#### Chemical Engineering Journal 233 (2013) 305-314



Contents lists available at ScienceDirect

# **Chemical Engineering Journal**

Chemical Engineering Journal

#### journal homepage: www.elsevier.com/locate/cej

# Highly active Bi/BiOI composite synthesized by one-step reaction and its capacity to degrade bisphenol A under simulated solar light irradiation



# Chun Chang, Lingyan Zhu\*, Yu Fu, Xiaolong Chu

Key Laboratory of Pollution Processes and Environmental Criteria, Ministry of Education; Tianjin Key Laboratory of Environmental Remediation and Pollution Control, College of Environmental Science and Engineering, Nankai University, Tianjin 300071, PR China

# HIGHLIGHTS

• A novel Bi/BiOI composite was firstly fabricated via a facile approach.

- The ratio of Bi in composites was adjusted by solvothermal temperature and duration.
- Metallic Bi promotes the separation of the photogenerated hole-electron pairs.
- The BOI-180-24 could remove BPA efficiently under simulated solar light irradiation.
- Photogenerated holes, superoxide radicals and singlet oxygen were active species.

#### ARTICLE INFO

Article history: Received 10 May 2013 Received in revised form 18 July 2013 Accepted 13 August 2013 Available online 22 August 2013

Keywords: Bi/BiOl One-step solvothermal synthesis Bisphenol A (BPA) Photocatalytic mechanism

#### ABSTRACT

A novel 3D Bi/BiOI composite was synthesized by a facile one-step solvothermal method and used for the degradation of bisphenol A (BPA) in water. The solvothermal temperature and reaction time affected the chemical compositions, crystallinity and morphology of the prepared materials. The proportion of metallic Bi in the materials increased as the solvothermal temperature and reaction duration increased. The photocatalyst prepared at 180 °C for 24 h (BOI-180-24) contained approximate 12.5% metallic Bi and displayed the best photocatalytic performance to BPA under simulated solar light irradiation. Metallic Bi might transfer the photogenerated electrons to  $O_2$  to produce superoxide radicals. Simultaneously, it also inhibited the recombination of the hole–electron pairs. As a result, the as prepared Bi/BiOI displayed much higher photocatalytic degradation and mineralization efficiency to BPA than pure BiOI. About 92.8% of 40 mg L<sup>-1</sup> BPA was degraded after 90 min reaction using 1 g L<sup>-1</sup> BOI-180-24 as catalyst under simulated solar irradiation, while 79.0% of TOC was removed at the same time. Photogenerated holes, superoxide radical species and singlet oxygen were responsible for the photodegradation while the superoxide radical species were more predominant in the Bi/BiOI photocatalytic reaction system. Only one intermediate (m/z 133) was observed by LC–MS/MS and a simple degradation pathway of BPA was proposed.

© 2013 Elsevier B.V. All rights reserved.

# 1. Introduction

Bismuth oxyhalides (BiOX, X = Cl, Br, I) are a new family of promising photocatalysts which exhibit excellent photocatalytic performance because of their layered tetragonal crystal structure and suitable band gaps. Among them, BiOI displays the greatest absorption in the visible light region due to the smallest band gap ( $\sim$ 1.8 eV). To explore its application in water treatment, much attention has been drawn to further improve the photocatalytic activity of BiOI under simulated solar light irradiation. One of the efforts is to dope BiOI with foreigner metal or non-metal elements.

Until now, many BiOI composites, such as Ag/BiOI [1], Pt/BiOI [2], BiOCl/BiOI [3], BiOBr/BiOI [4,5], TiO<sub>2</sub>/BiOI [6,7], ZnO/BiOI [8], AgI/ BiOI [9], Bi<sub>2</sub>O<sub>3</sub>/BiOI [10] have been successfully synthesized and they displayed improved photocatalytic efficiency as compared to pure BiOI. Except for doping with foreign elements, self-doping has been used to tune the properties of semiconductors [11]. Recently, it was reported that the photocatalytic activity of BiOI could be significantly enhanced by iodine self-doping [12]. However, there is no report on the synthesis of Bi/BiOI so far.

Bisphenol A (BPA, 2,2-bis(4-hydroxyphenyl)propane) is an important building block material and used extensively as the monomer to manufacture polycarbonate plastic and epoxy resins, such as food containers and utensils [13,14]. The total global production capacity of BPA was about 3.7 million metric tons in 2003, and increased to 5.2 million metric tons in 2008 [15]. Due

<sup>\*</sup> Corresponding author. Address: The College of Environmental Science and Engineering, Nankai University, Weijin Road 94, Tianjin 300071, PR China. Tel.: +86 22 23500791; fax: +86 22 23508807.

E-mail address: zhuly@nankai.edu.cn (L. Zhu).

<sup>1385-8947/\$ -</sup> see front matter @ 2013 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.cej.2013.08.048

to its large production and wide application, a large amount of BPA has been released into the aquatic environment. Unfortunately, it could cause adverse effects to human beings and wildlife, such as ovarian disease in women [16], thyroid hormone disruption [17], and carcinogenicity in adult rodents [18] and is regarded as a representative endocrine disrupting chemical (EDC). Thus, a great concern has been raised to remove BPA from water by different techniques, such as physical absorption [19], chemical remediation [20,21], and microbial degradation [22]. Among these methods, photocatalytic degradation is attracting widespread attention due to its effective activity and low toxicity.

The current study targeted to prepare a Bi/BiOl composite by a facile one-step solvothermal method. The effects of solvothermal temperature and reaction time on the compositions and morphologies of the photocatalysts were investigated and their photocatalytic activities to degrade BPA under simulated solar light irradiation were compared. The possible reaction mechanisms of Bi/BiOl to BPA were also explored by adding different scavengers of reactive species in the photocatalytic system. The possible degradation pathway of BPA was proposed by LC–MS/MS analysis.

#### 2. Materials and methods

#### 2.1. Materials and reagents

BPA (purity 99.5%) was purchased from Dr. Ehrenstorfer GmbH, Augsburg, Germany. Other materials and reagents are provided in Supporting information.

