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# N-Doped ZnO Nanoparticles Supported on ZnS based Blue Phosphors in the Photocatalytic Removal of Eriochrome Black-T Dye

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Photocatalysis appears one of the most viable solutions to remove organic pollutants from wastewater. One of the limitations of commercial application of photocatalysis is the low photoreactivity. It has been reported that ZnO has better photocatalytic activity compared to $TiO_2$; however, due to the value of its band-gap energy, about 3.4 eV, it is effective only under irradiation of UV light. In order to increase the photocatalytic performances of ZnO, the doping of its crystalline structure with nitrogen could make possible the exploiting of the visible light. Moving from our finding that N-doped $TiO_2$ coupled with another semiconductor, like ZnS based phosphors (ZSP), leads to enhanced photocatalytic activity, the aim of this work was to verify the effect of coupling N-doped ZnO (N-ZnO) with ZnS-based phosphors (ZSP) in the photocatalytic removal of eriochrome black-T (EBT), used as model dye, since the latter represents more than a half of the global dye production. To get ZSP supported N-ZnO nanoparticles (N-ZnO/ZSP), a modified sol-gel method was used. The nominal content of N-doped ZnO was varied from 15 to 70 wt%.

The photocatalytic tests were carried out with a pyrex cylindrical photoreactor equipped with an air distributor device, a magnetic stirrer to maintain the photocatalyst suspended in the aqueous solution, and four UV lamps (nominal power: 32 W) with wavelength emission centred at 365 nm. ZSP phosphors emit in visible region when activated with UV light. The visible light emitted by phosphors particles is able to photoexcite N-ZnO nanoparticles supported on their surface.

Photocatalytic results showed that, on unsupported N-doped ZnO nanoparticles, total EBT discoloration was reached after 2h of irradiation, however total organic carbon (TOC) removal was only 20 %. Also ZSP particles showed ability in EBT photodiscoloration, moreover leading to a higher TOC removal (about 47 % for both cases). A very interesting result has been found with N-ZnO/ZSP catalyst with a nominal content of N-ZnO equal to 30 wt %, for which the highest photoactivity was observed, allowing to obtain both the complete EBT discoloration and the total TOC removal within the same time of UV irradiation.

## 1. Introduction

Wastewaters from textile industries contain different types of synthetic dyes, the most of which are toxic and very stable to light, temperature and microbial attack. As a consequence, they are considered recalcitrant compounds and their removal is of great concern. Although conventional chemical and biological treatments have been applied for the removal of dyes from textile wastewater, these processes have low efficiency while photocatalytic processes for removing organic pollutants from wastewater are potentially a facile and cheap alternative solution (Hoffmann et al., 1995). For many years titania ($TiO_2$) based photocatalysts have received intense attention as promising photocatalytic materials for photocatalytic and photo-electrochemical applications (Fujishima and Honda, 1972). Recently, it has been reported that ZnO has better photocatalytic activity compared to that one of $TiO_2$ (Souza et al., 2013).

Really, due to the value of their band-gap energy, about 3.2 eV for $TiO_2$ and 3.4 eV (Vaiano et al., 2015) for ZnO (Kolodziejczak-Radzimska and Jesionowski, 2014), they are effective only under irradiation of UV light. Therefore, a very important topic is the increase of photocatalytic performances of $TiO_2$ and ZnO through the doping of their crystalline structure with non-metal ions to reduce the band gap to make possible the fruitful

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absorption of the visible light (Chen et al., 2008). Nitrogen is widely used as a dopant to modify the electronic structures of oxide semiconductors due to the comparable size to oxygen and the small value of formation energy required for the substitution of O (Asahi et al., 2001).

In this regard, N doping has been also applied to ZnO with the expectation of improving the light absorption property of ZnO in the visible region (Zheng and Wu, 2009). In our previous work, we found that the doping of $TiO_2$ with nitrogen (Vaiano et al., 2015b) and coupling it with another semiconductor, like ZnS-based phosphors, have led to an enhanced photocatalytic activity (Vaiano et al., 2014). Moving from our finding that N-doped $TiO_2$ coupled with another semiconductor, like ZnS based phosphors (ZSP), leads to enhanced photocatalytic activity (Sacco et al., 2015), the aim of this work was to show the effect of engineered coupling of N-doped ZnO with ZnS-based phosphors on the photocatalytic degradation of eriochrome black-T (EBT), used as model pollutant, since the latter represents more than a half of the global dye production.

