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Photocatalytic behaviour of $NiMnO_3/Mn_2O_3$ materials for degradation of Malachite Green and Methylene Blue dyes under UV irradiation

K. L. Zaharieva[1*], K. I. Milenova[1], S. V. Vassilev[2], S. S. Dimova[3], I. D. Stambolova[4], V. N. Blaskov[4]

[1] *Institute of Catalysis, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Bldg. 11, 1113 Sofia, Bulgaria*
[2] *Institute of Electrochemistry and Energy Systems, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Bldg. 10, 1113, Sofia, Bulgaria*
[3] *Institute of Polymers, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Bldg. 103A, 1113 Sofia, Bulgaria*
[4] *Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Bldg. 11, 1113 Sofia, Bulgaria*

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The present work describes a study of the photocatalytic behaviour of $NiMnO_3/Mn_2O_3$ materials for degradation of Malachite Green (MG) and Methylene Blue (MB) dyes as model contaminants under UV light irradiation. Samples were prepared by precipitation using nickel and manganese acetates as starting materials and sodium hydroxide precipitant, and then thermally treated at a different temperature – 450 and 650 °C. Powder X-ray diffraction analysis and Fourier-transform infrared spectroscopy were applied to study phase composition and structure of synthesized $NiMnO_3/Mn_2O_3$ samples. Photocatalytic measurements were carried out using MG or MB aqueous solution with starting concentration of 5 ppm. According to experiments using $NiMnO_3/Mn_2O_3$ photocatalysts calcined at 450 and 650 °C the degree of degradation of Malachite Green and Methylene Blue dyes after 120 minutes was increased as follows: $NiMnO_3/Mn_2O_3$, 450 °C, MB (10%) < $NiMnO_3/Mn_2O_3$, 650 °C, MB (13%) < $NiMnO_3/Mn_2O_3$, 650 °C, MG (67%) < $NiMnO_3/Mn_2O_3$, 450 °C, MG (78%). It was established that the $NiMnO_3/Mn_2O_3$ samples showed a much higher photocatalytic ability for degradation of Malachite Green relative to Methylene Blue dye under UV illumination..

Keywords: Malachite Green, Methylene Blue, degradation, $NiMnO_3/Mn_2O_3$, photocatalytic ability.

INTRODUCTION

Metal oxides can demonstrate an enormous number of structural geometries with an electronic structure that can possess semiconductor, metallic or insulator character and consequently show a very important role in various fields of physics, chemistry, and materials science [1]. Manganese oxides are famous to be active catalysts for various chemical processes such as dye degradation, water oxidation, organic synthesis, and CO and NO_x removal from waste gases [2]. Heterogeneous photocatalysis using metal oxides due to its potential application to both organic synthesis and environmental applications has attracted considerable attention [1,3].

Catalytic oxidation of Methylene Blue by H_2O_2 has been tested on manganese oxide loaded hollow silica particles (MHSPs). The MHSPs with hollow structure and high surface areas enhance the catalytic activity compared to the matching manganese oxide solid particles (MSPs) [2]. Xia *et al*. have prepared Mn_2O_3 microspheres by a two-step method in ethylene glycol system. The obtained samples were tested for photodegradation of Methylene Blue solution in the presence of H_2O_2 under ultraviolet illumination. The Mn_2O_3 microspheres exhibited moderate photocatalytic ability due to their particular structure [4]. In addition, Mn_2O_3 microspheres obtained by a hydrothermal route have been studied for purification of water polluted with Methylene Blue dye [5].

Han *et al*. have investigated a Mn_2O_3/MCM-41 composite for degradation of Methyl Orange (MO), Congo Red (CR), Methylene Blue (MB), and Rhodamine B (RB) with/without visible light irradiation at room temperature. The Mn_2O_3/MCM-41 composite demonstrated superb removal efficiency for RB and MB [6]. A Ni/α-Mn_2O_3 catalyst has been tested for reduction in aqueous phase of 4-nitrophenol and organic dye pollutants - Rhodamine B, Methylene Blue, Rose Bengal, Congo Red, and Methyl Orange in the presence of a mild reducing agent, $NaBH_4$ [7]. Yang *et al*. have prepared single-crystalline nanorods of beta-MnO_2, alpha-Mn_2O_3, and Mn_3O_4 using heat-treatment of γ-MnOOH nanorods obtained by a hydrothermal method. The synthesized manganese oxide nanorods manifested catalytic ability to oxidise and decompose Methylene Blue dye with H_2O_2 [8].

