

Article

Electrochemical Detection of Surfactant-Encapsulated Aqueous Nanodroplets in Organic Solution

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Abstract: We report enhanced electrochemical detection of single water-in-oil emulsion droplets using the nano-impact method. To detect the emulsion droplets, the water molecules in the droplets were directly oxidized (i.e., water splitting) without additional electroactive species when the droplets collided with the ultramicroelectrode. The water molecules in the emulsion droplet cannot be directly electrolyzed in an organic solvent because the emulsifier does not require a hydrophobic electrolyte. To enhance the signal intensity, the electrochemistry of sub-microscale single droplets was investigated considering the charge neutrality and limiting reagent. Therefore, effective electrolysis of the droplets was achieved. Approximately 10% of water molecules in the droplet (55.6 M H₂O) were oxidized based on calculations from the electrochemical peak analysis and DLS measurements.

Keywords: nanodroplet; single entity; collision; nanoelectrochemistry; single particle

1. Introduction

Nanoelectrochemistry has attracted tremendous interest in modern electrochemistry and has been studied using platforms such as nanoparticles [1–4], nanoelectrodes, nanogaps, nanojunctions, nanocavities, nanopores, nanochannels, and nanointerfaces [5–11]. The electrochemical reaction at the nanoscale is significantly different from that in the bulk solution. Recently, nanoelectrochemistry has been applied to single entities, such as emulsion droplets [12], liposomes [13–15], cells [16], micelles [17], nanobubbles [18] and vesicles [19]. Reaction monitoring in a single nano-entity is a challenging topic. A pure water droplet, which acts as a nanoreactor, is temporarily stable when dispersed in an immiscible organic solvent. In a real system, the surfactant is present in one or both liquids. A water droplet can be stabilized in an organic solvent using a surfactant (i.e., an emulsifier), which is called a water-in-oil emulsion (i.e., an inverse emulsion; W/O) [20–24]. In addition, organic media are not always pure and may contain chemical species. For example, gasoline and diesel fuels contain surfactants that act as corrosion inhibitors, dispersants, detergents, and anti-icing additives [25]. Therefore, a water droplet detection system must be developed that considers the surfactants included in the aqueous and/or organic phases.

Recently, single-liquid nanodroplets have been studied electrochemically using the ‘single particle collision’ (i.e., ‘nano impact’) method [26–31]. As a proof-of-concept, the suggested collisional detection method focuses on investigating the size distribution of a single droplet. This technique can be used to determine particle properties such as individual droplet size, droplet polydispersity, and droplet concentration in continuous media [32–36]. The reaction occurring inside a single liquid droplet enables single-entity electrochemistry. Studies have utilized reactions in single droplets for the controlled synthesis of single metal/nonmetal nanoparticles [37,38]. The liquid droplets can be dewetted or deformed when they land on the electrode surface, which can be used to control the electrochemical reactions inside single droplets. In single-droplet electrochemistry, the electrical contact area is a crucial factor determining the product of an electrochemical reaction.

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In the early stages, single water nanodroplets and single oil nanodroplets were first detected electrochemically by blocking the electrode area via adsorption of the droplet in the presence of redox species in the organic phase [39,40]. This method is a powerful tool for investigating liquid nanodroplets that do not contain redox species. However, these methods, which are based on the blockage of the electrode surface, cannot be used to obtain precise information about single droplets. For droplets of the same size, blockage of the amperometric current can differ depending on the shape of the droplet adsorbed on the electrode surface. In the presence of redox species in the droplets, a comparable electrochemical detection method is also suggested that uses the electrolysis reaction within the droplet [22,33,34]. In general, however, aqueous droplets in organic media seldom contain redox species inside them. Organic solvents may contain either water molecules or a hydrophobic/hydrophilic electrolyte (non-redox active) because the water content in such systems is mostly coming from humidity in the air and electrolytes are pre-dissolved in an organic solvent. As a simplified droplet detection system, water molecules are considered to be redox species that can be directly electrolyzed. In a previous study, we reported the direct electrolysis of water molecules in water nanodroplets in the absence of surfactants and lipophilic electrolytes [21].

However, only 0.81% of the water content in the surfactant-free water droplets was electrolyzed because the electrochemical conditions in the nanodroplets were not properly prepared. In the presence of a surfactant, the electrochemistry can be partially blocked by the surfactant, which can hinder charge (electron and ion) transfer at the water/metal and water/oil interfaces. Furthermore, in the absence of hydrophobic electrolytes in the organic phase, oxidation of water (water splitting) molecules in the emulsion was not observed.

