Solid State Tuning of TiO$_2$ Morphology, Crystal Phase and Size through Metal Macromolecular Complexes and its Significance in the Photocatalytic Response

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Abstract
A solid-state phase control of TiO$_2$ by the use of different macromolecular complex precursors is reported for the first time. During the formation of TiO$_2$ nanoparticles, chitosan and Poly(styrene-co-4-vinylpyridine) polymers can act as solid-state template producing areas after carbonization, where the TiO$_2$ nucleates. It seems that the location of metal centers through the polymeric chain (i.e. the distance between the metal centers) strongly influence the morphology and particle size of the photocatalyst. To demonstrate the application value of our different TiO$_2$ structures, the photocatalytic behavior was explored. The efficient photocatalytic decoloration of methylene blue on different polymorphic forms of nanostructured TiO$_2$ is confirmed. The best photocatalyst achieved 98% of discoloration rate in only 25 min when the pH of the solution is 9.5, improving the efficiency of the standard photocatalyst Degussa P25 without the addition of other phases or dopants. The novelty of the present work is that by means of an appropriate synthesis, can be tuned simultaneously the three main factors (morphology, size and crystalline phase) that allow modulating the photocatalytic response of titania material. This control has allowed an advance in the properties of the material, managing to increase the photoresponse in a short time.
Keywords: TiO$_2$ nanoparticles, Photocatalysis, solid-state synthesis, morphology, size and crystal phase.

1. INTRODUCTION

Organic pollutants have become one of the most serious environmental problems nowadays, due to their high toxicity and difficulty to be degraded.\textsuperscript{1-4} In this respect, the use of nanomaterials such as metal oxide in Advanced Oxidation Processes (AOPs) has attracted increased attention owing to their unique physical and chemical characteristics, and therefore its effectiveness as pollutant removal. Among all the semiconductors used for AOPs, titanium dioxide (TiO$_2$) stands out from others because of its high photochemical stability, low toxicity and cost to practical applications and scalability. TiO$_2$ also presents more availability to generate reactive oxygen species (ROS) which are responsible to degrade the organic pollutants. As a consequence, TiO$_2$ is the most used photocatalyst for various contaminants being the most effective and benign for the environment.

The photocatalytic properties of TiO$_2$ are strongly influenced by several factors, such as; particle size, crystal phase, morphology, crystalline defects, irradiation light, pH of suspension, specific surface area and preparation method of the photocatalytic material.\textsuperscript{5,6} Jang and co-workers\textsuperscript{7} mentioned that, among these factors, the most important are crystal structure and particle size, and therefore surface area related to the volume of the particle.

There are a large number of reports in the literature regarding TiO$_2$ with different sizes, crystalline phase morphologies and surface area, specifically applied to water remediation.\textsuperscript{8-10} However, the understanding of how these parameters affect photocatalytic properties and the order of influence on the performance of these properties is an important problem or bottleneck that prevents its practical application. Up to date, to the best of our
knowledge, it has not been possible to control several of these parameters simultaneously, and their impact on the degradation of organic pollutants.

In terms of morphology, several geometries were recently reported, such as for example spherical titania nanostructures or hierarchical nanofibers, nanowires and hollow-fibers.\textsuperscript{11-13} In this sense, Wang et al. recently reported that TiO\textsubscript{2} nanowires synthesized by the hydrothermal method presented an increased performance for hydrogen production.\textsuperscript{14}

Regarding their crystalline phases, anatase has received the most attention due to its high catalytic activity and electron mobility compared to the rutile and brookite phases,\textsuperscript{15,16} because it exhibits more defects than other phases and therefore it has more sites available for oxygen to generate ROS. On the other hand, various works have shown a higher photocatalytic performance when using a mixture of crystalline phases containing anatase and rutile, especially TiO\textsubscript{2} Degussa P25 (commonly used as commercial photocatalyst) than a pure phase.\textsuperscript{17} This improvement can be attributed to a synergic effect that is generated in the junction of the phases generating a decrease of the recombination of the hole-electron pairs.\textsuperscript{18}

Several other works can be found related to TiO\textsubscript{2} and persistent water pollutants using different morphologies, crystal phases and sizes such as; nanostructures, nanocomposites, or hybrid photocatalysts, among others.\textsuperscript{19-22} Lei and co-workers\textsuperscript{23} reported a mixture of TiO\textsubscript{2} phases, improving the photocatalytic activity to degrade an organic dye in comparison to pure crystalline phases of TiO\textsubscript{2}. Likewise, Juncheng et al.\textsuperscript{24} described the synthesis of uniform rhombic nanoplates with a high photocatalytic performance by controlling the morphology of these nanostructures through a novel solvothermal method. They attributed the enhanced photocatalytic properties of TiO\textsubscript{2} nanoplates to degrade
methylene orange (99.6%) at 24h to the exposed {010} facets and the high surface areas. In this regard, Li et al.\textsuperscript{25} have reported improvements in photocatalytic performance of TiO\textsubscript{2} to degrade methylene blue (MB) using CuS nanoflowers on a rutile surface. Additionally, Stoyanova and co-workers\textsuperscript{26} demonstrated that a decrease in particle size is linked to a better photocatalytic performance. Atitar et al. also studied the effect of the calcination temperature and phase transformation on photocatalytic performance.\textsuperscript{27}

One of the key parameters to control the shape and morphology of the catalyst is the synthetic method employed. Several methods to prepare TiO\textsubscript{2} nanostructures in solution using different conditions, such as the effect stabilizer, reductant and synthesis temperature have been developed.\textsuperscript{28} The major problem of using solution phase methods is that the incorporation of metal-oxide nanoparticles into solid devices is not straightforward, since solid-state isolation of nanoparticles causes particle agglomeration. The most widely used method for preparing powdered TiO\textsubscript{2} is the sol-gel solution method, because a controllable morphology, high purity and homogeneity are achieved.\textsuperscript{29} However, it has a number of disadvantages preventing the control of the factors that contribute to increasing the photoresponse. For example, a difficult control of particle growth (implying a reduction of the surface area), resulting also in more aggregate structures. In addition, the crystallinity of the powder could also decrease, even becoming amorphous (influencing the sites available for O\textsubscript{2}).\textsuperscript{30} The incorporation of metal-oxide nanoparticles generated directly from a solid-state approach will be of great applicability. From our best knowledge, solid-state methods have scarcely reported to preparing TiO\textsubscript{2} nanoparticles.\textsuperscript{31,32} For example, a solid-state metathesis reaction of TiCl\textsubscript{3} and Na\textsubscript{2}O\textsubscript{2} in presence of NaCl to give variable mixtures of anatase and rutile\textsuperscript{33} has been achieved. The reported photocatalytic activity of the obtained product
containing some anatase phase was comparable to a commercial TiO$_2$ standard. Other method consists of the anhydrous reaction of TiOSO$_4$ with Na$_2$CO$_3$ in presence of NaCl.$^{34}$ The average particle size, morphology and phase were strongly affected by the temperature of the post-milling heat treatment. The methods mentioned above, whether in solution or in the solid phase, have disadvantages with respect to the control of key factors in photocatalytic performance.

