Research Article

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Photocatalytic activity of NiFe_2O_4 and $\text{Zn}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$ modified by Eu(III) and Tb(III) for decomposition of Malachite Green

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Abstract: The mixed metal oxides NiFe_2O_4 and $\text{Zn}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$ with a spinel-like structure, pure and modified with the lanthanide ions Eu(III) and Tb(III), were prepared by a sol-gel process in which propylene oxide was used as a gelling agent and then tested as photocatalysts. The photocatalytic activity was studied under polychromatic visible light irradiation (halogen lamp) for the decomposition of the water pollutant Malachite Green in model solutions which were prepared under laboratory conditions. The modified samples showed a better activity under visible light irradiation than the pure samples. The highest activity under visible light irradiation was observed for $\text{Zn}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$ that was modified with 5 wt. % Eu(III) or Tb(III), and which showed the positive effects of the doping ions. Based on the cartographic data for the smooth and equal distribution of Tb(III) on the surface of $\text{Zn}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$ particles, the surface processes may have influenced the photocatalytic activity. The energy band gap of the samples was calculated, showing somewhat lower values for the doped samples than the pure ferrites.

Keywords: ferrites; lanthanide ions; photocatalytic activity; rate constants; band gap energy.

1 Introduction

Mixed metal oxides with a spinel-like structure can be presented with the formula $\text{M}'\text{M}''\text{O}_4$, where M' represents a divalent metal ion and M'' represents a trivalent metal ion such as Al, Cr, Fe, etc.; if M'' is Fe(III) these metal oxides are also called ferrites. They are technologically important systems and have been used in many applications including magnetic recording media for the storage and/or retrieval of information, magnetic fluids, magnetic resonance imaging enhancement, catalysis, magnetically guided drug delivery, sensors, pigments, etc. [1-3]. Recent investigations focus on their photocatalytic properties to elucidate their application for the degradation of water pollutants, as reviewed in [4]. Of special interest are both their ability to catalyze the photodegradation of water pollutants in visible light and their magnetic properties, which make it easy to separate the catalyst from the purified water after use. It has been found that some properties of these mixed metal oxides with a spinel-like structure can be influenced by modifying the lanthanide ions Ln(III) [5-14]. We therefore think it is worth investigating what influence some Ln(III) have on the photocatalytic activity of ferrites. There is limited information for the photocatalytic degradation of Malachite Green (MG) by ferrites. In our laboratory mixed metal oxides with a spinel-like structure were synthesized by mechanotreatment, both of the type MFe_2O_4 , where $\text{M} = \text{Zn}, \text{Ni}$ or Co , and of the type $\text{M}'\text{M}''\text{Fe}_2\text{O}_4$, where $\text{M}' = \text{Zn}$ and $\text{M}'' = \text{Ni}$ or Co ; these samples were tested for the degradation of MG under UV irradiation [15]. Because of NiFe_2O_4 and $\text{Zn}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$ showing especially promising behavior as photocatalysts, they were selected for the modification with lanthanide ions such as Eu(III) or Tb(III). The synthesized and characterized NiFe_2O_4 and $\text{Zn}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$ doped with Eu(III) or Tb(III) are presented in [16]. The X-ray diffraction and Mossbauer spectroscopy proved that the samples were monophasic ferrites. It was shown that Ln(III) ions affected the magnetic properties

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of ferrites, however, their influence was indirect and only due to their effect on the average particle size. The results of the investigation on the photocatalytic activity of these samples are discussed in this work.

2 Experimental and methods

The synthesis by the applied sol-gel method and the characterization of the samples NiFe_2O_4 and $\text{Zn}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$ by XRD and Mossbauer and Raman spectroscopy and those samples modified with Ln(III) ions ($\text{Ln} = \text{Eu}$ or Tb) are presented in detail in [16]. The samples were prepared by mixing the solutions of the nitrates in 96% ethanol, and then stirring the solutions for complete homogenization; propylene oxide was added in a molar ratio of 1:4 to the ethanol, then the solutions were continually stirred until a sol was formed. The sol was dried for 48h at 60°C and annealed for 5h at 550°C . Propylene oxide was used to make hydroxyl groups on the hydrated cations and to induce a polycondensation reaction between the ions of Fe^{3+} , Ni^{2+} and Zn^{2+} . The gel formation was almost immediate while other gelling agents took much longer to form a gel. In the text below the powdered samples tested as photocatalysts are referred to as NF-Ln1, NF-Ln5 and ZNF-Ln1, ZNF-Ln5 ($\text{Ln} = \text{Eu}$ or Tb), where NF or ZNF refers to the mixed metal oxides NiFe_2O_4 or $\text{Zn}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$, and the symbol of the Ln(III) ion is followed by its content (1 or 5 wt. %). In total, 10 samples (2 unmodified and 8 modified) were tested as photocatalysts, and the results are discussed below.

