

Photoelectrochemical Synthesis of Phthalocyanine

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Phthalocyanine has been synthesized photoelectrochemically with high current and quantum efficiencies at various p-type semiconductor electrodes. The reaction was followed by monitoring the absorption peak at 667 nm, which corresponds to phthalocyanine anion. Production of phthalocyanine was confirmed by X-ray diffraction, IR and UV-VIS spectroscopy, and elemental analysis. The highest current efficiency was 75%, and *ca.* 1 V was saved by using p-GaP as a photoelectrode compared with dark electrolysis at a gold electrode. Detailed study showed that a photoelectrochemically-formed intermediate was thermally converted to phthalocyanine anion (Pc^{2-}).

Phthalocyanine derivatives have quite interesting properties and are considered to have many useful applications such as dyes, organic conductors, sensors, photoactive materials and catalysts.¹ They are usually synthesized chemically, but the synthesis reaction requires high temperature and prolonged reaction time.^{2,3} Electrochemical syntheses of metal and metal-free phthalocyanines have been attempted and seem to be possible alternative routes.^{4,5}

In this paper, we report the photoelectrochemical synthesis of phthalocyanine (PcH_2) from phthalonitrile (PN) on various p-type semiconductor electrodes in ethanol and make it clear that the reaction proceeds with two steps, *i.e.*, the production of some intermediate by photoelectrochemical reduction of phthalonitrile and the formation of phthalocyanine from the intermediate in the dark at high temperatures.

Experimental

Phthalonitrile (>95%), ethyl alcohol (reagent grade, >99.5%) and lithium chloride (reagent grade) were purchased from Wako Pure Chemicals and were used without further purification. Single crystals of p-InP (Zn: $1.8 \times 10^{18} \text{ cm}^{-3}$), p-GaP (Cd: $2.8 \sim 4.4 \times 10^{17} \text{ cm}^{-3}$) and p-GaAs (Zn: $2.4 \times 10^{18} \text{ cm}^{-3}$) were obtained from Varian Associates, Fujitsu Laboratories and Morgan Semiconductor, respectively. Ohmic contacts were made by using an In-Zn alloy. Semiconductor electrodes were etched in HNO_3 -HCl (1:1) and rinsed with Milli-Q water and then with ethanol prior to the experiments.

Photoelectrochemical measurements were carried out in a three-compartment cell with an optical window and a water jacket through which temperature-controlled water was circulated. A Pt-Pt plate and an Ag/AgCl electrode were used as a counter and a reference electrode, respectively.

A potentiostat (Hokuto, HA-301) was used to control the potential and an external potential was provided by a function generator (Hokuto, HB-105). Potential-current and current-time relations were recorded on an X-Y-t recorder (Rika Denki, RW-11T).

A 500 W Xe lamp (Ushio, UXL500D-0) with an IR absorbing filter (Toshiba, IRA-20) was used as a light source. Light intensity was determined by using an optical meter (Anritsu, ML94A with MA-97A detector).

All the measurements and constant potential electrolysis were carried out in an ethanol solution containing 0.7 mol dm^{-3} LiCl and 0.1 mol dm^{-3} phthalonitrile. Electrolyte solution was deaerated by passing high purity nitrogen (99.99%) for at least 20 min before each experiment.

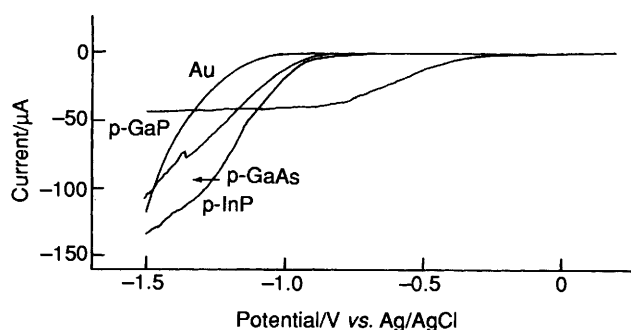


Fig. 1 Current-potential relations of various electrodes in an ethanol solution containing 0.7 mol dm^{-3} LiCl and 0.1 mol dm^{-3} phthalonitrile. Except for gold, the relations were measured under illumination.

Generation of phthalocyanine was followed by monitoring the absorption peak at 667 nm ($\log \epsilon = 5.4$), corresponding to phthalocyanine anion,⁶ by using a UV-VIS spectrometer (JASCO, U BEST-30).