Park and co-workers have reported an interesting method to obtain TiO$_2$ fused particles in nanopowder, by means of a solid titanium precursor (TiH$_2$) in a thermal plasma reactor, being able to control the size of the nanostructures remarkably (20-50nm) when compared to other processes, implying improved photocatalytic performance (95% of RhB degradation in 5h). Additionally, the particles obtained are resistant to heat treatment, both phases (anatase and rutile) being maintained in a range of 400-800 °C.$^{34}$ Yang et al$^{35}$ described an interesting synthetic route to get TiO$_2$ mesoporous single crystals with various morphologies in a controllable way by hydrothermal method using a silica template. They pointed out the morphology, size, and phase of the TiO$_2$ structures can be easily tuned by experimental conditions.

The most of solid state methods to synthetize TiO$_2$ have some disadvantages since their preparation involves the use of sophisticated and expensive instruments, and the chemistry involved in their generation processes is limited. Thus, most of them usually afford mixtures of anatase and rutile phase.$^{36-38}$

As a first result, we describe for the first time in this work a solid-state phase control, morphology and size of TiO$_2$ through the nature of the macromolecular complex precursor used. During the formation of TiO$_2$ nanoparticles, the Chitosan and Poly(styrene-
co-4-vinylpyridine) polymers act as solid-state templates producing areas after carbonization, where the TiO$_2$ will grow. It seems that the location of metal centers through the polymeric chain (i.e. the distance between the metal centers) strongly influence the morphology and particle size of the photocatalyst. Although Chitosan$^{39-43}$ and Poly(styrene-co-4-vinylpyridine)$^{44-46}$ stabilize metallic nanoparticles in solution, there are no reports of the behavior of solid-state template of these polymers. In this work, a versatile and novel method is reported to control morphology, size and crystalline phase, which can modulate the photocatalytic properties and potentially their practical application, through a solid state route. Finally, the very efficient photocatalytic degradation of methylene blue (MB) on different polymorphic forms of nanostructured TiO$_2$ is demonstrated.

2. EXPERIMENTAL SECTION

2.1 Preparation of precursors

Chitosan, Poly(styrene-co-4-vinylpyridine), Cp$_2$TiCl$_2$, TiOSO$_4$, TiO(acac)$_2$ were purchased from Sigma-Aldrich and used as received.

*Synthesis of (Chitosan)$^\cdot$(Cp$_2$TiCl$_2$) 1:1; precursor (I)*

Stoichiometric amounts of chitosan (0.703 g, 4.01 mmol) and Cp$_2$TiCl$_2$ (1.000 g, 4.01 mmol) were stirred in a Schlenk flask for 2 weeks at room temperature (RT) in dichloromethane (60 mL). The supernatant solvent was extracted with a syringe by decantation and then dried under low pressure to finally obtain a red-orange solid.

*Synthesis of (PS-co-4-PVP)$^\cdot$(Cp$_2$TiCl$_2$) 1:1; precursor (II)*

Stoichiometric amounts of PS-co-4.PVP (0.425 g, 4.01 mmol) and Cp$_2$TiCl$_2$ (1.000 g, 4.01 mmol) were stirred in a Schlenk flask for 2 weeks at room temperature (RT) in
dichloromethane (60 ml). The supernatant solvent was extracted with a syringe by
decantation and then dried low pressure. An orange solid was finally obtained.

Synthesis of (Chitosan)-(TiOSO$_4$) 1:1; precursor (III)

Stoichiometric amounts of chitosan (1.094 g, 6.25 mmol) and TiOSO$_4$ (1.000 g,
6.25 mmol) were stirred in a Schlenk flask for 2 weeks at RT in dichloromethane (60 mL).
The supernatant solvent was extracted with a syringe by decantation and then dried under
reduced pressure. Finally, a white solid was obtained.

Synthesis of (PS-co-4-PVP)-(TiOSO$_4$) 1:1; precursor (IV)

Stoichiometric amounts of PS-co-4-PVP (0.661 g, 6.25 mmol) and TiOSO$_4$ (1.000
g, 6.25 mmol) were stirred in a Schlenk flask for 2 weeks at RT in dichloromethane (60 mL). The supernatant solvent was extracted with a syringe by decantation and then dried
under reduced pressure. A white solid was finally obtained.

Synthesis of (Chitosan)-TiO(acac)$_2$ 1:1; precursor (V)

Stoichiometric amounts of chitosan (0.668 g, 2.55 mmol) and TiO(acac)$_2$ (1.000 g,
2.55 mmol) were stirred in a Schlenk flask for 2 weeks at RT in dichloromethane (60 mL). The supernatant solvent was extracted with a syringe by decantation and then dried under
reduced pressure. A yellow solid was finally obtained.

Synthesis of (PS-co-4-PVP)-TiO(acac)$_2$ 1:1; precursor (VI)

Stoichiometric amounts of PS-co-4-PVP (0.404 g, 1.54 mmol) and TiO(acac)$_2$ (1.000 g,
1.54 mmol) were stirred in a Schlenk flask for 2 weeks at RT in dichloromethane (60 mL). The supernatant solvent was extracted with a syringe by decantation and then dried under
reduced pressure. Finally, a pale yellow solid was obtained.

2.2 Pyrolysis of macromolecular complexes
The nanostructured TiO2 was obtained as follows; the macromolecular complexes were pyrolyzed in a porcelain crucible into an oven, model LEF-105S-1, LabTech brand in air at 500 °C, 600 °C, 700 °C and 800 °C for 4 h, with a heating rate of 10 °C/ min.

