IOWA STATE UNIVERSITY

College of Engineering

Next Generation Coatings Through Self-assembly and Nanotechnology

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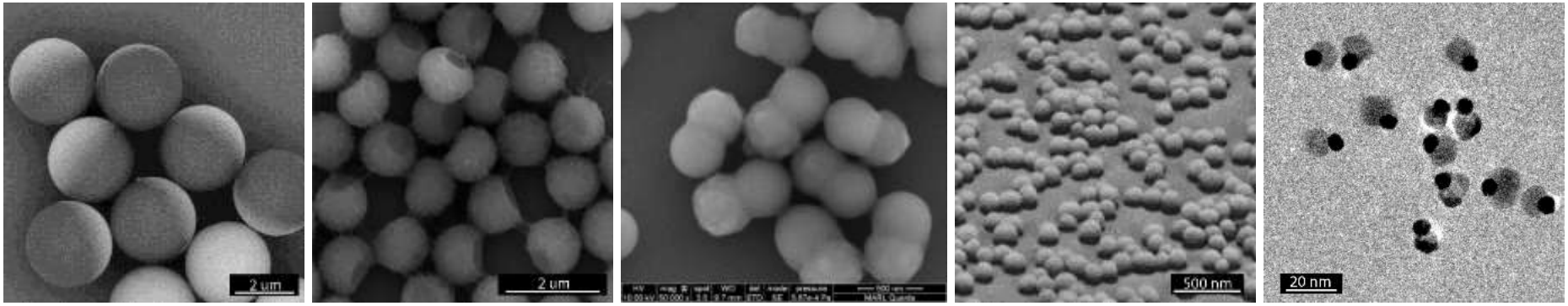


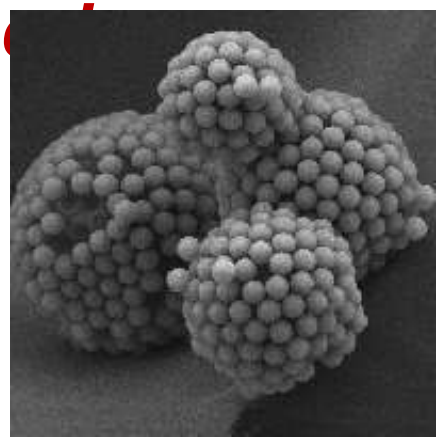
About me

- **Ph.D.** – University of Illinois at Urbana-Champaign
- **Postdoc** – MIT
- **Industry** – Dow Chemical (Rohm & Haas)
- **Professor** – Iowa State University

My lab – ***Soft Matter and Nano-engine***

(50+ publications & book chapters, 3 patents,
6 recent highlighted cover publications,
8 postdoc & graduates, 10+ undergrads,
funding from NSF, USDA and NASA)

http://sjiang1.public.iastate.edu/

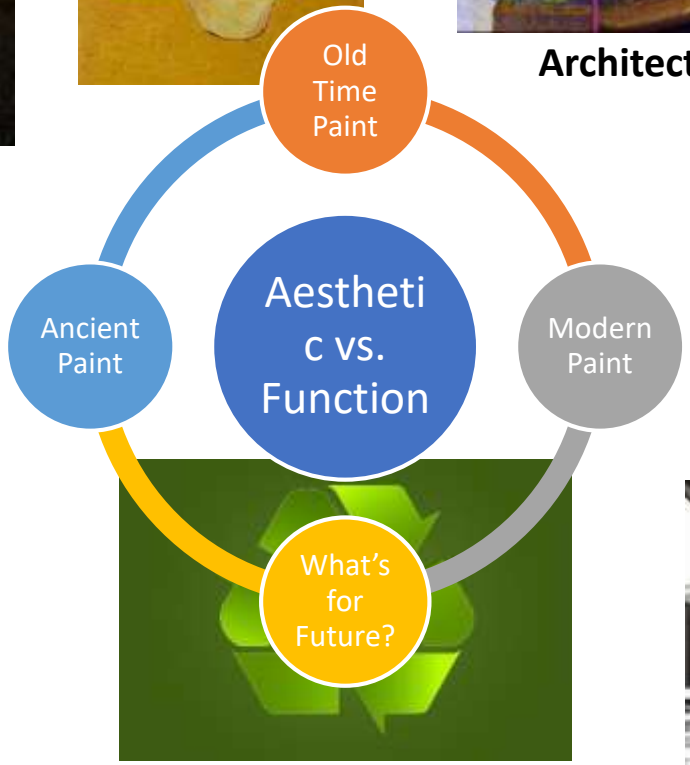


Next generation coating

Traffic Paint

Architecture Paint

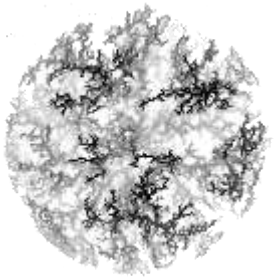
Painting of a Bison (c.15,000 BC)
From the Altamira Cave Complex



Marine Coating

Industry Coating

Outline



I. Biobased nano-composite coating

Self-assembly of nanoparticles under different biobased binders enables unique optical performance.

II. Janus particles coating additive

Janus particles *self-assemble* and stratify at interface and create hydrophobic coating surface.

I. Biobased nano-composite for UV-blocking and water-resistance coatings

1. Sustainability for food packaging
2. Coating design and nanotechnology
3. Binder comparison
4. Structure-property relationship

Sustainability – food packaging

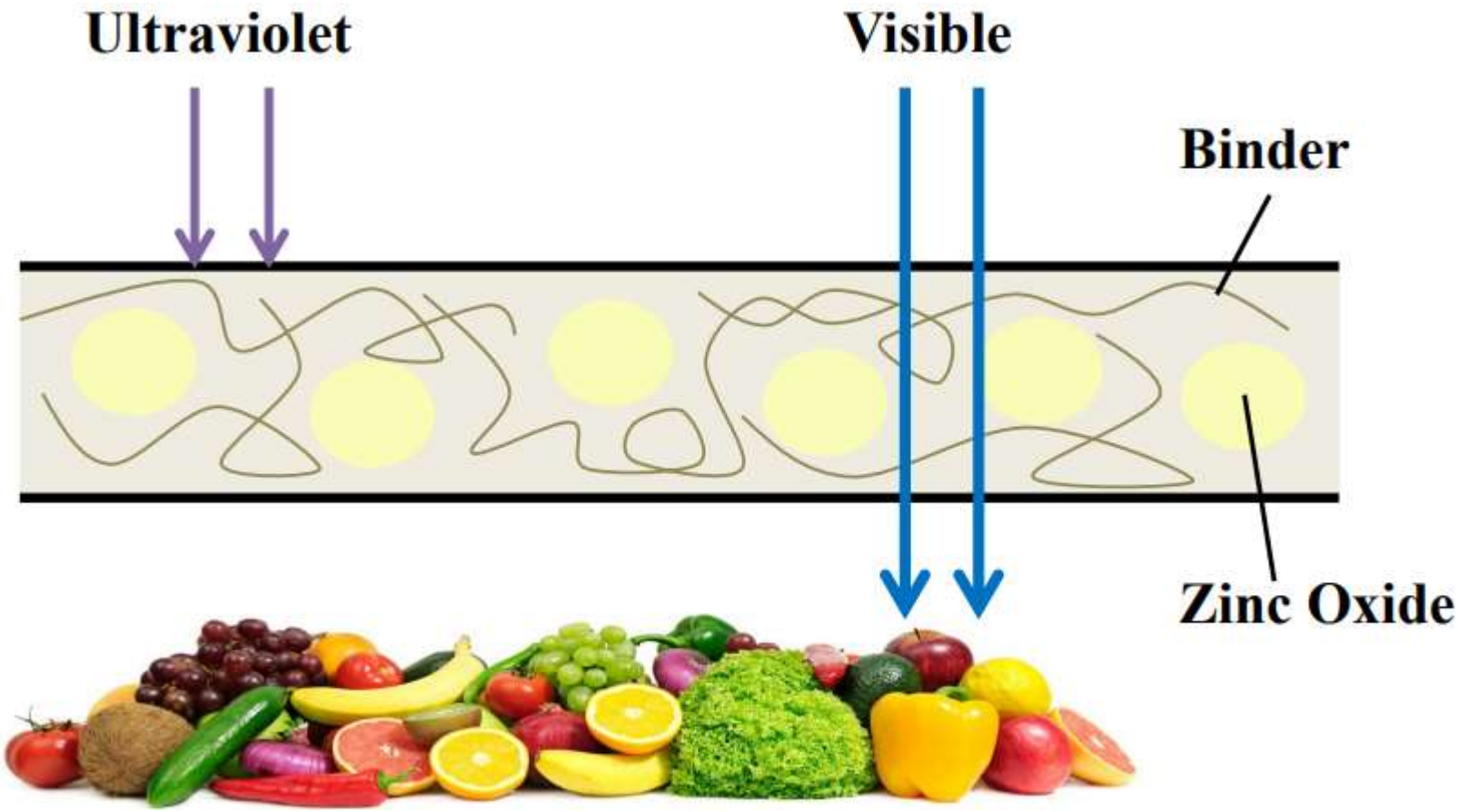
- Consumers want greener packaging
- Bio-based coating system is highly desirable
- Sensitive product, such as food, needs to be protected from UV light
- New LED lighting degrade food much faster

