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.

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35 1. Introduction

36 The high photocatalytic properties of titanium dioxide (TiO_2) make possible its use in many
37 fields of science such as anti-bacterial agent [1], UV protecting agent [2], solar energy conversion [3],
38 water splitting to produce hydrogen fuel, decomposing [4-8] and removal of organic or inorganic
39 pollutants [9-11] and also as photocatalyst in two-dimensional materials [12]. In this regard, organic
40 pollutants in water sources remain one of the biggest environmental problems today, as they are highly
41 toxic and difficulty to be degraded [7,13]. The effectiveness of the photocatalytic process depends on
42 several factors, such as the efficient generation of reactive oxygen species (ROS), which have a high
43 oxidizing power being able to oxidize and mineralize almost any organic pollutant (especially $\bullet\text{OH}$,
44 $E^\circ=2.8\text{ V}$). [14] Other factors include a wide range of light absorption, low recombination of electron-
45 hole pairs, availability of active sites for oxygen, electron-holes transfer capability, interphase
46 connection between pollutant-photocatalyst and removal of interfacial photocatalyst from aqueous
47 medium. [15-18] One of the most common persistent cationic organic pollutant is Methylene Blue
48 (MB), as widely used in cotton, wood and silk industry. When discharging in water sources, it can cause
49 harmful health on human beings and ecosystems through bioaccumulation. This dye can be mineralized
50 in aqueous media to CO_2 and H_2O or less toxic molecules using TiO_2 nanostructures, as these
51 photocatalyst materials are chemically stable and easily recoverable in solid phase to practical
52 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-agglomerate, impacting in a less separation of photo-generated electron-hole pairs. In this respect, the development of Ag-TiO₂ 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 TiO₂ materials. They also address the impact of the metal doping in TiO₂ 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 synthesized 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

HSCH₂COOH, MB, toluene and ethanol were commercially available from Sigma-Aldrich and were used without further purification. Degussa P25 TiO₂ (70% anatase and 30 % rutile) was used to generate nanocrystalline TiO₂ anatase (TiO₂NPs). 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

TiO₂NPs 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 TiO₂NPs suspended in toluene for 24h, and then washed with small amounts of toluene. After that, TiO₂-OOCCH₂SH was dispersed inside the Magnetron Sputtering chamber, where AgNPs are sputtered onto TiO₂NPs 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 ($\lambda = 1.540598\text{\AA}$) in the range $5^\circ < 2\theta < 80^\circ$ (40 kV, 30 mA) and a graphite monochromator. The TiO₂ anatase phase was indexed as a tetragonal lattice with the following lattice parameters: $a = 3.7867\text{\AA}$, $c = 9.5149\text{\AA}$, $\alpha = \beta = \gamma = 90^\circ$. The TiO₂ rutile phase was also indexed as a tetragonal lattice ($a = 4.5940\text{\AA}$, $c = 2.9586\text{\AA}$), while the silver measured lattice parameters are $a = 4.0862\text{\AA}$ (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 $\text{TiO}_2\text{-OOCCH}_2\text{S-Ag}$ 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 $\text{TiO}_2\text{-OOCCH}_2\text{S-Ag}$ 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 (1×10^{-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_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 $\text{TiO}_2\text{-OOCCH}_2\text{S-AgNPs}$ is shown in Fig. 2(a), XRD reflections for TiO_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_2 (see Fig. S1) to an anatase with only a low percentage of rutile. This suggests that the sintered TiO_2NPs will show better photocatalytic activity than TiO_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 $140\text{-}700\text{ cm}^{-1}$ region of the Raman spectrum of $\text{TiO}_2\text{-OOCCH}_2\text{S-AgNPs}$ (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 HOOCCH_2SH . This effective interaction can also be observed by the $\nu\text{Ag-S}$ and $\nu\text{C-O}_{\text{asymmetric}}$ 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 HOOCCH_2SH in the $690\text{-}1120\text{ cm}^{-1}$ region: $\nu\text{C-S}$ stretching band at 698 cm^{-1} , $\omega\text{C-H}$ wagging vibrational modes at 847 cm^{-1} and 891 cm^{-1} , and $\delta\text{C-H}$ bending modes at 1028 cm^{-1} and 1115 cm^{-1} . The vibrational frequency of the $\nu\text{S-H}$ 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 $\text{TiO}_2\text{-OOCCH}_2\text{S-Ag}$ 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. $\text{TiO}_2\text{-OOCCH}_2\text{S-Ag}$ 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 ± 0.3 nm, with adequate dispersion (ρ) of 4.9 ± 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 $40.3 \text{ nm} \pm 3.1$ and a dispersion of 22.9 ± 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 ($46.1 \text{ nm} \pm 4.1$) and more agglomerated fused nanoparticles ($\rho = 25.7 \pm 8.4$) with high dispersion than the systems obtained in presence of HOOCCH_2SH 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 $\text{TiO}_2\text{-OOCCH}_2\text{S-Ag}$. 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

