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Growth of ordered multi-walled carbon nanotubes over mesoporous 3D cubic Zn/Fe-KIT-6 molecular sieves and its use in the fabrication of epoxy nanocomposites

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ABSTRACT

Mesoporous three dimensional (3D) cubic Fe-KIT-6 molecular sieves with various Si/Fe ratios (Si/Fe: 50, 75 and 100) were synthesized hydrothermally and different weight percentage (wt.%) of Zn was loaded over them by wet impregnation. The synthesized materials were used as catalytic template for the growth of multi-walled carbon nanotubes (MWCNTs) using acetylene as a carbon precursor by chemical vapour deposition. The deposited carbon materials were purified and analysed by X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Raman spectroscopy techniques. The observation depicted that the Zn/Fe-KIT-6 template influence the high yield of ordered MWCNTs without major contamination. The purified MWCNTs were functionalized and investigated by Fourier transform infrared spectroscopy (FT-IR) and SEM techniques. The characterised MWCNT/functionalized-MWCNTs (*f*-MWCNTs) are used as filler material for the fabrication of epoxy composites. On comparison with different wt.% of loading viz., 0.5, 1.0 and 1.5 wt.%; 1 wt.% MWCNTs/*f*-MWCNTs filled epoxy resin showed the highest improvement in tensile strength, flexural strength and hardness as compared to neat and other epoxy systems. The rate of burning is decreased with respect to the wt.% of MWCNTs/*f*-MWCNTs. The *f*-MWCNT/epoxy composites were found to possess high thermo-mechanical properties compared to MWCNT/epoxy composites.

1. Introduction

Generally, mesoporous materials have a large uniform pore structures. Transition metal particles can be incorporated into the pore walls of the mesoporous molecular sieves that stabilize dispersed catalytic sites and also exhibit good structural stability. The mesoporous molecular sieves are of interest because of their remarkable properties, such as large surface area, large pore volume, narrow pore size distribution and the ease with which their surface can be functionalized [1]. Their uniform and tunable pore diameters make them well adopted for good catalytic supports. Among the different mesoporous materials, KIT-6 (Korean Institute of Technology-6) exhibits a cubic *Ia3d* symmetric structure with interpenetrating bicontinuous network of channels [2]. This provides highly opened spaces for direct access to guest species without pore blockage due to their unique three dimensional (3D) channel networks. In general, pure KIT-6 has limited catalytic activity, but active catalytic sites can be generated in KIT-6 by isomorphously substituting silicon with transition metals [3]. The metal particle plays an important role in the growth of carbon nanotubes (CNTs) and reports show a direct correlation between the size of the metal nanoparticles and the eventual tube diameter [4].

Iijima's landmark paper on a quasi one-dimensional new type of carbon named "CNTs" attracted a great deal of attention in various fields of research, due to their superior mechanical strength, electronic properties, large surface area for adsorption of hydrogen and high aspect ratio [5,6]. Generally, CNTs are synthesized by three different methods [7]: (i) arc discharge, (ii) laser evaporation and (iii) chemical vapour deposition (CVD). The first two methods employ the solid state carbon precursors needed for carbon evaporation at high temperature. The CVD utilises hydrocarbon gases as a carbon source and metal nanoparticles as the seeds for the growth of CNTs. The CVD has several advantages which include high purity, high yield, selective growth and vertical alignment [8]. The catalytically produced tubes are adequate for many applications, especially because they can be directly synthesized without major contamination by carbonaceous impurities.

During catalytic CVD, CNTs are grown by the catalytic decomposition of acetylene gas over the metal particles embedded in mesoporous catalytic supports. Transition metals have been widely used either in oxide or in metallic forms or as mixtures. Because,

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they possess a variety of properties that render them suitable for CNT synthesis such as equilibrium vapour pressure, solubility of carbon and carbon diffusion rate in the metal [9]. Various parameters including temperature and duration of the CVD, gas composition and flow rate can affect the nature of the carbon deposits in the resulting material [10]. Hence, the present work deals about the successful incorporation of Fe into the mesoporous KIT-6 with high structural regularity under low acidic conditions by hydrothermal method. Zn was loaded over Fe-KIT-6 using wet impregnation. The synthesized materials were characterised and used as a catalytic template for the growth of multi-walled carbon nanotubes (MWCNTs) using acetylene by CVD with different temperatures. The ultimate goal of this research is to understand the correlation between the Fe-KIT-6 and Zn/Fe-KIT-6 catalytic templates, on the quantity of CNTs produced and its functionalization.

Composites are the new class of materials providing superior properties compared to their microcomposite counterparts and are usually refer to a material at which at least one filler having the ultrafine dimensions in the order of a few nanometers. An addition of a small amount of nanoparticles can significantly improve the variety of properties which make these materials to be used in widespread applications such as in defence industries, automobile industries, aerospace, electrical and electronic industries. In general, any material can be used as nano fillers which appear in nano-scaled shape and size, but these particles have not gained much attention as MWCNTs. Because the MWCNTs, has a high potential to improve the mechanical, thermal [11] and electrical properties of polymers. The dispersion state of nanoparticles in the polymer matrix is of great importance for the mechanical properties of the composite. A homogeneous dispersion of the nanoparticles is believed to contribute to enhance the property improvement. However, a homogeneous dispersion in a polymeric matrix is a difficult task due to the strong agglomerating tendency of the nanoparticles. So, the effective dispersion of nanofillers into the polymeric matrix increases the overall performance of the composites. Carbon nanofillers like MWCNTs [12] and nanofibers have been used to reinforce various epoxy systems. The incorporation of MWCNTs and functionalized-MWCNTs (*f*-MWCNTs) into a thermosetting epoxy system enhanced the thermal and mechanical properties of the epoxy system. The homogeneous dispersion of the MWCNTs/*f*-MWCNTs causes strong interfacial adhesion between the epoxy resin and MWCNTs/*f*-MWCNTs that would result in the best performance of an epoxy composite system. The cross sectional morphology (fractured surface) of the composites was examined by scanning electron microscopy (SEM) technique. The *f*-MWCNTs filled composites could have high thermo-mechanical strength when compared with MWCNTs filled composites due to strong interfacial bonding between epoxy resin and *f*-MWCNTs [13].

