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 PII:
 S0022-4596(17)30359-6

 DOI:
 http://dx.doi.org/10.1016/j.jssc.2017.09.002

 Reference:
 YJSSC19931

To appear in: Journal of Solid State Chemistry

Received date: 4 August 2017 Revised date: 28 August 2017 Accepted date: 3 September 2017

Cite this article as: Jin-jin Ban, Guan-cheng Xu, Li Zhang, He Lin, Zhi-peng Sun, Yan Lv and Dian-zeng Jia, Mesoporous ZnO microcube derived from a metalorganic framework as photocatalyst for the degradation of organic dyes, *Journal of Solid State Chemistry*, http://dx.doi.org/10.1016/j.jssc.2017.09.002

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# Mesoporous ZnO microcube derived from a metal-organic framework as photocatalyst for the degradation of organic dyes

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## Abstract

A cube-like porous ZnO architecture was synthesized by direct two-step thermolysis of a zinc-based metal-organic framework [(CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>][Zn(HCOO)<sub>3</sub>]. The obtained ZnO microcube was characterized by powder X-ray diffraction, scanning electron microscopy, transmission electron microscopy and nitrogen adsorption and desorption isotherms. The mesoporous ZnO microcube was comprised by many nanoparticles, and inherited the cube shape from [(CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>][Zn(HCOO)<sub>3</sub>] precursor. With large surface area and mesoporous structure, the ZnO microcube exhibits excellent photocatalytic activities against methyl orange (MO) and rhodamine B (RhB) under UV irradiation, and the degradation rates reached 99.7% and 98.1% within 120 min, respectively.

**Graphical Abstract** 

Mesoporous ZnO microcube was synthesized via two-step thermolysis of metal-organic framework [(CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>][Zn(HCOO)<sub>3</sub>], and exhibit excellent photocatalytic activity towards MO and RhB.



## Keyword:

Mesoporous ZnO microcube, Metal-organic framework, Photocatalyst, Organic dye degradation

## 1. Introduction

Metal-organic frameworks (MOFs) are rapidly growing materials made up of metals or metal clusters and organic bridging ligands [1]. By combining organic and inorganic building blocks [2], MOFs have shown many attractive characteristics, such as high surface area, large pore volume and good thermal stability [3]. These special

properties have allowed MOFs to be applied in gas adsorption and storage [4], catalysis [5], drug delivery [6], and sensing [7]. MOFs have recently been found to be easily transformed into metal oxides [8], carbon materials [9] or carbon composite materials [10] through simple calcination under different atmospheres and conditions. Compared to other precursors [11], MOFs not only offer adjustable structure and size but also have stable framework and porosity [12]. MOFs have been used as templates to prepare different metal oxides [13]. Spindle-like MIL-88-Fe can be completely transformed to mesoporous  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> with the retained morphology by the two-step calcination [14]. The electrochemical performance of as-prepared  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> can be improved significantly due to interconnected nanometer-sized subunits. By heat treatment under mild conditions, porous CuO/Cu<sub>2</sub>O composites have been successfully prepared from Cu-BTC MOFs (BTC: 1,3,5-benzenetricarboxylic acid). The morphologies and sizes of Cu-BTC MOFs can be adjusted at controlled temperatures for different times. The porous CuO/Cu<sub>2</sub>O materials inherit the different shapes of Cu-BTC MOFs including cube, octahedron, rod and wire, and show excellent CO oxidation performance [15,16]. Therefore, MOFs with controlled features and porous structures are ideal candidates for precursors in solid state calcination to obtain different metal oxides with novel structures and properties [17].

Among new series of MOFs, [AmineH][M(HCOO)<sub>3</sub>] with perovskite-like structures templated by protonated amines have been synthesized recently [18]. Formate anion, HCOO<sup>-</sup>, is a suitable choice as a linker of MOFs, and it is the simplest carboxylate with the fundamental properties of carboxylate [19]. AmineH<sup>+</sup> cations are located in the channel/cages of the 3D anionic [M(HCOO)<sub>3</sub><sup>-</sup>] frameworks [20]. The crystal structures and morphologies of [AmineH][M(HCOO)<sub>3</sub>] can be modulated by employing different ammonium cations [21]. Among them,

 $[(CH_3)_2NH_2][Zn(HCOO)_3]$  is crystallized in the space group *R*3c. The Zn<sup>2+</sup> is octahedrally coordinated by six bridging formate ligands in an anti-anti mode, and the trigonal disordered  $(CH_3)_2NH_2^+$  cations are located in the 1D channel of the 3D

 $[Zn(HCOO)_3^-]$  framework (Fig. S1) [22].  $[(CH_3)_2NH_2][Zn(HCOO)_3]$  can be converted into metal oxide through simple thermal treatment in air, and a porous structure can be readily obtained due to the release of internally generated gas during calcination [23].

