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Insights into the formation of multiwall carbon nanotubes using simple flame pyrolysis method

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ABSTRACT

Herein, we discuss the formation of multiwall carbon nanotubes (MWCNTs) during the simple and effective flame pyrolysis of ferrocene solution in ethanol with the help of alcohol lamp. The method is unique and simple one to prepare impure MWCNTs in the best possible way. Systematic investigations showed that the in-situ generated maghemite plays an important role in the formation and development of the MWCNTs. The growth of the maghemite impregnated MWCNTs were thoroughly studied using sophisticated instruments viz. XRD, BET, HR-SEM, and TEM analysis in details and on the basis of these, the growth mechanism is discussed.

1. Introduction

Carbon nanotubes were extensively studied for diversified applications and were in main focus since their discovery by Ijima [1]. Carbon nanotubes possess unique structural and physical properties including high tensile strength coupled with high surface area, high electric as well as thermal conductivity [2,3], These properties made them ideal candidate for the numerous applications viz. electronic devices [4], composite materials [5–7], sensors [8], gas storing [9], catalytical supports [10–12], etc. For these extensive uses, their low cost and simple synthesis became essential. Various methods were developed to synthesis of carbon nanotubes which includes but not limited to either arc discharge [13–15] and high temperature furnaces [16–19]. Besides these methods, flame method emerged as energy efficient and is readily scalable for bulk synthesis of carbon nanotubes.

The synthesis of carbon nanotubes required three essential components, catalyst material, heat source and the carbon source [20]. Flame method is widely utilized for the synthesis of carbon nanotubes in the literature [20,21–23]. The commonly used catalyst materials includes Fe, Co and Ni containing compounds [11,24,25]. Firstly ferrocene, cobaltocene and nickelocene when used requires relatively low temperatures about 700 K [18,19] for their thermal decomposition than the threshold of soot formation which is approximately at 1300 K [20]. Secondly, the formation of carbon nanotubes requires fuel within the pyrolysis when using ferrocene or cobaltocene.

In recent years, Inamdar et al. gradually developed flame pyrolysis method using simple alcohol lamp [26–29]. In this the first report came in 2006 with the preparation of spherical 25 nm sized γ-Fe_2O_3 nanoparticles [26,27]. The next two reports came in 2012 and 2013 about preparation of faceted maghemite-carbon composite [28] and sulphur containing carbon nanoparticles [29] respectively. In a year another report came about flame synthesized N-containing turbostatic carbon nanoparticles in 2014 [30]. The latest report came last year in 2021, reporting electrochemical sensor using flame synthesized MWCNTs-iron oxide nanocomposite [8]. Herein, we discussed the insights into the formation of multiwall carbon nanotubes (MWCNTs) observed during the simple and effective flame pyrolysis of ferrocene solution in ethanol using an alcohol lamp [8]. In the present study carbon nanotubes were seen growing in the spirit lamp flame, where, ferrocene is utilized as both catalyst and carbon source. Ethanol, the fuel used in the lamp, acts as extra source of carbon.

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The advantages of the method are numerous viz. (i) the method does not requires high temperatures furnace nor circulation of inert gases, (ii) the synthesis can be done using stainless-steel alcohol lamp, (iii) its unique and simplest one to produce MWCNTs. (iv) the synthesis can be carried out at any ordinary laboratory using just ferrocene and alcohol lamp. Over the years, the flame pyrolysis method evolved as unique and simplest way to prepare various metal oxide and their carbon composites. The growth of impure MWCNTs is revisited in the best possible way utilizing sophisticated characterization techniques viz. HR-SEM and TEM along with BET analysis.

2. Experimental details

2.1. Synthesis using flame pyrolysis method

The experimental setup is as demonstrated in Fig. 1. It consists of a stainless steel /glass alcohol lamp equipped with cotton wick. In the typical preparation, 0.5 g ferrocene dissolved in 100 ml absolute ethanol used as feeding solution in the alcohol lamp. This resulted in 57 mg faceted maghemite sample (Sample-M) deposited on the cold surface of conical flask [26,28]. The second sample, composite (Sample-CM) weighing 107 mg collected around the cotton wick, was red-hot burned composite and fallen down after some time [8]. The sample preparation took around three hours.

