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Electrochemical Adventures in Microscale: Bubble Film-Mediated Electrochemical Sensing and Deposition

Nikoo Fahemi,[a] Shayan Angizi,[c] Amir Hatami(e) [a,b]*

[a] *Department of Chemistry, Institute for Advanced Studies in Basic Sciences, Zanjan-Iran.*

[b] *Department of Chemistry and Molecular Biology, University of Gothenburg, Gothenburg, Sweden.*

[c] *Department of Chemical Engineering, McMaster University. Hamilton, Canada.*

- *E-mail: amir.hatami@iasbs.ac.ir, amir.hatami@gu.se*

IASBS
UNIVERSITY OF GOTHENBURG
McMaster University

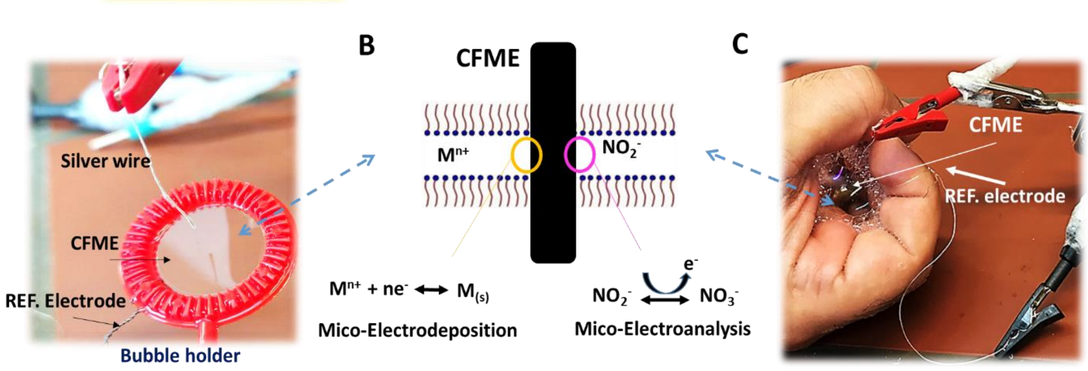
Abstrct

We describe a novel electrochemical cell design with a thickness of about ~27 µm that comprises a carbon fiber electrode (10 µm diameter) placed through a bubble wall (or stable surfactant film) which serves as the solution. To create a durable surfactant film, we employed a solution infused with non-ionic Triton-X100 surfactants. For electroanalysis, a modified carbon microelectrode with graphene oxide nanosheet (GO, as a sensing electrode) was placed through a soap bubble wall along with a 1 mm diameter silver wire as the counter/reference electrode [1]

Using this strategy, the proposed sensing system has successfully detected NO_2^- both on the hand and dissolved in Triton-X100 surfactants film [2-3]. This technique holds particular significance in criminal investigations, as the presence of NO2- ions on the hand is indicative of gunshot residue and can aid in identifying suspects. Therefore, this method enables rapid analysis with a low limit of detection of 28 µM and proves functionality for on-site sensing.

To perform electrodeposition in a bubble wall, different ions such as silver and palladium ions were dissolved within the bubble film. A bare carbon microelectrode was placed inside the bubble wall, and the suitable cathodic potential was applied. The deposited metallic film was analyzed by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy. The images obtained from the analysis revealed that the thickness of the bubble wall or electrochemical cell imposes limitations on the electrodeposition area at the microscale level. Furthermore, the lifespan of the bubble wall [3] played a crucial role in controlling the duration and thickness of the deposited film from nanoscale to microscale.

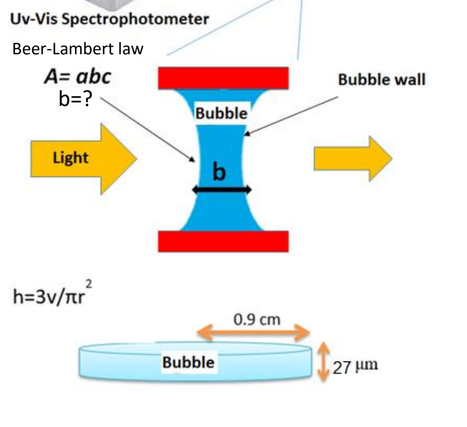
Experimental



(A) Schematic of the bubble wall structure and images of the experimental setups, microscale template free electrochemical deposition of metallic ions (B) and microelctroanalysis of nitrite (NO_2^-) oxidation on a hand (C), within tinny layer of soap bubble wall.

