Photocatalytic degradation of Reactive Black 5 and Malachite Green with ZnO and lanthanum doped nanoparticles

N Kaneva, A Bojinova and K Papazova
Laboratory of Nanoparticle Science and Technology, Department of General and Inorganic Chemistry, Faculty of Chemistry and Pharmacy, University of Sofia, 1164 Sofia, Bulgaria
E-mail: nina_k@abv.bg

Abstract. Here we report the preparation of ZnO particles with different concentrations of La$^{3+}$ doping (0, 0.5 and 1 wt%) via sol-gel method. The nanoparticles are synthesized directly from Zn(CH$_3$COO)$_2$.2H$_2$O in the presence of 1-propanol and triethylamine at 80°C. The conditions are optimized to obtain particles of uniform size, easy to isolate and purify. The nanoparticles are characterized by SEM, XRD and UV-Vis analysis. The photocatalytic properties of pure and La-doped ZnO are studied in the photobleaching of Malachite Green (MG) and Reactive Black 5 (RB5) dyes in aqueous solutions upon UV illumination. It is observed that the rate constant increases with the La loading up to 1 wt%. The doping helps to achieve complete mineralization of MG within a short irradiation time. 1 wt% La-doped ZnO nanoparticles show highest photocatalytic activity. The La$^{3+}$ doped ZnO particles degrade faster RB5 than MG. The reason is weaker N=N bond in comparison with the C–C bond between the central carbon atom and N,N-dimethylaminobenzyl in MG. The as-prepared ZnO particles can find practical application in photocatalytic purification of textile wastewaters.

1. Introduction
Textile wastewaters are a large problem for conventional treatment plants in the entire world. The release of these wastewaters in natural environments is very problematic to aquatic life [1] and mutagenic to human [2]. The traditional treatment techniques applied in textile wastewaters are not a complete solution to the problem due to the biological resistance of some dyes. There are many kinds of dyes available in the market. Based on the chemical structure of chromophore, 20-30 different groups of dyes can be discerned. Anthraquinone, phthalocyanine, triarylmethane and azo dyes are quantitatively the most important groups. The azo dyes, characterized by having an azo group consisting of two nitrogen atoms (-N=N-), are the largest class of dyes used in textile industry. Additionally, these dyes are the most problematic pollutants of textile wastewaters. Therefore, in this work, we have selected the dye Reactive Black 5 (RB5) as one of the most used reactive dyes for textile finishing. The other dye Malachite Green oxalate (MG) is used as a model pollutant in order to compare the particles behavior.

Many methods have been used to synthesize ZnO particles, for example, sol–gel [3, 4], hydrothermal [5] and co-precipitation [6]. Nowadays, various wet chemical methods have been consolidated and are now fashionable for synthesizing ZnO nanoparticles because they provide a simple and economic route as well as low temperature requirement. The addition of appropriate
surfactants can help to control the ZnO morphology. The morphology/surface area plays an important role in the photocatalytic activities of metal oxides. The reason is that doping of metal oxide and/or rare earth metals (like La) increases the surface defects [7, 8].

In our previous studies we have tested the photocatalytic degradation of Malachite Green and Reactive Black 5 using nanostructured films [9-12]. Thin films of zinc oxide were obtained by three different syntheses using different precursors: (i) zinc acetate dihydrate, 2-methoxyethanol and monoethanolamine [9], zinc oxide powder, polyethyleneglycol, ferrous (III) chloride, ZnCl₂ [10, 11], zinc acetate dihydrate, n-propanol and triethylamine [12]. Based on these results, we use the latter sol-gel method for synthesis of zinc oxide nanoparticles.

Recently, La-doped ZnO materials (nanoparticles, nanorods, nanowires etc.) have attracted much attention in the photocatalytic processes owing to their high photocatalytic activity in the degradation of organic contaminants. The reasons for this effect are the suppression of electron–hole recombination, large content of oxygen vacancies, and strong absorption of OH⁻ ions on the catalysts surface [13–15].

The zinc oxide particles are usually synthesized by sol–gel method, allowing good control of the size and morphology of the submicron particles. For this purpose, surfactants species, such as monoethanolamine and diethanolamine are applied in the preparation of ZnO particles, described in the literature [16, 17]. Recent reports on the preparation of pure and rare earth doped ZnO nanoparticles demonstrate the potentials for their applications in biomedical research [18, 19]. Here we investigate the application of such particles (undoped and doped) as a photocatalyst.

