NANOCOMPOSITES OF ZNO-DECORATED HPHT NANODIAMOND AS A PERSPECTIVE GREEN PHOTOCATALYSTS

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Abstract

Electrical and optical properties of zinc oxide, in particular the relatively wide direct band gap of ~3.3 eV predetermines ZnO as a photocatalytic material at room temperature. ZnO itself is non-toxic and the hydrothermal growth method we use to prepare its nanostructures is environmentally friendly. These facts contribute to the attractiveness of this material. Recently, we have focused on studying the influence of doping or of plasma surface treatment on the photocatalytic efficiency of ZnO. However, the main drawbacks are the high recombination rate of charge carriers and the poor in capturing visible light in a narrow spectral range. The solution is the use of ZnO as part of nanocomposites. In the past, ZnO-detonation nanodiamons (DND) composites were studied. The disadvantage of DND is the formation of clusters of different sizes, therefore we focused our attention on the use of HPHT nanodiamonds (NDs). We modified the surface of commercial HPHT NDs by oxidation in order to increase the concentration of hydroxyl-, carbonyl- and carboxyl- functional groups. The resulting ZnO-HPHT NDs composites were synthesized using a dehydration-condensation process between oxygen-containing functional groups on the NDs surface and hydroxyl groups on the ZnO surface. The prepared nanocomposites were characterized by SEM, EDX spectroscopy and secondary ion mass spectrometry (SIMS) and tested by photocatalytic dye degradation.

Keywords: HPHT NDs, ZnO, nanocomposites, photocatalyst, photocatalytic oxidation

1. INTRODUCTION

Zinc oxide (ZnO) represent semiconducting nanomaterial, which has been studied for its wide range of application beyond conventional optoelectronics. Its unique properties can be used for cultivation of mammalian cells, wound healing, inhibition of bacterial growth or in cosmetics for absorbing ultra-violet (UV) light. In addition, ZnO is an effective photocatalyst for the degradation of inorganic and organic pollutants [1]. The nanoparticles ZnO-NPs are the particles with the largest variety of synthesized structure. including one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) structures. The largest faction of ZnO represent one-dimensional structures such as needles, helixes, nanorods, ribbons, belts, wires and combs. 2D-ZnO can make up nanopellets or nanosheet. The last group of ZnO are 3D structures, whore include snowflakes, dandelion, flower [2]. This nanomaterial can be relative easily synthetized using different methods including sol-gel method, microwave heating synthesis, RF plasma synthesis or by hydrothermal growth method [3]. The latter is a simple and environmentally friendly method for the preparation of these nanoparticles since this method does not include any organic solvents or additional processing of the product [2,3]. This approach for the synthesis of ZnO brings many advantages such as the possibility of carrying out the synthesis at low temperatures or the high purity and the degree of crystallinity of the prepared material [4,5]. However, disadvantage of this method can requirement for expensive autoclaves and the difficulty of observing the crystal as it grows [6]. In our recent study, we investigated the photocatalytic properties of doped and plasma treated ZnO [1]. The main disadvantages of this materials are the high recombination rate of charge carriers and the poor use of visible light. The possible solution of this problem could be the use of ZnO as part of nanocomposites.

Hybrid zinc oxide (ZnO)/detonation nanodiamond (DND) composites have been the interest of study for many researchers over the years. DNDs form particles with the size around 5 ± 2 nm, while the diamond grains are unstable and spontaneously aggregate to clusters of different sizes [7]. Therefore, in this work, ZnO- HPHT NDs composites were prepared and studied. The use of HPHT nanodiamonds brings possible solution of the problem with DND. Detonation and High-pressure high-temperature (HPHT) methods are the two main methods applied for the synthesis of the commercially available nanodiamonds [8]. However, the final NDs products significantly differ in their structure (concentration of defects and embedded nitrogen) and also in their surface quality and reactivity [7]. In general, HPHT NDs create bigger and stable structures. Their other advantage over DNDs is certainly its monocrystalline character with low concentration of lattice defects. This is very essencial especially for their spintronic and sensing applications [9].

The studied ZnO-HPHT NDs composites were synthesized using a dehydration-condensation process between oxygen-containing functional groups on the NDs surface and hydroxyl groups on the ZnO surface. The prepared nanocomposites were then characterized by SEM, EDX, SIMS and tested by photocatalytic dye degradation (methylene blue MB).

