Flexible Nano-Photo-Electrochromic Film

Giovanni De Filpo,* Fiore P. Nicoletta, and Giuseppe Chidichimo

Department of Chemistry, University of Calabria, Arcavacata di Rende 87036 (CS), Italy

Received June 21, 2006

A flexible nano-photo-electrochromic poly(ethylene terephthalate) (PET)−TiO_2−PO_4−methylene blue (MB) based film was obtained by the deposition of TiO_2 nanoparticles on a PET conductive substrate. A further covalent chemical bond of MB molecules on the TiO_2 film by means of phosphate groups ensures the photo-electrochromic properties of this device. Indeed, MB molecules can change color both owing to the irradiation with red light, in the presence of electron donor molecules, and owing to the oxidation reaction with an oxidizing agent. Because the oxidation reaction of MB molecules occurs at the same electrode where the molecules are anchored, the film shows a very fast coloration time (600 ms). The thermal stability of the film and the anchoring of MB molecules on TiO_2 nanoparticles were investigated by the differential scanning calorimetry technique. The morphologies of the surface and cross section of the TiO_2 layer were studied by a scanning electron microscope. Moreover, the device was characterized in terms of light absorption by UV−visible spectroscopy and optical transmission by an optical line.

Introduction

Development of chromogenic materials for glazing smart windows has been actively pursued in recent years. The change in the optical properties of these materials may be activated by electricity, heat, or light. Examples of commonly used chromogenic materials are certain transition metal oxides such as WO_3 and MoO_3 and organic compounds such as viologens, diphthalocyanines, and conductive polymers.[1−8] The viologens are among the most studied chromogenic material, and the change in coloration is achieved by an oxidation−reduction reaction.

Electrochromism is defined as a reversible and visible change in the transmittance of a material as the result of an electrochemical oxidation or reduction.[9,10] The electroactive species change their optical absorption bands due to the gain or loss of an electron depending on their cathodic or anodic character. After the current pulse, which enables the electron transfer to/from the working electrode, the device becomes colored/bleached and persists in this state until a reverse electric pulse is applied or a competitive reaction takes place. Generally, the chromophore is either dissolved in a solution or incorporated in a polymeric film deposited on a transparent conducting substrate. Therefore, the coloring and bleaching rates are limited by the diffusion rate of the chromophore to the conducting substrates or by the migration rate of electrons within the polymeric film. As a consequence, the switching times of these devices are typically in the order of some tens of seconds even for relatively small area device. On the other hand, electrochromic conjugated polymers can have response times of a few seconds.[11] In particular, Reynolds obtained electrochromic devices based on poly(3,4-propylenedioxythiophene) derivatives with very rapid switching times ranging from 0.3 to 0.8 s.[12] Fitzmaurice et al. and Gratzel developed an ultrafast electrochromic device based on molecular monolayers anchored on a semiconductor surface.[13−16] The reversible process is based on the change of color of a suitable molecule that is colorless in the oxidized state and colored in the reduced state, adsorbed on the surface of a colorless semiconductor (usually TiO_2) on conducting glass. When a sufficiently negative potential is applied, electrons are injected from the conducting glass into the conduction band of the semiconductor reducing the adsorbed molecule and inducing its coloration. The ultrafast nature of this device is a direct consequence of the combination of a semiconducting nanostructured metal oxide electrode, modified by a redox chromophore, which colors upon being reduced with a conducting nanostructured metal oxide electrode, modified by a redox chromophore, which colors upon being oxidized.

---

* To whom correspondence should be addressed. E-mail: defilpo@unical.it.

