Photo-catalytic degradation of erythrosine and eriochrome black T dyes using $\text{Nd}_2\text{Zr}_2\text{O}_7$ nanostructures prepared by a modified Pechini approach

Sahar Zinatloo-Ajabshir, Masoud Salavati-Niasari*

Institute of Nano Science and Nano Technology, University of Kashan, Kashan, P. O. Box. 87317-51167, I. R. Iran

* Corresponding author. Tel.: +98 31 55912383; Fax: +98 31 55913201;

E-mail address: salavati@kashanu.ac.ir (M. Salavati-Niasari)

Abstract: $\text{Nd}_2\text{Zr}_2\text{O}_7$ (neodymium zirconate) nanostructures have been successfully prepared by a modified Pechini approach utilizing succinic acid as novel stabilization agent and propane-1,2-diol as new cross-linking agent in presence of tetraethylenepentamine as novel pH regulator and co-capping agent. Type of pH regulator and propane-1,2-diol dosage have been changed to study the influence of preparation factors on the shape and size of neodymium zirconate. The obtained neodymium zirconate was characterized by Fourier transform infrared (FT-IR) spectroscopy, UV-vis diffuse reflectance spectroscopy, X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), photoluminescence (PL) spectroscopy and energy dispersive X-ray microanalysis (EDX). To examine the catalytic characteristics of the obtained neodymium zirconate, the photocatalytic degradation of erythrosine and eriochrome black T dyes under ultraviolet illumination were performed.

Keywords: Neodymium zirconate; Nanostructure; Photocatalytic activity; Optical property; Electron microscopy.

1. Introduction

Much research has been focused on the preparation and study of the characteristics of nanostructured rare earth zirconium oxides ($\text{Re}_2\text{Zr}_2\text{O}_7$). $\text{Re}_2\text{Zr}_2\text{O}_7$ with excellent chemical and physical characteristics has been widely applied in the fields of photocatalyst, gas turbines, nuclear waste form, heat resistant oxide ceramics, oxygen monitoring sensors and proton solubility [1-12]. There are various ways for the synthesis of the rare earth zirconium oxides which involve sol-gel combined electrospinning, co-precipitation, solid-state reaction, sol-spray pyrolysis, hydrothermal, and Pechini polymeric process [13-22].

The characteristics and final uses of the nanometer-sized materials depend largely on their shape and size. Great attentions have been paid to the shape and size controlled production of nanometer-sized materials in the recent years [23-29]. The Pechini way is known as reliable, easy and cost effective way to control the shape and size of $\text{Re}_2\text{Zr}_2\text{O}_7$.

Herein, we report a modified Pechini approach for the synthesis of neodymium zirconate nanostructures. In this approach, succinic acid as novel stabilization agent and propane-1,2-diol as new cross-linking agent are utilized. This research presents the results of experiments on the dependence of the shape and size of the neodymium zirconate on the dosage of propane-1,2-diol and pH regulator type. Furthermore, the as-obtained neodymium zirconate nanostructures have been applied as the photocatalyst for the decomposition of erythrosine and eriochrome black T dyes under ultraviolet illumination.

2. Experimental

2.1. Materials and characterization

In this approach, zirconyl nitrate, liquor ammonia solution containing 25% NH_3 , propane-1,2-diol, ethylenediamine, neodymium nitrate, trimethylamine, succinic acid and tetraethylenepentamine with analytical

grade applied as-received without any further purification. Fourier transform infrared spectrum of as-prepared $\text{Nd}_2\text{Zr}_2\text{O}_7$ sample was obtained on a Shimadzu Varian 4300 spectrophotometer in KBr pellets in the 400–4000 cm^{-1} range. The UV-vis diffuse reflectance spectrum of the as-prepared nanostructured $\text{Nd}_2\text{Zr}_2\text{O}_7$ sample was recorded by a UV-vis spectrophotometer (Shimadzu, UV-2550, Japan). FESEM images of nanostructured $\text{Nd}_2\text{Zr}_2\text{O}_7$ sample were visualized by a Tescan mira3 field emission scanning electron microscope (FESEM). X-ray diffraction (XRD) pattern of the as-synthesized nanostructured $\text{Nd}_2\text{Zr}_2\text{O}_7$ sample was recorded by employing a diffractometer of Philips Company with X'PertPromonochromatized $\text{Cu K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). Transmission electron microscope (TEM) image of as-obtained nanostructured $\text{Nd}_2\text{Zr}_2\text{O}_7$ sample was taken on a JEM-2100 with an accelerating voltage of 200 kV. GC-2550TG (Teif Gostar Faraz Company, Iran) were used for all chemical analyses. Thermogravimetric analysis (TGA) of the as-synthesized product was carried out by a thermal gravimetric analysis instrument (Shimadzu TGA-50H) with a flow rate of 20.0 ml min^{-1} and a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$. The EDS analysis of the as-synthesized nanostructured $\text{Nd}_2\text{Zr}_2\text{O}_7$ sample was performed by a Philips XL30 microscope. The PL spectrum of the as-obtained nanostructured $\text{Nd}_2\text{Zr}_2\text{O}_7$ product was taken on a Perkin Elmer (LS 55) fluorescence spectrophotometer.

