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Effects of NO_2 and Nitric Acid on the Charge Acceptance of Organic Photoreceptors

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The charge acceptance of single layer organic photoreceptors consisting of α-type Cu phthalocyanine pigments and hydrazone charge transport materials dispersed in thermosetting acrylic polymer is found to decrease when the surface is exposed to ambient NO_2 gas. The electronic surface properties of the photoreceptors are investigated by treating the surface with HNO_3 aqueous solutions and by measuring the applied voltage current characteristics. Internal photoemission experiments determine the energy level relationship between metal electrodes and the photoreceptors. The hole injection from the treated surface can be attributed to the formation of acceptor-like states at the surface. The improvement of charge acceptance based on this conclusion is presented.

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Introduction

The electrophotographic applications of single layer organic photoreceptors (SLP) have recently been investigated extensively.[1] Ueda and Noda reported on the photoinduced discharge of one such photoreceptor consisting of α-type Cu phthalocyanine pigments and hydrazone charge transport materials dispersed in thermosetting acrylic polymer (CuPc/hydrazone/polymer SLP).[2]

Weiss reported that polymer films molecularly doped with tri(p-tolyl) amine were fatigued with respect to positive corona charging when exposed to the vapors over concentrated nitric acid and NO_2.[3] In the present article, we report the observation of reduction in the charge acceptance of CuPc/hydrazone/polymer SLP, when the SLP for positive charging is exposed to ambient NO_2 gas. In order to identify the mechanism of this effect, the electronic surface properties are investigated by treating the surface with HNO_3 aqueous solutions and by measuring the applied voltage-current characteristics. Based on our findings, a practical way for improving the charge acceptance is presented.

Experimental

The photoconductive layer (PCL) consists of α-type Cu phthalocyanine pigments and hydrazone charge transport material (CTM: 2-methyl-4-dibenzylaminobenzaldehyde diphenyl hydrazone) dissolved in thermosetting acrylic polymer (CuPc/hydrazone/polymer SLP).[2] The molecular structure of the CTM is shown in Fig. 1. The PCL of thickness about 20 microns is coated on an Al drum, where the surface is anodized as an effective blocking layer to charge injection. The photoinduced discharge curves with positive corona charging show no induction effect, because the PCL contains CTM.[2]

After exposing the PCL to ambient NO_2 gas for 2 h, the initial surface potential, i.e., the charge acceptance, is measured as a function of the gas density. A scorotron charger with a grid bias voltage of 500 V was used for corona charging. The results are shown in Fig. 2. The reduced charge acceptance recovers when the PCL is placed in normal ambient air for several minutes. Therefore, the charge acceptance once reduced, increases during repeated charging and exposure cycles in the normal ambient air. It is observed that the charge acceptance is not reduced when the PCL is exposed to O_2, CO_2, or CO ambient gas up to 2,500 ppm.

To investigate this effect, we simulate NO_2 adsorption with HNO_3 treatments. The free surface of CuPc/hydrazone/polymer SLP is treated with HNO_3 aqueous solution for 30 min and dried for more than 30 min at room temperature. The relation between the initial surface potential of the treated PCL and the normality, N, of HNO_3 aqueous solution is shown in Fig. 3. Once reduced after the treatment, the charge acceptance recovers during repeated charging and discharge cycles, as

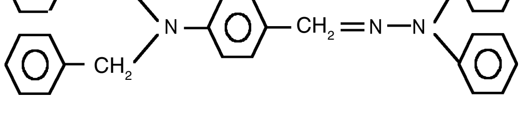

Figure 1. Chemical formulas of 2-methyl-4-dibenzylamino-benzalde-hyde diphenyl hydrazone.

