Single-step electrochemical synthesis of zinc oxide nanoflowers and multi-walled carbon nanotubes nanoconjugates

Ishu Singhal and B. S. Balaji
School of Biotechnology, Jawaharlal Nehru University, Delhi 110067, India
ishu_singhal@yahoo.com

Abstract. Zinc Oxide (ZnO) nanoparticles are investigated for use in various biomedical applications such as in the treatment of cancer because of their high targeting potential. Zinc oxide nanomaterials when conjugated with multi-walled carbon nanotubes (MWNT) show enhanced properties. In our present work, nano-conjugation between zinc oxide nanoflowers (ZnO NFs) and multi-walled carbon nanotubes has been successfully achieved. Here, we have used a two-electrode electrochemical setup for preparation as well as conjugation between ZnO nanoflowers and MWNT. The x-ray diffraction, Raman spectra, and transmission electron microscopy imaging for the ZnO NFs/MWNT nano-conjugate shows the successful synthesis of the nano-conjugate. The electrochemical method used here is a single step, economical, and without the use of any additional surfactant or capping agents. The only use of pure zinc electrodes as a precursor material favors high purity, easy and a less time-consuming purification process.

1. Introduction
Zinc Oxide (ZnO) nanomaterials are known to possess unique physical, chemical, optical and antimicrobial properties due to their high surface area to volume ratio. Owing to their remarkable properties, zinc oxide nanomaterials are used in many types of applications, like UV-absorbers in the textile industry due to their optical properties [1], in agriculture to improve the yield and quality of crops [2], as food additives and in the food packaging industry due to antimicrobial property [3], in sunscreens in the cosmetics industry as they not only scatter but also reflect ultraviolet A and B radiations [4], ZnO nanoparticles are investigated for use in various biomedical applications such as in the treatment of cancer because of their high targeting potential [5, 6] and so on. Zinc oxide nanomaterials when conjugated with multi-walled carbon nanotubes show enhanced properties. Decoration of ZnO quantum dots on multi walled carbon nanotubes were used as a good photosensitive UV photodetector due to their photo-elastic, high performance and photo-detection properties [7]. The ZnO nanomaterials when conjugated on multi walled carbon nanotubes (MWNT) protect the electronic properties of MWNT and can be used as a highly sensitive biosensor for the detection of carcinoma [8], malaria [9] etc.

Different methods have been used for the synthesis of ZnO/MWNT nano – conjugate in the past. Kaur et al. synthesized ZnO/MWNT conjugates by electrostatic interaction between ZnO functionalized with an amine group and MWNT functionalized with chlorine group [10]. Jiang et al. modified MWNT with sodium dodecyl sulphate (SDS) resulting in a negative charge on the MWNT surface, thereby enabling ZnO to be deposited via non – covalent interactions [11]. The sol-gel method has also been used for the synthesis of ZnO nanoparticles conjugated with MWNT by using amine-functionalized multi-walled carbon nanotubes [12]. Microwave-assisted synthesis has also been achieved by irradiating the mixture of zinc acetate dehydrate and MWNT [13]. Pulsed laser deposition was used by Gupta et al. for the preparation of ZnO nanocrystals which were then deposited on the MWNT surface using the hydrothermal method [14]. ZnO/MWNT conjugate was also prepared using atomic layer deposition, where ZnO was synthesized using zinc dust followed by coating on the outer and inner surface of MWNT [15].
All of these methods have resulted in the successful synthesis of zinc oxide nanomaterials conjugated with multi-walled carbon nanotubes. However, all of these synthesis methods are multistep and require costly materials such as precursor reagents, capping agents, surfactants, etc. and instruments. Here we are reporting for the first time, one-step electrochemical synthesis of zinc oxide nanoflowers (ZnO NFs) with multi-walled carbon nanotubes. In our developed electrochemical method, a pure zinc electrode is used as a precursor, therefore, no need for any additional metal salt and stabilizers. Additionally, the process can be optimized at a high current density to achieve high output yield. The conjugate prepared was characterized using transmission electron microscopy, X-ray diffraction, and Raman spectroscopy. All these characterization techniques showed and confirm the successful synthesis of ZnO NFs/MWNT nano-conjugate.

