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Improvement of Response Times in Photoelectrochromic Organic Film

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Some materials change color on absorption of light (photochromic materials)[1,2] and others on application of an external electric field (electrochromic materials).[3−5] Photoelectrochromic materials change color both on absorption of light and on application of an external electric field. Bechinger et al.[6] developed a photoelectrochromic device based on an inorganic WO_3 electrochromic film in combination with a dye-sensitized semiconductor electrode that produces a photovoltage sufficient to color the electrochromic film. Recently, a new organic photoelectrochromic film in which the same molecule, methylene blue, can change its color from blue to transparent on absorption of light and to come back blue owing to an oxidation reaction induced by an external electric field has been developed.[7] The major advantage of such a device is that it uses two distinct techniques for performing bleaching and coloring. In fact, it is possible to write on the film by means of a red laser beam and to erase by means of an electrical impulse. In the present work the active molecule, contained in the photoelectrochromic organic film, is methylene blue. It is well-known that it is a photoactive agent in the triplet state and that its photoreduction can occur in a solution containing appropriate electron donors.[8,9] At the same time, methylene blue changes color in response to an electrically induced change in its oxidation state.[10]

We have investigated the way to improve both the bleaching time when the photoelectrochromic organic film is illuminated with a He−Ne laser (writing laser) and the coloration time.

We have prepared five different photolelectrochromic solutions in concentration of 0.2 M of propylamine, dipropylamine, tripropylamine, triethylamine, and tributylamine (Aldrich), respectively, 0.05 M of methylene blue (anodic element and photoactive agent, Aldrich), and 0.05 M of ethyl viologen diperchlorate (cathodic element, Aldrich) in propylene carbonate (Aldrich) as solvent. Each solution was added to dipentaerythritol penta-acrylate (UV photopolymerizable monomer, Aldrich) and Irgacure 651 (UV photoinitiator, Ciba Geigy), at the levels of 70, 28, and 2 wt %, respectively. Glass cells with a gap of 25 μm, with internal surfaces covered by different thicknesses of conductive indium tin oxide (ITO) (45, 120, and 150 nm), were filled with the final solution and polymerized by UV light for 10 min to obtain a solid organic film in which the fluid photoelectrochromic solution is dispersed. The optical transmission of the samples was measured by means of the optical line described in the ref 7.

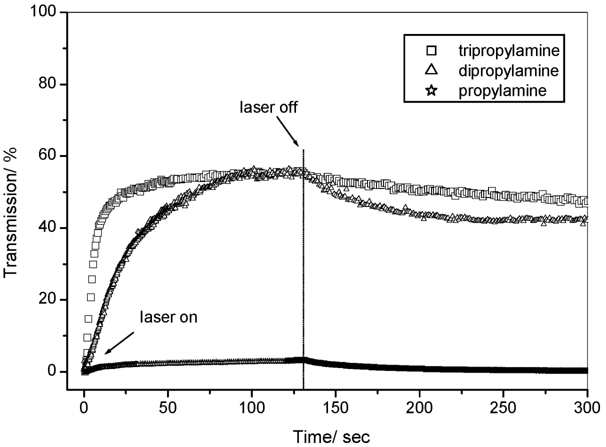

Figure 1. Optical transmission dependence versus time of the photoelectrochromic organic film containing (□) tripropylamine, (△) dipropylamine, and (☆) propylamine.

The variation of the optical transmission of three different photoelectrochromic organic films is shown in Figure 1. The optical transmission of the films in the original state is about 1%, with respect to the air. When they are illuminated with the red He−Ne laser beam (writing laser), a bleaching process begins as a consequence of the reaction[7] between the triplet state of methylene blue and the electron donor molecules, that is, propylamine, dipropylamine, and tripropylamine, a primary, a secondary, and a tertiary amine, respectively. The different bleaching rates are due to the different electron donor abilities of the three amines; in fact, the sample containing tripropylamine reaches the maximum of transparence (55% of transmission) in only 70 s and the sample containing dipropylamine reaches 40% of transmission in 100 s. In contrast, the sample containing propylamine shows a little variation of the optical transmission: about 3%. Such different behavior can be ascribed to the fact that the tertiary amine is the best electron donor because the nitrogen is bound with three electron donor groups that exercise a positive inductive effect on nitrogen that more easily donates its single electron.

For the same reason the secondary amine is somewhat less effective while the primary amine is not able to promote the photochemical reaction.