Herein, we report the sensitive electrochemical detection of water-in-oil emulsion droplets using the highly efficient oxidation of water molecules in a droplet. Surfactant-protected emulsion droplet dispersed in DCE solvent is investigated electrochemically based on the water oxidation (water splitting) reaction upon the collisional contact of the droplet on an electrode surface. The importance of a supporting electrolyte outside a single droplet in nanodroplet electrochemistry has been previously reported [20,34].

To consider the reaction efficiency in a single nanodroplet (i.e., water-in-oil emulsion droplet), reaction parameters such as the emulsifier, hydrophobic electrolyte, and hydrophilic electrolyte were carefully considered. By optimizing the reaction environment of a nanodroplet, electrolysis of a single nanodroplet has efficiently proceeded even with a surfactant-protected emulsion droplet. Therefore, an understanding of the reaction environment on nanodroplets is mandatory to detect the single entity electrochemically. In addition, this principle can be applied to elevate the electrolysis efficiency of water, which generates hydrogen gas as a reaction product.

During the water electrolysis in continuous aqueous media, bubbles are produced and cannot be removed rapidly from the electrode surface. The bubble is adsorbed on the electrode surface and covers the active reaction sites of the electrode to attenuate the production of hydrogen gas. This phenomenon would lead to high overpotential and high ohmic potential. Reducing bubbles is one of the key factors for water electrolysis. Injection of reactant water as a droplet could be a promising approach to removing the bubble effect on the electrode surface. Actually, ionic liquid as electrolytes for hydrogen production from water electrolysis was introduced for chemical stability and low reactivity of ionic liquid and effective hydrogen gas production from immiscible water ionic liquid properties [41]. Similarly, a water-in-oil emulsion system can also be utilized in efficient hydrogen gas production to effectively control the bubble adsorption on an electrode surface.

2. Materials and Methods

2.1. Reagents and Materials

Sodium chloride (NaCl, 99%), silver nitrate (AgNO₃, 99.9%), tetrabutylammonium hexafluorophosphate (TBAPF₆, 98%), and sodium dioctyl sulfosuccinate (AOT, 96%) were obtained from Alfa Aesar. 1,2-Dichloroethane (DCE, 99.8%) and tetrabutylammonium tetrafluoroborate (TBABF₄, 99%) were obtained from Sigma-Aldrich (St. Louis, MO, USA). Millipore water (>18 MW·cm) was used in all the experiments. Pt wire (99.99%; diameter, 10 µm) was supplied by Goodfellow (Devon, PA, USA). The Pt wire used as the counter electrode was purchased from Alfa Aesar. The reference electrode was an Ag wire with 10 mM AgNO₃ and 100 mM TBAPF₆ in acetonitrile (ACN, Thermo Fisher, Cleveland, OH, USA). All the reagents were used as received.

2.2. Electrochemical Instrumentation

Electrochemical experiment setups were composed of CHI 750E bipotentiostat (CH Instruments, Austin, TX, USA) with a three-electrode system. Every electrochemical measurement was performed inside a CHI 200B Faraday cage (CH Instruments, Austin, TX, USA). The three-electrode system is composed of an Ag/Ag⁺ nonaqueous reference electrode (10 mM AgNO₃ in acetonitrile, MF-2062, BASi, IN, USA), homemade ultramicroelectrode (Pt, Au, C) as a working electrode, and a Pt wire (diameter: 1 mm, length: 100 mm) as a counter electrode. The electrochemical cell was composed of a homemade Teflon cap assembled with a glass vial. A horn sonicator system was used to prepare the emulsion solution using a Q700 ultrasonic processor (Qsonica, Newtown, CT, USA) with a microtip probe at a pulse mode. The average size of the particle is investigated based on the dynamic light scattering (DLS) principle using a NanoBook 90 Plus particle size analyzer (Brookhaven Instruments Corporation, Holtsville, NY, USA).

