

Electronic structure and photocatalytic properties of $\text{In}_6\text{WO}_{12}$

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2007 J. Phys.: Condens. Matter 19 376213

(<http://iopscience.iop.org/0953-8984/19/37/376213>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 29/05/2010 at 04:41

Please note that [terms and conditions apply](#).

Electronic structure and photocatalytic properties of $\text{In}_6\text{WO}_{12}$

Haitao Zhang^{1,2,3}, Xinyi Chen^{1,3}, Zhaosheng Li^{1,2,3}, Lifei Liu^{1,3}, Tao Yu^{1,3}
and Zhigang Zou^{1,3,4}

¹ Eco-Materials and Renewable Energy Research Center (ERERC), Department of Physics, Nanjing University, Nanjing 210093, People's Republic of China

² Department of Materials Science and Engineering, Nanjing University, Nanjing 210093, People's Republic of China

³ National Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, People's Republic of China

E-mail: zgou@nju.edu.cn

Received 30 March 2007, in final form 29 July 2007

Published 22 August 2007

Online at stacks.iop.org/JPhysCM/19/376213

Abstract

In this paper, indium tungsten oxide $\text{In}_6\text{WO}_{12}$ was prepared by a solid-state reaction method. The sample that was obtained was characterized by x-ray diffraction (XRD), ultraviolet–visible (UV–vis) spectroscopy and Brunauer–Emmett–Teller (BET) measurement. According to the diffuse reflectance spectra of the sample, the band gap is estimated to be 3.3 eV. The photocatalytic properties of the $\text{In}_6\text{WO}_{12}$ sample were evaluated by photo-decomposing acetaldehyde. The experimental results showed that the acetaldehyde could be mineralized to CO_2 over $\text{In}_6\text{WO}_{12}$ under Xe lamp irradiation. The optimized crystal structure and calculated ground-state electronic structure of $\text{In}_6\text{WO}_{12}$ were also reported by using the standard CASTEP package.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Since the discovery of the photocatalytic property of TiO_2 three decades ago [1], the semiconductor photocatalytic process has attracted much attention [2]. Because of severe environment problems, the scientific interest in the photocatalytic degradation of organic pollution has grown quickly in recent years [3, 4].

Until now, most reports focused on the decomposition of organic pollution over TiO_2 -based photocatalysts [5–12]. Recently, CaBi_2O_4 [13] and CaIn_2O_4 [14] have been reported as photocatalysts which could photo-decompose organic pollution under visible light irradiation.

⁴ Author to whom any correspondence should be addressed.

However, the need for investigating new oxides which could photo-decompose organic pollutions are still urgent.

It is well known that WO_3 is a good photocatalyst for photocatalytic O_2 evolution [15]. Since the electronic structure of a material plays a crucial role in its photocatalytic properties [16], much effort has been made to adjust the electronic structure of metal tungstates [17, 18]. Tang *et al* reported the photophysical and photocatalytic properties of a new photocatalyst AgInW_2O_8 [19] with InO_6 octahedra. To the best of our knowledge, no one has reported the photocatalytic properties and electronic structure of $\text{In}_6\text{WO}_{12}$ with InO_6 octahedra. Research on the electronic structure and photocatalytic properties of $\text{In}_6\text{WO}_{12}$ should contribute to the research on other metal tungstates.

In this paper, we report the characterization and photocatalytic ability of $\text{In}_6\text{WO}_{12}$. The photocatalytic ability of $\text{In}_6\text{WO}_{12}$ was evaluated by photo-decomposing acetaldehyde. The optimized crystal structure and the calculated ground-state electronic structure of $\text{In}_6\text{WO}_{12}$ are also reported using the standard CASTEP package.

2. Experimental details

$\text{In}_6\text{WO}_{12}$ powder was prepared by using a solid-state-reaction method. Reagent-grade In_2O_3 and WO_3 in a stoichiometric ratio were ground and mixed thoroughly, and then heated in an aluminum crucible in air for 12 h at 1473 K [20].

The crystal structures of the samples were determined by the x-ray diffraction method (Utilma III, Tokyo, Japan). UV-vis diffuse reflectance spectra of the prepared sample were measured with a UV-vis spectrophotometer (Shimadzu UV-2550) at room temperature. The surface area of the photocatalyst was determined by BET measurement (Micromeritics-3000, from Micromeritics, USA) on nitrogen adsorption at 77 K after pre-treatment at 573 K for 2 h.