2. Material and methods
For the synthesis of the conjugated nanocomposite, a two-electrode electrochemical setup was used. The zinc electrodes, with a dimension of 70 mm length and 6 mm diameter, were spaced 40 mm apart and fixed. The electrolyte solution was prepared by adding 2 M sodium chloride (Merck) in 200 mL double distilled de-ionized water. 50 mg of MWNT is added in the prepared electrolyte solution and then further sonicated for 3 hours at room temperature. Here, no capping agent or additional metal salt was used. 200 ml of double-distilled de-ionized water was taken as the medium for the electrolyte cell to operate. The electrochemical cell was operated at a voltage of 3 V DC under a controlled and careful stirring rate of 400 RPM. The formation of gas bubbles is observed immediately. After a few minutes of operation, the electrolytic solution changed its color to an opaque grey precipitate. The experimental run was carried out for 5 minutes at a temperature of 60 °C. After the experimental run, the precipitate obtained was ultrasonicated for fifteen minutes. Further, the solution was kept separately for overnight stirring. The next day, the sample was washed and purified several times using ultracentrifugation and decantation method to achieve the pure sample in powder form for further morphological, structural and spectroscopic characterizations.

X-ray diffraction (XRD) was carried out using PANalytical XPert Pro X-ray diffractometer. Raman spectroscopy was carried using the combined confocal Raman AFM (atomic force microscope) system by WITec Denmark. Transmission electron microscopy (TEM) for all the samples was carried out using a Jeol 2100F microscope.

3. Results and discussion
The structural characterization of the as prepared ZnO NFs/MWNT nano-conjugate was carried out using X-ray diffraction. The graph is shown in Figure 1, and it can be observed that the zinc oxide nanoflowers are of wurtzite hexagonal in structure. The main peaks corresponding to the hkl values are (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), and (202). All of these peaks correspond to the hexagonal structure of zinc oxide [16]. The peak for multi-walled carbon nanotubes (MWNT) is also present which corresponds to its (002) plane [17].

![Figure 1. X-ray diffraction graph for the ZnO NFs/MWNT nano-conjugate.](image-url)
Raman spectroscopy for the as synthesized ZnO NFs/MWNT was also carried out for studying the vibrational properties of the nano-conjugate. The Raman spectra obtained is shown in Figure 2. It can be observed from the spectra that the disorder-induced D band and G band are present at 1343 cm\(^{-1}\) and 1576 cm\(^{-1}\) respectively. The bands at 2690 cm\(^{-1}\) correspond to the 2D band found in multi-walled carbon nanotubes. A weak G+D peak is also present in the spectra [18, 19]. The peaks present at 434 cm\(^{-1}\) corresponds to the higher frequency mode (E\(_{2H}\)) of ZnO. This peak is the characteristic peak for the wurtzite structure of ZnO nanoparticles. The peak present 329 cm\(^{-1}\) is for the multi-photon mode E\(_{2H}\)-E\(_{2L}\). The peak appearing at 569 cm\(^{-1}\) is assigned to the A\(_{1L}\)/E\(_{1L}\) mode for the hexagonal structure of ZnO. The acoustic combination of A\(_{1}\) and E\(_{2}\) modes can also be observed at 1101 cm\(^{-1}\) [20]. The presence of all the vibrational modes of zinc oxide and multi-walled carbon nanotubes confirms the synthesis of ZnO NFs/MWNT nano-conjugate.

![Figure 2. Raman spectra for the ZnO NFs/MWNT nano-conjugate.](image)

The morphological characterization was carried out using transmission electron microscopy. It can be observed from Figure 3(a) that the flower-like nanostructures with an average size range of 500 – 700 nm have been obtained. The image shows that these structures have formed with nanocrumb growing away from the centre [19]. It can also be observed from the image that these fusiform like nanoflowers are conjugated with multi-walled carbon nanotubes. The HRTEM (High-Resolution-TEM) image in Figure 3(b) shows that the lattice fringes are 0.27 nm for the ZnO nanoflowers and 0.37 nm for multi-walled carbon nanotubes [21]. The selected area electron diffraction (SAED) pattern is shown in Figure 3(c). The planes corresponding to (100), (101), (102), (110), and (103) for zinc oxide nanoflowers can be seen in the image [22]. Also, the planes (100), and (002) for multi-walled carbon nanotubes were also obtained [23].
Figure 3. Transmission electron microscopy of ZnO NFs/MWNT nano-conjugate, (a) TEM image, (b) HRTEM, and (c) SAED pattern.

