



Short communication

Photocatalytic activity of TiO₂ nanopowders supported on a new persistent luminescence phosphor

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ARTICLE INFO

Article history:

Received 11 September 2015

Received in revised form 29 October 2015

Accepted 30 October 2015

Available online 31 October 2015

Keywords:

TiO₂ nanoparticle

Persistent luminescence material

Photocatalysis

Methylene blue degradation

ABSTRACT

TiO₂ nanoparticles were supported on a new persistent luminescence (3ZnO:Ga₂O₃:2GeO₂):Cr³⁺ material. The sample was characterized by means of X-ray powder diffraction, scanning electron microscopy and radioluminescence. The photoactivity was evaluated for the degradation of methylene blue (MB) in aqueous solution especially in the darkness. A MB photodegradation occurred also in the absence of an external illumination. In fact, the persistent luminescence material stores and provides the necessary photons to the TiO₂ allowing the photocatalysis process even in the darkness.

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1. Introduction

Photocatalysis is an extremely fascinating field which has several applications, especially in the removal of pollutants in aqueous matrix and air [1–4], or for its antibacterial action [5–8]. Probably, the most used photocatalytic agent is the titanium dioxide in nanometric sizes. In order to activate the degradation process, the photocatalyst requires photo-excitation with light of appropriate wavelength, namely of energy equal to or greater than the band gap of the semiconductor. Thus, as a result of irradiation, the TiO₂ particle can behave either as an electron donor or acceptor for molecules in contact with the semiconductor. The greatest issue is the right choice of the radiation that best fits the absorption spectrum of the TiO₂ and increases its efficiency. Generally, TiO₂ has maximum adsorption in the UV region, at about 380 nm; consequently the direct use of the sunlight, the most available and cheaper radiation which can be chosen, does not allow to reach good results (UV in natural sunlight represents only 5%–8% of the solar spectrum). Therefore, several studies aimed at shifting the light absorption towards visible light and/or to increase the lifetime of the produced electron–holes pairs [9–12].

As an alternative route for the mentioned increase of efficiency, Zhang et al. [13] proposed to support the TiO₂ on a persistent luminescence material to allow the photocatalysis process also in the darkness. Specifically, exploiting the light stored inside the luminescent material

and using it as the irradiation source for the TiO₂ excitation. The persistent luminescence (PeL) materials are a peculiar class of compounds which can emit light even after the external excitation has been removed. PeL is a phenomenon often confused with the phosphorescence even if only at the macroscopic level they can be considered similar [14]. Generally speaking, a PeL material possesses an emission after the cessation of the excitation due to the peculiar capability to store the light adsorbed and to release it gradually; the emission duration varies according to the compounds but, in the most performing samples, it can reach several hours, e.g. in SrAl₂O₄:Eu²⁺, Dy³⁺ [15], in Zn₃Ga₂Ge₂O₁₀: Cr³⁺ [16] and Gd₂O₂CO₃:Yb³⁺ [17].

Although the combination of PeL phosphors and photocatalysts allows the photocatalysis without an external stimulation, very few reports are reported on this new peculiar class of materials [18]. Interesting results have been reached in the reduction of NO_x and gaseous benzene coupling the TiO₂ with BaAl₂O₄:Eu, Dy [19], CaAl₂O₄:Eu, Nd [20,21], and Sr₄Al₁₄O₂₅:Eu, Dy [22]; García et al. have documented an enhanced photodegradation activity supporting TiO₂ on bismuth doped strontium aluminates [23].

In this work, the TiO₂ has been supported on the new (3ZnO:Ga₂O₃:2GeO₂):Cr³⁺ matrix which was synthesized in a different way, from what was previously described in the literature [16], inducing a PeL in the sample which starts from very low wavelength. Exploiting the light stored in the PeL materials the photocatalytic activity, tested as degradation of the methylene blue in water, was studied not only under sunlight stimulation but also in absence of external excitation source.

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2. Experimental

2.1. Samples preparation

Three different materials have been synthesized. Sample A: $(3\text{ZnO}:\text{Ga}_2\text{O}_3:2\text{GeO}_2):1\% \text{Cr}^{3+}$; Sample B: TiO_2 ; Samples C, D and E: formed by B supported on A. For the specific synthesis see Supplementary data.

2.2. Photocatalytic tests (light and light/darkness)

Different kinds of methylene blue (MB) degradation tests were carried out in different conditions of external light exposure. During the Experiment L a lamp was kept always on; on the contrary during the Experiment L5/D and the Experiment L10/D different cycles in which, respectively, 5 and 10 min of light were alternated with 10 min of darkness, were performed. The aim of the Experiment L/D was to evaluate if a photocatalytic activity was still present also in the darkness thanks to the presence of the persistent luminescence material. For further information see Supplementary data.

