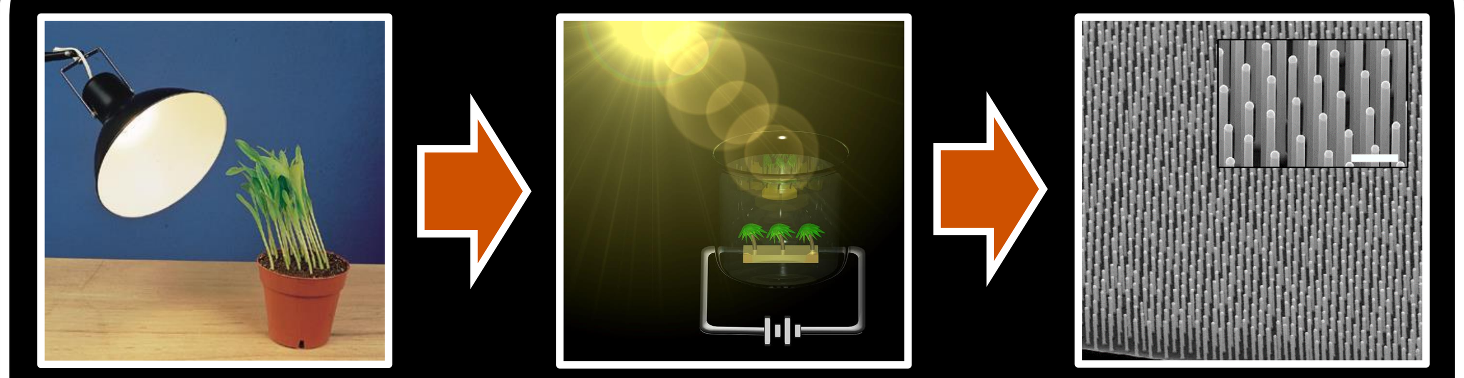
Inorganic Phototropic Growth of Semiconductor Mesostructures Directed by Interfacial Light Absorption Anisotropy

Caltech

Azhar I. Carim[1], Nicolas A. Batara[2], Anjali Premkumar[2], Madeline C. Meier[1], Kathryn R. Hamann[1], Harry A. Atwater[2] and Nathan S. Lewis[1]
[1]Division of Chemistry and Chemical Engineering, [2]Division of Engineering and Applied Science, Caltech, Pasadena, CA 91125, USA

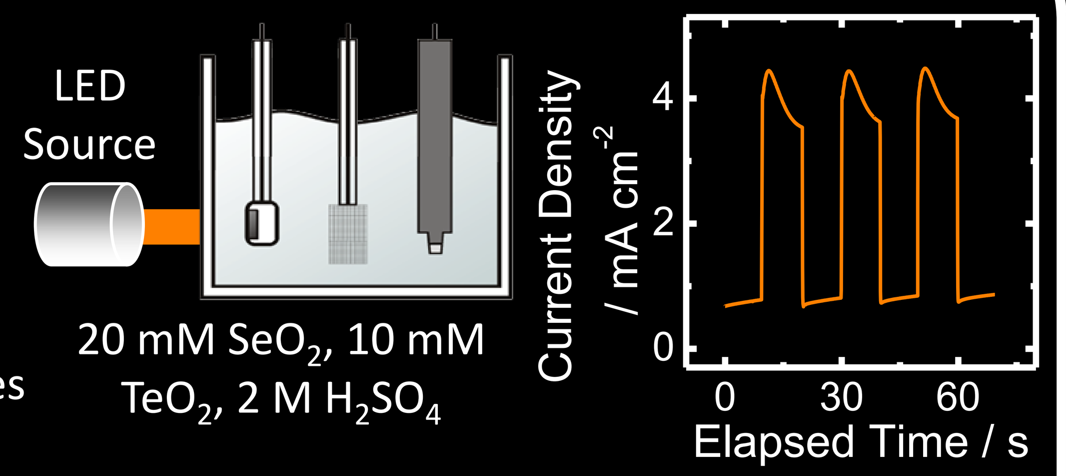
Motivation



In analogy to natural phototropism, utilize unstructured illumination and capitalize on inherent anisotropies in light-material interactions to optically instruct growth of complex mesostructures in three-dimensions without a template nor photomask.