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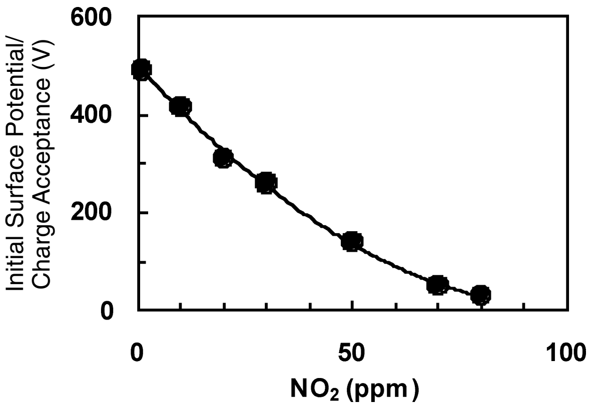

Figure 2. Initial surface potential measured after being placed in NO_2 gas for 2 h, as a function of the gas density for Cu phthalocyanine/polymer single layer photoreceptors.

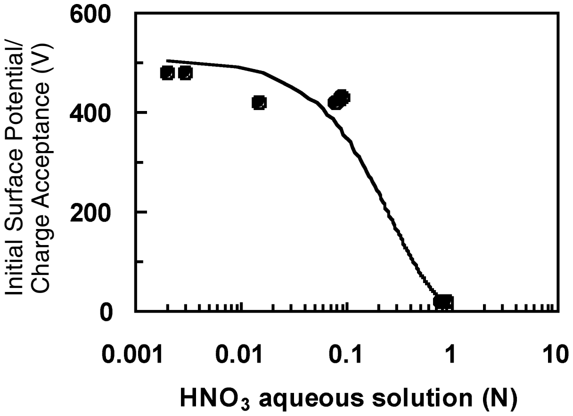

Figure 3. Initial surface potential for Cu phthalocyanine/hydrazone/polymer single layer photoreceptor after treated for 30 min, as a function of normality N of HNO_3 aqueous solution.

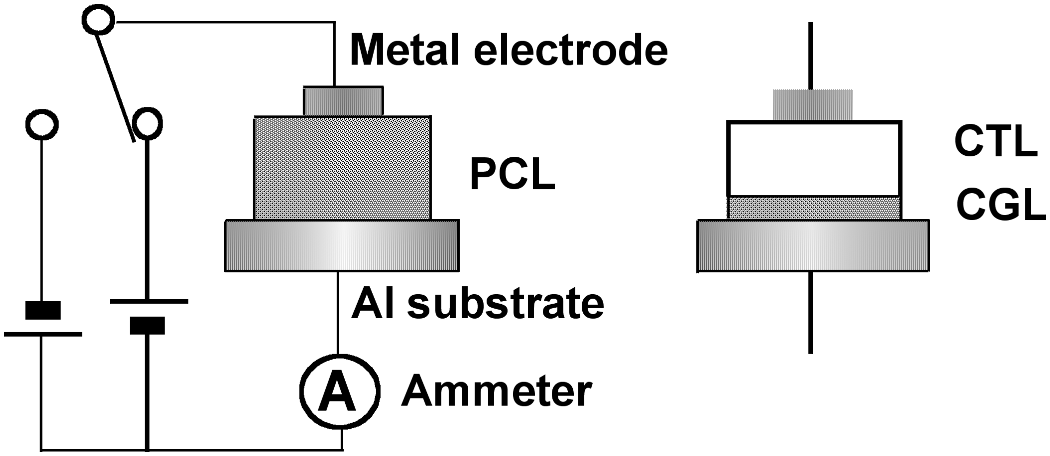

Figure 4. Experimental arrangement for measuring the applied voltage-current characteristics

in the case of NO_2 exposure (Fig. 2). However, such recovery is not observed when the treatment in HNO_3 aqueous solution lasts several hours. We believe the same mechanism operates in the HNO_3 aqueous solution treatment and in the NO_2 gas exposure.

Applied Voltage-Current Characteristics

The experimental arrangement of the applied voltage-current (V-I) characteristics is illustrated schematically in Fig. 4. The metal electrodes on the surface of PCL are prepared by vacuum deposition.