277 elemental mapping of these structures (see Fig. S3 in suppl.info) confirms the homogenous silver
278 deposition.

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

286 287 *3.2 Photocatalytic Behavior of TiO₂-OOCCH₂S-Ag systems*

288 Different photocatalytic activities are expected for the studied systems, given the diverse
289 physical features of TiO₂-OOCCH₂S-Ag materials. The photocatalytic behavior of all systems were
290 evaluated by quantifying the degradation of MB in aqueous solution under UV-Vis light (330-700 nm)
291 as irradiation source. The absorbance spectra over the entire MB degradation are shown in Fig. 5(a) for
292 TiO₂-OOCCH₂S-Ag-30 (the complete sets of spectra are shown in Fig. S5 of other sputter time
293 systems). The photocatalytic reaction of semiconductor materials can be followed as $-\ln(C/C_0) = kt$,
294 where k is the apparent rate constant of pseudo-first-order for this degradation process, as the
295 concentration of TiO₂-OOCCH₂S-AgNPs is kept constant. In Fig. S6, k value and degradation rate of the
296 obtained systems are exposed. In Table 2, a comparison of the photocatalytic performance for TiO₂-
297 OOCCH₂S-AgNPs samples is summarized. In absence of photocatalyst, a slight degradation of MB
298 (only 8.0 %) is observed, indicating a minor extent self-photodegradation of MB molecules under UV-
299 Vis irradiation (see Fig. 5b). For commercial TiO₂ (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 TiO₂NPs 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 30s. Therefore, the connection between TiO₂ 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 TiO₂ 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 TiO₂, 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_2SH . 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_2S -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 $\text{TiO}_2\text{-OOCCH}_2\text{S-Ag-30}$ 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 $\text{TiO}_2\text{-OOCCH}_2\text{S-Ag}$ 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.

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Supplementary Material

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

References

- [1] M.J. Santillán, Titania and titania–silver nanocomposite coatings grown by electrophoretic deposition from aqueous suspensions, *Surf. Coat. Technol.* 205 (2010) 2562-2571.
- [2] B. Faure, G. Salazar-Alvarez, A. Ahniyaz, I. Villaluenga, G. Berrioizabal, Y. De Miguel, L. Bergström, Dispersion and surface functionalization of oxide nanoparticles for transparent photocatalytic and UV-protecting coatings and sunscreens, *Sci. Technol. Adv. Mater.* 14 (2013) 023001.
- [3] P.V. Kamat, K. Tvrđy, D. Baker, J. Radich, Beyond Photovoltaics: Semiconductor Nanoarchitectures for Liquid-Junction Solar Cells, *Chem. Rev.* 110 (2010) 6664-6688.

