

# Generation, Properties and Applications of Oxygen Nanobubbles in Aeration

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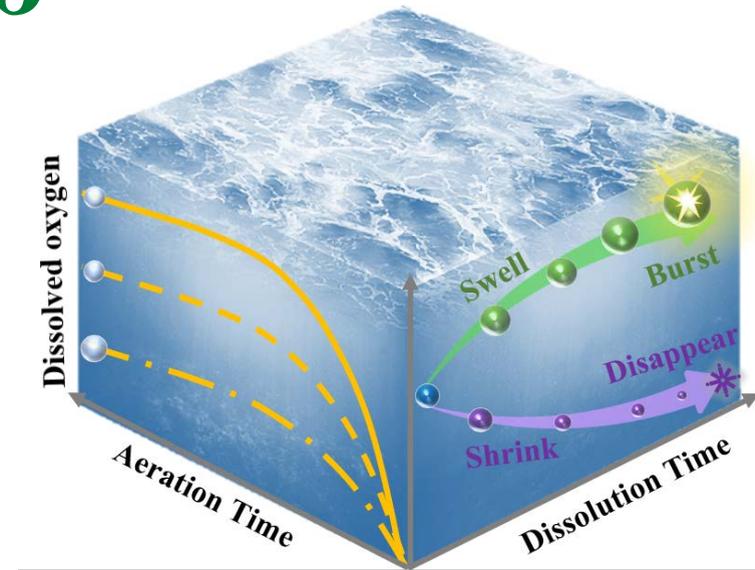
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# Research areas of nanobubbles at Zhang's lab



1. Agricultural applications of nanobubbles for smart irrigation (e.g., plant growth mechanisms and nutrient release soil characteristics)
2. Development of ozone nanobubble generation, characterization and disinfection
3. Aeration and dissolution behavior of oxygen nanobubbles in water for hypoxia remediation
4. Soil remediation (oil removal and other pollutant removal)

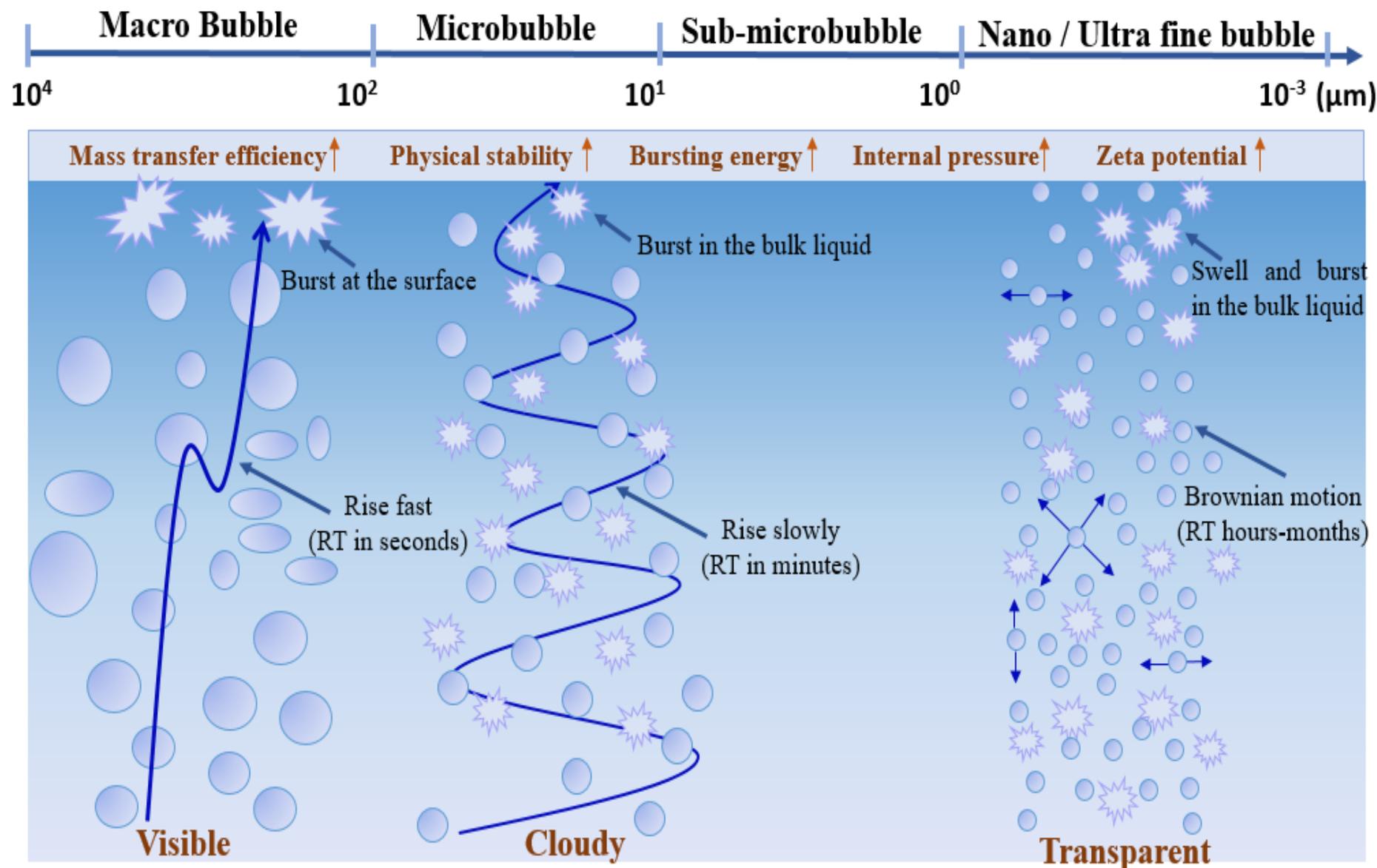


# Content

- Fundamentals of nanobubbles, chemistry, colloidal properties, and generation
- The method we produce nanobubbles in water
- Characterization of bubble properties
- Aeration studies using nanobubbles

# Nanobubbles and their properties

Nanobubbles (NBs) are nano-size gaseous bubbles with a diameter of less than 1  $\mu\text{m}$  according to the calculation of Peclet number for the ratio of buoyancy force and the Brownian motion

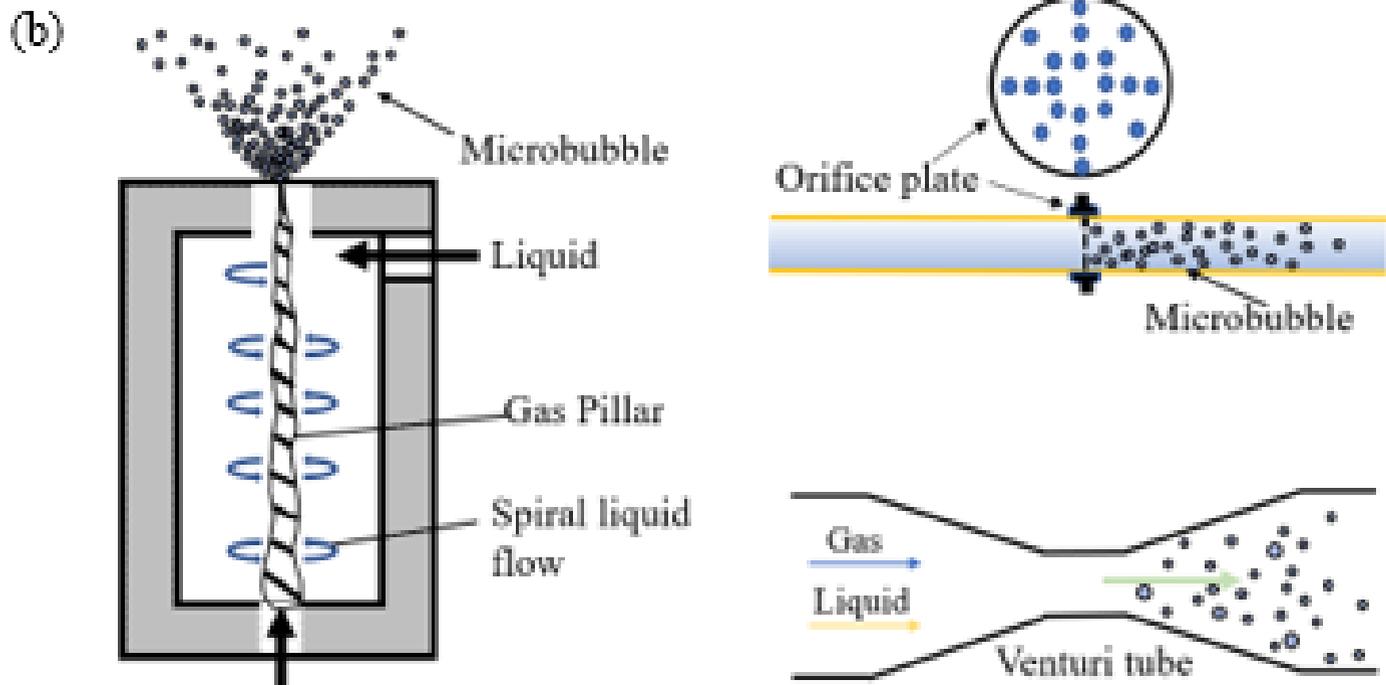
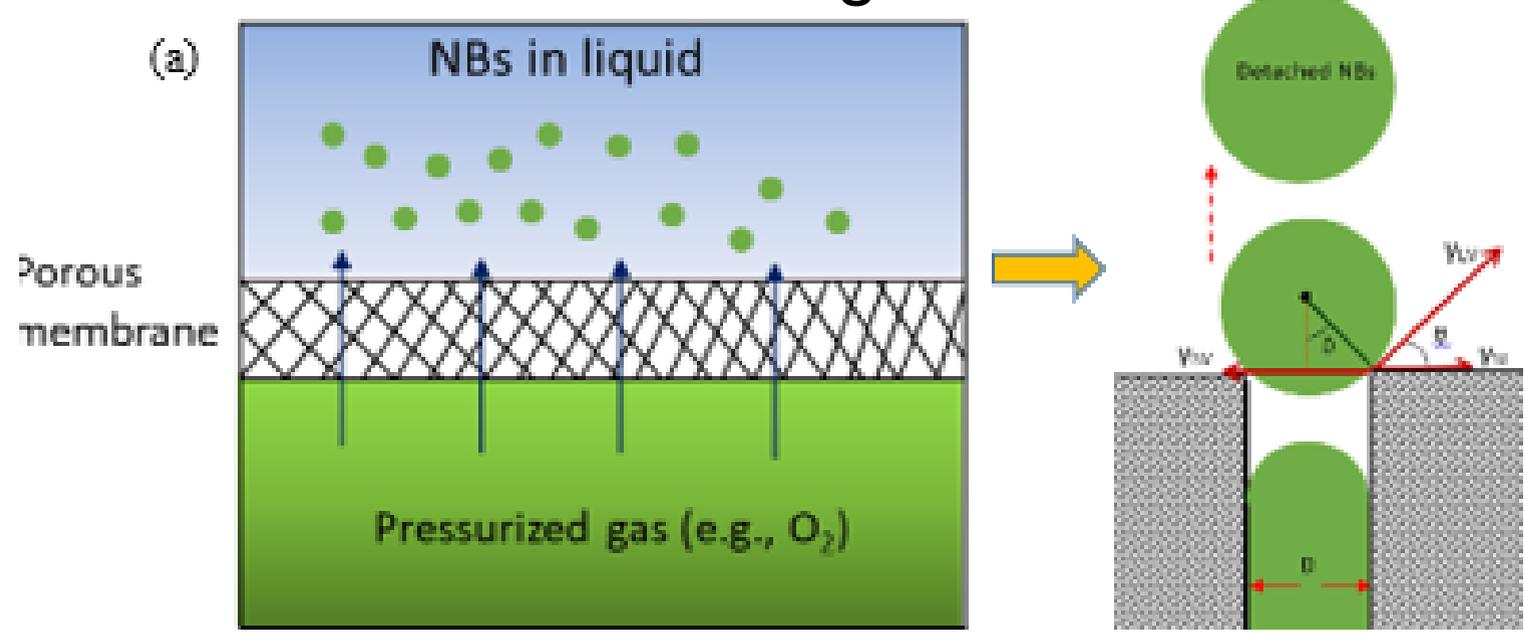


## Intriguing properties of NBs

- 1) Don't rise to the surface due to pronounced Brownian motion
- 2) Low rates of collapses or burst unless under disturbances such as sonication/laser irradiation or temperature variations
- 3) A long residence time in water (e.g., 24 h- several weeks)
- 4) High mass transfer rates or efficiency of air or other gases such as oxygen
- 5) Minor hydroxyl radical production under excitation/agitation
- 6) Surface hydrophobicity and negative charges

