

Increasing the Photoactivity of N-doped TiO₂ Photocatalysts Using Phosphors as Light Carriers

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The aim of the work was to increase the photoactivity of N-doped TiO₂ photocatalyst, active in visible light region, through the improving of the illumination efficiency. Microradiators like phosphors (namely, ZPS) which absorb an electromagnetic radiation by the external light source (UV) and, with no time delay, emit visible light, opportunely selected to be able to excite N-doped TiO₂ photocatalyst. Preliminary investigations were performed on physical mixtures of phosphors and N-doped TiO₂, evaluating the decolourization of methylene blue (MB). The simultaneous presence of N-doped TiO₂ and light carriers showed an increased decolourization activity, reaching about 100 % with a total TOC removal after 3 h of irradiation. To get core-shell photocatalysts, N-doped TiO₂ was supported on ZPS (NTiO₂-ZPS) by a modified sol-gel method. The content of N-doped TiO₂ was varied in the range 5-50 wt % to find an optimum loading. The photocatalytic activity of NTiO₂-ZPS was evaluated for the removal of MB under UV illumination. The performances of NTiO₂-ZPS showed an improved efficiency in decolourization process of MB, equal to 100 % after 90 min of irradiation, with a total TOC removal. The influence of several parameters, such as dye type and concentration has been studied.

1. Introduction

Textile dyes have become as toxic organic compounds the focus of environmental remediation efforts because of their natural biodegradability is increasingly troublesome owing to the improved properties of dyestuffs (Vajnhandl and Le Marechal, 2007). Colour interferes with penetration of sunlight into the water, retards photosynthesis, inhibits the growth of aquatic biota and interferes with solubility in water bodies (Vautier et al., 2001). Dyes removal using conventional oxidation methods is difficult, because a lot of pollutants are bio-recalcitrant (Souza et al., 2013, Šíma et al., 2013). Heterogeneous photocatalysis using oxide semiconductors is an interesting application owing to its potential in the resolution of environmental issues (Murcia et al., 2013, Bamuza-Pemu et al., 2013, Ruzmanova et al., 2013). The titanium dioxide (TiO₂) semiconductor photocatalyst has the potential to oxidize a wide range of toxic organic compounds into harmless compounds such as CO₂ and H₂O by irradiation with UV light (Driessen and Grassian, 1998). Due to the value of its band-gap energy (3.0-3.3 eV), TiO₂ absorbs about 5 % of sunlight in the UV region. A large number of approaches have been taken to reduce the band gap energy of TiO₂, such as doping with transition metal cations (Inturi et al., 2013) or more recently, doping with anions such as C (Zhang et al., 2013), S (Han et al., 2011) and N (Sannino et al., 2013a). The N-doped TiO₂ seems to be the most promising among all the so called second generation photocatalysts. However photocatalysts suffer for the layout of photocatalytic plants, where the most often found limitation regards the effective transferring of the light towards the overall amount of photocatalyst. The improving or a correct evaluation of the photocatalytic reactivity is correlated to wellness of the catalytic surface irradiation, and so the possibility to mix the photocatalyst with emitting phosphorescent particles (known generally as phosphors) as light carriers has been exploited (Ciambelli et al., 2011). In this case, the photocatalyst surface was completely irradiated (Sannino et al., 2013b) as shown by the considerably increase of the photocatalytic activity. The aim of this work was to investigate the effect of engineered coupling of N-TiO₂ with blue phosphors in photocatalytic degradation of methylene blue (MB) and methyl orange (MO). Reaction products were monitored both in liquid-phase, by decolourization and TOC analysis, and in gas-phase, by continuous analyses, measuring CO, CO₂ and SO₂ gaseous concentrations at the photo-reactor outlet.

