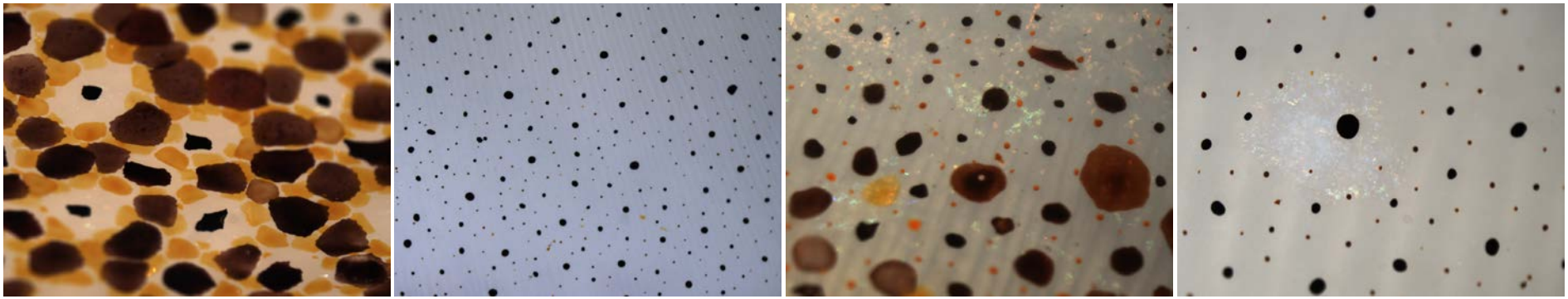
Thermal management in the ocean?

Unexpected Short-Wave Infrared Color Modulation from Nanostructures in Cephalopod Chromatophores



Leila Deravi

Biomaterials Design Group

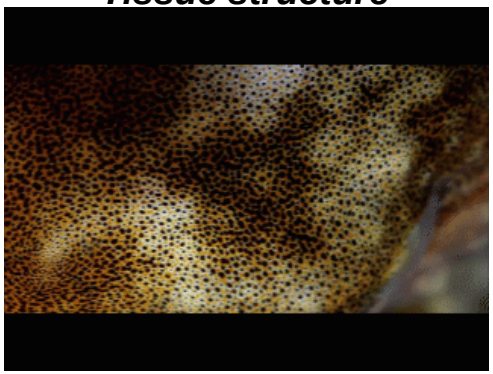
Northeastern University, College of Science

Department of Chemistry and Chemical Biology

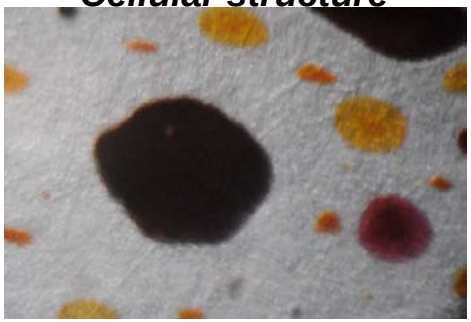
www.Northeastern.edu/biomaterialsdesign

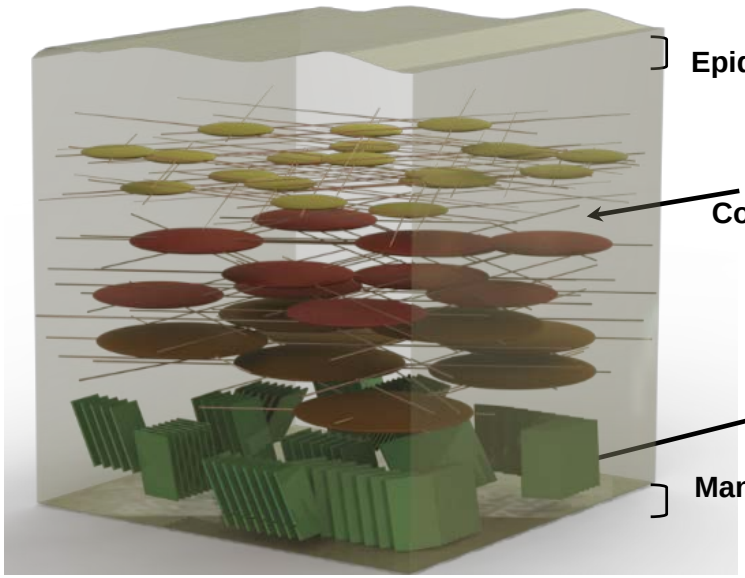
What components contribute to coloration in the chromatophore light organ?

