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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.

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

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http://dx.doi.org/10.1016/j.jphotochem.2016.10.003 1010-6030/© 2016 Elsevier B.V. All rights reserved. [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 TiO₂ 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 TiO₂ [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 bismuthdoped 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 Zn²⁺ aqueous solution to reach a pH around 9. The obtained whitish colloid was

 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

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).

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(NO₃)₃·5H₂O) 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 (HNO₃ 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 HNO₃ 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], Bi³⁺ 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(NO₃)₃·5H₂O (in HNO₃ 65%wt) to have a Bi/ Zn molar ratio of about 0.01. Then, the powders were dried in an oven at 90 $^\circ\text{C}$ and calcined at 300 $^\circ\text{C}$ 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 K α radiation (Cu K $_{\alpha 1} \lambda = 1.54056$ Å, K $_{\alpha 2} \lambda = 1.54433$ 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 prepared dropping the dispersed suspension of nanoparticles in isopropanol onto a holey-carbon supported copper grid and drying it in air at room temperature overnight.

Scanning Electron Microscopy (SEM) was carried out using a SEM Hitachi TM-1000 Microscope.

The BET surface area of the powders was determined from nitrogen adsorption-desorption isotherms at 77 K, using Coulter SA 3100 apparatus.

Dynamic Light Scattering (DLS) measurements were performed using a Malvern Zetasizer Nano ZS, based on the Photon Correlation Spectroscopy technique (PCS). For the analysis, zinc oxide nanopowders were suspended in a solution of KNO_3 0.01 M with a concentration of 0.3 g L^{-1} , to mimic the same conditions used during the photocatalytic processes.

To evaluate the nanoparticles isoelectric point, turbidimetric method was adopted. Thus, nanopowders were suspended in a solution of KNO₃ 0.01 M (constant ionic strength, concentration of ZnO powders equal to $0.3 \, \mathrm{g \, L^{-1}}$) and the natural pH was determined (around 7 for all samples, by using Amel Instrument 334-B pH-meter equipped with a combined glass electrode). Then, the absorbance was measured on an aliquot of each sample (wavelength range 400–600 nm, Shimadzu UV–vis spectrophotometer UV-2600), before varying suspensions pH with the addition of KOH (0.1 M or 1 M) towards alkaline region (up to 12). The acidic region (pH < 6.5) was not considered due to the dissolution of zinc oxide nanopowders.

Diffuse reflectance spectra (DRS) of the nanopowders were measured on an UV–vis spectrophotometer Shimadzu UV-2600 equipped with an integrating sphere; a "total white" $BaSO_4$ was used as reference.

2.4. Photocatalytic degradation of o-toluidine

All the as-synthesized bare and Bi-doped nanopowders were tested as photocatalysts for *o*-toluidine (target compound, Sigma-Aldrich, purity > 99%) photoremoval, in aqueous slurry. The initial concentrations of ZnO samples and pollutant were equal to 0.3 g L^{-1} and 25 ppm, respectively. The set-up was provided by a 750 mL cylindrical jacketed glass reactor and all the tests were carried out at spontaneous pH (around 7.0-7.5), for 6 h under UV irradiation (at 25 °C), with the lamp always located at 15 cm from the batch reactor. The pK_a of the *o*-toluidine pollutant (equal to 4.45 [27]) indicates that, in the present photocatalytic experimental conditions, the substance almost exists in the unprotonated form. The UV lamp is a Jesosil HG 500 W, λ 300–450 nm, with an effective power density of 57 mW cm⁻².

Direct photolysis (under 5%, after 6 h) is negligible. Furthermore, for all samples dark tests reveal that the adsorption of *o*-toluidine is lower than 10% with no mineralization degree.

