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The removal of encapsulated catalyst particles from carbon nanotubes using molten salts

Xuanke Li [a,b,*], Guanming Yuan [a], Andy Brown [b], Aidan Westwood [b], Rik Brydson [b], Brian Rand [b]

[a] *High Temperature Ceramic and Refractory Key Laboratory of Hubei Province, Wuhan University of Science and Technology, Wuhan, Hubei 430081, PR China*
[b] *Institute for Materials Research, University of Leeds, Leeds LS2 9JT, UK*

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Abstract

A novel method, using molten salts, is described for the removal of encapsulated nickel catalyst particles from multi-walled carbon nanotubes. The multi-walled carbon nanotubes, synthesised by the decomposition of methane and hydrogen over a NiO/SiO_2 aerogel catalyst, were treated in a LiCl–KCl eutectic molten salt and subsequently by hydrochloric acid to remove the nickel catalyst particles. The influence of the molten salt treatment on the microstructure of the carbon nanotubes was investigated by XRD, SEM and TEM analyses. The molten salt treatment promoted uncapping of the carbon capsules and the formation of strip-shaped carbon fragments. It was found that the hydrochloric acid treatment could then remove the nickel particles from the broken carbon capsules which was not possible prior to the molten salt treatment. The stability of carbon nanotubes in the molten salt is closely related to their ordered structure.

Keywords: Carbon nanotubes; Catalyst; Transmission electron microscopy

1. Introduction

Carbon nanotubes have been synthesised by laser ablation, arc-discharge and chemical vapour deposition (CVD) [1–3]. Catalytic CVD (CCVD) methods have been developed in recent years for the large-scale production and controlled synthesis of carbon nanotubes [4,5]. Highly purified nanotubes are in general required for further sophisticated measurements and practical applications. However, in virtually all methods a large amount of unwanted carbonaceous particles, catalyst and catalyst support particles contaminate the CCVD-synthesised carbon nanotubes [4,5].

There are several reports [6–11] on the purification of multi-walled carbon nanotubes (MWNTs). One of the purification methods is oxidation in air at temperatures around 750 °C. Although pure MWNTs can be obtained there is the risk of burning off up to 99 wt% of the sample after prolonged oxidation [6], owing to the small difference in reactivity between the MWNTs and the carbon nanoparticles. Another purification method is based on liquid-phase oxidation using a $KMnO_4/H_2SO_4$ solution [7]. A two-step acidic treatment within a microwave digestion system has been used to dissolve metal catalysts [12]. HNO_3 or HCl can rapidly absorb microwave heat and energy and completely dissolve any metal that resides in carbon nanotubes without damage [12]. A graphitisation procedure has been found to remove residual metal catalyst in the nanotubes by vaporisation. This also reduces the

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[*] Corresponding author. Address: High Temperature Ceramic and Refractory Key Laboratory of Hubei Province, Wuhan University of Science and Technology, Wuhan, Hubei 430081, PR China. Tel./fax: +0086 27 86551274.
E-mail address: prexli@leeds.ac.uk (X. Li).

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wall defects, as reflected in a reduced interlayer spacing between the graphene shells [13]. The purification of carbon nanotubes based on graphite intercalation has also been reported [14,15]. These methods use the difference in oxidation rates between the carbon nanotubes and a graphite intercalation compound (GIC). The intercalation compounds were subsequently heated in air and this resulted in a preferential destruction of the intercalated carbon. However, these various procedures for the removal of metal catalyst particles are not always, or even often, entirely successful because many of the particles become encapsulated by a multi-shell CVD carbon layer or are coated by carbon layers at the tips of the nanotubes. Thus, they are protected.

Syntheses in which molten salts are used as reaction aids are known to offer convenient and cost-effective routes to useful ceramic and metal [16,17] products at low temperatures in relatively short reaction times. Molten salt synthesis has also been used for the production of carbon nanotubes [18–20]. However, the use of molten salts in carbon reactions is novel and there is no other relevant literature. In this paper, a novel method of purifying carbon nanotubes is reported, which could effectively remove nickel metal particles from carbon nanotubes and multi-shell carbon nanocapsules. The results reveal that molten salt treatment can play a significant role in purifying MWNTs. The method is based on the concept that carbon nanotubes possess more rigid and ordered microstructure in their walls than near to the carbon nanotube tip.

