

# Enhanced Photocatalytic Degradation of Organic Pollutants in Wastewater Using Photocatalysts Coupled with Luminescent Materials

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The aim of this work was to study the effect of different luminescent materials (phosphors) as supports for visible light active N-doped TiO<sub>2</sub> (N-TiO<sub>2</sub>) photocatalyst to enhanced photocatalytic activity. Preliminary investigations were performed on physical mixtures of phosphors and N-TiO<sub>2</sub>, evaluating the decolourization of methylene blue (MB). Subsequently, to permit a higher capture of the light emitted by phosphors, the N-TiO<sub>2</sub> photocatalyst was supported on phosphors surface by modified sol-gel method. The effect of coupling has been tested in the degradation of different pollutants, like methylene blue (MB) and phenol (PHE). Finally, the best sample was tested also in the degradation of terephthalic acid (TPA). In all cases the presence of luminescent materials allowed to enhance the photocatalytic reaction rate if compared with the results obtained in the absence of phosphors.

## 1. Introduction

In the last years, heterogeneous photocatalysis has drawn lots of attention as a green method for the removal of different organic pollutants in wastewater (Ahmed et al., 2011). Among different semiconductors, TiO<sub>2</sub> is still the most promising photocatalyst due to being environmentally friendly, since its chemical stability, high oxidative power and low cost (Vaiano et al., 2016). However, it can only be activated by UV light because of the large band gap of about 3.2 eV (Dette et al., 2014). It is well known that the UV light just accounts for 5% of solar light, while the residual 45% and 50% of solar light are made up of visible light and near-infrared (NIR) light, respectively (Chen et al., 2010). In order to extend the absorption ability of TiO<sub>2</sub> to the visible-light region, many strategies, such as doping with heteroatoms, have been developed (Ruzmanova et al., 2015). Moreover, one of the main limitations for large scale application of photocatalysis is the photon transfer in the photocatalytic reactors (Spasiano et al., 2015).

To improve this feature it is possible to couple the photocatalyst with light emitting phosphorescent particles, substances that exhibit the phenomenon of luminescence (Vaiano et al., 2014).

Phosphors are materials having optically active centers that can absorb an incident radiation, which is re-emitted at shifted specific wavelengths (Li and Sakka, 2015). When phosphors are present together with a suitable photocatalyst, they can catch the radiation coming from external light sources and emit their specific radiation in the core of photoreactor, transferring additional photons to the photocatalyst in its close proximity (Vaiano et al., 2015), so improving the photons transfer also in the darker zones of a photoreactor (Sacco et al., 2015). Most commercial phosphors emit blue light when excited by UV light. Thus, to fruitfully capture the light emitted by phosphors, it is necessary to modify TiO<sub>2</sub> photocatalyst to make it active in visible region (Sacco et al., 2012). In this perspective, TiO<sub>2</sub> has been doped with nitrogen (N-TiO<sub>2</sub>) for exploiting also of the re-emitted radiation by phosphors. In this work, firstly it was evaluated the photoactivity of physical mixtures between N-TiO<sub>2</sub> and different commercial phosphors: ZnS-based phosphors (ZSP), BaMgAl<sub>10</sub>O<sub>17</sub>:Eu (BaMgP) and Sr<sub>2.90</sub>Eu<sub>0.03</sub>Dy<sub>0.07</sub>Al<sub>4</sub>Si<sub>11</sub> (SrSiP), having all blue emission. Subsequently, to permit a higher capture of the light emitted by phosphors the N-TiO<sub>2</sub> photocatalysts was supported on phosphors materials by modified sol-gel method (N-TiO<sub>2</sub>/phosphors). The N-TiO<sub>2</sub>/phosphors have been tested firstly analysing the decolourization of methylene blue (MB) dye and after analysing the degradation of a colourless target pollutant like phenol (PHE). Finally, the best sample was tested also in the degradation of terephthalic acid (TPA).

