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# Modification of $TiO_2$ and ZnO Particles Under Mechanical Stress with Polypropylene

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**Abstract** Solid-state process of introducing oxygen vacancies into the structure of $TiO_2$ and ZnO particles was studied. The phase transformations of metal oxides throughout the process were examined by X-ray diffraction (XRD). The influence of the loaded mechanical stress on the band gap was studied by diffuse reflectance spectroscopy (DRS). Mechanism of elimination of oxygen atoms from the surface of the oxides by co-milling with polyolefins, which can lead to creation of more effective materials for waste water treatment, was proposed.

**Keywords** High-energy ball milling · $TiO_2$ · ZnO · Oxygen vacancies

## 16.1 Introduction

Metal oxides such as $TiO_2$ and ZnO were extensively studied during the last decades because of their unique intrinsic properties and a wide range of possible applications as photocatalysts, photoelectrodes, antibacterial agents or gas sensors [1, 2]. One of the limiting factors of their practical application as photocatalysts is the width of the band gap, which corresponds to the required photon energy, necessary for the creation of electron-hole pairs. Both titanium dioxide and zinc oxide have wide

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band gaps (ZnO ~3.3 eV; $TiO_2$ ~3.2 eV) that enable photocatalysis only under UV light within the energy range 3–124 eV [3, 4]. With the aim of increasing the photocatalytic efficiency of these materials under solar light for degradation of organic pollutants, tuning of the band gaps is desirable.

Changes in metal oxides which accompany the process of high-energy ball milling (HEBM) have been previously investigated [5]. The process of HEBM, in contrast to the standard grinding used for comminution of materials, is aimed at accumulation of energy in the materials for further chemical transformations by introducing various defects such as dilation/shrinking of the lattice, vacancies, interstitial ions and atoms, dislocations [6]. These defects in turn alter the width of band gap of the material, which enables the employment of HEBM method for tuning of the material properties toward higher energy harvest.

## 16.2 Inducing Defects in Structure of Metal Oxides Under Mechanical Stress

An attempt to induce oxygen vacancies in $TiO_2$ (anatase) and ZnO was done in a planetary ball mill Pulverisette 7 premium line. The time of milling was varied from 60 min up to 180 min. As an oxygen subtracting agent polypropylene (PP) was used, since it is known that anion-containing polyolefins can decompose concurrently acting as reductants [7]. In Fig. 16.1, XRD patterns of samples co-milled with PP are shown. The formation of defects due to plastic deformations is one of the relaxation pathways under mechanical treatment, the others are heating, reduction of particles, amorphisation along with possible formation of polymorph. The last ones are observed in our case as well. During milling, $TiO_2$ transforms from anatase phase to rutile with the high-pressure phase of $TiO_2$, called $TiO_2$-II, as intermediate [5]. As seen from the XRD patterns, the percent of rutile phase is increasing with prolongation of the milling time which has a negative effect on the photocatalytic efficiency

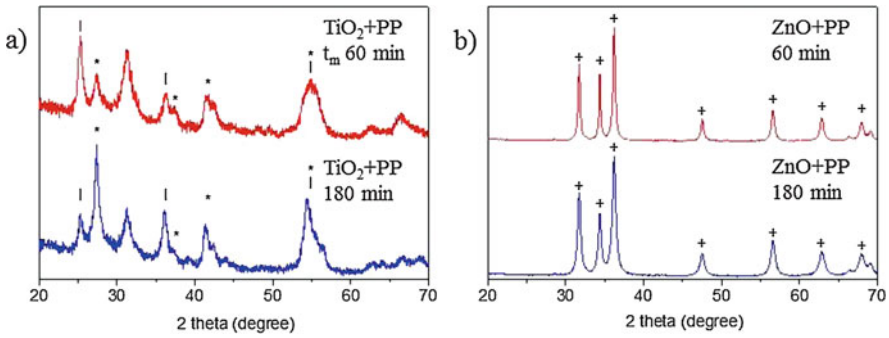


**Fig. 16.1** XRD patterns of (**a**) $TiO_2$ (l – anatase; ∗ – rutile) and (**b**) ZnO (+ – wurtzite ZnO), milled with PP for 60 and 180 min

of the materials. Together with the transition between different polymorphs, amorphisation process occurs which is seen from the broadening of the XRD peaks for both materials. In the case of ZnO, no peaks of new phase are observed which is in conformity with previous investigations of the structural changes during HEBM process [8]. As investigated by several researchers [9–11], ZnO crystals usually do not undergo reconstructions to other polymorphs during milling, except for small shrinkage of the lattice even when the presence of surface defects, particularly oxygen vacancies is shown by other techniques such as high resolution transmission electron microscopy (HRTEM) or by behavioral change revealed by photoluminescence (PL), Raman spectra, etc.

