Graphical abstract

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Articles

Preparation of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ composite and application in innocent treatment of ketamine by using sonocatalytic decomposition method

Hongbo Zhang ^a, Chunsheng Wei ^{a,b}, Yingying Huang ^a, Guanshu Li ^c, Qiong Wu ^a, Jun Wang ^{a,*}, Youtao Song ^{c,*}

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

^b National Police University of China, Shenyang 110854, P. R. China

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

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

A B S T R A C T

A novel sonocatalyst, $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ composite, was synthesized, and then, characterized by X-ray diffractometer (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). In order to evaluate the sonocatalytic activity of prepared $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ composite, the sonocatalytic degradation of ketamine, a kind of narcotic drug, was studied. In addition, some influencing factors such as mass ratio, heat-treated temperature and heat-treated time on the sonocatalytic activity of prepared $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ powders and ultrasonic irradiation time on the sonocatalytic degradation of ketamine were examined by using GC-MS machine. The experimental results showed that the $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ composite is a good sonocatalyst in the field of ultrasonic chemistry and the sonocatalytic degradation was a effective method for the innocent treatment of ketamine.

Preparation of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ composite and application in innocent treatment of ketamine by using sonocatalytic decomposition method

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

^b National Police University of China, Shenyang 110854, P. R. China

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

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Keywords: innocent treatment; ketamine; up-conversion luminescence agent ($\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$);

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

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

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Hongbo Zhang ^a, Chunsheng Wei ^{a,b}, Yingying Huang ^a, Guanshu Li ^c, Qiong Wu ^a, Jun Wang ^{a,*}, Youtao Song ^{c,*}

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

^b National Police University of China, Shenyang 110854, P. R. China

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

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

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

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1. Introduction

In the present-day world, the flooding of narcotic drugs has become a big threat, which is causing serious damage to the society and all mankind [1-3]. Since the criminals have mastered advanced production techniques, more and more types and amounts of narcotic drugs are being produced. Therefore, for confiscated narcotic drugs the effective destruction and treatment technologies are very necessary. Some traditional treatment methods of narcotic drugs were most often used in many country [4-8]. However, these technologies have still exhibited many disadvantages or limitations [9,10]. In addition, they may also lead to the second pollution [11,12]. The narcotic drugs are generally some special organic compound molecules with stable structure and fixed composition. It is difficult to thoroughly degrade and mineralize them. Of course, for these special organic compounds (narcotic drugs), if their structures or compositions are destroyed just a little, due to the small changes they will lose the toxicity. Considering the particularity of narcotic drugs, some Advanced Oxidation

Processes (AOPs) may be feasible methods [13,14].

Recently, the sonocatalytic degradation method has caused attention in the treatment of organic pollutants [15-20]. Sonocatalytic degradation of organic pollutants can be explained by the ultrasonic cavitation effect happened in aqueous medium, which leads to the sonoluminescence and “hot spot” [21-25]. During ultrasonic cavitation the produced “hot spot” can give transient high temperatures (5000 K) and high pressures (1000 atm) [26-29]. The transient high temperatures cause the thermal dissociation of water molecules to produce hydroxyl radicals ($\bullet\text{OH}$) which can degrade and destroy narcotic drugs [30,31]. Besides, the sonoluminescence resulted from ultrasonic cavitation effect can generate light with a comparatively wide range of wavelengths, which can excite the aromatic organic pollutants to become unstable in energy. However, in actual applications, the efficacy using ultrasonic irradiation alone to degrade organic pollutants is not high [28]. In order to efficiently carry out the degradation of organic pollutants under ultrasonic irradiation, the key is selecting some semiconductor materials as sonocatalyst to perform the sonocatalytic degradation reaction [32,33].

In the past, TiO_2 has been used as a sonocatalyst in the sonocatalytic degradation of organic contaminants by most researchers [34,35]. However, compared with some other semiconductor materials with wide-band gap and high oxidation potential, the TiO_2 is not best choice [36]. A lot of research showed that some perovskite niobates can enhance the efficiency of photocatalytic oxygen evolution at least by an order of magnitude [37,38]. Hence, KNbO_3 can be considered as a promising sonocatalyst [39,40]. The band gap (3.5 eV) of KNbO_3 is slightly wider than that (3.2 eV) of TiO_2 , so the KNbO_3 may display a high

sonocatalytic activity under ultrasonic irradiation [36]. Nevertheless, due to the wide-band gap, the KNbO_3 can only absorb high-energy light ($\lambda_{\text{max}} \leq 360 \text{ nm}$) to perform photocatalytic reaction. Using pure KNbO_3 the sonocatalytic degradation efficiency will be very low. Thus, it is necessary to provide sufficient high-energy light to maintain the high sonocatalytic activity.