#### 2.2. Synthesis and characterization of the photocatalysts

The photocatalysts were synthesized by a conventional solvothermal method [23]. 20 mL of  $0.15 \text{ mol L}^{-1}$  (1.4553 g) Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O dissolved in glycol was drop-wisely added into the same volume of 0.15 mol  $L^{-1}$  (0.4980 g) KI which was dissolved in glycol. The mixture was vigorously stirred at room temperature for 30 min, then was transferred to a 50 mL Teflon-lined autoclave, which was sealed in a stainless steel tank. A series of catalysts were synthesized at different temperatures (100, 140, 180, 225 and 250 °C) for 24 h to study the impact of temperature, which was defined as the temperature series; while another series of samples were synthesized at 180 °C for different time durations (1, 12, 24, 48, 72 h), which was defined as the time series. The product synthesized at 180 °C for 24 h was labeled as BOI-180-24. Other catalysts were labeled in a similar way. The autoclaves were naturally cooled to room-temperature. The solid products were washed three times with deionized water and ethanol respectively, and dried at 80 °C in oven for overnight. The characterization methods for the prepared samples are available in Supporting information.

# 2.3. Photoelectrochemical measurement

Photoelectrochemical measurement with a CHI 600D electrochemical system (Chenhua Instruments Co. Shanghai) was carried out in a conventional three-electrodes, a single-compartment quartz cell filled with 0.1 M  $Na_2SO_4$  electrolyte (30 mL), and a potentiostat. The ITO/photocatalyst electrodes served as the working electrode. A platinum black wire was used as a counter electrode with saturated calomel electrode (SCE) as a reference electrode. The photocurrents of the photocatalysts as light on and off were measured at 0.0 V.

#### 2.4. Sorption and degradation experiments

Batch experiments were conducted in a XPA-7 photochemical reactor (Xujiang Electromechanical plant, Nanjing, China) to investigate the prepared materials' photocatalytic activity to BPA. Simulated sunlight irradiation was provided by a 350 W xenon lamp (the color temperature of the light emitted was at about 6000 K, Institute of Electric Light Source, Beijing) with light intensity of 5.8 mW/cm<sup>2</sup>. The reaction system was cooled by circulating water and maintained at room temperature. In quartz test tubes, 0.0050 g of catalysts were added followed by adding 10 ml of BPA aqueous solution at 20 mg L<sup>-1</sup>. The solution was magnetically stirred during the reaction. Before irradiation, the suspension was stirred in the dark for 45 min to establish adsorption-desorption equilibrium of BPA on the catalysts. Approximately 0.6 ml of aqueous sample was withdrawn at certain time intervals and centrifuged under 8000 rpm before the analysis. Recycling tests were conducted to evaluate the stability of photocatalyst, and the detailed information is described in Supporting information.

#### 2.5. Instrumental analysis of BPA

BPA was analyzed employing a high performance liquid chromatograph (HPLC) and possible intermediates were investigated using a high performance liquid chromatograph coupled with mass spectrometer (LC–MS/MS). More detailed instrumental conditions are provided in Supporting information. UV–vis spectra of BPA solution were performed on a HACH DR/4000 UV–vis spectrophotometer. Total organic carbon (TOC) was measured with a Analytikjena mnlti N/C 3100 analyzer.

#### 3. Results and discussion

#### 3.1. Characterization of the prepared catalysts

The XRD patterns of the catalysts prepared at different reaction temperatures and durations are shown in Fig. 1. As shown in Fig. 1(a), the diffraction peaks of the catalysts prepared at low temperatures, such as 100 and 140 °C, are consistent with those of BiOI [JCPDS No. 73-2062], suggesting that pure BiOI crystal phase was formed. As the temperature increased to 180 °C, another phase appeared, with the diffraction peaks consistent with metallic Bi [JCPDS No. 85-1329], indicating that a part of BiOI molecules dissociated at high temperatures and the composite of Bi/BiOI was formed. With the increase of temperature, the characteristic peaks of BiOI became weak and eventually disappeared at 250 °C. Simultaneously, the peak intensity of metallic Bi increased gradually with the increase of reaction temperature. The characteristic peaks observed for metallic Bi are assigned to the diffraction planes of (003), (012), (104), (110), (202), (116), and (122), while the characteristic peaks of BiOI correspond to the diffraction from the (012), (110), (020), (122), and (124) planes. Similar situation occurred in the time series. At reaction time of 1 h, only the diffraction peaks of BiOI were observed, suggesting that BiOI was formed in the short duration of the reaction. As the reaction continued to 12 h, obvious peaks of Bi appeared, implying the formation of Bi/ BiOI. The peak ratio of Bi to BiOI increased gradually from 12 h to 72 h. The peak intensity of BiOI in the range of 1-24 h increased gradually, indicating the formation of better crystallites. The relative mass fraction of metallic Bi in the samples was estimated according to the following equation [24]:

$$W_t = \frac{I_i / R I R_i}{\sum_{i=1}^N I_i / R I R_i} \tag{1}$$



Fig. 1. XRD patterns of the prepared materials at different reaction temperatures (a) and durations (b).



Fig. 2. The TEM images of the prepared materials at different conditions.

where  $W_i$  is the mass fraction of phase i (%),  $I_i$  is the strongest integral intensity of phase i,  $RIR_i$  value from MDI Jade 5.0. In the temperature series, the estimated content of Bi was 12.5% and 68.9% in the samples prepared at 180 and 225 °C. It was difficult to estimate the content of metallic Bi in other samples due to the very low peak intensities of Bi or BiOI. In the time series, the content of metallic Bi was estimated to be 0, 8.3, 12.5, 17.6 and 26.7% in the composites prepared for 1, 12, 24, 48 and 72 h.

Morphologies of the prepared samples were characterized by TEM (Fig. 2) and SEM (Fig. S1). The images of TEM and SEM demonstrated the morphology evolution with the solvothermal temperature and reaction time. When the temperature was at 100–180 °C, the catalysts were mainly present as 3D hierarchical microspheres which were assembled by nano-sheets. The microsphere-like morphology was partially deformed at 180 °C. When the temperature further increased to 225–250 °C, the microsphere disappeared and mixed morphology of irregular flake-like and bulk particle dominated. The morphology of the prepared samples was affected by the reaction time in a similar way, as shown in Fig. 2 and Fig. S1. During the reaction for 1–12 h at 180 °C, regular microspheres were formed with diameter around several  $\mu$ m. As

the reaction continued to 24 h, the microspheres were deformed. When the reaction time extended to 48–72 h, the spherical structures were destroyed completely and nano-sheets morphology appeared. In addition, the white spherical spots corresponding to Bi nanoparticles generated due to the decomposition of BiOI were observed by FE-SEM (Fig. 3), which are anchored on the surface of BiOI microspheres. The EDX of the photocatalysts (Fig. 3) show that the "Bi" nanospheres contain almost pure metallic Bi.

