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A new approach: Synthesis, characterization and optical studies of nano-zinc aluminate ☆

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ABSTRACT

The present study reports a green chemistry approach for the biosynthesis of nano-zinc aluminate by a microwave method using high purity metal nitrates and aloe vera plant extract. Aloe vera extract simplifies the process and provides an alternative process for a simple and economical synthesis of nanocrystalline zinc aluminate. It is prepared by conventional and microwave method by with and without using the plant extract for comparison purpose. The obtained nanomaterials were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), high resolution scanning electron microscopy (HR-SEM), energy dispersive X-ray analysis (EDX), high resolution transmission electron microscopy (HR-TEM) diffuse reflectance spectroscopy (DRS) and photoluminescence (PL) spectroscopy. The XRD confirmed the formation of cubic structure of zinc aluminate. The formation of zinc aluminate phase is also confirmed by FT-IR. The change in morphology from nanorods to nanosheets from the conventional method to microwave method is clearly shown by HR-SEM. The optical properties were determined by DRS and PL spectra.

1. Introduction

Metal-oxide spinels are commonly used in many application fields such as semiconductor, biomedical, gas sensor, thin film technology, electroluminescent displays, as well as in heterogeneous catalysis, due to their high thermal resistance, catalytic, electronic and optical properties [1,2]. Among these materials, zinc aluminate ($ZnAl_2O_4$), with spinel structure belonging to Fd3m space group, offers many advantages, such as high thermal and chemical stability, hydrophobic behavior, high mechanical resistance, low sintering temperature, and high quantum yields [3–6]. Besides, it is a wide band gap semiconductor (3.8 eV) that can be used as a transparent conductor, dielectric material, optical material, and sensors [7]. Spinel metal oxides are produced by techniques such as hydrothermal methods, co precipitation, microemulsions, combustion, sol–gel, solvothermal, electrodeposition, microwave-assisted synthesis, non-aqueous routes, and also solid-state reactions [8,9]. On the other hand, the microwave-assisted synthesis route is yet another method for the synthesis of metal oxides and has been gaining significance in the synthesis of metal oxide nanomaterial [10]. Microwaves are used for many industrial and scientific purposes. Microwave use is a novel way of processing materials, due to its special characteristics as a heating source, including its environment friendliness, reduction in time, energy consumption and also its ability to produce unique microstructures [11–13]. Microwave heating is fundamentally different from conventional heating. In the microwave method, the heat is generated internally within the material instead of originating from external sources, and hence there is an inverse heating profile. The heating is very rapid as the material is heated by energy conversion rather than by energy transfer, which occurs in conventional methods [14,15].

Recently, synthesis using plant extract is an alternative synthetic route to prepare nanocrystalline inorganic materials. There are many reports on the synthesis of metal, semiconductor, and nanomaterial using aloe vera plant extracts. There is 99.5% water content in the aloe vera leaves. The rest is solid materials containing over 75 different ingredients including vitamins, minerals, enzymes, sugars, phenolic compounds, lignin, saponins, sterols, amino acids and salicylic acid. Aloe vera gel is widely used in the cosmetics industry as a hydrating ingredient in liquids, creams, sun lotions, lip balms, healing ointments etc. The gel is further used in pharmacology for wound healing, anti-inflammatory and burn treatment [16]. Aloe vera stable gel may be used as a bio-reducing agent in the preparation of metal oxide precursor powders. Recently, the extract of aloe vera plant has been successfully used to synthesize single crystalline triangular gold nanoparticles and spherical silver nanoparticles in high yield, by the reaction of aqueous metal source ions (chloroaurate ions for Au and silver ions for

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Ag) and the extract of the aloe vera plant [17]. Most recently, Maensiri et al. reported for the first time, the synthesis of nanoparticles of In_2O_3 by using aloe vera plant extract solution [17]. This is because of the long chain polysaccharides present within the aloe vera plant extract, which affords the homogeneous distribution of metal oxides. The advantage of this method includes (i) use of inexpensive, non-toxic and environmentally benign precursors and (ii) simple and time saving procedure [18].

The biological synthesis using aloe vera extract provides a simple efficient and green route for the synthesis of nanomaterials. The slow reduction of the nanomaterials along with the shape-directing effects of the constituents of the aloe vera extract plays a key role in the formation of the metal-oxide [19,20]. Our unique approach is to develop a 'greener approach' synthetic strategies to prepare the nanomaterials via several chemical pathways using benign reagents in the matrix in which they are to be used, thus, reducing the risk of exposure or eliminating the use and generation of the hazardous substances normally used. Due to the desire for eco-friendly processes, new green synthesis using plant extracts has acquired greater importance [21].

In the present work, we report for the first time, the synthesis of nano-zinc aluminate by a microwave method using metal nitrates and aloe vera extract solution as the precursors. Later, they are compared with the prepared by conventional method. The prepared nanomaterials were characterized by X-ray diffraction (XRD), fourier transform infrared spectroscopy (FT-IR), high resolution scanning electron microscopy (HR-SEM), energy dispersive X-ray analysis (EDX), high resolution transmission electron microscopy (HR-TEM) diffuse reflectance spectroscopy (DRS) and photoluminescence spectroscopy (PL).

