



# Assisted sonocatalytic degradation of pethidine hydrochloride (dolantin) with some inorganic oxidants caused by CdS-coated ZrO<sub>2</sub> composite



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## ARTICLE INFO

### Article history:

Received 5 April 2016

Received in revised form 13 May 2016

Accepted 16 August 2016

Available online 18 August 2016

### Keywords:

Sonocatalyst

CdS-coated ZrO<sub>2</sub> composite

Inorganic oxidant

Assisted sonocatalytic degradation

Pethidine hydrochloride (dolantin)

## ABSTRACT

CdS was synthesized via hydrothermal method and CdS-coated ZrO<sub>2</sub> composite was prepared via chemical precipitation method. And then they were characterized by X-ray diffractometer (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). After that, the sonocatalytic degradation of pethidine hydrochloride (dolantin) in aqueous solution was conducted adopting CdS-coated ZrO<sub>2</sub> composite as sonocatalyst with inorganic oxidant assisted. In addition, some influencing factors such as inorganic oxidant kind, including persulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>), perchlorate (NaClO<sub>4</sub>) and periodate (KIO<sub>4</sub>), inorganic oxidant concentration and ultrasonic irradiation time on sonocatalytic degradation of pethidine hydrochloride were examined by using gas chromatograph. The experimental results showed that the used inorganic oxidants can effectively assisted the sonocatalytic degradation of pethidine hydrochloride caused by CdS-coated ZrO<sub>2</sub> composite and the increase effects arrange as the order of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> > KIO<sub>4</sub> > NaClO<sub>4</sub>. And the best sonocatalytic degradation ratio (95.50%) of pethidine hydrochloride could be obtained when the conditions of 10.00 mmol/L K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, 1.00 g/L prepared CdS-coated ZrO<sub>2</sub> composite, 135 min ultrasonic irradiation (40 kHz frequency and 300 W output power), 100 mL total volume and 25–28 °C temperature were adopted. However, only using CdS-coated ZrO<sub>2</sub> as sonocatalyst without any inorganic oxidants merely reaches 20% degradation ratio of pethidine hydrochloride when other conditions are the same. The method of sonocatalytic degradation assisted with inorganic oxidants may be an efficient sonocatalytic system for degradation of pethidine hydrochloride.

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## 1. Introduction

Narcotic drugs abuse may do harm to people's health by making person produce the physical and mental dependence [1]. What is worse, it makes families into economic bankruptcy even leads to the harrowing break-up. Pethidine hydrochloride (dolantin) is a phenylpiperidine derivative, which is firstly synthetic analgesic drug to achieve the wide therapeutic use [2,3]. Acting as an opiate agonist, pethidine hydrochloride has the similar pharmacological effect with morphine [4]. Long-term abuse and accidental ingestion will result in dependence and damage of central nervous system (CNS), even lead to death [5,6]. On a global scale, many pharmaceutical factories in the production of pethidine hydrochloride

would discharge waste water containing pethidine hydrochloride into our environment [7]. On the other hand, every year some hospitals would also produce a lot of out-of-date pethidine hydrochloride. What's more, public security organ could seize a large number of pethidine hydrochloride every year. So the harmless treatment of pethidine hydrochloride is a major problem that we must face to. In the past, there were some methods to dispose pethidine hydrochloride, such as incineration, landfill, adsorption and so on [8]. Nevertheless, these methods are generally incomplete and insecure, even often bring secondary pollution. Therefore, it is indispensable to seek a better way to dispose pethidine hydrochloride. Perhaps, for a special biological active substance breaking its molecular structure and chemical composition to reach the harmlessness may be feasible.

The sonocatalytic technology combining with semiconductors has been received much attention in solving environmental problems [9–12]. Because of many advantages, such as strong

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penetrability, special transmission mode, high efficiency and simple operation, therefore, it can become an effective way to decompose the organic dyes in non- or low-transparent effluents [13–15]. Perhaps, this way should also be feasible to dispose narcotic drugs. In the past, sonocatalytic degradation of many organic pollutants employing titanium dioxide ( $\text{TiO}_2$ ) powder as sonocatalyst has been reported [16–19]. The bandwidth of  $\text{TiO}_2$  is 3.2 eV, and its valence band (VB) and conduction band (CB) electric potentials are 2.91 eV and  $-0.29$  eV [20], respectively. For most of organic pollutants,  $\text{TiO}_2$  is enough to effectively decompose them through photocatalytic or sonocatalytic reaction process [21,22]. Nevertheless, narcotic drugs are some stable substances chemically. Apparently, in order to destroy narcotic drugs, it is necessary to select some of broadband semiconductor oxides as sonocatalysts. Due to the bandwidth of 5.0 eV and relatively low VB electric potential of 3.91 eV,  $\text{ZrO}_2$  should have much stronger oxidation capacity under ultrasonic irradiation [23–25]. However, because of such wide bandwidth of  $\text{ZrO}_2$ , only a small portion of ultraviolet light in sonoluminescence can be used [26–28]. In order to broaden the response range towards light and avoid the recombination of electron ( $e^-$ )-hole ( $h^+$ ) pairs, using a narrowband semiconductor to combine with  $\text{ZrO}_2$  may be feasible [29–33]. CdS has bandwidth of 2.42 eV and is an applicable semiconductor. Being similar to photocatalytic reaction, such combination will enhance the sonocatalytic activity of  $\text{ZrO}_2$  [34–37].

In this paper, the nano-sized CdS was synthesized via hydrothermal method and the CdS-coated  $\text{ZrO}_2$  composite was prepared via chemical precipitation method. And then the CdS-coated  $\text{ZrO}_2$  composite was chosen as sonocatalyst to carry out sonocatalytic degradation of pethidine hydrochloride. In addition, it has been reported that the addition of inorganic oxidants could further enhance the sonocatalytic degradation efficiency of pollutants [38–41]. Therefore, in this study, some inorganic oxidants were used to assist sonocatalytic degradation. Through the reaction of inorganic oxidants with the electrons on the conduction band (CB) of  $\text{ZrO}_2$ , the reactive oxygen species (ROS) oxidants can be generated. The influences of inorganic oxidant kind and concentration as well as ultrasonic irradiation time on the sonocatalytic degradation of pethidine hydrochloride were studied. The degradation process and corresponding mechanism were tentatively proposed. It is wished that the sonocatalytic degradation method assisted with inorganic oxidants can be used to treat the narcotic drugs in aqueous solution.

