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Facile size-controlled preparation of highly photocatalytically active praseodymium zirconate nanostructures for degradation and removal of organic pollutants

Sahar Zinatloo-Ajabshir [a], Masoud Salavati-Niasari [a,*], Zahra Zinatloo-Ajabshir [b]

[a] Institute of Nano Science and Nano Technology, University of Kashan, Kashan, P.O. Box 87317-51167, Iran
[b] School of Pharmacy, Mazandaran University of Medical Sciences, Sari, P.O. Box 486717–887, Iran

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ABSTRACT

Highly photocatalytically active praseodymium zirconate ($Pr_2Zr_2O_7$) nanostructures were prepared by a new simple route with praseodymium nitrate and zirconyl nitrate as praseodymium and zirconium sources (at lower temperature). Benzene tricarboxylic acid as new stabilization agent and capping agent in presence of propylene glycol as connecting agent were applied to fabricate the nanostructured praseodymium zirconate for the first time. The as-obtained nanostructured $Pr_2Zr_2O_7$ was analyzed by UV–vis diffuse reflectance spectroscopy, energy dispersive X-ray microanalysis (EDX), Fourier transform infrared (FT-IR) spectroscopy, transmission electron microscopy (TEM), photoluminescence (PL) spectroscopy, field emission scanning electron microscopy (FESEM) and X-ray diffraction (XRD). Results of this investigation reveal that grain size, purity and shape of $Pr_2Zr_2O_7$ are controlled by altering preparation factors such as the kind of stabilization agent and alkaline agent. This is first attempt on the study of photocatalytic performance of the nanostructured praseodymium zirconate in various conditions. The effect of various factors including kind of pollutant, grain size of praseodymium zirconate nanostructures, praseodymium zirconate dosage and kind of light on photocatalytic behavior of products were evaluated.

1. Introduction

Praseodymium zirconate ($Pr_2Zr_2O_7$), which belongs to the class of rare earth-doped zirconium oxide materials, has been widely applied in high-temperature fuel cell, gas turbines, proton solubility, diesel engines, fluorescence centers and photocatalyst [1–5] owing to its specific and striking properties [6–9]. Up to now, synthetic methods such as complex precipitation, solid-state reaction, sol-gel, hydrothermal, sol-gel combined electrospinning and citrate gel have been reported for the fabrication of rare earth-doped zirconium oxide nanomaterials [10–17]. It is well known that the grain size and shape have a great impact on the behavior and final utilizations of the nanoscale materials. Hence, several preparation approaches have been introducing for grain size and shape controlling of the nanoscale materials [18–24]. Among of different approaches of the production of nanoscale materials, the Pechini way is well-known as a useful, cost-effective and simple process for grain size and shape controlling of the nanoscale materials.

This work reports a new simple way to prepare the nanostructured praseodymium zirconate with the aid of praseodymium nitrate and zirconyl nitrate and benzene tricarboxylic acid as new stabilization agent and capping agent in presence of propylene glycol as connecting agent. To our knowledge, it is the first time that benzene tricarboxylic acid as stabilization agent and capping agent in presence of propylene glycol as connecting agent are employed for the production of nanostructured praseodymium zirconate and the effect of factors such as the kind of stabilization agent and alkaline agent on the grain size, purity and shape of the nanostructured praseodymium zirconate by a new simple approach are investigated.

Organic dyes are the substantial chemicals applied in various industries, representing a great threat to the environment owing to their potentially carcinogenic nature and toxicity [25,26]. Today, water purification is known as one of the most significant fields in scientific research and organic dyes are the major contaminant kinds of wastewater. To date, much effort has been devoted to diminish or destruction of organic contaminants in the wastewater. Utilizing of photocatalysts is known as one of the most useful and promising routes for elimination organic contaminants from water [27–31]. This work is the first attempt on the study of

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

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photocatalytic performance of the nanostructured praseodymium zirconate in various conditions. The ability for the degradation of the organic contaminants including rhodamine B, methylene blue, methyl orange and eosin Y (as the model contaminants) were examined by photocatalysis experiments. The effect of various factors including kind of pollutant, grain size of praseodymium zirconate nanostructures, praseodymium zirconate dosage and kind of light on photocatalytic behavior of products were evaluated.