3. Results and discussion

All the synthesized samples were crystalline as demonstrated by XRD diffraction patterns (Fig. S1). The morphology of the particles was investigated through SEM analyses (Figs. S2 and S3). The Sample A had an inhomogeneous distribution of size and morphology, probably due to the performed solid state synthesis, that hampers an accurate control on these parameters. It is remarkable how the luminescent properties of the materials are not affected by the morphology, especially at micrometric level [24]. On the contrary, it was demonstrated [25,26] how the catalytic performances of TiO_2 decrease dramatically, increasing the particles sizes. The sol gel method allows the synthesis of catalytic nanoparticle with suitable dimension in order to obtain photoactivity, as demonstrated in our previous work [27]. The Sample C (Fig. 1) was confirmed to be formed by the TiO_2 particles supported on the Sample B surface: SEM-EDS investigation (Fig. 1 and for EDS see Fig. S4) showed the presence of the clearly detectable titanium signal; the XRD pattern of the Sample C was composed of the sum of spectra of Samples A and B (Fig. S1C). To investigate the specific surface areas, BET analyses were performed for Samples B and C. The TiO_2 nanoparticles had a surface area equal to $88.64 \pm 0.01 \text{ m}^2/\text{g}$; supporting them on the phosphor a notable decrease in the surface has been occurred, reaching the value of $4.49 \pm 0.01 \text{ m}^2/\text{g}$ (Sample C). Noteworthy that a so low surface area, respect to the unsupported nanoparticles, can be correlated to the ceramic nature and to the micrometric size of the phosphor.

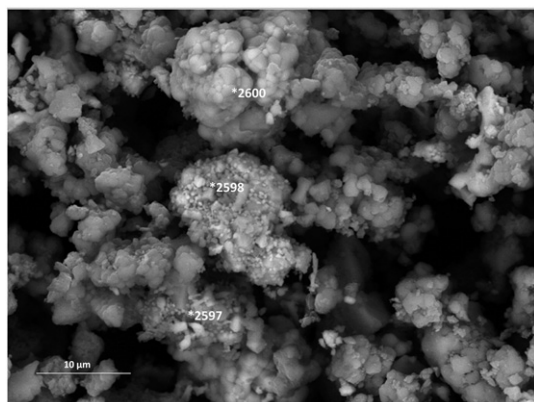


Fig. 1. SEM image of Sample C (magnification: $\times 2.50 \text{ K}$, HV: 20 KV).

The luminescent properties of Sample A were measured through radioluminescence (RL) and PeL. Two different peaks were detected: a narrow one was centred at $\sim 700 \text{ nm}$, inducing a red luminescence, and a second broad emission which practically covered all the visible range of electromagnetic spectrum. Consequently the emission from $\sim 350 \text{ nm}$ to $\sim 850 \text{ nm}$ induced a white emission in the sample (Fig. 2). Moreover, a white persistent luminescence was measured, which was visible by eye for about 15 min but could be instrumentally easily detected still after 30 min. This last property has been exploited to obtain the photocatalytic activity also in the absence of an external light source, substantially in the darkness.

Regarding the photocatalytic activity of TiO_2 on the MB decomposition, it was reported that the kinetic degradation of the dye follows a first order mechanism, ascribed to the equation: $\ln(C_0/C) = -k\Delta t$ [28], and that a complete mineralization of the colourant occurred [29,30].

Three different experiments have been performed: in the first the MB degradation has been conducted under the light always on for 70 min in total (Experiment L); in the subsequent tests a “dark” phase of 10 min was introduced, followed by a “light” phase respectively of 5 min (Experiment L5/D) and 10 min (Experiment L10/D). Through the latter it was possible to evaluate if the light emitted by the phosphor induced the photodegradation by the action of TiO_2 even in the dark interval, practically without external illumination. In order to evaluate the possible MB adsorption on the samples, a test in the darkness has been performed which showed how a very low amount of the dye has been absorbed. In particular the capture of MB occurred mainly in the first 20 min with an amount, respectively, of 0.5% for A and C and of 2.5% for B; these values remain essentially unchanged in the subsequent 50 min of stirring. Consequently the equilibrium phase prior to each experiment was set to 20 min. Moreover, it has been evaluated also the effect of the lamp on the MB solution. In this case the degradation occurred mostly in the first 30 min of light exposure reaching a reduction of the dye equal to 13% after 70 min (Fig. S4). Hence all the experiment yields have been calculated taking into account the degradation induced by the illumination, obviously depending on the time exposure. For the experiments conducted with the Sample A the degradation was estimated to be induced only by the lamp; consequently data correlated with Sample A are omitted in the explanation of the results because of no significant degradation has been evaluated.

Fig. 3.1 reports, during Experiment L, the MB percentage degradation using the Sample B and C. The former showed a MB removal equal to 66% after 70 min; the latter possesses a higher efficiency reaching a value of degradation equal to 79% (noteworthy that the overall reduction considering also the lamp contribution is major than 90%). The efficiency increase using the Sample C, which however has a lower surface area respect to B and consequently in principle a lower activity, was induced by the luminescent material; in fact, the TiO_2 is supported on the phosphor which plays as an “internal” light enhancing the nanoparticles excitation. This hypothesis is in accord with García et al. [23] that observed a better photoactivity of TiO_2 when it was supported on a persistent luminescence material. The inset in Fig. 3.1 reports the experimental degradation during the first 8 min of reaction; as shown the order of activity of Sample B and Sample C is reversed after about 5 min, indicating that the PeL material needs an enough time for charging after which emits sufficient photons to increase the photodegradation efficiency.

Yields significantly lower with respect to the previous test were obtained during Experiment L5/D: the MB degradation was estimated to be 34% for Sample B and only 25% for Sample C. The curves followed a typical step-by-step behaviour (Fig. S5) induced by the introduction of the “dark” phase. It is clear how during these intervals, so without an external stimulation, no photoactivity can be induced both in Sample B and C. While this is obvious in the case of Sample B because of the TiO_2 works only in presence of light, on the contrary for the Sample C the experiment suggested that the light interval of 5 min was not enough

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