

Sol-gel synthesized $x\text{In}-0.1\%\text{Gd}-\text{TiO}_2$ for the promoted activity on photocatalytic degradation of methyl orange

WENJIE ZHANG*, JIAO YANG XIAOBEI PEI

School of Environmental and Chemical Engineering, Shenyang Ligong University, Shenyang 110159, China

Asol-gel route was used to synthesize In-Gd co-doped TiO_2 materials. The material observed in the XRD patterns is anatase phase TiO_2 in tetragonal system. Some Ti^{4+} ions in the crystal lattice of anatase TiO_2 are substituted by In^{3+} and Gd^{3+} ions. The vibrations of Ti-O bond do not obviously change after doping of In and Gd ions. The maximum photocatalytic activity and the largest specific surface area are the characters of the $3\%\text{In}-0.1\%\text{Gd}-\text{TiO}_2$. Methyl orange decoloration efficiency is as high as 90% after 45 min of irradiation on the $3\%\text{In}-0.1\%\text{Gd}-\text{TiO}_2$ sample.

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1. Introduction

Organic pollutant from industrial wastewater and domestic sewage becomes a major environmental problem in the aquatic system. Photocatalytic oxidation of organic pollutant has been investigated for nearly half a century [1-3]. A hot topic is to synthesize powerful photocatalytic material in this field. The most widely studied material is TiO_2 [4-6]. Nevertheless, large scale industrial application of TiO_2 is not satisfactory. Modification on TiO_2 is still necessary to improve its activity [7,8].

Metal ion doping is an effective method to extend the lifetime of photogenerated electron-hole pairs during illumination. Consequently, photocatalytic activity of the doped substance can be promoted [9-11]. Although various elements are proven to be suitable dopants in TiO_2 -based materials, the simultaneous doping of two different elements is still a new approach. Liu and co-workers prepared La-B- TiO_2 through a facile solvothermal method [12]. Chen et al. prepared a $\text{In}_2\text{O}_3/\text{SnO}_2-\text{TiO}_2$ that can work under solar light irradiation [13]. The 0.5%Al-3%In- TiO_2 material was synthesized using Al and In as the co-dopants in our previous work [14]. The rate constant of the first order reaction is enhanced from 0.011 min^{-1} on 3%In- TiO_2 to 0.027 min^{-1} on 0.5%Al-3%In- TiO_2 .

The simultaneous doping of indium and gadolinium into TiO_2 was studied in this work. The novel In-Gd co-doped TiO_2 was synthesized through a sol-gel route. The $x\text{In}-0.1\%\text{Gd}-\text{TiO}_2$ photocatalyst was characterized using X-ray diffractometer, FT-IR/FIR spectrometer, and N_2 adsorption-desorption method. Photocatalytic decoloration of methyl orange (MO) was measured to show the activity of the material and the effect of doping on the activity.

2. Experimental

Synthesis of $x\text{In}-0.1\%\text{Gd}-\text{TiO}_2$ photocatalyst

In-Gd co-doped TiO_2 was synthesized through a sol-gel route. The precursor was made from two solutions. Solution A was composed of 4 mL anhydrous ethanol and 0.9 mL distilled water. Solution B was composed of 0.0027 g $\text{Gd}(\text{NO}_3)_3$, 0-0.1656 g $\text{In}(\text{NO}_3)_3$, 8 mL anhydrous ethanol, 2 mL tetrabutyl titanate and 0.1 mL concentrated hydrochloric acid. The mixture of solutions A and B was stirred for 60 min to form the gel. The gel was aged at room temperature for 12 h, and then was dried in the furnace at 80°C for 8 h. The powders were calcinated in an oven for 3 h. The product was named as $x\text{In}-0.1\%\text{Gd}-\text{TiO}_2$ [$x=n(\text{In})/n(\text{Ti})\times 100\%$]. Gadolinium doping content was fixed to 0.1%.

Characterization of photocatalysts

A D8 X-ray diffractometer was used to measure diffraction patterns of the materials, using monochromatized Cu $K\alpha$ at $\lambda=1.5416\text{\AA}$. Infrared and far infrared absorption spectra were recorded by a Frontier FT-IR/FIR spectrometer in the wavenumber between 50 cm^{-1} and 4000 cm^{-1} . Specific surface area and pore characters of the materials were measured by an F-sorb 3400 analyzer.

