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An efficient synthesis of graphenated carbon nanotubes over the tailored mesoporous molecular sieves by chemical vapor deposition

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ABSTRACT

The new hybrid of graphenated carbon nanotubes (g-CNTs) was superior to either CNTs or graphene. Mesoporous 3D cubic Ni/KIT-6 were synthesized hydrothermally through organic template route and then were used as catalytic template for the production of g-CNTs using acetylene as a carbon precursor by chemical vapor deposition (CVD) method. The deposited new hybrid carbon materials were purified and analyzed by various physico-chemical techniques such as XRD, TGA, SEM, TEM and Raman spectroscopy techniques. The graphitization of CNTs was confirmed by TGA and HRTEM studies. Thermal stability, surface morphology, and structural morphology of these materials were revealed by TGA, SEM and TEM analysis, respectively. Moreover, the tailored mesoporous Ni/KIT-6 molecular sieves were found to possess better quality and massive quantity of g-CNTs produced compared to other catalytic template route.

1. Introduction

Worldwide extensive and intensive researches on the preparation, characterization and applications of nanomaterial have been performed for the past 15 years. Generally, graphitic like CNTs and graphene are the attractive nanomaterials due to their specific electronic, chemical, and mechanical properties [1–3]. The new hybrid of graphenated carbon nanotubes (g-CNTs) was superior to either CNTs and/or graphene alone [4,5]. The fundamental advantage of an integrated g-CNT structure is the high surface area three-dimensional framework of the CNTs coupled with the high edge density of graphene. Deposition of graphene foliates with high density along the length of aligned CNTs can significantly increase the total charge capacity per unit of nominal area as compared to other carbon nanostructures [6]. The M41S family including MCM-41 and related mesoporous molecular sieves are of interest because of their remarkable properties such as large surface area (>1000 m^2/g), pore volume (>0.8 cm^3/g), narrow pore size distribution, and the ease fabrication with which their surface can be functionalized [7]. Among the mesoporous materials with uniform channels, large pore size, high specific surface area, and high thermal stability, KIT-6 exhibits a three-dimensional cubic *Ia*3*d* symmetric structure with interpenetrating bicontinuous network of channels [8]. Three dimensional pore structures of KIT-6 and its resistance against pore blockage of this phase could serve as an excellent candidate for catalytic applications. In general, the pure siliceous mesoporous has limited catalytic activity, but active catalytic sites can be generated in Si-mesoporous molecular sieves by isomorphously substituting silicon with transition metals like Fe, Co, Ni, etc. [9]. Several studies have been dedicated to the investigation of transition metal substituted mesoporous molecular sieves because of their wide range of applications in catalysis [10–13]. Apart from catalysis, the metal-embedded mesoporous molecular sieves have also been used as catalytic template for the synthesis of CNTs [14–18]. The metal particle plays an important role during CNT production and reports abound, showing a direct correlation between the size of the metal nanoparticles and the eventual tube diameter [19].

In the growth of g-CNTs, dispersion of metal particles over the support leads to the formation of well-graphitized g-CNTs. The present work deals with the synthesized Ni/KIT-6 as catalytic templates for the growth of g-CNTs by the CVD method using acetylene as carbon precursor. The ultimate aim of this study is to understand the correlation between the graphenes, CNTs, g-CNTs, and the quantity as well as quality of the g-CNTs produced for the numerous applications in nano-community.

2. Experimental

2.1. Materials

Pluronic P123 triblock co-polymer [poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol)] with

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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) and nickel(II) nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$) were used as a source of silica and nickel, respectively, for the synthesis of KIT-6. Hydrochloric acid (35 wt%) was purchased from Merck and used as a co-solvent for the synthesis of mesoporous 3D cubic KIT-6 molecular sieves. The gases namely acetylene (99.9%), argon (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 and HNO_3 were purchased from Merck and were used for the purification of g-CNTs. Solvents such as acetone and ethanol were purchased from Merck and double distilled water was used throughout this study. All the mentioned above chemicals were used without any further purification.

2.2. Synthesis of Ni/KIT-6

The mesoporous 3D cubic KIT-6 molecular sieves were synthesized hydrothermally using the gel composition of TEOS:0.017 P123:1.83 HCl (35 wt%):1.31 n-BuOH:195 H_2O [20]. The typical procedure for the synthesis of KIT-6 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 was added 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 condition. The dried material was ground well and then calcined at 550 °C for 12 h in atmospheric condition (heating rate: 5 °C/min) to remove the template. The different amount (wt% = 1.0, 2.0, 3.0, 4.0 and 5.0) of Ni was loaded individually over above synthesized pure KIT-6 using the wet impregnation method. In a typical procedure, an appropriate amount of nickel nitrate was dissolved in distilled water and sonicated for 15 min. The sonicated solution was added drop by drop with mesoporous 3D cubic 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 air.