In the photocatalytic measurements, a 300 W Xe lamp was used as the light source. The sample (1 g) was evenly spread over a dish with a diameter of 3.0 cm in a 500 ml pyrex vessel. The initial concentration of acetaldehyde was about 150 ppm. The final products of the photocatalytic oxidation of acetaldehyde were CO_2 and H_2O . To evaluate the photocatalytic activity, the amount of CO_2 was monitored using gas chromatography (Shimadzu, GC-14B) at given intervals.

The lattice parameters of the $\text{In}_6\text{WO}_{12}$ model were optimized, and then the ground-state energy band was also calculated by using the standard CASTEP package [21]. The CASTEP code is a plane-wave pseudo-potential total energy calculation method which is based on the density functional theory (DFT). In our calculation, the electronic wavefunctions were expanded in a plane-wave basis setup to a 380 eV cutoff. Calculations of the energy band and density of states (DOS) were both executed.

3. Results and discussion

Figure 1 shows a comparison of x-ray diffraction patterns of $\text{In}_6\text{WO}_{12}$ before and after the photocatalytic reaction. As shown in figure 1, the prepared sample crystallized in single phase (JCPDS#49-0336). The sharp peaks of $\text{In}_6\text{WO}_{12}$ indicate good crystallization of the prepared sample. By using the Scherrer formula, the average grain size of the samples was estimated to be about 67 nm. Analysis of the XRD patterns of the samples showed that the crystal structure of $\text{In}_6\text{WO}_{12}$ has not been changed after the reactions, which indicates that $\text{In}_6\text{WO}_{12}$ was stable under light irradiation.

Figure 2 shows the diffuse reflection spectra of $\text{In}_6\text{WO}_{12}$. The band gap energy can be estimated from a plot of $(\alpha h\nu)^2$ versus the photon energy ($h\nu$) [19]. The calculated energy

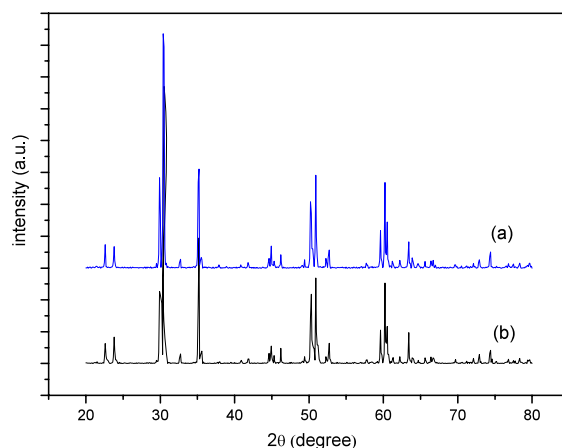


Figure 1. A comparison of x-ray diffraction patterns of $\text{In}_6\text{WO}_{12}$ powder before and after photocatalytic reactions: (a) after reactions; (b) before reactions.

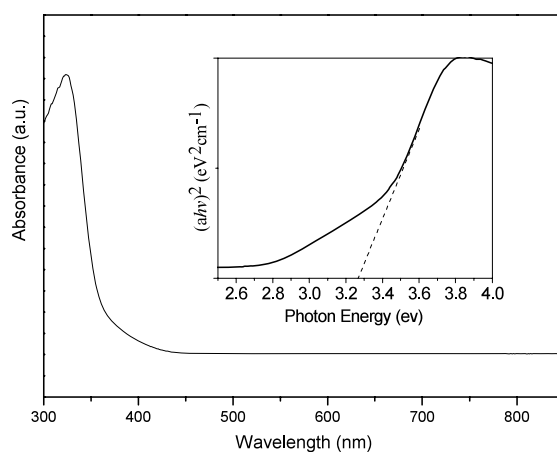


Figure 2. UV-visible diffuse reflectance spectra of $\text{In}_6\text{WO}_{12}$, inset is a plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$).

band gap (figure 5) showed that $\text{In}_6\text{WO}_{12}$ has a direct transition. The intercept of the tangent to the plot will give an approximation of the band gap energy for a direct band gap semiconductor. The band gap energy is estimated to be 3.3 eV (inset of figure 3) from the intercept of the tangents to the plot.

