SYNTHESIS AND CHARACTERISATION OF W-, Ag-, AND W/Ag- CO-DOPED TITANIA NANOPOWDERS, AND THEIR PHOTOCATALYTIC ACTIVITY

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Abstract

Tungsten, silver, and tungsten/silver co-doped titaniananopowders were synthesised via an aqueous sol-gel method. The dried gels were thermally treated at 2 different temperatures, and the occurrence of the amorphous phase was assessed, using the combined Rietveld-RIR method, on the X-ray powder diffraction data. Systematic studies of the crystal structure and of the optical properties of the powders – made with diffuse reflectance spectroscopy (DRS) – were performed. The energy band gap was calculated using the differential reflectance method; their morphology was investigated using field emission scanning electron microscopy and transmission electron microscopy analyses (FE-SEM and TEM, respectively). The photocatalytic activity of the samples was assessed in liquid-solid phase, under UVA-light and visible-light irradiation, monitoring the degradation of an organic dye. The influence of the phase composition, optical properties, dimensions, and specific surface area of the powders on the photocatalytic activity was thoroughly discussed.

Keywords: Sol-gel synthesis, nanostructures, X-ray diffraction, optical properties, doped titania, photocatalysis

Introduction

Titanium dioxide (TiO2) crystallises in a large number of polymorphs: the high-pressure columbite-like (Haines and Leger, 1993), baddeleyite-like (Sato et al., 1991), and cotunnite-like (c-TiO2) structures (Dubrovinsky et al., 2001), exist besides the well-known – in order of abundance – rutile, anatase, and brookite phases (Muscat et al., 2002). TiO2 is a common and widely used material in everyday life applications, not only for its well-established use in paints, as a whitening agent for food, and in personal care products or pharmaceuticals (Weir et al., 2012), but also for its use in electrochemical electrodes.
and solar cells (O’Regan and Grätzel, 1991). In particular, in recent decades, TiO$_2$ has been experiencing more and more attention after the discovery, in 1972, of the so-called “Honda-Fujishima effect” (Fujishima and Honda, 1972). This was photo-electrochemical water splitting, using a single-crystal titania electrode. As a result, in recent decades the degree of interest in semiconductor photocatalysis has grown exponentially, not only in the areas of water and air purification (Chen and Poon, 2009; Puddu et al., 2010), but also in wastewater treatment (Malato et al., 2009). Semiconductors (e.g. TiO$_2$, ZnO, α-Fe$_2$O$_3$, or CdS) are able to act as sensitisers for light-activated redox processes because of their electronic structure: when a photon matches or exceeds the band gap energy of the semiconductor, an electron is liberated from the valence band into the conduction band, leaving a hole behind (Hoffmann et al., 1995). The photo-generated pair (e$^-$-h$^+$) is able to reduce and oxidise a pollutant that is adsorbed on the photocatalyst surface (Fujishima et al., 2000). Amongst semiconductors, TiO$_2$ is indeed the most investigated photocatalytic material. TiO$_2$ is chemically inert and non-toxic; the reactions take place under mild operating conditions (e.g. a low level of solar or artificial illumination, room temperature (RT), and atmospheric pressure); no chemical additive is necessary; the possible intermediates of the reactions are not dangerous (or at least are less dangerous than the original pollutant) (Arsac et al., 2008); and even very recalcitrant and persistent pollutants can be degraded (Herrmann et al., 2007). Moreover, one peculiar characteristic of TiO$_2$ – simultaneous with the photocatalytic activity – is its antibacterial activity. When irradiated with light with a wavelength greater than the band-gap, TiO$_2$ photocatalysts can also be used to inactivate or kill bacteria that are on the photocatalyst surface, and hence to make those surfaces self-sterilising (Fujishima et al., 1999).