The V-I characteristics are shown in Fig. 5. With an Al electrode on untreated surface (Al/untreated surface), the current is negligible for both positive and negative applied voltages. On the other hand, a large current is observed for positive applied voltage with an Au electrode on untreated surface (Au/untreated surface). This means that holes can be injected from the Au electrode into the PCL.[4] The current is approximately proportional to the square of the applied voltage, indicating that it is space charge limited.

Also shown in Fig. 5 are the V-I characteristics of PCL's treated with 1N HNO_3 aqueous solution for 30 min. With an Al electrode (Al/treated surface), a large current is observed for positive applied voltage, indicating that hole injection from the Al electrode into the treated PCL becomes possible.

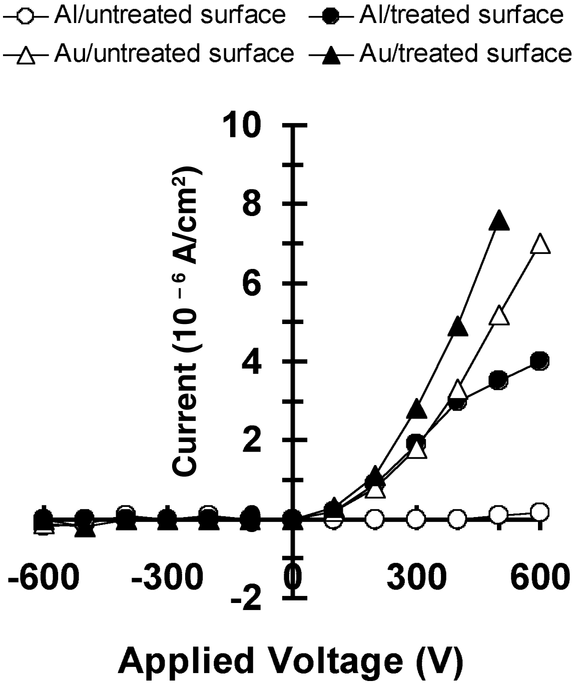

Figure 5. Applied voltage-current characteristics for the Cu phthalocyanine/hydrazonelpolymer single layer photoreceptors.

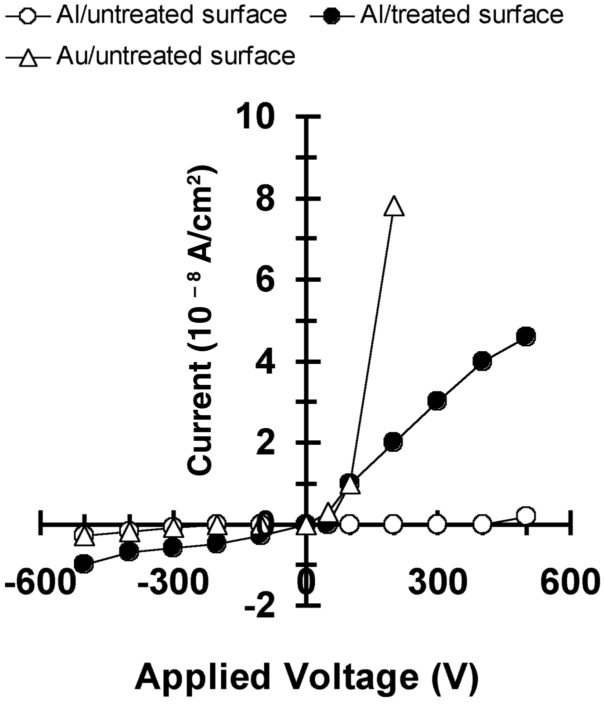

Figure 6. Applied voltage-current characteristics for the Cu phthalocyanine dual layer photoreceptors.

The CuPc/hydrazone/polymer SLP's with untreated surface have a good charge acceptance for both positive and negative corona charging. On the other hand, the SLP's with pre-treated surface show no charge acceptance for positive corona charging, but a high charge acceptance for negative corona charging. These results are consistent with the V-I characteristics shown in Fig. 5.

