

Structural-Dependent Photocatalytic Properties of Zinc Oxide

Ilya M. Sosnin

Institute of Advanced Data Transfer Systems, ITMO University, Kronverksky Pr. 49, bldg. A, St. Petersburg 197101, Russia

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Abstract. The present paper describes the effect of the structure of zinc oxide on its optical, electrical and photocatalytic properties. Examples of the influence of defects and lattice symmetry on photocatalytic activity are given. It is shown that oxygen vacancies allow to increase the rate of photocatalytic reaction due to donor properties and faceting allows to change the photocatalytic activity due to anisotropy of electric conductivity of zinc oxide. The mechanism of the influence of the dislocations and complex defects on zinc oxide photocatalytic properties is proposed. The present data can be used for development of photocatalysts based on zinc oxide, and for describing the photocatalytic properties of other semiconductors.

1. INTRODUCTION

Photocatalytic technology of water and air purification allows to reduce concentration of toxic substances below threshold limit value without formation of by-products. The purification is based on chemical degradation of pollutants interacting with photoelectrons on the surface of semiconductor nano- and microparticles. Behavior of electrons in a photocatalyst is determined by the most important semiconductor properties, such as band structure, electron mobility, carrier concentration, absorption coefficient of electromagnetic radiation, etc.

Overwhelming majority of photocatalysts have a crystal structure so their properties are directly dependent on lattice symmetry according to the Curie's principle [1]. Faceting of semiconductor particles influences the intensity of photocatalysis [2]. Moreover, photocatalytic properties of semiconductors are dependent on lattice distortions such as point defects [3,4], dislocations [5,6], grain boundaries [7]. At the present time there is no consensus on how structure of semiconductor impacts its photocatalytic properties. Comparison of optical and electronic properties of

semiconductor with the intensity of photocatalytic reaction can be used to reply to this scientific question and to design the photocatalysts for industrial and ecological application.

Zinc oxide is one of the most mentioned photocatalysts due to high effectiveness, low cost, and low toxicity. In this paper we review the structure and photocatalytic properties of zinc oxide. It is shown how morphology, crystal structure and lattice distortions of zinc oxide nano- and microparticles influence the rate of photocatalytic reaction.

2. ZINC OXIDE AND ITS APPLICATIONS

Only one allotropic modification of zinc oxide is stable at ambient conditions [8]. This modification has the wurtzite structure (Fig. 1) and it is described with space group $P6_3mc$, which belongs to hexagonal crystal system. There is one unique direction $[0001]$ in the crystal so zinc oxide displays anisotropy of structure and properties. Unit cell of wurtzite includes two interpenetrate hexagonal prisms, which have a six-fold rotate axis coinciding with the unique direction. Each of

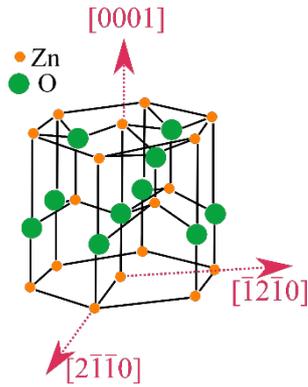


Fig. 1. Structure of unit cell of wurtzite-like zinc oxide.

these prisms consists of atoms of the same kind, therefore the crystal consists of oxygen and zinc sub-cells. Each anion is surrounded with four cations and vice versa, this tetrahedron coordination of atoms in unit cell means formation of sp^3 hybridization of atomic orbitals, which causes a chemical bond to take intermediate place between covalent and ionic types [9]. Combination of such chemical bond with non-centrosymmetric structure of wurtzite promotes pronounced piezoelectric properties of zinc oxide. In comparison with other wurtzite-like semiconductors zinc oxide has the largest piezoelectric constants [10].

Tensor of wurtzite piezoelectric constants has three independent components $e_{33} = 1.321$ C/m², $e_{31} = -0.573$ C/m² and $e_{15} = -0.48$ C/m² [11]. In a case of mechanical load along [0001] direction components e_{33} and e_{31} correspond to polarization caused by longitudinal and transverse deformation, respectively. The third component e_{15} describes the polarization arising as a result of shear deformation.