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* To whom all correspondence should be sent
E-mail: zaharieva@ic.bas.bg

Preparation of $NiMnO_3/Mn_2O_3$ powders using $MnSO_4 \cdot H_2O$ and $NiSO_4 \cdot 6H_2O$ precursors has been reported by Gao *et al*. [9]. Mn_2O_3 is a semiconductor metal oxide [10]. Kakvand *et al*. have prepared $NiMnO_3$/C nanocomposite electrode materials for electrochemical capacitors [11]. $NiMnO_3$ and $NiMnO_3$/nitrogen-doped graphene nanocomposites have been investigated as super-capacitors [12]. Gnanam *et al*. have determined the band gap energy (3.49, 3.43, 3.38, and 3.36 eV) of α-Mn_2O_3 nanoparticles prepared using sodium dodecyl sulphate (SDS) or different surfactants such as polyethylene glycol (PEG), cetyl trimethyl ammonium bromide (CTAB), and citric acid (CA) [13].

The present paper deals with a study of the photocatalytic efficiency of $NiMnO_3/Mn_2O_3$ materials about degradation of aqueous solutions of Malachite Green and Methylene Blue dyes under UV irradiation. Samples were obtained using precipitation technique by nickel and manganese acetates, followed by calcination at 450 and 650 °C. The synthesized products were characterized by powder X-ray diffraction analysis and FTIR spectroscopy.

EXPERIMENTAL

Synthesis and physicochemical characterization of $NiMnO_3/Mn_2O_3$ materials

$NiMnO_3/Mn_2O_3$ samples were prepared by precipitation technique using 0.25M $Ni(CH_3COO)_2 \cdot 4H_2O$ and 0.25M $Mn(CH_3COO)_2 \cdot 4H_2O$ mixed at a ratio of 1:2. 0.75M NaOH precipitant was added dropwise to a mixture of aqueous solutions of acetate precursors until pH reached 12 under continuous stirring. After precipitation, the suspension was further agitated for one hour. The precipitate was filtered and washed with distilled water several times. Finally, it was dried at 35 °C and calcined at 450 °C and 650 °C for 3 hours and 30 minutes in air atmosphere.

FTIR spectra of the synthesized materials were recorded on a Bruker-Vector 22 Fourier transform infrared spectrometer in the range of 400–4000 cm^{-1} using KBr tablets. Powder X-ray diffraction analysis (PXRD) of the investigated samples was performed by means of Philips PW 1050 instrument with Cu K_α-radiation. Phases in the prepared materials were established using ICDD database.

Photocatalytic study

The photocatalytic tests of degradation of Malachite Green (MG) and Methylene Blue (MB) with initial concentration of aqueous solution of the dye - 5 ppm were performed under UV-A illumination (18 W). The catalytic experiment was carried out in semi-batch slurry reactor using 0.15 g catalyst and 150 ml of dye solution under air flowing and stirring. To reach adsorption-desorption equilibrium state $NiMnO_3/Mn_2O_3$ powders were left in the dark for half an hour before turning on the UV light for period of time - 2 hours. The powder was divided from the aliquot solution by centrifugation. After that the change of absorbance during the photocatalytic investigation was monitored by UV-Vis absorbance spectrophotometer UV-1600PC in the wavelength range from 200 to 800 nm (λ_{max} = 615 nm for Malachite Green and 664 nm for Methylene Blue). The degree of dye degradation was computed using $((C_0 - C)/C_0) \times 100$, where C_0 and C were initial concentration before turning on the illumination and residual concentration of the dye solution after illumination for selected time interval.