By XRD the structural changes in long-range order can be seen but it is impossible to identify defects in short-range order. Since it is known that the impact of defects on photocatalysis is not unequivocal and the distribution of point defects plays a role, the surface oxygen vacancies are usually considered as favoring the photocatalysis preventing electron-hole recombinations and acting as active sites for adsorption, whereas the bulk oxygen vacancies have an opposite effect serving as recombination centers [1]. For investigations of the influence of HEBM on the electron structures of the materials, DRS measurements were performed.

## 16.3 Abstraction of Oxygen by Organic Constituent

As mentioned above, PP does not contain any anions for anionic exchange as, for example, polytetrafluoroethylene (PTFE) or polyvinylidene fluoride (PVDF). However, the process of subtraction of oxygen from the surface of the metal oxide can take place because of destruction of bonds. The ability of mechanical stress to destruct chemical bonds in polymer was studied earlier [12]. So we suggested mechanochemically induced destruction of hydrocarbon polymer with subsequent formation of reactive species that can react with the surface oxygen, creating oxygen vacancies without concomitant anion exchange [13]. The process of oxygen abstraction from the surface has greater impact on the band gap width than the reduction of $Ti^{4+}$ [14]. In Fig. 16.2, DRS spectra show a distinct shift towards visible light range for the milled samples. From these spectra the width of the band gaps was calculated by Kubelka-Munk function and the narrowing from 3.56 eV to 3.39 eV and from 3.27 eV to 3.16 eV for titanium dioxide and zinc oxide, respectively, was observed.

Because of the afore-mentioned possible presence of bulk defects which have lower impact on the band gap state [15] but can significantly change the photocatalytic properties of material, photocatalytic degradation of methylene blue was performed. Dye degradation upon irradiation is an indirect method for examination of the present defects. The increased efficiency of the process confirms the improved separation of e-h pairs. Prolonged milling led to decrease of the photocatalytic activity, whereas the sample of $TiO_2$ co-milled with PP for 60 min exhibited an increase in the activity during the first 60 min with subsequent decline after comparing to the pristine titanium dioxide.

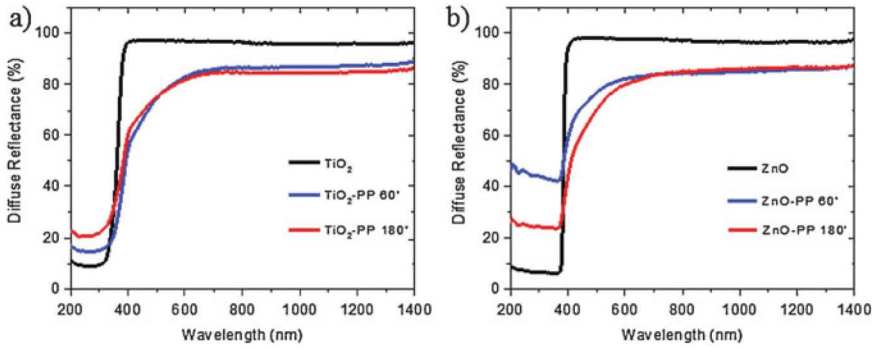


**Fig. 16.2** DRS spectra of (**a**) $TiO_2$ and (**b**) ZnO milled with PP for 60 and 180 min

## 16.4 Conclusions

The introduction of oxygen vacancies in ZnO and $TiO_2$ by solid-state process was demonstrated as a consequence of HEBM. The increased milling time revokes the positive effect of HEBM on the band gap state and the photocatalytic activity because of the unwanted process of amorphisation and polymorph transitions. However, this method is very attractive due to its simplicity for preparation of photocatalytic materials with enhanced efficiency for degradation of different organic pollutants.

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