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Short Communication

Synthesis and characterization of fly ash-zinc oxide nanocomposite

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ABSTRACT

Fly ash, generated in thermal power plants, is recognized as an environmental pollutant. Thus, measures are required to be undertaken to dispose it in an environmentally friendly method. In this paper an attempt is made to coat zinc oxide nano-particles on the surface of fly ash by a simple and environmentally friendly facile chemical method, at room temperature. Zinc oxide may serve as effective corrosion inhibitor by providing sacrificial protection. Concentration of fly ash was varied as 5, 10 and 15 (w/w) % of zinc oxide. It was found that crystallinity increased, whereas particle size, specific gravity and oil absorption value decreased with increased concentration of fly ash in zinc oxide, which is attributed to the uniform distribution of zinc oxide on the surface of fly ash. These nanocomposites can potentially be used in commercial applications as additive for anticorrosion coatings.

1. Introduction

Zinc oxide occurs in nature as the mineral zincite. Crystalline zinc oxide exhibits piezoelectric effect and is thermo chromic, changing from white to yellow when heated [1–3]. Nano zinc oxide are prepared by methods like aerosol, micro emulsion, ultrasonic, sol-gel method, conventional ceramic fabrication, evaporation of solutions and suspensions, evaporative decomposition of solution, solid state reaction, wet chamber synthesis and spray pyrolysis method [4,5]. It has been known that zinc oxide is a considerable material for semiconductor due to its wide band gap (3.37 eV) and its high excitation binding energy (60 meV) at room temperature [6]. Zinc oxide has been studied in many areas such as catalysts, electronics, optoelectronics and photochemistry in order to utilize its semiconductor characteristics [7,8]. Zinc oxide is also one of the most important corrosion inhibitor pigments in organic coatings [9].

Since wide scale coal firing for power generation began in the 1920s, many millions of tons of ash and related by-products have been generated. The current annual production of coal ash worldwide is estimated to be around 600 million tones, with fly ash constituting about 500 million tones at 75–80% of the total ash produced. Fly ash is generally gray in color, abrasive, mostly alkaline, and refractory in nature.

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To improve removal efficiencies and adsorption capacities, chemical modifications of fly ash is needed [10]. Research works have been undertaken to make fly ash better usable by its surface modification, subsequently trying to make useful products from the industrial waste. Shukla et al. coated fly ash with copper by electroless coatings using Sn–Pd catalyst, in order to impart electrical conductivity to it [11]. Rohatgi et al. prepared a series of aluminum and nickel coated fly ash using pressure infiltration technique [12]. Yu utilized fly ash to more easily separate titanium dioxide photocatalyst from the treated waste water by immobilizing it on fly ash by a precipitation method [13]. Recently, Panagopoulos et al. deposited zinc-fly ash composite coatings on mild steel to improve its wear and corrosion resistance [14]. However, we propose to prepare nano-sized zinc oxide coated fly ash by a simple, convenient and environmentally friendly facile chemical method, at room temperature, to be a material of potential importance for anti-corrosion in coatings; and thus providing an additional way to utilize the waste fly ash.

2. Experimental

2.1. Materials

Fly ash (FA) (composition: 57.13 wt% SiO_2, 34.24 wt% Al_2O_3, 2.84 wt% CaO, 0.91 wt% MgO, 2.78 wt% Fe_2O_3, 0.65 wt% K_2O and 0.91 wt% TiO_2; specific gravity: 2.20 g/cm^3 on Ignition (LOI): 2.90%) was obtained from Nashik Thermal Power Plant, Nashik, India. Zinc chloride, unburned carbon determined by Loss Chemicals such as zinc acetate dihydrate, oxalic acid dihydrate, diethanolamine, ethylene glycol were procured from M/s. S.D. Fine chemicals, Mumbai, India.

2.2. Preparation

10.9 g (0.05 mol) zinc acetate dihydrate was dissolved in distilled water at 60 °C till a transparent solution was formed. In another beaker 12.6 g (0.1 mol) oxalic acid dihydrate was dissolved in distilled water at room temperature to get a transparent solution. This oxalic acid solution was then slowly added, under continuous stirring, into zinc acetate dehydrate solution. To this mixture 0.52 g (0.005 mol) diethanolamine and 0.31 g (0.005 mol) ethylene glycol was slowly added. Then predefined amount of fly ash [5 (1.17 g), 10 (2.35 g) and 15 (3.52 g) % (w/w) of total quantity of zinc acetate dihydrate and oxalic acid dehydrate, nomenclatured as A1, A2 and A3, respectively] was added in order to get nanosized layer of zinc oxide (nano ZnO) coated fly ash. Obtained precipitate was filtered and washed 2–3 times with distilled water. This precipitate was dried in oven at 80 °C for 20 h. The resultant white powder was calcinated at 600 °C for 2 h. Thus, a white crystalline nano ZnO coated fly ash powder was prepared.

