Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2017

Supplementary Information

High-Pressure Zinc Oxide Phase as Visible-Light-Active Photocatalyst with Narrow Band Gap

Hadi Razavi-Khosroshahi^{1,*}, Kaveh Edalati^{2,3}, Ji Wu², Yuki Nakashima¹, Makoto Arita³, Yoshifumi Ikoma³, Masaaki Sadakiyo², Yuji Inagaki⁴, Aleksandar Staykov², Miho Yamauchi^{2,5}, Zenji Horita^{2,3} and Masayoshi Fuji¹

¹Advanced Ceramics Research Center, Nagoya Institute of Technology, Gifu, Japan

- ² International Institute for Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu University, Fukuoka, Japan
- ³ Department of Materials Science and Engineering, Faculty of Engineering, Kyushu University, Fukuoka, Japan
- ⁴Department of Applied Quantum Physics and Nuclear Engineering, Faculty of Engineering, Kyushu University, Fukuoka, Japan
- ⁵ Department of Applied Chemistry, Faculty of Engineering, Kyushu University, Fukuoka, Japan
- ⁶ Department of Mechanical Engineering, Faculty of Engineering, Kyushu University, Fukuoka, Japan

*Email: <u>razavi.khosroshahihadi@nitech.ac.jp</u> hrkhosro@gmail.com

- 1. General procedures and measurments
 - 1.1. High-pressure torsion (HPT)
 - 1.2. Photocatalytic Rhodamine B (RhB) degradation test
 - 1.3. Surface area analysis using pulsed nuclear magnetic resonance (NMR) and Brunauer-Emmett-Teller (BET) methods
- **2. Supplementary Figure 1.** TEM bright-field image, and (b) corresponding selected area electron diffraction (SAED) pattern of wurtzite powder.
- 3. Supplementary Figure 2. High-resolution TEM image of ZnO samples processed by HPT under 3 and 6 GPa. W and R refer to wurtzite and rocksalt phases, respectively.
- **4. Supplementary Figure 3.** Magnified view of XRD profiles, obtained by 24.772keV synchrotron radiation, for powder and samples processed by HPT under 3 and 6 GPa.
- **5. Supplementary Figure 4.** PL spectra, obtained using 488-nm laser excitation, for powder and samples processed by HPT under 3 and 6 GPa.
- 6. Supplementary Figure 5. Photocatalytic degeradation of RhB under UV light for powder and samples processed by HPT under 3 and 6 GPa (ΔC : degraded amount of RhB, C_0 : initial concentration of RhB).
- **7. Supplementary Figure 6.** Identical mass amount of ZnO powder before and after HPT processing used for photocatlytic degradation test.
- **8.** Supplementary Figure 7. XRD profile, obtained by CuKα radiation, for sample processed by HPT under 6 GPa after photocatalytic degradation test.
- **9.** Supplementary Figure 8. XRD profiles, obtained by CuKα radiation, for sample processed by HPT under 6 GPa after irradiation by Cukα X-ray for 160 and 320 min.
- **10.** Supplementary Figure 9. UV-vis diffused reflectance spectra of sample processed by HPT under 6 GPa before and after irradiation by Cuk α X-ray for 320 min.

- **11. Supplementary Figure 10.** XRD profiles, obtained by CuKα radiation, for sample processed by HPT under 6 GPa before UV irradiation and after UV irradiation for 33 days.
- 12. Supplementary Figure 11. Photocatalytic degeradation of RhB under UV light for anatase TiO₂ powders with two different particle sizes after normalizing by (a) powder mass and (b) surface area (ΔC : degraded amount of RhB, C_0 : initial concentration of RhB).
- **13. Supplementary Figure 12.** Photocatalytic degeradation rate of RhB under UV light for ZnO processed by HPT under 3 and 6 GPa compared with that for anatase TiO₂ powders with 20 nm and 500 nm particle sizes (ΔC : degraded amount of RhB, C_0 : initial concentration of RhB).
- **14. Supplementary Figure 13.** Magnetization curves at room temperature for powder and for sample processed by HPT under 6 GPa.
- **15. Supplementary Table 1.** Reported band gaps of ZnO processed with some representative methods.
- **16. Supplementary Table 2.** Specific surface area measured by BET and pulsed NMR, grain size measured by TEM, and morphology of grains for ZnO powder and samples processed by HPT under 3 and 6 GPa.
- **17. Supplementary Table 3.** Calculated and experimental band gaps together with calculated lattice parameters for wurtzite and rocksalt phases without oxygen vacancy and with 6.25% of oxygen vacancies.