Tissue structure

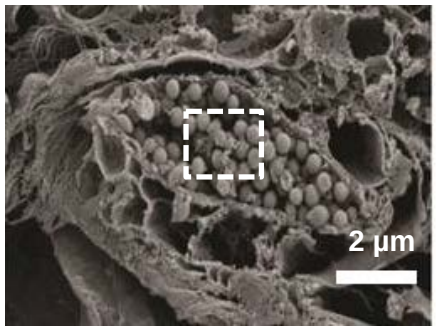


Cellular structure

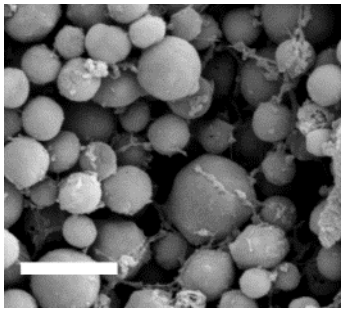




EM Pigment sac



Tethered pigment granules



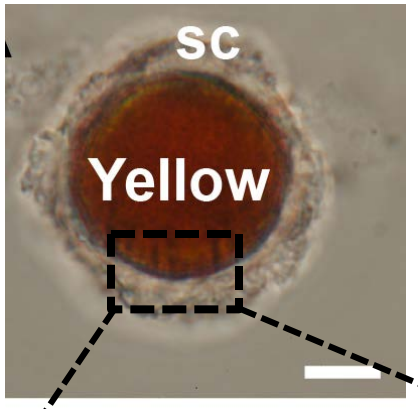
Granule diameter 528 ± 68 nm

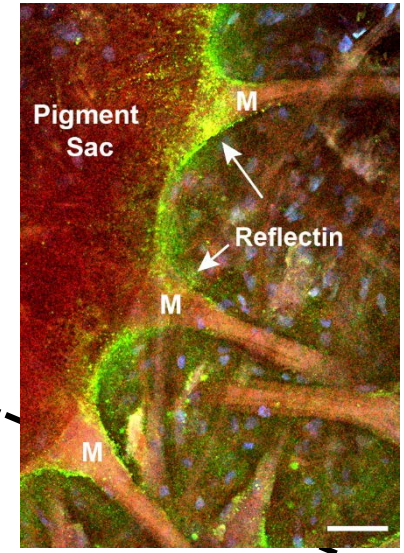
Hypothesis: ***Pigment granules behave as photonic nanostructures optimized to enhance the extraction and absorption of light for distributed skin patterning***

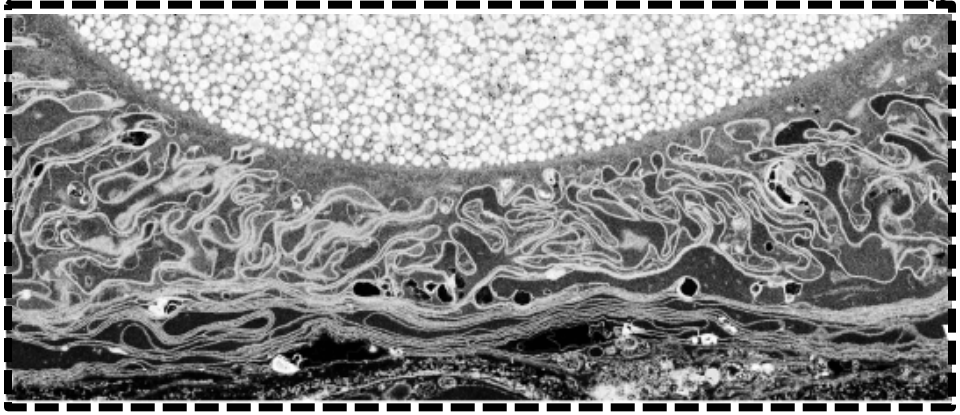
J.R Soc Interface, ***2014***

Structural iridescence in the chromatophore

→ ***Combination of pigmentary + structural coloration used to enrich color presented during actuation***





