

PREPARATION AND CHARACTERIZATION OF THE GRAPHITE/ZNO COMPOSITES

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Abstract

The composites graphite/ZnO were prepared using calcination method. Zinc chloride (ZnCl₂) and sodium carbonate (Na₂CO₃) were used for synthesis of zinc oxide (ZnO), whereas micromilled and natural graphite were used as the matrix for ZnO nanoparticles growing. During the reaction of ZnCl₂ with saturated aqueous solution of Na₂CO₃ new compound - Na₂Zn₃(CO₃)₄•(H₂O)₃ originates. During the calcination at the temperatures higher than 400°C this new precursor decomposes and ZnO nanoparticles are formed. The composites prepared within this research contained 10 and 50 wt.% of ZnO. Morphology of the composites was studied using scanning electron microscopy. Zinc content was determined using area EDS analysis. The X – ray diffraction method was used to study phase composition of the samples. The photocatalytic activity of prepared composites was determined by discoloration of organic dye acid orange 7 aqueous solution under UV irradiation.

Keywords: graphite, zinc oxide, composites, photocatalysis

1. INTRODUCTION

During number of the industrial production processes the toxic compounds originate and there are always many efforts to minimize their negative effect related to living environment [1]. One of the possible solutions for degradation of this harmful compounds is photocatalysis [2],[3],[4],[5]. The most frequently used photocatalyst is TiO₂, especially in its anatase form [6], other photocatalysts comprise for example CdS [7], CuS [8] and ZnO [9],[10], or their mixtures [11]. Nanoparticles are usually used due to the higher photodegradation efficiency in comparison to microparticles. There is also research focus on micro-sized composite materials containing nanoparticles instead of pure nanoparticles mainly due to nanoparticles negative influence to environment [12]. The environmental issue connected to the utilization of bare nanoparticles evoked the research activities focused on the fixing of the nanoparticles on the surfaces of suitable matrices [13]. Clays minerals like illite, montmorillonite, kaolinite, also porous silica, activated carbon, graphene, graphite, graphite oxide [14],[15] or carbon nanotubes [16] can be used as a matrix for the synthesis of photocatalytically active nanoparticles. Composites like graphene/ZnO show stronger light absorption in the visible light range in comparison to pure ZnO [17]. There are several publications showing ZnO as more photoactive than TiO₂ [18],[19] and number of the preparation method of ZnO particles has been already introduced. The most often utilized preparation techniques are summarized in review paper published by Moezzi et al. [20]. Hayat et al. [21] prepared ZnO using zinc nitrate hexahydrate, ammonium carbonate, ethanol and polyvinyl alcohol, thus prepared ZnO showed higher photodegradation activity against phenol.

In this study we synthesized graphite/ZnO nanocomposites by thermal decomposition of precursor obtained by reaction of ZnCl₂ and Na₂CO₃. The ZnO amount in the nanocomposites was determined by EDS area analysis. X – ray powder diffraction was used to reveal phase composition of the nanocomposites and SEM was used for observation of the morphology of the particles. The photodegradation activity was measured by discoloration of organic dye acid orange 7 aqueous solution under 1h UV irradiation.

2. MATERIALS AND METHODS

2.1 Materials

ZnCl₂ p.a. and Na₂CO₃ purchased from Lachema were used for the synthesis of Na₂Zn₃(CO₃)₄•3(H₂O) which is ZnO precursor in present work. Two graphite substrates with different particle size (micromilled – further assigned as Gra(1) and high purity natural graphite - further assigned as Gra(2)) were purchased from company Graphite Týn, spol. s r. o. and were used as a matrices for ZnO precursor growing. The azo-dye acid orange 7 (AO7) obtained from Synthesia a.s. was used to photodegradation testing. The distilled water was used during all the experiments.