## 2. Experimental

### 2.1. Materials and reagents

Cadmium chloride ( $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ ) and sodium sulphide nonahydrate ( $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ ) (Sinopharm Chemical Regent Co, Ltd., China) were used to prepare the nano-sized cadmium sulphide (CdS). Zirconium oxychloride ( $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ ) and ammonium hydroxide (Sinopharm Chemical Regent Co, Ltd., China) were used to prepare the nano-sized  $\text{ZrO}_2$ . Pethidine hydrochloride (99.99% purity, Tianjin Kaiyuan Reagent Corporation, China) was used to undergo the sonocatalytic degradation. Potassium persulfate ( $\text{K}_2\text{S}_2\text{O}_8$ ), sodium perchlorate ( $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ ) and potassium periodate ( $\text{KIO}_4$ ) (AR, Tianjin Kemiou chemicals Corporation, China) were purchased as assisted inorganic oxidants. Lidocaine (Sigma-Aldrich, MO, USA) was used as internal standard. All the reagents were of analytical purity grade, and were directly used without further purification.

X-ray powder diffractometer (XRD, D-8, Bruker-axs, Germany, Ni filtered Cu K $\alpha$  radiation in the range of  $2\theta$  from  $10^\circ$  to  $70^\circ$ ), transmission electron microscopy (TEM, JEOL JEM2100, Hitachi Corporation, Japan) and scanning electron microscopy (SEM, JEOL JSM-5610LV, Hitachi Corporation, Japan) were used to determine

the crystalline phase. X-ray photoelectron spectroscopy (XPS, Escalab 250XI, Thermo, America) was used to determine the element type and composition content of CdS-coated  $\text{ZrO}_2$  composite. Gas chromatograph Agilent 6890 (Agilent technologies, Massy, France) was used to inspect the sonocatalytic degradation ratio of pethidine hydrochloride in aqueous solution. Controllable Serial-Ultrasonics apparatus (KQ-300, Kunshan Company, China) was adopted to irradiate the pethidine hydrochloride aqueous solution, operating at ultrasonic frequency of 40 kHz and output power of 300 W through manual adjust. Apparatus of ultrasonic irradiation has been shown in our past work [42,43].

### 2.2. Preparation of nano-sized CdS powder

Nano-sized CdS particles were prepared by using a hydrothermal method. 6.0 mmol of  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$  was dissolved in 40 mL distilled water, then 6.0 mmol sodium sulphide  $\text{Na}_2\text{S}$  solution was added with continuous stirring for 30 min. Subsequently, the solution was transferred into a 50 mL polytetrafluoroethylene (PTFE) autoclave equipped with a stainless steel shell and maintained at  $100^\circ\text{C}$  for 4.0 h. After cooling to room temperature, the orange precipitation was collected through filter and washed several times alternately with ethanol and distilled water, and then vacuum-dried at  $80^\circ\text{C}$  3.0 h followed by calcination in air for 3.0 h at  $500^\circ\text{C}$  and grinded for the following experiments and characterizations.

### 2.3. Preparation of sonocatalysts CdS-coated $\text{ZrO}_2$ composite

$\text{ZrO}_2$  prepared by chemical precipitation method [44]. 5.80 mmol (1.8691 g) of zirconium oxychloride  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  was dissolved in 50 mL of deionised water and precipitated the hydroxides with an aqueous solution of 6.0%  $\text{NH}_3$  at pH 9.9 and stirred vigorously. The precipitate was filtered and washed to make it free from chloride ion and ammonia, and then dissolved in a small amount of water. After that 1.90 mmol (0.2810 g) of nano-sized CdS powder was added to the above solution with stirring vigorously. Then filtered and washed with distilled water. The washed product was dried at  $120^\circ\text{C}$  in air for 12 h followed by calcination in air for 3.0 h at  $350^\circ\text{C}$ . After fully grinding, the CdS-coated  $\text{ZrO}_2$  composite was obtained.

### 2.4. Characterization of the prepared CdS-coated $\text{ZrO}_2$ composite

The prepared CdS-coated  $\text{ZrO}_2$  composite 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  $2\theta$  from  $10^\circ$  to  $70^\circ$ ), scanning electron microscopy (SEM, JEOL JSM-5610LV, Hitachi Corporation, Japan), transmission electron microscopy (TEM, JEOL JEM2100, Hitachi Corporation, Japan) and X-ray photoelectron spectroscopy (XPS, Escalab 250XI, Thermo, America).

### 2.5. Measurements of sonocatalytic activity of the prepared CdS-coated $\text{ZrO}_2$ composite

Sonocatalytic degradation experiments of pethidine hydrochloride 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 CdS-coated  $\text{ZrO}_2$  composite, 2.70 g/L (10.00 mmol/L)  $\text{K}_2\text{S}_2\text{O}_8$ , 2.30 g/L (10.00 mmol/L)  $\text{KIO}_4$ , 1.23 g/L (10.00 mmol/L)  $\text{NaClO}_4$  and 10.00 mg/L pethidine hydrochloride 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. And then, the degradation of pethidine hydrochloride was performed under ultrasonic irradiation for 160 min. At 45 min interval, from the degradation liquid a certain of sample was removed and measured by gas chromatograph. The degradation ratios of pethidine hydrochloride were determined from the peak area ratio change of pethidine hydrochloride solution using the following equation:

$$\text{Degradation ratio (\%)} = [A_0/A_s - A_t/A_s]/(A_0/A_s) \times 100$$

where  $A_0$  is the initial peak area of pethidine hydrochloride 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.

In addition, the influences of inorganic oxidant kind and concentration on sonocatalytic degradation of pethidine hydrochloride were also investigated in detail.

