

Formation of Copper Phthalocyanine Films by Electrophoretic Deposition

Naoki Sato and Tetsuo Saji*

Department of Chemical Engineering, Tokyo Institute of Technology, Ohokayama, Meguro-ku, Tokyo 152-5882

(Received March 11, 1998; CL-980179)

A copper phthalocyanine (**1**) film was formed on an indium-tin oxide (ITO) electrode with a short deposition time by electrophoretic deposition using a 2-butanone dispersion containing **1** and a small amount of iodine. A spectroscopic study showed that the crystalline form of **1** is maintained throughout the film formation processes.

Films of copper phthalocyanine (**1**) and its derivatives continue to be the subject of numerous studies due to the following reasons:¹ (i) they are applicable to many devices as thin films; (ii) they are the most stable of the phthalocyanine compounds; and (iii) a variety of halogenated derivatives are commercially available. The technique for the preparation of these films is limited to vacuum sublimation because of their insolubility in most of organic solvents. Previously, we demonstrated the formation of a **1** thin film by the electrochemical oxidation of surfactants containing a ferrocenyl group.^{2,4} Furthermore, we reported the electroless plating of a **1** thin film by the reduction of the surfactant having an azobenzene group.⁵ On the other hand, formation of the phthalocyanine film using the electrophoretic deposition technique has not been reported except for a few cases in spite of many reports on the film formation of inorganic compounds using this technique.⁶

In this paper, we report the formations of **1** films by an electrophoretic technique, which enables control of the crystalline structure of the **1** film and a short film deposition time. In this technique, small charged particles are deposited onto the substrate under an applied electric field. In many cases, the adsorption of a proton on a particle has been used to obtain charged particles.⁷⁻¹² To get charged particles, we used the 2-butanone (acetone)/iodine system.^{12,13}

In this experiment, we mainly used 2-butanone in place of acetone due to its lower volatility than acetone. As the film-forming material, α -, β - and ϵ -type copper phthalocyanines (particle size 0.1–0.2 μm , **1a-c**, Dainichiseika Color & Chemicals (**1a**, **1b**), BASF Japan, Ltd. (**1c**)) were used. A 2-butanone dispersion containing iodine and **1** was prepared by twice sonicating the mixture for 10 min (Tomy Seiko Ultrasonic Disruptor Model UR-200P). **1** soon precipitated without iodine. The ITO and glassy carbon plates were used as cathodic and anodic electrodes, respectively. The distance between these two electrodes was kept at 1.0 cm. Film formations were done at 25°C.

Transparent blue films of **1a-c** were formed on the cathodic plate (ITO) by application of 30 V cm^{-1} between these two plates in a 2-butanone dispersion containing 0.7 mM (1 M = 1 mol dm^{-3}) iodine and 1 mM **1**. A similar blue film was formed using an acetone dispersion of **1b**.

Formation of a dispersion of **1** as a powder is ascribable to the formation of charged particles due to the adsorption of a proton by the reaction of 2-butanone with iodine in the presence of a small amount of water, which was estimated from the acetone/iodine system as shown in the following manner.^{12,13}

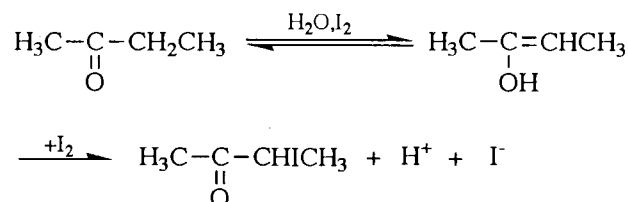


Figure 1 shows the absorption spectra of the **1a-c** films prepared by the electrophoretic deposition technique. The shape of these spectra at 500–800 nm (Q band) depends on the crystalline form of **1** used for the preparation of the dispersion. The frequencies, intensities, and width of the two peaks (Q band) are quite different among the three spectra. These characteristics are quite similar to those of the spectra reported by earlier workers.^{3,14} These results indicate that the crystalline structures of the **1** powders are maintained throughout the film formation processes. These results indicate that we can control the crystalline structure by the electrophoretic technique.

Figure 2a shows a scanning electron micrograph (SEM) of the surface of the **1b** film. This SEM shows that the film is

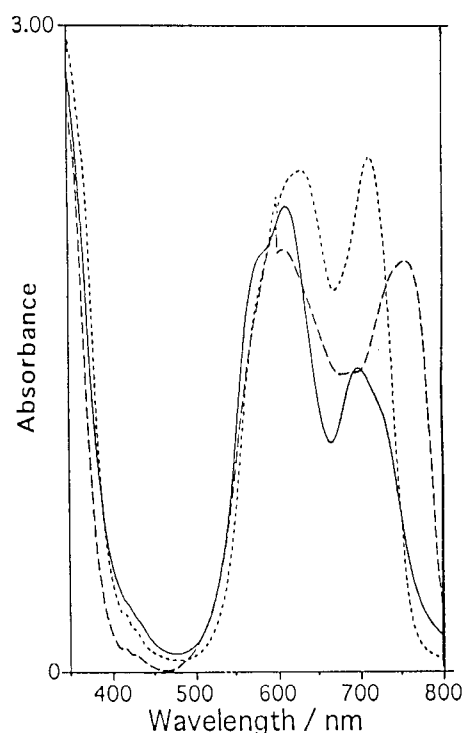


Fig. 1. Absorption spectra of **1** films on the ITO prepared by applying 30 V cm^{-1} for 5 s between the ITO and glassy carbon plates in a 2-butanone dispersion containing iodine and **1**. (—) 1mM **1a** and 0.5 mM iodine; (···) 1mM **1b** and 0.7 mM iodine; (--) 1mM **1c** and 1 mM iodine.

