J. Am. Chem. Soc. **1994,** *116,* 6053-6054

Electroless Plating of Organic Thin Films by Reduction of Nonionic Surfactants Containing an Azobenzene Group

Tetsuo Saji,* Ken-ichi Ebata, Kazuhiro Sugawara,
Shunlin Liu, and Ken Kobayashi

Department of Chemical Engineering
Tokyo Institute of Technology
Ohokayama, Meguro-ku, Tokyo 152, Japan

Received March 28, 1994

Redox-switched molecular aggregates are attracting increasing interest. For example, redox-switched complexes of a crown ether with ions,[1] micelles,[2] and vesicles[3] have been reported. Recently, we demonstrated that micelles formed by ferrocenyl surfactants can be dissociated into monomers by electrochemical oxidation,[2] and this phenomenon was applied to the electrochemical formation of organic thin films. Later studies showed that such techniques can be used to prepare thin films of a wide variety of organic compounds[4] and can be applied to the formation of devices. These methods require oxidative electrolysis and are unsuitable for film formation on base metal substrates, because the base metal substrates oxidize at the ferrocenyl surfactant electrolysis potential needed for film formation (+0.5 V vs SCE).[4]. This disadvantage can be overcome by using a surfactant which loses its amphiphilic function upon reduction. We report nonionic surfactants containing an azobenzene group that allow the formation of an organic thin film on base metals such as copper by electrolysis. We also report the formation of electroless organic films on base metals by simple immersion.

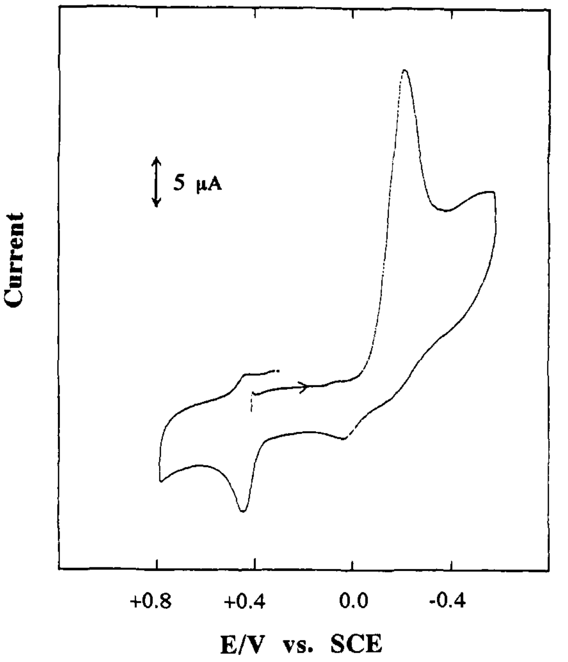
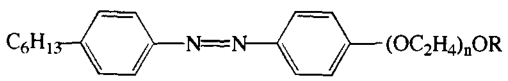


Figure 1. Cyclic voltammogram of 1 mM **1a** in 0.1 M HCl aqueous solution at 25 °C. Scan rate, 300 mV s^{-1}; working electrode (glassy carbon) area, 0.082 cm^2.



1a: n ≈ 16.8, R = CH_3
1b: n ≈ 21.4, R = H

Surfactants **1a** and **1b** were synthesized from 4-[(4-hexylphenyl)azo]phenol.[5] The critical micelle concentration (cmc) of these surfactants in a 0.1 M HCl aqueous solution was determined by the concentration dependence of the molar absorption coefficient to be 11 (**1a**) and 7 μM (**1b**).[6] The cyclic voltammogram (CV) of a 1 mM **1a** and 0.1 M HCl aqueous solution shows an irreversible reduction peak at -0.22 V vs SCE and a small oxidation peak at +0.43 V (Figure 1). After exhaustive controlled-potential electrolysis at -0.30 V overnight, the CV of this solution showed an oxidation peak at +0.42 V and a small adsorption peak at +0.1 V. With time the peak height at +0.42 V decreased. This oxidation peak may be assigned to aniline derivatives. In acidic solution, the reduction of azobenzenes is a four-electron reduction process with cleavage of the nitrogen-nitrogen bond, which leads to formation of the aniline derivatives.[7] Disruption of the micelles of **1a** and **1b** was proved by monitoring the uptake of a water-insoluble dye (aniline blue, **2**). A 1.0 mM **1a** and 0.1 M HCl aqueous solution solubilized 93 μM of **2**. In contrast, a solution of 1.0 mM reduced **1a** solubilized only 1.5 μM of **2**. The difference suggests that the micelles of **1a** are dissociated into monomers by reduction due to an enhancement in hydrophilic character. The results of **1b** were similar to those of **1a**.

As the film-forming materials, β-type copper phthalocyanine (particle size 0.1-0.2 μm, **3**) and perylene vermillion (C. I. Pigment Red 123, 0.03-0.04 μm, **4**), which are not soluble in water, were used. Compounds **3** and **4** may be dispersed by the surfactant, since this pigment is not soluble in most common organic solvents. A dispersion containing 1 mM **1a** (or **1b**), 0.1 M HCl, and **3** (or **4**) was prepared by sonicating the mixture for 10 min and stirring it for 3 days.

