**Controlled Ag-TiO₂ hetero-junction by combining physical vapor deposition and bifunctional surface modifiers**

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**Abstract**

A controlled physical method without any solvent was developed to growth Ag nanoparticles on TiO₂ through using mercaptoacetic acid as bifunctional surface modifier. The fabricated Ag-TiO₂ particles were proposed as an innovative photocatalytic material. The particle size, chemical nature, morphology and chemical bonding between the mercaptoacetic acid, silver and titania have been characterized by UV-vis Absorption Spectroscopy, Powder X-Ray Diffraction, Raman Spectroscopy, Transmission Electron Microscopy and Field Emission Scanning Electron Microscopy. Combining the photocatalytic activity of titania with the excellent electron acceptor abilities and visible absorption of small spherical silver nanoparticles, it was possible to demonstrate an efficient photo-induced degradation of cationic organic pollutant under UV-Vis light. The nanocatalyst material obtained at 30s of sputtered time under simulated sunlight provides almost complete degradation (97%) of methylene blue after 120 min. The particle-size and distribution of silver nanoparticles have been achieved for the first time by a physical method using controlled chemical bonding to bifunctional surface modifiers and the sputter deposition time.

**Keywords:** Controlled physical method, bifunctional surface modifiers, efficient photodegradation pollutant.
1. Introduction

The high photocatalytic properties of titanium dioxide (TiO$_2$) make possible its use in many fields of science such as anti-bacterial agent [1], UV protecting agent [2], solar energy conversion [3], water splitting to produce hydrogen fuel, decomposing [4-8] and removal of organic or inorganic pollutants [9-11] and also as photocatalyst in two-dimensional materials [12]. In this regard, organic pollutants in water sources remain one of the biggest environmental problems today, as they are highly toxic and difficulty to be degraded [7,13]. The effectiveness of the photocatalytic process depends on several factors, such as the efficient generation of reactive oxygen species (ROS), which have a high oxidizing power being able to oxidize and mineralize almost any organic pollutant (especially •OH, $E^o=2.8$ V). [14] Other factors include a wide range of light absorption, low recombination of electron-hole pairs, availability of active sites for oxygen, electron-holes transfer capability, interphase connection between pollutant-photocatalyst and removal of interfacial photocatalyst from aqueous medium. [15-18] One of the most common persistent cationic organic pollutant is Methylene Blue (MB), as widely used in cotton, wood and silk industry. When discharging in water sources, it can cause harmful health on human beings and ecosystems through bioaccumulation. This dye can be mineralized in aqueous media to CO$_2$ and H$_2$O or less toxic molecules using TiO$_2$ nanostructures, as these photocatalyst materials are chemically stable and easily recoverable in solid phase to practical applications and its scalability. [20]
Kamat pointed out [21] that some features such as shape- and size-controlled synthesis, new tools to understand the surface properties, and ease of chemical modification to tailor their surface properties have given many of these oxides prominence in recent years. However, TiO$_2$ is a semiconductor having a wide energy gap, preventing further absorption of photons (only absorbs UV light, which is less than 3% of incident solar light). It also presents a high recombination of hole-electron pairs and due their small size tends to agglomerate, avoiding the pollutant interaction on the photocatalyst surface. Therefore, the development of new photocatalysts modifying TiO$_2$ is one of the most important aims in photocatalysis for environmental applications. Cong and co-workers [22] mentioned the importance to improve the stability and the transmission of photo-generated electrons between the electron acceptor molecule and the conduction band of TiO$_2$ by chemical bond formation. They also mentioned that difficulties as poor quantum yield (associated with the rapid recombination of photogenerated electron-hole pairs ($e^-h^+$)), low adsorption capacity and difficulties to recover the photocatalyst, hampering the applications of these nanostructured semiconductors. In this regard, our group recently reported the impact of the shape, size, and distribution of semiconductor nanoparticles over photocatalytic degradation response, since they are controlling factors that dictate their physical and chemical properties [23].

Several studies confirm that the addition of noble metal nanoparticles such as gold (AuNPs) and silver nanoparticles (AgNPs), increase the photoresponse of TiO$_2$ [24-27]. Those NPs act as an electron acceptor material facilitating electron-hole separation due to formation of a Schottky barrier between semiconductor-metal junctions. Additionally, there is considerable interest in utilizing AgNPs to enhance the photocatalytic properties, because of its high oxygen adsorption reactivity [28], high efficiency and capacity to facilitate the excitation of electrons by creating a local electric field [29-31], and as a consequence improving the semiconductor photo-response. Chen and co-workers [32] recently
reported that some issues still occur in these kind of semiconductor-metal photocatalysts, such as a weak junction, easy separation and self-agglomeration, impacting in a less separation of photo-generated electron-hole pairs. In this respect, the development of Ag-TiO$_2$ compounds with better junctions is also a great challenge to efficiently separate the generated electron-hole pairs, thus increasing the photo-response.