Transparent UV-blocking coating

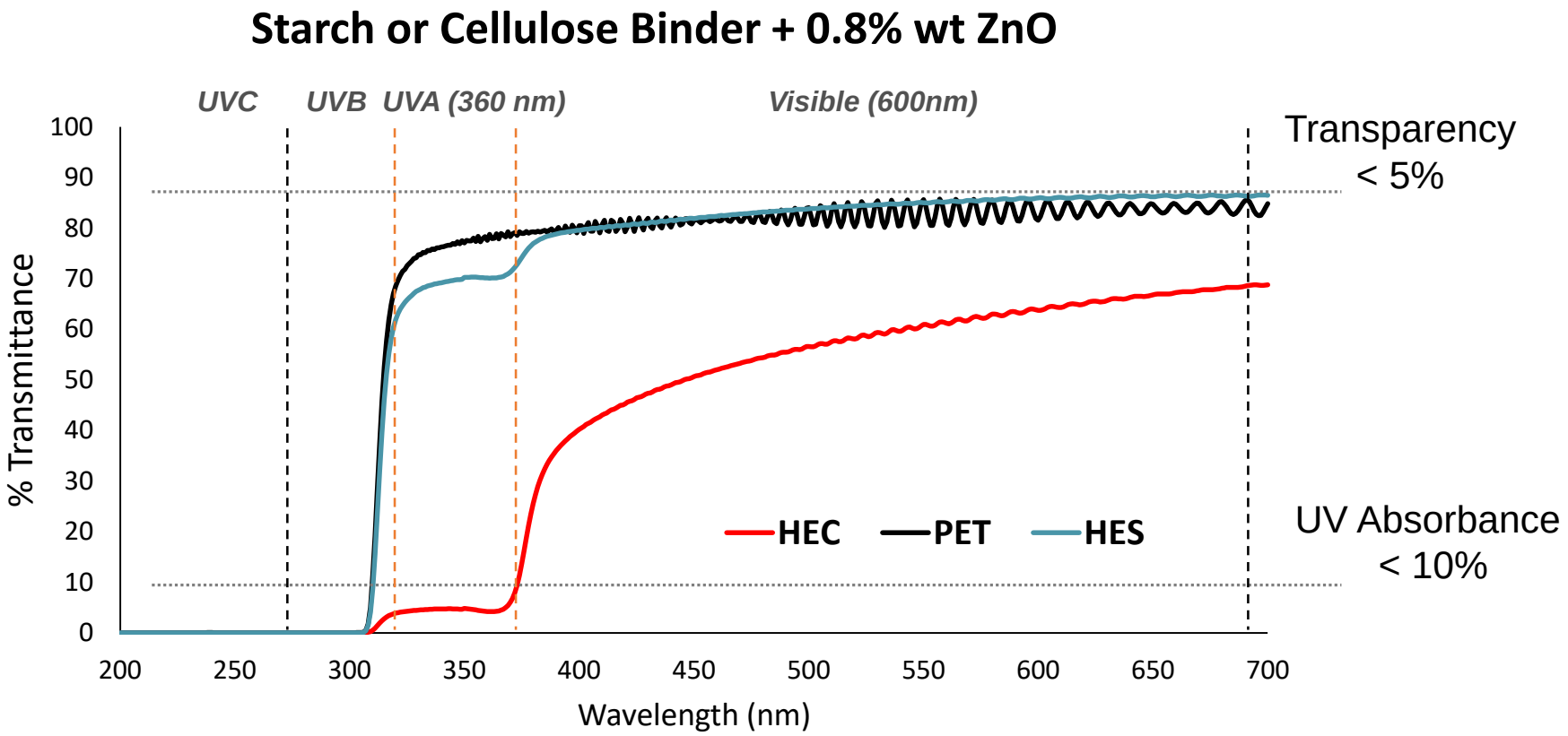
Develop a waterborne transparent bio-based UV-protective coating formulation for food packaging.

- **Binder:** Starch, cellulose, and their modified derivatives (HES, HEC)
- **Solvent:** Water based
- **Substrate adhesion:** Compatible and adhere well with flexible packaging substrate (PET, PVC)
- **UV blocking:** ZnO nanoparticles (< 10% transmittance from 200-390nm)
- **Transparency:** Maintain good visible transparency

Coating design

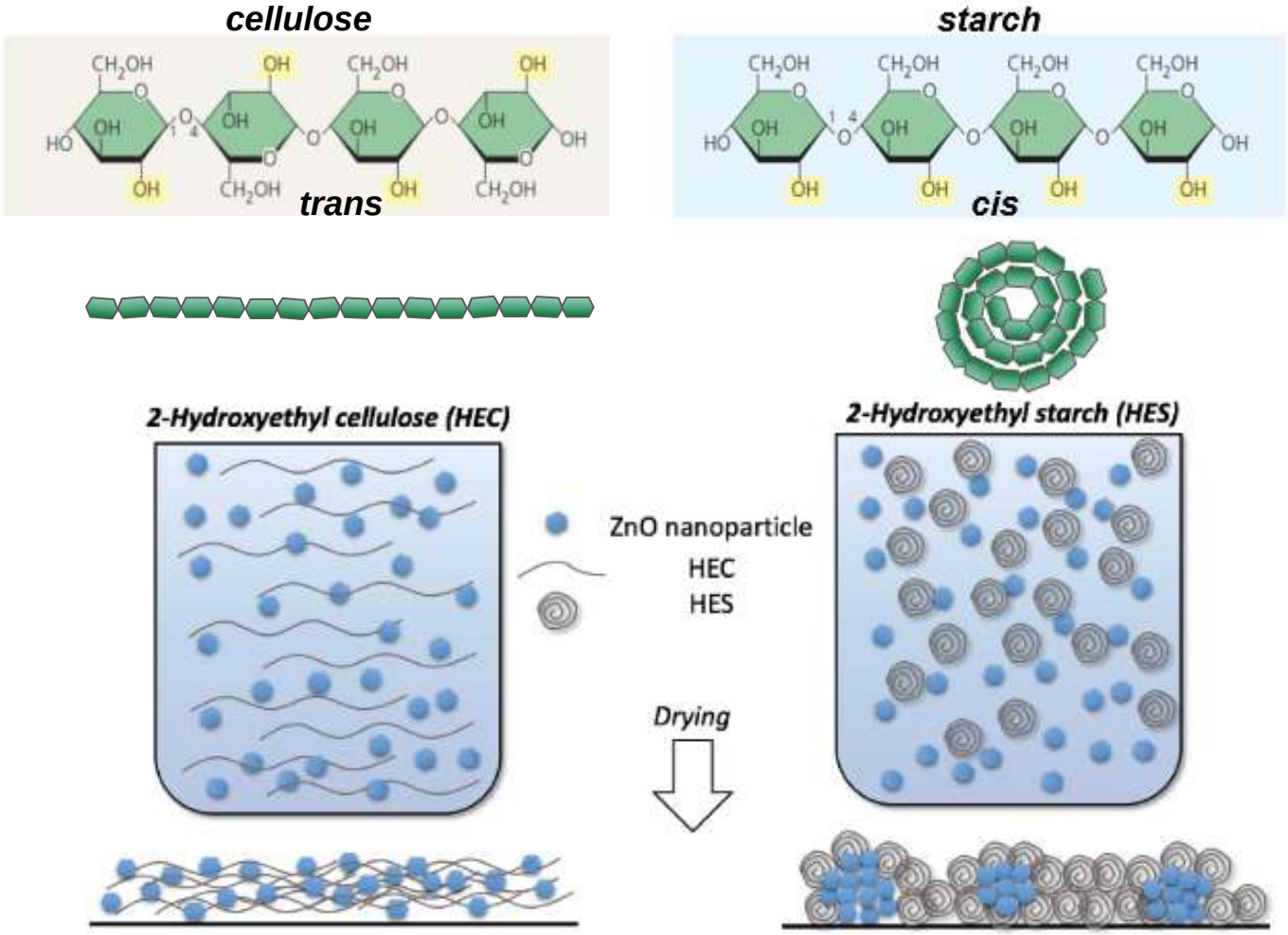


Coating performance



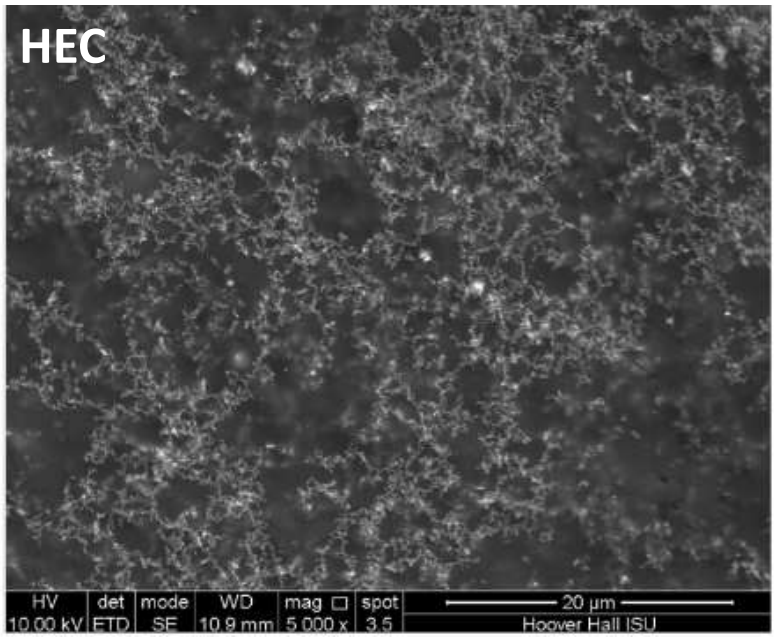
- **Coating formulated with HEC blocks UV much more efficiently than HES**
- **Significant improvements in UV blocking, while maintaining transparency**
  - ✓ **10% UV transmittance in UVA range**
  - ✓ **>70% transparency**

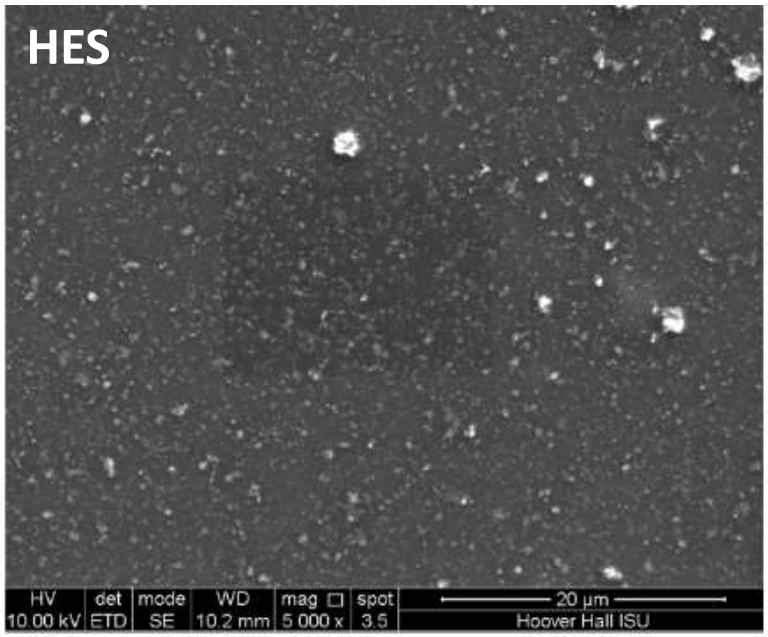
Binder comparison

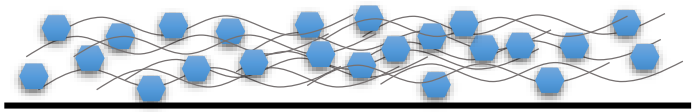


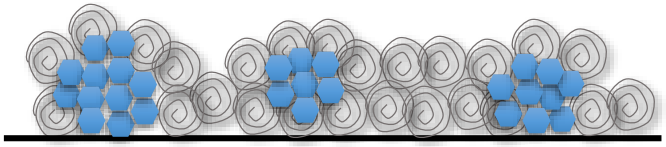
- **The behavior of the binders is highly dependent on persistence length, which impacts ZnO nanoparticle aggregation.**