2. Experimental

2.1 Catalysts preparation and characterization

N-doped TiO₂ (N-TiO₂) photocatalysts was prepared by sol-gel method starting from 97 % titanium tetraisopropoxide (TTIP) and added ammonia aqueous solution at 30 wt % with a molar ratio N/Ti=18.6 (Sacco et al., 2012). As light carriers, were used ZnS-based phosphors materials (ZPS) (model RL-UV-B-Y; Excitation Wavelength: 365 nm; Emission Wavelength: 440 nm) that emit in visible region when activated with UV light. Thus, to use the light emitted by phosphors, it is necessary to use TiO₂ photocatalyst active in visible region. The ZPS powders were mixed with N-TiO₂ powders for increase the photonic distribution. To get core-shell photocatalysts, N-TiO₂ was supported on ZPS surface by a modified sol-gel method. In particular, ZPS were dispersed in TTIP and after ammonia aqueous solution at 30 wt % (with a molar ratio N/Ti=18.6) was added. A progressive increase of N-TiO₂ amount, in the range 5-50 wt %, on the phosphors was realized. The content of N-TiO₂ on ZPS (NTiO₂-ZPS) was varied in the range 5-50 wt % to find an optimum loading. UV-Vis reflectance spectra of catalysts were recorded with a Perkin Elmer spectrometer Lambda 35. Equivalent band gap determinations were obtained from Kubelka-Munk theory by plotting $[F(R_{\infty}) \cdot hv]^2$ vs hv and calculating the x intercept of a line through $0.5 < F(R_{\infty}) < 0.8$.

2.2 Photocatalytic tests

The evaluation of the photocatalytic activity was carried out by following the reaction of decolourization of MB. In a typical photocatalytic test, the suspension is composed by 0.3 g of N-TiO₂ mixed with different amounts of ZPS. The total solution volume was 100 cm³ and MB or MO concentration was 7.5 ppm. The suspension was left in dark condition for 2 h to reach the adsorption equilibrium, and then light irradiation was performed for 3 h. The experiments were realized using a pyrex cylindrical photoreactor equipped with an air distributor device, magnetic stirrer to maintain the photocatalyst suspended in the aqueous solution, temperature controller and four UV lamps (nominal power: 32 W) with wavelength emission centred at 365 nm. Slurry samples were collected at fixed time and analysed to determine the change of dye concentration, measured with a Perkin Elmer UV-Vis spectrophotometer at 663 nm for MB concentration and at 464 nm for MO concentration. TOC of solution has been measured from CO₂ obtained by catalytic combustion at T=680 °C. CO₂ produced in gas-phase was monitored by continuous analyzers, measuring CO, CO₂ (Uras 14, ABB) and O₂ (Magnos 106, ABB) gaseous concentrations. The analysis of gas phase coming from the photoreactor was performed by means of a continuous CO, CO₂, and SO₂ non-dispersive infrared analyser (ABB Advance Optima).

3. Results and discussion

3.1 Catalysts characterization

The list of catalysts with their N-TiO₂ nominal content is reported in Table 1. X-ray diffraction analysis of N-TiO₂ sample showed the presence of signals typical of the titanium dioxide in the anatase phase (Sacco et al., 2012). The band-gap energy is also reported in Table 1. As shown in Table 1, with the increase of the amount of N-TiO₂ on ZPS, the band gap energy shifts from a value close to ZPS, for 5 %NTiO₂-ZPS and 15 %NTiO₂-ZPS samples, to a value close to NTiO₂ for 50 %NTiO₂-ZPS catalyst.

3.2 Photocatalytic activity tests

The behaviour of MB decolourization is represented in Figure 1a for N-TiO₂ compared to the physical mixture of the same photocatalyst with light emitting phosphorescent particles ZPS. In dark conditions both photocatalysts showed a decrease of MB concentration was observed during the first hour of the test and it was the same in the second hour indicating that the adsorption equilibrium of dye on catalyst surface was reached. In dark conditions both systems showed a decrease of MB concentration during the first hour of the test and it was the same in the second hour indicating that the adsorption equilibrium of dye on catalyst surface was reached. After the dark period, the solution was irradiated with UV lamps (Figure 1a). The results obtained with N-TiO₂ photocatalyst showed a decolourization activity lower than that one obtained when N-TiO₂ doped photocatalyst was mixed with ZPS with a total TOC removal. The presence of light carriers increased the effective activity in decolourization process of MB and in the removal of organic carbon, showing the presence of a limitation on in the photonic distribution and the overcoming of the photons transfer limitations that occur for only N-TiO₂.