2.2. Characterization techniques utilized

Transmission electron microscopy (TEM) images were recorded with an EM 912 Omega electron microscope operated at an accelerating voltage of 120 kV. High resolution scanning electron microscopy (HR-SEM) images were obtained using a Hitachi S-5500 microscope operated at an accelerating voltage of 30 kV. Powder X-ray diffractions (XRD) were measured with a Brucker D-8 diffractometer equipped with a Cu-Ka radiation (1.54 A°) (40 kV and 40 mA). The XRD pattern was recorded for 2θ values of 10–60, with scan rate of 0.05 degree per second. The nitrogen adsorption and desorption isotherm measurements were done in a Micromeritics ASAP 2000 at 77 K. Specific surface areas of the samples were determined by nitrogen isotherms using the BET (Brunauer–Emmett–Teller) equation.

3. Results and discussions

The details of the sample-M are already reported in the previous reports [26,28]. The XRD pattern of Fe_2O_3@MWCNTs nanocomposite (Sample-CM) is as shown in Fig. 2. The XRD pattern clearly exhibited two distinct diffraction peaks at 2 θ values of 27 and 42 indexed to (002) and (100) plane of graphite carbon structure and remaining peaks at 2θ values of 30, 35, 43, 51, 58 and 59 were indexed to cubic maghemite phase [8].

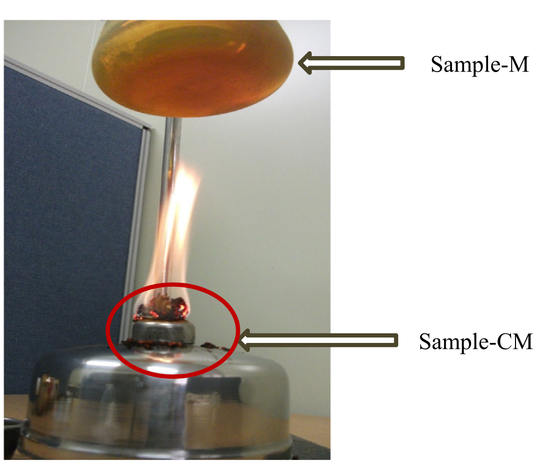

Fig. 1. Experimental setup of flame pyrolysis method.

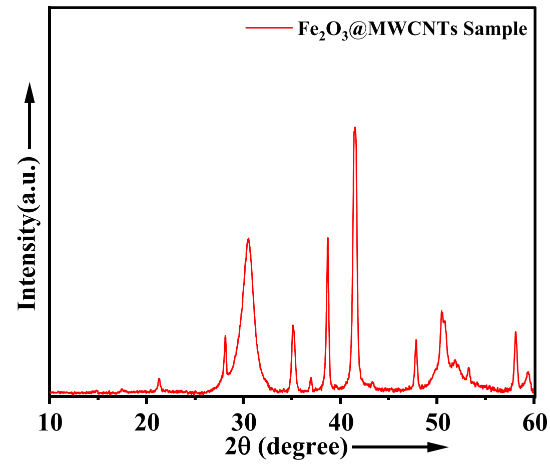

Fig. 2. XRD pattern recorded for the flame synthesized Fe_2O_3@MWCNTs sample.

The growth of MWCNTs were thoroughly studied using HR-SEM as shown in Fig. 3. The images were taken in two modes, the secondary electrons (SE) and transmission electrons (TE). The right-side images are in SE mode, while left-side images were in TE mode. The TE mode is advantages to see through the images, giving more clear idea of whether the nano-crystals are incorporated inside the CNTs or deposited onto surface. The SEM images in the Fig. 3 in TE mode revealed that the maghemite nano-crystals were filled inside the CNTs. The carbon nanotubes can be clearly seen in the images. The diameter of the nanotubes measured to be 70–80 nm. It has been observed that 40–50 nm sized maghemite crystals were impregnated as well as decorated on the surface of the carbon nanotubes. The nanotubes emerged as the graphene cloths bundled in the form of tube incorporating maghemite polyhedrons. The incorporation carbon precursors on maghemite crystals seems facilitating the growth of nanotubes. The carbon nanotubes were seen without any soot particles deposited on or around it, this ensures formation of pure maghemite-MWCNTs composite on the burning cotton wick.