In recent years, we used some up-conversion luminescence agents to combine with wide-band gap semiconductor materials to enhance the sonocatalytic activity and that achieved satisfactory results [41,42]. The up-conversion luminescence agents can absorb two or more low-energy photons generating one high-energy photon. The produced high-energy lights can excite wide-band gap semiconductor materials and help to realize the high sonocatalytic activity. As up-conversion luminescence agent, the $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ has been widely used in many fields due to its high conversion luminescence efficiency and chemical stability [43]. Therefore, in this work, we try to use $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ combined with KNbO_3 to prepare a novel $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ sonocatalyst performing the sonocatalytic degradation of ketamine under ultrasonic irradiation.

In this paper, $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ powder was prepared through sol-gel-hydrothermal method, and then combined with KNbO_3 by direct mixing and calcination methods as a new sonocatalyst for sonocatalytic degradation of ketamine. Meanwhile, some main influence factors on the sonocatalytic degradation activity of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ was investigated. Furthermore, the mechanism of up-conversion luminescence process of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ and the sonocatalytic degradation of ketamine caused by $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ under ultrasonic irradiation were also proposed.

2. Experimental

2.1. Materials and reagents

Niobium pentoxide (Nb_2O_5) and potassium hydroxide (KOH) (Sinopharm Chemical Reagent Co, Ltd, China) were used to prepare the potassium niobate (KNbO_3). Er_2O_3 (99.999 % purity), Y_2O_3 (99.999 % purity) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (analytically pure), citric acid (analytically pure) and HNO_3 (65-68 %, analytically pure) (Veking Company, China) were used to synthesize the $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ as up-conversion luminescence agent. Ketamine (99.99 % purity, the ministry of public security anti-drug information technology center, China) was used to undergo the sonocatalytic degradation for innocent treatment. All the reagents were of analytical purity grade, and were 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 $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ as sonocatalyst. X-ray powder diffractometer (XRD, D-8, Bruker-axs, Germany, Ni filtered Cu Ka radiation in the range of 2θ from 10° to 70°) and scanning electron microscopy (SEM, JEOL JSM-5610LV, Hitachi Corporation, Japan) were used to determine the crystalline phase and surface morphology. Energy dispersive X-ray spectroscopy (EDX, JEOL JSM-5610LV, Hitachi Corporation, Japan) was used to determine the element type and composition content. GC-MS machine (Agilent 7890A/5975C, Agilent Technologies Inc, USA) was used to inspect the sonocatalytic degradation processes and decomposition products of ketamine in aqueous solution. Controllable Serial-Ultrasonics apparatus (KQ-300, Kunshan Company, China) was adopted to irradiate the ketamine solution, operating at ultrasonic frequency of 40 kHz and output power of 300 W through manual

adjust.

2.2. Preparation of KNbO_3 powder

KNbO_3 particles were prepared by using a hydrothermal method following the work reported by Yan et al [44]. 3.57 g Nb_2O_5 and 37.69 g KOH were added into 19 mL distilled water, which was stirred vigorously for 30 min. Then the mixture was sealed in a Teflon-lined stainless steel autoclave and heated at 160 °C for 12 h. The products were washed with distilled water and ethanol several times, and then dried at 80 °C overnight. Finally, the KNbO_3 particles were obtained and stored for the sonocatalytic degradation.

2.3. Synthesis of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ as up-conversion luminescence agent

The $\text{Er}^{3+}:\text{YAlO}_3$ was synthesized by the sol-gel and calcination method [36]. Er_2O_3 and Y_2O_3 powders were dissolved in HNO_3 with magnetic stirring and heated until transparent. Appropriate amount of aluminum nitrate solution was added to the above transparent solution. Then citric acid was added as chelating agent and co-solvent. The remaining solution was stirred and heated at 50-60 °C until the transparent sol was successfully prepared. Then, the sol was heated at 80 °C for 30 min and the xerogel was finally obtained, which was ground into fine homogeneous powders. Subsequently, in order to remove residual organic components and nitrate ions the particles were calcined at 500 °C for 50 min, and then continue to heat to 1100 °C and kept for 2.0 h. At last, the sintered substance was allowed to cool down to the room temperature in atmosphere and taken out of the muffle furnace. After fully grinding, the nano-sized $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ powder was obtained and stored for preparing the sonocatalysts ($\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$).