The progressive degradation of *o*-toluidine over time (sampling aliquots every 90 min) was monitored by measuring the disappearance and mineralization percentages, by using LSV (Linear

Sweep Voltammetry) and TOC (Total Organic Carbon, TOC-VCPN Shimadzu Total Organic Carbon analyzer) analyses, respectively. As concerns the former, a 3 electrodes cell was used, in which the working electrode was a glassy carbon covered with Carbon NanoTubes (CNTs); a filament of Pt and a KCl saturated Ag/AgCl electrode as counter and reference electrodes, respectively. HCl 0.1 M was used as the supporting electrolyte and the potential was varied from +0.60 V to +1.00 V (*vs* Ag/AgCl). The *o*-toluidine molecule was detected at about 0.90–0.95 V; excellent results were obtained, characterized by linear increasing of *o*-toluidine peaks and a calibration plot with very good correlation [18].

In order to investigate the photodegradation mechanism of otoluidine, aliquots of raw reaction media were examined by using HPLC/MS technique (HPLC Agilent Technologies 1200 series instrument coupled with a Thermo Scientific LTQ Orbitrap XL analyzer). Chromatographic separations were carried out on a ZoRbax SB-C18 column (150 \times 0.5 mm, particle size 5 μ m), with a sample volume of $1 \,\mu L$ and a flux rate of $10 \,\mu L \,min^{-1}$. The separation step was made using a mobile phase composed of a first component A (H₂O+HCOOH 0.1%) and a second component B (acetonitrile, AcN) in non-isocratic conditions: $t = 0 \min$, A = 99% and B = 1%; t = 24 min, A = 1% and B = 99%. The stop time was fixed at 25 min, whereas the post time was of 8 min. The chromatographic effluent was then ionized by nano-ESI in positive mode [M+H]⁺. The ESI source settings were: capillary voltage 48 V; capillary temperature 220 °C; tube lens 120 V; spray voltage 2.40 kV. Mass spectrometric analyses were done in FTMS mode (35% normalized collision energy, scan range 50.00 – 600.00, resolution 30,000).

Moreover, Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR; Jasco 4200) analyses were carried out on used ZnO powders at the end of the reaction (after 360 min) to corroborate the HPLC/MS evidences.

3. Results and discussion

3.1. Physico-chemical characterizations of bare and Bi-doped ZnO nanopowders

Both bare and Bi-doped ZnO nanopowders were finely characterized on the morphological (N_2 adsorption isotherm, electron microscopy), surface (isoelectric point), optical (diffuse reflectance spectra) and structural (X-ray diffraction) points of view.

The surface area is an important parameter that characterizes a catalyst: actually, the rate of degradation mostly depends on its value, as the higher is the surface area, the faster is the adsorption of the organic molecule. In agreement with the literature [28], all bare samples have low S_{BET} values (ranging from 7 to 26 m² g⁻¹, Table 2, 2nd column). The acidic conditions of the sol-gel reactions do not modify the surface area value for both bare (Z_AcH and Z_NH samples) and doped ZnO nanoparticles. Instead, the different doping strategies (impregnation method *vs* sol-gel synthesis)

Table 2

Surface area (S_{BET}), average domain size (d^{XRD} and d^{TEM}), aggregates size (d_{aggr}), Bi/Zn atomic ratio obtained by EDX analysis, isoelectric point (iep) and band gap energy (*EG*) for each sample.

Sample	$S_{\rm BET}/m^2g^{-1}$	d ^{XRD} /nm	d ^{TEM} /nm	d _{aggr.} /nm	Bi/Zn ratio (EDX)	iep	EG/eV
Z_Ac	26	44	50	300 ± 40	-	8.0	3.21
Z_AcH	25	76	>100	n. d.	-	8.4	3.20
Z_AcH_Bi	22	78	>100	800 ± 100	0.026	9.0	3.20
Z_Ac_Bi_impr	2	81	>100	n. d.	0.068	8.0	<3.00
Z_N	9	50	60	600 ± 200	-	8.2	3.15
Z_NH	7	95	>100	n. d.	-	9.2	3.18
Z_NH_Bi	13	80	>100	700 ± 300	0.014	9.5	3.16
Z_N_Bi_impr	5	79	>100	n. d.	0.023	8.4	< 3.00

played a diverse role: indeed, Bi-impregnated samples are characterized by S_{BET} equal or lower than 5 m² g⁻¹, whereas those of Z_AcH_Bi and Z_NH_Bi are similar to the pure compounds (Table 2).

