Design and synthesis of carbon nanotubes for adsorption utilities: A proposed approach for direct preparation by mechanical milling at room temperature

Mohammad Hossein Khazaei Feizabad\textsuperscript{a}, Gholam Reza Khayati\textsuperscript{b}* , Sorayya Pouresterabadi\textsuperscript{c}

\textsuperscript{a}Department of Nano technology, Mineral Industries Research Center (MIRC), Shahid Bahonar University of Kerman, 7618868366 Kerman, Iran.

\textsuperscript{b}Department of Material Science and Engineering, Shahid Bahonar University of Kerman, 7618868366 Kerman, Iran.

* Corresponding Author: Email: khayatireza@gmail.com; Tel.: +98-34-32114053; Fax: +98-34-32114053; Mobile: +98-09151903477

Abstract

The carbon nanotubes (CNTs) were produced by mechanical milling of Hexane in the presence of two different catalysts (amorphous and crystalline Fe) at Ar atmosphere. Raman spectroscopy, Fourier-transform infrared spectroscopy, transmission electron microscopy, high-resolution scanning electron microscopy, Brunauer–Emmett–Teller (BET) and thermal analysis were employed to characterize the CNTs. The results showed that the amorphous catalyst induced more structural defects in CNTs respect to the crystalline catalyst. The ratio of single wall to multiwall CNTs of prepared samples were about 0.31 and 7.3 for crystalline and amorphous catalyst, respectively. Moreover, the BET results confirmed the higher adsorption capacity of the sample prepared by amorphous catalyst due to their higher structural defects.

Keywords: Carbon nanotubes; Mechanical milling; Amorphous catalyst; Crystalline catalyst; Hexane

1. Introduction

Carbon nanotubes (CNTs) is a combination of rolled graphitic sheet in the form of seamless cylindrical geometry. After discovery by Iijima (1991) [1], studying of this engineering material is the hot issue for many researchers due to unique characteristics, i.e., chemical, electronic, thermal and mechanical properties [2-6]. Such characteristics introduce CNTs as a good candidate for advanced application in engineering usages, e.g., field emission devices, scanning
probes, nanoscale electronic devices, hydrogen storages, chemical sensors and composite reinforcing materials [7-18]. To the best of our knowledge, CNTs have been prepared by various methods such as solar production, electric arc discharge, laser ablation of a carbon target, chemical vapor deposition, electrochemical synthesis, pyrolysis of benzene in the presence of hydrogen and reactive milling [19-29].

Compared to the fossil fuels, usage of hydrogen due to the zero emission as well as carbon free of combustion products are strongly preferred. Developments of proton exchange membrane fuel cells have a key role for replacement of hydrogen as a clean source of energy. In this regard, the evolution of on-board storage and release of hydrogen has administration effects. There are various techniques for storage of hydrogen, e.g., liquefaction, compression at high pressure and metallic hydrides. Outstanding characteristics of carbonaceous materials as physisorption agent introduces such structure as a good candidate for storage device. In this case, the gravimetric energy storage density carbonaceous materials are higher due to the lower atomic mass of its constituents. Significant safety and energy efficiency are the other advantages of such compounds. According to literature, employment of carbonaceous structures as hydrogen storage and transportation is the subject of many researches. CNTs, due to the high specific surface and microporous structure, showed excellent adsorb potential, especially hydrogen, in their nanostructure [30].

According to literature, the presence of defects in CNTs structure, significantly, enhanced the storage capacity of hydrogen. There are various approaches for the preparation of CNTs with a high density of defects, including oxidation of CNTs by oxygen at high temperature, alkali-metal addition, oxidation using chemical agents (HCl and HNO₃) in the presence of oxidizing agent and mechanical milling [31].

Respect to the prepared CNTs by arc discharge technique, the prepared CNTs using decomposition of carbon precursor (i.e., hydrocarbon) in the presence of appropriate catalyst possess higher defect density, e.g., localized kinks or bends. Chemical vapor decomposition (CVD) is one of the most common techniques that used from hydrocarbon decomposition for the preparation of CNTs. This technique has certain advantages including high yield, induction of high amount of defects in prepared CNTs and controllable growth. However, the prepared samples are usually have closed ends, tangled, long and as a consequence, restricted its usage as
gas adsorbing and desorbing agents, in which the open tips CNTs are preferred. To compensate these disadvantages; various techniques have been developed, including, scanning tunneling microscope voltage, ultra-sound power, chemical treatment and modification of prepared shorter and open-ended CNTs. Among these techniques, ball milling seems to be the cheapest and cleanest process for induction of such defects in CNTs without any further thermal and chemical treatment \[32\].

In this investigation proposed a novel approach for the preparation of CNTs using mechanical milling of Hexane (i.e., carbon precursor) directly. Employment of milling process to generate the mechanoochemical changes, e.g., solid-state reactions and phase transformation is the subject of many researches \[34, 35\]. Due to the mixing process and microstructure refinement during the mechanical milling, the reaction rate was dynamically increased as a function of milling time. Lowering the number of technical stages, removing the operational stages includes the employment of solvents as well as stabilizing additives, reproductively, simplicity, mass production, easy handling and removing of any heating treatment are the main advantageous of the proposed method for the preparation of CNTs.