Decoloration of methyl orange

The lab-scale reactor was made of a 100 mL quartz beaker and a 20 W UV-light lamp. The average irradiation intensity of the lamp at 253.7 nm was $1300 \mu\text{W}/\text{cm}^2$. 15 mg photocatalyst and 50 mL of 10 mg/L MO solution were used in each experiment. In prior to turn on the light, the suspension was ensured adsorption-desorption equilibrium

after stirring in the dark for 60 min. Adsorption percent of MO on the photocatalyst was measured at this moment. The irradiation time in the subsequent experiments was set to 30 min except for the prolonged time reaction. Absorbance of the solution was measured by a 721E spectrophotometer at the maximum absorption wavelength of MO, i.e. 466 nm. MO concentration was calculated according to Lambert-Beer theory.

3. Results and discussion

Fig. 1 presents XRD patterns of 3%In-0.1%Gd-TiO₂ and 0.1%Gd-TiO₂. The material observed in the patterns is anatase phase TiO₂ in tetragonal system. Doping of gadolinium and indium reduces the diffraction intensities and broadens the diffraction peaks. The crystallite size of anatase TiO₂ is calculated from the preferred (101) plane using Scherrer formula. The crystallite sizes of 3%In-0.1%Gd-TiO₂ and 0.1%Gd-TiO₂ is 9.7 nm and 10.3 nm, respectively. The crystallite size decreases very slightly after the subsequent doping of indium, although the indium doped TiO₂ has a obvious shrinking crystallite size as compared to the undoped TiO₂. A similar result was reported for La³⁺ doped mesoporous titania [15]. The Ti-O-La bond hinders crystallization and agglomeration of TiO₂ crystals during synthesis process. The diffraction peaks of anatase TiO₂ shift to lower angle after doping. In³⁺ and Gd³⁺ ions are incorporated into the crystal lattice of anatase TiO₂ by substituting Ti⁴⁺ ions, so that both of the ions can occupy the site of Ti⁴⁺ in TiO₂ crystal lattice.

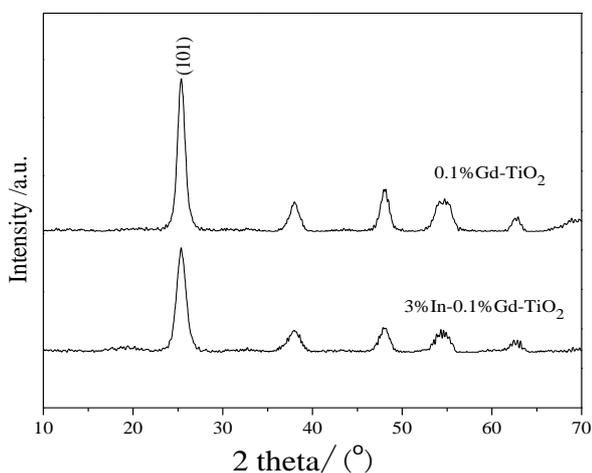


Fig. 1. XRD patterns of 3%In-0.1%Gd-TiO₂ and 0.1%Gd-TiO₂

FT-IR/Far IR spectra of xIn-0.1%Gd-TiO₂ samples are taken to determine the bonding characters in the materials, as shown in Fig. 2. Although the materials are prepared after calcination, there are still water molecules adsorbing on the surface of the materials. The absorption peaks at 3420 cm⁻¹ and 1640 cm⁻¹ are attributed to stretching and bending vibrations of surface hydroxyl and adsorbed water [16,17]. Bonding in metal oxide can be seen in the far IR

spectra. The broad absorptions around 464 cm⁻¹ and 345 cm⁻¹ are due to the vibration of Ti-O bond [18,19]. These vibrations do not obviously change after doping of In and Gd ions. The main Ti-O bond is maintained in the doped TiO₂ and is not noticeably influenced by the amount of dopants.

