

# Mechanochemical Doping of a Non-Metal Element into Zinc Oxide

J. WANG, J. F. LU, Q. W. ZHANG, S. YIN, T. SATO and F. SAITO

*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University,  
Katahira 2-1-1, Aobaku, Sendai, 980-8577 (Japan)*

E-mail: zhangqw@tagen.tohoku.ac.jp

## Abstract

We developed a method for narrowing the band gap in an oxide powder such as ZnO by doping other components such as S (sulphur) and N (nitrogen). The method consists of grinding a mixture of ZnO powder and non-metal element in air, followed by heating the milled sample at 400 °C. The former enables us to cause mechanochemical reaction between the components, and the latter allows us to enhance the bonding strength, as well as to remove the unreacted starting samples away from the surface of the oxide particles. The temperature has to be chosen in the heating operation so as to avoid any decomposition of the doped sample. The detailed information on doping S and N into ZnO powder, as well as its photo-catalytic reactivity, is shown in this report.

## INTRODUCTION

Photocatalytic reactions of semiconductors, such as decomposition of pollutants in water and air, have received great attention around the world for several decades. Most semiconductors are active only in the ultraviolet (UV) region because of the wide band gap. Now, it has become a target of researchers to extend the high reactivity of the photocatalysts towards the visible light range. Doping in order to narrow the band gap was fully investigated. Titanium dioxide ( $\text{TiO}_2$ ), for example, has been doped with not only various transition metal cations but also nonmetal elements such as nitrogen [1], fluorine [2], sulphur [3], and carbon [4]. Activity of the doped  $\text{TiO}_2$  samples in the visible-light region was demonstrated together with the shift of absorption edge of the light to a lower energy region.

Mechanochemical methods were employed to dope non-metal elements into oxide fine particles [5, 6]. In general, when a solid is ground with another material by using a high-energy ball mill, a solid-state reaction will occur between them, being accompanied by particle size

reduction down to the nanoscale. The mechanically induced solid-state reaction starts from particle surfaces and the yield is improved with an increase in milling time, as well as an increase in the energy input from the mill.

Zinc oxide (ZnO) is known to have piezoelectric, electron conductivity and transparent properties [7, 8]. These properties allow the material to be applied as catalysts, sensors, fluorescent and antibacterial materials. Much attention was paid to prepare a *p*-type ZnO by doping nitrogen and gallium into ZnO. Many methods, such as pulsed laser deposition, molecular beam epitaxy and metal oxide chemical vapour deposition, were proposed to deposit N-doped ZnO, and further investigations were made to understand the basic properties of nitrogen-doped ZnO. The main purpose of this paper is to provide information on the synthesis of nitrogen-doped and S-doped ZnO fine particles by means of mechanochemical operation, followed by calcining the ground products at 400 °C. In addition, characterizations such as light absorbance in visible light wavelength region and photocatalytic ability in antibacterial tests for the prepared ZnO sample were examined.

## EXPERIMENTAL PROCEDURE

The starting samples used in this work were ZnO, sulphur and urea ( $\text{CO}(\text{NH}_2)_2$ ) supplied by Wako Pure Chemical Industries (Osaka, Japan). Four grams of the mixtures of ZnO and sulphur (10 mass %) or urea at different molar ratios were put into a zirconia pot (45 cm<sup>3</sup> inner volume) with seven zirconia balls (15 mm in diameter), and they were subjected to grinding using a planetary ball mill (Fritsch Pulversette 7, Idar-Oberstein, Germany) at the rotational speed of 700 rpm for various periods of time in air. A reference sample was prepared by hand grinding using an agate mortar with a pestle. The ground samples and the reference sample were calcined at 400 °C for 1 h in air flow for nitrogen doping and in Ar gas flow for sulphur doping.