Amongst TiO$_2$ polymorphs, anatase and rutile are the most utilized in photocatalytic applications, although anatase is considered to be more photoactive than rutile (Ohno et al., 2001), because of its stronger reducing power and better hole-trapping ability (Augustynski, 1993). Anatase and rutile are wide band gap semiconductors – their band gap is equal to 3.23 and 3.02 eV, respectively – and this means that the photocatalytic reaction is promoted by light having UVA radiation. Consequently, titania exploits only 3–5% of the available solar energy in the photocatalytic reaction, being transparent for most of the solar radiation spectrum (Karvinen and Lamminmäki, 2003).

A possible means of extending the photocatalytic activity of titania into the visible region is doping it with transition metals (Choi et al., 1994; Fuerte et al., 2001). In particular, the doping of TiO$_2$ with WO$_3$ is able to improve the TiO$_2$ photocatalytic activity in several ways: it prevents the recombination of the electron-hole pairs (e$^-$-h$^+$) (Tatsuma et al., 2001), it may shift the light absorption band from the UVA to the visible region (Li et al., 2001), and it is able to increase the surface acidity of the photocatalyst; hence it can absorb more hydroxyl groups and, simultaneously, more organic reactants on its surface (Kwon et al., 2000). Furthermore, noble metal modification improves the photocatalytic activity of titania by accelerating liquid-solid photocatalytic reactions (Sakthivel et al., 2004), and by reducing the fast recombination of the photo-generated e$^-$-h$^+$ charge carriers (Kominami et al., 2002). Amongst noble metals, silver is particularly attractive due to its remarkable catalytic activity (Jana et al., 1999), its size-, as well as shape-dependent optical properties (Wang and Herron, 1991; Jin et al., 2003), its possible applications in biological and chemical sensing due to its localised surface plasmon resonance (Hutter et al., 2001); and also because of its long-established, well-known antibacterial properties, due to the so-called “oligodynamic effect” (Lansdown, 2010).

In this work, W-doped, Ag-doped, and W/Ag-co-doped titania were successfully synthesised via the sol-gel technique. The phase composition and crystal structure – by means of X-ray powder diffraction (XRPD)
and the Rietveld method – as well as the optical properties of the prepared samples, were thoroughly investigated. The photocatalytic activity – assessed in liquid-solid phase, by monitoring the degradation of an organic dye, under UVA-light and visible-light irradiation – of the samples was also tested. Results were explained taking into account the effects which the variation of crystallinity, crystalline phase, and optical and physical properties might exert on the photocatalytic activity of the samples.

**Experimental**

### Sample Preparation

Aqueous titanium(IV)hydroxide sols were made from the peptisation of hydrolysed titanium (IV) isopropoxide (Ti-i-pr, Ti(OCH(CH$_3$)$_2$)$_3$), using distilled water. One part of Ti-i-pr (Aldrich, 97%) was added to 4 parts of isopropyl alcohol (IPA, propan-2-ol) to make a 20% Ti-i-pr solution. This Ti-i-pr solution was hydrolysed by the dropwise addition of an excess of water (5:1 water:Ti-i-pr) as a 20% solution in IPA. The acid necessary to peptise the sol was also added to this water-IPA solution – concentrated HNO$_3$ (Aldrich, 65%, Sigma-Aldrich Corp., St. Louis, MO, USA), added in a ratio of Ti$_4^+$:HNO$_3$ of 5:1. This water-IPA-HNO$_3$ solution was added dropwise to a 20% Ti-i-pr solution (20% in IPA) with mechanical stirring, as above, although obviously this time without the addition of any acid to the highly basic mixture. As above, the IPA was removed on a rotary evaporator, and then replaced with water, which in this case had HNO$_3$ added. A higher ratio of 1.25:1 (5:4) Ti$_4^+$:HNO$_3$ was needed, probably due to some ammonia remaining in the dried gel. This was again evaporated to a gel, and then redispersed in more added water to form a sol in 30 min. The 1.0 mol% Ag$^+$ / 1.0 mol% W$^6+$ co-doped sol was made from a W$^6+$ doped sol made as above. To this sol, the stoichiometric amount of AgNO$_3$ was added afterwards. All sols were maintained at a 1M concentration, and were shown to be stable for over a week in all cases, and often several weeks. The volume of solvent/water before evaporation on the rotary evaporator was approximately 500 ml in all cases.