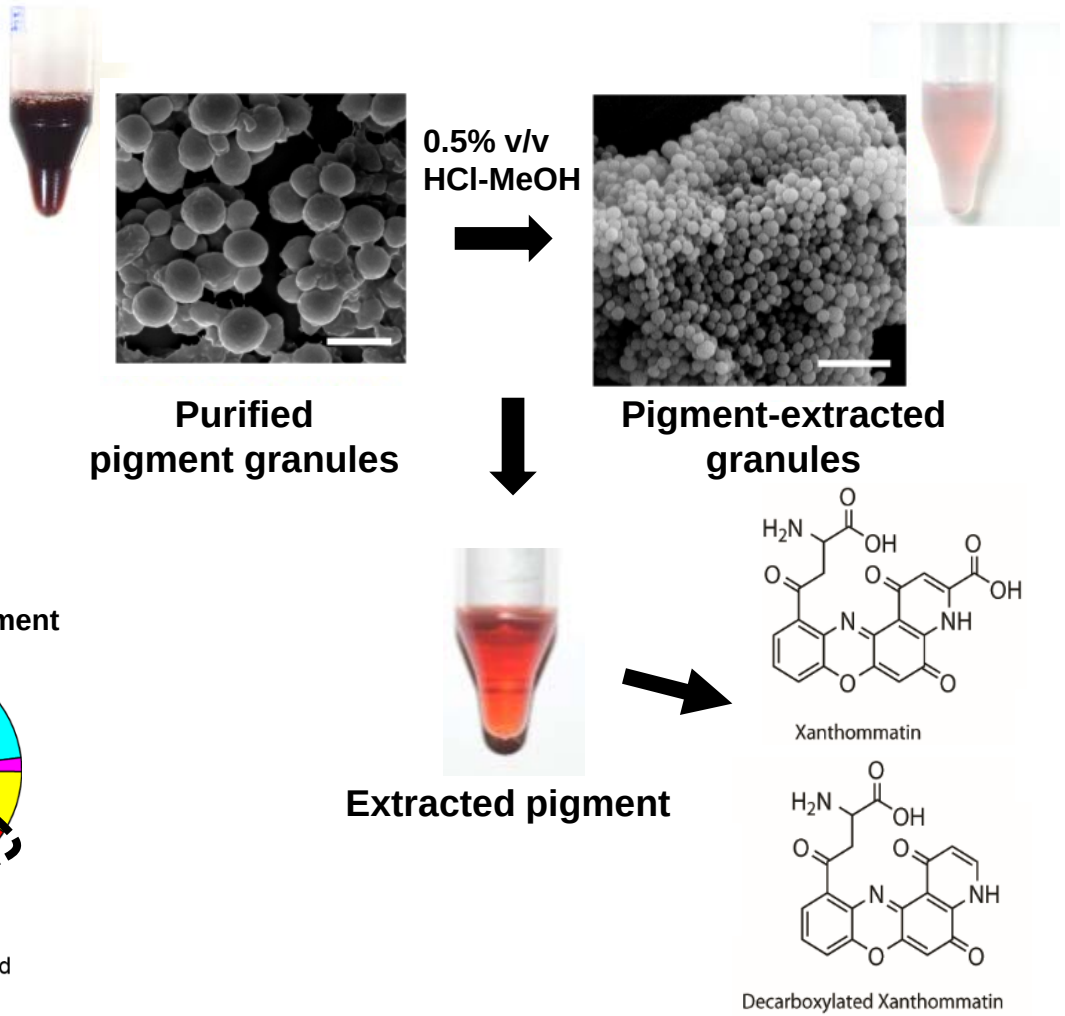


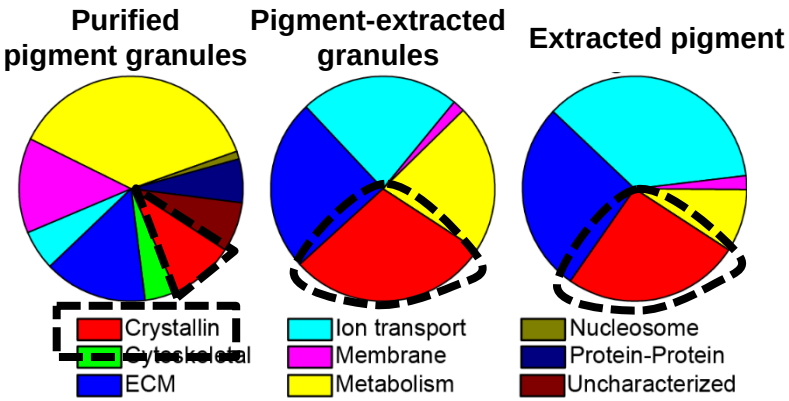
Williams, Senft, Yeo, et al. *Nature Communications* **2019.**

Steve Senft, Roger Hanlon @ MBL Woods Hole

What are the chromatophore pigment granules?

- We developed a process to selectively isolate and purify granules from the chromatophore
- We used the first annotated transcriptome of the chromatophore to assign proteins specific to the granules





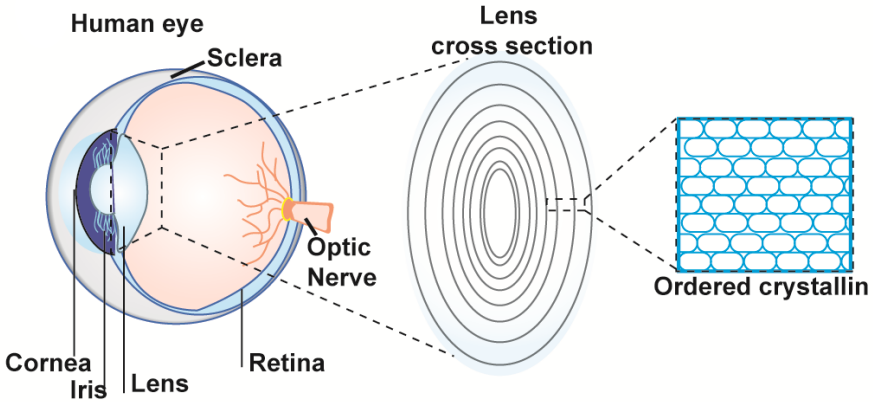
Lens crystallin is the most abundant single protein in the granules

Nature Communications, ***2019***

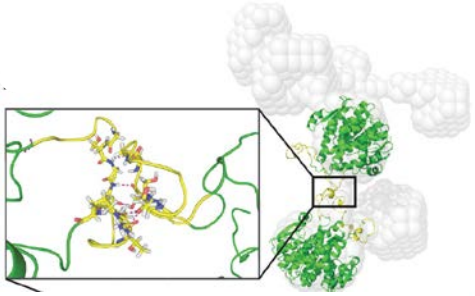
Langmuir, ***2016***

The role of crystallins in the light sensing

- Ordered crystallin (n~1.4) maintains the structural stability and transparency of the eye lens
- High concentrations (> 0.2 mg/mL) increase refractive index and decrease light scattering
- Crystallin (S- isoform) is observed as patchy colloids that form thermodynamically stable gels in squid eyes

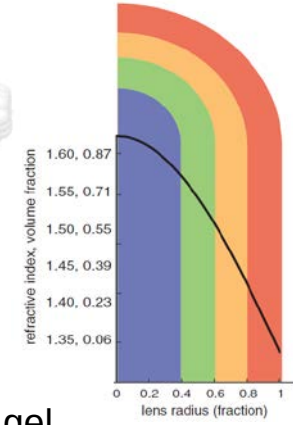


Crystallin dimers stabilized through unstructured dimers



Sweeny *Science*. 2017, 357,564

Lens radius vs. RI



Formation of a high density colloidal gel dominated by S-crystallin dimer interactions

Similar to the human and squid eye lens, does crystallin regulate both cellular structure and refraction of light within skin?

