Magnetron Sputtering Deposition of Ag/TiO\textsubscript{2} Nanocomposite Thin Films for Repeatable and Multicolor Photochromic Applications on Flexible Substrates

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It is reported on a reactive magnetron sputtering-based deposition method to synthesize, at room temperature, photochromic nanocomposite thin films consisting of Ag nanoparticles sandwiched between nanoporous TiO\textsubscript{2} layers. The fabrication process is compatible with large-scale production and functional flexible substrates. It is shown that when TiO\textsubscript{2} is deposited in the metallic mode, the formation of Ag metal nanoparticles induces localized surface plasmon resonances in the visible range and therefore the as-deposited samples are colored. In contrast, when TiO\textsubscript{2} is deposited in the compound mode, the trilayer samples are colorless because silver oxidizes during TiO\textsubscript{2} deposition. It is demonstrated that the colorless samples can be colored under ultraviolet (UV) laser exposure at 244 nm due to the reduction of oxidized silver and the formation of metallic Ag nanoparticles. Moreover, irradiation at 647 nm wavelength of colored samples (as-prepared or after UV exposure) gives rise to changes in the particle morphology that strongly modifies the film absorbance and results in a color transition from blue to orange. The choice of the irradiation wavelength allows controlling the color saturation of the sample up to the complete discoloration by using a visible laser at 488 nm. All these photochromic mechanisms are repeatable during cyclic processes.

1. Introduction

Photochromic materials change reversibly their colors under photonic excitation.[1] They have been suggested for a wide range of applications such as high-density multiwavelength optical data storage,[2] secure traceability, and rewritable color paper.[1] Since 2003, multicolor photochromism was reported in nanocomposites consisting of Ag nanoparticles loaded in TiO\textsubscript{2} matrix.[4–7] This multicolor behavior, which was reported in the presence of amorphous,[5,8] anatase,[4,6,9–13] or rutile[5,8,14] TiO\textsubscript{2}, is induced by photo-activated redox reactions coupled with morphological changes of Ag nanoparticles. From an optical point of view, this is characterized by the appearance or disappearance of an absorption band in the visible range due to localized surface plasmon resonances (LSPR) of the Ag nanoparticles.

Different processes have been proposed in literature for the synthesis of Ag/TiO\textsubscript{2} nanocomposite films. In many of them, Ag nanoparticles are formed from a silver salt reduced by (electro) chemical,[15,16] thermal,[16] or photocatalytic[4,6,8,10,14,17] route, either on a dense TiO\textsubscript{2} surface,[5,8,14] or in a nanoporous[4,6,9,10] or mesoporous[15–17] TiO\textsubscript{2} matrix. Some groups synthesize these films from commercial sols with anatase TiO\textsubscript{2} nanoparticles[4,7,9,10] by spin coating and postheat treatment at 500 °C. Other authors prepare mesoporous TiO\textsubscript{2} films by sol–gel technique coupled with evaporation induced self-assembly method.[15–17] Recently, some authors elaborated Ag/TiO\textsubscript{2} thin films on polyethylene terephalate (PET) sheets by sol–gel processes without damaging the substrate.[18,19] Some others authors prepared Ag/TiO\textsubscript{2} nanocomposites by magnetron sputter deposition without addressing their photochromic properties.[20–22] Zuo et al. used radio frequency (RF) sputtering of a TiO\textsubscript{2} polycrystalline and an Ag target on p-type Si wafers at room temperature.[20] Chakradhurana et al. used cosputtering of RF magnetron TiO\textsubscript{2} target and direct current (DC) magnetron of Ag target on Si wafers.[21] Recently, Dhar et al. combined RF magnetron sputtering of a TiO\textsubscript{2} target and DC sputtering of a Ag target at room temperature to deposit TiO\textsubscript{2}/Ag/TiO\textsubscript{2} trilayer thin films onto polyethylene naphtalate flexible substrates.[22] Other studies report the synthesis of photochromic Ag-embedded TiO\textsubscript{2} nanocomposite materials by magnetron sputter-deposition of TiO\textsubscript{2} and Ag thin layers at high Ar pressure, but they did not address the issue of functionalizing plastic substrates with such materials.[23–26]
Jian et al. deposited both sandwiched TiO$_2$/Ag/TiO$_2$ and over-coated Ag/TiO$_2$ structures films by dual-target helicon magnetron sputtering on quartz substrate at room temperature.\(^{[23]}\)

Dahmen et al.\(^{[24,25]}\) used DC sputtering of a Ag target and a Ti target in a Ar/O$_2$ atmosphere on glass, silicon and quartz substrates at room temperature with subsequent annealing at 300 °C. Zuo et al.\(^{[26]}\) used RF sputtering of a Ag target and a TiO$_2$ target on glass substrate at room temperature, followed by postgrowth annealing at 500 °C. The use of thermal treatments is not compatible with flexible substrates and thus limits the range of applications of such photochromic films.

