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Characterizing Nanoparticles Reactivity: Structure-Photocatalytic Activity Relationship

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Abstract. Nanoparticles are reactive, and their final interactions with the surrounding media are ultimately determined by their reactivity, which in turns depends on the nanoparticles morphology, surface chemistry and environment in which they are embedded. One simple and informative approach for the study of the reactivity of nanoparticles is the determination of their photocatalytic activity. In the present work, we briefly summarize the importance of different parameters such as the size, shape and agglomeration state on the photocatalytic activity of colloidal inorganic nanoparticles. The study of the use of nanoparticles as photocatalyts is relevant not only for its potential applications in environmental remediation issues but also it can provide relevant information about the role of these parameters at the nanoscale.

1. Introduction

The use of engineered nanoparticles (NPs) in photocatalysis has become one of the most investigated research fields during the last decade with potential applications in a variety of environmental remediation processes. The reasons include that currently treatment methods to degrade organic toxins, such as absorption by activated carbon or air stripping, need post-processing steps for the elimination of adsorbed contaminants. Other advanced oxidation technologies, especially those based on the use of strong oxidants, require hydrogen peroxide or ozone, which are expensive chemicals. In this sense, the main advantage of photocatalysis is that there is no further requirement for secondary disposal methods and that the photocatalysts are self-regenerated and can be reused or recycled [1].

Among other inorganic nanoparticles, oxide-based NPs are of specially interest due to their important photocatalytic activity. In some cases their band gap is in the range of UV-Visible light and the electrons required for initiating the photo-oxidation reactions can be easily excited even by sunlight. Moreover, the high reactivity of mater at the nanoscale makes them suitable for photocatalysis. In fact, TiO_2, ZnO and CeO_2 NPs are currently used for photocatalytic remediation technologies [2, 3]. In this context, the arising question is how to extract all this potential in the "real" use of engineered NPs. Recent advances in the synthesis of oxide NPs and the control over their size, shape and agglomeration state set new standards when talking about their uses as photocatalysts and it offers the

possibility to even increase the photocatalytic activity of these nanomaterials without the need of dopants or hybrid NPs [4-7].

However, and even taking into account the current effort on the characterization of NPs, there is still a lack of information and of specification regarding the relationship between size, shape and agglomeration state of oxide NPs and their photocatalytic activity.