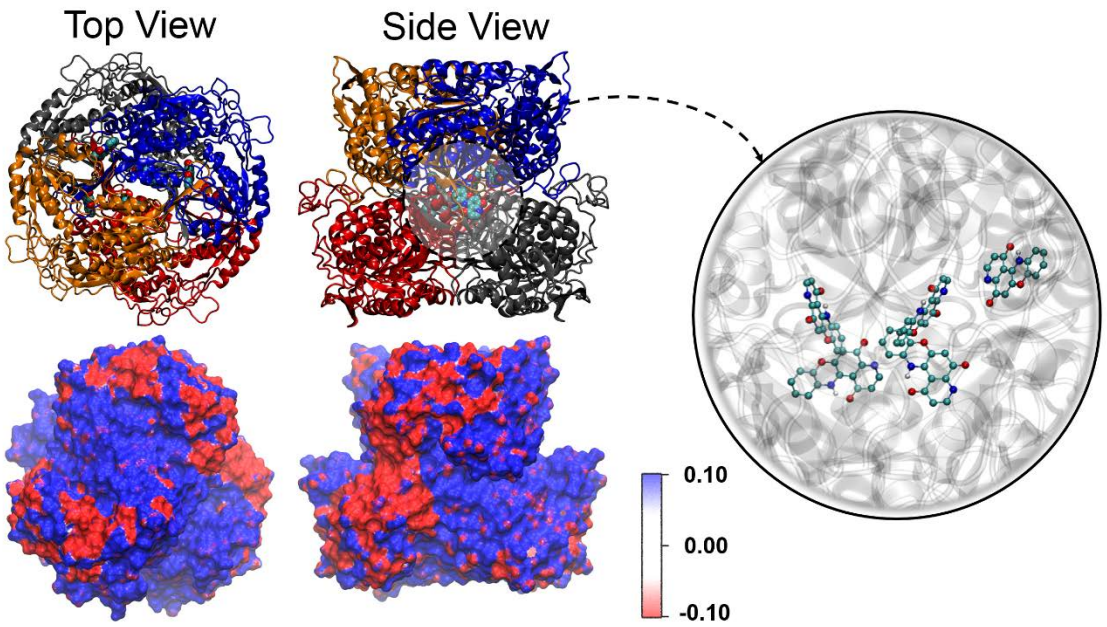
The relationship between pigments and proteins

- The abundance of crystallin and its affinity to xanthommatin suggests dual roles that contribute to:

i) The spherical nanostructure of the granule that aids in scattering

ii) The stabilization and/or sequestration of the pigment in the granule to aid in color retention

Molecular model of crystallins with pigment:

