pH-Responsive Pickering High Internal Phase Emulsions Stabilized by Waterborne Polyurethane

Speaker: Jianhui Wu

Supervisors: Prof. Wei Lin

Prof. To Ngai

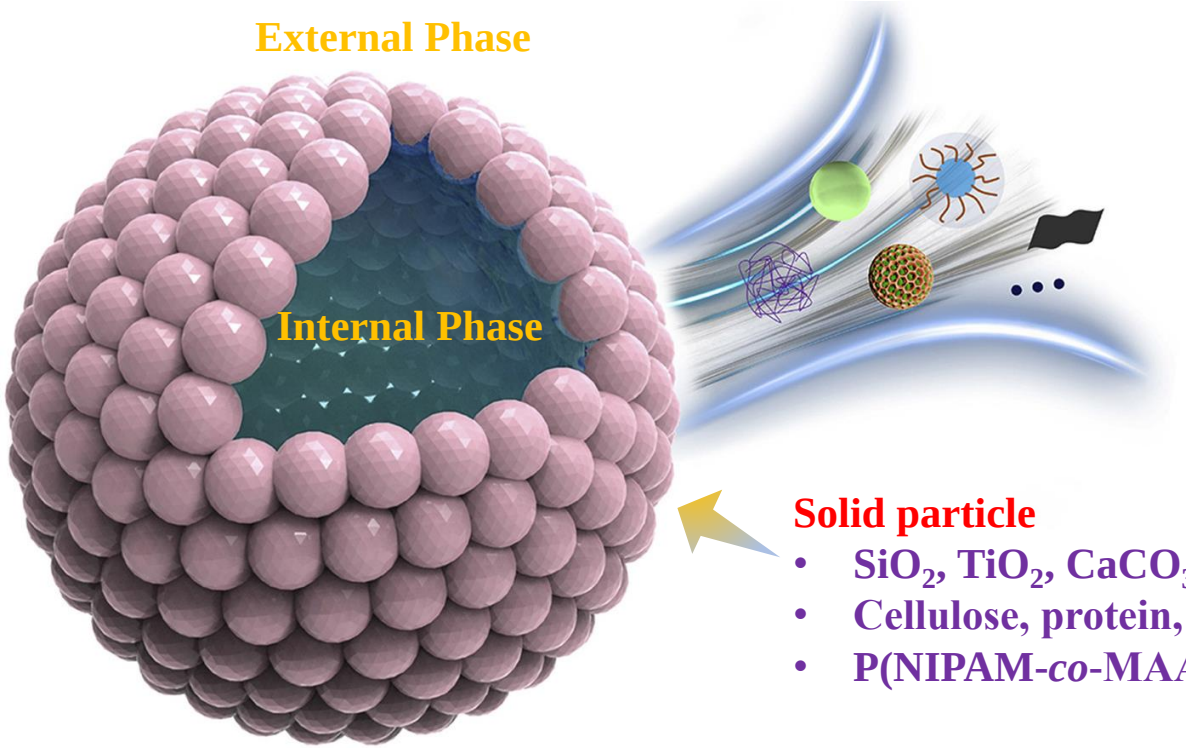
Date: 11/04/2021

四川大學
SICHUAN UNIVERSITY

CONTENTS

- Introduction
- Results and discussion
- Conclusions
- Acknowledgement

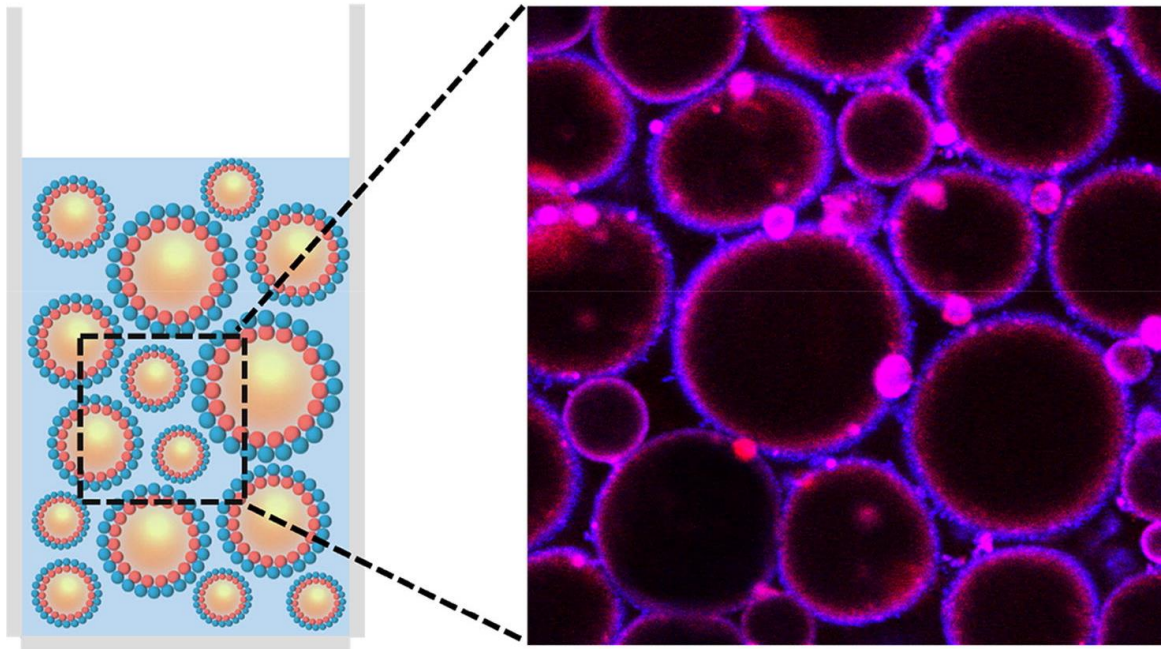
1. Introduction



Solid particle

- **SiO_2, TiO_2, $CaCO_3$…**
- **Cellulose, protein, …**
- **P(NIPAM-*co*-MAA)…**

Pickering emulsion: solid particles stabilized emulsion



Pickering High Internal Phase Emulsions (HIPEs, internal phase>74%)

Compared with traditional emulsion stabilized by small molecular surfactants, Pickering emulsion exhibits,

- **a wide variety of solid particles**
- **better stability**
- **lower toxicity**
- **higher efficiency**

W. Ramsden et al. *Proc. R. Soc.*, **1903**, *72*, 156.
S. U. Pickering et al. *J. Chem. Soc.*, **1907**, *91*, 2001.
Tao, S et al. *J. Colloid Interface Sci.* **2022,** *607*, 1491.
Guan, X et al. *Langmuir* **2021**, *37*, 2843.
Jiang, H et al. *Curr. Opin. Colloid Interface Sci.* **2020,** *49*, 1-15.

Application:

- **porous materials**
- **nutraceutical containers** → **long-term stability**
- **gels…**
- **oil transportation and recovery**
- **emulsion polymerization**
- **heterogeneous catalysis…** → **adjustable stability**

1. Introduction

The methods in industry to break up Pickering HIPEs are,

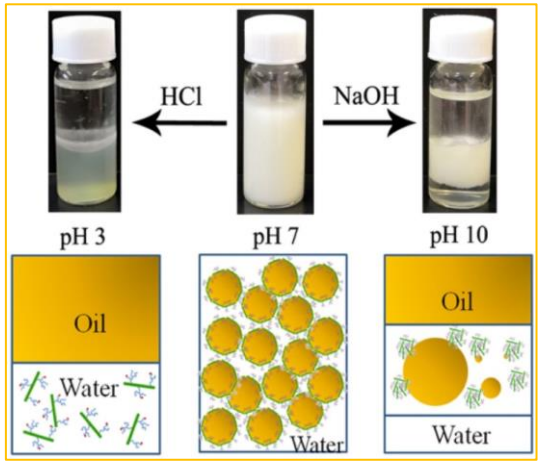
- **adding lots of chemical demulsifiers**
- **physical damage**

Disadvantage

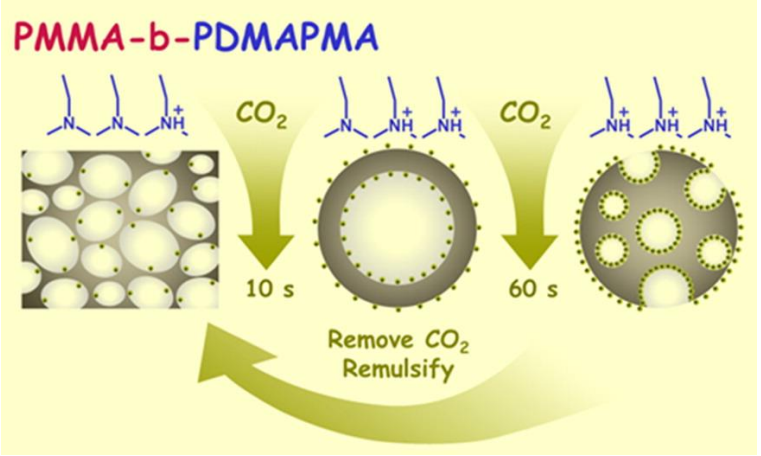
- generating extra additives
- large energy consumption
- high economic and environmental costs

Stimuli-responsive Pickering HIPEs with emulsification-demulsification cyclic property are desired.