2.3 Structural and microstructural characterization

*Powder X-Ray Diffraction* (PXRD) were carried out at RT using a Siemens D-5000 diffractometer. PXRD data was collected using Cu- Kα radiation (40 kV and 30 mA) and a graphite monochromator (λ = 1.540598Å). The TiO2 anatase phase was indexed as a tetragonal lattice (space group I41) with the following parameters: a = 3.7845 Å, c = 9.5143 Å, while the tetragonal TiO2 rutile phase (space group P42) lattice parameters were a = 4.5940 Å and c = 2.9586 Å.

*Scanning Electron Microscopy Field Emission* (FE-SEM) micrographs were performed using a Merlin FE-SEM microscope (Carl Zeiss).

*High-Resolution Transmission Electron Microscopy* (HR-TEM) and *Selection Area Electron Diffraction* (SAED) was performed using a JEOL 2000FX TEM microscope at 200 kV to characterize the average particle size, distribution and elemental and crystal composition. The average particle size was calculated using the DigitalMicrograph software. Reflectance diffuse were measured by *UV-Vis absorption spectroscopy* performed on a Shimadzu UV-2600 IRS plus spectrophotometer.

2.3 Photodiscoloration Experiments

MB was used as a model compound to test the morphology, crystal phase and particle sizes-dependent on photocatalytic properties. The TiO2 nanostructure activity was evaluated by measuring the decoloration rate of MB at 655 nm under UV-Vis illumination using a xenon lamp (150W) positioned 20 cm away from the photoreactor in a range 330-
680 nm at room temperature, to avoid the self-degradation and thermal catalytic effects of cationic dye MB. The short-wavelength components (λ < 340 nm) of the light were cut-off using a CuSO₄ optical filter (0.1 mol L⁻¹). 26 mg of the photocatalyst and 25 mL of MB aqueous solution (1 x 10⁻⁵ mol L⁻¹) were placed in a photoreactor vessel with continuous magnetic stirring. The suspension was stirred in the darkness for 60 min to establish an adsorption/desorption equilibrium, after which the photocatalytic decoloration of MB was initiated. Samples were withdrawn from the reactor at certain time intervals (5 min), and centrifuged to remove the particles.

### 3. RESULTS AND DISCUSSION

#### 3.1 Characterization of the Macromolecular precursors

The synthesis of the macromolecular complexes was carried out by direct reaction of the respective polymer with the Ti compound in CH₂Cl₂. In this media, the polymers are partially soluble and the Ti compounds are: Cp₂TiCl₂ – soluble, TiOSO₄ – insoluble, and TiO(acac)₂ – partially soluble. Subsequently, the suspension was slowly transforming into an insoluble solid that can be easily separated from the solution by decantation. The solid acquires the colour of their respective Ti compounds, ie. Cp₂TiCl₂ red-orange, TiOSO₄ white and TiO(acac)₂ yellow (see Supp. Info. Fig. S1). The macromolecular complexes were characterised by IR spectroscopy, ¹³C MAS NMR spectroscopy and TG/DTA analysis.

The presence of both polymers in the macromolecular complexes were confirmed by solid state ¹³C NMR analysis. As shown in Fig. S2 (see Supp. Info), and as also found in other reports,⁴⁷⁻⁴⁸ typical bands of Chitosan and PS-co-4-PVP were observed.⁴⁹⁻⁵¹
As shown in Figure S3, additional information of the coordination of Ti compounds to chitosan and PS-co-4-PVP arises from the IR spectra of the macromolecular complexes. Coordination was confirmed by the shifting of a broad band of $\nu$(OH)$+$ $\nu$(NH) observed in a range of 3422-3338 cm$^{-1}$ for (I), (III) and (V) complexes, compared to the same band observed for free chitosan at 3436 cm$^{-1}$. Furthermore, the NH$_2$ bending vibration is shifted to lower energy frequencies upon coordination. For macromolecular complexes with PS-co-4-PVP (II), (IV) and (VI), a shift of the characteristic vibration of $\nu$Py is observed in the range of 1576-1632 cm$^{-1}$.

TG/DTA analysis for the macromolecular complexes exhibits loss weigh patterns that are different to that of free chitosan (see Fig. S4), evidencing the coordination of the Ti moieties to the polymeric chain. However, the final weigh residue was in general slightly lower than the calculated values for TiO$_2$, probably due to a lesser coordination degree than 100%.

3.2 Pyrolytic products characterization

The pyrolysis (p) of different macromolecular complexes (I)-(VI) was studied at temperatures ranging from 500 to 800 °C (TiO$_2$(precursor)p-temperature). A summary of the different TiO$_2$ obtained phases, sizes and morphologies at each of the studied temperatures can be found in Table 1.

Figure S5 shows the PXRD patterns for the pyrolytic product at 800 °C from TiO$_2$(I)p to TiO$_2$(VI)p. PXRD patterns for other pyrolytic products at different temperatures can be found in Fig. S5 (supplementary information). It is well established that rutile is the stable phase, while both anatase and brookite are metastable. The irreversible anatase to rutile transformation has been studied widely at different temperatures. However, the
factors affecting this phenomenon, such as crystal phase transformation, are not fully understood.\textsuperscript{52} In this sense, as shown in Table 1, unexpected results were observed for the TiO\textsubscript{2}(III)p, as there is no phase transformation from anatase to rutile in all the studied temperature range (from 500 °C to 800 °C). This remarkable result could be attributed to a kinetic effect due to the metastable nature of anatase.\textsuperscript{53} Another interesting observation is the partial transformation of anatase to rutile for the products TiO\textsubscript{2}(II)p, TiO\textsubscript{2}(IV)p and TiO\textsubscript{2}(V)p, which could be attributed to the same kinetic factor involved in this phase process, as shown in Table S1.\textsuperscript{54}

The expected complete anatase to rutile transformation occurs for the pyrolysis of the precursors (I) and (VI). Additionally, it can be noted that for lower calcination temperatures, all the obtained products TiO\textsubscript{2}(I)p-TiO\textsubscript{2}(VI)p correspond to anatase. A small effect of the phase with the nature of the Ti salt linked to the polymeric chain of the polymer precursor –at fixed temperature- was also observed. For instance, at 800 °C the only precursor containing the TiOSO\textsubscript{4} salts linked to chitosan gives the anatase phase, while that both the precursor (I) and (VI) induces the rutile phase transformation.