2. Photocatalytic reaction

The principle of the photocatalytic reaction with oxide NPs is straightforward [2]. Upon adsorption of photons with energy higher than the band gap, electrons are excited from the valence band to the conduction band, creating electron-hole pairs. These charge carriers, in particular the electrons from the conduction band, migrate to the NP surface -where the reactions take place- and facilitate reduction reactions. The capture of holes and electrons by adsorbed species generate a variety of highly reactive radicals and intermediate species such as $OH\cdot$, O^{2-}, H_2O_2 capable of producing the oxidation of organic matter. In an aqueous media, the kinetic of the photocatalytic reactions mediated by NPs can be followed spectrophotometricaly by studying the degradation of organic dyes such as Rhodamine B (RhB), Methylene Blue or some phenol derivatives after photo-oxidation. These compounds have a characteristic absorption peak in the range of visible light which linearly depends on their concentration. As the reaction evolves the concentration of these compounds decreases and consequently the respective absorption peaks drop (figure 1). Thus, it is possible to follow the kinetics of the photocatalized reaction.
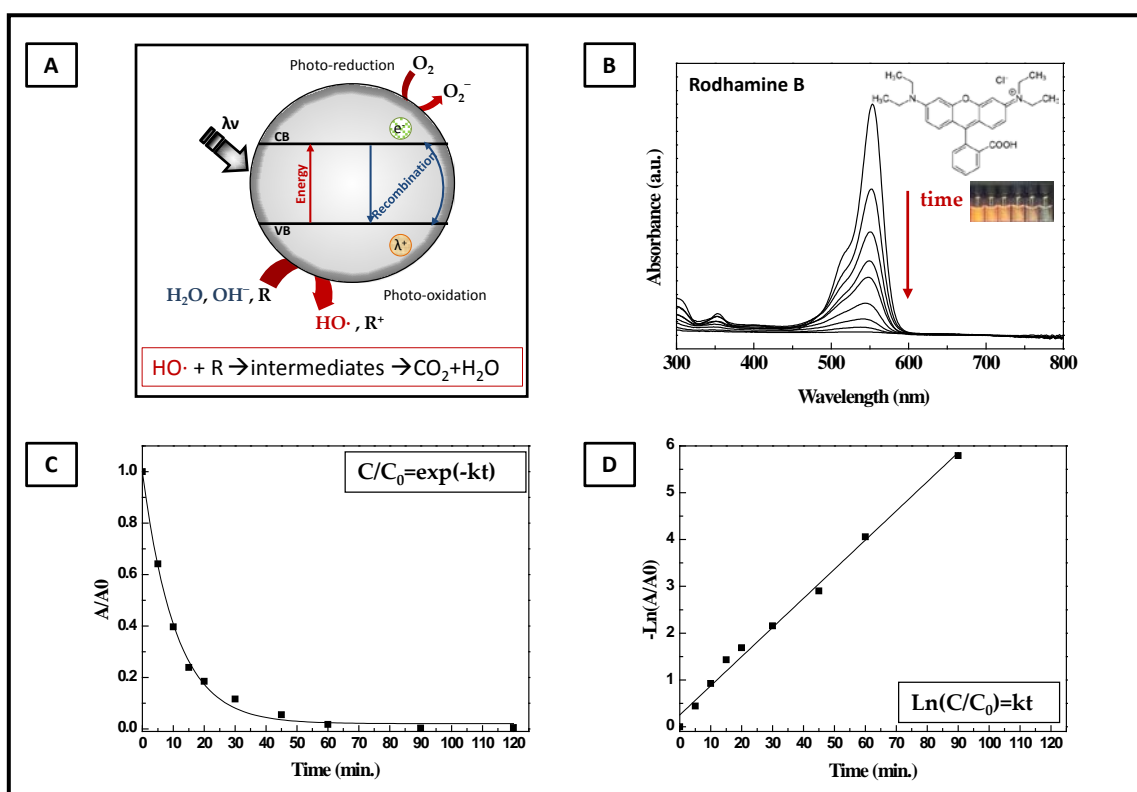
Figure 1. (A) Theoretical electron excitation process of an oxide-based NP. CB: Conduction Band. VB: Valence Band. (B) Temporal evolution of the absorbance of RhB in the presence of Degussa P25 NPs (0.6 mM). The reaction was done under 365 nm light and 8.9 mW/cm^2. (C) Maximum absorbance of the RhB as a function of time. (D) Logarithm of the maximum absorbance of RhB as a function of time.

The photocatalytic degradation using NPs is known to fit in a first ordered kinetic reaction. In the same conditions and normalizing the experiments by the total number of surface atoms, it is possible to compare the photocatalytic activity of two different NPs by comparing the kinetics rate of each reaction.

3. Experimental section

NPs used in this work, CeO_2, TiO_2 anatase, SiO_2 and ZnO, were synthetized in our laboratory following well-known aqueous sol-gel procedures and using tetramethyl ammonium hydroxide (TMAOH) as stabilizer [8-10]. Further purifications were performed by low speed centrifugation to ensure that no residues from these syntheses were in the samples during the experiments. The size and the shape of the NPs were determined by transmission electron microscopy (TEM) and their absorption spectra by UV-Vis spectroscopy.

In the case of CeO_2NPs, different shapes were obtained modifying reaction temperature during the synthesis and reagent concentration. In the case of TiO_2 NPs, the total amount of TMAOH used previous to the purification step leaded to different agglomeration states.

3.1. Preparation of particle suspensions

The concentration of NPs in the solutions were firstly adjusted with miliQ-water and further mixed with an aqueous solution of Rh B until 10 µM. At this concentration, when no degradation occurred, the absorbance was 1 (arbitrary units). Finally, the solutions were kept in dark under stirring for approximately 30 minutes for stabilization.

3.2. Photocatalytic activity

The samples were irradiated with a light source of 365 nm and 8.9 mW/cm^2 at 25ºC for a few hours. At different time points, aliquots of 1 mL were extracted and centrifuged at high speed in order to remove the NPs. Following absorbance of Rh B solution was measured. Since the absorbance is directly proportional to non-degradated Rh B this experiment can be considered a direct measurement of the photocatalytic activity of the NPs.

