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Synthesis and characterization of barium zinc ferrite nanoparticles: Working electrode for dye sensitized solar cell applications

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Abstract

Spinel type barium zinc ferrite ($Zn_{1-x}Ba_xFe_2O_4$) nanoparticles with compositions of barium ($x = 0.01$–0.15) were prepared by an auto combustion method using glycine as fuel and nitrates as precursors. The formation mechanisms of these ferrite nanoparticles are briefly discussed. The prepared samples were characterized by powder X-ray Diffraction analysis (XRD) and confirm the formation of pure phase zinc ferrite with cubic structure. The average crystallite size was found to vary from 39.5 nm to 47.6 nm. X-ray Photoelectron Spectroscopy (XPS) was used to analyze the elemental composition and oxidation states of the elements in the ferrite samples. Detailed photoelectron peaks of Zn 2p, Fe 2p, O 1s and Ba 3d with corresponding binding energy are presented in the XPS spectrum. The optical band gap values increased from 2.42 eV to 2.50 eV with increase in barium concentration as determined from UV–Diffuse Reflectance Spectroscopy (DRS) using Tauc relation. The current–voltage (J–V) curve for DSSC based on barium zinc ferrite nanoparticles sensitized with Eosin yellowish dye was characterized by J–V measurements. It exhibited a maximum optimal energy conversion efficiency of around 0.0027% for barium doped zinc ferrite nanoparticles whereas the cell based on the pure zinc ferrite nanoparticles gave efficiency of approximately 0.0014% and enhanced open circuit voltage and current are obtained.

Keywords: Zinc ferrite; Combustion method; Fuel; Nanoparticle; Oxidation state; Dye sensitized solar cells

1. Introduction

In the field of solar cell technology, currently much attention is directed to the development of dye-sensitized solar cell (DSSC). This is because the solar spectrum consists of ~5% UV ($\lambda = 200$–400 nm), ~52% infrared ($\lambda > 400$ nm) and ~43% visible ($\lambda = 400$–800 nm). Since visible light constitutes a large fraction of solar energy, one of the greatest challenges is to focus on ferrite materials that exhibit high efficiency when illuminated by visible light photons from solar spectrum. Ferrite materials like zinc ferrite have spinel structure of the type $A^{2+}B_2^{3+}O_4$ where A and B refer to the metal ions at tetrahedral and octahedral sites respectively in the oxygen lattice (Abedini Khorramia et al., 2011). Zinc ferrite ($ZnFe_2O_4$) belongs to the normal spinel ferrite system in bulk form whereas cubic spinel system in nanoscale forms. In addition to this, Zinc ferrite is an n-type semiconductor material that can be used in visible light photocatalytic applications due to its smaller band gap value (1.9 eV). It has the ability to absorb visible light from the solar spectrum and thus is a potentially useful solar energy conversion material (Suk Jang, 2009). Researchers are interested in ferrite materials for the development of water splitting for hydrogen energy production (Inoue et al., 2004), purification of water and air applications (Hoffman et al., 1995).

In the past, many methods like mechano chemical reaction (Yang et al., 2004), co-precipitation method (Ping, 2009), low temperature method (Li et al., 1996), sol–gel

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method (Gatelyte et al., 2011), wet-milling process (Ozcan et al., 2005), co-precipitation–air oxidation method (Li et al., 2010), hydrothermal synthesis (Shu-Hong et al., 2003), microwave-assisted solvothermal methods (Blanco-Gutierrez et al., 2011) and reviews have been used to produce nano $ZnFe_2O_4$ materials and have been reported in literature. Among them combustion method has great opportunities for large scale production of nanoparticles in a short span of time (20 min). It is cost effective and can produce pure phase nanoparticles with the desired shape. This method is mainly based on mixing the reactants that oxidize easily such as zinc nitrate, iron nitrate and an organic fuel which acts as a reducing agent. In order to initiate the ignition of the mixture, an external heat source is needed. This ensures the self-propagating character of an exothermic redox reaction. The fuel to metal nitrate ratio has to be carefully considered as they play a vital role in total combustion process. Barium with its interesting optical behaviour has been found to increase the optical property of various ferrites. However, no reports have been published on producing barium doped zinc ferrite by auto combustion method. In this investigation, pure and barium doped zinc ferrite with chemical compositions of $Zn_{1-x}Ba_xFe_2O_4$ ($x = 0.01$, 0.05, 0.10, 0.15) were synthesized by the auto combustion method. The crystalline phases of the samples were identified by X-ray diffraction. The surface phenomenon and oxidation state of these samples were characterized by X-ray Photoelectron Spectroscopy (XPS). Detailed surface analysis of core level spectra of Zn 2p, Fe 2p, Ba 3d and O 1s peak were recorded. The optical property of these samples was measured by using UV–Diffuse Reflectance Spectroscopy (DRS). DSSC was fabricated using barium zinc ferrite nanoparticles as a working electrode. The current–voltage measurements were performed for the DSSC prepared from barium zinc ferrite nanoparticles sensitized with Eosin yellowish dye.