Here we report for the first time on the synthesis and characterization of La-doped ZnO catalysts and their photocatalytic activity in the degradation of MG and RB5 at different initial concentrations: 3, 5, 7 and 10 ppm. All the materials have been characterized by SEM, XRD and UV–VIS analysis.

2. Experimental

2.1 Sample preparation

Zinc acetate dihydrate (> 99.5 %), 1-propanol (> 99.0 %) and triethylamine (> 99.5 %) were from Fluka. Lanthanum oxide (> 99.9 %) and acetic acid were from Sigma Aldrich. Malachite Green (C₅₂H₅₄N₄O₁₂, λₘₐₓ = 615 nm, dye content ≥90%, Croma GmbH) oxalate and Reactive Black 5 (C₂₆H₂₁N₅Na₄O₁₉S₆, λₘₐₓ = 585 nm, dye content 55%, Sigma-Aldrich) were used in the photocatalytic experiments. Distilled water was used in all experiments. All other chemicals and reagents were analytical reagent grade.

The synthesis of lanthanum acetate (III) was carried out following the reactions:

\[ \text{La}_2\text{O}_3 + 6\text{CH}_3\text{COOH} \rightarrow 2\text{La(CH}_3\text{COO)}_3 + 3\text{H}_2\text{O} \]

For this purpose, La₂O₃ powder was dissolved in a solution of CH₃COOH. The materials are mixed together in a round-bottomed flask and stirred at a room temperature. The resultant solution was heated at 80°C for 30 min and washed by repeated decantation with 25 ml portions of H₂O. The suspension was filtered and dried at 80°C for 2 h. The obtained product consisted of almost white, highly lustrous, brittle pieces, which were stirred with a mortar into fine particles and dried again at 80°C for 2 hours.

Zinc oxide particles with different concentrations of La³⁺ doping (0, 0.5 and 1 wt%) were synthesized by sol-gel method. Zinc acetate (Zn(CH₃COO)₂·2H₂O), lanthanum acetate (La(CH₃COO)₃) and ethylene glycol (C₂H₄(OH)₂) were dissolved in 1-propanol, and then triethylamine (TEA) was added to the solution as a stabilizer. The substances were mixed together in a round-bottomed flask with reversed condenser and stirred at a room temperature for 15 minutes. The obtained clear solution was heated at 80°C upon magnetic stirring for 30 min to obtain particles of average size of 150-230 nm. The resultant solution was clear and homogenous. The obtained
submicron particles were separated by centrifugation at 6000 rpm for 30 min, twice washed with pure 1-propanol and dried at open air to obtain pure and doped ZnO particles.

2.2. Sample characterization

The as-obtained pure ZnO particles and doped with different percent La$^{3+}$ were first imaged by a scanning electron microscope (SEM) JSM-5510 (JEOL), operated at 10 kV of acceleration voltage. The investigated samples were coated with gold by JFC-1200 fine coater (JEOL) before observation.

X-Ray diffraction (XRD) spectra were taken at room temperature by powder diffractometer (Siemens D500 with CuK$\alpha$ radiation within 2$\theta$ range of 30-70 deg at a step of 0.05 deg 2$\theta$ and counting time 2 s/step). This method was used for determination of samples crystallinity phase and composition.

The photocatalytic activities of ZnO and ZnO/La$^{3+}$ particles were investigated and compared by the photoinitiated decolorization of the dyes Malachite Green and Reactive Black 5 in aqueous solution (upon UV-light illumination). The concentration of ZnO particles was 0.12 mg/ml. The measurement was conducted in a cylindrical glass vessel of volume 150 ml, equipped with a magnetic stirrer and UV-lamp (main emission at 370 nm) [20]. The light power density at the sample position was 0.66 mW/cm$^2$. The light irradiation was measured with research radiometer of Ealing Electro-optics, Inc. The lamp (Sylvania BLB 18W) was fixed ~15 cm above the treated solution. The degradation process of MG and RB5 were monitored by absorbance spectroscopy after aliquot sampling at regular time intervals. Each aliquot sample (2 ml) returned back to the reaction vessel immediately after the spectrophotometrical measurement. The particles (ZnO and ZnO/La$^{3+}$) were then removed from the aliquot by centrifugation (6000 rpm, 3 min) before the UV-VIS spectrophotometric measurement of dyes concentration. After that, the aliquot, together with the photocatalyst particles were returned back to the glass reactor. In all experiments the optical absorbance spectra were measured by spectrophotometer Jenway 6400 in the wavelength range from 400 to 800 nm.