From structural investigations, X-ray diffraction lines show a single crystallographic phase (hexagonal wurtzite polymorph [22]) for all pure samples both synthesized starting from acetate (Fig. 1) and nitrate (Fig. S1) zinc precursors. On the contrary, the introduction of bismuth dopant gives different results, depending on the adopted synthetic route. When the bismuth salt was introduced directly during the synthesis, the final nanopowders do not show any additional external crystallographic phases (Fig. 1d and S1d). Whereas, in the case of impregnated samples, a weak peak (becoming more evident with the increasing of the Bi content [19]) appears at about 28° (Figs. 1 c and S1c) that could be assigned to the bismite polymorph (Bi₂O₃). Hence, the presence of a bismuth oxide segregated polymorph (bismite) could be hypothesized. Besides, by means of XRPD analyses and Quanto elaborations, average domain sizes were also determined. The values obtained for Z_Ac and Z_N are the lowest ones (Table 2, 3rd column), also compared to those calculated for Z_AcH and Z_NH samples. Indeed, the presence of nitric acid seems to provoke a particle size increase of about 40-50% (Table 2). Moreover, the same observations can be made for Bi-doped ZnO: actually the introduction of the dopant leads to the formation of bigger nanoparticles (Table 2, 3rd column), with domain sizes up to 80-90 nm.

To have a further confirmation of real particle dimensions and to evaluate samples morphology, HR-TEM analyses were subsequently performed. As concerns the bare compounds (Z_Ac and Z_N), HR-TEM images (Fig. 2a and b) reveal an ordered morphology of the powders and an average size in the range 50–60 nm for both samples (Table 2, 4th column), in agreement with data obtained by XRPD elaborations (Table 2, 3rd column). On the contrary, the doping procedure has led to morphological changes: actually, Bi-doped samples have more packed (agglomerates) and disordered nanoparticles (Fig. 2c–f) than the bare ones. In particular, those obtained through the addition of bismuth nitrate directly in synthesis show a heterogeneous morphology, with more elongated particles in the case of Z_NH_Bi (Fig. 2f). The increasing of nanoparticles sizes due to bismuth addition is also confirmed by HR-TEM technique. Indeed, d^{TEM} values (Table 2, 4th column) are higher than 100 nm for all doped compounds (both impregnated and not), corroborating the X-ray domain sizes.

Moreover, nanopowders morphology was also investigated by SEM analyses. The two home-made bare samples, Z_Ac and Z_N, are very different from each other: the former shows an extensive agglomeration of ZnO nanoparticles, to form compact and almost spherical agglomerates (size $20 \,\mu\text{m} \times 20 \,\mu\text{m}$) (Fig. S2a); whereas, the latter consists of a series of square-shaped platelet-like agglomerates, whose sizes seem even bigger with respect to Z_Ac agglomerates (Fig. S2b). Furthermore, the syntheses of pure ZnO in acidic medium have led to a modification of aggregates morphology, assuming a spongy-like conformation (Fig. S2c and d). This aspect is preserved in bulky Bi-doped samples, in which flowershaped nanoparticles can be detected. On the contrary, the impregnation technique has led to compact agglomerates formed by straight micrometric needles (Fig. S2g and h). By using EDX analysis, the effective presence of bismuth and its distribution into the crystals of all doped powders have been confirmed (Table 2, 6th column). In the case of bismuth addition in the synthetic step, a homogeneous dopant distribution (confirming the effective amount of dopant) occurs, while a segregation and edgeenrichment are appreciable for impregnated samples (higher Bi/ Zn ratios). This observation was previously made in our recent paper about Bi-doped zinc oxide commercial nanopowders [18].

