

Effect of TiO₂ surface modification in Rhodamine B photodegradation

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Abstract Commercial TiO₂ nanoparticles were superficially modified through polymeric resins obtained from polymerization of citrate complexes of Y³⁺ and Al³⁺ with ethylenglycol. The materials were treated at 450 °C for 4 h to obtain modified nanoparticles, which were characterized by HR-TEM, Zeta potential and surface area through N₂ fisisorption. Rhodamine B photodegradation by visible light irradiation and in presence of those modified nanoparticles was compared with the same process in presence of unmodified commercial TiO₂ nanoparticles. It was observed, by UV–visible spectroscopy, that the catalytic photoactivity in presence of modified nanoparticles was smaller than that observed with commercial TiO₂ nanoparticles. However, the surface modifier played an important role in the photodegradation kinetic process,

showing a non-linear relation between modifier amount and photodegradation rate, presenting a maximum value at 0.8% (w/w).

Keywords Photodegradation · Dye · Titanium dioxide · Photocatalysis · Water treatment

1 Introduction

Nowadays, the search for an adequate use of water is one of the main tasks to achieve a sustainable development. Several processes of water use implicate in the generation of toxic effluents or with high microbial /bacterial activity, inappropriate for reuse in agricultural activities and human use. Thus, in the last decades, water recycle becomes focus of attention of several research works [1–12].

An example to be analyzed is the textile production, an industrial activity that contributes to the generation of large quantities of liquid effluents. These wastes are often contaminated with organic dyes, used as one of the main components of textile inks. Recently, a catalyzed process which uses solar energy to promote breaking down of organic dyes has been studied [13–15]. In this process, a semiconductor inorganic material in nanometric scale (usually TiO₂) is used as catalyst to promote the degradation/oxidation of these organic dyes, as seen in Fig. 1. In the interface dye-semiconductor, the electron is injected to the semiconductor conduction band (CB) which can be captured by another species in the surroundings, as hydroxyl or O₂ groups. Due to the high surface area of nanostructured semiconductor systems and the adequate spectrum characteristic of the common dyes, the joined systems may absorb a high proportion of the incident solar energy flow (even high as 46%), despite that obtained

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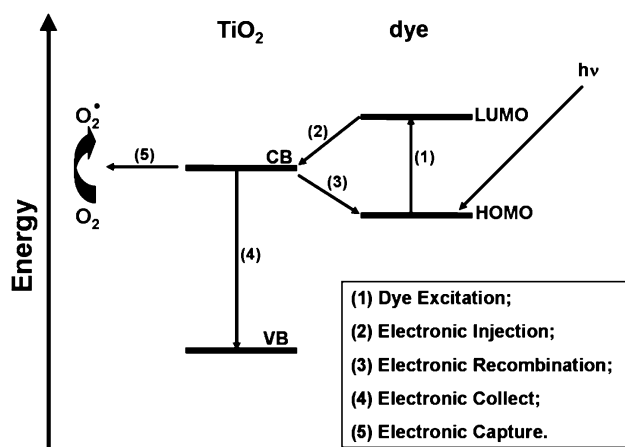