## 2. Experimental

### 2.1 Catalysts preparation and characterization

N-doped ZnO (N-ZnO) photocatalyst was prepared by sol-gel method starting from zinc sulphate (ZS) dissolved in 100 mL of deionized water and adding 30 wt % ammonia aqueous solution at with a molar ratio N/Zn=2. 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.

As support for N-ZnO, commercial ZnS-based phosphors materials (ZSP) (blue phosphors, provided by DB-Chemic, model RL-UV-B-Y, excitation wavelength: 365 nm, emission wavelength: 440 nm) were used.

To get N-ZnO supported on ZPS surface a modified sol–gel method was used. In particular, ZSP were dispersed in ZS solution and after ammonia aqueous solution at 30 wt % (with a molar ratio N/Zn= 2) was added. 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. A progressive increase of N-ZnO amount on the phosphors was realized. The content of N-ZnO on ZSP (N-ZnO/ZSP) was varied in the range 15-70 wt% to find an optimum loading. Physico-chemical characterization of samples has been performed with different techniques. 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 $[F(R\infty)\cdot h\nu]^2$ vs $h\nu$ and calculating the x intercept of a line through $0.5 < F(R\infty) < 0.8$. Laser Raman spectra were obtained at room temperature with a Dispersive Micro Raman (Invia, Renishaw), equipped with 514 nm laser, in the range 100-2500 $cm^{-1}$ Raman shift. X-ray diffraction (XRD) was carried out using an X-ray microdiffractometer Rigaku D-max-RAPID, using Cu-K$\alpha$ radiation and a cylindrical imaging plate detector.

### 2.2 Photocatalytic tests

The evaluation of the photocatalytic activity was carried out by following the decolourization and mineralization of EBT. In a typical photocatalytic test, the suspension contained 0.3 g of photocatalyst. The total solution volume was 100 mL and EBT initial concentration was 10 $mgL^{-1}$. The suspension was left in dark condition for 2 h to reach the EBT adsorption equilibrium on catalyst surface, and then UV light irradiation was performed for 2 h. The experiments were realized using a pyrex cylindrical photoreactor equipped with an air distributor device, a magnetic stirrer to maintain the photocatalyst suspended in the aqueous solution, a temperature controller and four UV lamps (nominal power: 32 W) with wavelength emission centred at 365 nm. The suspension was left in dark condition for 2 h to reach the EBT adsorption equilibrium on the catalyst surface, and then UV light irradiated the reactor for 2 h Slurry samples were collected at fixed time and analysed to determine the change of EBT concentration, measured with a Perkin Elmer UV-Vis spectrophotometer at 464 nm. TOC of aqueous solution was measured from $CO_2$ formed by catalytic combustion at T=680 °C. $CO_2$ produced in gas-phase was monitored by continuous analyzers, measuring CO, $CO_2$ (Uras 14, ABB) and $O_2$ (Magnos 106, ABB) gaseous concentrations.

## 3. Results and discussion

### 3.1 Materials characterization

The list of materials and their characteristics are reported in Table 1.

UV-Vis reflectance spectrum of N-ZnO catalyst (Figure 1) showed two absorption onsets: the first one at about 650 nm and the other one at about 450 nm evidencing the ability of N-ZnO to work in the presence of visible light irradiation. The Figure 1 shows also the photoluminescence spectrum of ZSP phosphors.

For 365 nm (wavelength of UV-lamp maximum emission) excitation, ZSP has a maximum emission at 440 nm wavelength. N-ZnO equivalent band- gap energy is 2.7 eV (Table 1).
This value implies that the activation energy of N-ZnO can be provided by the energy related to the wavelength emission of ZSP phosphors.