Vargas and co-workers [33] mentioned in a recent work that the concentration of photogenerated charge carriers and $e^-+-h^+$ recombination lifetimes are fundamentally important factors in the photocatalytic performance of TiO$_2$ materials. They also address the impact of the metal doping in TiO$_2$ and how these features are driving physical properties and therefore the photocatalytic process to degrade MB. They pointed out a clear red shift of the semiconductor band gap improving the visible harvesting light and then achieving an improvement photodegradation using Ag doping, attributed to better intensity of light radiation at the semiconductor interface generated by surface plasmon resonance of AgNPs.

AgNPs are typically synthetized by chemical reduction containing Ag precursors in solution phase [34], because a high reproducibility, less dispersion and small particles sizes are achieved comparatively with solid state methods. However, solid methods are often required to practical applications as photocatalysts, sensors, supported materials and solid matrices. [23] In this sense, with respect to wastewater remediation using photocatalytic nanomaterials; first, the catalyst obtained is in solution phase and therefore is difficult to remove it from treated water after photodegradation pollutant and therefore limit their practical application and scalability. [14] The second factor is that the prepared nanomaterial needs an appropriate stabilizer in solution phase to avoid agglomeration. Additionally, some reports have shown that the size, morphology, stability and properties of metal nanoparticles are strongly influenced by the experimental conditions, the different kinetics with reducing agents, and the
adsorption processes. [35,36] Therefore, the design of synthetic methods in which the size, morphology, stability and properties can be controlled has become a major topic of interest to get an efficient photocatalysts materials.

One interesting physical method is Physical Vapor Deposition (PVD), presenting several advantages including that there is no contamination from solvent or precursor molecules on the surface, the process is environmentally friendly, and there is no liquid waste. However, the greater dispersion and diameter of particles with respect to solution phase methods suggests new tools to improve them. [34-36] In this sense, our group made an innovation of this method through macromolecular systems, allowing the stabilization of ordered arrangements of metal nanoparticles, and thus improving the size dispersion and particle diameter. [37]

Here we report an alternative and more versatile method to growth AgNPs by PVD on nanocrystalline titanium dioxide using a bifunctional surface modifier such as the mercaptoacetic acid (HSCH₂COOH) type. Combining the efficient photocatalytic activity of titania with the excellent electron acceptor abilities and surface plasmon resonance of AgNPs, it was possible to achieve a very efficient organic pollutant photodegradation. The stability, particle-size and distribution of AgNPs were controlled and improved via chemical bonds between TiO₂, HOOCCH₂SH and AgNPs and an appropriated sputter time. A schematic representation of synthetic route of Ag on TiO₂ using bifunctional surface modifiers is illustrated in Fig 1.

Figure 1 here

2. Experimental

2.1 Chemicals and Starting Materials
HSCH$_2$COOH, MB, toluene and ethanol were commercially available from Sigma-Aldrich and were used without further purification. Degussa P25 TiO$_2$ (70% anatase and 30% rutile) was used to generate nanocrystalline TiO$_2$ anatase (TiO$_2$NPs). The AgNPs were carried out by Physical vapor deposition (magnetron sputter coater PELCO SC-6). The cathode used was of electrolytic grade (99.99% purity).

2.2 Synthesis of Photocatalytic Material

TiO$_2$NPs were obtained by heat treatment at 500 °C to achieve a sintering process. This heat treatment allows a crystal phase transition from 70% anatase and 30% rutile to mainly anatase. Once the anatase phase was obtained, a 1µM solution of mercaptoacetic acid was added drop wise to the TiO$_2$NPs suspended in toluene for 24h, and then washed with small amounts of toluene. After that, TiO$_2$-OOCCH$_2$SH was dispersed inside the Magnetron Sputtering chamber, where AgNPs are sputtered onto TiO$_2$NPs by using the bifunctional surface modifiers. The homogenous AgNPs were deposited on the substrate in an inert atmosphere (Ar) at room temperature. Vacuum: 1x10-5 atm; Current: 25mA; Exposure time: 10-80 seconds.

2.3 Structural Characterization

Powder X-Ray Diffraction (XRD) data were collected on a Siemens D 5000 powder diffractometer, with Cu Kα radiation (λ = 1.540598Å) in the range 5° < 2θ < 80° (40 kV, 30 mA) and a graphite monochromator. The TiO$_2$ anatase phase was indexed as a tetragonal lattice with the following lattice parameters: a = 3.7867 Å, c = 9.5149 Å, α = β = γ =90°. The TiO$_2$ rutile phase was also indexed as a tetragonal lattice (a = 4.5940 Å, c= 2.9586 Å), while the silver measured lattice parameters are a = 4.0862 Å (Ag) for a face centered cubic structure. Raman Spectra were recorded with a Renishaw
Raman RM1000 equipped with a 514.5 nm laser line and an electrically refrigerated CCD camera. Measurements were made at room temperature on solid samples. The morphology of TiO$_2$-OOCCH$_2$S-Ag photocatalysts was analyzed using a field-emission scanning electron microscope (FE-SEM) Nova 400 Nano operating at 25 kV and the elemental analysis was obtained with an Energy-Dispersive X-Ray Spectrometer (EDS). The High-Resolution Transmission Electron Microscopy (HRTEM) and Electron Diffraction (ED) were performed using a JEOL 2000FX microscope at 200 kV to probe the average size, distribution and elemental composition of nanoparticles. The optical properties and the photodegradation of MB were characterized by UV-Vis absorption spectroscopy performed on a Shimadzu UV-2600 spectrophotometer. The diffuse reflectance data of solid samples were transformed to absorbance using the Kubelka-Munk equation and TAUC model for indirect allowed optical transitions to determine the band gap value.

