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Flexible photochromic Ag:TiO_2 thin films fabricated by ink-jet and flexography printing processes

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The realization of flexible Ag:TiO_2 photochromic material using processes compatible with industrial scale production is demonstrated. A titanium precursor solution is printed on a plastic substrate. After incorporating silver, the coating shows a reversible photochromic behavior with a good contrast of color under laser exposures.

Authentication of goods[1], storage and displaying of time limited multicolored information[2,3,4] are parts of hot topics in current societies. Since few years, an innovative means is developed in order to address this issue. It is based on the photochromic behavior of some nanocomposite thin films. From few times, new inorganic[5] and organic/inorganic hybrid[6] materials demonstrated their photochromic performance and could compete with Ag:TiO_2 thin films. However the latter stay the most studied.[2,7,8,9] Different strategies have been proposed to fabricate such materials and one of them, based on the use of mesoporous films of amorphous TiO_2, has proven to give rise to a high color stability.[10,11] The mesoporous TiO_2 matrix is fabricated thanks to sol-gel and EISA methods[12] before incorporating silver ions. Under UV light exposure, the photocatalytic behavior of TiO_2[3] permits to reduce silver ions, which finally form Ag nanoparticles (NPs) with various shapes and sizes directly surrounded by TiO_2 or other compounds contained in the pores. This heterogeneity leads to an inhomogeneous broadening of the localized plasmon resonance (LSPR) of Ag NPs and gives the films a grey brown color.[2,13] Reversibly, under a visible light exposure Ag NPs can oxidized either partly or completely, which leads to a color change or to a total bleaching of the film. This oxidation results from the excitation of free electrons at the surface of particles, through their LSPR, and from their transfer to the TiO_2 conduction band.[2,14] Such materials were largely developed on rigid support.[1-9,13-15] However, if they could be fabricated on any kind of substrate, especially on flexible substrates like plastic sheets, their use could be of interest for smart cards and packaging manufacturing. Moreover, to permit the use of such materials in industry, adequate elaboration techniques have to be introduced. Printing technologies seem to be a good solution since they are already commonly used in industries. Few research studies considering inkjet[16,17,18,19] or flexography[20,21,22] to deposit sol gel recently began to appear in electronics,[17,18,20,19,22] photovoltaics and photocatalysis[16] areas. On the other hand, resistance of plastic substrate during laser exposure had been shown, in the case of the reduction of graphene oxide in conductive tracks.[23]

To the best of our knowledge, this communication describes for the first time, the production of a flexible mesoporous TiO_2 based photochromic material by printing processes, especially inkjet and flexography. Inkjet was first chosen because it permits directly[16,17,19] to print patterns or continuous layers[18] with precision by controlling the amount of released ink.[16,19] However, for high production volume, flexography printing was preferred.[21] This process is largely used in cardboard and wrapping films sectors[24] since it is the contact printing technology that requires the lowest contact pressure between the printing plate and the substrate.[20] The issue of the study was to fabricate a TiO_2:Ag thin film on polyethylene terephthalate (PET) sheets with processes adaptable to industry. Therefore, inkjet and flexography printing processes were adapted to a titanium precursor solution previously formulated[25] to fabricate a mesoporous film of amorphous TiO_2 on PET. The rheological properties were adapted to ensure the compatibility of the solution with printing processes and plastic substrate. Inkjet and flexography parameters were also adjusted according to previous results particularly to slow down the fast solvent evaporation. Optimized printed films were compared to spin-coated films. Finally, after incorporating silver ions the reversible photochromic behavior of the material was checked.

Ag:TiO_2 films were fabricated on clean untreated face of PET sheets (2 X 2 cm² and 5 X 7 cm²) Melinex ST504 from Dupont Teijin film. The titanium precursor solution was obtained by using a procedure previously published.[25] On the one hand, it consists in dissolving pluronic P123 copolymer (P123), whose removal from the film will form the porosity in the final titania matrix, in 1-propanol. On the other hand, titanium tetra-isopropoxyde (TTIP), the titania

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precursor, is mixed with benzoyl acetone (BzAc). The latter prevents the polymerization of the precursor in the solution. Then the two solutions are mixed together in presence of hydrochloric acid (HCl, 37%) and deionized water (H_2O). Molar ratios of the reagents are fixed at TTIP/P123/1-propanol/HCl/H_2O/BzAc = 1:0.026:29.77:0.017:31.11:0.5. The sol is aged at least two days before using. Rheological properties of the sol were measured using a Physica MCR 301 rheometer with the CP50-1 modulus. A digital tensiometer Kruss K10ST and the Nouy ring method were used to evaluate the surface tension of the sol. The wettability of the substrate by the sol and the surface energy of the substrate were evaluated by the measurement of the contact angle respectively between the sol and the PET film, and between four fluids (deionized water, polyethylene glycol 200, diiodomethane, glycerol) and the PET substrate, by image analysis (OCA 20, Data Physics).