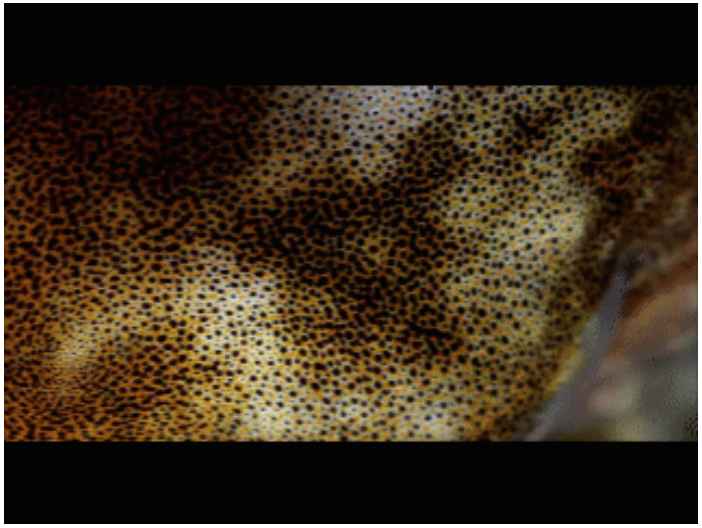


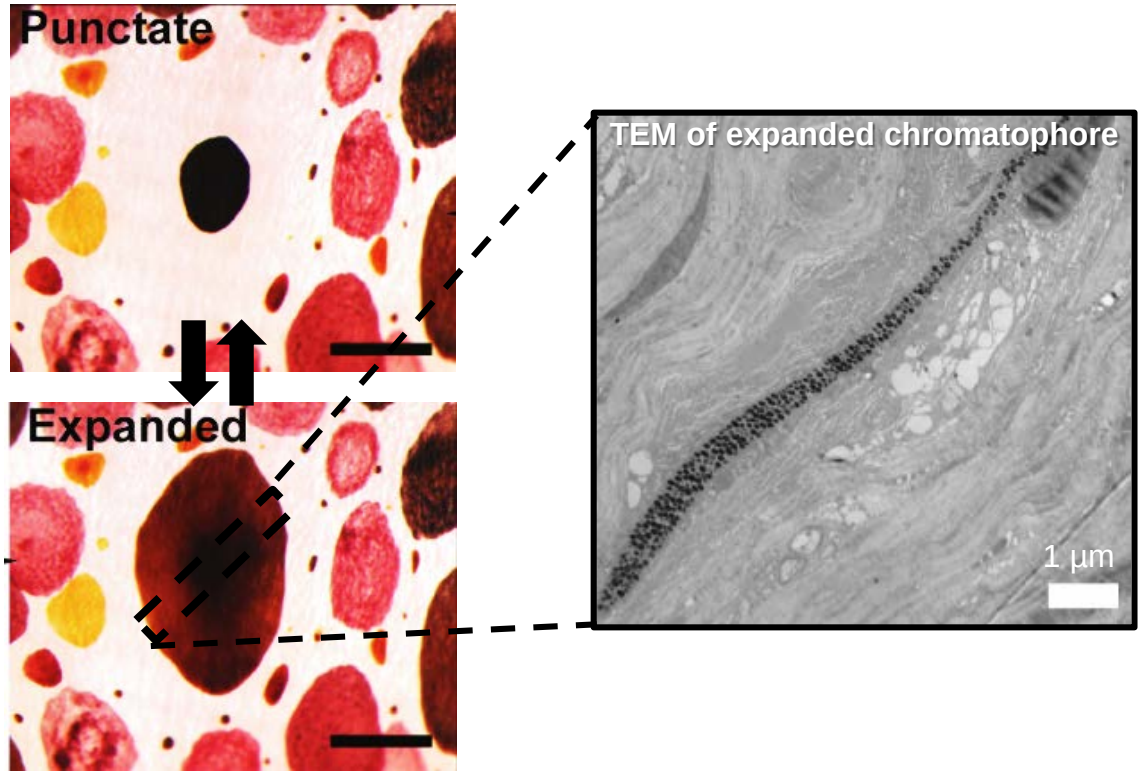
Average binding energy of pigment in crystallin tetramer	**-10.7 ± 0.2 kcal/mol**

Combinations of crystallin and pigments in the granules may play an important role in regulating color within the chromatocyte

Nature Communications **2019.**

What is the role of the granular structure in modulating color?



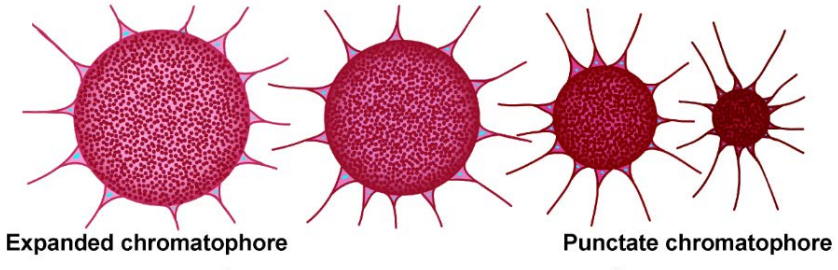


- Chromatophores experience a 5x change in presented surface area where granules are often 1-3 layers thick
- The color richness is still maintained but the mechanism is unknown

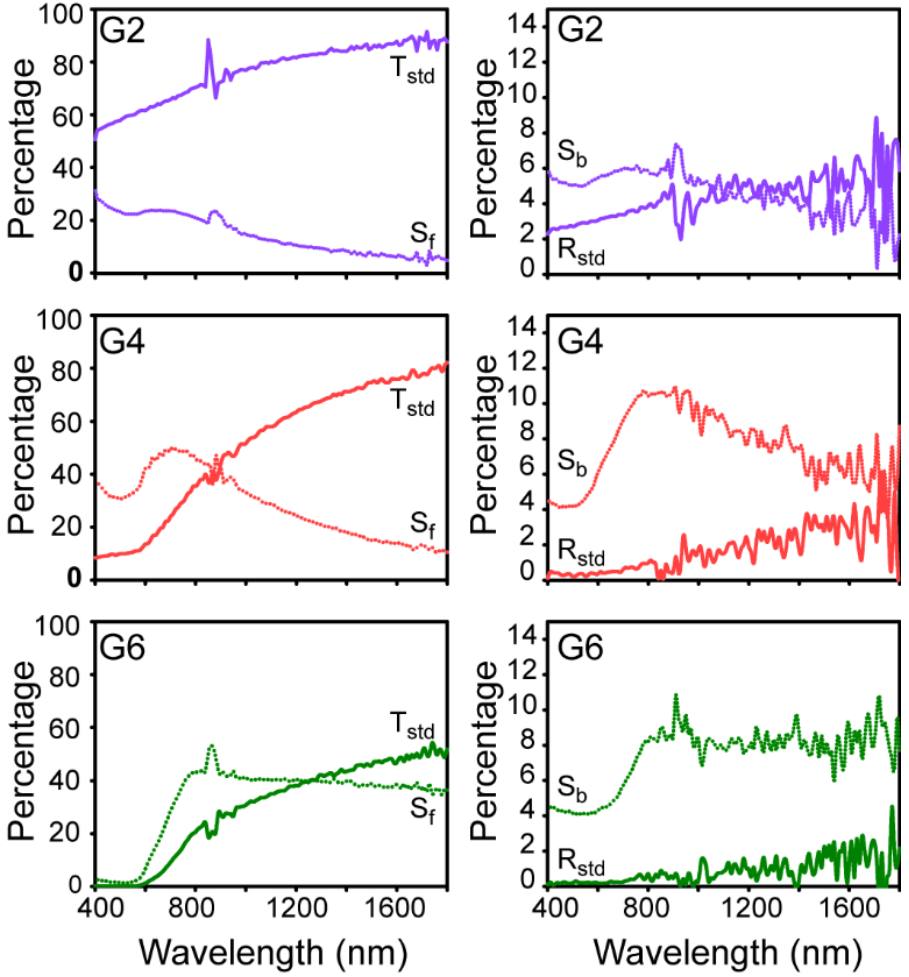
→ How do composition and nanostructure influence optics?