SEM micrographs



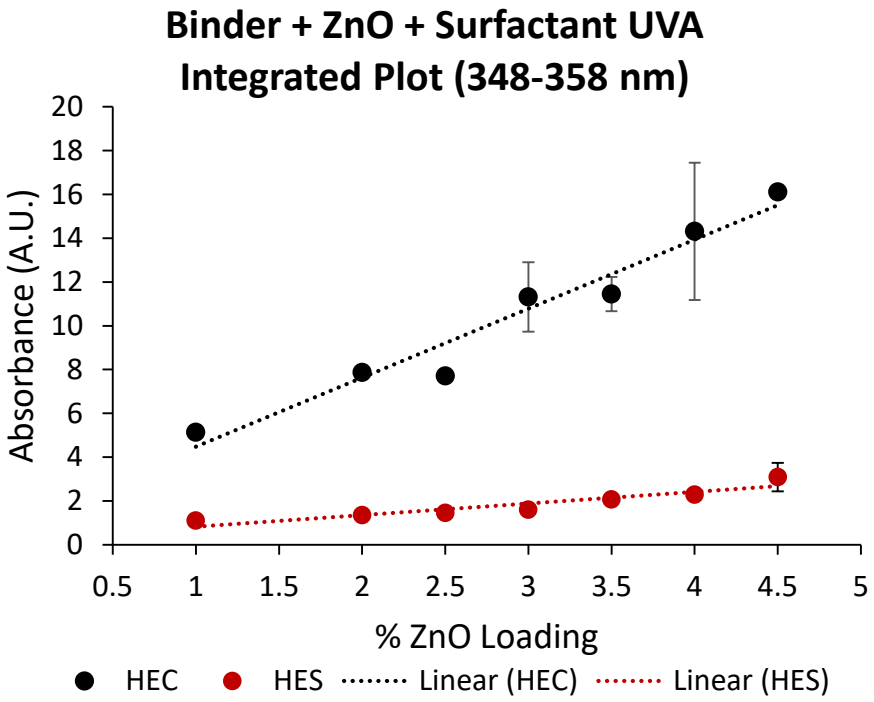


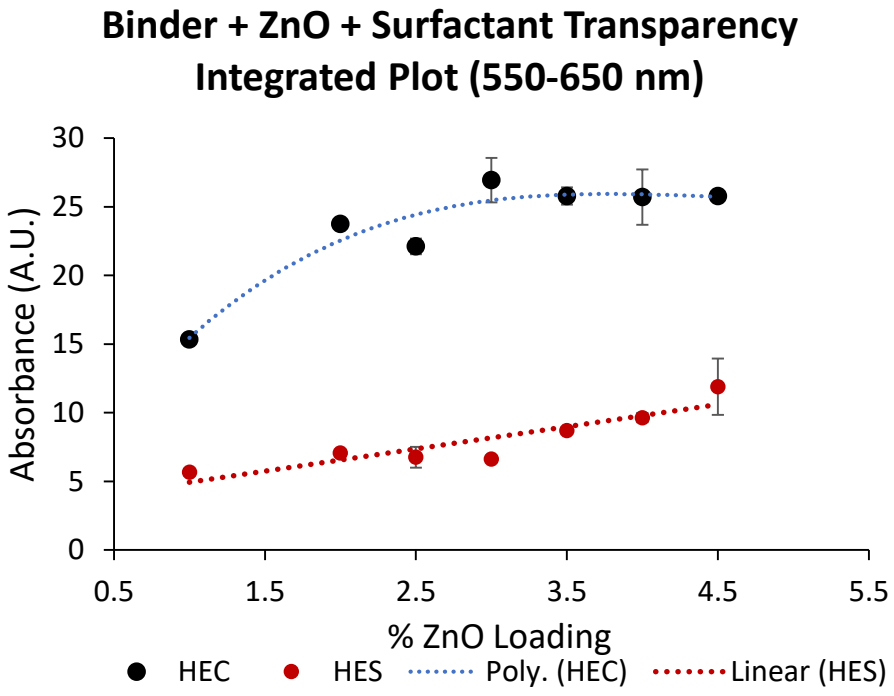




- **Unique fractal network of ZnO nanoparticles are formed with HEC**
- **New mechanism of stabilizing ZnO and achieving high UV-blocking efficiency and transparency**

ZnO loading

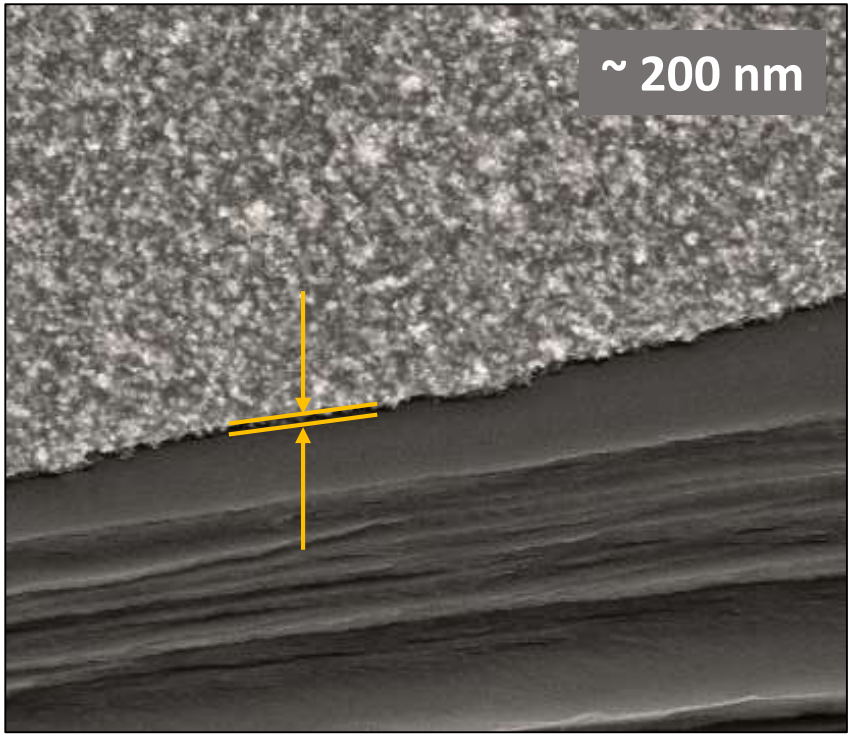


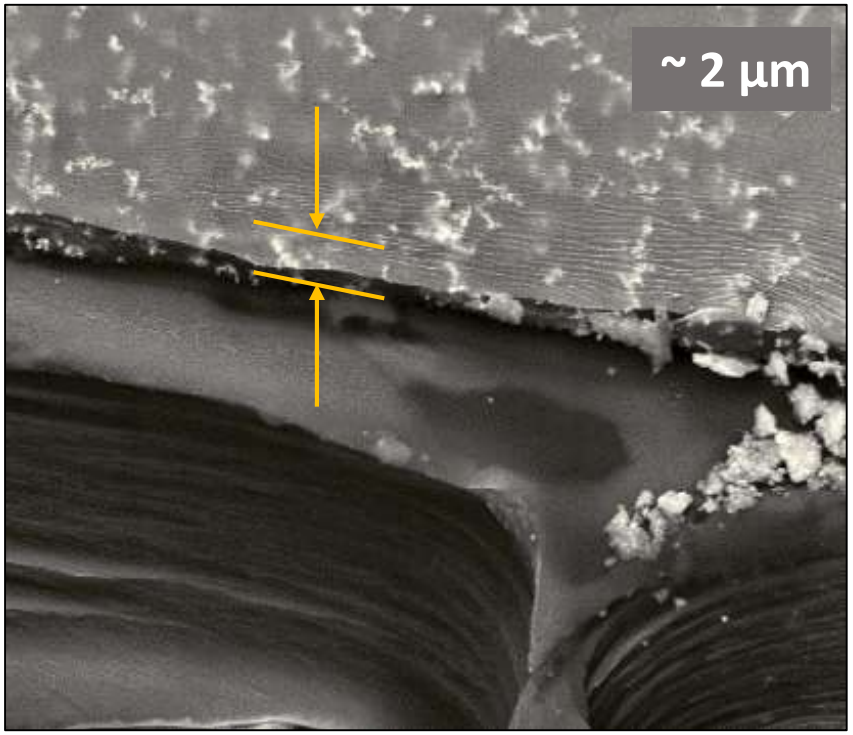


- **With HEC binder ZnO nanoparticle blocks UV much more efficiently.**
- **For visible spectrum, HEC shows a unique plateau, indicating a different mechanism of blocking visible light**

S. Jiang et al. ***Coating Trends and Technologies***, Chicago Conference (2016)

HEC thickness





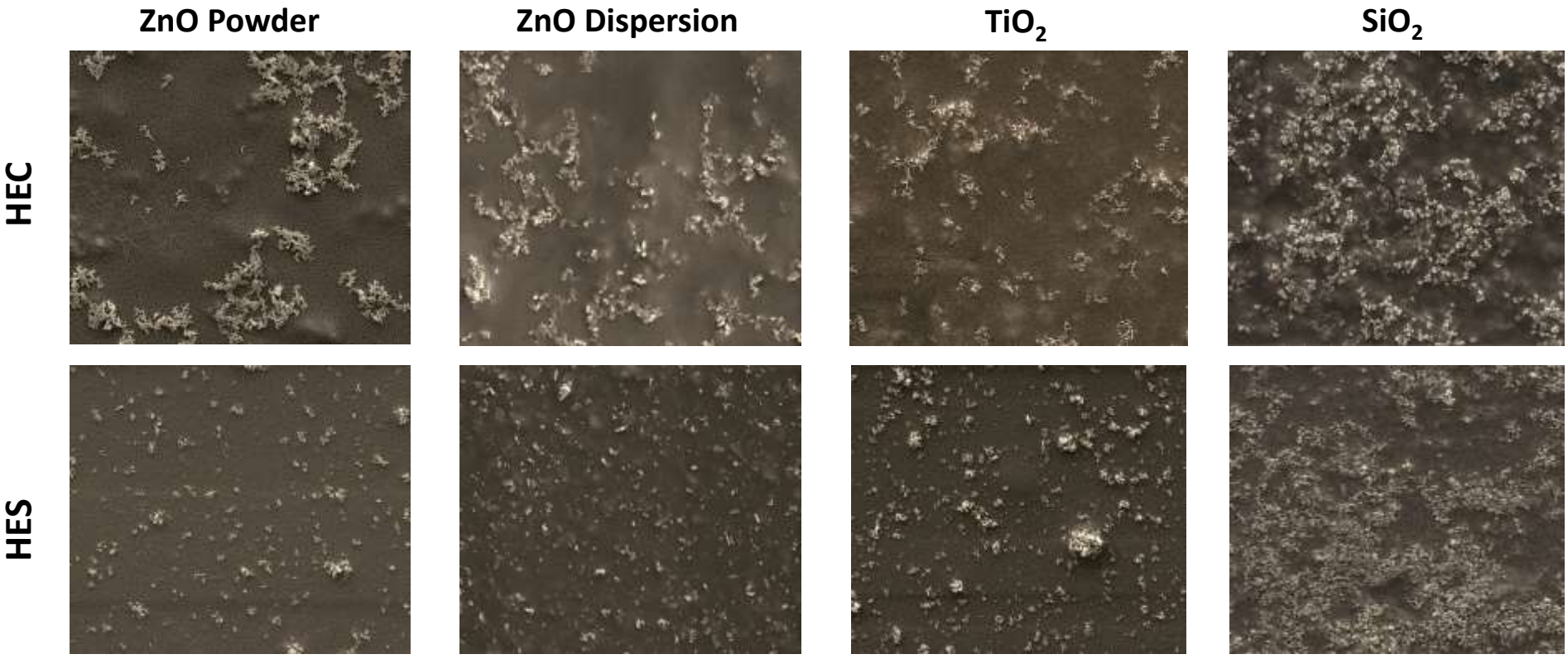
- **Our formulation is significantly thinner (0.2-2 µm than comparable coatings mentioned in literature (50 µm).**