2.4. Preparation of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ powders as sonocatalyst

The $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ catalysts were prepared through the ultrasonic dispersion and liquid boiling methods [45]. The $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ and KNbO_3 powders, whose mass ratios of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ and KNbO_3 were adopted as 0.00:1.00, 0.15:1.00 and 0.30:1.00, respectively, were added into a 200 mL beaker filled with 30 mL deionized water and then adequately dispersed by ultrasound of 40 kHz frequency and 300 W output power for 30 min. The suspended liquid was heated to boiling point and kept at constant temperature for 30 min. After filtration and lavation, the separated deposit was put into a crucible and heated in a muffle furnace at the calefactive rate of $2.0\text{ }^\circ\text{C}\cdot\text{min}^{-1}$. The temperature was controlled at 300 $^\circ\text{C}$, 400 $^\circ\text{C}$ and 500 $^\circ\text{C}$, respectively. After 60 min, the $\text{Er}^{3+}:\text{YAlO}_3/\text{KNbO}_3$ sonocatalysts were obtained.

2.5. Characterization of the prepared $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ powders

The prepared $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ particles as sonocatalysts were characterized by 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 spectroscopy (EDX, JEOL JSM-5610LV, Hitachi Corporation, Japan).

2.6. Measurements of sonocatalytic activity of the prepared $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$

Sonocatalytic decomposition experiments of ketamine were carried out in a 150 mL erlenmeyer flask placed in an ultrasonic irradiation apparatus (300 (length) $\times$ 180 mm (width) $\times$ 120 mm (height), KQ-300, 40 kHz, 300 W, six transducers, Kunshan ultrasonic apparatus Company, China) under air atmosphere. In the common experiment, 1.00 g/L

$\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ powder and 10.00 mg/L ketamine concentration in 100 mL total volume were adopted to perform the sonocatalytic degradation. Before ultrasonic irradiation, the above solutions were stirred for 30 min in the dark to achieve adsorption-desorption equilibrium of ketamine on the surface of catalyst particles. And then, the degradation of ketamine was performed under ultrasonic irradiation for 150 min. At a certain time interval, from the degradation liquid a certain of sample was removed and measured by gas chromatography-mass spectrometry (GC-MS). The degradation ratios of ketamine were determined from the peak area ratio change of ketamine solution using the following equation:

$$\text{Degradation ratio (\%)} = [A_o/A_s - A_t/A_s]/(A_o/A_s) \times 100$$

Where A_o is the initial peak area of ketamine solution, A_t is the instant peak area after a certain of ultrasonic irradiation time (t) and A_s is the peak area of internal standard peak area.

In addition, the influences of heat-treated temperature and heat-treated time on the sonocatalytic activity of the prepared $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ powders were also examined through the sonocatalytic degradation of ketamine in aqueous solution.

3. Results and discussion

3.1. XRD patterns of the prepared $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ powders

The XRD patterns of prepared KNbO_3 powder (a-1), synthesized up-conversion luminescence agent ($\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$) (a-2) and prepared $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ powders (a-3) were all given in Fig. 1(a). As can be seen in Fig. 1(a-1), it can be found that all given XRD patterns of prepared KNbO_3 powder are similar to the JCPDS card 32-0832 of KNbO_3 [46].

According to the characteristic diffraction angles at $2\theta = 22.04^\circ$, 31.56° , 45.02° , 51.04° , 56.04° and 65.82° , it can be confirmed that they correspond well with (110), (111), (220) and (002), (221), (311) and (222) planes, respectively. As shown in Fig. 1(a-2), the typical XRD diffraction peaks of synthesized $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ appear at $2\theta = 18.15^\circ$ (211), 33.50° (400), 41.50° (422), 46.62° (521) and 55.12° (532), respectively. Obviously, the XRD pattern of synthesized $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ is similar to the JCPDS #33-0040 file of $\text{Y}_3\text{Al}_5\text{O}_{12}$. It demonstrates that in the $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ the $\text{Y}_3\text{Al}_5\text{O}_{12}$ has formed and the Er^{3+} entered the crystal lattice of $\text{Y}_3\text{Al}_5\text{O}_{12}$ replacing the partial Y^{3+} ions. In addition, the movement of the characteristic diffraction peak in Fig. 1(a-2) from $2\theta = 37.94^\circ$ to $2\theta = 37.82^\circ$ also indicates that a small quantity of Er^{3+} ions slightly changes the basic crystal structure of $\text{Y}_3\text{Al}_5\text{O}_{12}$. From Fig. 1(a-3) it can be found that, beside the normal characteristic diffraction peaks of KNbO_3 , the prepared $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ catalysts also give the peaks of corresponding up-conversion luminescence agent ($\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$). It indicates that the $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ parts have combined with KNbO_3 forming $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ composites.