The influence of the precursor on the structure’s morphology was studied by SEM, which is summarized in Table 1. Different polymorphic forms were found such as; microfibers, dense plates and irregular structures, as shown in Figure 1. These morphologies depend on the nature of the precursor used to synthesize the macromolecular complex. Interestingly, for TiO\textsubscript{2}(III)p and TiO\textsubscript{2}(IV)p the presence of TiOSO\textsubscript{4} linked to the polymeric chain induce the formation of microfibers formed by fused nanoparticles on the surface, leading to large surface areas (see Figure 1), which are in concordance to literature mentioned above. This seems to be independent of the polymer and pyrolysis temperature.
Additionally, for the pyrolytic products TiO$_2$(V)p and TiO$_2$(VI)p, the TiO(acac)$_2$ salt strongly influences the obtaining of irregularly shaped structures and 3D mesh-like regions, which are typical for metal oxide nanostructures obtained by pyrolytic methods. These interesting results reveal an opportunity in the rational design and controlled synthesis of TiO$_2$ structures with different morphologies by polymeric precursors.

TEM analysis of the different samples is shown in Table 1. In all cases, there is a strong size dependence on the nature of the Ti precursor and the polymer. As expected, particle sizes increase when increasing the calcination temperature, as also reported in previous works.$^{35}$ However, it is very remarkable that, for the pyrolytic product TiO$_2$-A-(III)p-800, a bimodal distribution of nanoparticles was obtained (Figure 2c). As shown in Figure 2, despite of the high calcination temperature, the smallest particle sizes (6.9±0.2 nm), in form of anatase, were found for these conditions and in four analysed temperatures.

TEM analysis demonstrates that the microstructure observed for all cases are fused TiO$_2$ nanoparticles of different crystal phases, which are in agreement with previous works.$^{35}$ Some insight about the formation mechanism of the nanostructured materials from the precursor Chitosan●MXn and PS-co-4-PVP●MXn could be proposed using the mechanism of formation of nanostructured metallic materials from the precursor $\{\text{NP(O}C_8\text{H}_{12})_2(\text{OC}_6\text{H}_4\text{PPh}_2-\text{Mn(CO)}_2(\eta^5-\text{C}_5\text{H}_4\text{Me})_2}\}$. $^{56}$

The first step on heating involves the formation of a 3D network to produce a thermally stable matrix.$^{57}$ This step is crucial as it offset the sublimation. In our system, the first heating step could involve a cross linking of the Chitosan and PS-co-4-PVP polymers to give a 3D matrix, containing O-Ti-O and H$_2$N-Ti-NH$_2$ links (for the Chitosan polymer) and (pyridine)N-Ti-N(pyridine) bonds for the PS-co-4-PVP polymer. A schematic
representation of this process is provided in Figure 3. We believe that the following steps involve the starting of the organic carbonization, producing holes where the nanoparticles begin to nucleate. According to TG/DTA analysis, this occurs at ~ 128-401 °C for the Chitosan and 184-404 °C for PS-co-4-PVP polymer matrices. In this intermediate stage, a layered graphitic carbon host can act as a template, where the nanoparticles grow. After complete combustion this template disappears, but always remains carbon residues, which appears as an ultrathin carbon shell around the nanoparticles, which were evidenced by TEM analysis. It is clear that the precursor polymers play a key role during nucleation process of the TiO$_2$ into the anatase or rutile phase. However, this step is not completely elucidated. It is very remarkable the formation of the anatase phase for TiO$_2$(III)p in all the studied conditions, being this very promissory photocatalyst material for remediation processes, due to their phase and morphology.

As shown in Table 1, and the absorption edge extrapolation (Figure S7) confirms band gap energies higher than bulk values, which are in concordance to quantum confinement effect of smaller TiO$_2$ nanostructures. On the other hand, the tendencies regarding to crystal phase are in agreement to the previously reported band gap energies. However, there is no direct correlation of the morphology with respect to Eg. We can infer that the morphologies are related to the particle sizes that make up the structure. For example, microfibers are composed of small fused particles which are exposed to the surface, so they are associated with the size of the system. In this regard, the dense plates & irregular structures show lower band gap values, which we can attribute to their greater particles sizes. We can see that energy gaps must be considered in the irradiation to
quantify the photocatalyst performance, all of which are in the emission range of the solar spectrum (330 nm-680 nm equivalent to 3.75 eV-1.82 eV).

This novel reported method permits a control of the phase by selecting the appropriate Ti compound and the precursor polymer, ie. TiO\(_2\)(III)p precursor affords the formation of the anatase phase, and also the morphology and particle size can be tuned by the appropriated selection of these parameters (see Table 1). This method presents a clear advantage over another solid-state and solution methods, as an effective control of key parameters can be achieved governing the photocatalytic response for practical applications. Another additional advantage is that, from our method, TiO\(_2\) nanopowders are directly obtained, which can be used directly for their incorporation in a solid device avoiding an agglomeration process.

**3.4 Photocatalytic behavior of TiO\(_2\) nanostructures**

The photocatalytic performance of a persistent water pollutant for all TiO\(_2\) systems was investigated by quantifying the discoloration rate and pseudo-first-order rate constants of MB with UV-vis irradiation (330-670nm) and the better system are shown in Figure 4. The UV–vis absorption spectra and the normalized concentration changing of MB as a function of irradiation time for all TiO\(_2\) nanostructures obtained by (I)p-(VI)p precursors at different temperatures can be found in Figures S8 and S9, respectively. The kinetic analysis (Figure S10) is also summarized in Table 2. Without photocatalyst, we observed that the MB dye has a slight decoloration (~ 7%), indicating that the degradation of the organic pollutant by UV-vis light is scarce. A highest MB photodegradation (86.5%, see Figure 4a and 4b) at pH 6.5 and 25 min of irradiation time for TiO\(_2\) in anatase phase obtained from (III)p at 800°C have been achieved. It is very remarkable that highest extent degradation
was obtained after few minutes for the anatase microfibers formed by TiO$_2$ fused nanoparticles (TiO$_2$-A-(III)p-800), compared with commercial TiO$_2$ (Degussa P25) which only degraded 75.5% of MB at the same experimental conditions.