The decolourization process on photocatalysts is described by a first order kinetic Eq(1) with respect to the concentration of MB.

$$-\ln \frac{C}{C_0^*} = k_i \cdot t \quad (1)$$

Where:

C=concentration of MB at any given time;
 C_0^* =concentration of MB after dark adsorption;
 t= irradiation time;
 k_i =apparent kinetic constant.

The obtained results are plotted in Figure 1b showing that in presence of ZPS, apparent kinetic constant remarkably increased. For evaluating the effect of amount of ZPS in the MB decolourization process, 0.3 g of N-TiO₂ was physically mixed with different amount of phosphors (Figure 2). Increasing the dosage of ZPS from 0.6 to 1 g g⁻¹, the MB decolourization after one hour of irradiation increased. With a further increase of ZPS loading in the aqueous medium, the MB decolourization activity strongly decreased,

Table 1: Catalysts and their characteristics

Catalyst	TiO ₂ nominal content wt %	E _{bg} eV
ZSP	0	3.1
N-TiO ₂	100	2.5
5%NTiO ₂ -ZPS	5	3.1
15%NTiO ₂ -ZPS	15	3.0
30%NTiO ₂ -ZPS	30	2.7
50%NTiO ₂ -ZPS	50	2.6

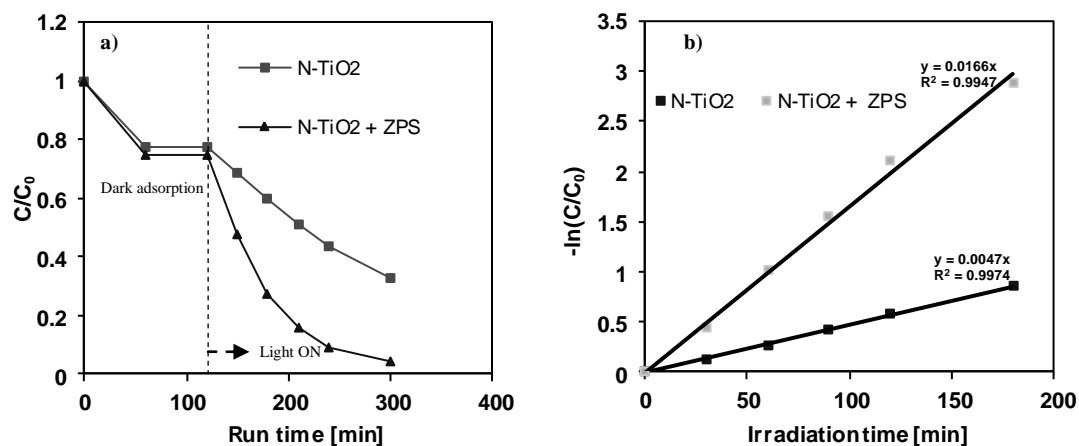


Figure 1: (a) Decolourization of MB (b) Evaluation of decolourization kinetic

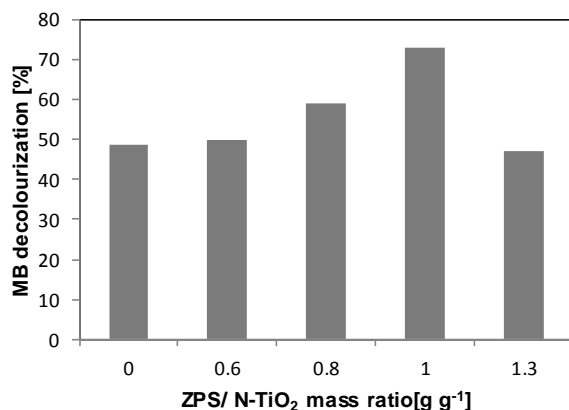


Figure 2: Evaluation of the effect of different amount of ZPS in physical combination with the similar amount of N-TiO₂ (0.3 g) on the decolourization of MB after one h