- 390 [4] A. Ayati, A. Ahmadpour, F. Bamoharram, B. Tanhaei, M. Mänttari, M. Sillanpää, A review on
391 catalytic applications of Au/TiO₂ nanoparticles in the removal of water pollutant, Chemosphere, 107
392 (2014) 163-174.
- 393 [5] Y. Lee, J. Joo, Y. Yin, F. Zaera, Evaluation of the Effective Photoexcitation Distances in the
394 Photocatalytic Production of H₂ from Water using Au@Void@TiO₂ Yolk–Shell Nanostructures, ACS
395 Energy Lett. 1 (2016) 52-56.
- 396 [6] B. D. Coday, B. Yaffe, P. Xu, T. Y. Cath., Rejection of Trace Organic Compounds by Forward
397 Osmosis Membranes: A Literature Review, Environ. Sci. Technol. 48 (2014) 3612-3624.
- 398 [7] C. Wang, J. Li, X. Lv, Y. Zhang, G. Guo, Photocatalytic organic pollutants degradation in metal–
399 organic frameworks, Energy Environ. Sci. 7 (2014) 2831-2867.
- 400 [8] R. Daghir, P. Drogui, D. Robert, Modified TiO₂ for Environmental Photocatalytic Applications: A
401 Review, Ind. Eng. Chem. Res. 52 (2013) 3581-3599.
- 402 [9] M. Yola, T. Eren, N. Atar, A novel efficient photocatalyst based on TiO₂ nanoparticles involved
403 boron enrichment waste for photocatalytic degradation of atrazine, Chemical Engineering Journal, 250
404 (2014) 288-294.
- 405 [10] M. Wang, J. Iocozia, L. Sun, C. Lin, Z. Lin, Inorganic-modified semiconductor TiO₂ nanotube
406 arrays for photocatalysis, Energy Environ. Sci. 7 (2014) 2182-2202.
- 407 [11] C. Xu, G. P. Rangaiah, and X. S. Zhao, Photocatalytic Degradation of Methylene Blue by Titanium
408 Dioxide: Experimental and Modeling Study, Ind. Eng. Chem. Res. 53 (2014) 14641-14649.
- 409 [12] I. Lightcap, T. Kosel, P.V. Kamat, Anchoring Semiconductor and Metal Nanoparticles on a Two-
410 Dimensional Catalyst Mat. Storing and Shuttling Electrons with Reduced Graphene Oxide, Nano Lett.
411 10 (2010) 577-583.
- 412 [13] W. Zhang, B. Jia, Q. Wang, D. Dionysiou, J Nanopart Res 17 (2015) 221-229.

- 413 [14] A. Kumar Mishra, Application of Nanotechnology in Water Research, Scrivener Publishing and
414 Wiley, 2014.
- 415 [15] C. Trelu, E. Mousset, Y. Pechaud, D. Huguenot, E. D. van Hullebusch, G. Esposito, M. A.
416 Oturana, Removal of hydrophobic organic pollutants from soil washing/flushing solutions: A critical
417 review, Journal of Hazardous Materials, 306 (2016) 149–174.
- 418 [16] L. M. Liz-Marzán, P. V. Kamat, Nanoscale Materials, Kluwer Academic Publishers, 2004.
- 419 [17] S. Sarkar, R. Das, H. Choi and Ch. Bhattacharjee, Involvement of process parameters and various
420 modes of application of TiO₂ nanoparticles in heterogeneous photocatalysis of pharmaceutical wastes –
421 a short review, RSC Adv., 4 (2014) 57250–57266.
- 422 [18] M. Dahl, Y. Liu, Y. Yin, Composite Titanium Dioxide Nanomaterials, Chem. Rev., 114 (2014)
423 9853–9889.
- 424 [19] Y. Li, Q. Du, T. Liu, X. Peng, J. Wang, J. Sun, Y. Wang, S. Wu, Z. Wang, Y. Xia, L. Xia,
425 Comparative study of methylene blue dye adsorption onto activated carbon, graphene oxide, and carbon
426 nanotubes, chemical engineering research and design 91 (2013) 361–368.
- 427 [20] S. Ameen, M. Shaheer, Y. Soon Kim, H. Shik Shin, Nanocomposites of poly(1-
428 naphthylamine)/SiO₂ and poly(1-naphthylamine)/TiO₂: Comparative photocatalytic activity evaluation
429 towards methylene blue dye, Applied Catalysis B: Environmental 103 (2011) 136-142.
- 430 [21] P.V. Kamat, Dominance of Metal Oxides in the Era of Nanotechnology, J. Phys. Chem. Lett. 2
431 (2011) 839-843.
- 432 [22] Y. Cong, X. Li, Y. Qin, Z. Dong, G. Yuan, Z. Cui, X. Lai, Carbon-doped TiO₂ coating on
433 multiwalled carbon nanotubes with higher visible light photocatalytic activity, Applied Catalysis B:
434 Environmental 107 (2011) 128-134.

