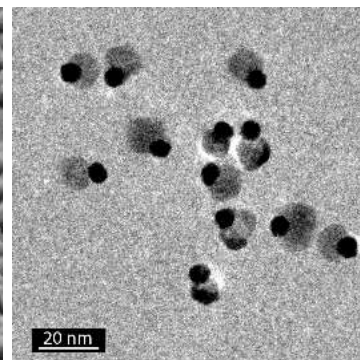
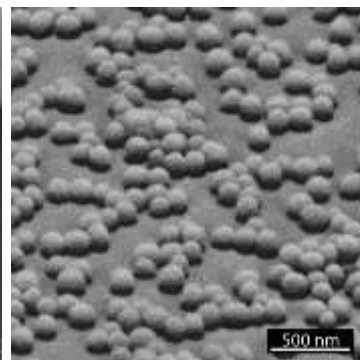
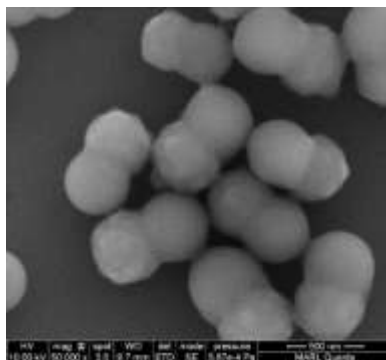
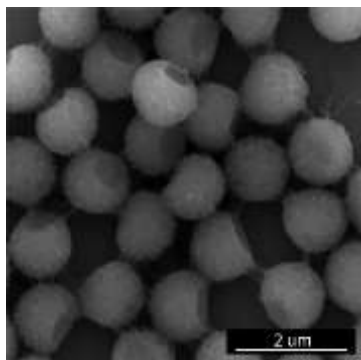
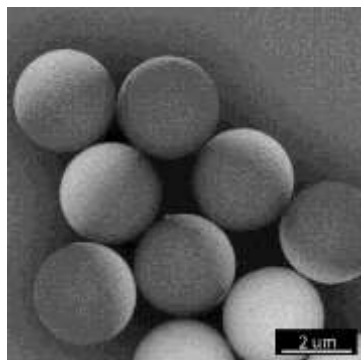


# Next Generation Coatings Through Self-assembly and Nanotechnology

Shan Jiang, Ph.D., Assistant Professor  
Materials Science and Engineering  
Iowa State University



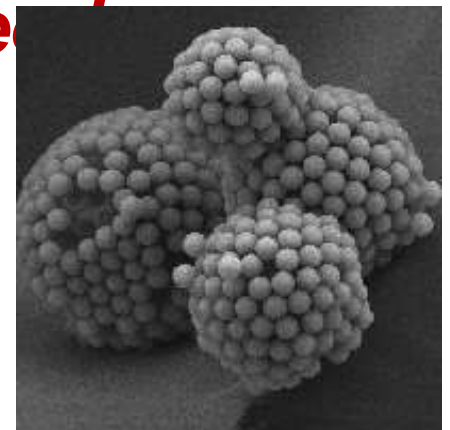
## About me

- **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-engineering***

(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



Old Time Paint



Architecture Paint



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

Ancient Paint

Aestheti  
c vs.  
Function

Modern Paint



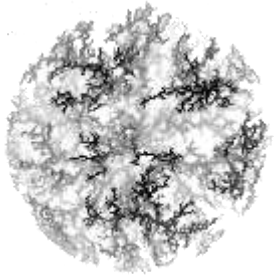
Marine Coating



Industry Coating

What's  
for  
Future?

# ■ 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

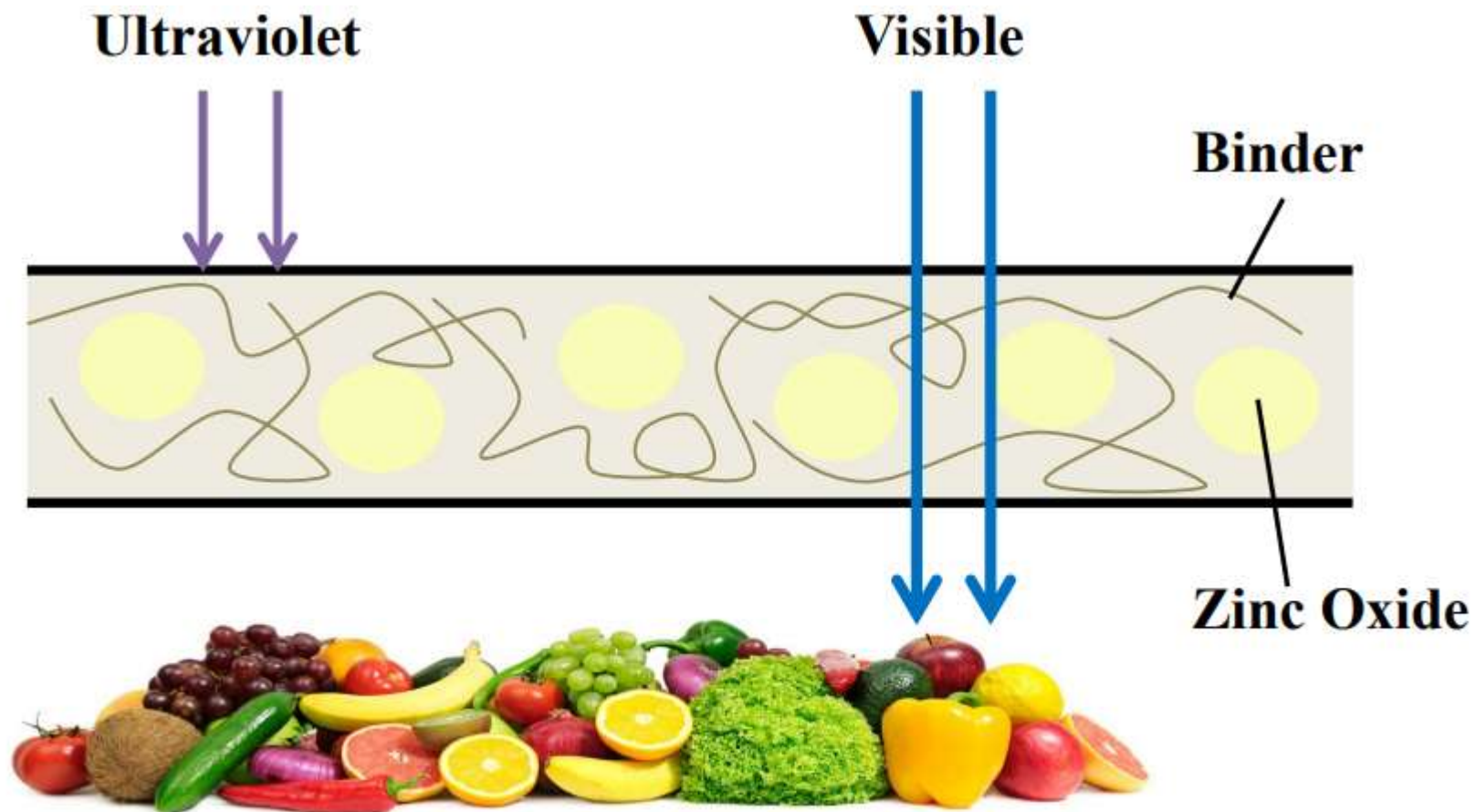
- Consumers want greener packaging
- Bio-based coating system is highly desirable
- Sensitive product, such as food, needs to be protected from UV light
- New LED lighting degrade food much faster

# ■ Transparent UV-blocking coating

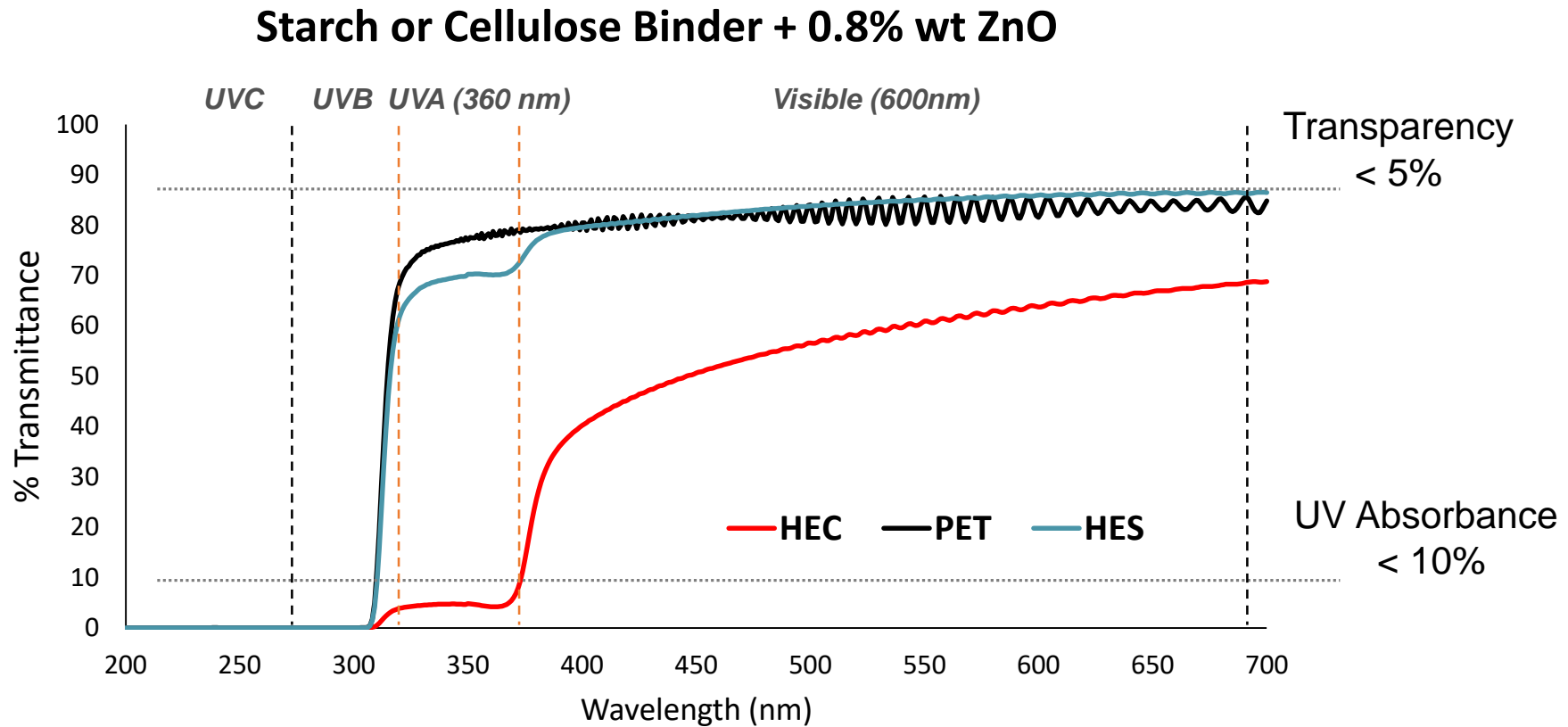
*Develop a waterborne transparent bio-based UV-protective coating formulation for food packaging.*