18. References

1. General procederes and measurments

1.1. High-pressure torsion (HPT)

The facility of high-pressure torsion (HPT) contained one pair of anvils with 50 mm diameter and 50 mm height. At the center of each anvil, there was a shallow hole with 10 mm diameters and 0.25 mm depth. The HPT anvils were made from a hard WC-11 wt% Co composite which allow processing the hard ZnO samples. Almost 0.5 g of commercially pure (99.8%) ZnO powder with an average particle size of ~20 nm was placed inside the lower anvil hole and compressed between the upper and lower anvils under the loads of 25 and 50 tons, which corresponds to nominal pressures of 3 and 6 GPa, respectively. The lower anvil was then rotated for N = 3 turns with respect to the upper anvil at room temperature with a rotation speed of 1 rpm. Powders were significantly compacted after HPT processing and discs with 10 mm diameter and 0.8 mm thickness were formed.

1.2. Photocatalytic Rhodamine B (RhB) degradation test

Photocatalytic activity of ZnO samples before and after HPT processing was examined by measuring the degradation rate of Rhodamine B (RhB) both under UV and visible light irradiation. A high-pressure Mercury lamp (Ushio, 500 W) was used as the UV light source and a Xenon lamp (Caster, 500 W) equipped with a 400 nm UV cutoff filter was used as the visible light source. The degradation test was maintained at room temperature by a cooling water circulation. Almost 10 mg of the ZnO photocatalyst mixed with 50 mg/L of RhB (300 mL) and the suspension was stirred in the dark for 2 h prior to light irradiation, in order to make sure that an adsorption-desorption equilibrium was reached. After light irradiation, 5 mL of suspension was sampled every 20 min, centrifuged, and the concentration of RhB solution was measured by using UV-vis spectrophotometer. After finishing the photocatalytic test, the ZnO samples were examined by X-ray diffraction (XRD) analysis to examine the stability of phases. Moreover, the active surface area of samples was examined by the Brunauer-Emmett-Teller (BET) method and by the pulsed nuclear magnetic resonance (NMR) technique, as described below.

1.3. Surface area analysis using pulsed nuclear magnetic resonance (NMR) and Brunauer-Emmett-Teller (BET) methods

Since the photocatalytic RhB degradation experiments were conducted in water, it is of importance to evaluate the surface area of powders in water. Therefore, in this study

pulsed nuclear magnetic resonance (NMR) method, in which the surface area is measured in water, is more appropriate than the Brunauer-Emmett-Teller (BET) method, in which the surface area of dry powders is measured by nitrogen gas absorption.

Surface area measurement by pulsed NMR is based on the evaluation of bound water in contact with the surface of ZnO. Since water molecules bound to ZnO have significantly shorter relaxation rate than that of free water molecules, the surface area can be measured by evaluation of relaxation rate.^{1, 2} After photocatalytic hydrogen generation test, 1 mL of sample mixture was inserted into an Acorn AreaTM, Xigo instrument and the surface area was measured by exciting the samples using a short radio frequency of 14 MHz. In addition, the BET specific surface area was also measured with a Belsorp-Max instrument, using the adsorption of nitrogen gas.



Supplementary Figure 1. TEM bright-field image and (b) corresponding selected area electron diffraction (SAED) pattern of wurtzite powder.

Note: The starting powder contains only wurtzite phase with an average grain size of 24 ± 10 nm.



Supplementary Figure 2. High-resolution TEM image of ZnO samples processed by HPT under 3 and 6 GPa. **W** and **R** refer to wurtzite and rocksalt phases, respectively.

Note: The average grain sizes are reduced to 12±5 and 11±5 nm after HPT processing under 3 and 6 GPa, respectively. It is found that the rocksalt phase disappears quickly under electron beam irradiation during TEM observations and transforms to the wurzite phase.



Supplementary Figure 3. Magnified view of XRD profiles, obtained by 24.772-keV synchrotron radiation, for powder and samples processed by HPT under 3 and 6 GPa.

Note: Magnified view of a XRD profiles confirms that peaks corresponding to the 002 and 101 planes of wurtzite phase shift to lower angles after HPT processing due to the lattice expansion. These shifts to lower angles correspond to the formation of oxygen vacancies.

5. Supplementary Figure 4



Supplementary Figure 4. PL spectra, obtained using 488-nm laser excitation, for powder and samples processed by HPT under 3 and 6 GPa.

Note: A broad and weak PL orange emission, which is observed at 587 nm after HPT processing, is due to recombination of photo-excited holes and ionized oxygen vacancies.