Table 1 abbreviates the researches that carried out by the employment of mechanical milling for preparation and modification of CNTs. In this regard, within the preparation approach, the graphitic precursor transferred to ultra-active amorphous carbon at first and then followed by high-temperature annealing to convert the amorphous phase to CNTs. While, in the latter approach the prepared CNTs by other technique, employed the mechanical milling to induce defects and enhanced the surface area. Both approach used high temperature during the preparation and it was considered as the main drawback for the extension of these techniques. It was worth to note that our proposed approach provides the possibility of CNT preparation at room temperature with significant defects in their structure. The main contribution of the current study are:

- Direct synthesis of the CNTs by mechanical alloying without any further heat treatment;
- Preparation of CNTs with a high density of defects as adsorbent agent;
- Usage of Fe and Fe\(_{0.7}\)Nb\(_{0.1}\)Zr\(_{0.1}\)Ti\(_{0.1}\) amorphous alloy as catalyst through the preparation of CNTs by mechanical milling.
2. Materials and method

In this study, the CNTs were prepared by mechanical milling of 10 mL Hexane ($C_6H_{14}$; Merck; 98.5%) in the presence of 10 gr powder of Fe or $Fe_{0.7}Nb_{0.1}Zr_{0.1}Ti_{0.1}$ as a catalyst. Fe (Merck, 99%, 10 μm), Nb (Alfa Aesar, 99.8%, <44 μm), Zr (Merck, 99.8%, 50 μm) and Ti (Alfa Aesar, 99%, <44 μm) were used as raw materials. The precursor and catalyst were subjected to the severe mechanical milling. Table 2 abbreviated the details of the milling process.

| Table 2 |
|---------------------------------------------------------------|
| To avoid from the oxidation of precursor and catalysts, the milling was carried out at Ar atmosphere. Also, the evaporation of carbon precursor was compensated by the addition of 5 mL of Hexane to the vial after 20 h of milling. Purification of CNTs was carried out by the employment of reflux technique to eliminate the catalyst particles. In this step, 8 gr of the as-milled sample was refluxed in 2 L of $H_2SO_4$ (6 M) for 6 h at the temperature of 80 °C. The solution was centrifuged at 4000 rpm for 15 min and washed 3 times by twice-distilled water. Finally, the products were dried at 50 °C for 30 min. Structural and phase changes were studied using X-ray diffraction (XRD) technique equipped with EQuniox 3000 powder diffractometer with Cu target. To investigate the morphological and the size of CNTs, high-resolution scanning electron microscopy (HRSEM) model Hitachi S-4160 and transmission electron microscopy (TEM) model Philips CM30 were used. Determination of the functional groups was done by Fourier transform infrared spectrum (FTIR) model TENSOR 27 in the range of 4000–400 cm$^{-1}$. Qualification of the products was carried out by Raman spectroscopy (Takram P50C0R10) with monochromatic light at 532.8 nm of the Nd:YAG laser as the excitation source in the range of 100-4400 cm$^{-1}$. Thermogravimetry (German NETZSCH-STA 409C thermal analyzer) was performed by selection of 7 ± 0.5 mg of each sample to study the purity of products in the air at the heating rates of 10 °C/min in the range of 30 to 800 °C. The reproducibility of results was confirmed by repetition of TG curves for three times. Nitrogen adsorption measurements at 77 K were carried out using a volumetric adsorption apparatus (Belsrp Mini ii, Bel Company, Japan). The amount of nitrogen adsorption for each measured point was set as 3 cc at 273 K and 760 mmHg. |

3. Results and discussion
3.1 Synthesis of CNTs

Fig. 1 illustrates the FTIR spectra of the prepared samples in the presence of Fe and Fe$_{0.7}$Nb$_{0.1}$Zr$_{0.1}$Ti$_{0.1}$ as a catalyst. As shown, the peaks at about 2934 cm$^{-1}$, 2850 cm$^{-1}$ and 1636 cm$^{-1}$ are attributed to the C-H stretching, O-H stretching and C-H bending, respectively. The peaks observed at 2934 cm$^{-1}$ due to C-H aliphatic bond and 1628 cm$^{-1}$ due to C=C bond confirmed the formation of CNTs. The evolution of weak peaks in the range of 1850-2000 cm$^{-1}$ and 1750-1845 cm$^{-1}$ can be related to the C=O bonds while the peak at 1270 cm$^{-1}$ is a sign of COOH bonds formation [36]. Moreover, the presence of a peak at 609 cm$^{-1}$ in Fig. 1 (a) confirmed the formation of carbides in sample that used Fe catalyst. Consequently, the induced energy by mechanical milling is able to provide the required energy for decomposition of Hexane to C and H [24, 37, 38]. In other words, prolonged milling (up to 100 h) provides the possibility of nucleation of free carbon as CNTs on the particles of catalyst.

Fig. 1.

The TEM images of as-prepared samples after 100 h of milling in the presence of various catalysts are shown in Fig. 2. Accordingly, in both samples, the catalyst particles act as nucleation sites for the formation of CNTs. Also, the encapsulations of catalyst particles are obvious phenomena in both of them.

Fig. 2.

To show the dissolution of C species in the catalyst particles, the peak shift in the Bragg angles are compared for (110) peaks of unmilled and milled Fe powder in the presence of Hexane after 100 h of milling (Fig. 3 (a)). As shown, the mechanical milling decreased the intensity of peak as well as peak broadening due to the grain refining and induction of strain in Fe powders. While, the dissolution of C species in milled sample caused to the peak shifting to the lower angles. The presence of Fe$_3$C and Fe$_5$C$_2$ confirmed by XRD results of this sample (Fig. 3(a)). It was necessary to note that, the possibility of carbide phase formation was increased after prolonged milling for the sample that used Fe as catalyst. Similar observation [39] has been confirmed the transformation of Fe to Fe$_3$C at first step and the growth of CNTs on cementite as an active site for nucleation at the next. In other research [40] emphasis that the stable carbide nanocrystals can act as the roots for the formation of nanotube.
To confirm the dissolution of C species in Fe\textsubscript{0.7}Nb\textsubscript{0.1}Zr\textsubscript{0.1}Ti\textsubscript{0.1} catalyst, (110) peaks of Fe as matrix were compared in samples prepared with and without Hexane after 100 h of milling (Fig. 3 (b)). Accordingly, increasing the milling time for both samples decreased the sharpness of the main peak significantly due to the formation of an amorphous alloy. Also, the obvious peak shifting of the main peak to the lower angles can be related to the dissolution of C species in catalyst from Hexane.