When a negative voltage is applied to the Al or Au electrode on CuPc/hydrazone/polymer SLP, no current is observed as shown in Fig. 5. This means that no electron can inject from the metal substrate into the positively corona charged PCL regardless of whether the substrate is Al or Au. This is consistent with the observation of high positive charge acceptance for CuPc/hydrazone/polymer SLP.

The V-I characteristics for CuPc dual layer photoreceptors (CuPc DLP) are shown in Fig. 6. The CTL contains the hydrazone CTM: 2-methyl-4-dibenzylaminobenzaldehyde diphenyl hydrazone, and the CGL contains CuPc pigments. The results are similar to that of CuPc/hydrazone/polymer SLP shown in Fig. 5.

The work functions of Al and Au are determined by the Kelvin method to be 3.9 and 4.9 eV, respectively. The ionization potentials of both the PCL of the SLP and the CTL of the DLP are 5.2 eV, determined from external photoemission experiments. The absorption edge ("band gap") of the PCL is 2.0 eV by fluorometry.

Internal Photoemission Experiment

Internal photoemission (photoinjection) of holes from a metal into an insulator can be used to determine the energy level relationships at the interface between metal electrodes and photoreceptors.[5] The sample is a CTL consisting of hydrazone CTM dissolved in thermosetting acrylic polymer. It has the same ionization potential of 5.2 eV as the one containing CuPc pigments. The CTL coated on an Al electrode is a transparent layer without CuPc pigments. The experimental setup (water cell) is illustrated in Fig. 7. Distilled water is held in a plastic box and sealed to the CTL. Monochromatic light reaches the Al electrode through the water electrode and the CTL. When a negative voltage is applied to the water electrode, holes generated in the Al electrode inject into the CTL.

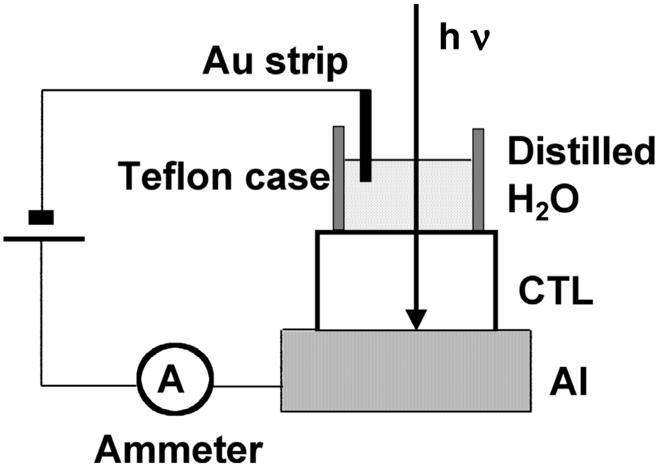

Figure 7. Experimental arrangement for observing the internal photoemission (water cell). Distilled water was held in a plastic box sealed to the CTL.

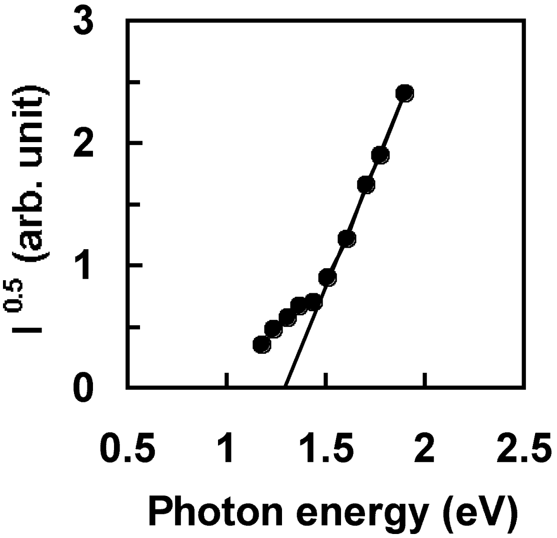

Figure 8. The threshold energy of 1.3 eV was determined for the interface between the Al electrode and the CTL.