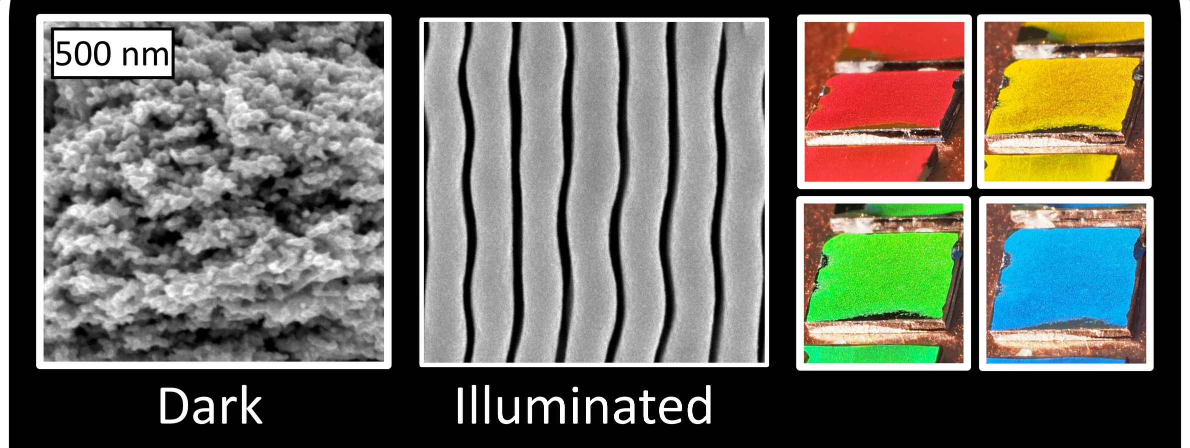
Inorganic Phototropic Growth

- Room temperature
- Isotropic solution
- Template-free
- Maskless
- Uncorrelated source
- mW cm^{-2} intensities
- µm min^{-1} growth rates



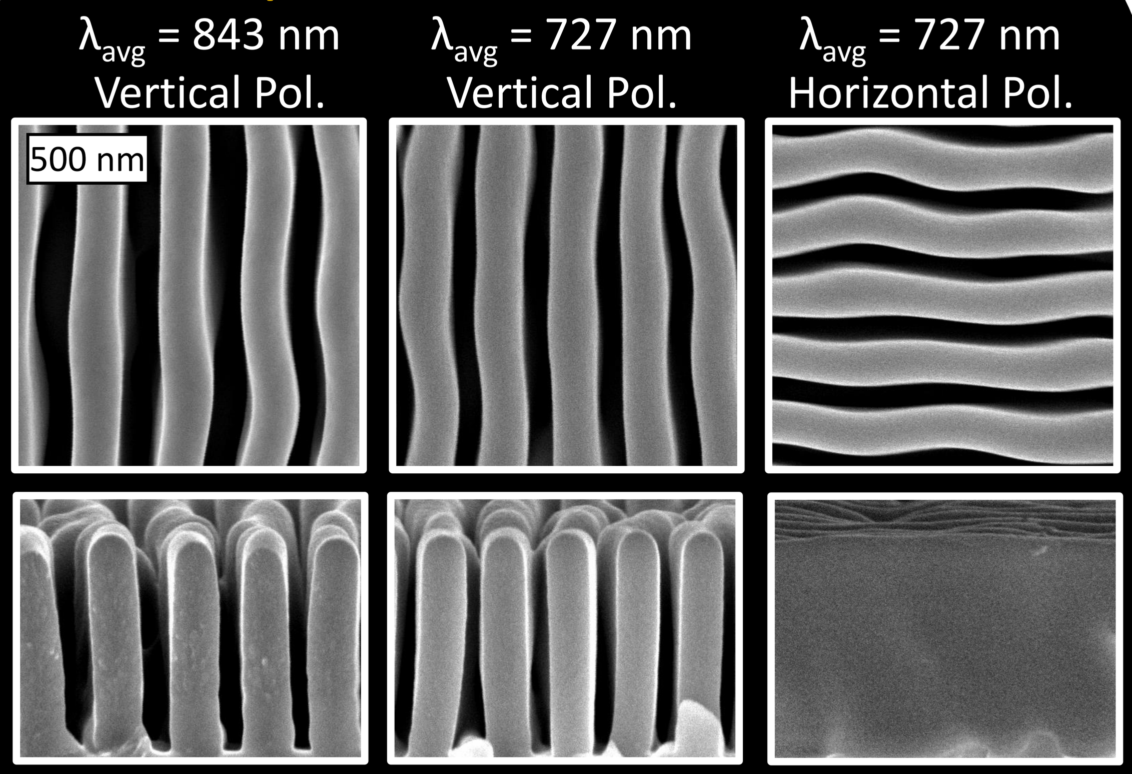
Electrodeposited semiconducting Se-Te from aqueous solution with 3-electrode cell using unpatterned LED illumination. Growth rate significantly enhanced under illumination (λ_{avg} = 521 nm, P = 13.5 mW cm^{-2}).