(1) Seeboth, A.; Schneider, J.; Patzak, A. *Sol. Energy Mater. Sol. Cells* **2000**, *60*, 263.
(2) Lampert, C. M. *Thin Solid Films* **1993**, *236*, 6.
(3) Sella, C.; Maaza, M.; Nemraoui, O.; Lafai, J.; Renard, N.; Sampeur, Y. *Surf. Coat. Technol.* **1998**, *98*, 1477.
(4) Jelle, B. P.; Hager, G. *Sol. Energy Mater. Sol. Cell* **1999**, *58*, 227.
(5) Sampanthar, J. T.; Neoh, K. G.; Ng, S. W.; Kang, E. T.; Tan, K. L. *Adv. Mater.* **2000**, *20*, 1536.
(6) Rauh, R. D.; Wang, F.; Reynolds, J. R.; Meeker, D. L. *Electrochim. Acta* **2001**, *46*, 2023.
(7) Byker, H. J. *Electrochim. Acta* **2001**, *46*, 2015.
(8) Walczak, R.M.; Reynolds, J. R. *Adv. Mater.* **2006**, *18*, 1125.
(9) Monk, P. M. S.; Mortimer, R. J.; Rosseinsky, D. R. *Electrochromism: Fundamentals and Applications*; Wiley-VCH: Weinheim, Germany, 1995.
(10) Rosseinsky, D. R.; Mortimer, R. J. *Adv. Mater.* **2001**, *13*, 783.
(11) Argun, A. A.; Cirpan, A.; Reynolds, J. R. *Adv. Mater.* **2003**, *15*, 1338.
(12) Welsh, D. M.; Kumar, A.; Meijer, E. W.; Reynolds, J. R. *Adv. Mater.* **1999**, *11*, 1379.
(13) Cinnsealach, R.; Boschloo, G.; Rao, S. N.; Fitzmaurice, D. *Sol. Energy Mater. Sol. Cell* **1998**, *55*, 215.
(14) Cinnsealach, R.; Boschloo, G.; Rao, S. N.; Fitzmaurice, D. *Sol. Energy Mater. Sol. Cell* **1999**, *57*, 107.
(15) Cummins, D.; Boschloo, G.; Ryan, M.; Corr, D.; Rao, S. N.; Fitzmaurice, D. *J. Phys. Chem. B* **2000**, *104*, 11449.
(16) Gratzel, M. *Nature* **2001**, *409*, 575.

10.1021/cm061438m CCC: $33.50

Differently, photochromic molecules changes their chromatic properties upon exposure to both natural and artificial ultraviolet (UV) light. The light radiation changes the molecular conformation of the dye molecules causing a shift of the light absorption peak which causes the color variation. If the radiation source is removed, dyes return to the original state, which may be colorless if no absorption falls in the visible region of the spectrum.[17,18]

Photo-electrochromic (PEC) materials change color both on absorption of light and on application of an external electric field. Bechinger et al. developed a PEC device based on an inorganic WO_3 electrochromic film in combination with a dye-sensitized semiconductor electrode.[19] This is able to generate electrons creating the voltage necessary to drive lithium ions into the electrochromic layer and coloring it.

The notable characteristic of the PEC device is the use of a dye-impregnated TiO_2 layer. A low concentration of the dye is used to maximize the transparency of the window.

Recently, our group developed a new organic PEC film in which methylene blue (MB) is the active molecule.[20] 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 with a consequent change of its color from blue to colorless.[21,22] At the same time MB, dissolved in a suitable solvent, can also be oxidized in the presence of an oxidative agent; as a consequence of the application of an external direct current (DC) electric field, when this electrochemical reaction occurs the color of the solution changes from light blue to intense blue.[23]

The main advantage of such a device is that it uses two distinct techniques to perform the bleaching and the 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.[20]

In the present paper we present a nano-photo-electrochromic PET$-$TiO$_2-$PO$_4-$MB flexible film. In comparison with the devices mentioned above, the peculiar characteristic of this film is the use of polymeric conductive support of poly(ethylene terephthalate) (PET) which makes the entire device flexible. In addition, the device is faster with regard to recoloring due to the deposition of a layer of TiO_2 nanoparticles linked to the PEC MB molecules.