RESULTS AND DISCUSSION

Results obtained by powder X-ray diffraction analysis are shown in figure 1. Two phases - $NiMnO_3$ (PDF-653695; PDF-895878) and Mn_2O_3 (PDF-721427; PDF-651798) were registered in the X-ray diffraction patterns of materials synthesized at 450 °C and 650 °C. In the powders, treated at 450 °C, the $NiMnO_3$ crystallographic phase prevails over other phase.

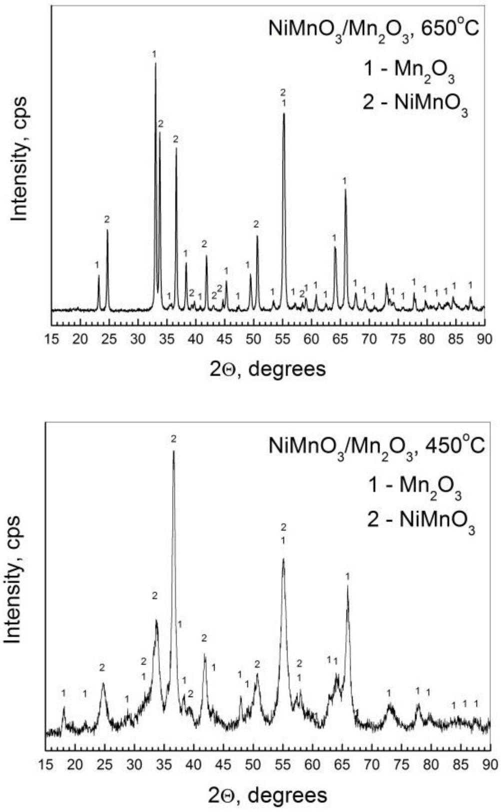

Fig. 1. PXRD patterns of $NiMnO_3/Mn_2O_3$ samples thermally treated at 450 and 650 °C.

Figure 2 displays FTIR spectra of investigated samples. Characteristic bands recorded in the range of 520−606 cm^{-1} are due to vibrations of the metal oxides [14−16]. The bands at about 3400 cm^{-1} and 1631 cm^{-1} arise from stretching and bending vibrations of OH groups of absorbed water molecules [16,17]. The vibrations observed at 1051, 1058, and 1197 cm^{-1} are probably due to the presence of other admixtures in the studied materials. The data acquired by FTIR spectroscopy are in agreement with results established using powder X-ray diffraction analysis.

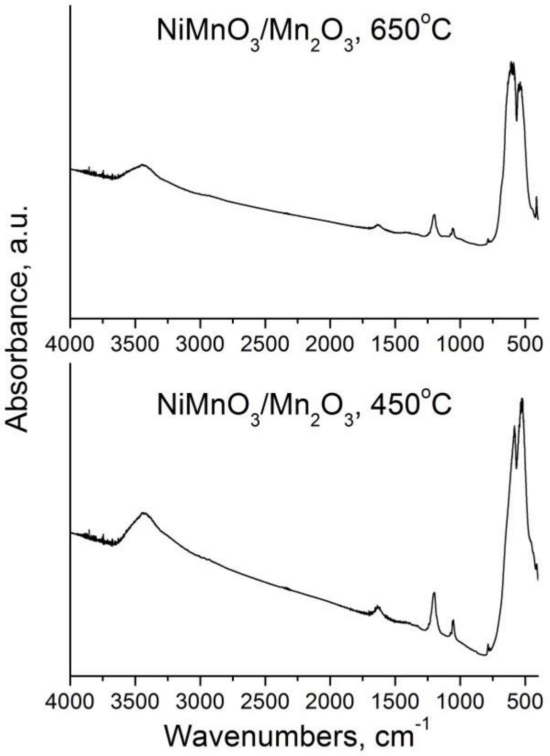

Fig. 2. FTIR spectra of $NiMnO_3/Mn_2O_3$ materials thermally treated at 450 and 650 °C.

Results from photocatalytic degradation measurements of model pollutant Malachite Green and Methylene Blue dyes under UV light using synthesized $NiMnO_3/Mn_2O_3$ as photocatalysts are shown and discussed in the following lines.

Calculated adsorption capacities and apparent rate constants of the investigated photocatalytic systems are presented in figure 3 and table 1, respectively.

