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Synthesis Nd_2TiO_5 nanoparticles with different morphologies by novel approach and its photocatalyst application

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Abstract Nowadays, in connection with the increasing pollution of the environment, several studies are performed in order to find new group of compounds which could replace chemical synthesis capping agents due to their high toxicity to ecosystem and difficulty in being degraded in the environment. In the current study, an attempt is made to synthesize neodymium titanate (Nd_2TiO_5) nanoparticles through a novel approach with the aid of capping agents such as alanine, leucine, and histidine in an aqueous solution and investigate their effect on the morphology and particle size of final products. According to the vibrating sample magnetometer result, Nd_2TiO_5 nanoparticles indicated a paramagnetic behavior at room temperature. In addition, methyl orange was chosen as a dye water pollution to evaluate its degradation by Nd_2TiO_5 nanoparticles under ultraviolet light irradiation. Furthermore, the photocatalysis results reveal that the maximum decolorization of 63 % for methyl orange occurred with Nd_2TiO_5 nanoparticles in 60 min under ultraviolet light irradiation.

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1 Introduction

Materials at the nanometer scale have been studied for decades because of their unique properties arising from the large fraction of atoms residing on the surface, and also from the finite number of atoms in each crystalline core. Especially, because of the increasing need for high area density storage, the synthesis and characterization nanocrystals have been extensively investigated [1–7]. Recently, extensive researches on the environmental problems, especially photocatalytic applications have been performed. The decolorization of hazardous organic dyes such as rhodamine B (RhB), methylen blue (MB), and methyl orange are very important, because their discharge from industrial applications causes severe adverse effects to the environment and greatly increases the water pollution and hence effectively disturbs the ecosystem [8–11]. Furthermore studies on thermophysical properties, including thermal expansion and heat capacity of Ln_2TiO_5 (e.g. Dy_2TiO_5, Gd_2TiO_5, Eu_2TiO_5), demonstrate their advantages of thermal stability with low swelling at high temperature (up to 1500 K), desired for control rod materials [12, 13]. In addition, the nanocluster form of yttrium titanate found its application in oxide-dispersion-strengthened steel when it was dispersed in ferritic alloy. This alloy is considered as the most promising structural material for advanced nuclear systems due to its greatly enhanced creep resistance at high temperature [14, 15] and exceptional radiation resistance originating from stabilized oxide nanoclusters. However, the structure and chemistry of the nanocluster oxides have not been fully understood, remaining one of the challenging scientific issues in nuclear materials research [16, 17]. In this report, for the first time, we had presented the preparation of Nd_2TiO_5 nanoparticles by sol–gel method in the presence of alanine,

leucine, and histidine without adding external surfactant. A simple approach for Nd_2TiO_5 nanoparticles synthesis by utilizing natural template permits the reaction to proceed usually in milder conditions. Although existing chemical approaches have effectively produced well defined Nd_2TiO_5 nanoparticles, these processes are generally costly and include the employ of toxic chemicals. The photocatalytic degradation was investigated using methyl orange (MO) under ultraviolet light irradiation [18–26].

2 Experimental

2.1 Characterization

X-ray diffraction (XRD) pattern was recorded by a Philips-X'PertPro, X-ray diffractometer using Ni-filtered Cu Kα radiation at scan range of $10 < 2\theta < 80$. Scanning electron microscopy (SEM) images were obtained on LEO-1455VP equipped with an energy dispersive X-ray spectroscopy. The electronic spectra were obtained on a Scinco UV–Vis scanning spectrometer (Model S-10 4100). The energy dispersive spectrometry (EDS) analysis was studied by XL30, Philips microscope. The magnetic measurement of sample was carried out in a vibrating sample magnetometer (VSM; Meghnatis Daghigh Kavir Co.; Kashan Kavir; Iran) at room temperature.

2.2 Synthesis of Nd_2TiO_5 nanoparticles

The amino acids, neodymium salt, ethanol, and tetra-n-butyl titanate (TNBT) were purchased from Merck Company and used without further purification. At first, a stoichiometric amount of TNBT and neodymium nitrate (1:1) was separately dissolved in ethanol in two A and B beakers, respectively. Then, amino acid as capping agent was dissolved in ethanol and added to the A solution under constant stirring. Afterwards, the neodymium nitrate solution was mixed with solution under stirring at room temperature. Subsequently, the final mixed solution was kept stirring to form a gel at 90 °C. Finally, the obtained product was calcinated at different temperatures for 3 h in a conventional furnace in air atmosphere, and calcination at different temperatures was carried out (Table 1).