Spontaneous Mesostructuring



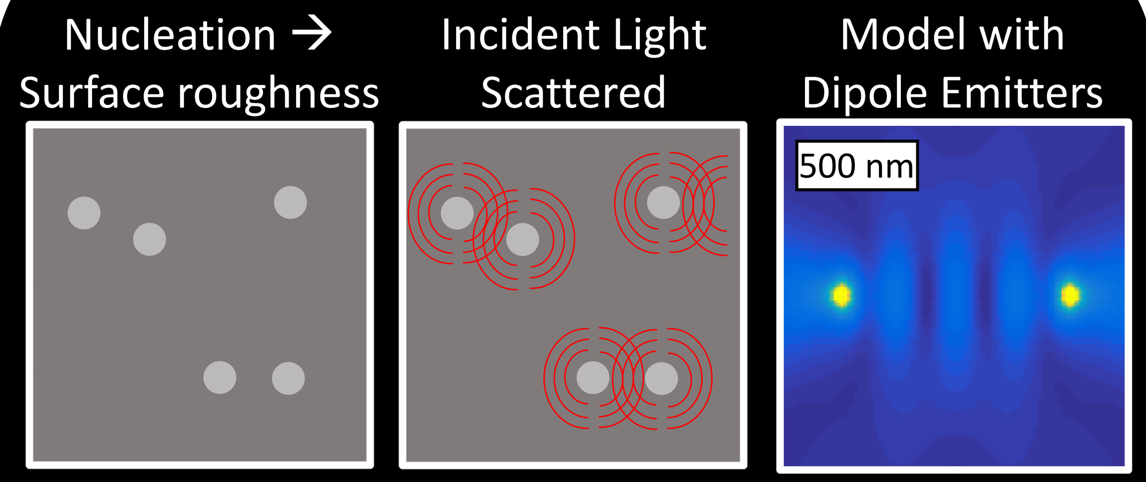
Dark growth unpatterned; polarized illumination (λ_{avg} = 528 nm) effected anisotropic pattern conformally over macroscale area, as highlighted by film iridescence.