Five series of experiments were carried out with: pure ZnO particles, doped with different percent La$^{3+}$ (0.5 and 1%). The effect of initial concentration of MG and RB5 (for 3, 5, 7 and 10 ppm) was also evaluated. All photocatalytic tests were performed at constant stirring rate (500 rpm) at room temperature (25°C).

3. Results and discussion

3.1. Structural characterization of ZnO and ZnO/La$^{3+}$ particles

The SEM images of the as-prepared ZnO and ZnO:La$^{3+}$ particles are shown in figure 1. As seen, the morphology is well ordered and spherical colloidal particles with average diameter size of about 150-230 nm are formed. The SEM investigation reveals that after lanthanum doping, the average size of ZnO colloidal particles is increased (figures 1b, c). The observed influence is expected to prove the photocatalytic efficiency of the ZnO. Particle size and surface area have key effects on the

Figure 1. SEM images of ZnO particles at different concentrations of La$^{3+}$ doping: (a) 0%; (b) 0.5 wt% and (c) 1 wt%.
photocatalytic activities of photocatalysts. The particle size distribution, determined from the SEM images is shown in figure 2. Average grain sizes of about 150, 210 and 225 nm are determined for the ZnO samples, doped with 0, 0.5 and 1 wt% respectively. There is a tendency of increasing the particle size with the rise of dopants concentration.

Figure 2. Statistical volume % distribution of ZnO particles doped at different concentrations of La$^{3+}$: (a) 0%; (b) 0.5 wt% and (c) 1 wt%.

X-ray diffractogram of the particles has been analyzed to obtain information about various crystalline aspects. Figure 3a shows XRD patterns of synthesized undoped ZnO nanopowders. The sharp and intense peaks indicate that the samples are of high crystallinity and ZnO nanoparticles have polycrystalline structure. The XRD peaks for (100), (002) and (101) planes indicate the formation ZnO of phase pure hexagonal wurtzite structure. The high intensity of (101) peak suggests that the growth of nanoparticles has taken place along this direction of crystallization of ZnO. No peaks due to impurities are observed. Figure 3b shows the XRD patterns of 1wt% La doped ZnO catalysts are similar to that of ZnO [21], suggesting that there is no change in the crystal structure upon La loading. This also indicates that La$^{3+}$ is uniformly dispersed onto ZnO nanoparticles [22].

Figure 3. XRD spectra of ZnO particles prepared by sol-gel and doped at: (a) 0 wt% and (b) 1 wt% La$^{3+}$.

3.2. Photocatalytic activity
In order to determine the photocatalytic activity of ZnO and La-doped ZnO, a series of experiments are carried out with Malachite Green (MG) and Reactive Black 5 (RB5) in aqueous suspensions. The experiments under UV light illumination exhibit a much higher decolorization rate of RB5 in comparison with MG solutions. The results show that the photocatalytic decolorization of MG and RB5 by ZnO colloids under UV illumination follows pseudo first-order kinetics.
The concentrations ratio \( \frac{C}{C_0} \), where \( C_0 \) is the initial concentration of dye and \( C \) is the concentration of dye after irradiation at selected time interval) is calculated to evaluate the degradation of the dyes. Curves of MG and RB5 degraded by ZnO colloids with different La\(^{3+}\) doping concentrations are shown in Fig. 4 and 5. As it represented in the figures at different concentration of the dye (3, 5, 7 and 10 ppm), undoped ZnO has a smaller ability to mineralize the dyes (about 81-89% in 180 min, calculated using the relation \( D = \left[ \frac{(C_0-C)}{C_0} \right] \times 100 \)) under UV-light irradiation. However, all of the La-doped ZnO photocatalysts exhibit higher photocatalytic activity than the pure ZnO. This may be attributed both to the better absorption in UV-light range and to the larger number of oxygen vacancies or defects, produced by La\(^{3+}\) doping. During the 180 min irradiation, the order of the photocatalytic activities of the La-doped ZnO with different La\(^{3+}\) doping concentrations is as follows: 1>0.5>0 wt%. This dependence of photocatalytic activity is observed for both dyes. The 1 wt% La-doped ZnO photocatalyst exhibits the highest photocatalytic efficiency for decolorization of MG and RB5 (94.22% and 99.43% after 180 min). That suggests that the doping of La\(^{3+}\) may enhance the photocatalytic activity of ZnO particles and there is an optimal doping concentration of La\(^{3+}\) ions in ZnO. The pure particles have the smallest photocatalytic activity and slowest degradation rate of the dye.