Contributions of optical scattering in perceived color

- Films containing a distribution of particles with multiple thicknesses inspired by chromatophore shape change



Control over sparse and dense arrays



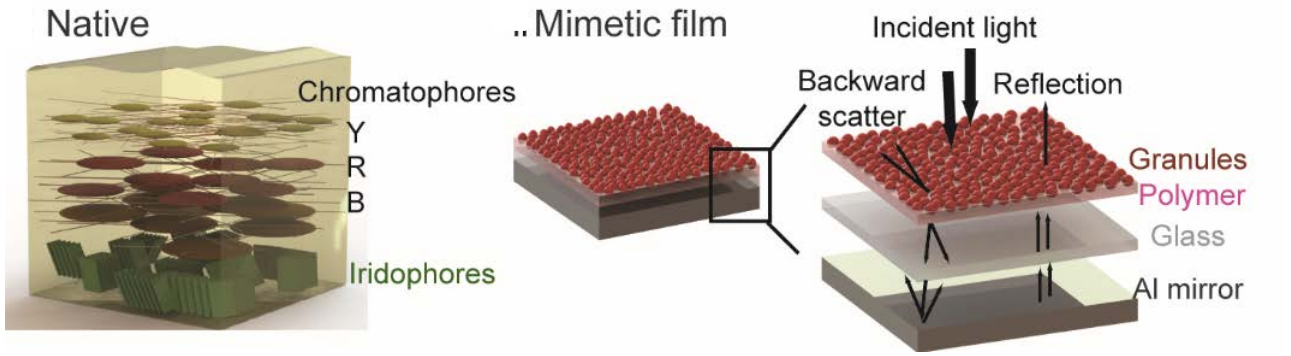
Scattering is the major contributor to transmitted and reflected color

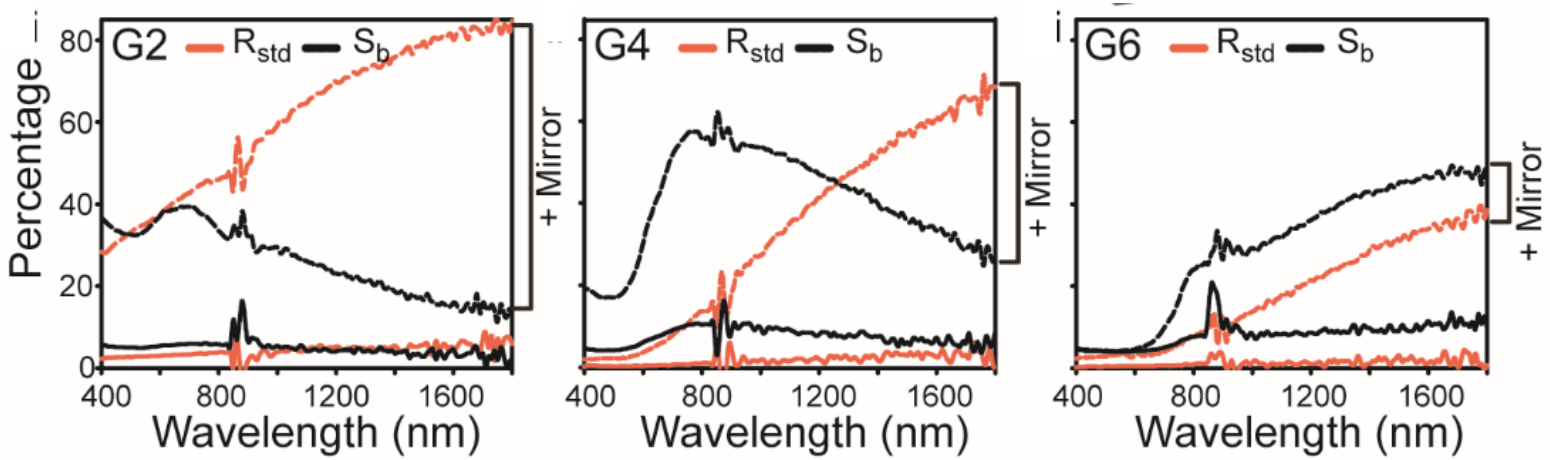
In collaboration with Richard Osgood CCDC-SC

Adv Opt Mater **2018**

Can we manipulate the direction of light to enhance color similar to squid?