Supplementary Figure 5. Photocatalytic degeradation of RhB under UV light for powder and samples processed by HPT under 3 and 6 GPa (ΔC : degraded amount of RhB, C_0 : initial concentration of RhB).

Note: The photocatalytic activity improves after HPT processing, while the improvement is more significant for the samples processed under 6 GPa due to the formation of rocksalt phase.



Supplementary Figure 6. Identical mass amount of ZnO powder before and after HPT processing used for photocatlytic degradation test.

Note: The volume of sample decreases significantly after HPT processing due to the consolidation of powders.



Supplementary Figure 7. XRD profile, obtained by $CuK\alpha$ radiation, for sample processed by HPT under 6 GPa after photocatalytic degradation test.

Note: The HPT-processed ZnO powder was collected and dried after photocatalytic test and examined by XRD. The XRD profile confirms that the rocksalt phase remained stable during the photocatalytic test.

9. Supplementary Figure 8



Supplementary Figure 8. XRD profiles for sample processed by HPT under 6 GPa after irradiation by Cukα X-ray for 160 and 320 min.

Note: The rocksalt phase is unstable when it is irradiated by high energy light sources such as CuK α X-ray. The rocksalt phase almost disappears when the irradiation time is 320 min.



Supplementary Figure 9. UV-vis diffused reflectance spectra of sample processed by HPT under 6 GPa before and after irradiation by Cuk α X-ray for 320 min.

Note: The visible-light absorbance and the absorbance-edge wavelength are reduced after irradiation by Cuk α X-ray for 320 min because of the iradiation-induced rocksalt-to-wurtzite phase transformation, as shown in supplementary Fig. 8.



Supplementary Figure 10. XRD profiles, obtained by CuK α radiation, for sample processed by HPT under 6 GPa before UV irradiation and after UV irradiation for 33 days.

Note: Long-term stability of rocksalt phase was examined by irradiating UV light to the sample processed by HPT under 6 GPa stirred in water by using a magnetic stirrer for 33 days. Comparing XRD profile before and after UV irradiation confirms that the rocksalt phase is stable under UV light for at least 33 days.



Supplementary Figure 11. Photocatalytic degeradation of RhB under UV light for anatase TiO₂ powders with two different particle sizes after normalizing by (a) powder mass and (b) surface area (ΔC : degraded amount of RhB, C_0 : initial concentration of RhB).

Note: Photocatalytic test was conducted on TiO_2 powders with the same crystal structure as anatase but with different particle sizes: (i) 20 nm with a surface area of 46

 m^2/g measured by the BET method, and (ii) 500 nm with a surface area of 8.1 m^2/g measured by the BET method. It is shown that photocatalytic reaction rate normalized by mass of TiO₂ is greater for the particle size of 20 nm when compared to that for the particle size of 500 nm. However, when the reaction rate was normalized by the surface area of each powder, both TiO₂ powders showed reasonably identical photocatalytic activity. These results suggest that the reaction rates should be normalized by the surface area to have a logical comparison between the photocatalytic activity of samples before HPT, and after HPT processing where a significant compaction occurs after HPT.



Supplementary Figure 12. Photocatalytic degeradation rate of RhB under UV light for ZnO processed by HPT under 3 and 6 GPa compared with that for anatase TiO₂ powders with 20 nm and 500 nm particle sizes (ΔC : degraded amount of RhB, C_0 : initial concentration of RhB).

Note: Photocatalytic activity of the rocksalt phase under UV light is clearly better than that of the wurtzite phase, and even better than the photocatalytic activity of anatase TiO_2 powders with particle sizes of 20 nm and 500 nm. It should be noted since the anatase phase can only absorb UV light, the photocatalytic activities were not compared under the visible light.



Supplementary Figure 13. Magnetization curves at room temperature for powder and for sample processed by HPT under 6 GPa.

Note: Magnetic properties of samples before HPT processing and after HPT processing were examined experimentally by using a superconducting quantum interference device (SQUID) magnetometer at room temperature. As can be seen, the powder sample before HPT processing shows no magnetic moment. However, the sample after HPT processing under 6 GPa, indicates a hysteresis curve with a very small saturation magnetic moment. This value is ~0.001 emu/g (~10⁻⁵ Bohr), which is an extremely small value and usually is neglected within the detection limits of the SQUID magnetometer.

15. Supplementary Table 1

Supplementary Table 1. Reported band gaps of ZnO processed with some representative methods.