The phase constitutions of the ground samples and calcined products were characterized by an X-ray diffraction analyzer (XRD) (Rigaku, RAD-B system, Tokyo, Japan). The bonding state of sulphur to zinc in the prepared samples was investigated by X-ray photoelectron spectroscopic analysis (XPS, PHI 5600 ESCA system, Ulvac-Phi Inc., Japan). Raman spectroscopic measurement was conducted to characterize the nitrogen doped ZnO sample (Model INF-300, Horiba, Japan). Light reflectance spectra of the products were recorded using a UV-VIS spectrometer (Model Lambda 35, Perkin Elmer, USA) in the range of wavelength from 190 to 800 nm. The pho-

tocatalytic ability in antibacterial test was carried out using the photo irradiation film covering method. A bacterial solution prepared with 1/500 ordinary bouillon and the prepared ZnO sample was dripped on the surface of a test strip, and this was adhered with film and stored while being irradiated with fluorescent light at 35 °C for 24 h. The number of bacteria on the test strip was measured. At the same time, as a reference, the test of bacterial solution without the prepared ZnO sample was carried out. The antibacterial activity can be evaluated by the decrease in numbers of remaining bacteria.

## RESULTS AND DISCUSSION

### *Preparation of sulphur-doped ZnO*

Figure 1 shows the XRD patterns of the prepared S-doped ZnO samples with various grinding times. With an increase in grinding time, the peak intensity of ZnO phase was observed to decrease, and the peaks broadened correspondingly. This means that the crystalline size of ZnO particles reduced by the grinding operation. A more interesting phenomenon is that peak shift to lower angle was clearly observed with an increase in grinding time. The peak shift to a smaller angle suggests that larger atoms of sulphur were doped into the ZnO crystal structures, leading to the expansion of crystalline planes as a result.

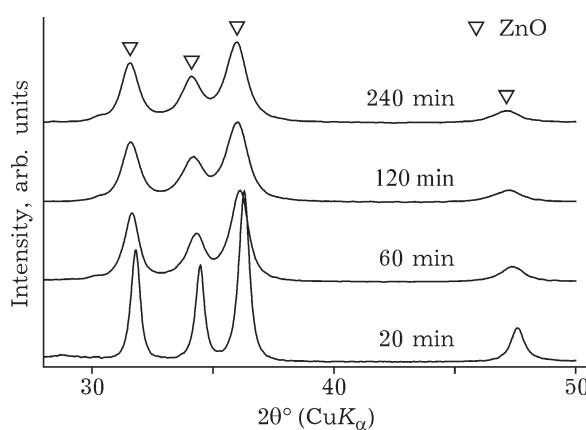


Fig. 1. XRD patterns of the sulphur-doped samples with various grinding times.

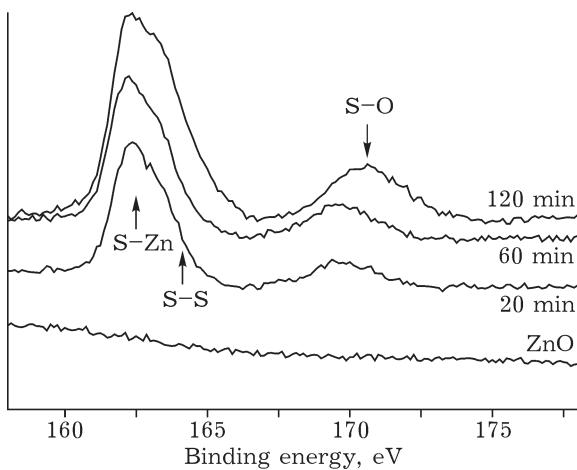


Fig. 2. XPS spectra of the sulphur-doped samples with various grinding times.

