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Original

ZnO nanoparticles with high degradation efficiency of organic dyes under sunlight irradiation / Sanna, Vanna; Pala, Nicolino; Alzari, Valeria; Nuvoli, Daniele; Carcelli, Mauro. - In: MATERIALS LETTERS. - ISSN 0167-577X. - 162:(2016), pp. 257-260. [10.1016/j.matlet.2015.10.031]

Availability:

This version is available at: 11381/2807711 since: 2021-09-30T17:58:39Z

Publisher:

Elsevier B.V.

Published

DOI:10.1016/j.matlet.2015.10.031

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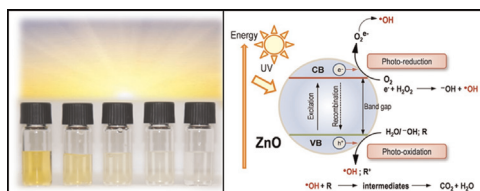
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Graphical Abstract

ZnO nanoparticles with high degradation efficiency of organic dyes under sunlight irradiation

Materials Letters ■ (■■■■) PP. 1–3

Vanna Sanna, Nicolino Pala, Valeria Alzari, Daniele Nuvoli, Mauro Carcelli



Highlights

- ZnO nanoparticles were fabricated by a simple and low cost precipitation method.
- Photodegradation activity of organic dye was evaluated under artificial sunlight.
- Nanoparticles possess excellent photocatalytic activity under sunlike irradiation.
- ZnO nanoparticles can be reusable because showed good recycling performance.
- Nanoparticles could be applied as low cost and a highly sunlight-active material.



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ZnO nanoparticles with high degradation efficiency of organic dyes under sunlight irradiation

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ARTICLE INFO

Article history:

Received 28 July 2015

Received in revised form

3 October 2015

Accepted 7 October 2015

Keywords:

ZnO

Nanoparticles

Sunlight

Photocatalysis

ABSTRACT

ZnO nanoparticles were fabricated by a simple and low cost precipitation method as photocatalytic agents for decomposition of dyes under solar light exposure. Q2

The ZnO nanoparticles showed excellent photodegradation efficiency and good recycling performance, supporting the potential application as economical and a highly sunlight-active material to treat wastewater containing azo dyes.

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1. Introduction

In order to decrease the damage caused by dye pollution to environment and human, the use of photocatalysts to convert organic compounds in contaminated water into nontoxic chemicals has been extensively investigated [1,2].

Recently, titanium dioxide (TiO₂) and zinc oxide (ZnO) nanoparticles are emerged as successful alternatives to conventional methods for the degradation of non-biodegradable pollutants [3,4]. TiO₂ is the most studied and used owing to its chemical and thermal stability, low cost, and nontoxicity. The basic principle of semiconductor photocatalysis involves photogenerated electrons and holes migrating to the surface that reduce and oxidize the adsorbed reactants, leading to the pollutant decomposition [5]. However, two types of defects limit the photocatalytic reactivity of such material: the excitation/activation by high energy UV irradiation and a low quantum yield rate, which resulted from a low rate of electron transfer to oxygen and a high rate of recombination between excited electron/hole pairs [6]. The electron–hole pairs can be formed by UV light at wavelength shorter than 387 nm, thus, only a small portion of the solar spectrum can be used for photooxidation reaction using TiO₂ [7]. In order to absorb visible light by increasing the charge separation and thus improve

the photodegradation, TiO₂ was doped by metal ions [8]. Besides, band gap narrowing of TiO₂ can be better achieved by using anionic dopants that enhance the thermal stability of catalyst [9].

In this scenario, ZnO nanoparticles have been emerged as a valid alternative to TiO₂ for the photodecomposition of organic pollutants and dyes [10,11], due to their ability to generate H₂O₂ more efficiently than TiO₂. This is directly related to a larger number of active sites with high surface reactivity [12], the relatively high band gaps (3.3 eV) at room temperature and the large exciton binding energy (60 meV). ZnO absorbs over a large fractions of solar spectrum than other photocatalysts, and remove organic contaminants under visible irradiation [13]. ZnO nanoparticles can be synthesized by various approaches [14], but the obtained nanoparticles are prone to aggregate due to the large surface area and high surface energy. In spite of this, and in order to also improve their water dispersion [15], other methods for the preparation of ZnO are expected.

Herein, we proposed a simple and economical precipitation method to prepare stable ZnO nanoparticles as catalysts with high photodegradation capacity under solar light irradiation and good recycling performance.

2. Experimentals

The detailed experimental procedures are described in Supporting information.

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<http://dx.doi.org/10.1016/j.matlet.2015.10.031>

0167-577X/© 2015 Published by Elsevier B.V.