2.4 Photocatalytic degradation

MB was used as a model compound for organic environmental contaminants to test the silver sputtered (particle-size, morphology, Ag deposition) dependent on photocatalytic behavior of the TiO$_2$-OOCCH$_2$S-Ag nanostructures. The photocatalytic activity was evaluated by measuring the bleaching rate of MB under UV-Vis illumination in a range of 330-700 nm at room temperature using a CuSO$_4$ filter (0.1mol/L), to avoid the self-degradation and thermal catalytic effects of this cationic organic pollutant. A quartz tube of 25 mL was used as a photoreactor vessel. The optical system used was a xenon lamp (150W) which was positioned 20 cm away from the photoreactor. 25 mg of the photocatalyst and 25 mL of MB aqueous solution (1$x10^{-5}$ mol/L) were placed with continuous magnetic stirring. Prior to irradiation, the suspension was stirred in the darkness for 30 min to establish an adsorption/desorption equilibrium, after which the photocatalytic degradation of MB was initiated.
Samples were withdrawn from the reactor at certain time intervals (30 min), and centrifuged to remove the particles. Photodegradation was monitored by measuring the absorbance of the solution at 655 nm under different time intervals.

3. Results and Discussion

3.1 Characterization

Once metal particles are deposited on TiO\textsubscript{2}, the color changed from white to yellow-pink. This change is indicative of small AgNPs (around 10-50 nm). The presence of anatase crystalline particles and their interaction with bifunctional surface modifiers and AgNPs were analyzed by two different techniques, XRD and Raman spectroscopy, as described below. The XRD pattern of TiO\textsubscript{2}-OOCCH\textsubscript{2}S-AgNPs is shown in Fig. 2(a), XRD reflections for TiO\textsubscript{2} correspond mainly to the anatase crystalline structure, although small amounts of the rutile crystal phase are still present. These results are evidencing the crystalline changes from a bi-crystalline structure of TiO\textsubscript{2} (see Fig. S1) to an anatase with only a low percentage of rutile. This suggests that the sintered TiO\textsubscript{2}NPs will show better photocatalytic activity than TiO\textsubscript{2} rutile phase as described in previous section, as anatase crystal structure has higher surface area and oxygen vacancies to interact with oxygen molecules to generate reactive species and degrade more efficiently the organic pollutant [32]. In addition, as shown in Fig. 2(a), XRD pattern also shows the reflections (220) and (311) of AgNPs, confirming the characteristic fcc crystal structure of Ag.

Figure 2 here
Kim and co-workers [38] mentioned that according to factor group analysis, anatase presents six Raman active modes, appearing at 144 cm$^{-1}$ ($E_g$), 197 cm$^{-1}$ ($E_g$), 399 cm$^{-1}$ ($B_{1g}$), 513 cm$^{-1}$ ($A_{1g}$), 519 cm$^{-1}$ ($B_{1g}$), and 639 cm$^{-1}$ ($E_g$) in an anatase single crystal [39]. In the 140-700 cm$^{-1}$ region of the Raman spectrum of TiO$_2$-OOCCH$_2$S-AgNPs (Fig. 2(b)), different bands were assigned to the TiO$_2$ anatase structure, at 140 cm$^{-1}$, 194 cm$^{-1}$, 393 cm$^{-1}$, 512 cm$^{-1}$ and 633 cm$^{-1}$, that are in good agreement with the reported afore mentioned Raman active modes of anatase. In addition, a weak vibrational band at 436 cm$^{-1}$ is observed. Milani and co-authors [40] assigned this vibrational mode to the corresponding $E_g$ rutile phase. The third band at 393 cm$^{-1}$ was assigned to Ti-O-Ti lattice vibration of anatase crystal phase [40]. However, when the TiO$_2$ interacts with Ag, this band shifted from 393 cm$^{-1}$ to 377 cm$^{-1}$, showing a weakening of the Ti-O-Ti bond, and also can be attributed to the effective interaction between TiO$_2$ and Ag through HOOCC$_2$SH. This effective interaction can also be observed by the $\nu$Ag-S and $\nu$C-O asymmetric stretching modes at 109 cm$^{-1}$ and 1636 cm$^{-1}$, attributed to the chemical bonds formed between the sulphur of the bifunctional surface modifiers and Ag, and between the carboxylate group and TiO$_2$. In this sense, five vibrational frequencies were attributed to HOOCC$_2$SH in the 690-1120 cm$^{-1}$ region: $\nu$C-S stretching band at 698 cm$^{-1}$, $\omega$C-H wagging vibrational modes at 847 cm$^{-1}$ and 891 cm$^{-1}$, and $\delta$C-H bending modes at 1028 cm$^{-1}$ and 1115 cm$^{-1}$. The vibrational frequency of the $\nu$S-H stretching mode was not observed at its characteristic wavenumber around 2580 cm$^{-1}$ (see Fig. S2 in supp.info), concluding that the S-H bond was dissociated to form a new chemical bond between Ag-S. The formation of this bond allows a hetero-epitaxial growth of AgNPs on sulphur site and stabilizes them in a uniform way. Therefore, the adsorption processes of AgNPs on TiO$_2$ surface, through chemical bonds, have been successfully achieved. This chemisorption between semiconductor and Ag achieve a better junction avoiding metal desorption on TiO$_2$ surface. On the other hand, the chemical bond formation improves
the stability and the transmission of photo-generated electrons, [22] suggesting our materials will be good candidates showing an efficient photocatalytic activity to degrade MB.