### 3. Results and discussion

#### 3.1. XRD patterns of the prepared CdS-coated ZrO<sub>2</sub> composite

The XRD patterns of prepared nano-sized CdS powder (a), nano-sized ZrO<sub>2</sub> powder (b) and CdS-coated ZrO<sub>2</sub> composite (c) were given in Fig. 1. As can be seen in Fig. 1(a), the XRD pattern of CdS

shows some sharp narrow peaks at  $2\theta = 24.7^\circ$  (1 0 0),  $26.5^\circ$  (0 0 2),  $28.3^\circ$  (1 0 1),  $36.6^\circ$  (1 0 2),  $43.8^\circ$  (1 1 0),  $48.1^\circ$  (1 0 3) and  $51.8^\circ$  (1 1 2), which are almost same as the JCPDS card 41-1049 of hexagonal wurtzite phase of CdS [45]. In Fig. 1(b), it can be seen that the diffraction signals at  $2\theta = 23.98^\circ$  (1 1 0),  $28.08^\circ$  (1  $\bar{1}$  1),  $31.32^\circ$  (1 1 1),  $34.64^\circ$  (0 0 2) and  $50.7^\circ$  (2 2 0) are related to the monoclinic ZrO<sub>2</sub> phase as the JCPDS card 83-0944 [46]. From Fig. 1(c) it can be found that the XRD pattern shows clearly the peaks corresponding to hexagonal CdS and monoclinic ZrO<sub>2</sub>, which indicates that the CdS and ZrO<sub>2</sub> have been successfully composited together to form the CdS-coated ZrO<sub>2</sub> composite.

#### 3.2. SEM and TEM images of the prepared CdS-coated ZrO<sub>2</sub> composite

In this section, the SEM images of nano-sized CdS, nano-sized ZrO<sub>2</sub> and CdS-coated ZrO<sub>2</sub> composite are depicted in Fig. 2(a–c), respectively. It can be seen that in Fig. 2(a) there are a lot of homogenous and spherical crystal particles with diameters in the range of 40–60 nm, which should pertain to the typical crystal form of nano-sized CdS particles. Fig. 2(b) shows that the nano-sized ZrO<sub>2</sub> particles aggregated into compact irregular shapes with diameters in the range of 50–70 nm. And the SEM image of Fig. 2(c) demonstrates that ZrO<sub>2</sub> and CdS have been combined to form a coated (core-shell) structure, and the ZrO<sub>2</sub> are uniformly coated

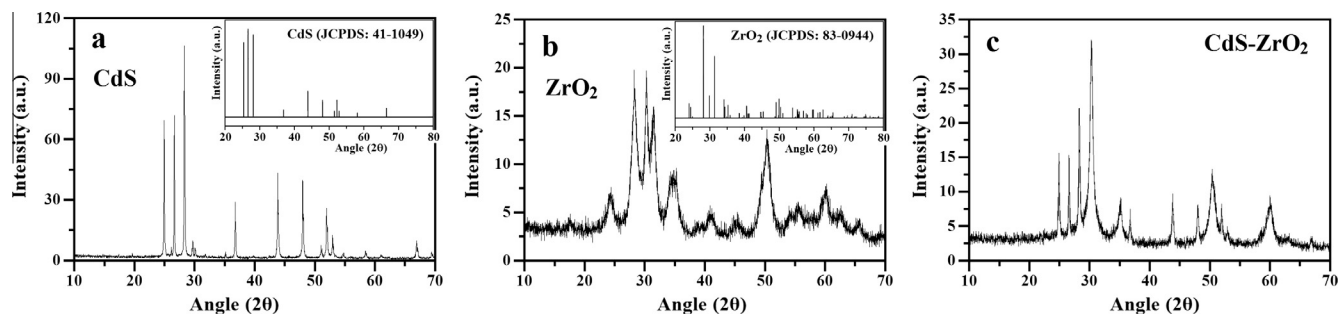


Fig. 1. XRD patterns of the prepared CdS (a), ZrO<sub>2</sub> (b) and CdS-coated ZrO<sub>2</sub> (c).

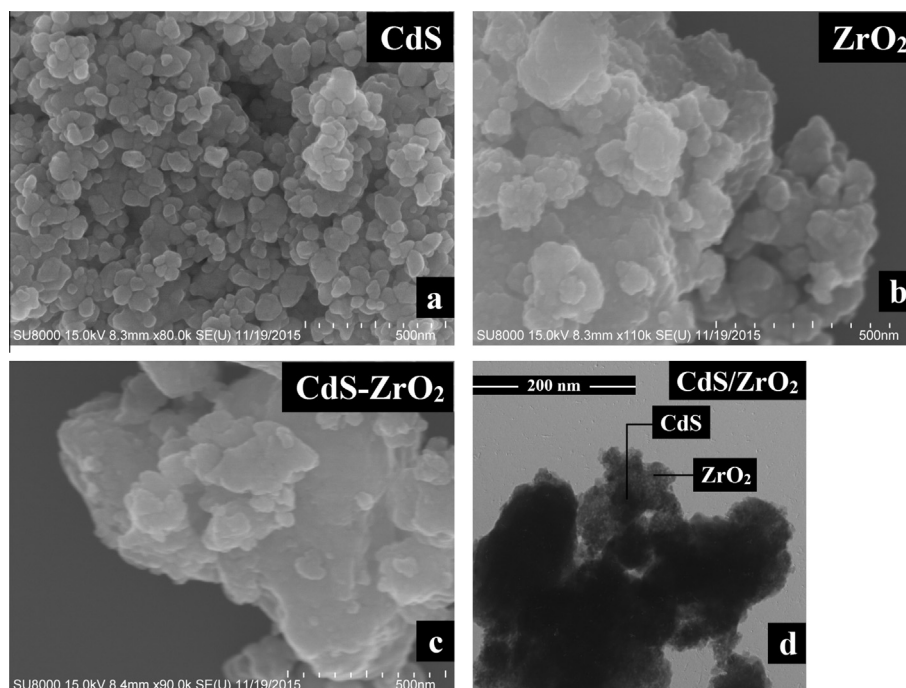


Fig. 2. SEM images of the prepared CdS (a), ZrO<sub>2</sub> (b) and CdS-coated ZrO<sub>2</sub> (c) and TEM images of the prepared CdS-coated ZrO<sub>2</sub> (d).

on the surface of nano-sized CdS particles, which led to an enlargement of the nanoparticle size. The diameters of CdS-coated ZrO<sub>2</sub> are in the range of 130–180 nm. These findings can prove that the nano-sized CdS particles have been coated with ZrO<sub>2</sub> films.