Fig. 3.

The growth mechanism of CNTs is a controversial issue from its discovery to date. Various mechanisms have been proposed by consideration of the reaction condition as well as post-deposition product characterization. Since in the present study, the catalyst particles were substrate-free, Hexane decomposed at the surface of catalyst particles to H and C species. H\textsubscript{2} flies away and C dissolved into the catalyst particles. The dissolved carbon diffuses through the catalyst toward the other zone of the catalyst due to the concentration gradient. Consequently, the concentration gradient encourages the C species to nucleate as CNTs at the other side of the catalyst [2, 41].

Moreover, respect to Fe\textsubscript{5}C\textsubscript{2} phase, all pathways at the surface of Fe\textsubscript{3}C have a significantly lower barrier for the migration of C and formation of C–C bond, i.e., C polymerization. The kinetically and thermodynamically aspects of the higher catalytic activity of Fe\textsubscript{3}C respect to Fe\textsubscript{5}C\textsubscript{2} have been proved by Mazzucco et al. [39]. Finally, the dissolution of excess C in catalyst particles during the milling ceases the CNT growth due to its poisoning with excess carbon [42] or the phase transformation of Fe\textsubscript{3}C to Fe\textsubscript{5}C\textsubscript{2} [39].

The XRD result of the sample that used Fe\textsubscript{0.7}Nb\textsubscript{0.1}Zr\textsubscript{0.1}Ti\textsubscript{0.1} catalyst (Fig. 3(b)) confirmed the formation of amorphous phase as well as its ability to act as a catalyst for CNT formation. In this sample, the dissolution of alloying elements (Nb, Zr, and Ti) in Fe matrix facilitate the diffusion of carbon in the amorphous catalyst.

HRSEM images of purified samples in Figs. 4(b) and 4(d) confirmed the formation of tubular products after 100 h of milling in both samples. Due to the formation of higher multiwall carbon nanotubes (MWCNTs) in the presence of Fe as well as higher amount of amorphous carbon in the presence of Fe\textsubscript{0.7}Nb\textsubscript{0.1}Zr\textsubscript{0.1}Ti\textsubscript{0.1}, the tubular morphology is more obvious at presence of Fe
catalyst (Figs. 4(a) and 4(b)) respect to the other sample (Figs. 4(c) and 4(d)). Similar results were confirmed in TG and Raman analyses at Figs. 5 and 6.

Fig. 4.

Fig. 5.

Fig. 6.

3.2 Quality determination of CNTs

To the best of our knowledge, Raman spectroscopy is a powerful technique for the characterization of CNTs types, i.e., single wall carbon nanotubes (SWCNTs) and MWCNTs. Generally, there are three types of Raman spectra during the CNTs characterization, i.e., radial breathing mode (RBM), first-order and second-order spectra. RBM is the out-of-plane phonon mode due to the coherent movement of C atoms in the radial direction and considered as the main sign of SWCNTs. The first order types were evolved in all graphite-like materials (such as MWCNTs) as a strong peak around 1580 cm\(^{-1}\) (G), named as high-frequency E\(_{2g}\) of the first-order mode. Additionally, bands around 1350 cm\(^{-1}\) (D) and 1620 cm\(^{-1}\) (D\('\)) were reported during the characterization of CNTs for the first-order type of Raman spectra. The characterization peak of the second-order Raman spectra observed in 2450 cm\(^{-1}\), 2705 cm\(^{-1}\) (G\('\)), 2945 cm\(^{-1}\) (D+G), 3176 cm\(^{-1}\) (2G) and 3244 cm\(^{-1}\) (2D\('\)) [43].

As shown in Figs. 5 (a) and (b), the formation of CNTs is confirmed in both samples. Accordingly, the evolution of a peak in a frequency lower than 200 cm\(^{-1}\) can be related to the symmetry RBM. It was necessary to note that the frequency of this peak is only a function of tube diameter (inversely proportional) and RBM cannot be usually detected for SWCNT with the diameter higher than 2 nm [44]. While, the outer sheet curvature of MWCNTs is similar to the graphene and the inner sheet is similar to SWCNTs [44]. The presence of RBM in high-quality MWCNTs composed of relatively small innermost tube diameter is possible as reported in the literature [45]. Since the lower frequency region structure in this study is broader than the bands arising from RBM (about FWHM 3-5 cm\(^{-1}\) for MWCNTs and 5-10 cm\(^{-1}\) for SWCNTs), it can be related to the structural defects as well as encapsulated catalyst particles in CNTs [44, 46] rather
than RBM. As shown, the first-order peaks of both samples overlapped due to the formation of carbon base impurities and imperfections [47, 48]. The Lorentzian function was employed to deconvolute the overlapping peaks and determine the type of every band (Fig. 6) [43].

The ideal CNTs show only one first-order band (G band) due to the lattice vibration of the ideal graphitic network with E2g symmetry around 1580 cm\(^{-1}\). While, in the presence of defects in CNTs network, additionally first-order bands (D or defect bands) were observed as a function of deviation from the ideal network. The relatively high intensity for D type peak belongs to D1 peak at the around of 1360 cm\(^{-1}\), corresponding to the lattice vibration of graphitic lattice with A1g symmetry. D2 is another first-order band at the about of 1620 cm\(^{-1}\) and revealed as a shoulder on G band. Similar to the G band; D2 band is a consequence of graphitic lattice mode vibration with E2g symmetry. The intensity of defects bands (D1 and D2) enhanced by increasing the wavelength of excitation as a consequence of resonance effects. The D1 band is believed to the defects in CNTs structure, e.g., the end of CNTs or foreign atoms in CNTs structure. While, D2 bands is a consequence of lattice vibration of graphene layers at the surface of the graphitic crystal [48].