4. Nanoparticles structure related photocatalytic properties

The photocatalytic activity of oxide-based NPs is largely controlled by (i) the light absorption properties, e.g. light absorption coefficient and spectrum, (ii) the energy of the band gap between the valence band and the conduction band, which needs to be below the energy of absorbed light, (iii) the electron-hole recombination rate inside and at the surface of the particle (iv) the absorption of the reactants and finally (v) reduction and oxidation rates on the surface by the electrons and holes [2]. These processes depend on the chemical composition and the nature of the oxide materials rather than just a fact of nanometric size of the material. While photocatalytic TiO_2 anatase, ZnO and CeO_2 NPs show high absorption below 400 nm and a bandgap around 3.2 eV, SiO_2 NPs with less absorbance in this range and a band gap of 1.1 eV do not show any photocatalytic activity (figure 2). Thus, even varying the parameters of SiO_2 particles, the efficiency of these NPs to photodegradate organic compounds is very low.

Crystallinity plays also an important role. The higher the crystallinity the fewer the bulk defects (kinks, steps…) and easier for the electron-hole pairs to reach the surface without recombination. For instance, anatase, rutile, brookite or amorphous TiO_2 NPs display different photocatalytic efficiencies, as well as monocrystalline or polycrystalline structured NPs [11, 12].

However, what ultimately define the effectiveness of a NP as photocatalyst is its intrinsic parameters such as size, shape and agglomeration state. These parameters affect the surface state of a NP and thus the place where the reaction takes place.
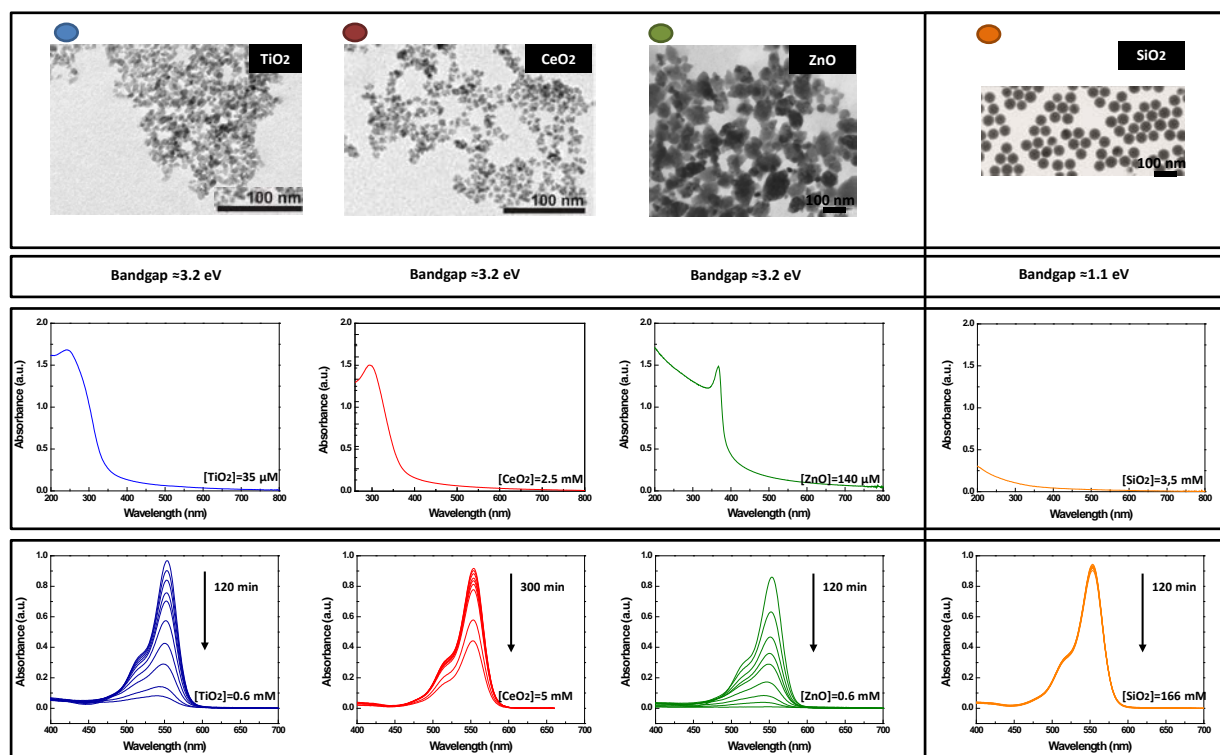
Figure 2. TEM images of different oxide-based NPs (first row), band gaps of NPs (second row), absorbances in the UV-Visible region showing band gaps of NPs (third row) and degradation of Rh B as a function of time under UV-Visible light; 365 nm 8.9 mW/cm (fourth row).