Experimental Section

The method used for the preparation of nanocrystalline films employs commercial TiO_2 (P25 by Degussa); a mixture of about 30% rutile and 70% anatase. To break the aggregates into separate particles, 12 g of the powder was ground in a porcelain mortar with about 4 mL of water and 0.4 mL of acetylacetone to prevent the reaggregation of the particles. Afterward, the powder was dispersed by the high shear force in the viscous paste, and it was diluted by adding dropwise 16 mL of water under continuous grinding. A total of 50 μL/cm^2 of the colloid was deposited on the conductive surface of the PET film (sheet resistance, 35 Ω/square) and spread on the surface by a spin-coater at 1200 rpm for 30 s. After drying in air at room temperature, the coated substrates were put into a Teflon-lined autoclave. A small amount of distilled water was added at the bottom of the reactor so that the sample was not in direct contact with water but with steam during the reaction. The reactor was placed in an oven at 100 °C for 12 h. After the hydrothermal treatment, the films were taken out, rinsed with water and afterward with methanol, and dried in an oven at 80 °C. The resulting film thickness was typically 0.4 μm.

The morphology of the film was investigated by a scanning electron microscope LEO 420 (by Zeiss).

The phosphate group was bounded to the surface of the TiO_2 nanospheres by immersing the PET$-$TiO$_2$ film in 50 mL of a buffer phosphate solution (1 M, pH 4.0) at 45 °C for 30 min.[24] After the immobilization of the phosphate group on the PET$-$TiO$_2$ film, the latter was immersed in 25 mL of a 10^{-3} M MB solution at pH 6.0 for 30 min at room temperature. The resulting PET$-$TiO$_2-$PO$_4-$MB film was washed several times with bi-distilled water until the wastewater that resulted was uncolored, which is indicative of the anchoring of the MB molecules on the TiO_2 nanospheres. Further drying of the film in an oven for 30 min at 60 °C was performed for removing the last traces of washing water.

The adsorbed quantity of MB molecules on the film with respect the phosphate group was determined by scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) spectroscopy. Differential scanning calorimetry (DSC) technique, by means of a MICRO DSC III (SETARAM), was useful to study the thermal stability of the film as well as the anchoring of the MB molecules on TiO_2 nanoparticles.

The absorption spectrum of the film was measured by the UV$-$vis spectrophotometer Jasco V550. The electrolytic solution is composed of 0.05 M ethyl viologen diperchlorate (cathodic element), 0.2 M triethylamine (electron donor molecule), and 0.5 M $LiClO_4$ (charge carrier). The 5 wt % of dipentaerythritol pentaacrylate (UV photopolymerizable monomer) and 1 wt % of Irgacure 651 (UV photoinitiator) were added to the electrolytic solution. The solution was absorbed through the pores of a microporous polar Nafion112 membrane (DuPont) by immersing the membrane in the solution overnight. Afterward, the membrane was put between PET$-$TiO$_2-$PO$_4-$MB and PET substrates, and the entire device was irradiated with UV light for 5 min to perform the polymerization of the acrylate monomer and to link in a stable way the flexible supports of PET$-$TiO$_2-$PO$_4-$MB and PET to the Nafion membrane. The resulting cell was sealed on the all sides with a cyanoacrylate glue.

The optical transmission of the sample was measured by means of a suitably chopped red He$-$Ne (632, 8 nm, 1 mW) laser beam (reading laser) perpendicular to the sample and incident on a photodiode. The signal goes from the photodiode to a lock-in amplifier EG&G 5209 connected to a computer for data recording. The writing red He$-$He (632, 8 nm, 5 mW) laser beam is set at an angle of about 6° with respect to the reading laser. The electric field was supplied to the sample by means of a power supplier AMEL Instruments 2049.

Results and Discussion

Fast response times to an electrical impulse is a fundamental property required for an electro-optical device to make

---

(17) Durr, H.; Bouas-Laurent, H. *Photochromism, Molecules and Systems*; Elsevier: Amsterdam, Holland, 1990.