The as-synthesised gels were dried in an oven at 80°C, and afterwards the dried gels were thermally treated at 450°C and 600°C in a static air flow. The thermal rate, from RT to the maximum temperature, was 5°C min$^{-1}$, followed by 2 h of soaking time. Undoped titania samples were referred to by Ti450 and Ti600 symbols, where the number represents the 2 maximum firing temperatures reached;
doped gels were instead indicated by adding the W- or Ag- chemical symbols; when co-doped, W/Ag- was the symbol added.

**Sample Characterisation**

The unit cell parameters of the prepared samples were determined using LaB₆ (National Institute of Science and Technology 660b) as the internal standard. XRPD data were collected by using a 0/20 diffractometer, Panalytical XˈPert Pro (PANalytical B.V., Almelo, Netherlands), equipped with a fast remote traffic microwave sensor (RTMS) detector, with graphite monochromated Cu Kα radiation (40 kV and 40 mA, 20-80° 2θ range, a virtual step scan of 0.0167° 2θ, and 50 s per step). Divergence and anti-scattering slits of 0.125° and 0.125°, respectively, were mounted in the incident beam pathway. The pathway of the diffracted beam included a Ni filter, a soller slit (0.01 rad), and an antiscatter blade (5 mm). The full profile fitting analyses were performed using XRPD data, and Rietveld refinements were accomplished with the general structure analysis system (GSAS) (Larson and Von Dreele, 2000) package and its graphical interface EXPGUI (Toby, 2001). The starting atomic parameters for anatase and rutile, described in the space groups I₄₁/amd and P4₂/mnm respectively, were taken from Howard et al. (1991); brookite ones, described in the space group Pbca, were obtained from Meagher and Lager (1979). In the full Rietveld refinements, these parameters were refined: scale-factors, zero-point, the background signal modelled using a 6th-order of the shifted Chebyshev polynomial function, unit cell parameters and profile coefficients – 1 Gaussian (G_w), an angle-independent term, and 2 Lorentzian terms, L_X and L_Y – peak correction for asymmetry, and sample displacement effects. For all XRPD measurements, the samples were carefully ground and mounted in aluminum sample holders using a side-loading technique. XRPD data were also used for the quantitative phase analysis (QPA). Data were collected using a 0/0 diffractometer, Panalytical XˈPert Pro, equipped with a fast RTMS detector, with graphite monochromated Cu Kα radiation (40 kV and 40 mA, 20-80 020 range, a virtual step scan of 0.0167° 2θ, and virtual time per step of 50s). Divergence and anti-scattering slits of 0.125° and 0.125°, respectively, were mounted in the incident beam pathway. The pathway of the diffracted beam included a Ni filter, a soller slit (0.01 rad), and an antiscatter blade (5 mm). Full QPA (i.e. determination of both the crystalline and amorphous content) was performed using the combined Rietveld–RIR method (Gualtieri, 2000; Gualtieri and Brignoli, 2004): 10 wt% corundum (National Institute of Science and Technology 676a) was added to the sample, and treated as an additional phase in the refinements. In this case, the refined weight fractions of each crystalline phase (X_w) were rescaled with respect to the known weight fraction of the added standard (X_s) in order to obtain the real crystalline phase weight fraction (X_c):

$$X_c = \frac{1}{1 - X_s} \left[ \left( \frac{X_w}{X_w} \right) X_s \right]$$ (1)

where X_w is the refined weight fraction of the internal standard. Knowing the weight fractions of all crystalline phases, the amorphous content (X_a) is calculated using the following equation:

$$X_a = 1 - \sum X_i$$ (2)

DRS was performed with a Shimadzu UV 3100 (Shimadzu Corp., Kyoto, Japan) spectrometer and spectra of the samples were acquired in the UV-Vis range (250-750 nm), with 0.02 nm in step-size and using BaSO₄ as the reference. The Kubelka-Munk function was applied with the aim of converting the diffuse reflectance into the absorption coefficient α:

$$\alpha \approx \frac{K}{S} \frac{(1-R_a)^2}{2R_a} = F(R_a)$$ (3)

where K and S are the absorption and scattering coefficients; the reflectance R_a
is equal to $R_{\text{sample}}/R_{\text{standard}}$ (Marfunin, 1979).