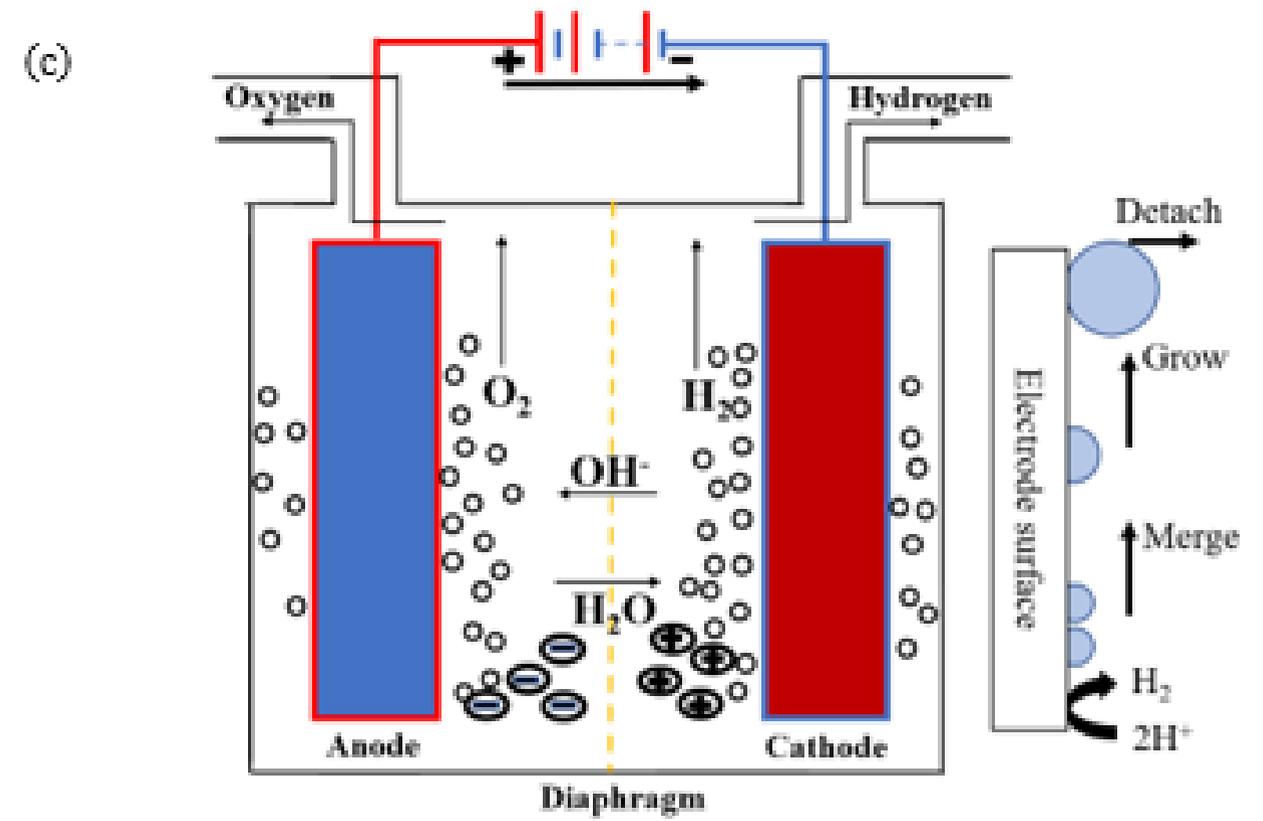
# Nanobubble generation methods

## Membrane bubbling



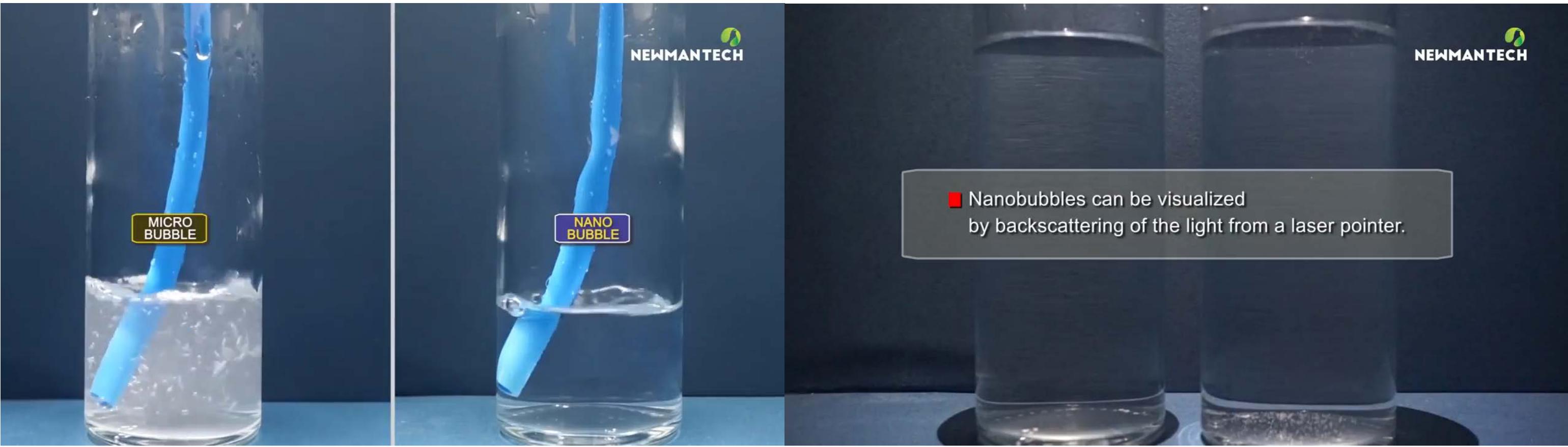
Hydrodynamic pressurization/depressurization

## Electrochemical redox reactions

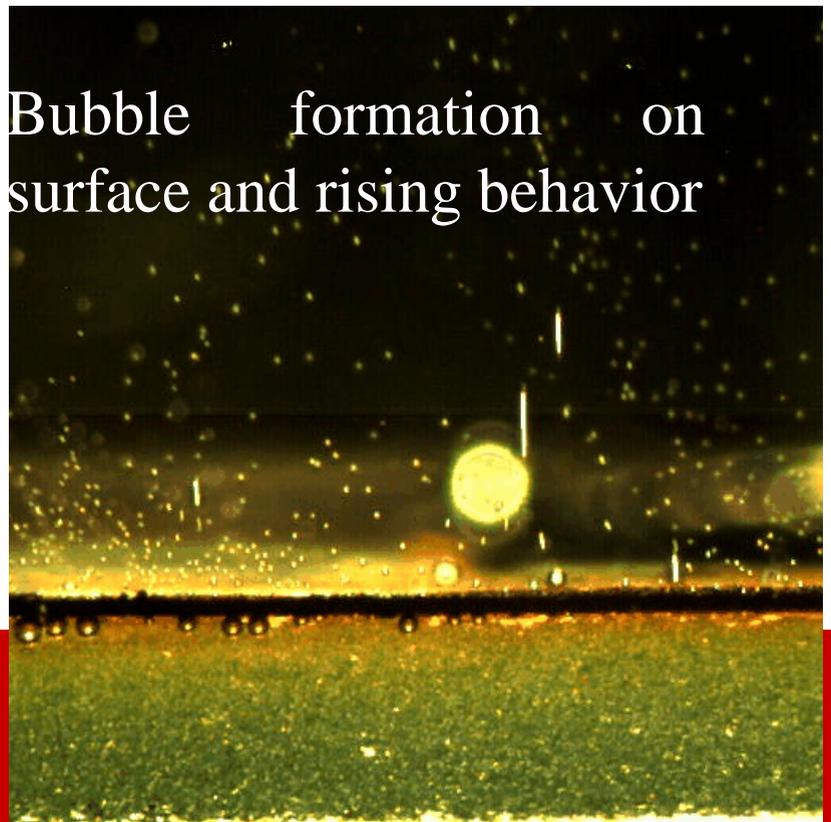
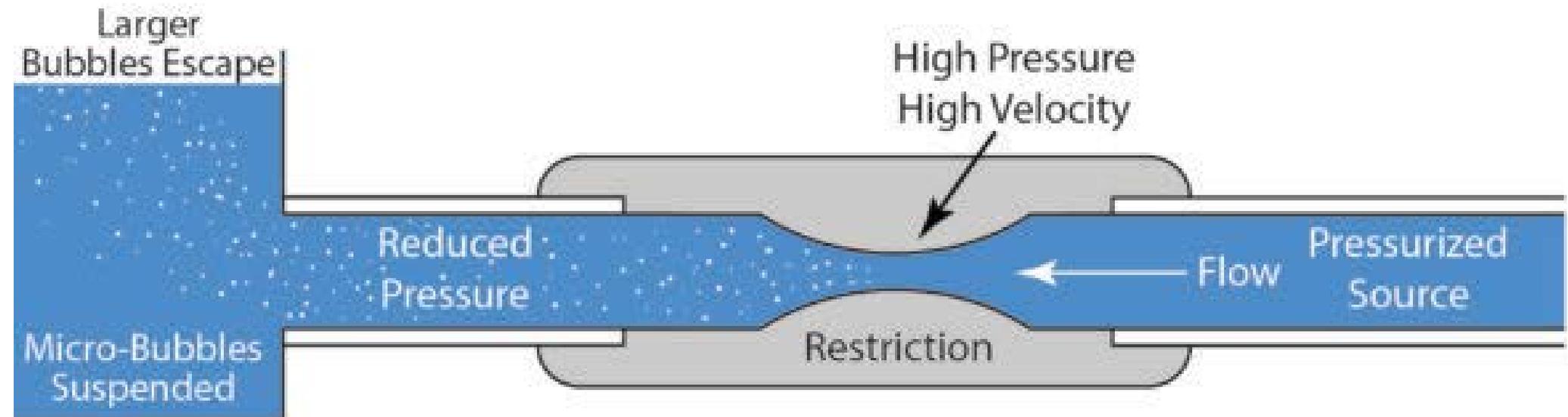


Wen Zhang, Shan Xue, Xiaonan Shi, Taha Marhaba. Chapter title: *Nanobubble Technology: Generation, Properties and Applications*. Book title: Emerging Nanotechnologies for Water Treatment; Chemistry in the Environment Series. *Royal Society of Chemistry*. Print ISBN: 978-1-83916-302-9. Publication year: 2022. <https://pubs.rsc.org/en/content/ebook/978-1-83916-389-0>

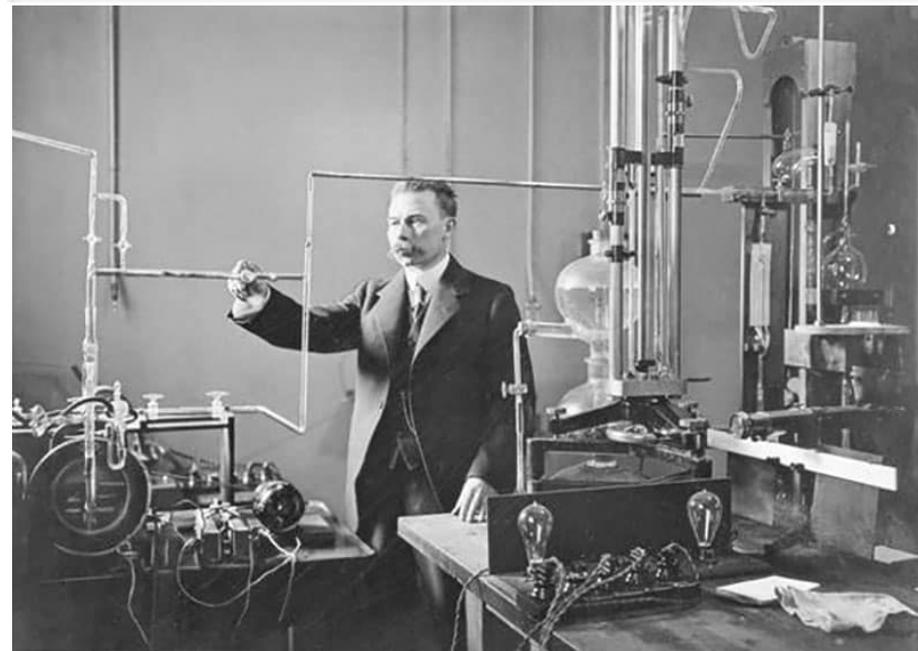
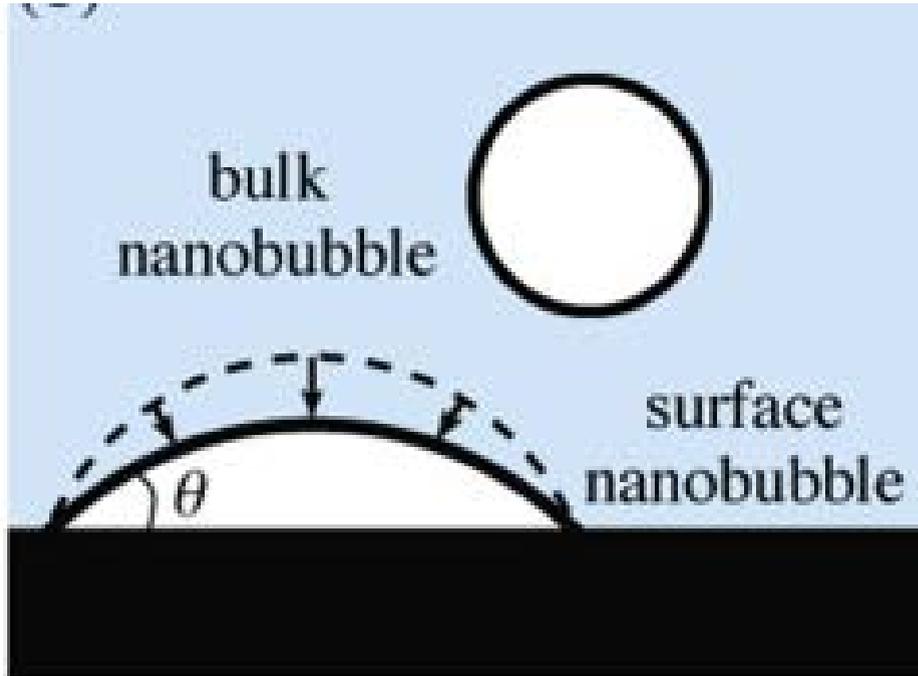
# Visual comparison of microbubbles and nanobubbles