For the purpose of the photocatalytic data interpretation, additional characterizations were done by the methods presented in this section.

Specific surface area, SSA, was determined using nitrogen at 77K by the Brunauer–Emmett–Teller (BET) method.

UV-Vis absorption spectra were recorded in the range 200–900 nm using an Evolution 300 UV-Vis spectrometer (Thermo Scientific).

TEM, transmission electron microscopy, investigations were performed on a JEOL 2100 transmission electron microscope.

Band gap energy calculations. The optical properties (absorption and optical band gap energy) of the samples were studied using UV-Vis spectroscopy. In all cases, broad absorption was observed in the 300–900 nm range of the spectra. The UV-Vis data were analyzed to determine the relationship between the optical band gap, absorption coefficient and energy ($h\nu$) of the incident photon for near edge optical absorption in semiconductors. The band gap

energy was calculated from the measured curves according to Tauc's equation [17] $\alpha h\nu = A(h\nu - E_g)^n$, where A is a constant independent of $h\nu$, E_g is the semiconductor band gap and n depends on the type of transition. In addition, the well-known approach to determine the semiconductor band gap energy from the intersection of linear fits of $(\alpha h\nu)^{1/n}$ versus $h\nu$ on the x-axis was used, n being 1/2 and 2 for direct and indirect band gap, respectively.

The photocatalytic tests were performed in a slurry (1 g catalyst L^{-1}), using a 10^{-5} M aqueous solution of Malachite Green oxalate (MG), (Chroma GmbH) as a model pollutant. The equipment and the procedure used were the same ones as for the photocatalytic measurements published in [15, 18–20]. After a 60-min “dark” period (to establish the equilibrium of the sorption process), the system was illuminated by a halogen lamp (Kanlux S.A., J-300W 118 MM, correlated color temperature 2710 K, 300 W, polychromatic, 300 - 800 nm, maximum at 600 nm), situated at 20 cm distance above the slurry, under continuous magnetically stirring (400 min^{-1}) and bubbling with air (45 L h^{-1}). The initial pH of the solutions was between 5.8 and 5.9. Periodically, a 5 mL aliquot was taken from the solution and filtered through a $0.20 \mu\text{m}$ Minisart filter. The dye concentration was determined spectrophotometrically by the band at 620 nm. The data obtained were plotted in coordinates $(C/C_0)/t$ and $-\ln(C/C_0)/t$ (where C_0 is the concentration after the “dark” period, and C is the concentration after t min irradiation), and apparent rate constants of the degradation process were determined assuming first-order kinetics. The sorption capacity was calculated as the ratio $(C_{00} - C_0)/C_{00}$, where C_{00} is the starting solution concentration (before the “dark” period). The MG degradation at moment t is determined by the formula: degradation, % = $(A_0 - A_t)/A_0 \times 100$, where A_0 is the initial absorption of the MG solution at $t = 0$ min, and A_t is the absorption at t min. The duration of visible irradiation was 150 min. The experiments were repeated in triplicate.

The pH value of the solution was found to be 5.8 in the beginning and 6.5 at the end of the test. The measurements of the ion concentrations in the filtrates made by atomic absorption spectroscopy showed a very low value for Zn(II) , namely 3.10^{-6} g/L , while Ni(II) and Fe(II) ions were not detected, obviously due to their concentrations under the detection limit of the applied method. These data show the stability of the catalysts in the pH interval 5.8–6.5 of the photocatalytic test.

Ethical approval: The conducted research is not related to either human or animal use.