The energy band gap ($E_g$) of the powders was calculated using the differential reflectance method (a method mainly applied for well-crystalline semiconductor materials). This method assumes that, plotting the first derivative of reflectance ($dR/d\lambda$) versus the wavelength ($\lambda$), the maximum value of such a plot corresponds to the band gap of the semiconductor material (Komornicki et al., 2004).

The morphology of the samples was investigated by TEM (Hitachi H9000, Hitachi Ltd., Tokyo, Japan), equipped with an energy dispersive x-ray spectroscopy (EDS) attachment (Bruker Quantax 400, Bruker Corp., Billerica, MA, USA), and FE-SEM (Hitachi SU-70, JP). The specific surface area (SSA) of the prepared samples was evaluated by the Brunauer-Emmett-Teller method (Micromeritics Gemini 2380, Micromeritics Instrument Corp., Norcross, GA, USA), using N$_2$ as the adsorbate gas.

**Evaluation of Photocatalytic Activity**

The photocatalytic activity of the prepared powders was evaluated in liquid-solid phase, monitoring the degradation of an organic dye – methylene blue (MB, Aldrich) – using a spectrometer (Shimadzu UV 3100, JP). The tests were performed at RT, in a cylindrical photocatalytic reactor (100 mm in diameter) containing an aqueous solution of the dye (1 L), at an initial concentration of 5 mg L$^{-1}$. The concentration of the photocatalyst in the slurry was 0.25 g L$^{-1}$. In order to mix the solution thoroughly, the slurry was magnetically stirred throughout the reaction; the reactor was covered with a watch-glass, so as to avoid the evaporation of the solution. The lighting of the reacting system was assured by placing 2 lamps at either side of the reactor; the distance between the lamps and the reactor was 5 cm. The UVA-light source was a germicidal lamp (Philips master PL-S 2P 9W/840, NL), having an irradiance of ~50 W m$^{-2}$ in the visible region and 600x10$^{-3}$ W m$^{-2}$ in the UVA region. In the experiments, the photocatalytic degradation of the MB was monitored by sampling about 4 mL of the slurry from the reactor, at regular time intervals. Before switching the lamps on, the suspension was stirred in the dark for 30 min, with the aim of allowing the adsorption of MB onto the powders. The powders in the samples were separated by centrifugation, and then the MB concentration in the liquid was determined, taking advantage of the Lambert-Beer law, by measuring the absorbance in a spectrometer at a wavelength of 665 nm, using distilled water as a reference. The photocatalytic reaction is a pseudo first-order reaction, hence, the extent of MB degradation was evaluated as the apparent first-order constant ($k'_{\text{app}}$):

$$\ln \left( \frac{C_0}{C} \right) = k'_{\text{app}} t$$

(4)

where $C_0$ is the initial concentration of orange II (OII) and $C$ is its concentration after a certain UVA-visible-light irradiation time $t$. The plot of $\ln \left( \frac{C_0}{C} \right)$ vs the irradiation time, gives a straight line, whose slope corresponds to the value of the pseudo first-order apparent rate constant ($k'_{\text{app}}$) (Al-Ekabiand Serpone, 1988). Commercial Aerioxide® TiO$_2$ P25 photocatalytic powder (Evonik Industries, Essen, Germany) was used for comparison.

**Results and Discussion**

**Morphology of the Fired Powders**

The fired powders consist of poorly crystallised, strongly aggregated, and sub-spherical-shaped particles, as shown by TEM analysis (Figure 1(a-d)). Undoped TiO$_2$ particles possess a broad particle size distribution, with dimensions ranging from tens of nanometres, up to ~50 nm (Figure 1(a)). W-doping gives the
powders a narrower grain size distribution, if compared to the undoped ones, and the mean particle size decreases as well (Figure 1(b)). Also the Ag-doped powders, at 450°C, possess a wide particle size distribution (Figure 1(c)); it is seen as well that an increase of firing temperature causes a growth in particle size. Moreover, in the Ag-doped sample fired at 600°C, rounded nanoscale Ag particles that are clustered around the larger titania ones, are clearly visible (Figure 1(d)).