Comparative coatings

Binder choice (with ZnO nanoparticles)	ZnO Content	Thickness (µm)	Transmittance	
			UVA (354 nm)	Visible (600 nm)
This study: HEC	**0.8%**	**0.2 - 2**	**6%**	**73%**
Neat resin	2%	40	8%	80%
Acrylic emulsion	2%	45	15%	57%
Benzophenone	1.5%	75	20%*	63%*
Starch + keferin	1%	130	2%*	79%*
Polylactide	1%	140	6%*	79%*
Polyurethane/ acrylic polymer resin	2%	2000	7%	85%

- **The proposed formulation is significantly thinner than those mentioned in literature, with similar UV-blocking, transparency, and ZnO loading.**

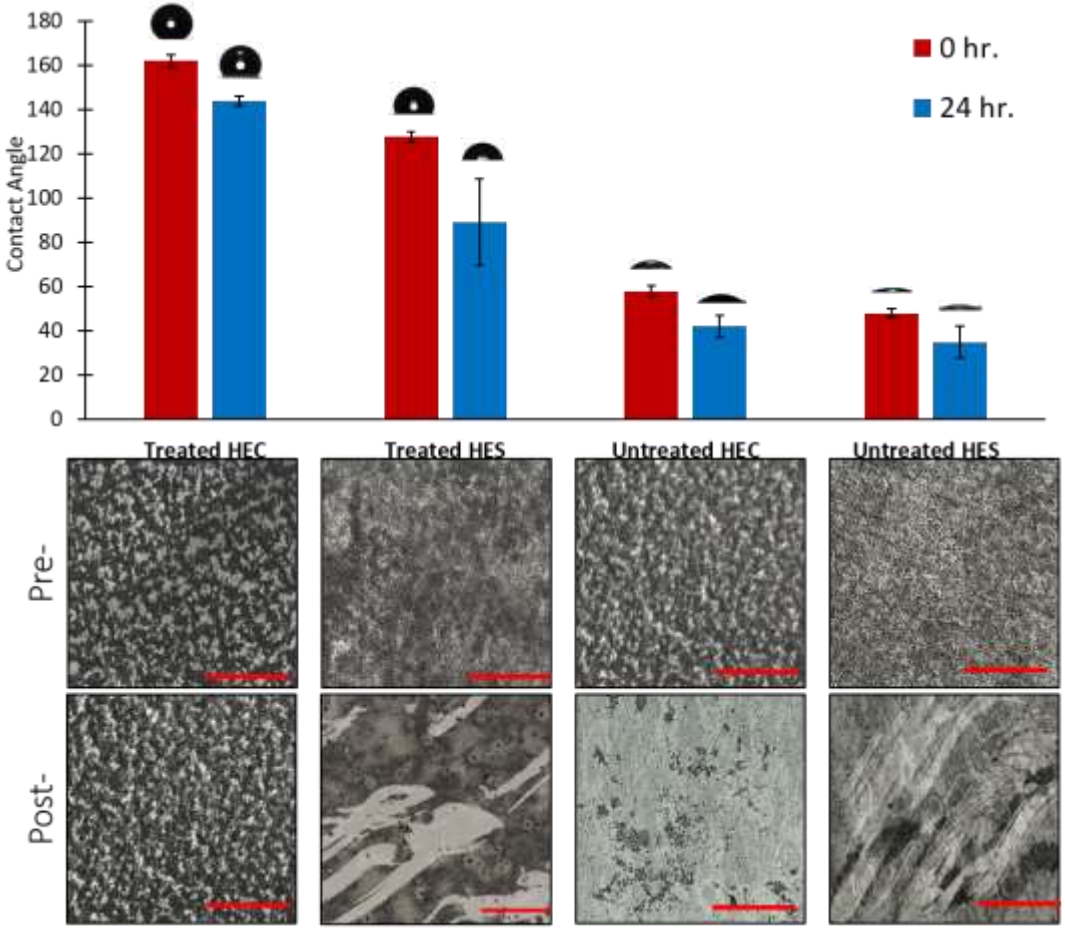
Meso-structure



- **The aggregation patterns observed with ZnO powder in HEC and HES can be generalized to other particles of similar size (30nm).**

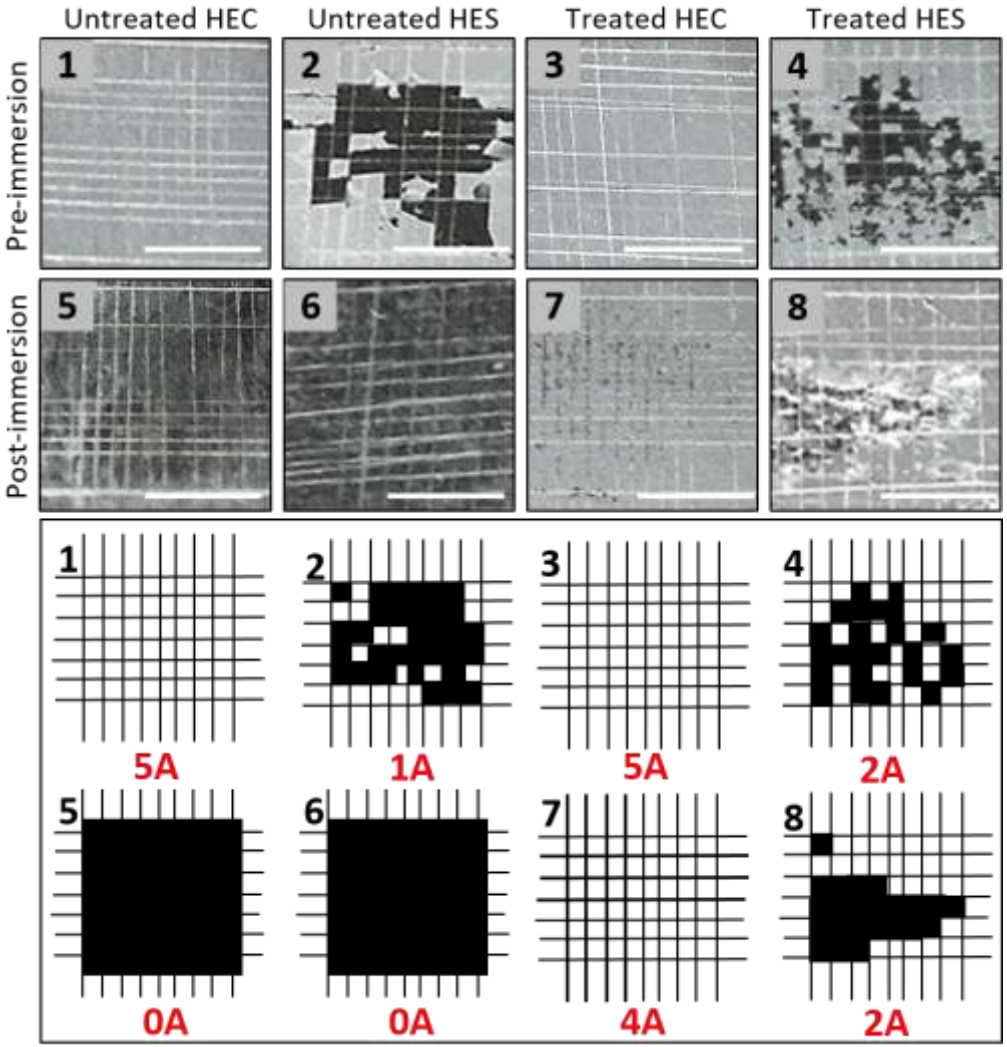
Immersion test after treatment

- The nanocomposite coatings were immersed in water for 1 day to assess robustness.
- The HEC maintained performance post-immersion (20° decrease); while HES decreases by 40°.
- Confocal film imaging reveals the surface morphologies responsible for the observed contact angles before and after immersion.



Crosshatch adhesion test

- Untreated HEC shows good adhesion before immersion, and HES does not.
- Upon immersion, both HEC and HES coatings are washed away.
- Treated HEC shows impressive adhesion before and after immersion.
- Treated HES shows improvement but does not perform as well as HEC.