Controlled-potential electrolysis of the dispersion containing 1.0 mM **1a**, 10 mM **3**, and 0.1 M HCl at an indium tin oxide (ITO) electrode maintained at -0.50 V was done for 30 min. A transparent blue film was formed on the ITO electrode. Similar

---

(1) (a) Kaifer, A.; Gustowski, D. A.; Echegoyen, L.; Gatto, V. J.; Schultz, R. A.; Cleary, T. P.; Morgan, C. R.; Goli, D. M.; Rios, A. M.; Gokel, G. W. *J. Am. Chem. Soc.* **1985**, *107*, 1958-1965. (b) Echegoyen, L. E.; Hyunsook, K. Y.; Gatto, V. J.; Gokel, G. W.; Echegoyen, L. *J. Am. Chem Soc.* **1989**, *111*, 2440-2443. (c) Medina, J. C.; Goodnow, T. T.; Kaifer, A. E.; Gokel, G. W. In *Electrochemistry in Colloids and Dispersions*; Mackay, R. A., Texter, J., Eds.; VCH: New York, 1992; Chapter 8. (d) Saji, T. *Chem. Lett.* **1986**, 275-276. (e) Saji, T.; Kinoshita, J. *J. Chem. Soc., Chem. Commun.* **1986**, 716-717.

(2) (a) Saji, T. Hoshino, K.; Aoyagui, S. *J. Am. Chem. Soc.* **1985**, *107*, 6865-6868. (b) Saji, T.; Hoshino, K.; Aoyagui, S. *J. Chem. Soc., Chem. Commun.* **1985**, 865-866.

(3) Medina, J. C.; Gay, I.; Chen, Z.; Echegoyen, L.; Gokel, G. W. *J. Am. Chem. Soc.* **1991**, *113*, 365-366.

(4) (a) Hoshino, K.; Saji, T. *J. Am. Chem. Soc.* **1987**, *109*, 5881-5883. (b) Saji, T. *Chem. Lett.* **1987**, 547-550. (c) Saji, T.; Hoshino, K.; Ishii, Y.; Goto, M. *J. Am. Chem. Soc.* **1991**, *113*, 450-456.

(5) Compound **1a** was prepared by the reaction of 4-[(4-hexylphenyl)-azo]phenol (AZOH) with α-methyl-ω-bromopoly(oxy-1,2-ethanediyl) (average MW ≈ 830) in 2-butanone in the presence of K_2CO_3: viscous solid, UV-vis (methanol) 349 nm ($\epsilon = 3.5 \times 10^4$); ^1H NMR ($CDCl_3$, 300 MHz) δ 0.88 (3H, CH_3-), 1.32 (6H, -CH_2-), 1.65 (2H, Ar-CH_2CH_2-), 2.67 (2H, Ar-CH_2-), 3.38 (3H, -OCH_3), 3.65 (63H, -OCH_2CH_2O-), 3.89 (2H, $ArOCH_2CH_2$-), 4.21 (2H, $ArOCH_2$-), 7.02-7.91 (8H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$ as solvent and internal standard [δ = 77.0]) δ 13.8, 22.3, 28.7, 31.0, 31.5, 35.6, 58.8, 67.5, 69.5, 70.4, 70.7, 71.8, 114.7, 122.5, 124.4, 129.0, 145.8, 147.1, 151.0, 161.0. Anal. Calcd for $C_{52.6}H_{91.2}N_{2.0}O_{17.8}$: C, 60.95; H 8.87; N, 2.70. Found: C, 60.60; H, 8.32; N, 2.79. Compound **1b** was prepared from AZOH in two steps. The reaction of AZOH with 1,2-dibromoethane in 2-butanone in the presence of K_2CO_3 gave [4-(2-bromoethoxy)phenyl][4-hexylphenyl]-diazene. This compound was converted to **1b** by the Williamson reaction with α-hydro-ω-hydroxypoly(oxy-1,2-ethanediyl) (average MW ≈ 1000) in 1,2-dimethoxyethane using NaH: solid, UV-vis (methanol) 349 nm ($\epsilon = 3.6 \times 10^4$); ^1H NMR δ 0.88 (3H, CH_3-), 1.32 (6H, -CH_2-), 1.65 (2H, Ar-CH_2CH_2-), 2.68 (2H, Ar-CH_2-), 3.64 (81.6H, -OCH_2CH_2O-), 3.90 (2H, $ArOCH_2CH_2$-), 4.23 (2H, $ArOCH_2$-), 7.03-7.91 (8H, ArH); ^{13}C NMR δ 13.9, 22.4, 28.8, 31.1, 31,5, 35.7, 61.6, 67.6, 69.5, 70.2, 70.5, 70.6, 70.8, 72.5, 114.8, 122.5, 124.5, 129.0, 145.9, 147.2, 151.0, 161.1. Anal. Calcd for $C_{60.8}H_{107.4}$-$N_{2.0}O_{22.4}$: C, 59.65; H, 8.78; N, 2.29. Found: C, 60.15; H, 8.91; N, 2.58.

