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Electrochemically Focus-Tunable Convex Lenses by Oil-Sessile Drop

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A sessile drop of nitrobenzene (NB) mounted on the transparent electrode immersed in the aqueous solution works as an optical lens of which focus can be controlled by electrode potential when the solution includes $K_3Fe(CN)_6$ and tetrapentylammonium (TPA⁺) chloride. $K_3Fe(CN)_6$ functions as a redox species, whereas TPACl does as supporting electrolyte as well as a surfactant. The focal length decreases in the reduction potential domain. The switching between the long and the short focuses is almost reversible for 1 h by the potential control, synchronized with voltammograms. The size of a real image of an object varies with the potential.
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Electrowetting is a phenomenon of varying a contact angle of a sessile drop on an electrode with electrode voltage.¹ Since it can control the size of drops reversibly,^{1,2} it has been applied³ to transport of microfluidics, laboratory-on-chip made of droplets, adjustable lenses, electronic displays, fast responding electronic paper, and fast micro-switches. Electrodes in these applications are coated with dielectric films in order to avoid electrolysis of liquid,⁴ because voltages required for variation of interfacial tension are as high as 100 V.¹ Voltage as low as 1 V can change the surface tension at the interface between two immiscible electrolytic solutions.^{5,6} The principle of electrowetting is based on variations of surface tension at liquid|electrode interface with electrode voltage. It has been called electrocapillarity, found by Lippmann.⁷

Electrowetting has also been found when faradaic reactions occur, as is exemplified by polarographic maximum currents.⁸ Its interpretation involves complications relevant to redox reactions.^{9,10} Examples are reactions at mercury drop electrodes,¹¹⁻¹⁴ at droplets with liquid|liquid interfaces,^{15,16} by thin film voltammetry,¹⁷ and at three-phase boundaries.¹⁸⁻²⁰ The faradaic reaction-controlled electrowetting occurs in a narrow voltage domain around the redox potential. This technique has been applied to change in size of droplets by voltage.²¹⁻²⁴

The voltage-dependency of the size means that the curvature radius of the sessile drop can be controlled with the voltage. Then the drop may work as a focal length-adjustable lens. This report is devoted to demonstration of the adjustable lenses by the redox reaction-control.

Materials and Methods

Water was deionized and distilled. Nitrobenzene (NB) was purified by dispersing active alumina powder and centrifuging it for 5 min. NB used for films was wet by immersion in water.

The indium-tin oxide (ITO)-coated glass plate (Kuramoto Co.), 40 × 4 mm² with 6.6 Ω sq and 81% transparency, was used for a transparent electrode. It was exposed to ozone gas for 5 min in order to make the ITO hydrophilic. The reference and the counter electrodes were Ag|AgCl (3 M KCl) and platinum wire, respectively. The water phase was deaerated for 20 min before voltammetric run.

A NB drop was formed by injecting a known volume of NB on the electrode. It was immersed in the aqueous solution including $K_3Fe(CN)_6$ + TPACl. The cell structure is illustrated in Fig. 1.

The focal length was regarded as the distance between the electrode and a real image when an object, a black dot 33 mm in diameter on a white paper, was located far from the electrode.

Results and Discussion

When a NB drop was mounted on the pyrolytic graphite electrode (PGE) with a basal plane, the voltammogram in the deaerated aqueous

solution of 2.0 mM $K_3Fe(CN)_6$ + 0.5 M TPACl showed a pair of the peaks at the first scan (Fig. 2a). The peaks are obviously ascribed to the redox reactions of $K_3Fe(CN)_6$ at the uncoated part of the PGE. The cathodic peaks were shifted in the negative direction by 50 mV at scans over the third iterative scan (Fig. 2b). The value of the shifted potential was closed to that of the cathodic peak of the emulsion of NB in aqueous solution including $K_3Fe(CN)_6$ and TPACl. Therefore the shift can be attributed to the reduction of emulsified $Fe(CN)_6^{3-}$ in the NB phase.

We observed the change in the projected area of the drop from the view normal to the electrode during the voltammetry (Fig. 3). The variation occurred at the potentials close to the peak potential in Fig. 2. It is attributable to the redox reaction of $Fe(CN)_6^{3-/4-}$. No variation of *S* was found without $Fe(CN)_6^{3-/4-}$. Since $Fe(CN)_6^{3-/4-}$ is monolayer-adsorbed at the NB|PGE,²⁵ the redox reaction can vary the interaction with TPACl to change the surface tension. The drop shrunk in the cathodic potential domain (Fig. 3, A1). It was difficult to determine the change in the height of the drop accurately. We estimated the height, *h*, from the area, *S*, of the drop in contact with the electrode and the volume of the drop, *V*, on the assumption that the sessile drop is a part of a sphere with radius, *r*. Since the volume and the area are given, respectively, by $S = \pi h(2r - h)$ and $V = \pi h^2(r - h/3)$, elimination of *r* yields $\pi h^3 + 3hS - 6V = 0$, (1). The values of *h* determined from *S* and *V* are 0.18 and 0.11 mm for Fig. 3(A1) and (A2), respectively. These values correspond to the curvature radii, 0.93 and 2.77 mm, of which cross-sections are illustrated in (B1) and (B2). The curvature radii were reproducible for the potential scan. Thus the drop is expected to work as a focus-tunable lens.