2.3. Characterization

Measurements of wide angle X-ray diffraction (XRD) were performed on a Rigaku Mini-Flex X-ray Diffractometer (Japan) with X-ray wavelength of Cu Kα = 0.154 nm. Fourier transform infrared (FTIR) spectroscopy was performed on a Perkin Elmer Spectrum 100 Spectrophotometer (USA) using KBr pellet. Scanning electron microscopy (SEM) analysis was done on a JEOL, JSM-6380 LA (Japan) 15 kV electron microscope. Specific gravity was measured by Pycnometer. Oil absorption value was measured according to the standard test method of pigments by Spatula Rub-out (ASTM D281).

3. Results and discussions

X-ray diffractograms obtained for the prepared nanocomposites are shown in Fig. 1. Fly ash showed its characteristic diffraction peak at around 27°, while ZnO showed its characteristic peaks at 31.7°, 34.4°, 36.2°, 47.5°, 56.5°, 62.7°, 66.3°, 67.8° and 68.9°, respectively. All peaks are in good agreement with the standard spectrum (JCPDS nos. 36-1451 and 79-0205) for ZnO. It was found that the peak intensities of ZnO decreased

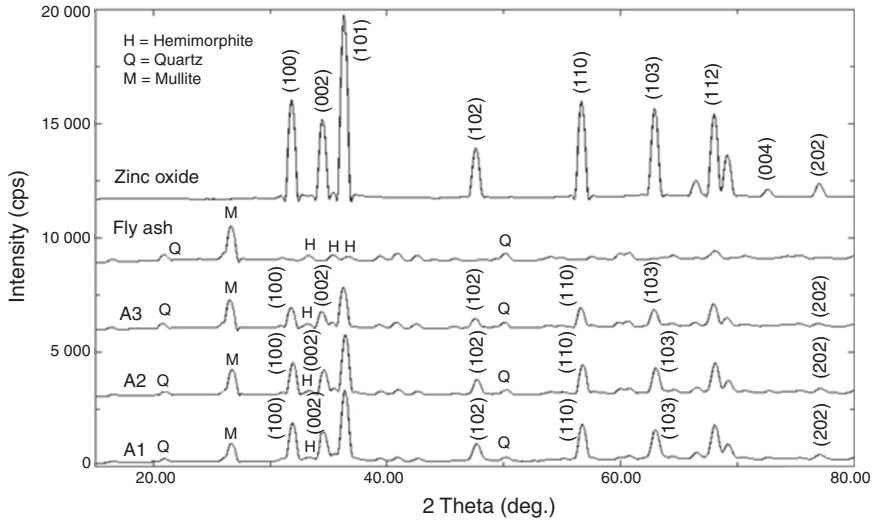

Fig. 1 – X-ray diffractograms obtained for the prepared nano ZnO coated flfly ash nanocomposites

