Nd₂Sn₂O₇ nanostructures: New facile Pechini preparation, characterization, and investigation of their photocatalytic degradation of methyl orange dye

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Abstract

Nd₂Sn₂O₇ (neodymium stannate) nanostructures were successfully produced through an improved Pechini process. For the first time, several organic acids as stabilization agent and capping agent, different pH control agents and propane-1,2-diol as esterification agent have been applied to produce Nd₂Sn₂O₇ nanostructures. In this investigation, tin (IV) chloride and neodymium nitrate were chosen as tin and neodymium sources. The neodymium stannate nanostructures were analyzed by PL, TEM, FESEM, FT-IR, XRD, UV–vis and EDX. Based on the morphological investigation, it was found that the size and shape of the neodymium stannate depended on the type of pH control agent and organic acid. Additionally, the photocatalytic activity of as-produced neodymium stannate has been studied by degradation of methyl orange dye as water contaminant.

Keywords: Ceramics; Neodymium stannate; Nanostructures; Photocatalytic; Electron microscopy.

1. Introduction

Lanthanide stannate (Ln₂Sn₂O₇) as one of the most attractive pyrochlore-type oxide have been widely employed in ionic/electric conductors, high temperature pigments, catalysts, hosts for radioactive waste and dielectrics

owing to their special and remarkable electrical, optical and magnetic characteristics [1-7]. To date, a few synthesis techniques for the preparation of lanthanide stannate nanostructures such as sol-gel, complex precipitation, solid-state reaction, Pechini and hydrothermal has been suggested [8-12]. It is generally accepted that the characteristics and applications of nanoscale materials are largely influenced by their size and shape. So, the size and shape controlled preparation of nanoscale materials have attracted extensive attention in recent years [13-19]. Pechini way is known as cost-effective and convenient approach for the synthesis of $\text{Ln}_2\text{Sn}_2\text{O}_7$ and provides an effective route to optimize the shape and size.

In this study, the $\text{Nd}_2\text{Sn}_2\text{O}_7$ (neodymium stannate) nanostructures are prepared by utilizing an improved Pechini process. This approach is cost-effective, facile and eco-friendly and provided a new route for optimizing shape and size of neodymium stannate. We present the role of the pH control agent and organic acid types on the shape and size of $\text{Nd}_2\text{Sn}_2\text{O}_7$. To our knowledge, it is the first time that several organic acids as stabilization agent and capping agent, different pH control agents and propane-1,2-diol as esterification agent are applied to produce neodymium stannate nanostructures.

2. Experimental

2.1. Materials and characterization

All the reagents applied for the preparation of neodymium stannate nanostructures were of analytical grade and were used as received. The Room temperature PL analysis of the as-obtained neodymium stannate nanostructures was done by employing a Perkin Elmer (LS 55) fluorescence spectrophotometer. Fourier transform infrared analysis of as-synthesized products was done by applying a Shimadzu Varian 4300 spectrophotometer in KBr pellets in the $400\text{--}4000\text{ cm}^{-1}$ range. GC-2550TG (Teif Gostar Faraz Company, Iran) were used for all chemical analyses. The EDS analysis of the as-obtained neodymium stannate nanostructures was done by applying a Philips XL30 microscope. The UV-vis diffuse reflectance analysis of the as-prepared neodymium stannate

nanostructures was done by applying a UV-vis spectrophotometer (Shimadzu, UV-2550, Japan). Thermogravimetric-differential thermal curve (TG-DTA) of the as-synthesized sample was obtained by applying a thermal gravimetric analysis instrument (Shimadzu TGA-50H) with a flow rate of 20.0 ml min⁻¹ and a heating rate of 10 °C min⁻¹. The morphological characteristics of the neodymium stannate nanostructures were examined by TEM (JEM-2100) and FESEM (Mira3 Tescan). XRD analysis of the as-obtained neodymium stannate nanostructures was carried out by applying a diffractometer of Philips Company with X'PertPromonochromatized Cu K α radiation (λ = 1.54 Å). The particle sizes of the samples were estimated by using Digimizer software on FE-SEM images.

