT:PSS coated FTO conductive substrate.

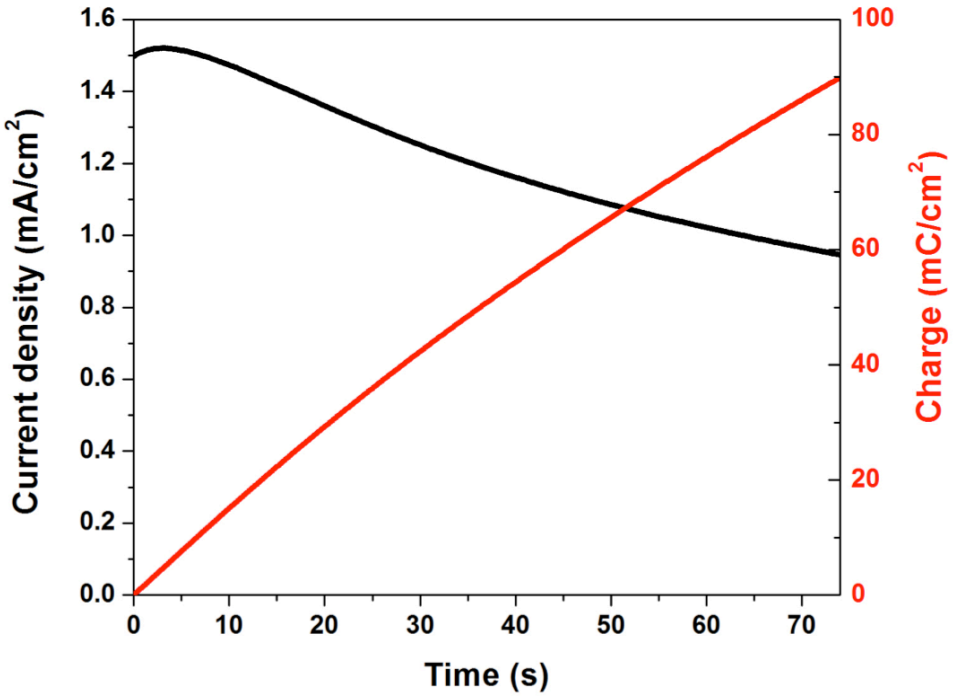


Figure S2

SEM image of an unmodified 450nm PEDOT thin film thickness.

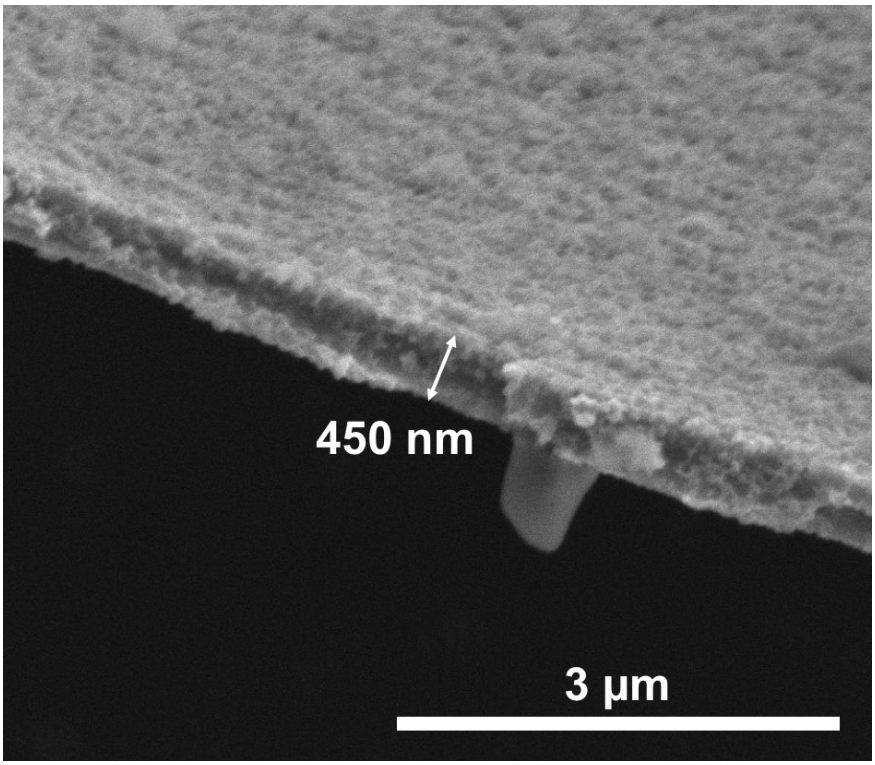


Figure S3

Reflectivity spectrum at an incidence angle of 8° for an unmodified 350 nm PEDOT film. (the thickness is the same as PEDOT nanocone) A similar reflectivity spectrum was observed with an unmodified 450 nm PEDOT. (Figure 2)

