Sol-gel preparation of porous In-TiO$_2$ photocatalyst using cetyltrimethylammonium bromide as template

Wenjie Zhang*, Xiaobei Pei and Jinlei Chen

School of Environmental and Chemical Engineering, Shenyang Ligong University, Shenyang, China

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ABSTRACT

A sol-gel method was used to prepare indium doped TiO$_2$ porous photocatalyst using cetyltrimethylammonium bromide as the template. The materials were studied by XRD, SEM, and N$_2$ adsorption-desorption methods. Photocatalytic activity of the materials was evaluated using methyl orange as the pollutant. Photocatalytic degradation efficiency is 91.8% on the sample In-TiO$_2$(0.12) after 60 min of irradiation. The degradation efficiency is nearly 35% larger than the sample without CTAB. The sample calcinated at 500 ℃ has both the maximum adsorption capacity and photocatalytic activity. The diffraction peaks of In-TiO$_2$ and In-TiO$_2$(0.12) are in accordance to the diffraction peaks of anatase phase TiO$_2$. The addition of CTAB leads to the increment of lattice parameters and cell volume. N$_2$ adsorption amount on In-TiO$_2$(0.12) is obviously larger than that on In-TiO$_2$. The average pore sizes of In-TiO$_2$ and In-TiO$_2$(0.12) are 23.3 nm and 16.3 nm, and the total pore volumes are 0.072 cm^3/g and 0.22 cm^3/g, respectively.

Key words: TiO$_2$, Indium, Photocatalysis, Cetyltrimethylammonium bromide

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INTRODUCTION

The application of TiO$_2$ as the main photocatalyst on degradation of organic pollutants has been widely investigated in recent decades. [1-3] However, large band gap and high recombination rate of charge carriers in TiO$_2$ has been considered to be the defects of this potential material. Metal ion doping can retard recombination of photogenerated electron-hole pairs in TiO$_2$, and improve its photocatalytic activity by extending charge carrier's lifetime. [4-6] Indium ion was used as dopant for TiO$_2$ photocatalyst by improving the crystallite structure and increasing life time of electron-hole pairs. [7-10]

Porous TiO$_2$ has large surface area, highly ordered porous structure, and well-defined pore size and porosity. [11-14] Porous material can be used to promote photocatalytic activity and to improve the efficiency of photo-electron-conversion. The increase of surface area can improve photocatalytic efficiency because of the large surface area exposed to pollutant. Surfactant such as CTAB (Cetyltrimethylammonium bromide) was used as a template agent in preparation of porous structured materials. [15-18] However, there is no literature reporting the use of CTAB to prepare porous indium doped TiO$_2$ photocatalyst.

In this work, CTAB was used as a template in sol-gel method to prepare porous indium doped TiO$_2$ material. XRD, SEM, BET, and BJH measurements were conducted to the material. Adsorption capacity and photocatalytic degradation of methyl orange on the material were investigated to ascertain the enhanced activity.

EXPERIMENTAL SECTION

SYNTHESIS OF THE MATERIALS

Indium doped porous TiO$_2$ was prepared by a modified sol-gel method using CTAB as the template. A certain

amount of CTAB and 0.0675 g $In(NO_3)_3 \cdot 4.5H_2O$ (n(In)/n(Ti)=0.03) were dissolved in 8 mL anhydrous ethanol, and then 2 mL tetrabutyl titanate and 0.1 mL concentrated hydrochloric acid were added into the former solution. Another mixed solution containing 0.9 mL distilled water and 4 mL anhydrous ethanol was then added into the precursor solution under stirring. A gel formed after 1 h under continuous stirring. The gel was aged at ambient temperature for 24 h and subsequently dried at 80℃ for 8 h. The obtained solid was grinded and calcinated for 3 h at temperature indicated later. The obtained powder samples were grinded again and marked as In-TiO$_2$(C), where C (mol/L) represented the concentration of CTAB in the precursor.

CHARACTERIZATION OF PHOTOCATALYST

X-ray diffraction measurement of the material was studied by a Rigaku D/Max-rB diffractometer using Cu Ka radiation. The XRD calculation of crystallite size was based on the Scherrer formula. The morphology of the material was studied by scanning electron microscopy (SEM. Hitachi, S-3400N). A thin layer of gold was coated on the sample to avoid charging. The specific surface area was determined by the multipoint BET method using the adsorption data in the relative pressure (P/P_0) range between 0.05-0.25. The desorption isotherm were studied to determine pore size distribution using the BJH (Barrett-Joyner-Halenda) method.