The following formula was used to estimate adsorption capacity:

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

where C_0 is initial dye concentration, C is dye concentration after 30 min in the dark, V is solution volume, and m is sample mass.

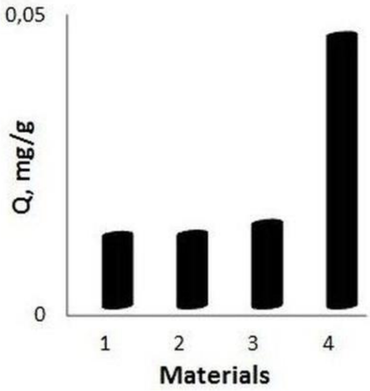

Fig. 3. Comparison of adsorption capacities of materials tested as photocatalysts for degradation of Malachite Green and Methylene Blue dyes: 1-$NiMnO_3/Mn_2O_3$, 650 °C, MG; 2-$NiMnO_3/Mn_2O_3$, 450 °C, MB; 3-$NiMnO_3/Mn_2O_3$, 450 °C, MG; 4-$NiMnO_3/Mn_2O_3$, 650 °C, MB.

Table 1. Calculated apparent rate constants (*k*) of tested photocatalysts and degree of degradation of investigated dyes after 120 minutes.

Sample	Used dye	k ($\times 10^{-3}$ min^{-1})	Degree of degradation, %
$NiMnO_3/Mn_2O_3$, 450°C	MG	11.6	78
$NiMnO_3/Mn_2O_3$, 650 °C	MG	7.9	67
$NiMnO_3/Mn_2O_3$, 450 °C	MB	0.7	10
$NiMnO_3/Mn_2O_3$, 650 °C	MB	0.5	13

The adsorption capacity of the investigated materials decreased in the following order: $NiMnO_3/Mn_2O_3$, 650 °C, MB (0.0450 mg/g) > $NiMnO_3/Mn_2O_3$, 450 °C, MG (0.0138 mg/g) > $NiMnO_3/Mn_2O_3$, 450 °C, MB (0.0120 mg/g) > $NiMnO_3/Mn_2O_3$, 650 °C, MG (0.0118 mg/g).

Apparent rate constants which followed pseudo first-order kinetics, were calculated using a logarithmic linear dependence $-\ln(C/Co) = k.t$. The apparent rate constants of samples calcined at 450 °C were higher than those calcined at 650 °C for degradation of Malachite Green dye (11.6×10^{-3} min^{-1} and 7.9×10^{-3} min^{-1}) and Methylene Blue (0.7×10^{-3} min^{-1} and 0.5×10^{-3} min^{-1}) were.

C/C_0 concentration changes of Malachite Green and Methylene Blue dye degradation as a function of UV illumination time are shown in figure 4. The calculated degree of degradation (Table 1) after 120 min UV illumination of Malachite Green dye is superior (67–78%) than that of Methylene Blue dye (10–13%) over the investigated $NiMnO_3/Mn_2O_3$ samples. The $NiMnO_3/Mn_2O_3$ materials demonstrated an enhanced photocatalytic efficiency toward photocatalytic degradation of Malachite Green dye compared to Methylene Blue dye.

It could be supposed that the MG degraded faster than the MB taking into account the chemical structure of the dyes. According to Berberidou *et al*. the degradation of MG may proceed in two pathways. The first involves a hydroxyl radical attack to the central carbon atom of MG, while in the second pathway the hydroxyl radical hits the N,N-dimethylamino group of MG producing a reactive cationic radical [18]. Methylene blue dye decolourizes slower due to difficult destruction of the single benzene rings in comparison with MG degradation.

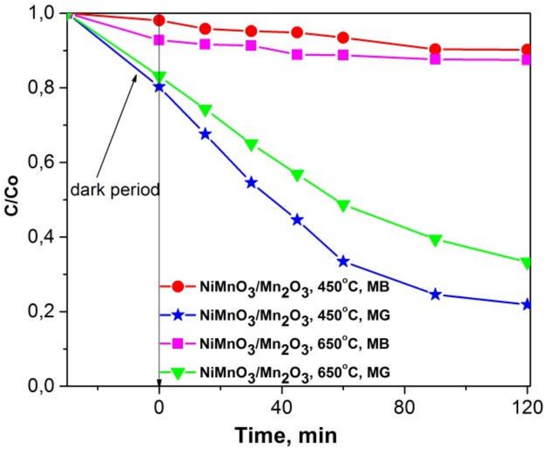

Fig. 4. C/C_0 concentration ratio of Malachite Green and Methylene Blue dyes as a function of UV irradiation time.