Figure 1: TEM micrographs of ZNF-Eu1 (a) and ZNF-Tb5 (b).

Table 1: Specific surface area (SSA) and average crystallite size of the samples.

Sample	SSA, m ² /g	Average crystallite size, nm [16]*	Sample	SSA, m ² /g	Average crystallite size, nm [16]*
NF	36	18	ZNF	32	18
NF-Eu1	42	14	ZNF-Eu1	42	16
NF-Tb1	56	9	ZNF-Tb1	42	15
NF-Eu5	79	13	ZNF-Eu5	50	16
NF-Tb5	77	9	ZNF-Tb5	50	15

*Values determined by the Scherrer equation; rounded up [16].

3 Results and discussion

3.1 Characterization of the samples

3.1.1 Average crystallite size and specific surface area (SSA)

The modified samples showed well-crystallized particles with size in the range of 9–18 nm (Table 1). The average crystallite size for the NF-Ln samples was observed to decrease with increasing Ln(III) content, while the size of the ZNF-Ln crystallites also decreased but to a lesser extent (Table 1). The low value for SSA for the pure NF and ZNF samples correlated well with their larger crystallite size of 18 nm (Table 1). The average crystallite size determined from XRD data (using Scherrer equation, about 15 nm, Table 1) and the evaluated particle size (between 15–20 nm) from the TEM micrographs can be seen in Figure 1 aligned well. TEM micrographs for ZNF-Eu1 (Figure 1, a) and for ZNF-Tb5 (Figure 1, b) are examples shown below. As the particles were closely packed, a particle size distribution analysis could not be made from these images.

The undoped samples NF and ZNF have fairly close values for their specific surface area (SSA), 36 and 32 m²/g, respectively and are the lowest among the investigated samples (Table 1).

The values for SSA for the modified samples NF-Ln and ZNF-Ln (Table 1) were found to be higher compared to the pure undoped NF and ZNF samples, as they increased with an increasing amount of dopant. It is known [21] that La₂O₃ is one of the best additives for inhibiting the sintering of high surface area gamma-Al₂O₃, which also has a spinel-like structure. The dopant is believed to decrease the rate of surface diffusion, which delays sintering and a loss of surface area. The effect of the dopant increased with the amount of Ln₂O₃ [21]. The research conducted for this paper showed similar trends: the values for SSA for the doped samples were higher than those for the unmodified samples; and those samples containing 5 wt. % of dopant showed higher SSA than those containing 1 wt. %, both for the NF-Ln and ZNF-Ln samples. The nature of the dopant (Eu or Tb) appears to be insignificant, with only NF-Tb1 showing a higher SSA than NF-Eu1.

Figure 2: TEM – micrographs for ZNF-Eu1, scale bar 500 nm (a), ZNF-Tb1, scale bar 500 nm (b), and ZNF-Tb5 scale bar 100 nm (c); based on them an energy dispersive X-ray microanalysis was made.

Figure 3: Elemental mapping of the sample ZNF-Eu1 (a). The equal distribution of Eu(III) on the surface is shown (b) and for comparison, the distribution of Fe(III) (c).

3.1.2 Data from the energy dispersive X-ray microanalysis

The TEM micrographs of the obtained samples were used to make an energy dispersive X-ray microanalysis in several points which were pointed out using digits on the micrographs (Figures 2 a, b, c). The content (wt. %) of Eu(III) in ZNF-Eu1, 1.0 ± 0.1 , as well as of Tb(III) in ZNF-Tb1, 4.0 ± 0.6 , and in ZNF-Tb5, 7.8 ± 1.4 was determined. The value obtained for Eu(III) was very close to the experimental stoichiometric value (1 wt. %). Eu(III) appear to be distributed equally on the particles' surface,

as shown by the elemental mapping (Figure 3). The higher value for Tb(III) both in ZNF-Tb1 and in ZNF-Tb5 suggests Tb(III) enrichment of the surface; the distribution appears to be homogeneous (Figure 4).

