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Structural, optical and photocatalytic activity of cerium doped zinc aluminate

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ABSTRACT

Zinc aluminate and cerium-doped zinc aluminate nanoparticles are synthesised by co-precipitation method. Ammonium hydroxide is used as a precipitating agent. The synthesised compounds are characterised by powder X-ray diffraction (XRD), Fourier transform Infrared spectroscopy (FT-IR), Ultraviolet diffuse reflectance spectroscopy (UV-DRS), Thermogravimetric analysis (TGA), Scanning electron microscopy (SEM) and Surface area measurements. The photocatalytic activity of zinc aluminate and cerium doped zinc aluminate nanoparticles are studied under the UV light and visible light taking methylene blue as a model pollutant. The amount of catalyst, concentration of dye solution and time are optimised under UV-light. Degradation of methylene blue under the UV-light is found to be 99% in 20 min with 10 mg of cerium doped catalyst. Compared to visible light degradation, the degradation of dye under UV-light is higher. Cerium doping in zinc aluminate ($ZnAl_2O_4$:Ce^{3+}) increased the photocatalytic activity of zinc aluminate.

1. Introduction

Spinel Oxide (AB_2O_4) is of two types (i) Normal Spinel (ii) Inverse spinel. In normal spinel, A (divalent metal) ion occupies tetrahedral side, and B (trivalent metal) ion occupies the octahedral site. Inverse spinel structure has a different cation distribution in that the entire A cations and half of the B cations occupy tetrahedral sites. Spinel aluminates (MAl_2O_4) are used as a catalyst [1], sensor [2], solid oxide fuel cell and highly conductive electrolyte [3,4]. $ZnAl_2O_4$ is a normal spinel with wide band gap 3.7 eV, it is suitable for UV optoelectronic devices, transparent conductors, and optical coating application in aerospace technology [5]. Zinc aluminate is used as a heterogeneous catalyst in many reactions, such as acetylation, methylation, dehydration, hydrogenation, dehydrogenation [6–10]. In recent years, the spinel oxides are used as photocatalyst for dye degradation. $ZnAl_2O_4$ nanoparticles are also reported as photocatalyst, e.g., in the degradation of textile dye and gaseous toluene [11,12]. Zinc aluminate nanoparticle has been synthesised by many methods such as hydrothermal method [13], sol-gel method [14], combustion method [15] and co-precipitation method. Among all the method of synthesis co-precipitation has advantages compared to other methods due to low-temperature preparation, purity and simple procedure.

The environmental problems associated with organic dyes from textile, paper and other industries remain to be the main concern. Photocatalytic degradation of organic dyes in the water using dissimilar semiconductor materials [16–20] has attracted the researchers to carry out this kind of work. The photocatalytic degradation using heterogeneous catalyst is observed to be a capable technology to decay harmful pollutants to non-toxic products [21,22]. More effort has been devoted to developing semiconductor photocatalysts with high photocatalytic activities in air purification, disinfection, and water treatment process [23,24]. The nanocatalyst is the most popular material for the photodegradation of dyes from the environment. Methylene blue is one of the dyes used in printing, paper, textiles, pharmaceutical and food industries [25,26]. The chemical formula of methylene blue (MB) is $C_{16}H_{18}N_3SCl$ and structure of it is given in Fig. 1. The maximum absorption peak of MB in the UV spectrum is 665 nm. The various side effects associated with methylene blue is mild bladder irritation, dizziness, headache, increased sweating, nausea, vomiting, diarrhoea, upset stomach, frequent urination.

Mechanochemically synthesised zinc aluminate photocatalytic activity is tested for the degradation of chromium acidic black diazo dye under UV light irradiation [27]. $ZnAl_2O_4$ nanospheres synthesised by wet chemical solution-phase method are reported for

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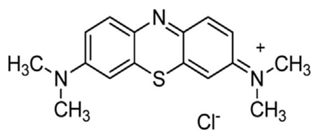

Fig. 1. Structure of methylene blue.

enhanced photocatalytic activity for the degradation of Rhodamine B dye [28]. Photocatalytic activity of $ZnO/ZnAl_2O_4$ microspheres is studied under UV light for the degradation of Methylene Blue dye [29]. In recent years, much effort has been devoted to the research of doped nanostructure material. Nickel doped zinc aluminate is reported for oxidative coupling of methane [30]. Cerium ion doped compounds are mostly used in the photocatalysis [31–33]. Cerium doped zinc oxide is reported for the degradation of Rhodamine B dye under UV light and visible light [34]. Cerium doped titanium oxide is testified for the photocatalytic reduction of carbon-dioxide [35]. Wang et al. reported cerium, lanthanum and vanadium doped titanium oxide for the degradation of Rhodamine B under solar light [36]. Rare earth doped $ZnAl_2O_4$ has been reported for luminescent properties with high emission quantum yields [37,38]. In the present work zinc aluminate ($ZnAl_2O_4$) and cerium doped zinc aluminate ($ZnAl_{2-x}Ce_xO_4$ x = 0, 0.01, 0.02 and 0.03) nanoparticles are synthesised by co-precipitation method. The degradation of methylene blue is studied to check the photocatalytic activity of zinc aluminate and cerium doped zinc aluminate in both UV light and visible light.