Safety

- No direct food contact
- Waterborne formulation involves no organic solvent
- ZnO blocking agent has been proven safe and widely used in cosmetics
- Biobased binder is food safe and environment friendly

Conclusions

- Invented a biobased, cost effective, printable, and transparent UV-blocking coating formulation
- Achieved high UV-blocking capability (< 10%) and transparency (~ 80%)
- Obtained very thin coating thickness (0.2 – 2 μm)
- Revealed unique cluster structures and new mechanism of improving UV-blocking performance

E.J. Olson, S. Jiang*, ***Patent Application***, 62/784,109 (2018)

II. Janus particles coating additive for high performance coating

1. Concept of Janus particles
2. Fabrication and stratification
3. Janus particles as coating additive

Janus particles

Polymer	ATRP, Block Copolymer	Tire, Plastic, Coating, Fiber
Surfactant	Micelles, Vesicles	Home & Personal care, Pharmacy
Liquid Crystal	MBBA, Phase diagram	LCD Display
Janus Particles	*Not explored yet*	

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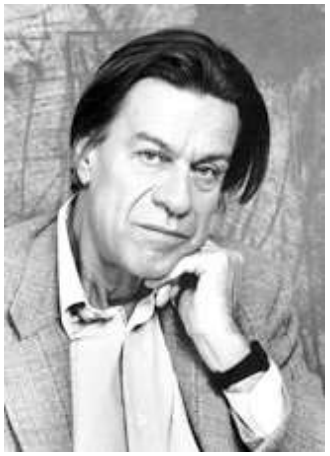
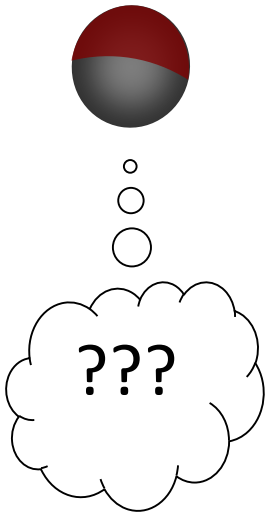
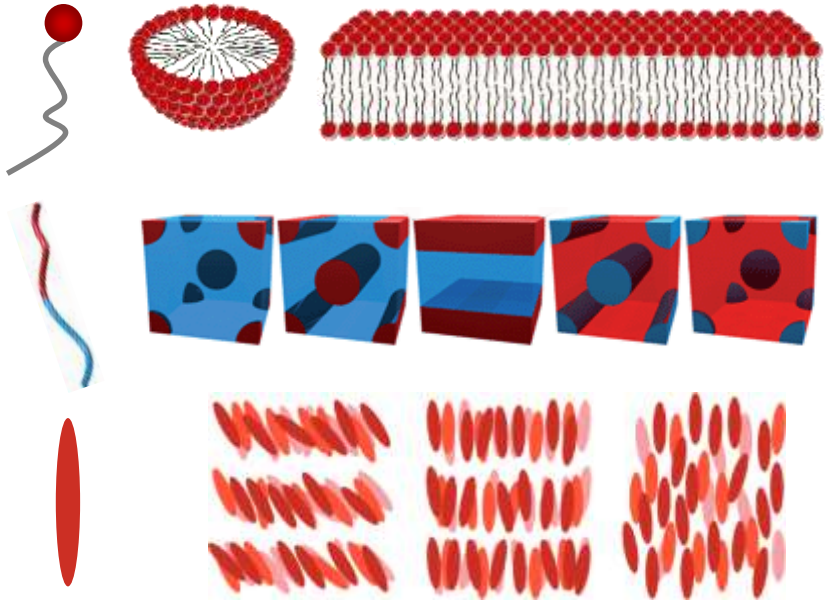


Complexity
& Flexibility

Plethora of applications

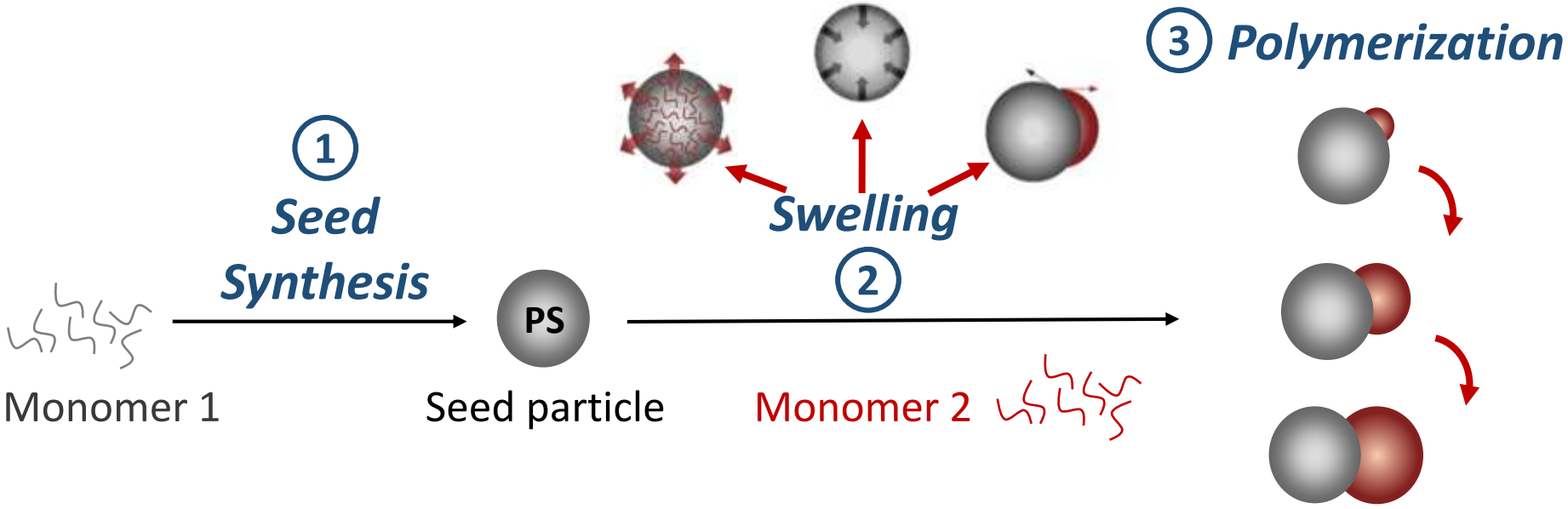
P. G. de Gennes, ***Rev. Mod. Phys.***, 64, 3 (1992)





S. Jiang, S. Granick, "*Janus particle synthesis, self-assembly and applications*," London: ***Royal Society of Chemistry*** (2012)

Seeded emulsion polymerization

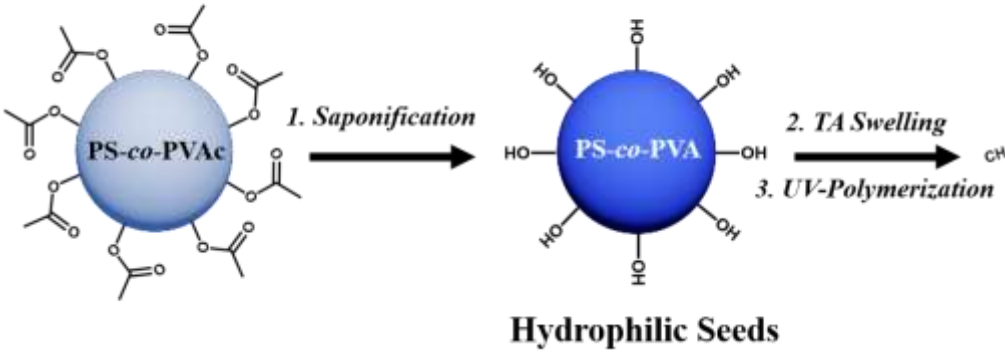


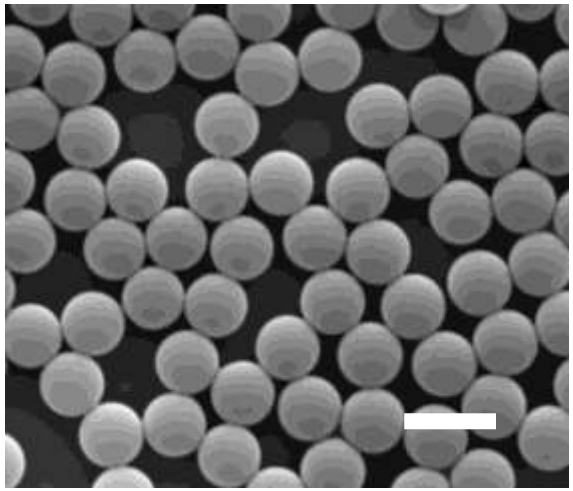
Free energy $\Delta\bar{G}_{m,p} = \Delta\bar{G}_m + \Delta\bar{G}_{el} + \Delta\bar{G}_t$

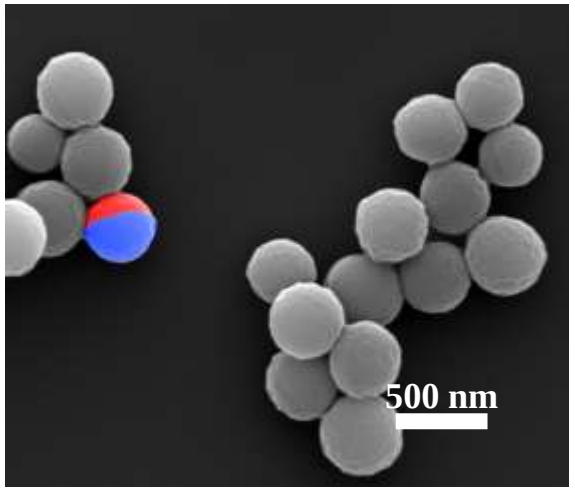
- monomer swelling polymer
- monomer mixing with polymer
- Elastic energy
- Interfacial tension

