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A novel synthesis method of nanostructured MgO-coated hollow carbon nanofibers via CO decomposition over Mg/MgO catalyst

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ABSTRACT

An easy and one-step synthesis method for preparation of oxide-coated carbon nanofibers (CNFs) by Mg/MgO catalyst has been reported. For this purpose, the mixture of Mg (metal) and MgO (fused magnesia) powders were heat treated at 1000 °C under reducing atmosphere of CO gas and the final product was comprehensively characterized by various analytical methods such as X-ray diffractometry, field emission scanning electron microscopy (FE-SEM), transition electron microscopy (TEM) and Raman spectroscopy. The results showed the formation of hollow CNFs with the average diameter and wall thickness of 100 nm and 25 nm, respectively. Furthermore, SEM micrographs have obviously revealed the presence of highly packed MgO nanoparticles (with average particle size of 30 nm) on the outer surface of fibers owing to catalytic reaction of Mg $_{(v)}$ and CO gasses. Considering the superior physical properties of the synthesized oxide-coated material such as great packing, high uniformity as well as the absence of structural defects, oxide-coated CNFs showed considerable enhancement in the oxidation resistance compared to the conventional carbon nanofibers. The synthesized oxide coated CNFs showed a weight loss of less than 5 wt% after exposing to high temperature at oxidative atmosphere highlighting the significant effect of the oxide coating. This effect was confirmed by a thermoanalytical technique using differential scanning calorimeter equipped with the online gas analyzer.

1. Introduction

Carbon nanofibers (CNFs) are cylindrical nanostructures with graphene layers arranged as stacked cones, cups or plates. Recently, CNFs are widely used in a wide variety of applications due to the unique features such as high mechanical strength at room and elevated temperatures, low density, and chemical inertness that have represented them as a promising candidate to revolutionize several fields in material science as well as nanotechnology [1,2].

Over the last decade, many studies have carried out on the synthesis of CNFs via different methods and various processing parameters including catalyst and reactant characteristics, temperature and atmosphere have been utterly investigated [3,4]. Among the developed methods, catalytic gas decomposition using metallic particles as a catalyst and an appropriate gaseous carbon source, i.e. CO and CH_4, is of more importance owing to the simplicity and scalability of the method [5]. Jiao and Seraphin have studied the effect of using different metals as the catalyst in CO gas decomposition process via two high-temperature heat treatment routes. They have reported that the products have a similar morphology, regardless of different synthetic methods. This result implies that the most important parameter involved in the formation of CNFs during gas decomposition process is catalyst features and its interaction with gas molecules [6]. Furthermore, Rana et al., have studied the synthesis of carbon nanotubes using cobalt nanoparticles via carbon monoxide decomposition in Mg/MgO system [7]. They claimed that the advantages of using Mg along with MgO could realize from the increase in carbon yield and final quality of carbon microstructure. Besides, some other studies have conducted on evaluating some catalyst/support systems such as Ni and Fe-MgO, Co-Al_2O_3, Co-MgO, for decomposition of CO to obtain carbon filaments [8–12]. Moreover, Pinheiro et al., have reported that MgO and Al_2O_3 as the catalyst support have the same effect on carbon precipitation but MgO is so much easier to be eliminated than alumina [13].

In the current study, the formation of hollow nanofibers in the MgO/Mg system was investigated. The catalytic decomposition of CO using Mg/Mg system could be known as the main idea of the present work leading to the formation of oxide coated CNFs. The formation of such coating has attributed to the heterogeneous reaction of Mg and CO components at current process condition. The development of a one-step synthetic method of nano-oxide coated CNFs could be of high importance, especially in the utilization of CNFs products in high-temperature bearing materials.

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2. Experimental procedure

Mg metal (Aldrich 13112, purity > 99%, 150–300 μm) and fused magnesia (Industrial grade, purity > 99%, 150–500 μm) powders were employed as starting materials and were used without any further purification. The powders were mixed homogeneously in highly pure methanol using magnetic stirrer via solvent-based mixing method. The weight ratio of Mg to MgO powder was 30:70, respectively. The prepared mixture was dried and heated at temperature of 1000 °C for 2 h in reducing atmosphere (Coke-bed prepared using graphite and carbon black powders), and the synthesized powder was characterized using different analytical techniques. The structural properties were analyzed by X-ray diffraction (XRD) using Philips X′pert diffractometer equipped with Cu Kα radiation (λ=1.541 Å), the operation voltage and current maintained at 40 kV and 40 mA, respectively. The morphology and chemical composition of the product were analyzed by scanning electron microscopy (SEM, JEOL) coupled with energy dispersive X-ray spectroscopy (EDX, JEOL Oxford). Besides, transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), and selected area electron diffraction (SAED) patterns (on a JEOL- 2010 microscope with an accelerating voltage of 100 kV) were employed for microstructural studies. Sample grids were prepared by sonicating powdered samples in ethanol for 30 min and evaporating one drop of the suspension onto a carbon-coated, holey film supported on a copper grid. Thermal analysis conducted using NETZSCH instrument (STA 449 F3 Jupiter) coupled with Quadrupole Mass Spectrometer (QMS) detector (Heating rate: 10 °C/min, atmosphere: air). Raman spectroscopy technique has also employed to characterize the degree of crystallinity in the microstructure of CNFs. The spectra were recorded at 2 cm^{-1} resolution using the liquid nitrogen cooled CCD devices as a detector and incident radiations around 514.5 nm. A curving fitting was applied for spectra in order to improve the accuracy in determination of spectroscopic parameters such as peak position, bandwidth, line shape, and band intensity.