Video sources: <http://newmantech.co.kr/nanoe/>



# The difference between surface and bulk NBs

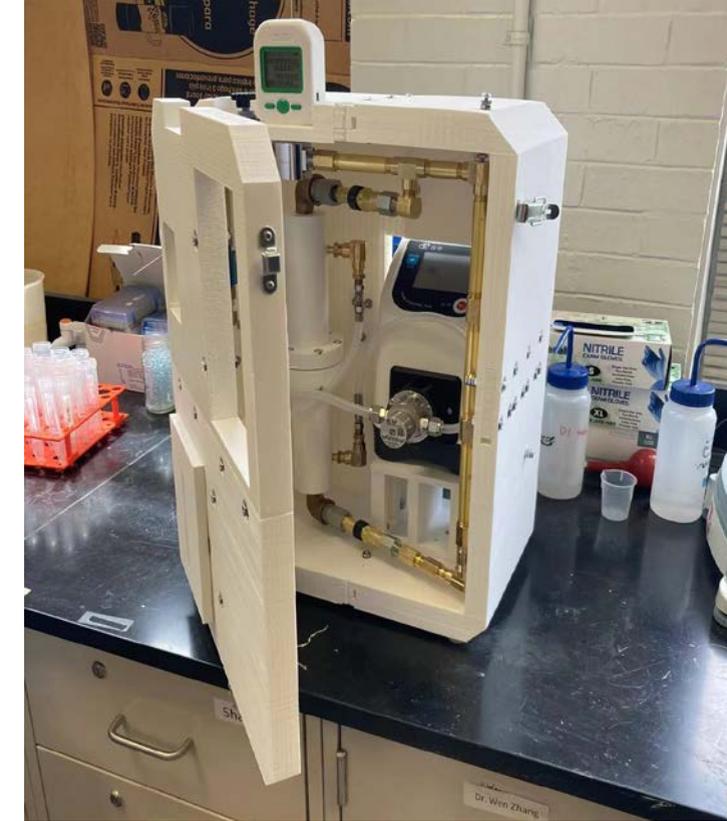
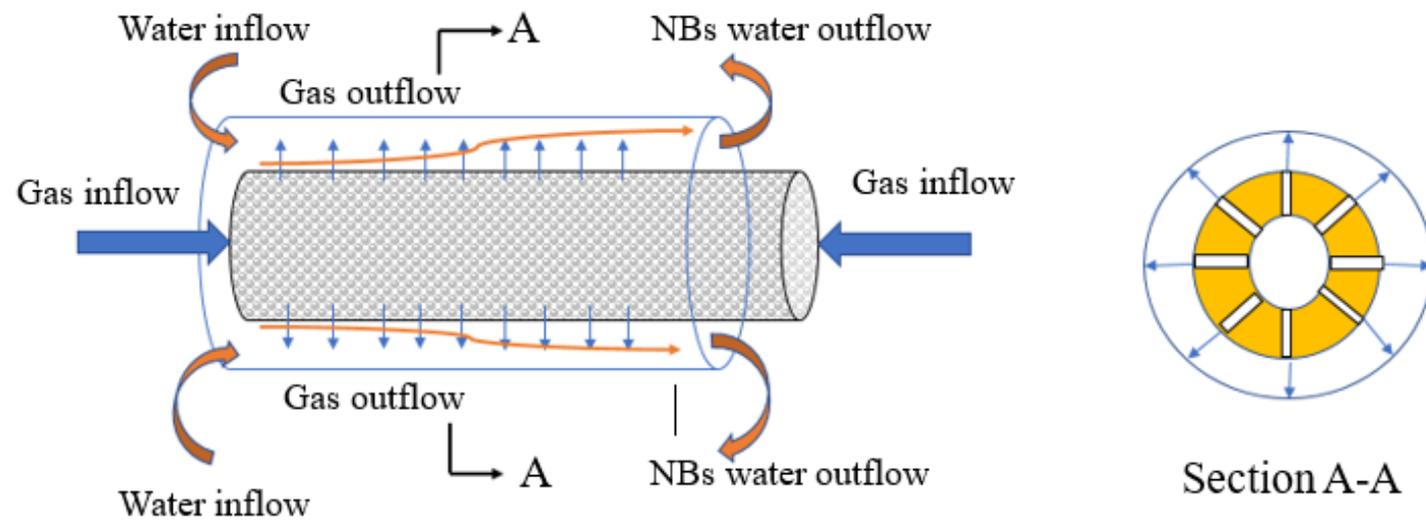


Martin Knudsen at work in a laboratory.  
(Courtesy: University of Copenhagen,  
Denmark)

- According to the pinning theory, surface NBs usually deform to **spherical-cap** compared to bulk suspended NBs and thus may have a larger radius of curvature than bulk NBs and a reduced Laplace pressure.
- According to the Knudsen number analysis, bulk NBs may NOT be a Knudsen gas type, whereas the surface NBs are a Knudsen type.
- A Knudsen gas is a gas with the mean free path of molecules ( $\lambda$ ) greater than bubble size (height or diameter).
- Moreover, the surface NBs are shown to have a similar order of magnitude of internal pressures with the bulk NBs, though the surface NBs may have deformed to spherical-cap compared to bulk NBs and thus may have a larger radius of curvature than bulk NBs and a reduced Laplace pressure.

# Nanobubble generation in Zhang's laboratory

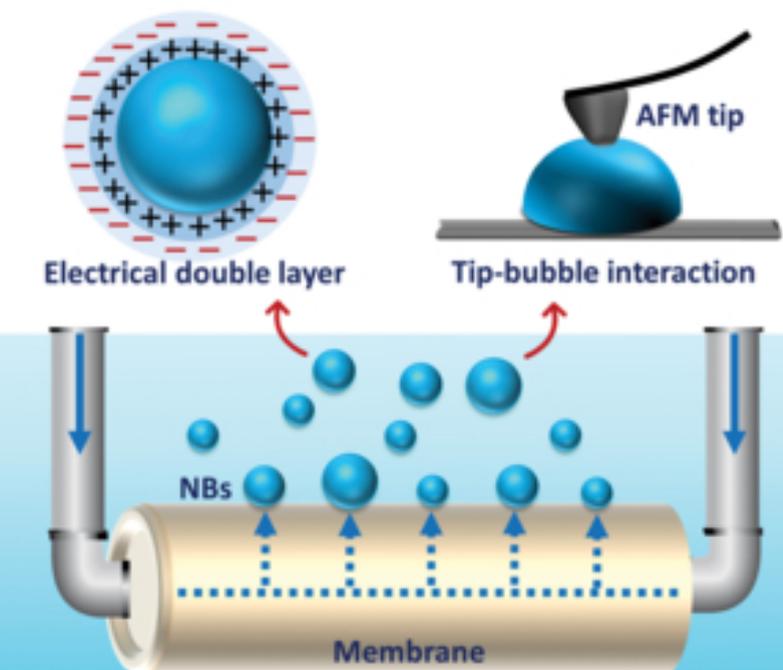
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## Major research findings in the past:

- Established a colloidal force balance model and a contact mechanics model that yielded consistent predictions of the internal pressures of various NBs (120 psi-240 psi or 8-16 atm).
- Dissolution kinetics of O<sub>2</sub> NBs are highly dependent on the initial bubble size as indicated by the changes of bubble size and DO.
- Smaller NBs raised up DO faster, whereas larger NBs could lead to higher equilibrium DO levels.
- The dissolving NBs may either swell or shrink according to the model prediction.

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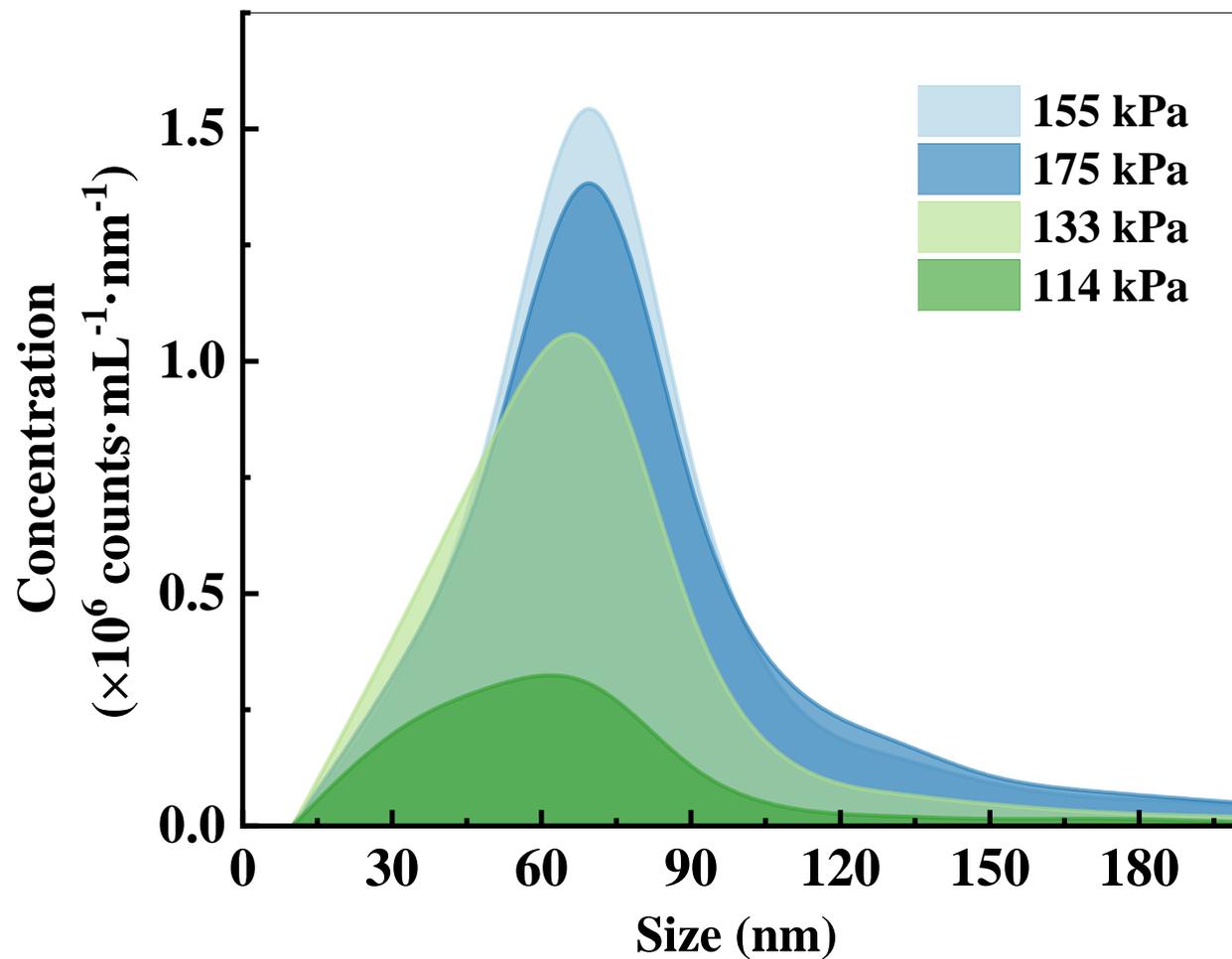
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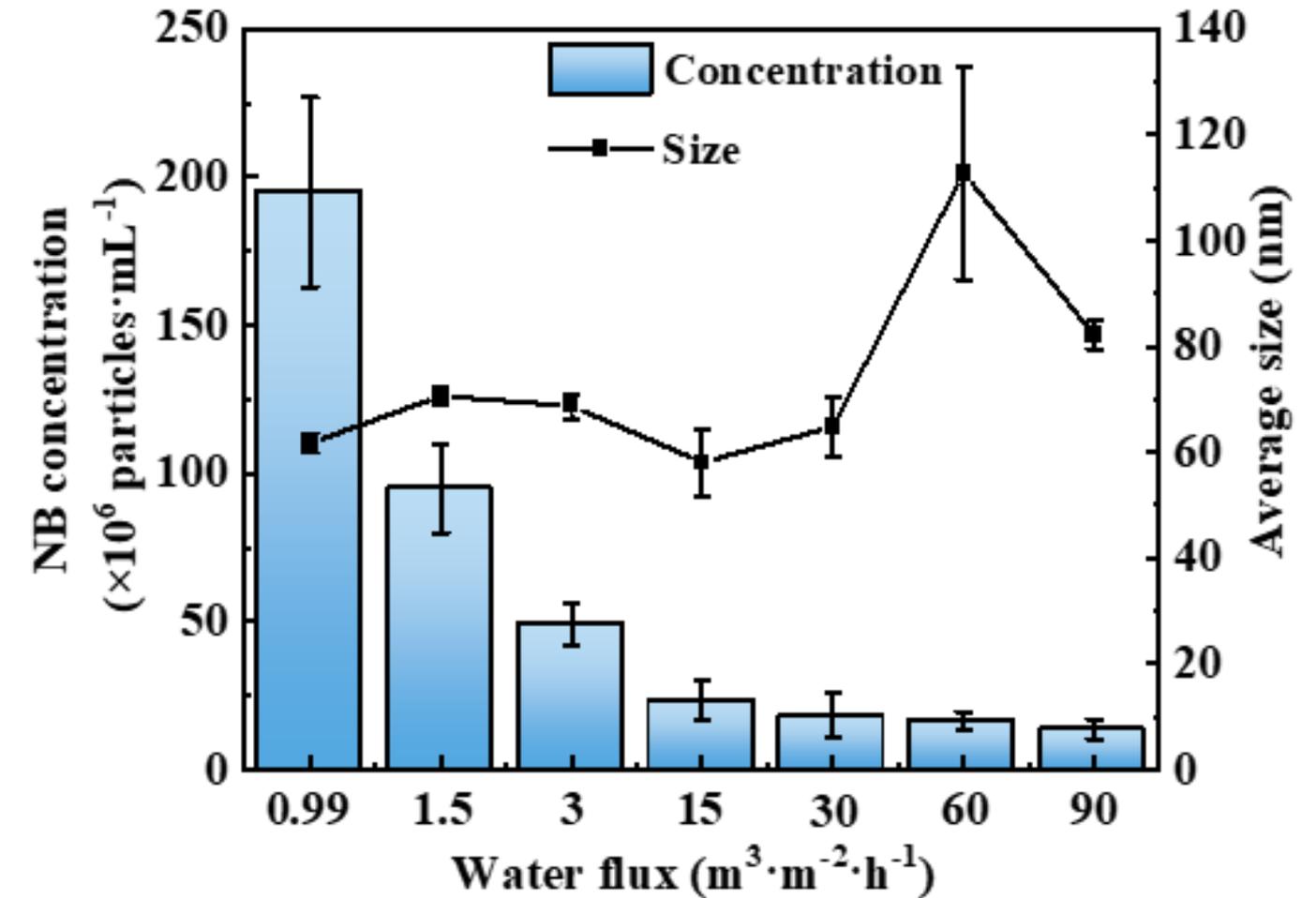
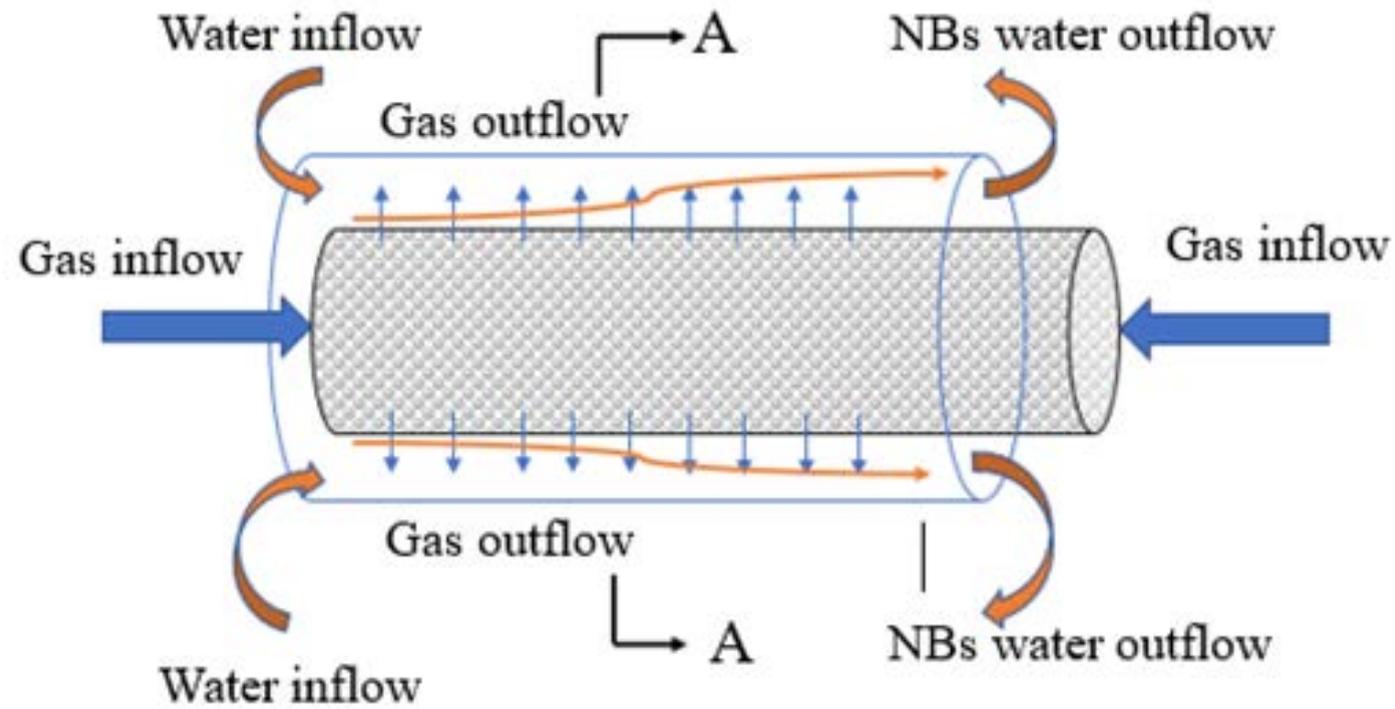
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# The concentration/size distribution of NBs measured by Horiba ViewSizer 3000