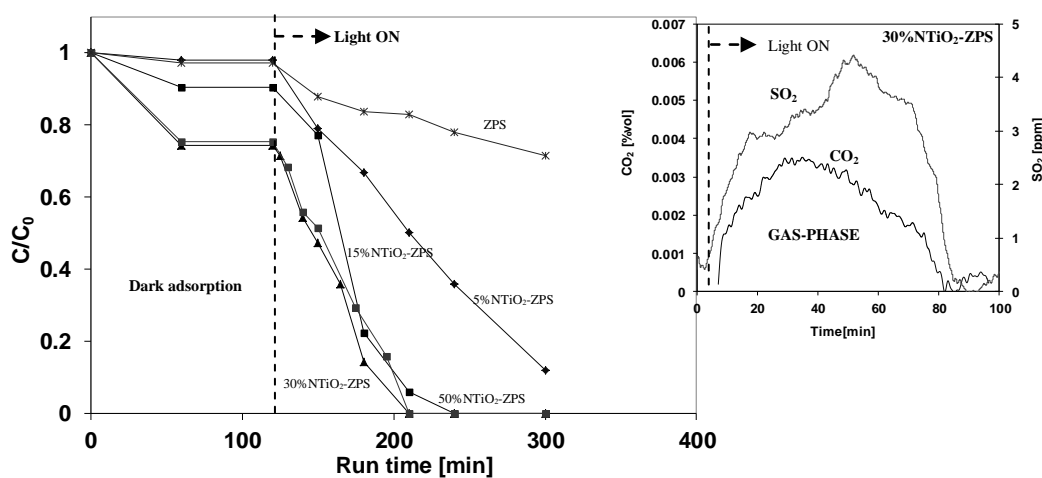


Figure 3: Comparison of core-shell photocatalysts performances by varying the extent of N-TiO₂ shell (indicated by the different weight percentages of N-TiO₂) in photocatalytic decolourization of MB and gas-phase analysis of 30%NTiO₂-ZPS

indicating that the light penetration through the solution becomes difficult. Therefore 1 g g⁻¹ of phosphor loading was found as the optimal value. However, the separation among the catalyst surface and the light emitted by the microcarriers remained high, since physically separated by the mere physical mixture with N-TiO₂.

Thus, the photocatalyst N-TiO₂ was supported on the surface of ZPS to get core-shell photocatalysts (Sannino et al., 2013a), to permit a higher capture of the ZSP emitted photons. The amount of N-TiO₂, however, have to be modulated, since it could be easily argued that a total coverage of ZPS by N-TiO₂ does not lead to the UV excitation of the covered phosphors (so no emission is possible), while a few amount of N-TiO₂ coating on ZSP will not give the desired photoactivity. So, the core-shell photocatalysts have to be able to absorb the UV light needed by the photoreaction in the proximity of the external light source (UV lamps), but leave a residual phosphors free surface able to harvest, and release, after UV light excitation, the further radiation at 440 nm useful to proceed with the photoreaction when the photocatalysts are in darker zones of the reactor. Figure 3 shows the comparison of the core-shell photocatalysts (NTiO₂-ZPS) in decolourization of MB. In all cases the equivalent amount of nominal N-TiO₂ is equal to 3 g L⁻¹. As it is possible to observe, the performances of NTiO₂-ZPS in the decolourization of MB were dramatically enhanced for all the samples. In particular, for the sample 30 %NTiO₂-ZPS, the total MB decolourization was obtained after 90 min of irradiation. In this case, the analysis of gaseous stream coming from the photoreactor during the irradiation revealed the presence of CO₂ and SO₂ (Figure 3). The CO₂ observed in the gas phase was due to the oxidation of MB which started at high reaction rate after few min of irradiation. Through a comparison between the amount of carbon consumed during the reaction (as

