PHOTOCATALYTIC ACTIVITY OF Eu_2O_3/ZnO AND Sm_2O_3/ZnO PREPARED BY MICROWAVE-ASSISTED HYDROTHERMAL METHOD

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Abstract

In this study Sm_2O_3/ZnO and Eu_2O_3/ZnO nanostructures were prepared using microwave-assisted hydrothermal method. Effect of Sm_2O_3 and Eu_2O_3 content and calcination temperature was investigated. The reusability of obtained photocatalysts was also studied. The prepared samples were investigated by using XRD, X-ray spectroscopy, scanning electron microscope. The photocatalytic activity was determined by degradation of methylene blue (MB) under Osram Vitalux illumination. Modified ZnO nanoparticles according to XRD analysis consists of ZnO with crystallite size in the range of 16-23 nm. Under solar light simulated radiation prepared ZnO nanostructures shown high photocatalytic activity. After 30 minute of irradiation more than 95 % of initial MB solution was degraded. The photocatalytic test revealed that ZnO containing Eu_2O_3 and Sm_2O_3 exhibits higher activity than pure unmodified ZnO.

Keywords: ZnO, hydrothermal synthesis, microwave, Eu_2O_3, Sm_2O_3, photocatalysis

1. INTRODUCTION

Textile industry is one of the main sources of dye pollution. Removing of dyes from water has received increased attention among the researched. Such methods as biodegradation, absorption and photocatalysis have been proposed for removal of hazardous compounds from wastewater [1].

Photocatalysis is advanced oxidation process (AOP) and is used to mineralize toxic compound and pollutants in order to purify water. During the photocatalysis highly reactive OH· radicals are generated that are able to degrade hazardous organics [2]. Photocatalysis is heterogeneous process involving semiconductor materials such as TiO_2 or ZnO [3]. When photocatalyst is irradiated with UV light, electron-hole pair is formed by transition of electron from valence band to conduction band [2].

ZnO is a wide band gap semiconductor (3.37 eV) with high exciton binding energy (60 meV) that is widely used as a photocatalyst [4]. It exhibits good mechanical, optical and chemical properties [5]. ZnO photocatalysts were prepared by sol-gel [6], precipitation [7] or hydrothermal method [8]. ZnO is stable, non-toxic and cheap to produce. Although recombination rate of photogenerated electrons and holes is high, which is limitation for ZnO photocatalytic performance [9]. It was reported that addition of Sm_2O_3 or Eu_2O_3 can increase photocatalytic activity [10,11].

The aim of this study is to obtain Sm_2O_3/ZnO and Eu_2O_3/ZnO photocatalysts with different dopant mass loading by microwave-assisted hydrothermal method and compare their photocatalytic activity, determine effect of calcination temperature and study reusability of photocatalysts.

2. EXPERIMENTAL

The photocatalysts were synthesized by aqueous microwave-assisted hydrothermal method. Certain amount of $Zn(CH_3COO)_2{\cdot}2H_2O$, $Sm(NO_3)_2$ or $Eu(NO_3)_3{\cdot}5H2O$ and 100 g of $NaHCO_3$ were mixed in 500 ml of deionized

water under vigorous stirring for 30 minutes. The mixture was transferred into sealed Teflon vessel and maintained at 200 ºC for 30 minutes under microwave radiation by using Anton Paar Masterwave BTR microwave system. The mixture was cooled down to 55 ºC and filtered and washed with deionized water and ethanol. Obtained samples with different Sm_2O_3 and Eu_2O_3 mass loading were dried in the oven at 90 ºC overnight and calcined at 400 - 600 ºC.

Phase composition of prepared powder was determined by X-ray diffraction analysis using Advance D8 Bruker AXS. Crystallite size was evaluated using X-ray diffraction software EVA12 based on the Scherrer formula. The amount of Sm_2O_3 and Eu_2O_3 was measured by X-ray fluorescence analysis using Pioneer S4, Bruker AXS. The specific surface (SSA) of powders was determined by the argon absorption-desorption method using apparatus based on Hrom-3 gas analysis. Size and shape of prepared particles was investigated using scanning electron microscopy (SEM). Photocatalyst activity test was carried out in 7.25 mg/L methylene blue (MB) solution. 100 mg of photocatalyst sample was added to 100 mL of MB solution. The mixture was kept in darkness for 30 min to achieve adsorption desorption equilibrium. The photocatalytic experiments were performed under irradiation of Osram Vitalux lamp (300 W) imitating solar light for 30 minutes. 2 mL of the solution was withdrawn and centrifuged at regular interval. Absorption of MB solution was measured at wave length of 662 nm.

