Experimental and theoretical study of the electronic properties of Cu-doped anatase TiO₂

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A good correlation was obtained between the electronic properties of Cu-doped anatase TiO₂ by virtue of both physical chemistry characterization and theoretical calculations. Pure and Cu-doped TiO₂ were synthesized. The composition, structural and electronic properties, and the band gap energy were obtained using several techniques. The method of synthesis used produces Cu-doped anatase TiO₂, and XRD, XPS and Raman spectroscopy indicate that Cu atoms are incorporated in the structure by substitution of Ti atoms, generating a distortion of the structure and oxygen vacancies. In turn, the band gap energy of the synthesized samples decrease drastically with the Cu doping. Moreover, periodic density functional theory (DFT-periodic) calculations were carried out both to model the experimentally observed doped structures and to understand theoretically the experimental structures obtained, the formation of oxygen vacancies and the values of the band gap energy. From the analysis of density of states (DOS), projected density of states (PDOS) and the electron localization function (ELF) a decrease in the band gap is predicted upon increasing the Cu doping. Thus, the inclusion of Cu in the anatase structure implies a covalent character in the Cu–O interaction, which involves the appearance of new states in the valence band maximum with a narrowing in the band gap.

1. Introduction

Titanium dioxide (TiO₂) is one of the most widely used semiconductors in photovoltaic and photocatalytic applications because of its commercial availability, optical and electronic properties, low toxicity and chemical stability. The presence of oxygen vacancies is one of the most interesting characteristics of TiO₂, which play a significant role in photocatalytic applications. In turn, surface modification of TiO₂ has been shown to be among the effective methods to improve the performance. Moreover, TiO₂-based nanocomposites with {001} facets play an important role in many applications. On the other hand, because TiO₂ has a wide band gap, which limits its application under sunlight, the effective use of visible light is one of the most important topics in research about TiO₂. Thus, a decrease of the band gap of this semiconductor improves its performance. It is well known that the doping of TiO₂ is one of the possible ways to decrease its band gap energy, and the presence of the dopant leads to improvements in some photovoltaic properties. The photocatalytic activity of the doped TiO₂ is well known, and for example, the following elements have been used as dopants: iron, chromium, carbon, bismuth. Recently, works about the use of carbon nanotubes (CNT) and graphene with TiO₂ have been reported for photocatalytic applications. Different elements have been used as dopants in photovoltaic applications, for example, niobium, vanadium, ytterbium, nitrogen, zinc, aluminium, tungsten. Moreover, copper has been commonly used as a dopant for different applications. Also, decreases of the band gap energy for Cu-doped TiO₂ samples have been reported in the literature, for example, Wang et al. obtained a value of 2.2 eV using a method of synthesis based on a metal plasma ion implantation, which is the lowest value found in the literature. The authors of this article previously carried out a study in which commercial TiO₂ (Degussa P25) was doped with Cu (as CuO) to produce surface doping. In this work its application to Dye-sensitized Solar Cells was studied in detail.

A fundamental understanding of the interaction of copper with TiO₂ is required to rationalize the experimental information on this topic, and first-principles calculations have been shown to be an interesting tool in the theoretical study of doped rutile and anatase TiO₂. Furthermore, recent theoretical studies focused on the electronic structure and optical properties of...
Cu-doped TiO$_2$ found that the Cu doping can induce doping states near the top valence band, and there is a Cu 3d-Ti 3d optical transition that enhances the visible absorption in the wavelength range of 400 to 1000 nm.$^{32}$

