

Accepted Manuscript

Sonocatalytic degradation of norfloxacin in aqueous solution caused by a novel Z-scheme sonocatalyst, mMBIP-MWCNT-In₂O₃ composite

Siyi Li, Guowei Wang, Jing Qiao, Ying Zhou, Xue Ma, Hongbo Zhang, Guanshu Li, Jun Wang, Youtao Song



PII: S0167-7322(17)34919-X

DOI: <https://doi.org/10.1016/j.molliq.2018.01.115>

Reference: MOLLIQ 8569

To appear in: *Journal of Molecular Liquids*

Received date: 16 October 2017

Revised date: 15 January 2018

Accepted date: 20 January 2018

Please cite this article as: Siyi Li, Guowei Wang, Jing Qiao, Ying Zhou, Xue Ma, Hongbo Zhang, Guanshu Li, Jun Wang, Youtao Song , Sonocatalytic degradation of norfloxacin in aqueous solution caused by a novel Z-scheme sonocatalyst, mMBIP-MWCNT-In₂O₃ composite. The address for the corresponding author was captured as affiliation for all authors. Please check if appropriate. Molliq(2017), <https://doi.org/10.1016/j.molliq.2018.01.115>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Sonocatalytic degradation of norfloxacin in aqueous solution caused by a novel Z-scheme sonocatalyst, mMBIP-MWCNT-In₂O₃ composite

Siyi Li ^a, Guowei Wang ^a, Jing Qiao ^a, Ying Zhou ^a, Xue Ma ^b, Hongbo Zhang ^a, Guanshu Li ^b,
Jun Wang ^{a,*}, Youtao Song ^{b,*}

^a College of Chemistry, Liaoning University, Shenyang 110036, P. R. China

^b College of Environment, Liaoning University, Shenyang 110036, P. R. China

Received 00 October 2017; received in revised form 00 October 2017; accepted 00 October 2017;

Available online 00 October 2017

ABSTRACT

In this study, a novel Z-scheme composite sonocatalyst, mMBIP-MWCNT-In₂O₃, is successfully fabricated by using hydrothermal and calcination methods. And then, the prepared sonocatalyst is characterized by X-ray diffractometer (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), UV-vis diffuse reflectance spectra (DRS), fourier transform infrared spectra (FT-IR) and X-ray photoelectron spectroscopy (XPS). The sonocatalytic activity of mMBIP-MWCNT-In₂O₃ composite is evaluated through the degradation of norfloxacin in aqueous solution under ultrasonic irradiation. Meanwhile, the impacts of ultrasonic irradiation time, used times and scavengers on the sonocatalytic degradation efficiency are researched by using UV-vis spectroscopy. The results indicate that the addition of MWCNT accelerates the electron (e⁻) transfer and restrains the recombination of electrons (e⁻) and holes (h⁺) in Z-scheme mMBIP-MWCNT-In₂O₃ sonocatalyst. In comparison, the formation of Z-scheme sonocatalytic system and the presence of and MWCNT make the mMBIP-In₂O₃ display much higher activity in the degradation of norfloxacin. The relatively high sonocatalytic degradation ratio of norfloxacin can be got when the 10.00 mg/L norfloxacin, 1.0 g/L mMBIP-MWCNT-In₂O₃, 150 min ultrasonic irradiation (40 kHz frequency and 300 W output power), 100 mL total volume and 25-28 °C temperature are used. Subsequently, several scavengers are used to confirm the formation of the hydroxyl radical

* Corresponding author. Tel.: +86 024 62207861; Fax: +86 024 62202053.

E-mail addresses: wangjun888tg@126.com (J. Wang); wangjun891@sina.com (J. Wang); ysong_tg@126.com (Y. Song)

<http://dx.doi.org/10.1016/j.molliq.2017.00.000>

0000-0000/© 2017 Elsevier Ltd. All rights reserved.

(•OH) and hole (h^+) for elucidating the sonocatalytic degradation mechanism. It is concluded that most of the norfloxacin in aqueous solution can be degraded by using mMBIP-MWCNT-In₂O₃ as sonocatalyst under ultrasonic irradiation.

© 2017 Elsevier B.V. All rights reserved.

Keywords: Modified Z-scheme sonocatalytic system; Multi-wall carbon nanotubes; mMBIP-MWCNT-In₂O₃ composite; Sonocatalytic degradation; Norfloxacin

ACCEPTED MANUSCRIPT

Sonocatalytic degradation of norfloxacin in aqueous solution caused by a novel Z-scheme sonocatalyst, mMBIP-MWCNT-In₂O₃ composite

Siyi Li ^a, Guowei Wang ^a, Jing Qiao ^a, Ying Zhou ^a, Xue Ma ^b, Hongbo Zhang ^a, Guanshu Li ^b, Jun Wang ^{a,*}, Youtao Song ^{b,*}

^a College of Chemistry, Liaoning University, Shenyang 110036, P. R. China

^b College of Environment, Liaoning University, Shenyang 110036, P. R. China

ARTICLE INFO

Article history:

Received 00 October 2017

Revised 00 October 2017

Accepted 00 October 2017

Available online 00 September 2017

Keywords:

Modified Z-scheme sonocatalytic system

Multi-wall carbon nanotubes

mMBIP-MWCNT-In₂O₃ composite

Sonocatalytic degradation

Norfloxacin

ABSTRACT

In this study, a novel Z-scheme composite sonocatalyst, mMBIP-MWCNT-In₂O₃, is successfully fabricated by using hydrothermal and calcination methods. And then, the prepared sonocatalyst is characterized by X-ray

* Corresponding author. Tel.: +86 024 62207861; Fax: +86 024 62202053.

E-mail addresses: wangjun888tg@126.com (J. Wang); wangjun891@sina.com (J. Wang); ysong_tg@126.com (Y. Song)

<http://dx.doi.org/10.1016/j.molliq.2017.00.000>

0000-0000/© 2017 Elsevier Ltd. All rights reserved.

diffractometer (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), UV-vis diffuse reflectance spectra (DRS), fourier transform infrared spectra (FT-IR) and X-ray photoelectron spectroscopy (XPS). The sonocatalytic activity of mMBIP-MWCNT-In₂O₃ composite is evaluated through the degradation of norfloxacin in aqueous solution under ultrasonic irradiation. Meanwhile, the impacts of ultrasonic irradiation time, used times and scavengers on the sonocatalytic degradation efficiency are researched by using UV-vis spectroscopy. The results indicate that the addition of MWCNT accelerates the electron (e⁻) transfer and restrains the recombination of electrons (e⁻) and holes (h⁺) in Z-scheme mMBIP-MWCNT-In₂O₃ sonocatalyst. In comparison, the formation of Z-scheme sonocatalytic system and the presence of and MWCNT make the mMBIP-In₂O₃ display much high activity in the degradation of norfloxacin. The relatively high sonocatalytic degradation ratio of norfloxacin can be got when 10.00 mg/L norfloxacin, 1.0 g/L mMBIP-MWCNT-In₂O₃, 150 min ultrasonic irradiation (40 kHz frequency and 300 W output power), 100 mL total volume and 25-28 °C temperature are used. Subsequently, several scavengers are used to confirm the formation of the hydroxyl radical (•OH) and hole (h⁺) for elucidating the sonocatalytic degradation mechanism. It is concluded that most of the norfloxacin in aqueous solution can be degraded by using mMBIP-MWCNT-In₂O₃ as sonocatalyst under ultrasonic irradiation.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Since the antibiotic came out, it has brought many benefits to humans. Particularly, norfloxacin, in China as one of the top five antibiotics, was used more than 5,000 tons in 2013 [1,2]. However, due to the mass production of norfloxacin, a series of social problems have been brought. A large amount of wastewater generated in the production of norfloxacin has entered lakes, rivers and underground water, resulting in water pollution, human eating by mistake and so on [3,4]. If these norfloxacin from various effluents are not dealt with in time, they may cause the damage to the organism and increase bacterial resistance after entering the body, which will seriously endanger the human health [5]. Therefore, the effective and rapid treatment method of norfloxacin as organic pollutant is

necessary and urgent.

As we all known, many traditional ways, such as chemical flocculation, adsorption and activated sludge, can be used to treat wastewater [6,7]. Nevertheless, these traditional treatment ways of organic contaminants generally show many disadvantages. In recent years, ultrasonic technology, as a new Advanced Oxidation Processes, has become a kind of green and efficient method to treat organic contaminants [8-10]. In particular, the ultrasonic technology displays a wide application prospect for the treatment of those low- or non-transparent organic pollutants. Ultrasonic degradation of organic pollutants is related to the cavitation effect resulted from ultrasonic irradiation [11]. When the ultrasound is used to irradiate to liquid, the cavitation bubbles occur, largen, condense and collapse [12]. Acoustic cavitation produces high pressure, high temperature and local hot spots and is accompanied by the sonoluminescence at the same time. The created extreme physical environment can cause the degradation of organic pollutant [13,14]. However, as reported previously, the degradation rate of organic pollutants is very low by using alone ultrasound. Recently, the sonocatalytic degradation concept, which is similar to photocatalytic reaction, was proposed. The use of sonocatalyst can give full play to the superiority of ultrasound, which can produce obviously synergistic effect and enhance the degradation efficiency of organic pollutants.

Many photocatalysts have been used tentatively to enhance the ultrasonic degradation of organic pollutants [15-17]. However, the lack of high activity and stability for sonocatalyst has severely limited the practical application of sonocatalytic degradation method. Recently, due to high photocatalytic activity and strong oxidation ability, BiPO_4 has attracted more and more attention. BiPO_4 mainly exists in three crystalline phases, that is, monoclinic structure (nBIP), monoclinic monazite structure (mMBIP) and hexagonal structure (HBIP) [18]. Considering the high photocatalytic performance,

simple synthesis condition and stable property, the mMBIP ($E_{VB} = +4.52$ eV, $E_{CB} = +0.20$ eV and $\Delta E_{bg} = +4.32$ eV) was selected as sonocatalyst in this study [19]. Nevertheless, mMBIP only can be excited by ultraviolet-light below 300 nm wavelength due to its wide band-gap (4.32 eV) [20]. In order to expand the light absorption range, the mMBIP was combined with a relatively narrow band-gap semiconductor photocatalyst (In_2O_3). In_2O_3 ($E_{VB} = +2.18$ eV, $E_{CB} = -0.62$ eV and $\Delta E_{bg} = +2.80$ eV) as a narrow band-gap semiconductor photocatalyst can absorb long wavelength visible-light [21,22]. Because the valence band of In_2O_3 is correspondingly close to the conduction band of mMBIP, an ideal Z-scheme photocatalytic system can be formed. Being similar to photocatalytic reaction, the ultrasound can be used to excite the photocatalyst, producing photo-generated electrons (e^-) and hole (h^+) in sonocatalytic system [23,24]. Apparently, the excited catalyst faces the problem of electron (e^-) and hole (h^+) recombination. The Z-scheme sonocatalytic system can effectively inhibit the recombination of electron (e^-) and hole (h^+) and broaden light absorption range [25,26].

For an ideal Z-scheme sonocatalytic system, it is important to accelerate the electron transfer from the conduction band of one sonocatalyst to the valence band of other sonocatalyst [27]. In recent years, some substances have been used as conducting channel to accelerate the electron transfer, for instance, noble metal, fullerenes and graphene, etc [28-30]. Nevertheless, noble metals as conducting channel can form small contact area and enhance resistance, which is detrimental to electron transfer [31]. Recently, the carbon nano-materials with large specific surface area and superior electron conductivity have been widely applied in the various branches [32-34]. In this paper, because of unique advantages the multi-walled carbon nanotubes (MWCNTs) was used as a conducting channel to accelerate the electron transfer, inhibiting recombination of electron (e^-) and hole (h^+).

In this article, mMBIP-MWCNT- In_2O_3 composite as sonocatalyst was prepared by means of

hydrothermal and calcination methods. The prepared sonocatalyst was characterized by X-ray diffractometer (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), UV-vis diffuse reflectance spectra (DRS), fourier transform infrared spectra (FT-IR) and X-ray photoelectron spectroscopy (XPS). The sonocatalytic activity of mMBIP-MWCNT-In₂O₃ composite was evaluated by degradation of norfloxacin under ultrasonic irradiation. At the same time, some major influencing factors are studied including ultrasonic time and used times. Moreover, the possible mechanism of sonocatalytic degradation of norfloxacin caused by mMBIP-MWCNT-In₂O₃ composite was proposed. The results show that the presence of MWCNT can obviously enhance the sonocatalytic activity of mMBIP-In₂O₃ composite in degradation of norfloxacin under ultrasonic irradiation. It can be considered that the prepared mMBIP-MWCNT-In₂O₃ composite is an excellent sonocatalyst and applicable in the degradation of norfloxacin in aqueous solution under ultrasonic irradiation.