2.2. Synthesis of $\text{Nd}_2\text{Zr}_2\text{O}_7$ nanostructures

In a typical experiment for the preparation of $\text{Nd}_2\text{Zr}_2\text{O}_7$ nanostructures, 1mmol of $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 1mmol of $\text{ZrO}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in distilled water. After adding 2 mmol of succinic acid as novel stabilization agent to the solution as well as regulating the pH of medium to 6 via adding (pH regulator) NH_3 solution drop-wise, 0.5 mmol of cross-linking agent (propane-1,2-diol) was added to the mixed solution. After that, the gel-like solution was allowed to evaporate. In the next step, to synthesize nanostructured $\text{Nd}_2\text{Zr}_2\text{O}_7$ (sample no. 1), the final porous solid mass was ground in the agate mortar (utilizing acetone) and calcined at $350 \text{ }^\circ\text{C}$ for 2 h and then at $700 \text{ }^\circ\text{C}$ for 4 h. Scheme 1 presents schematic diagram of preparation of $\text{Nd}_2\text{Zr}_2\text{O}_7$ nanostructures. Furthermore, the effects of the dosage of propane-1,2-diol and pH regulator type on the shape

and size of $\text{Nd}_2\text{Zr}_2\text{O}_7$ have been studied. The synthesis conditions of the prepared $\text{Nd}_2\text{Zr}_2\text{O}_7$ samples have been listed in Table 1.

2.3. Photocatalysis experiments

The photocatalytic activity of the nanostructured $\text{Nd}_2\text{Zr}_2\text{O}_7$ has been tested through the degradation of erythrosine and eriochrome black T solutions as model contaminants. In the experiment, the solution comprising the 120 mg of the nanostructured $\text{Nd}_2\text{Zr}_2\text{O}_7$ and 3 mg of the erythrosine or eriochrome black T contaminants in the quartz pipe have been applied. After aerating to achieve the adsorption–desorption equilibrium (in darkness for 30 min), the final mixture was irradiated by a 400 W ultraviolet light lamp. The erythrosine or eriochrome black T degradation efficiency has been determined as follow:

$$D.P.(t) = \frac{A_0 - A_t}{A_0} \times 100 \quad (1)$$

where A_0 and A_t are the absorbance of erythrosine or eriochrome black T solution before and after irradiation.

3. Results and discussion

In this study, succinic acid as novel stabilization agent and propane-1,2-diol as new cross-linking agent were applied to prepare $\text{Nd}_2\text{Zr}_2\text{O}_7$. Succinic acid act as stabilization agent and form chelates with rare earth metal cations, then the formed chelates polymerize with propane-1,2-diol by heating and produce solid polymer network. After calcining the final porous solid mass, the nanostructured $\text{Nd}_2\text{Zr}_2\text{O}_7$ is obtained. To examine the effect of propane-1,2-diol dosage on the morphology of $\text{Nd}_2\text{Zr}_2\text{O}_7$, FESEM images of synthesized $\text{Nd}_2\text{Zr}_2\text{O}_7$ samples with succinic acid:propane-1,2-diol molar ratio of 2:0.5, 2:1.5, 2:3, 2:5 and 2:7 were taken and depicted in Fig. 1 and 2, respectively. When 2:0.5 molar ratio of succinic acid:propane-1,2-diol was utilized, the high agglomerated particle-like structures of $\text{Nd}_2\text{Zr}_2\text{O}_7$ were obtained (Fig. 1a and b). Hence, in order to contribute to the preparation of nanostructured $\text{Nd}_2\text{Zr}_2\text{O}_7$ greater dosage of propane-1,2-diol was added. By changing the