2. Experimental

2.1. Materials and characterization

All the chemicals for the preparation of $Pr_2Zr_2O_7$ nanostructures including praseodymium nitrate, zirconyl nitrate, propylene glycol, citric acid, salicylic acid, ethylenediamine, succinic acid, propylenediamine, maleic acid, benzene tricarboxylic acid, liquor ammonia solution containing 25% ammonia and trimethylamine were purchased from Merck Company and were applied without further purification. Transmission electron microscope (TEM) images of the as-obtained praseodymium zirconate nanostructures were taken on a JEM-2100 with an accelerating voltage of 200 kV. Fourier transform infrared spectra of the as-prepared products were obtained on a Shimadzu Varian 4300 spectrophotometer in KBr pellets in the 400–4000 cm^{-1} range. Thermogravimetric-differential thermal analysis (TG-DTA) of the as-obtained sample was done by employing 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 EDS analysis of the as-produced praseodymium zirconate nanostructures was carried out by employing a Philips XL30 microscope. GC-2550TG (Teif Gostar Faraz Company, Iran) were used for all chemical analyses. The UV–vis diffuse reflectance spectrum of the as-produced praseodymium zirconate nanostructures was obtained on a UV–vis spectrophotometer (Shimadzu, UV-2550, Japan). Powder X-ray diffraction (XRD) patterns of the as-synthesized praseodymium zirconate nanostructures were recorded by applying a diffractometer of Philips Company with X'PertPromonochromatized Cu Kα radiation (λ = 1.54 Å). FESEM images of praseodymium zirconate nanostructures were visualized by employing a Tescan mira3 field emission scanning electron microscope (FESEM).

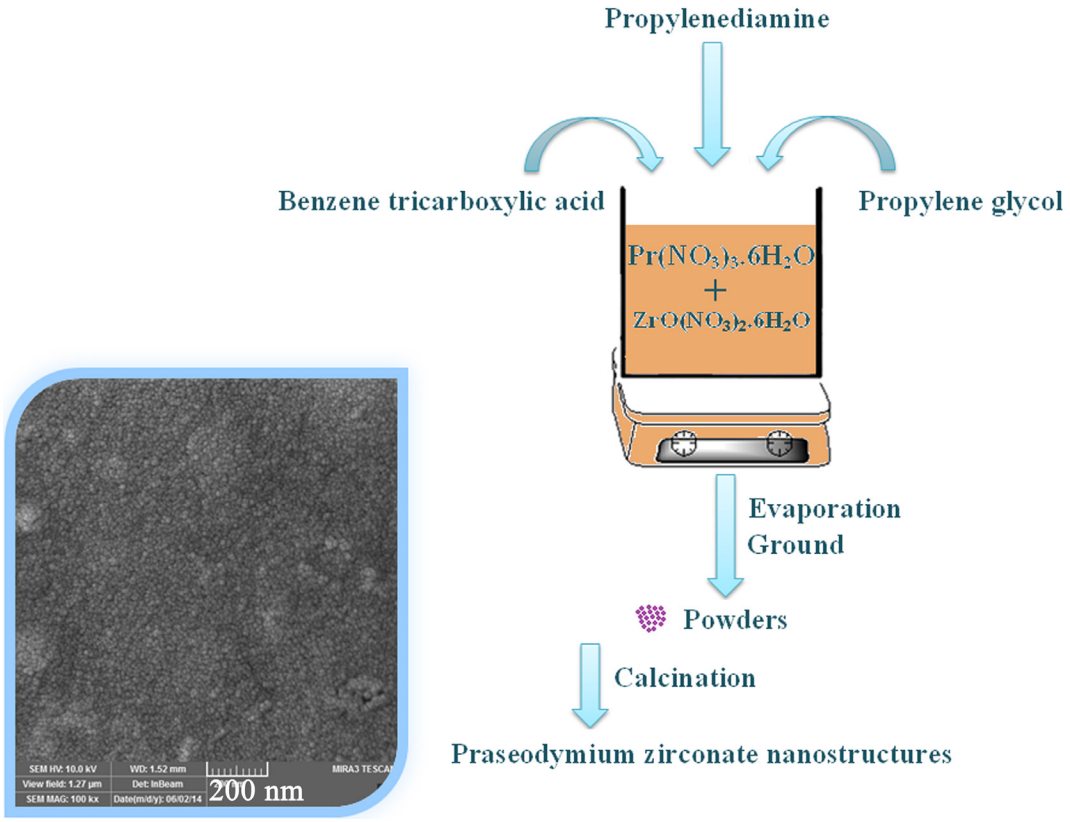

Fig. 1. Schematic diagram of the preparation of the praseodymium zirconate nanostructures.

Table 1
The preparation conditions of the praseodymium zirconate synthesized in this study.

Sample No.	Stabilization agent type	Alkaline agent	Figure of XRD patterns	Figure of FESEM images
1	Salicylic acid	Ammonia	5a	a and b
2	Maleic acid	Ammonia	5b	c and
3	Succinic acid	Ammonia	5c	e and f
4	Citric acid	Ammonia	5d	a and b
5	Benzene tricarboxylic acid	Ammonia	5e	c and d
6	Benzene tricarboxylic acid	Trimethylamine	5f	a and b
7	Benzene tricarboxylic acid	Ethylenediamine	–	9c and d
8	Benzene tricarboxylic acid	Propylenediamine	5g	e