2.2 Preparation of graphite/ZnO composites

The synthesis procedure can be divided into two parts including: i) reaction of ZnCl₂ with Na₂CO₃ when Na₂Zn₃(CO₃)₄•(H₂O)₃ originates and ii) thermal decomposition of Na₂Zn₃(CO₃)₄•(H₂O)₃ at selected temperatures. During the first step of the process graphite, ZnCl₂ and Na₂CO₃ saturated solution were stirred at room temperature to produce ZnO precursor. After stirring and filtration the obtained solid portion was dried at 100 °C. By the adjusting of ZnCl₂ and Na₂CO₃ ratio, the composites with 10 and 50 wt.% of ZnO were prepared. The dried graphite/ Na₂Zn₃(CO₃)₄•(H₂O)₃ composites which contained 10 and 50wt.% of ZnO were then calcined at the temperatures of 400, 500 and 600°C. The composites were designated as ZinGra(1)XY and ZinGra(2)XY, where X shows the ZnO amount (1 – 10wt.%, 5 – 50wt.%) and Y shows the calcination temperature (1 – drying at 100°C, 4 – calcination at 400°C, 5 – 500°C, 6 – 600°C).

2.3 Characterization methods

SEM - EDX

The scanning electron microscope Quanta FEG 450 (FEI) with EDS analysis APOLLO X (EDAX) was used as a microscopic method for characterization of morphology and elemental composition of the studied samples. Zinc content was determined using area EDS analysis.

XRPD

The diffractometer Bruker D8 Advance (Bruker AXS, Germany) equipped with detector VANTEC 1 was used to record the XRPD pattern under UV CoK α irradiation ($\lambda = 1.789$ nm). During the measurement the reflection mode was used and powder samples were pressed in a rotational holder. The database PDF 2 Release 2004 (International Centre for Diffraction Data) was used to evaluate the phase composition.

Photodegradation test

The photoactivity of samples was measured using organic dye acid orange 7 (AO7) discoloration under 1h long UV irradiation. In the first step, to achieve adsorption equilibrium the suspension of 7ml AO7 aqueous solution ($c_0=5 \cdot 10^{-3}$ mol·dm⁻³), 0.05 g composite and 93 ml distilled water was stirred for 24h. Next the suspension was exposed to 1h long UV irradiation (37W BLB tube OSRAM). The photoactivity was measured by the fiber optic spectrometer USB4000 (OceanOptics) using difference of the AO7 aqueous solution absorbance at 480nm after 24h stirring and the AO7 aqueous solution absorbance after 1h irradiation. The AO7 aqueous solutions were separate of samples by syringe filter filtration (45 μ m) before absorbance measurement. The total photodegradation activity is evaluated as a loss of the molar amount (Δn) of AO7 after 1 h long UV irradiation.

3. RESULTS AND DISCUSSION

The EDS analysis showed the amount of Zn in composites (in Table 1 recalculated into the amount of the oxides). The yield of the synthesis is approximately in the range 81 – 85 %. Relatively low yield of ZnO obtained during the synthesis can be probably attributed to the leaching of Zn²⁺ ions during the stirring of the

water suspension. Comparing the data shown in Table 1 it is evident that utilization of micromilled graphite in the case of composites ZinGra(1) had positive effect on yield of ZnO. This fact can be attributed to smaller particles of Gra(1) substrate in comparison of ZinGra(2) what is responsible for higher surface area of Gra(1).

Table 1 The ZnO amount in composites.

Sample	ZinGra(1)11	ZinGra(1)51	ZinGra(2)11	ZinGra(2)51
ZnO (wt.%)	8.4	42.3	8.1	41.2

The SEM images of particles of ZinGra(1)56 and ZinGra(2)56 composites are shown in Fig. 1 and Fig. 2 and the images clearly revealed the difference between ZinGra(1)56 particles and ZinGra(2)56 particles. The SEM image of ZinGra(2)56 composite reveals that the ZnO particles originate also aside the graphite substrate (see Fig. 2). As was mentioned earlier Gra(1) particles were micronized and probably consist of number of surface defects which are typical for particles obtained after the milling whereas these defects are favorable for capturing of reagents.