For the tertiary amine a slight coloration of the illuminated area is observed upon removal of the writing

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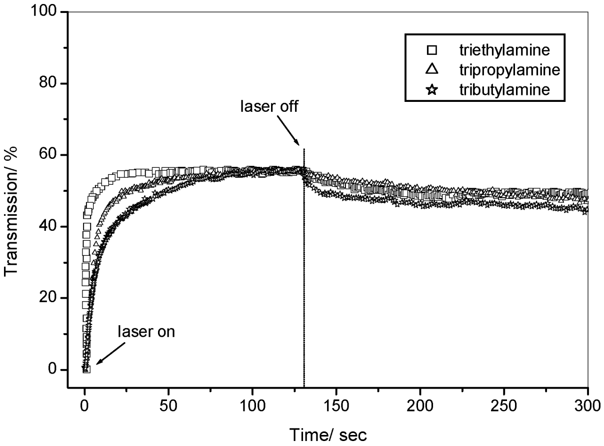

Figure 2. Optical transmission dependence versus time of the photoelectrochromic organic film containing tertiary amines: (□) triethylamine, (△) tripropylamine, and (☆) tributylamine.

laser and the optical transmission decreases, remaining at about 50% for a long time as shown in Figure 1. This is probably due to a small amount of oxygen, present in the film, that takes back the methylene blue triplet excited state to the ground state. To improve the bleaching time of the photoelectrochromic device, we have compared three samples containing different tertiary amines, that is, triethylamine, tripropylamine, and tributylamine. Figure 2 shows the optical transmission versus time for samples containing the three different tertiary amines. The bleaching times are 20, 70, and 100 s, respectively. Such different chromatic responses must be attributed to the different abilities of the tertiary amines to give up the electron pair as a consequence of the steric impediment on the nitrogen. In fact, the bleaching times of the films increase with the dimensions of the alkyl substituents on the nitrogen.

The electrochromic properties of methylene blue as anodic substance in the redox reaction with ethyl viologen diperchlorate can be helpful to convert the clear stable state of the film, after the writing process, into the original blue state. The application of a low external dc voltage (0.4 V) triggers the redox reaction of methylene blue with ethyl viologen-diperchlorate[10] on the corresponding electrodes, that is, the inner surfaces of the cell covered by ITO. As a result, the film changes color from clear to the intense blue, that is, the color of the methylene blue in its oxidized form, erasing process.

In Figure 3 we show the variations of the optical transmission of films containing triethylamine, supported on glass surfaces covered by different ITO thickness, that is, 45, 120, and 150 nm, upon the application of an external electrical impulse of 2 s. After the impulse, the color change that takes back the optical transmission to the original value occurs in about 170, 50, and 10 s for the samples with 45-, 120-, and 150-nm ITO thickness, respectively.

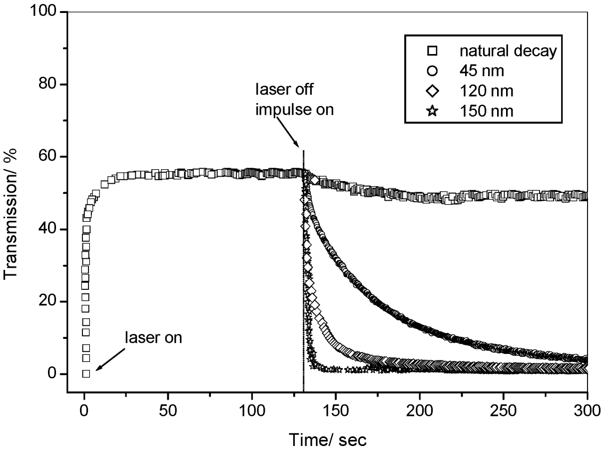

Figure 3. Optical transmission dependence versus time of the photoelectrochromic organic film containing triethylamine on different ITO thicknesses: (□) natural decay, (○) 45 nm, (◇) 120 nm, and (☆) 150 nm.

By means of atomic force microscopy (AFM), we have measured the average roughness of the films by a quantitative analysis obtained by a software treatment of AFM images[11] and we have obtained the values 1.9, 9.6, and 13.8 for the samples with 45, 120, and 150 nm of ITO surfaces, respectively.

The active area of the electrodes strongly depends to the surfaces roughness; then, the number of reduced and oxidized molecules at the corresponding electrodes in the time unit and, consequently, the coloring time of the films, changes as a function of the electrodes roughness, that is, the ITO thickness.

In conclusion, we have investigated the bleaching time dependence on different electron-donating abilities of amines and we have observed that it is possible to improve it by using a tertiary amine with ethyl groups bounded at the nitrogen. On the other hand, we have measured the coloring time dependence on ITO thickness, obtaining a coloration time of only 10 s for the sample with 150 nm of ITO thickness. This study enhances properties of the organic photoelectrochromic films for their possible practical application as electro-optical devices.

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