Fig. 2(d) shows the TEM image of the CdS-coated ZrO<sub>2</sub> composite particles. It can be seen that the nano-sized CdS particles displays the slightly regular shape with the average diameter about 50 nm. Besides, the ZrO<sub>2</sub> is uniformly dispersed on the surface of nano-sized CdS particles. Furthermore, the TEM results confirm

that the CdS-coated ZrO<sub>2</sub> composites form a coated (core-shell) structure with the diameters of 150 nm.

### 3.3. XPS spectra of the prepared CdS-coated ZrO<sub>2</sub> composite

X-ray photoelectron spectroscopy (XPS) is one of the most effective and most widely used analytical techniques in the surface analysis. In this section, it was mainly used to analyse the element and valence of the prepared CdS-coated ZrO<sub>2</sub> composite and the obtained results are given in Fig. 3. Thereinto, Fig. 3(o) shows the

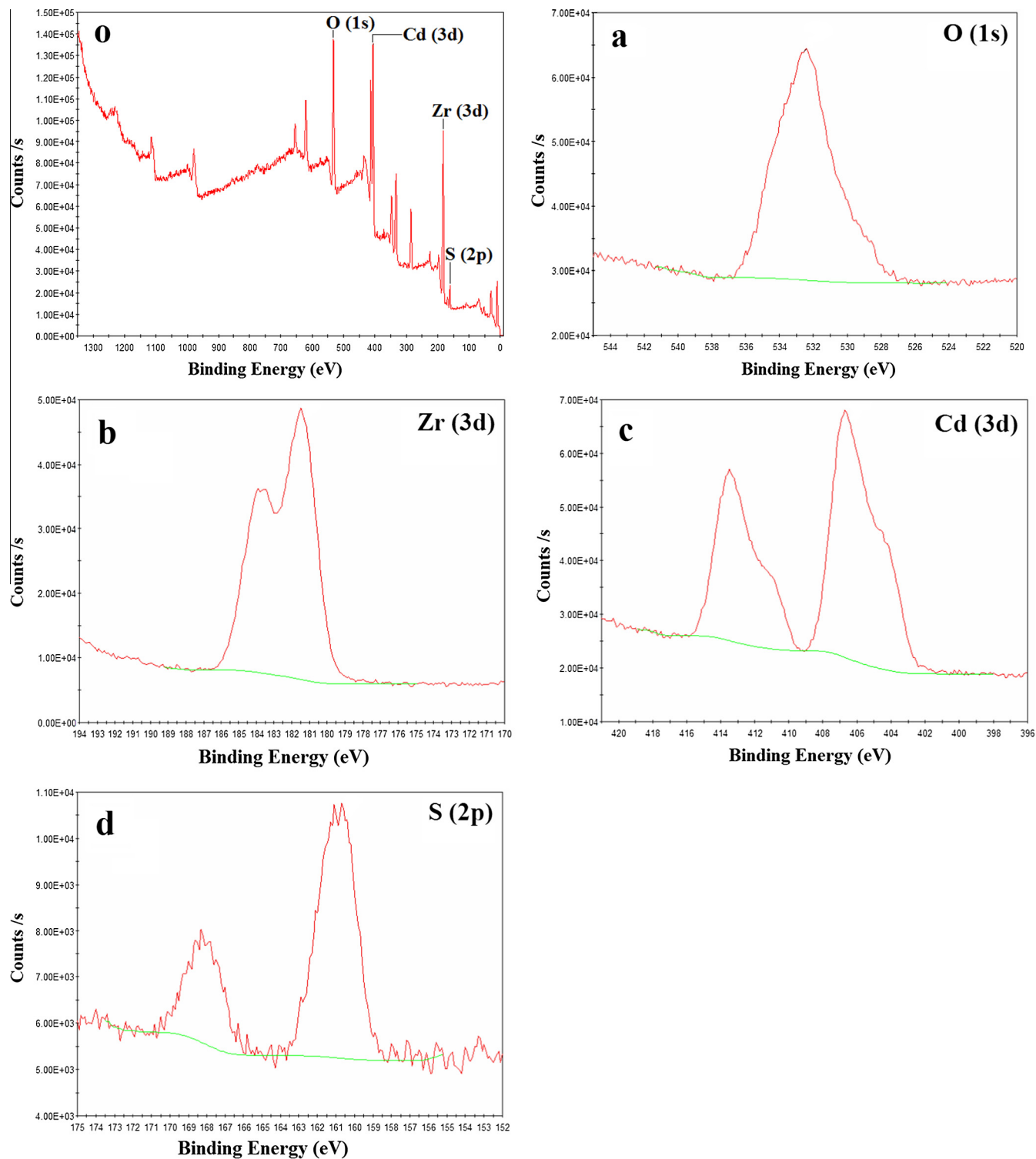


Fig. 3. XPS spectra of the prepared CdS-coated ZrO<sub>2</sub> as sonocatalyst.



fully XPS scanned spectra of the prepared CdS-coated ZrO<sub>2</sub> composite. As shown in Fig. 3(o), the strong peaks of Cd, S, Zr and O elements appear and the corresponding peaks are plotted carefully, which indicates that these elements compose the prepared CdS-coated ZrO<sub>2</sub> composite. Specifically, it can be seen that in Fig. 3 (a) the peak of O (1s) is at 532.1 eV. There is only one peak of O atom, which indicates that it is the O atom combined with Zr atom forming ZrO<sub>2</sub> rather than CdO. In Fig. 3(b), for Zr (3d) there are two peaks at 182.3 and 184.6 eV, which belongs to Zr (3d<sub>5/2</sub>) and Zr (3d<sub>3/2</sub>), respectively. These are consistent with that reported in literature [47]. From Fig. 3(c and d), the peaks at 406.63, 410.6 and 162.76 eV belong to the binding energies of Cd (3d<sub>5/2</sub>), Cd (3d<sub>3/2</sub>) and S (2p<sub>3/2</sub>), respectively. More specifically, EDX analysis reveals that the percent content of the elements (PP At.%) are Cd: 8.52%, S: 10.91%, Zr: 20.57% and O: 46.13%. It indicated that the chemical composition of the prepared CdS-coated ZrO<sub>2</sub> sample is very close to the calculated values of CdS-coated ZrO<sub>2</sub>. And these results are consistent with the XRD pattern presented above as well.