3. RESULTS AND DISCUSSIONS

3.1. Specific surface area

Specific surface area of samples prepared by microwave-assisted hydrothermal method is shown in **Table 1**. There was only marginal change in specific surface area observed after addition of Sm_2O_3 or Eu_2O_3. Specific surface area of prepared samples is in the range of 31.6 -35.8 m^2/g.

Table 1 Prepared samples and their specific surface area.

Sample	Composition, wt%	Specific surface area, m^2/g
SmZ-1	1% Sm_2O_3	34.8
SmZ-2	2% $Sm2O_3$	34.9
SmZ-4	4% Sm_2O_3	35.8
SmZ-10	10% Sm_2O_3	31.9
EuZ-1	1% Eu_2O_3	33.7
EuZ-2	2% Eu_2O_3	33.4
EuZ-4	4% Eu_2O_3	33.7
EuZ-10	10% Eu_2O_3	31.6

3.2. X-ray difraction

XRD patterns of Sm_2O_3/ZnO and Eu_2O_3/ZnO photocatalysts synthesized after calcination at 400 ºC are shown in the **Figure 1**. All intensive peaks correspond to a hexagonal ZnO structure (PDF 00-036- 1451) with 2θ angle values of 31.726°, 34.378° and 36.186 (PDF 01-078-4055). Sm_2O_3 and Eu_2O_3 phases are not detected however after calcination at 600 ºC, both phases Sm_2O_3 and Eu_2O_3 are observed indicating that at 400 ºC

these phases are x-ray amorphous. Slower XRD scan (10s per step, 1 step 2θ 0.01°) shown no shift of ZnO peaks indicating Sm_2O_3 and Eu_2O_3 did not fully incorporate into ZnO lattice.

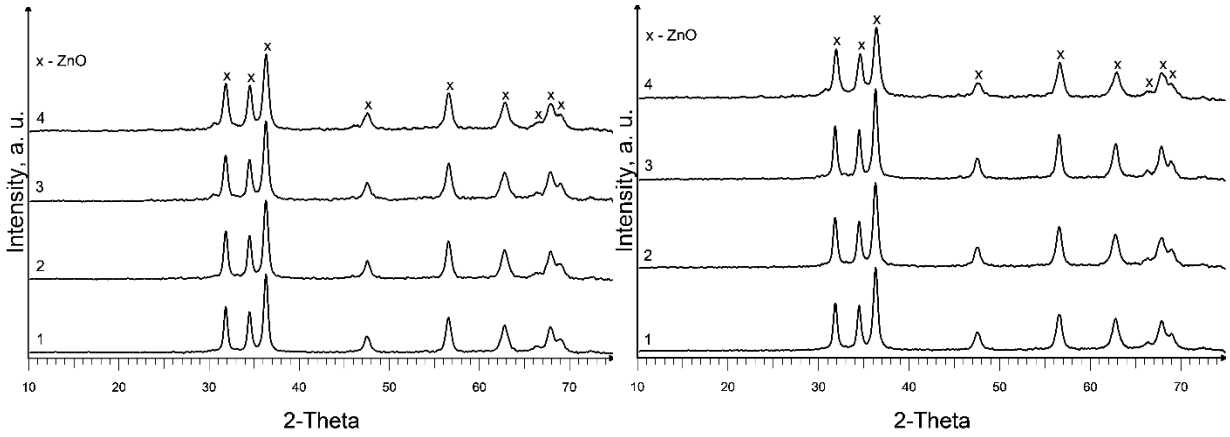

Figure 1 XRD patterns for the 1 - SmZ-1, 2 - SmZ-2, 3 - SmZ-4, 4 - SmZ-10 (left) and 1 - EuZ-1, 2 - EuZ-2, 3 - EuZ-4, 4 - EuZ-10 (right)

3.3. Morphology

Figure 2 represents obtained structure of ZnO synthesized by microwave-assisted hydrothermal method. Structure is flower-like and consists of nanosized thin plates. Plate thickness is about 65 nm. Such structure could be effective for light harvesting.