The decomposition rate and mineralization rate of acetaldehyde at different irradiation intervals were shown in figure 3. It could be found that the concentration of acetaldehyde decreased with increasing irradiation time. Furthermore, the CO_2 concentration also increased with the decrement of the acetaldehyde, which means that the acetaldehyde was not only decomposed but also mineralized to CO_2 . After 12 h of irradiation, acetaldehyde was decomposed completely, and about 70% of the acetaldehyde was mineralized to CO_2 . In fact, there was a change in trend between 5 and 9.5 h of irradiation time, which should be caused by adsorption/desorption of the gas on the surface of the sample or other factors [22, 23]. In order to observe the photocatalytic repeatability of the catalyst, the used $\text{In}_6\text{WO}_{12}$ was employed

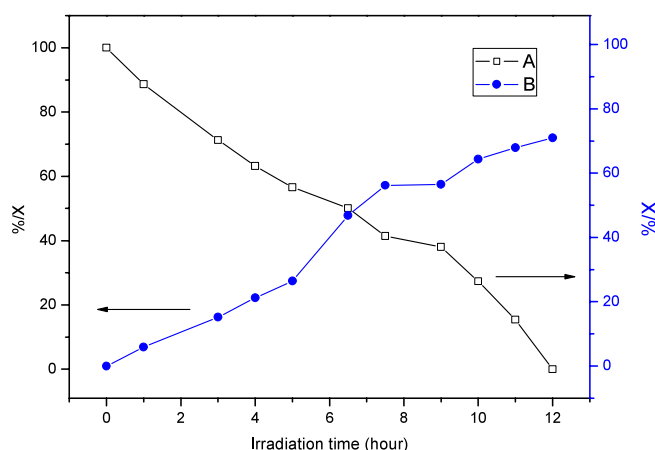


Figure 3. Photocatalytic acetaldehyde degradation at room temperature in air for 12 h (wavelength > 300 nm). (a) Degradation rate of acetaldehyde ($x\%$) over $\text{In}_6\text{WO}_{12}$. (b) Conversion rate of acetaldehyde into CO_2 ($x\%$) as a function of irradiation time.

Table 1. The experimental and calculated lattice parameters of $\text{In}_6\text{WO}_{12}$.

	Arris	Experimental data	Calculated data
Lattice parameters			
a (\AA)		6.2277	6.302
α (deg)		99.01	99.172

Table 2. The experimental and calculated coordinates of the atoms in $\text{In}_6\text{WO}_{12}$.

Atom	Wyckoff site	Experimental data			Calculated data		
		x	y	z	x	y	z
W	1a	0	0	0	0	0	0
In	6f	0.1397	0.3214	0.6044	0.1402	0.3243	0.6051
O	6f	-0.0426	0.0974	0.2969	-0.4450	0.1057	0.2980
O	6f	0.4057	0.5838	0.8219	0.4064	0.5806	0.8237

again to degrade acetaldehyde. It was found that the used $\text{In}_6\text{WO}_{12}$ showed similar activity to the fresh sample. $\text{In}_6\text{WO}_{12}$ lost its photocatalytic activity when a 420 nm cutoff filter was used, which is mainly because $\text{In}_6\text{WO}_{12}$ did not have any absorbance above 390 nm. Moreover, acetaldehyde degradation was not observed in dark conditions. Therefore the mineralization of acetaldehyde is in fact driven by light. The surface area of $\text{In}_6\text{WO}_{12}$ is about $0.8 \text{ m}^2 \text{ g}^{-1}$, which is much smaller than that of TiO_2 (about $50 \text{ m}^2 \text{ g}^{-1}$). This indicates that much higher efficiency could be expected by increasing the surface area of $\text{In}_6\text{WO}_{12}$.

The optimized lattice parameters and coordinates of the atoms in $\text{In}_6\text{WO}_{12}$ are listed in tables 1 and 2. Compared with the experimental results [24], it can be found that the calculated lattice parameters are in good accordance with the reported values. Furthermore, the calculated coordinates of the atoms in $\text{In}_6\text{WO}_{12}$ are also close to the experimental results.