On the other hand, ZnO is an environmental friendly oxide semiconductor with a direct wide band gap (3.37 eV) and a high exciton-binding energy of 60 meV [24]. ZnO can function as a photocatalyst to degrade organic pollutants in water under UV irradiation [25]. For photocatalytic degradation [26], MOF-derived ZnO shows excellent activity during catalysis due to favorable surface area [27] and large pore volume [28]. Recently, Li *et al.* have synthesized Zn-CPs (Zn-based coordination polymers) via a convenient one-pot method, which could be converted into ZnO with the retention of original morphology by simple thermal treatment [29]. The obtained ZnO exhibits excellent activity in the photocatalysis under open air condition owing to its large surface area and mesoporous structure. The ZnO sample can degrade rhodamine B (RhB) completely in 2 h [30]. In a word, pyrolyzing the MOFs are desirable alternatives for the porous zinc oxides to boost the photocatalysis processes.

Motivated by all these developments and to further contribute to the preparation of metal oxides with novel structures and properties, we herein successfully synthesized mesoporous ZnO microcube through two-step heat treatment of Zn-based MOF [(CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>][Zn(HCOO)<sub>3</sub>]. The obtained ZnO microcube, which was composed of numerous nanoparticles, managed to photocatalytically degrade organic dyes (methyl orange, MO and rhodamine B, RhB) effectively under UV light irradiation. After irradiation for 120 min, the degradation rates of MO and RhB reached 99.7% and 98.1% respectively.

#### 2. Experimental

#### 2.1. Materials

Zinc nitrate hexahydrate (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), 40% aqueous dimethylamine solution and formic acid (HCOOH) were purchased from Tianjing Fuchen chemical reagents factory, polyvinylpyrrolidone K30 (PVP K30) was purchased from Tokyo Chemical Industry Co., Ltd., ethanol (C<sub>2</sub>H<sub>5</sub>OH), edetate disodium (EDTA-2Na), benzoquinone (BQ) and tert-Butyl alcohol (t-BuOH), MO and RhB were commercially available and used as purchased without further purification.

#### 2.2. Characterization

Powder X-ray diffraction (XRD) patterns were collected on a Bruker D8 advance diffractometer with Cu-Ka radiation ( $\lambda = 1.54178$  Å) in the range of 10-80° at a scan rate of 2°·min<sup>-1</sup>. Morphological features were studied by field emission scanning electron microscopy (FESEM, Hitachi S-4800 microscope). Internal structures of the samples were observed by transmission electron microscopy (TEM, Hitachi H600 microscope) at an accelerating voltage of 200 kV. Thermogravimetric analysis (TGA) was performed on a Netzsch SDT 449F3 thermal analyzer with a heating rate of 10 °C·min<sup>-1</sup>. Nitrogen adsorption and desorption isotherms were obtained at the liquid nitrogen temperature (77 K) using a Quantachrome (ASIQ) instrument. The specific surface area and porous structural features of the samples were calculated by the Brunauer-Emmett-Teller (BET) method and the Barrett-Joyner-Halenda (BJH) method, respectively. Photocatalytic performances were investigated by a Model XPA-7 photocatalytic reactor (Xujiang Electromechanical Plant, Nanjing, China). UV-vis diffuse reflectance spectrum was recorded on a Hitachi 3900H spectrophotometer. UV-vis absorption spectroscopy of clarified solution was performed (UV Hitachi 3900H spectrophotometer) at room temperature at the wavelength from 200 to 700 nm.