## 2. Experimental

### 2.1 Catalysts preparation and characterization

N-TiO<sub>2</sub> was prepared by sol gel method starting from titanium(IV) isopropoxide (TTIP), as source of titanium dioxide and ammonia aqueous solutions (30% wt.) as dopant precursor at a molar ratio N/Ti=18.6. After 10 min of stirring, the precipitate was centrifuged and washed with deionized water for several times and calcinated at 450°C for 30 minutes (Sacco et al., 2012). ZSP, BaMgP and SrSiP (commercial blue phosphors, excitation wavelength: 365 nm, emission wavelength: 440 nm) were used as light carriers. The phosphors powders were mixed with N-TiO<sub>2</sub> for increasing the photonic distribution in the photoreactor (Vaiano et al., 2014). N-TiO<sub>2</sub> was supported on phosphors surface by a modified sol-gel method. In particular, blue phosphors were dispersed in TTIP solution and after ammonia aqueous solution at 30 wt % (with a molar ratio N/Ti= 18.6) was added (Sacco et al., 2015). The precipitate was washed with water and then centrifuged. Finally, the obtained powders were heated in air up to 450 °C and maintained at this temperature for 30 min. The content of N-TiO<sub>2</sub> in the final samples was 30 wt%.

Physico-chemical characterization of samples has been performed through X-ray diffraction (XRD) using an X-ray micro-diffractometer Rigaku D-max-RAPID, using Cu-K $\alpha$  radiation and a cylindrical imaging plate detection. The Brunauer Emmett and Teller (BET) surface area of the samples was measured from dynamic N<sub>2</sub> adsorption measurement at -196 °C, performed by a Costech Sorptometer 1042 after pretreatment at 150 °C for 30 min in He flow.

### 2.2 Photocatalytic tests

MB, PHE and TPA solutions were prepared by dissolving 10 mg, 50 mg and 15 mg respectively in 1L of MilliQ-grade water until to obtained an initial concentration equal to 10 ppm 50 ppm and 15 ppm. For the tests with physical mixtures, the suspension was composed by 3 g L<sup>-1</sup> of N-TiO<sub>2</sub> mixed with different amounts of phosphors. For the photocatalytic tests with N-TiO<sub>2</sub>/phosphors, the dosage of each photocatalyst in the reaction solution was 3 g L<sup>-1</sup>. The total solution volume was 100 mL. For all tests 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 (Philips, nominal power: 8 W each) with wavelength emission centred at 365 nm. Slurry samples were collected at fixed time and then they were centrifuged to remove the catalysts powders before the concentration measurement by a Perkin Elmer UV-Vis spectrophotometer at 663 nm for MB concentration, at 270 nm for PHE concentration and 241 nm for TPA concentration.

## 3. Results and Discussion

### 3.1. Characterization of the samples

The crystal phases of phosphors were determined by XRD analysis (Figure 1) indicating that crystal structure is mainly hexagonal for BaMgP and cubic for ZSP and matching well to the JCPDS data file #800020 and #260163. The diffraction intensity is maximum for BaMgP (107) plane (having 2 $\theta$ =33.51°), for ZSP (111) plane (having 2 $\theta$ =28.62°) and for SrSiP is 2 $\theta$ =30.66°.

The specific surface areas (SSAs) of all the samples analysed by BET method are reported in Table 1. In particular the specific surface areas were different, being 0.1, 1.1 and 3.5 m<sup>2</sup> g<sup>-1</sup> for ZSP, BaMgP and SrSiP, respectively.

Table 1: Characterization results for ZSP, BaMgP and SrSiP phosphors.

Sample	Specific surface area, (m <sup>2</sup> g <sup>-1</sup> )	Particle Diameter (μm)
ZSP	0.1	5-10
BaMgP	1.1	5-9
SrSiP	3.5	44