The IR transmittance spectra of all samples are demonstrated in Fig. 4. The broad absorption bands at  $3445 \text{ cm}^{-1}$  in Fig. 4(a) and  $3443 \text{ cm}^{-1}$  in Fig. 4(b) are corresponding to the stretching vibration absorption of hydroxyl function groups [25]. The presence of the sharp and strong absorption peaks at  $1577-1622 \text{ cm}^{-1}$  in Fig. 4(a),  $1625 \text{ cm}^{-1}$  in Fig. 4(b) are ascribed to the bending vibration absorption of free water molecules [26]. A band corresponding to symmetrical A<sub>2u</sub>-type vibrations of the Bi–O bond ( $512 \text{ cm}^{-1}$ ) was observed, and was in good agreement with the published results [25,27]. In addition, the absorption peaks at 793 cm<sup>-1</sup> in Fig. 4(a) and 772 cm<sup>-1</sup> in Fig. 4(b) are assigned to the asymmetrical stretching vibrations of Bi–O bonds [28,29]. Moreover, these peaks of Bi–O became smaller with the increase of temperature and time,



Fig. 3. The FE-SEM-EDX images of the prepared material at 180 °C for 24 h.



Fig. 4. FT-IR spectra of the prepared materials at different reaction temperatures (a) and durations (b); UV-vis DRS of the prepared materials at different reaction temperatures (c) and durations (d, inset at left corner: the band gap of the BOI-180-24 sample).

indicating the decomposition of BiOI due to the dissociation of Bi– O bond.

The UV–vis diffuse reflectance spectra of the catalysts prepared at different reaction temperatures and durations are also depicted in Fig. 4. As shown in Fig. 4(c), in the temperature series, the catalyst prepared at 100 °C displayed high photo-absorption capacity in the range of UV light to visible light around 630 nm. As the temperature increased to 140 °C, the light absorbance increased in the UV range while decreased slightly in the Vis range. This could be due to the different crystallinity and morphology. As the temperature further increased to 180 °C, the absorbance in the near infrared and visible light was greatly enhanced. This could be due to the appearance of metallic Bi in the catalyst, which showed very dark color. Another reason for the high absorption capacity of BOI-180-24 might be due to the surface plasmon resonance (SPR) of metallic Bi nanoparticles. It is well accepted that noble metals such as Au, Ag and Pt display plasmonic properties, which may increase the light absorption of the doped materials [30–37]. Recently, Toudert et al reported that as a non-noble metal, Bi also displays SPR property in near ultra-violet and Vis range if the particle size of metallic Bi is larger than 100 nm [38]. In the present study, the particle size of metallic Bi was about 100-200 nm (from the FE-SEM), and the emitted light wavelength was 300-1500 nm. With oscillations in the electromagnetic field, the weakly bound electrons of the metallic Bi nanoparticles respond collectively, resulting in the SPR [39]. This would help to improve the light absorbance of the composite. Due to the increase of metallic Bi in the samples prepared at high temperatures, such as 225–250 °C, the light absorbance in UV range decreased slightly while it was still very strong in the near infrared and visible light due to their dark color. In the time series (Fig. 4(d)), the catalyst prepared at 1 h demonstrated high optical absorbance capacity in the range of UV light to visible light about 630 nm. The catalysts prepared for longer reaction time 12-72 h displayed similar spectra, which showed high absorption in both UV and Vis ranges. For a crystalline semiconductor, their optical band gap could be calculated from the classic Tauc approach by using the following equation  $\alpha hv = A(hv - E_g)^{n/2}$  [40], where  $\alpha$ , v,  $E_g$ , and A are the absorption coefficient, the light frequency, the band gap, and a constant, respectively. Eg of BOI-180-24 sample could be estimated from the intercept of tangents to the plots was 2.06 eV from the Fig. 4(d, inset).

XPS was conducted to further investigate the chemical states of Bi element in the composite of Bi/BiOI, as shown in Fig. 5. The XPS of Bi element in the catalyst were fitted into a doublet corresponding to Bi  $4f_{7/2}$  and Bi  $4f_{5/2}$ . The Bi  $4f_{7/2}$  peak of Bi/BiOI was consisted of two components, which were attributed to metallic Bi and Bi<sup>3+</sup> respectively. However, the peak at 156.7 ev ascribed to metallic Bi was lower than that of pure metallic Bi (156.9 eV) [41] while the peak of  $Bi^{3+}$  (158.8 eV) was lower than that of pure BiOI (159.0 eV, Fig. 5a, lower panel). In the O 1s spectrum of Bi/BiOI (Fig. 5b, up panel), two peaks could be separated. The peak at 529.5 eV was attributed to the Bi-O bonds in [Bi<sub>2</sub>O<sub>2</sub>] slabs of BiOI [8] and the peak at 530.6 eV was originated from I–O bonds in BiOI [2], which shifted toward lower energy after the formation of heterojunction structure of the composite. The binding energies of I 3d<sub>5/2</sub> (618.6 ev) and I 3d<sub>3/2</sub> (630.1 ev) of Bi/BiOI displayed consistent binding energy as compared with pure BiOI (Fig. 5c, lower panel). These results indicate that the composite was not a simply physical mixture of metallic Bi and BiOI. There is an interaction between them and this interaction is of importance for electron or hole transferring and enhancing photocatalytic performance.

The N<sub>2</sub> adsorption/desorption isotherms were used to investigate the porous structure of the photocatalyst prepared at 180 °C for 24 h (BOI-180-24 displays the highest photocatalytic performance, which will be discussed later), and shown in Fig. S2. The isotherm of the BOI-180-24 was identified as type IV according to the international union of pure and applied chemistry (IUPAC) classification with a distinct hysteresis loop observed in the range of 0.87–1.00  $P/P_0$ , indicating its mesoporous property. In addition, the pore size distribution obtained from the isotherms in Fig. S2 (inset) reveals that there were a number of pores less than 50 nm in the sample (BOI-180-24), corresponding to mesoporous structure (the adsorption average pore size by BET is 21.75 nm). The BET specific surface area ( $S_{\text{BET}}$ ) of the BOI-180-24 was 47.99 m<sup>2</sup> g<sup>-1</sup>, and the single point adsorption total pore volume of pores at  $P/P_0 = 0.9790$  was 0.2609 cm<sup>3</sup> g<sup>-1</sup>.