Optical Growth Control



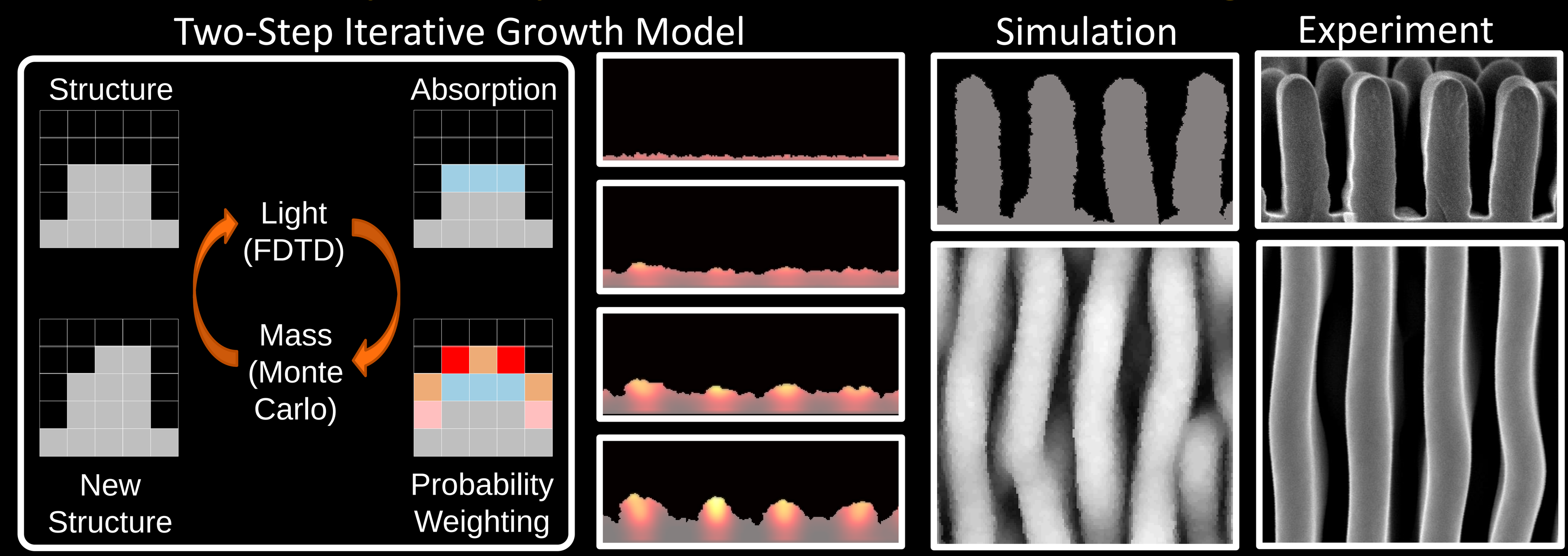
Feature size and pitch scale with wavelength. Polarization sets in-plane orientation.

Initial Growth Mechanism



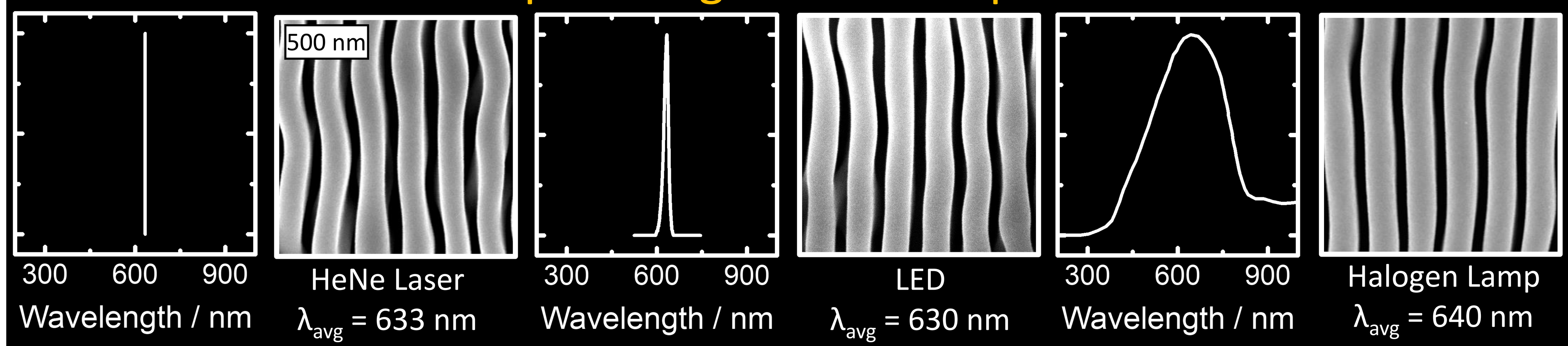
Initial film nuclei scatter the incident illumination. This optical interaction was modeled using two dipole emitter sources: interference fringes were observed between the sources. This spatially-oscillating light intensity profile effects spatially-anisotropic rates of photoelectrochemical growth.

