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Synthesis and characterization of novel spinel $Zn_{1.114}La_{1.264}Al_{0.5}O_{4.271}$ nanoparticles

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ABSTRACT

Novel spinel $Zn_{1.114}La_{1.264}Al_{0.5}O_{4.271}$ nanoparticles were synthesized using low–temperature gel combustion method and characterized by XRD, XPS, FE–SEM, TEM, BET, UV–Vis, FT–IR and fluorescence analyses. The XPS analysis revealed that the number of Zn^{2+} ions in the O_h holes was ~2.7 times greater than that in the T_d holes confirming the synthesized compound was not a mixture of different metal oxides but it was a normal spinel material. The average crystallite size measured for the sharpest peak at $2\theta \approx 33^\circ$ in the XRD diagrams was about 25 nm for the fuel/metals ratios of 1:3 and 2:3, but it was ~15 nm for the fuel/metals ratios of 10:3 and 20:3. The FE–SEM micrographs showed puzzle like, leaf and spherical morphologies for the nanoparticles synthesized using starch, poly(vinyl alcohol) and glycerin fuels, respectively. Interestingly, with increasing the fuel/metals ratio, the calcination time was decreased significantly from about 24 h to about 15 min. The N_2-physisorption data illustrated that varying both the fuel type and pH of the solution affected the BET surface areas and pore volumes. The band gap of the nanoparticles synthesized with glycerin fuel was slightly greater (3.24 eV, smaller electron conductivity) than those of nanoparticles obtained using starch and poly(vinyl alcohol) fuels (3.11 and 3.12 eV, respectively). Accordingly, the semiconductor $Zn_{1.114}La_{1.264}Al_{0.5}O_{4.271}$ nanoparticles can find promissing applications as catalysts (in chemical synthesis), electrocatalysis (cathodic and anodic materials in solar cells and fuel cells), ceramics (in high temperature catalytic reactions as highly stable materials) and adsorbents (in air/wastewater treatments).

1. Introduction

The synthesis of nanosized metal oxides has become of great interest due to the novel and invaluable properties of these materials [1–6]. Combustion is a simple and suitable method for the synthesis of nanoparticles such as advanced ceramics, catalysts and nanomaterials [7] that is based on the principles of the propellant chemistry [8] in which a thermally induced redox reaction takes place between an oxidant and a fuel. The monophasic nanopowders with homogeneous microstructure can be prepared with this method at lower temperatures or shorter reaction times, in comparison with other conventional methods like solid-state synthesis [9,10] or nitrate method [11]. The process of thermal decomposition of citrate precursor [12–16] has indicated good results among various synthetic approaches. Recently, this method has been modified to produce nanosized oxides through a process of sol–gel auto–combustion [17–19]. Indeed, when nitrate citrate gels are heated, they will burn in a self-propagating reaction to convert the precursor mixtures directly into the products [20,21]. Starch has been used as environmentally benign fuel in a combustion-based synthesis of zinc aluminate oxides [22] and also $Co_xZn_{1-x}Al_2O_4$ blue pigments [23]. Similarly, poly(ethylene glycol) was utilized for the green synthesis of $La_{1-x}Sr_xMnO_3$ nanoparticles [24]. Also, nanocrystalline ceria-based powders including CeO_2, $(YO_{1.5})_{0.2}(CeO_2)_{1.8}$, $(NdO_{1.5})_{0.2}(CeO_2)_{1.8}$, $(SmO_{1.5})_{0.2}(CeO_2)_{1.8}$ and $(GdO_{1.5})_{0.2}(CeO_2)_{1.8}$ have been prepared using combustion synthesis with ethylene glycol as a fuel and nitrate as an oxidizer [25]. Because of the importance of the fuel role in the combustion synthesis, the decomposition behaviors and burning characteristics of ammonium nitrate/polytetrahydrofuran/glycerin composite propellant were investigated [25].

