

## Synthesis and investigation of composite photocatalysts on the base of nickel and zinc oxides

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Photocatalytic activities of NiO<sub>0.8</sub>ZnO<sub>0.2</sub>-ZnO samples obtained by precipitation from various starting materials (chlorides and nitrates) followed by thermal treatment at two different temperatures (450 °C or 650 °C) were compared. Powder X-ray diffraction and FTIR spectroscopy were used to characterize the investigated catalysts. Oxidative photodegradation of Malachite Green dye on NiO<sub>0.8</sub>ZnO<sub>0.2</sub>-ZnO catalysts over a period of 2 hours using UV light was studied. Photodegradation degree of the Malachite Green dye using NiO<sub>0.8</sub>ZnO<sub>0.2</sub>-ZnO obtained from chlorides and treated at 450 °C or 650 °C, are 89 and 86%, respectively. Samples from nitrate precursors calcined at 450 °C or 650 °C exhibited a higher photocatalytic degradation activity 99 and 94%, respectively.

**Key words:** photocatalysts, photodegradation, Malachite Green, dye, pollutant.

### INTRODUCTION

Synthetic dyes are one of the most important pollutants from the textile industry [1]. They may cause serious health and environmental problems because of their stability, and toxicity [2]. Heterogeneous photocatalysis, being highly efficient advanced oxidation means, has been applied as an environmentally friendly, cost effective, and green process for successful degradation of many harmful organic compounds [3]. Recently there has been an increasing tendency of applying thermally and chemically stable semiconductor metal oxides as photocatalysts in aqueous systems [4]. In the recent years, scientists are excited by the opportunity to create low cost photocatalytic materials of high catalytic activity [5]. Due to modified electronic and structural properties, nanocomposites can possess enhanced photocatalytic activity in comparison with monocomponent oxides [6]. The role of incorporated foreign material such as metal/metal oxide, ceramic or polymer is to trap and transfer photoexcited electrons on the semiconductor surface and overcome the problem of recombination of the electron-hole pairs. NiO-ZnO coupled systems have demonstrated excellent photocatalytic efficiency under UV

and visible light irradiation, when compared to individual ZnO and NiO due to the effective separation of photogenerated electron-hole pairs. [7]. Low lattice mismatch between NiO and ZnO is important for the formation of p-n heterojunction [8]. Zinc oxide hybrid photocatalyst [9] and NiO-ZnO composites [10] were also studied as photocatalysts for water pollutant degradation.

NiO photocatalytic activity for bleaching of Rose Bengal [11] and degradation of Rhodamin-B dye under visible light has also been examined [12]. NiO-ZnO composites have been investigated for photodecomposition of Methylene Blue under UV [13] and visible light [14,15] irradiation and of Methyl Orange under UV light [4,16]. NiO-coupled ZnO photocatalysts have been tested for degradation of 2,4-dichlorophenol [7]. Introduction of Ni as dopant into ZnO can be efficient way to improve the activity of ZnO photocatalyst [17,18]. Composites on the base of ZnO-NiO supported on zeolites were also studied [3,19].

The aim of this work was to compare the photocatalytic activities towards degradation of Malachite Green dye of NiO<sub>0.8</sub>ZnO<sub>0.2</sub>-ZnO samples prepared from different precursors (chlorides and nitrates) and calcined at a different temperature (450 or 650 °C).

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## EXPERIMENTAL

*Sample preparation and physicochemical investigation*

Composite samples on the base of mixed nickel oxide and zinc oxide powders were synthesized by precipitation of nickel and zinc nitrates, or nickel and zinc chlorides of Ni to Zn salt solution ratio of 1:2. For this purpose aqueous solutions of 0.25M  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (VWR Prolabo BDH chemicals), 0.25M  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Valerus Co.), 0.25M  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (Valerus Co.), and 0.25M  $\text{ZnCl}_2$  (Valerus Co.) were applied. An aqueous solution of 0.75M NaOH (Valerus Co.) used as a precipitant was added dropwise to the mixture upon stirring until  $\text{pH} = 12$  and kept further under stirring for an hour. The precipitates were filtered, washed with distilled water several times, dried at 35 °C, and calcined in air at 450 °C or 650 °C for 3 hours and 30 minutes. Samples obtained from nitrates and calcined at 450 °C and 650 °C were denoted as H450 and H650, respectively. Those obtained from chloride precursors and calcined at 450 °C and 650 °C are indicated as X450 and X650, accordingly.