2.3. Preparation of the Water-in-oil Emulsion

The water-in-oil inverse emulsion solution was prepared according to the following procedures: 10 mL of 100 mM sodium chloride aqueous solution was prepared using distilled water, and 200 µL of 100mM NaCl aqueous solution was added to 5.0 mL of DCE solution containing 1 mM sodium dioctyl sulfosuccinate (AOT). The aqueous/DCE mixture solution was vortexed for 20 s, then homogenized with a horn ultrasonicator (700 W, 30% of amplitude) in the pulse mode (1 cycle: on for 7 s, and off for 3 s) for 1 min. The molar concentration of the prepared emulsion droplet (C_{em}) was calculated using Equation (1):

$$C_{em} = \frac{n_{em}}{V} = \frac{N_{em}}{N_A V} = \left(\frac{V_w}{V_{em}} \right) \frac{1}{N_A V} \quad (1)$$

where n_{em} is the moles of emulsion droplets, N_{em} is the number of droplets, N_A is Avogadro's constant, V is the volume of the solution, V_w is the volume of the aqueous solution, and V_{em} is the average volume of a single emulsion droplet. As shown in Equation (2), the volume of a single emulsion droplet was estimated from r_{em} which is the average radius of the droplet obtained using DLS. It is assumed that all emulsion droplets are spherical in shape and have the same radius.

$$r_{em} = \sqrt[3]{\frac{3V_{em}}{4\pi}} \quad (2)$$

2.4. Preparation of Pt ultramicroelectrode (Pt-UME)

The UME was prepared according to a procedure developed in our laboratory. Briefly, a 10 µm Pt wire (Goodfellow) was sealed in a borosilicate glass capillary (1.5 mm Outer Diameter × 0.75 mm Inner Diameter, Sutter), which was sonicated in hexane, toluene, IPA, ethanol, and water, respectively. The electrode was then polished with silicon

carbide abrasive sandpaper (400, 1000, 1200, 2000, and 2500 grit; Buehler, Lake Bluff, IL, USA) until a mirror-like surface was observed.

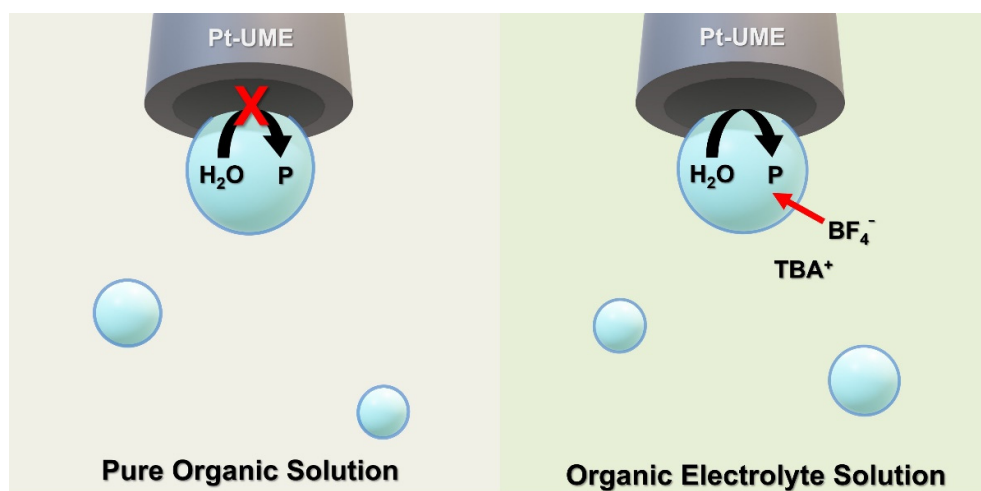
The active area was monitored by standard redox electrochemistry in 1 mM ferrocenemethanol (FcMeOH) solution and estimated by the following equation:

$$i_{lim} = 4nD_{Red}R_{UME}C_{Red}$$

where i_{lim} is the limiting current, n is the number of electrons in the redox reaction, D_{Red} , and C_{Red} is the diffusion coefficient and concentration of redox species, respectively, and R_{UME} is the radius of Pt-UME. The obtained electrode area was almost 10 μm in diameter when we assume it has a flat circular shape. Before each electrochemical experiment, all UMEs were polished using 4000-grit SiC sandpaper (R&B Co. Ltd. Daejeon, Korea) and 1 μm , 0.5 μm , and 0.1 μm diamond lapping film (R&B Co. Ltd. Daejeon, Korea) was also used to obtain a mirror-like finish on the UME surface.

3. Results and Discussion

As a detection target, a water-in-oil emulsion droplet is prepared by mixing an aqueous solution of 100 mM NaCl with 1,2-dichloroethane (DCE) through the ultrasonic process. To study the homogeneous water droplets in the organic phase, 1mM sodium dioctyl sulfosuccinate (AOT), which serves as an inverse emulsion stabilizer, was dissolved in the DCE continuous phase. Surfactant-encapsulated water-in-oil droplets were studied, which are a more probable type of water droplet in organic solvents than pure water droplets (Scheme 1).