In the case of bulk electrolysis, after the reaction had been terminated, 5 cm^3 of HCl was added to the solution (20 cm^3) and precipitate was collected by a membrane filter (Nucleopore, PC MEMB 2 μm). The reaction product was identified by IR (JASCO, IR-700) and UV-VIS spectroscopy (HITACHI, U3300), X-ray diffraction (Rigaku Denki, Model 2013) and elemental analysis.

Results and Discussion

Current-Potential Relation.—Fig. 1 shows current-potential relations for p-InP, p-GaP and p-GaAs under illumination and of Au in the dark in an ethanol solution containing 0.1 mol dm^{-3} phthalonitrile and 0.7 mol dm^{-3} LiCl at 75°C . While the current becomes significant when the potential is more negative than -1 V at a gold electrode in the dark, photocurrent starts to flow at more positive potentials at all semiconductor electrodes investigated. The order of shift is p-GaP ($E_g = 2.5 \text{ eV}$) > p-GaAs (1.4 eV) > p-InP ($E_g = 1.3 \text{ eV}$) and seems to be related to the energy gap of the semiconductor. The smallest shift is at p-InP and the largest at p-GaP.

Confirmation of Phthalocyanine Production.—Fig. 2 shows the visible spectra of an ethanol solution containing 0.1 mol dm^{-3} phthalonitrile and 0.7 mol dm^{-3} LiCl before and after potentiostatic photoelectrolysis for 20, 40 and 60 min at 75°C . The absorption peak around 670 nm, which was absent before

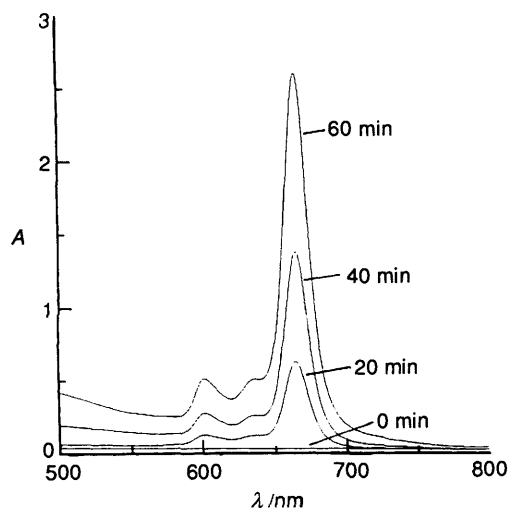


Fig. 2 Absorption spectra of an ethanol solution of the 0.7 mol dm^{-3} LiCl - 0.1 mol dm^{-3} phthalonitrile obtained during photoelectrolysis at p-GaP. The potential was -1.0 eV and the solution temperature was 75°C .

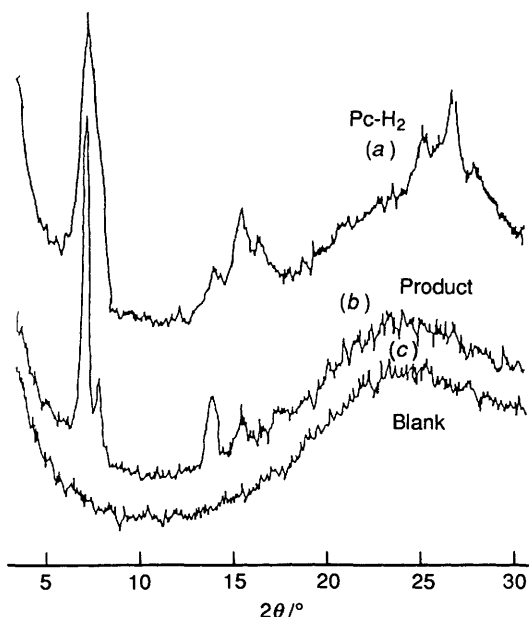


Fig. 3 X-Ray diffraction patterns of commercially available phthalocyanine (top) and the product of the photoelectrolysis (middle). The measurements were carried out for powders pressed on glass. As a comparison, XRD pattern of the glass substrates is also shown (bottom).