- **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

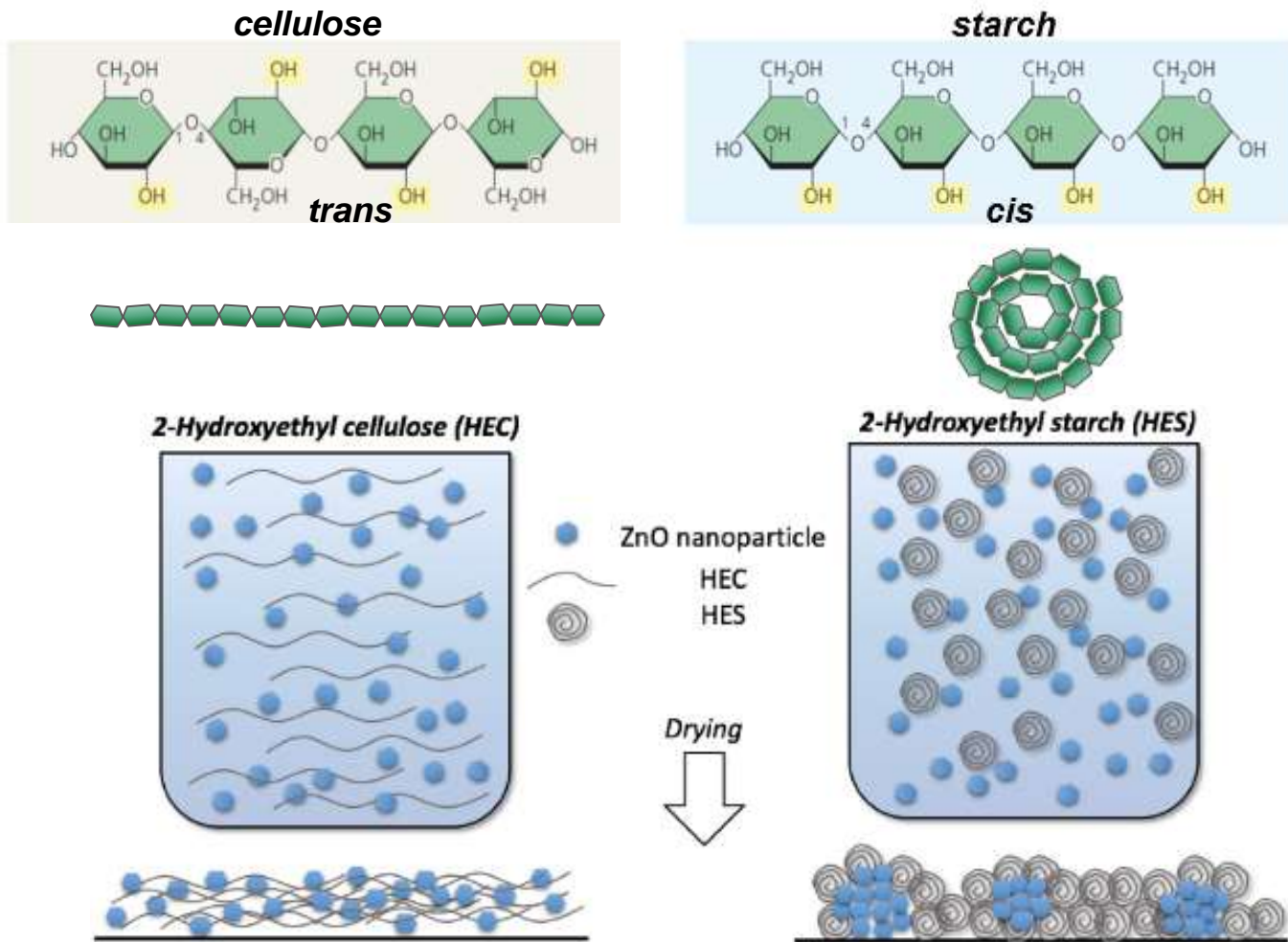


# Coating performance



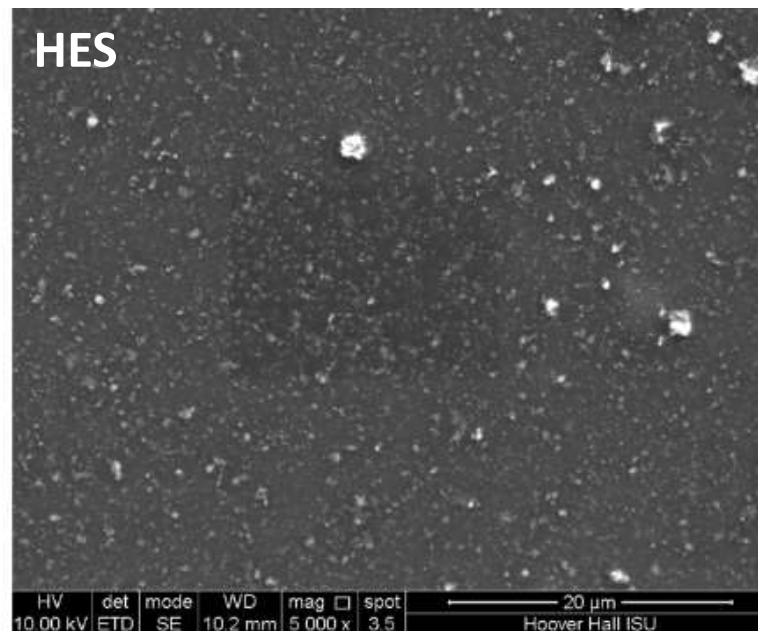
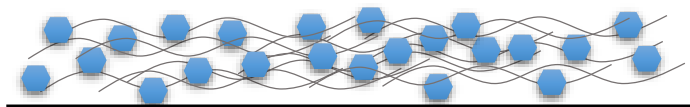
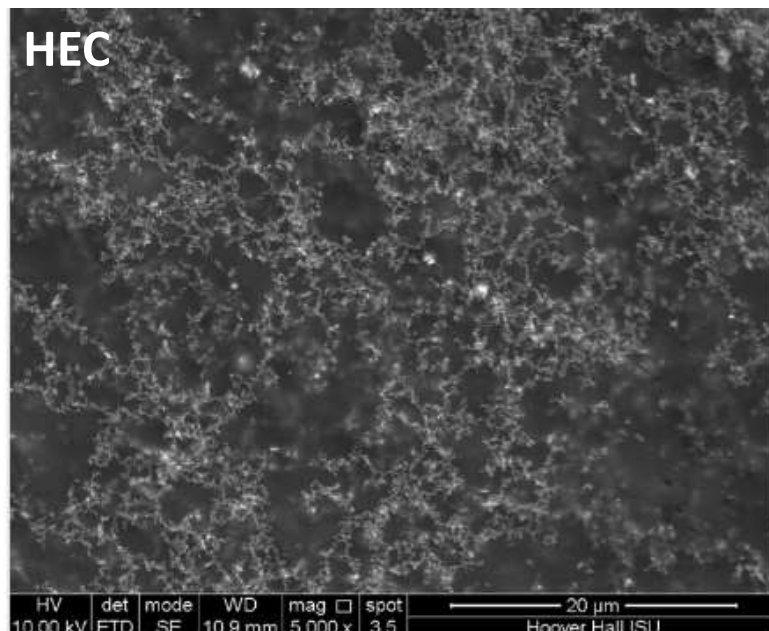
- Coating formulated with HEC blocks UV much more efficiently than HES
- Significant improvements in UV blocking, while maintaining transparency
  - ✓ 10% UV transmittance in UVA range
  - ✓ >70% transparency