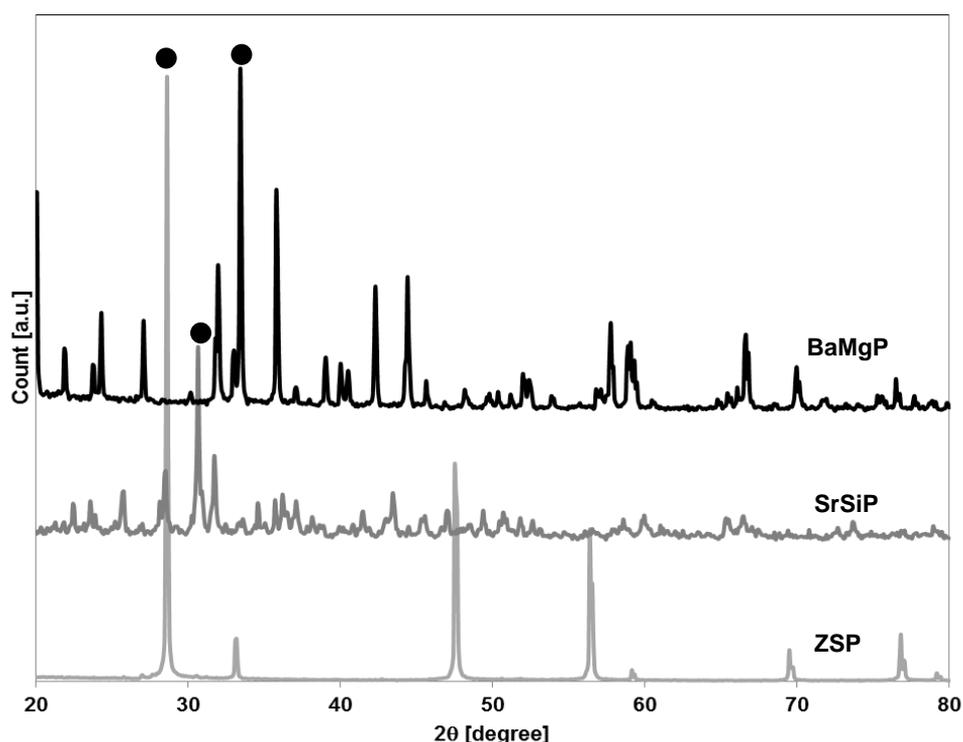


Figure 1: XRD spectra of ZSP, BaMgP and SrSiP phosphors

### 3.2 Photocatalytic activity tests

Figure 2 shows the photocatalytic results of MB decolourization using physical mixture of N-TiO<sub>2</sub> with different amount of light emitting phosphorescent particles after 30 min of UV irradiation. The results obtained showed a decolourization during the irradiation for all the physical mixtures. In particular, the best results were obtained using 0.15 g of BaMgP and 0.1-0.15 g of SrSiP leading to a degradation of 50% after 30min of UV irradiation. A lower activity was achieved when N-TiO<sub>2</sub> photocatalyst was instead mixed with ZSP phosphors (36%). However, the separation among the catalyst surface and the light emitted by the phosphors remained high, since physically separated by the mere physical mixture with N-TiO<sub>2</sub>.

To permit a higher capture of the light emitted by phosphors, N-TiO<sub>2</sub> was supported on the phosphors surface. Figure 3 shows the comparison of the N-TiO<sub>2</sub>/phosphors in decolourization of MB. As it is possible to observe, the performances of N-TiO<sub>2</sub>/phosphors in the decolourization of MB were dramatically enhanced with respect to unsupported N-TiO<sub>2</sub>. In particular, for N-TiO<sub>2</sub>/BaMgP and N-TiO<sub>2</sub>/ SrSiP and N-TiO<sub>2</sub>/ZSP, the MB decolourization obtained after 30 min of UV irradiation was 64, 52 and 41%, respectively. After 120 min of irradiation, only N-TiO<sub>2</sub>/BaMgP and TiO<sub>2</sub>/ZSP samples allowed to obtain the total MB decolourization. The efficiency of N-TiO<sub>2</sub>/BaMgP and N-TiO<sub>2</sub>/SrSiP and N-TiO<sub>2</sub>/ZSP was also evaluated in degradation of PHE (Figure 4) showing that all the samples are able to degrade also pollutants different from MB. As for the case of MB dye, the performances of N-TiO<sub>2</sub>/BaMgP and N-TiO<sub>2</sub>/ SrSiP and N-TiO<sub>2</sub>/ZSP in the degradation of PHE were dramatically enhanced with respect to pure N-TiO<sub>2</sub>, but, in the case of PHE, the trend of degradation was different compared with that one obtained for the MB decolourization. In fact, as shown in the Figure 4, the best degradation results was obtained for the N-TiO<sub>2</sub>/ZSP sample that after 90 min of irradiation led to a PHE degradation value equal to 82%, while it was 51% and 31% for N-TiO<sub>2</sub>/BaMgP and N-TiO<sub>2</sub>/SrSiP, respectively. Finally, the N-TiO<sub>2</sub>/ZSP sample was used in the photocatalytic degradation of TPA (Figure 5). Also in this case the photoactivity of the N-TiO<sub>2</sub>/ZSP sample was higher than N-TiO<sub>2</sub>. In particular after 150min of UV irradiation the TPA degradation was equal to 39 and 61% for N-TiO<sub>2</sub> and N-TiO<sub>2</sub>/ZSP, respectively.