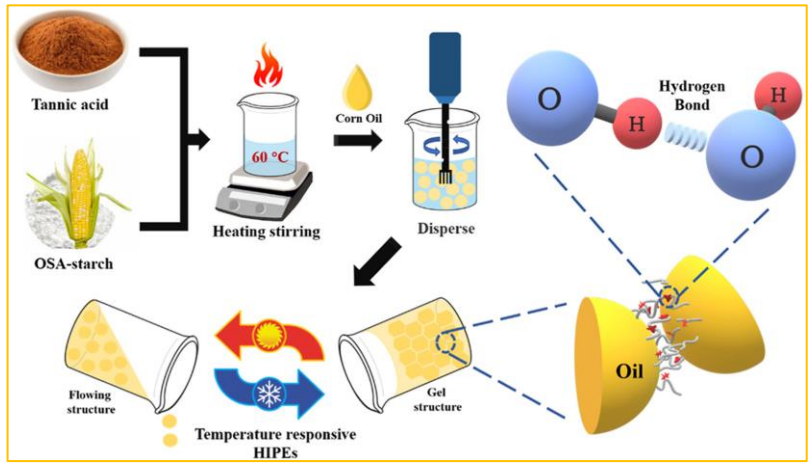
- pH
- CO_2
- temperature
- redox…



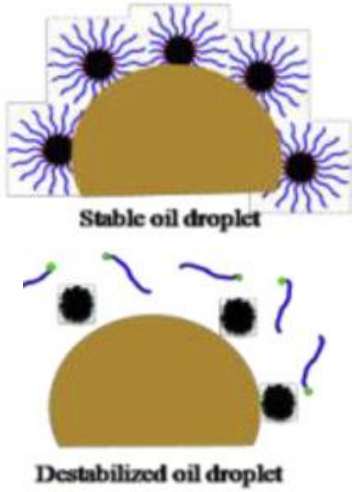
pH-responsive



CO_2-responsive



temperature-responsive



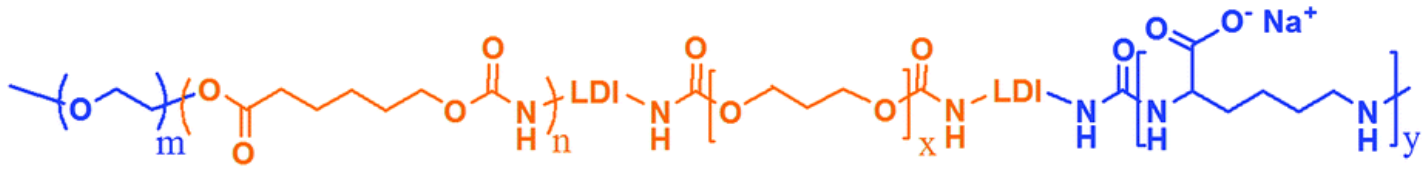
redox-responsive

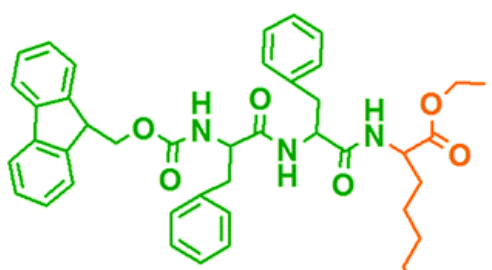
Li, W. X et al. *Carbohydr. Polym.* **2020,** *229*, 115401.
Hao, L et al. *Ind. Eng. Chem. Res.* **2018,** *57* (28), 9231.
Chen, Y et al. *Langmuir* **2016,** *32* (42), 11039.

Liu, Y et al. *Food Hydrocolloids* **2020,** *109*.
Yuan, J et al. *Polymer* **2018,** *158*, 1-9.
Shi, Y et al. *ACS Appl. Mater. Interfaces* **2020,** *12* (47), 53385.

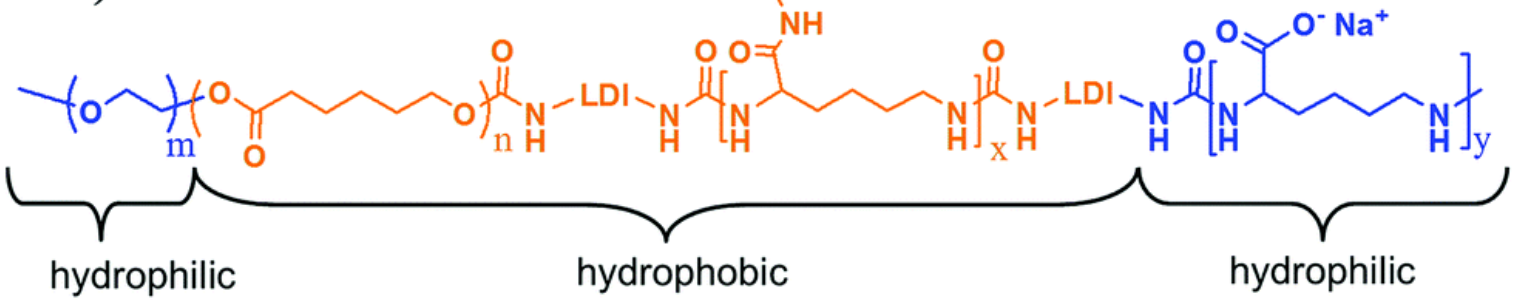
1. Introduction

a) **Waterborne polyurethane structure (WPU) structure**

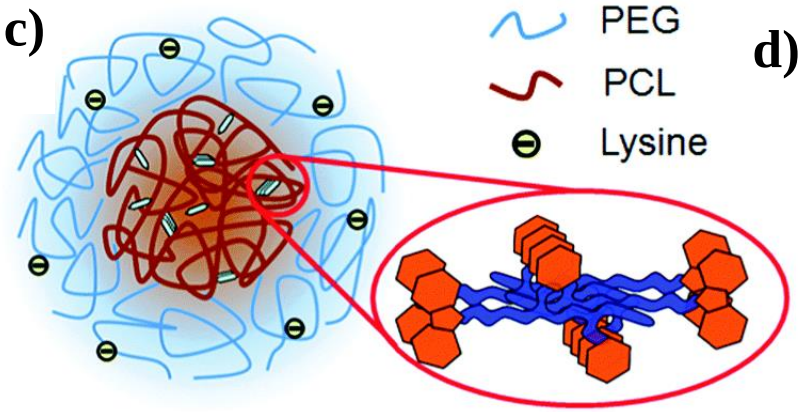




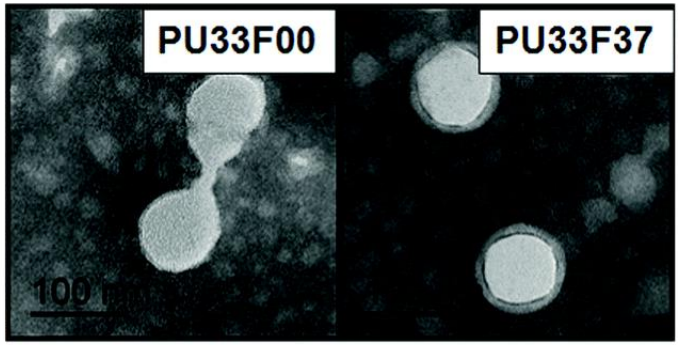
b)



c)

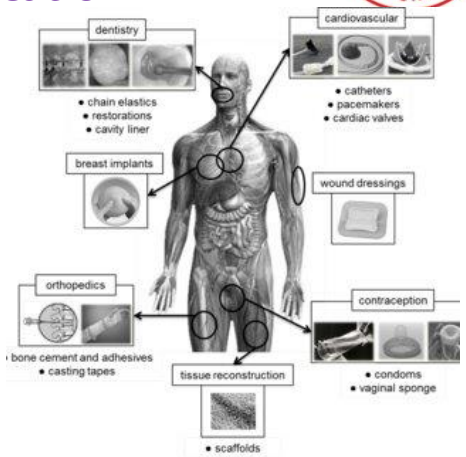


d)