(18) Yao, J. N.; Hashimoto, K.; Fujishima, A. *Nature* **1992**, *355*, 624.

(19) Bechinger, C.; Ferrere, S.; Zaban, A.; Sprague, J.; Gregg, B. A. *Nature* **1996**, *383*, 608.

(20) Macchione, M.; De Filpo, G.; Mashin, A.; Nicoletta, F. P.; Chidichimo, G. *Adv. Mater.* **2003**, *4*, 327.

(21) Lutoshkin, V. I.; Volkon, S. V. *Russ. Theor. Exp. Chem.* **1977**, *13*, 371.

(22) Mills, A.; Wang, J. *J. Photochem. Photobiol., A* **1999**, *127*, 123.

(23) Varaprasad, D. V.; Agrawal, A.; Zhao, M.; Allemand, P. M.; Dornan, C. A.; Lynam, N. R. European Patent 0 612 826 A1, 1994.

(24) Dias, S. L. P.; Fujiwara, S. T.; Gushikem, Y.; Bruns, R. E. *J. Electroanal. Chem.* **2002**, *531*, 141.

Scheme 1. Schematic Representation of the Photochromic Reaction of MB with an Electron Donor Molecule (:NR_3)

$$^{1}MB_0^{+} \leftrightarrow {}^{1}MB^{*+} \rightarrow {}^{3}MB^{*+}$$

(blue)

$$^{3}MB^{*+} + :NR_3 \rightarrow MB^{\cdot} + {}^{\cdot}NR_3^{+}$$

(clear)

$$^{3}MB^{*+} + O_2 \rightarrow {}^{1}MB_0^{+} + O_2$$

(blue)

it attractive for a probable application. In light of this, the aim of this work was the improvement of a previous PEC device making faster the oxidation of the MB molecules at the electrodes.[20] Indeed, the coloration rate of the PEC film depends on the number of MB molecules oxidized at the electrode in the unit of time.[25] In a previous work, the coloring time dependence on the indium tin oxide (ITO) thickness of the conductive substrates was already measured, obtaining a coloration time of 10 s for the sample with 150 nm of ITO thickness.[25] Therefore, it is evident that this kind of process strongly depends on the roughness of the electrode surface.

To notably increase the electrode active surface and the number of oxidized MB molecules, consequently, a transparent layer of nanocrystalline TiO_2 film was deposited on the electrode according to the method described by Zhang;[26] see experimental section.

MB is an organic dye that strongly absorbs in the visible region of the spectrum. When a MB molecule absorbs red light, it undergoes a transition to an excited single state.[16,17] This state can either return to the ground state or convert to an excited triplet state. The latter is a better electron acceptor than the ground-state form, owing to its reasonable life time (450 μs).[22] In the presence of an electron donor molecule, it subsequently reduces, changing its color from blue to colorless. The sequence of described reactions is shown in Scheme 1.

MB can be oxidized in the presence of an oxidative agent, as a consequence of the application of an external electric DC field.[23] When this electrochemical reaction occurs, its color changes from colorless to intense blue.

In practice, when an electrolytic solution, containing both the electron donor molecule and the oxidizing agent, is in contact with the PET$-$$TiO_2$$-$$PO_4$$-$MB film, it is possible to use both the photo- and electrochromic properties of MB. Such a specific series of operations allow us to obtain a flexible nano-photo-electrochromic PET$-$$TiO_2$$-$$PO_4$$-$MB based film.

By applying a voltage on the nanostructured TiO_2 electrode, MB molecules, bonded to the electrode surface, are oxidized, and a fraction of ethylviologen molecules present in the electrolytic solution are reduced on the opposite electrode.

The overall process results very fast. Indeed, the oxidation rate is not dependent on the diffusion rate of the molecules toward the electrode. Besides to be able to transport electrical charges, TiO_2 nanoparticles, because of their dimensions (25 nm in diameter), offer a very high surface area (50 m^2/g). In this way it has been possible to oxidize a great amount of MB molecules per surface unit.