Fig. 1 Possible electronic transitions in the photodegradation process

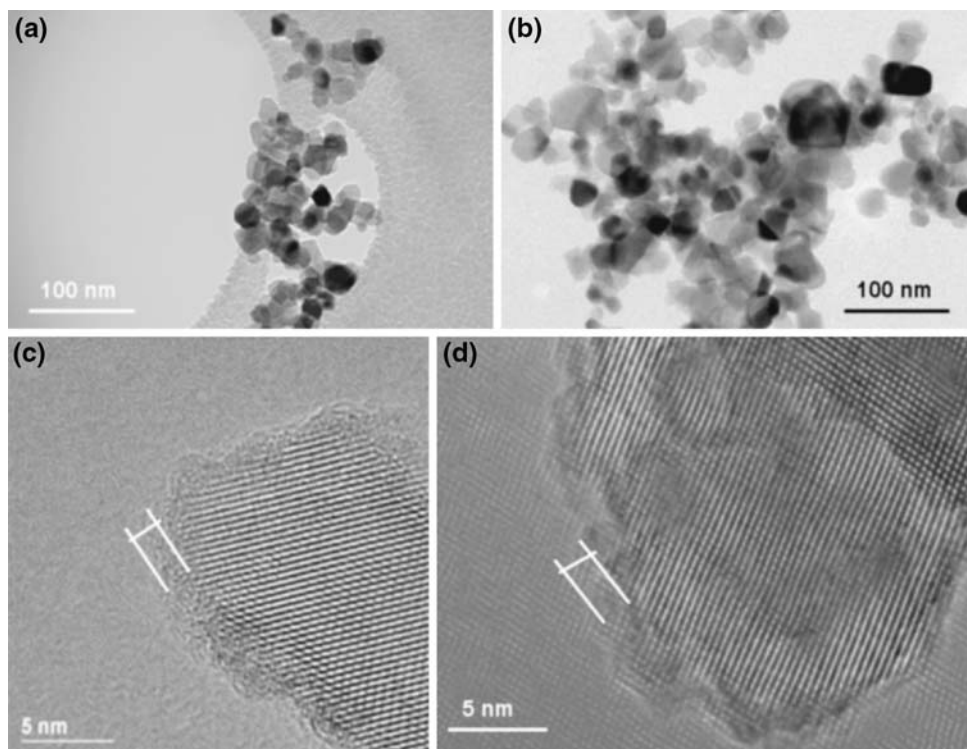
efficiencies, in solar simulation under AM 1.5 conditions, are still low (around 7–11%) [16–20].

Meanwhile, the electron in the semiconductor's CB can return to organic dye (electronic recombination) or also combine with a hole in the semiconductor valence band (VB) (electronic collect). These facts are drawbacks to the photocatalyzed process and must be avoided to improve the photodegradation efficiency. Indeed, the efficiency improvement is one of the major goals in this research field. In this sense, one way to improve photocatalysis efficiency is the control of the electronic recombination between the semiconductor and the organic dye,

minimizing electron loss in the interface semiconductor/dye [21]. This control can be achieved by modifying the semiconductor's surface, which can lead significant improvements in adsorbing kinetics of the dye at solid surface or avoiding electronic recombination by generating a high energy barrier to the return of the electron to the dye.

The key in this proposal is a proper selection of the intermediate material and the processing method. Among these proposals of surface modification, one of them is deposition of high-dielectric oxides, like Y₂O₃, ZrO₂, MgO and Al₂O₃ in the TiO₂ surface, generating an insulating oxide coating or modifying the surface by forming an intermediate phase (such as titanates). Those oxides may be deposited by several methods, like nitrates decomposition [21], sol-gel based [22] and others. In a recent work, Maciel et al. [23] demonstrated the possibility of apply the sol-gel modified route—also known as in-situ polymerizable complex method (IPC) [24]—for obtain Al₂O₃ encapsulated with La₂O₃. The IPC method has the advantages of good stoichiometric control, even in complex oxide structures, and the ability of a fine deposition control of large number of oxides. Thus, in this work we obtained surface-modified TiO₂ nanoparticles (using two insulating oxides—Y₂O₃ and Al₂O₃) by the modified-IPC method, and analyzed its effect in Rhodamine B photodegradation kinetics under visible light. The results will support future investigations about photodegradation systems based in surface-modified nanoparticles.

Fig. 2 TEM and HR-TEM images: (a) and (c) TiO₂ nanoparticles modified with Y₂O₃; (b) and (d) TiO₂ modified with Al₂O₃