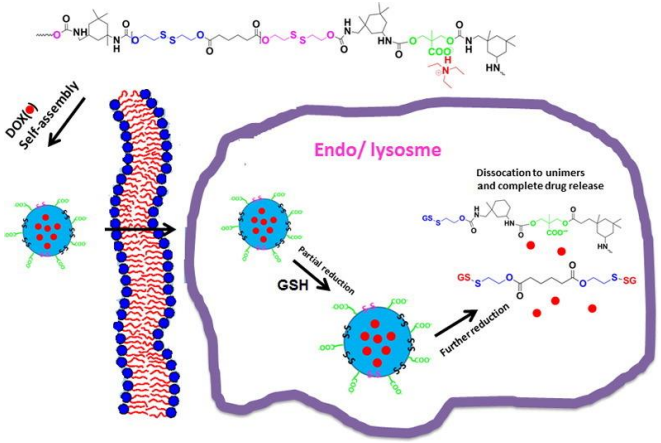


Application

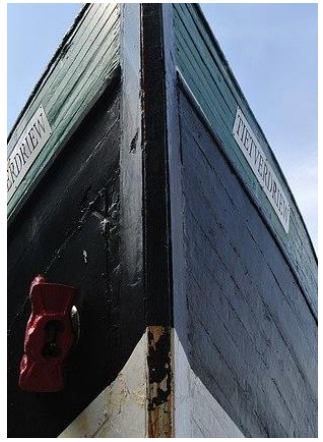
Leather finishing



Medical implants and devices



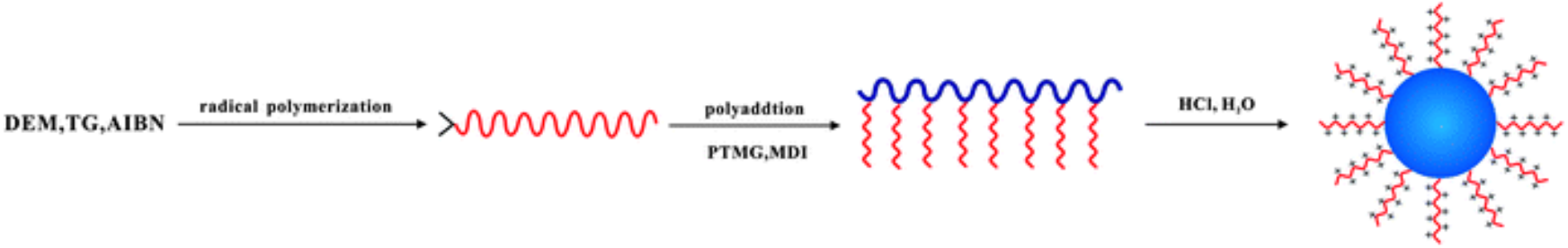
Drug release

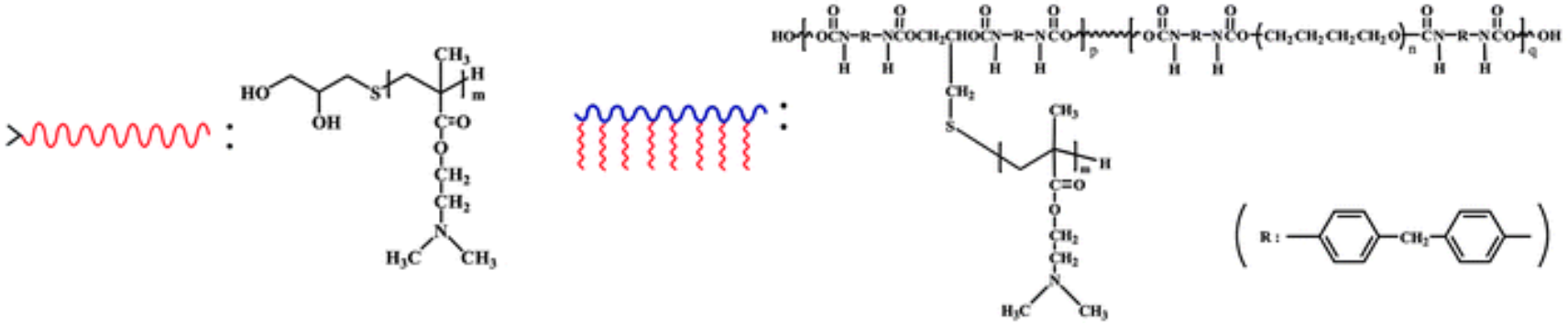


Marine coating

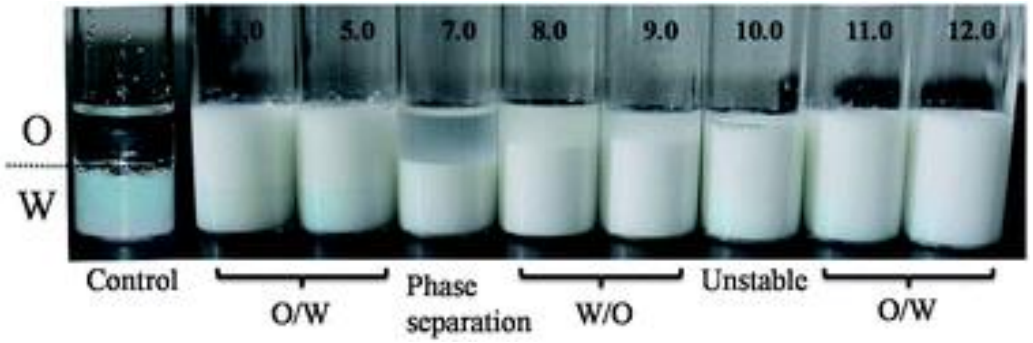
Gomez, I. J. et.al *ACS Applied Polymer Materials* **2019,** *1* (11), 3064. Pan, J et.al *ACS Sustain. Chem. Eng.* **2020,** *8* (3), 1671. Wang, C et.al. *RSC Advances* **2017,** *7* (44), 27522. Chen, K et.al *ACS Sustain. Chem. Eng.* **2018,** *6* (12), 16616. Omrani, et al. *Mater. Sci. Eng. C-Mater. Biol. Appl.***2017,** *70*, 607. Zhang, F et al.. *J. Mat. Chem. B* **2018,** *6* (26), 4326.

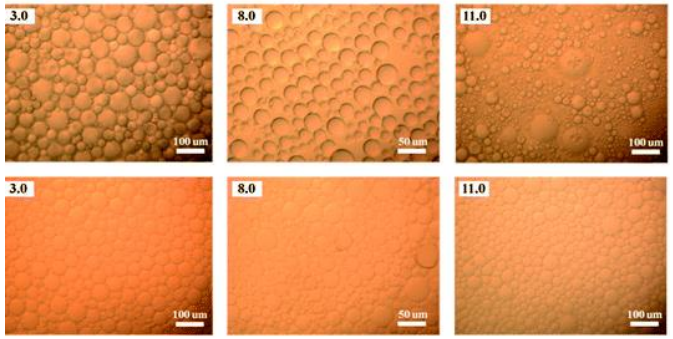
1. Introduction





PU-*g*-PDEM





- In 2013, our group first described the cationic PU-*g*-PDEM graft copolymer as a particulate emulsifier to achieve pH-responsive emulsions. After then, a series of cationic WPU nanoparticles were used as particulate emulsifiers to stabilize emulsions.
- However, it is hard to achieve the demulsification of those cationic WPU-based emulsions by adjusting the pH value, which restricts its applications in various fields where an emulsification−demulsification process is needed.

Ma, C et al. *J. Mater. Chem. A* **2013**, *1* (17), 5353.
Yuan, J et al. *RSC Adv.* **2016,** *6* (64), 58970.
Yuan, J et al. *Polymer* **2018,** *158*, 1

To solve this problem, we design and use anionic waterborne polyurethane as a novel particulate emulsifier for the generation of higher pH-responsive Pickering HIPEs.