The UV-Vis absorption spectra of TiO$_2$-OOCCH$_2$S-Ag with different sputter times were recorded by Diffuse Reflectance Spectroscopy (see Fig. 3). The optical properties evolution of TiO$_2$ interacting to Ag and characteristic surface plasmon bands of Ag nanostructures at different sputter times (10s-80s) are shown in Fig. 3a and 3b, respectively. As in shown in Fig 3c, at 30s of sputtered time, AgNPs show their characteristic surface plasmon band at 409 nm, attributed to small particles (around 10-50 nm) and a spherical morphology. To analyze the evolution of size and morphology by changing the optical properties of the material, different PVD sputtering times were performed, finding that when the sputter time increases to 80s, the absorption band is shifted to 444 nm, and a second band appears at 599 nm (see Fig. 3d) as a weak peak, which is attributed to larger nanoparticles with different morphology than spherical shape. In this sense, UV-vis absorption spectroscopy can be used to study the morphological evolution of Ag nanostructures [42,43], since they exhibit bands at different frequencies, depending on their particle size and shape. Maiyalagan and co-workers [43] reported silver nanorods showing two plasmon bands in the UV–Vis absorption spectrum, one at 424 nm and the other at wavelengths ranging from 500 to 680 nm depending on the nanorods length. Therefore, from 40s of sputtered time, larger nanostructures begin to form with two absorption peaks attributed to transverse and longitudinal plasmon absorptions, and therefore we can estimate the optimal sputter time to generate small and spherical AgNPs (~10 nm of particle size). It was found that 30s is the necessary time to completely cover the TiO$_2$ surface in order to avoid this kind of nanostructures, which will show a less photocatalytic performance. This behavior can be attributed to a less surface area to carry out the chemical reactions induced by light between TiO$_2$ doped with Ag.
Another important aspect that can be studied from optical measurements is the shifting of the semiconductor energy gap attributed to metal doping. The calculated band-gap values from Tauc model of TiO$_2$ at different sputtered Ag are summarized in table 1. The characteristic broad absorption maxima were found between 370-250 nm for pure TiO$_2$, typical of the electronic transition associated to energy gap of this semiconductor. TiO$_2$-OOCCH$_2$S-Ag samples are evidencing a red shift to the absorption edge of TiO$_2$ attributed to Ag doped material. This shifting improves the visible harvesting light and therefore an enhancement on the photocatalytic properties is expected. This behavior is attributed to Ag inducement of intermediate levels in the band gap of TiO$_2$ impacting in a positive photoinduced charge carriers within elongated lifetimes. [33]

The previously described results, from the best of our knowledge this is the first report that allows to demonstrate the control of stability, size, morphology and crystalline phase of Ag. These is achieved by controlling the deposition time of physical vapor deposition and the modification of the surface of the semiconductor with bifunctional molecules. This control should be reflected in an efficient photocatalytic response, as previously discussed at the introduction section.

Particle size, chemical analysis and morphological evolution were analyzed by TEM. Fig. 4 shows representative low-magnification TEM and SEM images for AgNPs on TiO$_2$ at different sputter times, observing agglomerates composed of fused TiO$_2$ assemblies interacting to AgNPs (Fig 4a). HRTEM image (inset in Fig 4b) shows the interface between Ag and TiO$_2$ nanoparticle, indicating the heterojunction formation, through close interfacial contact, which will facilitate the separation of electron-hole pairs. [31]

HRTEM analysis in Fig. 4c and associated electron diffraction pattern, exhibit characteristic atomic lattice spacing in the TiO$_2$ structure corresponding to the anatase phase. The optimized system,
as determined from optical properties of silver, shows an average particle size of $13.2 \pm 0.3$ nm, with adequate dispersion ($\rho$) of $4.9 \pm 1.0$ nm (see histograms in Fig. S5) and individual particles.

