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Theoretical and photo-electrochemical studies of surface plasmon induced visible light absorption of Ag loaded TiO₂ nanotubes for water splitting

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Vertically aligned TiO₂ nanotubes (TiO₂-NTs), obtained by anodization in organic electrolyte, are decorated with 15 nm Ag nanoparticles prepared by a micro-wave assisted polyol synthesis. The Ag/TiO₂ system is characterized by electronic microscopies in order to build a *Finite Differential Time Domain* (FDTD) model to simulate the interaction of light with the system. By combining UV-visible spectroscopy and FDTD simulations, the observed red shift in the surface plasmon resonance wavelength of the Ag nanoparticles, deposited on TiO₂, is explained. The Ag/TiO₂-NT system is used as photoanode in a photoelectrochemical water splitting setup and shows an increasing *Incident Photon to Current Conversion Efficiency* (IPCE) in the visible light domain with an increasing amount of deposited Ag. The spectral position of this activity enhancement coincides with the one expected from the FDTD calculations for the surface plasmon resonance of the Ag nanoparticles deposited on TiO₂. Published by AIP Publishing. [<http://dx.doi.org/10.1063/1.4964827>]

Vertically aligned TiO₂ nanotubes (TiO₂-NTs) grown on top of a conductive substrate by electrochemical anodization have attracted much interest since they have been discovered in the early 2000s.^{1–3} They are now used as photoanodes either in the photoelectrochemical cell proposed in the 70s by Fujishima and Honda for water-splitting⁴ or for the photo-oxidation of various organic pollutants.⁵ The main drawback of this material comes from the large band gap of TiO₂ of 3.2 eV, for the anatase phase, limiting its photoelectrochemical conversion to UV light ($\lambda < 390$ nm).

Several approaches are investigated to extend the absorption spectrum of TiO₂ to the visible part of the solar spectrum. However, there is up to now no ultimate technique and some drawbacks are always present. A well studied one is chemical doping by the substitution of O²⁻ anions by C⁴⁻, N³⁻, and F⁻,^{6,7} allowing the absorption of larger wavelengths often at the price of increasing electron/hole pairs recombination.⁸ Another way is the coupling of TiO₂ with organic dyes, as proposed by Grätzel.⁹ These molecules allow absorbing a large portion of the solar spectrum but are sometimes sensitive to degradation and oxidation. One can also cite the formation of heterojunctions, with either a polymeric semiconducting material,¹⁰ acting as a photosensitizer, or another metal oxide semiconductor with a smaller band gap than TiO₂.¹¹ Finally, the approach studied in the present paper is the functionalization of the semiconductor with metallic nanoparticles to make use of their plasmonic properties,^{12–14} such as Au^{15,16} and Ag.^{17,18} We choose to work on this approach because the metallic nanoparticles are more resistant to experimental conditions, are easy to synthesize and have both catalytic and optical interesting properties.

In this paper, we focus on the functionalization of TiO₂ nanotubes with the Ag nanoparticles having a surface

plasmon resonance (SPR) peak in the blue part of the visible spectrum, i.e., close to the TiO₂ band gap energy. The energy transfer mechanism between a surface plasmon activated metallic nanoparticle and a semiconducting material is now explained as comprising two main mechanisms that are still frequently discussed. The first is the SPR-mediated charge injection from the metal to the semiconductor,¹⁹ and the second is the near-field enhancement of the electrical field.²⁰ According to the cited papers, those mechanisms can occur simultaneously.

We built an FDTD (*Finite Differential Time Domain*) model, derived from the experimental parameters, to give insight into the behavior of this particular interface between SPR-activated Ag nanoparticles and TiO₂ when under illumination. The FDTD calculations are based on the resolution of the Maxwell equations in time domain. The model leads to several information (field exaltations, transmission, and so on) necessary to study the wave propagation in different materials for different nanostructured systems.²¹ The results are then compared with the experimental results obtained by the UV-visible spectroscopy and photoelectrocatalytic (PEC) measurements.