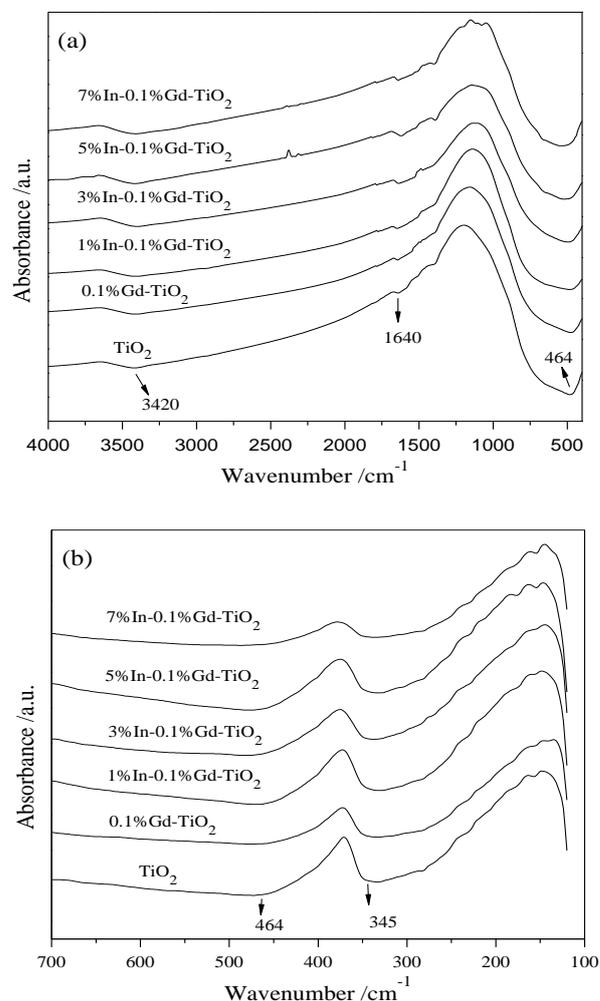


Fig. 2. FT-IR/FIR spectra of xIn-0.1%Gd-TiO₂ samples. (a) FT-IR, (b) FT-Far IR

Fig. 3(a) shows N₂ desorption isotherm of 3%In-0.1%Gd-TiO₂. The desorption isotherm can be regarded as a typical mesoporous type. The 3%In-0.1%Gd-TiO₂ contains macropores, proven by the abrupt enlarging pore volume at high relative N₂ pressure [16]. Fig. 3(b) shows the pore size distribution in the range between 2 and 18 nm. Pores in the size below 10 nm are found in the 3%In-0.1%Gd-TiO₂ sample.

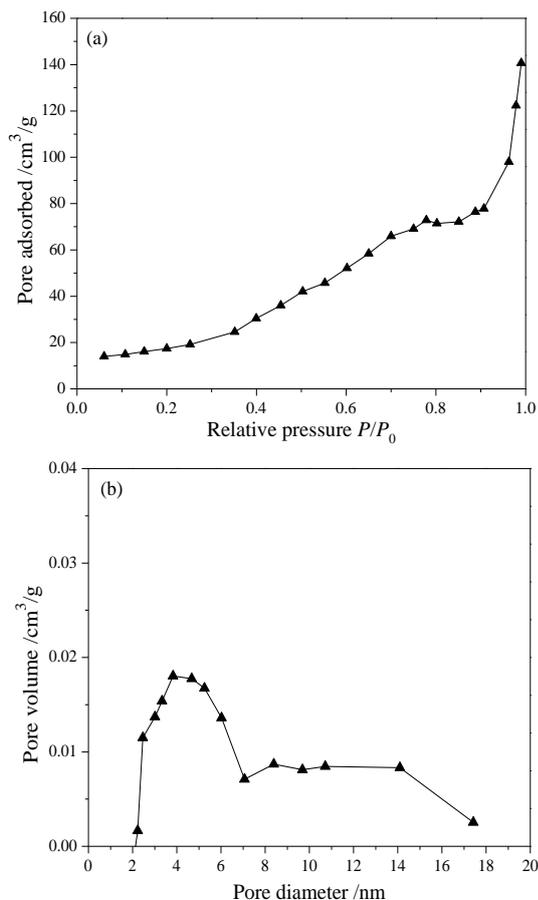


Fig. 3. (a) N_2 desorption isotherm and (b) BJH pore size distribution of 3%In-0.1%Gd- TiO_2