The agglomeration degree of both pure and doped compounds has been further evaluated by dynamic light scattering measurements. The grain size analysis gives single mode distribution for all



Fig. 1. XRPD spectra of a) Z_Ac, b) Z_AcH, c) Z_Ac_Bi_impr and d) Z_AcH_Bi nanopowders.



Fig. 2. TEM images of a) Z_Ac, b) Z_N, c) Z_Ac_Bi_impr, d) Z_N_Bi_impr, e) Z_AcH_Bi and f) Z_NH_Bi.

the synthesized samples (Fig. S3). In particular, the agglomerates size ($d_{aggr.}$) measured for the Z_Ac is the half of the one relative to Z_N (Table 2, 5th column). The addition of bismuth tends to increase the agglomeration process thus leading to bigger particles. The $d_{aggr.}$ values for Bi-ZnO samples by impregnation are not reported since their relative aqueous suspensions are not stable.

Complementary surface characteristics, related to the local surface chemistry, can be obtained from the stability (isoelectric

point, iep) measurements. Actually, stable suspensions were also required to enhance the photocatalytic performances by modulating the pH conditions. For all the synthesized samples, the iep was evaluated by means of turbidimetry. In this method, the absorbance decreases when the pH of the slurry is close to the particles iep, while it increases when the iep is far from the suspension pH. Fig. 3 shows data relative to Z_Ac series, as representative samples: the iep value can be extrapolated from the intersection of the two linear trends. For both bare ZnO



Fig. 3. Isoelectric point (iep) determination of Z_Ac series obtained by turbidimetric method.

nanopowders, the iep values (around 8.0) seems to be similar to the ones already reported in the literature [29]. Then, a predictable iep shift towards more alkaline pH is obtained when the synthesis was performed under acidic conditions (Z_AcH, Table 2, 7th column). Besides, the addition of bismuth species in the synthetic route leads to a further alkaline iep shift (9.0, Fig. 3 and Table 2): actually pure Bi₂O₃ possesses a iep value of around 9.4 [25,30], thus confirming the effective doping of ZnO lattice. Instead no



Fig. 4. Kubelka-Munk elaboration of the diffuse reflectance spectra of Z_Ac series.

appreciable iep variations in the case of Bi-doped samples obtained by impregnation method (Z_Ac_Bi_impr) occur, probably due to the negligible amount of segregated Bi_2O_3 phase in the whole powder. Actually, it may be hypothesized that the alkaline pH shift is principally ascribable to the presence of dopant ions uniformly distributed in the ZnO lattice, rather than to the formation of a segregated phase by impregnation method. Moreover, similar results were also achieved for the samples using nitrate salt as zinc precursor (Table 2 and Fig. S3).

Diffuse Reflectance Spectroscopy (DRS) analyses were subsequently performed to verify the effect of bismuth doping on the band gap energy (EG) of bare nanopowders. In particular a reduction of band gap values is expected in order to exploit the solar light, also for the photocatalytic processes [23]. The apparent values of EG, calculated by the Kubelka-Munk equation (Figs. 4 and S4 for Z_Ac and Z_N series, respectively), are reported in Table 2 (8th column). It is possible to note that the band gap energies strongly depend on the doping method: actually, only the impregnation process allows a great reduction of the band gaps (lower than 3.00 eV, see Table 2), further confirmed by the typical yellow color of these compounds. Indeed, the relative DRS curves (Figs. 4 and S4) are modified with respect to those of bare samples for the appearance of intra-gap level (or mid-state) [24,25]. On the contrary, when the bismuth precursor is introduced in the synthesis, only a small reduction of the band gap is obtained (lower yellowish color).

