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Communication

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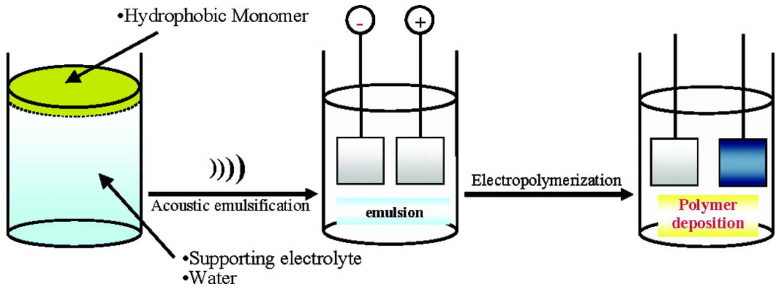

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Electropolymerization of an Immiscible Monomer in Aqueous Electrolytes Using Acoustic Emulsification

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Water is a most ideal medium for synthetic chemistry from the aspects of operational costs, safety, and greening,[1] but many organic materials are water-insoluble or only sparingly soluble. To overcome the solubility problem in water, synthetic processes employing surfactant-stabilized emulsions and suspensions have been developed. However, the presence of surfactants might cause other problems, such as difficulty in their separation from the reaction mixtures and production of wastes, and therefore, it is desired to conduct emulsion synthetic processes in the absence of surfactants.

Although electrosynthesis has been established as a powerful tool in organic and polymer syntheses, it still is in the development stage to fulfill its potential as a "green" methodology. In this situation, the electrochemical transformations of immiscible materials in aqueous electrolytes have been also investigated.[2] Mechanically stirred emulsions of immiscible liquid materials in water can be electrolyzed,[3] but generally, it is not possible to obtain high electron transfer rate between the droplet and the electrode since the size of droplets is usually larger than the micrometer range. Hence, the use of special surfactants allowing solubilization of the immiscible materials as microemulsions (where the oil droplets are typically between 10 and 100 nm in diameter) in aqueous media was unavoidable to obtain a practical reaction rate.[4,5]

On the other hand, ultrasonic irradiation provides stable emulsions without the need for surfactants simply by mechanical forces which arise at the liquid/liquid phase boundaries.[6] This has been termed "acoustic emulsification". Furthermore, it is also known that emulsions prepared by acoustic emulsification have the characteristic of giving narrow droplet size distributions in the submicrometer range.[7] Hence, it can be expected that these droplets would be electrolyzed smoothly at the electrodes, and therefore, a practical reaction rate would be obtained even without any emulsifying reagents. Herein, we wish to report the realization of direct electropolymerization of an immiscible monomer, such as 3,4-ethylenedioxythiophene (EDOT), in aqueous media using an acoustic emulsification. EDOT is the most intensively investigated monomer in the past decade because of the very high conductivity and excellent environmental stability of its polymer (PEDOT).[8]

The demulsification of EDOT emulsified in aqueous media containing 1.0 M $LiClO_4$ was monitored at 25 ± 2 °C with photographic recording. As shown in Figure 1, the demulsification was observed immediately after emulsification by mechanical stirring, while the turbidity still remained even for 60 min after the ultrasonic treatment. In addition, by the dynamic light scattering method, the mean size of EDOT droplets formed by the acoustic emulsification was found to be 211 nm.[9]

Immediately after the emulsification, the electropolymerization of EDOT was carried out by a cyclic potential scanning for 50 cycles in the range of -1.0 to $+1.2$ V vs SCE, at 50 mV s^{-1}. Figure 2 shows cyclic voltammograms in the course of the electropolymerization from both mechanically and acoustically emulsified solutions and an untreated solution. From the oxidation and reduction peak currents of the voltammograms, the polymerization was found to hardly proceed in an untreated solution, and the rate was gradually decreased during the potential scanning in mechanically emulsified solution.

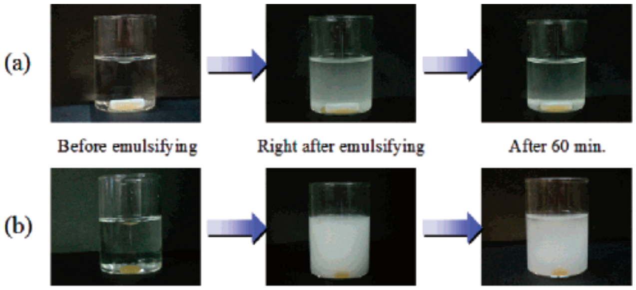

Figure 1. Photographic observations of emulsification and demulsification of EDOT (7.5 mmol) in 1.0 M $LiClO_4$ aqueous solution. Emulsifying method: (a) mechanical stirring (1500 rpm), (b) ultrasonication (20 kHz, 22.6 W cm^{-2}) for 60 s.