The schematic crystal structure of $\text{In}_6\text{WO}_{12}$ is shown in figure 4. The ball-and-stick model and the polyhedron model for $\text{In}_6\text{WO}_{12}$ are shown in figures 4(a) and (b), respectively. We can find that in $\text{In}_6\text{WO}_{12}$ the uniform InO_6 octahedral network should be beneficial for charge transfer to the surface [25].

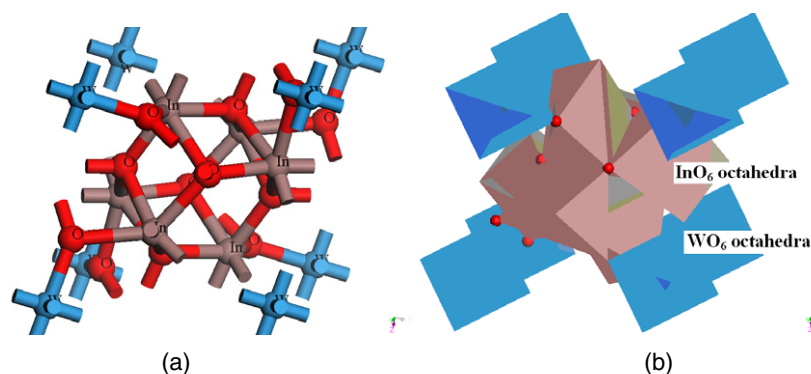


Figure 4. Schematic crystal structure of $\text{In}_6\text{WO}_{12}$: (a) ball-and-stick model; (b) polyhedron model.

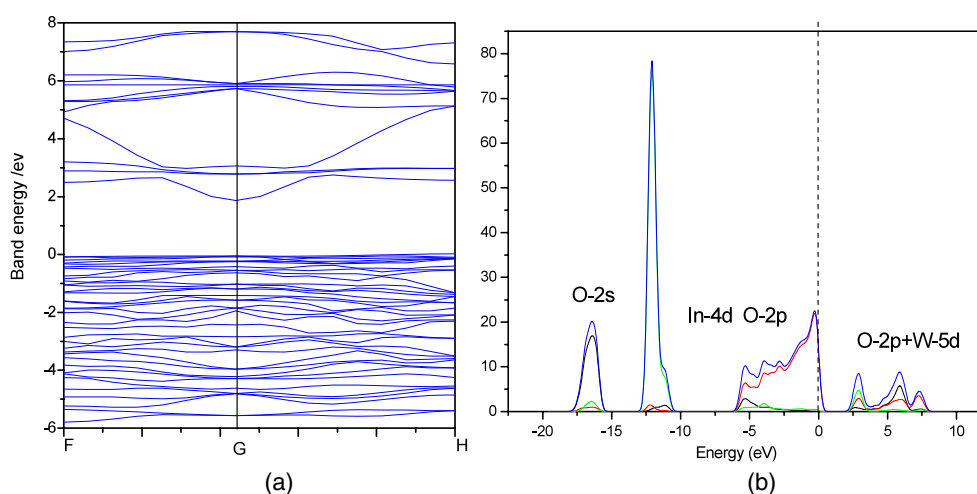


Figure 5. The energy band structure (a) and density of states (DOS) (b) of $\text{In}_6\text{WO}_{12}$.

Figure 5 shows the band structure and the total density of states (DOS) for $\text{In}_6\text{WO}_{12}$. The calculated band gap energy is 2.0 eV; the difference between the calculated value and the experimental value (3.3 eV) could be caused by neglecting the correlation effects in the CASTEP package [23]. Three occupied bands and one unoccupied band are represented in the total DOS diagrams. In the total DOS diagram of $\text{In}_6\text{WO}_{12}$, the bands consist of O 2s, In 4d, O 2p and W 5d orbitals, in turn from the lowest band to the highest band. Among them, the highest occupied band is composed of O 2p, corresponding to the valence band (VB). The lowest unoccupied band mainly comprises O 2p and W 5d orbitals, corresponding to the conduction band (CB). Doping with alkali ions should not affect the valence or conduction bands of $\text{In}_6\text{WO}_{12}$, because of the small electronegativities of such ions. But, based on previous research [2], if the O is partially substituted by N or S, there will be a narrower band gap for $\text{In}_6\text{WO}_{12}$, which will facilitate the excitation of an electron from the valence band to the conduction band in the doped oxide semiconductor under visible light irradiation, thus increasing the photocatalytic activity of the material. Some of the above-mentioned studies are currently underway in our laboratory.