## 2.3. Preparation of [(CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>][Zn(HCOO)<sub>3</sub>] and ZnO

An ethanol solution (25 mL) of HCOOH (8 mmol), PVP K30 (0.5 g) and dimethylamine (8 mmol) was added to another ethanol solution of  $Zn(NO_3)_2 \cdot 6H_2O$  (1

mmol) and PVP K30 (0.5 g) under vigorous stirring. Precipitate formed from the transparent solution after 10 s, and the suspension was stirred for 1 h and incubated for 4 h at room temperature. Tiny white block crystals were collected by centrifugation and washed with ethanol three times.  $[(CH_3)_2NH_2][Zn(HCOO)_3]$  precursor was obtained by drying in a vacuum oven at 60 °C for 4 h.

The precursor  $[(CH_3)_2NH_2][Zn(HCOO)_3]$  was transferred into a ceramic boat and pyrolyzed by a two-step process in a temperature-programmed furnace as follows.  $[(CH_3)_2NH_2][Zn(HCOO)_3]$  was heated to 125 °C at a ramp of 1 °C·min<sup>-1</sup> in air and kept for 60 min. Then the intermediate was heated up to 225 °C with the same rate and maintained for 60 min, giving mesoporous ZnO microcube.

#### 2.4. Photocatalytic Experiments

A certain amount of ZnO sample (18 mg) was dispersed into 50 mL aqueous solution of MO (50 mL, 10 mg·L<sup>-1</sup>) and RhB (50 mL, 10 mg·L<sup>-1</sup>) respectively. Before UV irradiation, the suspensions were magnetically stirred in dark for 60 min to reach adsorption-desorption equilibrium. Then, the suspension was exposed to a 300 W UV light source. A small amount of solution (4 mL each) was collected at regular interval of time (20 min), and centrifuged at 10000 rpm to separate the porous ZnO catalyst. The clarified solution was measured with UV-vis absorption spectroscopy at the wavelength from 200 nm to 700 nm.

#### 3. Results and discussion

### 3.1. Preparation and characterization of [(CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>][Zn(HCOO)<sub>3</sub>]

 $[(CH_3)_2NH_2][Zn(HCOO)_3]$  was prepared by a facile solution-precipitation method. The XRD pattern of  $[(CH_3)_2NH_2][Zn(HCOO)_3]$  is shown in Fig. S2a. The simulated XRD pattern was obtained from single-crystal structure using the program Mercury. Clearly, all the diffraction peaks of the formed  $[(CH_3)_2NH_2][Zn(HCOO)_3]$ match well with those of the simulated pattern in the 20 range of 10-50°.

To check the thermal stability of the precursor, simultaneous TGA-DTA curves were plotted (Fig. S2b). TGA shows that the first weight loss starts at 120 °C and ends at 200 °C with the mass loss of 37.4%, and one endotherm peak is also observed in the DTA trace. It corresponds to the departure of a dimethylammonium cation and formate anion per chemical formula unit, and the observed mass loss is in good agreement with the calculated value (calcd. 37.2%). By heating, the second stage occurs in the temperature range of 230 °C - 300 °C, corresponding to the decomposition of formate ligands, and the observed mass loss (30.3%) is consistent with the theoretical value (30.7%). The final residue, estimated as ZnO, has the observed mass of 32.3%, being in good agreement with the calculated value (32.1%). In short, ZnO was obtained by pyrolyzing the [(CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>][Zn(HCOO)<sub>3</sub>] precursor.

Furthermore, the typical size and morphology of the as-synthesized  $[(CH_3)_2NH_2][Zn(HCOO)_3]$  were observed by FESEM. As shown in Fig. 1a, the precursor has a double-edge solid cube morphology, with a highly uniform size of ca. 4 µm. As evidenced the corresponding magnified sample in Fig. 1b, the microcubes have smooth surfaces.