4.1. The role of size in photocatalysis

At the nanoscale, the size of NPs plays an important role not only in determining the efficiency and selectivity of photocatalytic activity, but also in the reactivity of the NP in general. Whereas in bulk materials surface atoms contribute only a relatively small fraction of the total number of atoms, at the nanoscale almost all the atoms of the particle lay close or at the surface. Moreover, when the NP is small enough, the coordination number of the surface atoms is affected by the size. For spherical-shaped NPs, both the curvature radii and the percentage of defects increases as the diameter decreases and surface atoms become less coordinated, which results in a higher reactivity. For larger diameters, the surface of the crystals possesses a larger collection of steps and kinks, independent from the size of the NP, and therefore the reactivity is only determined by the quality of its surface [13]. In this sense, the smaller the size, the higher the photocatalytic activity is. However, other effects can deviate photocatalytic behavior from previous defined predictions, e.g. the surface is a defective site; therefore, the larger the surface area, the faster the recombination.

Quantum effect is also a consequent of the size [2]. In the bulk material, an electron excited by light absorption from the valence band to the conduction band finds a high density of electronic states, where it can exist with different kinetic energies. However, in the case of NPs, as the size decreases below a critical value these electronic states start to discretize and the existence of an electron-hole pair is conditioned by the probability to fit into one of these states. Generally, size quantization is translated into strong changes in the electronic properties of the NP affecting the charge-carrier dynamics and the band structure. In most cases, there is a blue shift in the absorption and an increase on the band gap leading larger redox potentials.

Although, none experiment to correlate all these effects is presented here, the results reported by Wang et al. are indicative of the state of the art of the research, and at the same time, the little progress that has been made so far. They found an optimal size of 10 nm for TiO_2 anatase in the decomposition

of chloroform and, interestingly, this activity decreases when the size of the particles used was decreased down do 6 nm [14]. Recently Cerunto et al. investigated methylene blue decomposition in the presence of TiO_2 NPs between 4 nm and 10 nm, founding a maximum efficiency around 6 nm [15]. Unquestionably, size quantization affects the photocatalytic activity of a particle but not in a predictable manner, at least not treating the size as a merely geometric factor. Optimal size conditions for photocatalysis are sought by taking these conclusions into account and may vary from case to case.

4.2. The role of shape in photocatalysis

The photocatalytic activity of NPs itself also depends on the shape [6, 16]. It is known that physicochemical properties of NPs are shape dependent, and for example the absorbance and the band gap vary depending on this parameter. However, if the relation between the physicochemical properties of NPs and size is complex, there is still a greater lack of information related to the shape.

Apart from the quantum effects induced by the shape, there is another important point which has to be taken into account. This is, as in the previous case, the number and the coordination state of the atoms at the surface. Sphere is the form with less surface area per unit of volume and when comparing the same number of total atoms distributed in other shapes such as stamps, belts or others, the number of surface atoms in these forms is always higher than that found in the case of spheres. Besides the number of the surface atoms, there the quality of the surface is also an important parameter. Atoms in flat surfaces such as stamps have both, a higher degree of coordination than in spheres, and less reactivity compared to the atoms on vortex and edges present in the anisotropic shapes [13]. Different shapes also implies different crystal faces exposed to the media and it is known that not all the crystal faces have the same photoreactivity [16].