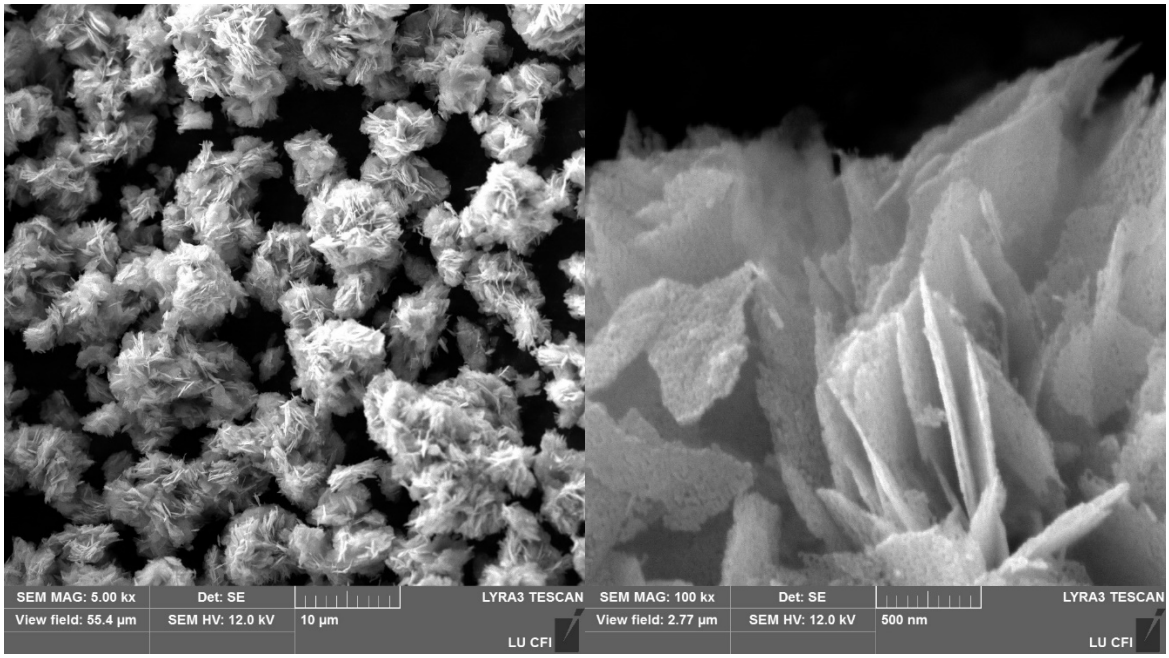

Figure 2 SEM micrographs of ZnO prepared by microwave-assisted hydrothermal method

3.4. Photocatalytic activity

Sm_2O_3/ZnO and Eu_2O_3/ZnO photocatalysts were used for the degradation of methylene blue dye under solar emitted light. **Figure 3** shows the change of concentration of methylene blue as a function of time in the presence of Sm_2O_3/ZnO and Eu_2O_3/ZnO. It can be seen Sm_2O_3/ZnO photocatalysts exhibit higher

photocatalytic activity compared to bare ZnO. More than 95 % of MB was degraded after 30 minutes of illumination. In the case of Eu_2O_3/ZnO photocatalysts, 95 % degradation rate was achieved by all samples except for EuZ-1. Photocatalytic activity of Eu_2O_3 is higher than of pure ZnO.