CONCLUSIONS

$NiMnO_3/Mn_2O_3$ materials were successfully prepared by precipitation technique using acetates as starting materials followed by thermal treatment at a different temperature of 450 °C and 650 °C. $NiMnO_3$ and Mn_2O_3 phases' occurrence was determined by powder X-ray diffraction analysis and FTIR spectroscopy. The photocatalytic behaviour of synthesized $NiMnO_3/Mn_2O_3$ samples was investigated in degradation reactions of aqueous solutions of Malachite Green and Methylene Blue dyes under UV irradiation for 120 minutes. In degrading Malachite Green dye the $NiMnO_3/Mn_2O_3$ samples exhibited a significantly higher photocatalytic efficiency than that in the case of Methylene Blue. The highest photocatalytic ability possessed a $NiMnO_3/Mn_2O_3$ catalyst calcined at 450 °C for degradation of Malachite Green dye (78%) in comparison with other studied samples.

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ФОТОКАТАЛИТИЧНО ПОВЕДЕНИЕ НА $NiMnO_3/Mn_2O_3$ МАТЕРИАЛИ ЗА РАЗГРАЖДАНЕ НА БАГРИЛАТА МАЛАХИТОВО ЗЕЛЕНО И МЕТИЛЕНОВО СИНЬО ПОД УВ ОБЛЪЧВАНЕ

К. Л. Захариева[1]*, К. И. Миленова[1], С. В. Василев[2], С. С. Димова[3], И. Д. Стамболова[4], В. Н. Блъсков[4]

[1] *Институт по катализ, Българска академия на науките, ул. „Акад. Г. Бончев“, бл. 11, 1113 София, България*
[2] *Институт по електрохимия и енергийни системи, Българска академия на науките, ул. „Акад. Г. Бончев“, бл. 10, 1113 София, България*
[3] *Институт по полимери, Българска академия на науките, ул. „Акад. Г. Бончев“, бл. 103А, 1113 София, България*
[4] *Институт по обща и неорганична химия, Българска академия на науките, ул. „Акад. Г. Бончев“, бл. 11, 1113 София, България*

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(Резюме)

В настоящата работа е изследвано фотокаталитичното поведение на $NiMnO_3/Mn_2O_3$ материали под действието на УВ облъчване за разграждане на багрилата малахитово зелено (МЗ) и метиленово синьо (МС) като моделни замърсители. Получени са образци чрез утаяване използвайки никелов и манганов ацетат и утаител натриева основа и след това термична обработка при различна температура - 450 и 650 °C. Рентгенов фазов анализ и инфрачервена спектроскопия с Фурие преобразуване бяха използвани за да се изследва фазовия състав и структурата на синтезираните $NiMnO_3/Mn_2O_3$ образци. Фотокаталитичните изследвания бяха проведени използвайки воден разтвор на багрилата МЗ и МС с начална концентрация 5 ppm. От фотокаталитичните тестове се установи, че степента на разграждане на багрилата малахитово зелено и метиленово синьо след 120 минути използвайки $NiMnO_3/Mn_2O_3$ фотокатализатори, накалени при 450 и 650 °C, нараства както следва: $NiMnO_3/Mn_2O_3$, 450^{o}C, МС (10%) < $NiMnO_3/Mn_2O_3$, 650^{o}C, МС (13%) < $NiMnO_3/Mn_2O_3$, 650^{o}C, МЗ (67%) < $NiMnO_3/Mn_2O_3$, 450^{o}C, МЗ (78%). Установено е, че $NiMnO_3/Mn_2O_3$ образци показват много по-висока фотокаталитична способност за разграждане на малахитово зелено отколкото на метиленово синьо под действието на УВ облъчване.