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Immobilization of Nuclear Waste Using Carbon Nanotubes Prepared by Laser Ablation in Liquid Method

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Abstract

Nuclear waste comes from many sources around us and considered as the main source of pollution which threats human's health and environments. Because of this, we must find a proper treatment, storage, and disposal method of nuclear waste over a long period of time. So, in this research the nuclear waste (Strontium hydroxide) was immobilized by Carbon nanotubes (CNTs). The Nd-YAG laser with wavelength 1064 nm, energy 750 mJ and 100 pulses was used to prepare CNTs. $Sr(HO)_2$ powder was added to the CNTs colloidal in calculated rate to get a homogenous mix of $CNTs\text{-}Sr(OH)_2$. The $Sr(HO)_2$ absorbs carbon dioxide from the air to form strontium carbonate so, the new solution is $CNTs\text{-}SrCo_3$. To dry the solution three drops from the new solution was placed on glass slides. To investigate the radiation damage on CNTs structure, the sample was irradiated with a beta source ($^{90}Sr/^{90}Y$) for different periods of time. The structure properties were measured using X-ray diffraction XRD, while the shape and size property was measured with scanning electron microscope SEM. The results showed homogenous distribution of nanoparticles with average particle size of about 20nm. The XRD spectra for all samples before and after β irradiation showed higher peaks at $2\theta = 25$ degree and when compared the XRD phase with standard card the resultant nanomaterial is strontium carbonite ($SrCo_3$). From SEM micrograph, $SrCo_3$ was well decorated on the surface of CNTs and there was not any remarkable difference in the corresponding due to beta radiation exposure.

Key words

Carbon Nanotubes (CNTs), nuclear waste, strontium hydroxide, laser ablation (PLAL).

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تثبيت النفايات النووية باستخدام انابيب الكاربون النانوية المحضرة بطريقة الاقتلاع بأستخدام الليزر

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الخلاصة

في محاولة للتخلص من النفايات النووية التي تشكل تهديدا على صحتنا وبيئاتنا. وجب علينا أيجاد طريقة مناسبة لتثبيت هذه النفايات النووية. لذلك، في هذا البحث تم تثبيت النفايات النووية (هيدروكسيد السترونتيوم) بواسطة أنابيب الكاربون النانوية (CNTs). استخدم في هذا البحث ليزر Nd-YAG بطول موجة 1064 نانومتر، بطاقة 750 mJ و 100 نبضة لتحضير CNTs. بعد ذلك تم إضافة مسحوق $Sr(OH)_2$ إلى محلول

CNTs النانوي بنسبة محسوبة للحصول على خليط متجانس من CNTs-Sr(OH)$_2$. Sr(OH)$_2$ الناتج يمتص ثنائي اوكسيد الكاربون من الهواء ليكون كاربونات لسترونتيوم لذلك، فان المحلول الجديد الناتج هو CNTs-SrCo$_3$. و لتجفيف المحلول وضعت ثلاث قطرات من المحلول الجديد على شرائح زجاجية. ولاستنتاج ضرر الاشعاع على سطح CNTs، شععت العينات بواسطة النظير المشع (^{90}Sr/^{90}Y) الباعث لجسيمات بيتا لفترات زمنية مختلفة. قيست خصائص السطح باستخدام حيود الاشعة السينية XRD بينما تم قياس خاصية الشكل والحجم عن طريق المجهر الإلكتروني الماسح SEM. اظهرت النتائج توزيع متجانس للجسيمات النانوية مع متوسط حجم للجسيمات حوالي 20nm. بينت اطياف XRD لجميع العينات قبل وبعد التشعيع ب β وجود قمم عالية تقريبا عند 2θ =25 درجة وعند مقارنة طور مع XRD مع البطاقة القياسية فان المادة النانوية الناتجة هي كاربونات السترونتيوم (SrCo$_3$). اظهرت الصورالمجهرية SEM، تزيين SrCOo$_3$ سطح أنابيب الكاربون النانوية CNTs بشكل جديد ولم يكن هناك أي اختلاف ملحوظ في المقابل بسبب التعرض لإشعاع بيتا.