The XRD patterns of prepared $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ with different mass ratio of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ and KNbO_3 from 0.0:1.0 to 0.3:1.0 are shown in Fig. 1(b). From Fig. 1(b) it can be found that, with the mass ratio further increase of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$, the characteristic diffraction peaks of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ gradually raise. The XRD patterns of prepared KNbO_3 powder heat-treated at different temperatures (from 300°C to 500°C) for 60 min were shown in Fig. 1(c). It can be seen that, when the prepared $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ powders are calcined for 60 min at 300°C , 400°C and 500°C , the diffraction peaks become sharper and higher with the increase of heat-treated temperature. That is, these X-ray diffractions revealed

that the increase of heat-treated temperature would be beneficial to the crystallinity of prepared $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ powders. From Fig. 1(d) it can be found that the heat-treated time in the range of 30-90 min also influences the crystal form of prepared $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ powders. However, the slight change of X-ray diffraction peaks indicates that the properly long heat-treated time does not much affect the crystallinity of prepared $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ powders.

Fig. 1.

3.2. SEM images of the prepared $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$

The scanning electron microscopic (SEM) images of prepared KNbO_3 , $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ and $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ powders were determined and the morphologies were studied in this section. As seen in Fig. 2(a), it can be seen that there are a large number of particles with an average size of approximately 50 nm, which is attributed to the $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ particles. As shown in Fig. 2(b), it can be found that there are a lot of cube-like crystal particles ranging from 200 nm to 250 nm in side length, which should belong to the typical crystal form of micron-sized KNbO_3 particles. From Fig. 2(c), it can be seen that some spherical particles with about 50 nm size attach to the cube-like morphology of particles with average 300 nm length and width. These findings prove that the $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ has been combined with KNbO_3 .

Fig. 2.

3.3. EDX spectra of the prepared KNbO_3

Fig. 3 shows the EDX spectra of the prepared KNbO_3 (a), $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ (b) and

$\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ (c) powders. As shown in Fig. 3(a), it can be seen that there are strong peaks which belong to O, Al, Er and Y elements. In fact, these elements compose the up-conversion luminescence agent ($\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$). Also, the atomic ratio given in Fig. 3(a) is basically the same as the atomic ratio of synthesized up-conversion luminescence agent ($\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$). As shown in Fig. 3(b), the strong peaks of O, Nb and K elements appear, which indicates that these elements compose the prepared KNbO_3 . Specifically, EDX analysis reveal that the percent contents of the elements (wt. %) are O: 28.858 %, Nb: 39.355 % and K: 21.016%. It indicated that the elemental composition of the prepared KNbO_3 sample is very close to the standard composition of KNbO_3 . And these results are consistent with the XRD pattern presented above as well. Lastly, as shown in Fig. 3(c), it can be clearly seen that all above peaks also appear in the EDX spectra of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$, which indicates that the prepared $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ contains the contents of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ and KNbO_3 . The corresponding ratio of each ingredient in the $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ is consistent with the theoretical calculating value.

Fig. 3.

3.6. Influence of ultrasonic irradiation time and corresponding reaction kinetics on sonocatalytic degradation of Ketamine

The relationships between sonocatalytic degradation ratios of ketamine and ultrasonic irradiation time (t) in the presence of prepared $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ powders with different mass ratios are given in Fig. 4(a). First of all, it can be found that the degradation ratios of ketamine raise along with increasing mass ratio of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ and KNbO_3 at any ultrasonic irradiation time. After 150 min of ultrasonic irradiation time, the degradation ratios reach

20.64 %, 44.83 % and 59.81 %, respectively, for 0.00:1.00, 0.15:1.00 and 0.30:1.00 mass ratios of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$. Apparently, it indicated that the presence of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ as up-conversion luminescence agent could obviously enhance the sonocatalytic activity of KNbO_3 . In a certain mass ratio range, along with the increasing $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ content the sonocatalytic activity of KNbO_3 can be gradually increased. It can be considered that the $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ as up-conversion luminescence agent under ultrasonic irradiation can emit the short wavelength (high energy) lights, which can be effectively absorbed by the KNbO_3 as sonocatalyst to carry out the sonocatalytic degradation and decomposition of pollutants. Of course, with the increase of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ dose, to a certain extent the sonocatalytic reaction surface or active site number of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ particles may be decreased, which will decrease the sonocatalytic activity of KNbO_3 . Thus, in order to obtain a high sonocatalytic activity an appropriate mass ratio of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ and KNbO_3 in $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ is necessary.