The relatively high-intensity peak within the local maximum peaks at the around of 1500 cm\(^{-1}\) belongs to the other type of D3 bands. It was suggested that this band is belonged to the amorphous carbon presence, i.e., organic molecules, fragments or functional groups [48]. Another peak at the around of 1350 cm\(^{-1}\) exhibits a shoulder at 1200 cm\(^{-1}\) (named as D4 band) is related to the C-C and C=C stretching vibration of the polyene-like structure as well as sp2-sp3 bands. In abbreviation, D1, D2, and D4 denoted to the presence of defects and imperfections of the graphitic lattice. While the D3 band belongs to the amorphous carbon constituents [48]. As shown in Fig. 6, with the exception of the D2 band, all other types of Raman peaks are observed in both samples.

Dresselhaus [49] employed the ratio of I\(_{D1}\) to I\(_G\) as criteria for determination of CNT quality. Accordingly, the I\(_{D1}/I_G\) ratio is lower than 0.45 for high-quality CNTs. Fig. 6 shows the deconvolution of Raman overlapping peaks for the two samples. According to Fig. 6(a), the sample prepared by Fe\(_{0.7}\)Nb\(_{0.1}\)Zr\(_{0.1}\)Ti\(_{0.1}\) shows higher I\(_{D1}/I_G\) (0.62) with respect to the other sample, with I\(_{D1}/I_G\) equal to 0.45 (Fig. 6(b)). As shown in XRD spectra of both sample after 100 h of milling (Fig. 3), prolonged milling to 100 h caused to the amorphization of
Fe$_{0.7}$Nb$_{0.1}$Zr$_{0.1}$Ti$_{0.1}$. While, the other sample is still in crystalline phase. The amorphization mechanism of these alloys was investigated in the literature [37, 50-52]. It can be concluded that the presence of a catalyst in the amorphous phase lead to the lower quality of prepared CNTs due to the lower crystallinity of catalyst, as well as enhanced the possibility of defect formation in CNTs structure.

From one hand, the formation of amorphous Fe based alloy (i.e., Fe$_{0.7}$Nb$_{0.1}$Zr$_{0.1}$Ti$_{0.1}$) is easier than the formation of amorphous phase during the milling of pure Fe [38] and from the other hand, the metallic catalyst acts as a substrate for nucleation of CNTs [42]. Consequently, the higher crystallinity, as well as well-shaped of Fe respect to Fe$_{0.7}$Nb$_{0.1}$Zr$_{0.1}$Ti$_{0.1}$ through the growth of CNTs, facilitate the formation of graphite layers to grow more easily as a consequence of the dynamic interaction between the carbon and Fe catalyst.

3.3 Purity determination of CNTs

According to the literature, MWCNTs with high crystallinity show more oxidation resistant respect to the other carbon allotropes, i.e., C$_{60}$, diamond, graphite, and soot [44]. It was necessary to note that some other factors, e.g., the walls number of MWCNTs, the type and amount of residual catalyst, the imperfection within the walls, and the presence of other carbon allotropes affected on MWCNTs oxidation behavior. It is well accepted that the oxidation temperature of carbon allotropes can be arranged from low to high as amorphous carbons, SWCNTs, MWCNTs and graphitic particles [44]. But the oxidation temperature of various carbon allotropes has not been well defined as a distinct value. Typically, the oxidation temperatures of MWCNTs reported in the range of 400–750 °C [44]. While the amorphous carbon species (200–300 °C) and SWCNTs (350–500 °C) have lower oxidation temperatures [44].

To determine the purification of products using TG curves, the mass changes during the heating must be exaggerated as oxidation peaks by determination of mass derivation versus the temperature (dM/dT). Since, every oxidation peak is related to the oxidation of one/more products species, it was possible to use peaks number as a threshold for the purity of the product. Fig. 7 shows the weight loss and its derivative as a function of temperature for both samples. As shown the TG curve in Fig. 7(a), the prepared sample in the presence of Fe shows a severe weight loss (about 55 wt.%) up to 270 °C as an overlap. Further analysis of dM/dT curve confirmed the presence of two peaks in the range of 50 to 270 °C due to the water evaporation
and amorphous carbon oxidation [44]. By consideration of dM/dT of this sample, the next weight loss is situated between 270 °C to 490 °C and can be related to the oxidation of SWCNTs. The last weight loss in the range 550 °C to 740 °C is related to the oxidation of MWCNTs. In summary, the TG diagram confirmed 55.3, 5.3, and 16.8 percentages weight loss of this sample due to water evaporation/amorphous carbon oxidation, SWCNTs oxidation, and MWCNT oxidation, respectively. The balanced weight (22.6 wt.%) is due to the residual catalyst. It can be seen that the ratio of SWCNTs to MWCNTs in this sample is about 0.31.

Fig. 7.