**X-ray Diffraction Analysis**

The powder diffraction patterns of the samples that were dried in an oven at 120°C (data were not reported here) interestingly show that, already at this temperature and with this synthesis method, poorly crystalline anatase, rutile, and brookite – at different amounts within the prepared powders – coexisted with the amorphous phase, and well-crystalline titanium hydrogen oxide hydrate. The powder diffraction patterns of the samples fired at 450°C are depicted in Figure 2(a). In these, the presence of W and/or Ag oxides was not detected. The incorporation of W into the titania lattice is predictable – the effective ionic radii of $[^6]Ti^{4+}$ and $[^6]W^{6+}$ are 0.61 and 0.60 Å, respectively (Shannon, 1976). On the other hand, the incorporation of Ag into the titania lattice is not likely (as was demonstrated by TEM observations), the $[^6]Ag^{+}$ ionic radius being 1.15 Å (Shannon, 1976). Thus, we deem that its amount in the mixtures (1 mol%), is lower than the x-ray detection limit.

From the QPA data (Table 1), it can be inferred that samples fired at this temperature (450°C) had quite a large amount of amorphous phase (values ranging from 21.6 wt%, to 27.3 wt%), a legacy of the un-crystallised titania in the starting sols.

![Figure 1. TEM micrographs of: a) sample Ti450; b) sample W-Ti450; c) Ag-Ti450; d) Ag-Ti600: the white circles indicate Ag nanoparticles, while the inset represents EDS analysis of them](image-url)
Table 1. Refinement parameters and phase composition of the undoped and doped titania samples. The phase composition was calculated from the Rietveld refinements of XRD patterns, using the NIST 676a internal standard. There were 3528 observations for every refinement; the number of anatase, rutile, and brookite reflections was 32, 31, and 154, respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>No. of variables</th>
<th>$R_p^2$</th>
<th>$R_{wp}$</th>
<th>$\chi^2$</th>
<th>Phases (wt%)</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>anatase</td>
<td>rutile</td>
<td>brookite</td>
<td>amorphous</td>
<td></td>
</tr>
<tr>
<td>Ti450</td>
<td>25</td>
<td>0.03</td>
<td>0.05</td>
<td>1.4</td>
<td>25.1±0.1</td>
<td>37.7±0.1</td>
<td>10.3±0.4</td>
<td>26.9±0.7</td>
<td></td>
</tr>
<tr>
<td>W-Ti450</td>
<td>23</td>
<td>0.03</td>
<td>0.05</td>
<td>1.5</td>
<td>26.8±0.1</td>
<td>36.7±0.1</td>
<td>10.7±0.3</td>
<td>25.7±0.6</td>
<td></td>
</tr>
<tr>
<td>W/Ag-Ti450</td>
<td>18</td>
<td>0.04</td>
<td>0.06</td>
<td>1.7</td>
<td>1.7±0.1</td>
<td>76.8±0.1</td>
<td>–</td>
<td>21.6±0.3</td>
<td></td>
</tr>
<tr>
<td>Ag-Ti450</td>
<td>25</td>
<td>0.02</td>
<td>0.05</td>
<td>1.2</td>
<td>33.7±0.1</td>
<td>25.3±0.1</td>
<td>13.7±1.0</td>
<td>27.3±1.3</td>
<td></td>
</tr>
<tr>
<td>Ti600</td>
<td>20</td>
<td>0.05</td>
<td>0.07</td>
<td>2.0</td>
<td>1.3±0.1</td>
<td>73.9±0.1</td>
<td>–</td>
<td>24.8±0.3</td>
<td></td>
</tr>
<tr>
<td>W-Ti600</td>
<td>21</td>
<td>0.06</td>
<td>0.06</td>
<td>1.5</td>
<td>13.4±0.1</td>
<td>61.4±0.1</td>
<td>–</td>
<td>25.2±0.3</td>
<td></td>
</tr>
<tr>
<td>W/Ag-Ti600</td>
<td>16</td>
<td>0.08</td>
<td>0.06</td>
<td>1.9</td>
<td>0.7±0.1</td>
<td>80.0±0.1</td>
<td>–</td>
<td>19.3±0.3</td>
<td></td>
</tr>
<tr>
<td>Ag-Ti600</td>
<td>18</td>
<td>0.06</td>
<td>0.06</td>
<td>1.4</td>
<td>6.1±0.1</td>
<td>75.7±0.1</td>
<td>–</td>
<td>18.2±0.3</td>
<td></td>
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</tbody>
</table>
The relative amount of the brookite phase is approximately the same in all the samples. The co-doped sample was the only exception, having no brookite, its composition being: 1.7 wt% anatase, 76.8 wt% rutile, and 21.6 wt% amorphous phase. Thus, the co-doping concentration – 1 mol% – favours brookite → rutile, and the anatase→to→rutile phase transformation (ART), at only 450°C. It has been reported that the ART mechanism changes with the Ag concentration (Chao et al., 2003), hence, an addition of 0.5 mol% Ag might favour rutile formation at the expense of brookite. Moreover, the reference sample (Ti450) and the W-doped one (W-Ti450), had virtually the same phase composition. On the other hand, Ag addition delayed the ART: this sample contained 33.7 wt% anatase, 25.3 wt% rutile, and 13.7 wt% brookite. Actually, there exist many contradictory reports on the crystallisation and phase transition of titania doped with silver. For instance, Chao et al. (2003) reported that Ag insertion favoured the ART; on the contrary, according to García-Serrano et al. (2009), Ag incorporation inhibited the ART in TiO₂ nanoparticles. Essentially, crystallisation and, consequently, the ART, are affected by several parameters, such as: the synthesis process, the starting materials, atmosphere, and the presence of impurities or doping species. Hence, we can assume that with this synthesis method, at a rather low temperature of 450°C, the Ag insertion increased the thermal stability of the anatase nanoparticles, hindering the crystallisation process and shifting the ART toward higher temperatures.