**Figure 3 here**

**Table 1 here**

Additional analysis, related to sputter exposure time, showed an increment of particle size and distribution when the time increases, showing aggregated nanostructures with an average size of $40.3 \pm 3.1$ nm and a dispersion of $22.9 \pm 5.3$ (see Fig. 3e). These results are in good agreement with the optical studies recently discussed, evidencing fused larger 1D systems. Finally, one of the most important aspect is when the AgNPs were generated without using bifunctional surface modifiers on TiO$_2$. Through the TEM images observed in Fig. 3f, it was confirmed the formation of larger ($46.1 \pm 4.1$) and more agglomerated fused nanoparticles ($\rho= 25.7 \pm 8.4$) with high dispersion than the systems obtained in presence of HOOCCH$_2$SH molecules. This study confirms that it is necessary to use this kind of molecules to stabilize and control their particle size, size distribution and surface coverage of AgNPs on nanocrystalline TiO$_2$, as when the particle size increases, the exposure surface decreases, impacting directly in a less photocatalytic degradation behavior.

**Figure 4 here**

Fig. 3(d) also shows a SEM image of TiO$_2$-OOCCH$_2$S-Ag. It can be observed that an assembly of Ag on TiO$_2$ was obtained, and that it is composed of uniform nanosized particles. The SEM-EDS
elemental mapping of these structures (see Fig. S3 in suppl.info) confirms the homogenous silver deposition.

The previously described results, in terms of size control, morphology and crystalline phase, are very important, since to our knowledge it is the first report that allows to demonstrate the control of these factors through the time of physical vapor deposition and the modification of the semiconductor surface with bifunctional molecules that allow to obtain small sizes, a metallic phase and different morphologies that are dependent of these parameters. The size, crystalline phase and shape, directly impact on physical and chemical properties of these materials, and it should be reflected in an efficient photocatalytic response.

3.2 Photocatalytic Behavior of TiO$_2$-OOCCH$_2$S-Ag systems

Different photocatalytic activities are expected for the studied systems, given the diverse physical features of TiO$_2$-OOCCH$_2$S-Ag materials. The photocatalytic behavior of all systems were evaluated by quantifying the degradation of MB in aqueous solution under UV-Vis light (330-700 nm) as irradiation source. The absorbance spectra over the entire MB degradation are shown in Fig. 5(a) for TiO$_2$-OOCCH$_2$S-Ag-30 (the complete sets of spectra are shown in Fig. S5 of other sputter time systems). The photocatalytic reaction of semiconductor materials can be followed as $-\ln(C/C_0) = kt$, where k is the apparent rate constant of pseudo-first-order for this degradation process, as the concentration of TiO$_2$-OOCCH$_2$S-AgNPs is kept constant. In Fig. S6, k value and degradation rate of the obtained systems are exposed. In Table 2, a comparison of the photocatalytic performance for TiO$_2$-OOCCH$_2$S-AgNPs samples is summarized. In absence of photocatalyst, a slight degradation of MB (only 8.0 %) is observed, indicating a minor extent self-photodegradation of MB molecules under UV-Vis irradiation (see Fig. 5b). For commercial TiO$_2$ (Degussa P25), about 54% of MB was degraded after
120 min. A highest extent of MB degradation (97%) at the same irradiation time was achieved using the photocatalyst with 30 s of Ag sputter time. This result evidenced that surface modification of TiO$_2$NPs with assembled spherical Ag nanoparticles within 13 nm of diameter improves the photocatalytic properties, which is attributed to the enhanced charge separation between electron-hole pairs by trapping photogenerated electrons on Ag sites. Moreover, when the sputter time is higher than 30 s, and consequently the AgNPs size increasing and therefore a less photocatalytic performance was observed. Ko and co-workers [44] mentioned that an excessive Ag deposition decreases the photoactivity due to the increased reflection of the incident light and more critically, interaction of negatively charged silver ions and positively charged holes. All these results are in good agreement with the optical and TEM studies, confirming that the optimal sputter time to generate the best photocatalyst should be around 30 s. Therefore, the connection between TiO$_2$ and AgNPs plays an important role for the photocatalytic activity, as the particle size and distribution can be controlled avoiding a decreased contact surface between the catalyst and organic pollutant, attributed to large metal nanoparticle size. An interesting result is observed when TiO$_2$ is exposed from 60 s to 80 s of sputter time, showing an increased photoresponse comparatively to 40 s and 50 s of exposure times of PVD, from 60% of degradation up to 79% at 70 s. This results could be explained by optical and TEM results, because at 30 s we have small spherical AgNPs deposited on semiconductor, but over this time an excess of Ag is generated on the surface of TiO$_2$, which causes an increase in the reflection of the incident light impacting in a less photocatalytic response, as mentioned before. When the exposure time is greater than 60 s, optical properties change due to the formation of 1D structures, which implies a decrease in incident light and therefore a decreased interaction between the charge of silver and the holes of the semiconductor impacting positively on photocatalytic activity.
For a better understanding of our photocatalytic performances, and in the same context against other state-of-the-art TiO$_2$-Ag materials, [45-51] the results are compared with other efficient catalysts in the literature. The comparison was performed with TiO$_2$ nanostructures doped with AgNPs, using MB and other similar persistent organic pollutants within different crystal phases, morphologies, sizes and their correlation with photocatalytic behaviour to degrade wastewater sources containing these kind of contaminants. This analysis (see table 3) was carried out considering the main conditions that dictate the photocatalytic activity, which were previously described. In spite of the great number of available works in the literature related to TiO$_2$ and AgNPs, the aforementioned control has not been reported, regarding to surface modifiers and PVD described in this work, and their impact in an efficient photocatalytic response.