Scheme 1. The schematic illustration of the electrochemical reaction of the water droplet when it contacts the electrode surface. There is no reaction without a supporting electrolyte in organic solution; however, the electrolysis of water molecules in droplets takes place in the presence of a supporting electrolyte in organic solution.

To investigate the electrolysis conditions of the surfactant-encapsulated emulsion droplets, cyclic voltammetry (CV) and chronoamperometry (CA) were conducted in the absence and presence of a hydrophobic electrolyte in the continuous DCE phase. The CVs were scanned from 0 V to 1.2 V (*vs.* Ag/Ag⁺), where water oxidation can occur thermodynamically. When the emulsion was injected into pure DCE (Fig. 1a black line), no anodic current response was observed until 1.2 V. However, in the presence of hydrophobic electrolyte in the organic phase, the oxidation of water started from around 0.85 V (Figure 1a, red line), resulting in a drastic current increase. In addition, current spikes were observed above the increasing current trend, owing to the continuous collision of the emulsion droplets. Figure 1b shows the CAs of the emulsions in DCE with and without 10 mM TBABF₄ in the organic phase. The electrode potential was maintained under an oxidative

condition of 1.0 V *vs.* Ag/Ag⁺. When the emulsions were injected into pure DCE (Figure 1b, black line), no spiky peak currents were observed. When the emulsion was injected into a DCE solution containing 10 mM TBABF₄, a collisional current spike originating from the collision and adsorption of the emulsion droplet on the UME, followed by simultaneous oxidation of the water molecules in the droplet was observed (Figure 1b, red line). Collisional current spikes were observed only in the presence of hydrophobic electrolytes in the organic phase in both the voltammetric and chronoamperometric measurements. Owing to the addition of the electrolyte to the solution, the resistance of the bulk solution decreased. Therefore, the background current increased slightly owing to the reduced *iR* overpotential.

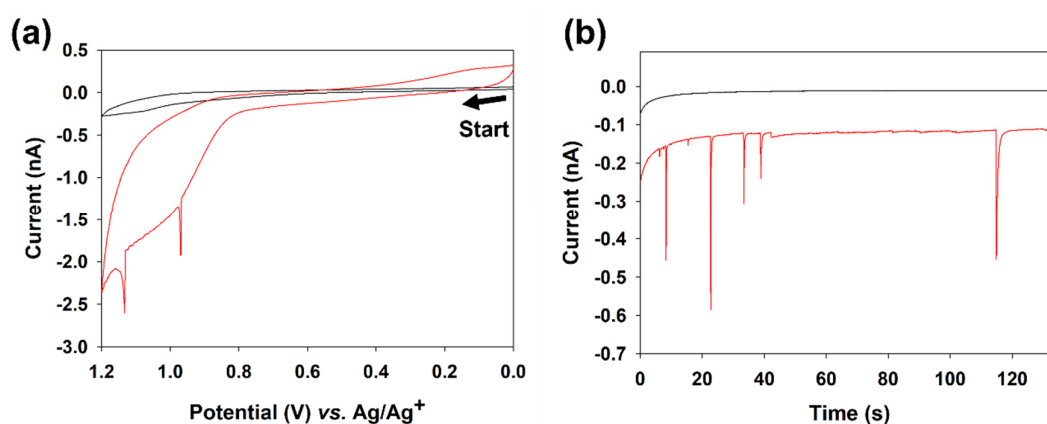
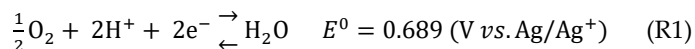


Figure 1. (a) CVs of the W/O emulsion droplets (0.1 M NaCl dissolved in aqueous phase) in pure DCE (black line) and in DCE containing 10 mM TBABF₄ (red line) on a Pt-UME at a scan rate 50 mV s^{−1}. (b) Amperometric *i-t* curves of the W/O emulsion droplets (0.1 M NaCl dissolved in aqueous phase) in pure DCE (black line) and in DCE containing 10 mM TBABF₄ (red line) on a Pt-UME biased at 1.0 V (*vs.* Ag/Ag⁺).