The spinel-type zinc aluminate ($ZnAl_2O_4$) nanoparticles have been applied as green and recyclable heterogeneous catalyst for the acetylation of amines, alcohols and phenols under solvent-free conditions [26]. Also, $M^{II}Cr_2O_4$-spinels were used as supports for

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Au nanoparticles in oxidation of CO [27]. Phenol methylation was performed over nanoparticulate $CoFe_2O_4$ inverse spinel catalysts [28]. The $LiMn_2O_4$ spinel cathode nanorods prepared from nanowire MnO_2 templates were capped with polyvinyl pyrrolidone (PVP) and coated with ZrC_2O_4 precursors in aqueous solution [29]. The size dependent gas sensing properties of spinel iron oxide nanoparticles was also investigated [30]. A highly sensitive formaldehyde chemical sensor based on hydrothermally prepared spinel $ZnFe_2O_4$ nanorods has been reported [31]. The $LiNi_{0.5}Mn_{1.5}O_4$ spinel (as cathode) and Si nanoparticles (as anode) were combined for utilizing in an advanced Li-ion battery that yielded much greater specific capacity than most existing Li-ion batteries [32]. The spinel metal oxide cathodes were used for intermediate temperature solid oxide [33,34] and microbial [35] fuel cells. Moreover, composite photoanodes of Zn_2SnO_4 nanoparticles modified with SnO_2 hierarchical microspheres were applied for dye-sensitized solar cells [36].

Herein, gel combustion method was applied for the synthesis of novel spinel nanosized $Zn_{1.114}La_{1.264}Al_{0.5}O_{4.271}$ particles using starch, poly(vinyl alcohol) and glycerin as environmentally benign green fuels. The effects of four parameters including pH, fuel type, calcination time and fuel/metal ratio on the size and morphology of nanoparticles were investigated. The XRD, XPS, FE–SEM, TEM, BET, UV–Vis, FT–IR and fluorescence analyses were performed to explore the structural, textural and spectroscopic properties of the nanoparticles.

2. Materials and methods

2.1. Materials

All materials were purchased from Merck and Sigma-Aldrich Companies and were used as received. They included aluminum(III) nitrate nonahydrate [$Al(NO_3)_3.9H_2O$, 99.997% trace metals basis], zinc(II) acetate dehydrate [$Zn(CH_3COO)_2.2H_2O$, ≥98%], lanthanum nitrate hexahydrate [$La(NO_3)_3.6H_2O$, ≥98%], water soluble starch, [$(C_6H_{10}O_5)_n$, Grade: GR for analysis ISO], ammonium hydroxide [NH_4OH, 25% NH_3 in water], poly(vinyl alcohol) [$(CH_2CHOH)_n$, M_W = 89,000–98,000] and glycerin [$OHCH_2CH(OH)CH_2OH$, ≥99.5%, Grade: ACS, Reag. Ph Eur].

2.2. Instruments and measurements

The Fourier–transform–infrared (FT–IR) spectrum was recorded on a Bruker FT–IR spectrometer. Elemental analysis was performed using EDAX accessory on FE–SEM instrument. X–ray diffraction analysis was obtained with an INEL EQUINOX 3000 X–ray diffractometer. The X-ray photoelectron spectroscopy (XPS) was recorded with an Axis Ultra DLD system (Kratos, U. K.) using an Al Kα radiation source (hυ = 1486.8 eV). The binding energy was calibrated by taking the C 1s peak (284.8 eV) as a reference. The XPS peaks were analyzed using a Shirley-type background and a nonlinear least-squares fitting of the experimental data based on a mixed Gauss/Lorentz peak shape. XPS quantification was performed by applying the appropriate relative sensitivity factors (RSFs) to the integrated peak areas. The field emission scanning electron microscopy (FE–SEM) micrographs were taken from Philips instrument (XL30), under vacuum, accelerated at 15 and 20 kV. The UV–Vis and fluorescence spectra were recorded using a Perkin Elmer spectrophotometer and a Perkin Elmer LS55 instrument, respectively. The surface area, pore volume and pore diameters were estimated by BET (Brunauer–Emmett–Teller) method from nitrogen adsorption–desorption isotherm data obtained at −196 °C on a constant–volume adsorption apparatus (QuantaChrome, NOVA2000). Prior to the adsorption–desorption measurements, all the samples were degassed at 200 °C in N_2 flow for 3 h. The TEM image was taken by a Zeiss EM 900 transmission electron microscope (TEM) apparatus. Intrinsic viscosity measurements were done by Ubbelhode viscometer and yielded the molecular weights of starch and poly(vinyl alcohol) equal to 56,669 and 112,903 g/mol, respectively.