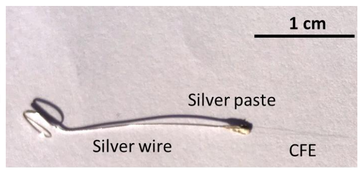
Estimation of bubble wall thickness and volume using spectrophotometric analysis

The Beer-Lambert law equation, A=εbc, relates the absorbance of a solution (in this case, the bubble wall) to the molar absorptivity (ε), the path length of light through the sample (b) in centimeters, and the concentration of the substance (Phenol red). After obtaining the molar absorptivity coefficient (ε) of organic color compound (phenol red), we determined the thickness of the bubble wall using the Beer-Lambert law equation and estimating b, which represents the bubble wall thickness. To do this, we placed the plastic ring containing the bubble with phenol red (8 ppm) inside the spectrophotometer next to the cuvette holder. The absorbance was then recorded at the maximum single wavelength of Phenol red (432 nm) within a short period (8-15 sec) after removing the bubble holder from the stock bubble solution. All measurements were performed and repeated at the fixed wavelength (432 nm) within the same time frame. Using the Beer-Lambert law, we estimated the bubble wall thickness to be 30 µm when using a 10% Triton X-100 solution for creating the bubble wall (Diameter of bubble holder is 0.9 cm). The same condition were used for nitrite sensing and electrodeposition processes.



Microsensor: fabrication, and modification

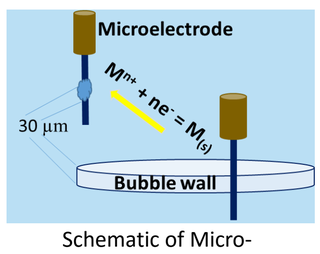
A microscale carbon fiber electrodes (MCFEs) with a diameter of 10 µm were fabricated by connecting a 1 cm carbon fiber (CF) to a silver wire (as a connection wire) using silver paste, as shown in Fig. 1.



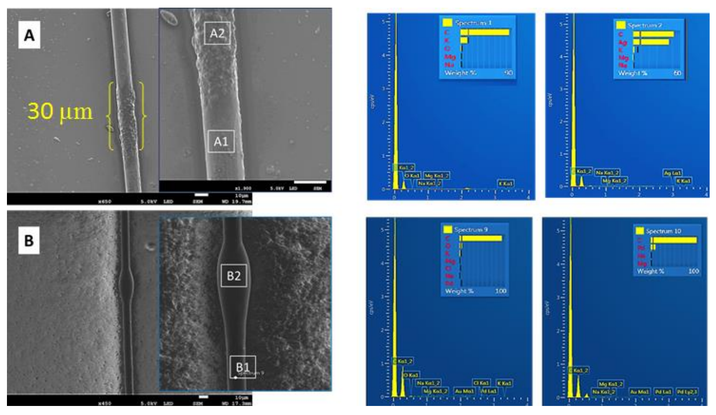
Optical image of the ultramicroelectrode
(D = 10 µm, L; 1 cm)

Results and discussion

The bubble wall thickness determines electrodeposition zone



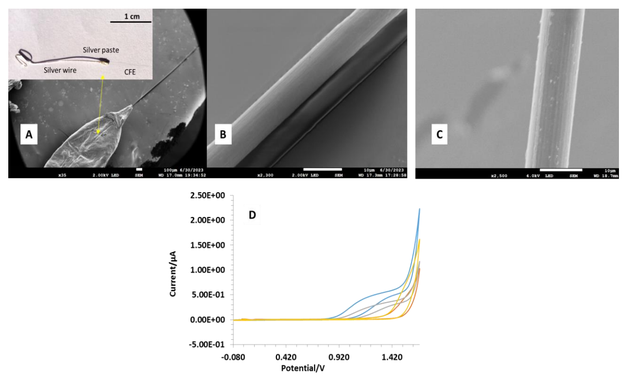
Schematic of Micro-Electrodeposition in a Bubble Wall Using a Microelectrode.



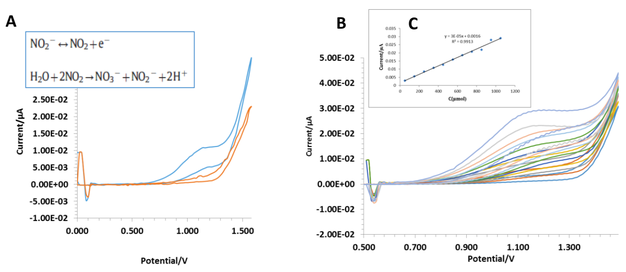
Top-view SEM images of MCFE coated with a thin layer of Ag film (above) and with Pd film (below) at various magnifications, along with the corresponding EDX analysis.