2.1 Synthesis and characterization of WPU

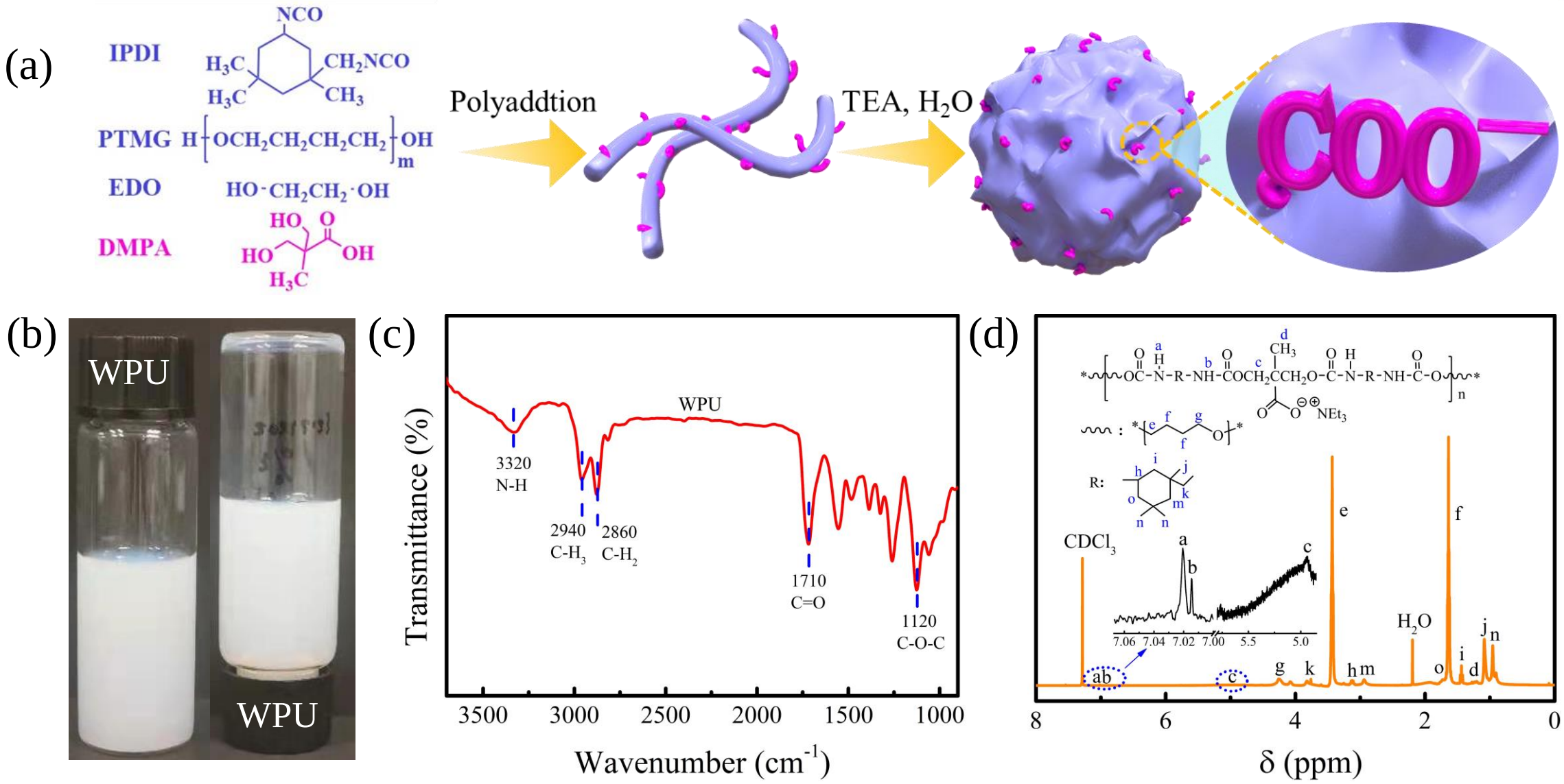


Fig. 2.1 (a) Schematic of the synthesis of WPU and their self-assembly in water. (b) the appearance of WPU dispersion. (c) FT-IR and (d) ^{1}H NMR spectra of WPU

2.1 Synthesis and characterization of WPU

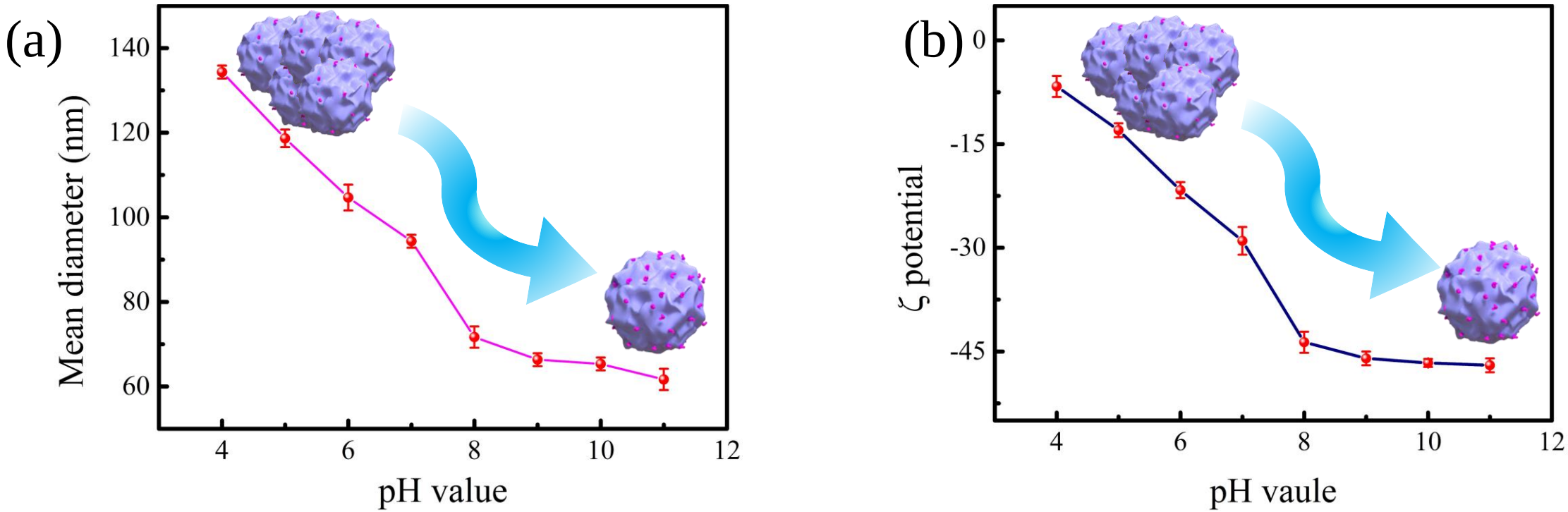


Fig. 2.2 pH dependence of (a) the mean particle diameter (b) ζ-potential of WPU nanoparticles in aqueous at a particle concentration of 10^{-4} wt% at 25 ^{o}C.

- **Phenomena:** with the increase of pH values, both the average particle size and ζ-potential of WPU decreased.
- **Reason:** the carboxyl deprotonation degree increases under alkaline conditions. The electrostatic repulsion between particles is therefore sufficient to prevent particle aggregation.
- **Result:** higher stability of the WPU dispersion under high pH conditions, which means the conformation of WPU nanoparticles could be controlled by varying the pH value.