Langmuir 2006, 22, 4037-4043

Synthesis of Janus particles

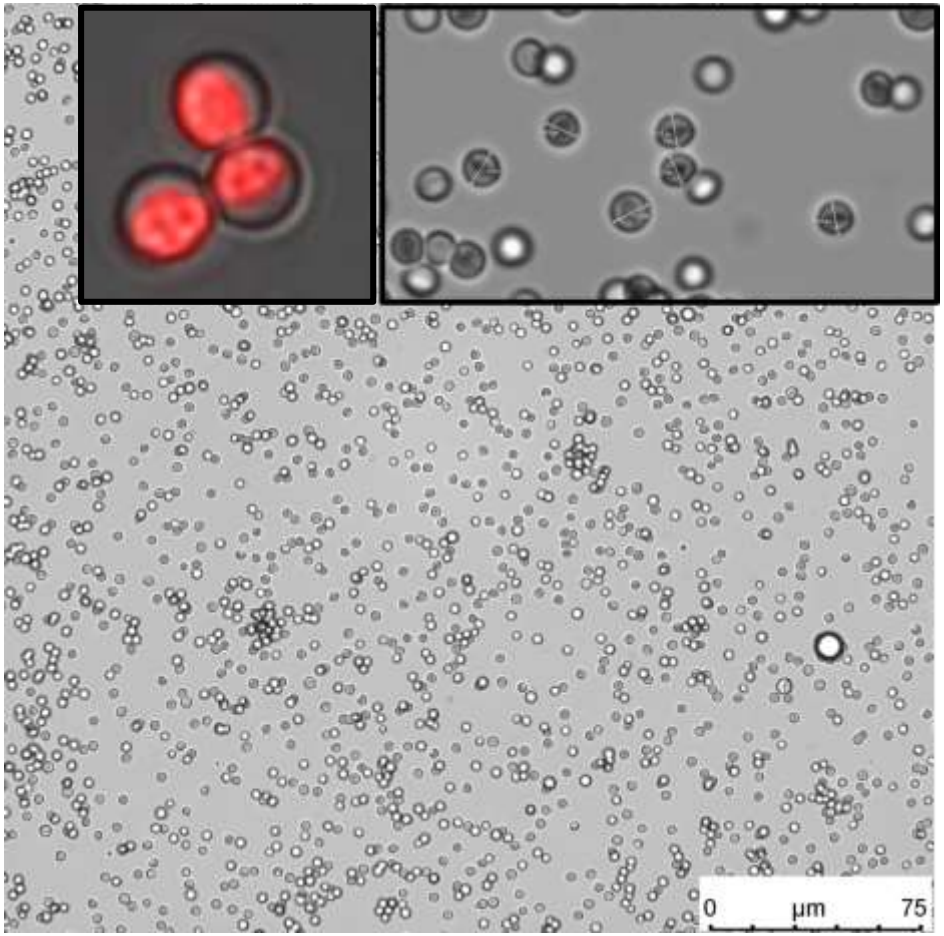


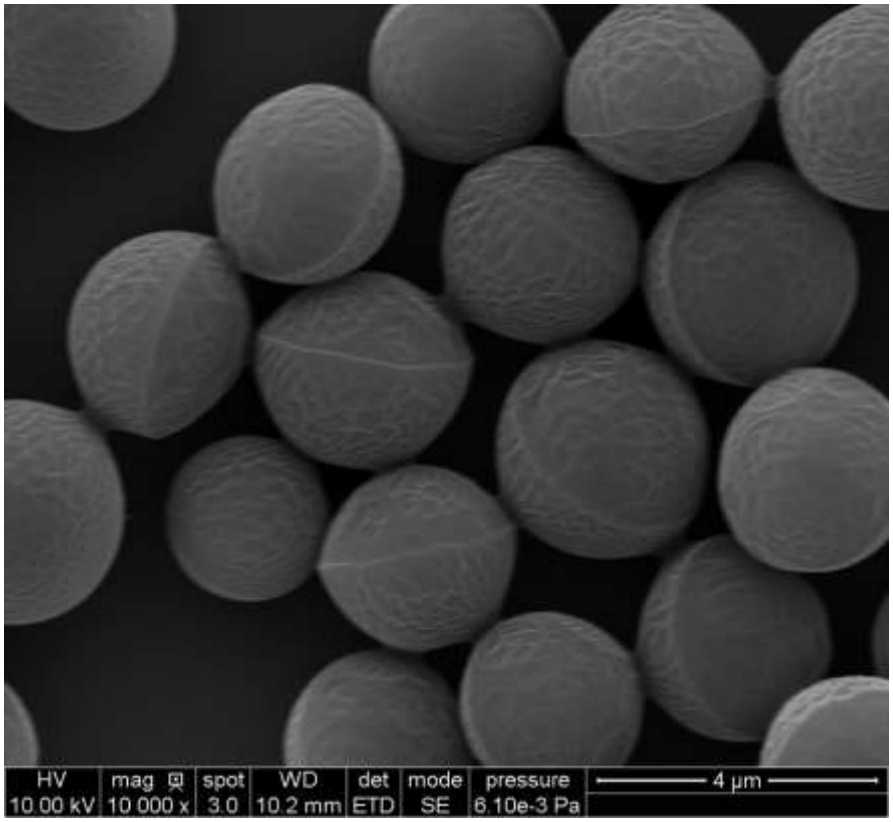




Journal of Colloid and Interface Science 543, 2019, 34–42

Characterization





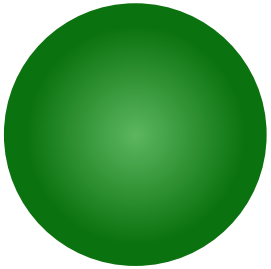
Seed surface – hydrophilic; Lobe surface – hydrophobic

Adsorption vs. stratification

Hydrophobic surface

Janus particles

Hydrophilic surface

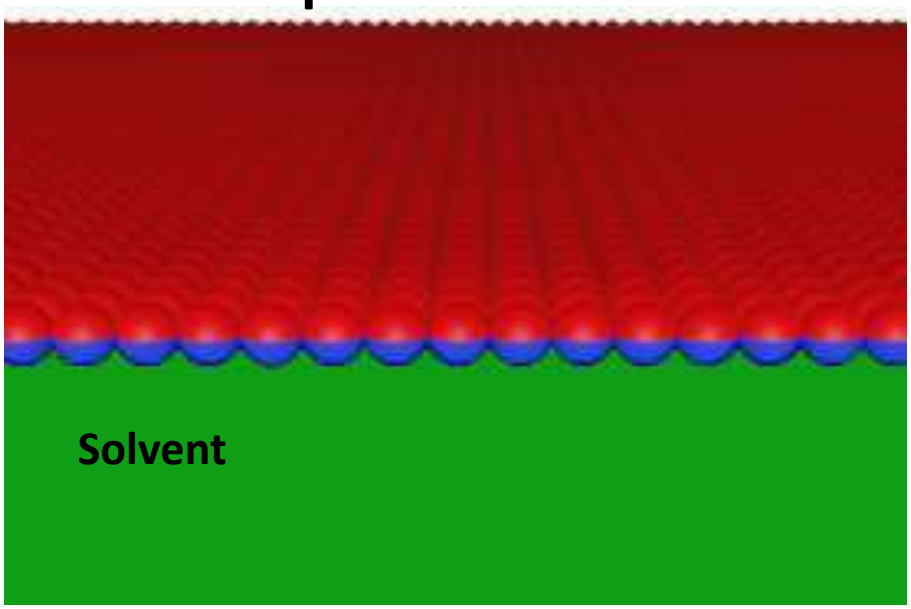


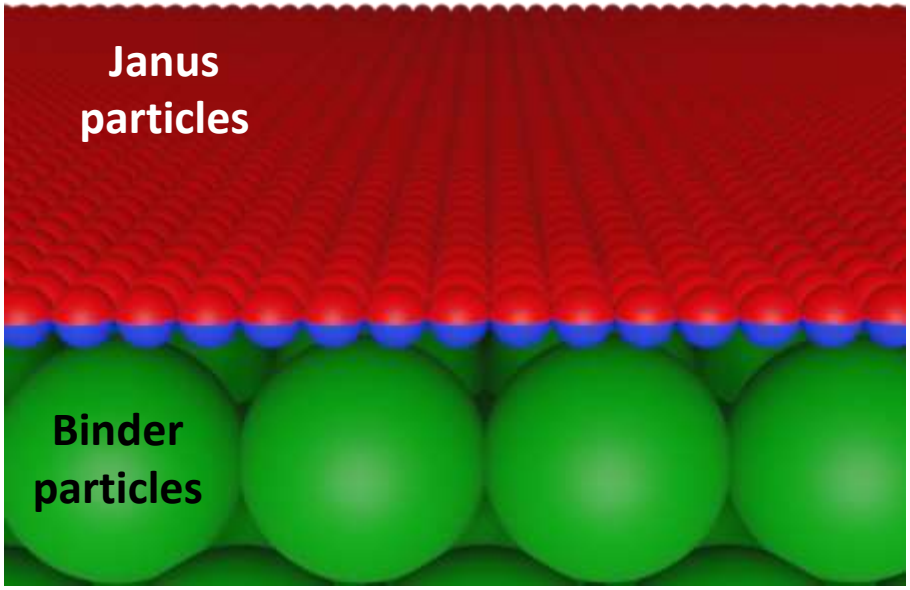
Homogeneous particles

Adsorption at interface

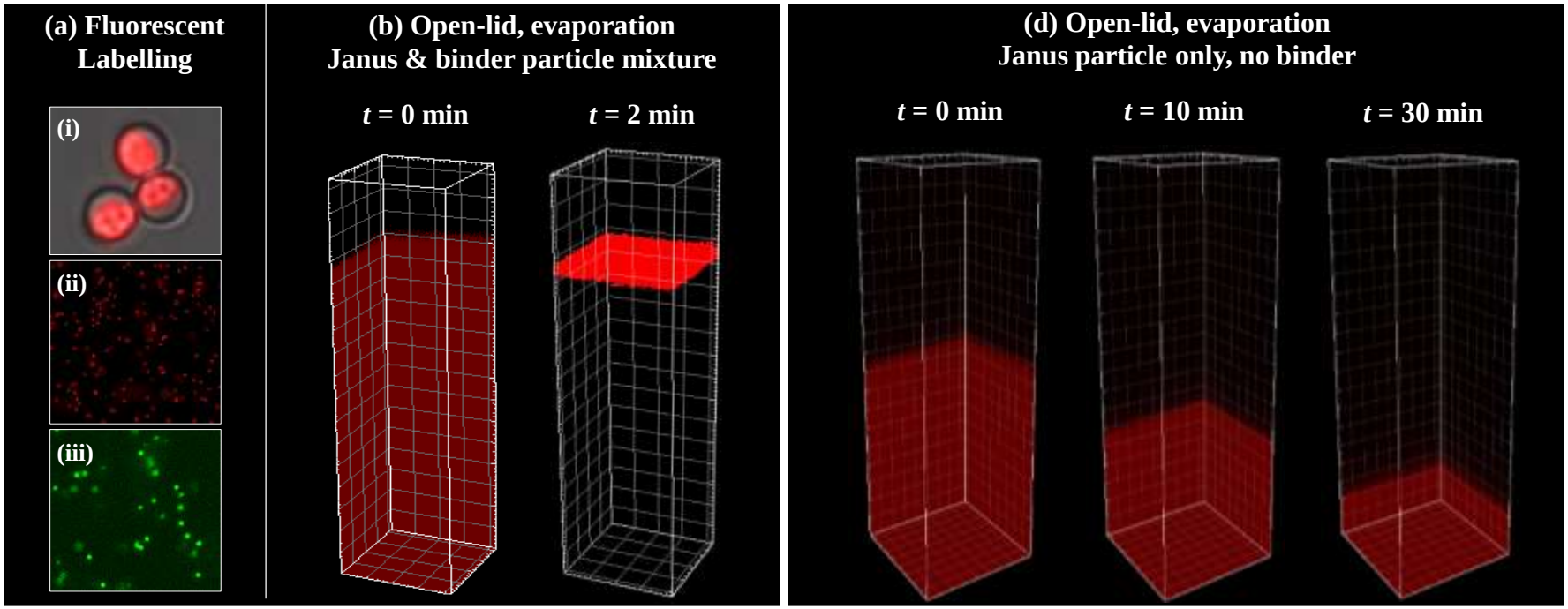
VS.