Analysis of dM/dT curve in Fig. 7 (b), revealing that the sample prepared in the presence of Fe_{0.7}Nb_{0.1}Zr_{0.1}Ti_{0.1} shows a weight loss peak up to 150 °C due to the water evaporation/oxidation of amorphous carbon. A small increase in the weight was observed in TG diagram between 150 °C to 240 °C as an overlap (about 0.7 wt. %). These peaks can be related to the oxidation of trace residual metallic or unalloyed metallic catalyst during the heating. At the range of 240 °C to 490°C, a drastic weight loss was observed as a consequence of SWCNTs oxidation. The last weight loss is evolved at the range of 490 °C to 800 °C as a broad peak due to the oxidation of MWCNTs. In summary, the TG diagram of the sample prepared in the presence of Fe_{0.7}Nb_{0.1}Zr_{0.1}Ti_{0.1} confirmed the 1.5, 14.6 and 2 wt.% loss as a consequence of water evaporation/amorphous carbon oxidation, SWCNTs oxidation, and MWCNT oxidation, respectively. While, the balanced weight (82.6 wt. %) was due to the residual catalyst. The ratio of SWCNTs to MWCNTs for this sample is about 7.3, i.e., higher than the ratio of the sample prepared in the presence of Fe.

As shown in TG analysis (Figs. 7(a) and (b)), during the purification of products by acid leaching, the most remained catalyst of Fe was removed and the residual mass can be related to the encapsulated Fe as carbide in CNTs (about 22.6 wt.%). While, the acid leaching has a lower effect on Fe_{0.7}Nb_{0.1}Zr_{0.1}Ti_{0.1} in other sample. This confirmed by lower weight losses of TG diagram (remaining of 82.6 wt.% in ashes) [44]. The higher tendency of the sample prepared in the presence of Fe_{0.7}Nb_{0.1}Zr_{0.1}Ti_{0.1} for the preparation of SWCNTs can be related to the microstructure of the metallic catalyst. In this sample, from one hand, the amorphous structure of the catalyst induced unordered surface in metallic catalyst and from the other hand provide a smaller nucleation site for the preparation of CNTs. While, in the crystalline catalyst (i.e., Fe) the
larger plate of crystalline catalyst act as nucleation sites for the preparation of CNTs. Consequently, the formation of MWCNTs is preferred in the presence of Fe [3]. As shown in Table 3, the higher stability of the CNTs in the sample that prepared in presence of Fe, confirmed the higher quality of this type, respect to the other sample.

Table 3

3.4 Adsorption characteristics of CNTs

Physical form and the structure of CNTs induce large surface area, i.e., about 1315 m²/g by theoretical approximation, for discreet SWCNTs. However, the measured surface areas of CNTs are significantly lower [53]. The properties of CNTs is strongly related to the impurities, the method of production, debundling of fibers, surface functionalization, CNT diameter and the number of walls [53]. Adsorption of nitrogen at 77 K is a general technique to estimate the specific surface area (SSA) of the material. Nitrogen can adsorb in the prepared CNTs including the curved portion of the outer surface, the groove situation produced by CNTs conjunction or the other defects sites [31,53]. The inner core of CNT is another situation for adsorption of nitrogen. Similar space provides at a bundle of three or more CNTs. Since the diameter of nitrogen is 3.64 Å and higher than the 3.4 Å of the space of MWCNT, it was impossible to adsorb in the space between the MWCNTs layers. According to literature, the preparation process plays a key role in determination of the ratio of closed to open prepared CNTs. Generally, supposed CNTs prepared as closed structure unless undergo to further treatment such as milling to open the end of CNTs [53].

Fig. 8 shows isotherm of both samples. In the case of Fe as catalyst (Fig. 8(a)), the isotherm curve is similar to the behavior of non-porous or macroporous adsorbent [54], indicating the monolayer-multilayer adsorption type of prepared CNTs. Point B, i.e., the start of the linear section of the isotherm, is a sign of the completion of coverage of monolayer and the start of multilayer adsorption. Such observation confirmed by the low ratio of SWCNTs/MWCNTs of this sample. For the sample prepared in the presence of Fe₀.₇Nb₀.₁Zr₀.₁Ti₀.₁ as a catalyst in Fig. 8(b) evolved a hysteresis loop, indicating the occurrence of capillary condensation in mesoporous. The first section of Fig. 8(b) is related to the monolayer-multilayer adsorption. As shown, both samples have the same path in isotherm curves. Since this sample has a higher ratio of SWCNTs/MWCNTs respect to the other sample, can act as mesoporous material.
SSA is another characteristic of BET. The SSA of samples prepared in presence of Fe$_{0.7}$Nb$_{0.1}$Zr$_{0.1}$Ti$_{0.1}$ and Fe as a catalyst were measured to be about 198.31 m$^2$/g and 81.14 m$^2$/g, respectively. Since the residual catalyst particles decreased the SSA, the higher amount of SSA of the sample prepared in the presence of Fe$_{0.7}$Nb$_{0.1}$Zr$_{0.1}$Ti$_{0.1}$ with a higher amount of residual catalyst is correlated to the higher amount of SWCNTs of this sample. It is worth to note that, the SWCNTs have higher SSA respect to MWCNTs as a consequence of lower shell and the higher surface of SWCNTs respect to the MWCNTs [53]. It seems that the amorphous carbons act as filling agent and decreased the adsorption potential of prepared CNTs. Moreover, such amorphous phase diminished the amount of SSA as a consequence of lower surface area respect to CNTs, inducing lower adsorption and desorption rate [55].