dosage of propane-1,2-diol from 0.5 to 1.5 and 3 mmol, the nanoparticles were obtained (Fig. 1c-f). When 2:5 and 2:7 molar ratio of succinic acid:propane-1,2-diol were applied, agglomerated micro/nanobundles were prepared (Fig. 2a-d). It seems that when the dosage of propane-1,2-diol from 0.5 to 3 mmol increases, the uniform and spherical neodymium zirconate nanoparticles prepares and also the grain size decreases (Fig. 1a-f). It seems that when the dosage of the propane-1,2-diol increases, the presence of excess propane-1,2-diol leads to the prepared nanoparticles embedded in polymer matrix became crystalline without interacting with other produced nanoparticles. By more increasing the dosage of propane-1,2-diol from 3 to 7, the presence of excess propane-1,2-diol can act as space-filling template and can induce the formed nanoparticles to assemble in the certain directions, and thus agglomerated micro/nanobundles were synthesized (Fig. 2a-d). Thus the the dosage of propane-1,2-diol plays a key role to control the shape and size of neodymium zirconate.

To examine the effect of pH regulator type on the morphology of $\text{Nd}_2\text{Zr}_2\text{O}_7$, the samples have been synthesized by utilizing (2:3) molar ratio of succinic acid:propane-1,2-diol as well as the trimethylamine (Fig. 3a and b), ethylenediamine (Fig. 3c and d), and tetraethylenepentamine (Fig. 3e and f). It can be seen that in the presence of tetraethylenepentamine as pH regulator, very uniform and spherical neodymium zirconate nanoparticles with fine size were formed (Fig. 3a-f). It seems that the tetraethylenepentamine with the highest steric hindrance effect (Scheme 2) can act as the best co-capping agent via hindering the aggregation of the formed nanoparticles. These results illustrate that tetraethylenepentamine as the best co-capping agent due to its high steric hindrance effect can control the size and morphology of $\text{Nd}_2\text{Zr}_2\text{O}_7$.

TEM image (Fig. 4a) was taken to examine the shape and size of the nanostructured $\text{Nd}_2\text{Zr}_2\text{O}_7$. The typical TEM image of the nanostructured $\text{Nd}_2\text{Zr}_2\text{O}_7$ in a molar ratio 2:3 (succinic acid to propane-1,2-diol) is depicted in Fig. 4a. This figure reveals that the prepared $\text{Nd}_2\text{Zr}_2\text{O}_7$ sample contains quasi-spherical nanoparticles with diameter from 20 to 80 nm.

Fig. 4b depicts the TGA curve of the as-obtained powders (sample no. 8 before calcining). As illustrated in this figure, the weight loss stages are two. One weight loss occurs in the temperature range 50–405 °C, and reveals 47 % weight loss, which may be related to the dehydration and depolymerisation of the polymeric remaining in the as-obtained powder. The other stage takes place at the 405–700 °C (displaying 22 % weight loss), which can be attributed to the complex decomposition and polymeric network combustion as well as removal of the nitrates and remaining carbonate intermediate and show the synthesis of Nd₂Zr₂O₇.

To confirm the purity and crystal structure of the as-obtained nanostructured Nd₂Zr₂O₇ (sample no. 8), XRD was applied. XRD pattern of the sample is depicted in Fig 5 and confirms preparation of pure cubic phase Nd₂Zr₂O₇ (JCPDS No. 78-1618). By utilizing Scherrer formula [27] and XRD data, the mean crystallite diameter of the sample was calculated to be about 28 nm.

The purity of the as-prepared Nd₂Zr₂O₇ (sample no. 8) was also confirmed by EDX. The EDS pattern of the Nd₂Zr₂O₇ sample (Fig 6) reveals the lines of Nd, Zr and O. Thus, the XRD and EDS results demonstrate that pure nanostructured Nd₂Zr₂O₇ is successfully prepared through the modified Pechini approach.

The surface of the as-obtained Nd₂Zr₂O₇ (sample no. 8) was examined by FTIR. Fig. 7 presents the FT-IR spectrum of the nanostructured Nd₂Zr₂O₇ sample. Two bands appear at 3440 and 1643 cm⁻¹ in the spectrum (Fig. 7) can be ascribed to the stretching and bending vibration of the surface adsorbed water [10, 27, 30]. In the spectrum, the characteristic band of Nd₂Zr₂O₇ seen at 405 cm⁻¹ [31].

The optical characteristics of the nanostructured Nd₂Zr₂O₇ sample prepared by 3 mmol of propane-1,2-diol and tetraethylenepentamine (sample no. 8) have been investigated by PL and DR-UV-vis spectroscopy. Fig. 8a presents the PL spectrum of Nd₂Zr₂O₇ sample (excitation wavelength = 270 nm). The emission peak at nearly 399 nm can be assigned to transition from the 4f band to the valence band of Nd₂Zr₂O₇.