Specific surface area, average pore size and total pore volume are the key characters of a porous material. As mentioned before, crystallite size of TiO_2 is reduced after doping of Gd and In. The shrinking of crystallite size can be regarded as one reason for the enlarged surface area. The BET surface area increases from $37.0 \text{ m}^2/\text{g}$ to $101.0 \text{ m}^2/\text{g}$ after doping 0.1% Gd into the TiO_2 . The BET surface area of 3% In-0.1% Gd- TiO_2 is $122.7 \text{ m}^2/\text{g}$. Adsorption and photocatalytic decoloration of pollutant occur on the material's surface. Doping of In and Gd puts extraordinary effect on the significant increase of surface area.

Fig. 4 shows adsorption and photocatalytic degradation of methyl orange on $x\text{In}-0.1\% \text{Gd}-TiO_2$ as the factor of indium doping content. Adsorption of methyl orange molecules on the surface of $x\text{In}-0.1\% \text{Gd}-TiO_2$ increases with rising In doping content. The adsorption efficiency is measured after adsorption-desorption equilibrium in the dark. Adsorption of methyl orange molecules on the $x\text{In}-0.1\% \text{Gd}-TiO_2$ depends on both surface properties and specific surface area. The adsorption capacity is in close relationship to the surface area. On the other hand, surface properties are also important factors in adsorption capacity. The specific surface areas of the $x\text{In}-0.1\% \text{Gd}-TiO_2$ with high indium content are much smaller than that of 3% In-0.1% Gd- TiO_2 . Surface polarity, bonding character and surface

morphology can greatly influence the adsorption capacity.

Photolysis alone cannot lead to decomposition of methyl orange in this work. Photocatalytic oxidation is the major pathway for methyl orange decoloration besides adsorption of the dye. Photocatalytic activity of $x\text{In}-0.1\% \text{Gd}-TiO_2$ also depends on the content of dopant. When In doping content is not more than 3%, photocatalytic degradation efficiency constantly increases with rising indium content. The 3% In-0.1% Gd- TiO_2 sample has the maximum photocatalytic activity. The degradation efficiency can be as much as 63% after 30 min of irradiation. However, further increase of indium content is not beneficial to the activity.

The effect of dopant concentration on photocatalytic activity can be attributed to low conduction band edge coming from the dopant. The dopant is also a kind of low energy trap for photogenerated electrons. The traps may become recombination centers of electrons and holes after excessive doping. As stated in this work, surface area is also affected by the dopant concentration. The maximum photocatalytic activity and the largest specific surface area are the characters of the 3% In-0.1% Gd- TiO_2 sample.

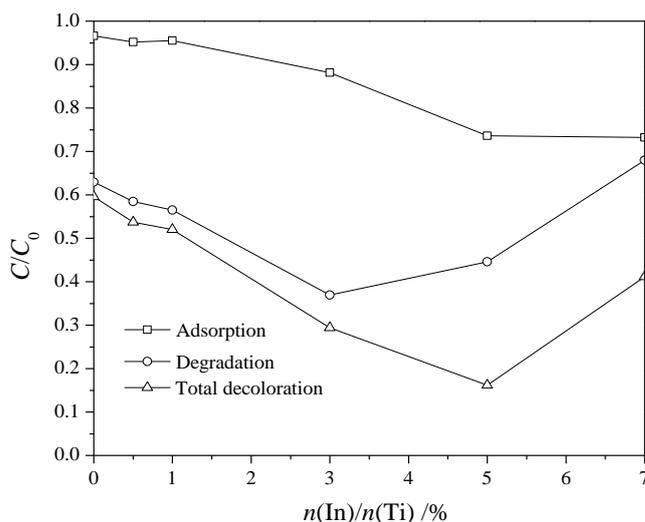


Fig. 4. Decoloration of methyl orange on $x\text{In}-0.1\% \text{Gd}-TiO_2$ as a factor of indium doping content