The increase of the firing temperature leads to a disappearance of brookite in all the samples: at 600°C, the only crystalline phases are anatase and rutile, (Figure 2(b) and Table 1). The amount of the amorphous phase in samples Ti600 and W-Ti600 slightly decreased, if compared to the same samples fired at 450°C. Sample Ti600 had a marked ART, its anatase content being equal to 1.3 wt%. Ag- and co-doped samples had, instead, a lower amount of the amorphous phase, namely, 18.2 and 19.3 wt%. Doping apparently favoured rutile formation, and accelerated the ART. Tungsten was the most effective in delaying the ART (anatase and rutile amounts in the W-doped sample were 13.4 wt% and 61.4 wt%, respectively). Actually, the incorporation of cations with a valence higher than 4+ into the anatase lattice is believed to retard the ART, due to the reduction of the oxygen vacancies and formation of interstitial Ti³⁺, thus repressing the atomic transfer in the anatase structure (Okada et al., 2001). Hence, we assume that the reactions amorphous / brookite → rutile, and anatase → rutile, occurred at a higher temperature, and the nanocrystals of brookite rapidly transformed into rutile, because of their high activation energy (Zhang and Banfield, 2000).

Considering the unit cell parameters, the insertion of tungsten leads to an expansion of the anatase lattice, both at 450 and 600°C (Figure 3(a,b)). On the other hand, the W/Ag- and Ag- doping virtually did not modify the anatase lattice of the powders fired at 450°C; on the contrary, at 600°C, the Ag- and the co-doping led to a contraction of the anatase lattice. Taking into account the modification that doping exerted on the rutile lattice (Figure 3(c)), tungsten and co-doping led to an expansion of the rutile lattice in the powders fired at 450°C; Ag-doping, virtually did not modify its lattice, confirming the aforementioned assumption that the incorporation of Ag into the titania lattice is not likely, because of ionic radii issues. Referring to the rutile in the powders fired at 600°C (Figure 3(d)), its lattice is virtually the same as the one of the W- and W/Ag-doped samples, while, at this firing temperature, the Ag-doping led to a contraction of the rutile lattice, as also in the case of anatase.