# Binder comparison



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

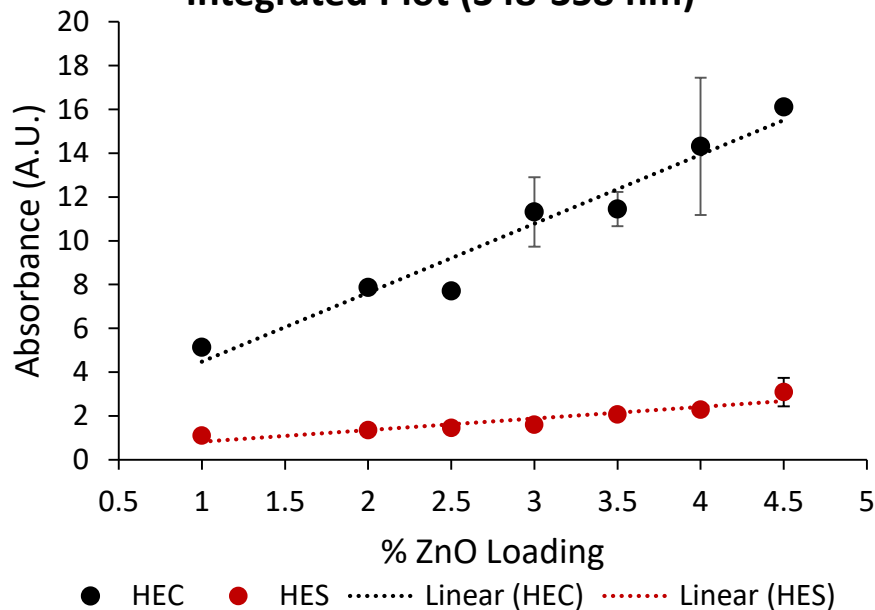
# SEM micrographs



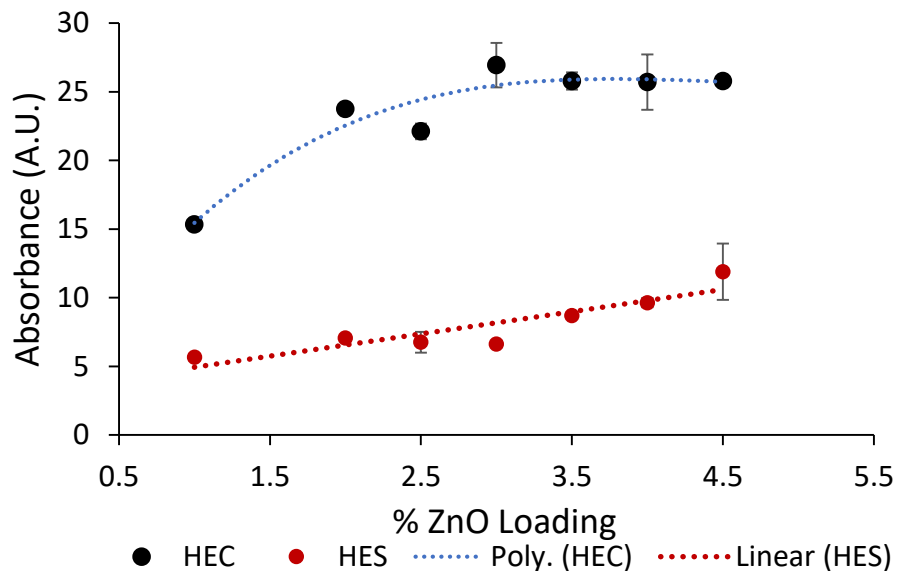
- Unique fractal network of ZnO nanoparticles are formed with HEC
- New mechanism of stabilizing ZnO and achieving high UV-blocking efficiency and transparency

# ZnO loading

**Binder + ZnO + Surfactant UVA  
Integrated Plot (348-358 nm)**

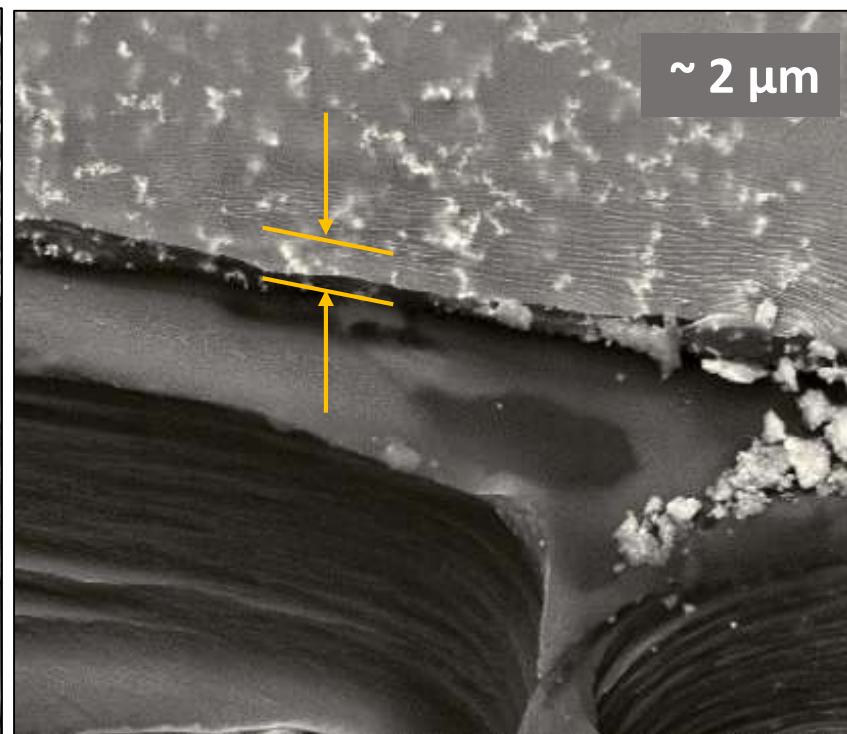
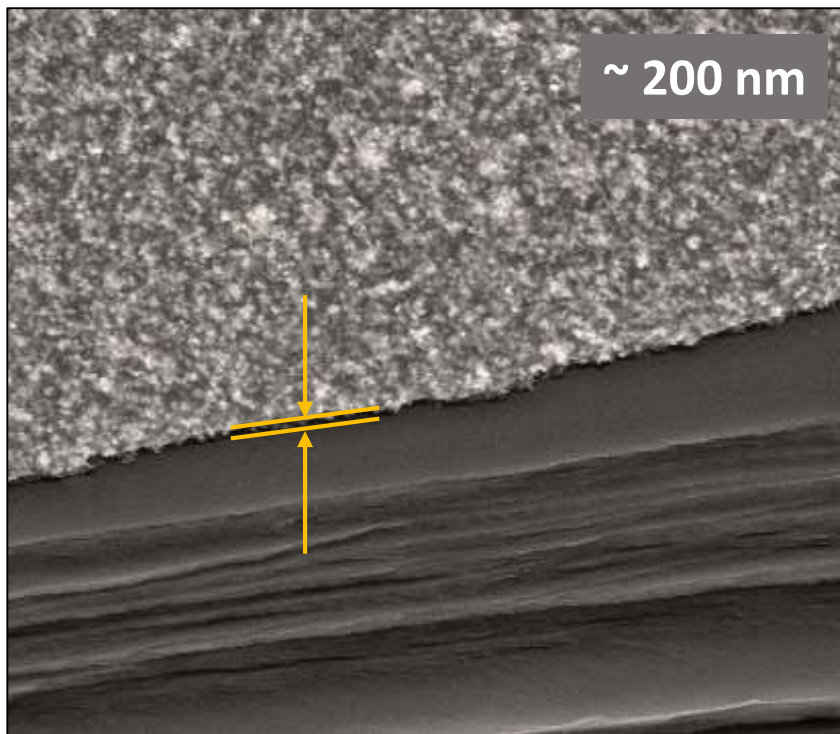


**Binder + ZnO + Surfactant Transparency  
Integrated Plot (550-650 nm)**



- 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

# 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 ( $\mu\text{m}$ )	Transmittance	
			UVA (354 nm)	Visible (600 nm)
<b>This study: HEC</b>	<b>0.8%</b>	<b>0.2 - 2</b>	<b>6%</b>	<b>73%</b>
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.

