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Nd_2O_3-SiO_2 nanocomposites: A simple sonochemical preparation, characterization and photocatalytic activity

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ABSTRACT

Nd_2O_3-SiO_2 nanocomposites with enhanced photocatalytic activity have been obtained through simple and rapid sonochemical route in presence of putrescine as a new basic agent, for the first time. The influence of the mole ratio of Si:Nd, basic agent and ultrasonic power have been optimized to obtain the best Nd_2O_3-SiO_2 nanocomposites on shape, size and photocatalytic activity. The produced Nd_2O_3-SiO_2 nanocomposites have been characterized utilizing XRD, EDX, TEM, FT-IR, DRS and FESEM. Application of the as-formed Nd_2O_3-SiO_2 nano and bulk structures as photocatalyst with photodegradation of methyl violet contaminant under ultraviolet illumination was compared. Results demonstrated that SiO_2 has remarkable effect on catalytic performance of Nd_2O_3 photocatalyst for decomposition. By introducing of SiO_2 to Nd_2O_3, decomposition efficiency of Nd_2O_3 toward methyl violet contaminant under ultraviolet illumination was increased.

1. Introduction

Preparation of nanostructures is currently under great studies owing to their remarkable uses [1–5]. Neodymium oxide (Nd_2O_3) has a wealth of effective features, which result in its uses in UV absorbent, colored glass, protective coatings, high-k gate dielectrics, and catalysts [6–10]. Various inquiries have been performed on the production ways of neodymium oxide such as hydrogen plasma-metal reaction, atomic layer deposition, precipitation, thermal decomposition and sol–gel auto-combustion [10–18]. Till now, several investigations have been assigned to produce of various nanostructures with ultrasonic approach as a simple and rapid route [19–22]. The acoustic cavitation (the creation, growth, and implosive collapse of bubbles in the solution) brings the influences of sonication. The high pressure and great local heating can be created after collapse of bubbles with very short lifetimes. Several chemical reactions may be driven with the created hot spots [23–25]. The shape and size determine the features and use efficiency of nanostructures. Control the shape and size of nanostructures has been investigated in the recent years [26–33]. There is very limited research on study of Nd_2O_3-SiO_2 nanocomposites [34]. In the present investigation, Nd_2O_3-SiO_2 nanocomposites with enhanced photocatalytic activity are produced through simple and rapid sonochemical route in presence of putrescine as a new basic agent, for the first time. The influence of the mole ratio of Si:Nd, basic agent and ultrasonic power are optimized to obtain the best Nd_2O_3-SiO_2 nanocomposites on shape, size and photocatalytic activity. It is the first time that the sonochemical route is applied for the fabrication of the Nd_2O_3-SiO_2 nanocomposites. Application of the as-formed Nd_2O_3-SiO_2 nano and bulk structures as photocatalyst with photodegradation of methyl violet contaminant under ultraviolet illumination is compared.

2. Experimental

2.1. Materials and characterization

Tetraethyl orthosilicate (TEOS), putrescine (tetramethylenediamine), $Nd(NO_3)_3 \cdot 6H_2O$ and trimethylenediamine were obtained from Merck. A UV–vis spectrophotometer (Shimadzu, UV-2550, Japan) has been applied to acquire DRS spectrum of the as-prepared Nd_2O_3-SiO_2 nanocomposites. GC-2550TG (Teif Gostar Faraz Company, Iran) were used for all chemical analyses. A diffractometer of Philips Company with Ni-filtered Cu Ka radiation has been applied to acquire XRD pattern of the as-obtained nanocomposites. Transmission electron microscopy (TEM, JEM-2100) and field emission scanning electron microscope (FESEM, MIRA3 FEG-SEM) have been applied to determine the morphology and size of the

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Table 1
The fabrication conditions of Nd_2O_3-SiO_2 nanocomposites.

Sample no	Basic agent	Ultrasonic irradiation	Si:Nd ratio	Power (W)	Figure of FESEM images
1	Trimethylenediamine	Yes	2:1	60	1a and b
2	Trimethylenediamine	Yes	3:1	60	1c and d
3	Trimethylenediamine	Yes	4:1	60	1e and f
4	Putrescine	Yes	2:1	60	2a and b
5	Putrescine	Yes	3:1	60	2c and d
6	Putrescine	Yes	4:1	60	2e and f
7	Putrescine	Yes	4:1	40	3a and b
8	Putrescine	Yes	4:1	80	3c and d
9	Putrescine	No	4:1	–	4a and b
10	Putrescine	Yes	0:1	60	–
11	Putrescine	Yes	1:0	60	–

as-formed Nd_2O_3-SiO_2 nanocomposites. A Philips XL30 microscope has been employed to evaluate the chemical composition of the as-obtained nanocomposites. The fabrication has been done applying an ultrasonic generator (MPI Ultrasonics; Switzerland). A Magna-IR, spectrometer 550 Nicolet has been applied to record FT-IR spectrum of the as-formed nanocomposites.