2.2. Synthesis of neodymium stannate nanostructures

Neodymium stannate nanostructures were synthesized through an improved Pechini process. In a typical preparation, 1mmol of neodymium nitrate and 1mmol of tin (IV) chloride were dissolved in distilled water. After adding 2 mmol of organic acid (benzene tricarboxylic acid) to the solution as well as adjusting the pH of the medium to 6 through addition (pH control agent) NH₃ solution drop-wise, 1.2 mmol of propane-1,2-diol as esterification agent was added the resultant solution. In the next step, the gel-like solution was allowed to evaporate. After that, to prepare neodymium stannate nanostructures, the resultant porous solid mass was ground in the agate mortar applying acetone and calcined at 350 °C for 3 h and then at 700 °C for 5 h (sample no. 2). Additionally, the effects of the type of pH control agent and organic acid on the size and shape of the neodymium stannate have been examined. The achieved results have been illustrated in [Table 1](#).

2.3. Photocatalytic studies

The photocatalytic performance of neodymium stannate nanostructures obtained from sample no. 8 was evaluated through the degradation of methyl orange solution as a target contaminant. For this aim, the solution comprising the 30 mg of the methyl orange contaminant and 120 mg of the neodymium stannate nanostructures in

the quartz reactor was utilized. After aerating in darkness to achieve the adsorption–desorption equilibrium (for 1/2 h), the resultant mixture was illuminated by the ultraviolet light (400 W mercury lamps). The methyl orange degradation efficiency was estimated 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 quantity of methyl orange solution before and after photodegradation by means of a UV–vis spectrometer.

3. Results and discussion

To examine the effect of various factors on the size and shape of the neodymium stannate, FESEM analysis has been applied. For studying the influence of the organic acid factor on the size and shape, sample no. 1 was synthesized without organic acid. Fig. 1a and b presents FESEM images of sample no. 1. It is noteworthy that irregular polyhedral-like structures with large size were prepared. So, in our experiment, several organic acids as stabilization agent are applied to control the shape and contribute to the production of nanostructured neodymium stannate. For this aim, the neodymium stannate samples were synthesized by utilizing the salicylic acid (sample no. 2), maleic acid (sample no. 3), succinic acid (sample no. 4), citric acid (sample no. 5) and benzene tricarboxylic acid (sample no. 6) as stabilization agent. The FESEM images reveal that less polyhedral-like structures (Fig. 1c and d), high agglomerated particles decorated by less uniform nanobundles (Fig. 1e and f), irregular scales-like nanostructures (Fig. 2a and b), less uniform sphere-like nanostructures (Fig. 2c and d) and uniform spherical nanoparticles (Fig. 2e and f) are synthesized by utilizing the salicylic acid, maleic acid, succinic acid, citric acid and benzene tricarboxylic acid as stabilization agent, respectively. By considering FESEM images in Figs. 1 and 2, it can be seen that by employing benzene tricarboxylic acid as stabilization agent with highest steric hindrance effect (Scheme 1), the uniform sphere-like nanoparticles with fine size can be formed (Fig. 2e

and f). All the applied organic acids can play as both stabilization agent and capping agent role through hindering the aggregation of produced nanoparticles. It seems that benzene tricarboxylic acid as stabilization agent can act as the best capping agent and leads to the nucleation occurrence rather than growth (Fig. 2e and f). So the applying the organic acid as stabilization agent and its type has a significant impact on the size and shape control of the neodymium stannate.

Moreover, the effect of the type of pH control agent on the size and shape of the neodymium stannate was studied (Fig. 3a-d). For this aim, the sample nos. 7 and 8 were synthesized by applying ethylenediamine (en) and triethylenetetramine (trien), respectively. Among these applied pH control agents (Scheme 1), trien creates the highest steric hindrance effect. Trien as pH control agent can act co-capping agent through impeding from the aggregation of the formed nanoparticles. The sample no. 8 exhibits the very homogeneous sphere-like neodymium stannate nanoparticles with fine particle size (Fig. 3c-d). Thus, an advantage of applying trien in presence of organic acid (benzene tricarboxylic acid) is that it causes to the very uniform spherical neodymium stannate nanoparticles with small grain size (Fig. 3c-d). Typical histograms of the particle sizes for the sample nos. 1–8 are seen in Fig. 4a-h, respectively. By comparing the particle size distribution of the samples, it is found that by using benzene tricarboxylic acid in the presence of trien, uniform sphere-like nanostructured neodymium stannate with small particle size forms.