4. Conclusion

In this study, the CNTs have been prepared by direct milling of Hexane as a precursor in the presence of two separate types of metallic catalysts (i.e., Fe and amorphous Fe$_{0.7}$Nb$_{0.1}$Zr$_{0.1}$Ti$_{0.1}$ alloy). By consideration of $I_{D1}/I_{G}$ ratio as criteria for determination of products quality, revealed that the employment of Fe was more appropriate than the using of Fe$_{0.7}$Nb$_{0.1}$Zr$_{0.1}$Ti$_{0.1}$ for the preparation of CNTs. While, by consideration of purity as criteria, the sample that was milled by Fe$_{0.7}$Nb$_{0.1}$Zr$_{0.1}$Ti$_{0.1}$ alloy was preferred. Also, milling in the presence of Fe$_{0.7}$Nb$_{0.1}$Zr$_{0.1}$Ti$_{0.1}$ produced higher SWCNTs respect to MWCNTs. While this behavior was reversed in the case of Fe. The BET surface areas are 198.31 m$^2$/g and 81.14 m$^2$/g for CNTs that prepared in the presence of Fe and Fe$_{0.7}$Nb$_{0.1}$Zr$_{0.1}$Ti$_{0.1}$ as a catalyst, respectively. The BET surface area increases with increasing the ratio of SWCNTs/MWCNTs. Since, the proposed method uses from simple and efficient technique, cheap and available raw materials to enhance the adsorption properties, it could be proposed as a good alternative for preparation of CNTs in such utilities.