2. Experimental

2.1. Synthesis of barium zinc ferrite nanoparticles

Pure and barium doped zinc ferrite nanoparticles with chemical composition $Zn_{1-x}Ba_xFe_2O_4$ ($x = 0.01$, 0.05, 0.10, 0.15) were prepared by the auto combustion method. All analytical reagents were used without further purification. Initially stoichiometric amounts of $Zn(NO_3)_2{\cdot}6H_2O$ (Merck), $Fe(NO_3)_3{\cdot}9H_2O$ (Himedia, 98–100% purity), $Ba(NO_3)_2$ (Himedia, 99%purity) were dissolved in 20 ml of distilled water, then 10 ml of nitric acid (HNO_3) was mixed with the aqueous solution which resulted in a clear solution. Appropriate amounts of fuel (reducing agent) were slowly added to the above solution and the mixture was stirred continuously until it was completely dissolved. To evaporate the water content in the solution, the mixture was heated in a magnetic stirrer with a hot plate at 100 °C for 2 h and it became a dark brown viscous gel. For further heat treatment, the gel obtained was kept on a hot plate at 200 °C for 15 min. The process of auto-ignition started and produced a dry brown resin with the emission of a large amount of gaseous fumes. Brownish zinc ferrite ash was obtained after the completion of the combustion process. The time taken between the initial ignition and the end of the reaction forming a zinc ferrite powder was less than 20 s. Finally, as-prepared nanoscale zinc ferrites samples were kept out of the hot plate and ground using an agate mortar and pestle to form fine powders. The entire reaction process is illustrated in Fig. 1. The fine powders were stored for characterization. The obtained samples were indicated as ZF, ZBF1, ZBF5, ZBF10 and ZBF15.

2.2. Preparation of working electrode and treatment with dye

The doctor blade technique was used to prepare the thin layer of nanostructured films (Katsaros et al., 2002). In typical process, the colloidal paste was prepared using the following steps; (i) First, 0.1 g of $ZnFe_2O_4$ nanoparticles was ground with the help of appropriate amounts of distilled water and acetylacetone for 10 min to form a viscous paste. (ii) The viscous paste was slowly added with 0.3 ml of distilled water until desirable viscosity was attained. (iii) Finally, 20 μl of surfactant (Triton X-100) was slowly added with grinding for 10 min. The resulting $ZnFe_2O_4$ paste is uniformly dispersed on the conducting substrate using the doctor blade technique. After coating, the films were dried in air atmosphere at room temperature. Then, the films were heat treated at 450 °C for 20 min. For fabricating the DSSC, these calcined films were then soaked into the solution containing ethanol and Eosin yellowish dye for 24 h at room temperature. The dye-sensitized electrodes were then rinsed with absolute ethanol to remove the physisorbed dye molecules on the surface.

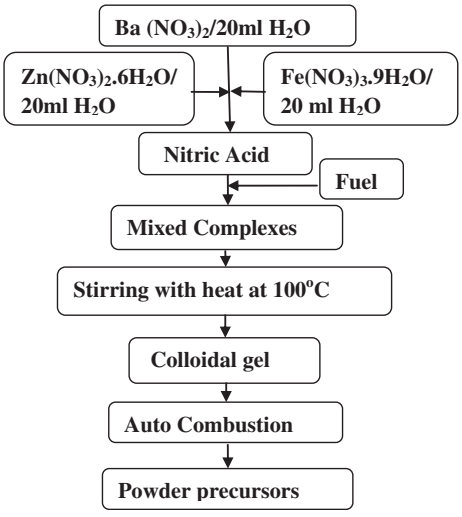

Fig. 1. Synthesis scheme of the $Zn_{1-x}Ba_xFe_2O_4$ ($x = 0.01$, 0.05, 0.10, 0.15) nanoparticles by auto combustion method.