Fig. 4.

In order to further compare the sonocatalytic degradation ratios of ketamine caused by different mass ratios of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ and KNbO_3 , the first-order reaction kinetics is constructed to investigate the sonocatalytic degradation of ketamine. Therefore, the curves of $\ln(C_t/C_0)$ (C_t : instantaneous concentration and C_0 : initial concentration) against ultrasonic irradiation time (t) can be obtained as shown in Fig. 4(b). It can be found that, for three courses (0.00:1.00, 0.15:1.00 and 0.30:1.00 systems), the approximate linear relationships indicate that these sonocatalytic degradation reactions basically follow the first-order reaction kinetics ($\ln(C_t/C_0) = -kt$), where k is the rate constant. The calculated reaction rate constants

and corresponding correlation coefficients are 0.0039 min^{-1} ($R^2 = 0.9655$), 0.0027 min^{-1} ($R^2 = 0.9778$) and 0.0014 min^{-1} ($R^2 = 0.9323$), respectively, for 0.30:1.00, 0.15:1.00 and 0.00:1.00 $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ systems. By comparison, the sequence based on the reaction rate constants was also $0.30:1.00 > 0.15:1.00 > 0.00:1.00$. It confirmed again that the $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ systems can effectively decompose ketamine molecules under ultrasonic irradiation.

3.5. Influences of heat-treated temperature and heat-treated time on sonocatalytic activity of prepared $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ powders

In general, for most of oxides and inorganic salts as catalysts, their catalytic activities are affected by heat-treated temperature and heat-treated time. This is because the heat-treated temperature and heat-treated time decide their crystalline form, crystalline phase, crystallinity, surface property as well as chemical composition. Here, the influences of heat-treated temperature and heat-treated time on the sonocatalytic activity of the prepared $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ powders were examined through the sonocatalytic degradation and decomposition of ketamine. As shown in Fig. 5(a), the sonocatalytic degradation ratio of ketamine in the presence of 1.00 g/L prepared $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ powders gradually increases with the rises of heat-treated temperature from 300 °C to 500 °C for 60 min. It indicates that the rises of heat-treated temperature are conducive to enhancing the sonocatalytic activity of the prepared $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ powders. The XRD determination (Fig. 1(c)) of the prepared $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ powders demonstrated that the rises of heat-treated temperature could enhance the crystallinity and stabilize the crystalline phase. Apparently, along with the rises of heat-treated temperature, more and more

crystal $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ particles become the highly active sonocatalyst. Because of the above reason, the highest degradation ratio was attained in the presence of prepared $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ powders calcined at 500 °C for 60 min and the corresponding sonocatalytic degradation ratio was 73.08 %.

Fig. 5.

From Fig. 5(b) it can be found that the sonocatalytic degradation ratio of ketamine in the presence of prepared $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ powders increases at first with the rises of heat-treated time from 30 min to 90 min at 400 °C, and then decreases slightly. It indicates that the increase of heat-treated time from 30 min to 60 min is conducive to enhancing the sonocatalytic activity of the prepared $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ powders. However, the increase of heat-treated time from 60 min to 90 min tends to reduce the sonocatalytic activity of the prepared $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ powders. It is because the composite structure of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ and KNbO_3 changes from loosening to tightness with the increase of heat-treated time from 30 min to 60 min, which results in the raises of sonocatalytic activity of the $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ powders. However, in the heat-treated process from 60 min to 90 min, the crystal form tends to be perfect, which causes the active sites to be reduced. Thus, it showed the decreasing sonocatalytic activity. Therefore, the $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ and KNbO_3 can combine perfectly when the heat-treated time reaches 60 min, which gives the highest sonocatalytic degradation ratio of ketamine. Because of the above reason, the heat-treated time of 60 min is favorable to handle the prepared $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ powders as an employed condition in the further experiments.

