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A unique and facile preparation of lanthanum ferrite nanoparticles in emulsion nanoreactors: Morphology, structure, and efficient photocatalysis

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ABSTRACT

Lanthanum ferrite nanoparticles ($LaFeO_3$ NPs) with light absorption properties in the visible region were successfully synthesized in CTAB (cetyltrimethyl ammonium bromide) emulsion nanoreactors at room temperature. The morphology, size, structure, elemental composition, and optical properties of these particles were characterized by field emission scanning electron microscope (FE-SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), fourier transform infrared spectroscopy (FT-IR), X-ray fluorescence (XRF), and ultraviolet–visible absorption (UV–Vis) spectroscopy. Through this method, highly crystalline and well-dispersed perovskite $LaFeO_3$ NPs with a phase-pure were successfully obtained. The band gap energy (E_g) of the $LaFeO_3$ NPs was calculated by UV-Vis spectroscopy at the wavelength of about 517 nm and is observed to have a value of 2.43 eV. The photocatalytic activities of $LaFeO_3$ NPs were evaluated by the degradation of toluidine blue O (TBO, used as a probe) dye under visible light irradiation, which exhibits a high photocatalytic TBO dye degradation activity as compared to the commercial P-25 titania powder. This phenomenon is due to smaller band gap energy and changing from bulk to nanostructure. The higher photocatalytic activity is also related to the photo absorption.

1. Introduction

In recent years, photocatalysis technology has received universal attention due to its applications in organic synthesis and the abatement of pollutants in water and air. In this context, many semiconductor photocatalysts have been recently explored. Among various oxide semiconductor photocatalysts, titanium dioxide (titania) has attracted intensive attention with the benefits of low cost, non-toxicity, excellent photocatalytic activity, and high chemical stability [1,2]. Unfortunately, titania can only absorb ultraviolet (UV) light which is only 3–5% of solar light due to its large band gap of 3.0 eV above, which limits its practical applications [3]. An attractive type of photocatalyst with a perovskite structure newly exploited as an effective photocatalyst in the visible region [4]. As a ferromagnetic insulator, $LaFeO_3$ with a typical ABO_3-type perovskite structure has attracted considerable part among the researchers due to its wide applications in various catalytic activities, as electrode material in solid oxide fuel cells, electronic and magnetic materials, gas sensors, and as electrodes in high temperature environments. In addition, it has been found that $LaFeO_3$ is visible light photocatalytic active due to its unique optoelectronic properties and narrow band gap [5].

Previous studies have reported that the specific surface area increases with decreasing average particle size of a

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photocatalyst in the nanometer regime. In general, morphology, crystal phase, band gap energy, and particle size are believed to play important roles in the photocatalytic activity of semiconductive oxides. Therefore, for a practical application in photocatalysis, the production of desired morphologies is important in terms of controlling the crystallinity and composition. Size, morphologies, and crystalline phases of nanostructures associated with their properties have been highly dependent on the synthesis method. The $LaFeO_3$ are usually synthesized via solid-state reactions at high temperatures (~1000 °C). Therefore, this methods lead to the production of the particles with large size and might also result in secondary phases as impurities due to high temperature treatment. Besides, high temperatures cause of the formation of non-controlled particle size and lower surface area. Several methods have been previously proposed for the synthesis of $LaFeO_3$ nanostructures, such as solid-state reaction [6], Microwave-assisted [7] combustion synthesis [8], sol–gel route [9], soft-chemistry method [10], etc. These approaches are the complex multistep processes, low yield energy-intensive and time-consuming, which limit their use in industrial applications. Consequently, the development of facile and effective process for nanostructures preparation is of practical interest. Synthesis of nanostructures within the emulsion nanoreactors gives a proper control of size and composition by exploiting the low formation temperature [11]. These emulsion nanoreactors are spherical in shape and favored the formation of spherical NPs during synthesis. Also, it is possible to control the shape and size of particles by adjusting the processing parameters such as different $^{(water)}/_{(surfactant)}$ molar ratios, solvents, reaction temperature and time. Furthermore, these emulsion nanoreactors can be employed to produce very fine particles of catalysts, which are efficient for photocatalytic processes [12]. So, this procedure is one of the most preferred candidates.