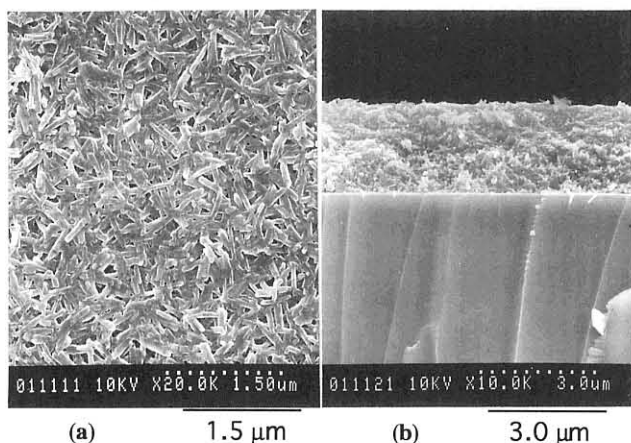


Fig. 2. Scanning electron micrographs of a surface (a) and a cross (b) section of a **1b** film on the ITO prepared by application of 30 V cm^{-1} for 60 s between the ITO and glassy carbon plates in a 2-butanone dispersion containing 1 mM iodine and 1 mM **1b**.

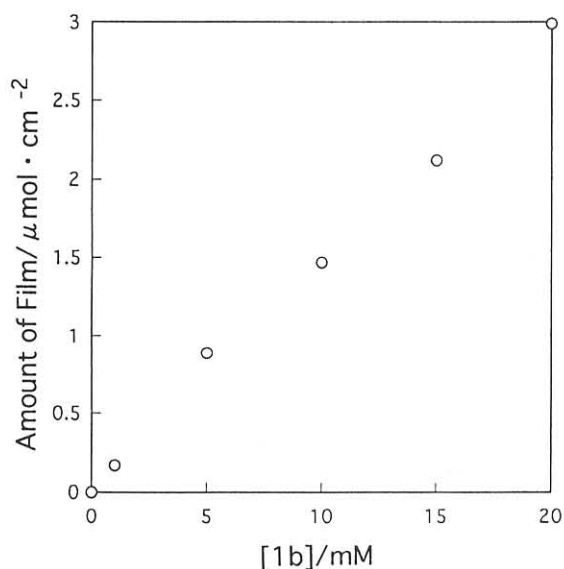


Fig. 3 Amount of the film vs. concentration of **1b**. These films were prepared by applying 30 V cm^{-1} between the ITO and glassy carbon plates in a 2-butanone dispersion containing 0.7 mM iodine and **1b** for 10 s.

composed of $0.1\text{--}0.2 \mu\text{m}$ particles. The shape and the length of these particles are the same as those used for the preparation of the dispersion. These results also support the conclusion from the above absorption spectra. The SEM of the cross section (Fig. 2b) shows that the thickness of the film is uniform. The thickness of the **1b** film was 1.2 and $2.3 \mu\text{m}$ for deposition time of 10 and 60 sec, respectively. The amount of the film increases with the concentration of **1b** (Fig. 3). When a dispersion containing 20 mM **1b** and 0.7 mM iodine was used, the thickness was $28 \mu\text{m}$ for the 10 s deposition time. Such a short deposition time may be an advantage over other methods.

To our knowledge, this is the first report of the formation of the **1** film using an electrophoretic deposition technique. Such an electrophoretic deposition technique provides a convenient method to prepare the films of copper phthalocyanine compounds.

This work was partially supported by a Grant-in-Aid for Scientific Research of the Priority Area of "Electrochemistry of Ordered Interfaces" (No. 09237221 and 10131221) from the Ministry of Education, Science, Sports and Culture, Japan.

References

- 1 For recent reviews, see: "Phthalocyanines: Properties and Applications", ed by C. C. Leznof, **1** (1989); **2** (1993); **3** (1993); **4** (1996).
- 2 T. Saji, *Chem. Lett.*, **1988**, 693.
- 3 T. Saji and Y. Ishii, *J. Electrochem. Soc.*, **136**, 2953 (1989).
- 4 T. Saji, K. Hoshino, Y. Ishii, and M. Goto, *J. Am. Chem. Soc.*, **113**, 450 (1991).
- 5 T. Saji, K. Ebata, K. Sugawara, S. Liu, and K. Kobayashi, *J. Am. Chem. Soc.*, **116**, 6053 (1994).
- 6 For example, K. Sekiya, Z. Kanazawa, and Y. Miyamoto, *Extended Abstracts of The 53rd Autumn Meeting of The Japan Society of Applied Physics*, **3**, 1039 (1992).
- 7 K. Tamaribuchi and M. L. Smith, *J. Coll. Interface Sci.*, **22**, 404 (1966).
- 8 M. Barraclough, N. E. Bolton, A. H. Collins, and J. M. Andrews, *IEEE Trans., Magnetics*, **MAG-3**, 531 (1967).
- 9 R. W. Powers, *J. Electrochem. Soc.*, **122**, 490 (1975).
- 10 J. H. Kennedy and A. Foissy, *J. Electrochem. Soc.*, **122**, 482 (1975).
- 11 S. Sugiyama, A. Takagi, and K. Tsuzuki, *Jap. J. Appl. Phys.*, **30**, 2170 (1991).
- 12 Y. Tokuoka, T. Kishi, and T. Nagai, *DENKI KAGAKU*, **42**, 80 (1974).
- 13 N. Koura, T. Tsukamoto, H. Shoji, and T. Hotta, *J. Appl. Phys.*, **34**, 1643 (1995) and references therein.
- 14 E. A. Lucia and F. D. Verderame, *J. Chem. Phys.*, **48**, 2674 (1968).