2. EXPERIMENTAL PART

2.1 Photocatalyst preparation

2.1.1 Treatment of HPHT nanodiamonds

The commercial type Ib HPHT (high-pressure, high-temperature) diamond powder of size about 30 nm was purchased from Microdiamant AG., Switzerland. The powder was oxidized by air at 510 °C for 6 h followed by the wet chemical treatment in a mixture of concentrated H_2SO_4 and HNO_3 at 75 °C for 3 days to increase the carbonyl surface coverage. After dilution of the reaction mixture was removed by centrifugation. Subsequently the nanodiamonds were washed with 0.1 M NaOH and 0.1 M HCl. Finally, the particles were washed five times with MilliQ water. The solution was lyophilized.

2.1.2 Preparation ZnO nanostructures

The process of synthesis zinc oxide by hydrothermal growth method was previously reported [3]. Briefly, equimolar aqueous solutions of 25 mM $Zn(NO_3)_2 \cdot 6H_2O$ and HMTA at 90 °C for 3 h. The precursor salt residue was removed from the sample by washing 3 -times with deionized water followed by centrifugation at 18 000 rpm (RCF: 23542g) for 20 min. Finally, the powder was dried by lyophilization.

2.1.3 Preparation of ZnO-NDs composites

The ND-ZnO nanocomposite was synthesized via a simple dehydration condensation process between the oxygen-containing functional groups on NDs and the hydroxyl groups on the surface of ZnO nanostructures 10 mg ND was first added to 20 ml water and ultrasonicated for 30 min. Then 100 mg ZnO powder was added into the suspension of NDs and stirred for 1 h and allowed to react overnight at r.t. The obtained light gray powder was dried at 130 °C for 6 h.

2.2 Structural analysis of the photocatalyst ZnO-ND

2.2.1 SEM analysis and EDX spectroscopy

Structural observations on ZnO-ND nanocoposite were performed with field emission scanning electron microscopy (SEM – JEOL 7600 FEG), and chemical compositions were analysed using energy dispersive (EDS) X-ray spectroscopy (Oxford Instruments INCA microanalysis system with X-Max 50 detector) at 10 kV. Original JOEL PC SEM software Ver. 2.1.0.9 (Tokyo, Japan) was used to collect SEM images and process the results, and INCA software was used for EDS-chemical composition analysis.

2.2.2 SIMS spectrometry

Mass spectrometry measurements were performed using a ToF-SIMS IV (ION-TOF, Germany) reflectron type time-of-flight mass spectrometer equipped with a bismuth ion source. Pulsed 25 keV Bi^+ were used as primary ions with a current of 1 pA with total primary ion dose density below the static limit of 10^{13} ions cm^{-2}. Secondary ion mass spectra were measured by scanning over a selected 100x100 μm^2 analysis area. Imaging was performed by selecting masses of interest and recording their intensities with respect to the position of the primary ion beam in the fields of view 250 x 250 μm^2. The lateral resolution of measured 2D images was about 1 µm. Measurements were performed in positive and negative polarities. The samples in a powder form were deposited on silicon substrate with double-sided graphite tape without any other procedures.

2.2.3 Characterisation of photocatalytic properties

Testing the efficiency of the ZnO-ND photocatalyst was realized through the photodegradation of MB. 20 mg of photocatalyst was added to 15 ml of MB aqueous solution (MB concentration was 10 ppm). The suspension was allowed to stir in a completely dark environment for half an hour before photocatalytic degradation to reach adsorption-desorption equilibrium. Subsequently, the suspension was exposed to UV radiation THORLAS LED 365 nm, 880 mW (min), 1000 mA. At regular 10-minute intervals, 2 mL samples were taken and filtered through a PVDF filter (diameter 13 mm, with a pore size of 0.22 µm. MB concentration was monitored by measuring the absorbance by a Beckman Coulter DU 730 UV/Vis spectrophotometer at a wavelength 662 nm. (For comparison, the photocatalytic efficiency of the prepared ZnO nanostructures was tested in an identical way).

3. RESULTS AND DISCUSSION

The SEM image as synthesized ZnO-ND nanocoposite is presented in **Figure 1**. The SEM image at 5 000 times magnification, it shows the homogeneous distribution of ZnO on the NDs surface. The elemental compositions of ZnO-ND nanocomposite were determined by EDX spectroscopy. The results are presented in **Table 1**.