- We placed a highly reflective aluminum (Al) mirror underneath the granule films and measured R_{std} and S_b





We can enhance the reflected and scattered color from chromatophore pigment granules, even when they are only one particle layer thick

In collaboration with Richard Osgood CCDC-SC

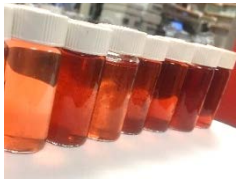
Adv Opt Mater **2018**

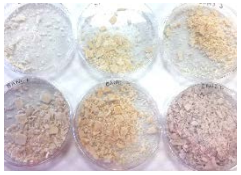
A new class of multi-functional materials inspired by/ derived from cephalopods

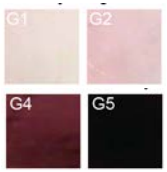
What else can we do?

Color

- Paints, specialty chemicals



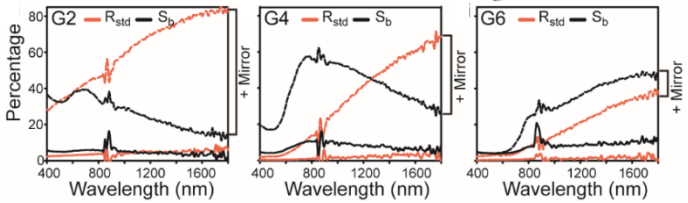




Color filtering

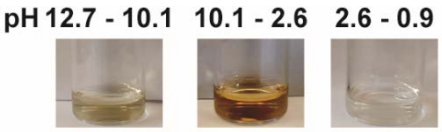
- UV through short- wave IR filters

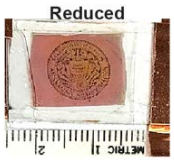
Sunscreen	SPF $_{calculated}$
XanthoChrome	**22**
Avobenzone	8
Oxybenzone	11



Color changing/ camouflage

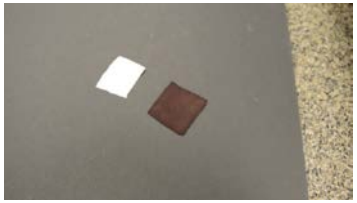
- pH sensors (optical probes)
- Electro-chromics





Reflective colorants

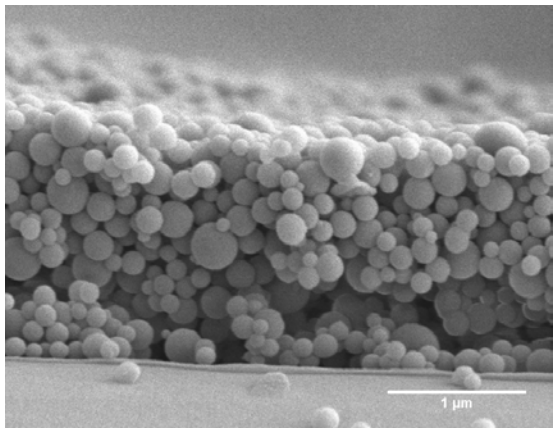
- Textiles/apparel
- Tactical shelters

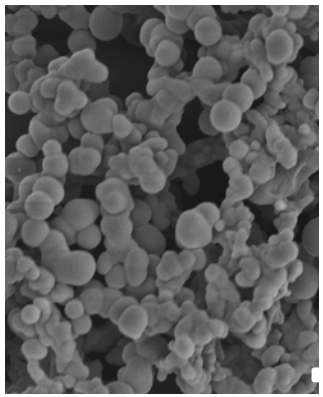


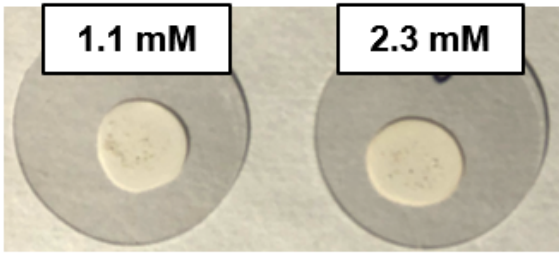
Technological hurdles remain in:

- Translocating the pigments for ‘on demand’ patterning local → global (the role of electrical control at low operational voltages)
- Scaling and quality control management of pigments (moving away from proteins)

- Here's what we know about the biology and chem so far.
- Hurdle in materials: scale, manufacturing, p