To determine a suitable potential for emulsion detection in an organic electrolyte solution, CA was conducted at various potentials in the Pt UME (Figure 2a). The experiments were conducted at potentials from 0.4 V to 1.2 V with 0.2 V intervals. When 0.4 V was applied, anodic peak currents were not observed. At 0.6 V and 0.8 V, the spiky current peaks were observed, resulting from the oxidation of the collided emulsion droplets. However, the current peaks were comparatively small because the overpotential was not sufficiently high for water oxidation. When the potential was increased to 1.0 V and 1.2 V, relatively large spiky peaks were observed. Based on the experimental results shown in Figure 2b, 1.0 V was chosen as the optimal electrode potential for the detection of emulsion droplets using the CA method because it showed high peak currents and maintained a stable background current.

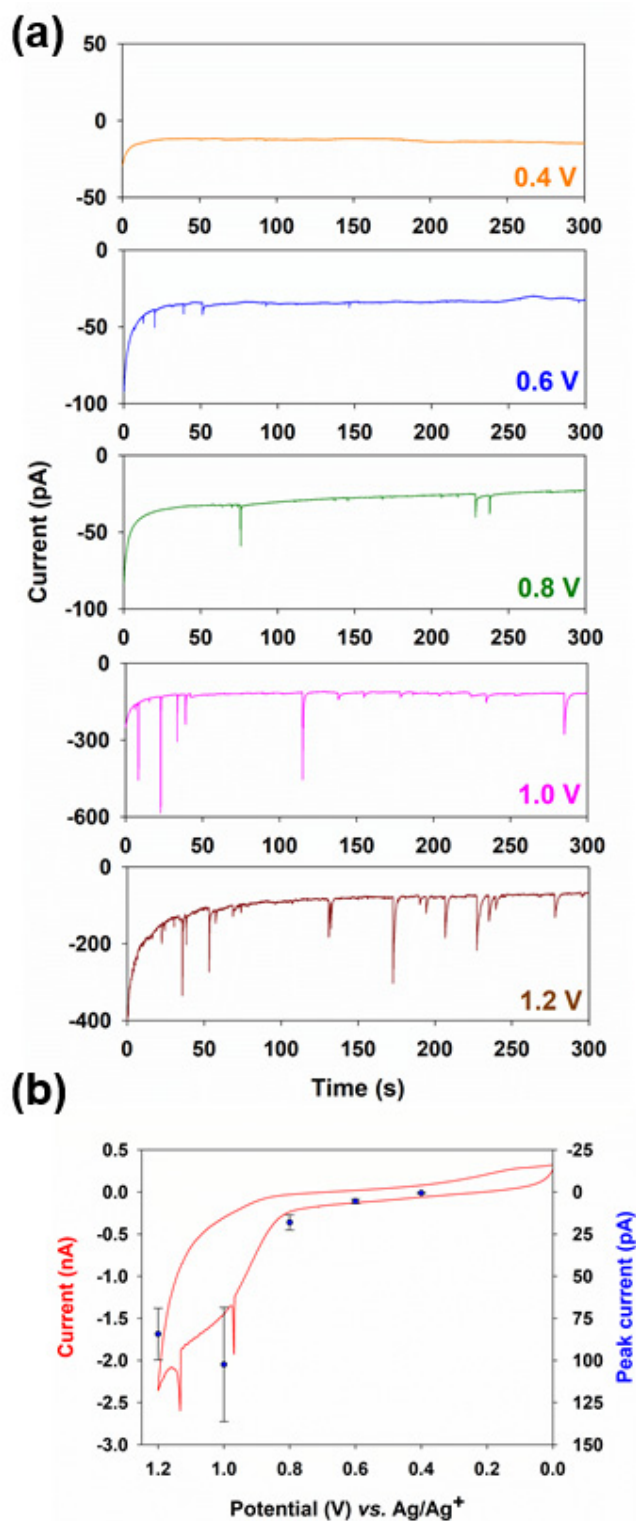


Figure 2. (a) Amperometric *i-t* curves of W/O emulsion droplet on Pt-UME at various applied potentials (0.4, 0.6, 0.8, 1.0, and 1.2 V vs. Ag/Ag⁺) in DCE electrolyte solution containing 10 mM TBABF₄ (b) Collisional peak heights obtained from W/O emulsion in the DCE electrolyte solution were plotted together with a cyclic voltammogram of the same solution depending on the applied electrode potentials.