3.2. The photocatalytic performances of bare and Bi-doped ZnO

LSV and TOC analyses were carried out to evaluate the *o*toluidine disappearance and mineralization during the photocatalytic experiment, performed in ZnO aqueous slurries by using both bare and Bi-doped nanopowders. The adopted experimental conditions (see experimental section) were considered optimal to guarantee hydrogen bonding/electrostatic interactions between oxygen atoms of ZnO and the N—H group of *o*-toluidine molecules, as widely reported in the literature [31,32]. Indeed, Eskizeybek et al. [31] deeply studying polyaniline (PANI)/ZnO system observed that a shift of the characteristic IR PANI peaks towards lower wavenumbers is due to the interactions between the PANI chains and ZnO nanoparticles, which affect the electron densities (*i.e.* density increase) and bond energies of polyaniline.

Photocatalytic results are reported in Fig. 5 in terms of both disappearance (a and c) and mineralization (b and d) degrees. Firstly, it is worth noting that the change in the synthetic conditions (introduction of nitric acid, Z_AcH and Z_NH samples) provokes a dramatic decrease of mineralization, whereas the disappearance percentage is almost preserved: this effect is particularly evident when zinc acetate is used as precursor. Furthermore, the impregnation method allows to reduce the Δ values between disappearance and mineralization percentages (Fig. 6) evidencing that the almost entire amount of disappeared *o*-toluidine is transformed into CO₂ and H₂O. On the contrary, the



Fig. 5. % LSV disappearance (a and c) and% TOC mineralization (b and d) of o-toluidine (25 ppm) by using both bare and Bi-doped samples.



Fig. 6. Photocatalytic results by UV irradiation as difference between the disappearance and the mineralization percentages $(\Delta).$

samples directly doped in the synthesis (Z_AcH_Bi and Z_NH_Bi) are characterized by both a lower degree of disappearance and a lower mineralization with respect to the bare compounds, probably as the result of the strong acidic conditions used for these syntheses. The presence of bismuth has allowed to reduce the gap between disappearance and mineralization degrees (Δ), leading to a lower amount of intermediate species, while the acidic conditions strongly reduce the pollutant photoremoval.

Table 3

LC/MS *o*-toluidine (*o*-tol) and intermediates (azo dimer, OH-dimer, BzOH, NH₂-BzH) abundance after 3 and 6 h (legend: +++ = 10^8 , ++ = 10^7 , += 10^6 , o = 10^5 , -= none). All species have been revealed as proton adducts, $[M + H]^+$.

Sample	o-tol		azo dimer		OH-dimer		BzOH		NH ₂ -BzH	
	3 h	6 h	3 h	6 h	3 h	6 h	3 h	6 h	3 h	6 h
Z_Ac	+++	++	+	+	0	0	+	+	+	+
Z_AcH	+++	++	+	++	-	+	+	+	-	++
Z_AcH_Bi	+++	+++	+	+	0	+	+	+	+	+
Z_Ac_Bi_impr	+++	+++	+	+	-	-	0	0	0	0
Z_N	+++	++	++	0	+	-	+	+	+	+
Z_NH	+++	++	++	++	-	+	+	+	+	++
Z_NH_Bi	+++	+++	+	+	-	+	0	+	+	+
Z_N_Bi_impr	+++	+++	+	+	-	-	0	0	-	0

3.3. Study of o-toluidine by-products: the proposed photodegradation mechanism

The study about o-toluidine photoremoval and the recognition of the possible by-products, formed during the photocatalytic process, can lead to a better comprehension of its photodegradation mechanism. The scheme reported by An et al. [17] (suggested in the case of TiO₂ thin films in gas phase) was the starting point for the development of a more complex global mechanism, thanks to the recognition of further by-products. The importance of determining by-products formed during the process comes from the partial mineralization degree (achieved at the end of the process) due to the accumulation of stable intermediates. Thus, a complex kinetic pathway [18] involving many surface reaction steps occurs. The study was conducted using concomitantly HPLC-MS and FTIR analyses. By means of HPLC-MS, the otoluidine peak is always detected (o-tol, m/z 108, 6.0 min RT, Fig. 7) confirming that the photocatalytic processes were not able to totally destroy the starting pollutant molecules. Furthermore, several by-products were identified: *i*) a dimer compound (azo dimer, m/z 211, 19.0 min RT) and the corresponding OH-dimer (OHdimer, m/z 227, 23.5 min RT) where a methyl group was oxidized to an new alcohol group; *ii*) BzOH (m/z 124, 4.7 min RT) and NH₂-BzH



Fig. 7. Extracted [M+H]⁺ ion chromatograms for the Z_Ac sample (as representative sample) after 3 h of photoreaction.