- 435 [23] C. Diaz, L. Barrientos, D. Carrillo, J. Valdebenito, M.L. Valenzuela, P.Allende, H. Geaney, C.
436 O'Dwyer, Solvent-less method for efficient photocatalytic α -Fe₂O₃ nanoparticles using macromolecular
437 polymeric precursors , New J. Chem. 40 (2016) 6768-6776.
- 438 [24] R. Dastjerdi, M. Montazer, A review on the application of inorganic nano-structured materials in
439 the modification of textiles: Focus on anti-microbial properties, Colloids and Surfaces B: Biointerfaces
440 79 (2010) 5-18.
- 441 [25] R. Dastjerdi, M.R. Mojtahedi, A.M. Shoshtari, Comparing the Effect of Three Processing Methods
442 for Modification of Filament Yarns with Inorganic Nanocomposite Filler and their Bioactivity Against
443 Staphylococcus aureus, Macromolecular Research 17 (2009) 378-387.
- 444 [26] H. Eom, J.Y. Jung, Y. Shin, S. Kim, J.H. Choi, E. Lee, J.H. Jeong, I. Park, Strong localized surface
445 plasmon resonance effects of Ag/TiO₂ core-shell nanowire arrays in UV and visible light for
446 photocatalytic activity, Nanoscale, 6 (2014) 226-234.
- 447 [27] E. Grabowska, A. Zaleska, S. Sorgues, M. Kunst, A. Etcheberry, C. Colbeau-Justin, H. Remita,
448 Modification of Titanium(IV) Dioxide with Small Silver Nanoparticles: Application in Photocatalysis, J.
449 Phys. Chem. C. 117 (2013) 1955-1962.
- 450 [28] S. Ko, C. Banerjee, J. Sankar, Photochemical synthesis and photocatalytic activity in simulated
451 solar light of nanosized Ag doped TiO₂ nanoparticle composite, Composites: Part B. 42 (2011) 579-583.
- 452 [29] A. Mills and S. Le Hunte, An overview of semiconductor photocatalysis, J. Photochem. Photobiol.
453 A: Chem. 108 (1997) 1-35.
- 454 [30] F. Meng and Z- Sun, Enhanced photocatalytic activity of silver nanoparticles modified TiO₂ thin
455 films prepared by RF magnetron sputtering, Materials Chemistry and Physics 118 (2009) 349-353.
- 456 [31] M. Dahl, Y. Liu, Y. Yin, Composite Titanium Dioxide Nanomaterials, Chem. Rev. 114 (2014)
457 9853-9889.