*Table 1: Materials and their characteristics*

| Material | Nominal N-ZnO content [wt%] | N-ZnO average crystallite size (101) [nm] | Equivalent band gap energy [eV] |
|---|---|---|---|
| ZSP | - | - | 3.1 |
| N-ZnO | 100 | 33 | 2.7 |
| 15N-ZnO/ZSP | 15 | 17 | 3.0 |
| 30N-ZnO/ZSP | 30 | 19 | 2.9 |
| 50N-ZnO/ZSP | 50 | 31 | 2.8 |
| 70N-ZnO/ZSP | 70 | 32 | 2.7 |

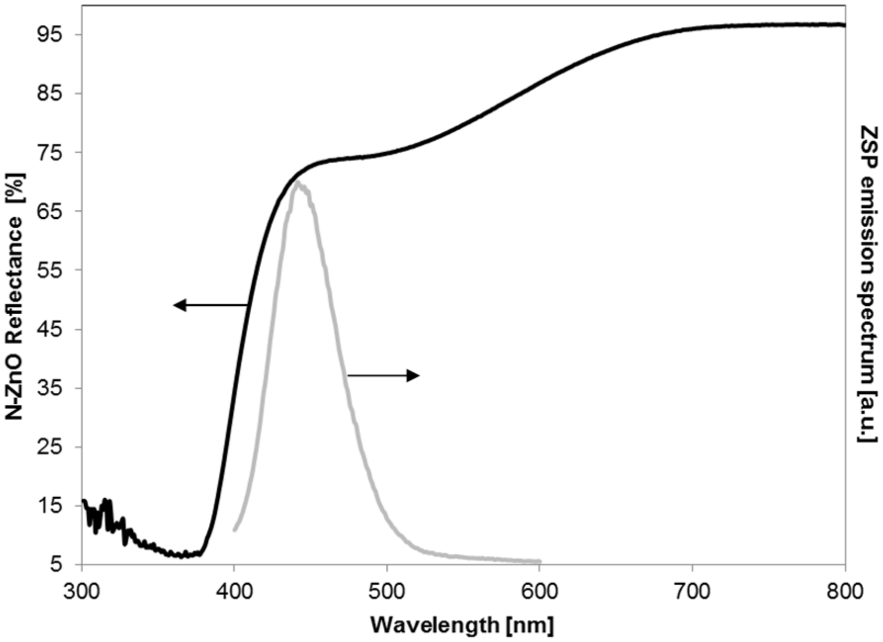

*Figure 1: UV–VIS DRS spectra of N-ZnO and emission spectrum of ZSP phosphors.*

Moreover, the increase of N-ZnO amount in N-ZnO/ZSP photocatalysts caused a decrease of band-gap values from 3.1 (band-gap of ZSP) to 2.7 eV (band gap of 70N-ZnO/ZSP), the same value of pure N-ZnO.
The Raman spectra of N-ZnO, ZSP and N-ZnO/ZSP photocatalysts are reported in Figure 2. The spectrum of phosphors (Figure 2a) displays strong signals at 352 cm$^{-1}$ and less intensive bands at 182, 220, 404, 425, 456, 619, 643 and 674 cm$^{-1}$ due to the Raman active fundamentals of ZnS (Ciambelli et al., 2011). Five bands appear in the Raman spectrum of N-ZnO: 275, 436, 508, 581 and 640 cm$^{-1}$. The band at 436 cm$^{-1}$ is attributed to the mode of undoped ZnO (Tu et al., 2006), the other signals to the presence of nitrogen as dopant for ZnO (Kerr et al., 2007).
15N-ZnO/ZSP, 30N-ZnO/ZSP, 50N-ZnO /ZSP and 70N-ZnO/ZSP samples showed all the bands related to ZSP phosphors and an additional signal at 436 cm$^{-1}$ due to ZnO. An increase of this last signal occurred by increasing the N-ZnO content (as shown in Figure 2b), indicating a progressive coverage of ZSP surface by N-ZnO. Similarly results were obtained also from XRD analysis (not shown).
The average crystallite size of N-ZnO in all the samples was calculated by Scherrer's equation using the full width at half maximum of (101) XRD peak. The average crystallite size of N-ZnO was about 33 nm, while,

when N-ZnO is supported on ZSP surface, its crystallite size was 17 nm for 15N-ZnO/ZSP and it increased up to 32 nm with the increasing the N-ZnO amount.

### 3.2 Photocatalytic activity results

In order to verify that EBT was converted by a photocatalytic reaction, blank experiments were performed. Tests carried out in dark conditions with all the investigated photocatalysts did not evidence any oxidation activity.