2 Materials and methods

Colloidal dispersions containing 2 g of commercial TiO₂ nanoparticles (P25; ca. 80% anatase and 20% rutile, Degussa Co.) in 50 mL of deionized water were prepared. A polymeric resin was obtained by queling a metal ion from a salt (Y₂(CO₃)₃ and Al₂(CO₃)₃, Aldrich Co.) with citric acid (Mallinckrodt), followed by polymerization against ethylene glycol (Mallinckrodt). Details of the resin preparation can be obtained in Ref. [25]. The obtained resins were added into colloidal dispersions to obtain dispersions containing 0.4%; 0.8%; 1.2%; 2.4% in weight of Y₂O₃ per weight of TiO₂. In another set, the same method was utilized for modification with Al₂O₃, with a density-based correction to maintain the total volume of the added phase. These dispersions were sonicated for 10 min and the

aqueous solvent was removed using a rotaevaporator. The solid resultant was pulverized and calcined at 450 °C for 4 h. The resultant nanoparticles were characterized by TEM (Philips CM 200) and the zeta potential of the dilute suspensions were measured in a Zeta Potential Meter (Brookhaven Inst. Corp. Zetaplus). The measurements of the surface area were carried out in ASAP 2000 equipment using the BET isotherm.

For the dye photodegradation studies, colloidal dispersions were prepared by adding 50 mg of modified or as-received TiO₂ powder to a 50 mL Rhodamine B aqueous solution (RhB, Mallinckrodt, 10⁻³ g L⁻¹). Prior the

Table 1 Samples chemical compositions and some physical chemical characteristics of modified and unmodified nanoparticles

Sample	NP modifier ^a	% (w/w)	IE ^b	Surface area (m ² g ⁻¹)	I _{v,m} I ^c (10 ⁻⁷ × mol L ⁻¹ /min)
1	TiO ₂	–	2.6	80.8	7.1
2	TiO ₂ · Y ₂ O ₃	0.4	5.8	51.5	5.1
3	TiO ₂ · Y ₂ O ₃	0.8	3.5	51.7	6.0
4	TiO ₂ · Y ₂ O ₃	1.2	5.3	50.8	5.9
5	TiO ₂ · Y ₂ O ₃	2.4	4.6	49.9	4.3
6	TiO ₂ · Al ₂ O ₃	0.3	3.6	50.2	4.6
7	TiO ₂ · Al ₂ O ₃	0.6	4.5	47.2	4.8
8	TiO ₂ · Al ₂ O ₃	0.9	5.1	51.5	4.2
9	TiO ₂ · Al ₂ O ₃	1.7	5.4	49.4	4.0

^a NP = nanoparticle

^b IE = isoelectric point, obtained graphically by Zeta potential measurements (see graphs in Fig. 3a, b)

^c Photodegradation average velocity: $I_{v,m}I = I(c_{RhBf} - c_{RhB0})I / (t_f - t_0) = I\Delta c_{RhB} / \Delta t$