PHOTOCATALYTIC ACTIVITY

The activity of the In-doped TiO$_2$ photocatalyst was evaluated by methyl orange (MO) decolorization. The mixed solution of MO and photocatalyst (V=50 mL, C(MO)=10 mg/L, C(catalyst)=300 mg/L) was put into a 100 mL column size quartz reactor. The suspension was stirred for 60 min to reach adsorption-desorption equilibrium. Subsequently, a 20 W UV-light lamp with main irradiation wavelength at 253.7 nm was used as a light source to excite the photocatalytic reaction. The average irradiation intensity striking the reaction solution was 1300 μW/cm^2. The MO solution could not be decolorized under irradiation without the existence of photocatalyst. After UV irradiation for 30 min, 5 mL of the suspension was removed and filtrated by millipore filter (pore size 0.22 μm) to measure the change of MO concentration. Total decoloration of the dye is composed of two parts, adsorption of the dye on surface of photocatalyst after adsorption-desorption equilibrium and photocatalytic degradation of the dye under UV light irradiation with the existence of photocatalyst.

RESULTS AND DISCUSSION

THE EFFECTS OF CTAB CONCENTRATION AND CALCINATION TEMPERATURE

Photocatalytic activity of indium doped TiO$_2$ prepared using different concentration of CTAB is shown in Figure 1. Decoloration efficiency of the dye increases with extending reacting time on all the samples without apparent losing of photocatalytic activity. When CTAB concentrations are 0.08 and 0.12 mol/L in the precursor, the samples possess enhanced photocatalytic activity as compared to the sample without using CTAB. Photocatalytic degradation efficiency is 91.8% after 60 min of irradiation on the sample In-TiO$_2$(0.12). The degradation efficiency is nearly 35% higher than the sample without using CTAB. However, the sample prepared using 0.3 mol/L of CTAB has nearly the same activity to the In-TiO$_2$ sample without using CTAB. That means excessive addition of template CTAB is not beneficial to further activity enhancement. This may be due to the collapse of porous structure in the material using excessively high concentration of CTAB.

Calcination temperature can also influence the adsorption capacity and photocatalytic activity of In-TiO$_2$(0.12). Calcination temperature can simultaneously influence the amount of methyl orange adsorbed and degraded on the materials, as shown in Figure 2. The sample calcined at 500℃ has the maximum adsorption capacity and photocatalytic activity. 8.2% of the initial methyl orange can be adsorbed on the sample after adsorption-desorption equilibrium, and 48.2% of the dye can be degraded after 30 min of irradiation. Phase formation is not adequate in the sample prepared at low temperature since the organic substances cannot be burnt out thoroughly. On the other hand, the samples calcined at high temperature have low activity and adsorption capacity too. Photocatalytic activity is related to physical-chemical properties of the materials, such as phase composition, porous character, and surface area. The characterization results of the materials will be discussed later.

CHARACTERIZATION OF THE MATERIALS

Figure 3 shows XRD patterns of In-TiO$_2$ and In-TiO$_2$(0.12). The diffraction peaks of the two samples are in accordance to the diffraction peaks of anatase phase TiO$_2$. There are no diffraction peaks of indium-containing substances such as In$_2$O$_3$ and other phases of TiO$_2$ in the spectra. The addition of template CTAB does not influence anatase TiO$_2$ formation apparently. According to Full Width at Half Maximum analysis of the anatase TiO$_2$ (101) diffraction peak and based on the Scherrer formula, the average crystallite sizes of In-TiO$_2$ and In-TiO$_2$(0.12) samples are 13.2 nm and 15.5 nm, respectively. The crystallite size of In-TiO$_2$(0.12) is only a little larger than that of In-TiO$_2$.

As can be seen from Figure 3, X-ray diffraction peaks of (101) crystal plane of In-TiO$_2$(0.12) sample shift to lower angle region, demonstrating the cell expansion caused by the addition of CTAB. Lattice parameter of TiO$_2$ and In-TiO$_2$ are listed in Table 1. The addition of CTAB also leads to increment of lattice parameters and cell volume. Template CTAB is surrounded by tetrabutyl titanate precursor molecules in the sol-gel process, leading to cell expansion in some extent after the template molecules are burnt out during calcination process.