First, the TiO₂-NT electrodes are prepared by electrochemical anodization and then characterized by scanning electron microscopy (SEM) (*Jeol*[®] JSM-6700F), transmission electron microscopy (TEM) (*Jeol*[®] 2100F), and X-ray diffraction (XRD) (*Brucker*[®] D8 Advance). The experimental parameters for the synthesis are available in the [supplementary material](#). The detailed growth mechanism of these nanostructures is well described in several reviews.^{22–24}

The Ag nanoparticles are prepared by a micro-wave assisted polyol synthesis with PVP (Polyvinylpyrrolidone) as capping agent. Synthesis parameters are detailed in the [supplementary material](#) as well, and growth mechanism can be found in the literature.^{12,25} The as prepared Ag nanoparticles

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are deposited by drop casting on the surface of vertically aligned TiO₂-NTs. The absorption behavior of the Ag/TiO₂-NT system is studied both experimentally and by *FDTD* simulations. The parameters of the model for the *FDTD* simulation are determined by the results obtained by the characterization of the TiO₂-NTs and the Ag nanoparticles with SEM, TEM and UV-visible spectroscopy. The calculations are performed with the *FDTD—Lumerical*[®] software and were focused on the light absorption properties of the system.

Fig. 1(a) shows an SEM image of the TiO₂-NTs after annealing under air for 5 h at 550 °C. The length of the nanotubes is $3.7 \pm 0.2 \mu\text{m}$, the inner diameter is $50 \pm 5 \text{ nm}$ and the outer diameter is $105 \pm 5 \text{ nm}$. Those dimensions are the ones used to design the *FDTD* model. The TiO₂ nanotubes were also characterized by XRD, and the results are presented in the [supplementary material](#).

Fig. 1(b) shows a TEM image of the resulting Ag colloidal solution. The Ag colloidal solution is composed of spherical nanoparticles with an average size of 15.4 nm and a standard deviation of 4.6 nm. This size distribution is in good accordance with the work of Komarneni *et al.*,²⁶ who used similar synthesis conditions. From these observations, we used the spherical Ag nanoparticles with a diameter of 15 nm to build the *FDTD* model.

The as prepared Ag colloids in water are characterized by the *Inductive Coupled Plasma-Atomic Emission Spectroscopy* (ICP-AES) to determine the concentration of Ag in order to make mass controlled deposits on the TiO₂-NT layer. Determined concentration of the colloid is 198 mg of Ag per

kg of colloidal solution. With an original mass of AgNO₃ of 0.003 g ($0.0044 \text{ mol}\cdot\text{L}^{-1}$) used for the synthesis, the yield of the reaction is 41%. The deposits of different mass of Ag between 0.05 wt. % and 1.0 wt. % were made by drop casting. Evaporation of the solvent is made at 80 °C. Fig. 2(a) shows TEM images of a portion of the TiO₂-NT film exhibiting Ag nanoparticles, which seem to be located on the internal tube walls.

The Ag nanoparticles colloid and TiO₂-NTs with various loadings of Ag are then analyzed by the UV-visible spectroscopy (*Varian*[®] 100 spectrometer). The Ag colloidal solution was characterized in the transmission mode, and the TiO₂-NTs in diffuse reflectance configuration using *Labsphere*[®] DRA-CA-301. The reflectance signal (*R*) for the TiO₂-NTs is used to obtain the Kubelka-Munk function *F*(*R*) with Equation (1). The Kubelka-Munk is similar to the absorption for solids but takes into account the reference spectra²⁷

$$F(R) = \frac{(1 - R)^2}{2R}. \quad (1)$$

Fig. 3(a) shows the resulting spectrum for the Ag colloid (black dashed line). The curve is composed of a single absorption peak, which corresponds to the surface plasmon resonance peak, and is centered at 402 nm. The position of the peak is coherent for the shape and size of Ag nanoparticles in water.^{12,26}

Fig. 3(a) also shows the Kubelka-Munk curves (*F*(*R*)), derived from reflectance spectra, of the TiO₂-NTs before (black line) and after (colored lines) deposition of various masses of Ag. All the TiO₂-NT samples, with and without Ag, show a main absorption edge starting at 390 nm. This corresponds to the TiO₂-anatase band gap of 3.2 eV, as confirmed by the Tauc curves²⁸ (not shown here) derived from the UV-visible spectra. The spectra reach a maximum at 360 nm and exhibit oscillations at $\lambda > 450 \text{ nm}$ coming from the interferences of the light beam with the thin TiO₂-NT layer.²³

The curves for the same sample but with increasing amount of deposited Ag exhibit an absorption shoulder, which tends to increase until 1.0 wt. % of deposited Ag. This absorption, resulting from the presence of the Ag nanoparticles, reaches a maximum at 440 nm, which is coherent with the observation made by Yang *et al.*²⁹ with a similar system. The position of this absorption shoulder is nevertheless redshifted compared to the position of the absorption peak for the Ag colloidal solution in water (dashed black line).