2. Experimental

2.1. Reagents and apparatus

Bismuth nitrate pentahydrate Bi(NO₃)₃·5H₂O (analytically pure) and phosphoric acid (H₃PO₄, 85 %, analytically pure, Sinopharm Chemical Reagent Co, Ltd, China) were used to synthesize the BiPO₄ particles. Ammonium hydroxide (ammonium water, 25 %, analytically pure, Sinopharm Chemical Reagent Co, Ltd, China) and Indium nitrate hydrate (In(NO₃)₃·4.5H₂O, analytically pure, Sinopharm Chemical Reagent Co, Ltd, China) were used to prepare the In₂O₃. Norfloxacin (NF) (98 % purity, Sinopharm Chemical Reagent Co, Ltd, China) was used to undergo the sonocatalytic degradation. All the reagents were of analytical purity grade and directly used without further purification.

Muffle furnace (SX2-4-10, Great Wall Furnace Company, China) and oven (101-1, Shanghai Experiment Apparatus Company, China) were used to prepare the mMBiPO₄-MWCNT-In₂O₃ as sonocatalyst. Controllable Serial-Ultrasonics apparatus (KQ-300, six transducer, Kunshan Company, China) was adopted to irradiate the norfloxacin in aqueous solution, operating at ultrasonic frequency of 40 kHz and output power of 300 W through manual adjust.

2.2. Preparation of sonocatalysts

2.2.1. mMBIP

BiPO₄ (mMBIP) powders were synthesized through hydrothermal processes. Firstly, 4.37 g Bi(NO₃)₃·5H₂O (9.0 mmol) and 90 mL H₃PO₄ (6.0 mol) were put into a beaker while stirring magnetically for 1.0 h to form a homogeneous solution. Subsequently, the obtained suspension was transferred into Teflon-lined stain-less steel autoclaves and the temperature was maintained at 200 °C for 72 h. After cooling down to room temperature, the monoclinic monazite BiPO₄ (mMBIP) was obtained by filtering off. The sample was washed with distilled water for several times and then dried at 80 °C for 24 h.

2.2.2. mMBIP-MWCNT

2.19 g Bi(NO₃)₃·5H₂O (4.5 mmol), 45 mL H₃PO₄ (3.0 mol) and 0.15 g MWCNT were put into a beaker while stirring magnetically for 1.0 h to form a homogeneous solution. Subsequently, according to synthesizing of mMBIP, mMBIP-MWCNT is synthesized under the same condition.

2.2.3. In₂O₃

The In₂O₃ was prepared by gradually adding 12 % ammonium water solution into In(NO₃)₃ aqueous solution under the condition of magnetic stirring, until the pH of the mixed solution was equal

to 8.0. Meanwhile, the white precipitation, $\text{In}(\text{OH})_3$, was produced. After filtration, the precipitation was washed with distilled water for several times, and then dried at 90 °C for 14 h. Lastly, the white In_2O_3 powder was obtained after heating at temperature of 300 °C in muffle furnace for 6.0 h.

2.2.4. mMBIP- In_2O_3

1.00 g mMBIP and 1.00 g In_2O_3 (3.6 mmol) were taken into 20 mL mixed solution of 1:1 volume ratio water and ethanol. After ultrasonic dispersion for 20 min and centrifugation, the mixture was dried at 70 °C for 14 h. The powder was transferred into a muffle burner and heated at 300 °C for 6.0 h and the mMBIP- In_2O_3 composite as sonocatalyst was obtained after fully grinding.

2.2.5. mMBIP-MWCNT- In_2O_3 composite

1.00 g mMBIP-MWCNT and 1.00 g In_2O_3 (3.6 mmol) were taken into 1:1 volume ratio of water-ethanol solution. Then, the mMBIP-MWCNT- In_2O_3 composite as sonocatalyst was prepared by using similar method as described above.

2.3. Characterization of the prepared mMBIP-MWCNT- In_2O_3 composite

X-ray powder diffractometer (XRD, D-8, Bruker-axs, Germany, Ni filtered Cu $K\alpha$ radiation in the range of 2θ from 10° to 70°), scanning electron microscopy (SEM, JEOL JSM-5610LV, Hitachi Corporation, Japan) and Energy dispersive X-ray analysis (EDX, JEOL JSM-5610LV, Hitachi Corporation, Japan), UV-vis diffuse reflectance spectroscopy (DRS, UV-3600, SHIMADZU, Japan), fourier transform infrared spectra (FT-IR, Nicolet 5700, Beckman Coulter, America), X-ray photoelectron spectroscopy (XPS, XSAM800, Shimadzu-Kratos, Japan) were used to characterize the prepared samples.

2.4. Measurements of sonocatalytic activity of the prepared samples

Sonocatalytic degradation experiments of norfloxacin were performed in a 150 mL erlenmeyer flask placed in an ultrasonic irradiation apparatus (300 (length) × 180 mm (width) × 120 mm (height), KQ-300, 40 kHz, 300 W, six transducers, Kunshan ultrasonic apparatus Company, China) under air atmosphere. In the experiment, 1.0 g/L mMBIP-MWCNT-In₂O₃ powder and 10.00 mg/L norfloxacin concentration in 100 mL total volume solution were applied to perform the sonocatalytic degradation. Before ultrasonic irradiation, the above solution was stirred for 30 min in the darkness to achieve the adsorption-desorption equilibrium. And then, the sonocatalytic degradation of norfloxacin was implemented under ultrasonic irradiation for 150 min. From the irradiated liquid a certain of sample was removed at a specific time interval and measured by UV-vis spectrometer (Cary 50, Varian Company, USA). The degradation ratios of norfloxacin were determined based on the absorbance change of norfloxacin solution at 272 nm, 323 nm and 327 nm, respectively, using the following equation:

$$\text{Reduction ratio (\%)} = (1 - A_t/A_0) \times 100 \%$$

Where A_0 is the initial absorbance of norfloxacin solution, A_t is the instant absorbance after a certain of ultrasonic irradiation time (t).

Moreover, the various influencing factors such as ultrasonic irradiation time, used times and scavengers on sonocatalytic activity of mMBIP-MWCNT-In₂O₃ composite were also investigated through the sonocatalytic degradation of norfloxacin in aqueous solution.

3. Results and discussion

3.1. XRD patterns of the prepared samples

In order to determine the crystal structure and phase composition of the samples, X-ray

diffraction (XRD) analyses were performed. The XRD patterns of prepared mMBIP, In_2O_3 , mMBIP- In_2O_3 and mMBIP-MWCNT- In_2O_3 were given in Fig. 1. As shown in Fig. 1(mMBIP), three distinct characteristic diffraction peaks were found at 18.5° , 22.8° and 37.0° , respectively, which can be perfectly indexed to the (101), (011) and (200) planes of mMBIP (JCPDS: 43-0637) [35]. It proves that mMBIP has been successfully synthesized by hydrothermal method. In Fig. 1(In_2O_3), the XRD pattern of prepared In_2O_3 shows three distinct characteristic diffraction peaks at $2\theta = 21.50^\circ$, 30.58° and 35.47° , which correspond to (211), (222) and (400) crystal planes of In_2O_3 , respectively. The given XRD pattern of prepared In_2O_3 is consistent with JCPDS: 06-0416 of the cubic bixbyite-type indium oxide (c- In_2O_3) [36,37]. It proves that the synthesized In_2O_3 is cubic bixbyite-type indium oxide (c- In_2O_3). From Fig. 1(mMBIP- In_2O_3), the XRD pattern shows characteristic diffraction peaks of mMBIP and c- In_2O_3 . In addition, the intensities of all peaks become large, which implies that mMBIP and In_2O_3 may combine each other. In comparison to Fig. 1(mMBIP- In_2O_3), in Fig. 1(mMBIP-MWCNT- In_2O_3) it can be found that, besides the normal characteristic diffraction peaks of mMBIP and In_2O_3 , the peaks corresponding the MWCNT were obviously detected at 26.00° , 42.86° and 44.48° , which could be assigned to (002), (100) and (101) crystal phases of (JCPDS: 00-026-1080) [38,39]. It demonstrates that the mMBIP-MWCNT- In_2O_3 composite has been prepared successfully.

Fig. 1.

3.2. SEM images of prepared samples

The morphologies of mMBIP, In_2O_3 , mMBIP- In_2O_3 and mMBIP-MWCNT- In_2O_3 powders were investigated by scanning electron microscopy (SEM) observation and the results were showed in Fig. 2. In Fig. 2(mMBIP), mMBIP particles present cuboid structure, whose length, width and height are

1.5-2.0 μm , 1.0-1.5 μm and 50-100 nm, respectively. From Fig. 2(In_2O_3), it can be seen that the In_2O_3 consists of small and irregularly spherical particles. From Fig. 2(mMBIP- In_2O_3), it can be found that there are many cuboid-like crystal particles, which should belong to the typical crystal form of mMBIP particles. Then, it can also be seen that many granular nanoparticles with smaller diameter in 40-50 nm attach to the surface of mMBIP particles, which should be approximately spherical In_2O_3 nano-sized particles. It can be confirmed the mMBIP- In_2O_3 composites have successfully be prepared. Lastly, in Fig. 2(mMBIP-MWCNT- In_2O_3), it can clearly be observed that the MWCNTs with line style are sandwiched between mMBIP and In_2O_3 particles. Through the above results, it can be confirmed that the mMBIP-MWCNT- In_2O_3 composite powders have also been prepared successfully, forming expectedly designed Z-scheme mMBIP-MWCNT- In_2O_3 .

Fig. 2.

3.3. EDX spectrum of prepared mMBIP-MWCNT- In_2O_3 composite

To confirm the elemental kind and chemical component, the Energy Dispersive X-Ray (EDX) spectrum of the prepared mMBIP-MWCNT- In_2O_3 was determined. In Fig. 3, the strong peaks corresponding O, P, Bi, In and C atoms can be found, which proves that these elements compose the mMBIP-MWCNT- In_2O_3 without any impurity. In particular, the presence of carbon element indicates that the MWCNT as conductive channels has been inserted between mMBIP and In_2O_3 particles, forming mMBIP-MWCNT- In_2O_3 composites. In addition, the atomic ratio of O, P, Bi, In and C in Fig. 3 is close to the feed ratio in the preparation of mMBIP, MWCNT and In_2O_3 . Furthermore, these results are consistent with the above XRD patterns.

Fig. 3.

3.4. UV-vis diffuse reflectance spectra of the prepared mMBIP, In_2O_3 and mMBIP-MWCNT- In_2O_3

UV-vis diffuse reflectance spectroscopy (UV-vis DRS) was employed to determine the optical absorption properties of the mMBIP, In_2O_3 and mMBIP-MWCNT- In_2O_3 in the range of wavelength from 200 to 800 nm, and the results are represented in Fig. 4. As shown in Fig. 4(mMBIP), the mMBIP has intense absorption in near ultraviolet region, and the absorption edges of mMBIP appear at approximately 290 nm. It proves that the prepared mMBIP can absorb far ultraviolet light. Meanwhile, from Fig. 4(In_2O_3), it can be seen that the intense absorption edges of In_2O_3 appear at approximately 450 nm. It proves that the prepared In_2O_3 can absorb partial visible light. From Fig. 4(mMBIP-MWCNT- In_2O_3), it can be found that, compared with mMBIP, the light absorption range of the mMBIP-MWCNT- In_2O_3 as sonocatalyst was greatly expanded. Based on the optical diffuse absorption spectra of prepared mMBIP and In_2O_3 , the band-gaps were calculated by using the following equation:

$$\alpha h\nu = A(h\nu - E_{\text{bg}})^{1/2}$$

Where α , h , ν , E_{bg} and A represent absorption coefficient, plank constant, light frequency, band-gap and a constant, respectively. As shown in Fig. 4(mMBIP and In_2O_3), the calculated band-gaps (E_{bg}) of the as-prepared mMBIP and In_2O_3 were 4.54 eV and 3.02 eV, respectively. The calculated band-gaps were very close to those in literature references [16,18]. The results show that mMBIP and In_2O_3 as a wide-band semiconductor and a narrow-band semiconductor, respectively, could utilize short-wavelength light and long-wavelength light. Apparently, the combined mMBIP and In_2O_3 (mMBIP-MWCNT- In_2O_3) can utilize ultraviolet light and partial visible light in sonoluminescence.