## 3.2. Structural and morphology characterization of ZnO microcube

ZnO microcube was obtained by calcining the  $[(CH_3)_2NH_2][Zn(HCOO)_3]$ precursor in air with a two-step temperature program (Scheme 1). The crystallographic structure and phase purity of the calcined product ZnO were analyzed by XRD (Fig. 2a). The as-synthesized porous ZnO corresponds well to the hexahedron wurtzite structure of pure ZnO (PDF#36-1451), without any impurity phases like Zn or Zn(OH)<sub>2</sub>. The typical morphology of microcube is shown in Fig. 1e and 1f. Obviously, ZnO inherits the cube-shape of the  $[(CH_3)_2NH_2][Zn(HCOO)_3]$ precursor. In comparison to the precursor, the ZnO cube constructions are little shrunk and the sizes of the cubes are ca. 3.5 µm. Interestingly, the ZnO microcube comprises numerous tiny particles with an average diameter of ca. 100 nm. As presented in inset of Fig. 1f, ZnO is a visible porous structure inside but not a solid box. During the

transformation from  $[(CH_3)_2NH_2][Zn(HCOO)_3]$  to ZnO upon thermal decomposition, the cube shape remains basically unchanged, except the double edges disappear (Fig. 1f).

In this study, uniform ZnO microcubes were obtained by pyrolyzing MOF precursor in air by a two-step process. [(CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>][Zn(HCOO)<sub>3</sub>] was firstly pyrolyzed at 125 °C for 60 min. The second step was to further raise the temperature up to 225 °C that was kept for 60 min. In order to verify this pyrolysis process, the morphology of intermediate was observed (Fig. 1c and 1d). The intermediate has similar size and double-edge shape to those of the precursor. According to TGA, the intermediate is Zn(HCOO)<sub>2</sub>. There are many holes on the surface of the intermediate (Fig. 1d) owing to partial removal of dimethylammonium cation and formate anion. By heating, the residual formate ligands were removed and porous ZnO microcube was produced. In order to explore the calcining condition, we tried to synthesize the ZnO microcube with a one-step pyrolyzation, and [(CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>][Zn(HCOO)<sub>3</sub>] was directly pyrolyzed at 225 °C for 60 min. Aggregated ZnO particles were obtained instead of well-defined mesoporous ZnO microcubes (Fig. S3), which may be caused by the quick release of the gas. Therefore, the two-step pyrolysis was favorable to keep the cubic shape and form the porous structure.

In order to characterize the porous structure, we analyzed the nitrogen adsorption-desorption isotherms and BJH pore size distribution (Fig. 2b). The obtained ZnO microcube displays a typical IV-type adsorption isotherm with a distinct hysteresis loop in the range of ca. 0.4-1.0 P/P<sub>0</sub>. The pore size distribution (inset of Fig. 2b) reveals the presence of mesoporous structure. As suggested by several sharp peaks at about 2.2 nm, 3.5 nm and 5.7 nm, the pore sizes of ZnO microcube are not uniform due to the arrangement of solid ZnO particles. The BET surface area is 19.82 m<sup>2</sup>·g<sup>-1</sup>. Collectively, the ZnO microcube has a developed porous structure containing interconnected mesopores.

#### 3.3. Photocatalytic performace

ZnO is a well-known effective semiconductor photocatalyst used frequently to solve environmental pollution. In this study, the UV-vis diffuse reflectance spectrum of ZnO microcube was recorded by UV-vis spectrophotometer in the range from 250 to 800 nm (Fig. 3). It can be clearly seen that the basal absorption of the ZnO microcube occurs near wavelength of 400 nm. The band gap energies ( $E_g$ ) can be estimated by Kubelka-Munk transformation. The  $E_g$  of ZnO microcube is calculated to be 3.2, and the ZnO microcube exhibits absorption in the UV region (insets of Fig. 3). MO and RhB were often chosen as the typical organic dyes to examine the photocatalytic activities of photocatalysts. The photocatalytic performance of the mesoporous ZnO microcube was evaluated by MO and RhB, respectively.

To reach adsorption-desorption equilibrium, the dye suspensions including ZnO catalyst were stirred in dark for 60 min. The adsorption capacity of ZnO toward RhB is slightly higher than that of MO (Fig. 4), and it also gives the absorption spectra of RhB and MO solutions with increasing degradation time using ZnO as the catalyst. Initially, MO and RhB show maximum absorption intensities at about 545 nm and 460 nm, respectively. With increasing UV irradiation time, the absorption intensities of dyes decrease remarkably, indicating reduction in their concentrations. The colors of the dyes also become lighter (insets of Fig. 4a, b). During the whole reaction process, no other peaks appear in the absorption spectra, suggesting that the dyes had been completely degraded in the presence of ZnO photocatalyst. The UV-visible spectra shown in Figure 4b reveal a progressive hypsochromic shift of the main absorption which can be attributed the removal one by one of the ethyl group [31].