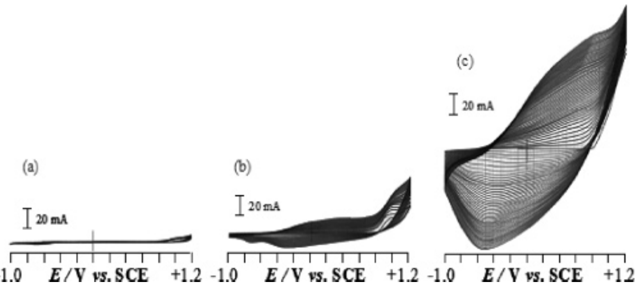

Figure 2. Cyclic voltammograms for electropolymerization of EDOT (7.5 mmol) with 50 cycles of potential scanning in 1.0 M $LiClO_4$ aqueous solution untreated (a) and emulsifying treated by mechanical stirring (1500 rpm, b) and ultrasonication (20 kHz, 22.6 W cm^{-2}, c).

In sharp contrast, the polymerization proceeded very smoothly, and the progress of the polymerization could be observed clearly even after 50 cycles of scanning in acoustically emulsified solution.[10] However, the polymerization of the emulsified EDOT hardly occurred in 1.0 M Li_2SO_4 and 1.0 M $LiNO_3$ aqueous solutions, although stable droplets having the submicrometer size were obtained by the ultrasonic treatment. It is well-known that $LiClO_4$ is relatively soluble in an organic medium. In fact, it was found that ca. 4.0 ppm of the lithium ion could be detected from EDOT droplets in 1.0 M $LiClO_4$ aqueous solution by inductively coupled plasma spectrometry (ICP), while microdroplets in both 1.0 M Li_2SO_4 and 1.0 M $LiNO_3$ aqueous solutions hardly contained any lithium ion. From the above facts, it is likely that the electron transfer takes place between the electrode and droplets of the monomer but not the monomer dissolved in an aqueous phase (Figure 3). In this kind of electron-transfer system, $LiClO_4$ dissolved in the droplets should play the role of the supporting electrolyte and contribute to the formation of an electric bilayer inside the droplets.

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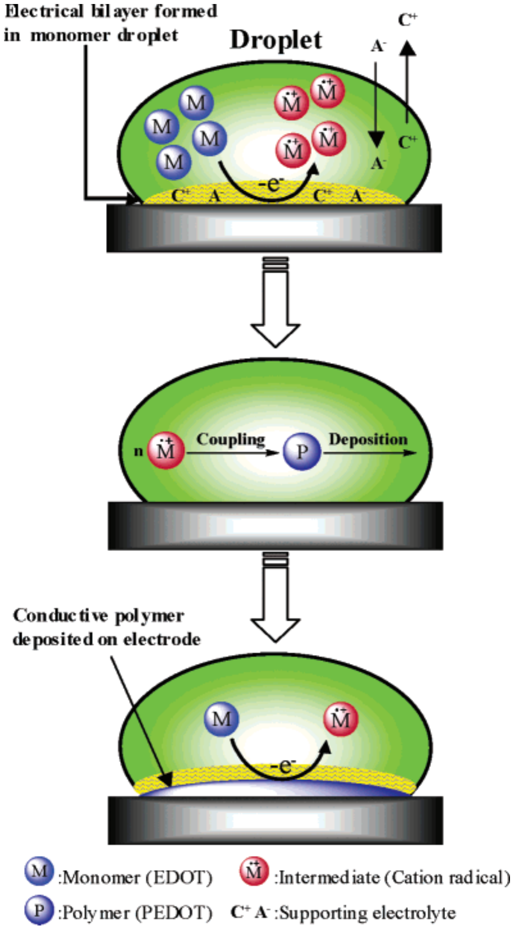

Figure 3. Schematic illustration of the polymerization of an immiscible monomer, such as EDOT, in an aqueous solution.

The electrical conductivity of PEDOT films deposited electrochemically on the anode substrate from the acoustically emulsified solution was also measured by the four-probes method, and it was found to be ca. 30 S cm^{-1}. It is well-known that conductivities of PEDOT films generally range from 1 to 100 S cm^{-1}. Thus, the electrical conductivity of the film obtained by the present procedure is comparable to that obtained by the conventional methods, including the chemical and electrochemical polymerizations in organic solvents.[8a,b,11]

In summary, we have developed a novel electropolymerization of an immiscible monomer, such as EDOT, in aqueous electrolytes using acoustic emulsification. This new methodology has many practical advantages and characteristics: (a) the formation of stable monomer droplets in aqueous electrolytes without added surfactants using ultrasonic treatment; (b) very smooth electropolymerization in aqueous electrolytes via the direct electron transfer between the electrode and the immiscible monomer droplets; (c) good conductivity after doping of the polymer film formed. It is hoped that the present methodology will be applied to various electrochemical reactions that are useful for polymer and organic syntheses.

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Supporting Information Available: Materials and procedures for emulsification treatment, polymerization, electrical conductivity, supporting electrolyte concentration in organic (EDOT) phase, DLS measurements, and SEM photographs. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) See Supporting Information.

(10) From SEM photograph of PEDOT film, large grains were deposited on the anode substrate; see Supporting Information.

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