Fig. 5(a) presents methyl orange adsorption and degradation efficiencies on TiO_2 , 0.1% Gd- TiO_2 and 3% In-0.1% Gd- TiO_2 with prolonged illumination time. The Gd-In co-doped 3% In-0.1% Gd- TiO_2 has the largest adsorption capacity and the maximum photocatalytic activity. More than 90% of methyl orange molecules are decolorized on 3% In-0.1% Gd- TiO_2 after 45 min of irradiation. The total removal efficiency is only 40% on TiO_2 . Photocatalytic activity of 3% In-0.1% Gd- TiO_2 is also compared with the commercial Degussa P25 under the same condition in this work. The first order reaction rate constant is 0.059 min^{-1} on 3% In-0.1% Gd- TiO_2 , while it is 0.031 min^{-1} on Degussa P25 at the same time.

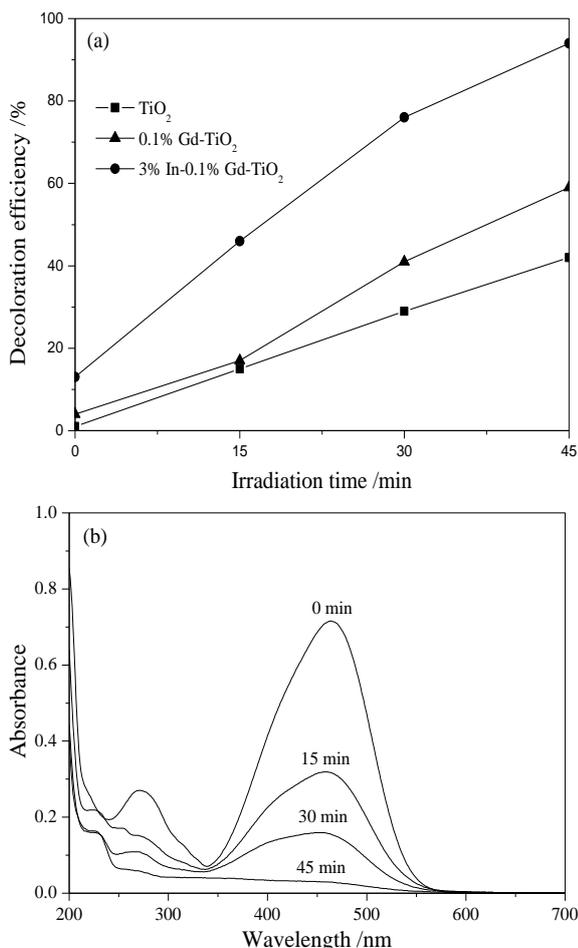


Fig. 5. (a) Decoloration of MO with extending irradiation time. (b) UV-Vis absorption spectra of MO aqueous solution during degradation

Fig. 5(b) shows UV-Vis absorption spectra of methyl orange aqueous solution during photocatalytic decomposition process in presence of 3%In-0.1% Gd-TiO₂. The methyl orange molecule has conjugated chromophores, which have a broad absorption peak at 466 nm. The functional groups in methyl orange molecule are decomposed with extending irradiation time. The absorption intensity of the spectrum decreases during photocatalytic decomposition process. The possible intermediates produced during oxidation cause the slight shift of the spectrum. The absorbance intensity becomes very weak after 45 min of reaction on 3%In-0.1% Gd-TiO₂. The conjugated chromophores absorbing in the visible region disappears. The undecomposed intermediates such as benzene ring has a slight absorbance in the short UV region.

4. Conclusions

The preparation of xIn-0.1% Gd-TiO₂ photocatalyst through a sol-gel route was studied. Anatase phase TiO₂ in tetragonal system is the only phase in the materials although indium content varies. The variation of indium content in xIn-0.1% Gd-TiO₂ does not put noticeable effect

on the Ti-O bond. The BET surface area increases from 37.0 m²/g to 101.0 m²/g after doping 0.1% Gd into the TiO₂. The BET surface area of 3%In-0.1% Gd-TiO₂ is 122.7 m²/g. The adsorption capacity and photocatalytic activity of TiO₂ are improved with a suitable dopant concentration in the material. The 3% In-0.1% Gd-TiO₂ sample has the maximum photocatalytic activity on methyl orange degradation.

Acknowledgments

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^{*}Corresponding author: wjzhang@aliyun.com