Zinc oxide is a direct bandgap semiconductor. The electrical resistivity of defect-free zinc oxide, depending on the crystallographic direction, differs by 4–10 times [12]: 1.6 and 17 $\Omega\cdot\text{cm}$ in the [0001] and $\langle 11\bar{2}0 \rangle$ close-packed directions, respectively [13]. In zinc oxide electrons serve as charge carriers, since its Fermi level is located 0.2 eV below the conduction band. The band gap of zinc oxide is 3.37 eV, that corresponds to the photon energy of electromagnetic radiation in the near ultraviolet part of the spectrum. The optical absorption coefficient of zinc oxide is 10^{-5} cm⁻¹; therefore, the depth of photon penetration into the crystal is 100 nm [8,14].

Due to these properties, zinc oxide is used in optoelectronics, electronics, as a piezoelectric, and it is also one of the most common photocatalysts. As a result of its amphoteric properties, zinc oxide is susceptible to corrosion in both slightly acidic and slightly

alkaline media. As a photocatalyst, it can be recommended for the final purification of wastewater from petrochemical enterprises from highly toxic substances (for example, from phenol [15]).

3. ROLE OF CRYSTAL DISTORTION IN PROPERTIES OF ZINC OXIDE

The spatial arrangement of crystal defects significantly affects the optical and electrical properties of semiconductor materials. While point defects create local distortions of the band structure, linear defects lead to the formation of chains of changed energy states. Since zinc oxide is an n-type semiconductor, when considering the photocatalytic properties, defects exhibiting donor properties are of greatest interest. It is known that an oxygen vacancy exhibits donor properties in zinc oxide, but the energy of the level associated with an oxygen vacancy remains a subject of discussion.

Bateman [16] indicated that the ionization energy of an oxygen vacancy is 0.2 eV. Zhang et al. [17] presented the results of modeling, which show that the oxygen vacancy creates an additional level located 0.2 eV below the conduction band. This viewpoint is refuted by Janotti and Van de Walle [18] claiming that the oxygen vacancy is a deep donor, which lies 1 eV below the conduction band. The depth of the level caused by the oxygen vacancy determines how much the energy of the photon that can be absorbed by zinc oxide is reduced.

Unlike the vacancy, a dislocation is a linear defect, therefore, local additional levels due to dangling chemical bonds are located along its line and form a chain of levels. Soleimanian and Aghdaee [19] described the dependence of the optical properties of thin zinc oxide films on the dislocation density. The films were annealed at different temperatures from 350 °C to 600 °C, and their dislocation density was estimated by X-ray reflection broadening analysis. A decrease in the dislocation density from $\sim 10^{15}$ m⁻² to $\sim 10^{14}$ m⁻² was observed with an increase in the annealing temperature and was accompanied by an increase in the band gap from 3.36 eV to 3.47 eV.

The electrically conductive properties of dislocations in zinc oxide films were studied by Miyamoto et al. [20], who showed that the electron mobility in the film increases to a maximum of 145 cm²·V⁻¹·s⁻¹ under the condition of a minimum dislocation density. It is reported that the electrical conductivity of the films is affected by edge dislocations, while screw and mixed ones have a weak effect. The authors suggested that the edge dislocation generates a chain of acceptor levels,

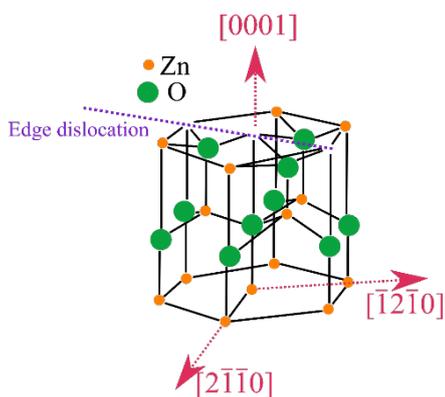


Fig. 2. An edge dislocation lying in $(000\bar{1})$ -O plane.

because of which it captures conduction electrons, reducing the electrical conductivity of the crystal.