- 458 [32] C. Xu, P. Chen, J. Liu, H. Yin, X. Gao, X. Mei, Fabrication of visible-light-driven Ag/TiO₂
459 heterojunction composites induced by shock wave, *J. Alloys Comp.* 679 (2016) 463-469.
- 460 [33] J. Vargas-Hernández, S. Coste, A. García-Murillo, F. Carrillo-Romo, A. Kassiba, *J. Alloys Comp.*
461 710 (2017) 355-363.
- 462 [34] H. Wender, P. Migowski, A. Feil, S.R. Teixeira, J. Dupon, Sputtering deposition of nanoparticles
463 onto liquid substrates: Recent advances and future trends, *Coordination Chemistry Reviews* 257 (2013)
464 2468-2483.
- 465 [35] M. Nakamoto, Y. Kashiwagi, M. Yamamoto, Synthesis and size regulation of gold nanoparticles by
466 controlled thermolysis of ammonium gold(I) thiolate in the absence or presence of amines, *Inorg. Chim.*
467 *Acta*, 358 (2005) 4229-4236.
- 468 [36] A. Roucoux, J. Schulz, H. Patin, Reduced Transition Metal Colloids: A Novel Family of Reusable
469 Catalysts?, *Chem. Rev.* 102 (2002) 3757-3778.
- 470 [37] L. Barrientos, P. Allende, C. Orellana, P. Jara, Ordered arrangements of metal nanoparticles on
471 alpha-cyclodextrin inclusion complexes by magnetron sputtering, *Inorganica Chimica Acta* 380 (2012)
472 372-377.
- 473 [38] H. Choi, Y. Jung, S. Kim, Size effects in the Raman spectra of TiO₂ nanoparticles, *Vibrational*
474 *Spectroscopy* 37 (2005) 33-38.
- 475 [39] T. Ohsaka, Temperature Dependence of the Raman Spectrum in Anatase TiO₂, *J. Phys. Soc. Jpn.* 48
476 (1980) 1661-1668.
- 477 [40] T. Mazza, E. Barborini, P. Piseri, P. Milani, Raman spectroscopy characterization of TiO₂ rutile
478 nanocrystals, *Phys. Rev. B* 75, (2007) 045416.

- 479 [41] S. Ameen, M. Akhtar, Y. Kim, H. Shin, Nanocomposites of poly(1-naphthylamine)/SiO₂ and
480 poly(1-naphthylamine)/TiO₂: Comparative photocatalytic activity evaluation towards methylene blue
481 dye, *Applied Catalysis B: Environmental* 103 (2011) 136-142.
- 482 [42] G. Lee, S. Shin, Y. Kim, S. Oh, Preparation of silver nanorods through the control of temperature
483 and pH of reaction medium, *Materials Chemistry and Physics* 84 (2004) 197-204.
- 484 [43] T. Maiyalagan, Synthesis, characterization and electrocatalytic activity of silver nanorods towards
485 the reduction of benzyl chloride, *Applied Catalysis A: General* 340 (2008) 191-195.
- 486 [44] S. Ko, C. Banerjee, J. Sankar, Photochemical synthesis and photocatalytic activity in simulated
487 solar light of nanosized Ag doped TiO₂ nanoparticle composite, *Composites: Part B*. 42 (2011) 579-583.
- 488 [45] M.F. Abdel Messih et al. Facile approach for homogeneous dispersion of metallic silver
489 nanoparticles on the surface of mesoporous titania for photocatalytic degradation of methylene blue and
490 indigo carmine dyes *Journal of Photochemistry and Photobiology A: Chemistry* 335 (2017) 40–51.
- 491 [46] A. Yu et al. Rapid synthesis of colloidal silver triangular nanoprisms and their promotion of TiO₂
492 photocatalysis on methylene blue under visible light, *Catalysis Communications* 90 (2017) 75–78.
- 493 [47] T. Lee et al. Improvement of photocatalytic activities of Ag/P25 hybrid systems by controlled
494 morphology of Ag nanoprisms, *Materials Chemistry and Physics* 192 (2017) 78-85.
- 495 [48] D.I. Çifçi, Decolorization of methylene blue and methyl orange with Ag doped TiO₂ under UV-A
496 and UV-Visible conditions: process optimization by response surface method and toxicity evaluation,
497 *Global NEST Journal* 18 (2016) 371-380.
- 498 [49] M. Hussain et al. Ag-TiO₂ nanocomposite for environmental and sensing applications, *Materials*
499 *Chemistry and Physics* 181 (2016) 194-203.