In this article, we use magnetron sputtering as a convenient approach to grow, at room temperature and without any thermal annealing, Ag/TiO$_2$ thin films on flexible PET substrates, whose characteristics have been optimized to get multicolor photochromic properties. Magnetron sputtering has the advantage of being compatible with large-scale production and we present original routes to synthesize two different types of films exhibiting cyclic multicolor photochromism. In situ spectral characterizations are used to monitor the differential reflectance changes during the deposition and spectral transmittance characterizations are performed after laser exposure at various wavelengths in the ultraviolet (UV) and visible range. The laser-induced modifications observed in the optical spectra are interpreted in light of the morphological changes arising in the nanostructures, which are characterized by transmission electron microscopy.

2. Results and Discussion

2.1. Synthesis and Characterization of TiO$_2$ Thin Films

TiO$_2$ layers were grown on PET, NaCl, quartz, and Si substrates from a Ti target by operating in a reactive Ar/O$_2$ atmosphere at relatively high Ar pressure (1 Pa) in order to obtain porous films. Two deposition modes were used, depending on the O$_2$ partial pressure: the metallic sputtering mode (MSM) where the Ti target remains metallic and the compound sputtering mode (CSM) where the Ti target is completely poisoned. Structural properties of the TiO$_2$ films were studied from in-plane views by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energy-filtered selected area electron diffraction (EF-SAED). Typical HAADF-STEM images obtained for 40 nm thick films together with the corresponding EF-SAED patterns (inset) are shown in Figure 1, which reveals a high porosity for both modes. Nevertheless, it is worth noting that TiO$_2$ films synthesized in the MSM exhibit a smaller intergrain distance (13.0 ± 0.1 nm vs 14.7 ± 0.1 nm) and smaller TiO$_2$ grains. Moreover, the diffraction patterns show no obvious sign of crystallization meaning that the TiO$_2$ films are completely amorphous or poorly crystallized (see Figure S1 in the Supporting Information).

The optical properties of such nanoporous TiO$_2$ layers are very close for both modes. For example, Figure 2a shows the transmittance spectra of 133 nm thick MSM and 132 nm thick CSM TiO$_2$ films deposited on a quartz substrate. Both films exhibit an absorption band in the UV range. The sharp transition observed around 380 nm corresponds to the TiO$_2$ optical bandgap.\(^{[27]}\) In the visible and near infrared (IR) range, the films are highly transparent and their spectra exhibit interference fringes arising from finite thickness effects. Figure 2b shows the spectral variations of the refractive index in the visible and near IR ranges deduced from ellipsometry measurements. The refractive indices are very close for both modes and lower than the values tabulated for anatase,\(^{[29]}\) rutile or amorphous TiO$_2$,\(^{[28]}\) consistent with porous layers.

2.2. Synthesis and Characterization of Ag/TiO$_2$ Nanocomposites

TiO$_2$(10 nm)/Ag(10 nm)/TiO$_2$(10 nm) trilayers were formed by alternate depositions on PET substrates. The buffer and the
capping TiO$_2$ layers (10 nm thick) were synthesized in the same sputtering mode, either MSM or CSM, and the effective Ag thickness was $t_{\text{Ag}} = 4$ or 8 nm. The adhesion of the films on the PET substrate was successfully tested (according the American Society for Testing and Materials D3359-97 protocol—see Figure S2 in the Supporting Information) and gave no visual evidence of film removal after withdrawal of the adhesive tape. The films exhibit also good strength after bending the PET substrate (see Figure S3 in the Supporting Information). In addition, no apparent color evolution of the as-deposited samples was noted after storage in ambient air and away from direct sunlight exposure for several months. Actually, we studied (not reported here) the influence of the TiO$_2$ capping layer thickness on the ageing of the sample optical properties and found that it is improved when increasing the thickness of the capping layer. But this increase also decreases the photochromic performances of films and the best compromise was found with the thickness of 10 nm reported in this article.