In addition, to eliminate oxide phases, the synthesized powder was washed with sulfuric acid (2 M, H_2SO_4) and washed powder was subsequently separated and dried for further study of carbon nanofibers. Finally, hydration test of the samples was conducted using vapor bath (100 °C) for an exposure time of 24 h. Fig. 1 shows the fellow chart of the mentioned experimental procedures.

3. Results and discussion

The XRD patterns of raw materials and as-synthesized product are demonstrated in Fig. 2. As seen, all diffraction peaks of the product are indexed to MgO and carbon phases that indicates that complete reaction between Mg and CO has occurred after heat treatment at

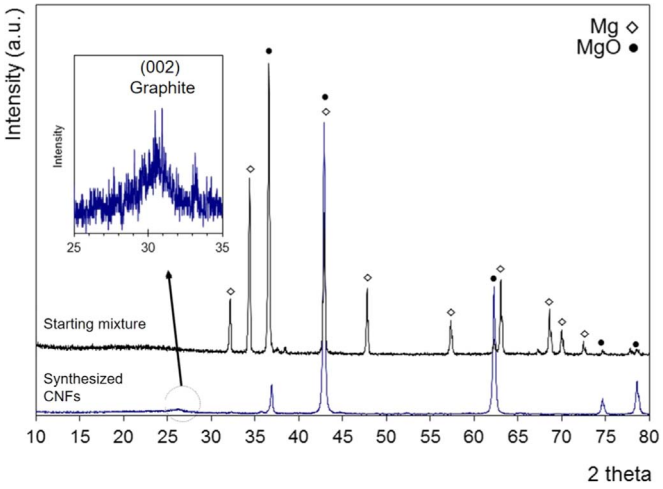

Fig. 2. XRD Patterns of starting Mg/MgO mixture and the synthesized product.

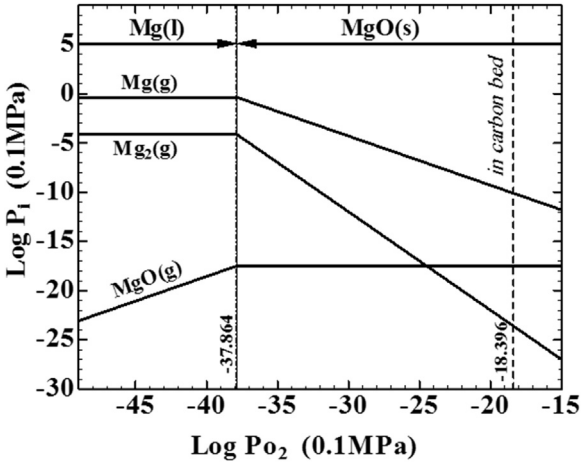

Fig. 3. Equilibrium partial pressure of components in Mg-O system at 1000 °C.

above-mentioned circumstances, leading to the formation of MgO and carbon phases. The weak and broad peak around 25° can be attributed to (002) basal planes of graphite phase and the presence of a deviation in diffraction angle compared to that of pure graphite phase is ascribed to the semi-crystalline nature of carbonaceous phase of CNFs [14]. Furthermore, no peak assigned to metallic Mg phase was observed highlighting the high purity of the final product.

To better study the possible reactions between starting components,

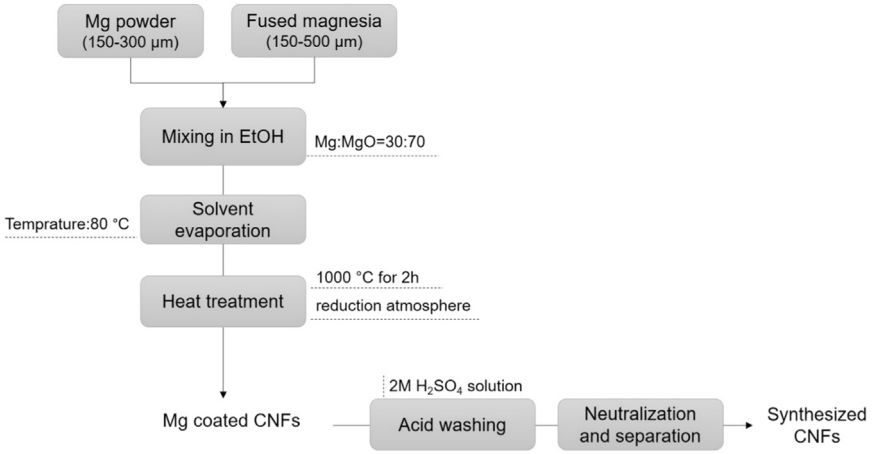

Fig. 1. The fellow chart of the applied experimental procedures to synthesize of oxide coated carbon nanofibers.