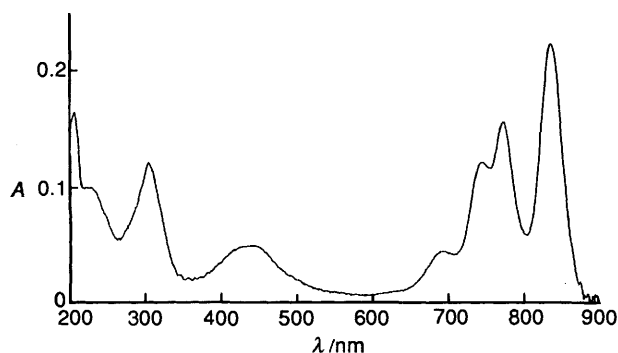


Fig. 4 UV-VIS spectrum of a conc. H_2SO_4 solution of the photoelectrolysis product

the photoelectrolysis, grew with time. The peak position agrees with that of phthalocyanine anion (Pc^{2-}).⁶ No change was observed when the reaction was carried out at room temperature.

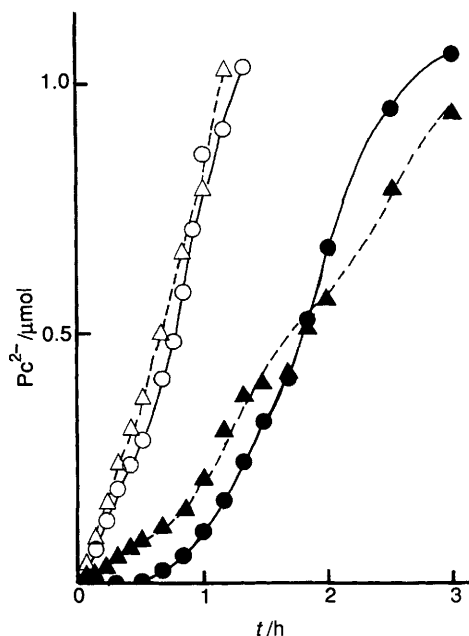


Fig. 5 Time course of Pc^{2-} formation at 75°C after the photoelectrolysis at room temperature. Photoelectrolysis potential and charge passed are: -0.8 V , 1.0 C (●); -1.0 V , 1.0 C (▲); -0.8 V , 1.5 C (○); -1.0 V , 1.5 C (△).

After the reaction had been terminated the solution was acidified by addition of HCl . Black powder was precipitated and the solution became clear. Elemental analysis of the product and phthalocyanine obtained commercially were carried out (C, 75.2; H, 3.3; N, 21.5% for the product and C, 75.0; H, 3.3; N, 21.7% for phthalocyanine) (*cf.* Calc. for phthalocyanine: C, 74.7; H, 3.5; N, 21.8%). IR spectra of the product and phthalocyanine were essentially the same. The above results and X-ray diffraction analysis (Fig. 3) confirm that the product is phthalocyanine.

The UV-VIS spectrum of a conc. H_2SO_4 solution of the product is shown in Fig. 4 and coincides with that of commercially available phthalocyanine, suggesting that the product is phthalocyanine in monomer form.⁷

Reaction Mechanism.—Although the photoelectrochemical formation of Pc^{2-} was not observed at room temperature as mentioned above, Pc^{2-} did form if the solution was heated after the photoelectrolysis had been carried out at room temperature. Fig. 5 shows the time course of Pc^{2-} formation when the solution was heated to 75°C just after the photoelectrolysis had been carried out at room temperature by using p-GaP as an electrode. Obviously there is no clear difference between the time course obtained for the solution photoelectrolysed at -0.8 V and that at -1.0 V since the charge passed is the same. The more charge was passed the faster the formation of Pc^{2-} . No change was observed if the solution was heated without photoelectrolysis. These results suggest that a certain intermediate is formed during the photoelectrolysis, even at room temperature, and is converted to Pc^{2-} by heating. Thus, the concentration of the intermediate controls the conversion rate.

Fig. 6 shows the time course of Pc^{2-} formation when the solution had been heated to various temperatures just after 1.0 C had been passed by photoelectrolysis at room temperature by using p-GaP as an electrode at -1.0 V . Not only was the formation rate higher, but also the final concentration if heated at higher temperatures. When the heating temperature was low, the absorption peak around $500\text{--}550 \text{ nm}$ grew, suggesting that the intermediate was converted to some species different from Pc^{2-} .