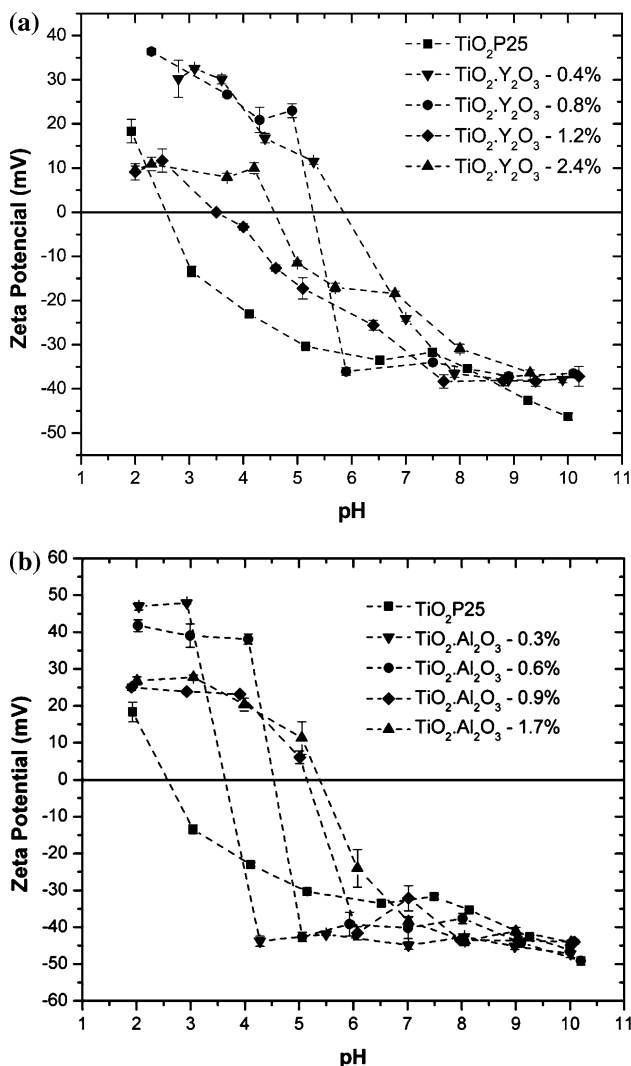


Fig. 3 Zeta potential measurements comparing unmodified nanoparticles with: (a) modified with Y₂O₃ and (b) modified with Al₂O₃. The dot lines were drawn to aid the eyes

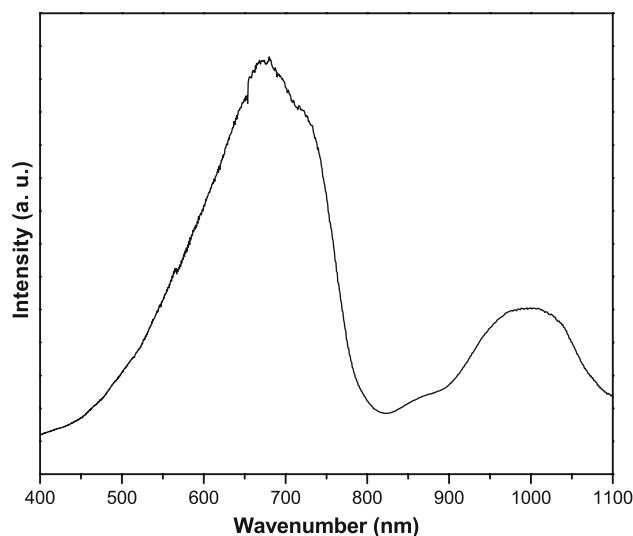


Fig. 4 Radiation source spectrum used in the dye photodegradation. Note that there is not radiation in the U.V. region

