In-Situ UV-Visible Spectroscopic Behavior of Copper Tetrakis(*n*-butoxycarbonyl) phthalocyanine and Oxygen Reduction Catalysis

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The physicochemical properties of metal phthalocyanines (MPcs) and their modified forms have received much attention due to their potential applications in the fields of photoelectrochemical reactions,[1] organic semiconductors,[2] analytical applications,[3] catalysis of chemical reactions,[4] and electroreduction of carbon dioxide.[5] In addition to these applications, there are a number of studies on the electrocatalytic reduction of molecular oxygen using transition metal phthalocyanines.[6~9]

We have recently studied the electrochemical and a potential-modulated electroreflectance (ER)[10,11] spectroscopic behavior of copper tetrakis(*n*-butoxycarbonyl) phthalocyanine (tbcCuPc)[12] film adsorbed on a pyrolytic graphite electrode (PGE) using CV and ER techniques. The rate constant of the redox reaction of tbcCuPc on the PGE was evaluated by potential-modulated UV-visible ER spectroscopy. The cyclic voltammogram (CV) exhibits two consecutive one-electron reductions, which are processes occurring at the ligand of tbcCuPc on the PGE. The reduction on the ligand of the complex has also been reported by van den Ham et al. for the CuPc complex.[7] Their results showed that FePc exhibits a specific catalytic activity for the reduction of molecular oxygen, which is related to two consecutive one electron processes of the central metal. However, the cathodic reduction processes do not occur at the central metal in the case of CuPc and ZnPc as well as in our result for tbcCuPc. Zagal *et al.*[4] studied the effect of the metal on the electrocatalytic activity of several transition metal complexes of Pc including CuPc.

We found that the tbcCuPc adsorbed on a pyrolytic graphite electrode (PGE) acted as a catalyst for the reduction of molecular oxygen. Thus, we investigated the electrocatalytic reduction of molecular oxygen and in situ spectroscopic behavior on the tbcCuPc-adsorbed PGE in a phosphate buffer solution.

Experimental Section

In situ UV-visible (vis) spectra were obtained using a spectrometer equipped with an optical fiber, CCD, xenon lamp, etc., supplied by Ocean Optics Co. The CVs of a tbcCuPc solution were obtained with an EG&G PAR 273 potentiostat/galvanostat. Instrumentation for ER measurements was described in a pervious report.[10] Incident angle of monochromatic light was about 45° to the electrode surface. The reflected light from the electrode surface contained an ac and dc as a result of a sinusoidal modulation of the electrode potential. The intensities of both the dc and ac components of the reflected light were detected by using a lock-in-amplifier.[11]

The Kawamura Institute of Chemical Research (Chiba, Japan) supplied copper tetrakis (n-butoxycarbonyl) phthalocyanine (tbcCuPc). Tetraethylammonium tetrafluoroborate used as supporting electrolyte was electrometric grade, and dried under vacuum of 1×10^{-5} torr. The pyrolytic graphite was obtained from Union Carbide Co. and contained about 1 % impure planes in a cleaved ab-plane, as verified by X-ray diffraction. The graphite electrode was polished with 1 μm alumina powder to produce a mirror finish hydrophobic surface. The electrode was cleaned by sonication in water to remove the embedded alumina. Wetting the electrode with a tbcCuPc/chloroform solution formed the tbcCuPc layer coated on PGE. The chemicals for the buffer solution were used as purchased from Wako Chemicals Co. (Japan). The buffer solution of pH 7 was made of NaH_2PO_4/Na_2HPO_4. The distilled water for an aqueous media (18 MΩ/cm resistivity) was purified by a Milli-Q system. All the electrode potentials were referred to a silver/silver chloride electrode in a saturated potassium chloride solution. The counter electrode was a platinum wire. The electrochemical and spectroelectrochemical measurements were performed at 25 °C in an argon atmosphere.

Results and Discussion

Figure 1 shows (a) the UV-Vis spectrum for 1×10^{-4} M tbcCuPc in chloroform solution and (b) the spectrum recorded for tbcCuPc adsorbed on PGE using an in situ spectroscopic technique. Compared with those observed for tbcCuPc in the solution phase, the bands for the adsorbed species are broadened and shifted to longer wavelengths. The band broadening may result from the aggregate formation and extensive interactions between π-electrons in the electronic orbital of Pc with π-electron clouds on the basal plane of the pyrolytic graphite. Mho *et al.* reported the similar result from other Pc complexes.[13] They reported that the bands of Co(II)Pc and Fe(II)Pc were particularly broad on the highly oriented pyrolytic graphite (HOPG) electrode. The interaction of Pc with π-electrons may be maximized at the basal plane of HOPG because the greatest orbital overlap is achieved when the macrocycles are oriented parallel to the basal plane of the carbon. In the case of the adsorbed species, the oligomerization or polymerization of the species on the carbon electrode gives band broadening and red shift.