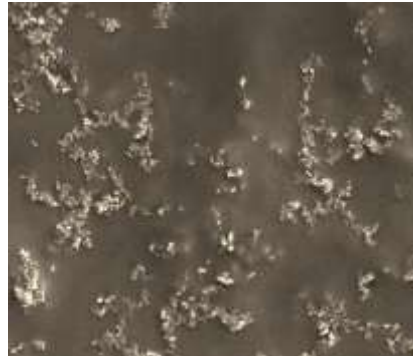
# Meso-structure

ZnO Powder

ZnO Dispersion

TiO<sub>2</sub>SiO<sub>2</sub>

HEC



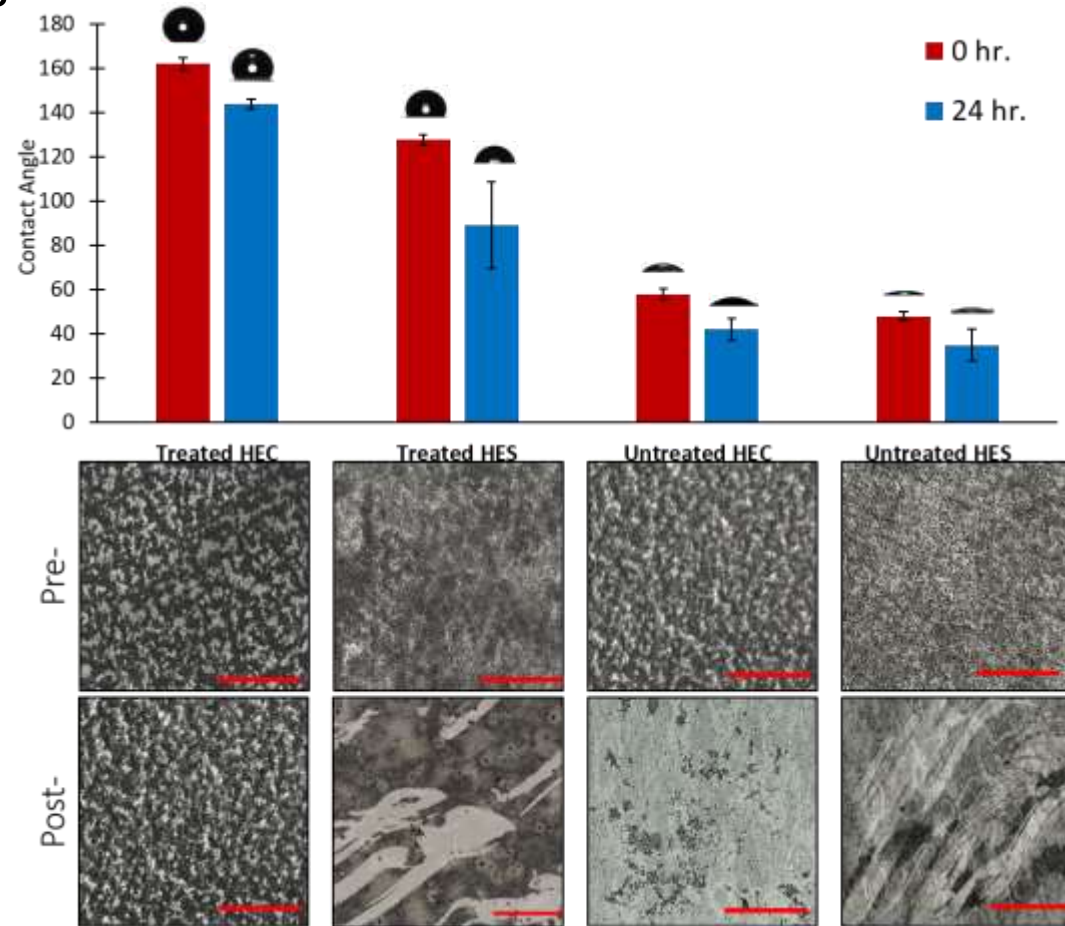
HES



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

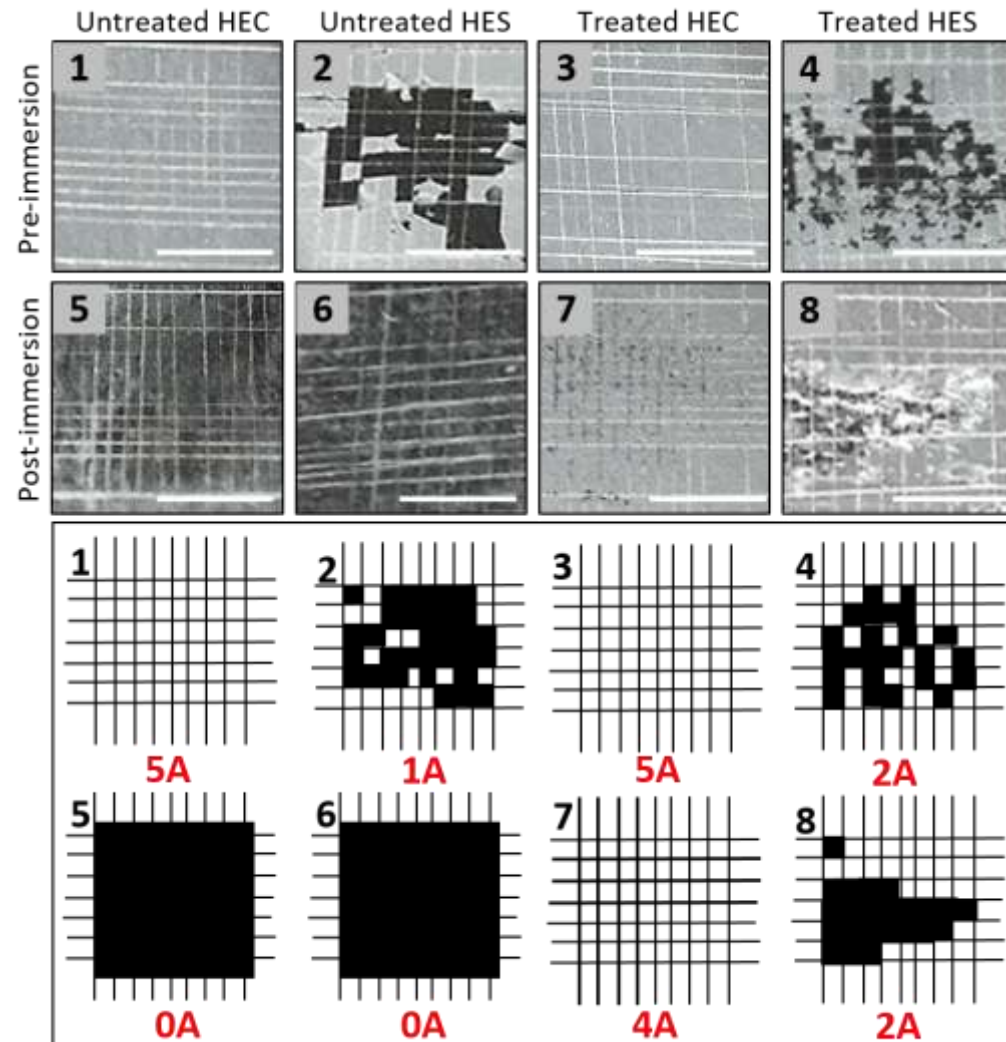
# Immersion test after treatment

- 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

FILM



# ■ Conclusions

- Invented a biobased, cost effective, printable, and transparent UV-blocking coating formulation
- Achieved high UV-blocking capability ( $< 10\%$ ) and transparency ( $\sim 80\%$ )
- Obtained very thin coating thickness ( $0.2 - 2 \mu\text{m}$ )
- Revealed unique cluster structures and new mechanism of improving UV-blocking performance

## **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

Pierre Gilles de Gennes, Nobel Prize,



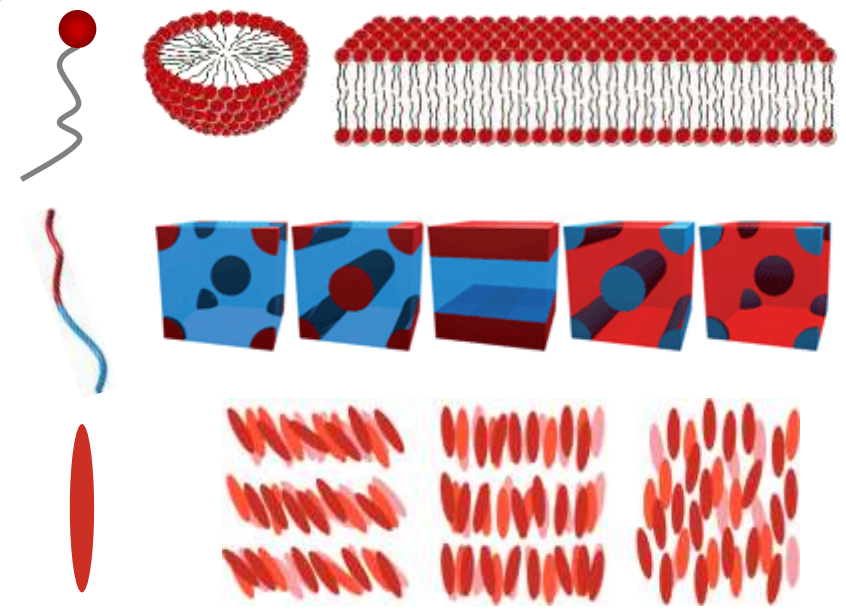
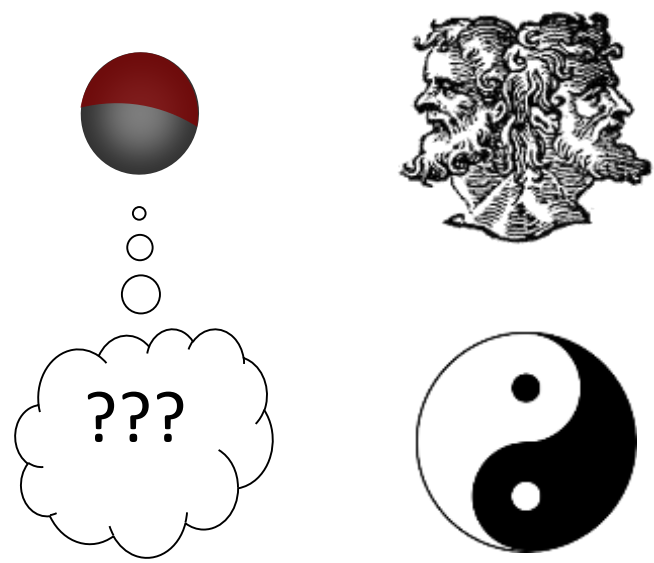
Polymer	ATRP, Block Copolymer	Tire, Plastic, Coating, Fiber
Surfactant	Micelles, Vesicles	Home & Personal care, Pharmacy
Liquid Crystal	MBBA, Phase diagram	LCD Display
Janus Particles	Not explored yet	