Optically-Based Growth Modeling

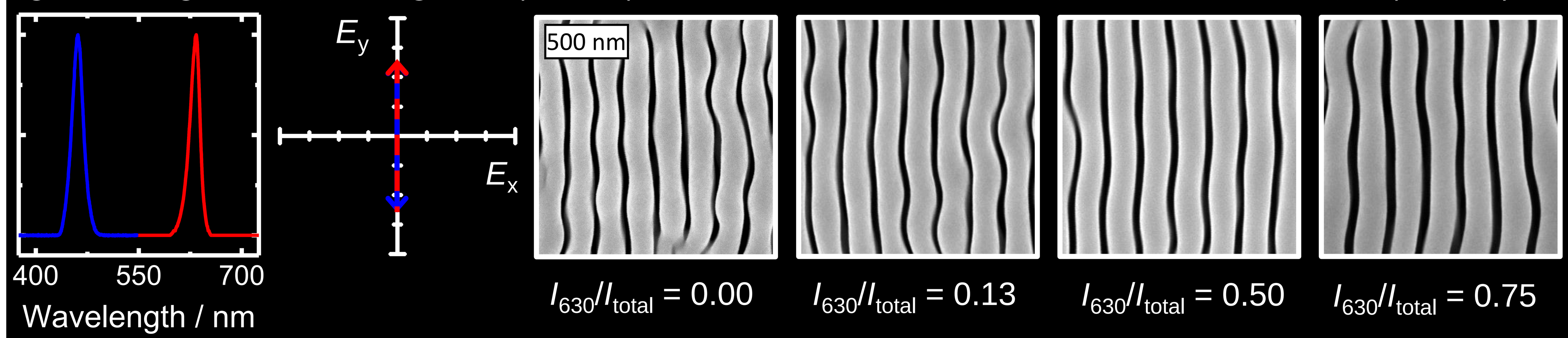


Simulations using iterative model: FDTD method first utilized to calculate light absorption profile. Then, a Monte Carlo method used to add mass preferentially to high absorption areas. No empirical inputs beyond the material complex refractive index. Experimental agreement suggests morphologies are fully optically determined.