As shown in Figure 5, we investigated the influence of morphology, size and crystal phase of our photocatalytic materials to discoloration of MB to establish a correlation of these key factors in the photocatalytic behavior. These results demonstrate that the structures with better performances are those of microfiber morphology and then irregular structures. The morphologies that showed smaller photocatalytic yields are those of dense plates and dense & irregular, which are in concordance to their optical properties obtained by DRS and smooth and greater surfaces observed by SEM, avoiding the high photocatalytic response. We attribute these results to microfibers’ structures, due are composed of fused small particles exposed to the surface, which leads to greater chemical reactivity to interact to MB and an anatase phase, in agreement to the optical properties.$^{54}$ If we analyse our systems that have the same morphology and similar sizes, we can find a correlation of how much the crystalline phase influences the photocatalytic performance (see Figure 5). The results allow showing the influence exerted by the crystal phase on the photocatalytic performance, being the following: mixture $>$ anatase $>$ rutile. For example, if we compare TiO$_2$-A-(I)p-500 and TiO$_2$-M-(I)p-600, both have the same morphology (granular) and similar sizes (11 and 12 nm) but the crystal phase is different (anatase and mixture, respectively). TiO$_2$-M-(I)p-600 shows a 20.4% of decolouration rate comparatively with 10.9% for TiO$_2$-A-(I)p-500, evidencing that mixture is better than anatase. These results are in concordance with Bacsa and co-workers.$^{58}$ They have attributed this behaviour to that a mixture of phases has a greater charge separation than a
pure phase between the interface, because the electrons are strongly retained in the electronic bands of the rutile, decreasing the charge recombination of the electron-hole pairs, which leads to an increase in their photoresponse.

As shown in Figure 5, if we compare the sizes of the systems when the phases and morphologies are the same, it can be observed that the behavior of the photocatalytic activities increases as the size decreases. These results are in agreement with those described in the literature, which report that decreasing the sizes increases the chemical reactivity and therefore the photocatalytic performance is greater.59

It is very interesting to note in Table 2, that the TiO$_2$(III)p samples for all temperatures show the same phase and morphology, therefore the photocatalytic properties were the expected according to their particles sizes as mentioned above. Therefore, from these remarkable results, the present approach provides the first evidence of a highly efficient photocatalytic decoloration using pristine TiO$_2$ systems in a short time. Additionally, according to our results, we can estimate the order of factors that control the photocatalytic properties, using a statistic study by Principal Component Analysis (PCA), as shown in Figure S11. The PCA has evidenced that the main components that impact on the photoresponse are size and crystal phase, since they explain 85% of the variance. According to the statistical analysis and the structural and band gap energies we can attribute the following order: Particle size > crystal phase > morphology (in close relation to the features of the surfaces)

The photodegradation process can be further quantitatively interpreted through fitting to the Pseudo-first order reaction model (assuming that the photocatalyst concentration is constant), in which apparent constant (k) of MB photodegradation can be
determined according to the following expression: \( \ln(C/C_0) = -kt \), where \( C_0 \) and \( C \) are the concentrations of MB at initial and a certain irradiation time, and \( k \) is the slope of the fitting line. This apparent rate constant is a very good parameter to compare the photoresponse of the studied systems. In this regard, the pseudo-first-order rate constants reported in Table 2 are in good agreement and have the same trends to the discoloration rate results and reveal that the best photocatalyst TiO\(_2\)-A-(III)p-800 provides 118.8 times higher degradation rate than TiO\(_2\)-M-(I)p-700. The normalized results summarized in Table 2 still show the same trend in performance and confirm that the TiO\(_2\)-A-(III)p-800 has the most efficient photodegradation activity. In addition, the catalytic activities and trend in performance measured herein are consistent with those measured in previous reports highlighting the quality of the TiO\(_2\) nanostructures and their different phases.\(^{15,16}\)

To analyze our results in a comprehensive way, and in the same context against other state-of-the-art TiO\(_2\) materials, we have compared them with other efficient catalysts in the literature. The comparison was performed with pure TiO\(_2\) phases, using MB and other persistent organic pollutants within different crystal phases, morphologies, sizes and their correlation with photocatalytic performance to degrade water pollutants. This analysis (see Table 3) was carried out considering the main conditions that dictate the photocatalytic activity, which was described in the introduction section. In spite of the great number of available works in the literature related to TiO\(_2\), the three aforementioned factors have not been controlled simultaneously, and also their order of importance to control the photochemical reactions.

From the comparative analysis of state-of-the-art materials with the ones here reported, our remarkable results arise on very high efficient photodiscoloration of MB in a
short time, and also in a better comprehension and control of the main factors that govern the photocatalytic response of TiO$_2$. Our results suggest that, in order to achieve very efficient photocatalytic properties, we must use a system that has fibers formed of fused nanoparticles, anatase phase and small sizes less than 10 nm. In order to outperform the activity of Degussa P25, up to now, the addition of another phase was necessary to enhance efficiency. From our knowledge, the present results (TiO$_2$-A-(III)p-800) showed the most efficient photocatalyst reported in the literature, in a short time, using pure TiO$_2$ without the addition of any other phase or dopant. In this regard, to take advantage of the TiO$_2$-A-(III)p-800 abilities, we have analyzed the pH effect on the rate of the photocatalytic process, because is the major factor influencing the discoloration rate.\textsuperscript{71} Fig S12 shows the discoloration percentage as a function of pH for TiO$_2$-A-(III)p-800 and commercial TiO$_2$. An improvement of MB discoloration rate in alkaline medium was observed for both compounds. The highest photodegradation was observed in alkaline medium to pH 9 for TiO$_2$-A-(III)p-800 and commercial TiO$_2$ P25, reaching 98% and 77% respectively. According to the literature, these improvement is expected because in an alkaline medium the adsorption of MB is considerably enhanced.

Finally, another important aspect to be considered for the practical application of the photocatalyst is its separation of the treated water for its reusability and scalability. These aspects were investigated by the photocatalytic efficiency of TiO$_2$-A-(III)p-800 for several cycles. The photocatalyst was removed 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 4d. The four cycles carried out for the photodegradation of
MB showed that the efficiency of TiO$_2$-A-(III)p-800 remains high, the percentage of photodegradation (~86%, pH 6.5) is practically unchanged compared to the first use.

4. SUMMARY AND CONCLUSIONS

A simple solid state synthetic pathway using macromolecular complexes has been developed to prepare TiO$_2$ nanostructures in different morphologies, crystalline phases and sizes. The proposed mechanism suggests a cross linking of the Chitosan and PS-co-4-PVP polymers to give a 3D matrix when it heated. Subsequently, the following steps involve the formation of holes that act as nucleation centers of the nanostructures. Therefore, it can be concluded that the precursor polymers and the nature of the Ti precursor play a fundamental role in the mechanism of formation of fused TiO$_2$ nanoparticles. The obtained TiO$_2$ nanostructures present an efficient photocatalytic decoloration a short time and the factors controlling their photocatalytic properties are the size and then crystal phase and subsequently the morphology, in close relation to the features of the surface. This three aforementioned factors have not been controlled simultaneously, and also their order of importance to control the photochemical reactions. The best photocatalyst was able to degrade the MB (discoloration rate) by 98% in only 25 min measured at 655 nm, in alkaline medium. These important results allow the rational design of a photocatalyst to control the characteristics of the material and water pollutants to achieve very efficient performances concerning the treatment and removal of recalcitrant. In this sense, the improvement of chemical reactivity towards other family substrates, such as phenols, anionic and azo dyes...
which are hazardous pollutants or chemical transformations could improve the performance of these catalysts.