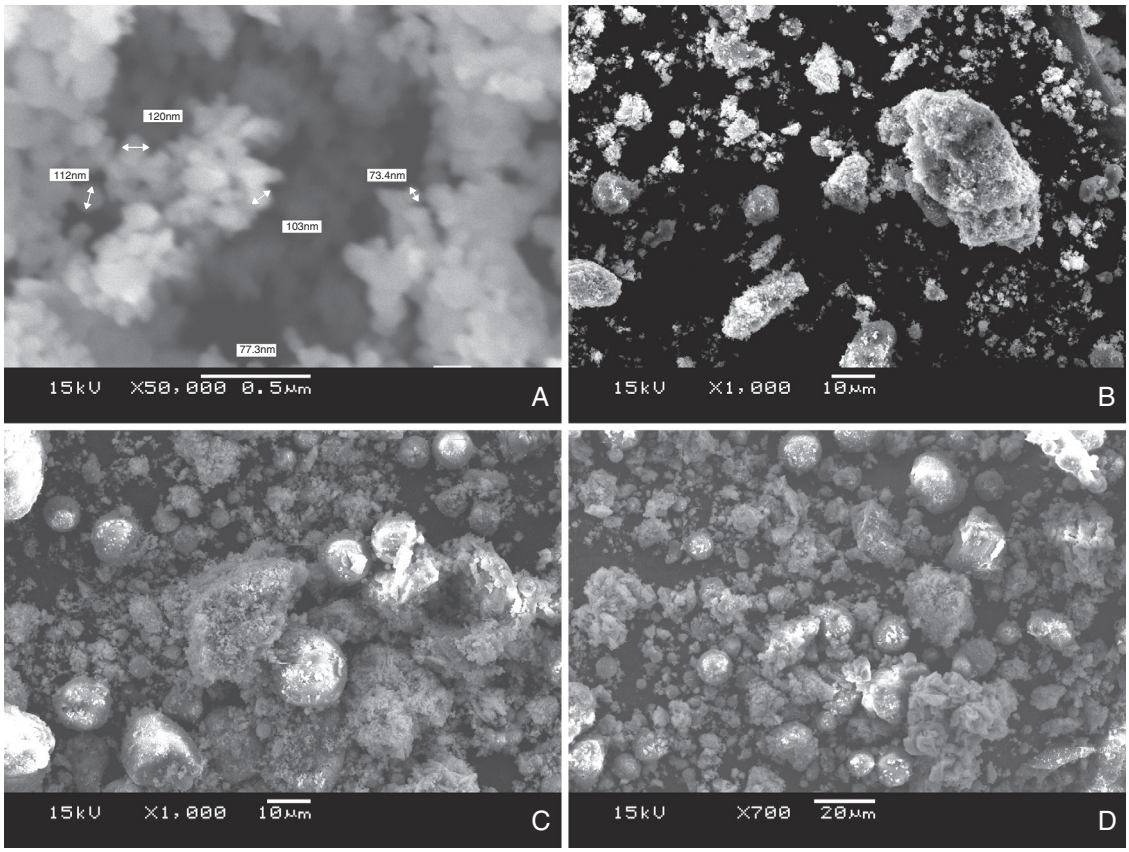

Fig. 2 – SEM micrographs obtained for ZnO and the prepared nano ZnO coated flfly ash nanocomposites

with increased concentration of fly ash. This suggests that there are kinds of interactions between ZnO and fly ash. Addition of fly ash had no effect on the crystallization performance of ZnO, as there is no change in the diffraction peak positions of ZnO.

Nano ZnO was found to have diameter size ranging between 80 and 110 nm (Fig. 2A), while SEM micrographs for A1, A2 and A3 were shown in Fig. 2B–D, respectively. It is clearly evident of nano ZnO deposition on the surface of fly ash. As the concentration of fly ash increased, more surface area of it became available for ZnO to deposit upon. This led to the decrease in the thickness as well as the surface roughness of the nano ZnO coatings on the surface of fly ash. However, surface roughness is uniform for particular concentration of fly ash. Also, the particle size of the composite decreased with increased concentration of fly ash.

FTIR spectra obtained for ZnO, fly ash, A1, A2 and A3 are shown in Fig. 3. FTIR spectra of ZnO show distinct Zn–O absorption band at 458.9 cm^{-1}, while in the FTIR of fly ash, distinct Si–O–Si peak is obtained at about 1100 cm^{-1}. Peak at about 3600 cm^{-1} is due to the moisture adsorbed on the surface of the composite. It was found that the characteristic peak of ZnO decreased in intensity with increased concentration of fly ash in the composite. It can also be seen that the characteristic peaks of ZnO and fly ash shifted toward right with increased concentration of fly ash in the composite, which can be attributed to the interactions happening between ZnO and fly ash.

Specific gravity of fly ash is 2.93 and that of nano ZnO is 5.5. Specific gravity values obtained for A1, A2 and A3 were 5.2, 4.8 and 4.6, respectively. It was found that the specific gravity of the composite decreased with increased concentration of fly ash. This was attributed to the low density of fly ash as compared to ZnO, leading to the decrease in the specific gravity of the composite. These specific gravity values were useful in primer formulation calculations [15].

Oil absorption value of pigment is also very useful in formulating the paint. This value for ZnO, A1, A2 and A3 are 5.5, 8.5, 9.0 and 12.1, respectively. It was determined that the oil absorption value of composite material increased with increased concentration of fly ash. There are several reasons for it. Firstly, fly ash was added maintaining the same concentration of ZnO every time. Thus, the addition of fly ash increases the surface area for adsorption of oil. Also, addition of fly ash increases the surface area for ZnO to coat on, decreasing the level aggregates and making it more uniform, again leading to the increase in surface area of ZnO to adsorb more oil.