Fig. 4.*3.5. FT-IR spectroscopy spectra of the prepared samples*

The characterization based on FT-IR spectra of mMBIP-MWCNT-In₂O₃ was carried out to get further information on the material composition and structural characteristic. Typical FT-IR spectra of the prepared mMBIP, In₂O₃, mMBIP-In₂O₃ and mMBIP-MWCNT-In₂O₃ are shown Fig. 5. From Fig. 5(mMBIP), the very intense absorption bands centered at 1107 cm⁻¹, 991 cm⁻¹ correspond to the ν₃ anti-symmetry stretching vibration of the PO₄ group. The absorption bands centered at 631 cm⁻¹ and 554 cm⁻¹ are assigned to δ (O-P-O) and ν₄ (PO₄), respectively [40]. It can prove that mMBIP has been prepared. The bands centered at 3432 cm⁻¹ and 1633 cm⁻¹ are probably due to ν (O-H) and δ (H-O-H) of the water adsorbed, respectively, in the surface of the mMBIP [41]. From Fig. 5(In₂O₃), the appearance of three sharp absorption peaks at 540 cm⁻¹, 565 cm⁻¹ and 600 cm⁻¹ can be assigned to the phonon vibrations of In-O bonds, which indicates the formation of the cubic In₂O₃ [42,43]. In Fig. 5(mMBIP-In₂O₃), it can be found that the normal characteristic absorption bands of mMBIP and In₂O₃ appear around 1107.69 cm⁻¹, 995.40 cm⁻¹, 632.71 cm⁻¹ and 554.44 cm⁻¹. And the peaks have slight movement and enhancement. From this it can be deduced that the mMBIP and In₂O₃ have successfully combined. From Fig. 5(mMBIP-MWCNT-In₂O₃), the peak at 601 cm⁻¹ was reasonably assigned to the C-H stretching vibration and the band at 1631 cm⁻¹ was assigned to the C=O stretching vibration. The existence of MWCNT in the mMBIP-MWCNT-In₂O₃ composite could also be confirmed using FT-IR spectroscopy. An absorption band centered at 1637 cm⁻¹ was due to C=C stretching vibrations [44]. Besides, no impurity or solvent residue absorption peak or absorption band was detected. From whole Fig. 5, it can be concluded that the mMBIP-MWCNT-In₂O₃ has successfully been prepared.

Fig. 5.*3.6. XPS spectra of prepared mMBIP-MWCNT-In₂O₃ composite*

The chemical composition of mMBIP-MWCNT-In₂O₃ composite and the chemical states of the constituent elements were analyzed by means of XPS as is shown in Fig. 6. It indicates that the prepared composite contains Bi, P, In, O and C elements and the corresponding peaks are plotted. As shown in Fig. 6(Bi), the two peaks at 159.85 and 165.21 eV are attributed to Bi (4f_{7/2}) and Bi (4f_{5/2}) of Bi³⁺ in mMBIP, respectively. From Fig. 6(P) the P (2p) peak can be found at 132.7 eV, and the peak is ascribed to the P⁵⁺ in mMBIP [45]. As seen in Fig. 6(Bi, P and O), the presented peaks at 159.85 eV and 165.21 eV (Bi 4f), 132.7 eV (P 2p) and 530.61 eV (O 1s) are closely agreed with the composition of mMBIP. For the In (3d), the two peaks located at 444.3 eV and 451.9 eV are attributed to In (3d_{5/2}) and In (3d_{3/2}), respectively, which are the characteristic peaks of In³⁺ species in In₂O₃ [46]. From Fig. 6 (In and O), the appearance of characteristic peaks of 444.3 eV (In 3d_{5/2}), 451.9 eV (In 3d_{3/2}) and 530.61 eV (O 1s) indicates that the In₂O₃ has been synthesized. Besides these characteristic peaks, there is also one peak at 282.5 eV, which belongs to C (1s), indicating the existence of MWCNT [47]. From whole Fig. 6, it can be concluded that the mMBIP-MWCNT-In₂O₃ has successfully been prepared.

Fig. 6.*3.7. UV-vis spectra of norfloxacin solutions during sonocatalytic degradation*

The UV-vis spectra of norfloxacin (10.00 mg/L) solution in the presence of mMBIP-MWCNT-In₂O₃ with ultrasonic irradiation time (0-150 min at 30 min intervals) and the corresponding sonocatalytic degradation ratios calculated based on three main absorption peaks (at

272 nm, 323 nm and 327 nm) were shown in Fig. 7. Since the norfloxacin has double bond and conjugated double bonds, the $\pi \rightarrow \pi^*$ electron transition can occur under the excitation of the matching wavelength. In addition, there are some heteroatoms containing solitary electrons in double bond, so the $n \rightarrow \pi^*$ electron transitions will also occur. From the UV-vis spectra in Fig. 7(a), it can be seen that there are three peaks at the wavelengths of 272 nm, 323 nm and 327 nm, respectively. Among them, the strongest peak appears at 272 nm wavelength, which should belong to the $\pi\text{-}\pi^*$ electron transition of double bond, conjugated double bond and benzene ring. Two relatively weak peaks appear at the 323 nm and 327 nm wavelength, respectively, which belong to the $n\text{-}\pi^*$ electron transitions of heteroatoms in double bond. When the ultrasonic irradiation time reached 150 min, the calculated degradation ratio based on the maximum absorption peak at 272 nm is 69.07 %. Similarly, other two absorption peaks at 323 nm and 327 nm also show an obviously decreasing trend along with ultrasonic irradiation time. Within 150 min, the calculated degradation ratios are 65.00 % and 69.39 %, respectively. The change of these absorption peaks in the ultraviolet region can be used to evaluate the degradation process of norfloxacin and measure the degradation ratio. As given in Fig. 7(b), the calculated reduction ratios according to peak at 272 nm gradually increase with increasing ultrasonic irradiation time and they are 23.52 %, 33.97 %, 47.43 %, 59.77 % and 69.07 %, respectively, at 30 min, 60 min, 90 min, 120 min and 150 min under given experimental conditions. The calculated reduction ratios according to the peak at 323 nm are 18.08 %, 33.33 %, 42.23 %, 56.47 % and 65.00 %, respectively, at 30 min, 60 min, 90 min, 120 min and 150 min. And the calculated reduction ratios according to the peak at 327 nm are 23.78 %, 33.82 %, 47.56 %, 60.42 % and 69.39 %, respectively, at 30 min, 60 min, 90 min, 120 min and 150 min. From Fig. 7(b), it can be thought that the degradation ratios of norfloxacin based on these three peaks are very close at any ultrasonic irradiation time. This

suggests that the degradation of norfloxacin is synchronous, possibly due to holes (h^+) degradation and no intermediate product. Therefore, the degradation ratio can be calculated using the change in absorption peaks. The results showed that most of the norfloxacin can be degraded by prepared mMBIP-MWCNT- In_2O_3 under ultrasound irradiation for 150 min. It is also possible that the use of mMBIP-MWCNT- In_2O_3 for the sonocatalytic degradation of norfloxacin in aqueous solutions is a viable method.

Fig. 7.

3.8. The effects of used times and scavengers on sonocatalytic degradation of norfloxacin caused by mMBIP-MWCNT- In_2O_3

In order to evaluate the activity and stability of the sonocatalyst, it is very significant to study the influence of used number. Therefore, the sonocatalytic activities in degradation of norfloxacin used mMBIP-MWCNT- In_2O_3 as sonocatalyst in several times recycles were researched and discussed and the corresponding results were provided in Fig. 8(a). It can be clearly seen that the sonocatalytic degradation ratio was only slightly decreased within five times recycle use and still close to 60 %. It illustrates that the mMBIP-MWCNT- In_2O_3 composite has a rather stable sonocatalytic activity and can be reused many times. The results showed that the mMBIP-MWCNT- In_2O_3 composite was an excellent sonocatalyst for degradation of norfloxacin under ultrasonic irradiation.

In order to study the sonocatalytic degradation reaction mechanism of norfloxacin, it is very important to identify the presence of hydroxyl radical ($\bullet OH$) and formation of hole (h^+). It was reported that the DMSO was regarded as excellent hydroxyl radical ($\bullet OH$) scavenger, and the EDTA has the nature scavenging holes (h^+) in the past [48,49]. The experiments in each group were carried

out under ultrasonic irradiation within 150 min. In Fig. 8(b), the sonocatalytic degradation ratio of norfloxacin without any scavengers was close to 70 %. After adding those scavengers (DMSO and EDTA), the degradation ratios were all lower obviously than that of the blank reference and were 51.32 % and 28.05 %, respectively. In particular, the degradation ratio after adding hole scavengers decreases most apparently, which demonstrates that hole (h^+) oxidation on the valence band of mMBIP with more positive potential plays a major role in sonocatalytic degradation of norfloxacin under ultrasonic irradiation. The added EDTA molecules react with holes (h^+), producing some low active materials, at the same time preventing sonocatalytic degradation of norfloxacin. Moreover, the hydroxyl radical ($\bullet OH$) oxidation plays the second role in sonocatalytic degradation of norfloxacin. Thus, sonocatalytic degradation of norfloxacin is through the combined action of holes (h^+) and hydroxyl radicals ($\bullet OH$) but mainly through holes (h^+) oxidation.

Fig. 8.

3.9. Influences of ultrasonic irradiation time and corresponding reaction kinetics on sonocatalytic degradation of norfloxacin

The sonocatalytic degradation ratios of norfloxacin along with ultrasonic irradiation time were researched for five systems, US/mMBIP-MWCNT-In₂O₃, US/mMBIP-In₂O₃, US/mMBIP, US/In₂O₃ and US, within 150 min at intervals of 30 min and the results were shown in Fig. 9(a). For all these five systems, with the extension of ultrasonic irradiation time, the sonocatalytic degradation ratios showed a gradually increasing trend. Under ultrasonic irradiation for 150 min, the sonocatalytic degradation ratios are 69.07 %, 53.68 %, 29.39 %, 22.56 % and 14.93 %, respectively, for US/mMBIP-MWCNT-In₂O₃, US/mMBIP-In₂O₃, US/mMBIP, US/In₂O₃ and alone US. The order of

sonocatalytic degradation ratios from high to low is US/mMBIP-MWCNT-In₂O₃ > US/mMBIP-In₂O₃ > US/mMBIP > US/In₂O₃ > US at any ultrasonic irradiation time. Apparently, the highest degradation ratio can be obtained for used US/mMBIP-MWCNT-In₂O₃ system. Meanwhile, under the same experimental conditions, the sonocatalytic degradation ratio of norfloxacin in the presence of US/mMBIP-MWCNT-In₂O₃ increases much faster than those in the presences of other four systems with the increase of ultrasonic irradiation time. The results obviously showed that, compared with single ingredient sonocatalyst (mMBIP or In₂O₃), the combination (mMBIP-In₂O₃) of sonocatalysts could obviously enhance the sonocatalytic degradation efficiency. Furthermore, the use of MWCNT can further enhance the sonocatalytic activity of mMBIP-In₂O₃. It indicates that the MWCNT as conducting channel plays a very important role in mMBIP-MWCNT-In₂O₃ for degradation of norfloxacin under ultrasonic irradiation.