#### 3.4. Gas chromatography of pethidine hydrochloride solutions during sonocatalytic degradation

Gas chromatography is a beneficial tool in the study on degradation process of narcotic drug as well as in the calculation of degradation ratio. The gas chromatograms of pethidine hydrochloride solution (10.00 mg/L) under 135 min ultrasonic irradiation in the presence of different kinds of inorganic oxidants (10 mmol/L) are given in Fig. 4. It can be seen that there are two peaks for original solution. One peak appears approximately at Rt (retention time) = 4.87 min, which should be the adsorption peak of pethidine hydrochloride. And the other one peak at Rt = 5.63 min belong to the lidocaine internal standard. There are no interfering peaks at the retention times of pethidine hydrochloride and the internal standard. Also, there is no carryover problem (memory effect) in this experiment. When the prepared CdS-coated ZrO<sub>2</sub> composite was adopted as sonocatalyst without any inorganic oxidants, the peak of pethidine hydrochloride reduced to a certain extent, which showed that only the presence of prepared CdS-coated ZrO<sub>2</sub> composite would degrade pethidine hydrochloride to some degree, but it is a little inconspicuously. When adding different inorganic oxidants, compared with original solution, it can be seen that the absorption peaks of pethidine hydrochloride all give an apparent decrease, and the reduced order is original solution

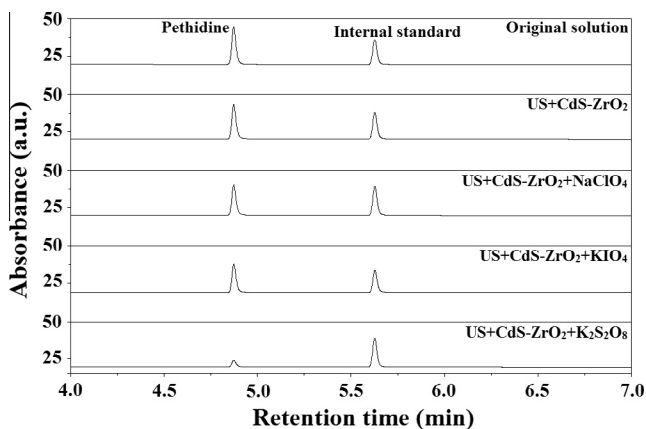


Fig. 4. Gas chromatography of pethidine hydrochloride solutions and comparison of sonocatalytic degradation caused by prepared CdS-coated ZrO<sub>2</sub> in the presences of different kinds of inorganic oxidants (experimental conditions: 10.00 mg/L pethidine hydrochloride concentration, 1.00 g/L CdS-coated ZrO<sub>2</sub> addition amount, 135 min ultrasonic irradiation time and 300 W output power and 40 kHz frequency ultrasonic irradiation).

< US/CdS-coated ZrO<sub>2</sub> < US/CdS-coated ZrO<sub>2</sub>/NaClO<sub>4</sub> < US/CdS-coated ZrO<sub>2</sub>/KIO<sub>4</sub> < US/CdS-coated ZrO<sub>2</sub>/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>. Especially, when the K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> was used to assist CdS-coated ZrO<sub>2</sub> under ultrasonic irradiation, the peak of pethidine hydrochloride declined drastically and that nearly disappeared. It showed that the pethidine hydrochloride in aqueous solution was almost degraded completely. It also indicates that the prepared CdS-coated ZrO<sub>2</sub> composite as a sonocatalyst assisted with inorganic oxidant can effectively degrade pethidine hydrochloride.

#### 3.5. Influence of inorganic oxidant kind and concentration on sonocatalytic degradation

In order to find out the effects of inorganic oxidant kind and concentration on the sonocatalytic degradation of pethidine hydrochloride, a series of experiments were carried out within the range (0.00–15.00 mmol/L) of inorganic oxidant concentration at 5.00 mmol/L intervals for three kinds of inorganic oxidant (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, KIO<sub>4</sub> and NaClO<sub>4</sub>). The amount of the prepared CdS-coated ZrO<sub>2</sub> composite was fixed as 1.00 g/L and the obtained results are presented in Fig. 5. First, it can be seen that, for these three systems, US/CdS-coated ZrO<sub>2</sub>/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, US/CdS-coated ZrO<sub>2</sub>/KIO<sub>4</sub> and US/CdS-coated ZrO<sub>2</sub>/NaClO<sub>4</sub>, the similar change trend appears. That is, the sonocatalytic degradation ratios of pethidine hydrochloride in the presence of 1.00 g/L prepared CdS-coated ZrO<sub>2</sub> composite within 135 min of ultrasonic irradiation all ascend gradually with the rises of inorganic oxidant concentration from 0.00 mmol/L to 10.00 mmol/L for K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, KIO<sub>4</sub> and NaClO<sub>4</sub>. And then, they slightly decrease with the further rises of inorganic oxidant concentration from 10.00 mmol/L to 15.00 mmol/L. It indicates that for these three systems the addition of inorganic oxidants apparently enhances the ability of sonocatalytic degradation indeed. However, too much inorganic oxidants may change the surface property of CdS-coated ZrO<sub>2</sub> composite particles, which is likely to decrease the sonocatalytic activity.