Introduction

Nowadays nanostructure science is a broad and interdisciplinary area of research and development activity that has been growing explosively worldwide in the past few years due to their miraculous properties compared to macro-sized materials. Nanomaterial has spread in commercial use, including sunscreens, cosmetics, textiles, and sports equipment while, in medical science the nanomaterial can be used as drug delivery and biosensors. Industrial nanoscale is using in many applications for examples, nuclear fuels production, structural materials, separation techniques and waste management [1]. Carbon nanotubes (CNTs), have attractive properties that can be employed for nuclear waste management [2]. CNTs are classified into single-walled (SW) and multiwalled (MW), as a displayed in the transmission electron microscope image (TEM image) (Fig.1 a, b and c). The shape of the wall is a flat molecular network of carbon-atoms called graphene, the graphite is composed of overlaying graphene sheets. The CNTs end caps include pentagonal rings to fit the geodesic curvature. The inter wall distance in MWNTs is about a few angstroms [3].

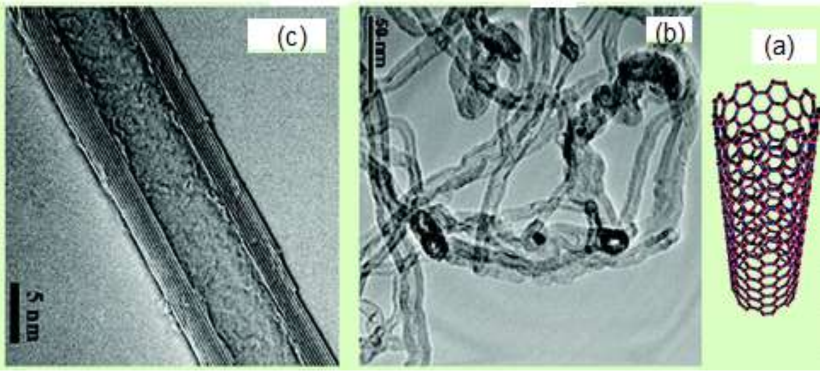


Fig.1: (a) TEM- image of the CNT structure, (b) "bundle" of CNTs in a raw form produced by (CVD) method and (c) TEM image of a MWNT up to ten walls can be counted [4].

There are several methods to produce CNTs, such as chemical vapor deposition (CVD), arc discharge and laser ablation in liquid. This type of materiel exists in physical forms: as a powder or bucky-paper. CNTs were used to adsorb several trace contaminants from water [5], and also was suggested to be used as a super absorbent for dioxin removal. There is still a lacking accommodating of the basic physics and chemistry of the interaction between a CNT surface and adsorbed species [6].

In this study, we briefly seeks the possibility of using CNTs to immobilize nuclear waste (Strontium hydroxide) to prevent leaching ions to the environment which causes nuclear waste pollution that effects human beings and environment by taking into consideration the three basic concepts to radioactive waste treatments. These are "concentrate and contain", "delay and decay" and "dilute and disperse". The study focused specifically on the first concept "Concentrate and contain" which is the process where the radioactive waste is reduced to a small volume and stored indefinitely, so that the activity is not released to the environment [7].

Strontium is a one type of alkaline-earth metal, soft and silver-yellow. Its physical and chemical properties are like that of calcium and barium. The strontium has three allotropic crystalline forms, one of them ^{90}Sr with a half-life of 29.1 years. ^{90}Sr is used in many fields such as in industry to measure the thickness of paper, rubber, plastic, and metal foils. While in medical applications, it is used for the treatment of some eye and skin diseases. The most important applications of ^{90}Sr is as isotopic energy source. It is also used in various research applications, including radioisotope thermoelectric generators (RTG) or for nuclear auxiliary power (SNAP) devices to power remote such as satellites, weather stations, and navigational buoys [8].

Strontium effects

In the environment strontium occurs naturally, to make up approximately 0.02–0.03% of the earth's crust. The major commercial strontium minerals are celestite ($SrSo_4$) and strontianite ($SrCo_3$). While the minor component of strontium may occur deposits with other mineral or associated with rock salt like limestone and dolomite [8]. The radioactive type of strontium, like ^{89}Sr and ^{90}Sr, does not occur spontaneously in nature, but they occur as a result of human activities, i.e. they are produced by nuclear fission. ^{90}Sr is a long-lived fission product, it is an unstable nuclide that decays by emitting beta particle to be converted into stable zirconium. ^{89}Sr and ^{90}Sr are produced in limited quantities from scientific and industrial applications. Low activity ^{90}Sr is used for commercial and medical purposes. It is placed in double walled capsules to prevent radiation hazard due to the radiation produced from radioactive Strontium.^{90}Sr also used for a scientific purposes such as in the United States Department of Energy national laboratories "Pacific Northwest National Laboratory" it's present one of the largest sources of ^{90}Sr in the world [9]. For industrial purposes, the United States uses strontium to produce glass, ceramics and on the television faceplate glass. All color televisions and other devices that containing cathode-ray tubes (CRT) contain the strontium in the faceplate glass of the tube to block the emitted x-ray [10]. The other type of non-radioactive Strontium is a Strontium hydroxide, $Sr(OH)_2$, which is used sometimes to extract sugar from molasses because it forms a soluble saccharide from which the sugar can be easily regenerated by the action of carbon dioxide [11].