Obviously, the concentrations of the two dye solutions decrease gradually. Fig. 5a shows the calibration curves for the degradation rates of two dyes with or without porous ZnO photocatalyst under UV irradiation within 120 min. The photocatalytic degradation percentage of MO/RhB was calculated by the following equation: Deg% =  $(A_0-A)/A_0 \times 100\%$ , where  $A_0$  and A are the absorbances of MO/RhB at time 0 and time t, respectively. The MO degradation percentage for ZnO reached 99.7% in 120

min under UV irradiation, and that of RhB also approached 98.1% after the same irradiation time. For comparison, the degradation rates of two dyes under UV light irradiation without photocatalyst were also tested (Fig. 5a). Without ZnO photocatalyst, the dyes hardly degraded under UV light irradiation. Only RhB underwent mild self-degradation. We chose commercial ZnO as bare ZnO to compare the photocatalytic performance of the mesoporous ZnO microcube. At the same conditions, the photocatalytic degradation percentage of bare ZnO is more lower than mesoporous ZnO microcube (Fig. 5a). The MO degradation rate for bare ZnO was 76.2% in 120 min under UV irradiation, and that of RhB approached 80.5% after the same irradiation time. At the same time, the photocatalytic activity of the mesoporous ZnO microcube was also compared to various ZnO samples in the other literature. All the comparative data are sorted in Table S1. With the equivalent conditions, the mesoporous ZnO microcube has an upper level for photocatalytic performance under UV to degrade MO and RhB.

Moreover, the dynamic photocatalytic degradation of organic dye can be described using the Langmuir-Hinshelwood mechanism,  $\ln C_0/C_t = kt$  (Fig. 5b). The determined slopes provide quantitative estimation for the photocatalytic activity of the sample. The photodegradation rate of the dyes follows the pseudo first-order kinetics, and the determined reaction constant k of MO is much higher than that of RhB (inset of Fig. 5b).

The photocatalytic stability is also key for the applications of a photocatalytic material. The recycled performance of ZnO microcube is also evaluated in Fig. 6, and the irradiation time for each test was 120 min. The photocatalytic efficiency of ZnO microcube just decrease a little for two dyes (1% for MO, 3% for RhB) after three recycles, which caused by the mass reduction of the catalyst during the recovery process. Therefore, ZnO microcube exhibits excellent photocatalytic performance and stability for the catalytic reduction of MO and RhB.

As mentioned above, the high photocatalytic activity of ZnO can mainly be attributed to the structure of the mesoporous ZnO microcube. In fact, the photocatalysis includes two steps. The first step is absorption during which dye molecules are absorbed on the surface of the ZnO. Secondly, the electron-hole ( $e^ h^+$ ) pairs inside the ZnO matrix degrade the dye molecules to CO<sub>2</sub> or H<sub>2</sub>O. The higher adsorption capacity is in accordance with the higher photocatalytic activity of photocatalyst samples. The larger surface area of ZnO facilitates photocatalytic reaction, and the special structure of ZnO matrix provides more surface active sites for the photocatalytic reaction. Meanwhile, the efficiency of electron-hole separation is improved. The separation of electrons ( $e^-$ ) from holes ( $h^+$ ) prevents charge recombination, thereby augmenting the photocatalytic activity of ZnO. Taken together, the geometric configurations of the mesoporous ZnO microcube from MOFs may contribute to the outstanding photocatalytic performance.

The active species were also investigated to discuss the photocatalytic mechanism under two organic dyes in Fig. 7. The holes ( $h^+$ ), superoxide radical anion ( $\cdot O_2^-$ ) and hydroxyl radicals ( $\cdot OH$ ) are the probable active species taking part in organic dyes photodegradation. In this study, the edetate disodium (EDTA-2Na), benzoquinone (BQ) and tert-Butyl alcohol (t-BuOH) are often adopted as the traps for  $h^+$ ,  $\cdot O_2^-$  and  $\cdot OH$  in photodegradation reaction, respectively. It is clearly seen the maximum photocatalytic degradation were took place without any scavenger (Fig. 7). As the addition of the scavengers, the photocatalytic reaction was seriously suppressed in two dyes. Moreover,  $h^+$  and  $\cdot O_2^-$  are the main active species in the photodegradation process because the photodegradation efficiencies of two dyes decrease more quickly when EDTA-2Na and BQ are individually added.