2.2. Synthesis of Nd_2O_3-SiO_2 nanocomposites

Nd_2O_3-SiO_2 nanocomposites were obtained through simple and rapid sonochemical route. First, a solution involving stoichiometric value of putrescine as basic agent was added into the solution involving 20 mg of $Nd(NO_3)_3{\cdot}6H_2O$ under ultrasonic waves (for 1/12 h). Next, a methanolic solution involving stoichiometric value of TEOS was added into the above mixture under ultrasonic waves (for 1/12 h). The Nd_2O_3-SiO_2 nanocomposites (sample 6) were obtained after washing (with methanol and distilled water), air-drying and calcining (at 650 °C for 120 min) the formed precipitate. For investigation of the influence of ultrasound on size, photocatalytic activity and shape of Nd_2O_3-SiO_2 nanocomposites, one sample has been obtained without sonication. In Table 1 the fabrication conditions of Nd_2O_3-SiO_2 nanocomposites have been summarized.

2.3. Photocatalytic measurements

Application of the as-formed Nd_2O_3-SiO_2 nano and bulk structures as photocatalyst with photodegradation of methyl violet contaminant under ultraviolet illumination has been compared. For this goal, the reaction suspension comprising 3 mg of the methyl violet contaminant and 120 mg of the as-fabricated structures in the glass reactor has been employed. The above suspension has been subjected to the UV illumination (125 W mercury lamp) after aerating (within 1/2 h in darkness) for gaining the adsorption–desorption equilibrium. The methyl violet contaminant decomposition efficiency has been obtained as follow:

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

where A_0 and A_t are the UV–visible absorbance quantity of methyl violet contaminant solution before and after decomposition.

3. Results and discussion

In the present investigation, Nd_2O_3-SiO_2 nanocomposites have been obtained through simple and rapid sonochemical route. The influence of the ratio of Si:Nd and basic agent type on shape and size of Nd_2O_3-SiO_2 nanocomposites have been evaluated (Figs. 1a-f and 2a–f). Fig. 1a–f reveals the morphology of Nd_2O_3-SiO_2 nanocomposites fabricated with 2:1, 3:1 and 4:1 ratios of the Si:Nd as wells as trimethylenediamine as basic agent. The formation of irregular microstructures comprising the agglomerated nanoparticles (sample 1), high agglomerated micro/nanobundles (sample 2) and less homogenous nanobundles (sample 3) is depicted in Fig. 1a–f. When the putrescine as basic agent and 2:1, 3:1 and 4:1 ratios of the Si:Nd are applied, irregular micro/nanobundles (sample 4), relatively homogenous nanobundles (sample 5) and homogenous spherical Nd_2O_3-SiO_2 nanocomposites (sample 6) are fabricated. It is observed that molar ratio of Si:Nd = 4:1 and putrescine are very effective and beneficial to fabricate fine and homogenous spherical Nd_2O_3-SiO_2 nanocomposites (Fig. 2e and f). Putrescine as basic agent with longer chain may bring greater steric hindrance effect and may play the more favorable capping agent role for control the shape and size of Nd_2O_3-SiO_2 nanocomposites.

In the other side, the influence of the sonication power on the shape and size of the Nd_2O_3-SiO_2 nanocomposites has been evaluated (Fig. 3a–d). Ultrasonic irradiation brings bubbles which creates very great temperature and energy after destruction. This phenomenon brings favorable quantities of energy for fabrication of nanostructures. It is observed that with altering ultrasonic power from 60 (sample 6) to 40 (sample 7) and 80 W (sample 8) the grain size and homogeneity of Nd_2O_3-SiO_2 nanocomposites are changed (Figs. 2e and f and 3a–d). Optimum and ideal power for fabrication of fine and homogenous spherical Nd_2O_3-SiO_2 nanocomposites is 60 W (Fig. 2e and f). Nd_2O_3-SiO_2 nanostructures fabricated at other powers are non-uniform and have large size (Fig. 3a–d).

To obtain the power output, within tests the temperature of the mixture has been recorded against time. By applying the T against t information, dT/dt may be calculated. The power output has been obtained as follow [35,36]:

$$\text{Power output} = M\ (dT/dt)\ c_P \tag{2}$$

where M and c_P are mass and heat capacity of the applied solvent. The solvent applied in ideal reaction (for sample 6) has been distilled water. The power output has been estimated 16.2 W.

The formation of irregular and non-uniform microstructures/bulk structures (prepared with magnetic stirring for 1/3 h and without sonication) is depicted in Fig. 4a and b. It is observed that ultrasound irradiation is very effective and beneficial to fabricate homogenous spherical Nd_2O_3-SiO_2 nanocomposites (Fig. 2e and f). The influence of ultrasonic irradiation on the size and shape of Nd_2O_3-SiO_2 nanocomposites is demonstrated in Scheme 1. Ultrasonic approach is known as a simple and rapid route for control the shape and size of