3.4. Gas chromatography of ketamine solutions during sonocatalytic degradation

The gas chromatograms of ketamine solution (10.00 mg/L) after different ultrasonic irradiation time are given in Fig. 6. It can be found that one strong adsorption peak appears at R_t (retention time) = 9.0 min, which can be confirmed to be ketamine adsorption peak by mass spectrometry. And the other adsorption peak at R_t = 11.2 belongs to that of internal standard (SKF255A). Moreover, from Fig. 6 it can be seen that the peak area ratio of ketamine and internal standard (SKF255A) give more and more significant decrease along with the increase of ultrasonic irradiation time. It indicates that most of ketamine molecules have been destroyed by prepared $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ particles under ultrasonic irradiation. In addition, after a period of reaction time, some new weak adsorption peaks appear. It indicates that the ketamine molecules can be decomposed to some small molecular fragments, which can be proved by mass spectrometry.

Fig. 6.

3.7. Process of sonocatalytic degradation of ketamine molecules in the presence of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ powders under ultrasonic irradiation

In order to confirm the real process of sonocatalytic degradation of ketamine molecules caused by $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ powders under ultrasonic irradiation, the decomposition products of ketamine molecules were analyzed by using GC-MS machine. The gas chromatogram of ketamine before and after ultrasonic irradiation and the corresponding mass spectra of the main decomposition products were provided in Fig. 7. From Fig. 7 (b), it can be found that, after ultrasonic irradiation, some new peaks appear at R_t = 3.633 min, 4.038 min,

4.444 min, 4.646 min, 5.278 min, 6.621 min, 7.178 min, 7.938 min and 8.659 min, respectively. It indicates that the molecular structure and chemical composition of ketamine molecules have been destroyed in the presence of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ powders under ultrasonic irradiation. Particularly, from Fig. 7 (b-n (n = 1 - 9)) it can be confirmed that the main decomposition products of are 2-chlorophenylacetylene ($R_t = 3.633$ min), 2-chlorobenzaldehyde ($R_t = 4.038$ min), 2-chlorobenzonitrile ($R_t = 4.444$ min), 2-chloroacetophenone ($R_t = 4.646$ min), 2-chlorobenzamide ($R_t = 5.278$ min), 2-amino-2-phenylcyclohexanone ($R_t = 6.621$ min), 1-(2-chlorophenyl)-N-methylpent-4-en-1-amine ($R_t = 7.178$ min), 2-phenylcyclohexanone ($R_t = 7.938$ min) and 2-amino-2-(2-chlorophenyl)cyclohexanone ($R_t = 8.659$ min), respectively. Apparently, these substances, as general organic compounds, will not cause people to be damaged and addicted in spirit and body.

Fig. 7.

In a word, it experimentally proved that the sonocatalytic decomposition caused by prepared $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ powders as sonocatalyst under ultrasonic irradiation displays the potential application prospect in the innocent treatment of various narcotic drugs.

3.8. Mechanism of sonocatalytic degradation of narcotic drugs caused by $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ powders under ultrasonic irradiation

In the past, as a novel advanced oxidation technology the sonocatalytic degradation method of organic pollutants has not been regarded thoroughly. Hence, there has been no ready-made mechanism and satisfying explanation yet on the sonocatalytic degradation of

organic pollutants including narcotic drugs caused by various semiconductor sonocatalyst under ultrasonic irradiation. In order to better understand the sonocatalytic degradation process of narcotic drugs and improve the sonocatalytic activity of semiconductor sonocatalyst, the possible sonocatalytic degradation mechanism of ketamine caused by $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ powders under ultrasonic irradiation is proposed as shown in Fig. 8. The proposal of sonocatalytic degradation mechanism is mainly based on both sonoluminescence and “hot spot” resulting from the ultrasonic cavitation effect [24]. This may be one of the well known and acceptable mechanisms. Therefore, in this study, in combination with the up-conversion luminescence the mechanism of sonocatalytic degradation in the presence of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ powder under ultrasonic irradiation is tentatively proposed as follows.

Firstly, it has been well known that the sonoluminescence caused by ultrasonic cavitation effect can generally generate various wavelength lights including short and long wavelength lights. As a wide band-gap ($E_{\text{bg}} = 3.2\text{-}3.5$ eV) semiconductor photocatalyst, the prepared KNbO_3 can only absorb short wavelength lights ($\lambda_{\text{max}} \leq 360$ nm) and can not absorb the most of the long wavelength lights ($\lambda_{\text{min}} \geq 360$ nm). In order to enhance the sonocatalytic activity of KNbO_3 , providing adequate ultraviolet lights is necessary. $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$, as a recognized up-conversion luminescence agent, can absorb the long wavelength (low energy) lights and then emit short wavelength (high energy) lights. Therefore, the use of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ can transform the visible lights in sonoluminescence from ultrasonic cavitation effect into ultraviolet lights, which as high energy lights can effectively activate the wide band-gap KNbO_3 semiconductor to carry out sonocatalytic degradation reaction. Secondly, as well