Our remarkable results arise in a very high efficient photodegradation of MB in a short time compared to state-of-the-art materials. Secondly, a better comprehension and control is achieved by using bifunctional modifiers such as HOOCCH$_2$SH. Our physical method allows the control of the deposition time of the metal in order to obtain small and spherical particles, generating a strong heterojunction through chemical bonds to TiO$_2$. This allows the modulation of the photocatalytic properties, by controlling the main factors that dominate these photo-induced chemical reactions, such as morphology, particle size and optical properties were controlled through a novel and versatile synthetic route, using an appropriate surface modifier and experimental conditions.

An important aspect to be considered for the practical application of the photocatalyst is its separation of the treated water and its reusability. These aspects were investigated by the photocatalytic efficiency of our best material TiO$_2$-OOCCH$_2$S-Ag-30 for multiple cycles. The photocatalyst was separated by filtration from the dispersion after degradation of MB, washed with water and ethanol and dried at RT. Subsequently, it was reused to photochemically degrade a fresh MB solution. The results of
photocatalyst reusability are shown in Figure 5d. The four cycles carried out for the photodegradation of MB showed that the efficiency of TiO$_2$-OOCCH$_2$S-Ag-30 remains high, the percentage of photodegradation (~97%) is practically unchanged compared to the first use efficiency.

Figure 5 here
Table 2 here

4. Conclusions

Through the use of a surface modifier, it has been possible to achieve a chemical bond between Ag and TiO$_2$, which impacts on an improved stability and transmission of the photogenerated electrons, avoiding the metal desorption from the surface of the semiconductor. By means of a chemical bond it has been possible to dope to the semiconductor with spherical and small AgNPs, which present a superficial plasmon resonance in the visible zone, allowing to improve the separation of the pair $e^-$-$h^+$, a red-shifting the absorption edge of TiO$_2$. In addition, there is an increase of the photo-response of the material avoiding charge recombination, and impacting in an improved photo-catalytic performance.

The UV-Vis light photocatalytic activities were tested for photo-induced catalyst materials using a common organic pollutant. We have found that the best photocatalytic performance (97%) was achieved for TiO$_2$-OOCCH$_2$S-Ag with 30s of sputter time. The rest of the prepared photocatalysts using different sputter times also showed higher performance than pure TiO$_2$ nanoparticles. These results suggest that the use of bifunctional surface modifiers enable the control of particle sizes, morphologies and stability of AgNPs on TiO$_2$ and thus improving the photocatalytic behavior of TiO$_2$. Our main results allow the rational design of a material to control the features of the photocatalyst and therefore achieve very
efficient behaviours concerning the treatment and removal of recalcitrant water pollutants such as methylene blue.

Acknowledgements

The authors acknowledge Vicerrectoría Académica UC grant VRA-39131781 for financial support. This research has received funding from Consejo Superior de Investigaciones Científicas, Spain under grant I-COOP LIGHT 2015CD0013. The use of Servicio General de Apoyo a las Investigación (SAI, University of Zaragoza) is also acknowledged.

Supplementary Material

Supplementary data associated with this article can be found, in the online version, at doi:

References


Figure Caption

**Figure 1.** Schematic representation of synthetic route of Ag nanoparticles on nanocrystalline TiO$_2$ using mercaptoacetic acid as bifunctional surface modifiers.

**Figure 2.** XRD diffractogram of TiO$_2$-OOC-CH$_2$-S-AgNPs, showing white TiO$_2$ powder and pink TiO$_2$ powder interacting with silver (a), Raman Spectrum of pure TiO$_2$ and TiO$_2$-OOC-CH$_2$-S-AgNPs obtained by 30 s of sputter deposition (b).

**Figure 3.** Optical properties of TiO$_2$-OOC-CH$_2$-S-AgNPs photocatalytic materials. Tauc plots derived from UV-vis reflection spectra for TiO$_2$-OOC-CH$_2$-S-AgNPs at different sputter times (a), UV-Vis absorption spectra of AgNPs on TiO$_2$ recorded by Diffuse Reflectance Spectroscopy (the inset shows silver plasmon band at 411 nm) (b), UV-visible Kubelka-Munk reflectance spectra of pure TiO$_2$ and TiO$_2$-OOC-CH$_2$-S-AgNPs at 30s (c) and deconvoluted spectrum of Ag plasmon bands at 444 nm and 599 nm of TiO$_2$-OOC-CH$_2$-S-AgNPs at 80s of sputter time (d).