# 3.2. Photocatalytic performance of the prepared catalysts under different conditions

Fig. 6 shows the photocatalytic degradation of BPA by the photocatalysts prepared at different reaction temperatures Fig. 6(a) and durations Fig. 6(b). The following pseudo first-order reaction kinetic model may be used to describe the degradation reaction of BPA:

$$C_{\text{BPA},t}/C_{\text{BPA},0} = e^{-k_{\text{obs}}^{\iota}}$$
<sup>(2)</sup>

where  $C_{\text{BPA,t}}$  is the concentration of BPA in aqueous phase (mg L<sup>-1</sup>),  $C_{\text{BPA,0}}$  is the initial concentration of BPA (mg L<sup>-1</sup>),  $k_{\text{obs}}$  is the pseudo first-order rate constant (min<sup>-1</sup>) and t is the reaction time (min). The pseudo first-order reaction kinetic model fitted the experimental data very well with regression coefficient  $R^2 > 0.9629$  in all cases. A linear fitting of  $\ln(C/C_0)$  and t would give the reaction rate constant  $k_{\text{obs}}$ . The degradation rate constants ( $k_{\text{obs}}$ ) of BPA by the photocatalysts prepared at different temperatures and durations are also shown in Fig. 6 (inset). In the temperature series, the  $k_{\text{obs}}$  was small (0.0123–0.0161) with the catalysts prepared at 100 and 140 °C, but it suddenly increased to 0.0398 with the catalyst prepared at 180 °C, and then decreased to extremely small (0.0008–0.0020) with the



Fig. 5. The XPS spectra of the Bi/BiOl composite (BOI-180-24, up panel) and pure BiOl (BOI-140-24, lower panel). (a) Bi 4f; (b) O 1s and (c) I 3d.



**Fig. 6.** The photocatalytic degradation of BPA by the prepared materials at different temperatures (a) and durations (b) in the degradation of BPA under the simulated solar light irradiation and their pseudo first-order rate constants (inset) (photocatalyst, 0.5 g  $L^{-1}$ ; BPA, 20 mg  $L^{-1}$ , pH = 6.28).

catalysts prepared at higher temperatures 225 and 250 °C. In the time series, the  $k_{obs}$  was 0.0056, 0.0113, 0.0398, 0.0261, and  $0.0222 \text{ min}^{-1}$  with the catalysts prepared at 1, 12, 24, 48 and 72 h, respectively. The photocatalytic efficiency increased as the solvothermal reaction time increased from 1 to 24 h, and decreased slightly as the reaction time increased from 24 to 72 h. It is apparent that the degradation efficiency was affected by the dosage of metallic Bi in the catalysts. As shown in Fig. S3. The degradation efficiency in 60 min irradiation increased gradually from 33.2% to 90.3% as metallic Bi content increased from 0% to 12.5% and then decreased to 72.7% as the content increased to 26.7%. As the metallic Bi content further increased, the degradation of BPA was negligible. The highest degradation efficiency was achieved by the catalyst BOI-180-24, which contained around 12.5% Bi. About 90.3% of BPA at initial concentration 20 mg  $L^{-1}$  was photodegraded by 0.5 g  $L^{-1}$  BOI-180-24 with simulated solar light for 60 min. It is well known that doping a certain amount of metal elements into a photocatalyst might improve the migration efficiency of photogenerated electrons and suppress the recombination of hole-electron effectively. In the present study, metallic Bi could act as electron trap and facilitate the separation of photogenerated hole-electron pairs on BiOI and enhance the photodegradation [1,42]. However, as the doping amount of metallic Bi increased, they could behave as recombinant centers. It was widely reported that over abundance of metal or non-metal impurities would become the recombination centers of electrons and holes, and finally resulting in the decrease of degradation rate [43,44]. Besides, metallic Bi is not reactive under solar light irradiation. As the doping amount of metallic Bi increased, the photoactive sites decreased, leading to reduced photocatalytic efficiency.

Photoeletrochemical performance could be used to evaluate the efficiency of photogenerated charge interface separation [45]. Fig. S4 shows a comparison of the photocurrents of the prepared materials under visible light irradiation. The photocurrent intensity generated by BOI-180-24 electrode was triple of that induced by other samples (BOI-100-24, BOI-250-24, BOI-180-1, BOI-180-72), suggesting more efficient separation of photogenerated hole–electron pairs in BOI-180-24, and there was a more efficient interfacial charge transfer between the electron donor and electron acceptor.

# 3.3. Photocatalytic reaction mechanism

A series of batch experiments were performed to examine the photocatalytic reaction mechanisms responsible for the degradation of BPA under simulated solar light irradiation by adding different scavengers (KI as scavenger for hole and the surface hydroxyl groups ( $\cdot$ OH<sub>ads</sub>) [46,47], NaF as scavenger for  $\cdot$ OH<sub>ads</sub> [47], methanol and ISO as scavengers for  $\cdot$ OH<sub>bulk</sub> ( $\cdot$ OH in the aqueous suspension) [46,48,49], benzoquinone (BQ) as scavenger for super-oxide radical species [50,51], and NaN<sub>3</sub> as scavenger for singlet oxygen [52,53]) in the reaction system.

Different concentrations of KI were applied to evaluate the contribution of hole and  $OH_{ads}$  in photocatalytic degradation of BPA, as shown Fig. 7(a). The BPA removal rate decreased with increasing KI concentration, indicating that photogenerated holes and  $OH_{ads}$ might contribute to the photocatalytic oxidation of BPA to a certain extent. Because both hole and  $OH_{ads}$  were generated on the surface of photocatalyst, the photocatalytic oxidation of BPA might occur on the surface of photocatalyst but not in the bulk solution.

 $F^-$  is very stable against oxidation even by the valence holes produced by Bi/BiOI due to the high redox potential of the couple  $F/F^-$  (3.6 V) [54]. Fig. 7(b) shows that photocatalytic degradation of BPA was not significantly affected by NaF at different concentrations. This suggests that  $OH_{ads}$  did not play a pivotal role, while the photogenerated holes played an important role in the photocatalytic degradation of BPA.

Isopropanol and methanol are usually employed as a diagnostic tool of 'OH<sub>bulk</sub> mediated mechanism because they are easily oxidized by 'OH and have poor affinity to semiconductor surface in aqueous media [55]. Different concentrations of isopropanol and methanol were dosed to assess their effects on the photodegradation of BPA. As shown in Fig. 7c and d, both isopropanol and methanol did not show distinct inhibitory effects on the photocatalytic efficiency. These results indicate the contribution of 'OH<sub>bulk</sub> is negligible in the photocatalytic process. For Bi/BiOI, the standard redox potential of the top valance band (1.59 V vs. NHE) of Bi<sup>V</sup>/Bi<sup>III</sup> is smaller than that of 'OH/OH<sup>-</sup> (1.99 V vs. NHE) [56] and 'OH/H<sub>2</sub>O (2.27 v vs. NHE) [57]. Thus, the photogenerated holes on the surface of BiOI were incapable of directly oxidizing adsorbed OH<sup>-</sup> groups to 'OH.