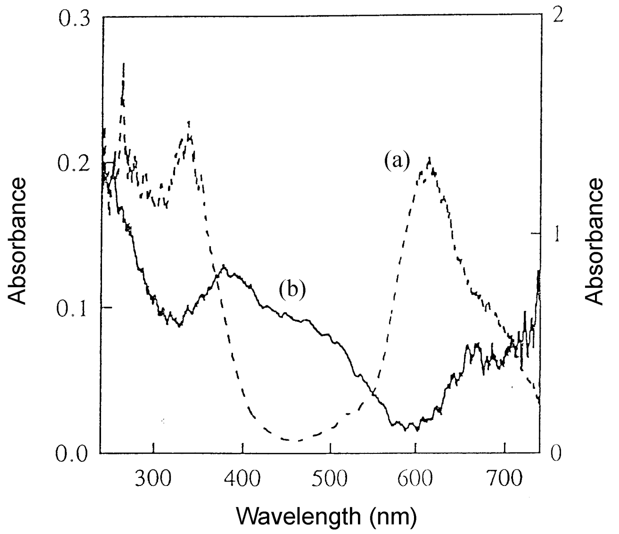

Figure 1. UV-Vis. spectra for (a) 1.0×10^{-4} M tbcCuPc in chloroform and (b) adsorbed tbcCuPc on PGE in a phosphate buffer solution (pH=7.04).

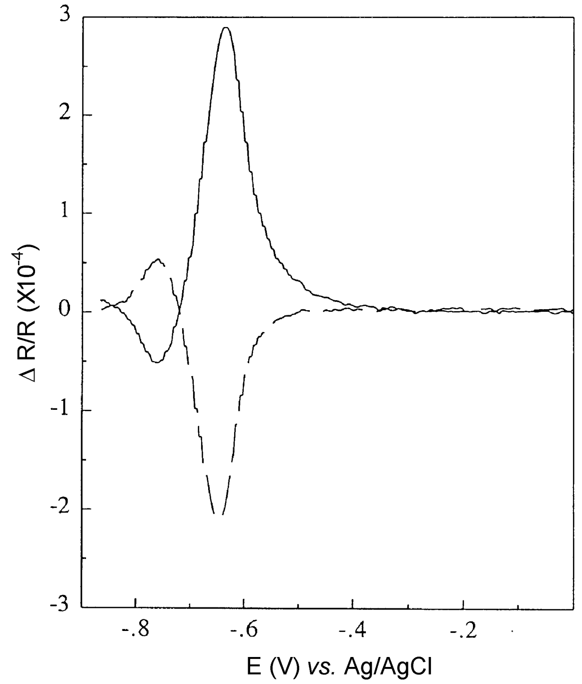

Figure 2. ER voltammogram of the tbcCuPc adsorbed on PGE in the phosphate buffer solution (pH 7.04) recorded at 600 nm, f=14 Hz, and ΔE_{ac}=30.65 mV with scan rate of 2 mV/sec. The solid and dashed lines indicate real and imaginary parts, respectively.

Figure 2 represents an ER voltammogram (ERV), which is very effective to determine a formal potential,[10] recorded for tbcCuPc adsorbed on PGE in a phosphate buffer solution at 600nm, which is a wavelength determined from ER spectra.[12] The ERV shows two peaks at -650 mV and -760 mV, which are the formal potentials and are close to the redox peak potentials in CV.

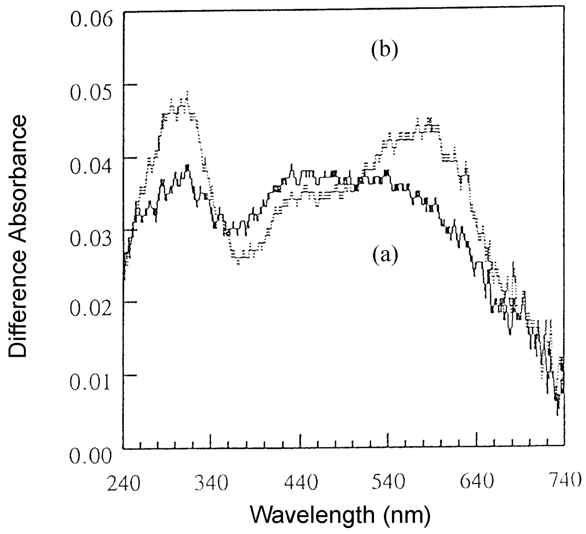

Figure 3. The difference spectra between the reduced and neutral states of the tbcCuPc adsorbed on PGE at -650 mV(a) and -760 mV(b), respectively.