Stratification





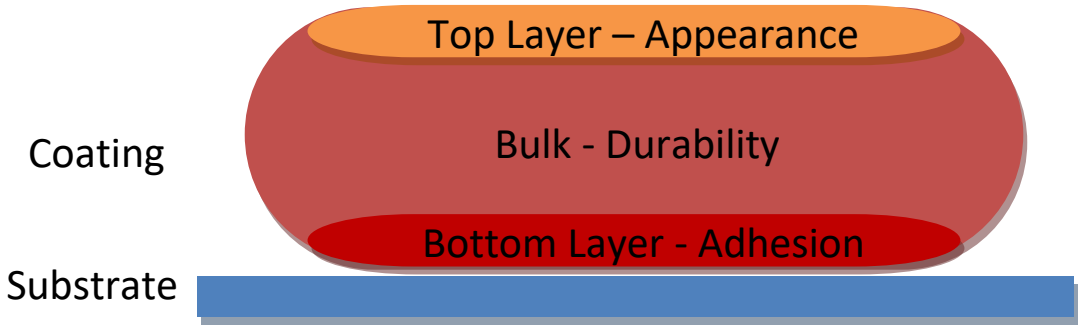
Ultrafast dynamics



- Self-stratification of Janus particles happens quickly, simple calculation shows the dynamics is 3 orders of magnitude faster than Brownian particles in bulk
- Without mixing with homogeneous particles, Janus particles will not adsorb at the interface

Self-stratified coating

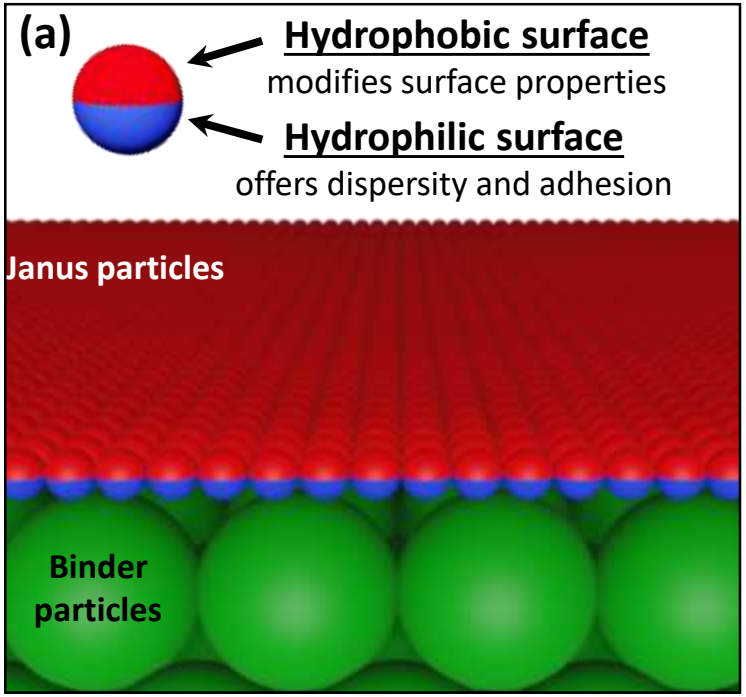
1. Janus particles can quickly self-stratify at the interfaces and change the coating surface properties independent from the bulk.
2. New concept: Janus particles can be used as a scalable and effective coating additive, and self-stratification offers a new approach to design coatings with superior properties.



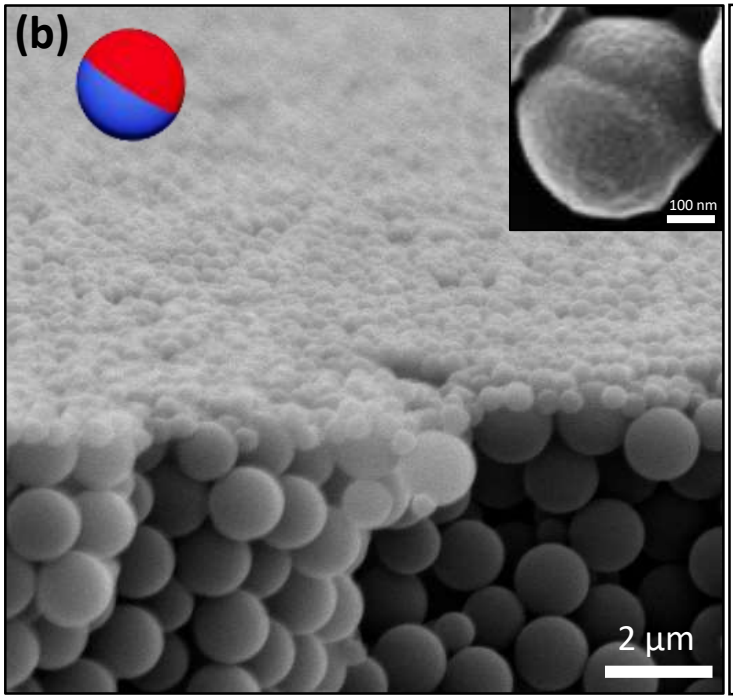
S. Jiang et al. ***Chem. Soc. Rev.*** 46, 3792 (2017)

Janus particles - a new coating additive

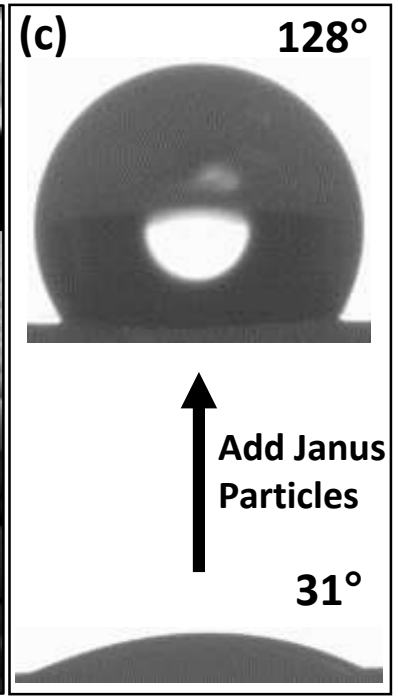
Theoretical Illustration of Self-stratified Coating



Electron Image of Self-stratified Coating

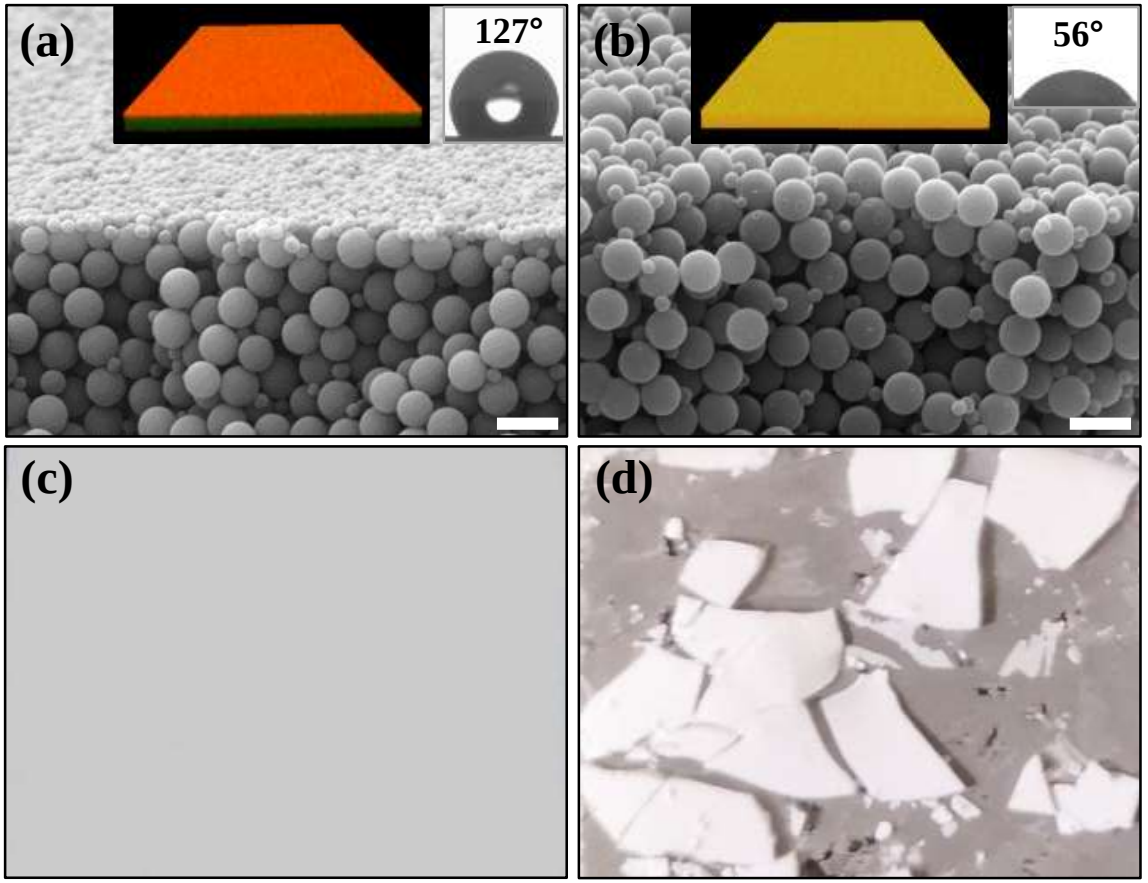


Hydrophobicity Enhancement



Small quantity of Janus particles are needed to cover the surface and change the surface-related coating properties. The bulk materials of the coating film remain intact

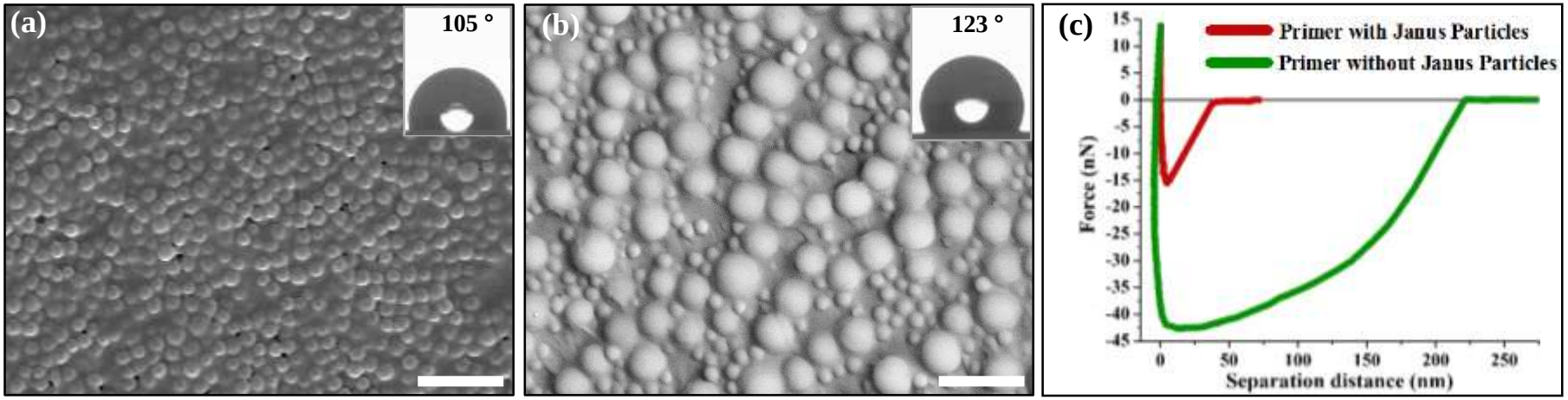
Superior performance



- Self-stratified coating shows high water contact angle
- Self-stratified coating has much better solvent resistance