Table 1 Lattice parameters of TiO$_2$ and In-TiO$_2$

Sample	$a(=b)$ /10^{-1} nm	c /10^{-1} nm	V /10^{-3} nm^3
In-TiO$_2$	3.7901	9.4784	136.16
In-TiO$_2$ (0.12)	3.7955	9.4809	136.58

Figure 4 shows the SEM images of In-TiO$_2$ and In-TiO$_2$(0.12). Small particles scatter among large particles in the samples. The size of large particles is as large as 1 μm, whereas the small particles are in the size below 100 nm. Some of the small particles are produced during grinding. There are more small particles in In-TiO$_2$(0.12). The existence of CTAB is beneficial to produce small particles because of the porous structure in the sample.

N$_2$ desorption isotherms of In-TiO$_2$ and In-TiO$_2$(0.12) are shown in Figure 5. The volume of N$_2$ adsorbed on the surface increases with increasing partial pressure of N$_2$. The increase of adsorbed N$_2$ is not large when N$_2$ partial pressure is below 0.6, since N$_2$ molecules are adsorbed on the surface in single or multiple layers. A drastic increase of adsorbed N$_2$ volume appears after N$_2$ relative pressure is larger than 0.7, which is caused by capillary condensation of N$_2$ in the micropores of the samples. N$_2$ adsorption amount on In-TiO$_2$(0.12) is obviously larger than that on In-TiO$_2$. Porous structure produced after the addition of template CTAB is responsible for the larger N$_2$ adsorption capacity on In-TiO$_2$(0.12).

As presented in Figure 6, In-TiO$_2$ and In-TiO$_2$(0.12) samples are composed of micropores and macropores, distributing in the range below 200 nm. Micropore size is mainly in the range between 1.5 and 20 nm. There are also macropores in the size between 30 nm and 200 nm in the two samples. The addition of CTAB does not apparently change distribution range of pore size although pore volume increases obviously after addition of CTAB. Micropores in the samples can be regarded as the result of the addition of the template CTAB. Meanwhile, the macropores are mainly inter-particle holes coming from particles aggregation.

The average pore sizes of In-TiO$_2$ and In-TiO$_2$(0.12) are 23.3 nm and 16.3 nm, and the total pore volumes are 0.072 cm^3/g and 0.22 cm^3/g, as being calculated using BJH method. Total pore volume increases sharply after the addition of CTAB. Specific surface area depends on particle size and porous structure. Table 2 lists specific surface areas of In-TiO$_2$ prepared with different CTAB concentration. Surface area increases apparently for the samples prepared using CTAB as template. The increasing surface area is responsible for the enhanced adsorption capacity. The sample In-TiO$_2$(0.12) can adsorb 8.2% of the initial dye on its surface, whereas only 2.2% of the dye can be adsorbed on the surface of sample In-TiO$_2$. CTAB concentration has slight effect on surface area of the samples. Surface area of the In-TiO$_2$(C) samples varies noticeably when CTAB concentration changes from 0.08 mol/L to 0.2 mol/L. The sample In-TiO$_2$(0.12) has the maximum surface area of 59.4 m^2/g. However, further increase of CTAB concentration leads to a slight dropping of surface area on sample In-TiO$_2$(0.20).

Table 2 Specific surface areas of In-TiO$_2$ prepared with different CTAB concentration

Sample	In- TiO$_2$	In-TiO$_2$(0.08)	In-TiO$_2$(0.12)	In-TiO$_2$(0.20)
BET surface area /m^2/g	39.1	57.0	59.4	53.2

Specific surface areas of In-TiO$_2$(0.12) samples calcinated at different temperature are listed in Table 3. Calcination temperature also influences pore formation and surface area. The sample calcinated at 500℃ has the maximum surface area of 59.4 m^3/g. Low calcination temperature is not capable of removing all of the organic substances from the sample, leading to smaller surface area of sample In-TiO$_2$(0.12) calcinated at 450℃. Meanwhile, particles aggregation and collapse of porous structure inside the material also lead to shrinking surface area of the sample calcinated at 600 ^{o}C.