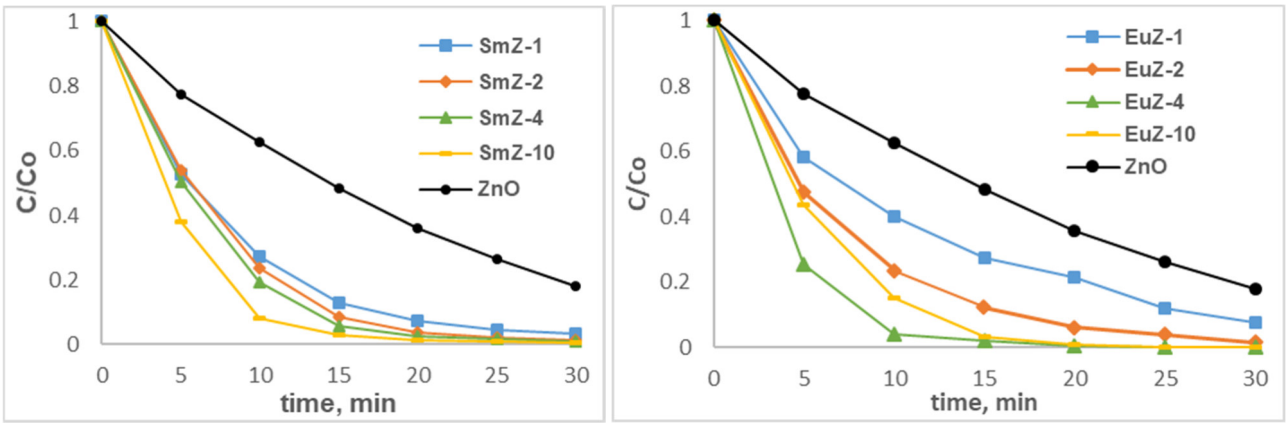

Figure 3 Change in concentration of MB as a function of time in presence of Sm_2O_3/ZnO (left) and Eu_2O_3/ZnO (right)

For more precise evaluation of photocatalytic activity, prepared samples have been compared by degradation kinetic studies. The kinetic of photocatalytic degradation of MB can be expressed with pseudo first-order rate law (1).

$$-ln\frac{C}{C_0} = kt \quad (1)$$

where:

C_0 - initial concentration (mg/l)
C - concentration after irradiation (mg/l)
k - pseudo-first order constant (s^{-1})
t - time, (s)

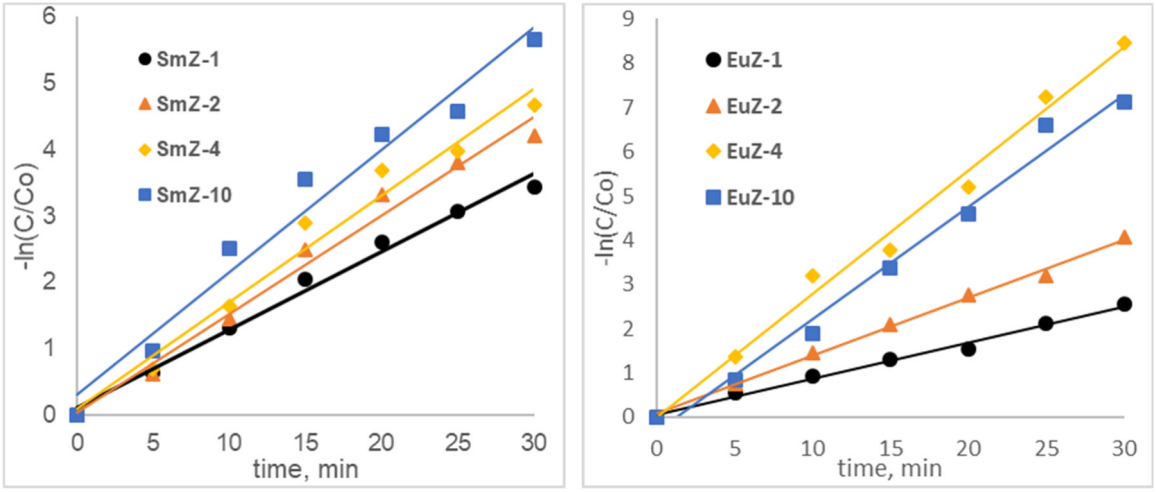

Figure 4 Kinetic study of MB degradation in presence of Sm_2O_3/ZnO (left) and Eu_2O_3/ZnO (right)

As shown in **Figure 4**, photocatalytic degradation reaction of MB follows first-order rate law. The rate constants were calculated and found to be 0,0021, 0,0025, 0,0028, 0,0035 s^{-1} for SmZ-1, SmZ-2, SmZ-4 and SmZ-10

photocatalysts, 0,0015, 0,0023, 0,0047, 0,0036 s^{-1} for EuZ-1, EuZ-2, EuZ-4 and EuZ-10 photocatalysts respectively. SmZ-10 and EuZ-4 shown the best photocatalytic performance among all samples and were further used to investigate calcination temperature effect on photocatalytic activity and possible reusability of photocatalysts.