2.3. Synthesis of g-CNTs

The synthesis of g-CNTs was carried out over Ni/KIT-6 by CVD method. The CVD setup consists of a horizontal tubular furnace and gas flow control units [17,21]. In a typical growth experiment, 200 mg of catalyst was placed in a quartz boat inside the quartz tube. The catalyst was purged in an argon gas at a flow rate of 100 mL/min for 30 min to remove the water and thus to pre-treat the catalyst and then hydrogen gas at a flow rate of 100 mL/min was purged for 30 min to reduce the Ni precursor. The reaction was carried out using acetylene as carbon source at 900 °C with a flow rate of 50 mL/min for 30 min. The furnace was then cooled to room temperature under argon atmosphere; the appearance of black material confirms the completion of the reaction. The obtained material was weighed, purified, and then characterized. The percentage of the carbon deposition due to the catalytic decomposition of acetylene was calculated from Eq. (1) [22,23]:

$$\text{carbon deposition yield}\,(\%) = \frac{m_{tot} - m_{cat}}{m_{cat}} \times 100 \tag{1}$$

where m_{tot} is the total mass of carbon product with catalyst and m_{cat} is the mass of catalyst.

2.4. Purification of g-CNTs

The technique for the removal of the silica phase by the presence of hydrofluoric acid (40 wt%) at ambient temperature was reported [24,25]. In brief, the carbon sample was immersed in an appropriate amount of HF, washed with distilled water and dried. The obtained sample was further treated with nitric acid and hydrochloric acid to remove the metal particles and then washed with distilled water and dried at 80 °C for 6 h in an air atmosphere [26–28]. The oxidized material was cooled to room temperature slowly and then characterized by various physico-chemical techniques.

2.5. Characterization methods

The synthesized mesoporous Ni/KIT-6 molecular sieves and g-CNTs were characterized by various physico-chemical techniques such as X-ray diffraction (XRD), N_2 sorption studies, thermogravimetric analysis (TGA), Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Raman spectroscopy. The XRD patterns of KIT-6 and Ni/KIT-6 molecular sieves were recorded in the 2θ range of 0.5–10°. The X-ray powder diffractograms of purified g-CNT samples were obtained on a PANalytical X'Pert diffractometer equipped with liquid nitrogen cooled germanium solid-state detector using Cu Kα radiation. The XRD patterns of g-CNTs were recorded in the 2θ range of 5–80° and at the step interval of 0.02° with the counting time of 5 s at each point. N_2 sorption isotherms were measured at −197 °C using a Micromeritics ASAP 2000. Prior to the experiments, the samples were dried at 130 °C and evacuated overnight for 8 h in flowing argon at the flow rate of 60 mL/min at 200 °C. Surface area, pore size, and pore volumes were obtained from isotherms using the conventional Brunauer–Emmet–Teller (BET) and Barrett–Joyner–Halenda (BJH) equations. TGA of the material was performed using a Mettler TA 3001 analyser. Samples of approximately 10 mg were heated in static air from 32 (room temperature) to 1000 °C at heating rate of 20 °C/min. SEM was performed on a JEOL with acceleration voltage of 4 kV by placing the g-CNT on non-conductive carbon tape. The TEM images of mesoporous Ni/KIT-6 and g-CNTs were obtained using a JEOL 3010 electron microscope operated at 300 kV. Samples for TEM were prepared by placing droplets of a suspension of the sample in acetone on a carbon-coated polymer micro grid supported on a Cu grid. Raman spectra were recorded with a Micro-Raman system RM 1000 Renishaw using a laser excitation line at 532 nm (Nd-YAG), 0.5–1 mW, with 1 μm focus spot in order to avoid photo-decomposition of the samples.

3. Results and discussion

3.1. Investigation of mesoporous KIT-6 molecular sieves

3.1.1. XRD analysis

The small-angle powder XRD patterns of calcined *Ia*3*d* cubic KIT-6 and Ni/KIT-6 molecular sieves are shown in Fig. 1. The high intensity peak in the 2θ range of 0.9–1.0° is due to (2 1 1) diffraction and a shoulder around at the range of 2θ = 1.1–1.2° due to (2 2 0) diffraction are observed. The weak peaks observed between 1.5° and 2.2° (2θ) due to (3 2 1), (4 0 0), (4 2 0), (3 3 2), (4 2 2) and (4 3 1) diffraction lines. The XRD pattern shows all the eight peaks corresponding to KIT-6 which confirms that the synthesized KIT-6 has highly ordered structured and high crystallinity. The XRD pattern shows excellent structural order with symmetry commensurate to a body-centered cubic *Ia*3*d* space group, which matches the reported data [20,29]. XRD patterns of the calcined material confirm that there is no structural