Plan-view HAADF-STEM images and the corresponding EF-SAED patterns of both types of trilayer films are shown in Figure 3. Ag nanoparticles (light-gray contrast) of irregular shape and random organization are observed within the MSM TiO$_2$ nanoporous matrix in dark-gray contrast (Figure 3a). Their average equivalent size can be estimated at about 17 ± 2 nm and the areal particle density is around 900 particles µm$^{-2}$. The diffraction pattern reveals the presence of Ag crystals with a face-centered-cubic structure and a lattice parameter of 0.408–0.409 nm (see Figure S1 in the Supporting Information).
Furthermore, we notice that the porosity of the TiO$_2$ matrix is still present (see Figure S4c in the Supporting Information). For CSM TiO$_2$ nanocomposite samples (Figure 3b,c), although we can note the presence of very few metal Ag particles with size larger than 20 nm, the contrast in the HAADF-STEM images is dominated by the nanoporous TiO$_2$ matrix. These results suggest that a large proportion of Ag is homogeneously distributed between the TiO$_2$ buffer and capping layers, either atomically dispersed or in the form of a continuous layer of amorphous silver oxide.$^{[30]}$ Moreover, the diffraction patterns show a narrow ring at $\approx 5.4$ nm$^{-1}$, which may suggest the presence of anatase TiO$_2$ crystals (see Figure S1 in the Supporting Information).

To better understand the mechanisms leading to different Ag growth morphologies depending on the sputtering mode used for TiO$_2$ deposition, the optical properties of Ag/TiO$_2$ nanocomposites were monitored in real time during the successive steps of the trilayer formation by using an in situ surface differential reflectance spectroscopy system.$^{[31]}$ From the very early stage of Ag deposition on both MSM and CSM TiO$_2$ buffer layers, Figure 4a,b shows the presence of a broad maximum in the differential reflectance spectra, corresponding to the LSPR of Ag nanoparticles. The formation of such Ag nanoparticles, whose average size increases in time, results from well-known nucleation and coalescence phenomena following the Volmer–Weber growth mechanism.$^{[32–34]}$ The LSPR band increases in amplitude and redshifts in position up to the near IR range with deposition time, in accordance with the development of larger and flatter Ag nanoparticles.$^{[31]}$ However, for the same Ag effective thickness, the resonance is less pronounced, more redshifted and broader when Ag is deposited on a CSM TiO$_2$ buffer layer than on a MSM one. From these results, it may be suggested that CSM TiO$_2$ gives rise to flatter nanoparticles with a larger dispersion in size and shape than those grown on MSM TiO$_2$.$^{[31]}$

Figure 4c,d displays the differential reflectance spectra measured before and after capping the Ag nanoparticles ($t_{Ag} = 4$ nm) by MSM and CSM TiO$_2$ layers, respectively. During the capping by MSM TiO$_2$, the LSPR band increases in amplitude and redshifts in position, in agreement with the change in the refractive index of their surrounding medium. In contrast, the capping by CSM TiO$_2$ causes a complete disappearance of the LSPR in accordance with the HAADF-STEM observations in which the contrast of metallic Ag particle is not present (Figure 3b). Actually, it should be noted that the nanoparticles grown on CSM TiO$_2$ layers are exposed to a greater oxygen partial pressure ($p_{O_2} = 3 \times 10^{-2}$ Pa) and during a longer time (deposition rate $v = 0.02$ nm s$^{-1}$) than nanoparticles grown on MSM TiO$_2$ layers ($p_{O_2} = 8 \times 10^{-3}$ Pa and $v = 0.2$ nm s$^{-1}$). Our results thus suggest that Ag nanoparticles strongly react with O$_2$ molecules and tend to confirm that oxidized silver is homogeneously dispersed within the TiO$_2$ matrix. Therefore, the as-grown trilayer samples are colored for MSM TiO$_2$ and uncolored for CSM TiO$_2$.