To explain this red shift, three *FDTD* simulations have been performed on a single 15 nm Ag spherical nanoparticle in the continuous media of H₂O, PVP and TiO₂. The resulting curves are presented in Fig. 3(b). In order to perform all the *FDTD* simulations, the real and imaginary parts of the dielectric constants of Ag were obtained using Equations (1) and (2) with the values of refractive index *n* and extinction coefficient *k* measured by Johnson and Christy³⁰

$$\varepsilon_1 = n^2 - k^2, \quad (2)$$

$$\varepsilon_2 = 2nk. \quad (3)$$

For the surrounding media, the values of the dielectric constants were found in the literature: $\varepsilon_m(\text{PVP}) = 2.25$ (Ref. 31)

FIG. 1. SEM image of the TiO₂-NTs (a). TEM image of the as prepared Ag colloid after washing treatment: inset is the corresponding size distribution in nm, measured on several images (b).

FIG. 2. TEM image of TiO_2 nanotubes after deposition of 1.0 wt. % of Ag nanoparticles (a). Proposed *FDTD* model for the Ag/ TiO_2 system (b).

and in the work of Landmann *et al.*³² for TiO_2 anatase. For H_2O , the dielectric constant of the *FDTD* software was used, $\epsilon_m(\text{H}_2\text{O}) = 1.77$.

The resulting simulated spectra show absorption peaks at 388 nm, 413 nm and 550 nm, respectively, for the Ag nanoparticle embedded in H_2O , PVP and TiO_2 anatase. In the case of Ag embedded in TiO_2 -anatase (purple dashed line), the curve also exhibits an absorption edge starting at 470 nm that corresponds to the absorption of the TiO_2 medium. For Ag in PVP, the position of the simulated absorption peak is slightly red shifted compared to the experimental absorption peak of the Ag colloid (Fig. 3(a), black dashed line) centered on 403 nm. This is probably because in the experimental case the PVP layer is only a few nanometers thick; thus, the water from the colloid has an impact

(blue shift) on the position of the peak, unlike the situation in the simulation with a continuous medium of PVP. In the case of the Ag nanoparticle in TiO_2 -anatase, the simulated absorption peak is strongly red-shifted, which shows how the position of the plasmon resonance band is strongly dependent on the surrounding medium. The increasing absorption shoulder observed on the experimental spectrum for the Ag loaded TiO_2 -NT samples (Fig. 3(a)) is positioned in between these two extreme cases (Ag in PVP and Ag in TiO_2) at 440 nm. This is due to the fact that the chemical environment of the Ag nanoparticles, when deposited on the TiO_2 -NTs, is composed mainly of PVP, but also of TiO_2 . This explains why the absorption coming from the Ag, when it is deposited on the TiO_2 -NTs, is red-shifted compared to absorption of the colloidal solution.

Fig. 2(b) depicts the model for the Ag/ TiO_2 system used for the *FDTD* calculations. This model has been built according to the TEM observations of the TiO_2 -NTs/1.0% Ag sample, where the number of Ag particles per μm of TiO_2 -NTs has been estimated to be 8 giving an average spacing between the nanoparticles of 70 nm. The *FDTD* model is built as follows: i) a 200 nm long and 100 nm in diameter TiO_2 -anatase Tube with a wall thickness of 50 nm, and ii) two 15 nm spherical Ag nanoparticles sitting on the inner wall of the tube. The two nanoparticles are separated by 70 nm. The system is illuminated by a plane wave that propagates along the z axis.

Fig. 3(b) also shows the absorption spectra obtained by the *FDTD* calculations for an empty TiO_2 -anatase tube (black line). The curve shows a main absorption edge that starts at 380 nm and reaches a maximum of absorption at 350 nm, which is coherent for TiO_2 , and is in good accordance with the experimental results obtained on Fig. 3(a) for the unmodified TiO_2 -NT samples. For the Ag/ TiO_2 system (red line), the only difference in the absorption spectrum compared to the TiO_2 tube alone is the presence of a sharp absorption peak located at 408 nm, which is attributed to the plasmonic resonance of the Ag nanoparticles present inside the tube. This peak is very sharp compared to the absorption shoulder observed on the UV-visible spectra, but this is due to the fact that in the *FDTD* model the Ag nanoparticles are perfectly spherical and have exactly the same size, whereas the colloidal solution contains a distribution of Ag nanoparticles with different sizes. Moreover, in the Ag/ TiO_2 samples, the Ag nanoparticles have also a position distribution and can sit on the internal or external surface of the nanotubes. Nevertheless, the position of this peak is red-shifted compared to the peak observed for the single Ag nanoparticle surrounded by water (blue dashed line) due to the presence of TiO_2 in the environment of the Ag nanoparticles.