Peoples can be exposed to low levels of (radioactive) strontium on breathing air or dust, drinking water, eating food, or by contact with soil that contains strontium. For most people, absorption of strontium is moderate. And not all types of strontium are considered as dangerous, only its compound (strontium chromate) offers danger to human health, even in small quantities. The toxic chromium that it contains is considered the one of the important reasons to cause the lung cancer, but the risks are greatly reduced if safety measures are followed when constructing buildings [12]. For children exceeding the limit dose of strontium, it may cause a health risk, because it can cause problems with bone growth. Strontium salts are not known to cause skin rashes or other skin problems [13]. Generally the radioactive strontium is a much more health risk than stable strontium [14].

Experimental work

CNTs has been prepared using the pulsed laser ablation in liquid technique (Fig.2). The laser used is Nd:YAG of a wavelength of 1064 nm at frequency 1Hz.

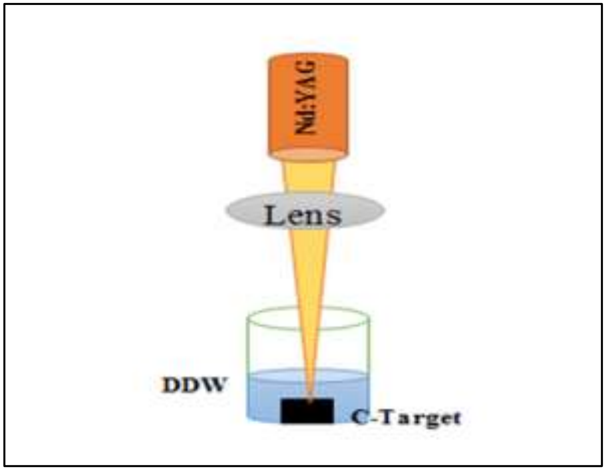


Fig.2: A schematic diagram of CNT-NPs preparation by the laser ablation in liquid technique.

To prepare CNT-NPs the Nd-YAG laser is focused using a lens onto the C-target. The C-target was placed in a glass container. That is immersed in 1ml of di-ionized water (DDW). All processes are done at room temperature. The Nd:YAG laser energy (750 mJ and the number of pulses=100) and the distance between the lens and target equal to 4 cm. After preparation CNT-NPs, 0.43g of $Sr(OH)_2$ was diluted in 1 ml of CNT-NPs then, the new mix putting in the centrifuge for 2 minutes to get a homogenous mix of CNTs-$Sr(OH)_2$. 3 drops of this homogenous mixture were dropped one by one, onto a glass plate placed on a heater of temperature (60-80) C^o to dry the samples. The CNT-NPs were prepared at the University of Technology, at the laser lab.

To study the effect of nuclear radiation, after low and medium term storage, on the structure properties of carbon nanotubes, the sample were irradiated with Beta particles emitted from radioisotope $^{90}Sr/^{90}Y$ radioisotopes source. The source is of 0.6 Ci activity and exposure dose 6×10^4 Gy/hr. The samples were placed at 15 cm from the source, and the samples were irradiated for different period of time as shown in Table 1.

Table 1. The time of exposure to gamma rays and the doses of irradiation Beta particle.

Dose rate	Time of exposure samples of Beta radiation
$\boldsymbol{6 \times 10^4 Gy/hr}$	1 hr
$\boldsymbol{1008 \times 10^4 Gy}$	168 hr

Beta irradiation process was done in University of Baghdad, College of Science, Department of Physics, in Nuclear Laboratory.