3. Results and discussion

ZnO nanoparticles with a mean diameter of 41.7 ± 8.2 nm, PI of 0.132 ± 0.04 (Fig. 1a), and spherical shape (Fig. 1b) were successfully prepared by a modified precipitation method [16].

The XRD pattern of the nanoparticles (Fig. 1c) can be well indexed to hexagonal wurtzite structural ZnO (JCPDS card no. 36-1451). The average crystalline size, calculated from the XRD pattern by using the Debye-Scherrer formula [17], was found to be 36 nm.

As shown in Fig. 1d, the exciton absorption at 378 nm represents the characteristic single peak of hexagonal ZnO nanoparticles [18]. The calculated E value was 3.4 eV, very close to the band gap of intrinsic ZnO powder [19].

Fig. 2a shows typical UV-Vis spectrum of methyl orange (MO, 10 mg/L), in the presence of ZnO catalyst (100 μ g/mL) at different irradiation times. As it can be seen, the intensity of the peak at 462 nm progressively decreases until it disappears almost completely within 60 min irradiation time. Furthermore, without the presence of either catalyst or the UV radiation, for all considered times, any change in the absorbance values was not observed. These results can be explained based on the large band gap value that delays the process of electron-hole recombination, which significantly increases the photocatalytic activity [1,20].

To determine the effect of catalyst loading, the experiments were performed without ZnO, and in the presence of different catalyst concentrations (0.05–0.75 mg/mL) for a fixed dye solution (10 mg/L), at pH 9.0, for 2 h. As depicted in Fig. 2b, both in the darkness and in the absence of ZnO the MO photodegradation was negligible. Conversely, the photocatalytic ability of the nanoparticles is strongly related to the increasing of catalyst-loading such as to the irradiation time. The MO degradation resulted of

47%, and 82%, in the presence of 0.05 and 0.1 mg/mL of ZnO, respectively, after irradiation for 60 min. At higher ZnO concentrations, the complete MO decolorization has been reached within 45 min. The increase of the photocatalyst loading determines an increased number of active sites and, consequently, leads to enhanced production of $\text{OH}\bullet$ radicals, increasing the percentage of photodegradation [21]. On the other hand, the increase of ZnO concentration over 0.25 mg/mL does not determine a linear increase in photocatalytic efficiency, due to a decrease in UV light penetration as a result of light scattering effect.

To study the pH effect on the decolorization efficiency, experiments were performed in pH range 3–11, at a constant dye concentration (10 mg/L), and catalyst loading of 0.1 g/L, for 60 min. With the enhance of the pH from 3 to 5 a fast increase of decolorization was observed (from 66.2% to 80.4%), followed by a gradually increase at pH 7 (85.5%), and the maximum value at pH 9 (90.3%) (Fig. 2c). A further increase to pH 12, instead, determined a reduction of degradation efficiency (82%) related to zero point charge of ZnO (9.0 ± 0.3). More specifically, below pH 9, the ZnO surface is positively charged and covered by the dye molecules. Above this pH, the surface, negatively charged by adsorption of hydroxide ions, favors the formation of $\text{OH}\bullet$, thus enhancing the photodegradation efficiency [1,20].

The influence of initial MO concentration on the degradation efficiency was studied by varying the dye concentration (5.0–25.0 mg/L), under pH 9, and ZnO nanoparticles (100 μ g/mL) as constant, until 120 min of irradiation time. With the increase of initial dye concentration, the degradation decreases remarkably (Fig. 2d). After 60 min, the decolorization efficiencies were found 53.6, 62.4, 76.8, 82.3, and 86.6% for MO concentration of 25, 15, 10, 7.5, and 5.0 mg/L, respectively. The almost complete degradation of MO occurred at 120 min for the highest MO concentrations,