2. Experimental section

2.1. Materials

Zinc nitrate (99% purity) and aluminum nitrate (98% purity) were used as the starting material (Merck chemicals, India) and were used as received without further purification. The aloe vera leaves were collected from local agricultural fields, Chennai, Tamil Nadu.

2.2. Aloe vera extracts preparation

A 2 g portion of thoroughly washed aloe vera leaves were finely cut and the obtained gel was in dissolved 10 ml of de-ionized water, and stirred for 45 min to obtain clear solution. The resulting extract was used as an aloe vera extract solution. Metal nitrate salts and the plant extract (used in the mixture) were chosen by considering the total reducing and oxidizing agent valences of the raw materials and were quantified in equivalence of NOx reduction N_2O to N_2 at low temperatures. But nowadays, plant extract has been used as both reducing and capping agent for the synthesis of nanomaterials. The plant extract plays not only a fuel role, but also has a coordinating action, capturing the involved metal ions in the amylose helix of the aloe vera, in well-defined sites, and impeding the separation of metal oxides [22]. The method proposed here opens new perspectives regarding the usage of aloe vera plant extract in materials synthesis. It also represents a successful start to enlarge the very selective family of fuels with natural, diverse, and less-polluting members, namely the plant extract [23].

2.3. Preparation of zinc aluminate by conventional method (CM)

Zinc nitrate and aluminum nitrate were dissolved in de-ionized water and then mixed with aloe vera extract solution under constant stirring for 5 h, at room temperature until a clear transparent solution was obtained. The molar ratio of Zn/Al was kept as 1:2. The solution was dried in an air oven at 120 °C for 5 h. The powders were then sintered at 400 °C at a heating rate of 5 °C/min for 3 h in muffle furnace and were labeled as $ZnAC_1$ (prepared by conventional method).

2.4. Preparation of zinc aluminate by microwave method (MWM)

The clear transparent solution prepared as mentioned in the previous section was then placed in a domestic microwave-oven (2.45 GHz, 750 W) for 15 min. Initially, the solution boiled and underwent dehydration followed by decomposition with the evolution of gases. It vaporized the solution and instantly became a solid and they were labeled as $ZnAM_1$ (prepared by microwave method).

For comparison purpose, the zinc aluminate samples were also prepared without using the plant extract by both conventional and microwave heating and were labeled as $ZnAC_2$ and $ZnAM_2$ respectively.

2.5. Characterization of zinc aluminate nanostructures

The structural studies were carried out using a Philips X'pert diffractometer for 2θ values ranging from 10° to 80° using Cu Kα radiation at λ = 0.154 nm. A Perkin Elmer infrared spectrophotometer was used for the determination of the surface functional groups of the nanomaterials. Morphological studies and energy dispersive X-ray analysis of nanomaterials have been performed using a Joel JSM6360 high resolution scanning electron microscope. The samples were coated with gold by a gold sputtering device for the better visibility of the surface morphology. Stereo-scan LEO 440 and a high resolution transmission electron microscope (HR-TEM). The diffuse reflectance UV–visible spectra of the nanomaterials were recorded using Cary100 UV–visible spectrophotometer. The emission properties were recorded using Varian Cary Eclipse Fluorescence spectrophotometer.

3. Results and discussion

3.1. X-ray diffraction studies (XRD) studies

To study the crystallization process and phase identification, the powder X-ray diffraction (Fig. 1a–d) analyses were performed on $ZnAl_2O_4$ samples. Fig. 1a and c shows the XRD pattern of ZAC_2 and ZAM_2. Absence of characteristic peaks of $ZnAl_2O_4$ confirmed

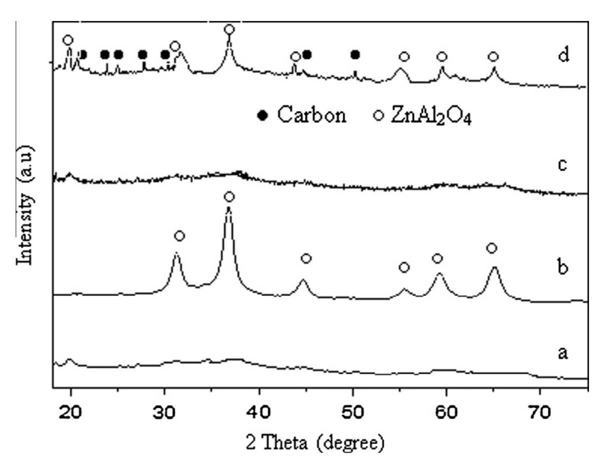

Fig. 1. XRD pattern of $ZnAl_2O_4$: (a and c) ZAC_2 and ZAM_2 prepared without using plant extract, (b and d) ZAC_1 and ZAM_1 prepared using plant extract.