The size and shape of neodymium stannate nanostructures produced by employing the organic acid (benzene tricarboxylic acid) as stabilization agent and trien as pH control agent were additional elucidated by TEM images. Fig. 5a-c presents the TEM images of sample no. 8 which contains quasi-spherical neodymium stannate nanoparticles with diameter in the range of 8 to 22 nm.

TG/DTG curve of as-formed powders (sample no. 8 before calcination steps) is depicted in Fig. 6. It can be observed that four endothermic mass loss stages happened. Two happened endothermic mass loss in the 25–320

°C (indicating 34.65 % mass loss) correspond to the dehydration and depolymerisation of the polymeric residual in the as-formed powders. The other occurred endothermic stages at the 320–700 °C (showing 28.16 % mass loss) are ascribed to complex decomposition and polymeric resin combustion as well as deletion of the nitrates and residual carbonate intermediate and reveal the preparation of neodymium stannate nanostructures.

FT-IR spectra of sample no. 8 before and after calcination steps are depicted in Fig. 7a and b, respectively. In the Fig. 7a, the peaks appear at 1694 and 1615 cm^{-1} can be related to C=O stretching vibration of stabilization agent (benzene tricarboxylic acid) and O–N=O asymmetric stretching vibration of the nitrates [20]. The bands located at 1546, 1391 and 756 cm^{-1} in the Fig. 7a can be ascribed to the (C=O) vibration, the COO^- stretching vibration and the N–O stretching vibration of the nitrates, respectively [20–21]. In the Fig. 7b, the band appear at 3426 cm^{-1} can be corresponding to the $\nu(\text{OH})$ stretching vibration of the surface adsorbed H_2O molecules [15]. The bands located at 615 and 425 cm^{-1} in the Fig. 7b are ascribed to (Sn–O) and (Nd–O $^\prime$) stretching vibrations, respectively [22].

The chemical purity of the neodymium stannate nanostructures (sample no.8) was examined by EDS analysis (Fig. 8). This pattern presents only the presence of Nd, Sn, and O elements in the sample no.8 and synthesis of pure neodymium stannate.

XRD analysis was applied to determine the mean crystallite diameter and crystal phase of the as-obtained neodymium stannate (sample no.8). Fig. 9 depicts XRD pattern of this sample. All the diffraction peaks in this pattern are well-matched to cubic $\text{Nd}_2\text{Sn}_2\text{O}_7$ (JCPDS No. 13-0185). By applying Scherrer formula [15], the mean crystallite size of the as-obtained neodymium stannate (sample no.8) from the XRD result were estimated to be about 20 nm. Thus, these obtained EDS and XRD results reveal that cubic neodymium stannate nanostructures with high level of purity have been successfully synthesized by employing the organic acid (benzene tricarboxylic acid) as stabilization agent and trien as pH control agent.

The optical characteristics of as-produced neodymium stannate nanostructures (sample no. 8) have been examined by PL and DR-UV-vis spectroscopy. The PL spectrum of the as-obtained neodymium stannate nanostructures (sample no. 8) is depicted in Fig. 10a. The emission band at nearly 397 nm has been appeared in the spectrum (excitation wavelength = 310 nm). This emission peak can be ascribed to $^4I_{9/2} \rightarrow ^4S_{9/2}$ transition [22].

Fig. 10b depicts the DR-UV-vis spectrum of neodymium stannate nanostructures (sample no. 8). This figure presents the absorption peak at 357 nm. The energy gap (E_g) as an effective factor on photocatalytic features can be estimated based on the DR-UV-vis data employing Tauc's equation [17]. The E_g of the neodymium stannate nanostructures (sample no. 8) has been calculated via extrapolating the linear section of the plot of $(ah\nu)^2$ versus $h\nu$ to the energy axis (Fig. 10c). The E_g amount of the neodymium stannate nanostructures has been determined to be 3.25 eV. From the determined E_g amount, it is apparent that the as-synthesized neodymium stannate nanostructures may be applied as the photocatalyst.