Figure 2 shows the XPS spectra of the prepared S-doped ZnO samples with various grinding times. Compared with the spectrum of the original ZnO sample where no information on S 2p was detected, the prepared samples exhibit several peaks in the spectra related to the sulphur bondings, and the peak intensity increases with an increase in grinding time. Peak positioned around 170 eV results from the S–O bonding due to the absorbed SO<sub>2</sub> molecules on TiO<sub>2</sub> surface. The peak around 162 eV results from bonding between S and metal (here zinc), confirming that sulphur was combined with zinc rather than only absorbed on the surface. The satellite of the large peak around 162 eV suggests the existence of peak positioned at 164 eV, which corresponds to sulphur itself. The XPS spectroscopic analysis indicates the doping of sulphur atoms into the ZnO crystal structures and the complicated existence states of sulphur composition in the prepared samples.

Figure 3 shows the UV-visible absorbance curves of the prepared samples. Compared with the original ZnO sample in which absorbance occurs only in the ultraviolet range under 400 nm, extension of the absorbance was clearly observed with the prepared samples forward into the visible range with wavelength as long

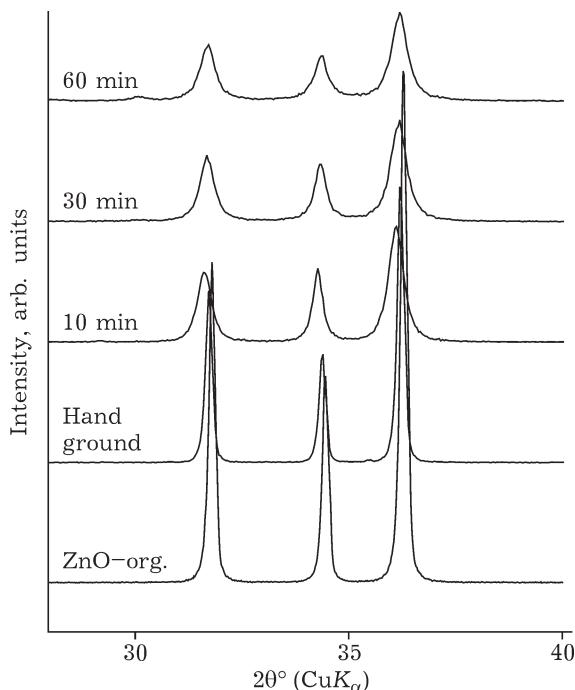


Fig. 4. XRD patterns of the mixture of ZnO and 5 % urea ground for different periods of time.

as 500 nm. The extension of absorbance reflects the doping effects of sulphur confirmed both by XRD and XPS analyses.

#### Preparation of nitrogen-doped ZnO

Figure 4 shows XRD patterns of the mixture of ZnO and 5 % urea ground for different periods of time, together with the ZnO sample and the mixture prepared by hand mixing using an agate mortar with a pestle. When compared to the XRD pattern of the ZnO sample, the patterns of the ground mixtures are clearly seen to be broad, and the peak intensities decrease with an increase in grinding periods of time. This indicates that disordering of the crystallines of ZnO sample is facilitated. In addition, there is no new peak formed in these patterns of the ground products. However, it is seen that each peak position is slightly shifted towards a lower angle. According to the additional XRD analysis for the 1 h ground mixtures at different urea ratios: 0 % (ZnO-0), 1 % (ZnO-1), 2 % (ZnO-2), 5 % (ZnO-5), 10 % (ZnO-10), a similar shift in the peak position was observed, in contrast to the peak of sample 0 % (ZnO-0). These results indicate that ZnO and urea do not exist just as a mixture after