Table 3 Specific surface areas of In-TiO$_2$(0.12) samples calcinated at different temperature

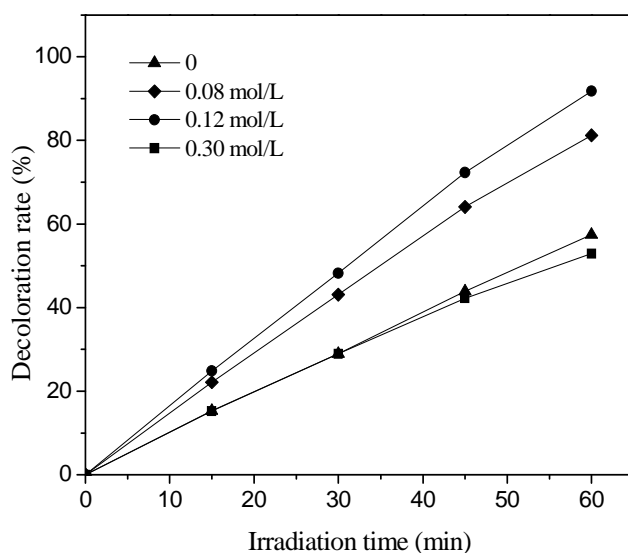| Calcination temperature / ℃	450	500	600
BET surface area /m^2/g	49.7	59.4	24.3

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Fig. 1: Photocatalytic activity of In-TiO$_2$ prepared using different concentration of CTAB. The samples were calcinated at 500 ℃

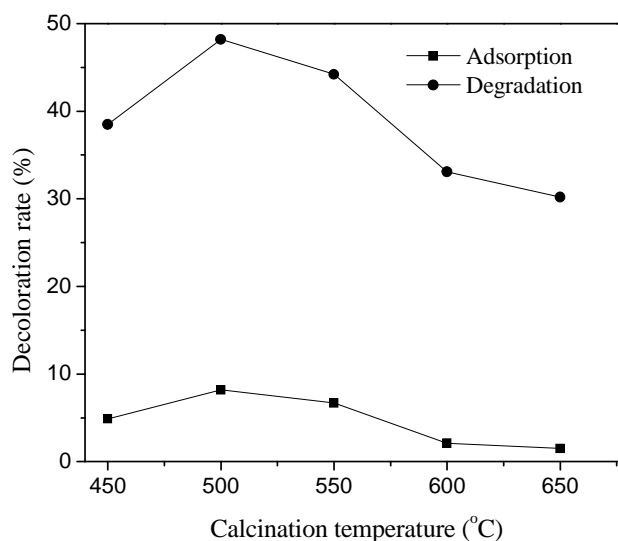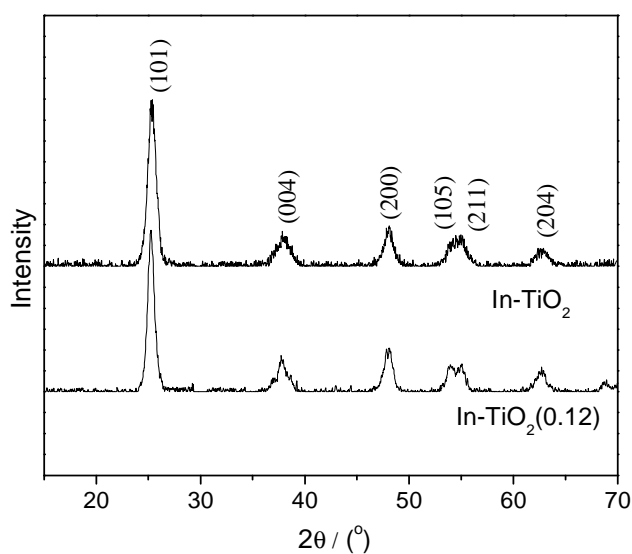**Fig. 2: Photocatalytic activities of In-TiO$_2$(0.12) as the factor of calcination temperature**

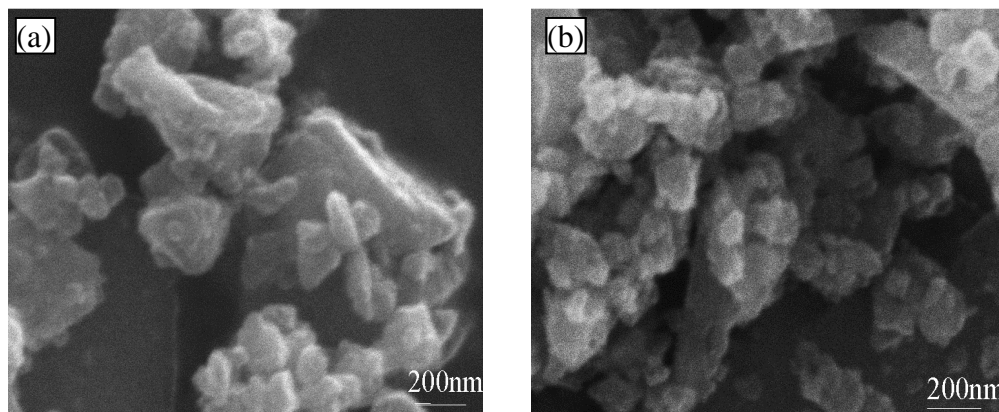**Fig. 3: XRD patterns of In-TiO$_2$ and In-TiO$_2$(0.12). The samples were calcinated at 500 ℃**