Photodegradation of methyl orange solution as a target contaminant under UV light illumination has been employed to evaluate the photocatalytic performance of neodymium stannate nanostructures (sample no. 8). Fig. 11 depicts the obtained result. No methyl orange dye was practically deleted after 50 min without employing UV light illumination or as-produced neodymium stannate nanostructures owing to the negligible contribution of the self-decomposition. With applying photocatalytic calculations by Eq. (1), the methyl orange dye degradation percentage was about 87 after 50 min illumination of UV light. This obtained photocatalytic result reveals that as-synthesized neodymium stannate nanostructures have excellent capability to be applied as effective and desirable nanometer-scale substance for photocatalytic uses under UV light.

The proposed mechanism of the photocatalytic degradation of the target contaminant can be assumed as:

In comparison to other works, presented in [Table 2](#), our approach is more facile, low-cost as well as low energy and time consumer. In this report, we presented an improved Pechini process to prepare $Nd_2Sn_2O_7$ with the aid of organic acid (benzene tricarboxylic acid) as stabilization agent in the presence of trien as pH control agent in milder conditions and lower reaction times. The novelty of this study compared to other reports is that for the synthesis of $Nd_2Sn_2O_7$, benzene tricarboxylic acid as new stabilization agent in the presence of trien as novel pH control agent was used. Results of this work indicate that the application of benzene tricarboxylic acid in the presence of trien leads to the synthesis of the products with high purity, uniform sphere-like shape and small particle size at lowest temperature.

4. Conclusions

This work presents a novel and facile approach for the large-scale production of neodymium stannate nanostructures with various shapes through an improved Pechini process. Utilizing of several organic acids as stabilization agent and capping agent, different pH control agents and propane-1,2-diol as esterification agent is the novelty of this investigation. Neodymium stannate samples with the different shapes and particle sizes have been formed through alteration the kind of pH control agent and organic acid. The as-obtained neodymium stannate nanostructures may be applied as effective and desirable nanometer-scale substance for photocatalytic

uses under UV light such as elimination of methyl orange dye, since this contaminant photodegradation was calculated to be 87 % after 50 min.

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References

- [1] S. Park, H.J. Hwang, J. Moon, Catalytic combustion of methane over rare earth stannate pyrochlore, *Catal. Lett.* 87 (2003) 219–223.
- [2] K.W. Li, H. Wang, H. Yan, Hydrothermal preparation and photocatalytic properties of $\text{Y}_2\text{Sn}_2\text{O}_7$ nanocrystals, *J. Mol. Catal. A* 249 (2006) 65–70.
- [3] E. Lopez-Navarrete, V.M. Orera, F.J. Lazaro, J.B. Carda, M. Ocana, Preparation through aerosols of Cr-doped $\text{Y}_2\text{Sn}_2\text{O}_7$ (pyrochlore) red-shade pigments and determination of the Cr oxidation state *J. Am. Ceram. Soc.* 87 (2004) 2108–2113.
- [4] B.J. Wuensch, K.W. Eberman, C. Heremans, E.M. Ku, P. Onnerud, E.M.E. Yeo, S.M. Haile, J.K. Stalick, J.D. Jorgensen, Connection between oxygen-ion conductivity of pyrochlore fuel-cell materials and structural change with composition and temperature, *Solid State Ionics* 129 (2000) 111–133.
- [5] K. Matsuhira, Y. Hinatsu, K. Tenya, H. Amitsuka, T. Sakakibara, Low-temperature magnetic properties of pyrochlore stannates, *J. Phys. Soc. Japan* 71 (2002) 1576–1582.
- [6] F. Matteucci, G. Cruciani, M. Dondi, G. Baldi, A. Barzanti, Crystal structural and optical properties of Cr-doped $\text{Y}_2\text{Ti}_2\text{O}_7$ and $\text{Y}_2\text{Sn}_2\text{O}_7$ pyrochlores, *Acta Mater.* 55 (2007) 2229–38.
- [7] S.M. Wang, G.J. Zhou, M.K. Lu, Y.Y. Zhou, S.F. Wang, Z.S. Yang, Synthesis and characterization of lanthanum stannate nanoparticles, *J. Am. Ceram. Soc.* 89 (2006) 2956–2959.
- [8] S. Fujihara, K. Tokumo, Multiband orange-red luminescence of Eu^{3+} ions based on the pyrochlore-structured host crystal, *Chem. Mater.* 17 (2005) 5587–5593.

