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Synthesis and characterization of ZnO@zinc terephthalate metal organic framework

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Abstract

Zinc oxide nano particles prepared using starch as capping agent were prepared and then incorporated into a zinc terephthalate framework. ZnO@Zinc terephthalate framework composites were then characterised by FTIR, XRD, SEM and thermogravimetric analysis. N_2 adsorption isotherms were obtained to calculate BET surface area and pore parameter of the framework.

Keywords: Zinc oxide, Nano particles, MOF, zinc terephthalate, BET

1. INTRODUCTION

Metal-organic frameworks (MFs) otherwise called inorganic coordination polymers are formed from metal or metal ion clusters which are linked by multitopic organic linkers [1–3]. Porous network structures have been used in the fields including storage of gas [4], sensing [5], catalysis [6] and for medicinal filed and as ailments in biomedicine [7, 8]. Functionality and acidic and basic moieties in the microporous structures gives them unique identification mark among other inorganic polymers. Supramolecular entities make them more flexible for host guest interactions [9, 10]. Properties of materials used in the field of ceramics, biopolymers can be enhanced by incorporating the nanomaterials into the porous metal organic framework [11].

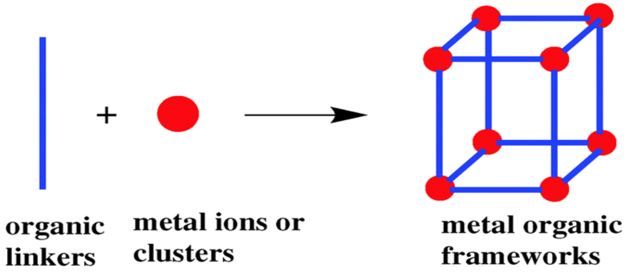


Fig 1: Formation of MOF's.

The present work focuses on the synthesis and characterisation of Zinc oxide nanoparticles @ Zinc terephthalate MOF.

2. EXPERIMENTAL

2.1. Preparation of Zinc terephthalate framework (H6J)

$Zn(NO)_3.6H_2O$ (0.012 mol) and terephthalic acid (0.012 mol) were dissolved in Dimethyl formamide with mild stirring, and 3 mL of trimethyl amine (TEA) was added to the solution drop wise and the system was and heated at 100 °C for 3 hours in an air oven. The resulting crystals were collected and dried.

2.2. Preparation of ZnO @ Zinc Terephthalate MOF (H7J)

Prepared Zinc terephthalate framework and Zinc acetate was dissolved in dilute HCl solution. Then solution of NaOH was added to the above solution until precipitation occurs, refluxed for 2 hours. The precipitates were then collected by filtration. The compound was dried at 60°C. These compounds are named as ZnO@ Zinc terephthalate framework (H7J).

ZnO@Zinc terephthalate framework (H7J) was then calcined at 450 °C for 3 hrs. This calcined product was named as H8J.

2.3. Preparation of zinc oxide nanoparticles using starch as capping agent (H9J)

0.01 M starch solution was prepared in 100 ml water. 100 mL of 0.1 M zinc acetate solution was added drop wise to the starch solution. Then 100 mL of 1 M NaOH solution was added to it till the pH was 12 and the mixture were stirred continuously for 3 hours. The resulting precipitate was filtered, washed, dried and calcined at 450 °C for 3 hours.

The nanoparticles and the MOF's were characterised by FTIR, XRD, SEM, BET and thermogravimetric analysis.

3. RESULTS AND DISCUSSIONS

3.1. FTIR Analysis

Figure 2 shows the FTIR spectrum of Zinc terephthalate framework (H6J), ZnO@Zinc terephthalate framework (H7J), Calcined ZnO@Zinc terephthalate framework (H8J) and ZnO nanoparticles (H9J).