- [50] Y. Zhang, T. Wang, M. Zhou, Y. Wang, Z. Zhang, Hydrothermal preparation of Ag-TiO₂ nanostructures with exposed {001}/{101} facets for enhancing visible light photocatalytic activity, *Ceramics International* 43 (2017) 3118–3126.
- [51] R.M. Kulkarni et al. Ag-TiO₂ nanoparticles for photocatalytic degradation of lomefloxacin, *Desalination and Water Treatment* 57 (2016) 16111–16118.

Figure Caption

Figure 1. Schematic representation of synthetic route of Ag nanoparticles on nanocrystalline TiO₂ using mercaptoacetic acid as bifunctional surface modifiers.

Figure 2. XRD diffractogram of TiO₂-OOC-CH₂-S-AgNPs, showing white TiO₂ powder and pink TiO₂ powder interacting with silver (a), Raman Spectrum of pure TiO₂ and TiO₂-OOC-CH₂-S-AgNPs obtained by 30 s of sputter deposition (b).

Figure 3. Optical properties of TiO₂-OOC-CH₂-S-AgNPs photocatalytic materials. Tauc plots derived from UV-vis reflection spectra for TiO₂-OOC-CH₂-S-AgNPs at different sputter times (a), UV-Vis absorption spectra of AgNPs on TiO₂ recorded by Diffuse Reflectance Spectroscopy (the inset shows silver plasmon band at 411 nm) (b), UV-visible Kubelka-Munk reflectance spectra of pure TiO₂ and TiO₂-OOC-CH₂-S-AgNPs at 30s (c) and deconvoluted spectrum of Ag plasmon bands at 444 nm and 599 nm of TiO₂-OOC-CH₂-S-AgNPs at 80s of sputter time (d).

Figure 4. TEM images of the TiO₂-OOC-CH₂-S-AgNPs. TEM examination in (a) and (b) confirms small and spherical AgNPs interacting to TiO₂ (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 TiO₂) of obtained system at 80 s of sputtered time (d). TEM images of TiO₂-OOCCH₂S-AgNPs (e) and TiO₂-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 TiO₂-OOCCH₂S-Ag-30. (b) Normalized concentration of MB as function of irradiation time showing the best performances of TiO₂-OOCCH₂S-Ag with different sputter times and commercial TiO₂ (Degussa P25). (c) Pseudo-first order kinetic of photocatalytic reactions for this degradation process. (d) Variation in the efficiency of the TiO₂-OOCCH₂S-Ag-30 for the degradation of MB with cycling. The exposure time in each cycle was 25 min.

Figure 1:

Figure 2:

570 **Figure 3:**

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593 **Table 1.** Optical properties of TiO₂-OOCCH₂S-Ag systems at different sputter times

Photocatalyst	Sputter Deposition time (s)	Band gap energies of TiO ₂ (eV)	λ (nm) of AgNPs at maximum absorbance	AgNPs estimated D(nm) through absorption band
TiO ₂	0	3.20	-	-
TiO ₂ -OOCCH ₂ S-Ag-10	10	3.04	408	25
TiO ₂ -OOCCH ₂ S-Ag-20	20	2.98	408	25
TiO ₂ -OOCCH ₂ S-Ag-30	30	2.95	409	26
TiO ₂ -OOCCH ₂ S-Ag-40	40	2.87	410	26
TiO ₂ -OOCCH ₂ S-Ag-50	50	2.85	410	26
TiO ₂ -OOCCH ₂ S-Ag-60	60	2.80	414	29
TiO ₂ -OOCCH ₂ S-Ag-70	70	2.70	414	29
TiO ₂ -OOCCH ₂ S-Ag-80	80	2.60	444 and a weak band at 599	50 and 158

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595 **Table 2.** Kinetic data for the photodegradation process of MB with all TiO₂-OOCCH₂S-Ag systems