In this paper we introduce a synergistic study of Cu-doped TiO$_2$ from an experimental and theoretical point of view. Cu-doped TiO$_2$ samples synthesized using a method based on a hydrolysis reaction at low temperature were characterized, with particular emphasis on the analysis of the band gap energy values obtained. Internal doping and a drastic decrease of the band gap energy were obtained. On the basis of these experimental observations, periodic density functional theory (DFT-periodic) calculations were carried out both to model the experimentally observed doped structures and to rationalize theoretically the experimental decrease in the band gap energy. Thus, the Vienna Ab initio Simulation Package (VASP)$^{33-36}$ with the projector-augmented wave method (PAW)$^{37,38}$ were used. The structures CuTi$_{37}$O$_{75}$, CuTi$_{17}$O$_{35}$ and CuTi$_{11}$O$_{23}$ were studied considering the oxygen vacancies and CuTi$_{2}$O$_{15}$ (23 atoms) were studied considering the oxygen vacancies to simulate the experimental stochiometries of CuTi$_{2}$O$_{7.5}$, CuTi$_{1.5}$O$_{1.5}$ and CuTi$_{1}$O$_{2.5}$. The study of density of states (DOS) and projected density of states (PDOS) clearly indicates that the 3d- and 2p-states of the Cu and O, respectively, play a crucial role in the decreasing band gap energy upon increasing the doped percentage. Moreover, the analysis of the electron localization function (ELF)$^{39}$ sheds light on the bonding character of the Cu-doped TiO$_2$. Thus, we appreciate an increase in the covalent character of the Cu–O interaction in Cu-doped TiO$_2$ in comparison to TiO$_2$.

2. Materials and methods

2.1. Experimental section

Cu-doped TiO$_2$ samples were synthesized using a low temperature hydrolysis reaction designed in our laboratory using titanium n-butoxide as a precursor.$^{40}$ The synthesis procedure can be summarized as follows: (a) 100 mL of deionised water was cooled at 4 °C in order to slow down the hydrolysis reaction, thereby it is possible to control the crystallinity of the samples; (b) during the cooling process a stoichiometric amount of CuCl$_2$·2H$_2$O (purity 98%, Panreac) was added to obtain theoretical proportions of Cu/TiO$_2$ of 2.5%, 5.0%, 7.5%; (c) then, 10 mL of titanium n-butoxide (purity 97%, Sigma-Aldrich) was added drop wise under magnetic stirring; (d) after this, the solution was homogenised for 30 min under magnetic stirring; (e) next, 4 mL of HNO$_3$ (purity 65%, Merck Suprapur) was added, and the mixture was stirred for 2 h; (f) then, the surplus solvent was evaporated under vacuum at 333 K using a rotatory evaporator, and subsequently on a hotplate at 373 K until complete removal; (g) finally, as-prepared Cu-doped TiO$_2$ samples were annealed in air for 1 h at 723 K. Also, pure TiO$_2$ was synthesized using the same procedure in order to compare the results obtained.

In order to characterize the Cu-doped TiO$_2$ samples, several instrumental techniques were used to find the proportion of Cu and its location in the structure, the crystalline phases, and the band gap energy. To understand the effect of Cu in the structure, samples of pure TiO$_2$ were characterized. Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) was used to determine the composition of the Cu-doped TiO$_2$ samples. This was performed using an Iris Intrepid spectrometer, supplied by Thermo Elemental$.^{41}$ The structural study was performed using several techniques. X-Ray Diffraction (XRD) was used to characterize the different crystalline phases in the samples, using an X-ray powder diffractometer supplied by Bruker$.^{42}$, model D8 Advanced. The 2θ scans were recorded using Cu K$_{α}$ radiation of wavelength 1.54 Å in the range 20–75° with 0.02° step size. In turn, XPS experiments were performed using monochromatized Al K$_{α}$ radiation (1486.6 eV), and a 20 eV pass energy to collect the spectra. Binding energy scale was referred to the C1s signal at 284.8 eV, and given with an accuracy of 0.1 eV. The spectra was collected using a Kratos Axis UltraDLD spectrometer. The crystalline structure was further analysed by Raman spectroscopy. The Raman spectra were collected in a backscattering geometry using a Jobin Yvon U1000 double monochromator equipped with a Hamamatsu R-943 PMT, and a DPSS 532 nm laser supplied by Oxiuss$.^{43}$ Finally, UV-Vis spectroscopy in diffuse reflectance mode was used to obtain the band gap energy for the Cu-doped TiO$_2$ samples. Thus, it is possible to find a relationship between the band gap energy and the amount of Cu used for doping the semiconductor. The system used was assembled in our laboratory and it comprised a Xenon lamp, model ASB-XE-175, supplied by Spectral Products$,^{44}$ and a spectrometer, model USB2000+, supplied by Ocean Optics$.^{45}$

