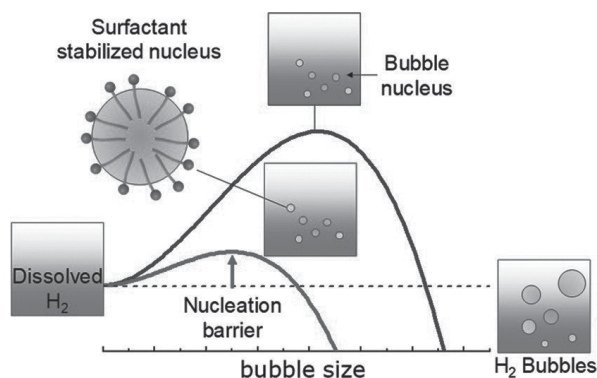


## Bubble Nucleation-based Electrochemical Detection of Surfactants

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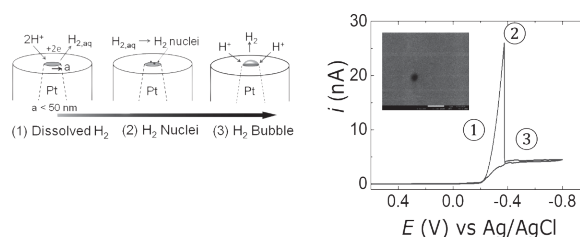
The formation and evolution of vapor and gas bubbles in a liquid body is a phenomenon of vast fundamental and applicative interest, for example, in commercial electrolytic processes in cavitation, in biomedical applications, and functional material fabrication.<sup>1</sup> Here, we present a new application of gas bubbles for surfactant detection. Our method is based on the interactions between gas nuclei and surfactant molecules during electrochemical gas bubble nucleation. According to classical nucleation theory (CNT), nucleation of a gas bubble requires a supersaturation of dissolved gas because of the energy barrier of establishing a new gas–liquid interface (Scheme 1). In the presence of surfactant molecules, gas nuclei can be stabilized because of the reduced surface tension of the gas–liquid interface, leading to a decrease of the supersaturation level required for bubble nucleation.<sup>2</sup> In our method, we take advantage of the high surface activity of surfactant analyte to affect the bubble nucleation and transduce the change in the supersaturation level required for bubble nucleation to electrochemical signal for highly sensitive and specific detection of surfactant analytes.



**Scheme 1.** Bubble-Nucleation-Based Electrochemical Method for Surfactant Detection

To electrochemically probe the bubble-nucleation condition, we adopted a nanoelectrode-based approach developed by Luo and White.<sup>3</sup> In this approach, a sub-50-nm Pt nanoelectrode is used to perform hydrogen evolution reaction (HER) in acid solutions. As the nanoelectrode potential is scanned negatively, the HER current increases exponentially until it reaches a peak

value (ipeak). Past ipeak, the HER current immediately drops to a minimal value, which corresponds to the nucleation and formation of a gas bubble at the nanoelectrode, blocking the electrode surface (Scheme 2). The supersaturation level of dissolved H<sub>2</sub> gas required for H<sub>2</sub> bubble nucleation is proportional to the ipeak value.



**Scheme 2.** Peak current provides information regarding the bubble nucleation.

Perfluoroalkyl Substances (PS) are persistent and globally distributed environmental contaminants. Analytical methods used for PS detection are currently dominated by chromatography in combination with mass spectrometry. These methods are highly sensitive and selective but expensive (typically > \$100/sample) and unsuitable for low-cost, on-site screening. Our detection method takes advantage of the high surface activity of PS, which affects the electrochemical bubble nucleation, and then transduces the change of nucleation condition to electrochemical signal for PS quantitation. The nanoscale dimension of the electrodes provides exquisite sensitivity for detecting slight changes near or at the electrode surface, while fast electrochemical measurements allow studying the dynamics of bubble nucleation. When PS concentration increases, the solution surface tension decreases, resulting in a lower nucleation energy barrier. Consequently, a lower supersaturation concentration is required for H<sub>2</sub> nanobubble nucleation resulting in a reduction of bubble nucleation current. Using this method, we demonstrate the quantitation of perfluorinated surfactants in water, with a remarkable limit of detection (LOD) down to 80 µg/L and a linear dynamic range of over three orders of magnitude. With the addition of a preconcentration

step, we have achieved the LOD range covering 70 ng/L, the health advisory for perfluorooctane sulfonate and perfluorooctanoic acid in drinking water established by the US EPA. The experimental results are in quantitative agreement with the model we derived from classical nucleation theory. We further tested the specificity of this method for detecting surfactant analytes by adding an excess of nonsurfactant interference, polyethylene glycol (PEG, 400 g/mol), which has a similar molecular weight as PFOS. The addition of PEG leads to a negative shift of the HER onset potential as compared to the PFOS-only sample, but the ip<sub>peak</sub> does not show any notable difference. Apart from that, we have also tested different concentrations of humic acid and lysozyme. We observed no trend in the peak current compared to that of the blank. These results show the exceptional specificity of our method for surfactant analytes. This research provides the proof of principle study of a bubble

nucleation-based sensing platform, which will be further developed toward a low-cost and portable tool for on-site detection of PS compounds in water. In addition, our method has the potential of further developing into a universal electrochemical detector for surfactant analysis due to its surface activity-based detection mechanism.

### References

1. Kronberg, B.; Lindman, B., Surfactants and polymers in aqueous solution. John Wiley & Sons Ltd., Chichester: 2003.
2. Blander, M.; Katz, J. L., Bubble nucleation in liquids. *AIChE J.* 1975, 21 (5), 833-848.
3. Luo, L.; White, H. S., Electrogeneration of single nanobubbles at sub-50-nm-radius platinum nanodisk electrodes. *Langmuir.* 2013, 29 (35), 11169-11175.