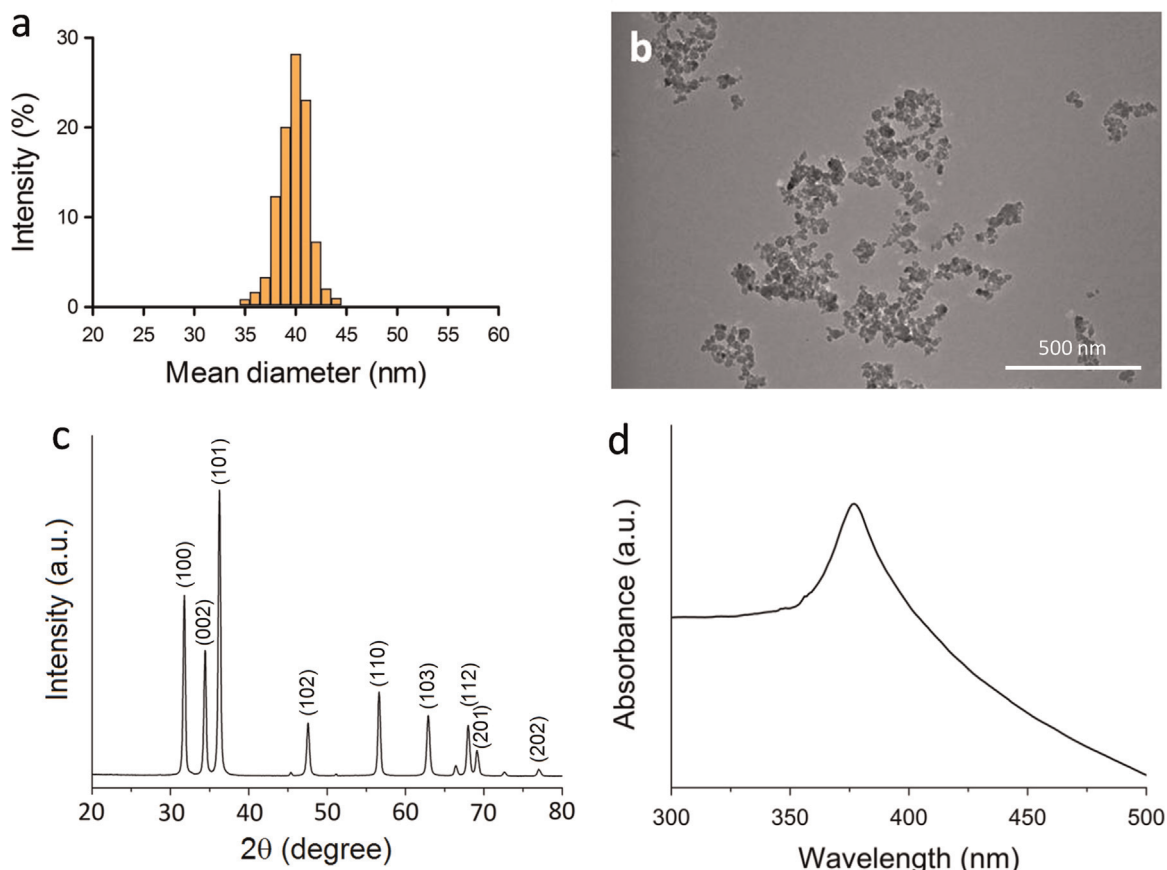


Fig. 1. (a) Particle size distribution, (b) TEM image, (c) XRD pattern, and (d) UV-vis spectrum of ZnO nanoparticles.