2.2. Computational framework

DFT-periodic calculations were performed using the Vienna Ab initio Simulation Package (VASP)$^{33-36}$ with the projector-augmented wave (PAW) method.$^{37,38}$

The number of plane waves in VASP was controlled by a cut-off energy, which in our calculations was set to $E_{\text{cut}} = 500$ eV in order to satisfactorily describe the system.$^{28}$ The electron exchange and correlation were treated within both the local density approximation (LDA)$^{41}$ and the generalized gradient approximation (GGA).$^{42}$ In the case of GGA, Perdew–Burke–Ernzerhof (PBE)$^{43}$ functionals were used. Both the cell shape and atomic positions were optimized using a conjugate-gradient algorithm, where the iterative relaxation of atomic positions was stopped when the forces on the atoms were less than 0.01 eV Å$^{-1}$. Also, a Gaussian smearing with $k_B T = 0.1365$ eV was applied.

The anatase structure is characterized by the tetragonal space group $I4/amd$. A Monkhorst–Pack grid$^{44}$ of $4 \times 4 \times 2$ k-points mesh for sampling the Brillouin zone for anatase bulk (12 atoms) was found enough to reach negligible changes in the optimized cell parameters and energy. The resulting cell parameters were $a = 3.749$ Å, $c = 9.502$ Å for LDA; and $a = 3.811$ Å, $c = 9.710$ Å for GGA-PBE, in agreement with the experimental values ($a = 3.782$ Å, $c = 9.502$ Å).$^{45}$

The cells Ti$_{12}$O$_{64}$ (96 atoms), Ti$_{16}$O$_{32}$ (48 atoms) and Ti$_8$O$_{16}$ (24 atoms) were optimized as anatase models for doping. The implantation of Cu into the structure was performed on substitutional positions. The Cu atom substitutes the Ti atom in TiO$_2$ taking into account the equivalent sites. Close attention was paid to
oxygen vacancies and we report the most stable configuration for each composition. Thus, the structures CuTi$_{31}$O$_{63}$, CuTi$_{15}$O$_{31}$ and CuTi$_{5}$O$_{15}$ were optimized to simulate the experimental stoichiometries of CuTi$_{25}$O$_{78}$, CuTi$_{12}$O$_{35}$ and CuTi$_{11}$O$_{23}$. The selected structures are adequate to represent the experimental concentrations within DFT with periodic boundary conditions framework. The density of states (DOS) and projected density of states (PDOS) for the relaxed structures were obtained using the tetrahedron method with Bloch corrections and a mesh of 12 $\times$ 12 $\times$ 12 k-points. Spin-polarized calculations were performed for the Cu-doped TiO$_2$. For all the systems, DFT + $U$ calculations were performed to take into account the on-site Coulomb interaction, applying a $U$ value of 5 eV.

Electron localization function (ELF) images and structures images were obtained by using the vaspview software and ChemCraft.

To calculate reaction energies, the energy of the O$_2$ molecule was obtained with VASP, using the same PAW potentials, cutoff energy and other precision parameters as in the other calculations.

### 3. Results and discussion

ICP-AES was used to characterize the atomic composition of the samples. Table 1 shows the amount of Cu introduced into the structures as a percentage of the mass of Cu in relation to the mass of TiO$_2$. The percentage of Cu incorporated into the TiO$_2$ structure was around 80% with respect to the initial amount of Cu added, that is, 2.5%, 5.0% and 7.5%. From these values the stoichiometric formula of the samples was calculated and is shown in Table 1.