In pure DCE solution, CA was performed at various anodic potentials to observe emulsion droplet collisions in the Pt UME (Figure 3). For the consideration of highly resistive organic solvent without supporting electrolyte, CA experiments were conducted at potentials from 1.0 V to 1.8 V with 0.2 V intervals. However, no collisional current spikes were observed in any of the experiments, including a high anodic potential of 1.8 V. The result indicates that hydrophobic electrolytes are required to detect the AOT-encapsulated emulsion droplets. For the detection of surfactant-free droplets (e.g., pure water droplets only containing hydrophilic electrolytes in an aqueous phase), the water droplets can be detected in the absence of hydrophobic electrolytes in DCE [22]. Although the surfactant species are dissolved in the organic phase, they are also present at the interface of the aqueous and organic solutions. Therefore, the electrochemistry of the aqueous droplet can be affected by the interface material.

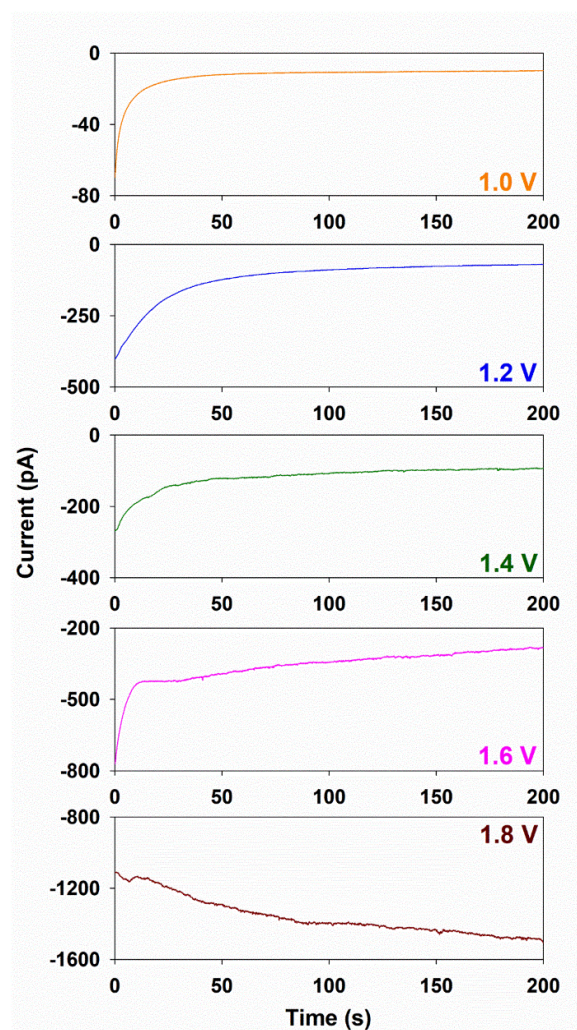


Figure 3. Amperometric *i*-*t* curves of W/O emulsion droplets on Pt-UME at various applied potentials (1.2, 1.4, 1.6, 1.8, and 2.0 V *vs.* Ag/Ag⁺) in pure DCE solution.

Using the CA data obtained from the collision experiments, the collision frequency was measured based on the concentration of the emulsion droplets. A plot of the collision frequency as a function of the emulsion concentration is shown in Figure 4. The upper and lower error bars were calculated as three times the standard deviation. It was observed that the collision frequency was proportional to the injected emulsion droplets when the

droplet concentration was less than ca. 300 pM. At lower droplet concentrations, the emulsion droplet behaved as a randomly moving independent particle, and a low probability of interaction was observed between the particles. Therefore, the increased number of emulsion droplets due to the increased emulsion injected suggests that collisions of emulsion droplets on UME are more likely to result from the stochastic diffusion process. The following Equation (3) was derived from a regression analysis of the experimental collision frequencies (Figure 4, blue line).

$$f_{exp} = 0.00044C_{em} \quad (3)$$

where f_{exp} is the collision frequency of the experiment and C_{em} is the concentration of the W/O emulsion.

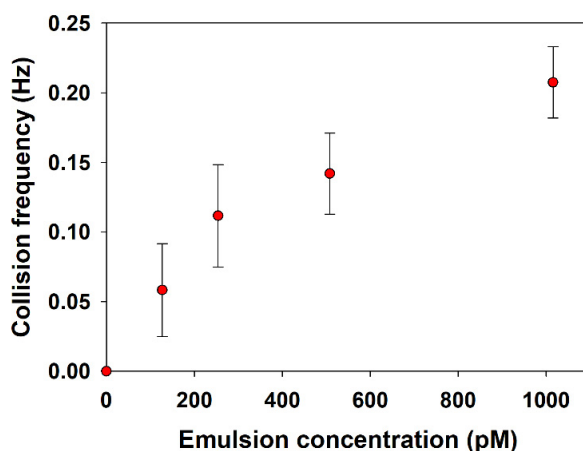


Figure 4. Plot of the collision frequency (Hz) as a function of the W/O emulsion concentration (pM). The error bars indicate the 3 times of the standard deviation of 6 independent measurements. All experiments were conducted on a Pt-UME biased at 1.0 V (vs. Ag/Ag⁺).