References

[1] Iijima, S. “Helical microtubules of graphitic carbon”. Nature, 354, pp. 56-58 (1991).
[2] Terrones, M. “Science and technology of the twenty-first century: synthesis, properties, and applications of carbon nanotubes”. Annual review of materials research, 33, pp. 419-501 (2003).
[3] Wang, R., Xie, L., Hameed, S., et al. “Mechanisms and applications of carbon nanotubes in terahertz devices: A review”, Carbon, 132, pp. 42-58 (2018).
[4] Hou, P.-X., Liu, C. and Cheng, H.-M. “Purification of carbon nanotubes”, Carbon, 46, pp. 2003-2025 (2008).
[5] Krueger, A. “Carbon materials and nanotechnology”, John Wiley & Sons, (2010).
[6] Fazelirad, H., Ranjbar, M., Taher, M. A., et al. “Preparation of magnetic multi-walled carbon nanotubes for an efficient adsorption and spectrophotometric determination of amoxicillin”, Journal of Industrial and Engineering Chemistry, 21, pp. 889-892(2015).
[7] Sun, L., Wang, X., Wang, Y., et al. “Roles of carbon nanotubes in novel energy storage devices”, Carbon, 122, pp. 462-474 (2017).
[8] Rashad, A.M. “Effect of carbon nanotubes (CNTs) on the properties of traditional cementitious materials”, Construction and Building Materials, 153, pp. 81-101 (2017).
[9] Rahimian-Koloor, S. M., Hashemianzadeh, S. M. and Shokrieh, M. M. “Effect of CNT structural defects on the mechanical properties of CNT/Epoxy nanocomposite”, Physica B: Condensed Matter, 540, pp. 16-25 (2018).
[10] Mirmohammadi, S.A., Sadjadi, S. and Bahri-Laleh, N. “10 - Electrical and Electromagnetic Properties of CNT/Polymer Composites”, Carbon Nanotube-Reinforced Polymers: From Nanoscale to Macroscale, pp. 233-258, Elsevier, (2018).
[11] Wang, Y., Li, D., Sun, W., et al. “Synthesis and field electron emission properties of multi-walled carbon nanotube films directly grown on catalytic stainless steel substrate”, Vacuum, 149, 195-199 (2018).
[12] Gao, S., Liu, H., Xu, L., et al. “Hydrogen storage properties of nano-CoB/CNTs catalyzed MgH2”, Journal of Alloys and Compounds, 735, pp. 635-642 (2018).
[13] Liu, X. Q., Li, C. J., Yi, J. H., et al. “Enhancing the interface bonding in carbon nanotubes reinforced Al matrix composites by the in situ formation of TiAl3 and TiC”, Journal of Alloys and Compounds, 765, pp. 98-105 (2018).
[14] Yang, P., You, X., Yi, J., et al. “Influence of dispersion state of carbon nanotubes on electrical conductivity of copper matrix composites”, Journal of Alloys and Compounds, 752, pp. 376-380 (2018).
[15] Liao, J. and Tan, M.-J. “Mixing of carbon nanotubes (CNTs) and aluminum powder for powder metallurgy use”, Powder Technology, 208, pp. 42-48 (2011).
[16] Barzegar-Bafrooei, H. and Ebadzadeh, T. “Synthesis of nanocomposite powders of γ-alumina-carbon nanotube by sol–gel method”, Advanced Powder Technology, 22, pp. 366-369 (2011).
[17] Hosseini, A., Ghoreyshi, A. A., Pirzadeh, K., et al. “Enhancement of hydrogen storage on multi-walled carbon nanotube through KOH activation and nickel nanoparticle deposition”, Scientia Iranica, 24, pp. 1230-1240 (2017).
[18] Yousefzadeh, M., Amani-Tehran, M., Latifi, M., et al. “Morphology and Mechanical Properties of Polyacrylonitrile/Multi-Walled Carbon Nanotube (PAN/MWNWs) Nanocomposite Electrospun Nanofibers”, Scientia Iranica, 17, pp. 60-65 (2010).
[19] Laplaize, D., Bernier, P., Maser, W. K., et al. “Carbon nanotubes: The solar approach”, Carbon, 36, pp. 685-688 (1998).
[20] Su, Y. and Zhang, Y. “Carbon nanomaterials synthesized by arc discharge hot plasma”, Carbon, 83, pp. 90-99 (2015).
[21] Amans, D., Diouf, M., Lam, J., et al. “Origin of the nano-carbon allotropes in pulsed laser ablation in liquids synthesis”, Journal of Colloid and Interface Science, 489, pp. 114-125 (2017).
[22] Yilmaz, M., Raina, S., Hsu, S. H., et al. “Growing micropatterned CNT arrays on aluminum substrates using hot-filament CVD process”, Materials Letters, 209, pp. 376-378 (2017).
[23] Huang, T., Fang, H., Mao, S., et al. “In-situ synthesized TiC@CNT as high-performance catalysts for oxygen reduction reaction”, Carbon, 126, pp. 566-573 (2018).
[24] Guler, O. and Evin, E. “Carbon nanotubes formation by short-time ball milling and annealing of graphite”, Optoelectronics and Advanced Materials–Rapid Communications, 6, pp. 183-187 (2012).
[25] Chen, Y., Fitz Gerald, J., Chadderton L., et al. “Investigation of nanoporous carbon powders produced by high energy ball milling and formation of carbon nanotubes during subsequent annealing”, Journal of Metastable and Nanocrystalline Materials, 2-6, pp. 375-380 (1999).
[26] Chen, Y., Conway, M., Gerald, J. F., et al. “The nucleation and growth of carbon nanotubes in a mechano-thermal process”, Carbon, 42, pp. 1543-1548 (2004).
[27] Pierard, N., Fonseca, A., Konya, Z., et al. “Production of short carbon nanotubes with open tips by ball milling”, Chemical physics letters, 335, pp. 1-8 (2001).
[28] Jeong, S. W., Son, S.Y. and Lee, D.H. “Synthesis of multi-walled carbon nanotubes using Co–Fe–Mo/Al2O3 catalytic powders in a fluidized bed reactor”, Advanced Powder Technology, 21, pp. 93-99 (2010).
[29] Sano, N., Kinugasa, M., Otsuki, F., et al. “Gas sensor using single-wall carbon nanohorns”, Advanced Powder Technology, 18, pp. 455-466 (2007).
[30] Ghosh, S. and Padmanabhan, V. “Adsorption of hydrogen on single-walled carbon nanotubes with defects”, Diamond and Related Materials, 59, pp. 47-53 (2015).
[31] Chen, M., Yu, H.-W., Chen, J.-H., et al. “Effect of purification treatment on adsorption characteristics of carbon nanotubes”, Diamond and Related Materials, 16, pp. 1110-1115 (2007).
[32] Liu, F., Zhang, X., Cheng, J., et al. “Preparation of short carbon nanotubes by mechanical ball milling and their hydrogen adsorption behavior”, Carbon, 41, pp. 2527-2532 (2003).
[33] Pierard, N., Fonseca, A., Colomer, J. F., et al. “Ball milling effect on the structure of single-wall carbon nanotubes”, Carbon, 42, pp. 1691-1697 (2004).
[34] Khayati, G. R. and Janghorban, K. “The nanostructure evolution of Ag powder synthesized by high energy ball milling”, Advanced Powder Technology, 23, pp. 393-397 (2012).
[35] Zhong, Y., Chaudhary, V., Tan, X., et al. “Kinetic study of the mechanochemical synthesis of Nd2(Fe,Co)14B hard magnetic nanoparticles”, Journal of Alloys and Compounds, 747, pp. 755-763 (2018).
[36] Routray, K. L., Saha, S. and Behera, D. “Effect of CNTs blending on the structural, dielectric and magnetic properties of nanosized cobalt ferrite”, Materials Science and Engineering: B, 226, pp. 199-205 (2017).
[37] Khazaei Feizabad, M. H., Sharafi, S., Khayati, G. R., et al. “Effect of process control agent on the structural and magnetic properties of nano/amorphous Fe0.7Nb0.1Zr0.1Ti0.1 powders prepared by high energy ball milling”, Journal of Magnetism and Magnetic Materials, 449, pp. 297-303 (2018).
[38] Suryanarayana, C. “Mechanical alloying and milling”, CRC Press, (2004).
[39] Mazzucco, S., Wang, Y., Tanase, M., et al. “Direct evidence of active and inactive phases of Fe catalyst nanoparticles for carbon nanotube formation”, Journal of Catalysis, 319, pp. 54-60 (2014).
[40] Tsui, F. and Ryan, P. “Self-organization of carbide superlattice and nucleation of carbon nanotubes”, Journal of nanoscience and nanotechnology, 3, pp. 529-534 (2003).
[41] Jia, X. and Wei, F. “Advances in Production and Applications of Carbon Nanotubes”, Topics in Current Chemistry, 375, pp. 18 (2017).
[42] Kumar, M. “Carbon nanotube synthesis and growth mechanism”, Carbon Nanotubes-Synthesis, Characterization, Applications, pp. 147-170 (2011).
Mohammad Hossein Khazaei Feizabad received his Ph.D. in Nano Materials engineering from Shahid Bahonar University of Kerman (Iran) in 2019 and M.Sc. in Materials Science engineering at Department of Materials Science & Engineering, Shiraz university of Shiraz (Iran). He received his B.Sc. (Honor Student) in Materials Science from Sistan & Baluchestan University of Zahedan. He has published more than 15 scientific papers in the field of synthesis and characterization of
Gholam Reza Khayati is currently a faculty of Materials Science and Engineering at Shahid Bahonar University of Kerman. He received his Ph.D. in materials science from Shiraz University of Shiraz (Iran) and M.Sc. in Materials Science and Engineering at Department of materials Science & Engineering, Tehran University (Iran). He received his B.Sc. (Honor Student) in materials Science from Shahid Bahonar University of Kerman, in 2004. He has published more than 40 scientific papers in the field of synthesis and characterization of nanostructures materials.

Sorayya Pouresterabadi is received his M.Sc. in Materials Science engineering from Shahid Bahonar University of Kerman (Iran) and B.Sc. in Materials Science engineering at Department of Materials Science & Engineering, Shahid Bahonar University of Kerman (Iran) in 2018.

| Table captions |
|----------------|
| Table 1. Abbreviation of the researches that carried out by mechanical milling for the preparation and modification of carbon nano tubes. |
| Table 2. Practical parameters of milling and the details of planetary ball mill. |
| Table 3. Comparison of the initiation and oxidation temperatures of prepared samples in the presence of Fe and Fe$_{0.7}$Nb$_{0.1}$Zr$_{0.1}$Ti$_{0.1}$ as a catalyst. |
Figure captions

Fig. 1. FTIR spectra of as-prepared sample after 100 h of milling before purification in the presence of (a) Fe and (b) Fe$_{0.7}$Nb$_{0.1}$Zr$_{0.1}$Ti$_{0.1}$ catalyst.