known, the temperature of “hot spot” produced by ultrasonic cavitation effect in water medium can achieve a very high temperature (more than 1000 °C). Such high temperature sufficiently breaks down some water molecules (H_2O) producing hydroxyl radicals ($\bullet\text{OH}$), but the number is not much. Fortunately, these heat energies of “hot spot” can also excite the KNbO_3 powder like lights to perform sonocatalytic degradation reaction.

Fig. 8.

Under high energy light excitation the electrons in the valence band (VB) of KNbO_3 semiconductors are transited to the conduction band (CB). At the same time, the holes are inevitably generated on the surface or inside of KNbO_3 particles. Through a series of chemical reactions, these highly reactive electrons and holes can generate various reactive oxygen species (ROS) to perform the degradation of narcotic drugs. On the one hand, the generated holes on the valence band (VB) can directly decompose the narcotic drugs on the surface of KNbO_3 crystal particles until degraded them completely. On the other hand, the generated holes oxidize the water (H_2O) molecules absorbed on the surface of KNbO_3 crystal particles producing hydroxyl radicals ($\bullet\text{OH}$), which indirectly degraded the narcotic drugs in aqueous solution or destroyed the structure of narcotic drugs. During the oxidation course, the narcotic drugs are decomposed to a series of intermediate products, losing their toxic effects on physical. At the same time, the generated electrons react with the molecular oxygen (O_2) dissolved in aqueous solution and produce the superoxygen radical anions ($\bullet\text{O}_2^-$), which also become the hydroxyl radicals ($\bullet\text{OH}$) through a series of chemical reactions. These hydroxyl radicals ($\bullet\text{OH}$) with strong oxidation ability can degrade the surrounding narcotic drug molecules, leading to volatile degradation by-products or CO_2 , H_2O and mineral acids through

entire mineralization.

4. Conclusions

In this paper, the $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ as sonocatalyst was prepared by using sol-gel method and hydrothermal method. And then, the sonocatalytic activity was evaluated through the degradation of ketamine in aqueous solution under ultrasonic irradiation. The prepared $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ powders with 0.30:1.00 mass ratio heat-treated at 400 °C for 60 min displays the best sonocatalytic activity during sonocatalytic degradation of ketamine. For given experimental conditions of 150 min ultrasonic irradiation time, 1.00 g/L $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ (with 0.30:1.00 mass ratio heat-treated at 400 °C for 60 min) and 10.00 mg/L ketamine concentration, the sonocatalytic degradation ratio can reach above 60 %. In addition, GC-MS spectra indicate that most of ketamine molecules have been decomposed into a series of non-toxic products, such as 2-chlorophenylacetylene, 2-chlorobenzaldehyde, 2-chlorobenzonitrile, 2-chloroacetophenone), 2-chlorobenzamide, 2-amino-2-phenylcyclohexanone, 1-(2-chlorophenyl)-N-methylpent-4-en-1-amine, 2-phenylcyclohexanone, 2-amino-2-(2-chlorophenyl)cyclohexanone and so on. Thus, it can be seen that the sonocatalytic degradation method can harmlessly treat narcotic drugs.

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Content of Figures:

Fig. 1. XRD patterns of (a-1) KNbO_3 powder (heat-treated at 400 °C for 60 min), (a-2) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ powder (heat-treated at 1100 °C for 120 min) and (a-3) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ powders (heat-treated at 400 °C for 60 min) and (b) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ with different mass ratio heat-treated at 400 °C for 60 min, (c) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ with 0.15:1.00 mass ratio at different heat-treated temperature for 60 min and (d) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ with 0.15:1.00 mass ratio at 400 °C for different heat-treated time.

Fig. 2. SEM images of (a) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ powder heat-treated at 1100 °C for 120 min, (b) KNbO_3

powder heat-treated at 400 °C for 60 min and (c) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ with 0.15:1.00 mass ratio heat-treated at 400 °C for 60 min.

Fig. 3. EDX spectra of (a) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ powder heat-treated at 1100 °C for 120 min, (b) KNbO_3 powder heat-treated at 400 °C for 60 min and (c) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ with 0.15:1.00 mass ratio heat-treated at 400 °C for 60 min.