Moreover, at any concentration of inorganic oxidants the sonocatalytic degradation ratios of pethidine hydrochloride keep a settled order all along, namely, US/CdS-coated ZrO<sub>2</sub>/NaClO<sub>4</sub> < US/CdS-coated ZrO<sub>2</sub>/KIO<sub>4</sub> < US/CdS-coated ZrO<sub>2</sub>/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>. It indicates that the adding proper concentration of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (about 10.00 mmol/L) can obviously assist the sonocatalytic degradation of pethidine

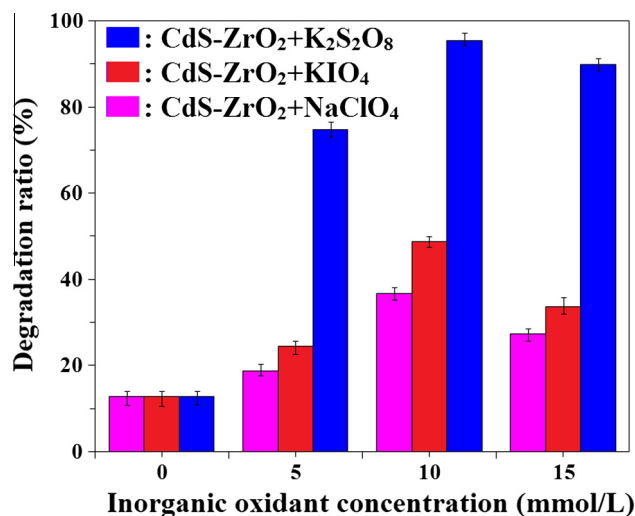


Fig. 5. The influence of inorganic oxidant concentration on the sonocatalytic degradation of pethidine hydrochloride caused by prepared CdS-coated ZrO<sub>2</sub> (experimental conditions: 10.00 mg/L pethidine hydrochloride concentration, 1.00 g/L CdS-coated ZrO<sub>2</sub> addition amount, 135 min ultrasonic irradiation time and 300 W output power and 40 kHz frequency ultrasonic irradiation).

hydrochloride (10.00 mg/L) in aqueous solution. Of course, a much higher concentration of inorganic oxidants probably results in generating the excessive  $\cdot\text{OH}$  radicals instantaneously. These excessive  $\cdot\text{OH}$  radicals would maybe recombine, and then form less reactive  $\text{H}_2\text{O}_2$  molecules, which leads to a slight decrease the sonocatalytic degradation ratio of pethidine hydrochloride. In addition, utilizing of a higher concentration of inorganic oxidants is likely to give rise to the adsorption of anion species on the surface of CdS-coated  $\text{ZrO}_2$  composite particles, which prevents the degradation reaction on the surface of sonocatalyst [48].

Above all, the highest degradation ratio was attained in the presence of prepared CdS-coated  $\text{ZrO}_2$  composite assisted with 10.00 mmol/L inorganic oxidants including  $\text{NaClO}_4$ ,  $\text{KIO}_4$  and  $\text{K}_2\text{S}_2\text{O}_8$ , and the corresponding relative sonocatalytic degradation ratio was 36.90%, 48.90% and 95.50%, respectively. The results demonstrated that the combination of CdS-coated  $\text{ZrO}_2$  composite and inorganic oxidants was more efficient to decompose the pethidine hydrochloride than CdS-coated  $\text{ZrO}_2$  sonocatalyst individual, which may be due to the synergistic influence of various highly reactive radicals generated. And the positive influence of inorganic oxidants assisted sonocatalytic degradation of pethidine hydrochloride caused by CdS-coated  $\text{ZrO}_2$  composite was found to be in the order of  $\text{K}_2\text{S}_2\text{O}_8 > \text{KIO}_4 > \text{NaClO}_4$ .

### 3.6. Influence of ultrasonic irradiation time and corresponding reaction kinetics on sonocatalytic degradation of pethidine hydrochloride

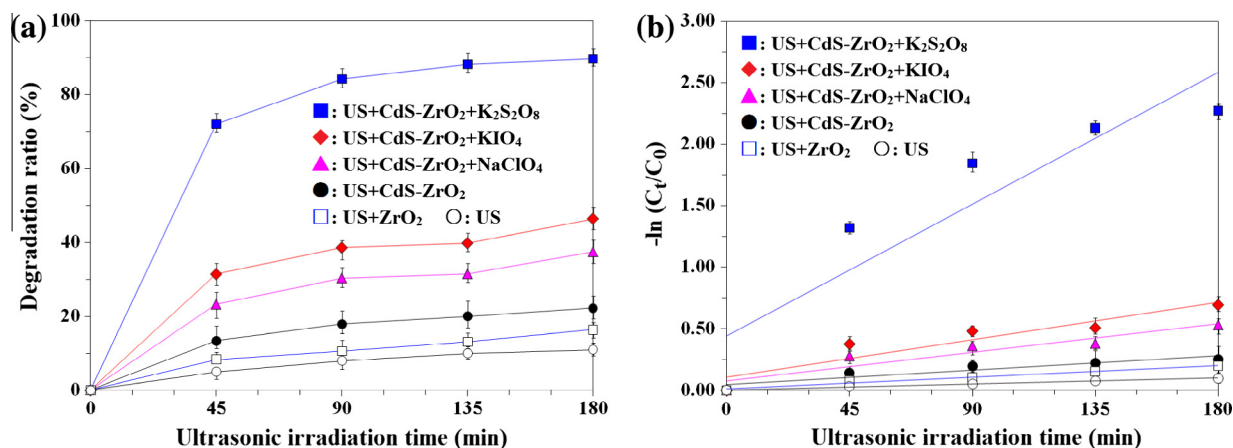
The comparison of sonocatalytic degradation ratios of pethidine hydrochloride at different ultrasonic irradiation time was carried out for six systems (US/CdS-coated  $\text{ZrO}_2$ , US/CdS-coated  $\text{ZrO}_2/\text{NaClO}_4$ , US/CdS-coated  $\text{ZrO}_2/\text{KIO}_4$ , US/CdS-coated  $\text{ZrO}_2/\text{K}_2\text{S}_2\text{O}_8$ , US/ $\text{ZrO}_2$  and US) and the corresponding results were given in Fig. 6. It can be observed from Fig. 6(a) that, on the one hand, all sonocatalytic degradation ratios of pethidine hydrochloride in these six systems increase with the increase of ultrasonic irradiation time. And the sequence based on the sonocatalytic degradation ratios is essentially  $\text{US} < \text{US}/\text{ZrO}_2 < \text{US}/\text{CdS-coated } \text{ZrO}_2 < \text{US}/\text{CdS-coated } \text{ZrO}_2/\text{NaClO}_4 < \text{US}/\text{CdS-coated } \text{ZrO}_2/\text{KIO}_4 < \text{US}/\text{CdS-coated } \text{ZrO}_2/\text{K}_2\text{S}_2\text{O}_8$ . Apparently, the sonocatalytic degradation ratio in the presence of CdS-coated  $\text{ZrO}_2$  composite assisted with  $\text{K}_2\text{S}_2\text{O}_8$  increases much faster with the increase of ultrasonic irradiation time than other five systems under the same conditions. On the other hand, within 180 min ultrasonic irradiation, the sonocatalytic degradation ratios reached 11.00%, 16.40%, 22.20%, 37.40%,