The XRD patterns of the pure TiO$_2$ and Cu-doped TiO$_2$ are shown in Fig. 1. A good correlation is observed with the reference, TiO$_2$ JCPDS 21-1272 for anatase and TiO$_2$ JCPDS 21-1276 for rutile, anatase being the predominant phase. These results differ from those obtained for samples synthesized using a typical hydrothermal method, wherein the rutile phase is not produced when the samples are annealed at 723 K, but it is well-known that the synthesis method used, the nature of the dopant and the doping level affect the crystalline structure obtained. Moreover, from all Cu-doped TiO$_2$ patterns, XRD does not reveal the presence of any crystalline phase of copper species (according to reference JCPDS 45-0937), and only the peaks of the anatase and rutile phases are observed. Thus, it may be concluded that Cu ions are uniformly dispersed within the anatase crystalline structure. Moreover, a positive shift of the peak (101) of the anatase phase ($2\theta = 25.28^\circ$, TiO$_2$ JCPDS 21-1272) in the synthesized samples is observed. The 2θ values obtained are 25.28$^\circ$ for pure TiO$_2$, and 25.42$^\circ$, 24.46$^\circ$ and 25.46$^\circ$ for 2.5%, 5.0% and 7.5% Cu-doped TiO$_2$. This shift can be attributed to a perturbation in the crystalline phase. The small difference between the ionic radii of Cu ($r$(Cu$^{2+}$) = 0.72 Å) and Ti ($r$(Ti$^{4+}$) = 0.68 Å) does not preclude the introduction of Cu into the anatase structure, but it leads to tension in the surrounding area and, as a consequence, the displacement of the peaks associated with the anatase phase.

From XRD patterns, it is possible to calculate several properties of the crystals, such as the percentage of anatase phase, the mean crystallite size, and the anatase lattice parameters. The percentage of anatase phase is calculated using the equation $A(\%) = 100/[1 + 1.265(I_A/I_R)]$ where $I_A$ is the intensity of the reflection (110) of the rutile phase, and $I_A$ is the intensity of the anatase peak (101) signal. In turn, the average crystallite sizes of all the samples were estimated using the Scherrer equation: $d = 0.89\lambda/(\beta \cos \theta)$, where $\lambda$ is the X-ray wavelength used, $\beta$ the diffraction angle, and $\theta$ is the full width at half maximum of the most intense diffraction peak (FWHM). Finally, the peak positions of the anatase (101) and (200) reflections were used to calculate the lattice parameters using the Nelson–Riley method, according to the equation

$$a^2 = \left[\frac{\lambda}{2\sin \theta}\right]^2 \left[h^2 + k^2 + l^2 \left(\frac{a^\prime}{c}\right)^2\right]$$

The values obtained for the properties noted above are shown in Table 2. From these values, we can observe that the anatase phase is the predominant phase in the samples.

<table>
<thead>
<tr>
<th>Initial % Cu added</th>
<th>Real % Cu</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>&lt;0.10$^a$</td>
<td>TiO$_2$</td>
</tr>
<tr>
<td>2.5</td>
<td>2.03 $\pm$ 0.03</td>
<td>CuTi$<em>{31}$O$</em>{35}$</td>
</tr>
<tr>
<td>5.0</td>
<td>4.10 $\pm$ 0.01</td>
<td>CuTi$<em>{15}$O$</em>{31}$</td>
</tr>
<tr>
<td>7.5</td>
<td>5.76 $\pm$ 0.07</td>
<td>CuTi$<em>{5}$O$</em>{15}$</td>
</tr>
</tbody>
</table>

$^a$ Percentage lower than the detection limit of the analytical method.

<table>
<thead>
<tr>
<th>% Cu</th>
<th>A/%</th>
<th>d/nm</th>
<th>a/Å</th>
<th>c/Å</th>
<th>V/Å$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>72.7</td>
<td>11.4 $\pm$ 0.2</td>
<td>3.770</td>
<td>9.575</td>
<td>136.1</td>
</tr>
<tr>
<td>2.5</td>
<td>73.5</td>
<td>9.6 $\pm$ 0.3</td>
<td>3.782</td>
<td>9.090</td>
<td>130.0</td>
</tr>
<tr>
<td>5.0</td>
<td>70.4</td>
<td>8.5 $\pm$ 0.5</td>
<td>3.769</td>
<td>9.384</td>
<td>133.3</td>
</tr>
<tr>
<td>7.5</td>
<td>70.8</td>
<td>8.0 $\pm$ 0.7</td>
<td>3.792</td>
<td>9.335</td>
<td>134.2</td>
</tr>
</tbody>
</table>

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Footnotes:


46. Spin-polarized calculations were performed.

47. Typical hydrothermal method.

48. Electron localization function (ELF).

49. TiO$_2$ JCPDS 21-1272.


52. Cu-doped TiO$_2$.


60. Cu-doped TiO$_2$.


63. Cu-doped TiO$_2$.

64. Cu-doped TiO$_2$.


68. Cu-doped TiO$_2$.


70. Cu-doped TiO$_2$.


Moreover, the average crystallite size decreases when the amount of Cu in the samples increases. As the radius of Cu$^{2+}$ is very close to the radius of Ti$^{4+}$, Cu$^{2+}$ is relatively easy to penetrate into the Ti$^{4+}$ position, and we can see from Table 2 that the cell parameters of pure TiO$_2$ and Cu-doped TiO$_2$ are close, although we can observe how the $a$ and $c$ parameters change slightly and that the cell volume of the Cu-doped TiO$_2$ is always less than that of pure TiO$_2$. This may be due to the introduction of Cu$^{2+}$ into the structure of TiO$_2$, which produces changes in the distance between atoms and generates oxygen vacancies to maintain the local charge neutrality, as discussed below. These oxygen vacancies can generate variations in lattice parameters that may be due to tensile and compressive strain in the structure, as it is possible to observe in the structure modelled below. The relative force between tensile and compressive strain defines the values of lattice parameters. Therefore, we can conclude that Cu$^{2+}$ penetrates into Ti$^{4+}$ positions, but it generates distortion of the anatase TiO$_2$ structure, and a decrease in crystallinity, as discussed above.

On the other hand, an XPS characterization has been developed. Table 3 shows the values of the binding energies (BE) of Ti 2p$_{3/2}$ and Cu 2p$_{3/2}$ for the samples synthesized, which are compared with reference values found in the literature. From these values, Ti$^{4+}$ is the major Ti species in our samples. In turn, the BE for Ti 2p$_{3/2}$ is 464.2 eV for pure TiO$_2$ and 2.5% and 5.0% Cu-doped TiO$_2$ and 464.1 eV for 7.5% Cu-doped TiO$_2$. Therefore, the separation of the peaks of Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ was around 5.6 eV, which is also consistent with previous results for Ti$^{4+}$.24 In turn, in order to study the presence of Cu in the structure, we compare the binding energies of Cu 2p$_{3/2}$ with values found in the literature. As we can observe, the values are very similar. Moreover, the presence of Cu$^{2+}$ is usually observed by shake-up satellites with high intensities around 9 eV higher than the main Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$ peaks. The shake-up satellites in our samples are shown in Fig. 2A. So, the Cu signals obtained show a good correlation with reference CuO signals.

Moreover, the Auger signal of Cu LMMa was registered, and using the Cu 2p$_{3/2}$ BE, the modified Auger parameter ($\alpha'$) was calculated in order to know the location of Cu$^{2+}$ ions in the structure. As comparison, values obtained from a sample of commercial CuO and values obtained in the literature were used. $\alpha'$ was calculated according to

$$\alpha' = \text{BE(Cu 2p$_{3/2}$)} + \text{KE(Cu LMMa)} \quad (2)$$

$\alpha'$ values are shown in Table 3. The results obtained for all the samples are similar, and there is a good concordance with values found in the literature. Moreover, the valence band (VB) of the samples in a range between 30 and $-5$ eV was registered, and they are shown in Fig. 2B. It is possible to observe a peak about 3.8 eV typical for CuO in all samples. The typical peak corresponding to the VB for Cu$_2$O appears at 2.8 eV,62 and this is not observed in our samples. In turn, Fig. 2C shows the valence band near to Fermi level for no doped TiO$_2$ and 5.0% Cu-doped TiO$_2$. A change in the maximum of the valence band is observed, and a decrease in the band gap energy can be obtained. The values of band gap energy are discussed in detail from the UV-Vis results below.

So, from XPS analysis, we can confirm the presence of Cu$^{2+}$ in our samples, and this fact does not involve any change of the oxidation state of Ti. Moreover, from the results shown above, Cu$^{2+}$ ions are located in an oxide matrix in the structure of our samples. Therefore, the XPS results provide evidence of the substitution of Ti$^{4+}$ by Cu$^{2+}$ in the structure of TiO$_2$, and this generates oxygen vacancies, as we can see from the Raman results discussed below.