For the sake of quantitatively comparing the sonocatalytic degradation reaction rates of norfloxacin for above five systems, their reaction kinetics were researched. In general, the first-order model is very intuitive, whose rate constants can be used to directly compare their sonocatalytic degradation reaction rates. In this text, the data of $-\ln(C_t/C_0)$ (C_t : instantaneous concentration and C_0 : initial concentration) for a first-order reaction as a function of ultrasonic irradiation time (t) were calculated. In Fig. 9(b), all calculated values of $-\ln(C_t/C_0)$ are nearly linear with the ultrasonic irradiation time (t) from beginning to end. Thus, sonocatalytic degradation reactions of norfloxacin for these five systems, US/mMBIP-MWCNT-In₂O₃, US/mMBIP-In₂O₃, US/mMBIP, US/In₂O₃ and alone US, can all be confirmed to be pseudo first-order kinetics reactions. The kinetic equations corresponding to US/mMBIP-MWCNT-In₂O₃, US/mMBIP-In₂O₃, US/mMBIP, US/In₂O₃ and alone US are $-\ln(C_t/C_0) = 0.0075t + 0.0074$ ($R^2 = 0.9928$), $-\ln(C_t/C_0) = 0.0049t + 0.0238$ ($R^2 = 0.9928$),

$-\ln(C_t/C_0) = 0.0017t + 0.052$ ($R^2 = 0.9444$), $-\ln(C_t/C_0) = 0.0015t + 0.035$ ($R^2 = 0.9783$) and $-\ln(C_t/C_0) = 0.001t + 0.0105$ ($R^2 = 0.9941$), respectively. The corresponding rate constants are 0.0075 min^{-1} , 0.0049 min^{-1} , 0.0017 min^{-1} , 0.0015 min^{-1} and 0.001 min^{-1} , respectively. By comparison, the sequence based on the reaction rate constants was also $\text{US/mMBIP-MWCNT-In}_2\text{O}_3 > \text{US/mMBIP-In}_2\text{O}_3 > \text{US/mMBIP} > \text{US/In}_2\text{O}_3 > \text{US}$. It can be confirmed that the $\text{US/mMBIP-MWCNT-In}_2\text{O}_3$ shows a best activity in degradation of norfloxacin under ultrasonic irradiation. At the same time, it can be concluded that the $\text{mMBIP-MWCNT-In}_2\text{O}_3$ is an excellent sonocatalyst in degradation of norfloxacin under ultrasonic irradiation.

Fig. 9.

3.10. Possible mechanism and process of sonocatalytic degradation of organic pollutants caused by mMBIP-MWCNT-In₂O₃ composite under ultrasonic irradiation

In order to better understand the sonocatalytic degradation process and enhance degradation efficiency of organic pollutants, it is necessary to research the related mechanism. The possible mechanism on sonocatalytic degradation of norfloxacin caused by prepared $\text{mMBIP-MWCNT-In}_2\text{O}_3$ under ultrasonic irradiation is proposed as shown in Fig. 10. It was reported that the sonocatalytic degradation of organic pollutants was related to the cavitation effect resulted from ultrasonic irradiation [50,51]. High temperature, high pressure and other extreme conditions caused by cavitation effect can decompose some water molecules (H_2O) and produce certain amount of free radicals, including hydrogen radicals ($\cdot\text{H}$) and hydroxyl radicals ($\cdot\text{OH}$). The hydrogen radicals ($\cdot\text{H}$) can react with the oxygen molecule (O_2) and form superoxide radical ($\cdot\text{O}_2^-$). Organic pollutants can be degraded by generated hydroxyl radicals ($\cdot\text{OH}$) and superoxide radical ($\cdot\text{O}_2^-$) to H_2O , CO_2 and inorganic ions

[52]. However, the cavitation effect can only produce a small amount of free radicals, so the use of ultrasound alone can not be perform large-scale treatment of wastewater.

Since the sonoluminescence caused by ultrasonic cavitation effect contains a wide range of wavelength light, being similar to the photocatalytic degradation process, the use of semiconductor photocatalysts combining ultrasonic irradiation is very effective to enhance the sonocatalytic degradation efficiency. Currently, many novel semiconductor sonocatalysts, such as BiPO_4 , PbO_2 , In_2O_3 , ZrO_2 etc, have been reported [53-55]. Under ultrasonic irradiation, they display obvious sonocatalytic activity in degradation of organic pollutants. In general, a wide band-gap semiconductor can use short-wavelength (ultraviolet light) and a narrow band semiconductor can use long-wavelength (visible light). In order to make better use the wide range wavelength of light, the combination of a wide band-gap semiconductor (mMBIP) and a narrow band semiconductor (In_2O_3) is used in this work. Because the conduction band potential ($E_{\text{CB}} = +0.20 \text{ eV}$) of mMBIP is relatively close to the valence band potential ($E_{\text{VB}} = +2.18 \text{ eV}$) of In_2O_3 compared with the band-gap ($E_{\text{bg}} = +4.32 \text{ eV}$) of mMBIP, mMBIP and In_2O_3 can form an ideal Z-scheme sonocatalytic system (mMBIP- In_2O_3). The Z-scheme sonocatalytic system can effectively inhibit the recombination of electron (e^-) and hole (h^+). Furthermore, such combination can produce more negative conduction band and more positive valence band, therefore, a Z-scheme sonocatalytic system with more strong oxidizability and more strong reducibility was obtained [56]. The more negative conduction band of In_2O_3 contributes to form superoxide radicals ($\bullet\text{O}_2^-$). Then, these superoxide radicals ($\bullet\text{O}_2^-$) become hydroxyl radicals ($\bullet\text{OH}$) through a series of chemical reactions [46,57]. Meanwhile, the more positive valence band of mMBIP can directly degrade organic pollutants into H_2O , CO_2 and inorganic ions.

In order to accelerate the transfer of the electrons (e^-) from conduction band of mMBIP to the

valence band of In_2O_3 , and restrain the recombination of the electrons (e^-) on conduction band of In_2O_3 and the holes (h^+) on valence band of mMBIP simultaneously, it is essential to enhance the flow rates of electrons (e^-). In this study, MWCNT with large specific surface area and superior electron conductivity is used as conducting channel to accelerate electrons flow. The results show that the addition of MWCNT greatly enhances the sonocatalytic degradation efficiency. In short, the sonocatalytic activity of the novel Z-scheme sonocatalytic system, mMBIP-MWCNT- In_2O_3 , is much higher than that of mMBIP or In_2O_3 , and also higher than that of mMBIP- In_2O_3 in sonocatalytic degradation of norfloxacin in aqueous solutions under ultrasonic irradiation.

The possible process is thought as following:

Ultrasonic irradiation (cavitation effect) \rightarrow light (sonoluminescence) + heat (hot spot)

$\text{H}_2\text{O} + \text{heat (hot spot)} \rightarrow \bullet\text{OH} + \bullet\text{H}$

$\bullet\text{H} + \text{O}_2 \rightarrow \bullet\text{O}_2^- + \text{H}^+$

mMBIP-MWCNT- $\text{In}_2\text{O}_3 + \text{light (short wavelength)} \rightarrow [\text{mMBIP}]^* \text{-MWCNT-}\text{In}_2\text{O}_3$

$[\text{mMBIP}]^* \text{-MWCNT-}\text{In}_2\text{O}_3 \rightarrow h^+/\text{VB/mMBIP} + e^-/\text{CB/mMBIP}$

mMBIP-MWCNT- $\text{In}_2\text{O}_3 + \text{light (long wavelength)} \rightarrow \text{mMBIP-MWCNT-}[\text{In}_2\text{O}_3]^*$

$\text{mMBIP-MWCNT-}[\text{In}_2\text{O}_3]^* \rightarrow h^+/\text{VB}/\text{In}_2\text{O}_3 + e^-/\text{CB}/\text{In}_2\text{O}_3$

$h^+/\text{VB}/\text{In}_2\text{O}_3 + e^-/\text{CB}/\text{mMBIP} \rightarrow \text{light} + \text{heat}$

$\text{norfloxacin} + h^+/\text{VB}/\text{mMBIP} \rightarrow \text{D}^+ \rightarrow \rightarrow \text{D}^{++} \rightarrow \rightarrow \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{NO}_3^- + \text{F}^-$

$e^-/\text{CB}/\text{In}_2\text{O}_3 + \text{O}_2 \rightarrow \bullet\text{O}_2^-$

$\bullet\text{O}_2^- + \text{H}^+ \rightarrow \text{HO}_2$

$\text{HO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \bullet\text{OH}$

$\text{H}_2\text{O}_2 + \text{heat (hot spot)} \rightarrow 2\bullet\text{OH}$

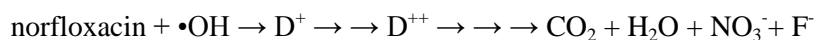
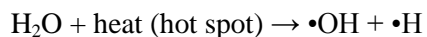


Fig. 10.

4. Conclusions

In this work, by using hydrothermal and calcination methods, a novel Z-scheme sonocatalyst, mMBIP-MWCNT-In₂O₃ was successfully fabricated. And then, its sonocatalytic activity was evaluated through the degradation of norfloxacin in aqueous solution under ultrasonic irradiation. The combination of mMBIP and In₂O₃ can form an ideal Z-scheme mMBIP-MWCNT-In₂O₃ with a more negative conduction band and a more positive valence band, which effectively restrains the recombination of electrons (e⁻) and holes (h⁺) and provides strong sonocatalytic degradation ability. The presence of MWCNT with specific surface area and superior electron conductivity accelerates the electron (e⁻) transfer from conduction band of mMBIP to valence band of In₂O₃, further enhancing the sonocatalytic activity. The prepared mMBIP-MWCNT-In₂O₃ composite gives the highest sonocatalytic ratio of norfloxacin compared with mMBIP-In₂O₃, mMBIP, In₂O₃ and onefold ultrasound. The corresponding degradation ratios are 69.07 %, 53.68 %, 29.39 %, 22.56 %, and 14.39 %, respectively, for US/mMBIP-MWCNT-In₂O₃, US/mMBIP-In₂O₃, US/mMBIP, US/In₂O₃ and US. The investigation on used times confirmed a high reusability of the mMBIP-MWCNT-In₂O₃ composite. Therefore, the prepared mMBIP-MWCNT-In₂O₃ composite is considered to be a stable sonocatalyst with excellent activity. It can be predicted that the mMBIP-MWCNT-In₂O₃ composite has broad application prospects to treat organic pollutants in aqueous solution.

Acknowledgements

The authors greatly acknowledge the National Science Foundation of China (21371084 and 31570154), Key Laboratory Basic Research Foundation of Liaoning Provincial Education Department (L2015043), Liaoning Provincial Department of Education Innovation Team Projects (LT2015012) and Undergraduate Teaching Reform Projects of Liaoning University (JG2016YB0034) for financial support. The authors also thank our colleagues and other students for their participating in this work.

References

- [1] M.J. Huang, T. Zhou, X.H. Wu, J. Mao, Distinguishing homogeneous-heterogeneous degradation of norfloxacin in a photochemical Fenton-like system ($\text{Fe}_3\text{O}_4/\text{UV}/\text{oxalate}$) and the interfacial reaction mechanism, *Water Res.* 119 (2017) 47-56.
- [2] X.M. Ma, Z. Ma, T. Liao, X.H. Liu, Y.P. Zhang, L.L. Li, W.B. Li, B.R. Hou, Preparation of $\text{BiVO}_4/\text{BiOCl}$ heterojunction photocatalyst by in-situ transformation method for norfloxacin photocatalytic degradation, *J. Alloy Compd.* 702 (2017) 68-74.
- [3] J.F. Gou, Q.L. Ma, X.Y. Deng, Y.Q. Cui, H.X. Zhang, X.W. Cheng, X.L. Li, M.Z. Xie, Q.F. Cheng, Fabrication of $\text{Ag}_2\text{O}/\text{TiO}_2$ -Zeolite composite and its enhanced solar light photocatalytic performance and mechanism for degradation of norfloxacin, *Chem. Eng. J.* 308 (2017) 818-826.
- [4] S.B. Hua, L. Lia, M.Y. Luo, Y.F. Yuna, C.T. Chang, Aqueous norfloxacin sonocatalytic degradation with multilayer flower-like ZnO in the presence of peroxydisulfate, *Ultrason. Sonochem.* 38 (2017) 446-454.
- [5] T. Zhou, X.L. Zou, X.H. Wu, J. Mao, J. Wang, Synergistic degradation of antibiotic norfloxacin in a novel heterogeneous sonochemical $\text{Fe}^0/\text{tetraphosphate}$ Fenton-like system, *Ultrason. Sonochem.* 37 (2017) 320-327.
- [6] N.A. Jamalluddin, A.Z. Abdullah, Low frequency sonocatalytic degradation of Azo dye in water using Fe-doped zeolite Y catalyst, *Ultrason. Sonochem.* 21 (2014) 743-753.
- [7] M.K. Jørgensen, M. Nierychlo, A.H. Nielsen, P. Larsen, M.L. Christensen, P.H. Nielsen, Unified understanding of physico-chemical properties of activated sludge and fouling propensity, *Water Res.* 120