Fig. 8b reveals the DR-UV-vis spectrum of as-obtained nanostructured $\text{Nd}_2\text{Zr}_2\text{O}_7$ (sample no. 8). The absorption band at 359 nm appears in the spectrum of the nanostructured $\text{Nd}_2\text{Zr}_2\text{O}_7$ sample. The energy gap (E_g) as a key factor on photocatalytic performance can be calculated by utilizing DR-UV-vis data and Tauc's formula [27, 32, 33]. The E_g of $\text{Nd}_2\text{Zr}_2\text{O}_7$ sample has been estimated through extrapolating the linear section of the plot of $(ah\nu)^2$ versus $h\nu$ to the energy axis (inset in Fig. 8b). The E_g value of $\text{Nd}_2\text{Zr}_2\text{O}_7$ sample has been calculated to be 3.3 eV. The calculated E_g value reveals that the as-obtained nanostructured $\text{Nd}_2\text{Zr}_2\text{O}_7$ (sample no. 8) may be utilized as the photocatalyst.

The photocatalytic performance of as-obtained nanostructured $\text{Nd}_2\text{Zr}_2\text{O}_7$ (sample no. 8) has been examined by monitoring the degradation of erythrosine solution as a model contaminant, under UV illumination. Fig. 9 depicts the photocatalysis experiment result. No erythrosine contaminant was practically decomposed after 50 min without utilizing the nanostructured $\text{Nd}_2\text{Zr}_2\text{O}_7$ or UV light corresponding to the negligible contribution of the self-decomposition. Applying photocatalytic calculations by Eq. (1), the erythrosine contaminant photodegradation was about 88 % after 50 min. The suggested mechanism of the photocatalytic decomposition of the erythrosine contaminant can be explained as follows:

The photocatalytic behaviors of $\text{Nd}_2\text{Zr}_2\text{O}_7$ products with various shapes and different grain sizes prepared by ammonia (sample no. 3) and tetraethylenepentamine (sample no. 8) were compared under UV illumination. Fig. 10 illustrates the observed results. As depicted in Fig. 10, the photocatalytic behavior of $\text{Nd}_2\text{Zr}_2\text{O}_7$ product synthesized by tetraethylenepentamine is obviously better than other product. Applying photocatalytic calculations by Eq. (1), the erythrosine contaminant photodegradation was about 88 % by sample no. 8 (very uniform and spherical neodymium zirconate nanoparticles with smaller particle size) and 65 % by sample no. 3 (less uniform neodymium zirconate nanostructures with larger particle size) after 50 min. Typical histograms of the particle sizes for the sample nos. 3 and 8 are illustrated in Fig. 11a and b, respectively. By comparing the particle size distribution of the neodymium zirconate samples, it can be found that by applying the tetraethylenepentamine as pH regulator and co-capping agent, very uniform and spherical neodymium zirconate nanoparticles with fine grain size are formed. Based on the results of the photocatalytic tests as well as grain size and shape of neodymium zirconate samples, the sample no. 8 with smaller grain size (Fig. 3e and f) that has larger surface area demonstrates the great performance for decomposition in comparison to sample no. 3 (Fig. 1e and f). Thus grain size and shape of nanostructures is a substantial factor on decomposition of organic contaminant by photocatalyst. The neodymium zirconate sample with smaller grain size due to larger surface area demonstrates great photocatalytic efficiency. It seems that when the particle size of $\text{Nd}_2\text{Zr}_2\text{O}_7$ diminishes, the ratio of surface area to volume, existing active sites on $\text{Nd}_2\text{Zr}_2\text{O}_7$ surface as well as transfer amount of interfacial charge-carrier improved and therefore the photocatalytic efficiency enhanced [34]. Hence, privilege of employing of tetraethylenepentamine as pH regulator and co-capping agent is that it leads to synthesize nanostructured $\text{Nd}_2\text{Zr}_2\text{O}_7$ product with better photocatalytic behavior. In addition, repeated destruction reactions were done to determine the stability of the as-obtained nanostructured $\text{Nd}_2\text{Zr}_2\text{O}_7$ (sample no. 8). It can be seen that the as-formed nanostructured $\text{Nd}_2\text{Zr}_2\text{O}_7$ did not show any significant loss of activity after five consecutive reaction cycles, demonstrating the high stability of catalyst. The destruction percentage was decreased to 78%

after six cycles. This result indicated that the as-formed nanostructured $\text{Nd}_2\text{Zr}_2\text{O}_7$ has high potential to be utilized as an effective and suitable kind of photocatalyst under UV illumination.