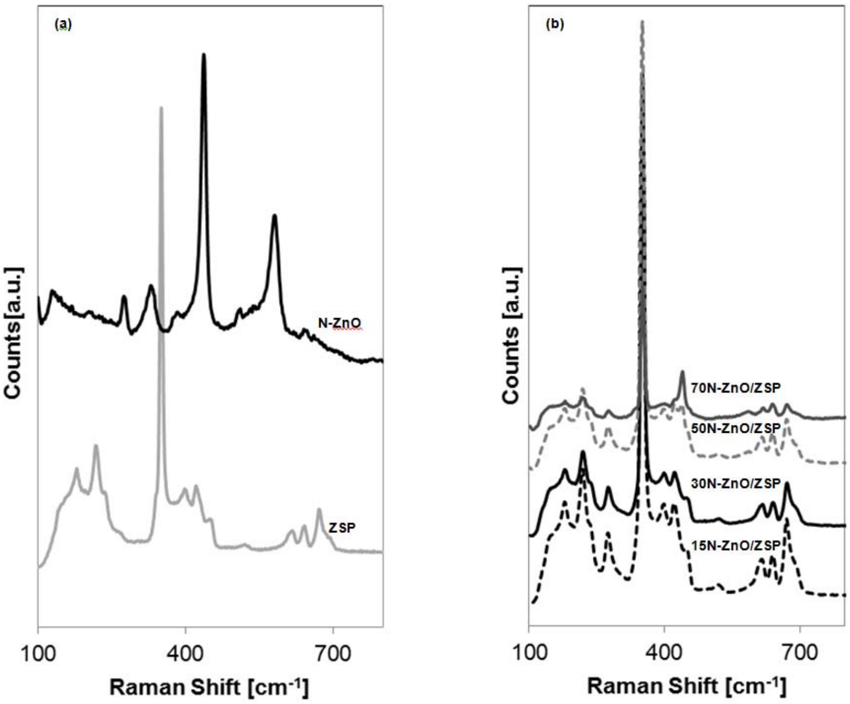

*Figure 2: Raman spectra of a) ZSP, N-ZnO, and b) 15N-ZnO/ZSP, 30N-ZnO/ZSP, 50N-ZnO/ZSP and 70N-ZnO/ZSP*

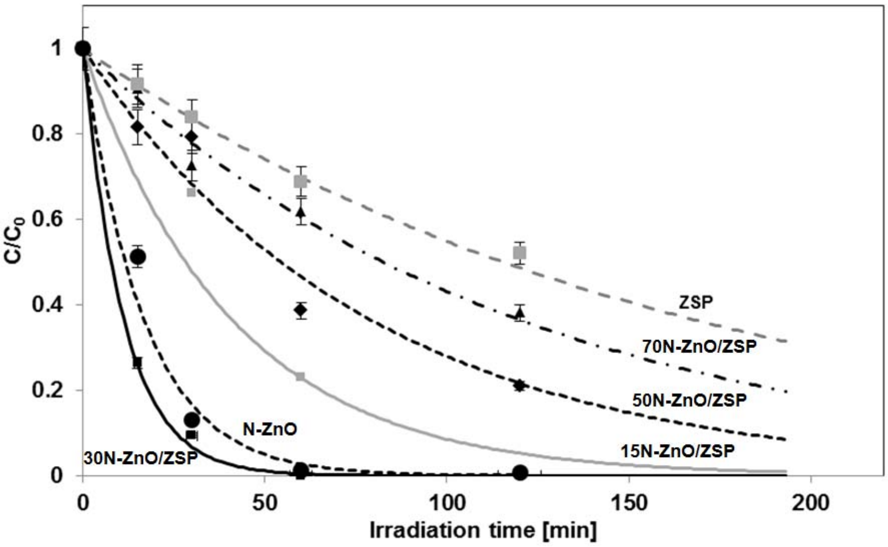

*Figure 3: Effect of the amount of N-ZnO on ZSP surface on EBT photocatalytic discoloration*