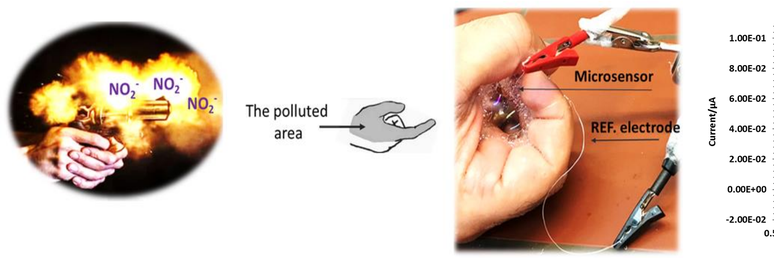
Micro-electroanalysis of nitrite within the bubble wall and fingers !

SEM images of the CFE (a-b) and (c) modified CFE with GO. The inset in a shows the optical image of the ultramicroelectrode associated with SEM. (d) CV curves in 200 µM nitrite,1.0 M TX-100 and electrolyte with a scan rate of 0.1 Vs−1 in solution and bubble wall: (Green) bare MCFE, (Red) MCFE@GO electrode in the absence of nitrite, (Blue) bare MCFE, (Black) MCFE@GO electrode in the presence of 200 µM nitrite.



(a) CVs of the MCFE@GO (a) 0.0 (b) 200 µM nitrite in bubble wall. (b) CVs of the MCFE@GO between +0.10 and +1.20 V at a scan rate of 0.1 V s-1 with 50- 1050 µM of nitrite in 1 mM PBS (pH 6.00) and TX-100 10% V/V, (c) the relationship between the oxidation peak currents and the nitrite concentrations.





Schematic and principle of nitrite Ion detection Using the modified ultramicroelectrode (CFE@GO) within the formed bubble wall, showed on the left. On the right, a simulation of microelectroanalysis for different concentrations of nitrite ions within bubble wall and on hand (Control in blue, 100 µM in red, and 300 µM in green).

Conclusion

In summary, we have developed innovative applications for a bubble wall as a thin layer of water using microscale electrochemistry. Initially, we successfully determined the thickness and volume of the bubble (electrochemical reaction media) using UV-Vis spectroscopy. Subsequently, we utilized the bubble to conduct electrochemical deposition within a microscale zone. The thickness of the bubble wall, containing metal ions, precisely controlled the deposition area of metallic films (Ag and Pd films) on the electrode surface. Importantly, the length of the deposition area correlated with the estimated thickness of the bubble wall. In the second part of our work, we demonstrated the ability of a surfactant solution to dissolve nitrite ions, which our microelectrode could detect at micromolar levels within a matter of seconds. Therefore, we propose that this developed technique could be explored as an innovative approach for detecting nitrite ions, a crucial aspect of forensic investigations involving gunshot residues. Nitrite ion analysis plays a pivotal role in criminal investigations, as their presence serves as a significant indicator of recently discharged firearms. Remarkably, when compared to existing analytical methods, the proposed approach is remarkably rapid, simple, and exhibits suitable sensitivity. Additionally, we have devised a new method for on-site analysis, performed by hand, which eliminates the need for complex sampling and laboratory-based analysis. In conclusion, we believe that this work has the potential to break current barriers and introduce innovations in the field of microelectrochemistry. It also opens up new applications involving bubbles.

References

Zhang, X., Hatamie, A., & Ewing, A. G. (2020). Nanoelectrochemical analysis inside a single living cell. Current Opinion in Electrochemistry, 22, 94-101.

Braide-Azikiwe, Dandisonba Chinwe Bamidele, Katherine B. Holt, David E. Williams, and Daren J. Caruana. "Soap film electrochemistry." Electrochemistry communications 11, no. 6 (2009): 1226-1229.

Vannoy, Kathryn J., Nicole E. Tarolla, Philip J. Kauffmann, Rebecca B. Clark, and Jeffrey E. Dick. "Detecting Methamphetamine in Aerosols by Electroanalysis in a Soap Bubble Wall." Analytical Chemistry 94, no. 16 (2022): 6311-6317.