- [9] L. Kong, I. Karatchevtseva, Mark G. Blackford, N. Scales, G. Triani, Aqueous Chemical Synthesis of $\text{Ln}_2\text{Sn}_2\text{O}_7$ Pyrochlore-Structured Ceramics, *J. Am. Ceram. Soc.* 96 (2013) 2994–3000.
- [10] K.E.J. Eurenus, E. Ahlberg, C.S. Knee, Proton Conductivity in $\text{Sm}_2\text{Sn}_2\text{O}_7$ Pyrochlores, *Solid State Ionics* 181 (2010) 1577–1585.
- [11] T.H. Yu, H.L. Tuller, Ionic Conduction and Disorder in the $\text{Gd}_2\text{Sn}_2\text{O}_7$ Pyrochlore System, *Solid State Ionics* 86–88 (1996) 177–182.
- [12] J. Yang, Y. Su, H. Li, X. Liu, Zh. Chen, Hydrothermal synthesis and photoluminescence of Ce^{3+} and Tb^{3+} doped $\text{La}_2\text{Sn}_2\text{O}_7$ nanocrystals, *J. Alloys Compd.* 509 (2011) 8008–8012.
- [13] Z. Salehi, S. Zinatloo-Ajabshira, M. Salavati-Niasari, Novel synthesis of $\text{Dy}_2\text{Ce}_2\text{O}_7$ nanostructures *via* a facile combustion route, *RSC Adv.* 6 (2016) 26895–26901.
- [14] S. Zinatloo-Ajabshir, M. Salavati-Niasari, Facile route to synthesize zirconium dioxide (ZrO_2) nanostructures: Structural, optical and photocatalytic studies, *J. Mol. Liq.* 216 (2016) 545–551.
- [15] F. Beshkar, S. Zinatloo-Ajabshir, M. Salavati-Niasari, Simple morphology-controlled fabrication of nickel chromite nanostructures *via* a novel route, *Chem. Eng. J.* 279 (2015) 605–614.
- [16] S. Zinatloo-Ajabshir, M. Salavati-Niasari, M. Hamadani, Praseodymium oxide nanostructures: novel solvent-less preparation, characterization and investigation of their optical and photocatalytic properties, *RSC Adv.* 5 (2015) 33792–33800.
- [17] S. Mortazavi-Derazkol, S. Zinatloo-Ajabshir, M. Salavati-Niasari, Novel simple solvent-less preparation, characterization and degradation of the cationic dye over holmium oxide ceramic nanostructures, *Ceram. Int.* 41 (2015) 9593–9601.

- [18] S. Zinatloo-Ajabshir, M. Salavati-Niasari, Preparation of nanocrystalline cubic ZrO_2 with different shapes via a simple precipitation approach, *J. Mater. Sci. Mater. Electron.* 27 (2016) 3918–3928.
- [19] S. Moshtaghi, S. Zinatloo-Ajabshir, M. Salavati-Niasari, Preparation and characterization of BaSnO_3 nanostructures via a new simple surfactant-free route, *J. Mater. Sci. Mater. Electron.*, 27 (2016) 425–435.
- [20] S. Čulubrk, Z. Antić, M. Marinović-Cincović, Ph.S. Ahrenkiel, M.D. Dramićanin, Synthesis and luminescent properties of rare earth (Sm^{3+} and Eu^{3+}) Doped $\text{Gd}_2\text{Ti}_2\text{O}_7$ pyrochlore nanopowders, *Opt. Mater.* 37 (2014) 598–606.
- [21] F.L. Morales, T. Zayas, O.E. Contreras, L. Salgado, Effect of Sn precursor on the synthesis of SnO_2 and Sb-doped SnO_2 particles via polymeric precursor method, *Front. Mater. Sci.* 7 (2013) 387–395.
- [22] Y. Tong, Y. Wang, Salt-assistant combustion synthesis of nanocrystalline $\text{Nd}_2(\text{Zr}_{1-x}\text{Sn}_x)_2\text{O}_7$ ($0 \leq x \leq 1$) solid solutions, *Mater. Charact.* 60 (2009) 1382–1386.
- [22] A. Alemi, R. Ebrahimi Kalan, Preparation and characterization of neodymium tin oxide pyrochlore nanocrystals by the hydrothermal method, *Radiat Eff. Defects Solids* 163 (2008) 229–236.
- [23] Y.N. Wang, Y.Ch. Chen, Sh.L. Yao, Ch.Y. Wu, Microwave dielectric properties of neodymium tin oxide, *Ceramics International* 40 (2014) 2641–2645.
- [24] Zh. Qu, Ch. Wan, W. Pan, Thermophysical properties of rare-earth stannates: Effect of pyrochlore structure, *Acta Materialia* 60 (2012) 2939–2949.