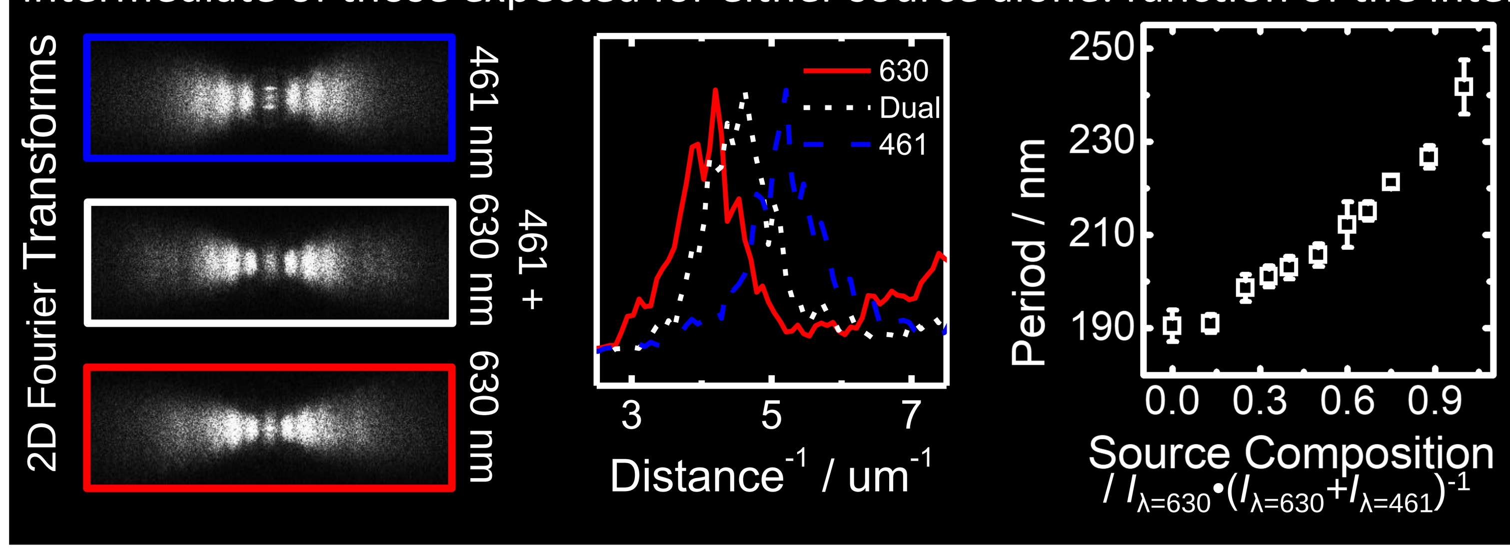
Self-Optimizing Growth Response



Similar patterns with equivalent morphological periods observed for growth using a HeNe laser, a narrowband light emitting diode, and halogen lamp with spectral FWHM values of <<1 nm, 30 nm, and 420 nm, respectively.

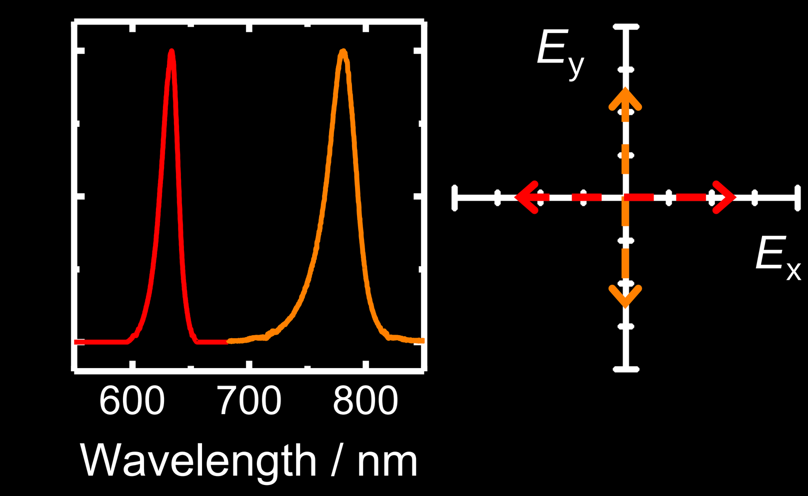


Simultaneous illumination with λ_{avg} = 461 and 630 nm sources resulted in patterns with periodicities intermediate of those expected for either source alone: function of the intensity ratio between sources.