Otherwise, the samples synthesized were analysed by Raman spectroscopy. The anatase phase of TiO$_2$ shows a tetragonal structure with six active Raman modes: $A_1g$ ($519$ cm$^{-1}$), $B_1g$ ($399$ cm$^{-1}$ and $519$ cm$^{-1}$), and $E_g$ ($144, 197$ and $639$ cm$^{-1}$).63–65 Fig. 3A shows the Raman spectra obtained. In these spectra, we can assign peaks to the vibrational modes of the anatase phase, and we observe a very low-intensity band at approximately $445$ cm$^{-1}$ which can be related with the $E_g$ mode of the rutile structure ($446.5$ cm$^{-1}$).66 However, in the Cu-doped TiO$_2$ spectra no peak was observed which could be assigned to CuO (according to literature, peaks at $297$ (A$g$), $344$ (B$g$) and $629$ cm$^{-1}$ (B$g$)67,68), in agreement with the XRD results.

Furthermore, it was observed that the $E_g(1)$ peak ($144$ cm$^{-1}$) shows a shift towards higher wavenumbers (Fig. 3B), while the $E_g(3)$ peak ($639$ cm$^{-1}$) shows a shift towards lower wavenumbers (Fig. 3C). It is well-known that when TiO$_2$ is rendered nonstoichiometric, anatase Raman peaks are shifted and broadened.69,70 The incorporation of dopants with oxidation states less than Ti$^{4+}$ causes the generation of oxygen vacancies to conserve local charge neutrality within the anatase-lattice.69,71 Thus, as with XRD, the substitution of Ti by Cu provokes structural distortions of the anatase, and oxygen vacancies in the structure.

UV-Vis spectra for the pure and doped TiO$_2$, in diffuse reflectance mode (DRS), are shown in Fig. 4A. The spectrum of pure TiO$_2$ shows a band edge absorption near $370$ nm, which is typical for the band gap of anatase TiO$_2$ nanoparticles.72 In contrast, Cu-doped TiO$_2$ spectra show an absorption band
below 550 nm, and a broad band at 500–800 nm. These bands are assigned to Cu in the samples, as the theoretical calculations shown below confirm. The band between 500 and 800 nm are assigned to the $2E_g - 2T_{2g}$ transitions of Cu$^{2+}$. This implies that Cu doping facilitates the transition of the electrons from the valence band to higher electronic states. Thus, the band gap energies of pure and doped TiO$_2$ were calculated from DRS spectra using the Kubelka–Munk formula and Tauc plot. The Kubelka–Munk formula is $f(R) = (1 - R)^2/2R$, where $R$ is the reflectance. As TiO$_2$ is an indirect semiconductor material, the plot of $[f(R)\cdot h\nu]^{1/2}$ versus $h\nu$ (Tauc plot) will show a linear region if the band gap is determined by direct transition. In the linear region, the equation $[f(R)\cdot h\nu]^{1/2} = K(h\nu - E_g)$, where $h\nu$ is the photon energy, $E_g$ the band gap energy, and $K$ is a characteristic constant for each semiconductor material, must be satisfied. Thus, the band gap energy can be obtained by extrapolating the Tauc plot to the $h\nu$ axis. Fig. 4B shows the Tauc plots for pure and Cu-doped TiO$_2$ samples, and the values of the band gap energy obtained are shown in a table included as an inset in this figure. It shows that the band gap energy decreases with Cu doping and this effect increases when the amount of the dopant increases. Furthermore, the band gap energy values obtained are lower than those reported in the literature. Several authors have reported values from 2.40 eV to 3.00 eV. Also, using metal plasma ion implantation, Wang et al. obtained a value of 2.20 eV for Cu-doped TiO$_2$.

Based on the results of the physical chemistry characterization, we can conclude that we obtained internally doped anatase TiO$_2$ by substituting Ti$^{4+}$ for Cu$^{2+}$ in the structure, which generates oxygen vacancies and distortions in the anatase structure. Moreover, we have not obtained evidence of the presence of any species of Cu in the samples. Also, the band gap energy of the doped TiO$_2$ synthesized decreased drastically.