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Photocatalyst	decoloration rate η (%)	Apparent photodegradation rate constant k (10^{-2} min^{-1})
TiO ₂ P25 (Degussa)	54.0	0.74 $\pm$ 0.04
TiO ₂ -OOCCH ₂ S-Ag-10	71.4	1.11 $\pm$ 0.08
TiO ₂ -OOCCH ₂ S-Ag-20	71.0	1.01 $\pm$ 0.10
TiO ₂ -OOCCH ₂ S-Ag-30	97.0	1.95 $\pm$ 0.09
TiO ₂ -OOCCH ₂ S-Ag-40	63.6	0.82 $\pm$ 0.15
TiO ₂ -OOCCH ₂ S-Ag-50	58.3	0.71 $\pm$ 0.06
TiO ₂ -OOCCH ₂ S-Ag-60	72.5	1.08 $\pm$ 0.12

TiO ₂ -OOCCH ₂ S-Ag-70	79.2	1.30 ±0.06
TiO ₂ -OOCCH ₂ S-Ag-80	76.3	1.18 ±0.02

597 **Table 3.** Recent State-of-the-art related to photocatalytic performances of different TiO₂ –Ag nanomaterials to degrade persistent
 598 organic water pollutants in comparison with our best photocatalyst.

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Organic Water pollutant (concentration)	Photocatalyst (concentration)	Irradiation light	Reaction Kinetics	decoloration rate	irradiation time	Major observation
Methylene Blue, MB						
MB (2x10 ⁻⁵ M)	Mesoporous Ag/TiO ₂ nanoparticle (1g L ⁻¹)	Hg lamp	Pseudo first-order kinetic	95%	120 min	TiO ₂ nanoparticles with Ag was synthesized by sol-gel route using chitosan as template.[45]
MB (5 ppm)	Ag colloid-TiO ₂ (50ml/500ml MB)	fluorescent lamp (8W)		78%	5h	Synthesis of colloidal silver triangular nanoprisms. The polyvinylpyrrolidone is responsible of uniform formation of particles. [46]
MB (40 μM)	Ag/P25 powder (0.2 g L ⁻¹)	fluorescent lamp (10 W) UV light lamp (10 W) red LED light (10W)	Pseudo first-order kinetic	82%	4h	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]
MB (20 mg L ⁻¹)	1.0% weight ratio of Ag-TiO ₂	UV-Vis light lamps (8W)	Pseudo first-order kinetic	99%	120min	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]
MB (30μM)	Anatase Ag-TiO ₂ nanostructures	Xenon lamp (300 W)	Pseudo first-order kinetic	73%	18min	Ag-TiO ₂ nanocomposites prepared by hydrothermal and co-precipitation method,

						have an excellent photocatalytic activity performance. The Ag particle size is about 15-20nm on surface of TiO ₂ . [49]
Rhodamine B (10 mg L ⁻¹)	Ag-TiO ₂ nanocomposites (0.6 g L ⁻¹)	Xe lamp (800W)		96%	270 min	Nanocomposites material of Ag nanoparticles dispersed TiO ₂ nanocubes. The most efficient photocatalytic performance are nanoparticles containing 2% silver. [50]
Rhodamine B (20 mg L ⁻¹)	Ag/TiO ₂ heterojunction composites (2 g L ⁻¹)	Xe lamp (500W)		88%	120 min	88% degradation was possible after 120 min of irradiation time. The Ag/TiO ₂ photocatalyst was synthesized by shock wave which possess large surface area. The surface TiO ₂ rutile phase is covered with Ag nanoparticles. [32]
Lomefloxacin (LMF) (20 M)	Ag-TiO ₂ nanoparticles (100 mg L ⁻¹)	Hg Lamp (8W)	Pseudo first- order kinetic	95%	60min	Ag doped TiO ₂ nanoparticles with anatase phase was synthesized by liquid impregnation method. Ag-TiO ₂ nanoparticles with a particle size of 13-17 nm. [51]