Figure 3 shows the difference spectra between the neutral (at open circuit potential) and reduced states of tbcCuPc adsorbed on the PGE at the potential of -650 mV (Figure 3a), which is considered as the first formal potential of this compound determined by ER voltammogram. The absorbance band at 300 nm and broad bands around 420 and 520 nm, were observed in the spectrum. In this case, the reference spectrum was taken at the open circuit voltage. As the applied potential went to -760 mV (Figure 3b), which corresponds to the second formal potential of tbcCuPc adsorbed on PGE, the absorption intensity around 300 nm and 600 nm increased while the band at 450 nm did not increase. Thus, the bands at 300 and 600 nm are due to the species generated at the second reduction potential rather than at the first one as shown in Figure 3. The difference spectra between the reduced and neutral states show that the reduction of tbcCuPc may change the structure of the adsorbed tbcCuPc on PGE. Although spectra obtained at the formal potentials may not give an information of fully reduced state of the O_2-phthalocynine adduct, we could not obtain the spectra at more negative potentials than -760 mV, due to instability of the compound. Phthalocyanine is also known to undergo a dimerization or oligomerizaton reaction even at a reasonably low concentration by reduction.[7,14~15] There are three isosbestic points in the spectrum around 340, 510 and 690 nm. These are the very similar wavelengths in the ER spectra for tbcCuPc adsorbed on PGE in a phosphate buffer solution.[12]

Figure 4 shows the CV recorded for the oxygen reduction with (a) a bare PGE in a phosphate buffer solution (pH= 7.04) after deaeration by argon gas, (b) a bare PGE in air saturated buffer solution, (c) the tbcCuPc modified PGE in a deaerated buffer solution, and (d) the tbcCuPc modified PGE in an air saturated buffer solution. While the reduction peak for O_2 dissolved in the blank electrolyte solution appears at -0.67 V at a bare PGE (i_{pc}=28 μA), the peak appears at -0.55 V at the tbcCuPc-adsorbed PGE (i_{pc}=30 μA). The tbcCuPc and oxygen reduction peaks are superimposed in the CV and the current increase was observed in this case. The onset potential of the oxygen reduction was -0.26 V (Figure

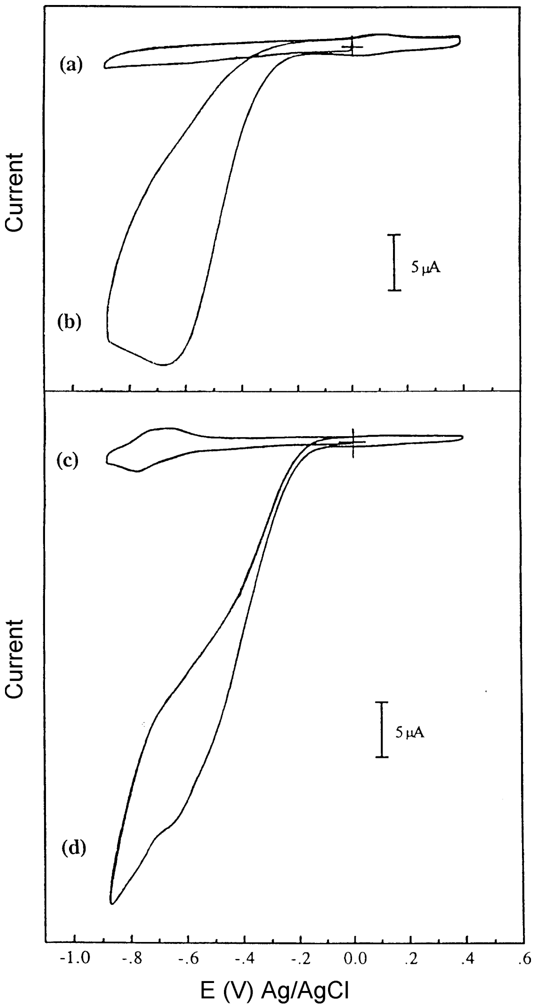

Figure 4. CVs recorded for the reduction of O_2 with (a) bare PGE in an argon gas purged phosphate buffer solution, (b) bare PGE in an air saturated buffer solution, (c) tbcCuPc adsorbed PGE in the argon gas purged buffer solution, and (d) tbcCuPc adsorbed PGE in the air saturated buffer solution. The scan rate was 100 mV/s.

4(b)) at a bare electrode and was shifted to -0.15 V (Figure 4(d)) at the tbcCuPc- adsorbed PGE. The reduction peak of dissolved oxygen at the tbcCuPc-adsorbed electrode appears at a more positive potential, of about 110 mV, than that at a bare PGE. The increase of the current and the potential shift to positive direction indicates that the tbcCuPc-adsorbed PGE catalyzes the reduction of molecular oxygen.

In conclusion, the band broadening and red shift by the adsorbed species compared to that observed in the solution phase suggests aggregate formation and extensive interactions of π-electrons in the electronic orbital of Pc with π-electron clouds on the basal plane of the pyrolytic graphite. Thus, the reduction of the molecular oxygen could be catalyzed by the aggregated species ($[H_2tbcCuPc]_{agg}$) on the PGE.

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