Complexity & Flexibility



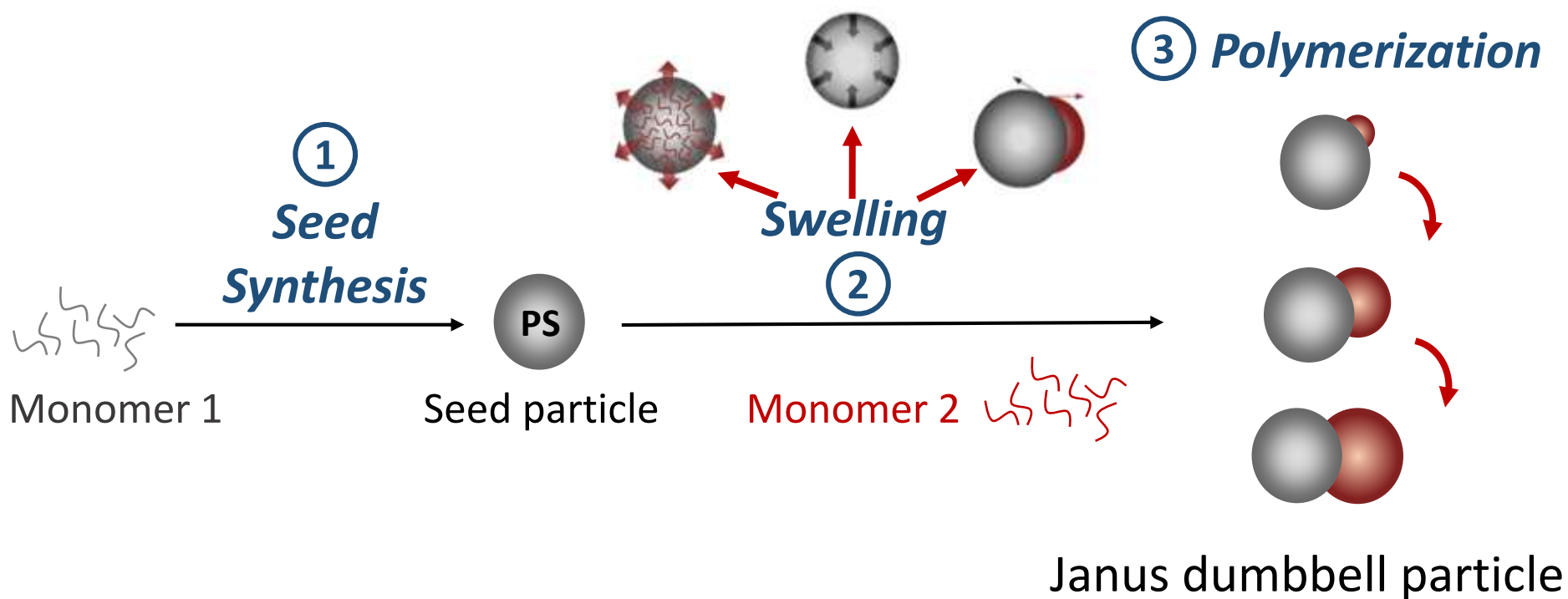
Plethora of applications

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



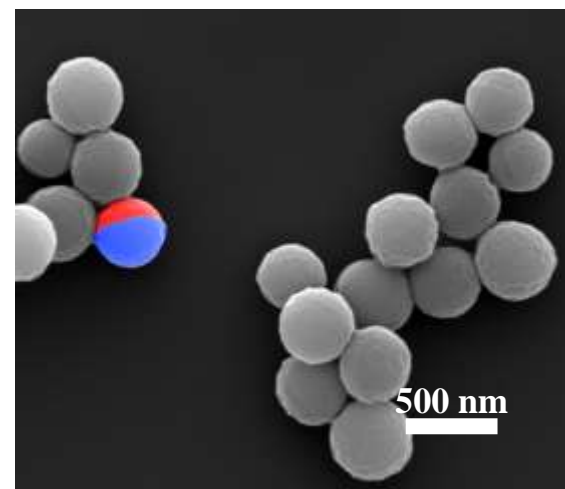
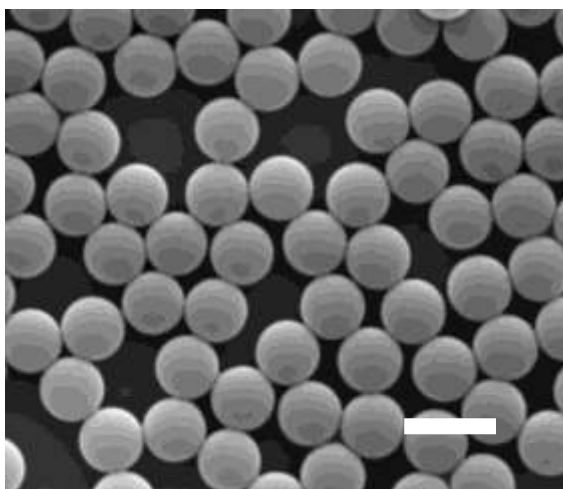
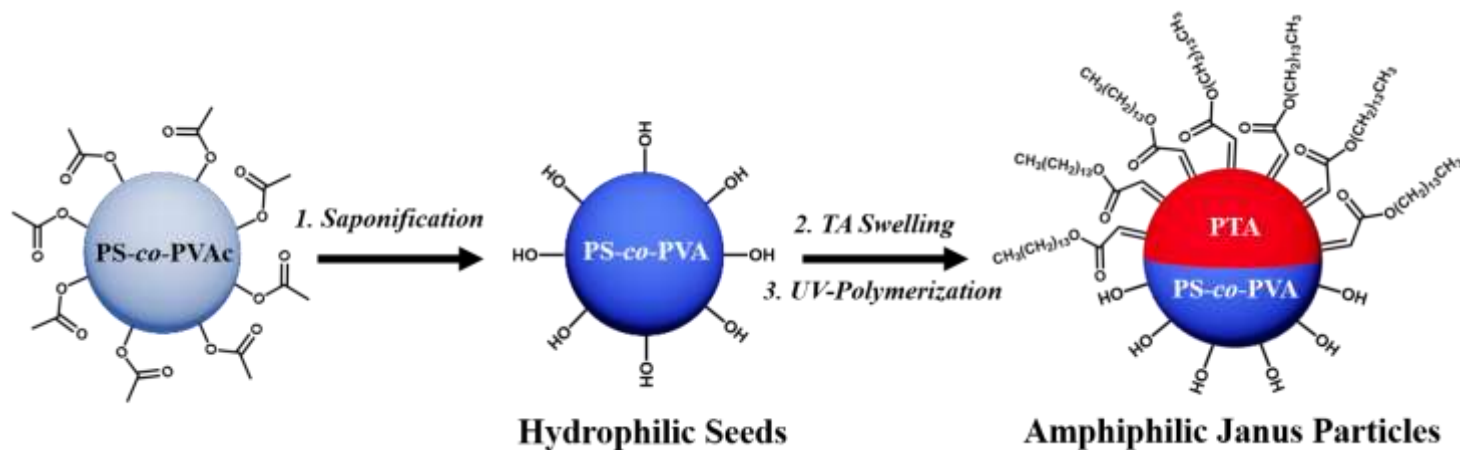
**Free energy**

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

monomer swelling polymer      Elastic energy      Interfacial tension

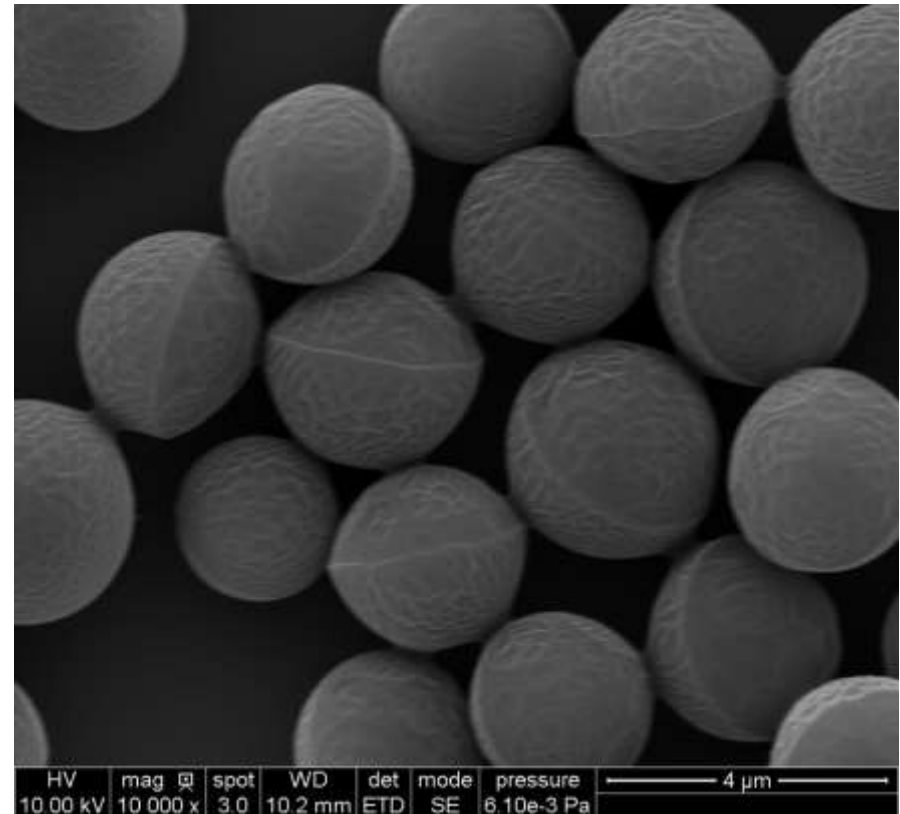
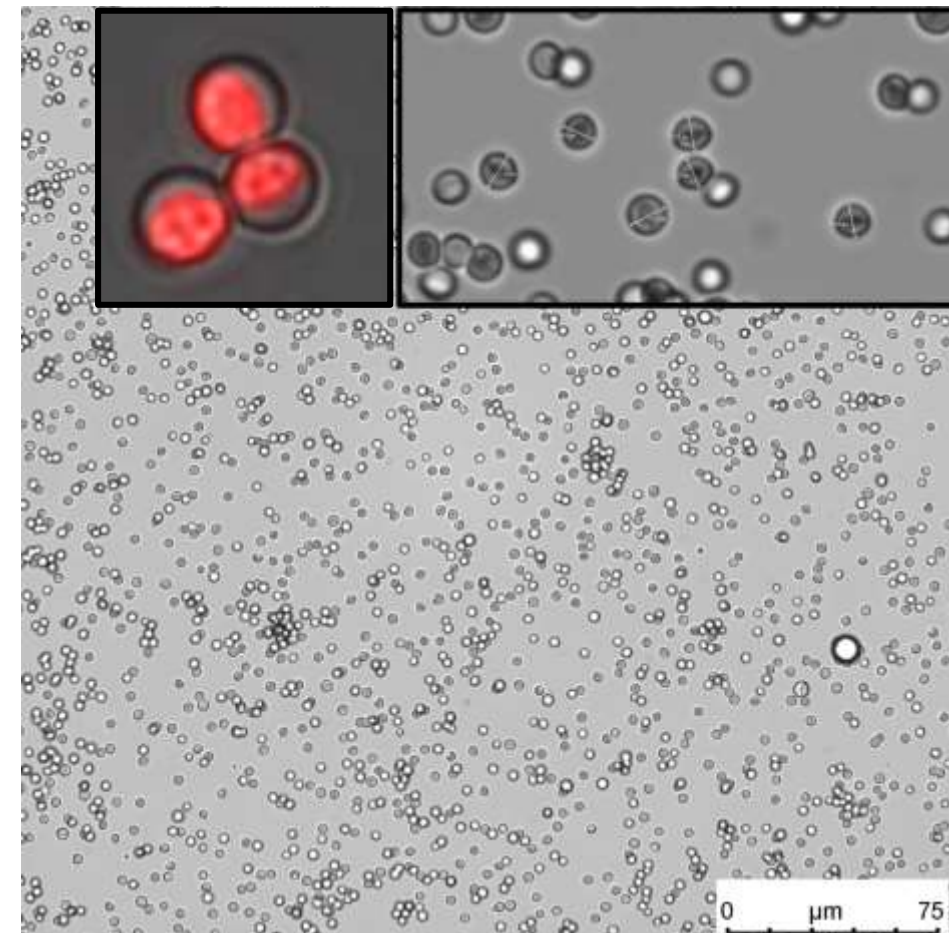
monomer mixing with polymer