Physicochemical characterization of the samples was performed applying FTIR spectroscopy and powder X-ray diffraction (PXRD) analysis. FTIR spectra were recorded on a Bruker-Vector 22 instrument in the range of 400–4000  $\text{cm}^{-1}$  using KBr discs of studied material. PXRD patterns of the samples were collected on a Philips PW 1050 apparatus with  $\text{Cu K}_\alpha$  radiation. ICDD database was used for phase determination.

*Photocatalytic study*

Oxidative photodegradation of aqueous solution of Malachite Green dye of 5 ppm concentration was investigated in a semi-batch slurry reactor using 0.15 g of  $\text{NiO}_{0.8}\text{ZnO}_{0.2}$ -ZnO catalysts catalyst and 150 ml of dye solution under constant stirring in air flow. The photocatalytic experiments were performed using a UV-Vis absorbance spectrophotometer in the wavelength range from 200 to 800 nm ( $\lambda_{\text{max}} = 615$  nm) and polychromatic UV-A lamp illumination (18 W) with maximum of the emission at 365 nm and illumination intensity of 0.66  $\text{mW}\cdot\text{cm}^{-2}$ . Tested systems were left in the dark for about 30 min before switching on the UV irradiation for 2 hours in order to reach adsorption-desorption equilibrium state. First, sample aliquots of the suspension were taken from the reaction vessel and second the powder was separated from the aliquot solution by centrifugation.

Dye degradation degree was calculated using the dependence  $((C_0 - C)/C_0) \times 100$ , where  $C_0$  and  $C$  are initial concentration before turning on the illumination and residual concentration of the dye solution after illumination for selected time interval, respectively.

## RESULTS AND DISCUSSION

PXRD patterns of the investigated samples are presented in figure 1.  $\text{NiO}_{0.8}\text{ZnO}_{0.2}$  (PDF-750271) and ZnO (PDF-897130) phases were determined in the materials.

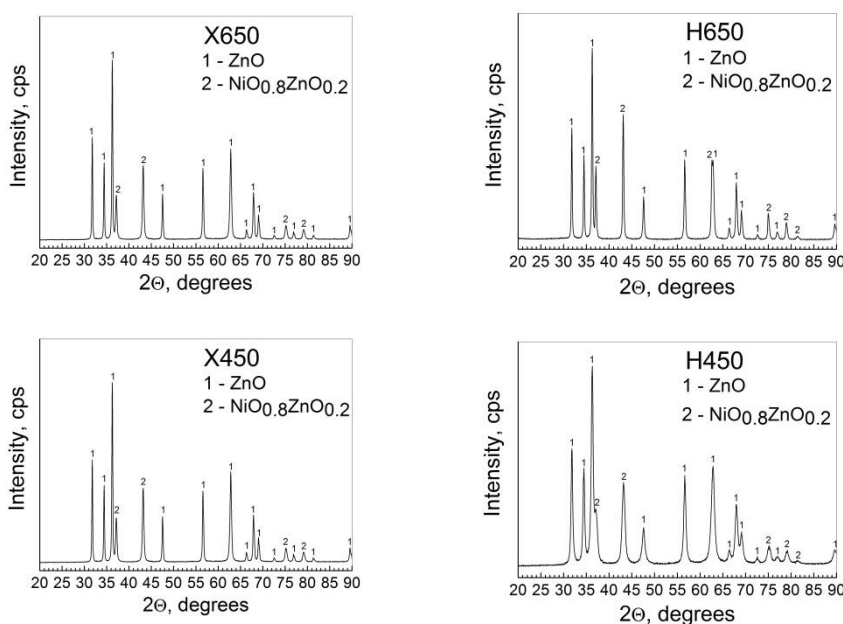


Fig. 1. PXRD patterns of  $\text{NiO}_{0.8}\text{ZnO}_{0.2}$ -ZnO materials calcined at 450 and 650 °C.

FT-IR spectra of the investigated materials in the range of 400–4000  $\text{cm}^{-1}$  are displayed in figure 2. Absorption bands at about 3432–3442 and 1636  $\text{cm}^{-1}$  were observed in the infrared spectra of  $\text{NiO}_{0.8}\text{ZnO}_{0.2}\text{-ZnO}$  samples ascribed to the stretching and bending vibrations of O–H bonds [20,21]. The presence of vibrational bands registered at around 1058 and 1197  $\text{cm}^{-1}$  could be due to other admixtures in the investigated materials. The bands observed in the region above 436  $\text{cm}^{-1}$  belong to the stretching vibrations of zinc oxide [22,23]. The results obtained by FT-IR spectroscopy are in agreement with data from PXRD analysis.