Compatibility

Mixed with a commercial primer



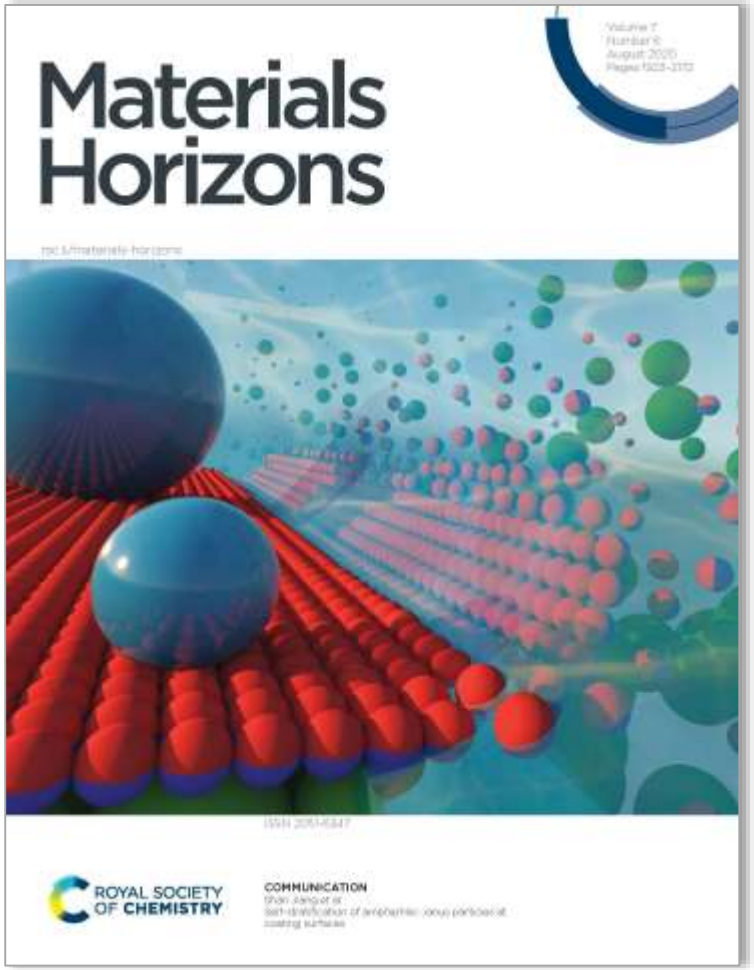
- **Janus particles can self-stratify even in a commercial primer product**
- **The stratified coating shows much higher surface hardness**

Commercialization

- Affordable materials in large quantity
- Easy to scale-up (lab synthesis over 10g/batch)
- Fast polymerization rates
- Narrow molecule weight distribution

Summary

- Janus particles self-stratify to the surface when mixed with homogeneous particles
- The dynamics is very fast, and stratification is complete
- Stratification converts coatings to hydrophobic surfaces



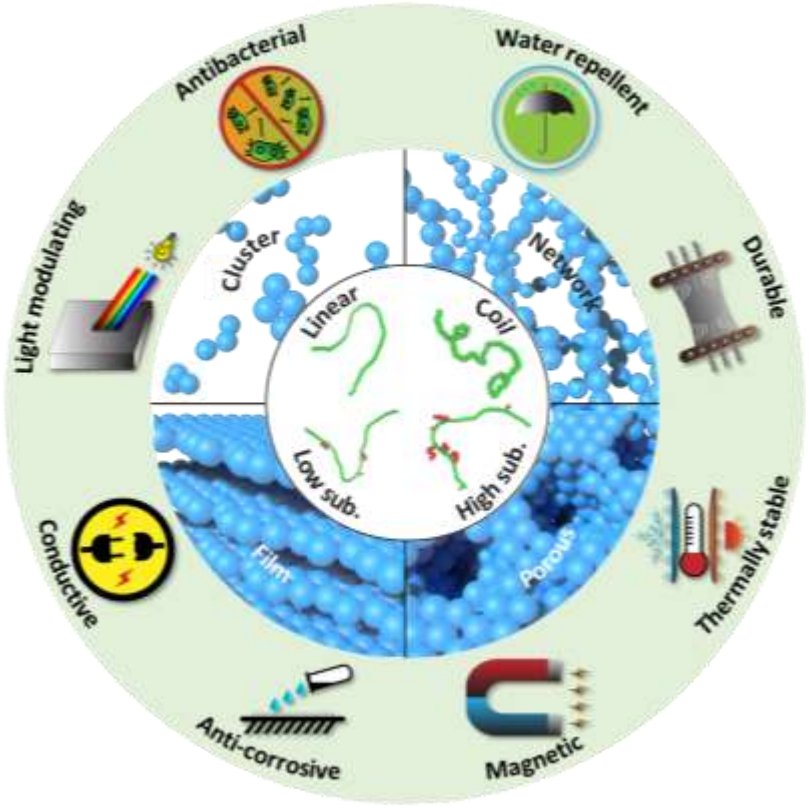
Li et al. ***Mater. Horiz.*** 7, 2047 (2020)

Email: sjiang1@iastate.edu

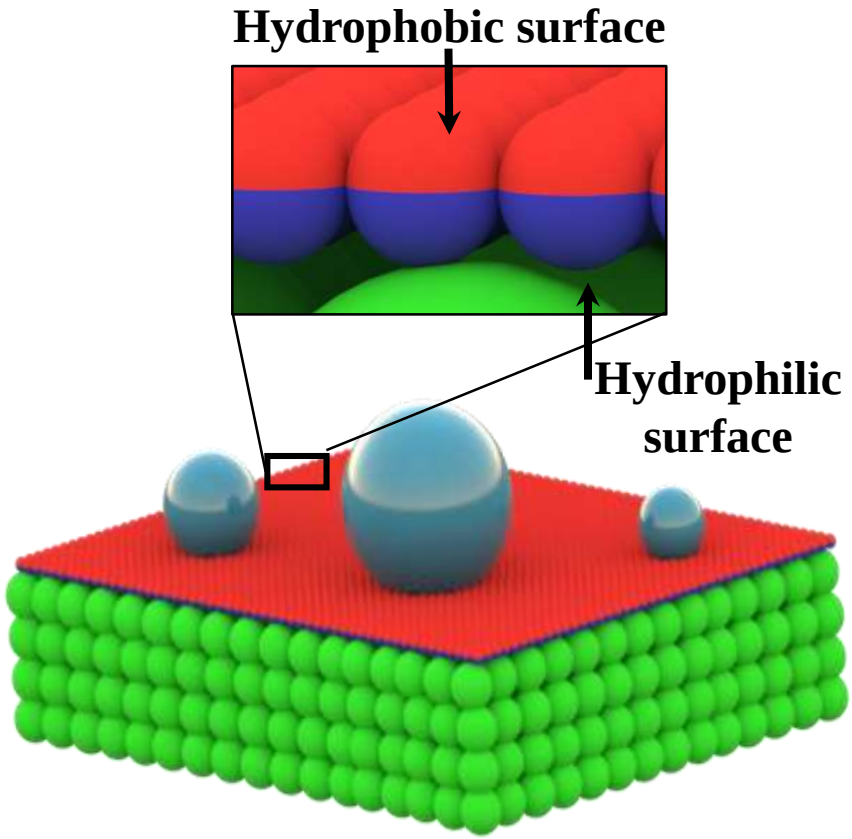
Next generation industry coating

Sustainability + Performance

Nanoparticle assembly & functionality



Janus particles & stratification



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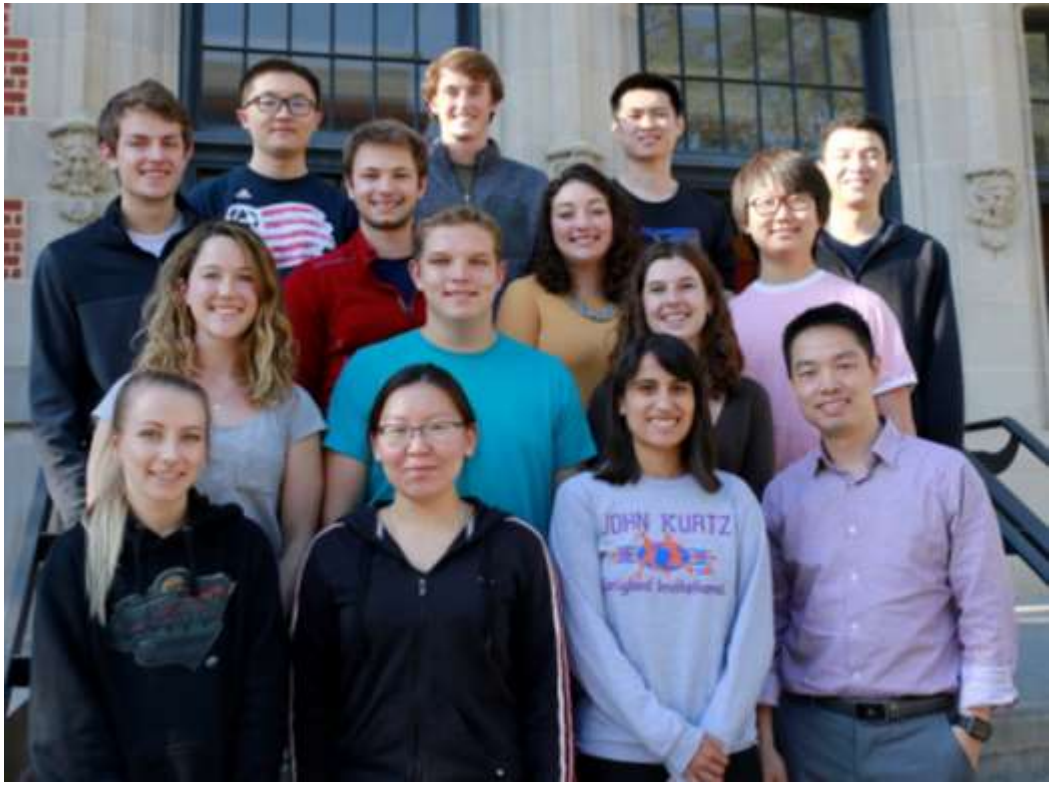
Prof. Minglin Ma, Cornell University



USDA

Polymer and Food Protection Consortium

Startup Fund

Diamond Vogel

NSF

Non-tenured faculty award

3M

Inland SIEGWERK

RIF grant