



Short communication

## Fast, self-supplied, all-solid photoelectrochromic film

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### ARTICLE INFO

#### Article history:

Received 25 November 2009

Received in revised form 13 January 2010

Accepted 17 January 2010

Available online 25 January 2010

#### Keywords:

Photoelectrochromic film

SWNT

Nanomaterials

### ABSTRACT

This paper describes the fabrication and the characterization of a new nanostructured and self-supplied photoelectrochromic device. The main properties of this film are its all-solid nature, its fast coloration time as well as its fast bleaching time. The photoelectrochromic film was manufactured by coating dye functionalized TiO<sub>2</sub> nanoparticles (dye-TiO<sub>2</sub>) on a layer of WO<sub>3</sub> nanoparticles. In order to improve their electrical conductance, both the dye-TiO<sub>2</sub> and WO<sub>3</sub> layers were properly doped with single wall carbon nanotubes (SWNT) bearing COOH groups. A layer of PEDOT/PSS was cast between the dye-TiO<sub>2</sub> layer and the ITO counter electrode, without the use of any fluid component. When exposed to the light, SWNT doped dye-TiO<sub>2</sub> layer generates electrons that reduce the WO<sub>3</sub> layer. As a consequence of this redox reaction, the film changes its color if the two external electrodes are not short-circuited. On the contrary, a fast bleaching of the device can be achieved by shortcircuiting the electrodes.

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### 1. Introduction

Electrochromics are materials that change their color upon application of an electric field. There are two main categories of electrochromic devices:

1. Those that change color upon intercalation of small ions (e.g. Li<sup>+</sup> and H<sup>+</sup> present in fluid electrolyte solutions) into a metal oxide (e.g. WO<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>, and TiO<sub>2</sub>), cast as amorphous or polycrystalline thin films onto conducting transparent substrates.
2. And the others, in which the chromatic change is the consequence of a redox reaction of a chromophore dissolved in a solution or incorporated in a polymer film cast on a conducting transparent substrate.

For satisfactory electro-optical applications an electrochromic device must be characterized by long-term stability, a rapid switching, and a large chromatic change. Unfortunately, in both kinds of the above described devices the coloring and bleaching times are generally too long (several minutes) due to low diffusion of ions in metal oxides and of chromophores in conducting substrates, or due to the long migration time of electrons within the polymer films. Nevertheless, electrochromics are the subject of a number of papers and applications in the literature as smart windows, i.e. devices that are able to control the incident daylight and glare according

to occupant comfort. Even if the applications are currently limited to side and rear-view mirrors, sunglasses, sun-roofs and, in general, small area glazing, a number of leading manufacturers have now demonstrated the commercial viability of products incorporating electrochromic materials. Furthermore, in the last decade several new types of photovoltaic devices have been developed giving new impulse to researches devoted to lower the demand on precious non-renewable fuels for lighting and cooling. When a photovoltaic cell is coupled to electrochromic substrates it is possible to change the device color by using the photocurrent generated by the electrochromic layers, which are generally dye functionalized (or dye-sensitized) in order to absorb a larger range of the sunlight frequencies [1–4]. Therefore, the resulting photoelectrochromic devices are able to feed themselves by simple exposure to an electromagnetic radiation, i.e. they are self-supplied. In fact, the absorbance of a photoelectrochromic device increases when it is illuminated, i.e. the device turns colored, and decreases under short-circuit conditions, i.e. the device bleaches, without the need of any external power source. Consequently, these films are interesting from an applicative point of view for their electro-optical and energy saving properties. In addition, such self-supplied cells have the advantage, over conventional photovoltaics, of being rather simple devices and easy to be assembled.

After the pioneering works reported by Deb and co-workers [1] on dye-sensitized TiO<sub>2</sub> layers in photoelectrochromic configurations, the research on photoelectrochromics gained a renewed worldwide interest after the publication of works from Graetzel [4,19], which have been able to increase the solar energy conversion efficiency in a dye-sensitized TiO<sub>2</sub> thin film solar cell up to 11%.