- (2017) 117-132.
- [8] A. Khataee, F.T. Mohamadi, T.S. Rad, B. Vahid, Heterogeneous sonocatalytic degradation of anazolene sodium by synthesized dysprosium doped CdSe nanostructures, *Ultrason. Sonochem.* 40 (2018) 361-372.
- [9] A. Khataee, S.A. Oskoui, L. Samaei, ZnFe-Cl nanolayered double hydroxide as a novel catalyst for sonocatalytic degradation of an organic dye, *Ultrason. Sonochem.* 40 (2018) 703-713.
- [10] G.M.S. ElShafei, A.M. Al-Sabagh, F.Z. Yehia, C.A. Philip, N.A. Moussa, G. Eshaq, Metal oxychlorides as robust heterogeneous Fenton catalysts for the sonophotocatalytic degradation of 2-nitrophenol, *Appl. Catal. B: Environ.* 224 (2018) 681-691.
- [11] F.O. Ogutu, T.H. Mu, Ultrasonic degradation of sweet potato pectin and its antioxidant activity, *Ultrason. Sonochem.* 38 (2017) 726-734.
- [12] J. Li, B. Li, P. Geng, A.X. Song, J.Y. Wu, Ultrasonic degradation kinetics and rheological profiles of a food polysaccharide (konjac glucomannan) in water, *Food Hydrocolloid.* 70 (2017) 14-19.
- [13] K. Kerboua, O. Hamdaoui, Computational study of state equation effect on single acoustic cavitation bubbled phenomenon, *Ultrason. Sonochem.* 38 (2017) 174-188.
- [14] R. Balachandran, Z. Patterson, P. Deymier, S.A. Snyder, M. Keswani, Understanding acoustic cavitation for sonolytic degradation of pcesol as a model contaminant, *Chemosphere* 147 (2016) 52-59.
- [15] P. Nuengmatcha, S. Chanthai, R. Mahachai, W.C. Oh, Sonocatalytic performance of ZnO/graphene/TiO₂ nanocomposite for degradation of dye pollutants (methylene blue, texbrite BAC-L, texbrite BBU-L and texbrite NFW-L) under ultrasonic irradiation, *Dyes Pigments* 134 (2016) 487-497.
- [16] J.K. Im, J. Yoon, N. Her, J. Han, K.D. Zoh, Y. Yoon, Sonocatalytic-TiO₂ nanotube, Fenton, and CCl₄ reactions for enhanced oxidation, and their applications to acetaminophen and naproxen degradation, *Sep. Purif. Technol.* 141 (2015) 1-9.
- [17] S.X. Zuo, Y. Chen, W.J. Liu, C. Yao, X.Z. Lia, Z.Y. Lia, C.Y. Ni, X.H. Liu, A facile and novel construction of attapulgite/Cu₂O/Cu/g-C₃N₄ with enhanced photocatalytic activity for antibiotic degradation, *Ceram. Int.* 43 (2017) 3331-3336.
- [18] M.C. Gao, D.F. Zhang, X.P. Pu, H.Y. Ma, C.G. Su, X. Gao, J.M. Dou, Surface decoration of BiOBr with BiPO₄ nanoparticles to build heterostructure photocatalysts with enhanced visible-light photocatalytic activity, *Sep. Purif. Technol.* 170 (2016) 183-189.
- [19] Y.Y. Zhu, Y.J. Wang, Q. Ling, Y.F. Zhu, Enhancement of full-spectrum photocatalytic activity over

- BiPO₄/Bi₂WO₆ composites, *Appl. Catal. B: Environ.* 200 (2017) 222-229.
- [20] H.B. Li, G.Y. Huang, J. Zhang, S.H. Fu, T.G. Wang, H.W. Liao, Photochemical synthesis and enhanced photocatalytic activity of MnO_x/BiPO₄ heterojunction, *T. Nonferr. Metal. Soc.* 27(2017) 1127-1133.
- [21] X.Z. Bu, B.Z. Wu, T. Long, M.Z. Hu, Preparation, characterization and enhancement of the visible-light photocatalytic activity of In₂O₃/rectorite composite, *J. Alloy Compd.* 586 (2014) 202-207.
- [22] J.M. Yang, Z.P. Qi, Y.S. Kang, Q. Liu, W.Y. Sun, Shape-controlled synthesis and photocatalytic activity of In₂O₃ nanostructures derived from coordination polymer precursors, *Chinese Chem. Lett.* 27 (2016) 492-496.
- [23] Y.Y. Huang, H.B. Zhang, C.S. Wei, G.S. Li, Q. Wu, J. Wang, Y.T. Song, Assisted sonocatalytic degradation of pethidine hydrochloride (dolantin) with some inorganic oxidants caused by CdS-coated ZrO₂ composite, *Sep. Purif. Technol.* 172 (2017) 202-210.
- [24] A. Hassani, A. Khataee, S. Karaca, C. Karaca, P. Gholami, Sonocatalytic degradation of ciprofloxacin using synthesized TiO₂ nanoparticles on montmorillonite, *Ultrason. Sonochem.* 35 (2017) 251-262.
- [25] J.Q. Li, H.J. Hao, Z.F. Zhu, Construction of g-C₃N₄-WO₃-Bi₂WO₆ double Z-scheme system with enhanced photoelectrochemical performance, *Mater. Lett.* 168 (2016) 180-183.
- [26] X.J. Ye, S.S. Zhao, S.G. Meng, X.L. Fu, L. Bai, Y. Guo, X.C. Wang, S.F. Chen, Remarkable enhancement of photocatalytic performance via constructing a novel Z-scheme KNbO₃/Bi₂O₃ hybrid material, *Mater. Res. Bull.* 94 (2017) 352-360.
- [27] L.X. Yin, H. Zhang, X.G. Kong, J.F. Huang, D.D. Zhang, C.Q. Liu, J.M. Fang, F. Zhang, Red AgCl/SmOCl Z-scheme composites: Enhanced photocatalytic performance under sunlight, *Mater. Lett.* 210 (2018) 42-45.
- [28] B.D. Zhang, Z.P. Lin, J.L. Huang, L.M. Cao, X.X. Wu, X. Yu, Y.F. Zhan, F.Y. Xie, W.H. Zhang, J. Chen, W.J. Mai, W.G. Xie, H. Meng, Highly active and stable non noble metal catalyst for oxygen reduction reaction, *Int. J. Hydrogen Energ.* 42 (2017) 10423-10434.
- [29] H. Fleischner, Reducing an arbitrary fullerene to the dodecahedron, *Discrete Math.* 340 (2017) 2714-2722.
- [30] S. Schöche, N. Hong, M. Khorasaninejad, A. Ambrosio, E. Orabona, P. Maddalena, F. Capasso, Optical properties of graphene oxide and reduced graphene oxide determined by spectroscopic ellipsometry, *Appl. Surf. Sci.* 421 (2017) 778-782.

- [31] G.X. Zhang, Q.L. Wei, X.H. Yang, A.C. Tavares, S.H. Sun, RRDE experiments on noble-metal and noble-metal-free catalysts: Impact of loading on the activity and selectivity of oxygen reduction reaction in alkaline solution, *Appl. Catal. B: Environ.* 206 (2017) 115-126.
- [32] L. Zhou, L.R. Enakonda, M. Harba, Y. Saiha, A.A. Tapia, S.O. Chikh, J.L. Hazemann, J. Li, N. Wei, D. Garye, P.D. Gallo, J.M. Basset, Fe catalysts for methane decomposition to produce hydrogen and carbon nano materials, *Appl. Catal. B: Environ.* 208 (2017) 44-59.
- [33] B. Ouadil, O. Cherkaoui, M. Safi, M. Zahouily, Surface modification of knit polyester fabric for mechanical, electrical and UV protection properties by coating with graphene oxide, graphene and graphene/silver nanocomposites, *Appl. Surf. Sci.* 414 (2017) 292-302.
- [34] J. Han, M.G. Wang, Y.M. Hu, C.Q. Zhou, R. Guo, Conducting polymer-noble metal nanoparticle hybrids: Synthesis mechanism application, *Prog. Polym. Sci.* 70 (2017) 52-91.
- [35] Y.D. Wang, B.W. Li, G.S. Li, Y.Y. Huang, D.W. Fang, J. Wang, Y.T. Song, Photocatalytic conversion of nitrite in aqueous solution over nanocomposite photocatalyst $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{BiPO}_4$ using different photosources, *J. Ind. Eng. Chem.* 47 (2017) 74-85.
- [36] Y.Y. Wang, S.L. Xue, P. Xie, Z.Y. Gao, R.J. Zou, Preparation, characterization and photocatalytic activity of juglans-like indium oxide (In_2O_3) nanospheres, *Mater. Lett.* 192 (2017) 76-79.
- [37] X.X. Chen, R. Li, X.Y. Pan, X.T. Huang, Z.G. Yi, Fabrication of $\text{In}_2\text{O}_3\text{-Ag-Ag}_3\text{PO}_4$ composites with Z-scheme configuration for photocatalytic ethylene degradation under visible light irradiation, *Chem. Eng. J.* 320 (2017) 644-652.
- [38] M. Ahmad, E. Ahmed, Z.L. Hong, W. Ahmed, A. Elhissi, N.R. Khalid, Photocatalytic, sonocatalytic and sonophotocatalytic degradation of Rhodamine B using ZnO/CNTs composites photocatalysts, *Ultrason. Sonochem.* 21 (2014) 761-773.
- [39] H. Kose, S. Dombaycioglu, A.O. Aydın, H. Akbulut, Production and characterization of free-standing $\text{ZnO}/\text{SnO}_2/\text{MWCNT}$ ternary nanocomposite Li-ion battery anode, *Int. J. Hydrogen Energ.* 41 (2016) 9924-9932.
- [40] F. Xue, H.B. Li, Y.C. Zhu, S.L. Xiong, X.W. Zhang, T.T. Wang, X. Liang, Y.T. Qian, Solvothermal synthesis and photoluminescence properties of BiPO_4 nano-cocoons and nanorods with different phases, *J. Solid State Chem.* 182 (2009) 1396-1400.
- [41] D.M. Chen, Z. Kuang, Q. Zhu, Y. Du, H.L. Zhu, Synthesis and characterization of CdS/BiPO_4

- heterojunction photocatalyst, *Mater. Res. Bull.* 66 (2015) 262-267.
- [42] S.F. Chen, X.L. Yu, H.Y. Zhang, W. Liu, Preparation, characterization and activity evaluation of heterostructure $\text{In}_2\text{O}_3/\text{In}(\text{OH})_3$ photocatalyst, *J. Hazard. Mater.* 180 (2010) 735-740.
- [43] F. Zhang, X.Y. Li, Q.D. Zhao, Q.Z. Zhang, M. Tadé, S.M. Liu, Fabrication of $\alpha\text{-Fe}_2\text{O}_3/\text{In}_2\text{O}_3$ composite hollow microspheres: A novel hybrid photocatalyst for toluene degradation under visible light, *J. Colloid Interf. Sci.* 457 (2015) 18-26.
- [44] S. Zaman, K. Zhang, A. Karim, J.G. Xin, T. Sun, J.R. Gong, Sonocatalytic degradation of organic pollutant by $\text{SnO}_2/\text{MWCNT}$ nanocomposite, *Diam. Relat. Mater.* 76 (2017) 177-183.
- [45] J.X. Xia, J.Z. Zhao, J. Chen, J. Di, M.X. Ji, L. Xu, Z.G. Chen, H.M. Li, Facile fabrication of $g\text{-C}_3\text{N}_4/\text{BiPO}_4$ hybrid materials via a reactable ionic liquid for the photocatalytic degradation of antibiotic ciprofloxacin, *J. Photoch. Photobio. A* 339 (2017) 59-66.
- [46] J. Luo, X.S. Zhou, L. Ma, X.Y. Xu, H.T. Ruan, Z.B. Zhang, Facile fabrication and enhanced visible-light photocatalytic activity of $\text{In}_2\text{O}_3/\text{Ag}_2\text{CrO}_4$ composites, *Rsc Adv.* 6 (2016) 52627-52635.
- [47] X.F. Wang, J.C. Fan, F. Qian, Y.L. Min, Magnetic BiFeO_3 grafted with MWCNT hybrids as advanced photocatalysts for removing organic contamination with a high concentration, *Rsc Adv.* 6 (2016) 49966-49972.
- [48] Z. Kozmér, E. Takács, L. Wojnárovits, T. Alapi, K. Hernádi, A. Dombi, The influence of radical transfer and scavenger materials in various concentrations on the gamma radiolysis of phenol, *Radiat. Phys. Chem.* 124 (2016) 52-57.
- [49] B.A. Marinho, R.O. Cristóvão, J.M. Loureiro, R.A.R. Boaventura, V.J.P. Vilar, Solar photocatalytic reduction of Cr(VI) over Fe(III) in the presence of organic sacrificial agents, *Appl. Catal. B: Environ.* 192 (2016) 208-219.
- [50] J. Wang, Z. Jiang, Z.H. Zhang, Y.P. Xie, Y.H. Lv, J. Li, Y.Q. Deng, X.D. Zhang, Study on inorganic oxidants assisted sonocatalytic degradation of Acid Red B in presence of nano-sized ZnO powder, *Sep. Purif. Technol.* 67 (2009) 38-43.
- [51] M. Cui, J. Choi, Y. Lee, J.J. Ma, D. Kim, J. Choi, M. Jang, J. Khim, Significant enhancement of bromate removal in drinking water: Implications for the mechanism of sonocatalytic reduction, *Chem. Eng. J.* 317 (2017) 404-412.
- [52] G.W. Wang, Y.Y. Huang, G.S. Li, H.B. Zhang, Y.D. Wang, B.W. Li, J. Wang, Y.T. Song, Preparation of a