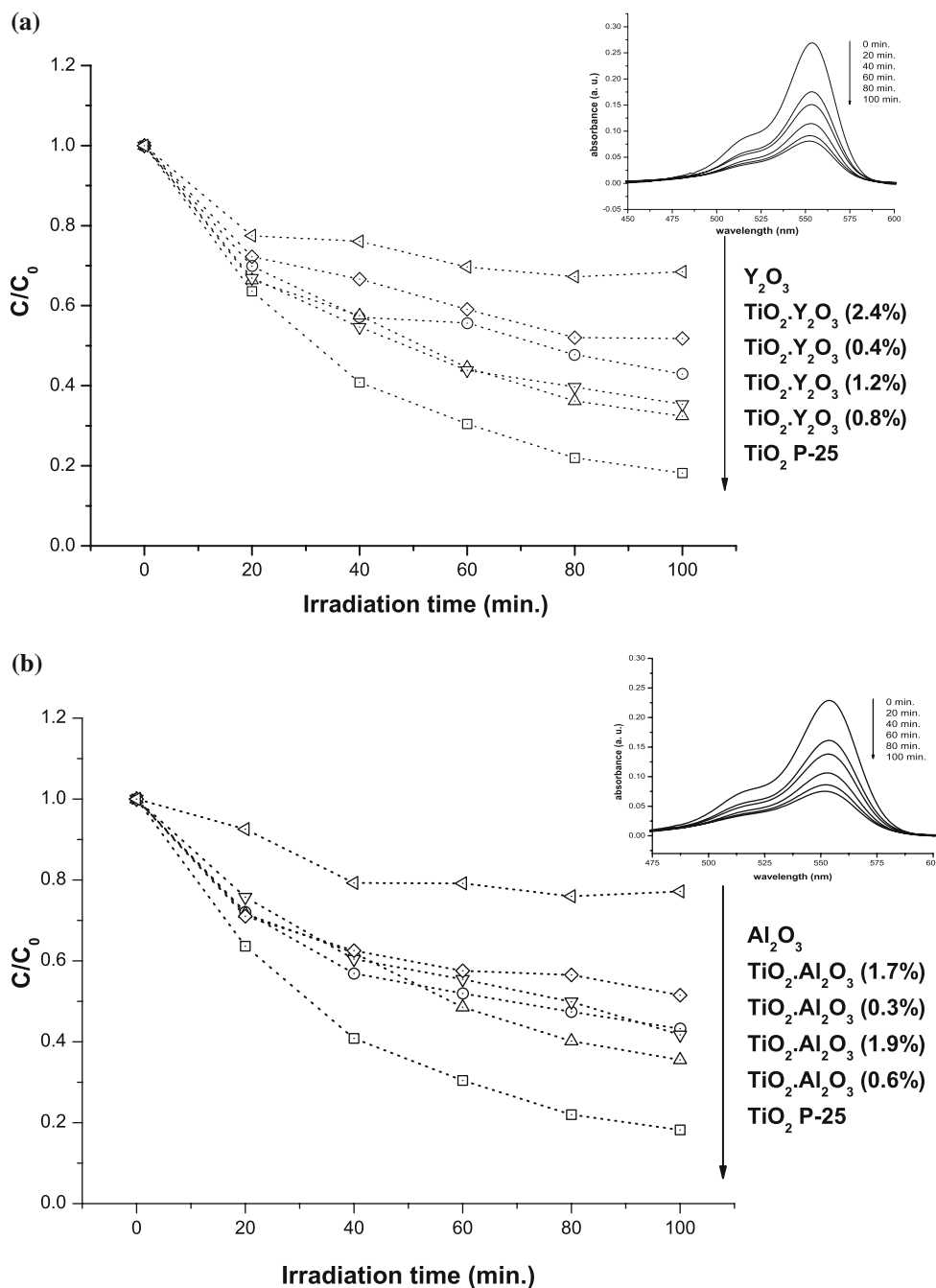
irradiation, the dispersions were sonicated during 10 min in an ultrasonic bath and magnetically stirred in the dark for 30 min to ensure establishment of an adsorption/desorption equilibrium between the TiO_2 , RhB and atmospheric oxygen. Thereafter, the dispersions were kept under constant air-equilibrated conditions. A 150 W halogen lamp was utilized to photodegradation analysis. At given irradiation time intervals, samples (5 mL) were collected, centrifuged and filtered (Millipore, pore size, 450 nm) to separate the TiO_2 nanoparticles. After, the filtrates were analyzed by UV–visible spectroscopy (Shimadzu model MultiSpec

1501) to monitor the temporal degradation of the dye. The RhB concentration was determined by the absorbance at 554 nm.

3 Results and discussion

TEM and HR-TEM images of the modified nanoparticles are shown in Fig. 2. All the modified nanoparticles exhibit a spherical morphology and similar size, despite agglomerate formation (Fig. 2a, b). Some of them exhibited a thin

Fig. 5 Photodegradation profiles: (a) TiO_2 modified with Y_2O_3 and (b) TiO_2 modified with Al_2O_3 . The dot lines were draw to aid the eyes. The inset shows the variation of absorption band intensity as function of the irradiation time



coating of some nanometers (Fig. 2c, d), forming a core-shell structure, while most part exhibited the formation of irregular islands in TiO₂ surfaces. The observed structures showed that the proposed method is effective to the modification of TiO₂ surface, despite the irregular distribution of the insulating oxides.

Zeta Potential measurements (Fig. 3) also confirmed the surface modifications. In spite of this fact, the Zeta potential measurements supply us with information about the average sample value, unlike the local information supplied by TEM analysis. In Table 1, we can see that the addition of different amounts of insulating oxide in the TiO₂ nanoparticles gives different values of isoelectric point (IE). Surface area measurements were employed to characterize TiO₂ powder and the modified nanoparticles, because surface area is an important parameter in heterogeneous photocatalysis [26]. The corresponding parameters are also listed in the Table 1. The comparison shows that heat treatment employed in the surface modification process turned out in a similar surface area decrease (approx. 37%) for all modified nanoparticles, when compared with unmodified nanoparticles. However, it was not possible to define the phase present at the surface (insulating oxide or an intermediate phase), due to the low contents of the modifier added.