Sample	Method	Band gap	Reference
		(eV)	
Silver modified ZnO	Liquid-phase process	3.00	3
Manganese doped ZnO	Aerosol spray pyrolysis	3.25	4
Oxygen vacancy induced ZnO	Vacuum deoxidation	2.85	5
	method		
Defect induced ZnO	Ball milling	2.60	6
Self-doped ZnO microrods	Liquid-phase process	3.05	7
Oxygen vacancy induced ZnO	Sol-gel	2.83	8
Carbon doped ZnO	Urea-assisted thermal	2.50	9
	decomposition		
Nitrogen doped ZnO thin film	Sputter deposition	1.75	10
Graphene hybridization of	In-situ reduction	3.09	11
ZnO			
Nitrogen doped ZnO	Heating ZnOHF under	1.95	12
	ammonia atmosphere		
Core/shell ZnO/CdS	Sol-gel	2.63	13
Bi ₂ O ₃ -ZnO heterostructure	Hydrothermal-thermal	3.09	14
	decomposition		
GaN:ZnO solid solution	Nitridation of ZnO	2.58	15
ZnO/CeO ₂ nanocomposite	Thermal decomposition	2.90	16
	method		
Carbon doped ZnO	Polymer assisted pyrolysis	2.98	17
Oxygen vacancy induced ZnO	Biogenic modification of	3.05	18
	ZnO by biofilm		

Note: The band gap achieved by stabilizing the high-pressure ZnO phase is the lowest level reported for pure ZnO so far. It should be noted that the band gaps were roughly estimated from UV-Vis spectra in the publications that the band gaps were not reported.

16. Supplementary Table 2

Supplementary Table 2. Specific surface area measured by BET and pulsed NMR, grain size measured by TEM, and morphology of grains for ZnO powder and samples processed by HPT under 3 and 6 GPa.

	Surface Area (m ² /g)		Morphology	Average Grain	
	BET	Pulsed NMR		Size (nm)	
Powder	35.34	44.41	Spherical	24 ± 10	
P = 3 GPa	2.28	1.80	Spherical	12 ± 5	
P = 6 GPa	1.83	0.96	Spherical	11 ± 5	

Note: The surface area is reduced after HPT processing due to the consolidation of powders, while the average grain size is also reduced due to the effect of large plastic strain.

17. Supplementary Table 3

Supplementary Table 3. Calculated and experimental band gaps together with calculated lattice parameters for wurtzite and rocksalt phases without oxygen vacancy and with 6.25% of oxygen vacancies.

Converted stress etcome	Supercell ·	Band gap (eV)		Lattice Parameters		
		Cal.	Exp.	a (Å)	b (Å)	c (Å)
Ideal Wurtzite	2 x 2 x 2	3.22	3.1	3.279	3.279	5.159
Wurtzite + O vacancy	2 x 2 x 2	2.91	2.8	3.260	3.260	5.230
Ideal Rocksalt	2 x 2 x 1	3.25	-	4.314	4.314	4.314
Rocksalt + O vacancy	2 x 2 x 1	1.73	1.9	4.307	4.307	4.311

Note 1: Errors are less than 1%. The ideal lattices are calculated based on $Zn_{16}O_{16}$ super lattice ZnO in Wurtzite and Rocksalt phases. The oxygen vacancy setups are created by removing one oxygen atom from the $Zn_{16}O_{16}$ super lattices. It is evident that the rocksalt phase containing oxygen vacancies exhibit excellent band gap for visible-light absorbance.

Note 2: The band gap estimated by calculations for the oxygen deficient cases is smaller than that of defect-free cases. It is mainly caused by the creation of extra electron states in the forbidden gap of the ideal oxides, due to the introduction of the oxygen vacancies. When an oxygen vacancy is created in the super lattice, charge neutrality condition requires the two electrons, which used to be on the orbitals of the removed O^{2-} ion, to stay in the supercell. Therefore, these two electrons must find new states to suit themselves, and these newly created states are usually higher in energy than the valence energy levels of the ideal lattice. Hence, these new states are usually in the band gap of the ideal lattice and reduce the band gap for the defected lattice, as can be seen in the plots of density of states in Figures 4(a-d). This band gap reduction due to the oxygen vacancy is commonly observed in periodic crystals, both experimentally and computationally. For example, band gap reductions due to oxygen vacancy was reported in wurtzite ZnO,¹⁹ tetragonal ZrO₂²⁰ and anatase TiO₂.²⁰