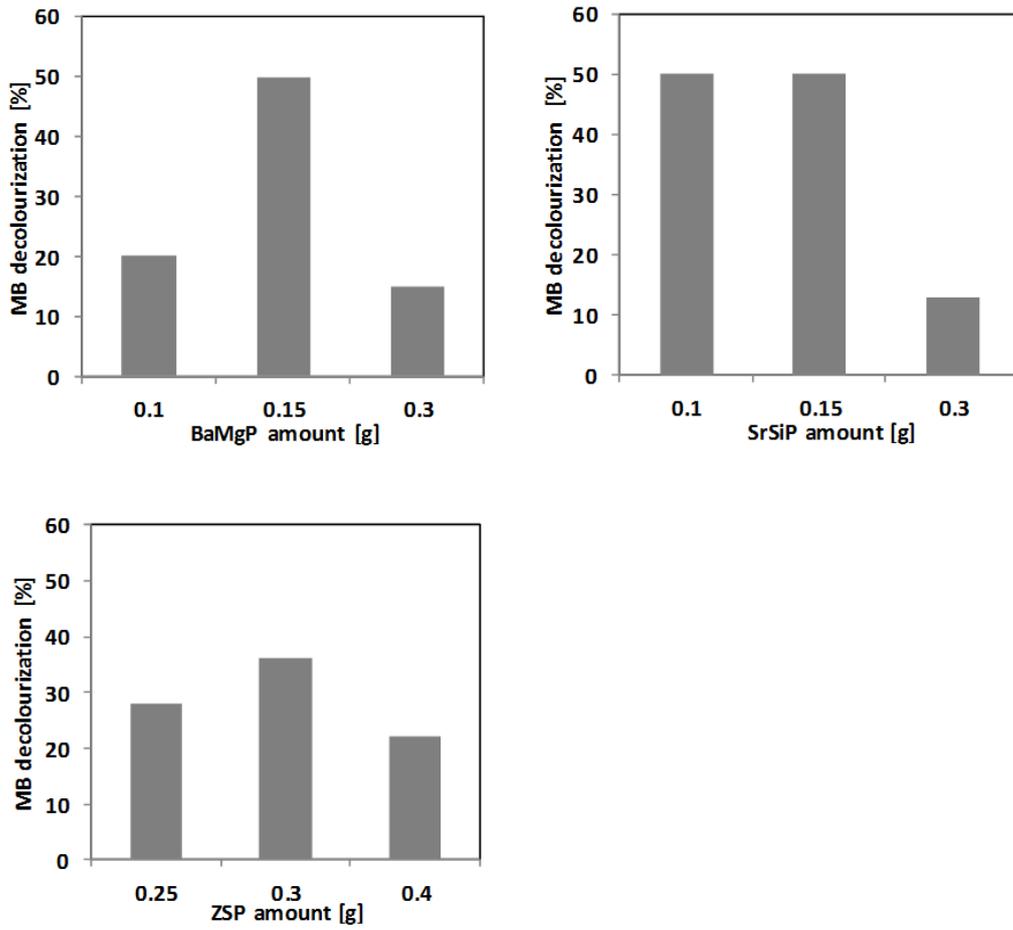


Figure 2: Evaluation of the effect of different amounts of ZSP, BaMgP and SrSiP phosphors physically mixed with N-TiO<sub>2</sub> (0.3 g) on the decolourization of MB after 30 min of UV irradiation.

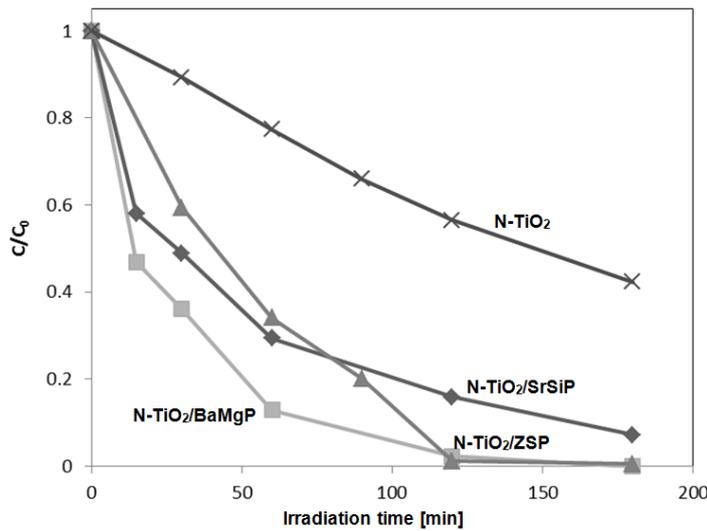


Figure 3: Comparison between photocatalytic performances of pure N-TiO<sub>2</sub> and N-TiO<sub>2</sub>/phosphors in the MB decolourization