2. Experimental

2.1. Material

Zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$, s.d fine 99.0%), aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$, s.d fine 98.0%), cerium nitrate ($Ce(NO_3)_3 \cdot 6H_2O$, s.d fine 99.0%), ammonia solution, methylene blue (s.d fine 97.0%)

2.2. Synthesis of photocatalyst

Zinc aluminate ($ZnAl_2O_4$) and cerium doped zinc aluminate ($ZnAl_{2-x}Ce_xO_4$ X = 0, 0.01, 0.02, 0.03) nanoparticles were prepared by co-precipitation method. Stoichiometric quantities of $Zn(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$ and $Ce(NO_3)_3 \cdot 5H_2O$ were weighed and dissolved in require amount of double distilled water and stirred for 10 min. The precipitating agent aqueous ammonia was added to the mixture of the solution to maintain the pH of 10.5 and stirred for 30 min. The precipitate was filtered and washed several times with distilled water and dried at 60 °C for 24 h. The synthesized compounds were heat treated at 300° C, 500° C and finally 700° C for four hours with intermittent grinding to obtain the pure phase.

2.3. Photocatalytic activity

Photocatalytic activity of zinc aluminate and cerium doped zinc aluminate nanoparticles were measured by the degradation of MB under UV and visible-light irradiation. In the typical photocatalytic degradation, 10 mg of zinc aluminate or cerium doped zinc aluminate catalyst were added to 100 ml beaker containing 10 ppm of MB (50 ml) solution and placed in dark condition for 60 min with stirring to attain the equilibrium between the MB and photocatalyst. After that the solution was exposed to UV light (265 nm, 32 w). In a similar way, the reaction was carried out and exposed to visible light (500 w, tungsten lamp) with hydrogen peroxide. 3 ml of sample were taken at regular intervals of time, centrifuged to remove the photocatalyst particles. The filtrates of MB solutions were analysed by measuring differences in the maximum absorption peak at 664 nm in the UV-visible spectrometer. The degradation efficiency was calculated using the following equation

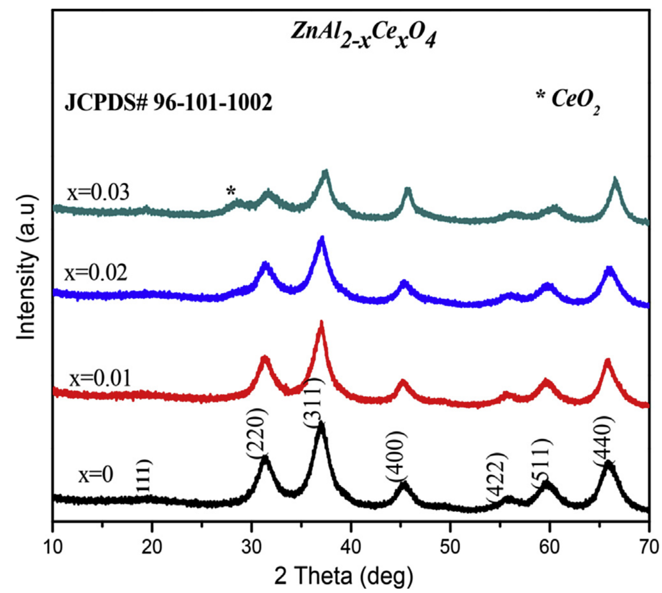

Fig. 2. Powder XRD pattern of zinc aluminate and cerium doped zinc aluminate ($ZnAl_{2-x}Ce_xO_4$, X = 0, 0.01, 0.02, 0.03) nanoparticles.

Table 1
Lattice parameter and Average crystalline size.

Sample	Lattice parameter (Å)	Average crystalline size (nm)
X = 0	7.981	7.483
X = 0.01	8.015	7.725
X = 0.02	8.095	7.805
X = 0.03	8.065	9.641

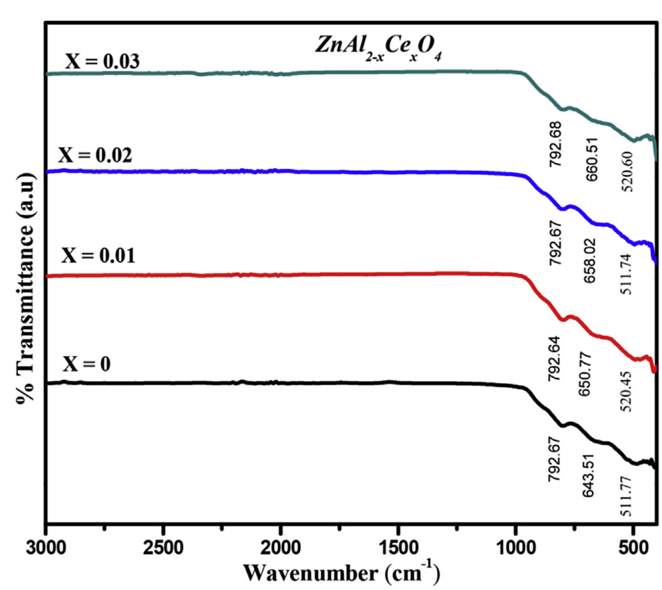

Fig. 3. FT-IR spectra of zinc aluminate and cerium doped zinc aluminate ($ZnAl_{2-x}Ce_xO_4$, X = 0, 0.01, 0.02 and 0.03) nanoparticles.