Note 3: Both wurtzite and rocksalt phases were considered as periodic crystals for both the primitive cells and the supercells cases. Due to the high symmetry of both phases, most of the possible oxygen vacancy sites are symmetry-related and therefore are symmetrically identical. For the periodic wurtzite phase, there are only two irreducible symmetry sites for oxygen, while all oxygen sites are symmetrically equivalent in the rocksalt phase. The calculations of the total lattice energies and band gaps of the wurtzite and rocksalt phases with different oxygen vacancy positions show that the total energies for the different defect sites only differ by less than 0.005 eV for the wurtzite phase and less than 0.003 eV for the rocksalt phase. Also, calculated band gaps differ by less than 0.002 eV for the wurtzite defect cases and less than 0.03 eV for the rocksalt defect cases. This high degree of consistency agrees well with the assumption of periodic crystals with high symmetry, as the coordination and chemical environments surrounding these symmetry-related oxygen vacancy sites are almost identical.

18. References

- 1. H. Y. Carr and E. M. Purcell, *Phys. Rev.*, 1954, **94**, 630-638.
- 2. S. Meiboom and D. Gill, *Rev. Sci. Instrum.*, 1958, **29**, 688-691.
- 3. R. Georgekutty, M. K. Seery and S. C. Pillai, *J. Phys. Chem. C*, 2008, **112**, 13563-13570.
- D. E. Motaung, I. Kortidis, D. Papadaki, S. S. Nkosi, G. H. Mhlongo, J. Wesley-Smith, G. F. Malgas, B. W. Mwakikunga, E. Coetsee, H. C. Swart, G. Kiriakidis and S. S. Ray, *Appl. Surf. Sci.*, 2014, **311**, 14-26.
- Y. Lv, C. Pan, X. Ma, R. Zong, X. Bai and Y. Zhu, *Appl. Catal. B-Environ.*, 2013, 138, 26-32.
- D. Chen, Z. Wang, T. Ren, H. Ding, W. Yao, R. Zong and Y. Zhu, J. Phys. Chem. C, 2014, 118, 15300-15307.
- 7. S. G. Ullattil, P. Periyat, B. Naufal and M. A. Lazar, *Ind. Eng. Chem. Res.*, 2016, 55, 6413-6421.
- J. Wang, Z. Wang, B. Huang, Y. Ma, Y. Liu, X. Qin, X. Zhang and Y. Dai, *ACS Appl. Mater. Interfaces*, 2012, 4, 4024-4030.
- X. Zhang, J. Qin, R. Hao, L. Wang, X. Shen, R. Yu, S. Limpanart, M. Ma and R. Liu, J. Phys. Chem. C, 2015, 119, 20544-20554.
- 10. K.-S. Ahn, Y. Yan, S. Shet, T. Deutsch, J. Turner and M. Al-Jassim, *Appl. Phys. Lett.*, 2007, **91**, 231909.
- 11. X. Bai, L. Wang, R. Zong, Y. Lv, Y. Sun and Y. Zhu, *Langmuir*, 2013, **29**, 3097-3105.
- 12. X. Zong, C. Sun, H. Yu, Z. G. Chen, Z. Xing, D. Ye, G. Q. Lu, X. Li and L. Wang, J. *Phys. Chem. C*, 2013, **117**, 4937-4942.
- S. Khanchandani, P. K. Srivastava, S. Kumar, S. Ghosh and A. K. Ganguli, *Inorg. Chem.*, 2014, **53**, 8902-8912.
- 14. S. Balachandran and M. Swaminathan, J. Phys. Chem. C, 2012, 116, 26306-26312.
- 15. K. Maeda, T. Takata, M. Hara, N. Saito, Y. Inoue, H. Kobayashi and K. Domen, *J. Am. Chem. Soc.*, 2005, **127**, 8286-8287.
- S. Rajendran, M. M. Khan, F. Gracia, J. Qin, V. K. Gupta and S. Arumainathan, *Sci. Rep.*, 2016, 6, 31641.
- A. S. Alshammari, L. Chi, X. Chen, A. Bagabas, D. Kramer, A. Alromaeh and Z. Jiang, *RSC Adv.*, 2015, 5, 27690-27698.
- S. A. Ansari, M. M. Khan, S. Kalathil, A. Nisar, J. Lee and M. H. Cho, *Nanoscale*, 2013, 5, 9238-9246.

- Y. Lv, W. Yao, X. Ma, C. Pan, R. Zong and Y. Zhu, *Catal. Sci. Technol.*, 2013, 3, 3136-3146.
- 20. H.-Y. T. Chen, S. Tosoni and G. Pacchioni, J. Phys. Chem. C, 2015, 119, 10856-10868.