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A typical photoelectrochromic device is generally made by coating a photoactive (dye/TiO<sub>2</sub>) layer with an electrochromic (WO<sub>3</sub>) layer, while an electrolyte solution, containing Li<sup>+</sup> ions and a redox couple (I<sup>-</sup> and I<sub>3</sub><sup>-</sup>), is between the electrodes. When the dye molecules are excited by light, they inject electrons via the TiO<sub>2</sub> conduction band to the WO<sub>3</sub>, and the consequent cell coloration is observed. If the cells are short-circuited, the electrons are transferred from the WO<sub>3</sub> to the electrode, causing the regeneration of I<sup>-</sup> ions in the electrolyte solution, the oxidation of WO<sub>3</sub>, and the consequent cell bleaching.

The first generation photoelectrochromic devices were characterized by long switching times (several minutes) and the presence of a liquid electrolyte, which reduced their long-term stability. A way to overcome such last drawback was the use of gelators in order to solidify the liquid electrolytes, but resulting in slower response devices.

Interesting photoelectrochromic cells were fabricated and characterized by Kuwabata et al., which made a composite film containing TiO<sub>2</sub> nanoparticles and anodic electrochromic materials as polyaniline or Prussian blue [5–7]. By using a photomask the composite thin film produces a photo-image when irradiated by UV light. Bechinger et al. developed photoelectrochromic windows and displays by pairing an inorganic WO<sub>3</sub> electrochromic electrode and a dye-sensitized semiconductor electrode, able to give a sufficiently high photovoltage to color the electrochromic film [8].

In the recent years our research group developed a flexible organic photoelectrochromic film formed by a layer of TiO<sub>2</sub> nanoparticles covered with methylene blue molecules, and coated on flexible conductive supports [9,10]. This device is able to change its color when irradiated with a laser beam.

The use of conductive polymers, e.g. polyaniline and PEDOT, allowed the manufacture of flexible photoelectrochromic films at low costs [1,11]. Recently, Krasovec et al. manufactured a photoelectrochromic film composed of a TiO<sub>2</sub> layer cast on a WO<sub>3</sub> substrate [12,13]. The authors used the electron photogeneration by TiO<sub>2</sub> nanoparticles, when exposed to light, to reduce the electrochromic WO<sub>3</sub> particles with a consequent color change of the device. However, the main drawbacks of such a device are the long coloration and bleaching times (about 10 min) due to the low electrical conductance of TiO<sub>2</sub> layer and to its low porosity that hampers the diffusion of lithium ions.

In this paper, the manufacture and the characterization of a new nanostructured and self-supplied photoelectrochromic device is described. Photoelectrochromic film was manufactured by coating dye functionalized TiO<sub>2</sub> nanoparticles (dye-TiO<sub>2</sub>) on a layer of WO<sub>3</sub> nanoparticles acting as electrochromic layer. In order to improve their electrical conductance, both the dye-TiO<sub>2</sub> and WO<sub>3</sub> layers were properly doped with single wall carbon nanotubes (SWNT) bearing COOH groups and a layer of PEDOT/PSS was cast between the dye-TiO<sub>2</sub> layer and the ITO counter electrode, without the use of any fluid component. As a consequence the most attractive properties of this film are its all-solid nature and its fast coloration time as well as its fast bleaching time, which last a few tens of seconds.

## 2. Experimental

COOH functionalized single wall carbon nanotubes (SWNT, 3–6 at% carboxylic acid, Sigma-Aldrich) were added to a 20 wt% water suspension of WO<sub>3</sub> nanoparticles (Aldrich, average diameter ≈50 nm) containing some drops of Triton X100 (Aldrich) as surfactant. The weight ratio was SWNT: WO<sub>3</sub> = 0.005: 1. The resulting mixture was cast on ITO coated glass supports (resistance 20 Ω/sq) by a spin-coater. The supports were kept in an oven for 30 min at 450 °C in air, and the thickness of the result-

ing layers was ≈0.5 μm. After such a treatment, no thermal degradation of SWNTs was observed by thermal gravimetric analysis/differential scanning calorimetry. Then, following the same procedure used for WO<sub>3</sub>, a second layer (thickness ≈0.5 μm) of TiO<sub>2</sub> nanoparticles (Aeroxide P25, Degussa, average diameter ≈25 nm) doped with 0.002 wt% of SWNT was cast above the WO<sub>3</sub> layer. The resulting SWNT-WO<sub>3</sub>/SWNT-TiO<sub>2</sub> double layer was dipped overnight in a 3 mM cis-bis(isothiocyanate)bis(2,2'-bipyridyl-4,4'-dicarboxylate)-ruthenium(II)/ethanol solution (Solaronix) in order to bind the dye to the surface of the TiO<sub>2</sub> nanoparticles. A further thermal treatment of the film at 60 °C for 12 h was used to remove the solvent. Control films without dyes did not give satisfactory results.