Without entering into detail, the differences in the physicochemical properties and the variation in the surface state of NPs associated with modifications in their shapes imply necessarily changes in their photocatalytic activity. Figure 3 shows the degradation rate of Rh B in the presence of CeO_2 NPs with different shapes under UV 365 nm light. Even being the specific surface area similar, small 3 nm spherical CeO_2 NPs seemed to be more photoreactive than stamps and belts.
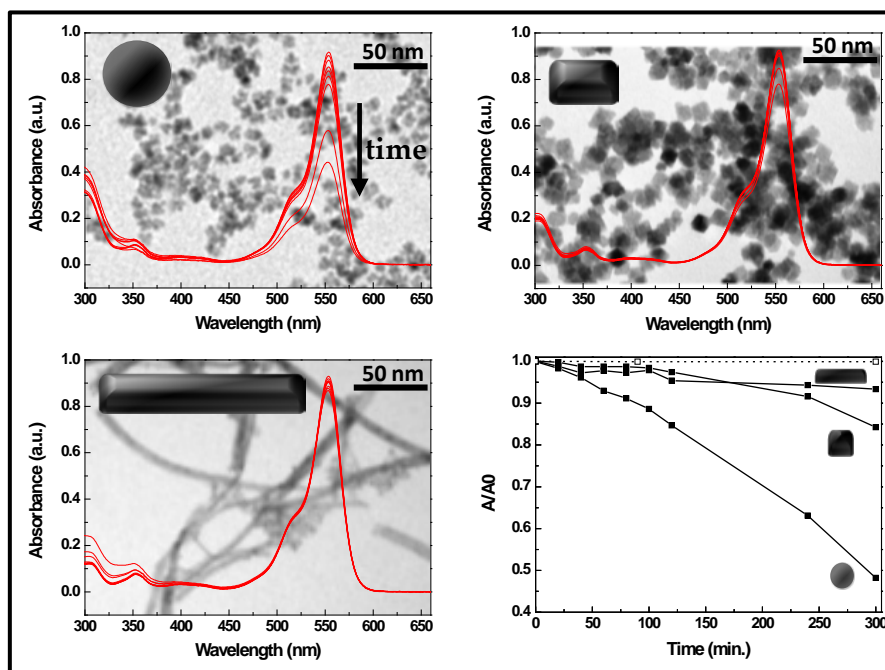
Figure 3. Evaluation of the photocatalytical properties of CeO_2 NPs of different shapes. Temporal evolution of Rh B peak of absorption in the presence of spheres, stamps and belts CeO_2NPs ($C_{0\text{-}CeO2}$=5 mM).