A piezoelectric drop on demand printer (Fujifilm Dimatix DMP-2831) was used for inkjet printing. Used cartridges contain up to 1.5 mL of ink and their 16 nozzles of 21 µm diameter spaced by 254 µm from each other permit to eject drop with a nominal volume of 10 pL. The drop ejection is activated by the deformation of a piezoelectric component that causes a short shrinkage of the chamber containing the ink volume. A micro-volume of ink is then pushed into the nozzles to be ejected as it is shown in figure 1a). In this study, a standard waveform elaborated by Fujifilm was adjusted to obtain uniform patterns. Moreover a voltage of 30 V was applied on all nozzles, the printhead was fixed at 0.25 mm from the PET substrate and a space of 30 µm was fixed between printed drops in order to form continuous patterns. Finally, a Peltier plate was used to cool down the substrate during printing.

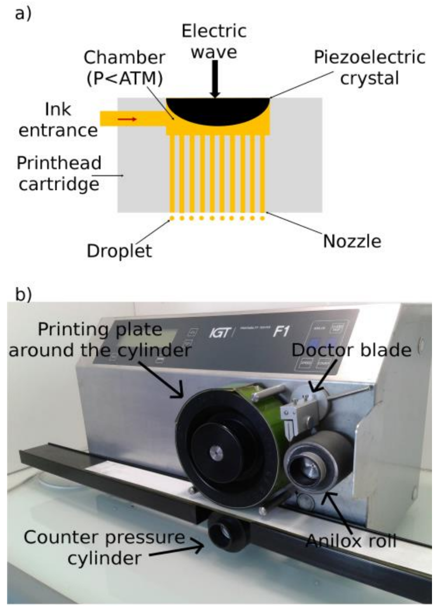


FIG. 1 Principle of: a) ink ejection in inkjet process and b) ink transfer in flexography process.

A flexo printability tester F1 from Certified Lab Consulting Company Limited was also used. Flexography is a method of direct printing mainly used for packaging substrates (paper, foil and film…). As figure 1b) shows, a resilient relief-image plate of rubber or photopolymer material is inked by an engraved cell structured, ink-metering 'anilox' cylinder. Thanks to a small pressure, the plate then transfers the ink to the desired regions of the substrate when they contact each other.[17] To optimize the printing, several parameters were studied: the cell dimensions of the engraved ceramic cylinder, the pressure between anilox roller and printing plate, and between printing plate and PET, the printing speed, and the number of coated layers.

After deposition, coated films were stabilized at 110°C for 2 hours and under UVA light (365 nm, I=310 µW/cm²) for 24 hours. They were annealed under an infrared rapid thermal annealing furnace (As-One, Annealsys), to ensure the polymerisation of TTIP in TiO_2 and create mesoporosity by eliminating P123 surfactant. Mesoporous films were then soaked 30 min in an aqueous ammoniacal silver solution $[Ag(NH_3)_2]^+NO_3^-$. All this part of the process had been described in a previous paper.[25] The films were stored for 12 hours at room temperature in darkness before using. Finally, obtained films were submitted to successive continuous wave (CW) laser exposures in order to highlight their photochromic behavior. Exposure conditions depend on the film absorbance and thickness. UV exposures were performed at 244 nm, with an intensity I=0.11 W/cm² during 8 min for flexography coated films and 10 min for inkjet printed films. Visible exposures were performed at 488 nm, I=5.6 W/cm² during 20 min on films made by flexography and at 4.6 W/cm² during 25 min on films made by inkjet.

The surface of mesoporous films was characterized thanks to microscopic observations with a Zeiss Axio Imager optical microscope. Their thickness and roughness were measured with the Dektak XT surface profiler with a diamond stylus of 2 µm on a profile of 500 µm. The adhesion of the films on the PET substrate was evaluated by scratch test, according to the D3359-97 procedure of the American Society for Testing and Materials. Finally, the UV-visible spectra of films were measured with a Perkin Elmer Lambda 900 UV/vis/NIR spectrophotometer.