When BQ, which is a scavenger for superoxide radical species, was added in the reaction system, the photocatalytic reaction was significantly inhibited, as shown in Fig. 7(e). The removal efficiency of BPA gradually decreased with increasing BQ concentration. Only 20.77% BPA was removed after 60 min of irradiation when the concentration of BQ was 0.5 mM. Moreover, the inhibitory effect was more obvious with the addition of BQ compared to other scavengers. This result reflects that superoxide radicals might be a predominant active species responsible for the photocatalytic reaction. Bi, as a trap of the photogenerated electrons, could efficiently pass electrons to  $O_2$  in the solution to produce



**Fig. 7.** Photocatalytic degradation of BPA by the BOI-180-24 under simulated solar light irradiation in the presence of different radical scavenging species. (a) potassium iodide (KI); (b) sodium fluoride (NaF); (c) methanol; (d) isopropanol; (e) benzoquinone (BQ) and (f) sodium azide (NaN<sub>3</sub>).

superoxide radicals ( $O_2^-$ ), which may react with  $H^+$  to form  $HO_2^-$ . It is reported that superoxide radicals, such as  $O_2^-$  and  $HO_2^-$ , are very active radicals for the ring cleavage of aromatic compounds [53].

$$0^{-}_{2} + h^{+} \to {}^{1}0_{2}$$
 (3)

As shown in Eq. (3), the singlet oxygen  $({}^{1}O_{2})$ , is also known as one of the highly reactive oxygen species via the energy or electron transfer of photogenerated hole and superoxide radical [50]. The formation of  ${}^{1}O_{2}$  can be detected by direct method such as nearinfrared phosphorescence [58], or indirect method based on use of probe reagent [53,59,60]. NaN<sub>3</sub> is an effective scavenger of  ${}^{1}O_{2}$ , thus NaN<sub>3</sub> at different concentrations (1, 5, 10 mM) was added in the reaction system. The results (Fig. 7(f)) show that the photocatalytic degradation of BPA attenuated with increase in the concentration of NaN<sub>3</sub>. <sup>1</sup>O<sub>2</sub> with high energy (22.5 kcal mol<sup>-1</sup>) can degrade BPA directly [61]. It implies that <sup>1</sup>O<sub>2</sub> was generated in the system under simulated solar light irradiation, and it made contributions towards BPA degradation to a certain extent. Based on above discussions, possible photocatalytic reaction mechanisms are illustrated in Scheme 1 and include: photogenerated electrons were transferred via Bi to O<sub>2</sub> to produce superoxide radicals (O<sub>2</sub><sup>-</sup>), which might also react with the photogenerated holes to produce singlet oxygen. The photogenerated holes, superoxide radicals and the singlet oxygen could degrade BPA efficiently.



**Scheme 1.** The possible mechanism of the photocatalytic performance improvement of Bi/BiOI.

#### 3.4. Mineralization and photocatalytic degradation pathway of BPA

The mineralization of organic pollutants is of great importance in the treatment of organic pollutants [62–64]. To evaluate the mineralization of BPA, TOC was monitored during the entire reaction process. About 92.8% of BPA was degraded (BPA, 40 mg L<sup>-1</sup>; photocatalyst, 1 g L<sup>-1</sup>; pH = 6.28) after 90 min reaction using BOI-180-24 as catalyst under simulated solar irradiation, while 79.0% of TOC was removed at the same time (shown in Fig. 8(a)). These results suggest that the composite displays high efficiency to degrade BPA and to mineralize BPA to CO<sub>2</sub> and H<sub>2</sub>O. Fig. 8(b) illustrates the UV–vis spectra of reaction solution during the reaction process. The absorption peak at 276 nm diminished gradually as



**Fig. 8.** (a) Time evolution of m/z 227 (BPA) and m/z 133 (intermediate product), and TOC removal; (b) time evolution of UV-vis spectra of BPA in the presence of BOI-180-24 sample under simulated solar light irradiation; mass spectra and proposed chemical structures of m/z 227 (c) and m/z 133 (d) (photocatalyst,  $1.0 \text{ g L}^{-1}$ ; BPA,  $40 \text{ mg L}^{-1}$ , pH = 6.28).



Scheme 2. The possible reaction pathway for BPA degradation (ROS: reactive oxygen species).

the reaction time increased, indicating that BPA was destroyed during the reaction.

The probable intermediates formed in the degradation process were identified by LC–MS/MS. Only one intermediate product at m/z 133 was observed, which was identified as 4-isopropenyphenol [15]. The mass spectra of m/z 227 (BPA) and m/z 133 (4-isopropenyphenol) are illustrated in Fig. 8(c) and (d). The 4-isopropenyphenol could be attributable to the attack of BPA by photogenerated holes at the tert-butyl carbon. No hydroxylated products were identified by LC–MS/MS, supporting that hydroxyl radical is insignificant in the photocatalytic degradation. In addition, superoxide radical species and singlet oxygen could also directly oxidize BPA. Scheme 2 illustrates the simple degradation pathway of BPA by BOI-180-24.

# 3.5. Stability of BOI-180-24 composite

The optical stability of Bi/BiOI composites for photocatalytic reaction under simulated solar light was investigated by recycling tests and the results are shown in Fig. S5. The results indicate that the composite is stable without distinct photocorrosion after five recycling runs.

# 4. Conclusions

A novel Bi/BiOI composite was fabricated via a facile one-step solvothermal process. Low reaction temperature and short reaction time favored the formation of pure BiOI, which would be gradually decomposed to Bi as the temperature went up and the reaction extended. Thus, composites of Bi and BiOI could be synthesized and their mass ratio could be tunable by adjusting the temperature and the reaction duration. The photocatalyst prepared at 180 °C for 24 h was a composite Bi/BiOI with the mass ratio of metallic Bi in the composite approximate 12.5%. It displayed very high photocatalytic performance to BPA under simulated solar light irradiation. The potential photocatalytic mechanisms of Bi/BiOI on BPA were also elucidated: photogenerated holes, superoxide radical species and singlet oxygen were responsible for the photocatalytic oxidation. Especially, the superoxide radical species was regarded as the predominant species to degrade BPA.