Then, the SWNT-dye-TiO<sub>2</sub> layer was covered by spin-coating with a 5 wt% aqueous solution of poly(3,4-ethylenedioxythiophene)poly(styrenesulfonate) (PEDOT/PSS, Bayer). A further thermal treatment of the film at 60 °C for 24 h was necessary to remove water.

Finally, the PEDOT layer was covered by an ITO layer by room temperature sputtering. This step was necessary to protect the PEDOT conductive surface and to allow the electrical connections.

Morphology characterization of the films was performed by a scanning electron microscope (SEM, LEO 420, LEICA). Sample cross sections were obtained by cutting cells after immersion in liquid nitrogen. Optical characterization was performed by UV–vis spectrophotometer (V 550, JASCO). Cell irradiation was performed from ITO layer side by an optical fiber connected to a suntest device (CPS, Atlas). The response times (both in open and short-circuit conditions) were measured by monitoring the absorbance as a function of time at the wavelength of 800 nm.

## 3. Results and discussion

The photoelectrochromic films were made by coating dye functionalized TiO<sub>2</sub> nanoparticles (dye-TiO<sub>2</sub>) on a layer of WO<sub>3</sub> nanoparticles, which were cast on an ITO coated glass support (working electrode). The WO<sub>3</sub> layer acts as the electrochromic layer. Strategies to lower the response times of a photoelectrochromic cell include the increase of electrical conductance of the composite film by doping the layers with different derivatives, acids, polymers, nanoparticles, and carbon nanotubes. A problem common to all these attempts is the non-uniform distribution of doping molecules/particles in the films. In order to improve the electrical conductance of both dye-TiO<sub>2</sub> and WO<sub>3</sub> layers, they were adequately doped with single wall carbon nanotube molecules functionalized with COOH groups (COOH-SWNT). The SWNT-dye-TiO<sub>2</sub> layer was covered by a PEDOT layer and, then, by an ITO layer acting as counter electrode. As reported in the experimental part, the doping of layers with COOH-SWNTs includes their thermal annealing at 450 °C for 30 min in air, which could damage COOH-SWNTs. In order to check the integrity of SWNTs after the annealing process, we performed a thermal gravimetric/differential scanning calorimetry analysis reported in Fig. 1. As one can see, no thermal degradation of SWNTs is observed up to 450 °C. When films are exposed to light irradiation, the SWNT-dye-TiO<sub>2</sub> layer generates electrons that are injected into the WO<sub>3</sub> layer, which is thus reduced. As a consequence of this redox reaction, the film changes its color if the two electrodes are not short-circuited. The bleaching of the device can be achieved by short-circuiting the device. In order to improve the electrical conductance of both TiO<sub>2</sub> and WO<sub>3</sub> layers and to favour a homogeneous water dispersion, we checked the amount of SWNTs functionalized with COOH groups to be added to nanoparticles suspensions [14,15]. A detailed morphology analysis of the resulting films by scanning electron microscope (SEM) allowed to choose the best SWNT percentage in both the

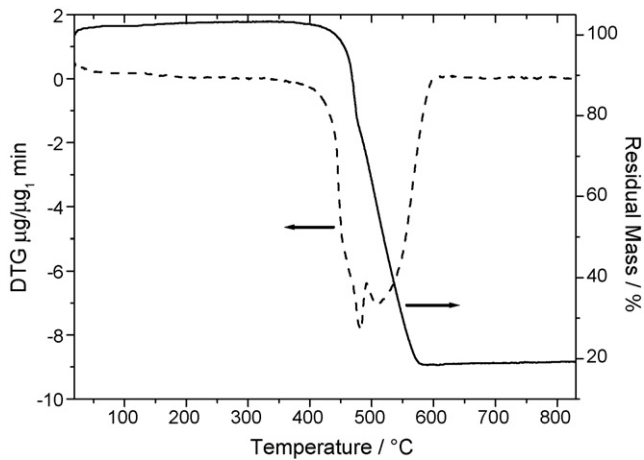


Fig. 1. Differential scanning calorimetry and thermal gravimetric analysis of COOH-SWNTs.