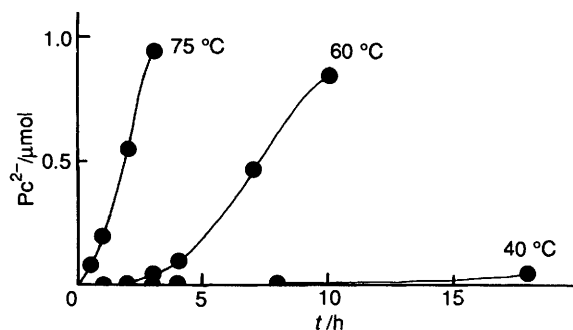


Fig. 6 Temperature dependence of Pc^{2-} formation, after the photoelectrolysis at room temperature. Photoelectrolysis potential and charge passed are -1.0 V and 1.0 C respectively.

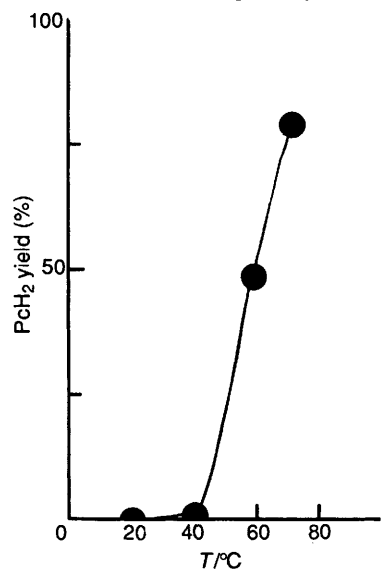


Fig. 7 Temperature dependence of final yield (quantum efficiency) of phthalocyanine. Experimental conditions are same as those in Fig. 6.

The temperature dependence of final yield (current efficiency) was also studied by actually measuring the mass of phthalocyanine. After photoelectrolysis at room temperature, the solution was heated to a certain temperature. The photoelectrolysis was carried out at p-GaP at -1.0 V and the charge passed was 1.0 C. The formation of Pc^{2-} was followed by UV-VIS measurement and HCl was added after prolonged heating to provide confirmation that the spectra did not change any more. Phthalocyanine was collected by the method mentioned before and its mass was measured. Current efficiency was calculated by assuming the following reaction scheme (1).



Fig. 7 shows the temperature dependence of the current efficiency. The current efficiency reached 78% at 75 °C. An almost negligible amount of phthalocyanine was formed below 40 °C. These results are essentially in good agreement with the results shown in Fig. 6.

If the heating was not carried out immediately after the photoelectrolysis, the yield was quite low even if the heating temperature was very high, suggesting the participation of a short-lived intermediate. If O_2 gas was passed after the photoelectrolysis and before the heating, the yield became ca. 50%. As already reported, phthalocyanine is not formed by the electrolysis of phthalonitrile in non-aprotic solvents such as DMF and acetonitrile, although the phthalonitrile radical is generated.⁸ Furthermore, it has been reported that alcohols play an important role in the chemical synthesis of phthalocyanine from phthalonitrile.⁹ Thus, we can conclude that (photo)electrolysis generates some intermediate, possibly radical anion from ethanol, and that the intermediate is converted to Pc^{2-} thermally.

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References

- 1 P. Sayer, M. Gouterman and C. R. Connell, *Acc. Chem. Res.*, 1982, **15**, 73.
- 2 P. A. Barrett, C. E. Dent and R. P. Linstead, *J. Chem. Soc.*, 1936, 1719.
- 3 H. Tomoda, S. Saito, S. Ogawa and S. Shiraishi, *Chem. Lett.*, 1980, 1277.
- 4 C. H. Yang, S. F. Lin, H. L. Chen and C. T. Chang, *Inorg. Chem.*, 1980, **19**, 3541.
- 5 M. A. Petit, V. Plichon and H. Belkacemi, *New J. Chem.*, 1989, **13**, 456.
- 6 P. Turek, J. J. Andre, A. Girandean and J. Simon, *Chem. Phys. Lett.*, 1987, **134**, 471.
- 7 M. Yudasaka, K. Nakanishi, T. Hara, M. Tanaka and S. Kurita, *Jpn. J. Appl. Phys.*, 1985, **24**, L887.
- 8 A. Gennard, F. Maran, A. Maye and E. Vianello, *J. Electroanal. Chem.*, 1985, **185**, 353.
- 9 H. Tomoda, E. Hibiya, T. Nakamura, H. Ito and S. Sato, *Chem. Lett.*, 1976, 1003.

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