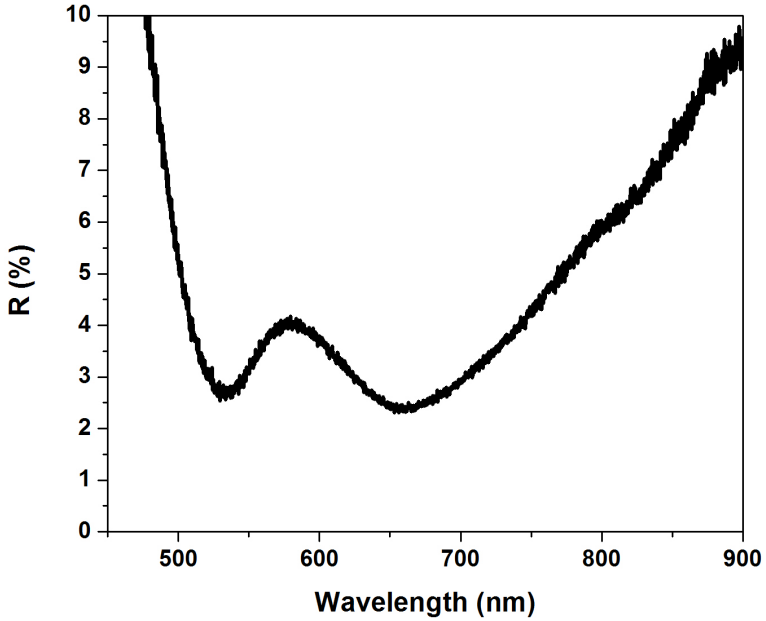


Figure S4

Reflectivity spectrum at an incidence angle of 45° (black spectrum) and 67.5° (blue spectrum) for a (a) PEDOT nanocone array film and (b) an unmodified PEDOT film.

