

Full length article

Multi walled carbon nanotube decorated cadmium oxide nanoparticles via pulsed laser ablation in liquid media

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HIGHLIGHTS

- Decoration of MWCNTs with metal oxide nanoparticles.
- Pulsed laser ablation in liquid media technique is used to make a decoration of MWCNTs.
- Metal oxide nanoparticles are fabricated and decorated MWCNTs in just one step.

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ABSTRACT

A simple synthesis method to produce multi walled carbon nanotubes (MWCNTs) decorated with metal oxide nanoparticles (e.g., cadmium oxide (CdO)) has been described by pulsed laser ablation of Cadmium sheets immersed in precursor solution from functionalized MWCNTs. The as-prepared of decoration composites of MWCNTs with CdO nanoparticles were characterized by Fourier transform infrared spectroscopy, UV–Visible spectrophotometer, transmission electron microscopy, scanning electron microscopy, Energy dispersive X-ray spectroscopy, and X-ray diffraction, which revealed that these decorations of CdO nanoparticles were uniformly distributed on the surface of MWCNTs with diameter about 22 nm. Also, the optical properties of MWCNTs were successfully enhanced after decoration via metal oxide nanoparticles. This work could be used to decorate MWCNTs via different metals oxides via pulsed laser ablation in liquid media technique to produce interesting new properties of MWCNTs composite.

1. Introduction

Recently, many researchers put a lot of attention for doping, mixing or decorating the elements with each other to produce a new compound or composite had more valuable properties. These properties could be represented as a mixture of all used precursor elements and could be changed based on the used precursor elements [1–3]. The importance of doping materials with each other open the way to the advance in technologies of the next generation in all fields. Especially when the attention are focused on nanoscale elements, the very promising class of materials, It is expected that more development on the all fields because they change the physical, chemical, electrical, optical, and mechanical properties completely as compared to their bulk phase [4,5].

Among these nanomaterials, there are, especially, metal oxides which are very wanted materials in all sectors of industry. From these oxides, cadmium oxide (CdO), an important n-type semiconductor, has high electrical conductivity, high carrier concentration, high

transparency in the visible range of the electromagnetic spectrum, and relatively inexpensive. All of that lead to being nano CdO appeared enormously in the several application fields such as solar cells, photo-transistors, photodiodes, transparent electrodes, gas sensors [6–8].

In another way, Multiwall carbon nanotubes (MWCNTs) provide special and extraordinary physicochemical properties such as mechanical strength, high surface to volume ratio, excellent electrical conductivity, flexibility and high chemical stability [9–11]. That entire make MWCNTs advocated for a plethora of diversified innumerable applications like nano-electronics, sensors, electro-chemical, field emission, X-ray generation, nano-tweezers, chemical force microscopy (CFM), storage of energy [12,13].

In the combination of CdO and MWCNTs, it has been considered to be a promising way to improve their electrochemical performance via their composite form [7,14]. In 2014, Feng et al. prepared CdO/Carboxylated MWCNTs nanocomposites via chemical precipitation method [15]. Followed by Glennon et al. prepared CdO/MWCNT by

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electrochemical deposition [16].

There are several methods are used so far to synthesis Metal oxide/MWCNTs composite like co-precipitation method [17], chemical vapor deposition [18], hydrolysis [19], and calcinations [20]. In general, from the nanofabrication method, Laser ablation in liquid media could be represented one of promising technique, but till now, no scientific report was mentioned that this technique could be used for the mission of production nanoparticles and decoration the tubes of MWCNTs. Actually, this method could represent one of the fascinating ways for producing very high-quality nanoparticles. That is due to the advantages of this technique as [21–23]:

- Desired chemical composition could be produced with the same schematic method without any further complicated preparation steps or using expensive solvents.
- Different laser ablation parameters could be used for controlling the shape and size nanostructures.
- The produced nanostructures have high stability without using surfactant or stabilizer based on extremely high colloidal stability for the synthetic process.
- This method could be represented as green synthetic method based on the nanostructure preparation is done inside liquid media without production of any fumes or gas. So, there is no side effect to the environment or humans.

Herein, the authors describe a method to prepare nanocomposites structure from MWCNTs decorated by CdO nanoparticles via a novel way. The novelty appeared in use pulsed laser ablation on Cd-sheet immersed in ultrapure water containing functionalized MWCNTs to produce and decorate the tubes of MWCNTs by metal oxide (e.g. CdO) in just one step. Then the produced nanocomposites observed by techniques of SEM, TEM, XRD, EDX, UV–Visible spectrophotometer and FT-IR employed for investigation of structural, optical, and morphological investigations.