Shuvalov et al. [21] reported that semiconductor crystals of $A^{II}B^{VI}$ compounds, which have a significant proportion of ionic bonds and edge dislocations lying in the $(000\bar{1})$ plane, exhibit both donor and acceptor properties. In zinc oxide negatively charged dislocations lie in the $(000\bar{1})$ -O plane (Fig. 2), and the electrical conductivity along these dislocation lines is increased.

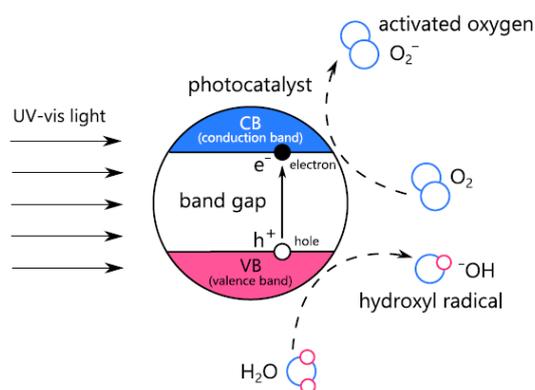
4. PHOTOCATALYTIC PROPERTIES OF ZINC OXIDE

To find the correlation between the structure and photocatalytic properties of a semiconductor, it is necessary to consider the mechanism of photocatalysis. The scheme of the mechanism of the photocatalytic process is shown in Fig. 3. It shows that the chemical reaction is initiated by an electron activated by electromagnetic radiation having energy of photon equal to the band gap of the semiconductor.

Reducing the size of a semiconductor crystal to less than 100 nm makes it possible to suppress the recombination of electrons and holes, increase the area of the active surface, and the lifetime of free carriers on this surface. For this reason, semiconductors in photocatalysis are used in the form of nano- and microscale dispersed particles. The morphology of zinc oxide particles affects the rate of photocatalysis due to the difference in faceting. The reasons for this effect may lie in the anisotropy of the electrical conductivity of zinc oxide crystals [12,13].

Jang et al. [23] presented the results of a comparison of the photocatalytic activity of zinc oxide particles of different morphology: nanoplates, nanorods, and microrods. The rate of photocatalytic decomposition of hydrogen peroxide in the presence of nanoplates was 2.5 times higher than in the presence of

(a) formation of oxidation agents



(b) catalytic decomposition

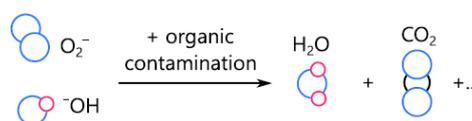


Fig. 3. Scheme of the photocatalytic process. Reproduced with permission from Ref. [22]. Copyright (2020), Elsevier.

nanorods. The authors explain this phenomenon by an increase in the total surface area covered with (0001) crystallographic planes. This area is $3.53 \text{ m}^2/\text{g}$ for nanoplates and $0.12 \text{ m}^2/\text{g}$ for nanorods.

Li et al. [2] noted that an increase in the ratio of the areas of crystallographic planes $\{10\bar{1}0\}$ to (0001) from 1.175 to 1.304 contributes to an increase of acetaldehyde decomposition rate constant from 1.1 to $4.6 (\text{mol}\cdot 10^{-7})/\text{min}$. In this case, the specific surface of particles decreased from 27.5 to $6.5 \text{ m}^2/\text{g}$. This dependence is not observed under the condition of a further decrease in the specific surface area to $1.2 \text{ m}^2/\text{g}$. Some authors claim that $\{10\bar{1}0\}$ planes exhibit higher photocatalytic activity than (0001) [24, 25], but they do not provide specific surface area data for these crystallographic planes.

The results of modeling the electronic structure and optical properties of different crystallographic planes, performed using the density functional theory, are presented by Zhang et al. [26]. Based on a comparison of the properties of four planes: $(10\bar{1}0)$, $(11\bar{2}0)$, (0001) -Zn, $(000\bar{1})$ -O, the authors concluded that (0001) -Zn plane exhibits maximum photocatalytic activity since Fermi level on this plane is located as close as possible to the edge of the conduction band, which contributes to an increase in electrical conductivity. Difference in structure of zinc-terminated (0001) -Zn and oxygen-terminated $(000\bar{1})$ -O planes is shown in Fig. 4.