2. Experimental

2.1. The preparation of NiO/SiO_2 binary aerogel

A NiO/SiO_2 binary aerogel was used as a catalyst for the synthesis of the multi-walled carbon nanotubes. Tetraethoxysilane (TEOS), $Ni(NO_3)_2 \cdot 6H_2O_2$ solutions in ethanol and acetic acid at a molar ratio of 1:0.4:0.01 were mixed using magnetic stirring for 24 h at room temperature to form an 'alcosol'. Then the 'alcosol' was placed in an autoclave and dried under the supercritical conditions of 250 °C and 7.0 MPa pressure for 0.5 h after which the ethanol was slowly discharged at 250 °C and the autoclave was cooled to room temperature with flowing nitrogen to obtain a binary aerogel.

2.2. The synthesis of multi-walled carbon nanotubes

The preparation of carbon nanotubes was carried out in a quartz tube (60 mm diameter) furnace equipped with temperature and gas-flow controls. 5 g of binary aerogel catalyst in a quartz boat was first heated to 680 °C under nitrogen which was then replaced by hydrogen for 30 min, followed by methane for a further 30 min to synthesise the carbon nanotubes. Subsequently, the methane supply was turned off, the furnace was heated to 800 °C under hydrogen atmosphere and then the methane was introduced again for 20 min to prepare carbon nanotubes with encapsulated nickel particles. After the reaction, the reaction gas was replaced by nitrogen and the furnace allowed to cool. The carbon product was then treated with hydrofluoric acid under magnetic stirring for 48 h to remove the silica support and those nickel particles which had not been encapsulated by carbon. Finally the sample was thoroughly washed in water in order to neutralise the specimen.

2.3. The molten salt treatment of carbon nanotubes with encapsulated nickel particles

Appropriate quantities of LiCl, KCl and carbon nanotubes with the remaining encapsulated nickel particles were mixed and heated in a covered alumina crucible at 950 °C for 5 h and subsequently cooled for 12 h to room temperature. The molten salt mixture compositions and temperature were chosen as a result of optimising initial runs. All of the heat treatments were carried out under a nitrogen atmosphere. The resulting mixture of molten salts and carbon nanotubes was washed in boiling water to dissolve the salts. The carbon nanotubes were then treated in boiling dilute hydrochloric acid (ca. 1 M) for 5 h and separated by filtration. The resulting samples were finally washed in deionised water to neutrality and dried at 110 °C for 5 h.

2.4. The characterisation of carbon nanotubes with encapsulated nickel particles

The phases present in the carbon nanotubes before and after molten salt treatment were determined by X-ray diffraction using Cu-K_α radiation. The surface morphology and elemental composition of the carbon nanotubes were investigated with a Carl Zeiss LEO 60 mm 1530 field emission scanning electron microscope (FEGSEM) and the morphology and microstructure of the carbon nanotubes examined in a Philips CM200 Field emission gun transmission electron microscope (FEGTEM).

3. Results and discussion

The X-ray diffraction profiles of the primary carbon nanotubes after HF treatment as well as the products after treatment in molten salt before and after washing with hydrochloric acid are shown in Fig. 1(a)–(c), respectively. The XRD profile of the primary carbon nanotubes in Fig. 1(a) shows that the sample is composed of carbon and nickel. There is one sharp reflection at about $2\theta = 26°$ and three weak reflections at about $2\theta = 42.8°$, 53.8° and 77.8° in Fig. 1(a) that can be attributed to the carbon nanotubes. The other five diffraction peaks in the XRD profile (Fig. 1(a)) at about $2\theta = 44.51°$, 52.84°, 76.36°, 92.94° and 98.44° correspond to (111), (200), (220), (311) and (222) crystal planes of fcc nickel. Since the primary carbon nanotubes had already been treated in HF acid, this XRD result indicated that the nickel was