TiO<sub>2</sub> and the WO<sub>3</sub> suspensions, in order to incorporate the maximum amount of SWNTs without changing the nanostructured layer homogeneity. Fig. 2a and b shows the top surface and the cross section of a TiO<sub>2</sub> film containing 0.002 wt% of SWNTs, respectively. As a result of the presence of COOH groups, SWNTs were well dispersed in water and such a good miscibility with water is beneficial for the fabrication of TiO<sub>2</sub> and WO<sub>3</sub> uniform films. Analyses of SEM confirm that incorporation of COOH-SWNTs up to 0.002 wt% into the TiO<sub>2</sub> film essentially yields a uniform TiO<sub>2</sub> film thickness, a regular surface morphology, and an adequate forward electron transfer through the SWNT-dye-TiO<sub>2</sub> layer. On the contrary, the pictures of samples with larger amounts of COOH-SWNTs (Fig. 2c and d shows the morphologies of TiO<sub>2</sub> films containing 0.008 wt% and 0.030 wt% of SWNTs, respectively) are characterized by the presence of some clusters making the structures spatially irregular and with a reduced electrical conductance [16].

The cluster formation is probably due to the heterogeneity of the starting suspensions because of the high SWNT concentration. In addition, the electrostatic interactions between COOH groups of SWNT and OH groups present on the TiO<sub>2</sub> surface, could be responsible for the observed macro-aggregates [16]. Similar results were obtained with the morphology of WO<sub>3</sub> layers (incorporation of COOH-SWCNs up to 0.005 wt%). This phenomenon in both the TiO<sub>2</sub> and the WO<sub>3</sub> layers is known to cause a loss in the electron transfer efficiency due to reduced connectivity between the SWCNTs and the TiO<sub>2</sub> particles

Fig. 3 shows the different layers of the used materials, from the left: SWNT-WO<sub>3</sub>/SWNT-dye-TiO<sub>2</sub>/PEDOT/ITO. Scheme 1 reports the diagram of energy levels of the previous layers and the electron diffusion paths through the device. The incident light promotes electrons from the HOMO to the LUMO dye orbitals. The energy gap between the two levels is about 1.6 eV and is related to the absorption of visible light with a wavelength up to 700 nm. Then, electrons move to the TiO<sub>2</sub> orbitals, as their energy levels have lower values than the dye LUMO ones. Successively, electrons transfer to the WO<sub>3</sub> levels and cause the reduction of WO<sub>3</sub> in W<sup>6+</sup><sub>1-x</sub>W<sup>5+</sup><sub>x</sub>O<sub>3-x/2</sub> with a consequent change of the absorption spectrum of the film, becoming deep blue [17,18].

The above described coloration process occurs if the external circuit is open. On the contrary, by short-circuiting the electrodes one let the W<sup>6+</sup><sub>1-x</sub>W<sup>5+</sup><sub>x</sub>O<sub>3-x/2</sub> oxidize to WO<sub>3</sub>, causing the film bleaching.

PEDOT layer is another novelty of this film compared to analogous devices. In facts, it allows an easier repopulation of the dye HOMO level by electron transfer from the ITO layer [23]. Such a conductive polymer layer plays the role of an electrical contact