We observed a real image of an object, a black dot on a paper, through the NB drop 3.2 mm in diameter which was mounted on the ITO glass. The image was projected on a CCD image sensor of a digital camera. The clear images for the dot, as shown in the inset of Fig. 4, indicate that the sessile drop should work as a convex lens.

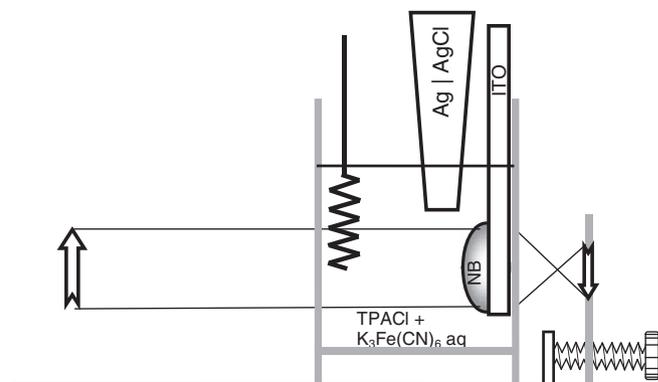


Figure 1. Illustration of the cell structure for measurements of functionality of a lens of a NB sessile drop.

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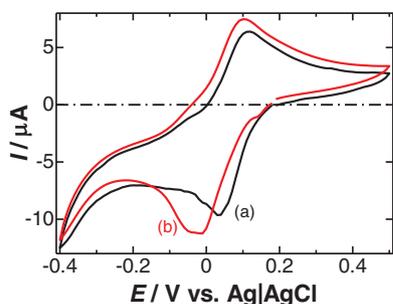


Figure 2. Voltammograms at (a) the first and (b) the third scan at the PGE mounted by a NB drop in 2 mM $K_3Fe(CN)_6$ + 0.5 M TPACl deaerated aqueous solution at the scan rate of 30 mV s^{-1} .

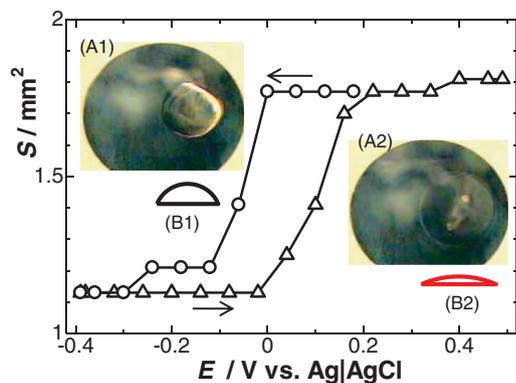


Figure 3. Dependence of the projected areas of the NB drop on the applied potential, and photographs of the 0.1 mm^3 drop at (A1) -0.12 and (A2) 0.30 V under the same conditions as in Fig. 2. Cross sections of the sessile drops, (B1) and (B2), were calculated from Eq. (1) at known values of S and V , for (A1) and (A2), respectively.

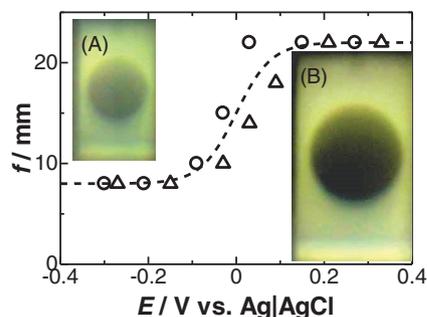


Figure 4. Dependence of the focal length of the NB drop on the electrode potential when the potential was shifted in the (circles) negative and the (triangles) positive directions in 2 mM $K_3Fe(CN)_6$ + 0.1 M TPAC solution. The insets are the real images of the object of a black dot on white paper shot at (A) -0.30 V and (B) 0.18 V.

We determined focal lengths, f , at various potentials by focusing the image. Since the object was located a few meters away from the drop, the distance between the real image and the drop is approximately equal to the focal length. Fig. 4 shows the dependency of f on the potential. The focal lengths varied by 2.5 times with the potential reversibly for 1 h. Hysteresis was found, as was similar to Fig. 3. It varied with scan rates. Speed of the varying focal length could not be measured by the present instrument. The potential variation of f is obviously caused by that of the contact angle owing to the redox reaction. The mechanism will be presented in a succeeding report.

Conclusions

The curvature radius of the NB drop varies with voltage when the drop is immersed into $K_3Fe(CN)_6$ + TPACl aqueous solution. The variation is ascribed to the redox reaction of $K_3Fe(CN)_6$ rather than electrocapillarity. The radii are small in the reduced potential domain. This variation can be applied to a convex lens. Real images are observed in the potential domain of the redox reaction. The focal length vs. the potential curve is a sigmoid. The focal length at the oxidation potential is 2.5 times larger than that at the reduction one.

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