2.2 Adsorption of WPU at the Oil–Water Interface

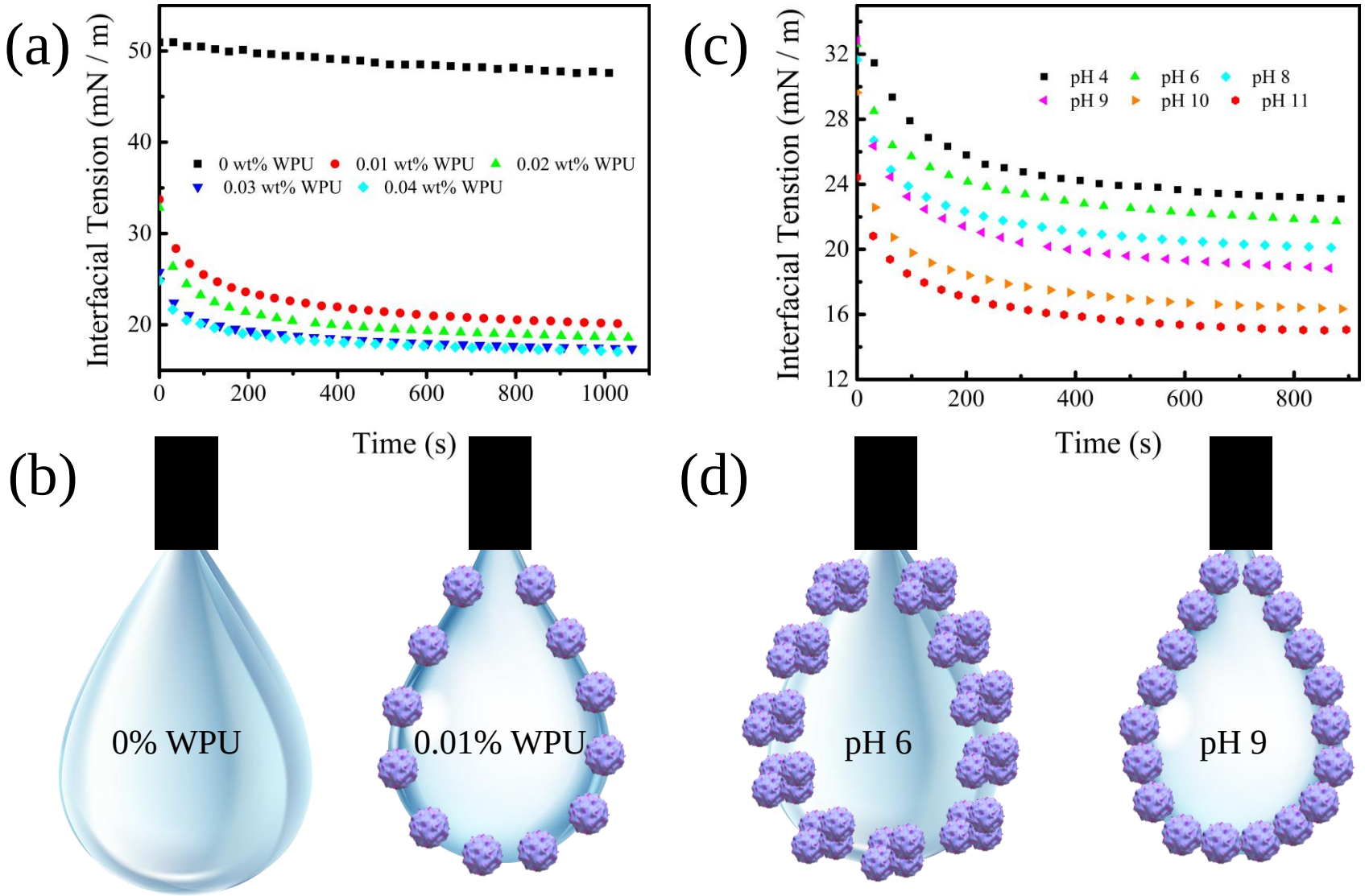
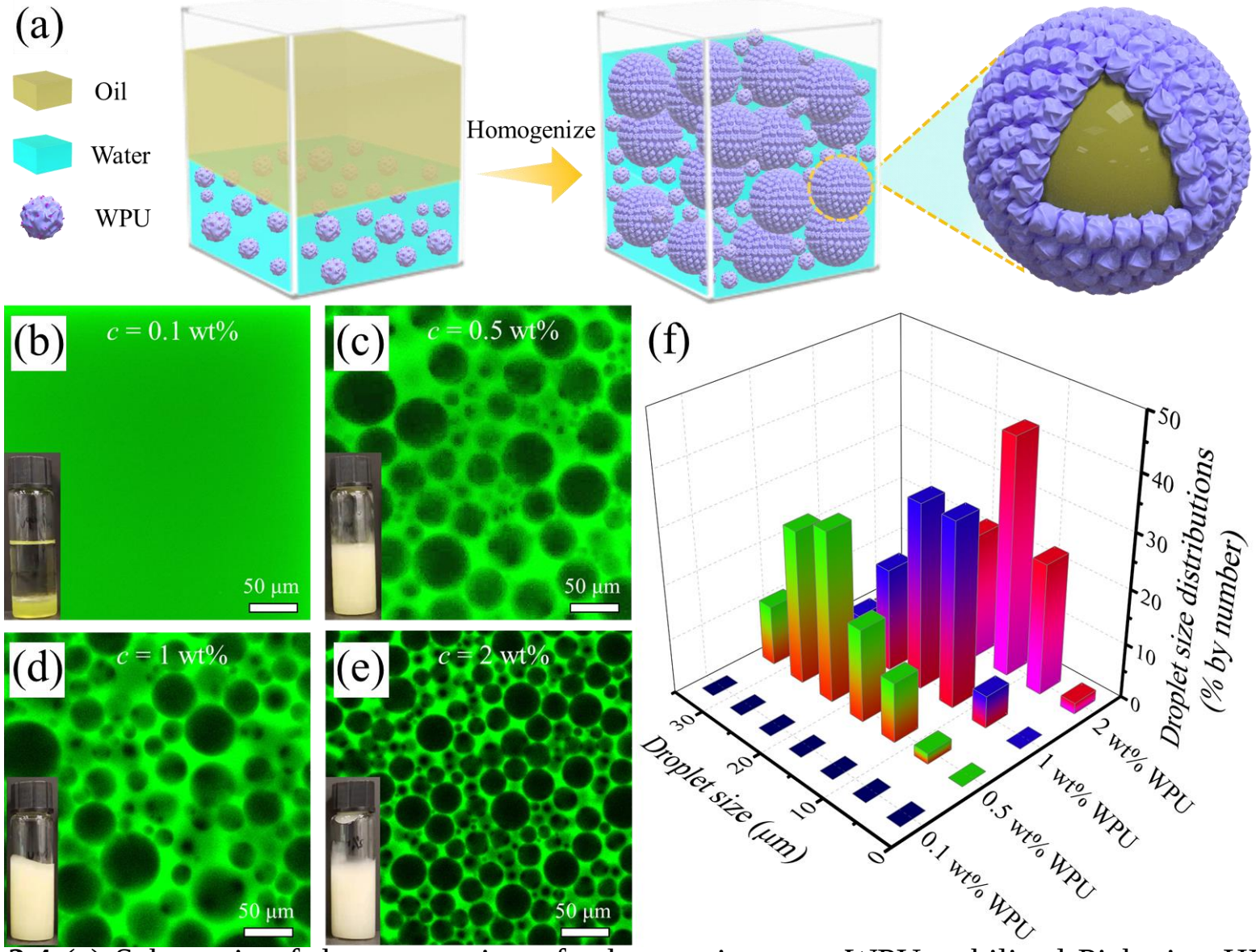


Fig. 2.3 Interfacial tension (γ) between *n*-hexane and water as a function of time (a) with different WPU concentrations (0-0.04 wt%) at pH 9.0 and (b) corresponding schematic illustration, (c) at different pH value with 0.01 wt% WPU concentrations and (d) corresponding schematic illustration.

- **Phenomena:** the interfacial tension between *n*-hexane and water decreased as the WPU concentration and pH value increased.
- **Reason:** the WPU nanoparticles have small average particle size at high pH value. That is, small particles in high-pH medium can adsorb onto interfaces faster and occupy the interface with a higher coverage ratio because of their higher diffusion rate and reduced steric hindrance.
- **Conclusion:** WPU nanoparticles are highly surface-active and could be ideal candidates for stabilizing O/W interfaces.

2.3 Effect of WPU Concentration on the Pickering HIPEs Stability



➢ **Phenomenon:**

(1) when the WPU concentrations exceeded 0.5 wt%, stable gel-like HIPEs were achieved.

(2) the mean droplet size of emulsions decreased with the increasing of WPU concentration.

➢ **Reasons:**

(1) the synergistic effect between WPU adsorbed droplets and network constructed by excess WPU in continuous phase which strongly limited the movement of emulsion droplets.

(2) more particles can stabilize larger interface at a constant oil-water ratio.

Fig. 2.4 (a) Schematic of the preparation of *n*-hexane-in-water WPU-stabilized Pickering HIPEs. (b-e) CLSM images of *n*-hexane-in-water Pickering HIPEs with different WPU nanoparticles concentrations and (f) the corresponding droplet size distributions. Insets are the pictures of the corresponding HIPEs. The internal phase fraction and pH value were kept at 80% and 9, respectively.