Table 1. The preparation conditions of the neodymium stannate produced in this investigation.

Sample No.	Organic acid kind	pH control agent	Figure of FESEM images
1	-	Ammonia	1a and b
2	Salicylic acid	Ammonia	1c and d
3	Maleic acid	Ammonia	1e and f
4	Succinic acid	Ammonia	2a and b
5	Citric acid	Ammonia	2c and d
6	Benzene tricarboxylic acid	Ammonia	2e and f
7	Benzene tricarboxylic acid	En	3a and b
8	Benzene tricarboxylic acid	Trien	3c and d

Table. 2 Characterization comparison of this work with the others work.

Method	Precursors	Morphology	Calcination temperature (°C)	Ref.
Improved Pechini process	Tin (IV) chloride, Neodymium nitrate, Benzene tricarboxylic acid, Propane-1,2-diol, Trien	Spherical nanoparticles (8–22 nm in diameter)	700	This work
Solid-state	Nd ₂ O ₃ , SnO ₂ (needed ball-milling in alcohol for 12 h)	Irregular microstructures	1200	[23]
Co-precipitation	Nd ₂ O ₃ , SnCl ₄ .5H ₂ O, Nitric acid, NH ₃ (needed ultrasonic oscillating)	Spherical structures (50–100 nm in diameter)	800	[24]
Complex precipitation	Neodymium nitrate, SnCl ₄ .5H ₂ O, oxalic acid, NH ₃ (needed stirring for 3, long time and high calcination temperature)	Irregular microstructures (100–500 nm in diameter)	>1200	[9]

Figure Captions:

Figure 1. FESEM images of the sample no. 1 was synthesized without organic acid (a and b) and the sample nos. 2 and 3 synthesized by utilizing the salicylic acid (c and d) and maleic acid (e and f).

Figure 2. FESEM images of the sample nos. 4, 5 and 6 synthesized by utilizing the succinic acid (a and b), citric acid (c and d) and benzene tricarboxylic acid (e and f).

Figure 3. FESEM images of the sample nos. 7 and 8 were synthesized by applying ethylenediamine (a and b) and triethylenetetramine (c and d).

Figure 4. (a–h) Particle size distribution of sample nos. 1–8, respectively.

Figure 5. TEM images of the neodymium stannate nanostructures (sample no. 8).

Figure 6. TG/DTG curve of as-formed powders (sample no. 8 before calcination steps).

Figure 7. FT-IR spectra of sample no. 8 before (a) and after (b) calcination steps.

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

Figure 9. XRD pattern of the the neodymium stannate nanostructures (sample no. 8).

Figure 10. PL spectrum (a) and DR-UV-vis spectrum (b) of the as-obtained neodymium stannate nanostructures (sample no. 8) and the curve of $(\alpha h\nu)^2$ against $h\nu$ (c).

Figure 11. photocatalytic methyl orange dye degradation of the as-synthesized neodymium stannate nanostructures (sample no. 8).

Scheme 1. Various organic acids applied as stabilization agent and different pH control agents.

Fig 1.

Fig 2.

Benzene tricarboxylic

Citric acid

Succinic acid

Maleic acid

Salicylic acid

Ammonia

Ethylenediamine

Triethylenetetramine

Scheme 1.

Fig 3.

Fig 4.

Fig 5.

Fig 6.

Fig 7.

Fig 8.

Fig 9.

Fig 10.

Fig 11.