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Tailored routes for home-made Bi-doped ZnO nanoparticles. Photocatalytic performances towards *o*-toluidine, a toxic water pollutant

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ABSTRACT

Herein we report the photodegradation of highly toxic *o*-toluidine in aqueous media (under UV irradiation), by using home-made bare and bismuth-doped ZnO nanoparticles. The latter powder was prepared by both a traditional impregnation method and by an innovative sol-gel synthesis, obtained using bismuth nitrate as precursor. Moreover, synthetic conditions (such as zinc salts and medium acidity) were varied in order to obtain different semiconductor nanopowders with diverse physico-chemical properties and, hence, photocatalytic performances. Both the disappearance and the mineralization of the pollutant molecule were followed by Linear Sweep Voltammetry and Total Organic Carbon techniques, respectively. Photocatalysis by-products were then identified by HPLC–MS (on eluates, after 3 h and 6 h) and ATR-FTIR (on used nanopowders) analyses. Thus, a new photodegradation pathway (with azo dimer derivatives in the first step) has been proposed. Bi-impregnated samples show high degree of mineralization, reducing the stability of the intermediates.

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1. Introduction

In the recent years, environmental remediation has become one of the most important topic of the actual scientific debate [1,2]. Especially due to human activity, we are witnessing to an exponential increase of pollutants concentration all over the world [3,4]. Indeed, several pollutants have been recognized as toxic agents, especially due to prolonged exposition. Among them, the aromatic amine, *o*-toluidine, is one of the substances recognized by the World Health Organization (WHO) with high genotoxic and carcinogenic properties for humans [5,6], declared to be a hazardous compound for both animals and environment [7,8]. Its presence in indoor and outdoor surroundings has to be related to its use as precursor for azo-dyes [9], in rubber industries and in pharmaceutical production [10]. Thus, both the monitoring and the decreasing of its concentration have become a fundamental research topic, in order to assure the maximum level of exposure for humans and reduce the risks related to its release.

The present work focused on the *o*-toluidine removal by means of photocatalytic processes. Actually, literature is plenty of studies about the use of photocatalysis (one of the main Advanced Oxidation Processes, AOPs) for the degradation of several organic pollutants [11–16]. An et al. [17] reported a study concerning the *o*-toluidine photoremoval by using TiO_2 thin films in the gas phase, under UV irradiation (with degradation efficiency of 98.7%). Moreover, *o*-toluidine photodegradation was already studied by our research group under UV/solar irradiation, with the adoption of bare and doped commercial zinc oxide photocatalysts [18,19]. Indeed, ZnO is a semiconductor whose properties are second only to TiO_2 [20] and it is characterized by high photosensitivity, low cost and no toxicity [21,22]. In the present work, the attention has been focused on the role played by bare and Bi-doped home-made ZnO nanoparticles on the *o*-toluidine photodegradation, reducing the gap between removal and mineralization percentages. All the

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powders were firstly synthesized by a sol-gel method, evaluating how structural, morphological, optical and surface properties can be influenced by changing the zinc precursor (zinc acetate or nitrate) and the acidity of the medium (nitric acid). Then, the nanopowders were further modified adding a dopant to increase their solar light adsorption (composed only by 5% of UV component) and hence to improve the photocatalytic performances for in situ applications. Several articles [18,23–25] have demonstrated the ability of bismuth dopant to reduce the band gap of semiconductors, shifting the adsorption edge of the pure semiconductor and thus modifying the separation rate of photoinduced charge carriers. Before appreciating the possible improvement under solar light due to the presence of bismuth, a detailed study about the photocatalytic performances of bismuth-doped nanopowders was done under UV light. Therefore, Bi-doped samples were both prepared by traditional impregnation method and by modification of the sol-gel route, introducing a bismuth precursor (bismuth nitrate) directly in the synthetic path.

All the as-synthesized nanopowders were then tested as photocatalysts, monitoring both the disappearance (by means of Linear Sweep Voltammetry (LSV), as already reported in our previous work [19]) and the mineralization degrees (by means of Total Organic Carbon (TOC) technique). Finally, the by-products identified by both HPLC/MS techniques on eluates (3 h and 6 h) and FTIR analyses on used powders (after 6 h of photocatalysis process) have allowed the proposal of a possible mechanism for *o*-toluidine photoremoval, expanding the mechanism reported in the recent literature [17,19].

2. Material and methods

All chemicals were of reagent grade purity and were used without further purification; doubly distilled water passed through a Milli-Q apparatus was used to prepare solutions and suspensions.