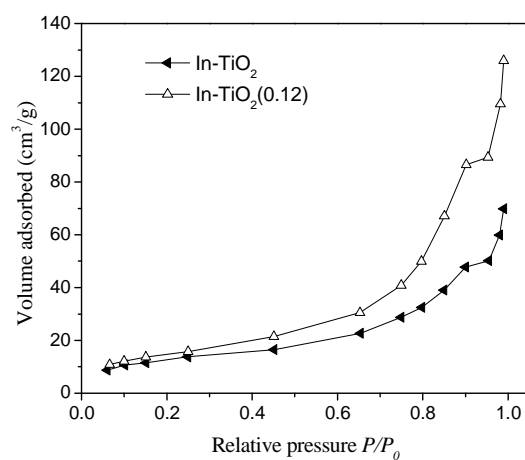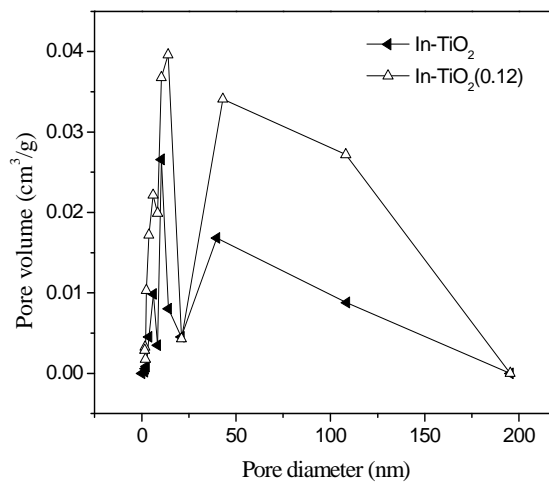**Fig. 4: SEM images of (a) In-TiO$_2$ and (b) In-TiO$_2$(0.12). The samples were calcinated at 500°C**

Fig. 5: N$_2$ desorption isotherms of In-TiO$_2$ and In-TiO$_2$(0.12). The samples were calcinated at 500°C
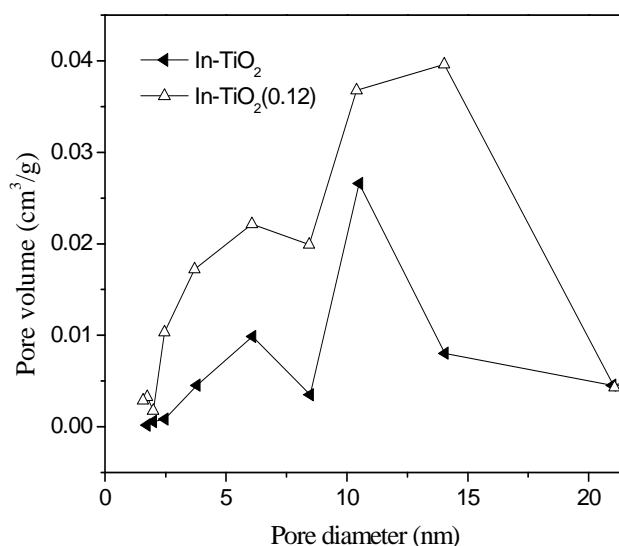
Fig. 6: BJH pore size distribution of In-TiO$_2$ and In-TiO$_2$(0.12). The samples were calcinated at 500 $^\circ$C

CONCLUSION

Indium doped TiO$_2$ photocatalysts were synthesized by sol-gel method to investigate the effect of CTAB template addition. 8.2% of the initial methyl orange can be adsorbed after adsorption-desorption equilibrium on In-TiO$_2$(0.12) which is calcinated at 500 $^\circ$C, and 48.2% of the dye can be degraded after 30 min of irradiation. The addition of template CTAB does not affect anatase TiO$_2$ formation, but it can lead to increment of lattice parameters and cell volume. Porous structure is responsible for the large N$_2$ adsorption capacity on In-TiO$_2$(0.12). Surface area increases apparently for the samples prepared using CTAB as template.

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