The photocatalytic performance of as-prepared nanostructured $\text{Nd}_2\text{Zr}_2\text{O}_7$ (sample no. 8) was also examined by monitoring the decomposition of eriochrome black T solution as a model contaminant, under illumination with UV light. About 84% of eriochrome black T contaminant was degraded after 50 min by as-prepared nanostructured $\text{Nd}_2\text{Zr}_2\text{O}_7$ (sample no. 8), as illustrated in Fig. 13. These obtained results suggest the nanostructured $\text{Nd}_2\text{Zr}_2\text{O}_7$ as favorable and effective photocatalyst under UV irradiation for removal of water contaminants.

4. Conclusions

In this work, we develop a new facile synthetic approach to pure $\text{Nd}_2\text{Zr}_2\text{O}_7$ nanostructures. In this synthetic approach, succinic acid as new stabilization agent and propane-1,2-diol as novel cross-linking agent are utilized. It is shown that the type of pH regulator and propane-1,2-diol dosage play key roles in controlling the shape and size of neodymium zirconate. The as-prepared nanostructured $\text{Nd}_2\text{Zr}_2\text{O}_7$ may be applied as favorable and effective photocatalyst kind under UV illumination in the photocatalytic uses such as removal of erythrosine and eriochrome black T contaminants, since these contaminants photodegradation were determined to be 88 and 84 % within 50 min, respectively.

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Table 1. The synthesis conditions of the prepared Nd₂Zr₂O₇ samples.

Sample No.	Propane-1,2-diol dosage (mmol)	pH regulator type	Figure of FESEM images
1	0.5	Ammonia	1a and b
2	1.5	Ammonia	1c and
3	3	Ammonia	1e and f
4	5	Ammonia	2a and b
5	7	Ammonia	2c and d
6	3	Trimethylamine	3a and b
7	3	Ethylenediamine	3c and d
8	3	Tetraethylenepentamine	3e and f

Figure Captions:

Figure 1. FESEM images of neodymium zirconate prepared using: (a and b) 2:0.5, (c and d) 2:1.5, and (e and f) 2:3 molar ratio of succinic acid to propane-1,2-diol.

Figure 2. FESEM images of neodymium zirconate synthesized using (a and b) 2:5 and (c and d) 2:7 molar ratio of succinic acid to propane-1,2-diol.

Figure 3. FESEM images of neodymium zirconate synthesized by utilizing (2:3) molar ratio of succinic acid:propane-1,2-diol as well as the trimethylamine (a and b), ethylenediamine (c and d), and tetraethylenepentamine (e and f).

Figure 4. TEM image (a) of the neodymium zirconate nanostructures (sample no. 3) and TGA curve (b) of the as-obtained powders (sample no. 8 before calcining).

Figure 5. XRD pattern of the neodymium zirconate nanostructures (sample no. 8).

Figure 6. EDS pattern of the neodymium zirconate nanostructures (sample no. 8).

Figure 7. FT-IR spectrum of the neodymium zirconate nanostructures (sample no. 8).

Figure 8. PL spectrum (a) and UV-vis diffuse reflectance spectrum (b) of the neodymium zirconate nanostructures (sample no. 8) (inset: the curve of $(\alpha h\nu)^2$ against $h\nu$).

Figure 9. Photocatalytic erythrosine contaminant degradation of the as-obtained neodymium zirconate nanostructures (sample no. 8).

Figure 10. Photocatalytic erythrosine contaminant degradation of the as-obtained neodymium zirconate products (sample nos. 3 and 8).

Figure 11. (a and b) Particle size distribution of sample nos. 3 and 8, respectively.

Figure 12. Recycling tests of as-obtained neodymium zirconate nanostructures (sample no. 8) for degradation of erythrosine under ultraviolet light.

Figure 13. Photocatalytic eriochrome black T contaminant degradation of the as-obtained neodymium zirconate nanostructures (sample no. 8).

Scheme 1. Schematic diagram of preparation of $\text{Nd}_2\text{Zr}_2\text{O}_7$ nanostructures.

Scheme 2. Various amines used as pH regulator.

Scheme 1.

Fig 1.

Fig 2.

Fig 3.

Scheme 2.

Fig 4.

Fig 5.

Fig 6.

Fig 7.

Fig 8.

Fig 9.

Fig 10.

Fig 11.

Fig 12.

Fig 13.