Hence, the current research is focused on the improvement of the thermo-mechanical properties with a neat epoxy resin by the addition of fillers such as MWCNTs and *f*-MWCNTs. MWCNTs with ultra-strong composite was prepared using Zn/Fe-KIT-6 catalytic template by CVD at 800 °C. The mesoporous 3D cubic Zn/Fe-KIT-6 catalytic templates produced MWCNTs with more number of graphene layers (walls). The synthesized CNTs were purified and functionalized with 1:3 ratios of H_2SO_4 and HNO_3 mixture. The synthesized MWCNTs/*f*-MWCNTs were used as filler material in the epoxy matrix. The neat epoxy matrix and different wt.% MWCNT/epoxy and *f*-MWCNT/epoxy composites were prepared by casting method. The thermo-mechanical properties such as flame retardancy, thermal stability, tensile strength, flexural strength and hardness were examined for neat epoxy matrix, MWCNT/epoxy and *f*-MWCNT/epoxy composites. The ultimate goal of this research is to fabricate the MWCNT/epoxy, *f*-MWCNT/epoxy composites and to compare their thermo-mechanical properties.

2. Experimental

2.1. Materials

Pluronic P123 triblock co-polymer [poly (ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol)] with molecular weight of 5800 ($EO_{20}PO_{70}EO_{20}$) and n-butyl alcohol (n-BuOH) purchased from Aldrich were used as the structure directing agent and co-surfactant, respectively. Tetraethylorthosilicate (TEOS) was used as a source of silicon for the synthesis of KIT-6. Hydrochloric acid (35 wt.%) was purchased from Merck and used as a co-solvent for the synthesis of metal-containing mesoporous 3D cubic KIT-6 molecular sieves. The gases namely acetylene (99.9%), nitrogen (99%) and hydrogen (99%) were used as carbon source, carrier gas and reducing agent, respectively. Analytical reagent (AR) grade of acids such as HF, HCl, HNO_3 and H_2SO_4 were purchased from Merck and were used for the purification and functionalization of CNTs. Solvents such as acetone and ethanol were purchased from Merck and double distilled water was used throughout this study.

Diglycidylether of Bisphenol-A (Araldite LY 556) and Trietha tetramine (Aradur HY 951) purchased from Javanthee Enterprises, Chennai, India, were used as the epoxy resin and hardener, respectively. These were used for the fabrication of composites. All the above said chemicals were of AR (Analar/Analytical) grade and used without any further purification.

2.2. Synthesis of Fe-KIT-6 and Zn impregnated Fe-KIT-6 (Zn/Fe-KIT-6)

The mesoporous 3D cubic Fe-KIT-6 molecular sieves with Si/Fe ratios of 50, 75 and 100 samples were synthesized hydrothermally using the gel composition of TEOS: 0.017P123: 1.83HCl (35 wt.%): 1.31n-BuOH: 195H_2O [14]. The typical procedure for the synthesis of Fe-KIT-6 is as follows: 6 g of Pluronic P123, 217 g of distilled water and 11.8 g of HCl were taken in a polypropylene bottle. The mixture was stirred for 3 h at 35 °C to prepare the template dissolved in distilled water and HCl. To this mixture, about 6 g of n-BuOH was added under constant stirring at 35 °C. After 1 h stirring, 12.9 g of TEOS and appropriate amount of ferric nitrate were added simultaneously to the homogeneous solution at the same temperature. The resulting mixture was stirred for 24 h at 35 °C and subsequently heated for 24 h at 100 °C in a hot air oven under static condition in a closed polypropylene bottle. The solid products obtained after the hydrothermal treatment were filtered without washing and dried for 5 h at 100 °C in atmospheric air. The dried material was ground well and then calcined at 550 °C for 12 h in atmospheric air (Heating rate: 5 °C/min) to expel the template. The different wt.% (0.25, 0.5 and 0.75) of Zn was loaded individually over Fe-KIT-6 using the wet impregnation. In a typical procedure, an appropriate amount of zinc acetate was dissolved in distilled water and sonicated for 15 min. The sonicated solution was added drop by drop with mesoporous 3D cubic Fe-KIT-6 under constant stirring at room temperature. The solution was dried under reduced pressure and then calcined at 550 °C for 4 h in atmospheric air.

2.3. Synthesis of MWCNTs

The synthesis of MWCNTs were carried out using Fe-KIT-6 with various Si/Fe ratios and the optimised Si/Fe ratio was taken further to study the effect of Zn by CVD. This CVD setup consists of a horizontal tubular furnace and gas flow control units. In a typical growth experiment, 200 mg of catalyst was placed in a quartz boat inside the quartz tube. The catalyst was purged in a nitrogen gas at a flow rate of 100 mL/min for 30 min to remove water and thus to