assessed by the analysis of TOC in liquid phase) and the amount of carbon released as CO_2 in the gaseous phase, the total carbon mass balance was closed to about 100 %. This allowed affirming that the MB is selectively converted to CO_2 . The effect of MB initial concentration on the photocatalytic activity was evaluated with two different initial MB concentrations: 7.5 and 95 ppm and in presence of the most active photocatalyst, 30 % NTiO_2 -ZPS, (Figure 4a). At fixed reaction times, the increase of MB initial concentration determined a decrease of the photocatalytic activity. This could be due both to the higher mass of dye to remove, but also to the increase of colour intensity of the solution, that reduces the light penetration into the aqueous medium, meaning that the path length of photons inside the solution decreases. However, also in this case, the core-shell photocatalyst is able to assure the total MB decolourization after about 1,200 min of irradiation. Finally, the efficiency of 30 % NTiO_2 -ZPS was also evaluated in decolourization of (MO) (Figure 4b) showing that it is able to remove also dyes different from MB.

4. Conclusions

Core-shell photocatalysts based on N- TiO_2 coating on ZSP were successfully synthesized. The optimal load of N- TiO_2 on the phosphors was individuated at 30 wt %, yielding in the right combination of the need of ZSP to absorb the UV light to be excited by the external light source (UV lamps), and the

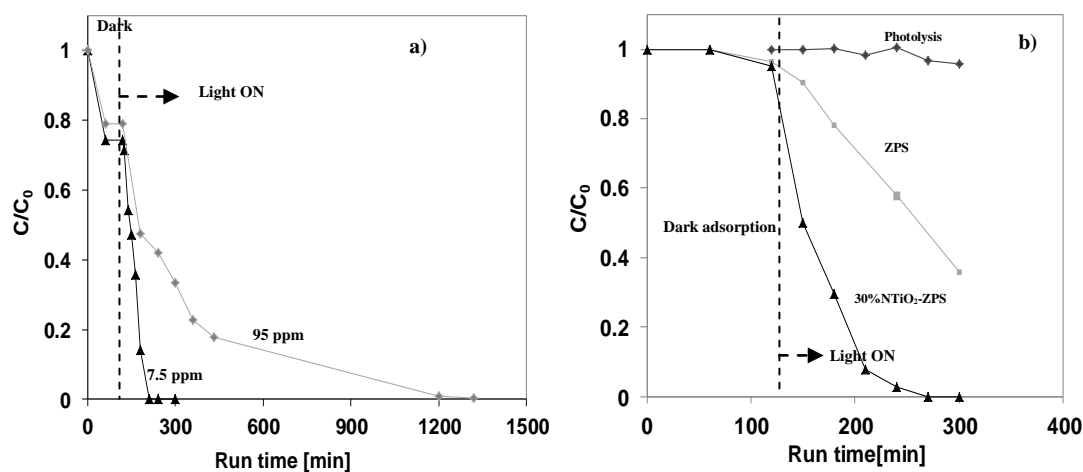


Figure 4: a) Evaluation of decolourization with different initial concentration of MB; photocatalyst: 30% NTiO_2 -ZPS; b) Evaluation of MO decolourization); photocatalysts 30% NTiO_2 -ZPS

presence of a suitable amount of active N- TiO_2 photocatalytic phase, so developing the ability to proceed with the photoreaction when the photocatalysts are in darker zones of the reactor. Core-shell photocatalysts demonstrated remarkably activity in the decolourization of organic dyes and in the removal of total organic carbon, overcoming photons transfer limitations that typically are present in the photoreactors used for wastewater treatment.

Acknowledgements

The authors wish to thank University of Salerno for funding project "orsa111873; processi chimici catalitici per la produzione di energia sostenibile e l'ambiente".

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