In order to gain insight into the energetics of the vacancy formation we have calculated the energy of the formal reactions:

$$\text{CuTi}_{31}O_{64} \rightarrow \text{CuTi}_{31}O_{63} \square + \frac{1}{2} O_2$$  \hspace{1cm} (3)

$$\text{CuTi}_{15}O_{32} \rightarrow \text{CuTi}_{15}O_{31} \square + \frac{1}{2} O_2$$  \hspace{1cm} (4)
CuTi$_7$O$_{16}$ → CuTi$_7$O$_{15}$ $\square$ + $\frac{1}{2}$ O$_2$  \hspace{1cm} (5)

where $\square$ denotes an oxygen vacancy. To model the dopant–vacancy system, it is necessary to identify the optimal configuration for the dopant and vacancy within the supercell. We identified the first coordination shell around the dopant as the most stable site for the vacancy to occur, in agreement with previous results for CuTi$_3$O$_{7.82}$. 

The energy associated with the vacancy formation reaction ($E$) can be described as:

$$E = E(\text{doped}) - E(\text{doped-vacancy}) + \mu_O$$  \hspace{1cm} (6)

where $E(\text{doped})$ is the total energy of the system containing the Cu atom and $E(\text{doped-vacancy})$ is the total energy of the system considering the vacancy formation; $\mu_O$ is the chemical potential of O. $\mu_O$ is determined from $\mu_O = 1/2 \cdot E(\text{O}_2) + \mu'_O$ where $E(\text{O}_2)$ is the total energy of an isolated oxygen molecule in a triplet state, and $\mu'_O = 1/2 \cdot k_B T \ln (p/p_0)$. 

Fig. 5 illustrates the dependence of the formation energy versus oxygen pressure as $\ln (p/p_0)$ at the experimental temperature of 723 K, while Table 4 shows the reaction energies under the particular case of oxygen-rich conditions, i.e. $(p/p_0) = 1$, for the most stable configuration at each Cu-doped percentage.
A perusal of Fig. 5 and Table 4 clearly suggests that the generation of oxygen vacancies is favoured at the experimental conditions, in order to conserve the local charge neutrality in the TiO$_2$ lattice.

In turn, the local geometry for the most stable configuration of the optimized structures is shown in Fig. 6, and some geometrical parameters which are modified with doping are shown in Table 5. Remarkably, in general the Cu–O distances diminish (ca. from 2.1 to 1.9 Å) upon increase of the Cu percentage which reinforces the Cu–O bond and it is indicative of its covalent character. Moreover, this reinforcement of the Cu–O bond and the oxygen vacancy generation introduces a logical distortion of the structure, as we observe experimentally from XRD and Raman results. If we look at the Ti atom on the left site where the vacancy is generated (Fig. 6B–D) it can be appreciated that the angle O$_\text{up}$–Ti–O$_\text{DOWN}$ (identified as $\alpha$ in Fig. 6) is ca. 26, 20.9 and 13.2$^\circ$ closer for the 2.5%, 5% and 7.5% Cu-doped structures, respectively, as compared to the parent TiO$_2$ (see Table 5). Consequently, the linear distances between those two oxygen atoms ($d_1$, see Fig. 6 and Table 5) increases from 3.36 to 3.75 Å for the 2.5% to 7.5% Cu-doped structures, respectively.