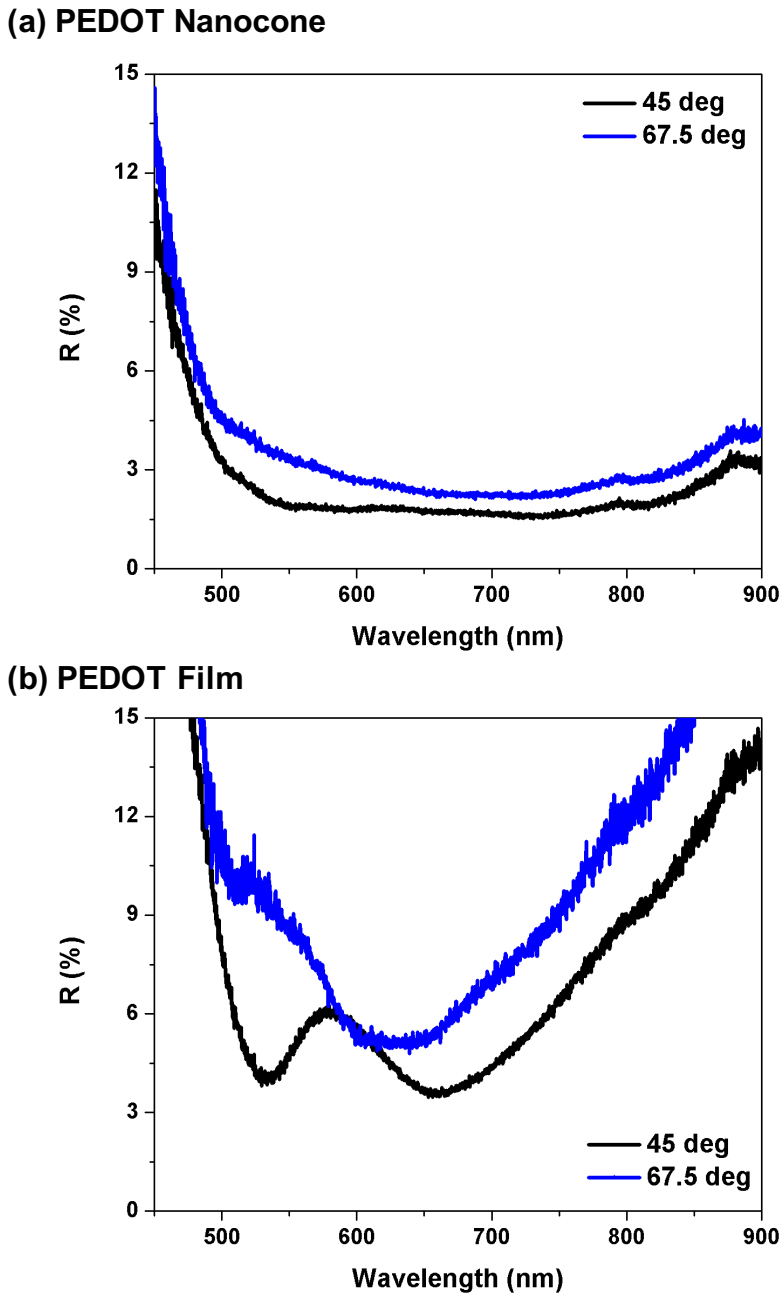


Figure S5

Electrochromic behavior of an unmodified PEDOT thin film. UV–visible absorption spectra of PEDOT film removed from solution after 20s under potentiostatic control at three potentials: -1.0V (blue spectrum), 0.0V (black spectrum) and +1.0V (red spectrum) vs. Ag/AgCl.

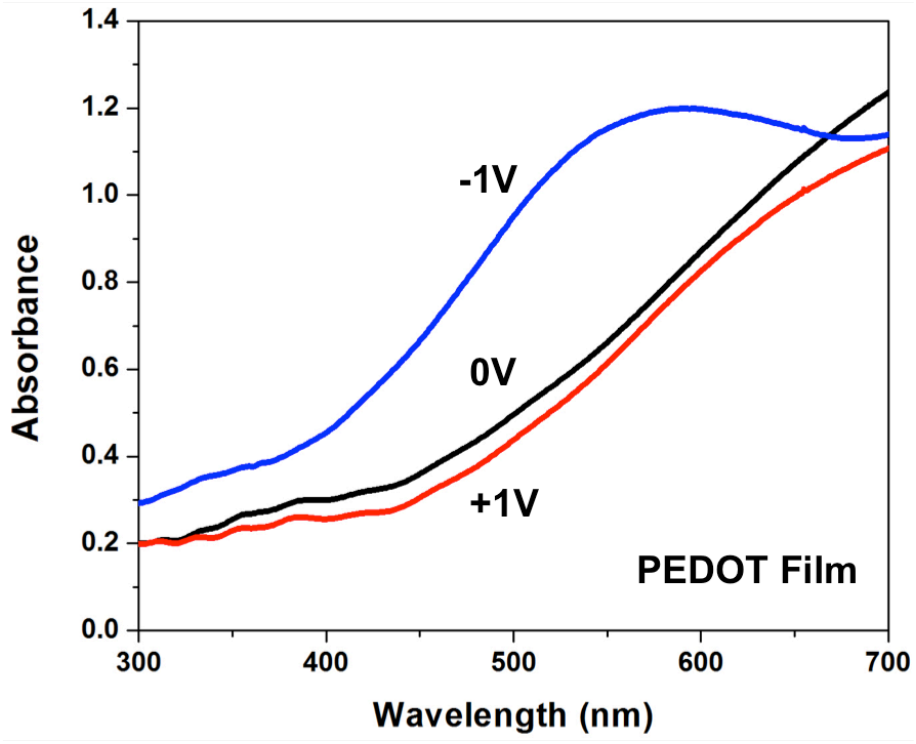


Figure S6

Three phase Fresnel reflectivity calculation (air; n1=1/film; n2=1.5+xi/substrate; n3=1.5) and plot of Reflectivity vs. theta (incident angle) . An increase in PEDOT film absorption as modeled by an increase in the imaginary component of the film RI from zero to 0.5 leads to a higher specular reflectivity at all incident angles.