2.3. Synthesis

The synthesis of $Zn_{1.114}La_{1.264}Al_{0.5}O_{4.271}$ powder was performed according to a gel combustion technique in which the metal salts (zinc acetate, lanthanum nitrate and aluminum nitrate) were used as oxidants and sources of Zn(II), La(III) and Al(III) cations. The synthetic procedure was based on a redox reaction and starch, poly(vinyl alcohol) and glycerin were used as fuels to reduce the reaction temperature and facilitate the synthesis process.

An aqueous solution containing appropriate amounts of $Al(NO_3)_3\cdot 9H_2O$, $Zn(CH_3COO)_2\cdot 2H_2O$ and $La(NO_3)_3.6H_2O$ was prepared in distilled water. Different molar stoichiometric amounts (1, 2, 10, 20) of each fuel was added to the solution and the mixture was stirred until a suspension was formed. It should be noted that for calculating the required amounts of starch and poly(vinyl alcohol) fuels, weights of their monomers were taken into account. Then, the suspension was heated up to 80 °C in order to become concentrated by evaporating water. The concentrated gel was placed in a furnace and heated up to 800 °C with the heating rate of 5 °C/min. The calcination time was different (from 15 min to 24 h) depending on the fuel/metals ratio. After calcination, the grayish powder of $Zn_{1.114}La_{1.264}Al_{0.5}O_{4.271}$ nanoparticles was obtained that was washed with acetone and dried. In these experiments, the pH value was also changed from 3.9, 7.0, 8.0 to 9.0 in order to examine the effect of the medium ionic strength on the size and morphology of the particles. The pH adjustments were done using HCl and NH_4OH solutions in order to prepare acidic, neutral and alkaline media.

3. Results and discussion

3.1. XPS analysis

In order to validate the spinel nature and the chemical purity of the green synthesized nanoparticles by gel combustion method, X-ray photoelectron spectroscopy (XPS) was carried out (Fig. 1). The wide scans (Figs. S1–S3) only exhibited the major Zn, La, Al and O peaks; hence sustaining the chemical purity of the surface of the nanoparticles. It is notable that the peak at the binding energy (BE) of 285 eV corresponding to the C 1s peak is almost always appeared in the XPS spectra of all samples which is attributed to the hydrocarbon contamination when the sample is prepared for the XPS analysis [37]. The $Zn_{1.114}La_{1.264}Al_{0.5}O_{4.271}$ formula indicates that one and half (1.5) number of the Al^{3+} ions in the well-known spinel $ZnAl_2O_4$ have been replaced by Zn^{2+} and La^{3+} ions. This analysis also confirms that the expected spinel structure is obtained for this new material. Furthermore, the existence of additional oxide ions (equal to an additional negative charge of −1.022) can be related to the inevitable presence of hydrocarbon contamination [37].

Fitting of the XPS peaks was performed by Gaussian deconvolution technique (Figs. S1–S3) and in all cases the reduced chi-squared values were below 0.50 confirming the accuracy of the fittings. It is seen in Fig. S1a that the fitted peak near 75 eV (Al 2p) is comprised of two peaks which are related to the Al–O(–Zn) (A, 75.36 eV) and Al–O(–La) (B, 74.07 eV) bonds. It was reported that the Al peaks at 76.8 eV and 121.7 eV corresponding to Al 2p and Al 2s were ascribed to the Al^{3+} ions located at the tetrahedral and octahedral sites, respectively [38]. In another work, the binding