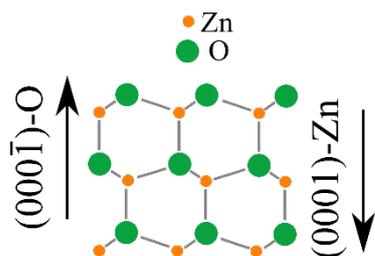


Fig. 4. Model of arrangement of atoms on $(000\bar{1})$ -O and (0001) -Zn planes.

Among the point defects that affect the properties of zinc oxide, oxygen vacancies were studied in the most detail. The donor properties of oxygen vacancies increase the concentration of free electrons in zinc oxide and accelerate the photocatalytic reaction. Bora et al. [27] showed the results of photocatalytic testing of zinc oxide nanorods containing oxygen vacancies. The rods were annealed at different temperatures from 90 °C to 450 °C. The concentration of oxygen vacancies was estimated using photoluminescence spectra and compared with the rate constant of the photocatalytic oxidation of phenol. The activity increased as the annealing temperature increased to 250 °C and then decreased. The authors explain this by the diffusion of oxygen vacancies to the surface of the rods. Oxygen vacancies act as active centers of the photocatalyst. A further increase in the annealing temperature favors the passivation of surface oxygen vacancies.

The role of dislocations in the photocatalytic properties of zinc oxide has not yet been studied. However, based on an increase in electrical conductivity along edge dislocations lying in the (0001) plane, it can be assumed that an increase in the density of such dislocations promotes an increase in the photocatalytic activity of zinc oxide particles. In addition, the presence of internal stresses will contribute to the additional generation of charges due to pronounced piezoelectric properties [10]. It should be noted that dislocations can form atmospheres by interaction with point defects, for example, with vacancies. In this case, it can be assumed that point defects will absorb photons with energies below the band gap of defect-free zinc oxide and supply free electrons through dislocations to the particle surface.

5. CONCLUSION

The photocatalytic activity of zinc oxide nanoparticles is affected by the symmetry of the crystal structure, the presence of oxygen vacancies, the type and density of dislocations, and the faceting. The photocatalytic

activity of zinc oxide rises with an increase in electrical conductivity, the (0001) plane being the most active. Edge dislocations lying in the $(000\bar{1})$ -O plane contribute to an increase in electrical conductivity, and possibly photocatalytic activity. Oxygen vacancies increase the concentration of free electrons and allow to rise the photocatalytic activity. Energy levels in the band gap caused by oxygen vacancies reduce the energy of a photon that can be involved in a photocatalytic reaction. The presented data about the effect of the structure of zinc oxide on the optical, electrically conductive properties can be used in the design of photocatalysts.

It should be noted that the present correlations can be used for description of photocatalytic properties of other semiconductors. For example, Li et al. [28] reported that in a case of Cu_2S photocatalytic activity of $\{110\}$ facets is higher than that of $\{001\}$ planes. Octahedron particles of Cu_2O are more active than Cu_2O cubes due to faceting with planes (111) and (100) , respectively, as was shown by Xu et al. [29]. Effect of native defects in tungsten trioxide was shown by Li et al. [30] to be similar to that in zinc oxide, meaning the optimal concentration of oxygen vacancies is necessary to manifest enhanced photocatalytic activity. Moreover, there are some papers, illustrating impact of dislocations in semiconductor particles on photocatalysis. Han et al. [5] reported that band gap reduces along the Shockley partial dislocation-induced multiple faults in $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$. Ren et al. [31] described titania nanowires with edge dislocations displaying higher photocatalysis efficiency by up to 1.8 times in comparison with defect-free titania nanoparticles.

These examples allow to conclude that correlations between defect structure of semiconductor and its photocatalytic activity are valid not only for zinc oxide. So, it is possible to create a map of semiconductors for prediction of their photocatalytic activity based on structure, optical and electrical properties according to the approach presented in this paper.

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