4.3. The role of agglomeration state in photocatalysis

Finally, the agglomeration state of NPs is also an important parameter to be taken into account. The degree of agglomeration has relevant consequences on the final behavior of the NPs which often translates into a loss of their nanometric properties. A direct consequence of agglomeration is the decrease of the free surface, and thus an expected decrease in the photocatalytic activity. Additionally, large sizes difficult the organic molecules to reach the surface. Figure 4 shows two cases of 5-10 nm a TiO_2 anatase NPs dispersed in water; one composed of 100 nm agglomerated and other well dispersed nearly individual particles. The photocatalytic activities of the two samples are different, being the first one less efficient in the photodegradation process than the second one.
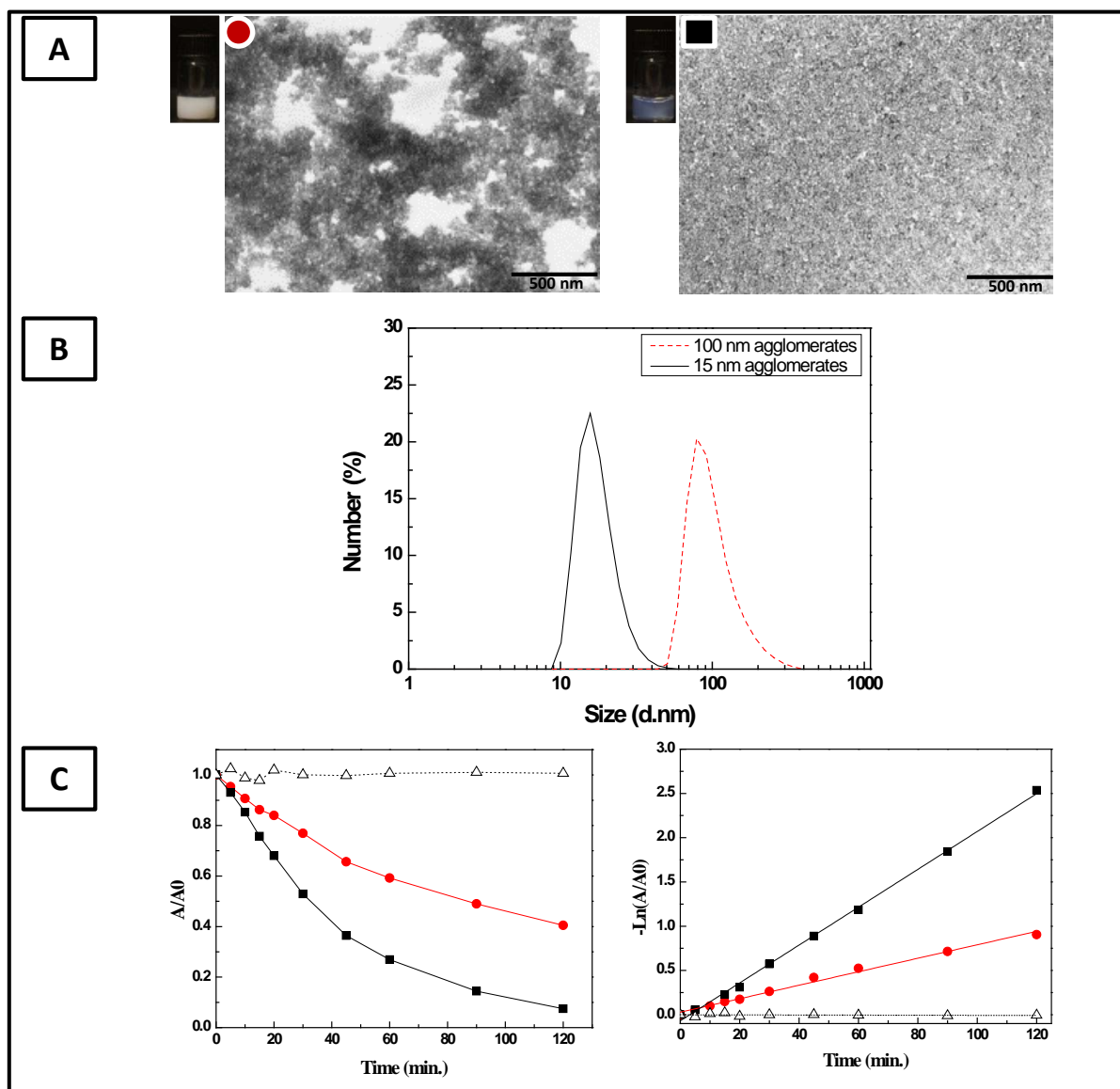
Figure 4. (A) TEM images of: (left) 100 nm and (right) 15 nm agglomerates TiO_2 NPs. (B) Dynamic Light Scattering measurement of both samples. (C) Temporal evolution of the RhB absorbance ($C_{0\ TiO2}$=0.6 mM): △control without NPs, ● 100 nm agglomerates and ■ 15 nm agglomerates.

5. Conclusions

There are many parameters that can affect the photocatalytic activity of NPs. Some of them, size, shape and aggregation have been briefly discussed in the present work.

Taking into account above considerations and the specific cases showed, it is expected for NPs that: (i) small particles are more photocatalytic than larger particles, (ii) atoms on flat surfaces in stamp or belt like shapes have a higher degree of coordination than in spheres, therefore possessing a lower photocatalytic activity compared to those atoms in edges or vortices, (iii) particles lose their nanometric properties and therefore also their efficiency when agglomerates.

However, this is just a general trend and not necessarily has to be always fulfilled. Usually, modifications of physicochemical properties associated to the variation of these parameters are proved for a specific photodegradation process and it is difficult to predict the efficiency of a particular NP as photocatalyst.

Moreover, nowadays there is a huge effort in understanding how NPs interact with the environment, bringing new parameters that are discovered to play an important role in the NPs behavior, e.g. surfactant used, corrosion, dissolution… Hence, the photocatalytic activity of NPs not only depends on the intrinsic properties of the particle but also on the environment in which the NPs are embedded and their evolution over time.

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