- Nanobubble concentration in the DI water reach up to:  $4 \times 10^8 \pm 3.31 \times 10^7$  bubbles·mL<sup>-1</sup>
- Nanobubble mean size:  $70 \pm 12.2$  nm



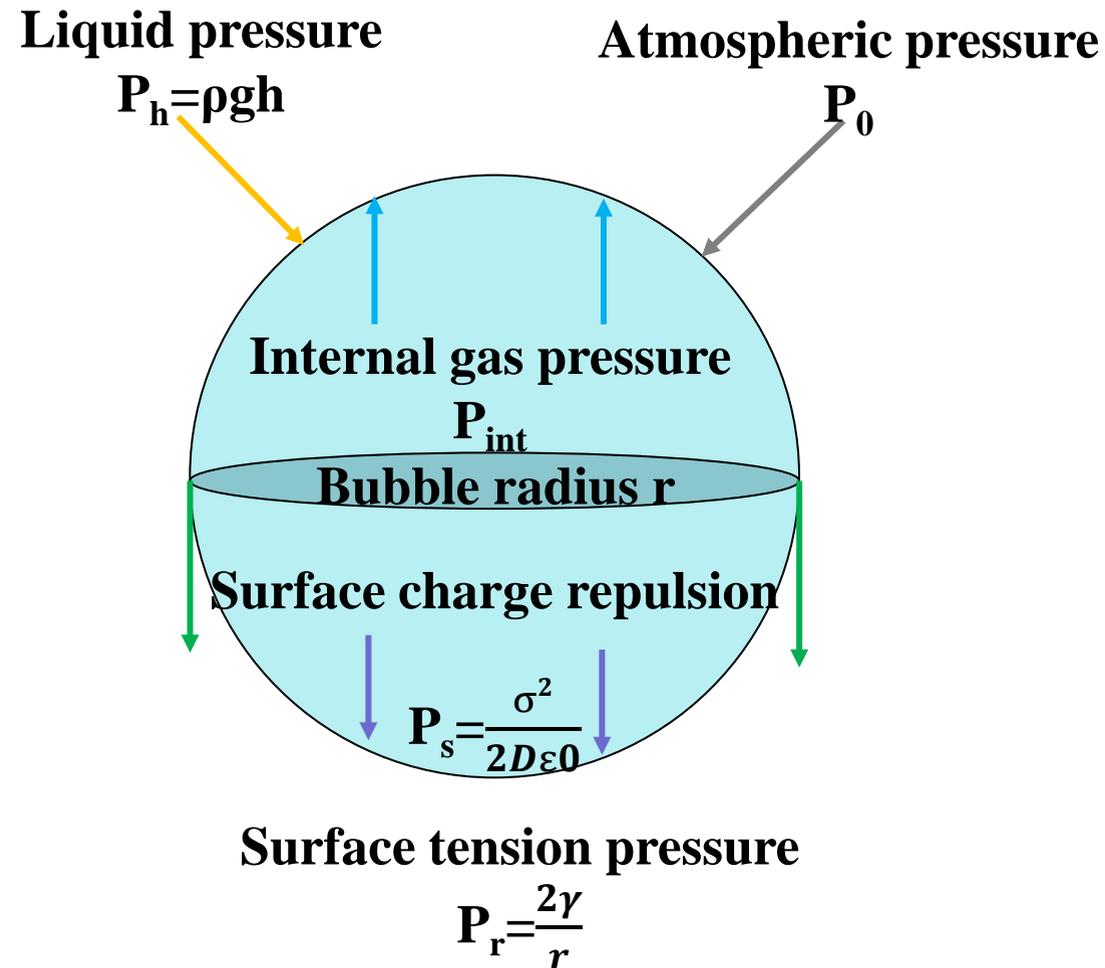
# The effects of water flow rate, gas pressure and wettability of membrane surface on bubble concentration



- The concentration of NBs decreased with the increase of the water flux, due to the reduced time of gas/liquid contact and bubble formation or transfer
- The average size of NBs remained stable when the water flux or cross-flow velocity is less 30 m/h.
- The bubble size had slight increase with the increase of the water flux, suggesting that high shear flows are not beneficial for nanobubble formation at the membrane/water interface.

# Modeling Analysis of Colloidal Stability of NBs in Water

## Colloidal force balance model



The suspended or bulk NBs in water could be stabilized by the outbound and inbound pressures from a number of interfacial forces.

The outbound pressure ( $P_{out}$ )

$$P_{out} = P_s + P_{int} \quad (1)$$

The inbound pressure ( $P_{in}$ )

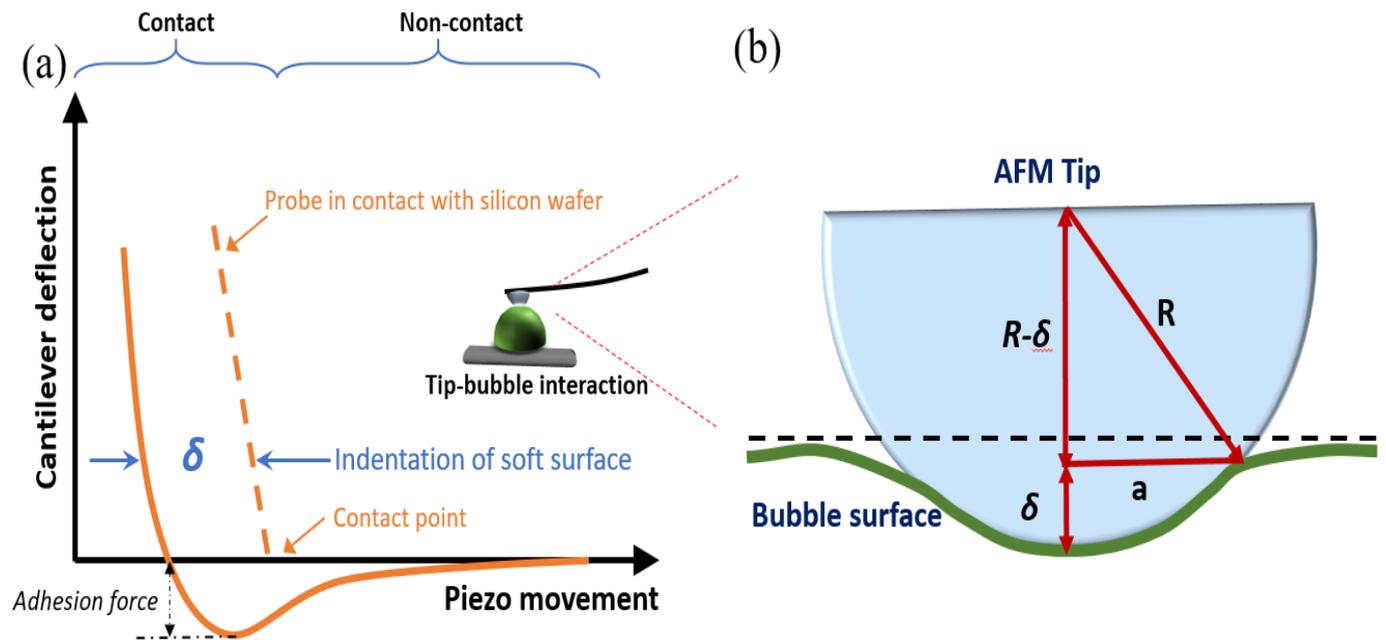
$$P_{in} = P_r + P_0 + P_h \quad (2)$$

When the bulk NBs are stabilized in water ( $P_{in} = P_{out}$ ), the NB's internal pressure ( $P_{int}$ ):

$$P_{int} = \frac{2 \cdot \gamma}{r} + (P_0 + \rho \cdot g \cdot h) - \zeta^2 \left( \frac{\epsilon}{\lambda_D} \right)^2 \frac{\epsilon_0}{2 \cdot D} \quad (3)$$

where  $D$  is the relative dielectric constant of the gas bubbles (assumed unity) and  $\sigma$  is the surface charge density ( $C \cdot m^{-2}$ ),  $\epsilon_0$  is the dielectric permittivity of a vacuum,  $8.854 \times 10^{-12}$  ( $C \cdot V^{-1} \cdot m^{-1}$ ),  $\epsilon$  is the dielectric constant of water, 80.36 (20 °C),  $\zeta$  is the zeta potential of NBs (V),  $z$  is the distance from the particle's surface to the slipping plane (0.335 nm),  $r$  is the bubble radius (nm), and  $\lambda_D$  is the Debye length (nm).  $\gamma$  is the water surface tension ( $72.80 \text{ mN} \cdot \text{m}^{-1}$  at 20 °C),  $g$  is the gravity acceleration ( $9.80 \text{ m} \cdot \text{s}^{-2}$ ),  $\rho$  is the density of water ( $\text{kg} \cdot \text{m}^{-3}$ ), and  $h$  is the height of water (m).

# Direct experimental measurement of the internal pressure of surface NBs in water



## Contact mechanics model

Johnson-Kendall-Roberts (JKR) model

$$E^* = \frac{F_{adh} \cdot R \cdot \sqrt{2 \cdot R - \delta}}{9 \cdot \delta^{3/2} \cdot (R - \delta)^2}$$