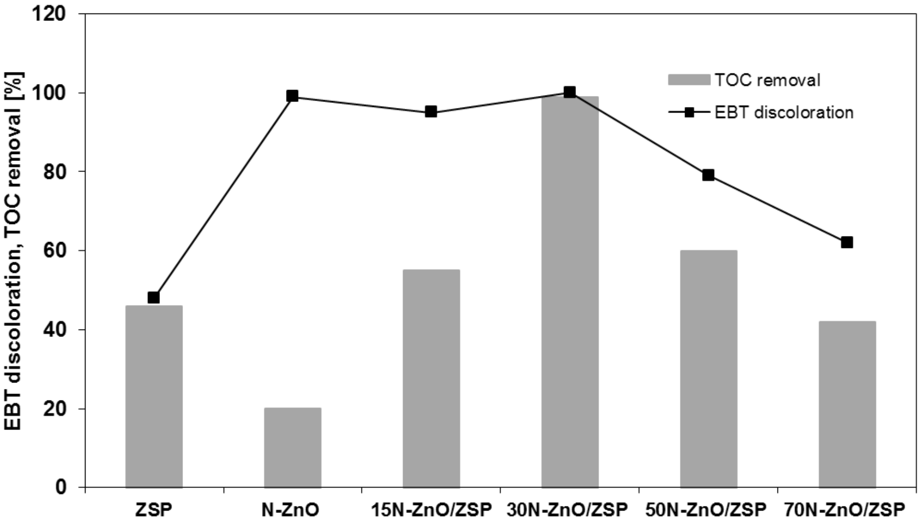

*Figure 4: Effect of the amount of N-ZnO on ZSP surface on the performances in the EBT photocatalytic discoloration and TOC removal*

Moreover, additional control tests were carried out in the presence of EBT and irradiating the photoreactor with UV lamps (photolysis reaction) and in the absence of photocatalyst. Also in this case, no degradation of the target dye was observed.

In Figure 3, the behavior of EBT discoloration on all the samples is reported. The Figure shows that ZSP alone has photocatalytic activity. It is likely due to the ability of ZSP to photogenerate surface SH group and OH radicals in the presence of water and UV irradiation (Kim and Kang, 2012). Moreover, after 60 min of irradiation EBT discoloration was 32, 77, 62 and 39 % for ZSP, 15N-ZnO/ZSP, 50N-ZnO/ZSP and 70N-ZnO/ZSP, respectively. It is very important to underline that almost total EBT discoloration was achieved after 60 min of irradiation with N-ZnO and 30N-ZnO/ZSP catalysts. However, 30N-ZnO/ZSP showed a higher photocatalytic activity with respect to unsupported N-ZnO for irradiation time lower than 60 min.

It must be always remembered that the observed discoloration of EBT does not necessary correspond to the oxidation and mineralization of the dye. For this reason, in order to determine the real effectiveness of the photocatalysts in the EBT removal, TOC analysis of liquid samples collected after 2 h of irradiation was performed.

The results are summarized in Figure 4, where TOC removal data were coupled with EBT discoloration results. It is evident that even if unsupported N-ZnO led to total EBT discoloration, the TOC removal was only about 20 % (Figure 4). Higher values of TOC removal were obtained for all other catalysts, however only with ZSP alone and 30N-ZnO/ZSP photocatalyst the same values of EBT discoloration and TOC removal were obtained. Really, while with ZSP they were only about 47 %, only in the presence of 30N-ZnO/ZSP almost total EBT discoloration together with total TOC removal was achieved. This result gives a clear evidence of the effect of coupling N-ZnO with a photoactive support, such as phosphors, to enhance the photocatalytic activity for both discoloration and mineralization.

## 4. Conclusions

Nitrogen doped ZnO (N-ZnO) photocatalyst was supported on ZnS based phosphors (ZSP) via sol-gel routine. N-ZnO nanoparticles of small crystallite size were deposited on the surface of ZSP with N-ZnO loading varying in the range 15-70 wt%. With the increase of N-ZnO loading, the size of primary nanoparticles on the ZSP support increased, being always smaller than that of pure N-ZnO.

The catalytic results showed that N-ZnO/ZSP photocatalysts are very efficient to remove eriochrome black-T dye (EBT) under UV irradiation. The photocatalyst N-ZnO/ZSP with N-ZnO loading of 30 wt% was the most active, allowing to achieve the almost complete EBT discoloration together with total TOC removal after 2 h of UV irradiation. This study gives a clear evidence of the photocatalytic activity enhancement due to the innovative catalyst formulation consisting of ZSP phosphors as support for visible light-active ZnO. The resulting effect is due to the utilization by N-ZnO of the re-emitted radiation by ZSP after its excitation by UV source. The combined effect of the two catalyst components opens novel perspective on the route towards enough high performance in advanced oxidation processes based on photocatalysis.

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