Results and discussion

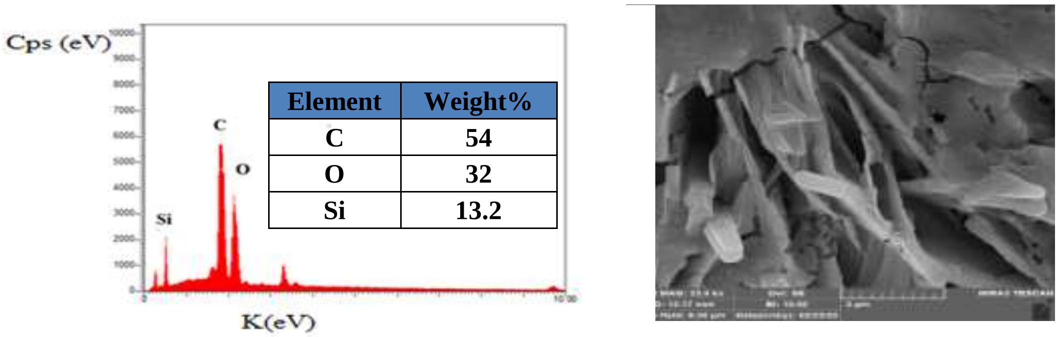
One way-to dispose nuclear waste is by long-time storing until it decays to its safe levels it must be immobilized during this time. This research focused on the effect of beta radiation on the samples of carbon nanotubes that were used to immobilize nuclear waste $Sr(OH)_2$, the research aims to find the effect of radiation on the physical properties (structure properties) of carbon nanotubes wall, which stimulates changes of the carbon nanotubes, that were used to immobilize nuclear waste and evaluated the damage caused by the radiation on the CNTs-microstructure to estimate the size of the risk resulting from storing waste in this way. The second aim of this research is to find a new way to reduce the volume of nuclear waste by converting it into a nanomaterial.

The impact of radiation on CNTs is of 3-types: the atomic displacement by momentum and energy transfer; second, ionization and charge trapping; and the third is the photochemical effects. However, the fewer effect on the net damage depends on the type, the energy of the radiation and the total dose. Previous studies have shown that the bonds in carbon nanotubes are strong because they are in the form of a network of nanotubes, which showed resistance to radiation damage.

To investigate the effect of beta irradiation on the surface and texture of the samples x-ray diffraction analysis (XRD) and scanning electron microscopy (SEM) was employed.

CNT-NPs characteristics

The morphology of the prepared CNTs was examined using SEM. The chemical composition of the resulted NPs was calculated by energy dispersive spectroscopy EDS (Fig.3).



Element	Weight%
C	54
O	32
Si	13.2

A **B**

Fig.3: (A) SEM image for CNTs at laser energy 750mJand no. of pulses 100pulse and (B) EDS spectrum and weight percentage of elements in carbon nanotubes sample.

The CNTs- structure was tube-shaped containing spherical NPs of size in the range 15-25 nm. The laser energy is an essential parameter that affects the structure of carbon nanotubes prepared by laser ablation technique. The mechanism of nanotube generation in laser ablation of graphite sample in DDW start by photo-thermal operation. Then, the target temperatures increases as the number of pulses increases leading to melting and finally the spread of ablated particles from the target. The strong confinement of Plasma happens due to the change of the liquid dynamics causing expansion and ablation of materials. The Shockwave generated have high pressure that is generated between the target and the liquid [15]. Fig.3, displays the interaction of the chemical elements inside the solution which depends on the behavior of the target structure and the excitation source and the Wight percentage for each element. The EDS- results clarified the existence of C, O, and Si (which is related to glass plate).

X-ray diffraction (XRD)

The technique that was used to characterize the crystal composition, grain size, and preferring orientation in polycrystalline or powdering solid samples was the X-ray diffraction (XRD). X-ray diffractometer was used to investigate the amorphous phase or crystalline phase for the carbon nanotubes that contains strontium hydroxide as nuclear waste. The X-ray diffraction data were recorded by using Cu Kα radiation (1.5406 A) and the intensity peaks were calculated by the 2θ of the range (20°–80°). For all samples, the diffraction peaks appeared at angles 2θ of 25.39°, 31.51°, 45.28°and 50.22° corresponding to the reflection from the (100), (002), (111) and (200) crystal planes, respectively.

For all samples, the XRD spectra showed that indicates the presence of the crystalline phase which is strontium carbonite. It was clear from XRD spectra for all the samples that the location of the peaks was not affected by increasing the radiation dos. The appearance of the higher peaks at 2θ = 25 degree signify that the phase of material has not changed. In other words, the absence of a new substance, i.e. the immobilization material represented by carbon nanotube was not affected by radiation, as shown in Figs.4, 5 and 6.