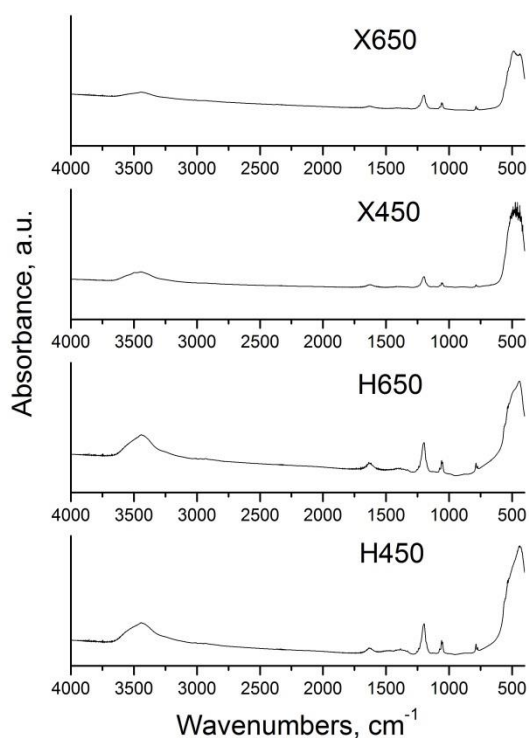


Fig. 2. FTIR spectra of  $\text{NiO}_{0.8}\text{ZnO}_{0.2}\text{-ZnO}$  samples calcined at 450 and 650  $^{\circ}\text{C}$ .

Adsorption capacity of the investigated materials was calculated using the formula:

$$Q = \frac{(C_0 - C) \cdot V}{m}$$

where  $C_0$  is initial dye concentration,  $C$  is dye concentration after 30 minutes in the dark,  $V$  is solution volume, and  $m$  is photocatalyst weight.

Sample adsorption capacity (Figure 3) decreased in the following order: H450 (0.051  $\text{mg/g}$ ) > X450 (0.044  $\text{mg/g}$ ) > H650 (0.040  $\text{mg/g}$ ) > X650 (0.025  $\text{mg/g}$ ). Samples calcined at 450  $^{\circ}\text{C}$  had higher adsorption capacity than those treated at 650  $^{\circ}\text{C}$ .

Figure 4 presents  $C/C_0$  concentration ratio of MG dye degradation with UV illumination time. Calculated degradation degree of Malachite Green dye increases in the order: X650 (86%) < X450 (89%) <

H650 (94%) < H450 (99%) (Table 1). Data on apparent rate constants (calculated using logarithmic linear dependence  $-\ln(C/C_0) = k \cdot t$ ) of the studied catalysts are given in Table 1. Apparent rate constant values of  $\text{NiO}_{0.8}\text{ZnO}_{0.2}\text{-ZnO}$ , 450  $^{\circ}\text{C}$ , chlorides and  $\text{NiO}_{0.8}\text{ZnO}_{0.2}\text{-ZnO}$ , 650  $^{\circ}\text{C}$ , chlorides are  $11.8 \times 10^{-3} \text{ min}^{-1}$  and  $13.9 \times 10^{-3} \text{ min}^{-1}$ , respectively, while those of  $\text{NiO}_{0.8}\text{ZnO}_{0.2}\text{-ZnO}$ , 450  $^{\circ}\text{C}$ , nitrates and  $\text{NiO}_{0.8}\text{ZnO}_{0.2}\text{-ZnO}$ , 650  $^{\circ}\text{C}$ , nitrates increased to  $26.0 \times 10^{-3} \text{ min}^{-1}$  and  $17.9 \times 10^{-3} \text{ min}^{-1}$ , accordingly.

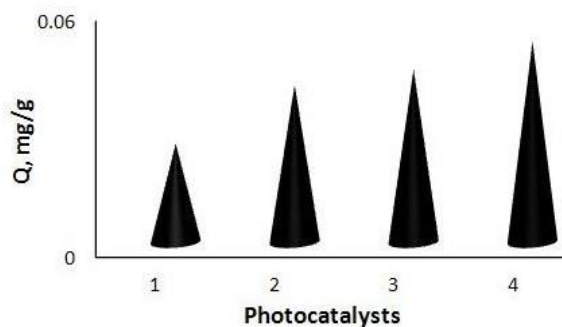


Fig. 3. Comparison of photocatalyst adsorption capacities: 1-X650, 2-H650, 3-X450, and 4-H450 for degradation of Malachite Green dye.

