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Green synthesis of $Dy_2Ce_2O_7$ ceramic nanostructures using juice of Punica granatum and their efficient application as photocatalytic degradation of organic contaminants under visible light

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ABSTRACT

An effective and simple route is developed for production of $Dy_2Ce_2O_7$ nanostructures by applying juice of Punica granatum as fuel and metal nitrates. Juice of Punica granatum has for the first time been exploited as a new fuel for simple synthesis of various structures of $Dy_2Ce_2O_7$ in terms of shape, photocatalytic efficiency and particle size at different time and temperature for production. TEM, Raman, DRS, XRD, FESEM and EDS are exploited for study and characterization the obtained nano-sized structures of $Dy_2Ce_2O_7$. Photocatalytic efficiencies have been evaluated with destruction of erythrosine and methylene blue pollutants under visible illumination over the various structures of $Dy_2Ce_2O_7$. Results clearly demonstrated that the nano-sized structures of $Dy_2Ce_2O_7$ obtained by application of juice of Punica granatum as new fuel at 450 °C for 4 h revealed excellent photocatalytic efficiency for the destruction of erythrosine and methylene blue pollutants.

1. Introduction

There is an increasing interest in preparation and study of the rare earth-doped cerium oxide compounds exhibiting efficient and attractive performance in solid oxide fuel cells, electrochemical devices, ceramic materials and photocatalyst and so on [1–8]. A number of approaches like combustion, co-precipitation, Pechini, salt-assisted aerosol decomposition, mechanochemical and solvothermal are available for the preparation of rare earth-doped cerium oxide compounds [9–14].

As far as we know, nanostructured compounds can exhibit various efficiencies depending over their grain size as well as morphology. Hence, great attempt has been invested in the modification of morphology and grain size [15–20]. Combustion procedure is cost effectiveness and has been applied to obtain the modified compounds in terms of morphology and grain size.

Exploiting sunlight in visible-light-driven photocatalysis has been offered as a quite effective strategy in resolving environmental issues as well as wastewater treatment [21–23]. Thus, to obtain the visible-light photocatalysts that can effectively act, simple and cost effective procedures should be rapidly presented.

The production of nanostructured compounds with green procedures that apply renewable and non-hazardous reagents (natural sources) instead of chemical compounds for overcoming environmental pollution issues, has been attracted growing interest. So, to prepare the nanostructured compounds in the large-scale with application of natural sources as non-hazardous and plentiful reagents, green and cost effective procedures should be rapidly introduced [24,25]. This study demonstrates an effective and simple route for production of $Dy_2Ce_2O_7$ nanostructures by applying juice of Punica granatum as fuel and metal nitrates. Juice of Punica granatum has for the first time been exploited as a new fuel for simple synthesis of various structures of $Dy_2Ce_2O_7$ in terms of shape, photocatalytic efficiency and particle size at different time and temperature for production. The fuel that utilizes for production of various structures of $Dy_2Ce_2O_7$ in this research is biodegradable and non-hazardous. Punica granatum Juice is rich in sugar (fructose & glucose) that can function as reductants and presumably can

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Table 1
The optimizing synthetic factors for $Dy_2Ce_2O_7$.

Sample no	Fuel	Calcination conditions	Dy:Ce	Figure of FESEM images
1	Punica granatum juice	850 °C/4 h	1:1	1a and b
2	Punica granatum juice	750 °C/4 h	1:1	1c and d
3	Punica granatum juice	650 °C/4 h	1:1	1e and f
4	Punica granatum juice	550 °C/4 h	1:1	2a and b
5	Punica granatum juice	450 °C/4 h	1:1	2c and d
6	Punica granatum juice	450 °C/3 h	1:1	4a
7	Punica granatum juice	450 °C/5 h	1:1	4b
8	–	450 °C/4 h	1:1	4c and d
9	Punica granatum juice	450 °C/4 h	1:0	5a and b
10	Punica granatum juice	450 °C/4 h	0:1	5c and d

be responsible to modify size and morphology due to making efficacious steric hindrance impact in the preparation. Also, photocatalytic efficiencies have been evaluated with destruction of erythrosine and methylene blue pollutants under visible illumination over the various structures of $Dy_2Ce_2O_7$.