# Synthesis of Janus particles



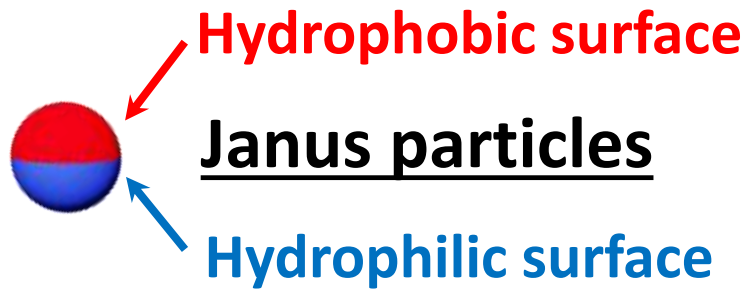
# 24

## ■ Characterization



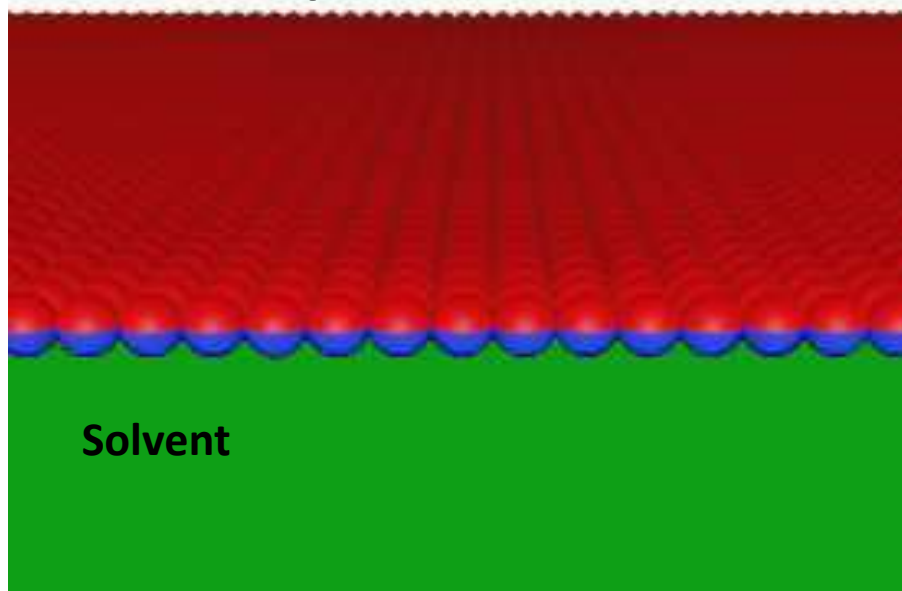
Seed surface – hydrophilic; Lobe surface – hydrophobic

# ■ Adsorption vs. stratification

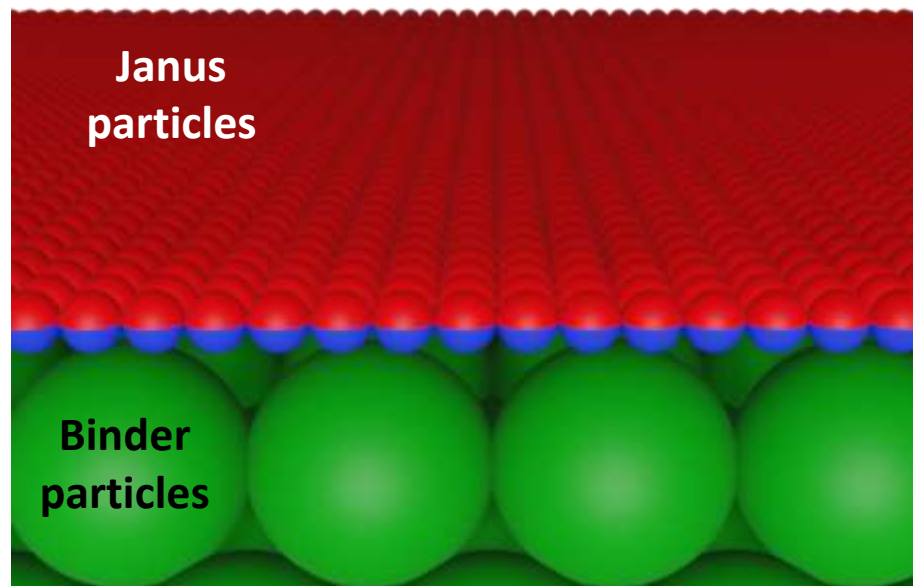


VS.