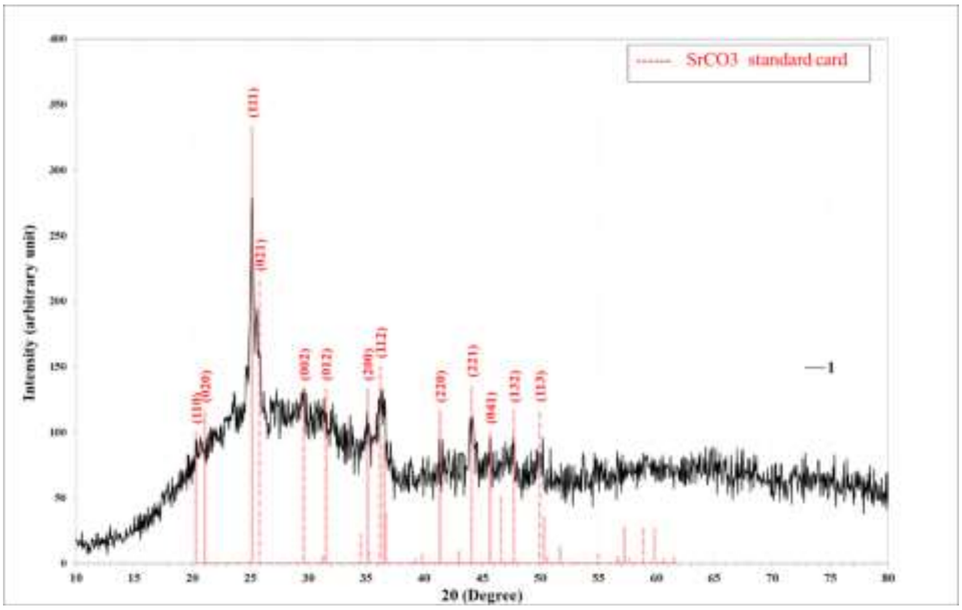


Fig.4: X-ray diffraction CNTs-Sr(OH)$_2$ before exposure to Beta irradiation.

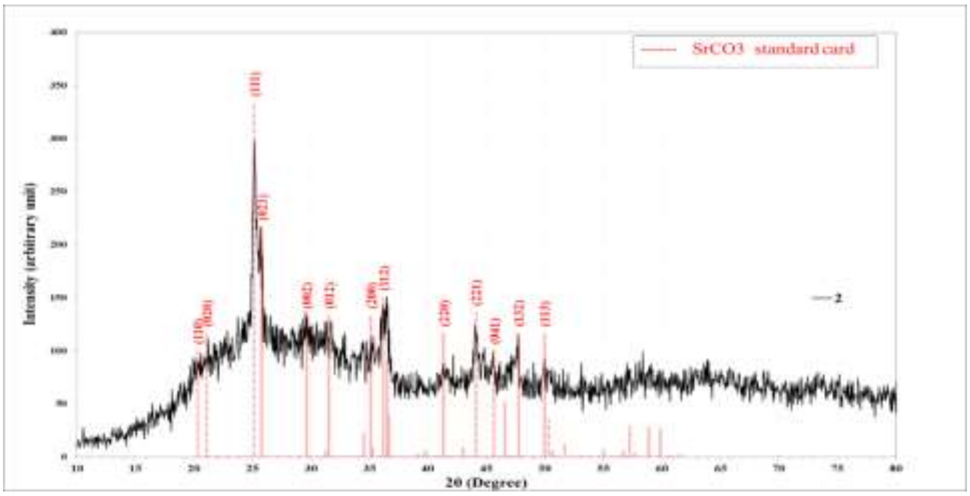


Fig.5: X-ray diffraction CNTs-Sr(OH)$_2$ after exposure to1hr Beta irradiation.