2. Materials and methods

2.1. Used materials

Cd metal granulated sheets ($\geq 99.9\%$) were purchased from BDH chemical Ltd pool, England. The solvent of Nitric acid (HNO_3) and Hydrochloric acid (HCl) are obtained from El-Nasr Pharmaceutical Chemicals Company, Egypt. All reagents were analytical grade and used without further purification.

2.2. Functionalization of MWCNTs

Firstly, MWCNTs were purified from any impurities by washing with 5 M HCl solution to make sure that there are not any remaining catalyst from the preparation process of MWCNTs. Secondly, the surface of tubes was functionalized by oxidation with HNO_3 solution (65%). Typically, 150 mg of MWCNTs was added to 150 ml HNO_3 under refluxing and stirring for 6 h at 85°C followed by washing with ultrapure water several times until the pH reached to 7. Finally, the functionalized MWCNTs were dried at 90°C overnight.

2.3. Preparation of nano composite

CdO/MWCNTs nanocomposites structures were synthesized by pulsed laser ablation of cleaned Cd sheets (99.99%) in liquid media from functionalization MWCNTs as shown in Fig. 1. The target was put at the bottom of a glass vessel filled with 5 ml of the used solution. The laser beam was focused on the surface of the Cadmium target. The liquid depth above the target surface was about 0.7 mm. An acoustic optically Q-switched Nd-YAG laser ($\lambda = 1064\text{ nm}$) with 7 ns pulse duration, was used and adjusted to operate at 10 Hz repetition rate

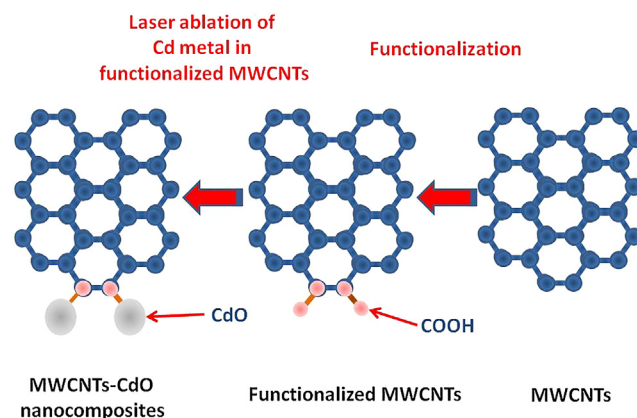


Fig. 1. Schematic diagram of functionalization of MWCNTs and the decoration by CdO nanoparticles using pulsed laser ablation in liquid media.

(Continuum laser, PRLI 8000, Electro-optics, Inc., Wyandotte, MI, USA). The laser pulse energy applied on the target was 60 mJ. The laser beam was focused on the target surface using a lens of focal length of 70 mm. The ablation was carried out for 10 min. During this process, the solution was stirred by mechanical rotator to enhance the growth of the produced nanocomposites

2.4. Characterization techniques

A Fourier-transform infrared spectroscopy (FT-IR) was employed to demonstrate the chemical composition of prepared samples using KBr method by JASCO 6100 spectrometer, Japan. The transition spectra of the used materials were studied by a Jasco 570 UV–VIS–NIR spectrophotometer, Japan. The morphology and topography of the prepared samples were analyzed by field emission scanning electron microscopy (FE-SEM) by Quanta FEG 250, Republic of Czech and high-resolution transmission electron microscope (HRTEM) of the type JEOL-JEM-1011, Japan. The crystalline structure of samples was characterized using X-ray (XRD) diffractometer (Schimadzu 7000, Japan). The chemical composition of the prepared samples was investigated Energy dispersive X-ray spectroscopy (EDX) measurements using TEAM® software attached to scanning electron microscopy on a Quanta FEG 250 electron microscope. The ultra structure images of SEM and TEM were solved via using open access ImageJ simulation program to gain more information.

3. Results and discussions

3.1. Optical analyses

Fig. 2 shows the UV–visible transition spectra of MWCNTs, their functionalization and their composite with CdO nanoparticles. As can be seen, the MWCNTs have a characteristic peak appeared around 250 nm for MWCNTs, which is in good agreement with the value reported in the previous literature [24,25]. After functionalization process, the transition peaks around 250 nm became stronger and red shifted due to the electronic transition of $n \rightarrow \pi^*$ of a pair of non-bonding electrons ($=\text{O}$) of the carboxylic groups ($-\text{COOH}$) attached to the walled surface of MWCNTs, showing that the functionalization was efficient for MWCNTs to be modified. This observed red shift in the characteristic band of MWCNTs indicates the existence of more carboxylic groups on the surface of MWCNTs. In another way, there is a blue shift in the case of formation CdO-MWCNTs nanocomposites. That is due to quantum confinement property of CdO nanoparticles and $n \rightarrow \pi^*$ between the n-orbital of the oxygen species of CdO and π^* of MWCNTs [6].

The FT-IR spectra of MWCNTs, their functionalization, and

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