An electron in Al receives the photon energy and undergoes a transition to a previously unoccupied state in the conduction band leaving a deep (energetic) hole that may then enter the transport levels in the CTL. Internal photocurrent is measured as a function of photon energy. For the interface between Al and CTL, the threshold energy value of 1.3 eV is determined from the photocurrents shown in Fig. 8.

Discussion

Consider the contact between a metal electrode with a work function W_M and a photoreceptor with an ionization potential I_P, as illustrated in Fig. 9. The Schottky barrier is given by,

$$\Phi_B = W_M - I_P \quad (1)$$

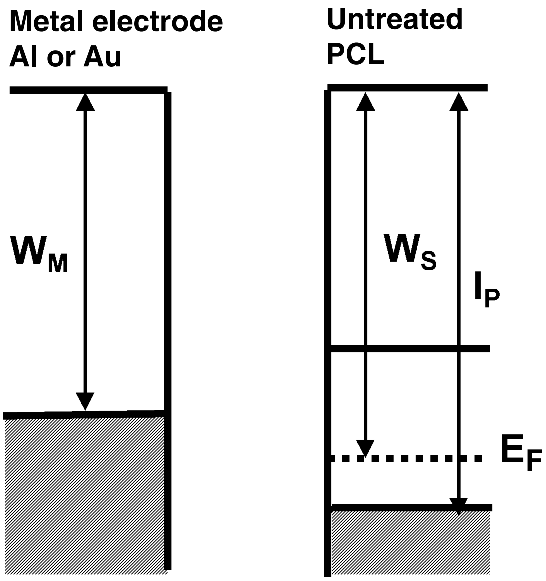

Figure 9. Energy level of the metal electrode and the untreated PCL.

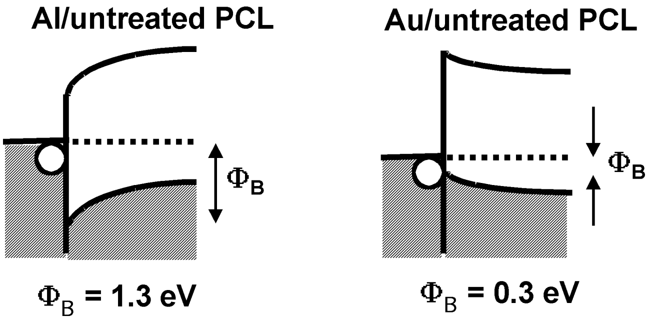

Figure 10. Energy level relationship at the interface between the metal electrodes and the CuPc/hydrazonelpolymer SLP. W_S = 4.6 eV, W_{Al} = 3.9 eV and W_{Au} = 4.9 eV.

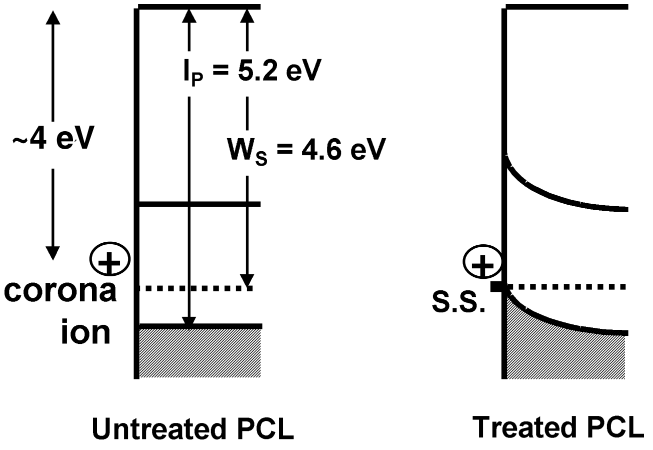

Figure 11. Energy level shifting by the surface.