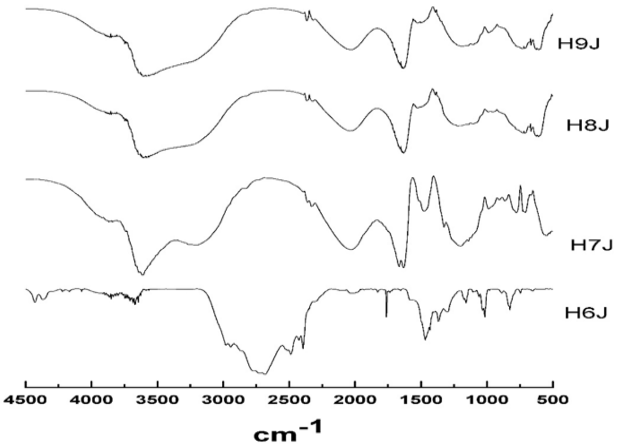


Fig 2: FTIR spectrum of ZnO@Zinc terephthalate framework composites.

In Zinc terephthalate framework, the peaks at 1400 and 1762 cm^{-1} corresponds to the symmetric and anti-symmetric vibration of –CO group in H_2BDC respectively. Peaks ranging from 1300–825 cm^{-1} correspond to in-plane C–H bending which identifies the possibility of formation of zinc terephthalate framework. The peaks in ZnO@ Zinc terephthalate framework with a slight deviation of fingerprint values show the possibility of entrapping other moieties in the framework. Peaks at 1400–1500 cm^{-1} corresponds to C=O bonds. Peaks at 3600 cm^{-1} corresponds to OH stretching vibrations which indicates the formation of zinc oxide. In Zinc oxide nanoparticles using starch as capping agent shows peaks at 450–500 cm^{-1} corresponds to metal oxide bond (Zn–O) and the broad peak at 3500 cm^{-1} range corresponds to water molecules. The IR spectrum of calcined ZnO@MOF is exactly similar to that of zinc oxide prepared by starch as capping agent, which reveals the possibility of the degradation of ZnO@MOF structure to ZnO.

3.2. X-ray diffraction analysis

Figure 3 represents the XRD pattern of Zinc terephthalate frame works and its ZnO composites. The powder XRD pattern of Zinc terephthalate (H6J) frameworks shows characteristic peaks at 2θ values in the range of 5° to 30° such as at 6.5, 9, 13, 15, 23.7, 24.0, 26.3 and 30. Similar XRD patterns are reported for Zinc terephthalate framework prepared from different zinc precursor [12].

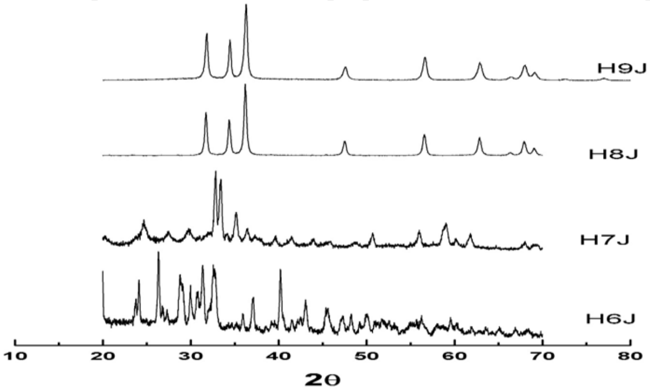
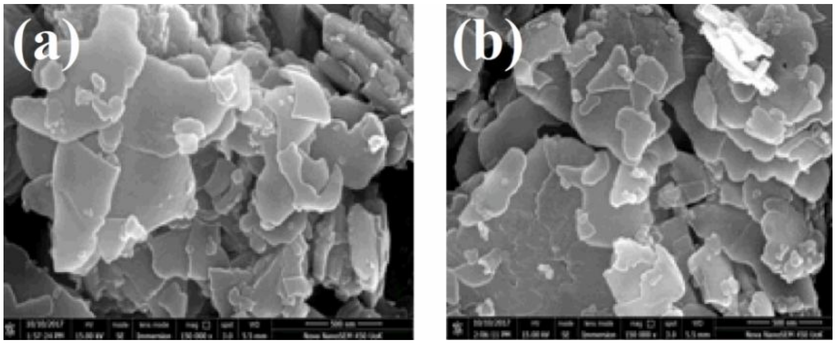