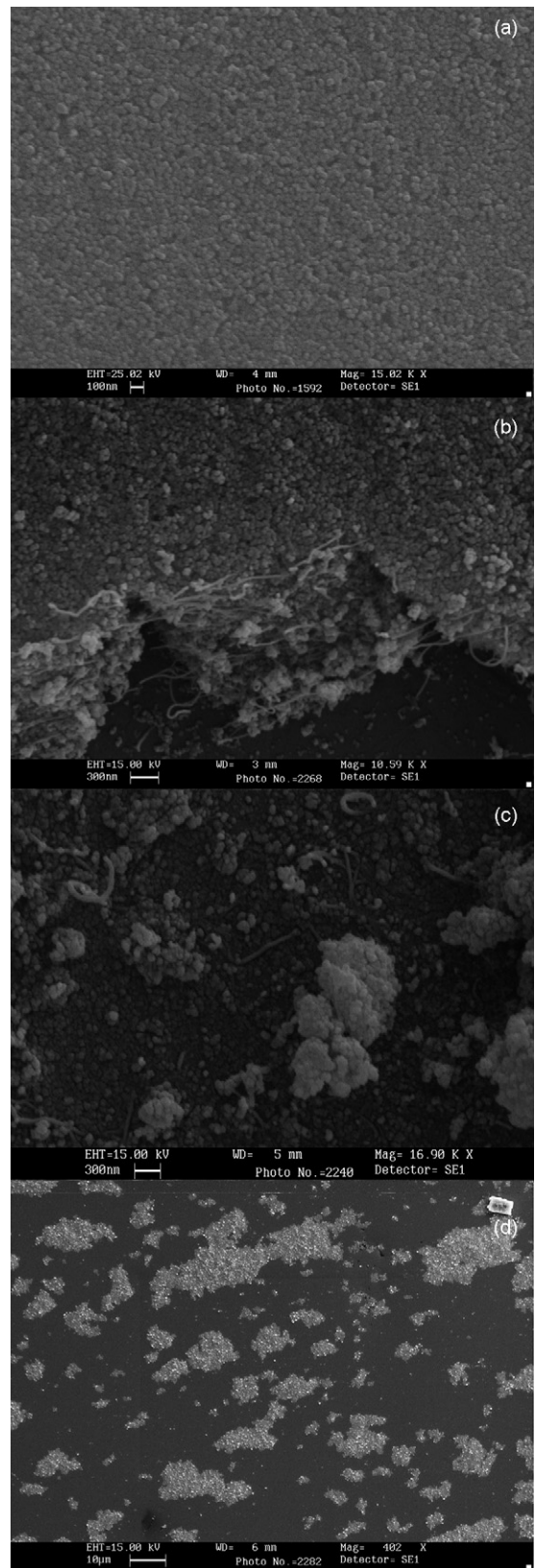
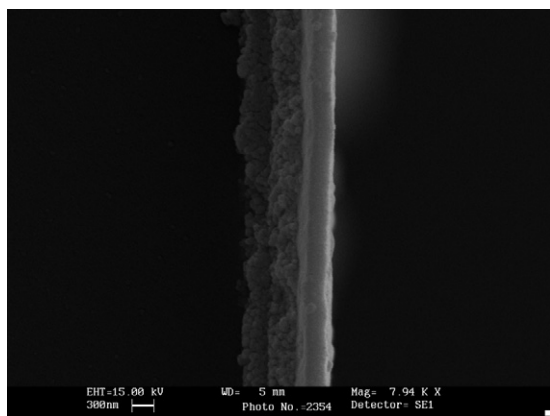


Fig. 2. SEM images of top surface and cross section of TiO<sub>2</sub> film incorporating 0.002 wt% (a and b) and of top surface of TiO<sub>2</sub> films incorporating 0.008 and 0.030 wt% of SWNTs (c and d, respectively).



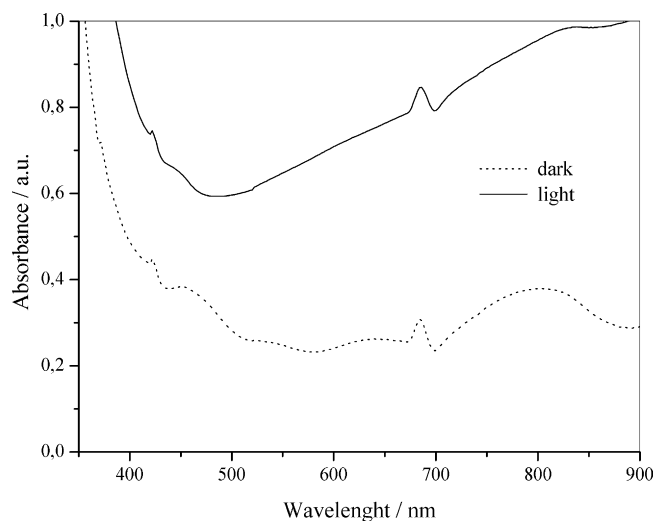
**Fig. 3.** SEM image showing the sequence of different layers. From the left: SWNT-WO<sub>3</sub>/SWNT-dye-TiO<sub>2</sub>/PEDOT/ITO. The glass substrate at the left end of the picture is not visible being far from the SEM focus as a consequence of the stub preparation.