**Optical Properties**

The DRS of the synthesised powders are depicted in Figure 4(a) and (b). As expected, the undoped sample showed no absorption in the visible region. Its spectrum, at both firing temperatures, consisted of a single
absorption band, below approximately 410 nm, ascribed to the metal-ligand charge transfer in titania. Doped and co-doped samples (stored in the dark), besides that band, also showed an absorption tail in the visible region, at approximately 430 nm, at both firing temperatures. The exception was the co-doped sample fired at 600°C, in which the thermal treatment led to a disappearance of that absorption tail (Figure 4(b)).

The energy band gaps of the powders were calculated by the differential reflectance method (Table 2). The resulting curves were successfully fitted with a Gaussian function, and the maximum values were found from the fitting. The subsequent band gap energies of the samples were all assigned to rutile, since they are consistent with its expected $E_g$ value, that is 3.02 eV (411 nm), referred to Table 2. Exceptions were the Ag-doped and the co-doped samples, at both the firing temperatures. These samples also showed a shoulder, centred at approximately 423 nm (2.93 eV), that can be attributed to Ag mid-gap states, that are in the titania forbidden band. In particular, silver doping creates middle Ag 4$d$ states, whose transitions between Ti 3$d$ states are the source of the visible absorption (Guo and Du, 2012).

**Photocatalytic Activity**

Photocatalytic activity results, reported as the relative pseudo first-order apparent rate constant ($k_{app}$) during the reactions – under UVA and visible-light exposure – are depicted in Figure 5(a-d).

Under UVA light irradiation, the reference sample, Aerioxide® TiO$_2$ P25 powder, had the best photocatalytic activity of all the sets of powders, fired both at 450 and 600°C, leading to a full degradation of the dye, in approximately 4 h of irradiation time (Figure 5(a), and (b)). Undoped sample Ti450 was the best photocatalyst amongst the synthesised powders fired at 450°C, leading almost to a complete degradation of the dye after 7 h of irradiation time (Figure 5(a)). Between the doped and co-doped samples, W-Ti450 had the better photocatalytic activity, followed by the co-doped sample and the Ag-doped one. In this case, dopants should behave as electron-hole recombination centres (Serpone et al., 1994; Sclafani and Herrmann, 1998; Di Paola et al., 2002). Moreover, the amount of amorphous phase also has to be taken into account, lowering the relative photocatalytic active centres on such samples (Tobaldi et al., 2010). The increase of the firing temperature to 600°C, Figure 5(b),
Figure 3. Unit cell parameters \((a = b)\) Vs unit cell volume of: a) anatase fired at 450°C; b) anatase fired at 600°C; c) rutile fired at 450°C; d) rutile fired at 600°C

Figure 4. Diffuse reflectance spectra – in the \(\lambda\) range of 375-550 nm – of the samples fired at: a) 450°C, and b) 600°C
led to a decrease of the photocatalytic activity of all the tested samples. Such a decrease was more marked for the undoped and the Ag-doped samples with the lowest SSA. On the contrary, the photocatalytic activity of the W- and co-doped samples did not suffer dramatically with the increase of firing temperature. Actually, the W- and co-doped samples are the ones with the highest SSA values at this firing temperature, and this made such behaviour possible.