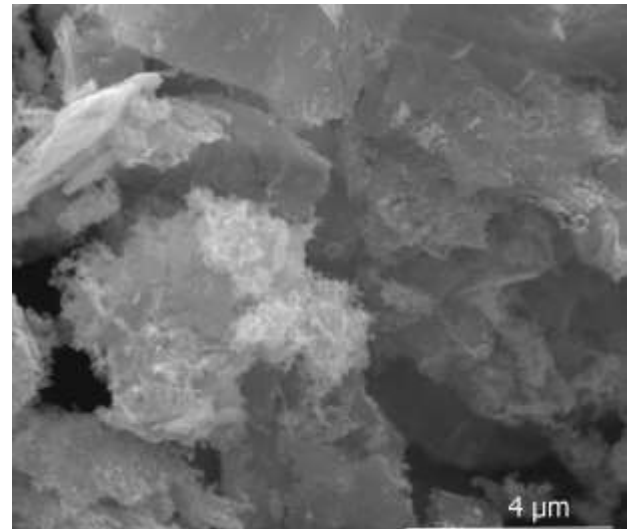
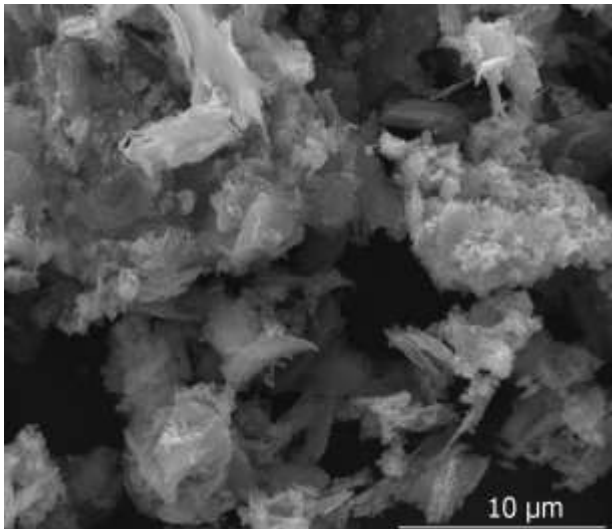


Fig. 1 The ZinGra(1)56 particles SEM images.

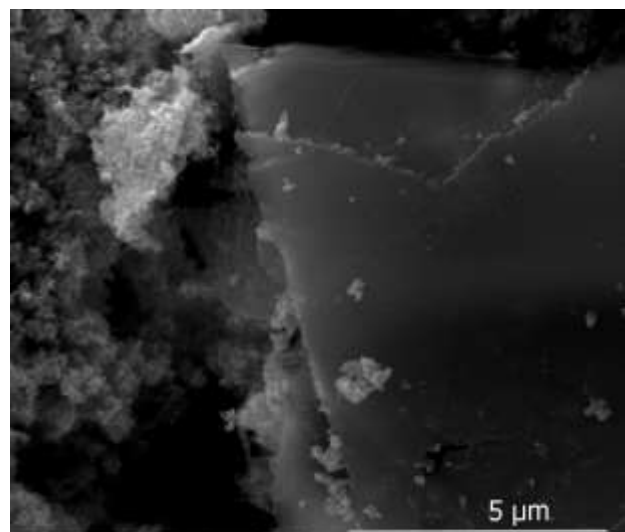
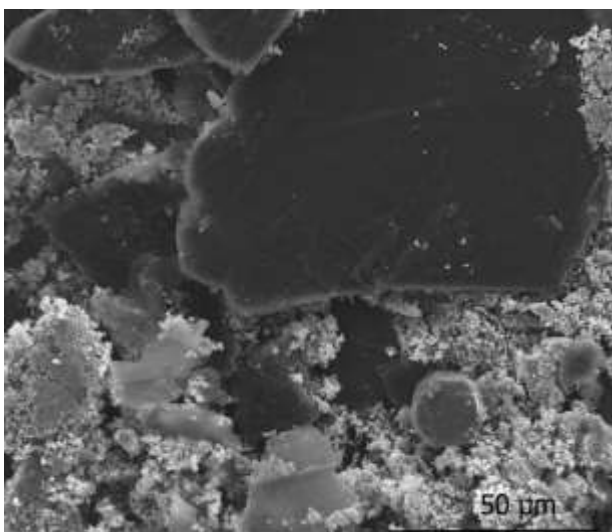


Fig. 2 The ZinGra(2)56 particles SEM images.

The XRPD patterns of ZinGra(1) and ZinGra(2) composites are shown in Fig. 3 and 4. Diffraction patterns of dried composites confirmed the origination of $\text{Na}_2\text{Zn}_3(\text{CO}_3)_4 \cdot (\text{H}_2\text{O})_3$ as a result of ZnCl_2 and Na_2CO_3 reaction and also that ZnO originates during the calcination at the temperature above 400°C . In both cases, the intensity of ZnO diffraction lines increases with calcination temperature what is connected to the precursor decomposition.