The growth of MWCNTs in the current results is seen catalysed by the maghemite particles forms in-situ in the flame. Carbon nanotubes grows mainly in three steps, adsorption of hydrocarbons on catalyst surface, diffusion of carbon species through decomposition of adsorbed hydrocarbons and lastly precipitation of crystalline graphite [9,31–34]. The other factors viz. influence of catalyst, carbon concentration and temperature of the flame also impact the growth of carbon nanotubes significantly in diffusion and precipitation steps [9,35]. The morphologies of carbon nanotubes depend mostly on particle size and curvature of the catalyst, the deposition of carbon atoms for deposition prefers surface with low curvature of catalyst particles [9]. The maghemite particles here showed strong affinity to the substrate. During the growth of the carbon nanotubes, few maghemite particles seen getting trapped in and on the surface of tubes (refer Fig. 3 and Fig. 4).

The growth of MWCNTs is facilitated by the presence of maghemite nanocrystals which acted as catalyst for the further growth of the nanotubes in the air-flame environment. The method neither needs high temperatures furnace nor requires circulation of any gases, the method simple pyrolysis of the ferrocene precursor solution with the help of a stainless-steel alcohol lamp. We strongly believe that this method might be unique and simplest one to pro-

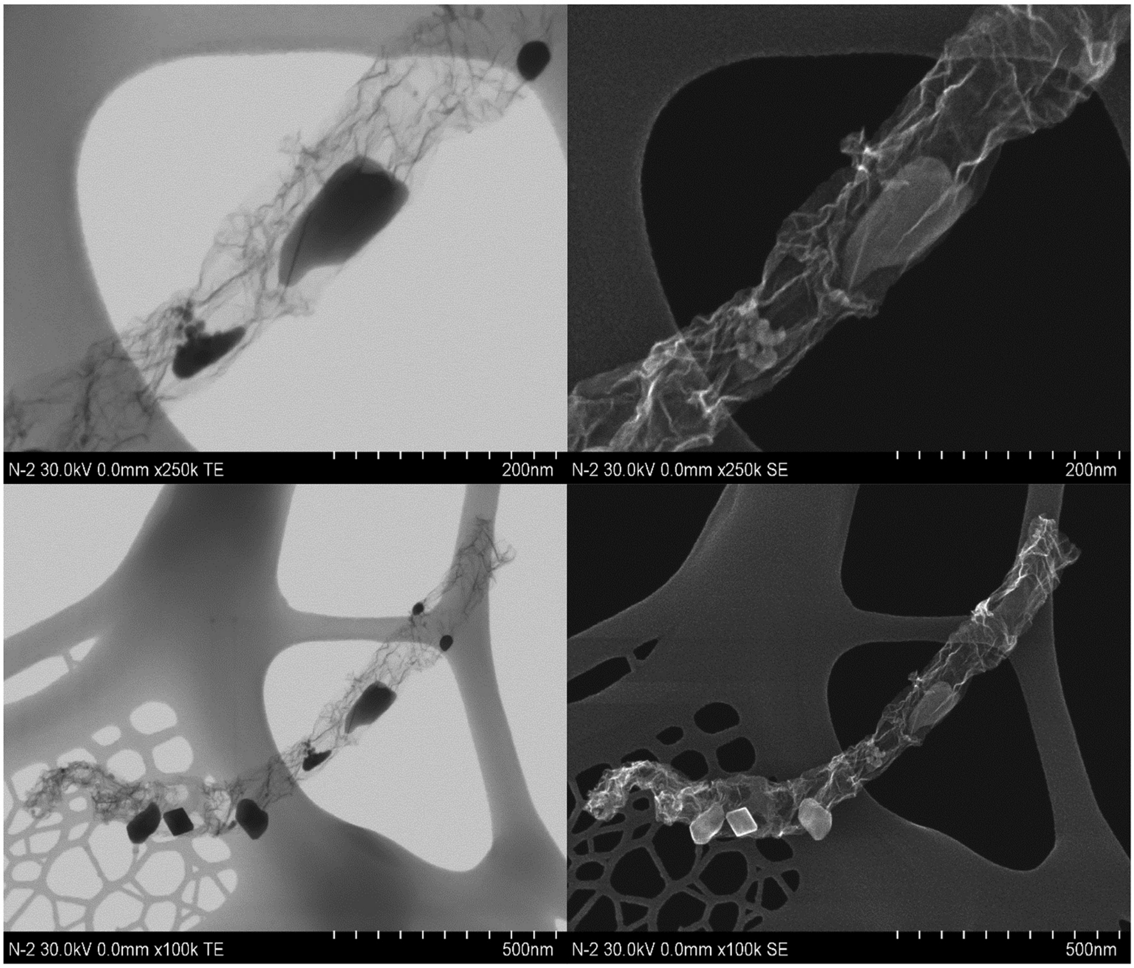

Fig. 3. HR-SEM images in SE mode and TE mode of multi-walled carbon nanotubes grown using flame pyrolysis method.

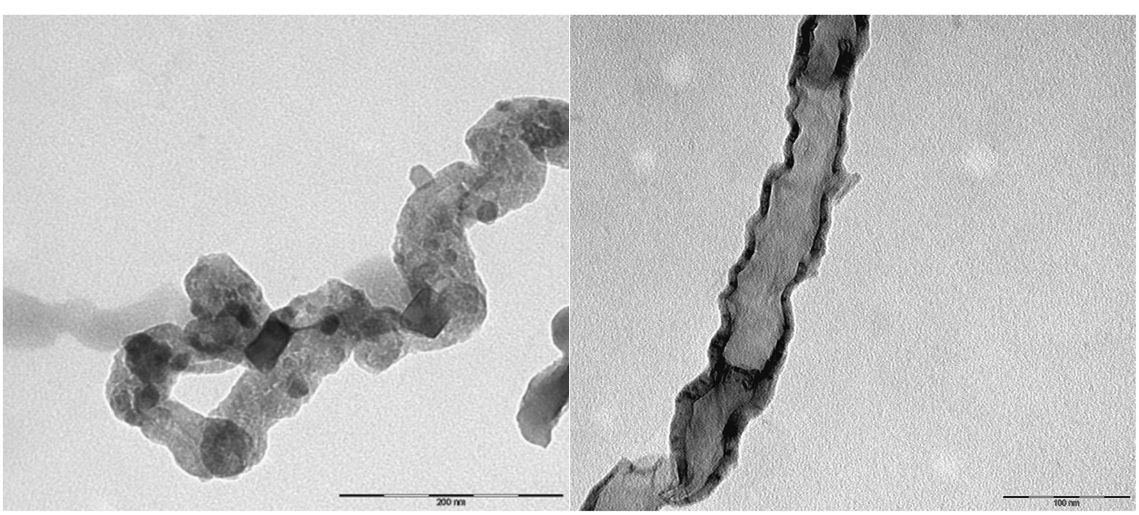

Fig. 4. TEM images of multi-walled carbon nanotubes grown using flame pyrolysis method.

duce MWCNTs without requirement of any sophisticated furnaces or gas circulation setups. The synthesis of MWCNTs using this method can be carried out at any simple laboratory using just ferrocene and alcohol lamp.

The growth of MWCNTs were also studied using TEM analysis as shown in Fig. 4. The carbon nanotubes with diameter of 70–80 nm were clearly seen in the images. In the TEM images too, the MWCNTs were seen filled with maghemite crystals. The diameter of the multiwall carbon nanotubes was observed similar to that of the HR-SEM analysis.

CNTs are a type of nanomaterial that has attracted increasing interest because of their beneficial characteristics, including their