Derjaguin-Muller-Toporov (DMT) model

$$E^* = \frac{F_{loading} + F_{adh}}{\sqrt{R \cdot \delta^3}}$$

The internal pressure of NBs

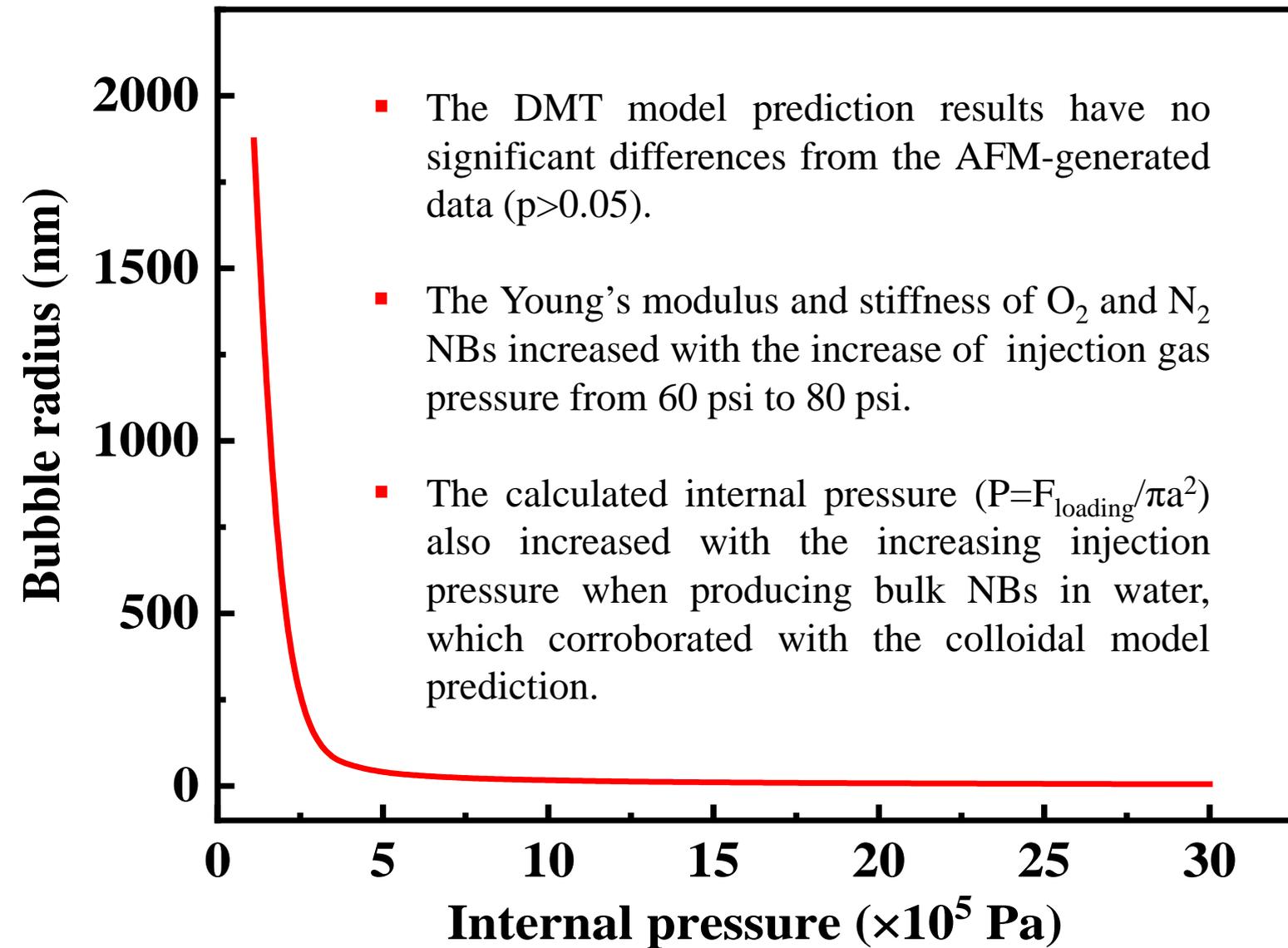
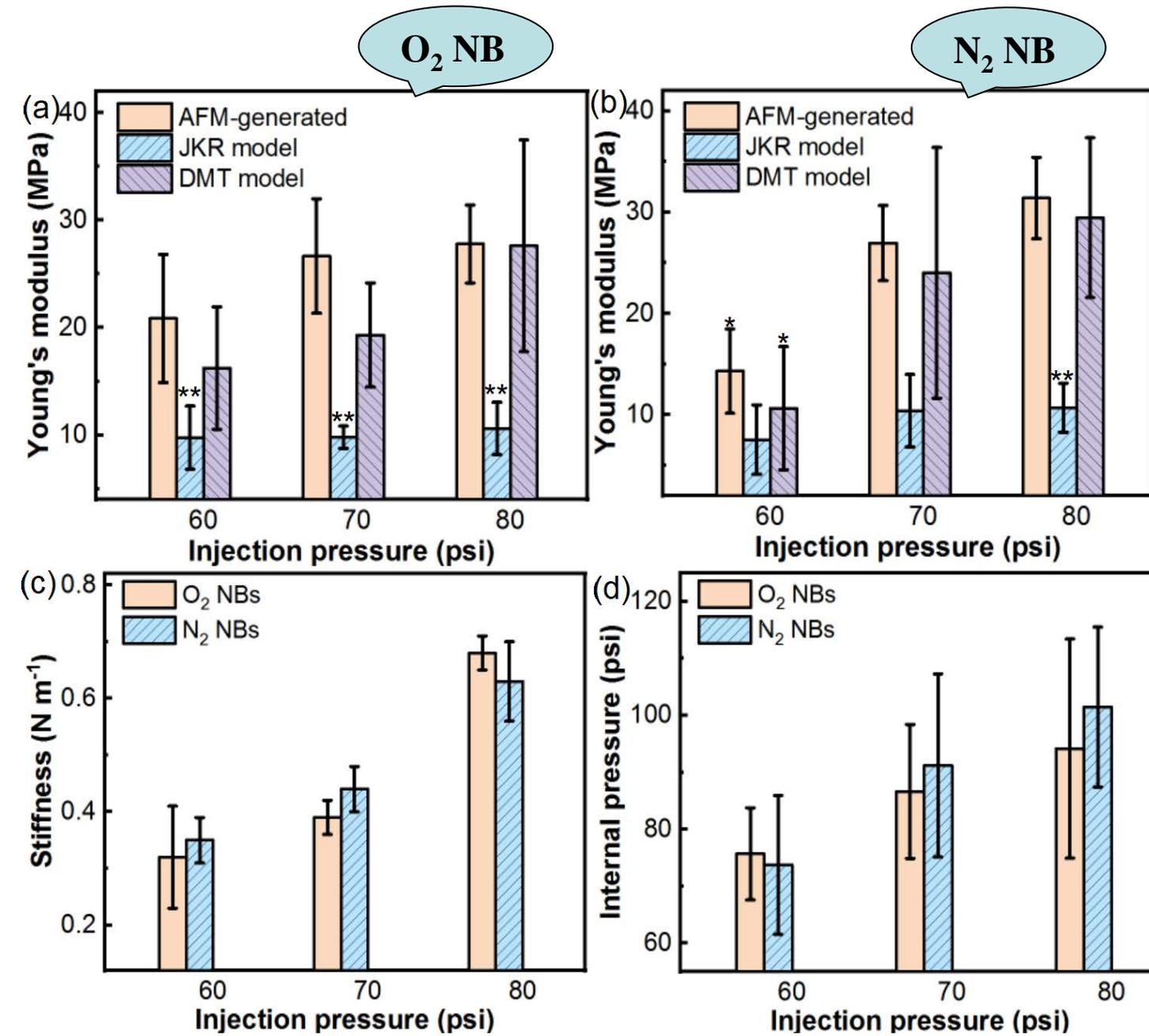
$$P_{int} = \frac{F_{loading}}{\pi \cdot a^2} \quad (R - \delta)^2 + a^2 = R^2$$

where the loading force ( $F_{loading}$ ) is the compression force that the AFM probe tip exerts on the sample surface 500pN and  $a$  is the radius of the spherical contact area, which is related to the indentation ( $\delta$ ) and the AFM tip radius ( $R$ ).  $W$  is the adhesion energy per unit area ( $J \cdot m^{-2}$ ) and  $E^*$  is the reduced Young's modulus (MPa), adhesion force ( $F_{adh}$ ) read directly from the force-distance curve.

$E^*$  is related to the Poisson's ratios ( $\nu_s$  and  $\nu_T$ ) and the Young's moduli ( $E_s$  and  $E_T$ ) of the sample and tip

$$E^* = \left[ \frac{3}{4} \left( \frac{1 - \nu_s^2}{E_s} + \frac{1 - \nu_T^2}{E_T} \right) \right]^{-1} \approx \left[ \frac{3}{4} \left( \frac{1 - \nu_s^2}{E_s} \right) \right]^{-1}$$

# Assessment of mechanical properties of surface NBs in water



$$P_{\text{int}} = \frac{2 \cdot \gamma}{r} + (P_0 + \rho \cdot g \cdot h) - \zeta^2 \left( \frac{\epsilon}{\lambda_D} \right)^2 \frac{\epsilon_0}{2 \cdot D}$$

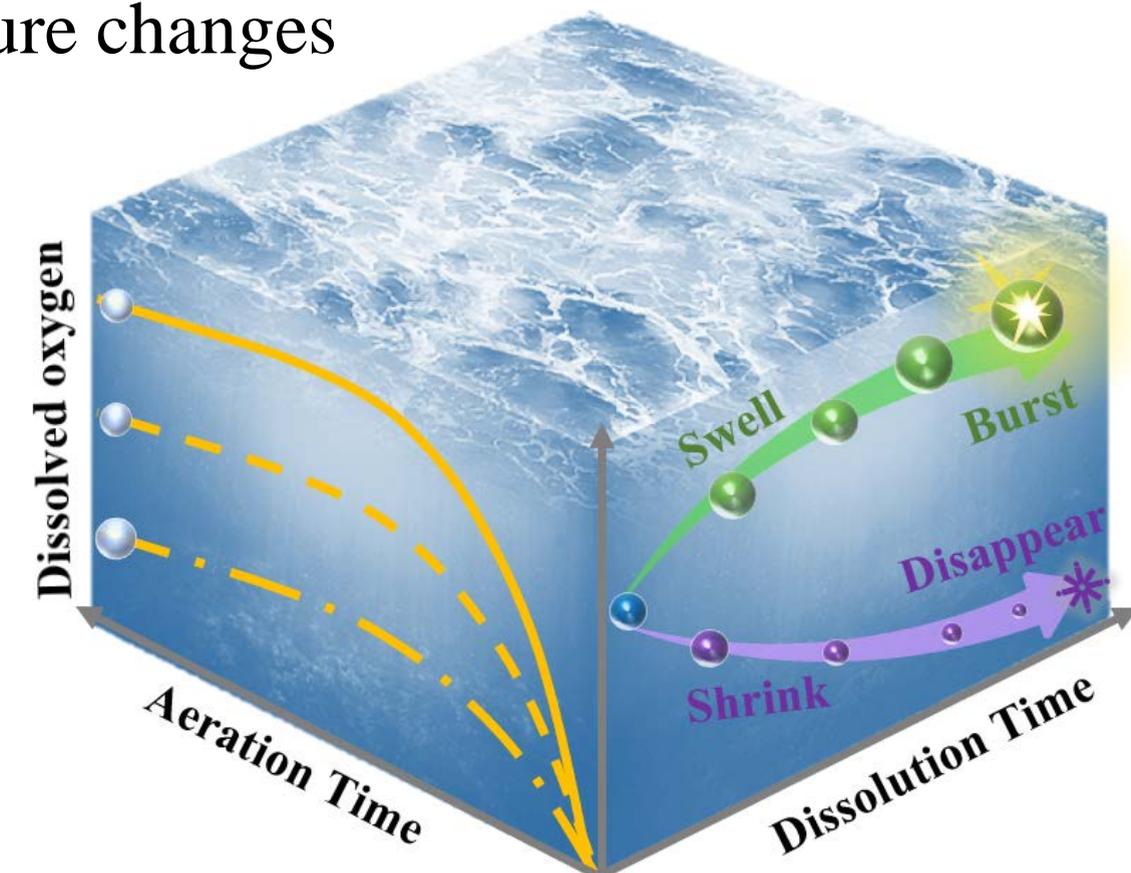
# Dissolution Behavior of Oxygen Nanobubbles in water

There are three wide-reported reasons for high colloidal stability and longevity:

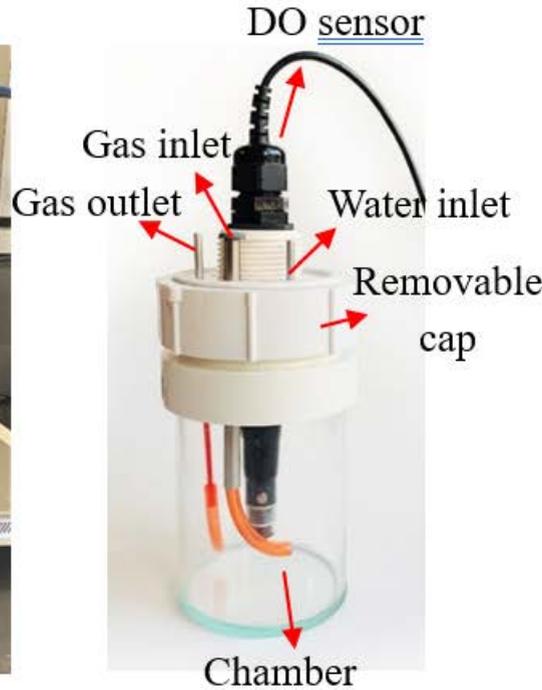
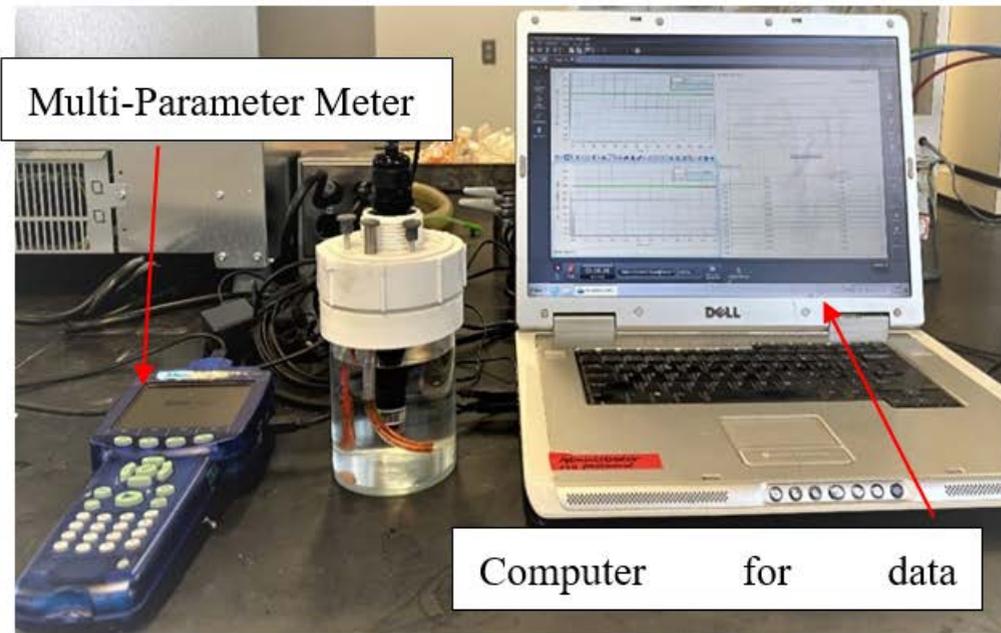
- Selective adsorption of anions such as  $\text{-OH}$
  - Hydrogen bonding network
  - Local oversaturation of gas molecules such as air or oxygen
- The high internal pressures lead to fast dissolution rate or driving force of dissolution according to the Henry's law.
  - The dissolution leads to the size changes and internal pressure changes



The dissolution behavior and mechanisms of bulk NBs in liquid



# Volumetric mass transfer coefficient ( $K_L \cdot a$ ) and the change of DO during the aeration using $O_2$ NBs



The bulk mass transfer efficiency in aeration is often described by :

$$V \frac{dC}{dt} = K \cdot A \cdot \left( \frac{P_a}{K_H} - C \right) \quad \ln\left(\frac{C_s - C_t}{C_s - C_0}\right) = -(K_L \cdot a) \cdot t$$

$$C_s = \frac{P_{int}}{K_H} \quad \text{where } C_s \text{ is the saturation concentration of oxygen in water and follows the Henry's law}$$