FIG. 3. Absorption spectra of TiO_2 nanotubes with different amounts of deposited Ag (plain lines) and UV-visible spectrum of the Ag colloidal solution in water (dashed line) (a). *FDTD* absorption spectra of an empty TiO_2 tube (black line), the Ag/ TiO_2 system (red line) and a single Ag nanoparticle in different continuous media (blue, green, and purple dashed lines). The schemes represent the different *FDTD* simulation corresponding to each curve (b).

The presence of this red-shift in the FDTD simulation is in good accordance with the one observed on the experimental curves from the Fig. 3(a).

The TiO₂-NT electrodes with various Ag loadings are then used as photoanodes in a photoelectrochemical water splitting setup for hydrogen generation. Details about the measurements of the photoelectrocatalytic activity are presented in the [supplementary material](#).

Fig. 4(a) shows the results for the *Incident Photon to Current Conversion Efficiency* (IPCE) measurements for TiO₂-NT (black line) and Ag/TiO₂-NT photoanodes (color lines). The curves show a main activity edge starting at 400 nm that is coherent with the absorption results from Fig. 3(a). The IPCE reaches a 15% maximum at 300 nm for the unmodified TiO₂-NT electrodes. When Ag is present, however, the curve exhibits a peak at 360 nm followed by a plateau. The presence of this peak can originate from the filling of surface states induced by the presence of Ag and/or PVP at the interface with the nanoparticles. This increase in photocurrent is then due to a diminution of electron/hole pairs recombination because holes are used either to fill these states, located above the valence band, or to oxidize the PVP present on the Ag nanoparticles.

However, the FDTD simulations showed that the main contribution of Ag was located at 408 nm and no particular activity enhancement is observed at that particular wavelength. First, it is probably due to the large activity of the TiO₂ in that region that is probably hiding any contribution made by the Ag SPR. Also, it is important to point out the differences between the FDTD model and the experimental situation. In the first case, the TiO₂ tube is perfectly smooth

and the Ag nanoparticles are perfectly spherical and from identical size. On the contrary, in the experimental case, the tube surfaces are rough and the Ag nanoparticles can have a slightly non-spherical shape and have a size distribution.

Nevertheless, as shown in Fig. 4(b), in the region where the SPR of the Ag nanoparticles is maximum, the IPCE increases with the amount of deposited Ag up to 0.17% at 450 nm for the sample TiO₂-NTs/1.0% Ag. This observation is in good accordance with the absorption results from Fig. 3(a), meaning that the visible light absorbed by the Ag/TiO₂ system is converted into current. As on the absorption spectra, the main IPCE edge of TiO₂ is not red shifted, meaning that the presence of Ag does not reduce its band gap. Nevertheless, one can see that the unmodified TiO₂-NTs have a non-zero IPCE in the visible region. This small activity can be attributed to the presence of surface states and/or oxygen vacancies located above the valence band of TiO₂. It is possible that it is that activity that is amplified by the near field electromagnetic and scattering mechanisms of the surface plasmon resonance of the Ag nanoparticles, as explained by Linic *et al.*²⁰

In summary, the deposition of Ag nanoparticles, with controlled size and shape, which have a surface plasmon resonance centered at 400 nm, on the surface of vertically aligned TiO₂-NTs, induces visible light absorption, up to 440 nm, due to the modification of the dielectric constant of the environment surrounding the nanoparticles. The proposed FDTD model, designed from the experimental observations, confirms this behavior by exhibiting similar red shift in the position of the surface plasmon resonance in the Ag nanoparticles when deposited on TiO₂.

The Ag/TiO₂-NT system was used as photoanode in a photoelectrochemical water splitting experiment, and its activity has been measured in terms of IPCE. The red shifted surface plasmon resonance of the Ag nanoparticles induces an increase in activity under visible light, which tends to increase with the amount of deposited Ag.

The increased activity induced by Ag is located in the same region as the one usually observed for anionic doped or co-doped TiO₂ materials.³³ This means that the Ag nanoparticles could be deposited on the doped or co-doped TiO₂ based nanomaterials to further increase their activity under visible light. These results gave interesting information for understanding the behavior of surface plasmon enhanced light converting setups such as solar cells and photoelectrocatalytic systems.

See [supplementary material](#) for all the experimental details concerning the preparation of the vertically aligned TiO₂ nanotubes and the Ag nanoparticles.

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FIG. 4. IPCE curves for the TiO₂ photoanode with increasing amount of deposited Ag (a). Zoom in the region where the activities in the visible light increases with the increasing loading of Ag (b). Applied potential is 0.168 V vs. RHE, pH = 10.

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