It is worth noting that the process implemented by Zuo et al.$^{[26]}$ using RF sputtering of a TiO$_2$ target gives rise to samples colored by the presence of Ag nanoparticles like in our MSM nanocomposite samples, whereas the samples obtained by
Dahmen et al.\textsuperscript{[24,25]} using DC sputtering of a Ti target in reactive \textit{Ar}/\textit{O}_2 atmosphere are similar to our uncolored CSM nanocomposite samples. Dahmen et al. performed a thermal annealing at 300 °C in order to get colored samples and therefore metallic Ag nanoparticles. With the other techniques described in the introduction, Ag salt is introduced in the form of ionic compound once the TiO\textsubscript{2} film is created and the samples are also uncolored.\textsuperscript{[2,3,35–37]}

2.3. Multicolor Photochromic Behavior

MSM and CSM TiO\textsubscript{2} nanocomposite samples were exposed to a visible laser emitting at 647 nm (irradiance of 8.59 W cm\textsuperscript{-2}) and to a UV laser emitting at 244 nm (irradiance of 0.12 W cm\textsuperscript{-2}). In order to study the effects of visible and UV laser exposures on both kinds of samples, their transmittance spectra were measured after different durations of laser irradiation. In \textbf{Figure 5a}, the visible laser irradiation over 120 min of the MSM TiO\textsubscript{2}/Ag(4 nm)/MSM TiO\textsubscript{2} nanocomposite causes the progressive disappearance of the initial absorption band (including the excitation wavelength at 647 nm) and the appearance of a new, narrower, absorption band centered at 480 nm, at the origin of the color change shown in the optical images. It takes almost one hour to obtain the final color. Similarly, in \textbf{Figure 5b}, a UV laser irradiation of the CSM TiO\textsubscript{2}/Ag(8 nm)/CSM TiO\textsubscript{2} nanocomposite sample during 10 min induces the appearance of a broad absorption band centered at 650 nm, characteristic of metallic Ag particles, and the initially colorless sample gets a bluish color (see optical images). The UV irradiation effect is much faster as it takes two minutes to obtain the final color. These results suggest that photochromism is a complex phenomenon in its dynamics, which remains poorly understood to date, and motivate the need for further experimental and theoretical studies.

To show the reversibility of the photochromic behavior of both samples investigated in \textbf{Figure 5}, \textit{vis}–\textit{UV} or \textit{UV}–\textit{vis} cycles were performed. A UV laser irradiation of a visible irradiated film induces the appearance of a broad absorption band at large wavelength, giving back to the sample its bluish color. Moreover, the exposure of a UV irradiated sample to visible

\begin{figure}[h]
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\includegraphics[width=\textwidth]{figure5.png}
\caption{Transmittance spectra after successive laser exposures with the corresponding optical pictures (2.62 × 1.96 mm\textsuperscript{2}). a) MSM TiO\textsubscript{2}/Ag(4 nm)/MSM TiO\textsubscript{2} nanocomposite sample exposed at 647 nm wavelength (8.59 W cm\textsuperscript{-2}, red dotted line) and b) CSM TiO\textsubscript{2}/Ag(8 nm)/CSM TiO\textsubscript{2} nanocomposite sample exposed at 244 nm wavelength (0.12 W cm\textsuperscript{-2}). Exposure times are written on top of the optical pictures using the same color code as the corresponding transmittance curves.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6.png}
\caption{Changes in the transmittance at 647 nm wavelength and optical pictures (2.62 × 1.96 mm\textsuperscript{2}) during photochromic cycles performed using successive laser exposures at 244 nm (30 min at 0.12 W cm\textsuperscript{-2}) and 647 nm (1 h at 8.59 W cm\textsuperscript{-2}) wavelengths for a) a MSM TiO\textsubscript{2}/Ag(4 nm)/MSM TiO\textsubscript{2} nanocomposite sample and b) a CSM TiO\textsubscript{2}/Ag(4 nm)/CSM TiO\textsubscript{2} nanocomposite sample deposited on PET substrates.}
\end{figure}
laser induces the disappearance of the initial absorption band along with the appearance of a new absorption band centered at 480 nm. Figure 6 shows that the color and spectral changes are fairly repeatable during these cyclic processes.