 $(m/z \ 122, \ 20.1 \ min \ RT)$ that differ only for the presence of an alcoholic group (2-aminobenzyl alcohol, BzOH), that could be further oxidized to an aldehyde group (2-aminobenzaldehyde, NH₂-BzH). Hence, the mechanism involves the equilibrium reaction between the starting *o*-toluidine molecule and its azo dimer, characterized by the presence of a double N=N ligand. Then, several reactions could be hypothesized as follows: *i*) the attack of a hydroxyl radical on the methyl group of the azo dimer (giving rise

to the OH-dimer compound); *ii*) the breaking of the double N=N ligand with the formation of the amine group (BzOH compound); and *iii*) the oxidation of $-CH_2OH$ of BzOH to an aldheyde group (NH₂-BzH compound). Although the MS analysis cannot be considered as a quantitative study, the relevant abundance of the different [M+H]⁺ intermediates was considered in order to obtain an estimation of their variation during the reaction time (after 3 h and 6 h, Table 3). The starting *o*-toluidine pollutant



Fig. 8. ATR-FTIR spectra subtraction relative to used nanopowders: a) from zinc acetate and b) from zinc nitrate.

amount remains almost high for the synthesized samples during the whole reaction. All the photocatalytic powders favor the formation of the azo dimer, followed by the corresponding oxidized one (OH-dimer); particularly, Z_Ac seems to promote a higher accumulation of these by-products with respect to Z_N (for which they are present in traces or they are completely removed after 6 h). In all cases the production of BzOH and NH₂-BzH is already evident at half of the photocatalytic reaction time. The acidic sol-gel condition leads to a higher amount of by-products with respect to Z_Ac and Z_N, as a result of the dramatic decrease of mineralization percentage. These results are fully in agreement with the Δ values, as reported in Fig. 6. On the contrary, impregnated Bi-doped samples are characterized by a significant reduction of by-products: both after 3 h and 6 h, they are present only in traces (i.e. as soon as they are formed, they are almost completely destroyed). Hence, it is possible to state that bismuth, added through impregnation, is able to reduce the gap between disappearance and mineralization with an important environmental benefit. Instead, when bismuth salt is added directly in the synthetic route, the required acidic conditions are probably the main reason for the increased disappearance/mineralization gap (thus loosing the main benefit of bismuth doping, see Fig. 6).

Moreover, FTIR technique was adopted to corroborate the previous HPLC–MS data. By analyzing the used powders after the photocatalytic tests, several peaks could be ascribable to characteristic functional groups of by-products adsorbed molecules. In the case of bare compounds (see Fig. 8), *o*-toluidine (δ_{C-C} =1180 cm⁻¹ [33], δ_{N-H} =1260 cm⁻¹ [33] and $\nu_{C=Cring}$ =1580 – 1640 cm⁻¹ [34]) and few by-products (NH₂-BzH and BzOH observing the



Fig. 9. The proposed mechanism for o-toluidine photodegradation.

 $\nu_{C=0} = 1680 - 1720 \text{ cm}^{-1}$ [35,36], $\nu_{C=0} = 1450 \text{ cm}^{-1}$ [36]) are detected on the surface of Z_Ac and Z_N (no differences are evident between the two synthesized bare samples). Then, a new intermediate could be hypothesized owing to the appearance of a sharp peak at $1350 \, \text{cm}^{-1}$ (ν_{NO2} [37]), probably the consequence of the further NH₂-BzH oxidation. Furthermore, comparing the spectra obtained for the two sets of doped samples, the impregnated powders (Z_Ac_Bi_impr and Z_N_Bi_impr) after 6 h of photocatalysis are characterized by a lower amount of adsorbed molecules on their surface, confirming the drastic reduction of Δ (Fig. 6) by the addition of bismuth. On the contrary, when bismuth is introduced in synthesis, the same peaks detected for bare compounds are still evident (Fig. 8), thus confirming the inefficiency in reducing the disappearance-mineralization gap (as already shown in Fig. 6). Therefore, the amount of adsorbed molecules is higher with respect to impregnated samples and, in particular, even the peak of o-toluidine is well-defined for Z_AcH_Bi and Z_NH_Bi samples, indicating the low disappearance degree (see Fig. 6).