- novel sonocatalyst, Au/NiGa₂O₄-Au-Bi₂O₃, nanocomposite, and application in sonocatalytic degradation of organic pollutants, *Ultrason. Sonochem.* 38 (2017) 335-346.
- [53] L. Liu, L. Ding, W.J. An, S.L. Lin, J.S. Hu, Y.H. Liang, W.Q. Cui, Cu₂O NPs decorated BiPO₄ photo-catalyst for enhanced organic contaminant degradation under visible light irradiation, *Rsc Adv.* 6 (2016) 29202-29209.
- [54] X. Chen, Y.T. Liu, X.N. Xia, L.L. Wang, Popcorn balls-like ZnFe₂O₄-ZrO₂ microsphere for photocatalytic degradation of 2,4-dinitrophenol, *Appl. Surf. Sci.* 407 (2017) 470-478.
- [55] X.Y. Duan, J.R. Li, W. Liu, L.M. Chang, C.W. Yang, Fabrication and characterization of a novel PbO₂ electrode with a CNT interlayer, *Rsc Adv.* 6 (2016) 28927-28936.
- [56] T.T. Nguyen, Y. Asakurac, S. Kodad, K. Yasuda, Dependence of cavitation, chemical effect, and mechanical effect thresholds on ultrasonic frequency, *Ultrason. Sonochem.* 39 (2017) 301-306.
- [57] H. Cao, M.X. Wan, Y.Z. Qiao, S.S. Zhang, R.X. Li, Spatial distribution of sonoluminescence and sonochemiluminescence generated by cavitation bubbles in 1.2 MHz focused ultrasound field, *Ultrason. Sonochem.* 19 (2012) 257-263.

Content of Figures:

Fig. 1. XRD patterns of prepared mMBIP, In_2O_3 , mMBIP- In_2O_3 and mMBIP-MWCNT- In_2O_3 .

Fig. 2. SEM images of prepared mMBIP, In_2O_3 , mMBIP- In_2O_3 and mMBIP-MWCNT- In_2O_3 .

Fig. 3. EDX spectra of prepared mMBIP-MWCNT- In_2O_3 .

Fig. 4. UV-vis diffuse reflectance spectra (DRS) of mMBIP, In_2O_3 and mMBIP-MWCNT- In_2O_3 and calculated band gap of mMBIP and In_2O_3 .

Fig. 5. FT-IR spectra of mMBIP, In_2O_3 , mMBIP- In_2O_3 and mMBIP-MWCNT- In_2O_3 .

Fig. 6. XPS spectra of mMBIP-MWCNT- In_2O_3 , Bi (4f), P (2p), In (3d), O (1s) and C (1s).

Fig. 7. (a) UV-vis spectra of norfloxacin solutions with ultrasonic irradiation and (b) comparison of degradation ratios calculated by UV-vis spectra. (10.00 mg/L norfloxacin concentration, 1.00 g/L mMBIP-MWCNT- In_2O_3 (5.0 wt% MWCNT content and 1:1 mMBIP and In_2O_3 molar ratio) addition amount, 100 mL total volume and 0-150 min ultrasonic (300 W output power and 40 kHz frequency) irradiation time.)

Fig. 8. Influences of used times (a) and scavengers (b) on sonocatalytic activity of mMBIP-MWCNT- In_2O_3 (5 wt% MWCNT content and 1:1 mMBIP and In_2O_3 molar ratio). (10.00 mg/L norfloxacin solutions concentration, 1.00 g/L sonocatalyst addition amount, 100 mL total volume and 150 min ultrasonic irradiation (300 W output power and 40 kHz frequency) time.)

Fig. 9. The influence of ultrasonic irradiation time (a) and corresponding reaction kinetics (b) on the sonocatalytic degradation of norfloxacin. (10.00 mg/L norfloxacin solutions concentration, 1.00 g/L (mMBIP-MWCNT- In_2O_3 , mMBIP- In_2O_3 , mMBIP and In_2O_3) addition amount, 100 mL total volume and 150 min ultrasonic irradiation (300 W output power and 40 kHz frequency) time.)

Fig. 10. Sonocatalytic degradation mechanism of norfloxacin in the presence of mMBIP-MWCNT- In_2O_3 under ultrasonic irradiation (mMBIP: mMBiPO₄).

Figures:

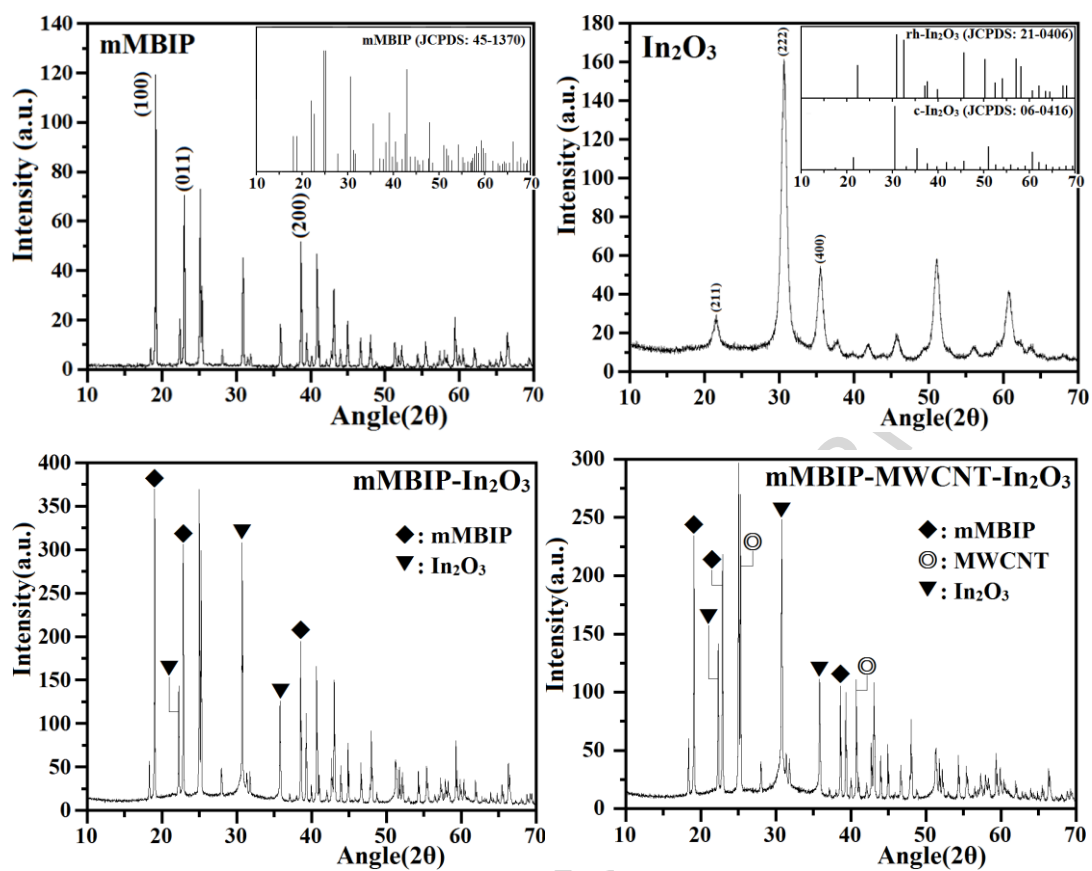


Fig. 1. XRD patterns of prepared mMBIP, In₂O₃, mMBIP-In₂O₃ and mMBIP-MWCNT-In₂O₃.

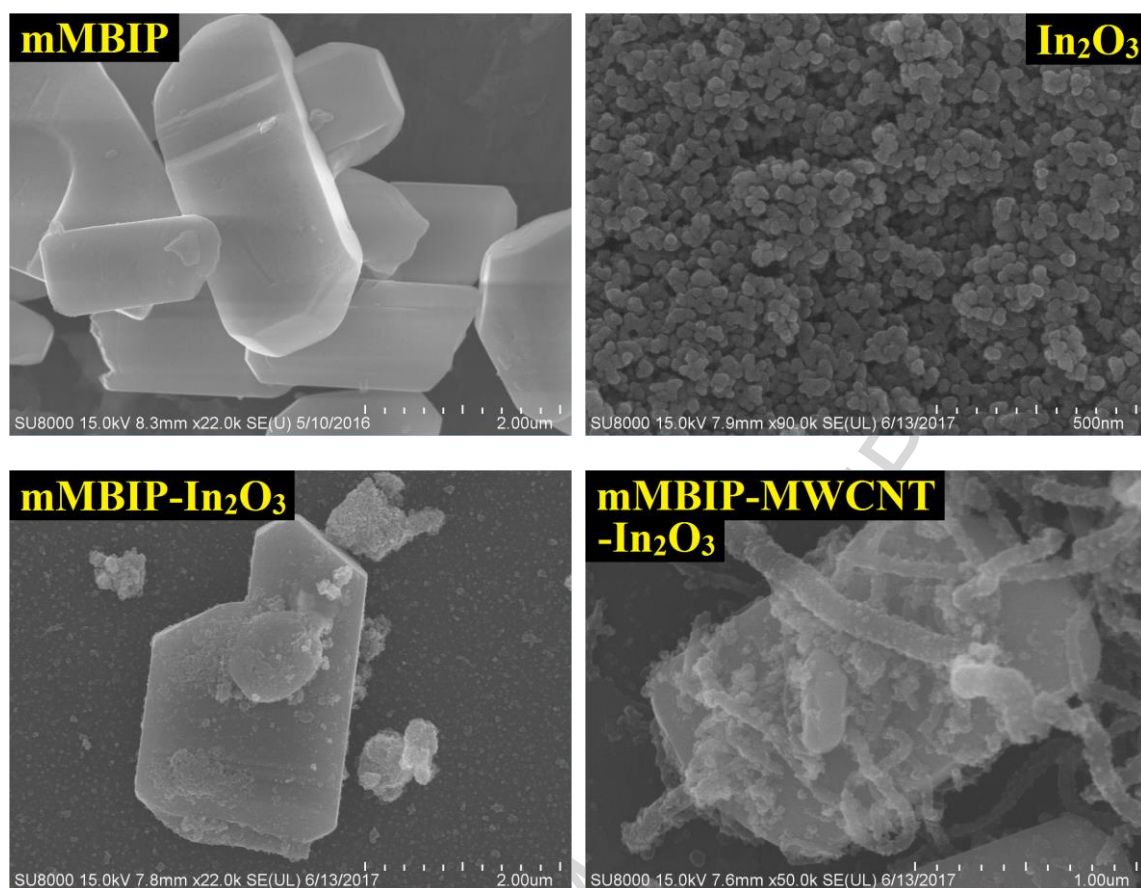


Fig. 2. SEM images of prepared mMBIP, In₂O₃, mMBIP-In₂O₃ and mMBIP-MWCNT-In₂O₃.