A typical HAADF-STEM image of the MSM TiO$_2$/Ag(4 nm)/MSM TiO$_2$ sample after visible laser irradiation (8.59 W cm$^{-2}$ at 647 nm) during 120 min is shown in Figure 7a. It can be compared with Figure 3a corresponding to the same sample before exposure. Clearly, the visible laser exposure causes a decrease in the average size of the Ag nanoparticles (from about 17 to 8 nm) combined with an increase of the areal particle density from 900 to 3650 particles µm$^{-2}$. Accordingly, the corresponding EF-SAED pattern shows diffraction rings broader than those observed before exposure (see Figure S1 in the Supporting Information). These observations are consistent with the optical changes viewed in Figure 5a since small particles exhibit generally more spherical shapes compared to larger ones and give rise to absorption at smaller wavelengths. In the as-deposited sample, particles exhibit different morphologies (see Figure 3a), which are expected to resonate at different wavelengths giving rise to the broad LSPR observed in Figures 4c and 5a. An incident monochromatic light induces therefore the oscillation of free electrons in specific Ag nanoparticles. Actually, the disappearance of the initial absorption band may be explained by the selective response of large nanoparticles, whose LSPR band includes the excitation wavelength (647 nm). Excited electrons at the surface of the particles can move to trapping centers, like adsorbed oxygen in the nanoporous TiO$_2$ matrix, and Ag$^+$ ions can be released leading to the decrease of the nanoparticle size. Then, some ions can recombine with electrons, generating new smaller Ag nanoparticles and resulting in an increase of the areal particle density. It should be noted that while the structure and color of such irradiated samples remain stable for several months, we observed, however, a slow and gradual evolution of the as-deposited MSM TiO$_2$ nanocomposite films stored in ambient air over several months, resulting in structures similar to those displayed in Figure 7a.

In the case of colorless samples as those obtained by other techniques, authors proposed to irradiate them by a UV laser in order to use the photocatalytic behavior of TiO$_2$ to generate electron–hole pairs. The UV-induced reduction of oxidized Ag allows obtaining metal particles and consequently colored samples. Similarly, we observed that UV irradiation at 244 nm of colorless CSM TiO$_2$ nanocomposite samples induces the appearance of a broad absorption band characteristic of metallic Ag nanoparticles. A typical HAADF-STEM image of the CSM TiO$_2$/Ag(8 nm)/CSM TiO$_2$ sample after UV laser irradiation during 10 min is shown in Figure 7b, which evidences the formation of a high density (7200 particles µm$^{-2}$) of small particles with an average size of 5 nm. The EF-SAED profiles of the corresponding samples before and after irradiation are very similar (see Figure S1 in the Supporting Information), except the presence of a narrow peak at $\approx$4.9 nm$^{-1}$ due to the laser-induced formation of some isolated large Ag crystals. To verify that the small particles observed in Figure 7b correspond to Ag nanoparticles, we conducted an elemental chemical mapping of Ag by combining STEM with energy electron loss spectroscopy (EELS) (Figure 8). The bright zones in the HAADF-STEM image (zoom in Figure 8a) are correlated with an increase of the intensity in the AgM$_4$,M$_5$ energy range (Figure 8b). This promotes the presence of metallic Ag nanoparticles within the films, which may have been formed by the photoreduction of oxidized silver dissolved in the TiO$_2$ matrix followed by coalescence or Ostwald ripening processes. The observed resonance around 650 nm in Figure 5b could be explained by the interactions between very close particles and/or the formation of disk-shaped particles.
As observed in Figure 6, after irradiation at 647 nm, the as-prepared MSM and the UV irradiated CSM TiO$_2$ nanocomposite samples become orange. It is worth noting that, contrary to what had been observed on Ag containing mesoporous TiO$_2$ films elaborated by sol–gel process,$^{[18]}$ the complete discoloration of the film is not reached even after a 1 h exposure time under monochromatic light. However, the choice of the visible laser wavelength enables multicolor photochromism as illustrated in Figure 9a with a UV irradiated CSM TiO$_2$ nanocomposite sample. Whereas the irradiation at 647 nm induces the appearance of a strong absorption band around 480 nm, this absorption band is less marked (and the color is less saturated) when the irradiation wavelength is smaller. It is counterbalanced by a larger absorption at larger wavelengths. This may be explained by the elimination of the small particles and the formation of even smaller and more spherical nanoparticles combined with the growth of some bigger particles. It may be noticed that after irradiation at 488 nm, the sample becomes almost achromatic. A cyclic irradiation with two visible wavelengths (647 and 488 nm) allows changing repeatedly from an orange to an achromatic sample as shown in Figure 9b.