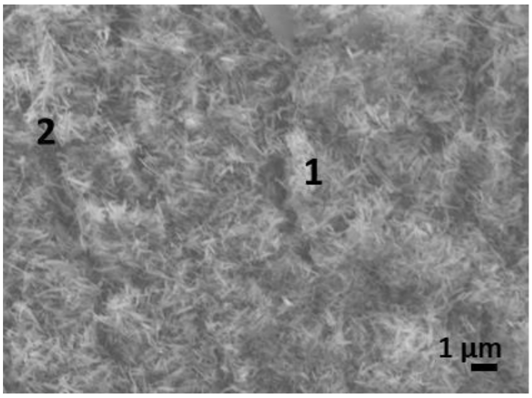


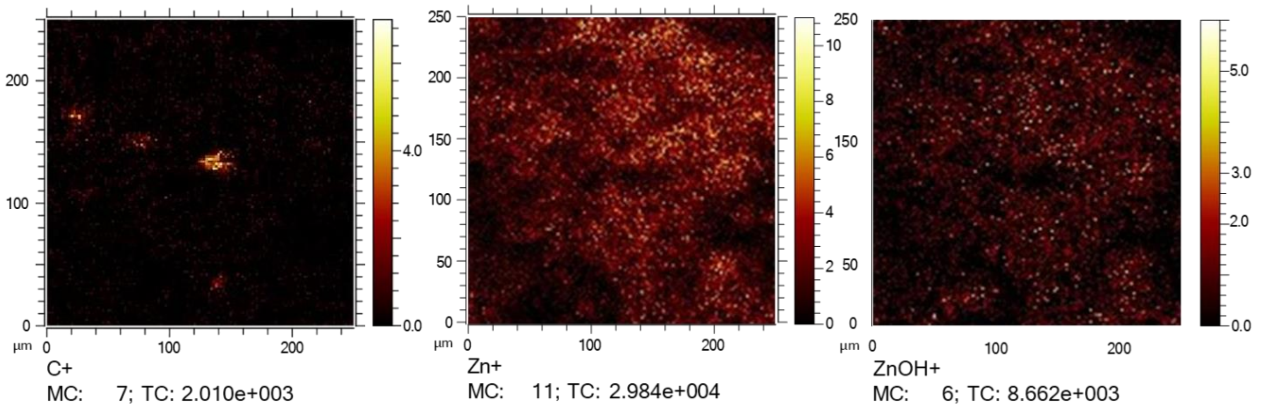
Figure 1 The SEM image of the ZnO-ND nanocomposite with marking of the positions for measuring the EDX spectrum

Table 1 The table of the elemental composition of the ZnO-ND nanocomposite in the marked SEM positions (**Figure 1**) in mass percentage

Position in the SEM image	**wt%**		
	C	**Zn**	**O**
1	19.10	57.79	23.11
2	15.84	60.20	23.97

Secondary ion mass spectrometry of the ZnO-ND nanocomposite sample identified the following ions and fragments with the corresponding isotopic distribution in positive polarity: C+, Zn+, ZnOH+. The following ions and fragments originating from the nanodiamond structure and ZnO coating were identified in negative polarity a: C, O-, OH-, CO_3-, ZnO-, ZnOH-, ZnO_2-. Due to the high sensitivity of SIMS at the ppm level, impurities originating probably from the synthesis process, such as Na+, F-, Cl, were identified.

The images were measured over the area of 250 x 250 μm2. The brighter is the yellow colour, the higher is the emission of selected secondary ion from given area. The darker or black colour means the low or no emission of selected secondary ions. The numbers below each image denote the maximum number of detected ions as counts in the single shot measurement (MC) and the total number of detected ions as counts (TC). The total ion image represents the distribution of all secondary ions detected during SIMS analysis in selected polarity. The **Figure 2** represents the 2D distribution of the selected species in the positive polarity. The distributions of Zn+ and ZnOH+ represent the homogeneous coverage of nanodiamond with ZnO.

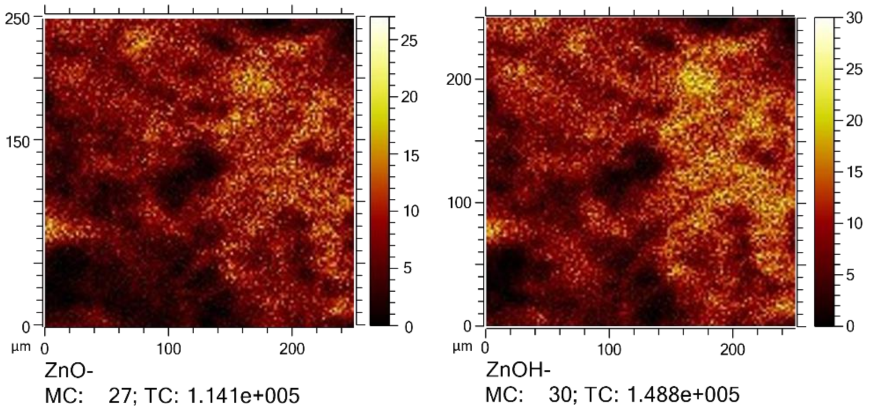


C+
MC: 7; TC: 2.010e+003

Zn+
MC: 11; TC: 2.984e+004

ZnOH+
MC: 6; TC: 8.662e+003

Figure 2 SIMS 2D images obtained in positive polarity for the homogeneous coverage of nanodiamond ZnO