ASSOCIATED CONTENT

Supporting Information available: $^{13}$C MAS NMR and IR spectra, TG/DTA curves of all macromolecular complexes and pure polymers. PXRD, crystal phase quantification and degradation curves of MB for TiO$_2$ systems are available on the ACS Publications website

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**Figures Caption**

**Figure 1.** SEM images of (A) TiO$_2$-A-(III)p-800 showing a microfiber and (B) increased image of fused nanoparticles forming this structure, (C) and (D) showing the same microstructure for TiO$_2$-M-(IV)p-800, (E) TiO$_2$-M-(VI)p-500 evidencing irregular and (F) TiO$_2$-M-(I)p-600 dense plates morphologies.
Figure 2. HRTEM images for TiO$_2$-A-(III)p microfibers composed of fused particles at different temperatures (A) 500 °C, (B) 600 °C, (C) 700°C and (D) 800 °C showing the crystal planes of anatase phase. The insets show the electron diffraction patterns of TEM images.
Figure 3. Schematic representation of the proposed mechanism in the formation of TiO$_2$ nanostructures. In the first step, at room temperature the formation of the 3D matrix occurs. Subsequently, the increase in temperature causes the decomposition of the polymer matrix and the formation of TiO$_2$ nanostructures.
Figure 4. (A) Photodiscoloration curves of MB in presence of our best photocatalyst (TiO$_2$-A-(III)p-800). The inset shows changing of MB before and after photochemical reaction. (B) Normalized concentration of MB as function of irradiation time showing the best performances of TiO$_2$ nanostructures with different precursors and TiO$_2$ P25. (C) Pseudo-first order kinetic of photocatalytic reactions for this process. (D) Variation in the efficiency of the TiO$_2$-A-(III)p-800 for the degradation of MB with cycling. The exposure time in each cycle was 25 min.
Figure 5. Graphical analysis of different parameters which are relevant for the photocatalytic properties. % discoloration as function of (A) phase, (B) morphology and (C) size.