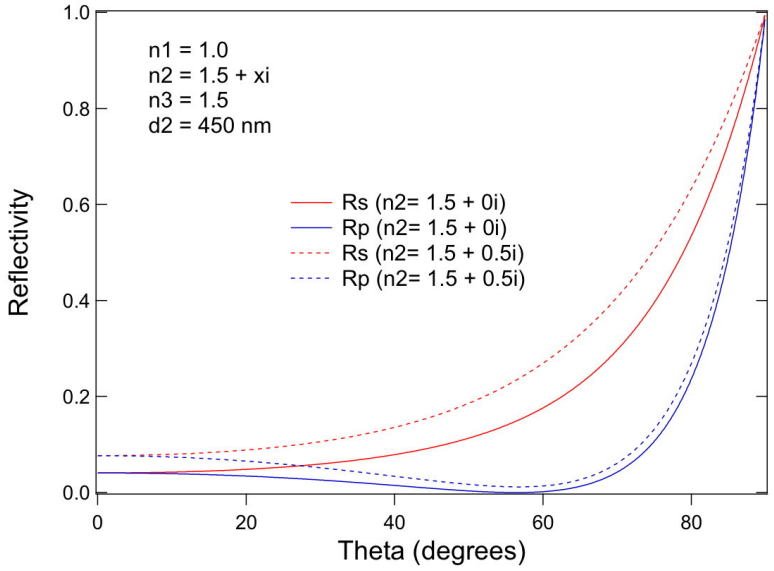
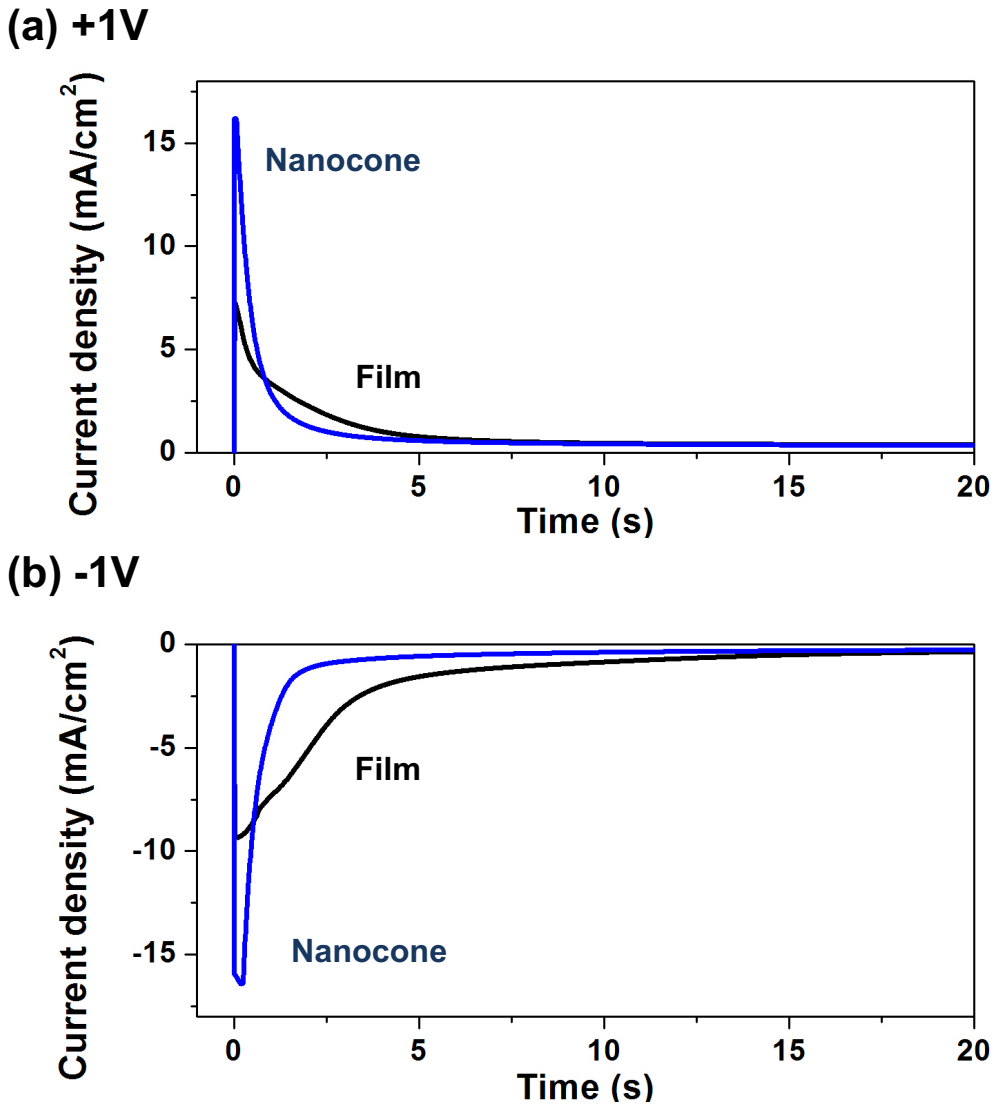


Figure S7

Chronoamperometry curves of PEDOT nanocone array (blue spectrum) and unmodified PEDOT thin film (black) by applied potential (a) +1.0V and (b) -1.0V during 20s in 0.1M $LiClO_4$ (aqueous) electrolyte.



References

(1) Kim, Y. H.; Sachse, C.; MacHala, M. L.; May, C.; Müller-Meskamp, L.; Leo, K. *Adv. Funct. Mater.* ***2011***, 21, 1076–1081.

(2) Park, H.; Shi, Y.; Kong, J. *Nanoscale* ***2013***, 5, 8934–8939.