ZnO-
MC: 27; TC: 1.141e+005

ZnOH-
MC: 30; TC: 1.488e+005

Figure 3 SIMS 2D images obtained in negative polarity for the homogeneous coverage of nanodiamond ZnO

The **Figure 3** represents the 2D distribution of the selected species in the negative polarity. ZnO^- and $ZnOH^-$ distributions representing the ZnO coverage of the nanodiamond sample are homogeneous. The intensity distributions of ZnO species in both polarities correspond to the total ion distribution and the intensities variations within one image are given by topographical effect of the sample.

Results of degradation processes were further fitted to first-order rate kinetic based on the Langmuir-Hinshelwood model. Langmuir–Hinshelwood (LH) kinetics is the most commonly used kinetic expression to explain the kinetics of the heterogeneous catalytic processes. The kinetics of the photodegradation MB follows an apparent first order, like the Langmuir-Hinshelwood mechanism.

$$ln(c_0 / c) = k_s \cdot t \tag{1}$$

where:

k_S- the rate constant (min^{-1})

c_0- the initial concentration of MB (mg/l)

c-the concentration of MB at reaction time of t (mg/l)

The values of the degradation rate constants indicate the rate of MB degradation (detected by MB decolorization). The larger the rate constant, the faster the reaction takes place, i.e. degradation of MB.

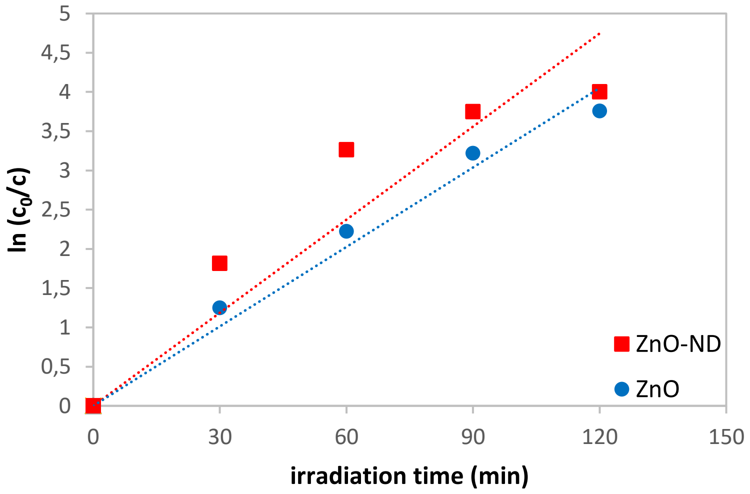


Figure 4 Graph of function of time and photocatalytic degradation MB kinetics, the straight lines represent the linear fit from the Langmuir-Hinshelwood model

All the plots of $ln(c_0/c)$ vs t follow a linear relationship with a correlation coefficient (R^2) and the slope (**Figure 4**) deduced from each fit provides an estimate of k_S, as presented in **Table 2**.

Table 2 Comparison of rate constants k_s and correlation coefficients R^2 for photocatalysts ZnO and ZnO-ND

Photocatalyst	**R^2**	**k_s**
ZnO	0.9931	0.0338
ZnO-ND	0.9595	0.0396

4. CONCLUSION

Zinc oxide has unique optoelectronic properties. One of them is the band gap region (3.2 ev), which predetermines its use as a photocatalyst. Its indispensable advantage is cheap and environmentally friendly preparation. However, it exhibits a high recombination rate of charge carriers. One of the solutions is the use of ZnO as a component of composites. In our study, attention was first focused on the ZnO-NDs nanocomposite, while HPHT nanodiamonds were used as NDs. ZnO was prepared by the method of hydrothermal growth. By oxidizing commercial NDs, we increased their surface concentration of hydroxyl, carbonyl and carboxyl functional groups. This allowed us to prepare a ZnO-ND nanocomposite by dehydration condensation process. We examined the morphology of the composite using SEM microscopy. We confirmed the elemental composition using EDX and SIMS spectrometry was used to study the structure. We tested the photocatalytic efficiency of the composite through the photodegradation of methylene blue. By comparing the degradation of MB under identical conditions with the use of ZnO as a photocatalyst, we found that the rate of degradation when using ZnO-ND was 1.17 times faster.

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