#### Acknowledgements

The authors gratefully acknowledge the financial support of Ministry of Education (Grant 708020); Tianjin Municipal Science and Technology Commission (10SYSYJC27200), Ministry of Science and Technology (2009BAC60B01, 2012ZX07529-003), Ministry of Environmental Protection (201009026) and the Fundamental Research Funds for the Central Universities.

#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2013.08.048. Materials and reagents; Some characterization and instrument analysis methods; Recycle test. The SEM images of the prepared materials at different reaction temperatures and durations. The N<sub>2</sub> adsorption–desorption isotherms and pore size distributions of the prepared materials BOI-180-24. Photocurrent responses of the prepared materials at different temperatures and durations. The results of the recycling tests of BOI-180-24.

#### References

- [1] H. Liu, W.R. Cao, Y. Su, Y. Wang, X.H. Wang, Synthesis, characterization and photocatalytic performance of novel visible-light-induced Ag/BiOI, Appl. Catal. B 111 (2012) 271–279.
- [2] C.L. Yu, J.C. Yu, C.F. Fan, H.R. Wen, S.J. Hu, Synthesis and characterization of Pt/ BiOI nanoplate catalyst with enhanced activity under visible light irradiation, Mater. Sci. Eng. B 166 (2010) 213–219.
- [3] T.B. Li, G. Chen, C. Zhou, Z.Y. Shen, R.C. Jin, J.X. Sun, New photocatalyst BiOCl/ BiOl composites with highly enhanced visible light photocatalytic performances, Dalton Trans. 40 (2011) 6751–6758.
- [4] J. Cao, B.Y. Xu, B.D. Luo, H.L. Lin, S.F. Chen, Novel BiOl/BiOBr heterojunction photocatalysts with enhanced visible light photocatalytic properties, Catal. Commun. 13 (2011) 63–68.
- [5] J. Cao, B.Y. Xu, H.L. Lin, B.D. Luo, S.F. Chen, Chemical etching preparation of BiOl/BiOBr heterostructures with enhanced photocatalytic properties for organic dye removal, Chem. Eng. J. 185 (2012) 91–99.
  [6] X. Zhang, L.Z. Zhang, T.F. Xie, D.J. Wang, Low-temperature synthesis and high
- [6] X. Zhang, L.Z. Zhang, T.F. Xie, D.J. Wang, Low-temperature synthesis and high visible-light-induced photocatalytic activity of BiOl/TiO<sub>2</sub> heterostructures, J. Phys. Chem. C 113 (2009) 7371–7378.
- [7] G.P. Dai, J.G. Yu, G. Liu, Synthesis and enhanced visible-light photoelectrocatalytic activity of *p*-*n* junction BiOI/TiO<sub>2</sub> nanotube arrays, J. Phys. Chem. C 115 (2011) 7339–7346.
- [8] J. Jiang, X. Zhang, P.B. Sun, L.Z. Zhang, ZnO/BiOI heterostructures: photoinduced charge-transfer property and enhanced visible-light photocatalytic activity, J. Phys. Chem. C 115 (2011) 20555–20564.
- [9] H.F. Cheng, B.B. Huang, Y. Dai, X.Y. Qin, X.Y. Zhang, One-step synthesis of the nanostructured Agl/BiOI composites with highly enhanced visible-light photocatalytic performances, Langmuir 26 (2010) 6618–6624.
- [10] Y.Y. Li, J.S. Wang, H.C. Yao, L.Y. Dang, Z.J. Li, Chemical etching preparation of BiOl/Bi<sub>2</sub>O<sub>3</sub> heterostructures with enhanced photocatalytic activities, Catal. Commun. 12 (2011) 660–664.
- [11] I. Djerdj, D. Sheptyakov, F. Gozzo, D. Arčon, R. Nesper, M. Niederberger, Oxygen self-doping in hollandite-type vanadium oxyhydroxide nanorods, J. Am. Chem. Soc. 130 (2008) 11364–11375.
- [12] X. Zhang, L.Z. Zhang, Electronic and band structure tuning of ternary semiconductor photocatalysts by self doping: the case of BiOI, J. Phys. Chem. C 114 (2010) 18198–18206.
- [13] J.G. Hengstler, H. Foth, T. Gebel, P.J. Kramer, W. Lilienblum, H. Schweinfurth, W. Volkel, K.M. Wollin, U. Gundert-Remy, Critical evaluation of key evidence on the human health hazards of exposure to bisphenol A, Crit. Rev. Toxicol. 41 (2011) 263–291.
- [14] Y.B. Wetherill, B.T. Akingbemi, J. Kanno, J.A. McLachlan, A. Nadal, C. Sonnenscheing, C.S. Watson, R.T. Zoeller, S.M. Belcher, In vitro molecular mechanisms of bisphenol A action, Reprod. Toxicol. 24 (2007) 178–198.
- [15] C.Y. Wang, L.Y. Zhu, C. Song, G.Q. Shan, P. Chen, Characterization of photocatalyst Bi<sub>3.84</sub>W<sub>0.16</sub>O<sub>6.24</sub> and its photodegradation on bisphenol A under simulated solar light irradiation, Appl. Catal. B 105 (2011) 229–236.
- [16] T. Takeuchi, O. Tsutsumi, Y. Ikezuki, Y. Takai, Y. Taketani, Positive relationship between androgen and the endocrine disruptor, bisphenol A, in normal women and women with ovarian dysfunction, Endocr. J. 51 (2004) 165–169.
- [17] R.T. Zoeller, R. Bansal, C. Parris, Bisphenol-A, an environmental contaminant that acts as a thyroid hormone receptor antagonist in vitro, increases serum thyroxine, and alters RC<sub>3</sub>/neurogranin expression in the developing rat brain, Endocrinology 146 (2005) 607–612.
- [18] R.A. Keri, S.M. Ho, P.A. Hunt, K.E. Knudsen, A.M. Soto, G.S. Prins, An evaluation of evidence for the carcinogenic activity of bisphenol A, Reprod. Toxicol. 24 (2007) 240–252.
- [19] B. Pan, D.H. Lin, H. Mashayekhi, B.S. Xing, Adsorption and hysteresis of bisphenol A and 17 alpha-ethinyl estradiol on carbon nanomaterials, Environ. Sci. Technol. 42 (2008) 5480–5485.
- [20] Y.H. Cui, X.Y. Li, G.H. Chen, Electrochemical degradation of bisphenol A on different anodes, Water Res. 43 (2009) 1968–1976.
- [21] E.M. Rodriguez, G. Fernandez, N. Klamerth, M.I. Maldonado, P.M. Alvarez, S. Malato, Efficiency of different solar advanced oxidation processes on the oxidation of bisphenol A in water, Appl. Catal. B 95 (2010) 228–237.
- [22] Y.T. Xie, H.B. Li, L. Wang, Q.A. Liu, Y. Shi, H.Y. Zheng, M. Zhang, Y.T. Wu, B. Lu, Molecularly imprinted polymer microspheres enhanced biodegradation of bisphenol A by acclimated activated sludge, Water Res. 45 (2011) 1189–1198.
- [23] X. Zhang, Z.H. Ai, F.L. Jia, L.Z. Zhang, Generalized one-pot synthesis, characterization, and photocatalytic activity of hierarchical BiOX (X = Cl, Br, I) nanoplate microspheres, J. Phys. Chem. C 112 (2008) 747–753.
- [24] Y. Cheng, M. Shigeta, S. Choi, T. Watanabe, Formation mechanism of titanium boride nanoparticles by RF induction thermal plasma, Chem. Eng. J. 183 (2012) 483–491.
- [25] Y.N. Wang, K.J. Deng, L.Z. Zhang, Visible light photocatalysis of BiOl and its photocatalytic activity enhancement by in situ ionic liquid modification, J. Phys. Chem. C 115 (2011) 14300–14308.
- [26] N.B.-M. Kalish, E. Shandalov, V. Kharlanov, D. Pines, E. Pines, Apparent stoichiometry of water in proton hydration and proton dehydration reactions in CH<sub>3</sub>CN/H<sub>2</sub>O solutions, J. Phys. Chem. A 115 (2011) 4063–4075.
- [27] C.H. Wang, C.L. Shao, Y.C. Liu, L. Zhang, Photocatalytic properties BiOCl and Bi<sub>2</sub>O<sub>3</sub> nanofibers prepared by electrospinning, Scr. Mater. 59 (2008) 332–335.
- [28] K. Gurunathan, Photocatalytic hydrogen production using transition metal ions-doped γ-Bi<sub>2</sub>O<sub>3</sub> semiconductor particles, Int. J. Hydrogen Energy 29 (2004) 933–940.