2. Experimental

2.1. Materials and characterization

Dysprosium(III) nitrate pentahydrate and ceric ammonium nitrate with analytical grade were exploited without any separate purification stages. Crystal structures of the formed structures of $Dy_2Ce_2O_7$ have been identified with a diffractometer of Philips Company with Ni-filtered Cu Ka radiation. A Philips XL30 microscope has been applied to examine the purity of the formed structures of $Dy_2Ce_2O_7$. DRS spectrum for the formed structures of $Dy_2Ce_2O_7$ has been collected with a UV–vis spectrophotometer (Shimadzu, UV-2550, Japan). FT-IR spectrum for the formed structures of $Dy_2Ce_2O_7$ has been acquired on a Magna-IR, spectrometer 550 Nicolet. The morphology of the formed structures of $Dy_2Ce_2O_7$ has been revealed with a field emission scanning electron microscope (FESEM, MIRA3 FEG-SEM) as well as a transmission electron microscopy (TEM, JEM-2100).

2.2. Preparation of nanostructures of $Dy_2Ce_2O_7$

Nanostructures of $Dy_2Ce_2O_7$ have been synthesized with an effective and simple procedure applying juice of Punica granatum as new fuel. First, a mixture was prepared through slow addition of proper quantity of Punica granatum juice as new fuel to the solution (1.4 mmol of dysprosium(III) nitrate pentahydrate and 1.4 mmol of ceric ammonium nitrate in distilled water) and was kept strenuously stirred at 45 °C within 1/3 h. After evaporation, the formed viscous gel was dried (at 100 °C) and subsequently heated at various time and temperature (Table 1). The dependence of morphology and grain size on utilization of Punica granatum juice was also examined.

2.3. Investigation of photocatalytic activity

Photocatalytic efficiencies have been evaluated with destruction of erythrosine and methylene blue pollutants under visible illumination over the various structures of $Dy_2Ce_2O_7$. For investigation of photocatalytic activity, 60 mg of each of the various structures of $Dy_2Ce_2O_7$ was dispersed in aqueous solution of erythrosine or methylene blue (1.5 mg). Before turning on the light (125 W Osram lamp), the obtained suspension was kept in darkness under magnetic agitation for 1/2 h to attain the adsorption–desorption equilibrium. The erythrosine or methylene blue dye destruction rate has been computed as follow:

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

where A_0 and A_t are the quantity of UV–visible absorbance for erythrosine or methylene blue dye solution before and after decomposition.

3. Results and discussion

This study presents an effective and simple route for production of $Dy_2Ce_2O_7$ nanostructures by applying juice of Punica granatum as fuel and metal nitrates. Juice of Punica granatum has for the first time been exploited as a new fuel for simple synthesis of various structures of $Dy_2Ce_2O_7$. The fuel that utilizes for production of various structures of $Dy_2Ce_2O_7$ in this research is biodegradable and non-hazardous. So, its application can be desirable for overcoming environmental pollution issues. Punica granatum juice is rich in sugar (fructose & glucose) that can function as reductants and presumably can be responsible to modify size and morphology due to making efficacious steric hindrance impact in the preparation. The dependence of the morphology and grain size of $Dy_2Ce_2O_7$ on the time and temperature for production was investigated and the findings are represented in Figs. 1, 2 and 4.

Samples 1, 2, 3, 4 and 5 prepared at 850, 750, 650, 550 and 450 °C illustrate irregular microstructures (Fig. 1a and b), agglomerated micro/nanobundles (Fig. 1c and d), non-uniform micro/nanobundles (Fig. 1e and f), beehive-like nanostructures (Fig. 2a and b) and homogenous nanostructures (Fig. 2c and d). It seems that variation of temperature to 850 °C can cause to increment in the kinetic energy that can be reason for assemble and fuse the primary nanoparticles to each other in the definite directions and ergo form various structures of $Dy_2Ce_2O_7$.

XRD patterns corresponding to samples 1–5 prepared at several temperatures are displayed in Fig. 3a-e. The presence of the bands related to dysprosium oxide in Fig. 3a reveals the production of pure $Dy_2Ce_2O_7$ at 750, 650, 550 and 450 °C. All the diffraction bands of Fig. 3b-e are consistent with pure fluorite (standard) $Dy_2Ce_2O_7$ [26]. The mean diameter of crystallite corresponding to the structures of $Dy_2Ce_2O_7$ prepared at 750, 650, 550 and 450 °C are 28, 26, 20 and 17 nm computed applying Scherrer formula.

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