46.40% and 89.70%, respectively, for US, US/ $\text{ZrO}_2$ , US/CdS-coated  $\text{ZrO}_2$ , US/CdS-coated  $\text{ZrO}_2/\text{NaClO}_4$ , US/CdS-coated  $\text{ZrO}_2/\text{KIO}_4$  and US/CdS-coated  $\text{ZrO}_2/\text{K}_2\text{S}_2\text{O}_8$ . Therefore, a conclusion was drawn that some inorganic oxidants can efficiently assist the sonocatalytic degradation of pethidine hydrochloride in the presence of CdS-coated  $\text{ZrO}_2$  composite. It can be speculated further that most of the pethidine hydrochloride molecules could be soon degraded completely in the US/CdS-coated  $\text{ZrO}_2/\text{K}_2\text{S}_2\text{O}_8$  system.

In addition, in order to infer the sonocatalytic degradation rates of pethidine hydrochloride for these four systems, the reaction kinetics were studied. Here, the data of  $-\ln(C_t/C_0)$  for first-order reaction as a function of ultrasonic irradiation time (t) was calculated [49]. In fact, as shown in Fig. 6(b), the results indicate that all calculated values of  $-\ln(C_t/C_0)$  are approximately linear with the ultrasonic irradiation time (t) all through. That is, the sonocatalytic degradation processes of pethidine hydrochloride for these six systems are all conformed to be pseudo first-order kinetics reactions. The kinetic equations corresponding to US, US/ $\text{ZrO}_2$ , US/CdS-coated  $\text{ZrO}_2$ , US/CdS-coated  $\text{ZrO}_2/\text{NaClO}_4$ , US/CdS-coated  $\text{ZrO}_2/\text{KIO}_4$  and US/CdS-coated  $\text{ZrO}_2/\text{K}_2\text{S}_2\text{O}_8$  are  $-\ln(C_t/C_0) = 0.0005t + 0.004$  ( $R^2 = 0.9926$ ),  $-\ln(C_t/C_0) = 0.0011t + 0.012$  ( $R^2 = 0.9778$ ),  $-\ln(C_t/C_0) = 0.0013t + 0.0458$  ( $R^2 = 0.8608$ ),  $-\ln(C_t/C_0) = 0.0026t + 0.077$  ( $R^2 = 0.8828$ ),  $-\ln(C_t/C_0) = 0.0034t + 0.108$  ( $R^2 = 0.8724$ ) and  $-\ln(C_t/C_0) = 0.0119t + 0.4426$  ( $R^2 = 0.8449$ ), respectively. The rate constants are  $0.0005 \text{ min}^{-1}$ ,  $0.0011 \text{ min}^{-1}$ ,  $0.0013 \text{ min}^{-1}$ ,  $0.0026 \text{ min}^{-1}$ ,  $0.0034 \text{ min}^{-1}$  and  $0.0119 \text{ min}^{-1}$ , respectively. Thus, the order of sonocatalytic degradation rates for these six systems can be judged as  $\text{US} < \text{US}/\text{ZrO}_2 < \text{US}/\text{CdS-coated } \text{ZrO}_2 < \text{US}/\text{CdS-coated } \text{ZrO}_2/\text{NaClO}_4 < \text{US}/\text{CdS-coated } \text{ZrO}_2/\text{KIO}_4 < \text{US}/\text{CdS-coated } \text{ZrO}_2/\text{K}_2\text{S}_2\text{O}_8$ .

### 3.7. Possible mechanism and process on sonocatalytic degradation assisted with inorganic oxidants

In general, under ultrasonic irradiation, the micro-bubbles in liquid form, vibrate, grow and aggregate acoustic energy, finally formed cavitation bubbles fast collapse in almost adiabatic process accompanied by the generation of localized high temperatures and high pressures. It is called as ultrasonic cavitation effect [19]. It is known that the sonoluminescence caused by ultrasonic cavitation could produce the light with a wide wavelength range. The bandwidth of  $\text{ZrO}_2$  as a wide-band conductor material is about 5.0 eV. And the bandwidth of CdS as a narrow-band conductor material is about 2.4 eV. The prepared CdS-coated  $\text{ZrO}_2$  composite with core-shell structure should have wide light response range due



**Fig. 6.** The influence of ultrasonic irradiation time (a) and the corresponding reaction kinetics (b) on the sonocatalytic degradation of pethidine hydrochloride (experimental conditions: 10.00 mg/L pethidine hydrochloride concentration, 1.00 g/L sonocatalyst addition amount, 10 mmol/L inorganic oxidant concentration and 300 W output power and 40 kHz frequency ultrasonic irradiation).