2.4 Effect of the Internal Phase Fraction on the Pickering Emulsion Stability

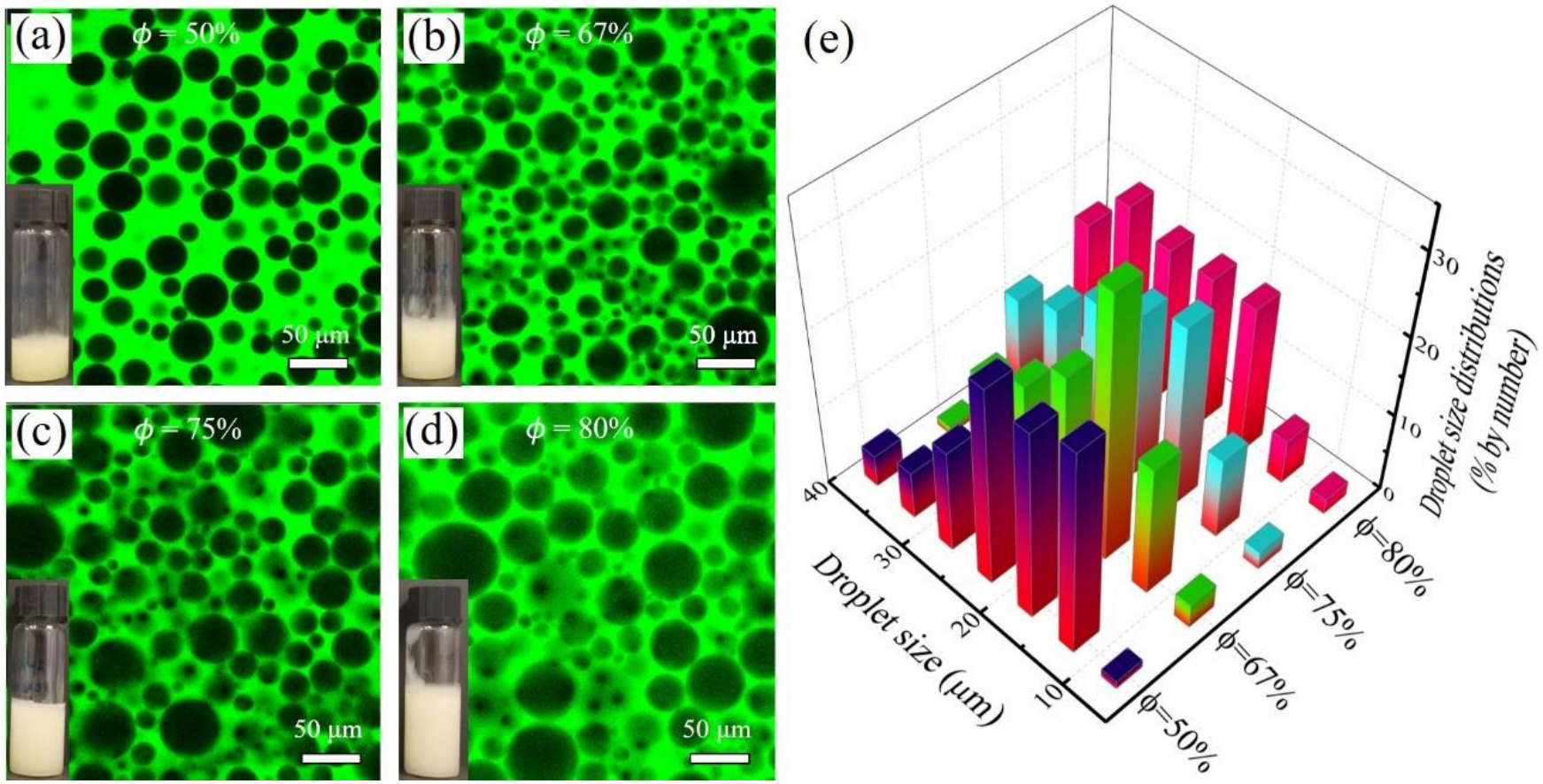


Fig. 2.5 (a-d) CLSM images of n-hexane-in-water emulsions with different internal phase fraction and (e) the corresponding droplet size distributions. Insets are the pictures of the corresponding emulsions. The WPU concentration and pH value were kept at 1 wt% and 9, respectively.

- **Phenomena:**
  with the increasing of the internal phase fraction,
  (1) the viscosity of emulsions was recognizably improved.
  (2) the mean droplets size of emulsion increased.

- **Reasons:**
  (1) the increasing steric hinderance between droplets.
  (2) there would be less particles adsorbed on each droplet surface at higher internal phase fraction to ensure the invariant interface area, thus causing larger droplet size.

2.5 Effect of the Type of Oils (polarity) on Pickering HIPEs Stability

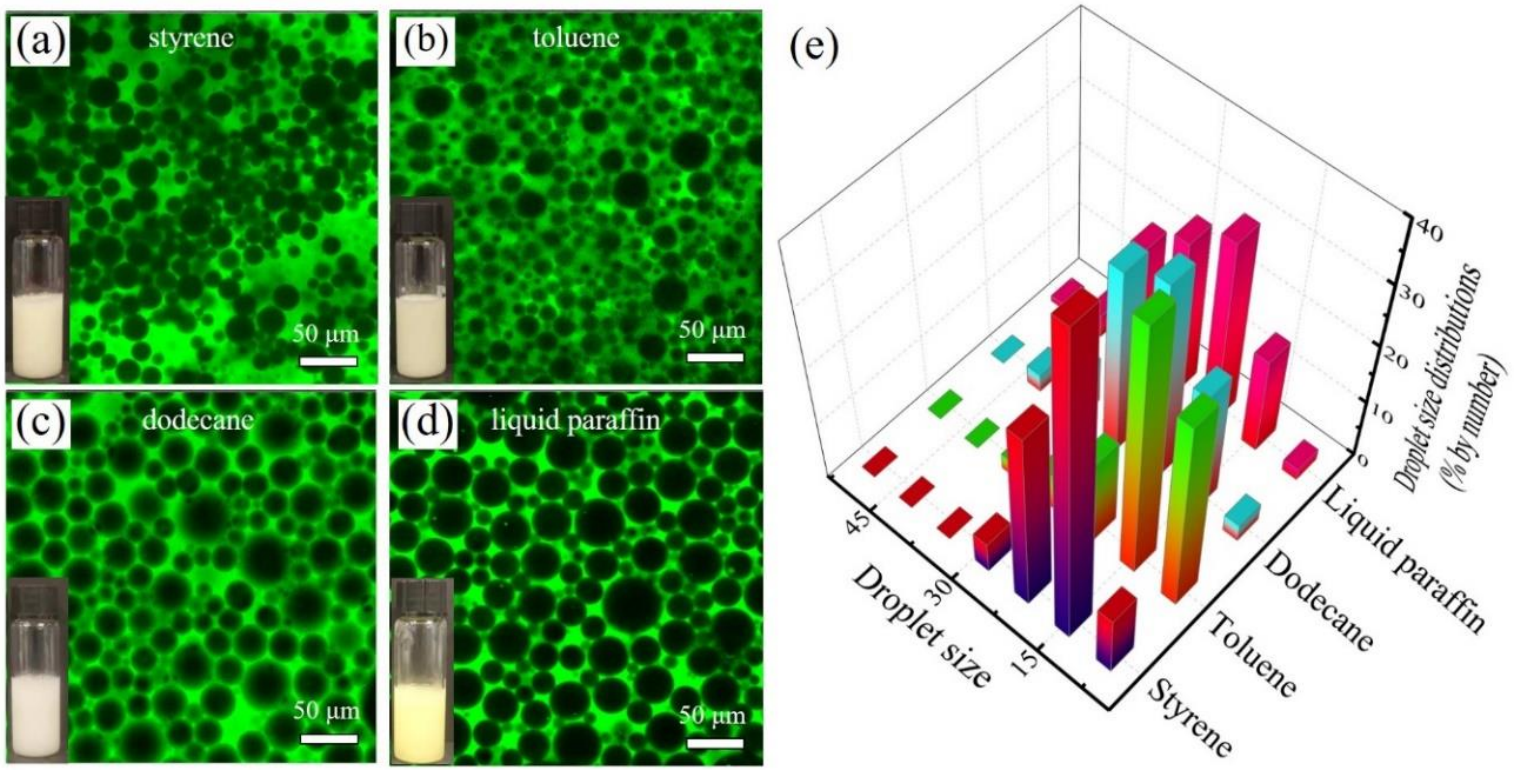


Fig. 2.6 CLSM images of Pickering HIPE stabilized by 1 wt% WPU nanoparticle using (a) styrene, (b) toluene, (c) dodecane, (d) liquid paraffin as oil phase. and (e) the corresponding droplet size distributions. Insets are the pictures of the corresponding HIPEs. The internal phase fraction and pH was kept at 80% and 9, respectively.

Table 1 Oil/water interfacial tension (γ_{OW}) values and dielectric constant of the Oils

Oil	styrene	toluene	dodecane	liquid paraffin
γ_{OW} (mN / m)	32	34	49	53
ε (F / m)	2.4	2.4	2	1.9
Droplet size (μm)	16	17	23	26

- **Phenomena:**
  (1) four stable Pickering HIPEs containing different oil phases were obtained.
  (2) the sizes of the HIPEs decreased with increasing the polarity of internal phase.

- **Reasons:**
  (1) The possibility reason is that the WPU nanoparticles exhibited a higher affinity to polarity oil, thus lead to more nanoparticles adsorbed onto the O/W interface.

- **Conclusion:**
  WPU particulate emulsifiers could stabilize various oils, which is beneficial to further practical applications.

Wan, Z et al. *J. Agric. Food. Chem.* **2017,** *65* (11), 2394-2405.
Binks, B. P et al. *PCCP* **2000,** *2* (13), 2959-2967.