However, when the droplet concentration is increased, a greater chance of interaction is expected between the droplets. Coalescence occurs during the injection of emulsion droplets into an organic medium. Furthermore, in the presence of hydrophobic electrolytes in the organic phase, the droplets can agglomerate to form larger droplets because the electrostatic repulsion between the charged droplets can be reduced at a high ionic strength. In our experiment, at higher emulsion droplet concentrations, the coalescence of the emulsion droplets resulted in a lower collision frequency than that expected from the linear trend.

The theoretical collision frequency can be evaluated by considering the diffusion and migration of W/O emulsion droplets toward the UME. In this system, only the diffusional movement of the droplet was considered because the migration effect can be ignored using supporting electrolytes in an organic solvent. The theoretical collision frequency is given by Equation (4):

$$f_{em} = 4D_{em}C_{em}r_eN_A \quad (4)$$

where f_{em} is the theoretical frequency of the W/O emulsion owing to diffusion toward the working electrode, D_{em} is the diffusion coefficient of the W/O emulsion droplet, C_{em} is the concentration of the W/O emulsion, r_e is the radius of the working electrode, and N_A is Avogadro's number. D_{em} was calculated using the Stokes–Einstein relationship (Equation (5)):

$$D_{em} = \frac{k_B T}{6\pi\eta r_{em}} \quad (5)$$

where k_B is the Boltzmann constant, T is the temperature (298 K), η is the viscosity of water at 25 °C, and r_{em} is the radius of an emulsion droplet. Consequently, the theoretical frequency of collision (f_{em}) from the 127, 254, 508, and 1016 pM emulsion droplet was 2.1, 4.1, 8.3, and 16.5 Hz and the experimental frequency (f_{exp}) was estimated to be 0.058, 0.112, 0.142, and 0.208 Hz, respectively. The f_{em} values of the water droplet collisions were approximately 35–80 times higher than the f_{exp} values. The lower experimental frequency (f_{exp}) might be attributed to the invalid collision of the emulsion droplets on the UME; that is, the collision of droplets did not lead to an electrochemical reaction, possibly owing to incomplete contact on the UME. The adsorption of the injected emulsion droplet on the surface of the electrochemical cell and glass sheath of the electrode also reduced the experimental collision frequency.

Upon adsorption of the emulsion droplet onto the Pt UME, the electrochemical reaction started instantly on the biased Pt UME. The electrolysis of water molecules in the emulsion droplets exhibited a high current magnitude because the tiny droplets contained a highly condensed reactant (i.e., 55.6 M water molecules). The shape of the anodic current peaks showed a sharp increase and exponential decay with time. The current peaks were analyzed to determine the size of each water droplet. Therefore, the number of charges from each collision event was calculated by integrating the peak areas in CA. Assuming a spherical droplet, the diameter of each droplet (d_{drop}) was calculated using Equation (3).

$$d_{drop} = \sqrt[3]{\frac{6Q}{n\pi F C_{redox}}} \quad (6)$$

where Q is the measured charge and n is the number of electrons transferred per molecule. F is the Faraday constant and C_{redox} is the concentration of the redox species in a droplet. In our experiments, the electrochemical redox species is water. Therefore, the water concentration in the droplets was ca. 55.6 M. During oxidation, each water molecule generates two electrons. Therefore, n is 2.

The size distribution of the droplets, calculated using Equation (6), is shown in Figure 5 (blue bars), and that obtained from the DLS measurements is shown in Figure 5 (red line). Previous studies using electroactive redox species have demonstrated similar size distributions using both the electrochemical collision method and DLS measurements [22,34]. However, in our experiments, comparing each average size obtained through the electrochemical collision method (~171 nm) and DLS measurements (~363 nm), the two results indicated considerable differences. The size of the emulsion droplets obtained electrochemically was underestimated because the oxidation of water molecules in the droplets did not proceed completely until the water was depleted. During the oxidation of water in a neutral solution, two water molecules produce one oxygen molecule and four protons. The produced oxygen molecules can form bubbles at the interface of the electrode, which can lead to a loss of electrical connection between the droplet and the UME, hindering the complete electrolysis of the water molecules in the droplet.