In this study, we describe a simple way, low-cost, time-saving, and economical approach with uniform shape and excellent monodispersity for the production of single-phase $LaFeO_3$ NPs synthesized within the emulsion nanoreactors. The present study has investigated the morphology, size, and structure of these particles. Also, toluidine blue O dye degradation was carried out to study the photocatalytic activity of present NPs under visible light irradiation.

2. Experimental

2.1. Materials

Cetyltrimethyl ammonium bromide (CTAB 98%) as surfactant, lanthanum(III) chloride heptahydrate ($LaCl_3 \cdot 7H_2O$ 99%) and iron(III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$ 99%) as precursor salts, and ammonia solution (NH_4OH 25%) as a reducing agent were purchased from Merck. Commercial P–25 titania powder (P-25, ca. 80% anatase, 20% rutile) from Degussa was used for the comparison of the photocatalytic activity. Isooctane/*n*-butanol (purity~99%) as the oil phase was supplied from Merck. Deionized and double distilled water was used for emulsion and solution preparation.

2.2. Characterization

The shape (or surface morphology), size, elemental composition, crystal structure, and optical properties of the lanthanum ferrite nanoparticles were characterized by FE-SEM, TEM, XRD, XRF, FT-IR, and UV–Vis spectroscopy. FE-SEM image was obtained on a Hitachi S–1460 field emission scanning electron microscope using accelerating voltage of 15 kV. TEM measurement for $LaFeO_3$ NPs was performed on a Philips model EM–208 S instrument operated at an accelerating voltage of 100 kV. Usually more than 100 particles from different parts of the grid were used to estimate the average size and size distribution of particles. XRD analysis of the lanthanum ferrite nanoparticles was carried out using a Philips diffractometer (Model TM-1800). Nickel filtered Cu-Kα radiation source was used to produce X-ray (λ=0.154 nm), and scattered radiation was measured with a proportional counter detector at a scan rate of 4°/min. The scanning angle was from 20° to 60°, operating at a voltage of 40 kV applying potential current of 30 mA. The elemental composition of the $LaFeO_3$ NPs was determined by Philips model PW-1480 Fluorescence Spectrometer operating at 4 kW with Rh Ka radiation source. FT-IR spectra (in the wavenumber range from 400 to 4000 cm^{-1}) were recorded using KBr disks on a Shimadzu FT-IR model Prestige 21 spectrometer. The UV–Vis absorption spectrum of the emulsion solution containing the lanthanum ferrite nanoparticles was measured using a Perkin-Elmer UV–Vis spectrometer equipped with a 1.0 cm quartz cell. (300–800 nm).

2.3. Preparation of the $LaFeO_3$ NPs

The emulsion nanoreactors was prepared using 59.29 wt % isooctane as the oil phase, 16.76 wt% CTAB as the surfactant, 13.90 wt% *n*-butanol as the co-surfactant, and 10.05 wt.% aqueous phase. Initially, the aqueous solution was added drop by drop into the oil phase with vigorous stirring at room temperature, leading to the formation of the water-in-oil emulsion nanoreactors. The resulted mixture was stirred for 5 min until a clear solution was obtained. Then, three emulsions with different aqueous phases containing 0.32 mmol $LaCl_3 \cdot 7H_2O$ (as emulsion A), 0.32 mmol $FeCl_3 \cdot 6H_2O$ (as mulsion B), and 0.68 mmol NH_4OH (as emulsion C) were prepared. Emulsion A was mixed to emulsion B; hereafter the resultant emulsion is called system I. After mechanical agitation for about 15 min, the emulsion C (reducing agent) was rapidly added to system I and the obtained transparent liquid was stirred for 30 min. Although the color of the emulsion changed from yellow to black after a few minutes, the time of 30 min stirring was applied to ensure complete reduction. Then, the obtained precipitate was separated by centrifugation and washed thoroughly by ethanol and deionized water for 5 min three times. The prepared precursor was dried in an oven at 30 °C for 6 h. Finally, the product was calcined during 4 h at 500 °C under air flux for a complete crystallization and surfactant elimination (the product after calcining at 300 °C and 400 °C for 4 h were still amorphous in structure). The heating rate was 10 °C/min and natural cooling was used. The resulting black product was lanthanum ferrite NPs. The nanoparticles were then naturally