**Figure 4.** TEM images of the TiO$_2$-OOC-CH$_2$-S-AgNPs. TEM examination in (a) and (b) confirms small and spherical AgNPs interacting to TiO$_2$ (the inset shows a TEM image of individual hetero-junction evidencing the interface region). HRTEM examination in (c) confirms single crystal structure indexed to anatase in the electron diffraction pattern. SEM image (the Inset shows the EDS analysis confirming the presence of Ag and TiO$_2$) of obtained system at 80 s of sputtered time (d). TEM images of TiO$_2$-OOCCH$_2$S-AgNPs (e) and TiO$_2$-AgNPs (without surface modifier) (f) at the same 80s of sputter time, showing the fused agglomerates.

**Figure 6.** (a) Photodegradation curves of MB in presence of our best photocatalyst TiO$_2$-OOCCH$_2$S-Ag-30. (b) Normalized concentration of MB as function of irradiation time showing the best performances of TiO$_2$-OOCCH$_2$S-Ag with different sputter times and commercial TiO$_2$ (Degussa P25). (c) Pseudo-first order kinetic of photocatalytic reactions for this degradation process. (d) Variation in the efficiency of the TiO$_2$-OOCCH$_2$S-Ag-30 for the degradation of MB with cycling. The exposure time in each cycle was 25 min.
Figure 1:

nanocrystalline TiO$_2$ anatase

mercaptoacetic acid in toluene for 24h

growth of AgNPs by PVD
Figure 2:

(a) X-ray diffraction pattern showing peaks corresponding to different crystallographic planes.

(b) FTIR spectrum with peaks indicating vibrational modes of Ag-S, C-S, and C-H groups.
Figure 3:

(a) 

(b) 

(c) 

(d)
Figure 4:
Figure 5.
Table 1. Optical properties of TiO$_2$-OOCCH$_2$S-Ag systems at different sputter times

<table>
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<tr>
<th>Photocatalyst</th>
<th>Sputter Deposition time (s)</th>
<th>Band gap energies of TiO$_2$ (eV)</th>
<th>λ (nm) of AgNPs at maximum absorbance</th>
<th>AgNPs estimated D(nm) through absorption band</th>
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<tr>
<td>TiO$_2$-OOCCH$_2$S-Ag-30</td>
<td>30</td>
<td>2.95</td>
<td>409</td>
<td>26</td>
</tr>
<tr>
<td>TiO$_2$-OOCCH$_2$S-Ag-40</td>
<td>40</td>
<td>2.87</td>
<td>410</td>
<td>26</td>
</tr>
<tr>
<td>TiO$_2$-OOCCH$_2$S-Ag-50</td>
<td>50</td>
<td>2.85</td>
<td>410</td>
<td>26</td>
</tr>
<tr>
<td>TiO$_2$-OOCCH$_2$S-Ag-60</td>
<td>60</td>
<td>2.80</td>
<td>414</td>
<td>29</td>
</tr>
<tr>
<td>TiO$_2$-OOCCH$_2$S-Ag-70</td>
<td>70</td>
<td>2.70</td>
<td>414</td>
<td>29</td>
</tr>
<tr>
<td>TiO$_2$-OOCCH$_2$S-Ag-80</td>
<td>80</td>
<td>2.60</td>
<td>444 and a weak band at 599</td>
<td>50 and 158</td>
</tr>
</tbody>
</table>

Table 2. Kinetic data for the photodegradation process of MB with all TiO$_2$-OOCCH$_2$S-Ag systems

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Decoloration rate η (%)</th>
<th>Apparent photodegradation rate constant $k$ ($10^{-2}$ min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$ P25 (Degussa)</td>
<td>54.0</td>
<td>0.74 ±0.04</td>
</tr>
<tr>
<td>TiO$_2$-OOCCH$_2$S-Ag-10</td>
<td>71.4</td>
<td>1.11 ±0.08</td>
</tr>
<tr>
<td>TiO$_2$-OOCCH$_2$S-Ag-20</td>
<td>71.0</td>
<td>1.01 ±0.10</td>
</tr>
<tr>
<td>TiO$_2$-OOCCH$_2$S-Ag-30</td>
<td>97.0</td>
<td>1.95 ±0.09</td>
</tr>
<tr>
<td>TiO$_2$-OOCCH$_2$S-Ag-40</td>
<td>63.6</td>
<td>0.82 ±0.15</td>
</tr>
<tr>
<td>TiO$_2$-OOCCH$_2$S-Ag-50</td>
<td>58.3</td>
<td>0.71 ±0.06</td>
</tr>
<tr>
<td>TiO$_2$-OOCCH$_2$S-Ag-60</td>
<td>72.5</td>
<td>1.08 ±0.12</td>
</tr>
<tr>
<td>Composite</td>
<td>Value</td>
<td>Error</td>
</tr>
<tr>
<td>-------------------------</td>
<td>--------</td>
<td>-------</td>
</tr>
<tr>
<td>TiO$_2$-OOCCH$_2$S-Ag-70</td>
<td>79.2</td>
<td>1.30 ±0.06</td>
</tr>
<tr>
<td>TiO$_2$-OOCCH$_2$S-Ag-80</td>
<td>76.3</td>
<td>1.18 ±0.02</td>
</tr>
</tbody>
</table>
Table 3. Recent State-of-the-art related to photocatalytic performances of different TiO$_2$–Ag nanomaterials to degrade persistent organic water pollutants in comparison with our best photocatalyst.