3.1.3 Energy of the band gap, E_g

The absorbance in the UV/Vis range (450–700 nm, spectra not included here) showed a clear maximum at around 400 nm. Based on these data, the band gap energy, E_g , was determined after plotting α/E , where α is the

Figure 4: Elemental mapping of the sample ZNF-Tb5 (a). The equal distribution of Tb(III) on the surface is shown (b) and for comparison, the distribution of Fe(III) (c).

absorption coefficient. The energy of the band gap of the samples characterized is in the range 1.57 – 1.61 eV (785 – 767 nm); a value of 1.57 eV (785 nm) was calculated for the pure NF and ZNF. These data are somewhat lower than those published in the literature for pure ferrites (1.9 eV for ZnFe_2O_4 [22, 23] and 2.19 eV for NiFe_2O_4 [24]), quite likely due to the difference in the synthetic procedure applied. The values calculated for Eu(III) doped (1.57–1.60 eV) as well as for Tb(III) doped (1.58 – 1.61 eV) NF-Ln and ZNF-Ln are close, and apparently do not correlate to the amount of Ln(III) added. Considering the synthetic procedure, it can be expected that the Ln(III) are present as oxides in the samples. In our former work, based on XRD and Mossbauer spectroscopy data, we deduced that Ln^{3+} most likely formed a second phase; however, due to their low amount, it was not directly observed in the diffractograms [16]. In the literature the calculated and experimental band gaps for the respective oxides show values in the range of 2.25 – 4.4 eV for Eu_2O_3 (i.e. 550 – 280 nm) and 3.7 – 4.4 eV for Tb_2O_3 (i.e. 334 – 280 nm) [25]. These values are higher than those calculated for our samples where the E_g values for the doped NF-Ln and ZNF-Ln approximate the value of the pure NF and ZNF.

3.2 Photocatalytic activity of the samples

The results for the photodegradation of Malachite Green (MG) under visible light irradiation in the presence of the synthesized photocatalysts are shown in Figure 5, where the C/C_0 dependence on the irradiation time is presented.

The data for the rate constants of the photocatalytic process along with the sorption of the photocatalysts are summarized in Table 2 and are illustrated additionally in histograms in Figure S1 (Supplementary material).

The degradation rate constants are divided by the SSA (rate constant/SSA) (an approach applied by us in [20]) and the “normalized” values ($\text{min}^{-1} \text{g. m}^{-2}$) are shown in Table 2. They can be compared with the “normalized” value for the well-known photocatalyst TiO_2 Degussa P25, $2.2 \times 10^{-4} \text{ min}^{-1} \text{g. m}^{-2}$, [20] (data obtained for TiO_2 Degussa P-25 decomposing Malachite Green with UV light irradiation, rate constant $11.6 \times 10^{-3} \text{ min}^{-1}$, with specific surface area $52 \text{ m}^2/\text{g}$ [20].) Figure 5 shows that after about 80 minutes of irradiation with visible light, a very similar degradation of the dye MG for the different catalysts is achieved. The photocatalysts show differences in their activity in the interval of 80–150 minutes. It is assumed that some deactivation of the catalyst surface took place, which could be proved after a second catalytic cycle test.

Based on the data in Table 2, some tendencies are mentioned in the discussion below.

3.2.1 Pure vs. doped ferrites and the content of the modifying ions

Comparing the pure undoped samples, ZNF appears to have a higher activity than NF, which must be due to the beneficial effects of adding Zn(II). Doping NF with Ln(III) does not seem to have a significant effect: the rate constants are the same within experimental error, except

Figure 5: Degradation curves (C/C_0 dependence on the irradiation time) under visible light irradiation for pure and doped NF (a) and ZNF samples (b).

Table 2: Photocatalytic activity of NF and ZNF, pure and modified with Eu(III) and Tb(III) ions, under irradiation with visible light.

Sample	Rate constant			
	$\text{n} \cdot 10^{-3} \text{ min}^{-1}$	to SSA, $\text{n} \cdot 10^{-4} \text{ min}^{-1} \cdot \text{g} \cdot \text{m}^{-2}$	Degradation after 150 min, %	Sorption, %
NF	3.43 ± 0.42	0.95 ± 0.1	38	62.40
NF-Eu1	3.30 ± 0.06	0.79 ± 0.01	37	64.11
NF-Tb1	3.40 ± 0.38	0.61 ± 0.07	38	58.86
NF-Eu5	3.50 ± 0.45	0.44 ± 0.05	38	63.15
NF-Tb5	4.10 ± 0.38	0.53 ± 0.05	43	66.53
ZNF	5.47 ± 0.38	1.71 ± 0.12	52	58.30
ZNF-Eu1	5.0 ± 0.2	1.19 ± 0.04	48	65.63
ZNF-Tb1	3.80 ± 0.23	0.90 ± 0.05	40	63.32
ZNF-Eu5	6.0 ± 0.6	1.20 ± 0.12	60	74.91
ZNF-Tb5	6.77 ± 0.20	1.35 ± 0.04	64	76.75