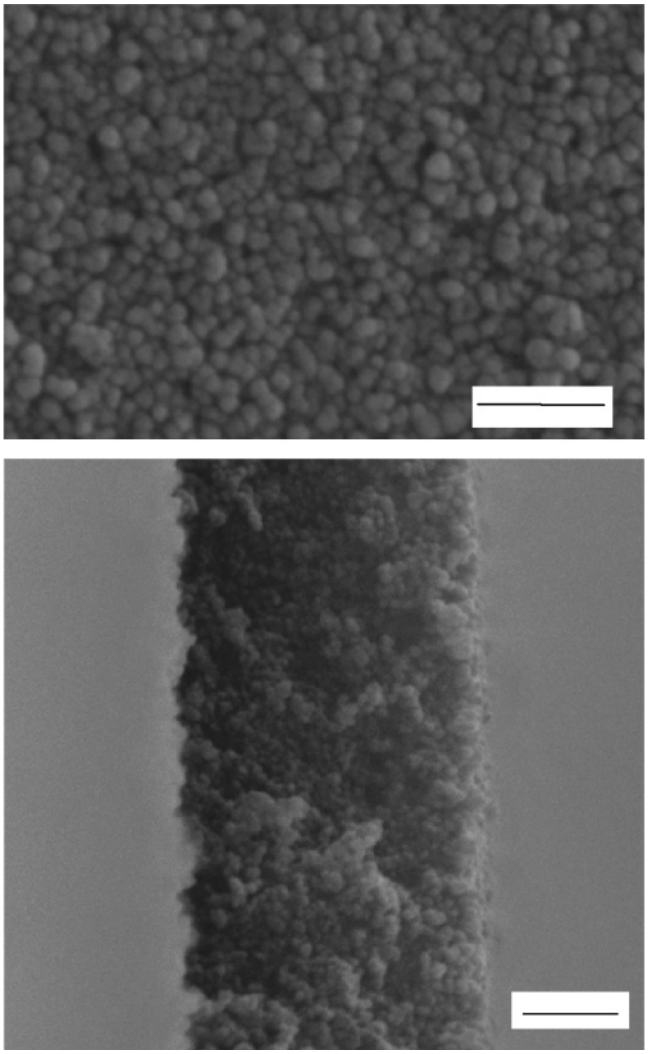

Figure 1. SEM images of the surface and cross section of the TiO_2 film. The bars are equal to 120 nm.

The morphology of the surface and cross section of the TiO_2 layer are shown in Figure 1. It is evident that the arrangement of the nanoparticles in the layer causes the formation of a highly porous film. Moreover, because of their mutual contact, the electrical charges can easily have a very high mobility on the overall surface.

The phosphate/sulfur (sulfur atom is present in MB molecules) molecular ratio was determined by microanalysis (EDX), and it was found to be 2:1; that is, for each pair of phosphate groups present on the surface of the TiO_2 nanospheres, there is one MB molecule anchored.

The Ti/phosphate ratio was not determined. In fact, titanium is present in the total volume of the of the particle so it was very difficult to have direct information about the amount of titanium present only on the particle surface. The synthesis strategy for chemically bonding chromophore molecules to TiO_2 nanoparticles by using PO_4 groups was already reported.[24,27] Nevertheless, to verify if the MB

---

(25) Macchione, M.; De Filpo, G.; Nicoletta, F. P.; Chidichimo, G. *Chem. Mater.* **2004**, *16*, 1400.

(26) Zhang, D.; Yoshida, T.; Furuta, K.; Minoura, H. *J. Photochem. Photobiol., A* **2004**, *164*, 159.

(27) Kalyanasundaram, K.; Gratzel, M. *Coord. Chem. Rev.* **1998**, *77*, 347.