Fig. 3: XRD pattern of ZnO@Zinc terephthalate framework composites

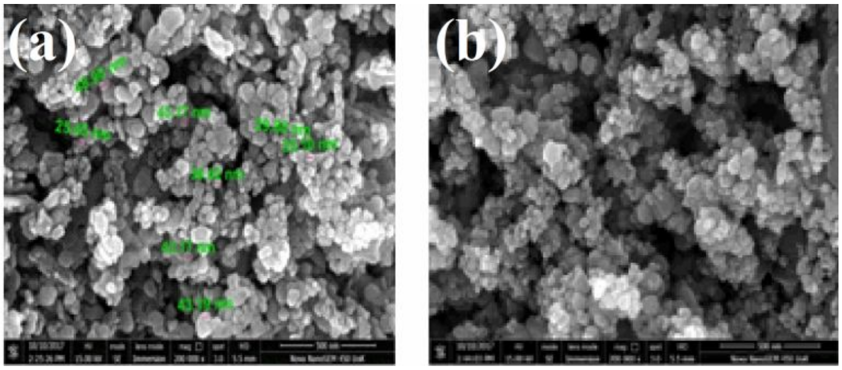
XRD pattern of ZnO@Zinc terephthalate framework reveals that the product is composed of both zinc terephthalate frameworks and ZnO nanoparticles as it is clear from the peaks observed at 31.7, 34.4 and 36.2 corresponds to pure zinc oxide, in addition to the above said peaks of the Zinc terephthalate framework structure. ZnO and calcined ZnO@MOF show same XRD pattern indicating the complete conversion of ZnO@MOF to ZnO nanoparticles and their average particle size calculated from Debye Scherer equation is 25nm.

3.3. SEM analysis

Figures 4 represent the scanning electron micrographs of zinc oxide @ zinc terephthalate frame work. It shows an irregular flaky crystalline morphology which is different from small crystals with well-defined cubic morphology for Zinc terephthalate framework reported by Biemmil et al. [12]. The destruction of the cubic morphology to this flaky morphology is attributed to the incorporation of ZnO nanoparticles.



Figs. 4: SEM images of zinc oxide @ zinc terephthalate frame work.



Figs. 5: SEM images of calcined zinc oxide @ zinc terephthalate frame work.

The SEM image of the calcined zinc oxide @ zinc terephthalate frame work is shown in Figure 5 Micrograph reveals that the flaky structure has been completely converted into granular morphology with particle size of 25-40 nm as calculated from XRD. This conversion of morphology clearly confirms the formation of Zinc oxide by the calcination of zinc oxide @ zinc terephthalate frame work, which is also clear from the XRD patterns

3.4. BET surface area analysis

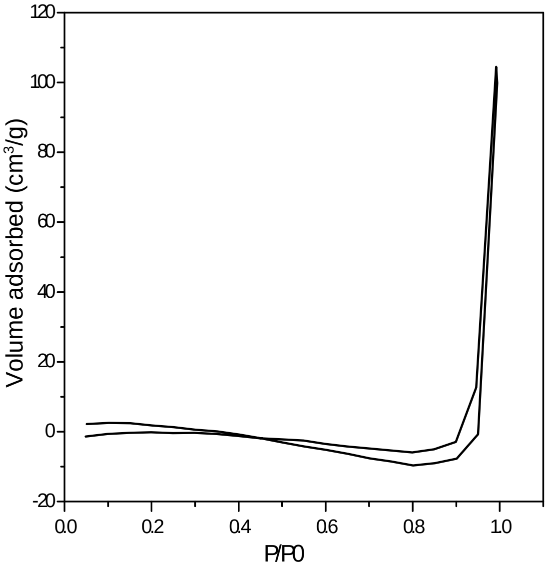


Fig. 6: Nitrogen adsorption and desorption isotherm of ZnO@zinc terephthalate frame work

The BET surface area and Pore parameter of zinc oxide@zinc terephthalate frame work were calculated according to the N_2 adsorption isotherms (Figure 6) at 77.35 K. The adsorption and desorption isotherms are almost same indicating that the configuration of MOF is retained during this process. Adsorption isotherm resembles type IV isotherm indicating the mesoporous nature of the framework. BET surface area of the compound is found to be 5.524 m^2/g. This value is insignificant when compared with BET surface area of zinc terephthalate framework, which is 839.6 m^2/g [13]. The decrease in BET surface area is attributed to the encapsulation of ZnO nanoparticles in Zinc terephthalate framework. Similarly pore volume is found to be 0.175 cc/g which is found to be smaller than the reported value of 0.34 cc/g [13].