2.6 pH-Responsive Behavior of the Pickering HIPEs

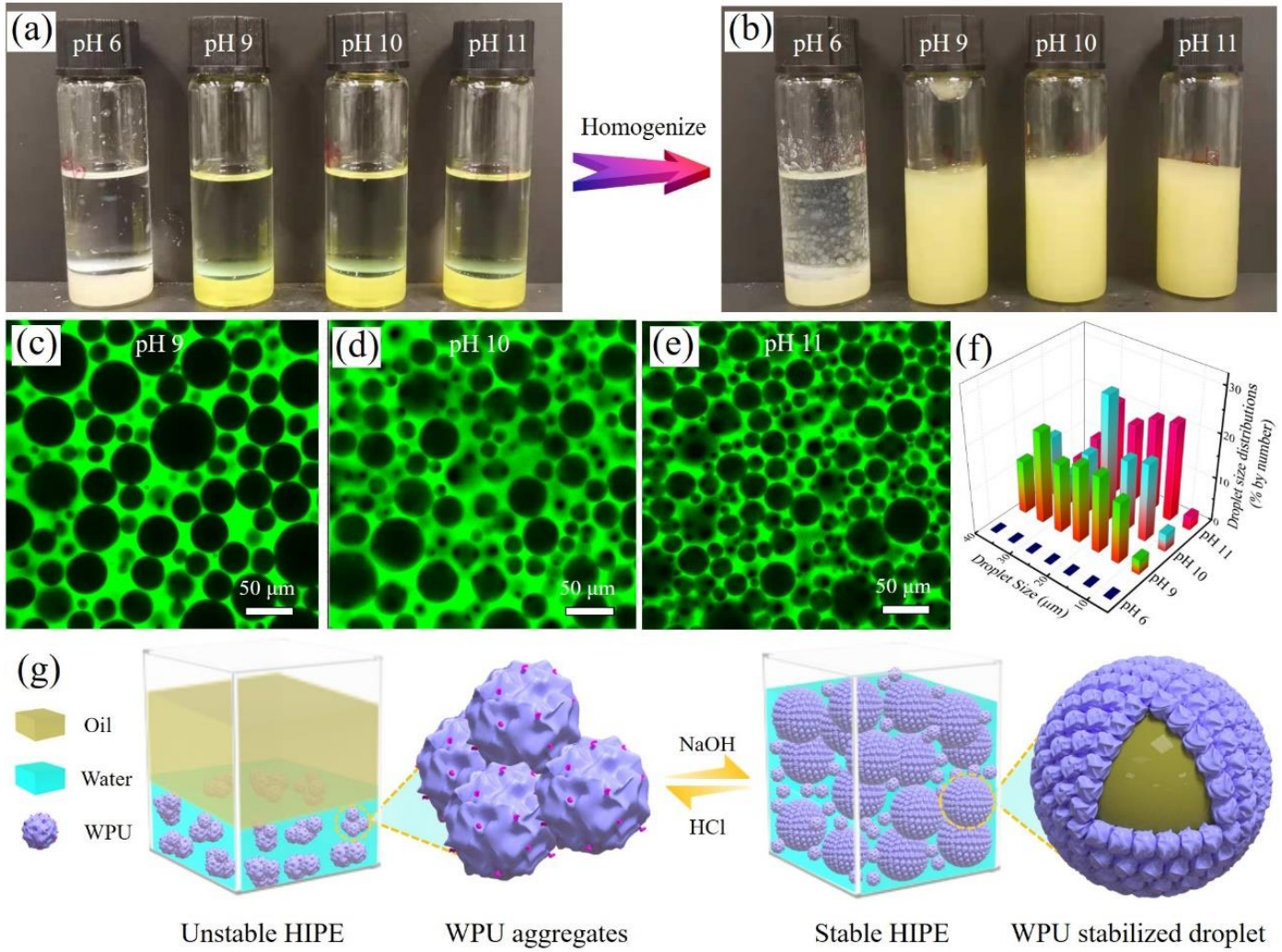


Fig. 2.7 Pictures of n-hexane-in-water Pickering HIPEs with different pH values (a) before and (b) after homogenization. (c-e) CLSM images of Pickering HIPEs with different pH values and (f) the corresponding droplet size distributions. (g) Schematic illustration of the pH-responsive behavior of WPU-based Pickering HIPEs. The WPU concentration and internal phase fraction were kept at 1% and 80%, respectively.

- **Phenomena:**

  (1) in weak acidic solution (pH 6), WPU could not stabilize the HIPEs.

  (2) the stable gel-like HIPEs were obtained in alkaline condition (pH ≥ 9.0).

  (3) the mean droplet size of HIPEs was reduced with the pH value shifted from 9 to 11.

- **Reasons:**

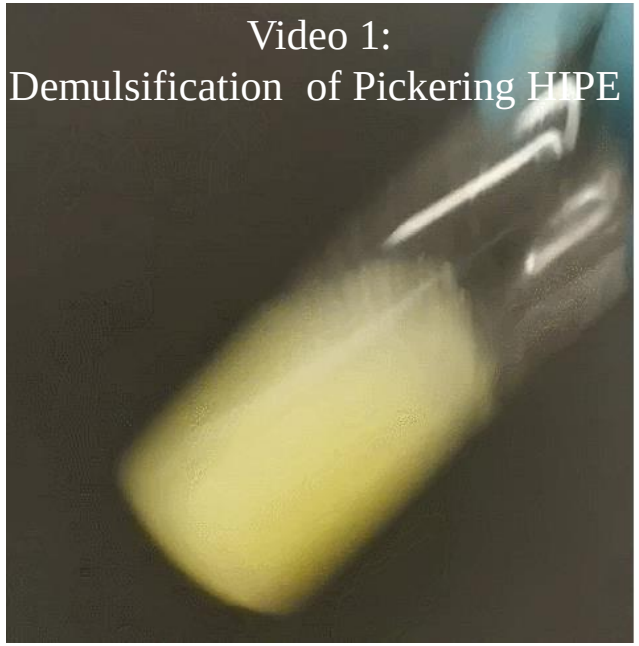
  (1) the lower deprotonation degree of WPU at acidic solution reduced the electrostatic repulsive force between the WPU particles.

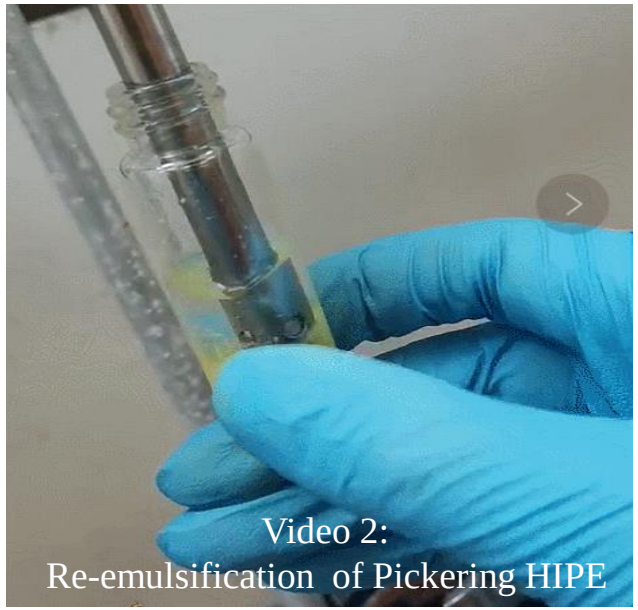
  (2) the WPU nanoparticles had smaller particle size and exhibited higher surface activity at higher pH value, which leaded to small average droplet size