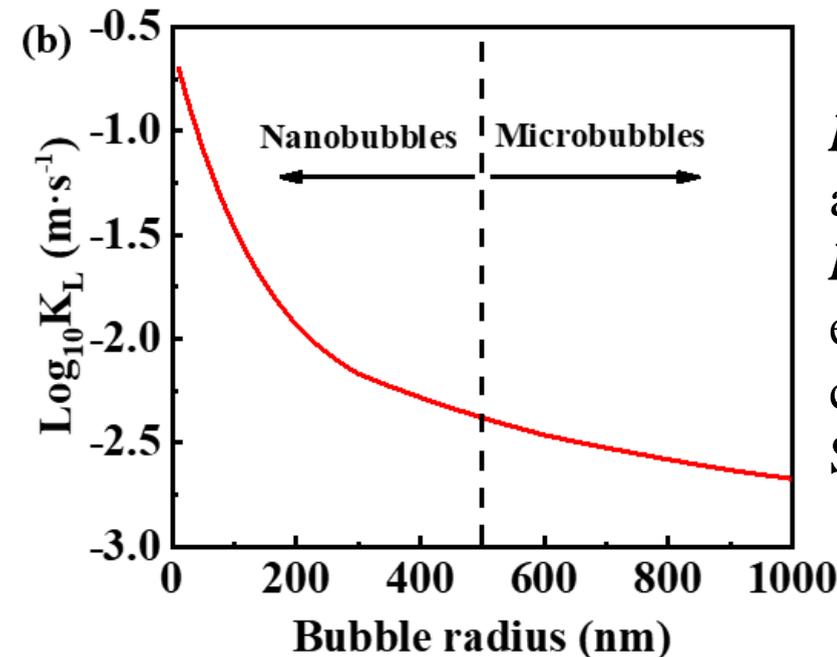
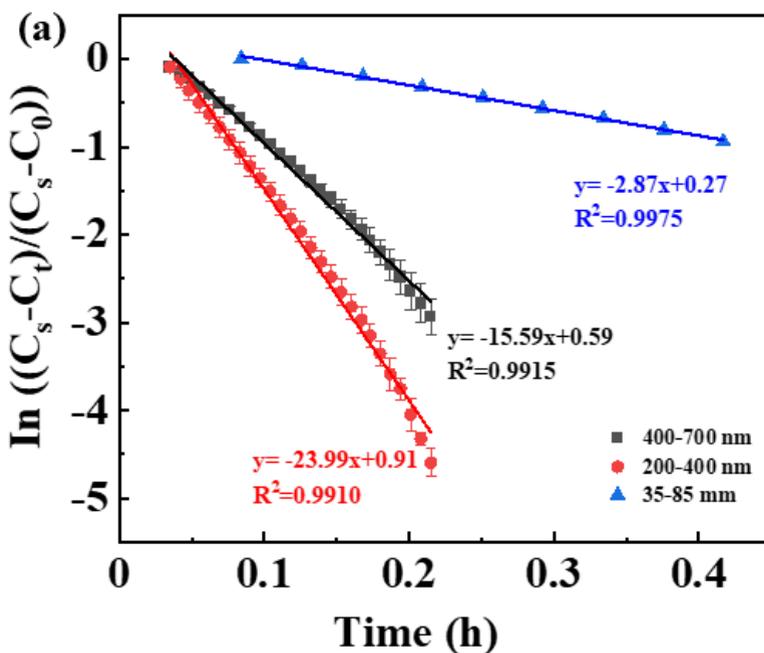
All NBs are treated as **spheres with a homogenous radius**, calculation of specific surface area ( $a$ ) using

$$\text{Eq: } a = \frac{N}{V'} \cdot 4\pi \cdot r^2 = \frac{1}{V'} \cdot \frac{3}{r} \cdot \frac{Q \cdot t \cdot P_{inj}}{P_{int}}$$

$K_L \cdot a$  is the volumetric mass transfer coefficient ( $h^{-1}$ ) is almost 5-8 times that for the  $O_2$  macrobubbles.

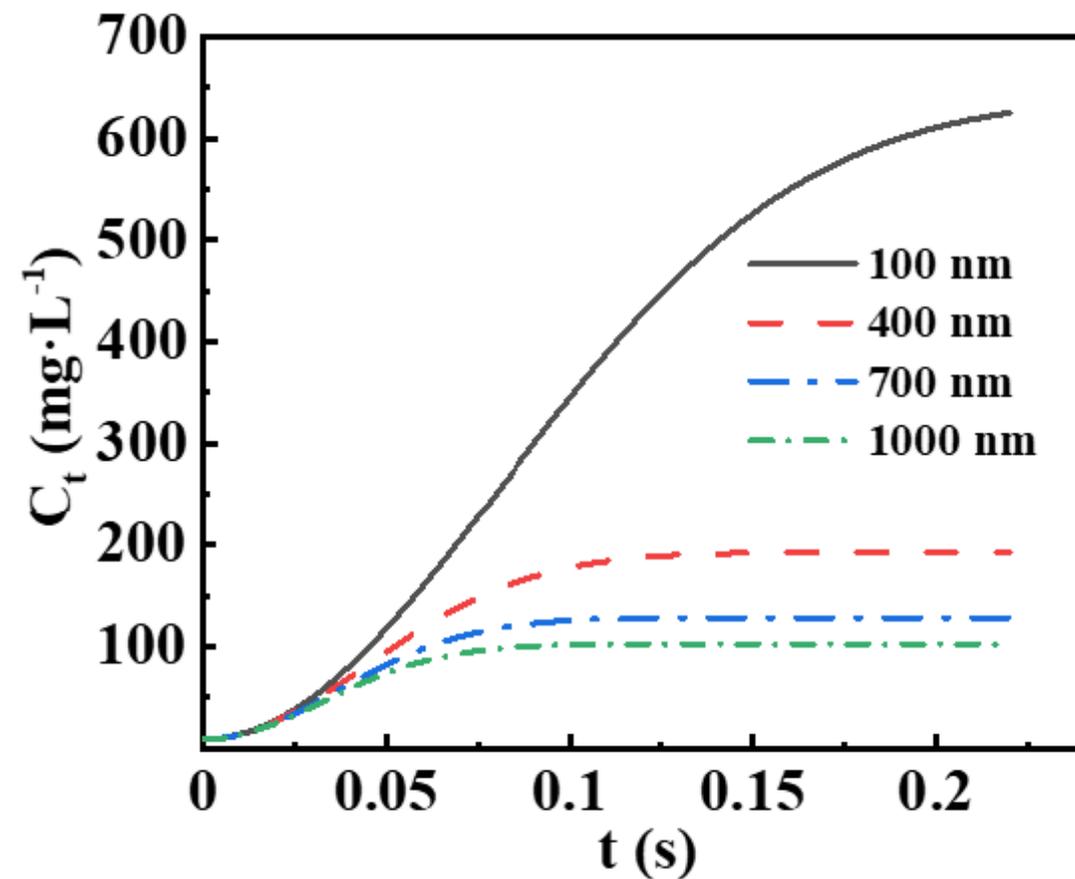
$K_L$  is the bulk liquid film coefficient that was estimated by the correlation of mass transfer coefficients using Schmidt Number ( $Sc$ ) and Sherwood Number ( $Sh$ ) by

$$K_L = Sh \cdot D' / (2 \cdot r)$$



where  $V$  is the volume of the solution ( $m^3$ ),  $C$  is the  $O_2$  concentration in the water ( $mol \cdot L^{-1}$ ),  $t$  is the aeration time ( $h$ ),  $K$  is the bulk transfer coefficient ( $m \cdot h^{-1}$ ),  $A$  is the air-water surface area ( $m^2$ ),  $P_a$  is the partial pressure of  $O_2$  that governs the DO following the Henry's Law,  $K_H$  is the Henry's law constant ( $770 L \cdot atm \cdot mol^{-1}$ , in water at 298.15 K), and  $P_a/K_H$  is the saturation concentration of  $O_2$  in water ( $C_s$ ,  $mol \cdot L^{-1}$ ). The integration of Eq. (1) with boundaries of  $C=C_0$  and  $C=C_t$  at  $t=0$  and  $t=t$ .  $P_{int}$  is internal bubble pressure,  $P_{inj}$  is specific injection pressure.

# Volumetric mass transfer coefficient ( $K_L \cdot a$ ) and the change of DO during the aeration using $O_2$ NBs

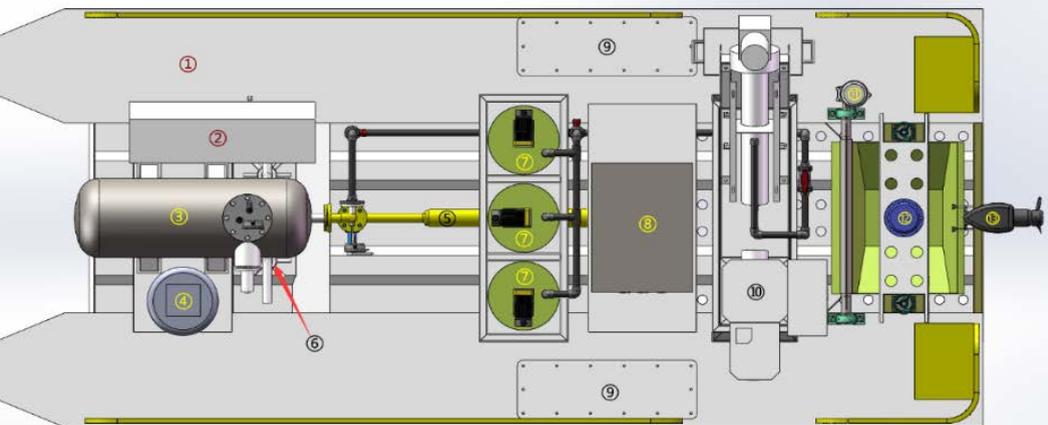
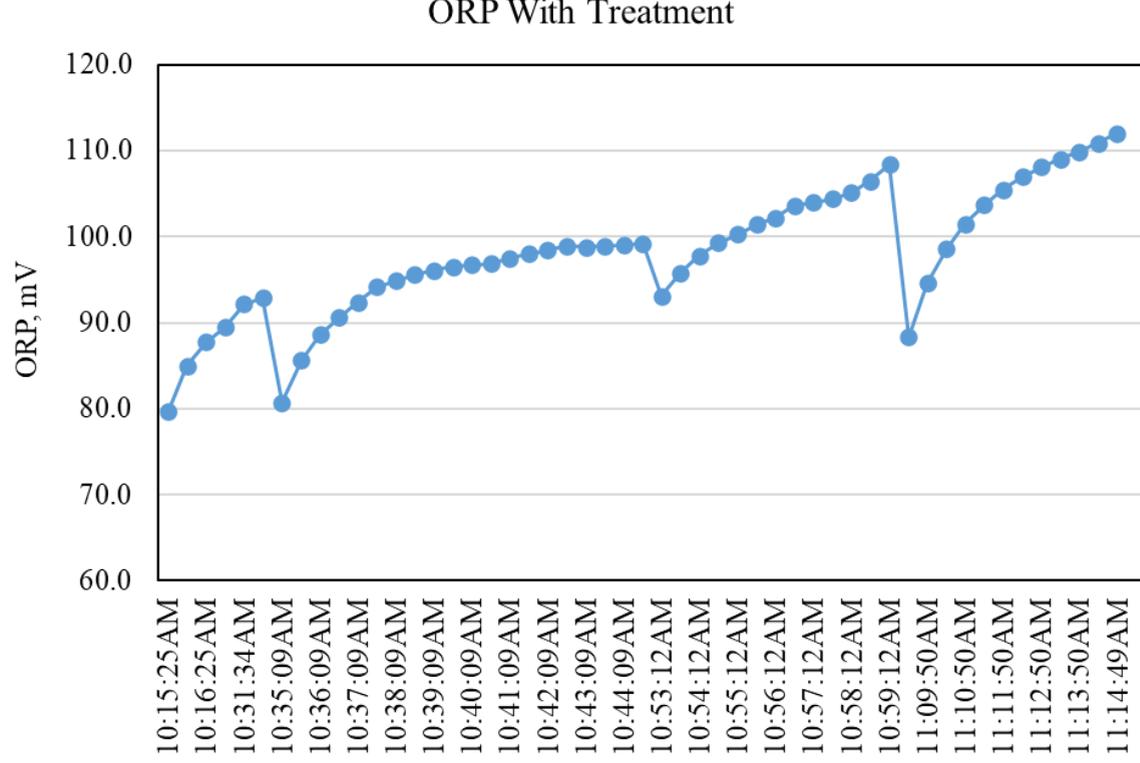
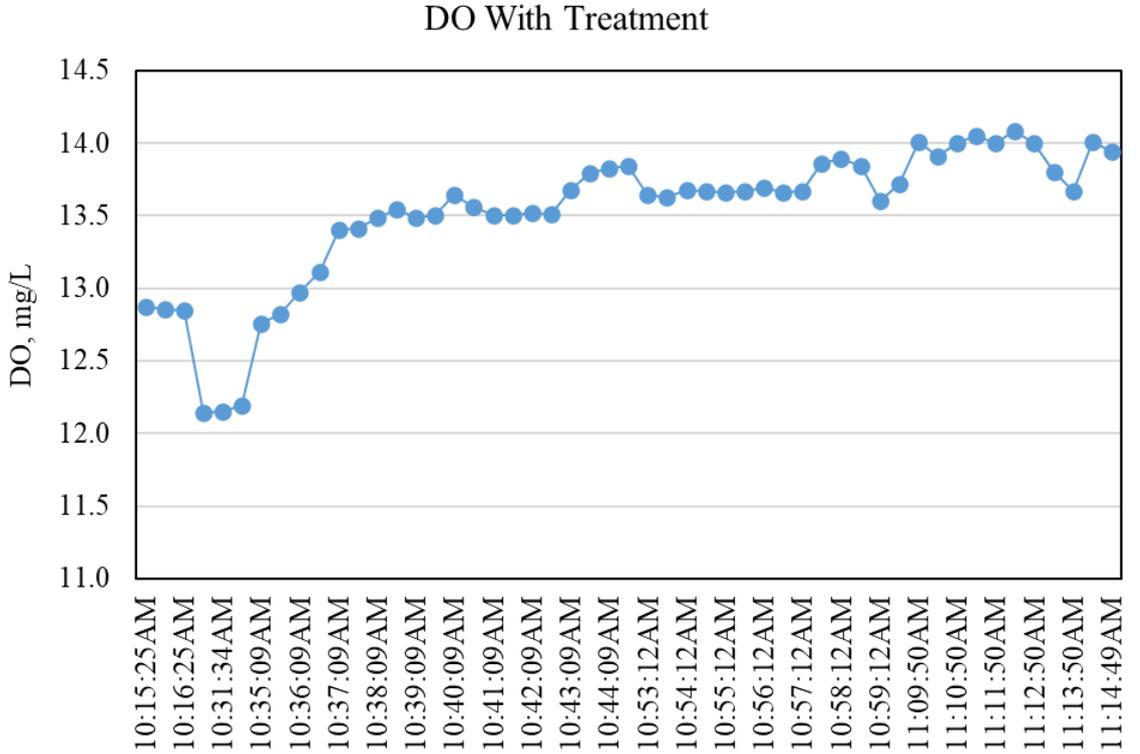


This result is predicted by assuming spherical bubbles are well dispersed in a closed water tank without any DO loss due to evaporation or bubble exit from liquid to air (at the initial aeration period of less than 0.2 s).