2.1. Synthesis of bare and Bi-doped ZnO nanoparticles via sol-gel route

In this work we adopted a sol-gel method, previously optimized in our laboratory [19] for both bare and bismuth-doped ZnO samples, based on the adoption of two different zinc precursors: zinc acetate, $Zn(CH_3COO)_2{\cdot}2H_2O$ (Z_Ac compounds) and zinc nitrate, $Zn(NO_3)_2{\cdot}6H_2O$ (Z_N compounds). A general synthetic procedure can be summarized as follows: the suitable amount of zinc salt was dissolved under vigorous stirring (at 300 rpm) into the appropriate solvent (*i.e.* ethanol or water for Z_Ac and Z_N, respectively) and at different temperatures, accordingly to the reagent used (Table 1). In the case of zinc acetate a cooling step in water/ice bath (T ~5 °C) comes after, for 5 min. Then, a suitable amount of 0.5 M NaOH (Table 1, 5th column, always in excess with respect to Zn salt) was slowly added to the Zn^{2+} aqueous solution to reach a pH around 9. The obtained whitish colloid was continuously stirred for 24 h and subsequently centrifuged and washed several times by the appropriate solvent (the same used for the synthesis). Then, all the powders were dried in an oven at 90 °C for a night and calcined at 300 °C for 6 h under O_2 stream (9 NL/h).

Table 1
Synthetic conditions adopted for both bare (acidic and not) and Bi-doped ZnO samples.

Sample	mol				T/°C
	Salt	Solvent	HNO_3	NaOH	
Z_Ac	0.015	3.4	–	3.4	80
Z_N	0.050	5.6	–	3.4	25
Z_AcH	0.015	3.4	0.10	11.4	80
Z_NH	0.050	5.6	0.10	14.0	25
Z_AcH_Bi	0.015	3.4	0.14	11.4	80
Z_NH_Bi	0.050	5.6	0.12	14.0	25

As concerns Bi-doped samples, a new synthetic route was adopted to introduce Bi-dopant directly into ZnO lattice, instead of the common impregnation method [18]. Thus, the suitable amount of bismuth nitrate ($Bi(NO_3)_3{\cdot}5H_2O$) was utilized to have Bi/Zn atomic ratio equal to 0.01 (as the most performing dopant percentage [18]). To avoid the poor solubility of the bismuth salt in both solvents (ethanol and water, used in the sol-gel method for pure samples), acidic synthetic conditions (HNO_3 65%wt, see Table 1) were adopted. Therefore, the protocol previously reported was modified in two points: *i*) the addition of nitric acid in the initial solution of the zinc salt (so that the final concentration of HNO_3 is equal to 0.5 M) and *ii*) the addition of the bismuth acidic solution before NaOH (0.5 M, Table 1). The as-prepared Bi-doped ZnO compounds were labeled as Z_AcH_Bi (from zinc acetate) and Z_NH_Bi (from zinc nitrate), respectively.

Moreover, due to the addition of nitric acid in both zinc salt solutions, two further syntheses were carried out to obtain pure zinc oxide, in order to understand if acidic conditions could modify the properties of bare compounds. Thus, the ZnO nanopowders were prepared using the same procedure described above with the quantities reported in Table 1. These samples were respectively named as Z_AcH and Z_NH.

2.2. Synthesis of Bi-doped ZnO via impregnation

In order to deeply study the role of the bismuth doping procedures on the properties of the synthesized photocatalysts, Z_Ac and Z_N calcined samples were also doped by impregnation method. Indeed, according to what already reported in the literature [26], Bi^{3+} cannot exist in aqueous solutions at pH higher than 4 since it forms $Bi(OH)_3$ compound, which is almost insoluble and tends to precipitate. Thus, taking into account the occurrence of basic conditions during the synthetic route described in the previous paragraph, the impregnation method (in acidic conditions) should be the more efficient one to dope ZnO nanoparticles with bismuth ions, due to their higher adsorption on zinc oxide surface. Hence, the doping was realized by adding a 0.1 M solution (1.23 mL) of $Bi(NO_3)_3{\cdot}5H_2O$ (in HNO_3 65%wt) to have a Bi/Zn molar ratio of about 0.01. Then, the powders were dried in an oven at 90 °C and calcined at 300 °C for 6 h. Samples (labeled as Z_Ac_Bi_impr and Z_N_Bi_impr, respectively) obtained after the calcination step showed a very intense yellow color.

2.3. Sample characterizations

X-Ray Powder Diffraction (XRPD) analyses were performed on a Philips PW 3710 Bragg-Brentano goniometer equipped with a scintillation counter and 1° divergence slit, 0.2 mm receiving slit, and 0.04° soller slit systems. We employed graphite-monochromated Cu Kα radiation (Cu $K_{\alpha1}$ $\lambda = 1.54056$ Å, $K_{\alpha2}$ $\lambda = 1.54433$ Å) at 40 kV × 40 mA nominal X-rays power. Diffraction patterns were collected between 20° and 80° with a step size of 0.1° and a total counting time of about 1 h. Quanto fitting program and the Scherrer equation were applied throughout to provide estimates of the average domain sizes.

High-Resolution Transmission Electron Microscope/Scanning Transmission Electron Microscope (HR-TEM) analyses were performed on LIBRA 200 EFTEM (Zeiss) instrument operated at 200 kV accelerating voltage. The microscope is equipped with an Energy-dispersive X-ray system (EDX – Oxford INCA Energy TEM 200) for elemental maps and analysis. The TEM grids were

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