Fig. 2. TEM images of as-prepared sample after 100 h of milling in the presence of (a) Fe and (b) Fe$_{0.7}$Nb$_{0.1}$Zr$_{0.1}$Ti$_{0.1}$.

Fig. 3. Comparison of the shape and position of Fe (110) peaks for (a) unmilled sample of Fe powders and milled sample in the presence of Fe catalyst and (b) milled samples of Fe$_{0.7}$Nb$_{0.1}$Zr$_{0.1}$Ti$_{0.1}$ with and without Hexane after 100 h.

Fig. 4. HRSEM images of the prepared sample in the presence of (a) Fe catalyst before purification, (b) Fe catalyst after purification, (c) Fe$_{0.7}$Nb$_{0.1}$Zr$_{0.1}$Ti$_{0.1}$ catalyst before purification, (d) Fe$_{0.7}$Nb$_{0.1}$Zr$_{0.1}$Ti$_{0.1}$ catalyst after purification.

Fig. 5. Normalization of Raman spectra by consideration of G band as criteria, the sample prepared in the presence of (a) Fe and (b) Fe$_{0.7}$Nb$_{0.1}$Zr$_{0.1}$Ti$_{0.1}$ catalyst.

Fig. 6. Deconvolution of Raman overlapping peaks for sample prepared in the presence of (a) Fe and (b) Fe$_{0.7}$Nb$_{0.1}$Zr$_{0.1}$Ti$_{0.1}$ catalyst.

Fig. 7. The weight losses and their derivatives as a function of temperature for sample prepared in the presence of (a) Fe and (b) Fe$_{0.7}$Nb$_{0.1}$Zr$_{0.1}$Ti$_{0.1}$ catalyst.

Fig. 8. N$_2$ adsorption isotherms for the CNTs: (a) prepared in the presence of Fe and (b) Fe$_{0.7}$Nb$_{0.1}$Zr$_{0.1}$Ti$_{0.1}$ as a catalyst.

Table 1.

| Ref.                  | Year | Preparation method  | Guler et al. [24] | Chen et al. [25] | Chen et al. [26] | Liu et al. [32] | Pierard et al. [33] | Proposed method   |
|-----------------------|------|---------------------|-------------------|------------------|------------------|------------------|---------------------|-------------------|
| Year                  |      |                     |                   |                  |                  |                  |                     |                   |
| 2012                  | 1999 | Mechanothermal process |                 |                 |                  |                  |                     |                   |
| 2004                  | 2003 | Mechanothermal process |                 |                 |                  |                  |                     |                   |
| 2004                  | 2004 | Chemical vapor deposition |               |                 |                  |                  |                     |                   |
| 2004                  |      | Mechanical milling |                   |                  |                  |                  |                     |                   |
| Precursor           | Graphite                          | Graphite                          | Graphite                          | Acetylene                  | Methane                  | Hexane                  |
|--------------------|-----------------------------------|-----------------------------------|-----------------------------------|----------------------------|--------------------------|--------------------------|
| Milling effect     | Ultra-active amorphous carbon     | Ultra-active amorphous carbon     | Ultra-active amorphous carbon     | Increase the surface area  | Increase the surface area| Synthesis and increase the surface area |
| Preparation        | 1600-1800                         | 1400                              | 1400                              | 700                        | 1000                      | Room temperature         |
| temperature (°C)   |                                   |                                   |                                   |                            |                          |                          |

Table 2.

| Characteristic         | Value                          |
|------------------------|--------------------------------|
| Vial rotation speed (rpm) | 350                           |
| Disc rotation speed (rpm)  | 250                           |
| Disc diameter (mm)       | 350                           |
| Vial diameter (mm)       | 90                            |
| Vial material            | Hardened chromium steel       |
| Vial capacity (mL)       | 150                           |
| Ball material            | Hardened carbon steel         |
| Parameter                          | Value                      |
|-----------------------------------|----------------------------|
| Ball diameter (mm)                | 15                         |
| Ball to powder weight ratio       | 20:1                       |
| Milling time (h)                  | 100                        |
| Rest time                         | 15 min for every 30 min milling |
| Milling type                      | Wet                        |
| Milling atmosphere                | Ar                         |
| Initial powder mass (g)           | 10                         |

| Type of catalyst | CNTs type | Initiation temperatures (°C) | Oxidation temperature (°C) |
|------------------|-----------|------------------------------|---------------------------|
| Fe               | SWCNTs    | 270                          | 410                       |
|                  | MWCNTs    | 550                          | 670                       |
| Fe$_{0.7}$Nb$_{0.1}$Zr$_{0.1}$Ti$_{0.1}$ | SWCNTs    | 240                          | 330                       |
|                  | MWCNTs    | 490                          | 680                       |
(a) 4000 3000 2000 1000
Wavenumber (cm⁻¹)

Transmittance%

- Hydroxyl groups (−OH)
- C-H stretching
- O-H stretching
- C=C bond
- COOH bonds
- Carbide formation

(b) 4000 3000 2000 1000
Wavenumber (cm⁻¹)

Transmittance%

- Hydroxyl groups (−OH)
- C-H stretching
- O-H stretching
- C=C bond
- COOH bonds
Fig. 3.
Fig. 4.
Fig. 5.
Fig. 6.
Fig. 7.
Fig. 8.