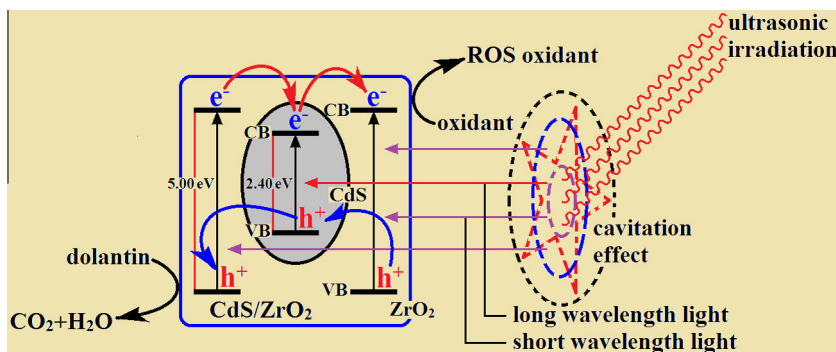
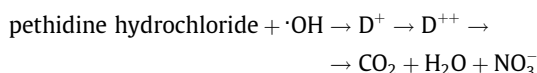
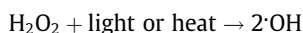
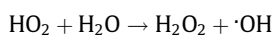
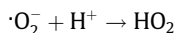
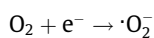
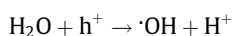
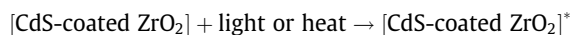


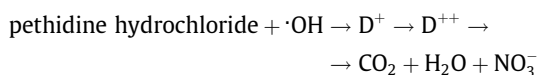
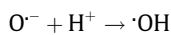
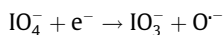
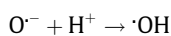
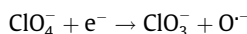
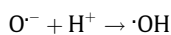
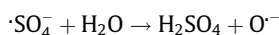
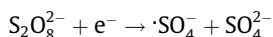
Fig. 7. Sonocatalytic degradation principle of pethidine hydrochloride in the presence of CdS-coated  $ZrO_2$  composite under ultrasonic irradiation.

to the combination of wide-band and narrow-band conductor materials. That is, the ultraviolet light is able to excite  $ZrO_2$ , and the visible light can excite CdS [50]. Since the research on the sonocatalytic degradation of pethidine hydrochloride has not been much yet, the corresponding mechanism can only be tentatively proposed as shown in Fig. 7. It can be considered that the long wavelength (visible) light with low energy from sonoluminescence penetrates  $ZrO_2$  shell of CdS-coated  $ZrO_2$  composite and then excites internal nano-sized CdS particles, so as a result the electron-hole pairs are generated. In the CdS, these photogenerated electrons from valence band (VB) get transferred to conduction band (CB). At the same time, the short wavelength (ultraviolet) light with high energy also from sonoluminescence is absorbed by  $ZrO_2$  and excites  $ZrO_2$  directly. Similarly, in the  $ZrO_2$  the photo-generated electrons from valence band (VB) of get transferred to conduction band (CB). The electrons on the conduction band (CB) of  $ZrO_2$  can be quickly consumed because of their strong reaction activity. And then the electrons on the conduction band (CB) of internal CdS cores transfer to the conduction band (CB) of  $ZrO_2$  shell.

In CdS-coated  $ZrO_2$  composite, the CdS core lies in the center of core-shell structure. As narrow-band conductor materials the CdS can continuously generate electrons and holes on the conduction band (CB) and valence band (VB), respectively, under visible light irradiation. Although these generated electrons and holes cannot directly take part in any chemical reaction, they continually enter the conduction band (CB) and valence band (VB) of external  $ZrO_2$  shell, respectively. Moreover, the generated holes can directly degrade the pethidine hydrochloride absorbed on the surface of CdS-coated  $ZrO_2$  composite particles. Also, they can oxidize the water molecules ( $H_2O$ ) to produce the hydroxyl radicals ( $\cdot OH$ ), indirectly destroying the pethidine hydrochloride in aqueous solution. At the same time, the photogenerated electrons react with the molecular oxygen ( $O_2$ ) dissolved in aqueous solution and then produce the superoxygen radical anions ( $\cdot O_2^-$ ). After a series of chemical reactions these superoxygen radical anions ( $\cdot O_2^-$ ) can also become the hydroxyl radicals ( $\cdot OH$ ) with strong oxidation capacity [42]. These hydroxyl radicals ( $\cdot OH$ ) can also degrade the surrounding pethidine hydrochloride, leading to volatile degradation by-products or  $CO_2$ ,  $H_2O$  and mineral acids through entire mineralization. The possible process is thought as following:



The valence band (VB) of  $ZrO_2$  has a relatively more positive potential. The produced holes can directly degrade the pethidine hydrochloride due to its strong oxidation ability. In order to further promote the oxidation reaction on the pethidine hydrochloride, the produced electrons on the conduction band (CB) can interact with various inorganic oxidants under ultrasonic irradiation and generate a large numbers of ROS oxidants. These generated ROS oxidants can also participate in the degradation of pethidine hydrochloride by radical oxidation pathways to assist the sonocatalytic degradation. The detailed process may be as following [51]:



#### 4. Conclusions

In this work, via hydrothermal method and chemical precipitation method the CdS-coated  $ZrO_2$  composite as sonocatalyst was prepared and then characterized by X-ray diffractometer (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). Adopting CdS-coated  $ZrO_2$  composite as sonocatalyst, the sonocatalytic degradation of pethidine hydrochloride in aqueous solution could be carried out. Particularly, some inorganic oxidants can effectively assist the sonocatalytic degradation of pethidine hydrochloride in

the presence of CdS-coated ZrO<sub>2</sub> composite. The sonocatalytic degradation of pethidine hydrochloride is related with inorganic oxidant kind and the increase effects arrange as the order of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> > KIO<sub>4</sub> > NaClO<sub>4</sub>. In addition, the sonocatalytic degradation ratio of pethidine hydrochloride increases with increasing inorganic oxidant concentration and ultrasonic irradiation time. The best sonocatalytic degradation ratio (95.50%) of pethidine hydrochloride could be obtained when the conditions of 10.00 mmol/L K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, 1.00 g/L prepared CdS-coated ZrO<sub>2</sub> composite, 135 min ultrasonic irradiation (40 kHz frequency and 300 W output power), 100 mL total volume and 25–28 °C temperature were adopted. It can be forecasted that the method of sonocatalytic degradation assisted with inorganic oxidants is an efficient sonocatalytic system for degradation of pethidine hydrochloride.

## Acknowledgements

The authors greatly acknowledge the National Science Foundation of China (21371084), Key Laboratory Basic Research Foundation of Liaoning Provincial Education Department (L2015043), Liaoning Provincial Department of Education Innovation Team Projects (LT2015012) and Youth Science Foundation of Liaoning University (2013LDQN14) for financial support. The authors also thank our colleagues and other students for their participating in this work.

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