(6) Hoshino, K.; Saji, T.; Suga, K.; Fujihira, M. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 2667-2676.

(7) See: Thomas, F. G.; Boto, K. G. In *Chemistry of the Hydrazo, Azo and Azoxy Groups Part 1*; Patai, S., Ed.; John Willey & Sons: London, 1976; Chapter 12, p 469.

0002-7863/94/1516-6053$04.50/0

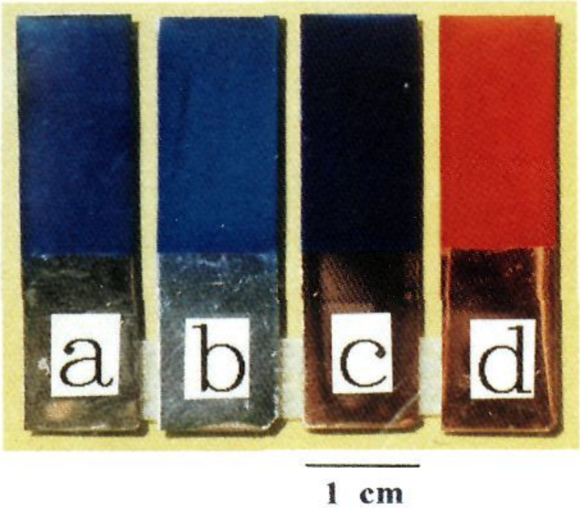


Figure 2. Photograph of the films prepared by immersing the substrate in the dispersion containing 1 mM **1a** (or **1b**), pigment and 0.1 M HCl for 20 min. (a) **1a**, 10 mM **3**, and nickel (substrate); (b) **1a**, 10 mM **3**, and aluminum; (c) **1b**, 15 mM **3**, and copper; (d) **1b**, 15 mM **4**, and copper.

blue films of **3** were also obtained on copper and stainless steel plates using the same electrolysis. In addition, a blue film of **3** was formed on copper, iron, lead, tin, zinc, nickel, and aluminum plates[8] by immersing them in the dispersion for 20 min without electrolysis (Figure 2a,b). Films of **3** and **4** were also formed by immersing these metal plates in a dispersion containing 1.0 mM **1b**, 15 mM **3** (or **4**), and 0.1 M HCl for 20 min (Figure 2c,d). However, a film was not formed on the ITO, silver, palladium, and platinum plates without electrolysis. Such electroless plating may be explained by the chemical reduction of **1a** and **1b** with the substrate, since the standard potentials of base metals are more negative and those of noble metals are more positive than those of **1a** and **1b** (approximately –0.1 V vs SCE at pH 1). Absorption spectra of aqueous dispersions prepared by washing these films with a 5 mM Brij 35 aqueous solution consisted of broad peaks and were very similar to that for an 5 mM Brij 35 aqueous dispersion of **3**.[9] The scanning electron micrograph of a cross section of the **3** film on a copper plate shows that the film is of uniform thickness (1 μm for 30 min immersion) and is composed of 0.1–0.2-μm particles which are the same as those used for dispersion (Figure 3). These agreements indicate that these films are mainly made of **3** and the crystalline form of **3** is maintained throughout the film preparation processes.

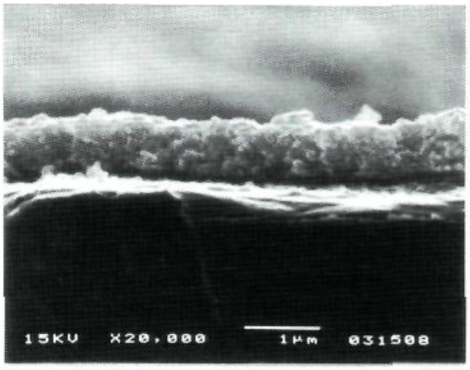


Figure 3. Scanning electron micrograph of cross section of a film prepared by immersing a copper plate in a dispersion containing 1 mM **1b**, 15 mM **3**, and 0.1 M HCl for 30 min.

Such film formation may be explained by the same mechanism as that using the ferrocenyl surfactant:[4a] **1a** (or **1b**) is reduced to the aniline derivative by the base metal, which loses its function as a surfactant due to enhancement of the tail group's hydrophilicity. The concentration of the surfactant in the vicinity of an electrode decreases to less than the cmc. The surfactant adsorbed on the particles is desorbed, which leads to the deposition of the particles on the electrode.

Present experiments show that the use of surfactants **1a** and **1b** makes it possible to prepare a thin film of an organic compound on a wide variety of conducting materials with or without electrolysis.

Acknowledgment. We thank Mr. R. Ohki for the electron micrograph data. This work was partially supported by a grant from the Iketani Science and Technology Foundation (No. 041029A) and by a Grant-in-Aid on Priority Areas from the Ministry of Education, Science and Culture of Japan (No. 06226221).

---

(8) These metal plates were cleaned by polishing with the metal polishing reagent PIKAL (Nihon Maryo-Kogyo Co., Ltd.) followed by sonication with acetone and chloroform for 5 min.

(9) Saji, T.; Ishii, Y. *J. Electrochem. Soc.* **1989**, *136*, 2953–2956.