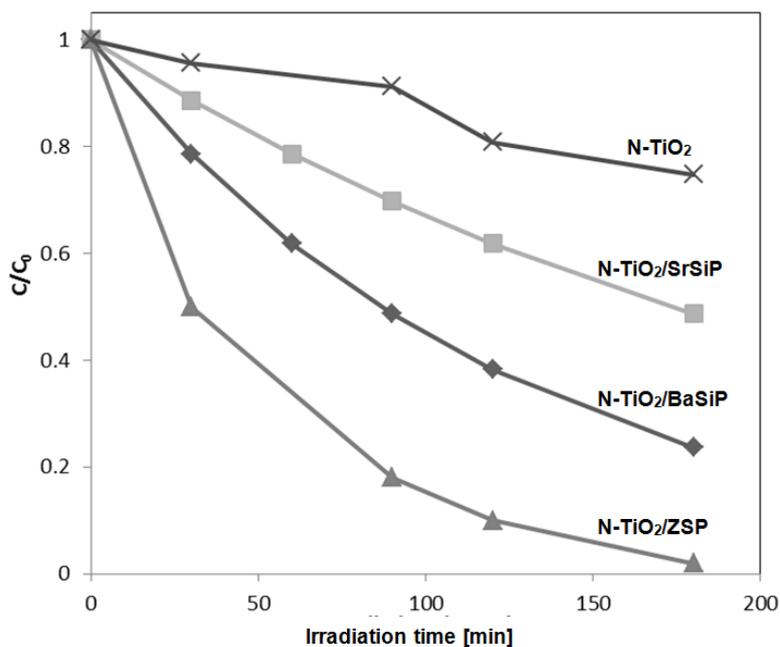


Figure 4: Comparison between photocatalytic performances of pure N-TiO<sub>2</sub> and N-TiO<sub>2</sub>/phosphors in the PHE degradation.

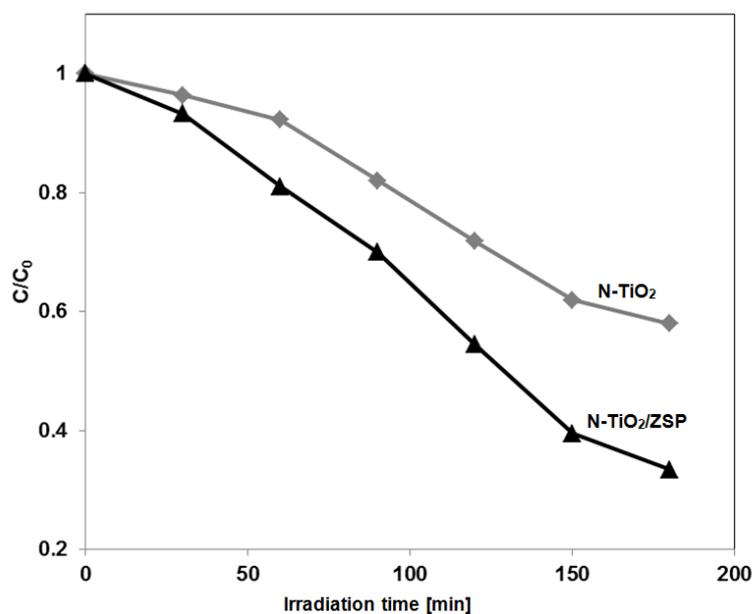


Figure 5: Photocatalytic performances of N-TiO<sub>2</sub>/ZSP and pure N-TiO<sub>2</sub> in the TPA degradation

### 3. Conclusions

Visible light-active N-TiO<sub>2</sub> photocatalyst was successfully immobilized on luminescent materials (phosphors) having all blue emission when excited by the external UV light source. The final nominal loading of N-TiO<sub>2</sub> in N-TiO<sub>2</sub>/phosphors composite was 30 wt%. N-TiO<sub>2</sub>/phosphors samples have been tested in the degradation of different organic pollutants, like methylene blue, phenol and terephthalic acid. In all cases the presence of luminescent supports for N-TiO<sub>2</sub> photocatalyst induced an enhanced photocatalytic reaction rate if compared with the results obtained with pure N-TiO<sub>2</sub>.

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