![Figure 4](image1.png) **Figure 4.** Photocatalytic activity of the Malachite Green at initial concentration: (a) 3 ppm, (b) 5 ppm, (c) 7 ppm and (d) 10 ppm in aqueous solution (under UV-illumination) with ZnO particles with different amounts of La\(^{3+}\) doping.

![Figure 5](image2.png) **Figure 5.** Photocatalytic efficiency of pure and doped ZnO particles for degradation of Reactive Black 5 at initial concentration of: (a) 3 ppm, (b) 5 ppm, (c) 7 ppm and (d) 10 ppm in water solution under UV-light illumination.
The ZnO particles obtained by sol-gel method possess higher activity and faster degrade RB5 in comparison to MG. The reason for decomposition of RB5 is OH radicals that attack first the azo groups and thus destructing the long conjugated p-systems [23]. As the N=N bonds are easier for destruction than the aromatic ring structures. This explains the higher photoactivity of ZnO films in the decomposition of RB5, compared to MG, which does not contain N=N bond. The N=N bond is weaker than the C–C bond between the central carbon atom and N,N-dimethylaminobenzyl in MG, which results in the formation of 4-(N,N-dimethylamino) methylbenzylone as most common intermediate [24].

The kinetics of the reaction is obtained by plotting the natural logarithm of the concentration ratios versus the irradiation time. Straight lines are obtained, indicating that the reactions are of first order kinetics. The particles with the lowest rate of reaction are the one that contains ZnO for degradation of Malachite Green ($k_{MG} = 0.0046\text{ min}^{-1}$) and Reactive Black 5 ($k_{RB5} = 0.0113\text{ min}^{-1}$) under UV-light illumination. The values of the rate constants increases with the dopant concentration increase ($0.5\text{wt}\%\text{ La}^{3+} - k_{MG} = 0.0091\text{ min}^{-1}$ and $k_{RB5} = 0.0122\text{ min}^{-1}$, $1\text{wt}\%\text{ La}^{3+} - k_{MG} = 0.0154\text{ min}^{-1}$ and $k_{RB5} = 0.0243\text{ min}^{-1}$). This means that the incorporation of La-doped ZnO in the particles increases the photocatalytic efficiency. These values are presented in figure 6.

![Figure 6](image_url)

Figure 6. Comparison of the apparent rate constants of photocatalysis of for doped ZnO particles at different initial concentration under UV-light illumination of: (a) RB5 and (b) MG.

Among the catalysts studied, 1.0 wt% La-doped ZnO is found to be more active, showing higher photocatalytic activity for the degradation of RB5 in comparison with MG. Thus, we can conclude that the optimum loading of La is 1 wt% which may be more efficient for separating photoinduced electron–hole pairs and enhance the photocatalytic activity.

4. Conclusions

A series of La-doped ZnO particles with different La doping content (0, 0.5 and 1 wt%) are prepared by sol-gel method and characterized by Scanning Electron Microscopy, X-ray diffraction and UV-VIS analyses. The colloidal particles (pure and doped) are spherical in shape with hexagonal wurtzite structures, which demonstrates that the dopant La$^{3+}$ ions have no effect on the crystal structure. The kinetics of photocatalytic reaction is systematically studied under UV at different variable system parameters – amount of lanthanum doping and initial concentration of Malachite Green and Reactive Black 5 in the reaction solution. The 1 wt% La-doped ZnO photocatalyst exhibits the highest photocatalytic decolorization efficiency, leading to as much as 99.43% photocatalytic degradation of
RB5 in 180 min. The photocatalytic efficiency of pure ZnO particles is lower than the activity achieved by La-doped sample, giving a thickness-based rate constant of pure ZnO $<<$ ZnO:La$^{3+}$(1%) under UV-light illumination. This fact is observed for both dyes. ZnO and ZnO:La particles are reproducible and stable. The doped particles have the highest photocatalytic activity in comparison to the undoped ones. All these observations prove that La-doped ZnO is a potential candidate for the practical application in photocatalytic degradation of organic contaminants from water solutions.

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