between the SWNT-dye-TiO<sub>2</sub> and ITO layer, aiding the electron transfer from the counter electrode to the dye. In addition, while traditional devices have fluid electrolyte solutions for the electron transfer, with the disadvantage to have a liquid phase dispersed in the film, the use of PEDOT allows protons to intercalate to balance the charge on the electrons and, consequently, the preparation of a self-supported and all-solid film with enhanced charge injection [23].

After cell irradiation from ITO glass side, the sample changes its color from an initial pale blue in a deep blue one. The film absorbance, before and after irradiation, as a function of wavelength is shown in Fig. 4. The absorbance increase in the visible range is due to reduction of WO<sub>3</sub> layer.

Fig. 5 shows the time behaviour of the optical transmittance,  $T$ , at the wavelength of 800 nm of our cell (full line). In dark conditions, the film is highly transparent ( $T \approx 84\%$ , normalization to the air). After irradiation in open circuit conditions, the film turns deep blue with a consequent transmittance decrease to 30% in about 8 s. Successively, by switching OFF the lamp but in open circuit conditions,  $T$  very slowly increases as a function of time.

If one shortcuts the electrodes, the film bleaches in about 30 s, allowing the transmittance to gain its original value. An increase in the response time can be observed if one lowers the light power. No change in the transmittance values is observed. Control films without SWNTs are characterized by longer response times (7–8 min) confirming that the increase of layer conductance [16] can give rise



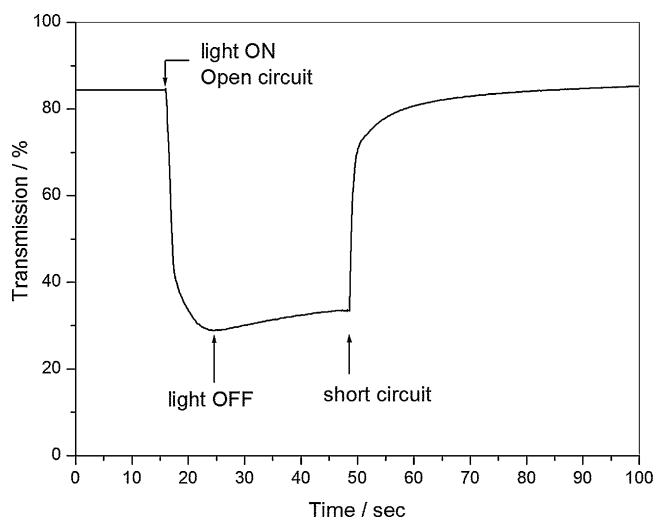
**Fig. 4.** Absorption spectrum of the photoelectrochromic device in its bleached (dark conditions) and colored state (under irradiation).

to more performant cells and the SWNTs represent the real novelty of our devices.

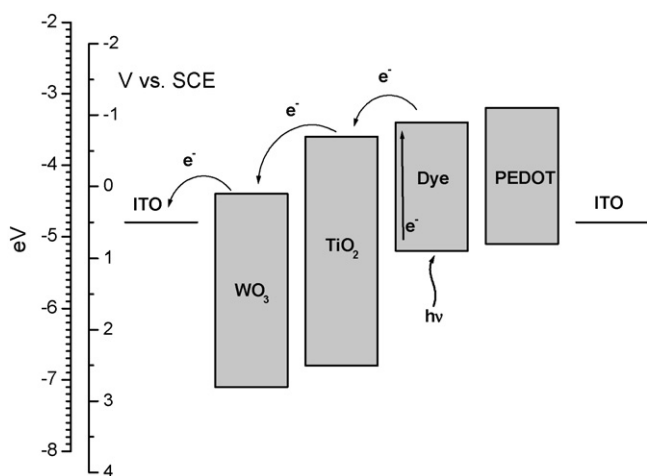
The obtained results on the response times of photoelectrochromic cells is due to the doping of the TiO<sub>2</sub> and WO<sub>3</sub> layers with 0.002 wt% COOH-SWCNs. Compared with the undoped ones, cells show a faster response (about two order of magnitude lower) and an excellent contrast ratio, (i.e. the percentage of transmittance change, see Fig. 6). The response time behaviour can be related to the increased electrical conductance of the film coming from improved miscibility of COOH-SWCNTs with water, increased interconnectivity between layer particles (TiO<sub>2</sub> and WO<sub>3</sub>) and COOH-SWCNTs, and the use of PEDOT layer.