To scrutinize the differences in the electronic properties of the pure and Cu-doped TiO$_2$, we studied the bond characteristics through the analysis of the electron localization function (ELF) in those systems. The ELF provides a direct space depiction of electron distribution, which is useful for study bonding features.$^{39}$ The local value of the ELF at a position can be interpreted as the probability of finding an electron at that locality given the existence of neighbouring electrons. The ELF ranges from 0 to 1. Thus, ELF values close to one corresponds to a region of the space where there is a high probability of finding electron localization, whereas an ELF value close to one-half corresponds to a region of electron gas-like behaviour.$^{39,87}$ By contrast, a value of 0 implies that electrons are fully delocalized or that there is no electron in that place. Fig. 7 depicts the ELF contour plots for TiO$_2$ (A, B) and for Cu-doped anatase (C, D). As can be seen, the electron localization on Ti is higher than on Cu, which implies the higher covalent features of Cu–O interaction as compared to Ti–O interaction, as reported elsewhere$^{84}$ for Os-doped anatase. Moreover, it can be observed in the enlarged area of Fig. 7D that the ELF of the oxygen atoms under the vacancy is slightly deformed and directed through the Cu atoms, which is corroborated by the 4.1 Å of the Cu–O distance (identified as $d_3$ in Fig. 7) as compared to the 4.3 Å of Ti–O distance (marked as $d_4$ in Fig. 7) in the TiO$_2$. Therefore, the O–Ti–O angle under the vacancy in the doped structure ($\beta$ in Fig. 7) is around 160$^\circ$, that is, ca. 20$^\circ$ less than in the TiO$_2$ (marked as $\gamma$). This result is consistent with the Cu–vacancy–Ti distance of 3.94 Å, which is longer than that of 3.80 Å for Ti–O–Ti. This distance is identified as $d_2$ in Fig. 6, and its values are shown in Table 5 for the structures studied.
To further understand the electronic properties that underlie the energetic effects mentioned above, we will discuss the electronic structure in terms of the density of states (DOS) and the projected density of states (PDOS). The calculated DOS of pure and Cu-doped anatase are shown in Fig. 8, and the calculated PDOS for CuTi$_7$O$_{15}$ is shown in Fig. 9 as an example of the PDOS obtained for Cu-doped structures. Our results indicate that the valence band of pure TiO$_2$ is mostly composed of O 2p states and the conduction band is dominated by the Ti 3d states, in agreement with previous results.$^{29,32}$ After Cu-doping the electronic structure undergoes changes, as seen in Fig. 8. The substitution of a Cu atom by a Ti one produces new states at the top of the valence band of the host. Increasing the percentage of Cu doping narrows the band gap (Fig. 8). In Table 6, the experimental and theoretical band gap energies are shown. Our theoretical results predict a decrease in the band gap energy upon increasing the amount of Cu in the doped structure. The highest band gap value corresponds to the CuTi$_{14}$O$_{63}$ supercell in agreement with the experimental results and it represents ca. 2% of Cu in the doped-structure. It is remarkable that both LDA + $U$ and PBE + $U$ methods present a similar trend as compared to our experimental data. Moreover, our results are consistent with the absorption band between 500–800 nm observed in the UV-Vis spectra for Cu-doped anatase shown above. Consequently, Cu doping promotes the visible absorption of TiO$_2$, which improves its performance in photovoltaic and photocatalytic applications.

Moreover, the PDOS analysis (Fig. 9) indicates that those new states in the total DOS consist mainly of O 2p-states and of Cu 3d-states, while a residual contribution of Ti 3d-states is also appreciated. The participation of the Cu and Ti 3d-states in the three doped structures increases by around 15% (10%) and 2% (2%), respectively, as measured by the area below the peaks for LDA + $U$ (PBE + $U$), while the participation of the O 2p-states decreases by around 13% (8%). Therefore, the overlap of the metal d orbitals with oxygen p levels in the same range of energies of the DOS suggests that some covalence bond character exists between Ti, Cu, and O atoms.$^{88}$
4. Conclusions

A good correlation between the experimental and theoretical results was obtained for Cu-doped anatase. The physical chemistry characterization of the pure and Cu-doped TiO_2 synthesized indicates that all the samples present a predominant anatase phase. XRD, XPS and Raman spectroscopy suggest that Cu^{2+} ions are incorporated into the anatase structure by substitution of Ti^{4+} ions, and distortions of the structure and oxygen vacancies are generated. Moreover, UV-Vis spectroscopy indicates that the band gap energy decreases drastically for Cu-doped TiO_2. In turn, the theoretical results predict a decrease in the band gap upon increasing the Cu doping, and allow us to understand the structures of the Cu-doped TiO_2 when oxygen vacancies are generated. The inclusion of Cu as a dopant agent implies a covalent character in the Cu-O interaction that implies the appearance of new states in the valence band maximum with a narrowing in the band gap.

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References