Table 1 shows that the viscosity and the surface tension of the sol are very close to the recommended range for inkjet and flexography processes. Particularly, the Dimatix user manual suggests a viscosity range from 10 to 12 mPa.s to get optimum performance however some authors[16] obtained satisfactory results with a sol with a viscosity value about 4 mPa.s. The difference of the viscosity value between the sol and 1-propanol (2.2 mPa.s)[26] can be mainly explained by the presence of TIPT complexed with BzAc and starting interactions between titanium alcoxyde, and the use of a high molecular weight nonionic surfactant, i.e. P123.

	Theoretical recommendation		Experimental values
	Ink Jet	Flexography	Sol
Viscosity at 20°C, 1000 s^{-1} (mPa.s)	[10-12][27]	[10 – 100][24]	6.50 ± 0.40
Surface tension (mN/m)	[28-42][27]	[24 – 40][24]	25.90 ±0.12

TABLE 1 Rheological properties of the solution and recommended values for printing processes

The sol viscosity appeared to be stable from the second day after formulation to at least three months. The surface tension is principally imposed by 1-propanol, which owns a surface tension value of 24.46 ± 0.15 mN/m. Note that this value is lower than the surface energy determined for the PET sheets, i.e. 38.5 mJ/m². Therefore a good spreading of the sol on the substrate is expected during the coating and was confirmed by the low contact angle, about 15.9°, measured when depositing a drop of the solution on a PET sheet. Consequently, thanks to a mixture in good proportions, the obtained precursor solution behaves like an ink for inkjet or flexography processes, which remains stable for at least three months.

The titanium precursor solution was printed by flexography and inkjet. Parameters of each process were adjusted to obtain the most uniform layer of TiO_2 matrix. Owing to the high volatility of the small sol droplets deposed by inkjet, the PET substrate was fixed on a Peltier plate. The latter permitted to maintain the temperature at 17°C and to slow down the solution evaporation rate in order to ensure a good merging between successive printed lines. If the temperature was higher than 17°C, the solution began to dry between each line. As illustrated in figure 2, at 28°C lines still merge but a pronounced coffee ring effect[28] is observed. This

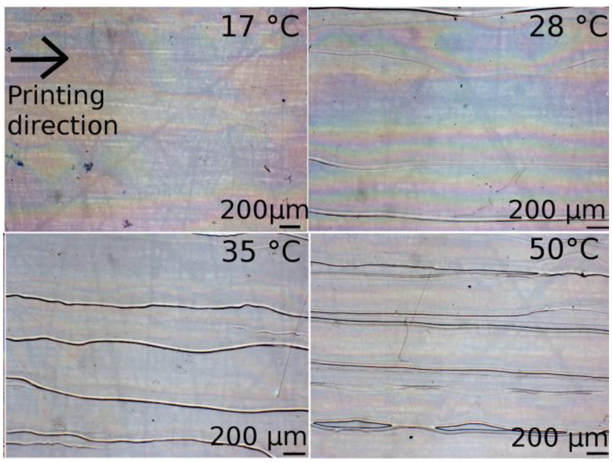


FIG. 2. Optical images taken in reflexion of the center of squares of 4 cm² inkjet printed on a PET sheet at different temperatures

effect, which corresponds to variations in the film thickness from the center to the edge of the line, results from the fast evaporation of solvent at the line edge. From 35°C, brown lines appear on pictures due to the partial covering by the "line in printing" of the previous line completely dried.

According to the principle of the flexography printing process, that is an automated ink pad with a double ink transfer, few matter were deposited on the substrate. Consequently, the film thickness was low and a little variation in the printing process could cause defects. So, to coat an adequate amount of titania ink, two layers were deposited with intermediate drying at room temperature during 5 min. The latter permitted to fix and homogenize the first layer on the substrate.

Optimized printed layers obtained in flexography and inkjet were compared to layer deposited by spin-coating Results are presented in Table 2. The surface of printed films has a similar quality than the one obtained by spin coating. The film coated by inkjet has a thickness very close to the one of spin-coated films whereas flexography printed films are thinner. Whatever the used coating process, the roughness of films replicates the bare PET one (5±3 nm) and their adhesion on PET is very satisfactory according to the scratch test. To resume, inkjet printing and flexography with adjusted parameters permit to obtain films with a quality very close to that given by spin coating.