The photocatalytic mechanisms could be explained as follow: When the photocatalyst is irradiated under UV light, photogenerated electrons ( $e^-$ ) in the valence band of ZnO are excited to the conduction band, leaving holes ( $h^+$ ) (Fig. 8). The activated electron ( $e^-$ ) migrates to the surface, and catches oxygen to produce

peroxide radicals ( $\cdot O_2^-$ ). The remaining hole reacts with water (H<sub>2</sub>O) or hydroxyl ions (OH<sup>-</sup>) to produce active species, such as hydroxyl radicals ( $\cdot OH$ ). With the strong oxidation of OH· and  $\cdot O_2^-$ , organic dye can mostly be oxidized to the final products carbon dioxide (CO<sub>2</sub>) and water (H<sub>2</sub>O).

The possible reactions for organic dye degradation are listed in Eqs:

 $ZnO + h\upsilon \rightarrow e^{-} + h^{+}$ 

 $e^- + O_2 \rightarrow \cdot O_2^-$ 

 $h^+ + H_2O \rightarrow OH \cdot$ 

 $\cdot O_2^- + OH \cdot + dye \rightarrow H_2O$ 

## 4. Conclusion

In summary, cube-shaped mesoporous ZnO was successfully synthesized by thermolysis of [(CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>][Zn(HCOO)<sub>3</sub>] precursor with a two-step process at moderate temperature. Composed of many nanoparticles, the ZnO microcube has a porous structure. The ZnO microcube exhibits excellent photocatalytic performance for the catalytic reduction of MO and RhB, with the degradation rates reaching 99.7% and 98.1% respectively within 120 min under UV light. The porous ZnO microcube efficiently photocatalyzed the degradation of the two dyes. We rationalized that the unique porous structure of ZnO microcube played an important role in the satisfactory photocatalytic performance. This study may provide a promising way for fabricating porous ZnO for photocatalysis, which may also be applicable to the preparation of other transition metal oxides.

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### Acknowledgements

This work was financially supported by National Natural Science Foundation of China (Nos., 21471127, 21361025, 21661029, 21663029), Natural Science Fund for Distinguished Young Scholars of Xinjiang Uygur Autonomous Region (No. 2013711008).

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Scheme 1. Schematic illustration for the synthesis of mesoporous ZnO microcube.

**Fig. 1** SEM images of [(CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>][Zn(HCOO)<sub>3</sub>] precursor (a, b), intermediate (c, d) and ZnO microcube (e, f). TEM images of ZnO microcube (insets of e, f).

**Fig. 2** XRD pattern of ZnO microcube (a); N<sub>2</sub> adsorption-desorption isotherms of ZnO microcube; inset: pore size distribution (b).

**Fig. 3** UV-vis diffuse reflectance spectrum of ZnO microcube (inset shows the energy band gap).

**Fig. 4** Variation of the absorption spectra for MO (a) and RhB (b) in the presence of mesoporous ZnO microcubes under UV irradiation at different time intervals.

**Fig. 5** Photocatalytic degradations of MO and RhB with mesoporous ZnO microcube and bare ZnO catalysts under UV irradiation (a); Fitting of kinetic data using the first order model (b).

**Fig. 6** The reuse activity of mesoporous ZnO microcube for photodegradation of MO and RhB.

**Fig. 7** Effect of scavengers on the photodegradation of MO (a) and RhB (b) with the mesoporous ZnO microcube catalysts.

**Fig. 8** Scheme for the photocatalysis using ZnO microcube catalyst under UV irradiation. CB: conduction band; VB: valence band.



Scheme 1.



Fig. 1



Fig. 3









Fig. 5



Irradiation Time (min)





Fig. 7





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# **Highlights:**

1 Cubic MOF  $[(CH_3)_2NH_2][Zn(HCOO)_3]$  was prepared by

solution-precipitation method.

2 Mesoporous ZnO microcube was obtained by a two-step calcination of MOF precursor.

3 ZnO microcube shows photocatalytic activity to MO and RhB under UV irradiation.

4 The  $h^+$  and  $O_2^-$  are main active species during the photodegradation

process.