for that of NF-Tb5, which is slightly higher. The tendency for increasing the rate constants of the photocatalysts in the presence of modifying agents is more obvious for the ZNF-Ln modified samples. The samples containing 1 wt. % Ln are somewhat less active than the unmodified ZNF, especially for the Tb-doped sample, while the samples containing 5 wt. % Ln are more active than the unmodified sample, also especially for the Tb-doped sample. The most active samples are ZNF-Tb5 and ZNF-Eu5 with rate constants of $(6.77 \pm 0.20) \times 10^{-3} \text{ min}^{-1}$ and $(6.0 \pm 0.6) \times 10^{-3}$

min^{-1} , respectively. They have neither the highest SSA nor the smallest average crystallite size. This fact confirms the statement [26, 27] that the characteristics and peculiarities of the surface structure can be responsible for the differences in the catalytic action, but the process of photodegradation is determined by additional factors. The size of the particles and crystallites may also affect the activity of the photocatalysts by influencing the processes of recombination of the electron-hole pairs, e^-/h^+ .

The increased activity of the modified ZNF with 5 wt. % Ln(III) under visible light irradiation corresponds to the element mapping data for homogeneous distribution of Tb on the surface of ZNF-Tb5 particles and to the enrichment with Tb. In this case there appears to be an influence of the surface processes on the activity.

3.2.2 The influence of the specific surface area and average crystallite size

It can be expected that the specific surface area is important for the photocatalytic process. The samples ZNF-Tb5 and ZNF-Eu5 demonstrate lower SSA compared with the values for NF-Tb5 and NF-Eu5 (50, and 77 and 79 m²/g, respectively) (Table 1). At the same time the higher SSA for NF-Tb5 and NF-Eu5 do not result in higher rate constants. The decrease of the average crystallite size is observed to a different extent for the modified NF-Ln and ZNF-Ln (Table 1). The rate constants of both NF-Ln and ZNF-Ln change in a similar way i.e. they show higher values in comparison with the pure samples. Data published for photocatalytic MG degradation by ferrites is rather limited. Additionally, the comparison is difficult because the photocatalysts tested are synthesized by different synthetic procedures [15, 18, 19].

3.2.3 The band gap energy as a factor in the photocatalytic process

According to [4], to absorb visible light energy, a photocatalyst with a maximum band gap of about 3.1 eV is required. It is known that spinel ferrites have a band gap of approximately 2.0 eV, so they should be capable of photocatalytic conversion of visible light energy to generate electron/hole pairs that in turn produce reactive oxygen species through redox processes for the degradation of pollutants [4]. The data for E_g obtained for our samples (see 3.1.3.) show that they may be applied for photodegradation under visible light, which is proved by the results in Table 2.

3.2.4 Comparing the influence of Eu(III) and Tb(III)

Considering the role of Eu(III) and Tb(III), the content of Ln(III) in the ferrite (1 or 5 wt. %) and the type of ferrite modified (NF or ZNF) have to be taken into account. Based on the role of Ln(III) on the photocatalytic activity of semiconductors such as TiO₂ [28], it can be expected