Fig. 4. (a) Influence of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ and KNbO_3 mass ratio and (b) the corresponding reaction kinetics on the sonocatalytic degradation of ketamine. (1.00 g/L $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ powders (heat-treated at 400 °C for 60 min), 10.00 mg/L ketamine concentration, 24-28 °C temperature, 100 mL total volume and 150 min ultrasonic irradiation time (300 W output power and 40 kHz frequency.)

Fig. 5. Influence of (a) heat-treated temperature and (b) heat-treated time on the sonocatalytic activity of prepared $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ powders with 0.15:1.00 mass ratio heat-treated at 300-500 °C for 30-90 min. (1.00 g/L $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ powders, 10.00 mg/L ketamine concentration, 24-28 °C temperature, 100 mL total volume and 150 min ultrasonic irradiation time (300 W output power and 40 kHz frequency.)

Fig. 6. Gas chromatography of ketamine solutions with different ultrasonic irradiation time. (1.00 g/L $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ powders (with 0.15:1.00 mass ratio heat-treated at 400 °C for 60 min), 10.00 mg/L ketamine solutions, 300 W output power and 40 kHz frequency.)

Fig. 7. Gas chromatographies of (a) ketamine and (b) sonocatalytic decomposition products and the corresponding mass spectra (from b-1 to b-9). (1.00 g/L $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ powders (with 0.15:1.00 mass ratio heat-treated at 400 °C for 60 min), 10.00 mg/L ketamine concentration, 24-28 °C temperature, 100 mL total volume and 150 min ultrasonic irradiation time (300 W output power and 40 kHz frequency).)

Fig. 8. Sonocatalytic degradation principle of narcotic drugs in the presence of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ powders under ultrasonic irradiation.

Figures:

Fig. 1. XRD patterns of (a-1) KNbO_3 powder (heat-treated at 400 °C for 60 min), (a-2) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ powder (heat-treated at 1100 °C for 120 min) and (a-3) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ powders (heat-treated at 400 °C for 60 min) and (b) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ with different mass ratio heat-treated at 400 °C for 60 min, (c) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ with 0.15:1.00 mass ratio at different heat-treated temperature for 60 min and (d) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ with 0.15:1.00 mass ratio at 400 °C for different heat-treated time.

Fig. 2. SEM images of (a) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ powder heat-treated at 1100 °C for 120 min, (b) KNbO_3 powder heat-treated at 400 °C for 60 min and (c) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ with 0.15:1.00 mass ratio heat-treated at 400 °C for 60 min.

Fig. 3. EDX spectra of (a) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ powder heat-treated at 1100 °C for 120 min, (b) KNbO_3 powder heat-treated at 400 °C for 60 min and (c) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ with 0.15:1.00 mass ratio heat-treated at 400 °C for 60 min.

Fig. 4. (a) Influence of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ and KNbO_3 mass ratio and (b) the corresponding reaction kinetics on the sonocatalytic degradation of ketamine. (1.00 g/L $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ powders (heat-treated at 400 °C for 60 min), 10.00 mg/L ketamine concentration, 24-28 °C temperature, 100 mL total volume and 150 min ultrasonic irradiation time (300 W output power and 40 kHz frequency.)

Fig. 5. Influence of (a) heat-treated temperature and (b) heat-treated time on the sonocatalytic activity of prepared $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ powders with 0.15:1.00 mass ratio heat-treated at 300-500 °C for 30-90 min. (1.00 g/L $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ powders, 10.00 mg/L ketamine concentration, 24-28 °C temperature, 100 mL total volume and 150 min ultrasonic irradiation time (300 W output power and 40 kHz frequency.)

Fig. 6. Gas chromatography of ketamine solutions with different ultrasonic irradiation time. (1.00 g/L $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ powders (with 0.15:1.00 mass ratio heat-treated at 400 °C for 60 min), 10.00 mg/L ketamine solutions, 300 W output power and 40 kHz frequency.)

Fig. 7. Gas chromatographies of (a) ketamine and (b) sonocatalytic decomposition products and the corresponding corresponding mass spectra (from b-1 to b-9). (1.00 g/L $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ powders (with 0.15:1.00 mass ratio heat-treated at 400 °C for 60 min), 10.00 mg/L ketamine concentration, 24-28 °C temperature, 100 mL total volume and 150 min ultrasonic irradiation time (300 W output power and 40 kHz frequency).)

Fig. 8. Sonocatalytic degradation principle of narcotic drugs in the presence of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$

powders under ultrasonic irradiation.