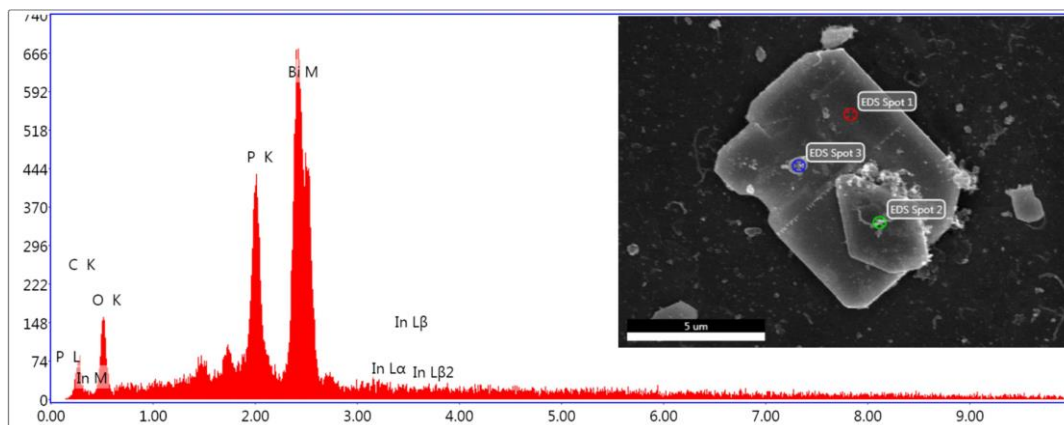


Fig. 3. EDX spectra of prepared mMBIP-MWCNT-In₂O₃.

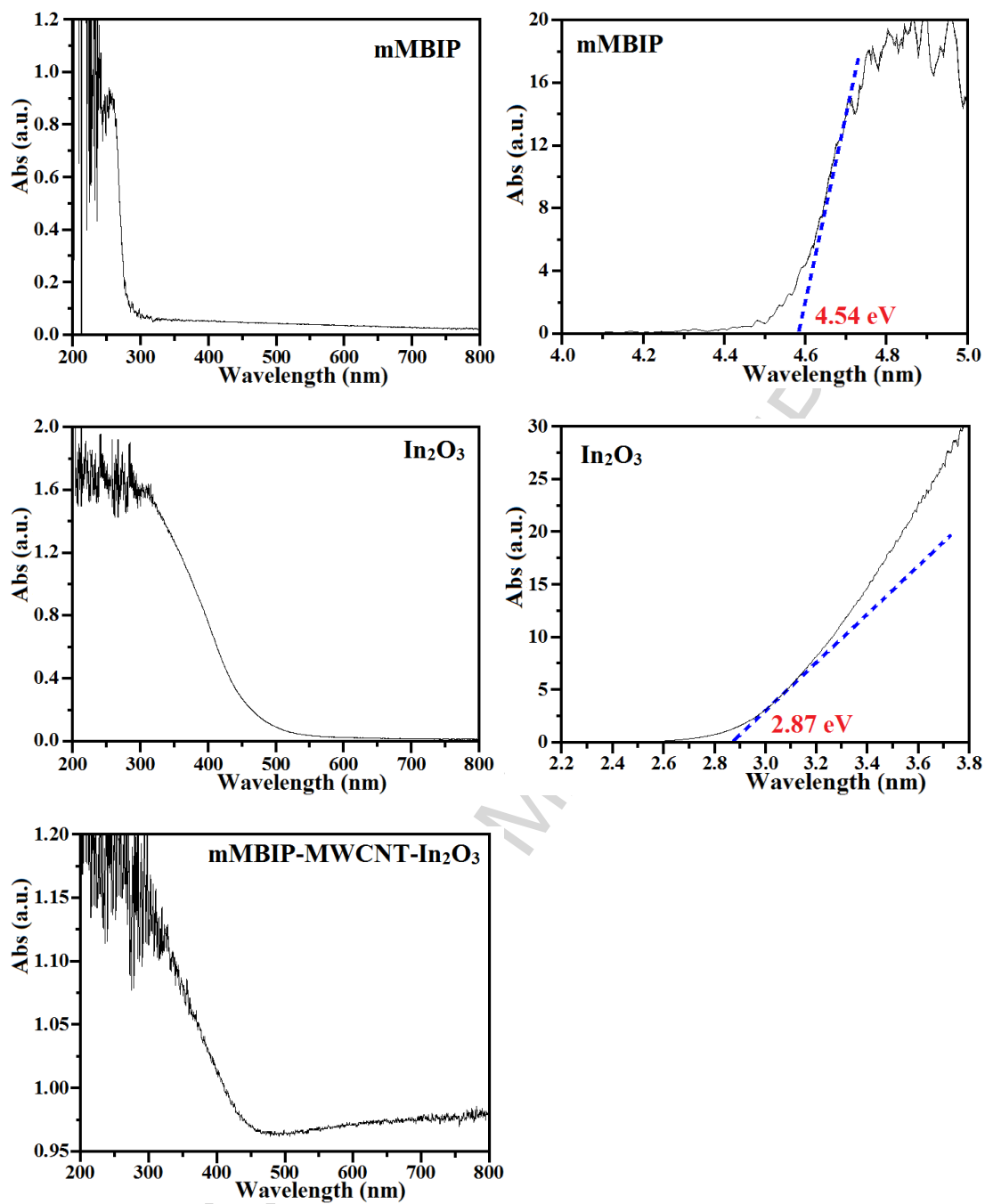


Fig. 4. UV-vis diffuse reflectance spectra (DRS) of mMBIP, In₂O₃ and mMBIP-MWCNT-In₂O₃ and calculated band gap of mMBIP and In₂O₃.

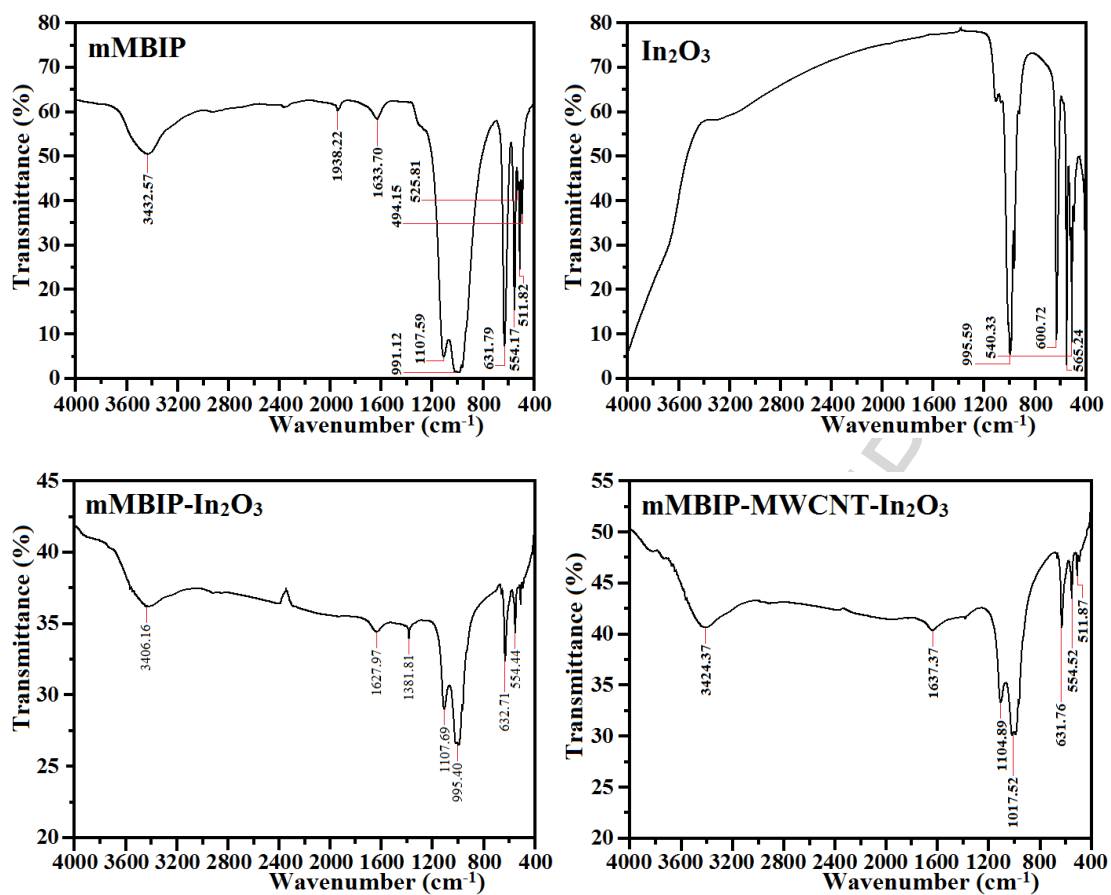


Fig. 5. FT-IR spectra of mMBIP, In₂O₃, mMBIP-In₂O₃ and mMBIP-MWCNT-In₂O₃.

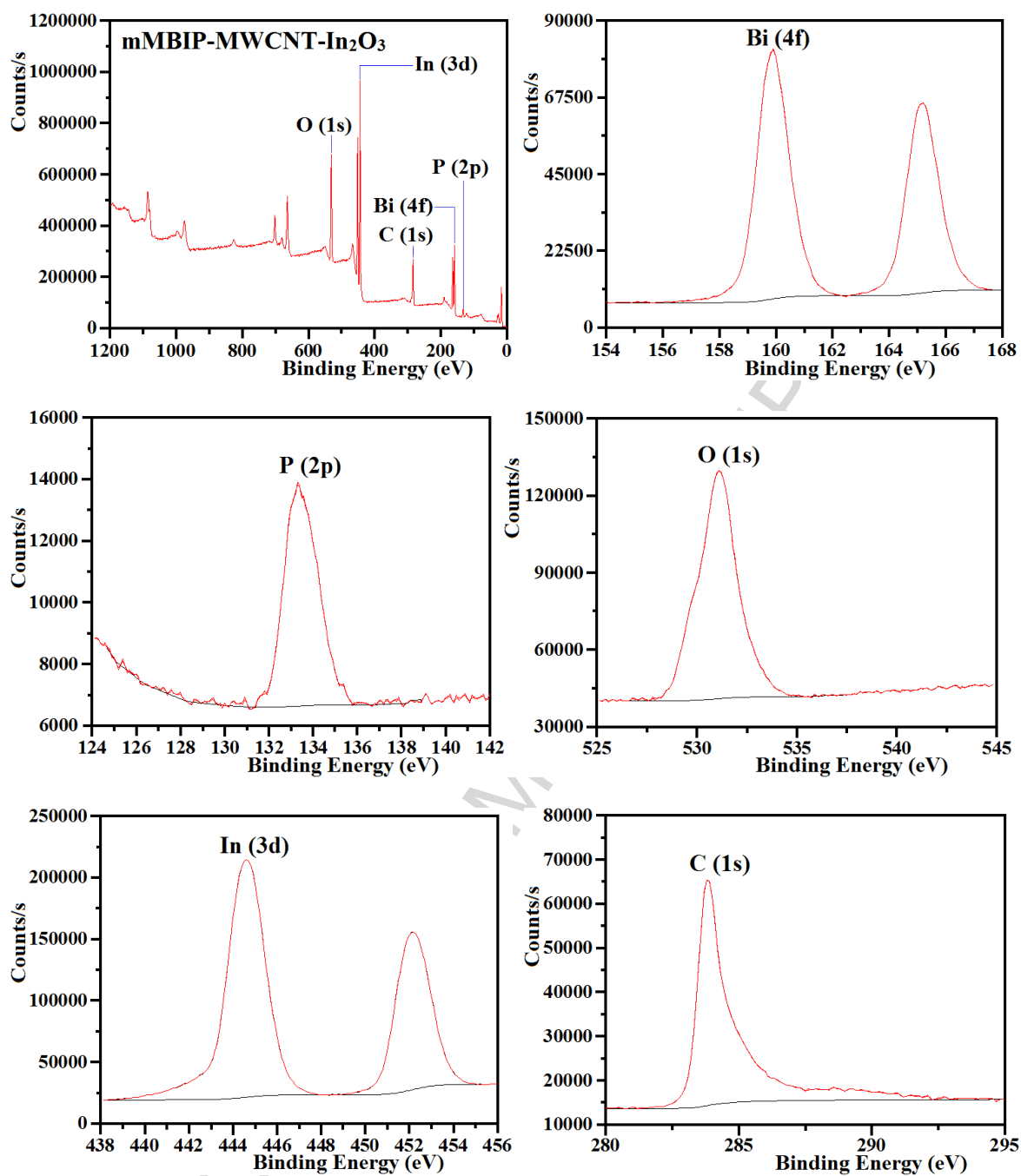


Fig. 6. XPS spectra of mMBIP-MWCNT-In₂O₃, Bi (4f), P (2p), In (3d), O (1s) and C (1s).