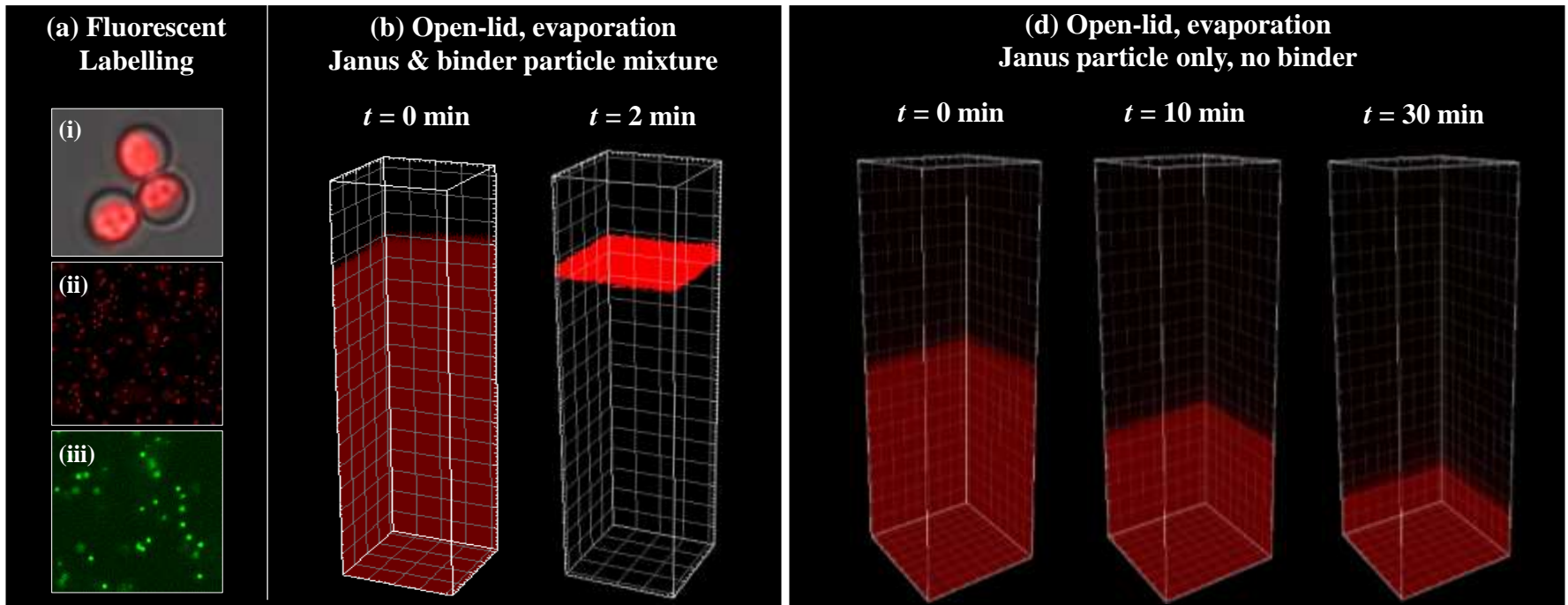
Adsorption at interface



Stratification



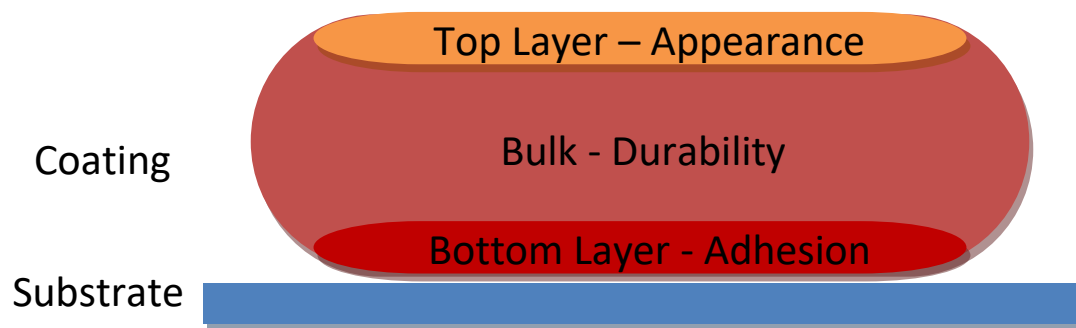
# Ultrafast dynamics



- 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

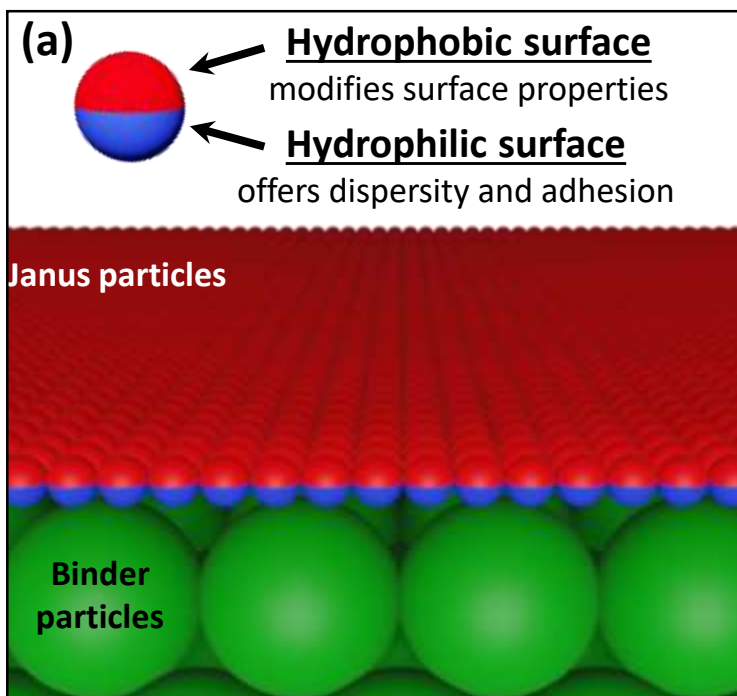
# Self-stratified coating

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.

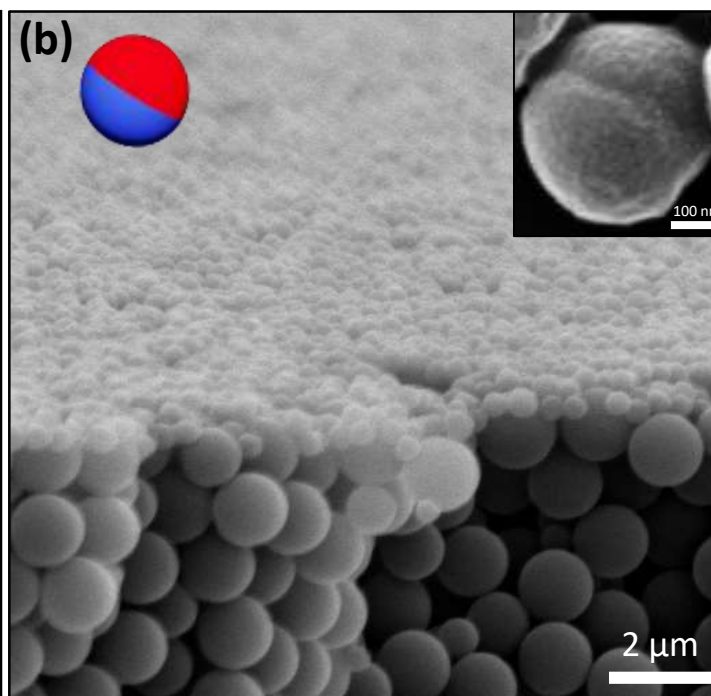


# Janus particles - a new coating additive

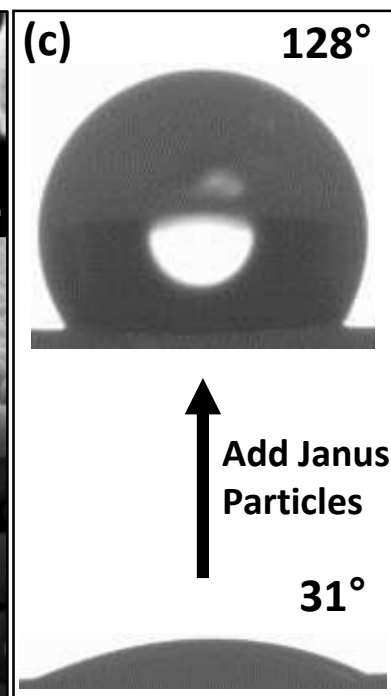
Theoretical Illustration of  
Self-stratified Coating