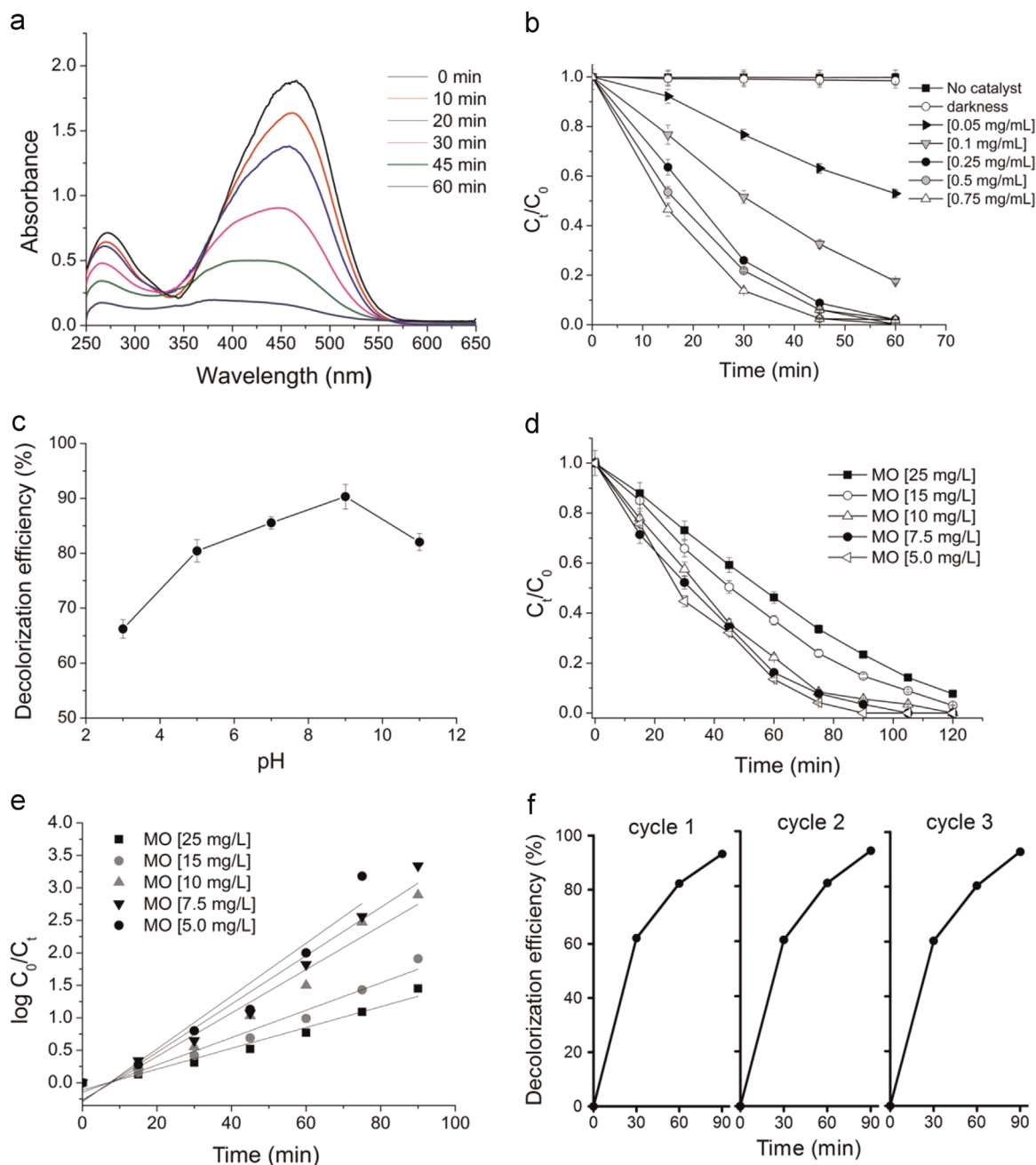


Fig. 2. (a) UV-vis spectrum of MO solution (10 mg/L) as a function of irradiation time in the presence of ZnO nanoparticles (0.1 mg/mL); (b) Influence of the ZnO nanoparticles concentration on decolorization of MO solutions for 60 min of exposure; (c) Influence of the pH on decolorization of MO solutions in the presence of ZnO nanoparticles (0.1 mg/mL); (d) Influence of the MO concentration on decolorization rate in the presence of ZnO nanoparticles (0.1 mg/mL); (e) Linear variation of $\log C_0/C_t$ vs time for the photocatalytic degradation of MO at different initial concentrations (5.0–25 mg/L) in the presence of 0.1 mg/mL ZnO nanoparticles; (f) Comparison of decolorization of MO solution (10 mg/L) and in three successive cycles of exposure (ZnO nanoparticles 0.1 mg/mL; under pH 9).

after 90 min for 10 and 7.5 mg/L concentrations, and 75 min for lowest dye concentration (5 mg/L).

As previously reported, the high MO concentration determines a competition between dye and OH^- ion adsorption on the catalyst surface. The presence of dye depresses the OH^- ion adsorption, resulting in the reduction on the OH^\bullet formation. Additionally, with increased dye molecules the solution became more intense colored and the path length of photons entering the solution decreased [1,2].

To date, only a handful studies have been attempted to evaluate the photodegradation efficiency of ZnO catalysts for organic MO dye under solar light exposure. It is reported that ZnO photocatalyst at a dose of 1 g/L, determined a complete degradation of

25 mg/L MO solutions within 90 min [22]. Interestingly, at the same MO concentration and time, we found 77% of decolorization efficiency by using a catalyst dose ten times lower (10 mg/L), suggesting an excellent photodegradation activity of fabricated nanoparticles.

To obtain the reaction kinetics, the $\log C_0/C_t$ vs the irradiation time was plotted, giving straight lines that indicate first order reactions (Fig. 2e). The corresponding parameters k and the correlation coefficient (R) of the decolorization process are summarized in Table 1. According to literature, the reaction rate constant decreases with increasing initial dye concentration [7]. The organic MO is first adsorbed on the surface of the nanoparticles and then the degradation occurs under irradiation. As the initial

Table 1
Pseudo-first order apparent constant values for the different initial concentrations of MO.

MO concentration (mg/L)	k (min^{-1})	R^2
25	0.0160	0.9741
15	0.0210	0.9718
10	0.0334	0.9617
7.5	0.0372	0.9649
5.0	0.0408	0.9333

concentration of MO increases, the molecules aggregate on the catalyst surface resulting in quenching of the excited molecules [8].

As illustrated in Fig. 2f, the photodegradation efficiency shares an overlapping behavior in each of the successive cycles, suggesting that nanoparticles were reusable and retain a good photodegradation efficiency.

4. Conclusions

In this study, ZnO nanoparticles have been obtained by a simple and low cost precipitation method.

Results demonstrated the importance of modulating the optimum degradation parameters, and the ability to setup a favorable combination suitable to obtain a high degradation rate. ZnO nanopowders possess excellent photocatalytic activity under sun-like irradiation for decolorization of MO, and retain a good recycling performance, suggesting that may be applied as an economical and highly sunlight-active material to treat wastewater containing azo dyes.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.matlet.2015.10.031.

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