<table>
<thead>
<tr>
<th>Organic Water pollutant (concentration)</th>
<th>Photocatalyst (concentration)</th>
<th>Irradiation light</th>
<th>Reaction Kinetics</th>
<th>decoloration rate</th>
<th>irradiation time</th>
<th>Major observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylene Blue, MB</td>
<td>Mesoporous Ag/TiO$_2$ nanoparticle (1gL$^{-1}$)</td>
<td>Hg lamp</td>
<td>Pseudo first-order kinetic</td>
<td>95%</td>
<td>120 min</td>
<td>TiO$_2$ nanoparticles with Ag was synthetized by sol-gel route using chitosan as template.[45]</td>
</tr>
<tr>
<td>MB (2x10$^{-5}$M)</td>
<td>Ag colloid-TiO$_2$ (50ml/500ml MB)</td>
<td>fluorescent lamp (8W)</td>
<td>78%</td>
<td>5h</td>
<td></td>
<td>Synthesis of colloidal silver triangular nanoprisms. The polyvinylpyrrolidone is responsible of uniform formation of particles. [46]</td>
</tr>
<tr>
<td>MB (5 ppm)</td>
<td>Ag/P25 powder (0.2 g L$^{-1}$)</td>
<td>fluorescent lamp (10 W) UV light lamp (10 W) red LED light (10W)</td>
<td>Pseudo first-order kinetic</td>
<td>82%</td>
<td>4h</td>
<td>Ag/P25 hybrid systems are synthesized from P25 powder and Ag nanospheres (5-15nm) by chemical reduction method and Ag nanoprism (75nm) by additional photochemical process. [47]</td>
</tr>
<tr>
<td>MB (40 µM)</td>
<td>1.0% weight ratio of Ag-TiO$_2$</td>
<td>UV-Vis light lamps (8W)</td>
<td>Pseudo first-order kinetic</td>
<td>99%</td>
<td>120min</td>
<td>Photocatalyst Ag doped TiO$_2$ was synthesized by sol-gel method. Different molar ratios of Ag as dopant were evaluated, (0.5%, 1%, 1.5% and 2%) being 1.0% weight ratio the most efficient. [48]</td>
</tr>
<tr>
<td>MB (20 mg L$^{-1}$)</td>
<td>Anatase Ag-TiO$_2$ nanostructures</td>
<td>Xenon lamp (300 W)</td>
<td>Pseudo first-order kinetic</td>
<td>73%</td>
<td>18min</td>
<td>Ag-TiO$_2$ nanocomposites prepared by hydrothermal and co-precipitation method,</td>
</tr>
</tbody>
</table>
have an excellent photocatalytic activity performance. The Ag particle size is about 15-20nm on surface of TiO₂. [49]

<table>
<thead>
<tr>
<th>Rhodamine B (10 mg L⁻¹)</th>
<th>Ag-TiO₂ nanocomposites (0.6 g L⁻¹)</th>
<th>Xe lamp (800W)</th>
<th>96%</th>
<th>270 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rhodamine B (20 mg L⁻¹)</td>
<td>Ag/TiO₂ heterojunction composites (2 g L⁻¹)</td>
<td>Xe lamp (500W)</td>
<td>88%</td>
<td>120 min</td>
</tr>
<tr>
<td>Lomefloxacin (LMF) (20 M)</td>
<td>Ag-TiO₂ nanoparticles (100 mg L⁻¹)</td>
<td>Hg Lamp (8W)</td>
<td>Pseudo first-order kinetic</td>
<td>95%</td>
</tr>
</tbody>
</table>

Nanocomposites material of Ag nanoparticles dispersed TiO₂ nanocubes. The most efficient photocatalytic performance are nanoparticles containing 2% silver. [50]

88% degradation was possible after 120 min of irradiation time. The Ag/TiO₂ photocatalyst was synthetized by shock wave which possess large surface area. The surface TiO₂ rutile phase is covered with Ag nanoparticles. [32]

Ag doped TiO₂ nanoparticles with anatase phase was synthetized by liquid impregnation method. Ag-TiO₂ nanoparticles with a particle size of 13-17 nm. [51]