After liberating the porosity of films by infrared annealing, SEM observations (not shown) on both inkjet and flexo printed films highlight the presence of open surface pores with diameter ranging from 2 to 6 nm which were associated to the P123 surfactant removal after IR radiations, as confirmed by IR analysis and as already demonstrated in a previous article.[25] Note that microscopic cracks appears after the annealing due to the constrains suffered by the film during the process. However they don't alter the film properties as already shown in the same previous article.[25] Silver ions were then incorporated in mesoporous films. The latter were exposed to UV then visible laser light to check their photochromic behavior. The film evolution was followed by UV-visible spectroscopy. After UV exposure (figure 3a, red1), a plasmon resonance band appears centered around 500 nm as resulting from the growth of silver nanoparticles and causing the coloration of the film[2,8,10,25]. As the resonance band is quite large, nanoparticles with different sizes and local environment are formed and explain the brown color of the film. The material was then exposed to visible

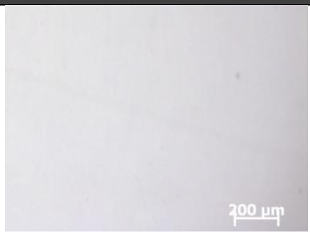
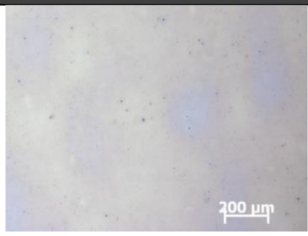
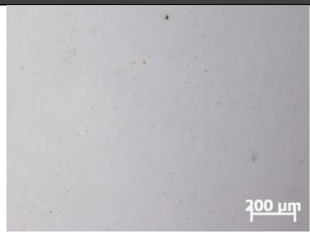
	Spin-coating	Flexography	Ink-jet
Surface state			
Roughness Ra (nm) measured on 500 µm profile	**4 ± 4**	**9 ± 6**	**8 ± 3**
Thickness (nm)	**271 ± 79**	**178 ± 53**	**211 ± 104**
Adhesion	**<< 5% of film damaged by tape removing**		

Table 2: Comparison between TiO_2 film coated by spin-coating, flexography and inkjet

light. The plasmon resonance band disappears (figure 3a, ox1) after the oxidation of nanoparticles and the bleaching of films[2,10,25,29]. Five cycles of uv / visible exposures were then performed. UV-visible spectra are reported in figure 3a for a flexography film. A slight red shift, observed from the second reduction, indicates that bigger particles are formed. Figure 3b shows the values of absorbance at 488nm during cycles on films from flexography and ink jet. Note that the difference of absorbance level between the two films is due to their different thicknesses. The inkjet coated films are thicker than the flexography coated films, they therefore contain more silver ions. Consequently, a higher quantity of photons, i.e a longer UV exposure time, is needed to totally reduce ions to form nanoparticles and a higher absorbance value is reached. After each UV and visible exposure similar values of absorbance are measured, demonstrating a repeatable photochromic behavior. Since laser exposures permit to color and bleach the material, the photochromic behavior can be used to mark updatable data at different scales: from macroscopic to micrometric for example, like in figure 3c.

Conclusions

To conclude, the realization of flexible photochromic materials with conventional printing processes has been demonstrated. A sol-gel titanium precursor solution was successfully printed by inkjet and flexography on plastic substrate thanks to adaptation of printing processes. After incorporating silver ions, the nanocomposite films showed a repeatable reversible photochromic behavior with a good contrast between the colored and bleached state. Consequently, the fabrication of flexible photochromic material using easily up-scalable printing processes can be industrially envisaged and offers a new means to store updatable data and to secure products in smart cards or goods packaging areas.

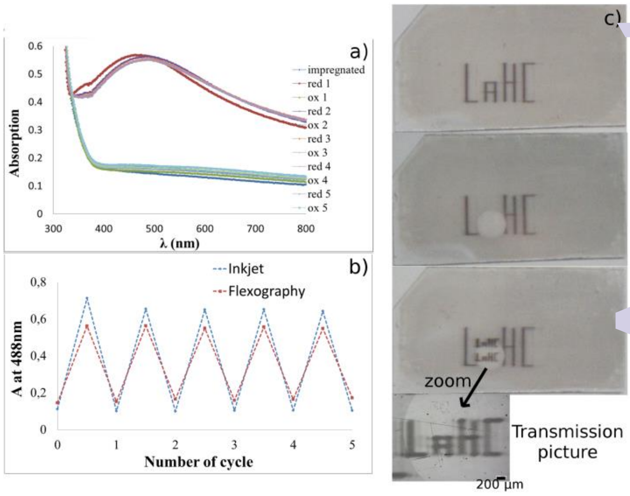


FIG. 3. Photochromic behavior. a) UV-vis absorption spectra of film from flexography after successive UV and visible exposure. b) Absorbance at 488nm for 5 cycles of UV/visible exposures for each kind of film. c) Picture of UV exposure inscription at different scales and visible exposure erasing on a film coated by flexography. (Zoom of the second inscription is an observation with optical microscope in transmission

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