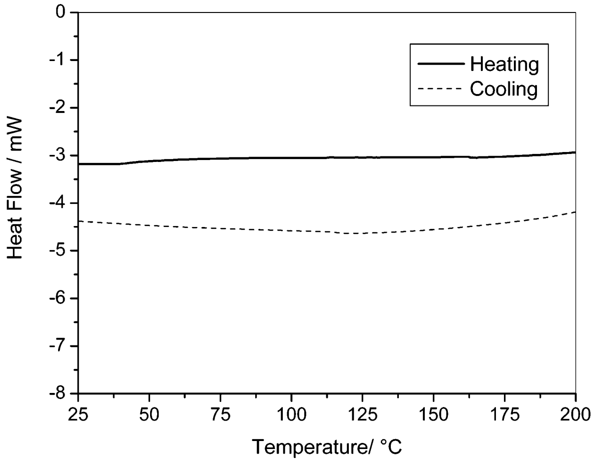

Figure 2. DSC thermogram of TiO_2-PO_4-MB nanoparticles. Heating rate 5 °C/min.

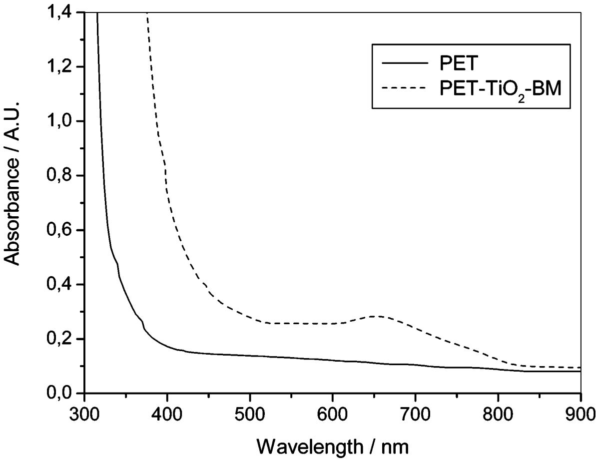

Figure 3. Absorption spectra of the flexible film containing MB molecules ($PET-TiO_2-MB$) and of the PET film.

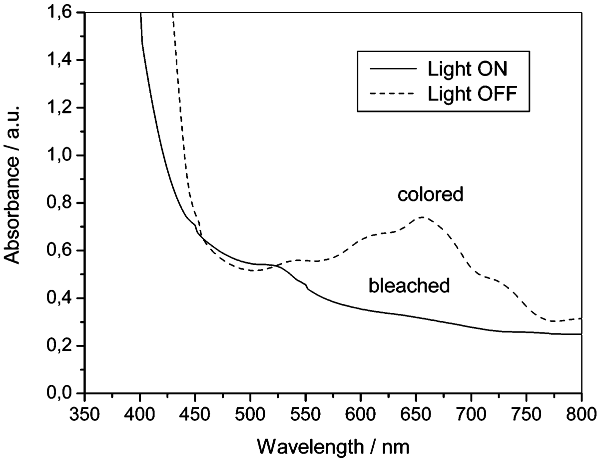

Figure 4. Absorption spectra of the nano-photo-electrochromic device before (colored) and after (bleached) irradiation with red light.

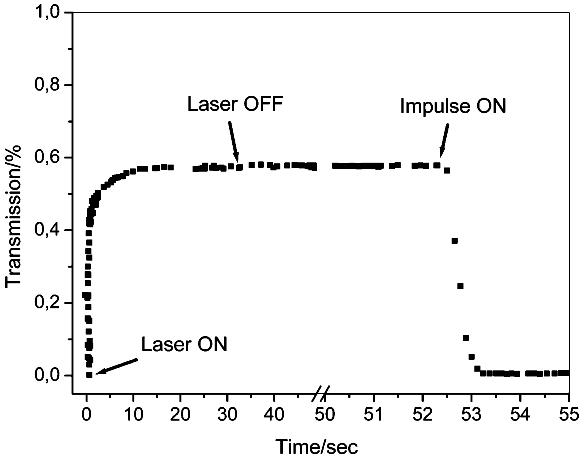

Figure 5. Optical transmission of the nano-photo-electrochromic film. The device was exposed to a red He−Ne laser, and an electrical impulse was applied on it.