Hence, starting from these results (from HPLC/MS and FTIR analyses) and on the basis of the recent literature [17-19], a general scheme of possible photoremoval pathways was developed (Fig. 9). A dimer photocatalytic reaction is the starting point for both bare and Bi-doped ZnO photocatalysts, followed by the formation of OH-dimer, BzOH and finally NH₂-BzH. Unfortunately, no successive by-products (reported in the second part of the proposed scheme, Fig. 9) were found; thus, the possible routes proposed for the degradation of NH₂-BzH cannot be confirmed with the present experimental analyses. However, these further compounds were proposed by merging our previous results on Bi-doped commercial ZnO [18,19] with the scheme reported by An et al. [17]. The only difference between bare and Bi-doped samples is from the kinetic point of view. Indeed, bismuth is likely to reduce the stability of the intermediates, leading to high mineralization degree, especially if it is introduced by impregnation method.

4. Conclusions

The present research work focused on the role played by homemade bare and Bi-doped ZnO nanopowders as photocatalysts towards the photoremoval of o-toluidine, a highly toxic water pollutant. The photocatalytic results were strictly dependent on the physico-chemical properties of zinc oxide nanoparticles: this is the reason why synthetic conditions (such as zinc precursors and medium acidity) have been varied. Furthermore, 1% Bi-doped compounds have been prepared by two different synthetic methods: a traditional impregnation procedure and a more innovative one, which was based on the direct introduction of bismuth nitrate as a synthesis reagent. Both bare and dopednanostructured (as confirmed by HR-TEM analyses) particles have low surface areas (which sharply decrease only in the case of bismuth impregnation) and they are structurally characterized by the main ZnO polymorph, i.e. the wurtzite phase. However, Biimpregnated samples show a small content of segregated Bi₂O₃ phase. Moreover, the impregnation method significantly modifies both the isoelectric point (that is influenced by the segregate Bi₂O₃ phase) and the band gap energy (<3.00 eV). These parameters, instead, are not affected by the direct introduction of bismuth precursor.

Concerning the photocatalytic performances, bismuth doping is able to reduce the mineralization/disappearance gap, decreasing the amount of by-products formed during the photodegradation process. This has been particularly verified for impregnated powders, whereas the gap obtained for Z_AcH_Bi and Z_NH_Bi samples is higher, probably due to the modification of the synthetic conditions. Actually, acidic medium may have a main role in reducing the performances in terms of mineralization degree and thus further studies should be carried out to find a better alternative to introduce the Bi species. Finally, a general *o*toluidine photoremoval mechanism was proposed on the basis of both FTIR technique on used nanopowders and HPLC/MS analyses on eluates (3 h and 6 h) during the photocatalytic remediation. The suggested mechanism is an expanded version of our previous work [18], based on the recognition of different by-products, especially the dimer compound (azo dimer), that have allowed a new additional pathway (with azo dimer derivatives in the first step of the photo-oxidative degradation). In particular, Bi-impregnated samples seem to reduce the stability of the intermediates, leading to high mineralization degree.

Thus, bismuth-doped ZnO could represent a forefront photocatalyst for the exploitation of solar light; however, more studies are required to increase the photocatalytic performances of these nanopowders enhancing their relative active surface area able to absorb higher amount of *o*-toluidine and by-products pollutant species.

Conflict of interest

The authors declare that they have no conflict of interest.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jphotochem.2016.10.003.

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