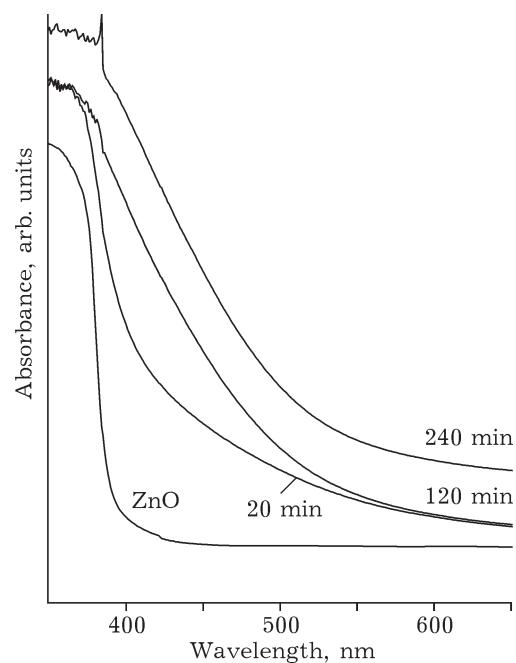


Fig. 3. UV-visible absorbance spectra of the sulphur-doped samples with various grinding times.

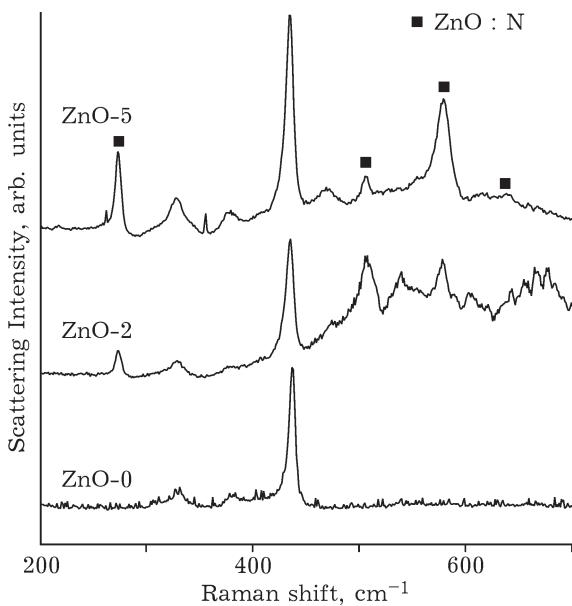


Fig. 5. Raman spectra of the products calcined at 400 °C after grinding the mixtures for 1 h.

grinding operation. A kind of reaction is expected to occur, resulting in the crystalline change of ZnO. One possible suggestion could be a slight intercalation of urea molecules into the ZnO crystals, leading to expansion of crystalline planes in ZnO structure.

Figure 5 shows the Raman spectra of the calcined products prepared from the mixture of ZnO ground with three different molar ratios of urea, 0, 2, and 5 %. In the spectrum of the product without urea addition, one sharp peak attributable to the typical E2 mode of wurtzite ZnO phase can be seen. However, regarding to other spectra of the products with urea, four new peaks positioned at 275, 506, 579 and 642 cm<sup>-1</sup> can be seen, and these are identified as N-related local vibrational modes (LVM) [9]. This is the direct evidence for N-doping to ZnO, and the intensity of these peaks increases correspondingly with an increase in the amount of urea added. This suggests that the amount of N doped into ZnO can be controlled by changing the ratio of urea in the mixture.

Figure 6 shows the Raman spectra of the calcined products of ZnO-5 after grinding for different periods of time. The spectra of the original ZnO and the hand ground samples are shown in this Figure. The spectrum of the hand ground sample is the same as that of the orig-