Table 1. Crystal phases, sizes, morphologies and band gap of obtained TiO₂ nanostructures.
<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Temperature (°C)</th>
<th>Phase</th>
<th>Size (nm)</th>
<th>Dispersion</th>
<th>Band gap (eV)</th>
<th>Morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂-A-(I)p-500</td>
<td>500</td>
<td>Anatase</td>
<td>11.1</td>
<td>±0.1</td>
<td>3.7</td>
<td>Dense plates</td>
</tr>
<tr>
<td>TiO₂-M-(I)p-600</td>
<td>600</td>
<td>Mixture</td>
<td>12.9</td>
<td>±0.3</td>
<td>3.4</td>
<td>Dense plates</td>
</tr>
<tr>
<td>TiO₂-M-(I)p-700</td>
<td>700</td>
<td>Mixture</td>
<td>11.2</td>
<td>±0.5</td>
<td>3.6</td>
<td>Dense &amp; irregular</td>
</tr>
<tr>
<td>TiO₂-R-(I)p-800</td>
<td>800</td>
<td>Rutile</td>
<td>24.3</td>
<td>±1.7</td>
<td>3.4</td>
<td>Irregular</td>
</tr>
<tr>
<td>TiO₂-A-(II)p-500</td>
<td>500</td>
<td>Anatase</td>
<td>12.8</td>
<td>±0.1</td>
<td>3.4</td>
<td>Dense plates</td>
</tr>
<tr>
<td>TiO₂-A-(II)p-600</td>
<td>600</td>
<td>Anatase</td>
<td>24.6</td>
<td>±9.5</td>
<td>3.3</td>
<td>Dense &amp; irregular</td>
</tr>
<tr>
<td>TiO₂-A-(II)p-700</td>
<td>700</td>
<td>Anatase</td>
<td>32.5</td>
<td>±3.3</td>
<td>3.2</td>
<td>Granular</td>
</tr>
<tr>
<td>TiO₂-M-(II)p-800</td>
<td>800</td>
<td>Mixture</td>
<td>33.1</td>
<td>±2.0</td>
<td>3.3</td>
<td>Granular</td>
</tr>
<tr>
<td>TiO₂-A-(III)p-500</td>
<td>500</td>
<td>Anatase</td>
<td>27.1</td>
<td>±1.1</td>
<td>3.3</td>
<td>Microfibers</td>
</tr>
<tr>
<td>TiO₂-A-(III)p-600</td>
<td>600</td>
<td>Anatase</td>
<td>17.3</td>
<td>±4.9</td>
<td>3.4</td>
<td>Microfibers</td>
</tr>
<tr>
<td>TiO₂-A-(III)p-700</td>
<td>700</td>
<td>Anatase</td>
<td>32.3</td>
<td>±1.8</td>
<td>3.3</td>
<td>Microfibers</td>
</tr>
<tr>
<td>TiO₂-A-(III)p-800</td>
<td>800</td>
<td>Anatase</td>
<td>6.9 and</td>
<td>±0.2 and</td>
<td>3.7</td>
<td>Microfibers</td>
</tr>
<tr>
<td>TiO₂-M-(III)p-800</td>
<td>700</td>
<td>Mixture</td>
<td>31.9</td>
<td>±2.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO₂-A-(IV)p-500</td>
<td>500</td>
<td>Anatase</td>
<td>11.1</td>
<td>±0.2</td>
<td>3.5</td>
<td>Irregular</td>
</tr>
<tr>
<td>TiO₂-A-(IV)p-600</td>
<td>600</td>
<td>Anatase</td>
<td>19.7</td>
<td>±1.3</td>
<td>3.4</td>
<td>Irregular</td>
</tr>
<tr>
<td>TiO₂-M-(IV)p-700</td>
<td>700</td>
<td>Mixture</td>
<td>35.1</td>
<td>±1.1</td>
<td>3.4</td>
<td>Microfibers</td>
</tr>
<tr>
<td>TiO₂-M-(IV)p-800</td>
<td>800</td>
<td>Mixture</td>
<td>30.3</td>
<td>±0.2</td>
<td>3.4</td>
<td>Microfibers</td>
</tr>
<tr>
<td>TiO₂-A-(V)p-500</td>
<td>500</td>
<td>Anatase</td>
<td>11.8</td>
<td>±0.7</td>
<td>3.5</td>
<td>Dense plates &amp; irregular</td>
</tr>
<tr>
<td>TiO₂-A-(V)p-600</td>
<td>600</td>
<td>Anatase</td>
<td>13.6</td>
<td>±0.6</td>
<td>3.4</td>
<td>Dense plates &amp; irregular</td>
</tr>
<tr>
<td>TiO₂-M-(V)p-700</td>
<td>700</td>
<td>Mixture</td>
<td>24.7</td>
<td>±1.0</td>
<td>3.2</td>
<td>Dense plates &amp; irregular</td>
</tr>
<tr>
<td>TiO₂-M-(V)p-800</td>
<td>800</td>
<td>Mixture</td>
<td>18.2</td>
<td>±0.9</td>
<td>3.3</td>
<td>Dense plates &amp; irregular</td>
</tr>
<tr>
<td>TiO₂-A-(VI)p-500</td>
<td>500</td>
<td>Anatase</td>
<td>7.9</td>
<td>±0.8</td>
<td>3.7</td>
<td>Irregular</td>
</tr>
<tr>
<td>TiO₂-M-(VI)p-600</td>
<td>600</td>
<td>Mixture</td>
<td>11.0</td>
<td>±0.4</td>
<td>3.6</td>
<td>Irregular</td>
</tr>
<tr>
<td>TiO₂-M-(VI)p-700</td>
<td>700</td>
<td>Mixture</td>
<td>38.6</td>
<td>±3.3</td>
<td>3.4</td>
<td>Irregular</td>
</tr>
<tr>
<td>Photocatalyst</td>
<td>Apparent photodegradation rate constant $k$ ($10^2$ min$^{-1}$)</td>
<td>Decoloration rate at 25 min, $\eta$ (%)</td>
<td>$R^2$ linear fit (%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------------</td>
<td>-------------------------------------------------------------</td>
<td>----------------------------------------</td>
<td>---------------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO$_2$-A-(Dp-500</td>
<td>0.40 ±0.04</td>
<td>10.9</td>
<td>93.9</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 2.** Kinetic data for the photodegradation process of MB with all TiO$_2$ systems obtained from (I)-(VI) precursors at different temperatures.
<table>
<thead>
<tr>
<th>TiO$_2$-M-(I)p-600</th>
<th>0.80 ±0.04</th>
<th>20.4</th>
<th>98.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$-M-(I)p-700</td>
<td>0.06 ±0.03</td>
<td>14.3</td>
<td>98.0</td>
</tr>
<tr>
<td>TiO$_2$-R-(I)p-800</td>
<td>1.30 ±0.10</td>
<td>30.0</td>
<td>93.8</td>
</tr>
<tr>
<td>TiO$_2$-A-(II)p-500</td>
<td>0.40 ±0.04</td>
<td>10.7</td>
<td>91.9</td>
</tr>
<tr>
<td>TiO$_2$-A-(II)p-600</td>
<td>0.33 ±0.03</td>
<td>6.6</td>
<td>88.8</td>
</tr>
<tr>
<td>TiO$_2$-A-(II)p-700</td>
<td>0.40 ±0.02</td>
<td>10.2</td>
<td>97.6</td>
</tr>
<tr>
<td>TiO$_2$-M-(II)p-800</td>
<td>1.00 ±0.06</td>
<td>22.6</td>
<td>97.2</td>
</tr>
<tr>
<td>TiO$_2$-A-(III)p-500</td>
<td>3.90 ±0.20</td>
<td>63.6</td>
<td>96.9</td>
</tr>
<tr>
<td>TiO$_2$-A-(III)p-600</td>
<td>4.10 ±0.20</td>
<td>65.3</td>
<td>97.4</td>
</tr>
<tr>
<td>TiO$_2$-A-(III)p-700</td>
<td>2.00 ±0.06</td>
<td>38.7</td>
<td>99.2</td>
</tr>
<tr>
<td>TiO$_2$-A-(III)p-800</td>
<td>7.13 ±0.01</td>
<td>86.5</td>
<td>99.8</td>
</tr>
<tr>
<td>TiO$_2$-A-(IV)p-500</td>
<td>2.40 ±0.01</td>
<td>45.2</td>
<td>97.8</td>
</tr>
<tr>
<td>TiO$_2$-A-(IV)p-600</td>
<td>3.10 ±0.01</td>
<td>55.0</td>
<td>98.0</td>
</tr>
<tr>
<td>TiO$_2$-M-(IV)p-700</td>
<td>0.20 ±0.02</td>
<td>4.9</td>
<td>91.1</td>
</tr>
<tr>
<td>TiO$_2$-M-(IV)p-800</td>
<td>4.00 ±0.20</td>
<td>63.0</td>
<td>97.1</td>
</tr>
<tr>
<td>TiO$_2$-A-(V)p-500</td>
<td>3.40 ±0.10</td>
<td>58.8</td>
<td>99.1</td>
</tr>
<tr>
<td>TiO$_2$-A-(V)p-600</td>
<td>1.30 ±0.04</td>
<td>26.8</td>
<td>99.2</td>
</tr>
<tr>
<td>TiO$_2$-M-(V)p-700</td>
<td>1.30 ±0.09</td>
<td>27.3</td>
<td>96.4</td>
</tr>
<tr>
<td>TiO$_2$-M-(V)p-800</td>
<td>0.60 ±0.03</td>
<td>13.5</td>
<td>98.0</td>
</tr>
<tr>
<td>TiO$_2$-A-(VI)p-500</td>
<td>1.70 ±0.03</td>
<td>33.7</td>
<td>99.7</td>
</tr>
<tr>
<td>TiO$_2$-M-(VI)p-600</td>
<td>2.40 ±0.02</td>
<td>47.7</td>
<td>95.9</td>
</tr>
<tr>
<td>TiO$_2$-M-(VI)p-700</td>
<td>2.60 ±0.02</td>
<td>50.5</td>
<td>94.6</td>
</tr>
<tr>
<td>TiO$_2$-R-(VI)p-800</td>
<td>0.50 ±0.02</td>
<td>14.0</td>
<td>98.5</td>
</tr>
<tr>
<td>TiO$_2$ P25 (Degussa)</td>
<td>6.7 ±0.36</td>
<td>75.5</td>
<td>98.0</td>
</tr>
</tbody>
</table>
Table 3. State-of-the-art related to photocatalytic performances and key factors (crystal phase, size and morphology) of different TiO$_2$ materials to degrade 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></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MB (1 x 10$^{-3}$ M)</td>
<td>Our best system TiO$_2$ in anatase phase from precursor (III) at 800°C (1.0 g L$^{-1}$)</td>
<td>Xe lamp (150W) with 340 nm cut-off filter, 330 nm &gt; $\lambda$ &gt; 680 nm</td>
<td>Pseudo first-order kinetic</td>
<td>86.5%</td>
<td>25 min</td>
<td>Up to 86% degradation was possible after 25 min of irradiation time to pH 6.5. The photocatalyst is composed by fused particles of anatase phase using a novel solid synthetic route.</td>
</tr>
<tr>
<td>MB (10ppm)</td>
<td>TiO$_2$ nanoparticles (2.5 g L$^{-1}$)</td>
<td>UV Lamp fig (40W)</td>
<td>Langmuir-Hinshelwood Pseudo first-order kinetic</td>
<td>71%</td>
<td>60min</td>
<td>Fused anatase and rutile particles with hexagonal and rectangular morphologies obtained by facile and low-cost bio-inspired synthesis were achieved. The average diameter was 22 nm. These systems were evaluated to degrade cationic dyes with an efficient photochemical response.$^{60}$</td>
</tr>
<tr>
<td>MB (50ppm)</td>
<td>TiO$_2$ nanofibers</td>
<td>Xenon lamp UV-Vis (150W) with AM 1.5 G filter $\lambda$ &gt; 400nm</td>
<td>NM</td>
<td>100%</td>
<td>180min</td>
<td>TiO$_2$ nanofibers were synthetized by electrospinning method and then a calcination treatment from 450-700°C was carry out. They studied the impact of calcination temperature on photocatalytic response, finding that the main factors involved in a better degradation of MB were particles size of nanofibers and defect</td>
</tr>
<tr>
<td>MB (10mg L(^{-1}))</td>
<td>TiO(_2) nanotubes (0.16g L(^{-1}))</td>
<td>Xenon visible light source (500W)</td>
<td>NM</td>
<td>99.1%</td>
<td>40min</td>
<td>An increased surface area, narrowed band gap and separated charge carriers were achieved in a defective TiO(_2) nanotube, showing an improved photocatalytic activity under visible irradiation.(^{62})</td>
</tr>
<tr>
<td>------------------------</td>
<td>--------------------------------------</td>
<td>-----------------------------------</td>
<td>-----</td>
<td>-------</td>
<td>------</td>
<td>------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>MB (0.01mM)</td>
<td>Mesoporous TiO(_2) (0.17g L(^{-1}))</td>
<td>UV light irradiation with eight tubes with a power source of 6 W, (\lambda=365) nm</td>
<td>NM</td>
<td>85%</td>
<td>60min</td>
<td>TiO(_2) fused nanoparticles in anatase phase, with sizes of 10-20 nm obtained through a facile hydrothermal method for efficient photodegradation of MB.(^{63})</td>
</tr>
<tr>
<td>MB</td>
<td>Hollow Titania Microspheres (HTS)</td>
<td>UV lamp 15W</td>
<td>Pseudo first-order kinetic</td>
<td>53%</td>
<td>90min</td>
<td>Hierarchical assembly, crystallinity, and surface chemistry of TiO(_2) materials were controlled. Specially, an exposed ({001}) facets and designed surface chemistry were correlated to photocatalytic degradation of azo molecules.(^{64})</td>
</tr>
<tr>
<td>MB (1 mM)</td>
<td>TiO(_2) nanoparticles</td>
<td>black light lamp (1mW)</td>
<td>NM</td>
<td>45%</td>
<td>20min</td>
<td>Quantitative determination of particle size and phase composition of TiO(_2) nanoparticles on the photocatalytic properties.(^{65})</td>
</tr>
</tbody>
</table>