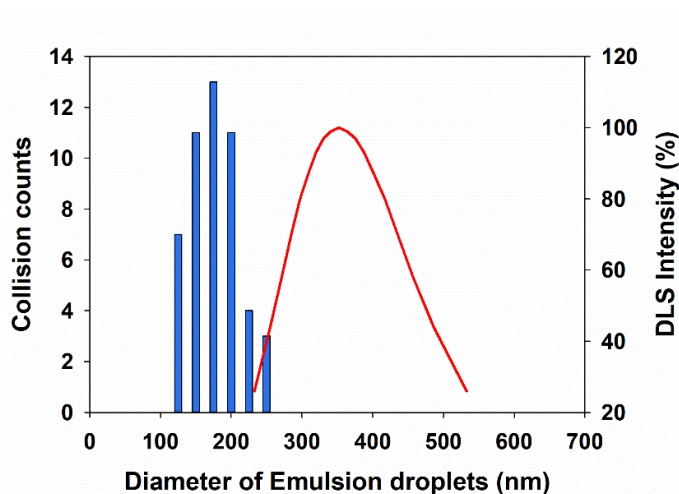
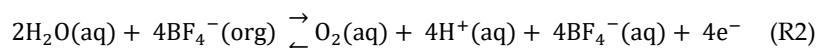


Figure 5. Comparison of the size distribution between the single W/O (water-in-oil) emulsion collision method (blue bars) and DLS measurement (red line).

By comparing the underestimated size and actual size of the droplets, the number of water molecules in the droplets that are oxidized can be calculated. Please note that the average size of the droplets from DLS measurement can contain large errors because the droplets are a polydisperse sample rather than a monodisperse. When a large particle is included in the sample, the large particle can have strong scattering and also can partly disturb the weaker scattering from the small particles. More accurate results could be obtained by using nanoparticle tracking analysis (e.g., Nanosight). If the water molecules in the 363 nm diameter (obtained from DLS) droplets react completely, a 269 pC of charge should be generated. The average charge obtained from the same sample using the electrochemical collision method was 28 pC. Comparing these two charge values, we can conclude that roughly ~ 10% of water molecules in the droplet were electrochemically oxidized, and the remainder were not oxidized. This result is significantly enhanced from a previous report of the 0.81% electrolysis efficiency in an electrolyte-free organic solvent [21]. Owing to the confined size of the reactor (i.e., the emulsion droplets), it is difficult to pump the reaction product out of the reactor for a continuous reaction in the droplets. If the produced charged product (e.g., protons) is not properly balanced inside the droplet, the electrolysis reaction is halted because charge neutrality inside the droplet is not maintained. The hydrophobic electrolyte anion (BF_4^-), which permeates to the aqueous droplet from the organic electrolyte solution, promotes the electrochemical water oxidation by maintaining the charge balance.



Therefore, we established efficient electrolysis conditions for surfactant-stabilized aqueous droplets in organic solvents based on an understanding of the reaction in a single entity. Using this system, we detected aqueous emulsion droplets without the addition of additional redox species. Furthermore, this principle can elevate water electrolysis efficiency under neutral conditions. In the bulk electrolysis of the water continuum, the adsorption of bubbles on the electrode surface results in a high ohmic potential drop and a large reaction overpotential. The efficient electrolysis of water emulsion droplets in an organic medium can be studied by reducing bubble adsorption on the electrode surface and controlling the hydrophobic surfactant on an organic solution.

4. Conclusions

Herein, we describe the electrochemical detection of surfactant-encapsulated aqueous droplets in organic electrolyte solutions. Previous studies on surfactant-free water

droplets have utilized the direct oxidation of solvent molecules in a pure organic solution. However, in the presence of a surfactant (e.g., an emulsifier) in an organic solvent, the water molecules are not electrochemically oxidized. In our experiments, the water molecules in the emulsion droplets are electrolyzed using a hydrophobic electrolyte. Although the water oxidation partly proceeds in an electrolyte-free organic solvent (0.81%), more efficient electrolysis occurs in an organic solvent in the presence of hydrophobic electrolytes. By enhancing the electrolysis efficiency, a high signal-to-noise ratio can be obtained for the electrochemical detection of emulsion droplets. Therefore, the electrochemical detection of nano/microdroplets can be utilized in the study of electrochemical sensors. Furthermore, this principle can be applied to elevate water electrolysis efficiency under neutral conditions.

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