In this work, the radiation source used in the photodegradation process was limited to visible—near IR spectra (see the spectrum of light source in Fig. 4). Thus, since the band gap energy of TiO₂ is estimated around 3.75 eV [27] (absorption at 310–330 nm), the direct formation of electron/hole pairs (excitons) in the semiconductor is not expected [28]. In our experimental condition, RhB photoexcitation originates the electron injection from RhB's lowest unoccupied molecular orbital (LUMO) to TiO₂ CB, as schematically disposed in Fig. 1. This injected electron can take three ways: it can return to RhB (electronic recombination, regenerating the dye), it can combine with a hole in the TiO₂ VB (leading to the electronic collect) or it can be captured by another specie at solid surface surroundings (electronic capture). The surface modification may have improved the electronic collect by imposing an energy barrier to the recombination, but may have decreased dye adsorption, by covering some active sites.

Figure 5a and b show the photodegradation profiles of Rhodamine B in presence of modified and unmodified TiO₂ nanoparticles. The decrease in RhB concentration with irradiation time and different profiles for each sample indicates that dye solution was degraded in all conditions and the catalyst performance is directly affected by the amount of modifier. The catalytic activities of the modified nanoparticles were smaller than the unmodified TiO₂ nanoparticles. In fact, the lower catalytic activity cannot be attributed only to the modifier or the surface area reduction

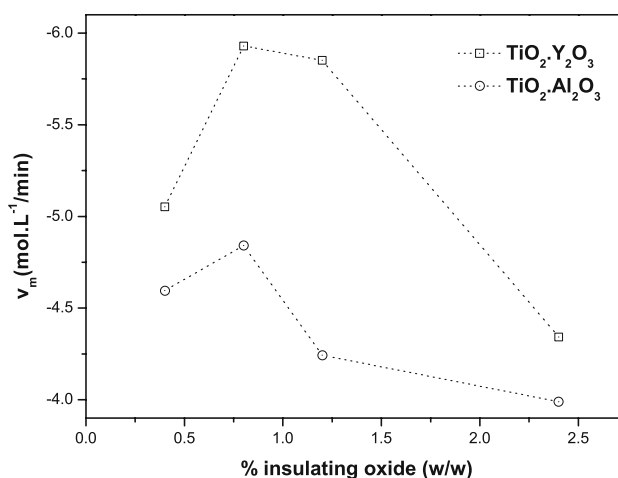


Fig. 6 Photodegradation average velocity as function of the insulating oxide amount. Note that y-axis is inverted because the photodegradation average velocity is negative

(caused by thermal treatment) and needs to be better investigated. However, it was observed that the addition of Y₂O₃ as surface modifier resulted in better performance than Al₂O₃, and both present the same optimum value for modified samples (approximately 0.8% w/w), as shown in Fig. 6, indicating some selective surface modification.

In order to verify the single oxides (Y₂O₃ and Al₂O₃) activities, the photodegradation process was also carried out in the presence of these pure oxides, as shown in Fig. 5a and b. Both oxides showed photocatalytic activities, but negligible when compared to the modified and unmodified TiO₂ nanoparticles.

4 Conclusions

Rhodamine B photodegradation using surface-modified TiO₂ nanoparticles as catalysts was observed through UV–visible spectroscopy. It was demonstrated, by Zeta potential measurements, that the IPC method was effective to obtain surface modifications, despite this surface modification is not homogeneous, as we can see by HR-TEM images. In RhB photodegradation carried out only in visible light, the modified TiO₂ nanoparticles presented the same optimum catalytic activity at modifier content (around 0.8% w/w) for two oxides observed, Y₂O₃ and Al₂O₃, with better results for Y₂O₃ modification. The pure oxides did not show significant photocatalytic activity, suggesting a synergistic effect in electron capture that should be better investigated.

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