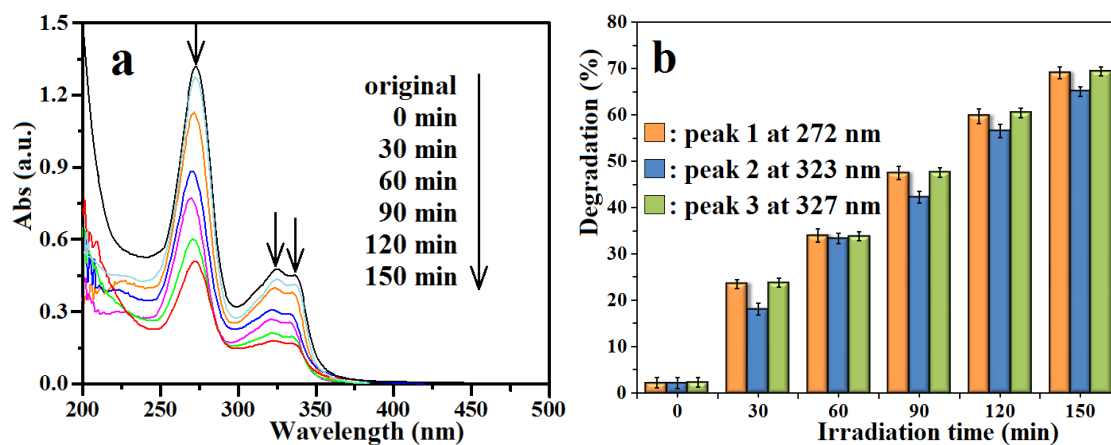


Fig. 7. (a) UV-vis spectra of norfloxacin solutions with ultrasonic irradiation and (b) comparison of degradation ratios calculated by UV-vis spectra. (10.00 mg/L norfloxacin concentration, 1.00 g/L mMBIP-MWCNT-In₂O₃ (5.0 wt% MWCNT content and 1:1 mMBIP and In₂O₃ molar ratio) addition amount, 100 mL total volume and 0-150 min ultrasonic (300 W output power and 40 kHz frequency) irradiation time.)

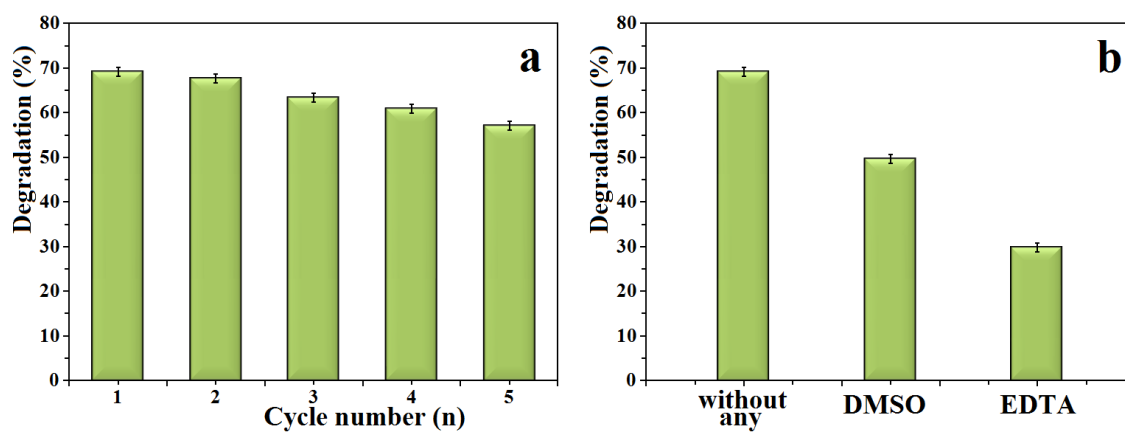


Fig. 8. Influences of used times (a) and scavengers (b) on sonocatalytic activity of mMBIP-MWCNT-In₂O₃ (5 wt% MWCNT content and 1:1 mMBIP and In₂O₃ molar ratio). (10.00 mg/L norfloxacin solutions concentration, 1.00 g/L sonocatalyst addition amount, 100 mL total volume and 150 min ultrasonic irradiation (300 W output power and 40 kHz frequency) time.)

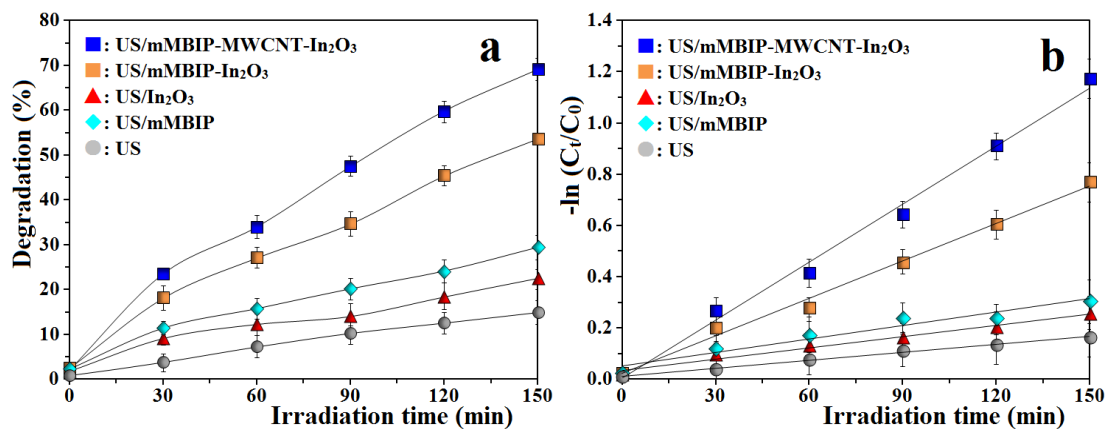


Fig. 9. The influence of ultrasonic irradiation time (a) and corresponding reaction kinetics (b) on the sonocatalytic degradation of norfloxacin. (10.00 mg/L norfloxacin solutions concentration, 1.00 g/L (mMBIP-MWCNT-In₂O₃, mMBIP-In₂O₃, mMBIP and In₂O₃) addition amount, 100 mL total volume and 150 min ultrasonic irradiation (300 W output power and 40 kHz frequency) time.)

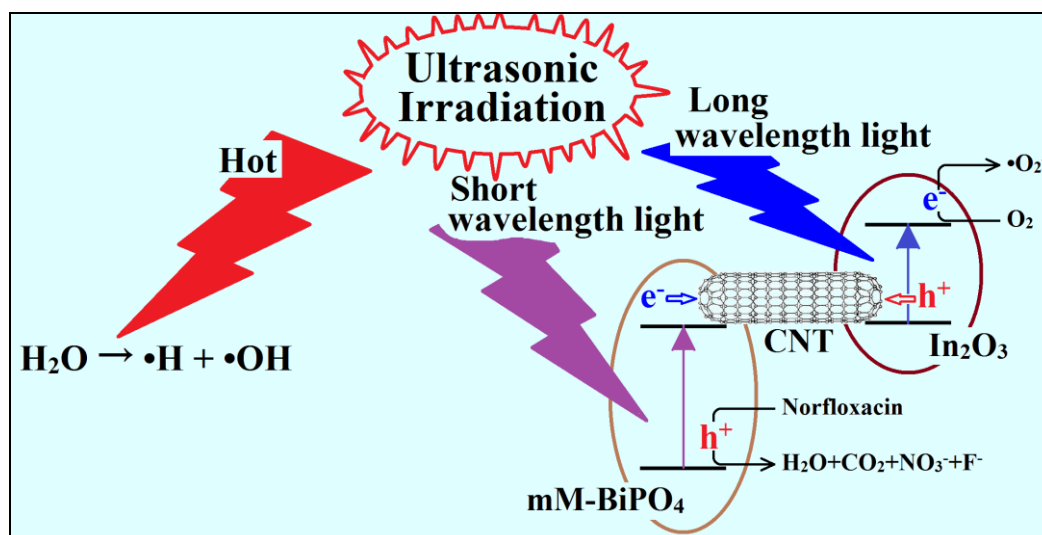


Fig. 10. Sonocatalytic degradation mechanism of norfloxacin in the presence of mM-BIP-MWCNT-In₂O₃ under ultrasonic irradiation (mMBIP: mMBiPO₄).

Graphical abstract

Journal of Molecular Liquids (2017) 000-000

Article

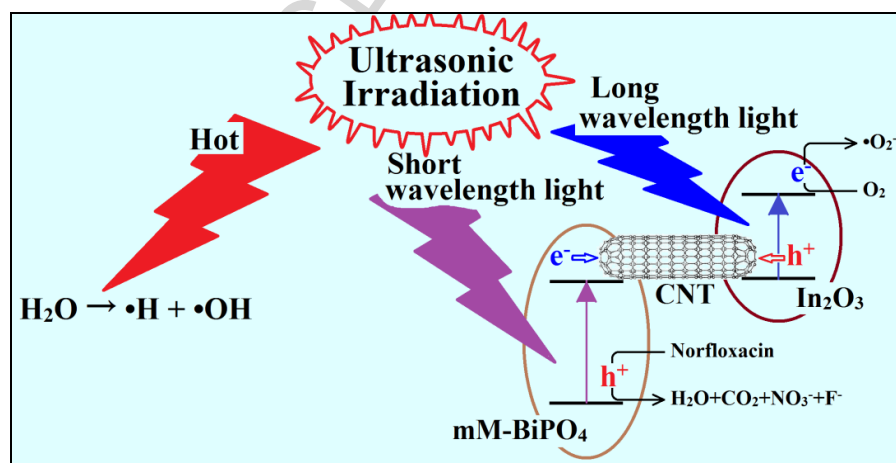
Sonocatalytic degradation of norfloxacin in aqueous solution caused by a novel Z-scheme sonocatalyst, mMBIP-MWCNT-In₂O₃ composite

Siyi Li ^a, Guowei Wang ^a, Jing Qiao ^a, Ying Zhou ^a, Xue Ma ^b, Hongbo Zhang ^a, Guanshu Li ^b, Jun Wang ^{a,*}, Youtao Song ^{b,*}

^a College of Chemistry, Liaoning University, Shenyang 110036, P. R. China

^b College of Environment, Liaoning University, Shenyang 110036, P. R. China

A novel Z-scheme composite sonocatalyst, mMBIP-MWCNT-In₂O₃, is successfully fabricated by using hydrothermal and calcination methods. The sonocatalytic activity of mMBIP-MWCNT-In₂O₃ composite is evaluated through the degradation of norfloxacin under ultrasonic irradiation. The addition of MWCNT accelerates the electron (e⁻) transfer and restrains the recombination of electrons (e⁻) and holes (h⁺) in Z-scheme mMBIP-MWCNT-In₂O₃ sonocatalyst. In comparison with the individual components (mMBIP or In₂O₃), the formation of Z-scheme sonocatalytic system and the presence of and MWCNT make the mMBIP-In₂O₃ display much higher activity in the degradation of norfloxacin. It is wished that the mMBIP-MWCNT-In₂O₃ composite would be an available catalyst in sonocatalytic degradation of organic pollutants.



Research Highlights

- Combination of mMBIP and In_2O_3 forms a novel Z-scheme sonocatalytic system.
- Formed Z-scheme sonocatalytic system can restrain combination of electron and hole.
- MWCNT as conducting channel can accelerate electron transfer in mMBIP- In_2O_3 .
- mMBIP-MWCNT- In_2O_3 can effectively degrade norfloxacin under ultrasonic irradiation.