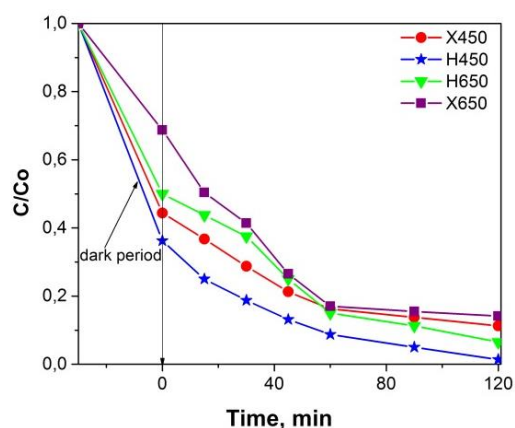


Fig. 4. Concentration  $C/C_0$  ratio of Malachite Green dye with UV illumination time.

**Table 1.** Calculated apparent rate constants of investigated photocatalysts and degradation degree of tested dye

Sample	$k$ ( $\times 10^{-3} \text{ min}^{-1}$ )	Degree of degradation, %
X450	11.8	89
H450	26.0	99
H650	17.9	94
X650	13.9	86

Materials prepared by nitrate precursors possessed higher photocatalytic activity in comparison with those prepared by chloride precursors. The photocatalytic reactivity decreases on rising the temperature of calcination of one type precursor samples. An increase from 400 to 500  $^{\circ}\text{C}$  caused a decrease in photocatalytic activity of ZnO-NiO sup-

ported on zeolite semiconductors due to changes in crystallite phase and particle size [3]. Under UV [24] and solar irradiation [25] commercial ZnO showed degradation of Malachite Green dye below 90%. We can conclude that the photocatalytic behaviour of NiO<sub>0.8</sub>ZnO<sub>0.2</sub>-ZnO materials for degradation of Malachite Green dye under UV-light irradiation is dependent on different synthesis conditions. The high photocatalytic activity of NiO-ZnO composite is probably due to increased separation rate of photogenerated electrons and holes [8,10].

## CONCLUSIONS

A precipitation method was used to obtain composite NiO<sub>0.8</sub>ZnO<sub>0.2</sub>/ZnO photocatalysts using two types of precursors, chlorides and nitrates, followed by calcination at 450 °C or 650 °C. XRD analysis confirmed the presence of ZnO (wurtzite) and NiO<sub>0.8</sub>ZnO<sub>0.2</sub> crystallographic phases. Photocatalytic activities of NiO<sub>0.8</sub>ZnO<sub>0.2</sub>-ZnO catalysts prepared under different synthesis conditions for dye degradation for a period of 2 hours using UV light were compared. All photocatalysts manifested a high catalytic activity. Among them, samples obtained from nitrate precursors treated at 450 °C photodegrade Malachite Green dye by 99% after 2 hours of illumination. Samples from chloride precursors exhibited a lower photocatalytic activity. An increase of the calcination temperature to 650 °C slightly decreased the degradation activity of samples prepared from the same precursor. Composite NiO<sub>0.8</sub>ZnO<sub>0.2</sub>-ZnO photocatalysts, synthesized from nitrate precursors could be suitable for purification of water polluted with Malachite Green textile dye.

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СИНТЕЗ И ИЗСЛЕДВАНЕ НА КОМПОЗИТНИ ФОТОКАТАЛИЗАТОРИ НА ОСНОВАТА НА СМЕС ОТ НИКЕЛОВ ОКСИД И ЦИНКОВ ОКСИД

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(Резюме)

Сравнена е фотокаталитичната активност на  $\text{NiO}_{0.8}\text{ZnO}_{0.2}\text{-ZnO}$  образци, получени при утаяване от различни изходни материали (хлориди и нитрати), последвано от термична обработка при две различни температури (450 °С или 650 °С). Рентгенов анализ и инфрачервена спектроскопия с Фурие трансформация са използвани за охарактеризиране на изследваните катализатори. Изучено е окислителното фоторазграждане на багрилото Малахитово Зелено върху  $\text{NiO}_{0.8}\text{ZnO}_{0.2}\text{-ZnO}$  образци за период от 2 часа, използвайки ултравиолетова светлина. Степените на разграждане на багрилото Малахитово Зелено от  $\text{NiO}_{0.8}\text{ZnO}_{0.2}\text{-ZnO}$  образци, получени от хлориди, третираны при 450 °С и 650 °С, са съответно 89 и 86%. Образците, получени от нитратни прекурсори обработени при 450 °С и 650 °С проявяват по-висока степен на фотокаталитична деградация (съответно 99% и 94%).