3.5. Effect of calcination temperature

Calcination temperature is important factor in nanostructure synthesis. It mainly affects specific surface area and number of defects in structure. The effect of calcination temperature on degradation of MB using SmZ-10 and EuZ-4 photocatalysts was studied in the temperature range of 400 - 600 ºC. **Figure 5** reflects photocatalytic activity of SmZ-10 and EuZ-4 samples at different calcination temperatures. It can be seen that in both cases there is marginal change in photocatalytic performance after calcination at 500 and 600 ºC despite the specific surface area decrease, from 31.9 to 22.5 m^2/g for SmZ-10 (after being calcined at 600 ºC) and from 33.7 to 22.4 m^2/g for EuZ-4 photocatalyst.

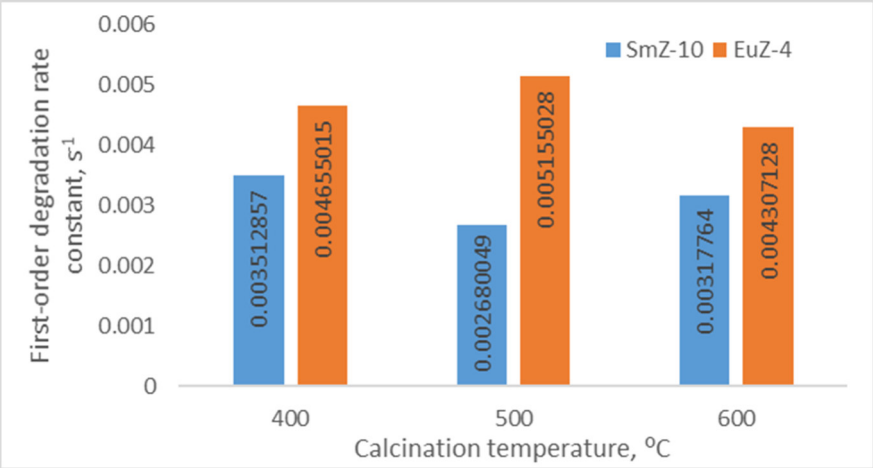

Figure 5 Effect of calcination temperature on photocatalytic activity of SmZ-10 and EuZ-4 samples

The photocatalytic activity trend for SmZ-10 for degradation of MB lies in the order 400º > 600º > 500º, for EuZ-4 order is 500º > 400º > 600º. It is also noted that for both samples the same trend is observed for absorption of MB in the dark. It is hypothesized that such difference can be explained by the change of absorption mechanism after calcination at higher temperatures.

3.6. Reusability of photocatalysts

From application point reusability of photocatalyst is vital factor. To test the reusability of SmZ-10 and EuZ-4 samples were used in degradation studies of MB solution for 5 cycles. After each cycle photocatalyst was washed with deionized water and ethanol followed by drying at 90 ºC for 4 hours. Both samples shown high stability and small loss of photocatalytic activity was observed after 5 cycles. Decolorization rate for SmZ-10 decreased from 99 % to 93 % and from 99 % to 94 % for EuZ-4 photocatalyst.

4. CONCLUSION

Flower-like Sm_2O_3/ZnO and Eu_2O_3/ZnO nanostructures were prepared by microwave-assisted hydrothermal method. The effect of dopant and its amount on photocatalytic activity has been studied. Methylene blue degradation tests shown that doped ZnO samples exhibit higher photocatalytic activity. Among them photocatalysts with 4% wt. of Eu_2O_3 and 10% wt. of Sm_2O_3 were found to be with highest degradation rate.

Obtained photocatalysts are stable and show little decrease in photocatalytic activity after 5 reuse cycles. Change in calcination temperature shown little effect on photocatalytic activity on studied samples.

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