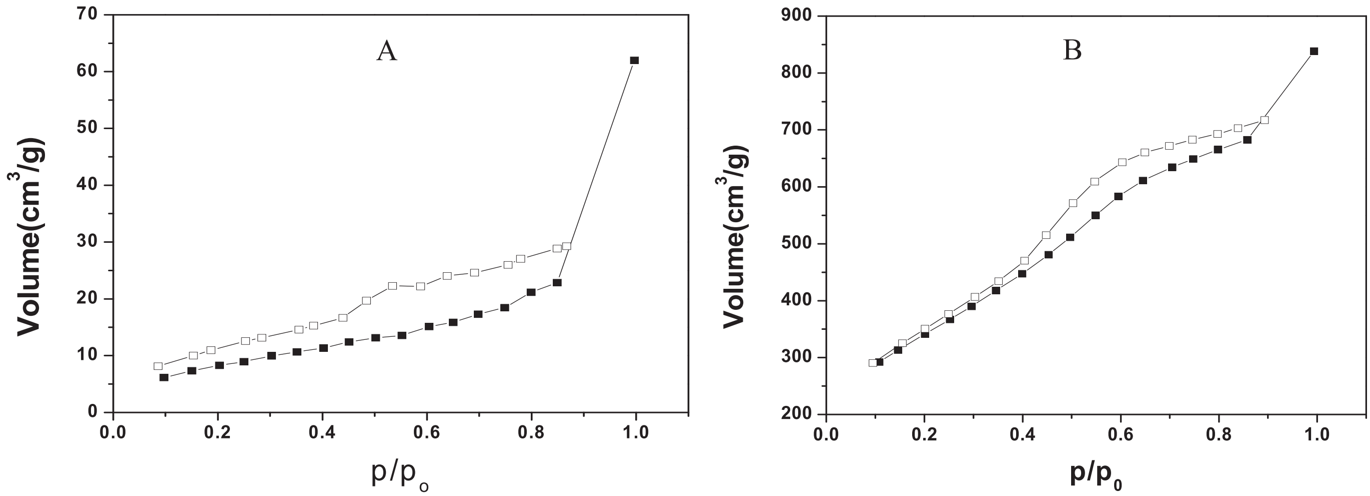

Fig. 5. **[A]** BET surface analysis of maghemite nanocrystals (Sample-M) and **[B]** maghemite-carbon nanotube composite (Sample-CM).

Table 1
Comparative surface area for the prepared samples and the reported values for the commercial MWCNTs samples.

MWCNTs sample	MWCNTs SIGMA	MWCNTs Sunnano	MWCNTs Shenzhen	Flame synthesized
Surface area, m^2/g	6.66 [38]	170 [38]	79.2 [38]	1224.21

small size, high porosity and large surface area, lower cost, distinctive electrical capabilities, and layered, hollow, and compact nature [10]. The CNTs' catalytic properties are improved by the increased surface area [36]. The incorporation carbon precursors on maghemite crystals facilitated the growth of nanotubes and also induced porosity to the maghemite-carbon nanotube composite. The induction of porosity is confirmed by the systematic study of the prepared samples using BET analysis as shown in Fig. 5. The sample-M exhibited BET surface area of 32.77 m^2/g (Fig. 5**A**) indicating very little porosity of the polyhedrons [28]. Whereas, the sample-CM exhibited surface area of 1224.21 m^2/g (Fig. 5**B**), which is more than 35 folds of the pure maghemite sample, indicates formation of CNTs along with maghemite nanocrystals. This suggests that the iron oxide nanoparticles trapped on and inside the surface of CNTs, as seen in SEM and TEM images, increased their surface area and hence increased the number of adsorption sites [37]. The as prepared Fe_2O_3@MWCNTs sample exhibited higher surface area than that reported in the literature for the commercial MWCNTs [38]. The comparison is as shown in the Table 1.

4. Conclusions

The multiwall carbon nanotubes (MWCNTs) embedded in or supported by maghemite nanocrystals were prepared by a one-step flame pyrolysis method. Overall, MWCNTs were formed during the simple flame pyrolysis of ferrocene solution in ethanol. Systematic investigations showed that the maghemite crystals were impregnated and decorated on the MWCNTs. The maghemite impregnated MWCNTs were found to be 70–80 nm diameter using both HR-SEM and TEM analyses. The obtained product maghemite-carbon nanotubes exhibited high BET surface area of 1224.21 m^2/g compared to maghemite exhibiting BET surface area of just 32.77 m^2/g. The method is the simple way to prepare impure MWCNTs in the form of maghemite- MWCNTs composite.

CRediT authorship contribution statement

Mahadev P. Shinde: Conceptualization, Writing – original draft. **Rajshekhar Karpoormath:** Conceptualization, Formal analysis, Methodology. **Shashikant P. Patole:** Formal analysis, Methodology, Resources. **Shaukatali N. Inamdar:** Conceptualization, Formal analysis, Investigation, Writing – review & editing.

Data availability

No data was used for the research described in the article.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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