**Other similar organic water pollutants**

| Malachite green, MG (10ppm) | TiO\(_2\) nanoparticles | UV Lamp | Langmuir-Hinshelwood Pseudo first- | 78% | 60 min | The same parameters were used with MB in this study. The photo-response allow an |
Rhodamine B, RhB and Methyl Orange MO (0.01 mM)

| (2.5 g L⁻¹) | Full-arc Xe lamp (300 W) with a cut-off filter, \( \lambda > 420 \text{ nm} \) | NH | 95.0\% for RhB | 30 min | The large exposed (101) facets of this TiO₂ in anatase phase has exhibited excellent photocatalytic activities due to high surface area.⁶⁶

Bisphenol A, BPA, (200 \( \mu \text{M} \))

| TiO₂ powder, Degussa P25 (0.5 g L⁻¹) | Xe arc lamp (300W) IR water filter and cut-off filter, \( \lambda > 320 \text{ nm} \) | Pseudo first-order kinetic | 75\% for BPA | 4 h | The degradation and mineralization studies were carried out to compare the photocatalytic performance of pure and fluorinated TiO₂. The better results were founded for pure TiO₂ in the case of mineralization.⁶⁷

Acetaminophen, Ace (1.3 \( \mu \text{M} \))

| TiO₂ powder, Degussa P25 (NM) | UVA/LED lamps, \( \lambda_{\text{max}} = 366 \text{ nm} \) | NH | 100\% | 8 min | This decomposition study reported a controlled periodic illumination by UVA/LED lamps, which exhibited a greater performance compared to continuous illumination under the same conditions.⁶⁸

RhB (NM)

| TiO₂ Nanopowder (0.3 g L⁻¹) | Visible light \( \lambda > 420 \text{ nm} \) | NH | 90 | 5 h | TiO₂ nanopowder obtained by thermal plasma synthesis enhances the photocatalytic performance to degrade RhB under visible light.⁶⁹

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²⁵ g L⁻¹ (40W) order kinetic efficient degradation of both cationic dyes at the same irradiation time and conditions.⁵⁰
Methyl orange 50 mL, 4×10^{-5} M
TiO_2 powder (10mg)
Xe Lamp 300W NM 90% 3h

The morphology, size, and phase of the anatase and rutile TiO_2 mesoporous single crystals were controlled by the hydrothermal synthetic way.\textsuperscript{36}
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