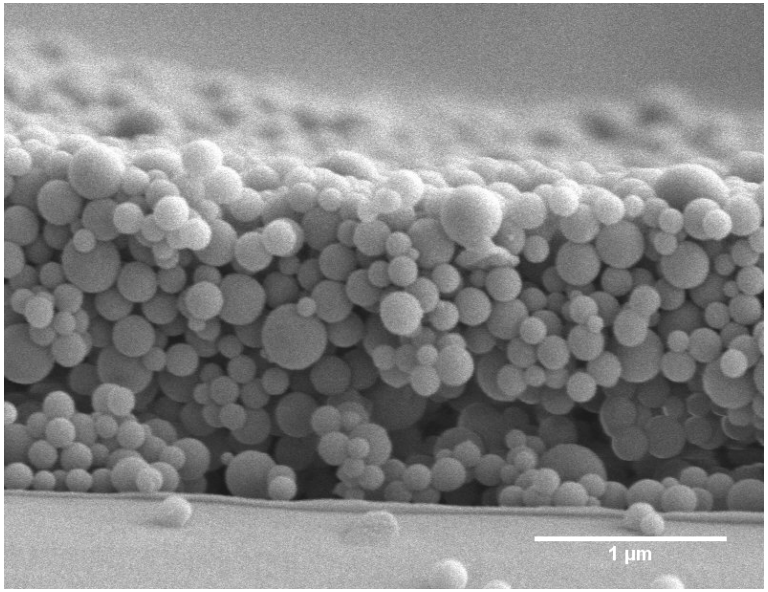




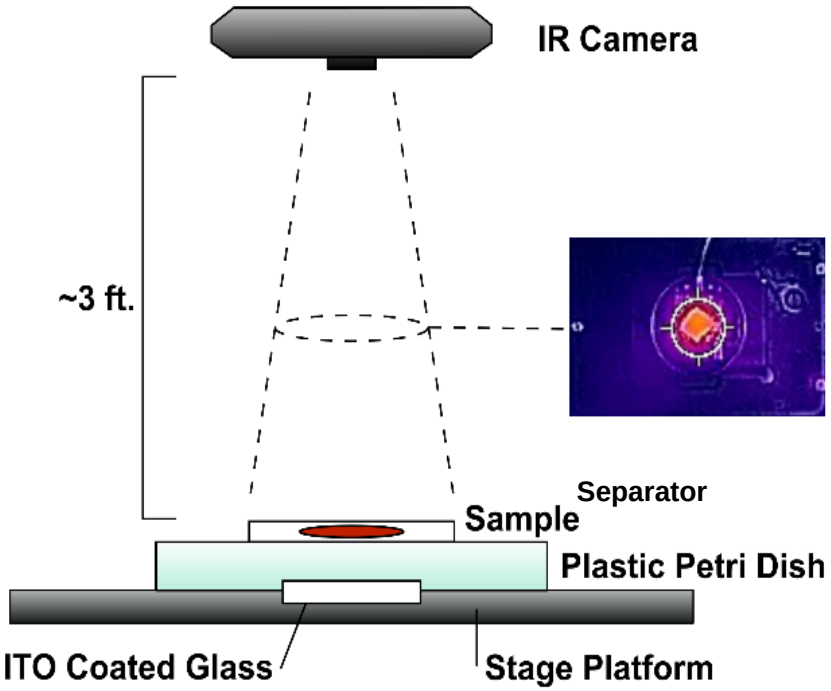
Sample	L*	a*	b*	C
1.1 mM	107.892	2.145	9.387	9
2.3 mM	108.317	2.440	9.583	9
4.6 mM	100.050	7.383	20.637	21

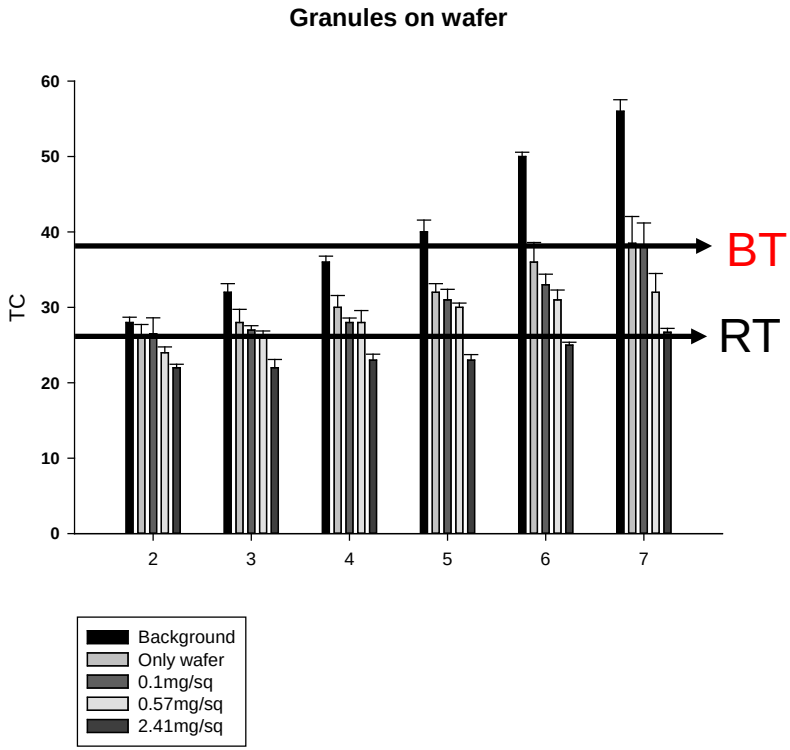
- If we can get past this, we can do X

Sample	L*	a*	b*
Uncoated	100.920	2.818	-70.
SiNP	99.845	2.358	9.08
XaNP	99.936	10.311	39.2
Reduced XaNP	93.017	13.988	17.8


1 µm

1b.





- **Granules have thermal concealing ability**