Table 1 The preparation conditions of the Nd_2TiO_5 nanoparticles

Sample no.	Temperature	Capping agent	Degradation (%)
1	900	Alanine	63
2	900	Leucine	–
3	900	Histidine	–

2.3 Photocatalytic experimental

The methyl orange (MO) photodegradation was examined as a model reaction to evaluate the photocatalytic activities of the Nd_2TiO_5 nanoparticles under ultraviolet light irradiations. The photocatalytic degradation was performed with 150 mL solution of methyl orange (0.0005 g) containing 0.1 g of Nd_2TiO_5. This mixture was aerated for 30 min to reach adsorption equilibrium. Later, in order to perform photocatalytic tests, the mixture was placed inside the photoreactor in which the vessel was 15 cm away from the ultraviolet source of 400 W mercury lamps at room temperature. Aliquots of the mixture were taken at definite interval of times during the irradiation (60 min) and after

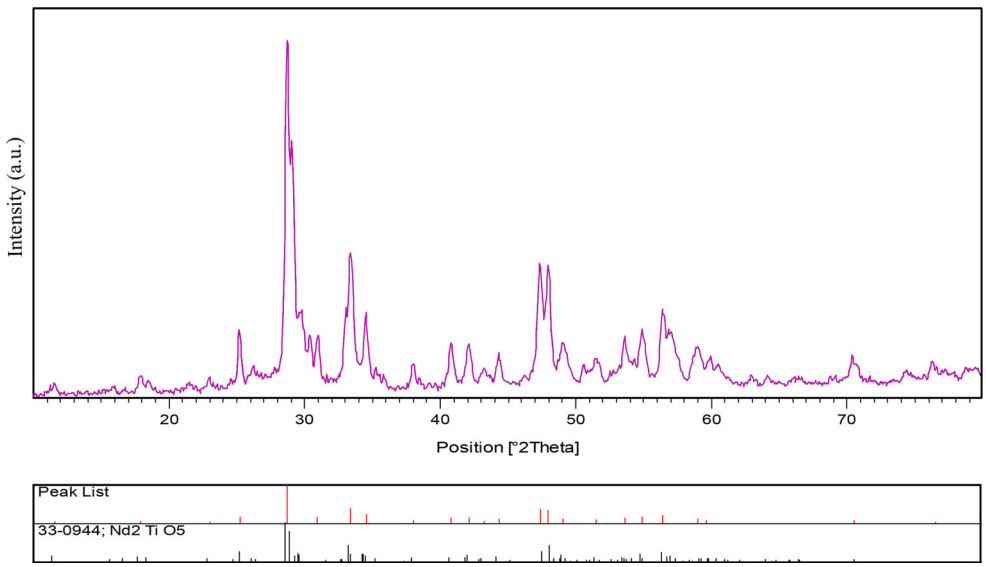


Fig. 1 XRD pattern of Nd_2TiO_5 nanoparticles calcined at 900 °C (sample 1)

centrifugation they were analyzed by a UV–Vis spectrometer. The methyl orange (MO) degradation percentage was calculated as:

$$\text{Degradation rate } (\%) = \frac{A_0 - A}{A_0} \times 100 \quad (1)$$

where A_0 and A are the absorbance value of solution at A_0 and A min, respectively.

3 Results and discussion

Crystalline structure and phase purity of as-prepared product has been determined using XRD. The XRD pattern of as-prepared Nd_2TiO_5 (sample 1) is shown in Fig. 1. Based on the Fig. 1, the diffraction peaks observed can be indexed to pure orthorhombic phase of Nd_2TiO_5 (a = 10.7251 Å, b = 11.3407 Å, and c = 3.8457 Å) with space group of Pnam and JCPDS no. 33-0944. No diffraction peaks from other species could be detected, which indicates the obtained sample is pure. From XRD data, the crystallite diameter (Dc) of Nd_2TiO_5 nanoparticles (sample 1) was calculated to be 16 nm using the Scherer equation: $D_c = K\lambda/\beta\cos\theta$ Scherer equationwhere β is the breadth of the observed diffraction line at its half intensity maximum, K is the so-called shape factor, which usually takes a value of about 0.9, and λ is the wavelength of X-ray source used in XRD. In the third millennium, current studies show that different type of capping agents such as ionic, polymeric; etc. play a fundamental role in synthesis procedures [27–38]. Moreover, capping agents are essential materials for preparation of many disperse systems such as solid/liquid dispersions (usually referred to as suspensions); therefore, in this research we examined the