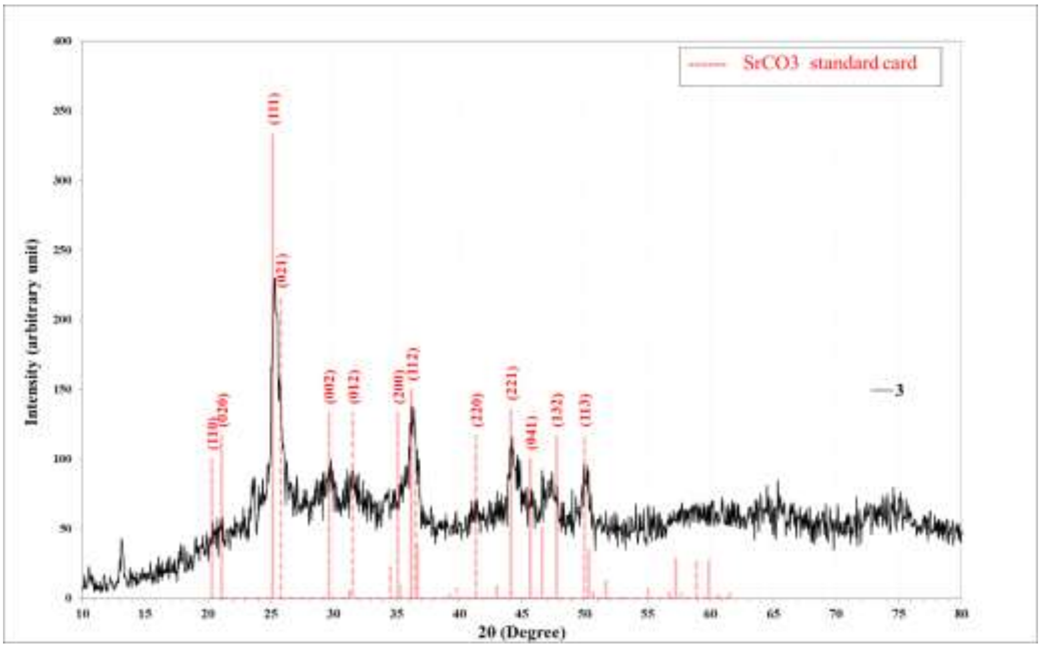


Fig.6: X-ray diffraction CNTs-Sr(OH)$_2$ after exposure to168hr Beta irradiation.

By comparing the results of the XRD spectra with the standard card, it was found that the resulting phase was strontium carbonate phase due to the nature of strontium hydroxide. The transformation of strontium hydroxide to strontium carbonate is because it absorbs carbon dioxide from air.

The resultant strontium carbonate is a white, tasteless and odorless powder. A carbonate, is a weak base so, it's reactive with acids. But otherwise it's stable and safe to work with. It is practically insoluble in water (1 part in 100,000). While the solubility increased significantly if the water is saturated with carbon dioxide, to 1 part in 1,000 [16].

Scanning electronic microscope (SEM)

Scanning electron microscope was utilized to study the surface morphology of carbon nanotubes, which contains strontium hydroxide as nuclear waste, before and after irradiation to reveal the possible textural transformation due to radiation. The SEM device was ARYA Electron Optic operating at 15 kV, beam current 10.000 nA, and magnification 12500. The SEM micrograph with different magnification of the samples (figs.7, 8 and 9), show formation of carbon nanotubes that were prepared using a laser ablation method. Moreover, it was found that CNTs-Sr (OH) 2 are well decorated on CNTs surface. SEM micrograph of the samples before and after beta irradiation showed that the carbon nanotube structure was not affected by beta radiation (no structure destruction) and that the nuclear waste Sr(OH)$_2$ was immobilized on the surface of carbon nanotubes. Although, there was a slight change in the diameters of nuclear waste, the diameter increased with increasing the radiation exposure time but, the average diameter remained fixed at 20 nm, the increasing in nuclear waste diameter is not an indication of the inefficiency of carbon nanotubes to immobilize waste. In all three SEM micrographs, CNTs-Sr(OH)$_2$ we're well decorated on the surface of CNTs and there was not no remarkable difference after beta irradiation. These results confirm (as seen in the SEM micrographs 5, 6 and 7) that nuclear waste Sr(OH)$_2$ was attached to the CNT surface and formed CNTs-Sr(OH)$_2$ nano-composites. The nuclear waste may be immobilized on the CNTs surface due to Van der Waals interactions.