Using the W_M of Al and the I_P of PCL given in the previous section, the Schottky barrier of Φ_B = 1.3 eV is obtained from Eq. 1. This value is in agreement with the result on the threshold energy in the internal photoemission experiment (Fig. 8). The high barrier prevents hole injection from Al electrode into the untreated PCL (Al/untreated surface), as schematically illustrated in Fig. 10. Similarly, a Schottky barrier of Φ_B = 0.3 eV is obtained for Au/untreated surface and is shown schematically in Fig. 10. The smaller barrier allows hole injection from Au electrode into the untreated PCL. We will apply this hole injection mechanism to the discussion of the treated surface.

The V-I characteristics of the Al/untreated surface in Fig. 5 correspond to high charge acceptance for positive corona charging which means that there is a large difference between the energies of the positive corona ions and of the hole transport level of the PCL. Therefore, we believe that the ionization potential of positive corona ions is nearly equal to the work function of Al, i.e., about 4 eV.

Surface States and Carrier Injection

The HNO_3 aqueous solution treatment and the NO_2 gas exposure produce surface states at the free surface of PCL. The barrier model with the surface states is shown in Fig. 11. A measurement by external photoelectric effect gives the ionization potential of PCL as 5.2 eV. This leads to a large barrier of 1.3 eV for Al/untreated surface of CuPc SLP, based on Eq. 1, and an equally large gap of about 1.2 eV between the energies of positive corona ions and the hole transport level of the PCL, assuming the ionization potential of positive corona ions to be about 4 eV as argued above.

We have observed hole injection from the Al electrode into the treated PCL as shown in Fig. 5. This indicates that a nearly ohmic contact is formed at the interface between the Al electrode and the treated PCL. Now suppose the HNO_3 aqueous solution treatment or the NO_2 gas exposure introduces acceptor-like states at the surface. Then the ionization potential for states near the surface is reduced. This leads to upward shifting of the energy levels, reduces the barrier, and facilitates hole injection from the positive corona ion as shown on the right hand side in Fig. 11.

We have no chemical evidence as to the details of the surface states at the photoreceptor surface. However, Weiss indicated that nitric acid and NO_2 convert the surface of the polymer films molecularly doped with tri(p-tolyl) amine from one that is blocking toward positive charge injection to one that is injecting.[3] This is due to the formation of amine radical cations near the film's surface. The oxidation is believed to occur via electron transfer between the amine and nitrogen dioxide or some other nitrogen oxide-derived species. In our experiment the radical cation caused by electron transfer from the hydrozone to NO_2 is expected to lead to acceptor-like states.

Improvement of the Charge Acceptance

For CuPc DLP in practical use nowadays, it is not necessary to consider the NO_2 problem seriously because the media are used with negative charging. However, when a reversal development process is applied to CuPc DLP, the corona discharge at the toner transfer station is positive and special care may be necessary. If DLP's [CTL (electron transport layer)/CGL/substrate] using positive charging are to be in practical use in the future, it may be not necessary to worry about the ambient gas problem.

Organic photoreceptors for use in electrophotographic processes may be overcoated to protect the surface from corona generated chemicals.[6] We have prepared a useful protective layer against NO_2 gas on the surface of CuPc/hydrazone/polymer SLP drums to prevent the reduction in charge acceptance. The SiO blocking layer with a thickness of 0.3 μm is vacuum deposited on the surface of PCL on Al substrates and aged at 55°C for 5 h. A thickness of 0.3 μm is found sufficient to prevent the NO_2 effect while leaving negligible residual potential. In contrast, neither Al_2O_3, SiC, SiO_2 nor Si_3N_4 are found to be effective as a protective layer. It is not clear why only SiO was effective at the moment.

Conclusion

It is concluded that the observed decrease of positive charge acceptance in CuPc/hydrazone/polymer SLP exposed to ambient NO_2 gas can be attributed to the formation of acceptor-like states at the surface that facilitate hole injection from the corona ions into the photoreceptor. We are able to identify a thin SiO on the surface as a useful protective layer against nitration of CuPc/hydrazone/polymer SLP.

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