- **Conclusion:**

  HIPEs stability has a close correlation with pH values

2.7 Reversibility and Recycling of Pickering HIPEs





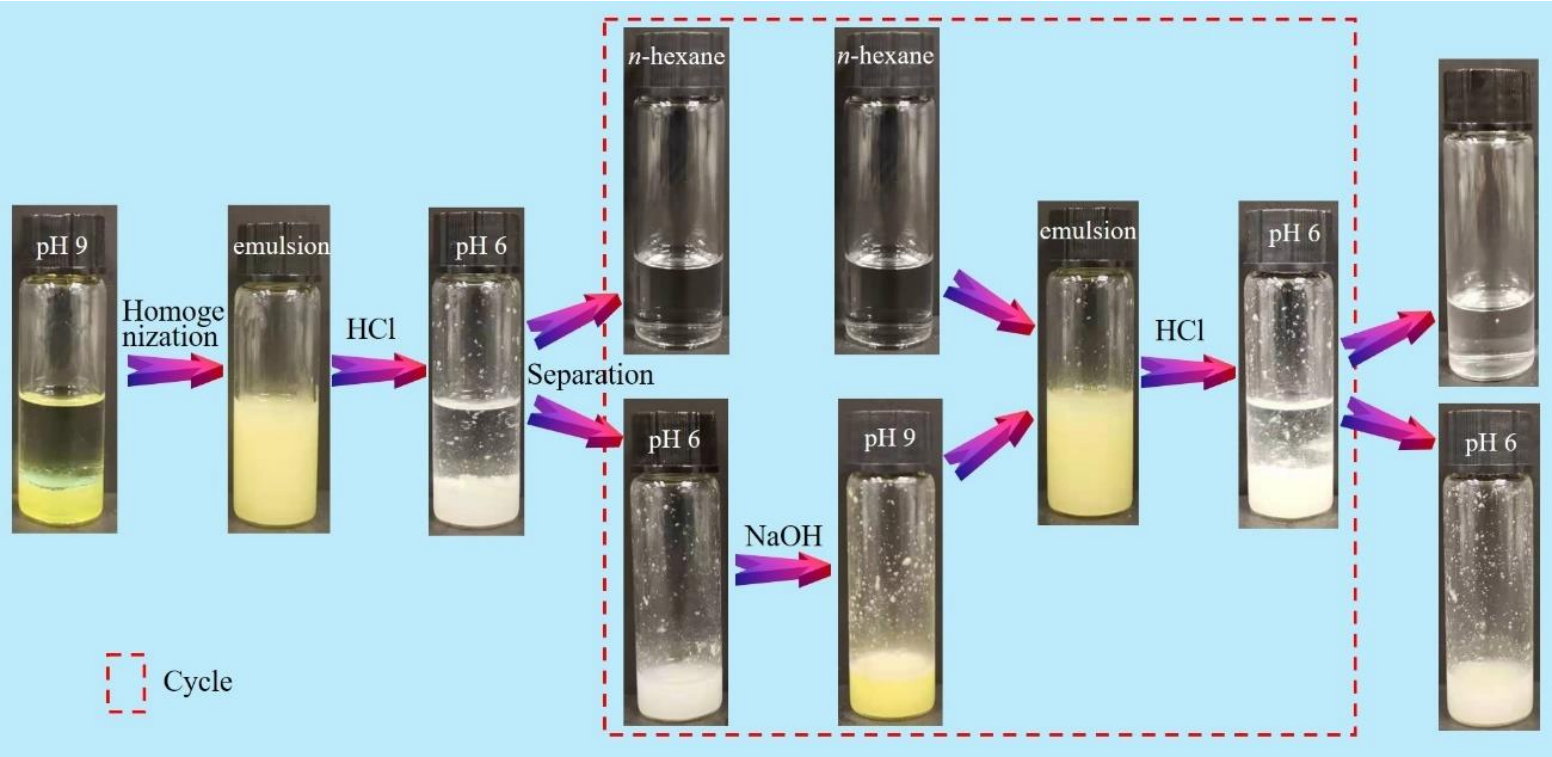


Fig. 2.8 The emulsification-demulsification process of the Pickering HIPEs and recycling of the emulsifiers can be achieved by adjusting the pH value.

- After adjusting the pH value of the stable Pickering HIPE from 9 to 6, demulsification occurred immediately by gentle hand shaking for 30 s.
- Again, the pH value of the separated aqueous phase was adjusted to around 9 for the next emulsification. A stable Pickering HIPE was reformed after homogenized.
- The emulsification–demulsification process can be cycle for four times, proving the reversibility of the emulsification.

2.8 Effect of the salt concentration on Pickering HIPEs Stability

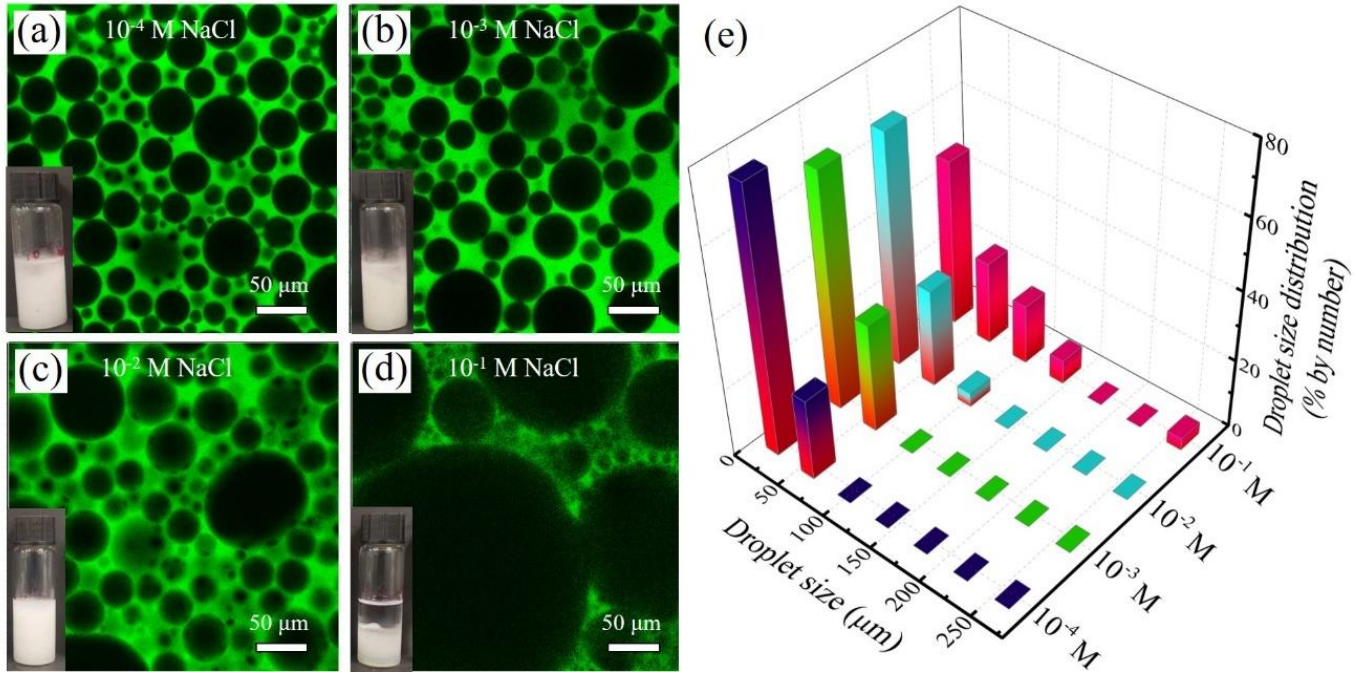


Fig. 2.9 (a-d) CLSM images of n-hexane-in-water Pickering HIPE with different NaCl concentrations and (e) the corresponding droplet size distributions. Insets are the pictures of the corresponding HIPEs. The WPU concentration, internal phase fraction and pH value were kept at 1 wt%, 80% and 9, respectively.

➢ **Phenomena:**

(1) when the salt concentration was less than 10^{-2} M, the stable emulsion fraction of Pickering HIPEs reached 100% while the droplet size is larger than that without additional salt.

(2) when the salt concentration increased to 10^{-1} M, a certain volume of *n*-hexane floated above the emulsion (**Fig. 2.9 (d) Insert**), which means the emulsion was not stable that only partial oil phase can be emulsified.

(3) the mean droplet sizes gradually increased with increasing NaCl concentration.

➢ **Reasons:**

(1) the increasing salt concentration reduces the electrostatic repulsive force between the WPU nanoparticles, so that the WPU nanoparticles aggregated with poor emulsification ability.

(2) the number of WPU nanoparticles in the aqueous phase decreased because of aggregation at high salt concentrations, which could also result in poor emulsifying ability and large droplet size.

3. Conclusions

- WPU has been successfully synthesized and introduced as a novel pH-responsive particulate emulsifier for the formation of Pickering HIPEs.

- Compared with other particles such as graphene oxide, and PNIPAM-*co*-MAA microgels, WPU-stabilized Pickering HIPEs exhibited higher pH sensitivity, which can be demulsified within seconds by adding a small amount of 1 M HCl solutions.

- Further, in contrast to the particles complexation with surfactants, because WPU do not rely on surfactant to elicit pH-responsiveness, the stability and usable lifetime of WPU-stabilized Pickering HIPEs are enhanced obviously, resulting in more sustainable emulsifier recyclability.

- Most importantly, a predominant advantage of WPU is that their structures and properties can be easily adjusted by changing the component of the building blocks, which means that they have the potential to be tailored for specific situations, wherein a narrow transition range or precise control is desired.

- The WPU-stabilized HIPEs could undergo four cycles of emulsification–demulsification without significant loss of stability.

- The attractive features of Pickering HIPEs by using WPU nanoparticles as pH-responsive particulate emulsifiers which can open new venues for oil transportation and recovery, emulsion polymerization, and heterogeneous catalysis.

4. Acknowledgement