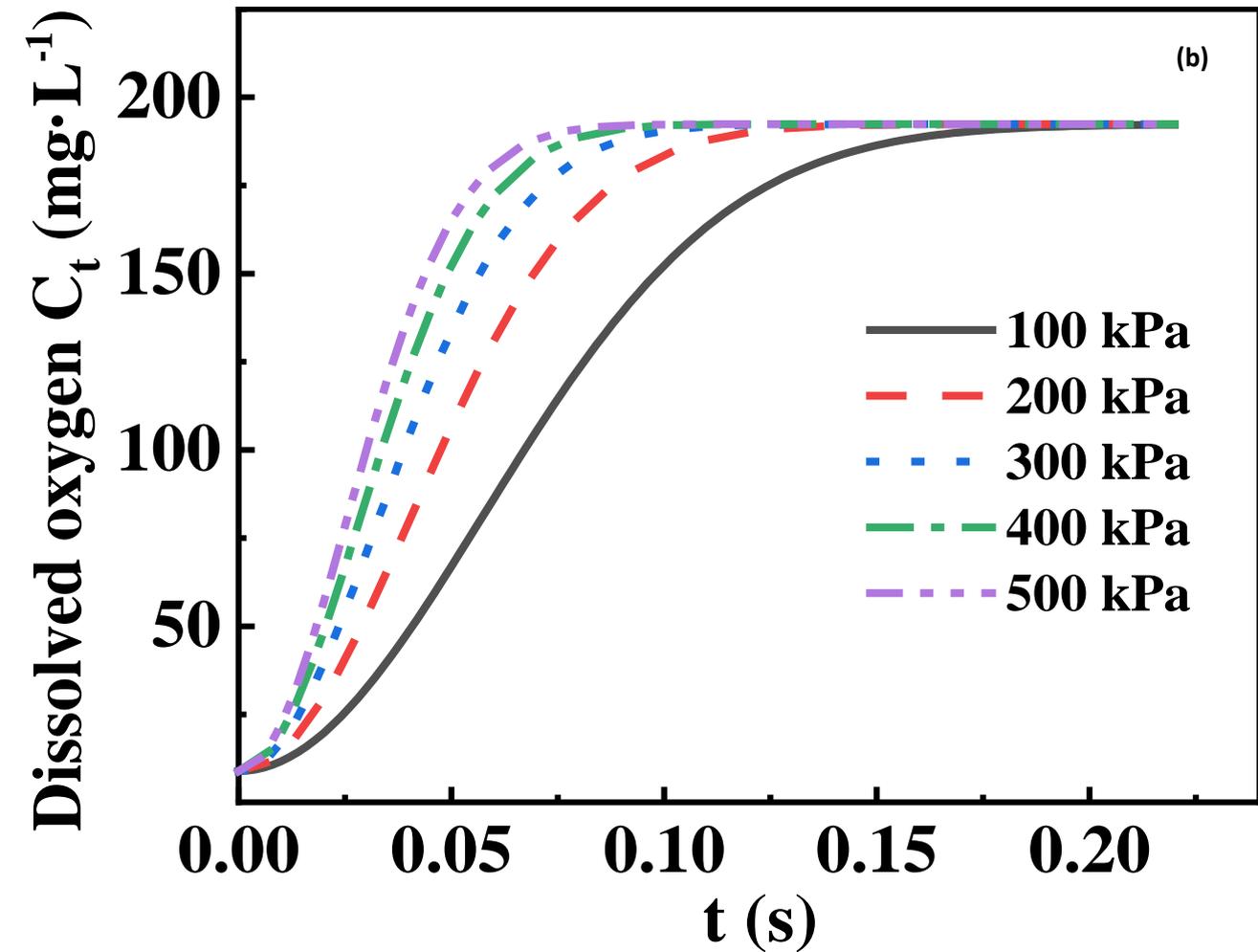
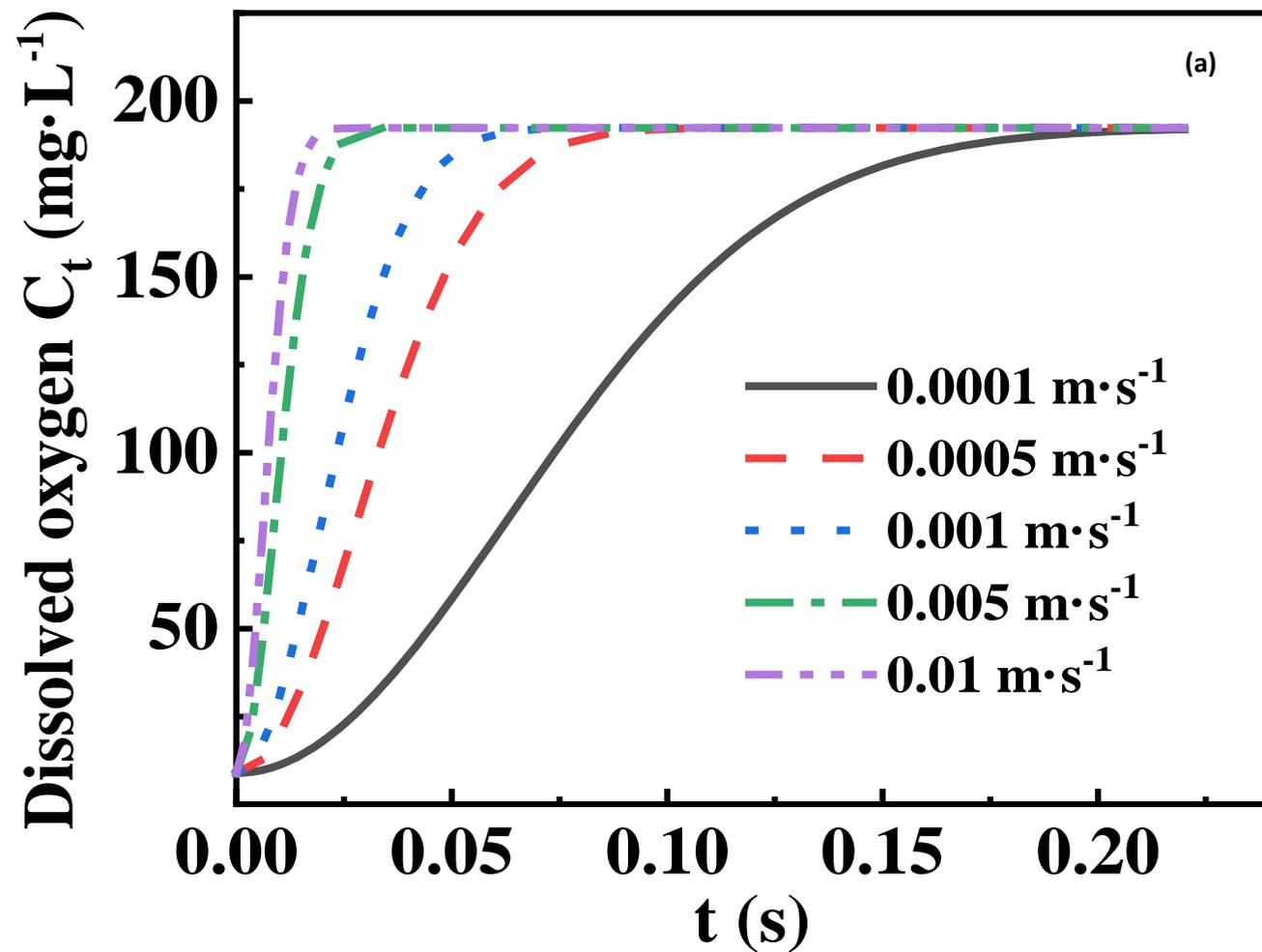
$$\ln\left(\frac{C_s - C_t}{C_s - C_0}\right) = -(K_L \cdot a) \cdot t$$

The rate of DO increase for 100-nm NBs is almost 4 times that of 1000-nm NBs, due to the high  $a$  term (the specific surface area of bubbles in liquid ( $m^2 \cdot m^{-3}$ )).

# Harmful Algal Bloom (HAB) mitigation by micro/nanobubbles integrated on a multifunctional algal scavenger boat under NJDEP funding support (2021-2024)

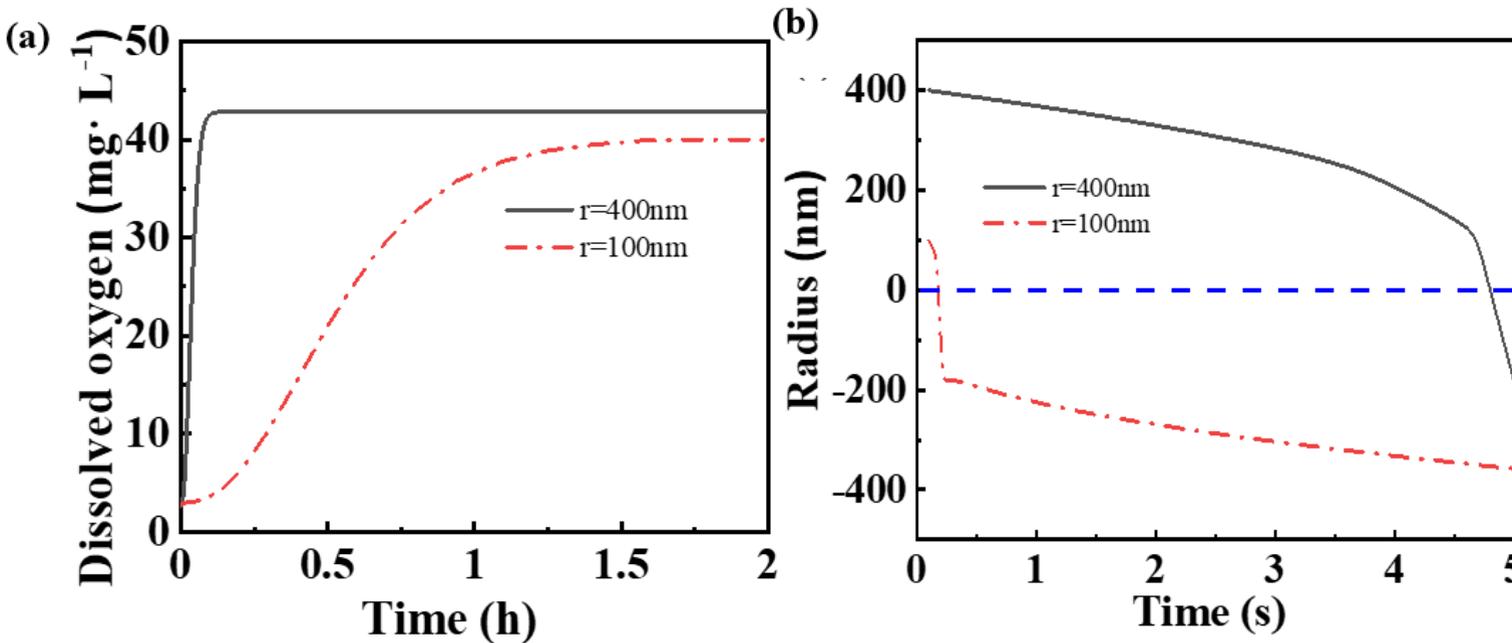
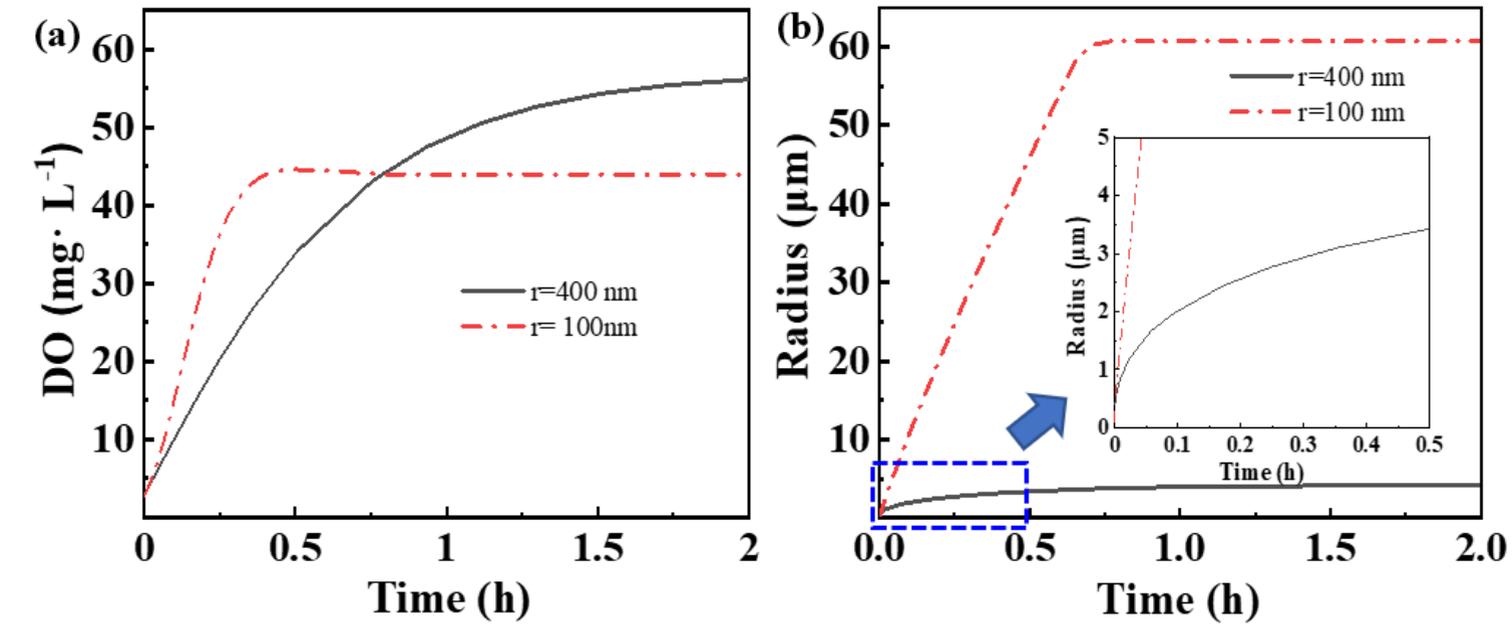