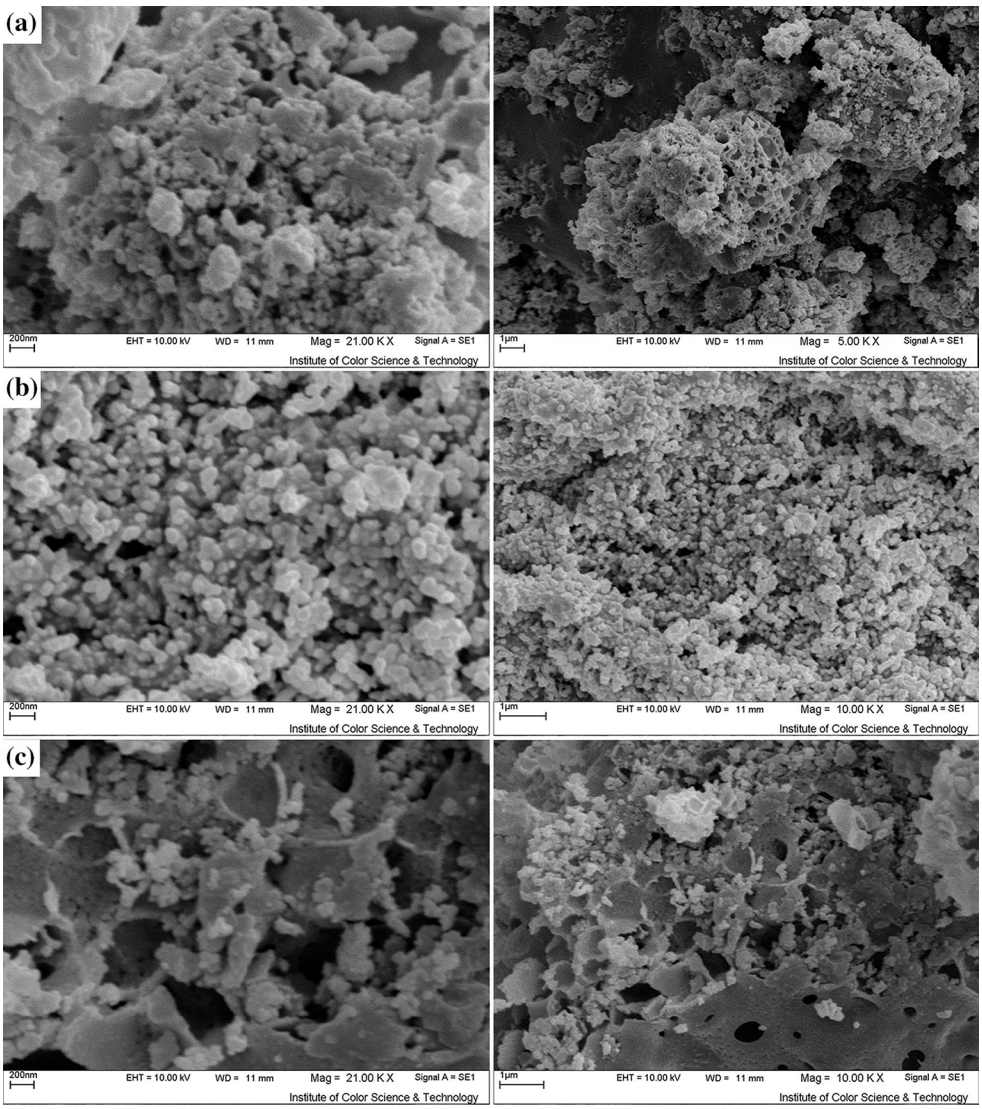


Fig. 2 SEM images of Nd_2TiO_5 nanoparticles calcined at 900 °C **a** sample 1, **b** sample 2 and **c** sample 3