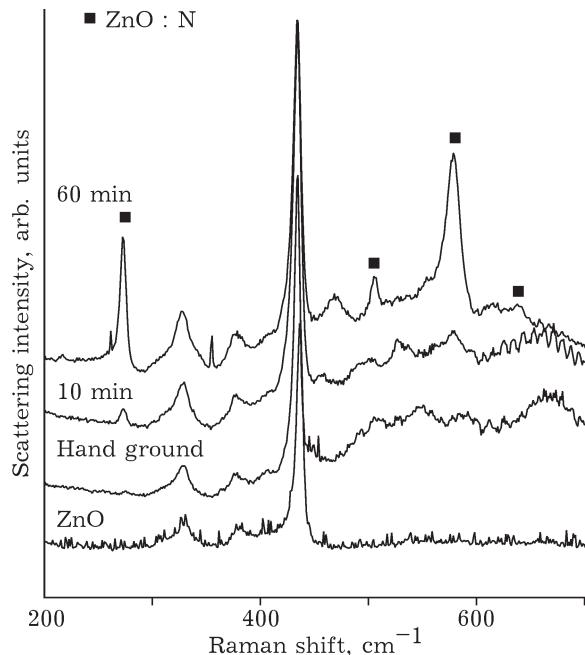


Fig. 6. Raman spectra of the products calcined at 400 °C after grinding the mixture of ZnO and 5 % urea for different times.

inal ZnO sample, and no other peaks corresponding to the N-related LVM are observed in these two spectra. This means that the calcination of the mixture of ZnO and urea does not cause any reaction, and only urea is simply burnt out by 400 °C. Thus, N cannot be doped into ZnO only by calcining the mixture at this temperature. On the contrary, the N-related LVM are observed in the spectra of the calcined products, and the peak intensity increases with an increase in grinding periods of time. This means that N was doped into ZnO when ZnO and urea were ground together before calcination, and the doped amount of N would increase as the grinding progresses. Taking the results shown in Figs 4 and 6 into account, it is clear that chemical bonding between Zn and N is strengthened by the combination of grinding and calcination. Zn–N bonding is not formed by calcination at 400 °C without grinding operation. Grinding operation stimulates chemical bonding between the two elements to form a precursor, and this precursor is solidified by thermal treatment. The extra urea is burnt out, leaving N-doped ZnO as a product.

Figure 7 shows SEM photograph of the calcined product after grinding the ZnO-5 mixture for 1 h. It is obviously noted that the sam-

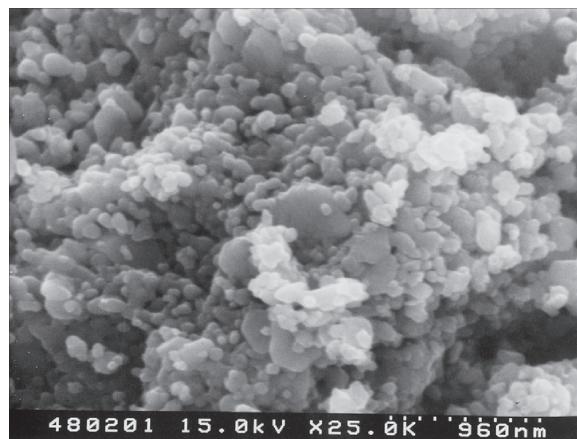


Fig. 7. SEM image of the calcined product after grinding the mixture of ZnO and 5 % urea for 1 h.

TABLE 1  
Change in the number of remaining bacteria over time

Bacteria	Initial	24 h	Reference
<i>St. aureus</i>	$1.7 \times 10^5$	<10*	$2.0 \times 10^4$
<i>E. Coli</i>	$2.2 \times 10^5$	<10*	$1.7 \times 10^7$

\*Not detected.

ple consists of agglomerates with primary particles having a few ten nanometers in size. From the width at half maximum intensity from XRD patterns, the calculated crystalline grain size is also in nanorange.

The N-doped ZnO was tested for antibacterial activity using photo irradiation film covering method. The killing effect of the sample on *Escherichia coli* and *Staphylococcus aureus* was examined. The results are shown in Table 1. When the doped ZnO was used, the existence

of remaining bacteria was hardly detected, compared with the tremendous numbers of bacteria left in the reference test. Intensive antibacterial evaluations, as well as other photocatalytic investigations, are planned to understand the correlation between antibacterial activity and doping effect.

## CONCLUSION

This paper shows the information on the synthesis of doped ZnO by the mechanochemical treatment and subsequent heating of the ground samples at quite a low temperature. Various analytical methods have confirmed that ZnO was doped successfully with nitrogen and sulphur. Grinding operation plays an important role in doping non-metal elements into the oxide.

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