that both Eu(III) and Tb(III) adsorbed as oxides on the surface of the spinel favor the separation of the charge carriers, and by that they suppress the recombination of electron/hole pairs and increase the activity of the doped photocatalysts. The powder XRD analysis of the samples [16] showed single-phase ferrites. No additional peaks corresponding to Ln(III) oxides were observed, which would be the case if we indeed had composite material (especially for the samples containing 5 wt % of Eu and Tb). This suggests that the Tb and Eu ions dissolve into the ferrite matrix and are with all likelihood present in the interlayer space of the ferrite. Their influence can be connected with the smaller crystallites size of 10-15 nm (Table 1), which is in agreement with the statement [29] that an average crystallite size of 20 nm is optimal for a high quantum yield. The values for the energy of the band gap E_g are very close to the doped samples NF-Ln and ZNF-Ln; a difference of 0.03 eV is not expected to be significant. The data from Table 2 show that the Tb(III) doped samples have higher rate constants than Eu(III). The only deviation from this trend is ZNF-Tb1, showing lower activity than ZNF-Eu1. Actually, the rate constant of ZNF-Tb1 under visible light has the lowest value among the ZNF-Ln doped samples. The SSA of Tb(III) doped samples is equal or slightly larger than the values of the Eu(III) doped samples. In this case, the SSA as a factor in influencing the photocatalytic activity, acts in synergy with the smaller radius of Tb(III). Generally, the influence of Ln(III) on the photocatalytic activity of ferrites needs further elucidation. The role is likely to be similar on the influence of Ln(III) on the reactivity of TiO₂ (investigated photocatalyst, active only under UV light when not modified) i.e. the complexation capability of Ln(III) gives a chance for better adsorption of the pollutants on the surface of the photocatalyst [30]. Considering the smaller radius of Tb(III), it has a better complexation ability than Eu(III), which may be a factor for the better activity of ZNF-Tb5 over ZNF-Eu5.

Taking into account that (i) Ln(III) ions do not enter the lattice cell [16, 31], but quite likely remain on the surface and (ii) the data from the energy dispersive X-ray microanalysis show that they are equally spread on the surface and (iii) the surface is enriched in Tb(III), it is likely that surface processes are essential for the catalytic activity of the ferrites modified with Ln(III). Tb(III) is a unique lanthanoid that has been reported to form mixed valence compounds with a nonstoichiometric structure [32], so there might be a process where Tb(III) disturbs the e-/h+ recombination by its variable oxidation state Tb(III) - Tb(IV).

3.2.5 Comparing NF vs ZNF

Under visible light irradiation, the pure ZNF shows a higher rate constant than the pure NF (Table 2). At the same time, the pure photocatalysts NF and ZNF have close values both for the average crystallite size and for the specific surface area (36 and $32 \text{ m}^2 \text{ g}^{-1}$ respectively, Table 1), equal values for the energy of the band gap according to our calculations (1.57 eV) as well as close values according to the literature data (2.19 and 1.9 eV [22-24]). This means that these factors are not the only ones responsible for the difference in the photocatalytic activity of NF and ZNF.

Among the modified samples, NF-Ln samples generally have lower activity than ZNF-Ln modified samples; among all the samples tested the lowest rate constant was found for NF-Eu1, i.e. $3.3 \times 10^{-3} \text{ min}^{-1}$. The rate constants for ZNF-Ln5 are almost twice as large as those for NF-Ln5. ZNF doped with 5 wt. % Ln(III) shows the highest photocatalytic activity.

4 Conclusions

The decomposition of Malachite Green in model solutions under visible light irradiation in the presence of NiFe_2O_4 and $\text{Zn}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$, pure and modified with Eu(III) and Tb(III) , was investigated. It was found that more than 60 % of the dye was decomposed after 150 min under visible light irradiation. The most active photocatalyst among the investigated samples was the three-component mixed metal oxide $\text{Zn}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$, modified with 5 wt. % Ln(III) , showing a high activity under visible light while the two components ferrite NiFe_2O_4 shows lower activity. The rate constants under visible light irradiation of the tested catalysts was found to increase in the order of $\text{ZNF} < \text{ZNF-Eu5} < \text{ZNF-Tb5}$. The positive influence of Tb(III) and Eu(III) on the photocatalytic activity at visible light irradiation is demonstrated.

The large number of factors influencing the process of decomposition of MG makes it difficult to distinguish and elucidate the role of each of them separately. Considering the lower energy of visible light and the availability of sunlight, the results are rather promising because the activation under visible light means lower cost for the photocatalytic cleaning and simple construction of the testing equipment. It is crucial for the application of the prepared catalysts that they are not hazardous; indeed no dissolution of catalyst metals was detected under the conditions of the photocatalytic test.

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