- [29] Z. Liu, X.X. Xu, J.Z. Fang, X.M. Zhu, J.H. Chu, B.J. Li, Microemulsion synthesis, characterization of bismuth oxyiodine/titanium dioxide hybrid nanoparticles with outstanding photocatalytic performance under visible light irradiation, Appl. Surf. Sci. 258 (2012) 3771–3778.
- [30] A. Tanaka, S. Sakaguchi, K. Hashimoto, H. Kominami, Preparation of Au/TiO<sub>2</sub> exhibiting strong surface plasmon resonance effective for photoinduced hydrogen formation from organic and inorganic compounds under irradiation of visible light, Catal. Sci. Technol. 2 (2012) 907–909.
- [31] Z. Han, L. Ren, Z. Cui, C. Chen, H. Pan, J. Chen, Ag/ZnO flower heterostructures as a visible-light driven photocatalyst via surface plasmon resonance, Appl. Catal. B 126 (2012) 298–305.
- [32] S.-W. Cao, J. Fang, M.M. Shahjamali, F.Y.C. Boey, J. Barber, S.C.J. Loo, C. Xue, Plasmon-enhanced hydrogen evolution on Au-InVO4 hybrid microspheres, RSC Adv. 2 (2012) 5513–5515.
- [33] H. Zhang, X.F. Fan, X. Quan, S. Chen, H.T. Yu, Graphene sheets grafted Ag@AgCl hybrid with enhanced plasmonic photocatalytic activity under visible light, Environ. Sci. Technol. 45 (2011) 5731–5736.
- [34] A. Primo, T. Marino, A. Corma, R. Molinari, H. García, Efficient visible-light photocatalytic water splitting by minute amounts of gold supported on nanoparticulate CeO<sub>2</sub> obtained by a biopolymer templating method, J. Am. Chem. Soc. 133 (2011) 6930–6933.
- [35] D.B. Ingram, S. Linic, Water splitting on composite plasmonic-metal/ semiconductor photoelectrodes: evidence for selective plasmon-induced formation of charge carriers near the semiconductor surface, J. Am. Chem. Soc. 133 (2011) 5202–5205.
- [36] P. Wang, B. Huang, Z. Lou, X. Zhang, X. Qin, Y. Dai, Z. Zheng, X. Wang, Synthesis of highly efficient Ag@AgCl plasmonic photocatalysts with various structures, Chem. Eur. J. 16 (2010) 538–544.
- [37] O. Rosseler, M.V. Shankar, M.K.-L. Du, L. Schmidlin, N. Keller, V. Keller, Solar light photocatalytic hydrogen production from water over Pt and Au/ TiO<sub>2</sub>(anatase/rutile) photocatalysts: influence of noble metal and porogen promotion, J. Catal. 269 (2010) 179–190.
- [38] J. Toudert, R. Serna, M. Jiménez de Castro, Exploring the optical potential of nano-bismuth: tunable surface plasmon resonances in the near ultraviolet-tonear infrared range, J. Phys. Chem. C 116 (2012) 20530–20539.
- [39] B. Ma, J. Guo, W.-L. Dai, K. Fan, Highly stable and efficient Ag/AgCl core-shell sphere: controllable synthesis, characterization, and photocatalytic application, Appl. Catal. B 130–131 (2013) 257–263.
- [40] H. Ma, J. Shen, M. Shi, X. Lu, Z. Li, Y. Long, N. Li, M. Ye, Significant enhanced performance for Rhodamine B, phenol and Cr(VI) removal by Bi2W06 nancomposites via reduced graphene oxide modification, Appl. Catal. B 121– 122 (2012) 198–205.
- [41] R. Nyholm, A. Berndtsson, N. Martensson, Core level binding energies for the elements Hf to Bi (*Z* = 72–83), J. Phys. C: Solid State Phys. 13 (1980) L1091.
- [42] Y. Zheng, C. Chen, Y. Zhan, X. Lin, Q. Zheng, K. Wei, J. Zhu, Photocatalytic activity of Ag/ZnO heterostructure nanocatalyst: correlation between structure and property, J. Phys. Chem. C 112 (2008) 10773–10777.
- [43] J. Ren, W.Z. Wang, S.M. Sun, L. Zhang, J. Chang, Enhanced photocatalytic activity of Bi2WO6 loaded with Ag nanoparticles under visible light irradiation, Appl. Catal. B 92 (2009) 50–55.
- [44] C. Young, T.M. Lim, K. Chiang, J. Scott, R. Amal, Photocatalytic oxidation of toluene and trichloroethylene in the gas-phase by metallised (Pt, Ag) titanium dioxide, Appl. Catal. B 78 (2008) 1–10.
- [45] T. Tran. T, P. Sheng, C.a. Huang, J. Li, L. Chen, L. Yuan, C.A. Grimes, Q. Cai, Synthesis and photocatalytic application of ternary Cu–Zn–S nanoparticlesensitized TiO<sub>2</sub> nanotube arrays, Chem. Eng. J. 210 (2012) 425–431.
- [46] Y. Chen, A. Lu, Y. Li, L. Zhang, H.Y. Yip, H. Zhao, T. An, P.-K. Wong, Naturally occurring sphalerite as a novel cost-effective photocatalyst for bacterial disinfection under visible light, Environ. Sci. Technol. 45 (2011) 5689–5695.