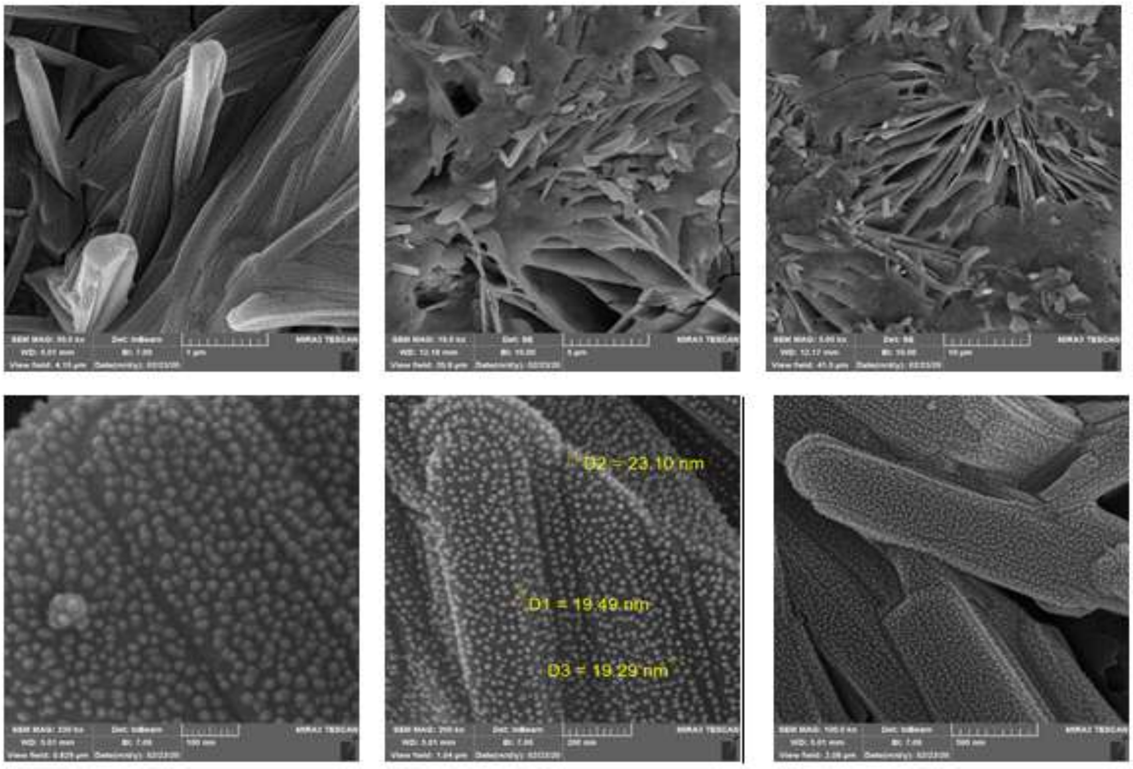


Fig.7: The SEM micrograph for CNTs-Sr$(OH)_2$ sample before exposure to Beta irradiation at different magnification.

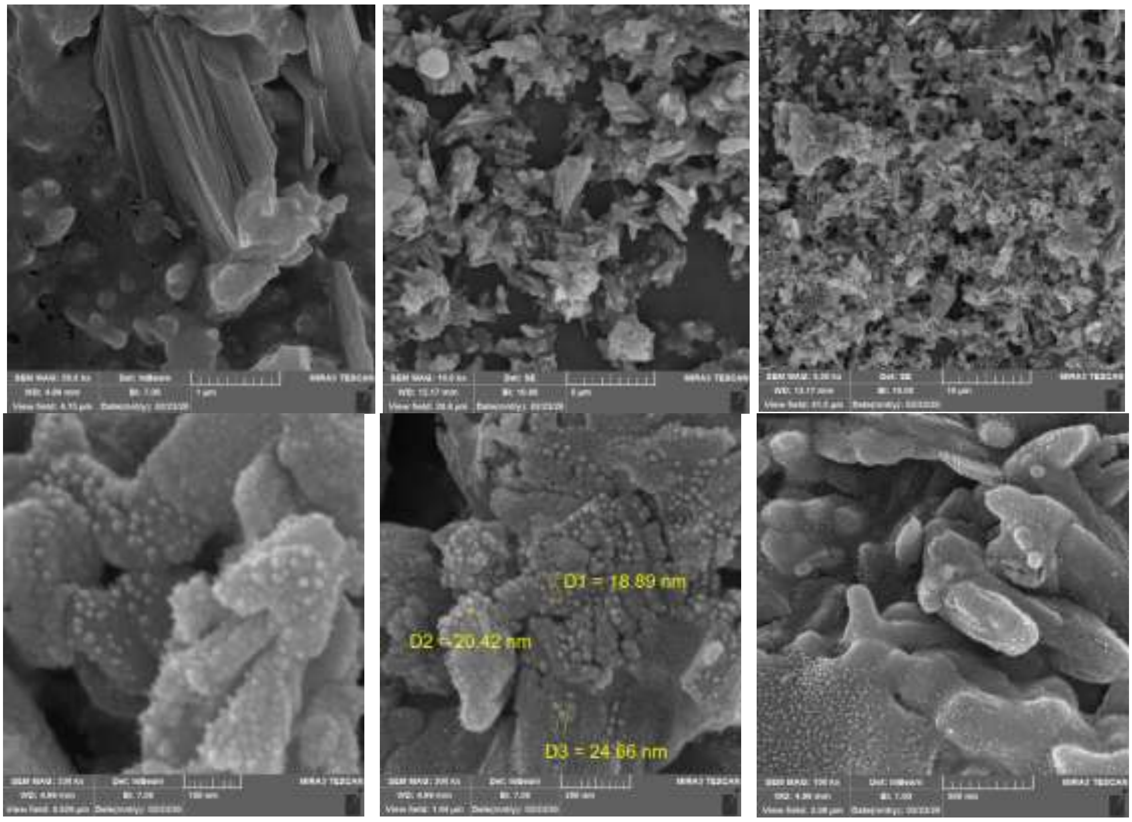


Fig.8: The SEM micrograph for CNTs-Sr$(OH)_2$ sample after exposure to 1 hr Beta irradiation.