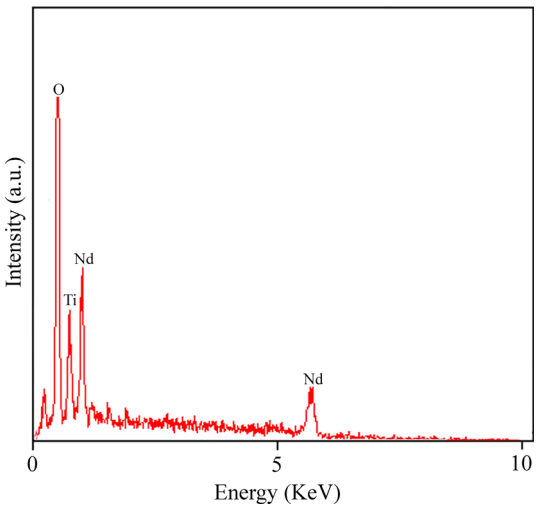


Fig. 3 EDS pattern of Nd_2TiO_5 nanoparticles calcined at 900 °C (sample 1)

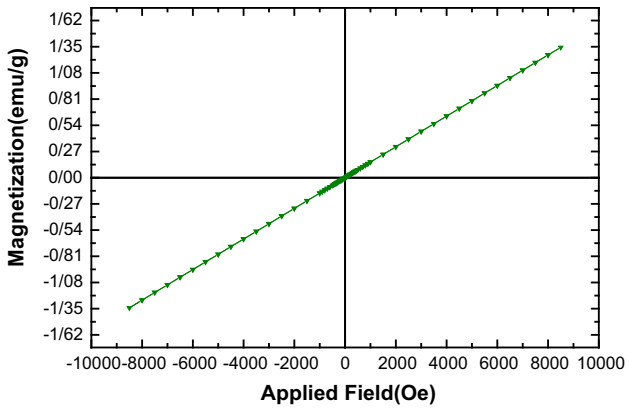


Fig. 4 VSM curve of Nd_2TiO_5 nanoparticles calcined at 900 °C (sample 1)

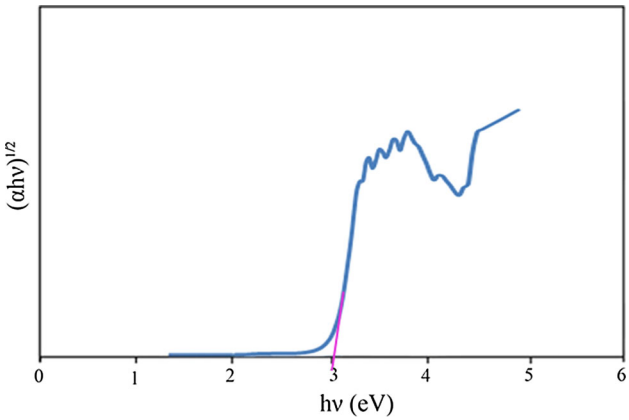


Fig. 5 DRS pattern of Nd_2TiO_5 nanoparticles calcined at 900 °C (sample 1)

effect of capping agents such as alanine, leucine, and histidine on the morphology and particle size of final products. Figure 2a–c shows the SEM images of the sample 1–3, respectively. In the presence of capping agents (alanine and leucine), the product mainly consists of spherical shape nanoparticles with average particle size 40–45 nm, as shown in Fig. 2a, b. Besides, in the presence of histidine as the capping agents the particle size of products were increased and products become agglomerate, as shown in Fig. 2c. Therefore, amino acids cause to increase the particle size of final products. Therefore, amino acids cause to increase the particle size of final products. Since in this study we used amino acids; therefore, the EDS analysis measurement was used to investigate the chemical composition and purity of Nd_2TiO_5 nanoparticles (sample 1), as shown in Fig. 3. According to the Fig. 3, the product consists of Ni, Ti, and O elements. Furthermore, neither N nor C signals were detected in the EDS spectrum, which means that the product is pure and free of any amino acids or impurity. The VSM magnetic measurement spectrum for the Nd_2TiO_5 (Fig. 4) shows the magnetic properties of Nd_2TiO_5 nanoparticles calcined at 900 °C. The Nd_2TiO_5 nanoparticle (sample 1) exhibits ferromagnetic behavior at room temperature with a saturation magnetization of 1.35 emu/g. The diffused reflectance spectrum of the as-prepared Nd_2TiO_5 nanoparticles is shown in Fig. 5. The fundamental absorption edge in most semiconductors follows the exponential law. Using the absorption data the band gap was estimated by Tauc's relationship:

$$\alpha = \alpha_0(h\nu - Eg)n/h\nu \quad (2)$$

where α is absorption coefficient, $h\nu$ is the photon energy, α_0 and h are the constants, E_g is the optical band gap of the material, and n depends on the type of electronic transition and can be any value between ½ and 3. The energy gap of the Nd_2TiO_5 nanoparticles (sample 1) is determined by extrapolating the linear portion of the plots of $(\alpha h\nu)^{1/2}$ against $h\nu$ to the energy axis, as shown in Fig. 5. The E_g value is calculated as 3.0 eV for the Nd_2TiO_5 nanoparticles. Photodegradation of methyl orange (MO) solution under UV light illumination was employed to evaluate the photocatalyst properties of the as-synthesized Nd_2TiO_5 nanoparticles (Fig. 6). No methyl orange was practically broken down after 60 min in the absence of Nd_2TiO_5 nanoparticles. The proposed mechanisms of the photocatalytic degradation of the methyl orange with the aid of Nd_2TiO_5 nanoparticles can be assumed as:

$$Nd_2TiO_5 + h\nu \rightarrow Nd_2TiO_5^{\cdot} + e^- + h^+ \quad (3)$$

$$h^+ + H_2O \rightarrow OH^{\cdot} \quad (4)$$

$$e^- + O_2 \rightarrow O_2^{\cdot -} \quad (5)$$

$$OH^{\cdot} + O_2^{\cdot -} + \text{methyl orange} \rightarrow \text{Degradation products} \quad (6)$$

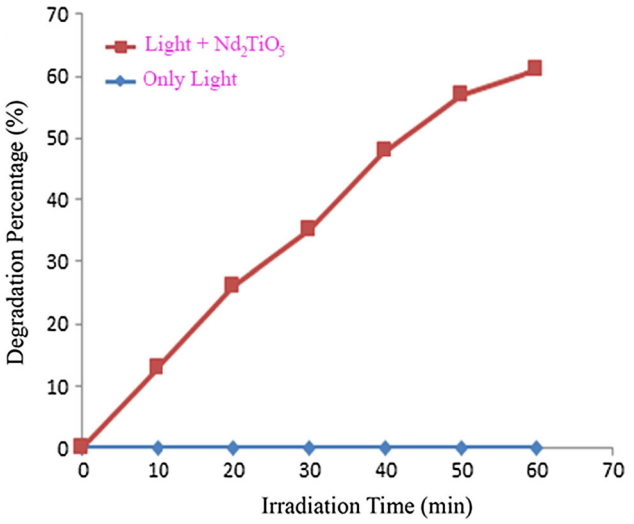
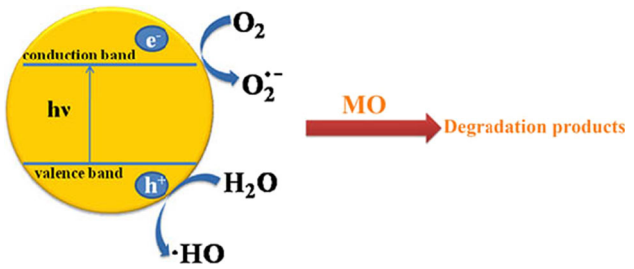


Fig. 6 Photocatalytic methyl orange degradation of Nd_2TiO_5 nanoparticles (sample 1) under ultraviolet light



Scheme 1 Reaction mechanism of methyl orange photodegradation over Nd_2TiO_5 nanoparticles under UV light irradiation

Utilizing photocatalytic calculations by Eq. (1), the methyl orange degradation was about 63 % after 60 min illumination of UV light in the presence of Nd_2TiO_5 nanoparticles (sample 1). Besides, the whole mechanism is shown in Scheme 1.

4 Conclusions

In this work, Nd_2TiO_5 nanoparticles were successfully synthesized by green method in an aqueous solution. EDS and XRD results proved high purity of the as-prepared Nd_2TiO_5 nanoparticles. In order to investigate the effect of polymeric surfactants on the morphology and particle size of final products several tests were performed in the presence of alanine, leucine, and histidine. Applying nanocrystalline Nd_2TiO_5 as the photocatalyst causes maximum 63 % degradation of methyl orange after 60 min irradiation of UV light. This result suggests that as-obtained nanocrystalline Nd_2TiO_5 as favorable material has high potential to be used for photocatalytic applications under UV light.

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