Electron Image of  
Self-stratified Coating

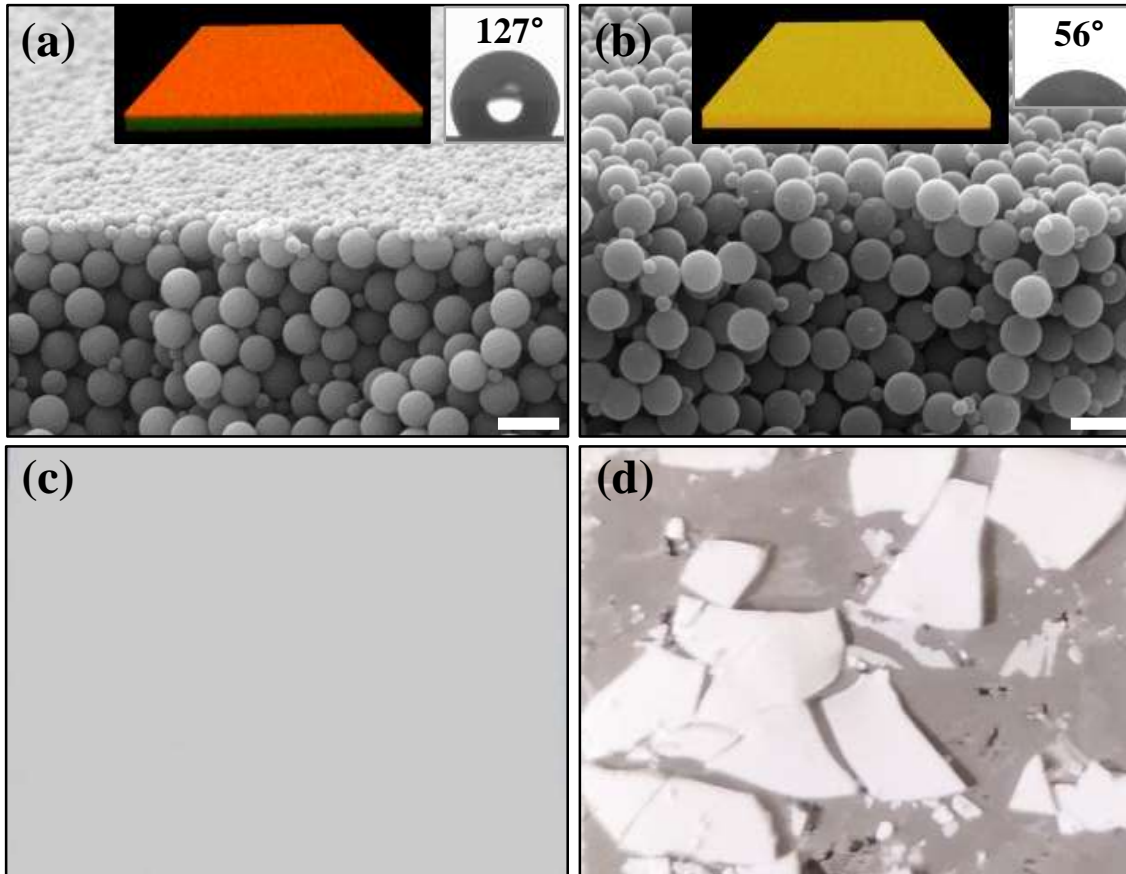


Hydrophobicity  
Enhancement



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

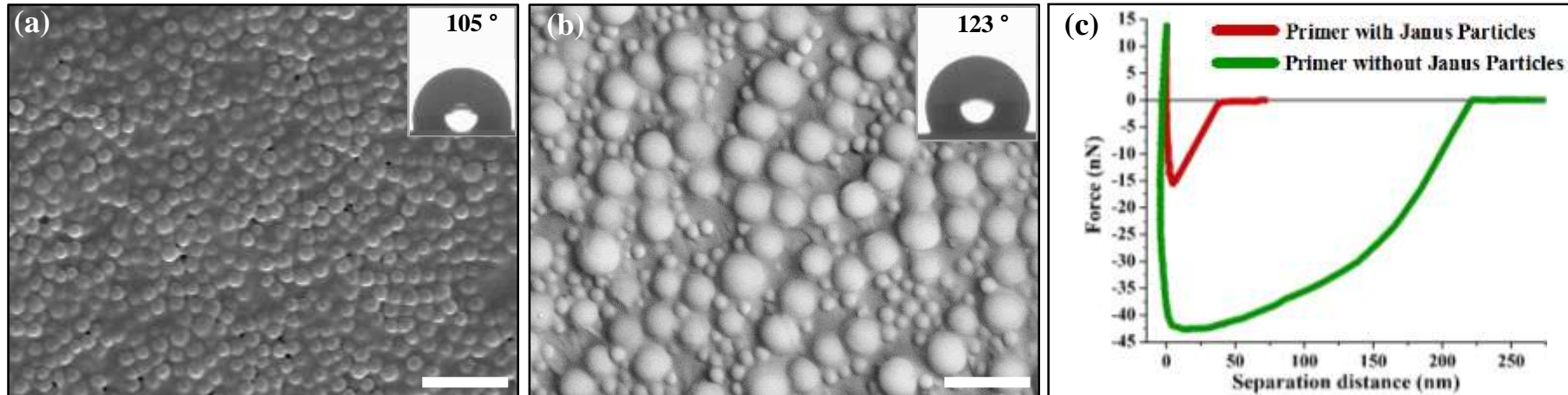
# ■ Superior performance



- 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

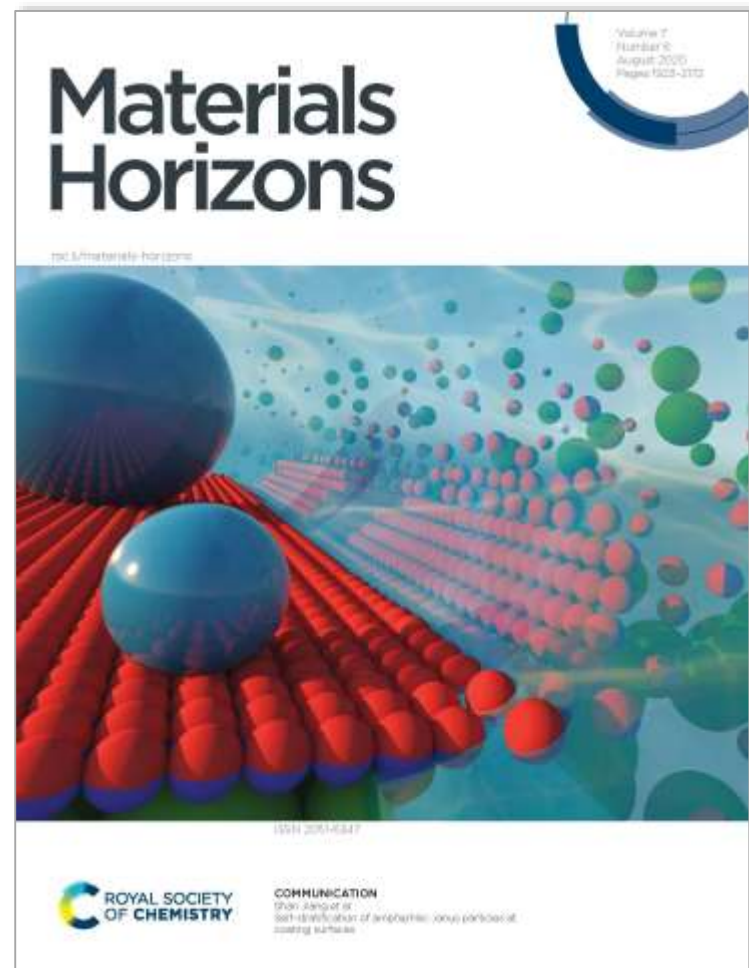
# Commercialization



- 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](mailto:sjiang1@iastate.edu)

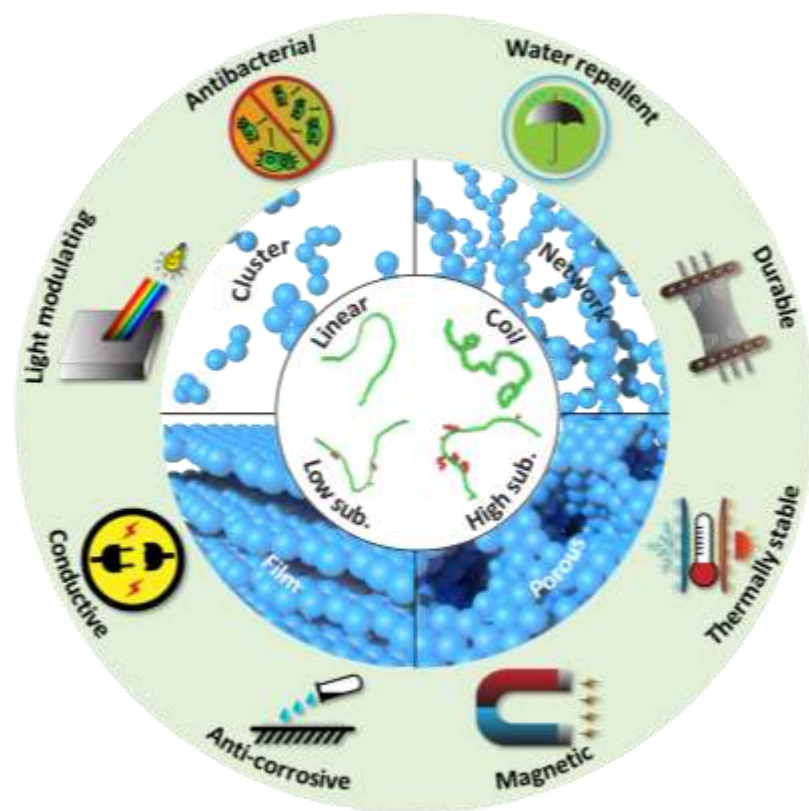
# Next generation industry coating

**Sustainability**

+

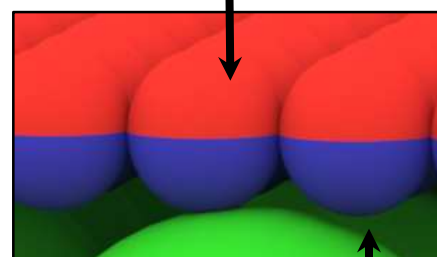
**Performance**

**Nanoparticle assembly  
& functionality**

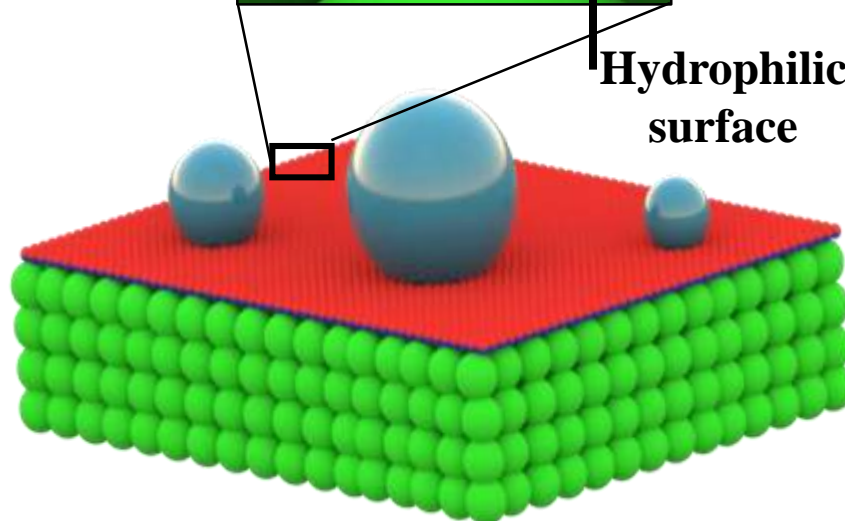


**Janus particles  
& stratification**

**Hydrophobic surface**

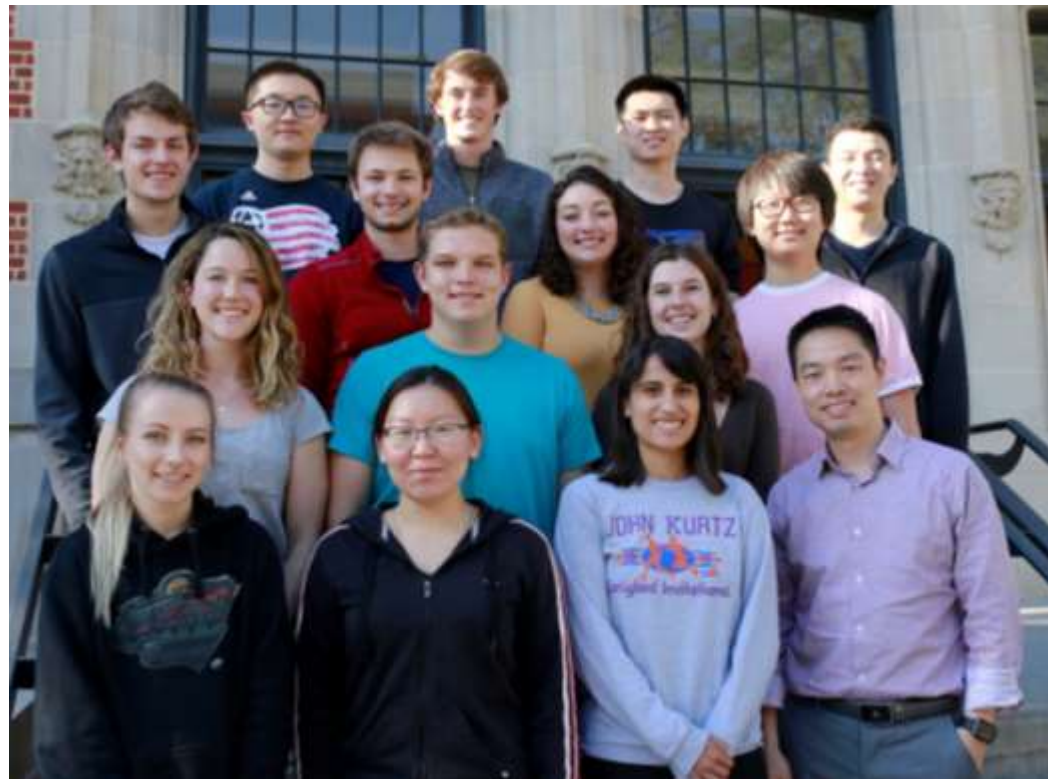


**Hydrophilic  
surface**



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Polymer and Food  
Protection Consortium



Startup Fund



3M  
Non-tenured faculty award



RIF grant