# Volumetric mass transfer coefficient ( $K_L \cdot a$ ) and the change of DO during the aeration using $O_2$ NBs



(a) when purging  $O_2$  NBs (400 nm) with different  $K_L$  (0.0001-0.01 m·s<sup>-1</sup>) under  $P_{inj} = 414$  kPa and (b) when purging  $O_2$  NBs (400 nm) with different injection pressures (100-500 kPa). Other important parameters used in the calculation include: the  $O_2$  gas flow,  $Q = 7.5 \times 10^{-6}$  m<sup>3</sup>·s<sup>-1</sup>, the volume of NB water,  $V = 4 \times 10^{-4}$  m<sup>3</sup>, DO concentrations in the water at time 0,  $C_0 = 9$  mg·L<sup>-1</sup>.

# Model prediction of DO and bubble size changes during dissolution of O<sub>2</sub> NBs in water



According to the Epstein-Plesset theory:

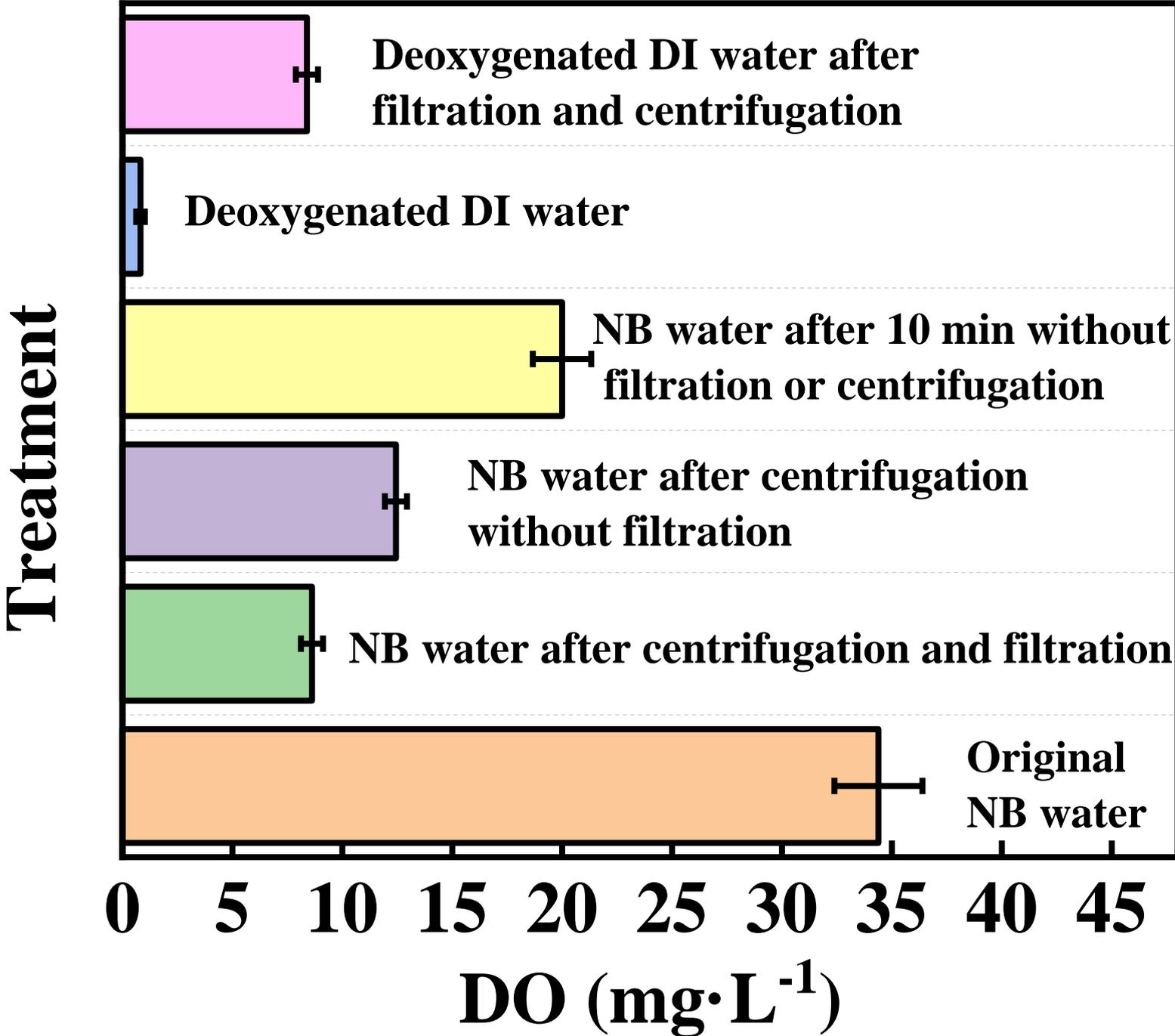
$$\frac{dr}{dt} = -\frac{D' \Delta c}{\rho_g} \left( \frac{1}{r} + \frac{1}{\sqrt{\pi D' t}} \right)$$

If we ignore the loss of oxygen, the increase of the dissolved gas concentration (c) will be proportional to the dissolution of the gas molecules from NBs, which yields the following equation

$$\begin{aligned} \frac{dc}{dt} &= \frac{N}{V} \frac{dn}{dt} = \frac{N}{V} \frac{d(P_{\text{int}} V')}{RT dt} \\ &= \frac{1}{RT} \frac{N}{V} \left( \frac{V' dP_{\text{int}}}{dt} + \frac{P_{\text{int}} dV'}{dt} \right) \\ &= \frac{1}{RT} \frac{N}{V} \left( -\frac{2\gamma V'}{r^2} + 4\pi r^2 P_{\text{int}} \right) \frac{dr}{dt} \end{aligned}$$

(a) The predicted DO levels during the dissolution of O<sub>2</sub> NBs in water (NBs were prepared with the initial radii of 100 and 400 nm). (b) The predicted bubble radius changes during the dissolution. The N/V of 10<sup>14</sup> #·m<sup>-3</sup> was used in the model calculation.

# Effects of filtration/centrifugation on the DO levels of O<sub>2</sub> NBs water

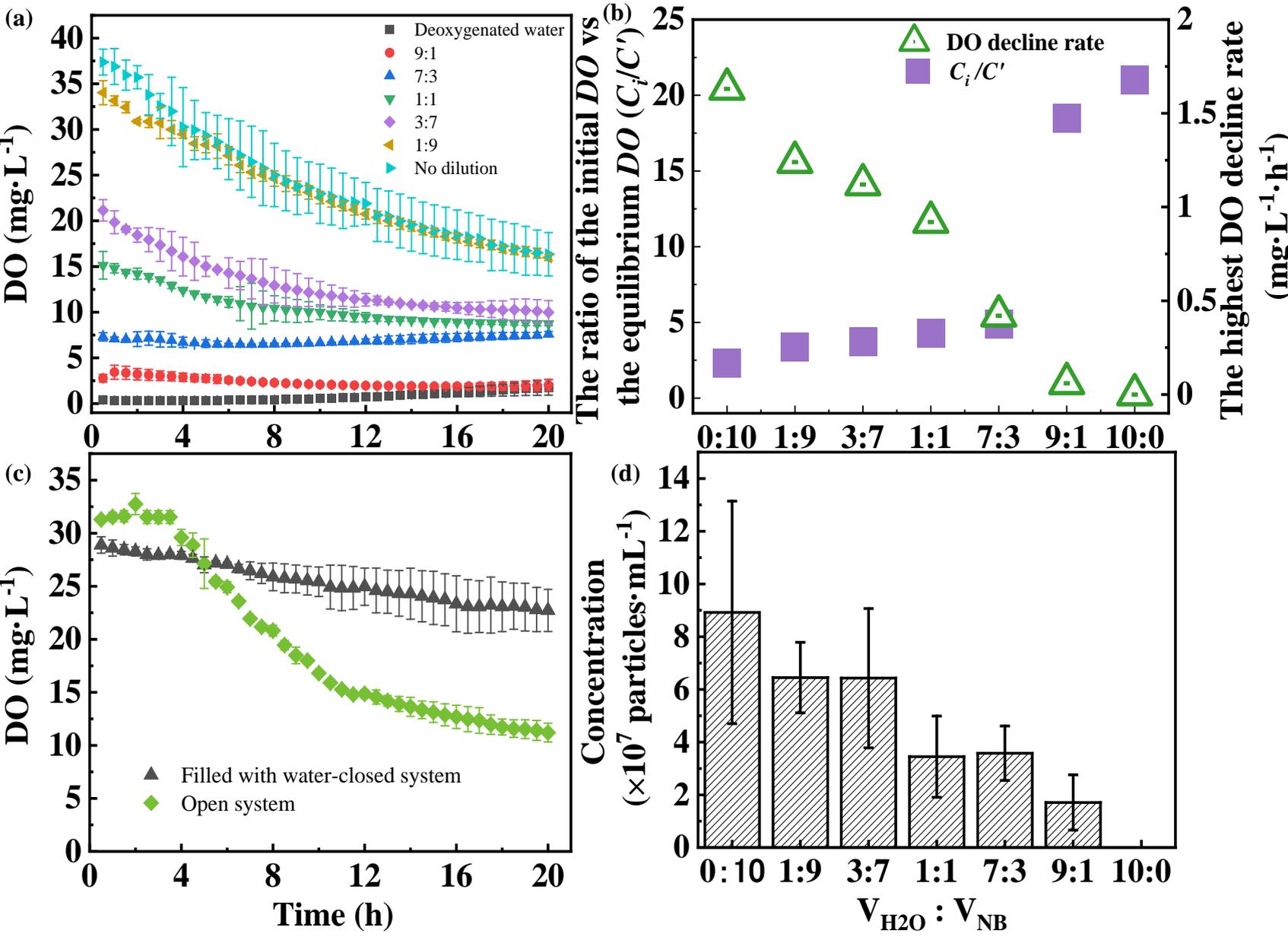


- ✓ The presence of O<sub>2</sub> NBs strongly dictates the DO level and follows the Henry's law.
- ✓ Once O<sub>2</sub> NBs are removed by filtration (or partially by natural dissolution), the DO level is shown to progressively reduce and eventually reach the equilibrium level ( $8.6 \pm 0.5 \text{ mg}\cdot\text{L}^{-1}$ ) with the ambient air.

DO levels in different conditions. The centrifugal speed and time were  $5300 \times g$  and 10 min.



# Observations of the DO changes after the dilution of the water suspension of O<sub>2</sub> NBs with DO-free water



- ✓ **Figure a** shows as the O<sub>2</sub> NB suspension was diluted with deoxygenated water, the initial DO levels ( $C_i$ ) declined proportionally as expected and all dropped to different stable levels ( $C'$ ).
- ✓ **Figure b** shows that increasing the dilution ratio (the volume of the spiked deoxygenated water divided by the volume of the NB suspension,  $V_{H_2O}/V_{NB}$ ) will **increase the ratio of  $C_i/C'$** .
- ✓ **Figure c** shows that when the liquid mixture was completely open to the air, the DO declined much faster ( $1.80 \text{ mg}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$ ) than that obtained ( $0.38 \text{ mg}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$ ) when the liquid mixture fully occupied the overhead space.
- ✓ **Figure d** shows that the average number concentration of O<sub>2</sub> NBs in water was proportionally reduced when varying the dilution ratio (0:10, 3:7, 7:3, 9:1) with deoxygenated water.

(a) DO levels versus the dissolution time under different dilution ratios ( $V_{H_2O}/V_{NBs}$ ) in an air-tight container, (b) The ratio of the initial DO vs the equilibrium DO ( $C_i/C'$ ) and the decline rate of DO under different dilution ratio, (c) DO levels versus the dissolution time of O<sub>2</sub> NBs in the container fully filled up and open to the ambient air, and (d) The influence of dilution ratios on the average concentration of O<sub>2</sub> NBs.

# Conclusion

- The mass transfer coefficient ( $K_L$ ) is highly dependent on bubble size.
- The dissolution model based on Epstein-Plesset (EP) theory predicts that the saturated dissolved oxygen (DO) level and the size variation are dependent on bubble size.
- During dissolution, NBs may either swell or shrink depending on the NBs number density
- The internal pressures of O<sub>2</sub> NBs dictate the dissolve oxygen level and also drives the dissolution.
- The experimental measurement and model prediction both revealed the bubble size decreases at high injection or internal gas pressures.
- The colloidal force balance model implies that NBs elicit much higher internal pressures (120~240 psi) than the injection gas pressures (60-80 psi).
- Increasing the solution temperatures (6–40 °C) reduced bubble sizes from approximately 400 to 200 nm, which are validated by colloidal model.

# Acknowledgement

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United States Department of Agriculture  
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# Questions?



**Thank you!**