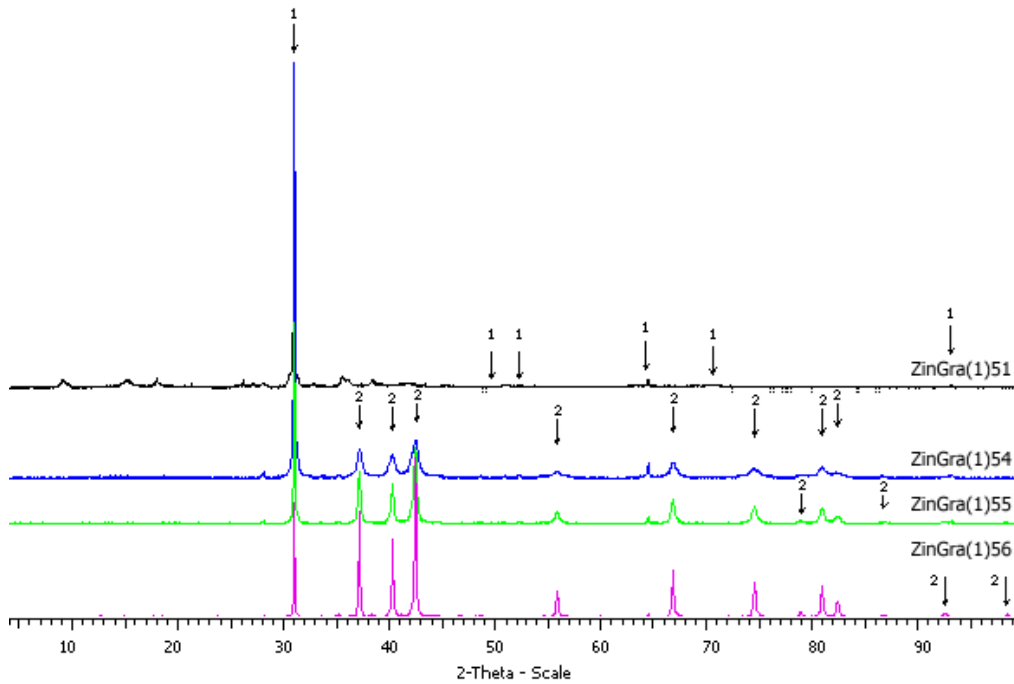


Fig. 3 The XRPD pattern of ZinGra(1) composites: 1..... $\text{Na}_2\text{Zn}_3(\text{CO}_3)_4 \cdot (\text{H}_2\text{O})_3$ precursor, 2.....ZnO.