- [47] S. Song, L. Xu, Z. He, J. Chen, X. Xiao, B. Yan, Mechanism of the photocatalytic degradation of C.I. reactive black 5 at pH 12.0 using SrTiO<sub>3</sub>/CeO<sub>2</sub> as the catalyst, Environ. Sci. Technol. 41 (2007) 5846–5853.
- [48] W. Wang, Y. Yu, T. An, G. Li, H.Y. Yip, J.C. Yu, P.K. Wong, Visible-light-driven photocatalytic inactivation of *E. coli* K-12 by bismuth vanadate nanotubes: bactericidal performance and mechanism, Environ. Sci. Technol. 46 (2012) 4599–4606.
- [49] C. Wang, L. Zhu, M. Wei, P. Chen, G. Shan, Photolytic reaction mechanism and impacts of coexisting substances on photodegradation of bisphenol A by Bi<sub>2</sub>WO<sub>6</sub> in water, Water Res. 46 (2012) 845–853.
- [50] Y.Y. Li, J.S. Wang, B. Liu, L.Y. Dang, H.C. Yao, Z.J. Li, BiOI-sensitized TiO<sub>2</sub> in phenol degradation: a novel efficient semiconductor sensitizer, Chem. Phys. Lett. 508 (2011) 102–106.
- [51] M. Yin, Z. Li, J. Kou, Z. Zou, Mechanism investigation of visible light-induced degradation in a heterogeneous TiO<sub>2</sub>/Eosin Y/Rhodamine B system, Environ. Sci. Technol. 43 (2009) 8361–8366.
- [52] H. Ji, F. Chang, X. Hu, W. Qin, J. Shen, Photocatalytic degradation of 2,4,6trichlorophenol over g-C3N4 under visible light irradiation, Chem. Eng. J. 218 (2013) 183–190.
- [53] J.W. Ng, X.P. Wang, D.D. Sun, One-pot hydrothermal synthesis of a hierarchical nanofungus-like anatase TiO<sub>2</sub> thin film for photocatalytic oxidation of bisphenol A, Appl. Catal. B 110 (2011) 260–272.
- [54] Y. Chen, S. Yang, K. Wang, L. Lou, Role of primary active species and TiO<sub>2</sub> surface characteristic in UV-illuminated photodegradation of acid orange 7, J. Photochem. Photobiol. A 172 (2005) 47–54.
- [55] L.-S. Zhang, K.-H. Wong, H.-Y. Yip, C. Hu, J.C. Yu, C.-Y. Chan, P.-K. Wong, Effective photocatalytic disinfection of *E. coli* K-12 using AgBr-Ag-Bi2WO6 nanojunction system irradiated by visible light: the role of diffusing hydroxyl radicals, Environ. Sci. Technol. 44 (2010) 1392–1398.
- [56] H.B. Fu, S.C. Zhang, T.G. Xu, Y.F. Zhu, J.M. Chen, Photocatalytic degradation of RhB by fluorinated Bi2WO6 and distributions of the intermediate products, Environ. Sci. Technol. 42 (2008) 2085–2091.
- [57] Y. Cui, J. Huang, X. Fu, X. Wang, Metal-free photocatalytic degradation of 4chlorophenol in water by mesoporous carbon nitride semiconductors, Catal. Sci. Technol. 2 (2012) 1396–1402.
- [58] Y. Nosaka, T. Daimon, A.Y. Nosaka, Y. Murakami, Singlet oxygen formation in photocatalytic TiO<sub>2</sub> aqueous suspension, Phys. Chem. Chem. Phys. 6 (2004) 2917–2918.
- [59] X.P. Wang, T.T. Lim, Effect of hexamethylenetetramine on the visible-light photocatalytic activity of C–N codoped TiO<sub>2</sub> for bisphenol A degradation: evaluation of photocatalytic mechanism and solution toxicity, Appl. Catal. A 399 (2011) 233–241.
- [60] P. Raja, A. Bozzi, H. Mansilla, J. Kiwi, Evidence for superoxide-radical anion, singlet oxygen and OH-radical intervention during the degradation of the lignin model compound (3-methoxy-4-hydroxyphenylmethylcarbinol), J. Photochem. Photobiol. A 169 (2005) 271–278.
- [61] D. Zhang, R. Qiu, L. Song, B. Eric, Y. Mo, X. Huang, Role of oxygen active species in the photocatalytic degradation of phenol using polymer sensitized TiO<sub>2</sub> under visible light irradiation, J. Hazard. Mater. 163 (2009) 843–847.
- [62] B. Subash, B. Krishnakumar, V. Pandiyan, M. Swaminathan, M. Shanthi, Synthesis and characterization of novel WO3 loaded Ag-ZnO and its photocatalytic activity, Mater. Res. Bull. 48 (2013) 63–69.
- [63] B. Subash, B. Krishnakumar, M. Swaminathan, M. Shanthi, Highly Efficient, solar active, and reusable photocatalyst: Zr-loaded Ag-ZnO for reactive red 120 dye degradation with synergistic effect and dye-sensitized mechanism, Langmuir 29 (2012) 939–949.
- [64] B. Subash, B. Krishnakumar, R. Velmurugan, M. Swaminathan, M. Shanthi, Synthesis of Ce co-doped Ag-ZnO photocatalyst with excellent performance for NBB dye degradation under natural sunlight illumination, Catal. Sci. Technol. 2 (2012) 2319–2326.