molecules were bonded, not simply absorbed, on TiO_2-PO_4 nanoparticles thermal properties of the TiO_2-PO_4-MB nanoparticles were investigated. It is well-known that the loss of chemical or electrostatic interactions is associated to a variation of enthalpy. In light of this, DSC performed on the TiO_2-PO_4-MB nanoparticles was a suitable technique for measuring the variation or heat flux associated to a probable desorbing of MB molecules from the surface of the nanoparticles. In Figure 2 is shown the DSC thermogram of a sample specimen of TiO_2-PO_4-MB nanoparticles heated from 25 °C up to 200 °C. Indeed, at higher temperatures MB molecules undergo thermal decomposition. It is evident that there is not any variation of heat flux associated with the sample heating, which clearly indicates that MB molecules are chemically bonded to nanoparticles as well as there not being any degradation phenomenon.

This result was also confirmed by the fact that the wastewater of the washed $PET-TiO_2-PO_4-MB$ film was uncolored even if the color of the film was blue due to the presence of the MB molecules.

Figure 3 shows the UV−vis spectra of $PET-TiO_2-PO_4-MB$ and PET films.

The $PET-TiO_2-PO_4-MB$ film, besides having the characteristic absorption of TiO_2 at 400 nm, also presents the typical absorbance of MB molecules at 660 nm. On the contrary, the PET film is perfectly transparent to the visible radiation up to 350 nm.

The resulting nano-photo-electrochromic film was characterized by means of UV−vis spectroscopy and an optical line described in detail in the experimental section. Figure 4 shows the absorption spectrum of the device. Before the exposition at the red light, the film presents the peak of absorption of MB molecules (660 nm), resulting in an intense blue coloration of the sample. After the red light irradiation, the device becomes transparent in about 20 s according to the process shown in the Scheme 1. The absorption maximum disappears, and its absorption changes notably.

The optical transmission of the film, reported in Figure 5, was measured by means of a He−Ne laser (reading laser), the intensity of which was decreased by a neutral density filter and a pinhole of 300 μm. Decreasing the power of the reading laser was necessary to avoid interference with the writing laser during the bleaching of the film.

The zero-time optical transmission of the device is about 1% with respect to the air; when it is illuminated with a second He−Ne laser beam (writing laser) the bleaching process starts as a consequence of the reaction between the triplet state of the MB molecules and the electron donor triethylamine molecules. In this case the optical transmission reaches 57% in 20 s. When the writing laser is switched off, the optical transmission of the film still maintains this value for 1 day.

On the contrary, the time necessary for re-coloring the sample, owing to the application of a 1 s electrical impulse of 0.4 V DC, is about 600 ms. Such a re-coloring time is notably smaller than our previous device and comparable with that of the electrochromic device of Reynolds et al.[12] The reason for the about 16 times reduction of the response time is that the MB molecules are anchored at the electrode. Indeed, because molecules do not migrate toward the electrode, the oxidation process is not dependent on the diffusion rate. In addition, the number of oxidized molecules per surface unit is very high because of the great surface of the TiO_2 nanoparticles.

Conclusions

A flexible nano-photo-electrochromic film was obtained by means of the deposition of TiO_2 nanoparticles on conductive PET. The PEC properties of this film are due to the presence of MB molecules bonded to the TiO_2 nanospheres.

A substantial reduction in the re-coloring time of about 16 times is obtained with respect the previous PEC film. This improvement was obtained thanks to the innovative assembly design of this device. Moreover, using plastic conductive PET supports was also helpful to improve the flexibility of the film to make it attractive from the applicative point of view. Indeed, polymer foils are easier to handle in processing steps, such as cutting of larger entities into smaller individual modules.

CM061438M