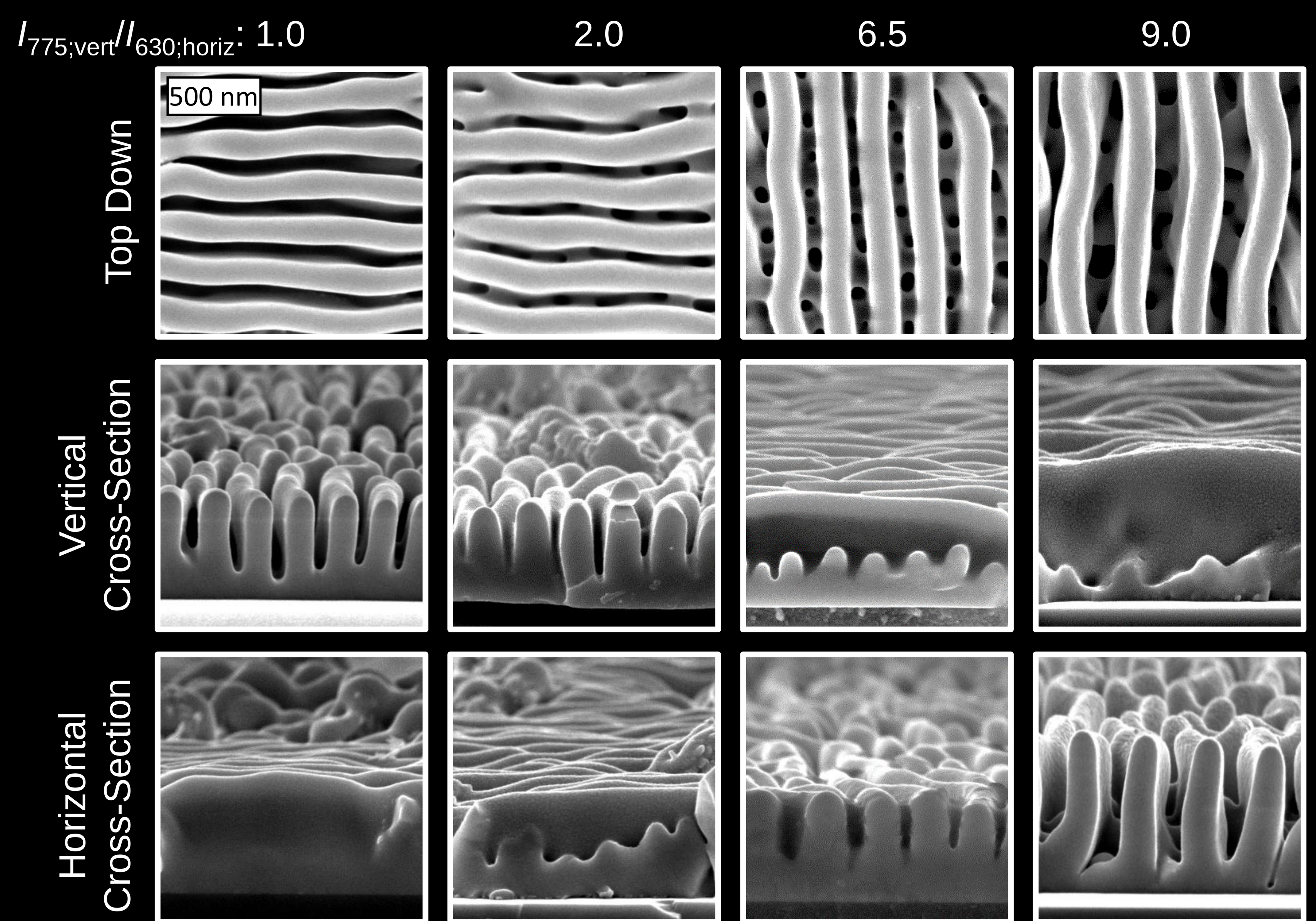


Fourier analysis indicated singular morphological periods for each illumination condition and was used to quantify. Period could be continuously tuned by varying intensity ratio. Growth self-optimizes to effect morphology that maximizes interfacial absorption.

Simultaneous Polarization Inputs



Simultaneous illumination with orthogonally polarized λ_{avg} = 630 and 775 nm sources resulted in morphologies exhibiting two intersecting, perpendicular patterns with two different periodicities. The relative heights of the two patterns was a function of the intensity ratio between the sources and could be tuned continuously.



Conclusions

Inorganic phototropic growth was effected via photoelectrodeposition of semiconducting Se-Te. Three-dimensional mesostructures were generated in a template-free manner over macroscopic areas. Morphologies were a function of all optical inputs utilized during growth.

Acknowledgements

This work was supported in part by the “Light-Material Interactions in Energy Conversion” EFRC funded by the DOE under Award No. DE-SC0001293 and in part by the NSF under Award No. DMR 1905963. AIC, MCM, and KRH acknowledge the NSF GRFP. Authors acknowledge R. Gerhart and N. Hart for cell fabrication.