3.5. Thermogravimetric analysis

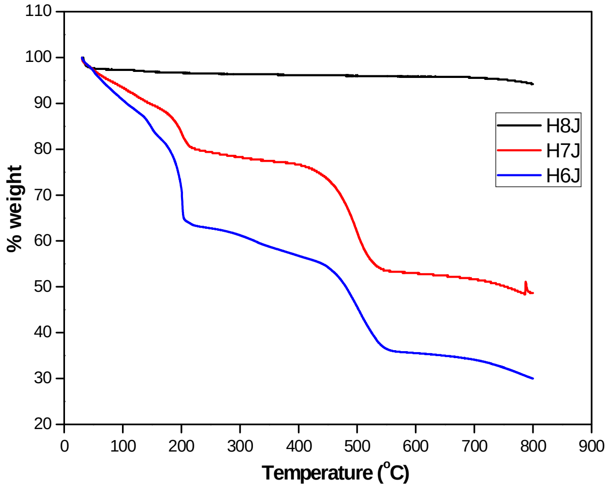


Fig. 7: TG curves of ZnO@Zinc terephthalate framework composites

Thermogravimetric analysis of ZnO@Zinc terephthalate framework composites are shown in Figure 7. Thermograms of both Zinc terephthalate framework and ZnO@Zinc terephthalate framework show two major weight losses. The first weight loss, between 40 to 206°C, is assigned to the removal of solvent molecules occluded within the pores of framework structure. The second weight loss from 440 to 550°C is attributed to the destruction of terephthalate molecules in the framework structure. The percentage of weight loss is found to be more for ZnO@Zinc terephthalate framework. Indicating incorporation of ZnO nanoparticles, which replaces the solvent molecules occluded in the framework. In the case of Zinc terephthalate framework, the first and second weight loss is 17% and 22% respectively, but it is 7.7% and 24% respectively for ZnO@Zinc terephthalate framework. The same kind of two stage decomposition thermogram for zinc terephthalate framework was reported by Loiseau et al [14]. Thermogram of calcined ZnO@Zinc terephthalate framework shows no significant weight loss in the whole temperature range of 40 to 800°C. This high thermal stability is attributed to the formation of ZnO nanoparticles by the calcination of ZnO@Zinc terephthalate framework.

4. CONCLUSIONS

FT-IR spectrum reveals the presence of characteristic functional group within the MOF structure and ZnO@MOF composites of terephthalate systems. The formation of ZnO nanoparticles is also evidenced from FTIR. The crystal structures of all these materials have been identified from XRD patterns. XRD pattern and FTIR spectrum of ZnO and calcined ZnO@Zinc terephthalate composites are found to be same indicating the degradation of framework to ZnO nanoparticles with average particle size of 25 nm. SEM images of ZnO@Zinc terephthalate show the flaky crystalline morphology which is different from the normal cubic structure of Zinc terephthalate framework. The destruction of cubic topology of framework structure is attributed to the incorporation of ZnO nanoparticles. SEM image of calcined ZnO@ Zinc terephthalate framework structure shows a granular morphology of size between 25-45 nm which clearly confirms the formation of zinc oxide. N_2 adsorption and desorption isotherm is a type-IV isotherm indicates mesoporous framework structure. Surface area and pore volume calculated from BET equation is less than that of reported value that confirms the encapsulation of ZnO in Zinc terephthalate framework. Thermal analysis shows a two stage decomposition thermogram for both Zinc terephthalate framework and ZnO@ Zinc terephthalate framework systems. But, the percentage of weight loss is found to be more for Zinc terephthalate framework structures compared to ZnO@ Zinc terephthalate framework composite systems. This indicates the encapsulation of ZnO in Zinc terephthalate framework

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