4. Conclusion

We have demonstrated the photocatalytic properties of a new photocatalyst, $\text{In}_6\text{WO}_{12}$. The photocatalytic activity of $\text{In}_6\text{WO}_{12}$ was evaluated by photo-decomposing acetaldehyde. The optimized crystal structure and calculated ground-state electronic structure of $\text{In}_6\text{WO}_{12}$ were also reported. The present work also provides useful information for searching for new photocatalysts.

Acknowledgments

The authors would like to acknowledge financial support from the National Natural Science Foundation of China (nos 20603017 and 20528302), the National High Technology Research and Development Program of China (no. 2006AA05Z113), the Science and Technology Research Program of the Ministry of Education (MOE) of China (no. 307012), as well as the Jiangsu Provincial Natural Science Foundation (nos BK2006718 and BK2006127) and the Jiangsu Provincial High Technology Research Program (no. BG3006030). Professor Z G Zou and T Yu would like to thank the Jiangsu Provincial Talent Scholars Program.

References

- [1] Fujishima A and Honda K 1972 *Nature* **238** 37
- [2] Asahi R, Morikawa T, Ohwaki T, Aoki K and Taga Y 2001 *Science* **293** 269
- [3] Zou Z G, Ye J H, Sayama K and Arakawa H 2001 *Nature* **414** 625
- [4] Hoffmann M R, Martin S T, Choi W and Bahnemann D W 1995 *Chem. Rev.* **95** 69
- [5] Zhang W, He Y and Qi Q 2005 *Mater. Chem. Phys.* **93** 508
- [6] Xie Y B 2006 *Nanotechnology* **17** 3340
- [7] Fernandez J, Kiwi J, Lizama C, Freer J, Baeza J and Mansilla H D 2002 *J. Photochem. Photobiol. A* **151** 213
- [8] Zhang X, Zhou M and Lei L 2005 *Mater. Chem. Phys.* **91** 73
- [9] Guaitella O, Thevenet F, Guillard C and Rousseau A 2006 *J. Phys. D: Appl. Phys.* **39** 2964
- [10] Wang H and Lewis J P 2006 *J. Phys.: Condens. Matter* **18** 421
- [11] Rohe B, Veeman W S and Tausch M 2006 *Nanotechnology* **17** 277
- [12] Kuo W S and Ho P H 2001 *Chemosphere* **45** 77
- [13] Tang J W, Zou Z G and Ye J H 2004 *Angew. Chem. Int. Edn* **43** 4463
- [14] Tang J W, Zou Z G and Ye J H 2003 *Chem. Phys. Lett.* **382** 175
- [15] Darwent J R and Mills A 1982 *J. Chem. Soc. Faraday Trans.* **359** 78
- [16] Tang J W and Ye J H 2005 *J. Mater. Chem.* **15** 4246
- [17] Kudo A and Kato H 1997 *Chem. Lett.* **5** 421
- [18] Kudo A and Hijii S 1999 *Chem. Lett.* **10** 1103
- [19] Tang J W, Zou Z G and Ye J H 2003 *J. Phys. Chem. B* **107** 14265
- [20] Rahmane M, Krishna K, Soga T, Jimbo T and Umeno M 1999 *J. Phys. Chem. Solids* **60** 201
- [21] Segall M D, Lindan P J D, Probert M J, Pickard C J, Hasnip P J, Clark S J and Payne M C 2002 *J. Phys.: Condens. Matter* **14** 2717
- [22] Liu W, Zhang T G, Stavropoulos P and Levy B 1996 *J. Phys. Chem.* **100** 19466
- [23] Kapoor P N, Uma S, Rodriguez S and Klabunde K J 2005 *J. Mol. Catal. A* **229** 145
- [24] Michel D and Kahn A 1982 *Acta Crystallogr. B* **38** 1437
- [25] Sato J, Kobayashi H and Inoue Y 2003 *J. Phys. Chem. B* **107** 7970