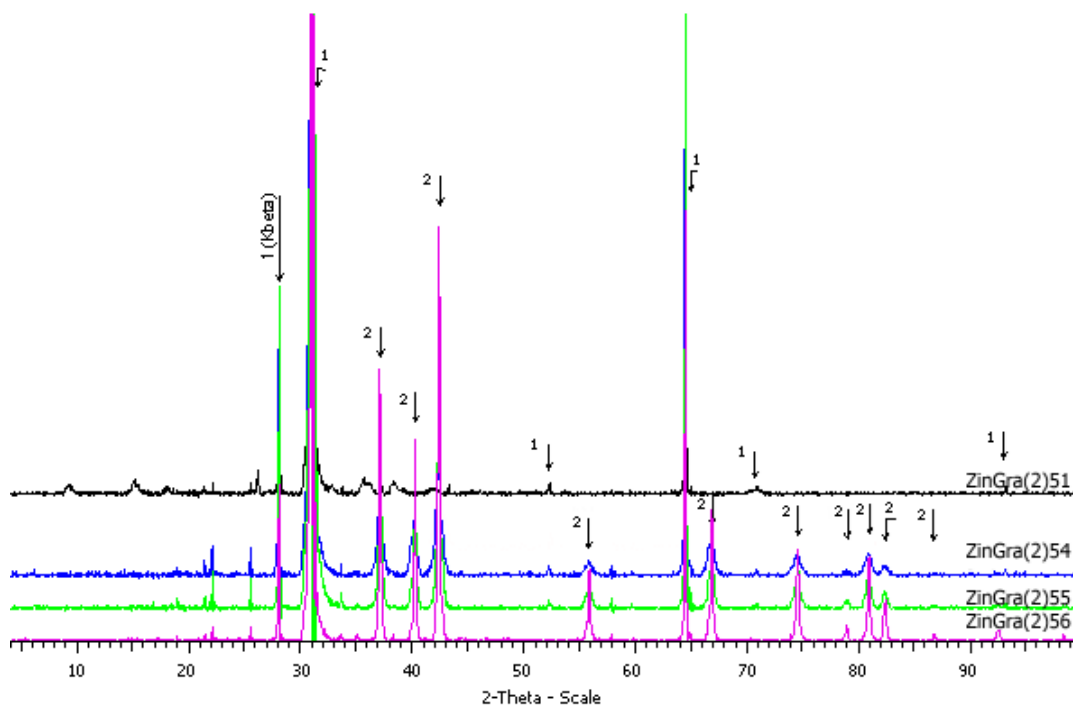


Fig. 4 The XRPD pattern of ZinGra(2) composites: 1..... $\text{Na}_2\text{Zn}_3(\text{CO}_3)_4 \cdot (\text{H}_2\text{O})_3$ precursor, 2.....ZnO.

The photodegradation activity of prepared composites is shown in Fig. 5. The tests did not confirm any photodegradation activity for composites dried at 100°C which according to XRPD analysis do not consist of any ZnO. The composites calcinated at temperatures 400, 500 and 600°C exhibited photodegradation activity. In both cases, ZinGra(1) and ZinGra(2), the composites containing 50 wt.% of ZnO show higher photodegradation activity in comparison to composites with 10 wt.% of ZnO. The results in Fig. 5 also revealed the composites prepared using Gra(1) substrate as more photodegradation active.

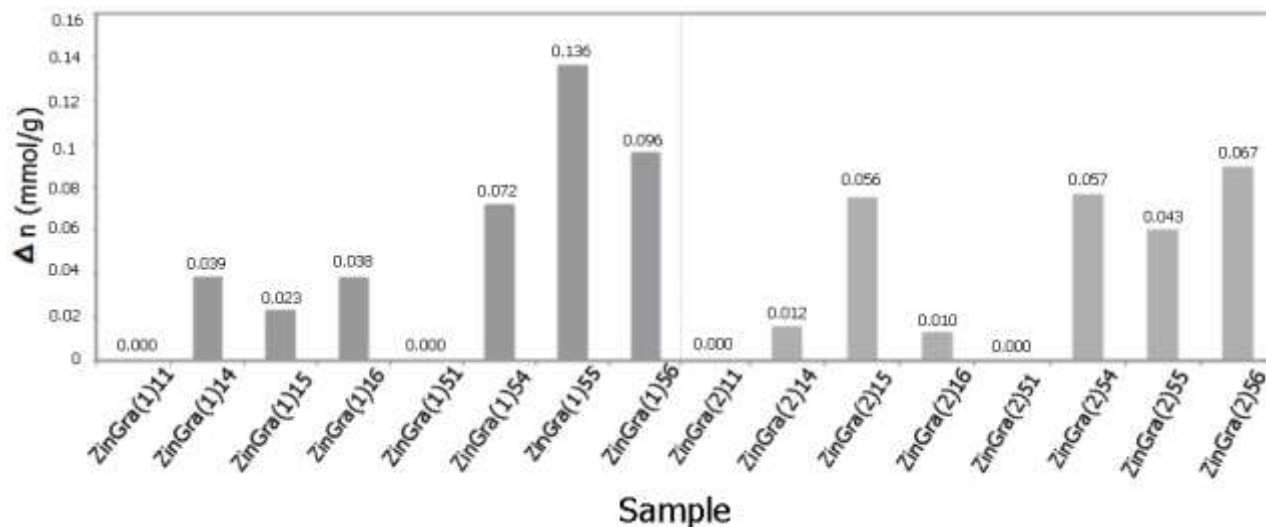


Fig. 5 The photocatalytic activity of ZinGra samples.

4. CONCLUSIONS

The graphite/ZnO composites containing approximately 8 and 43 wt.% of ZnO particles fixed on the surface of graphite were successfully prepared. The XRPD analysis confirmed the formation of $\text{Na}_2\text{Zn}_3(\text{CO}_3)_4 \cdot (\text{H}_2\text{O})_3$ which serves as precursor for ZnO. It was observed that the synthesis yield and the photodegradation activity of prepared composites is dependent on the graphite matrix. Generally, the yield of ZnO and the photodegradation activity were higher for composites with micromilled graphite.

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