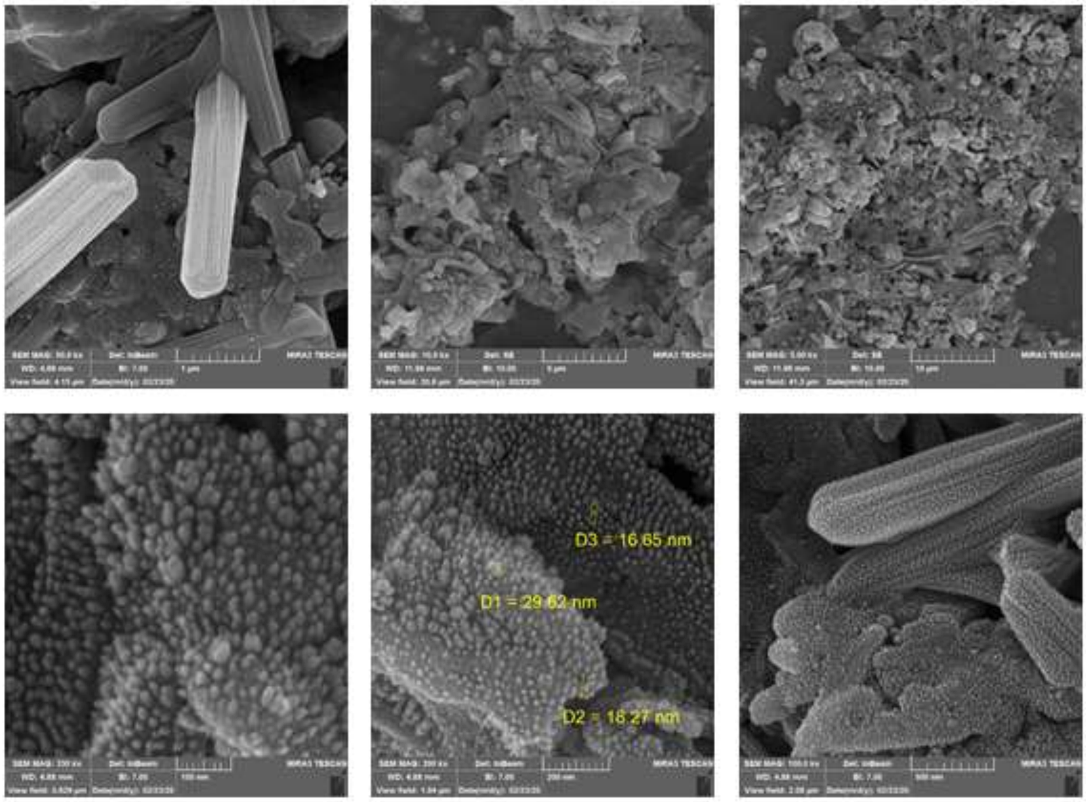


Fig.9: The SEM micrograph for CNTs-$Sr(OH)_2$ sample after exposure to 168 hr Beta irradiation.

Conclusions

The only way to dispose nuclear waste is by storing the radioactive waste to decay to safety radiation levels. Therefore, one must find a suitable method to immobilize nuclear waste to prevent leaching ions to the surroundings and so as to prevent radiation hazards that may threatens environment and humans. In this research the nuclear waste (Strontium Oxides) was immobilized by Carbon nanotubes (CNTs). Carbon nanotubes were produced using laser ablation technique which is regarded as safe, quick and are produced at room temperature.

As displayed, by the X-ray diffraction XRD and scanning electron microscope (SEM) it is a clear that carbon nanotubes initially indicates to be very good material to immobilize nuclear waste, but a mechanistic understanding of radiation damage to carbon nanotubes has not been reached, partially due to the limited number of studies to date and partially due to the complexities arising from tests with different methods to prepare carbon nanotubes and the different materials that must be added to support or strengthen the composition of carbon nanotubes (and structures), radiation sources (alpha, beta and gamma radiation), and test conditions (pressure and temperature).

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