Fig. 6a and b shows a sample just after irradiation in open circuit conditions and after circuit shortcutting, respectively. The sample looks deep blue and is rather opaque in Fig. 6a, but it looks pale blue when it is completely bleached.

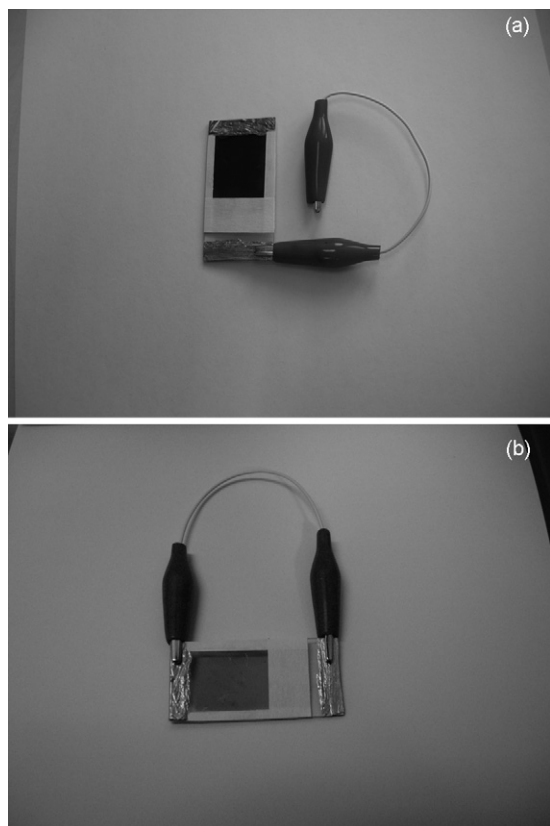
The device stability was checked by cycling both the coloration and the bleaching processes. In particular, after 100 irradiation cycles we did not observe any change in the initial and final values of transmittance, confirming the stability of devices.



**Fig. 5.** Behaviour of transmittance of the photoelectrochromic device. Under irradiation and open circuit conditions the devices turn colored. After switching off the light source and in short-circuit conditions, the devices bleach to the initial transmittance value in a few seconds.



**Scheme 1.** Energy level diagram for our photoelectrochromic device. See Refs. [19–22].



**Fig. 6.** Pictures showing: (a) the colored state in open circuit conditions, (b) the bleached state in short-circuit conditions.

#### 4. Conclusions

In conclusion, a new all-solid and self-supplied photoelectrochromic device was manufactured. It is able to modulate the optical transmittance by a color change induced after light exposure, and to return to the original state by shortcutting the electrodes. This process is long-term stable and does not need any external power supply. The coloration and bleaching times are 8 s and 30 s, respectively. Such values are smaller than similar device ones (about 600 s). The coloration and bleaching time reduction of about two order of magnitude was obtained by using SWNT functionalized with COOH groups in order to allow their easier and better dispersion in aqueous suspensions of TiO<sub>2</sub> and

WO<sub>3</sub> nanoparticles. The improved miscibility with water and the good incorporation of COOH-SWCNs in the TiO<sub>2</sub> and WO<sub>3</sub> films increase the uniformity of layers, their electrical conductance, and the electron transfer through the film, and, consequently, decrease remarkably the response times. Finally, the introduction of a conductive layer of PEDOT, cast between the dye-TiO<sub>2</sub> layer and the ITO counter electrode, avoids the use of any fluid or jellified electrolytic solutions as in similar cells, giving rise to a new, fast, self-supplied, and all-solid photoelectrochromic device and enabling thus new scientific prospects and/or applications. Work is in progress in order to enhance the device performance by using different dyes and thickness of layers without losing the contrast ratio in the transmittance.

#### Acknowledgment

MIUR is acknowledged for financial supports (EX-60% and PRIN).

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