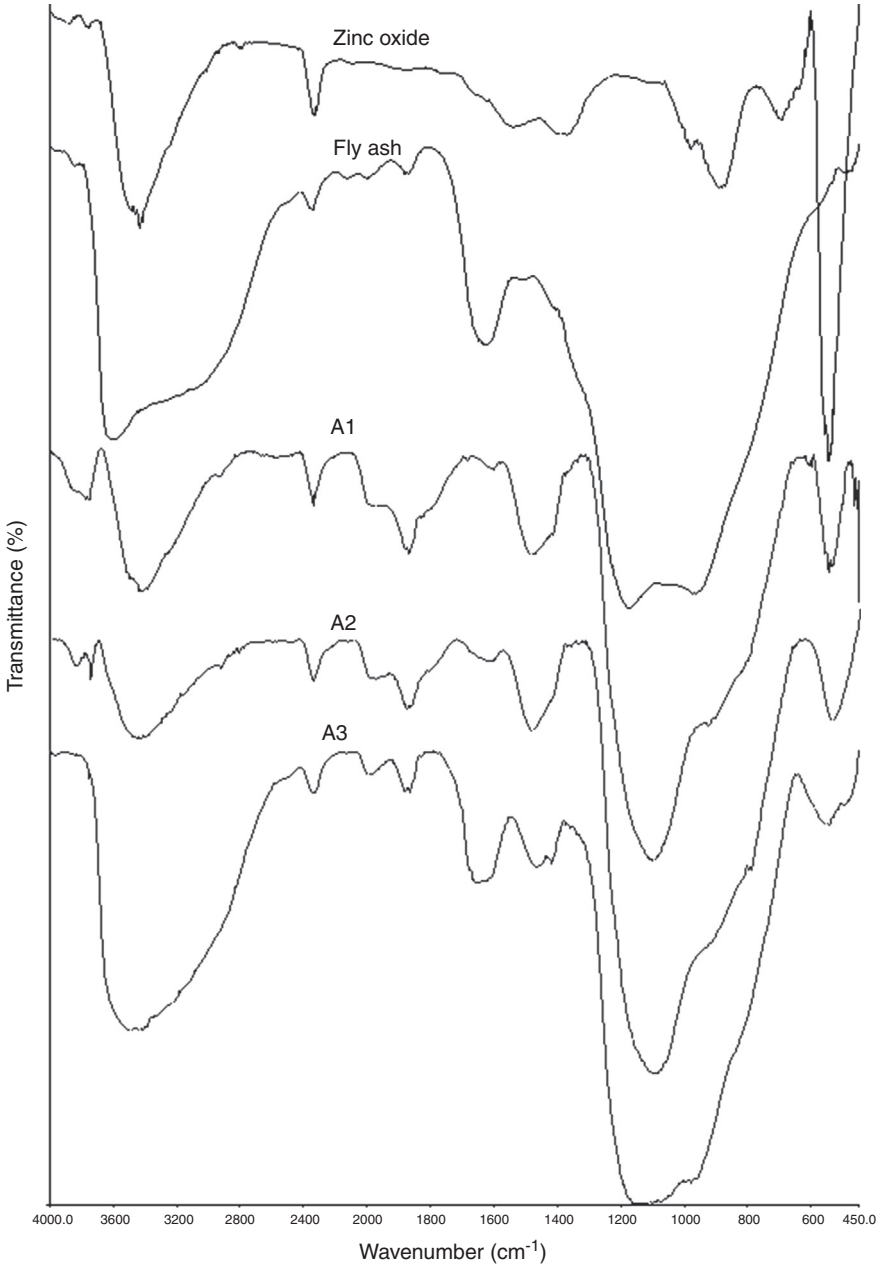

Fig. 3 – FTIR spectra obtained for ZnO, flfly ash, A1, A2 and A3

4. Conclusion

A novel and very simple procedure for preparing fly ash-zinc oxide nanocomposite using precipitation method was utilized in the current research work. Prepared fly ash-zinc oxide nanocomposites were characterized by XRD, FTIR, SEM, specific gravity and oil absorption value. These results reveal the coating of zinc oxide on the surface of fly ash with interactions happening between them. Prepared nanocomposites can be used as pigment in antistatic coatings and anti-corrosive coatings.

Conflicts of interest

The authors declare no conflicts of interest.

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