Visible-light exposure led to a lowering of the overall photocatalytic performance, even if every sample was shown to be active at both firing temperatures. Furthermore, their photocatalytic activity (the only exception being sample Ag-Ti600) was higher than that of the Aeroxide® TiO₂ P25, used as the reference (Figure 5(c), and (d)). Of the samples fired at 450°C, the best one was the undoped titania. Its superior activity should be due to the concomitant presence of nanostructured anatase, brookite, and rutile (Ding et al., 2000): to a certain extent, rutile, when nanostructured, is a visible-light active photocatalyst (Yin et al., 2004), since its band-gap is slightly shifted into the visible region, and, therefore, it has a higher visible light absorption compared to anatase. Moreover, brookite/rutile mixed systems have also recently been reported to be visible-light active photocatalysts (Pan et al., 2009; Xu and Zhang, 2009). Considering the lower photocatalytic activity of the doped and co-doped samples in this case, we can infer that the dopants acted as electron-hole recombination centres. It can be seen that firing at 600°C clearly resulted in powders with a lower photocatalytic activity under visible light. At this firing temperature, the photocatalytic activity of the undoped sample dramatically decreased because, if on the one hand the crystallinity increased, on the other the excessive coarsening of the particles led to a huge decrease of its SSA (Table 2). The photocatalytic activity of the doped and co-doped samples followed the trend: W>W/Ag>Ag. Even though the relative anatase/rutile amounts in those samples are approximately the same, sample W-Ti600

<table>
<thead>
<tr>
<th>Sample</th>
<th>( E_g ) (eV)</th>
<th>( \frac{dR}{d\lambda} )</th>
<th>( S_{\text{BET}} ) (m² g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti450</td>
<td>3.06±0.01</td>
<td>–</td>
<td>41.9</td>
</tr>
<tr>
<td>W-Ti450</td>
<td>3.04±0.01</td>
<td>–</td>
<td>64.6</td>
</tr>
<tr>
<td>W/Ag-Ti450</td>
<td>3.07±0.02</td>
<td>2.93±0.02</td>
<td>47.5</td>
</tr>
<tr>
<td>Ag-Ti450</td>
<td>3.08±0.01</td>
<td>2.96±0.02</td>
<td>49.2</td>
</tr>
<tr>
<td>Ti600</td>
<td>3.03±0.01</td>
<td>–</td>
<td>4.0</td>
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<tr>
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<td>–</td>
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<tr>
<td>W/Ag-Ti600</td>
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</tbody>
</table>

Table 2. Band gap energy \( E_g \) and specific surface area of pure, doped and co-doped titania. The energy band gap \( E_g \) is calculated with the diffuse reflectance \( dR/d\lambda \) method.
(that possessing the highest SSA within the set of samples fired at 600°C) is once again the best performing photocatalyst, and the increase of the firing temperature did not dramatically affect its photocatalytic activity under visible-light exposure.

Conclusions

Undoped titania and W-, Ag-, and W/Ag co-doped titania were successfully synthesised via an aqueous sol-gel method. The simultaneous presence of rutile, anatase, and brookite was detected in the dried gels thermally treated at 450°C, together with a significant amount of amorphous phase. At 600°C, the only crystalline phases were anatase and rutile. Brookitetercrystallised into rutile; tungsten addition was the more effective for delaying the ART.

The Ag- and co-doping gave the nanopowders a band gap contribution at around 2.93 eV (423 nm), due to the Ag mid-gap localised levels. Undoped titania and the doped and co-doped powders, fired at 450°C, showed an appreciable photocatalytic activity under visible-light irradiation, better than the Aeroxide® TiO₂ P25 powder – without the need of any oxygen supply – due to the concomitant presence of nanostructured anatase and rutile. Tungsten doped and co-doped powders, at this firing temperature, were shown to be less photo-active than the undoped sample, probably due to the electron-hole recombination. At the highest firing temperature, 600°C, only the W-doped powder kept its high photocatalytic performance – not suffering from the increase in firing temperature – both under UVA and visible-light exposure.

References


Augustynski, J. (1993). The role of the surface intermediates in the photoelectrochemical behaviour of anatase and rutile TiO
2


2

2

2

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2

2


2

2


2
–WO
2

2
-loaded TiO
2

Tungsten, Silver, and Tungsten/Silver Co-Doped Titania Nanopowders