### 3. Conclusion

In this article, we show that two types of photochromic Ag/ TiO$_2$ thin films (MSM TiO$_2$ nanocomposite and CSM TiO$_2$ nanocomposite materials) can be synthesized by magnetron sputtering on flexible PET substrates at room temperature. The adhesion and the mechanical resistance of such films on the PET substrate were successfully tested, and their photochromic behavior was investigated in detail. We have demonstrated that MSM TiO$_2$ nanocomposite materials are colored by the presence of Ag metallic nanoparticles after deposition. This initial color can be modified by exposing the films to visible laser light due to the selective oxidation phenomenon. Whereas CSM TiO$_2$ nanocomposite materials are initially colorless due to the lack of Ag metallic nanoparticles, we have demonstrated that such samples can be colored under UV laser exposure due to the photocatalytically induced formation of metal nanoparticles. Both types of samples give a large flexibility for cyclic and multicolor photochromic experiments without degrading the PET substrate. The selective oxidation phenomenon is characterized from an optical point of view by a high decrease of the absorption around the excitation wavelength connected with an absorption increase at low wavelengths (around 480 nm). We proposed a route to significantly broaden the absorption band over the whole visible spectrum by exciting the red-irradiated samples at 488 nm. These results open up new possibilities in a wide variety of applications requiring flexible substrates, such as innovative solutions in the fields of fight against counterfeiting and traceability for identity and credit cards, new generation of datamatrix, for instance.

### 4. Experimental Section

**Thin Film Deposition:** The film synthesis was performed at room temperature by using a high-vacuum (base pressure lower than $10^{-5}$ Pa) magnetron sputtering chamber equipped with three cathodes in confocal configuration. The target to substrate distance was 18 cm. Both reference TiO$_2$ films and Ag-TiO$_2$ nanocomposites were deposited under the following conditions:
TiO<sub>2</sub> films were deposited by sputtering a titanium (Ti) target using a DC power supply at constant power mode (300 W) under reactive (Ar + O<sub>2</sub>) atmosphere, at a total working pressure of 1 Pa. Two sputtering modes were selected:

- MSM, where the Ti target remained metallic. O<sub>2</sub> partial pressure was 8 × 10<sup>−3</sup> Pa and deposition rate was 0.2 nm s<sup>−1</sup>.
- CSM, where the Ti target was fully poisoned. O<sub>2</sub> partial pressure was 3 × 10<sup>−2</sup> Pa, the deposition rate was 0.02 nm s<sup>−1</sup>.

Ag growth was performed by sputtering a silver target in pure Ar atmosphere at constant power (24 W) using a DC power supply, at a total working pressure of 1 Pa. The Ag deposition rate (0.1 nm s<sup>−1</sup>) was deduced from the thickness (≈80 nm) measured by X-ray reflectometry for a thick Ag layer preliminary deposited onto a silicon substrate. The Ag effective thickness in nanocomposite samples was then obtained by the product of the deposition rate and the deposition time.

Nanocomposites consisting of TiO<sub>2</sub>/Ag/TiO<sub>2</sub> trilayers were fabricated by alternate depositions of TiO<sub>2</sub> and Ag layers and were grown on PET and NaCl substrates. The PET sheets were 175 µm thick, transparent (in the visible range), colorless, flexible, and resistant to thermal treatments until 180 °C. Two types of nanocomposite samples were obtained depending on the reactive mode, either MSM or CSM, used for the deposition of the buffer and the capping TiO<sub>2</sub> layers. It should be noted that after Ag deposition a timeout of about 300 s was included before subsequent growth to account for possible relaxation effects and morphological evolution toward closer to equilibrium shapes. Moreover, the deposition of the capping TiO<sub>2</sub> layer was preceded by the introduction of oxygen in the chamber. Therefore, slight changes in the optical response were observed between the end of the Ag deposition and the start of the capping-layer deposition (see Figure 4).

Note that no significant indirect heating of the films due to ionic bombardment occurred under the present deposition conditions, because of the relatively high pressure and large target-to-substrate distance used. The maximum temperature rise is estimated to be lower than 10 °C, based on a previous work from the authors involving the same magnetron sputtering device.

**Morphology and Structural Properties:** The structure and morphology of TiO<sub>2</sub> films and Ag/TiO<sub>2</sub> nanocomposites were investigated by HAADF-STEM and EF-SAED. The experiments were conducted using a JEOL 2200FS transmission electron microscope equipped with a Schottky-FEG operated at 200 kV. The inner collection angle was set to 50 mrad to minimize diffraction contrast in order to record mass-thickness contrast via the incoherent scattering of electrons at high angles (Rutherford scattering); the intensity in the image thus scales linearly with the sample thickness and with Z<sup>1.7</sup>, (Z being the atomic number of the encountered atomic species). A probe size of 0.7 nm was used to optimize the signal to noise ratio of HAADF-STEM images while keeping a spatial resolution allowing resolving the smallest particles.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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