The different synthesis routes for the preparation of zinc oxide nanostructures and multi-walled carbon nanotubes nano-conjugate are listed in Table 1. All of these methods have some advantages and some disadvantages. However, the electrochemical synthesis method used in this study provides different types of zinc oxide nanostructures depending on the parameters. This method is a single step, time-saving, and economical with high yield. Therefore, this method can easily be scaled up for industrial production of nanomaterials and their conjugates.

The different synthesis routes for the preparation of zinc oxide nanostructures and multi-walled carbon nanotubes nano-conjugate are listed in Table 1. All of these methods have some advantages and some disadvantages. However, the electrochemical synthesis method used in this study provides different types of zinc oxide nanostructures depending on the parameters. This method is a single step, time-saving, and economical with high yield. Therefore, this method can easily be scaled up for industrial production of nanomaterials and their conjugates.

**Table 1.** Different synthesis methods for ZnO nanostructures conjugated with MWNT, their advantages, and disadvantages.

| Synthesis Methods    | Nanomaterial                                      | Advantages                                                                                                                                  | Disadvantages                                                                                                                                                                                                 | Ref.  |
|----------------------|---------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------|
| Wet chemical method  | Quantum dots, nanoflowers, nanorod, nanoparticles | A simple and inexpensive method, can be grown on the substrate easily                                                                                                                                   | The density of the ZnO coating is not well controlled, difficult to maintain homogeneous thin films (due to cracks)                                                                                             | [24]  |
| Electrostatic interaction | ZnO Quantum dots interaction with SDS treated MWNT | Densely self-assembled conjugates are synthesized, augmenting photocatalytic properties                                                                                                                  | Difficult to optimize the size and shape of the ZnO on the surface. Purification (The surfactant is very hard to remove)                                                                                         | [11]  |
| Sol-gel method       | Nanoparticles                                      | Not much expensive and very simple method, uses only low temperatures                                                                                                                                   | There is a shrinking of large volume and possibility to crack due to drying                                                                                                                                 | [25]  |
| Microwave irradiation | Nanosphere                                        | Quicken the rate of the reaction, higher                                                                                                                                                               | Scalability is a problem. Need for expensive equipment                                                                                                                                                     | [26]  |
Hydrothermal method | Nanowire, and nanocrystals | Less temperature is enough for the synthesis. The composition of nanomaterials is under good control | Calcination at high temperature is required during the synthesis process | [27]

Ball milling | Nanoparticles | Scalable method of synthesis, no need of solvents | Chances for contamination due to the mechanochemical method of synthesis, Crystal defects occur Lounder noise due to the steel balls milling. | [24]

Atomic Layer Deposition | Nanoparticles | High control of the thickness of the deposition | The presence of functionalized groups modify the shape | [28]

Ultrasonic Spray Pyrolysis | Nanodots | Low cost, a high degree of control of size and shape can be accomplished. | Cannot be easily scaled up Hard to determine growth temperatures | [29]

Electrochemical | Nanoflowers | Low cost, high yield, economical, single-step, lesser experiment time, low temperature | Difficult to maintain the stoichiometric ratio. Current work |  

4. Conclusion
In the present work, nano-conjugation between zinc oxide nanoflowers and multi-walled carbon nanotubes has been successfully achieved. Here, we have used a two-electrode electrochemical setup for preparation as well as conjugation between ZnO nanoflowers and MWNT. The XRD and Raman spectra, TEM imaging for the ZnO NFs/MWNT nano-conjugate shows the successful synthesis of the nano-conjugate. XRD reveals that the zinc oxide nanoflowers achieved are of wurtzite hexagonal structure type. The flower-like nanostructures has an average particle size ranging between 500 – 700 nm. The electrochemical method used here is a single step, economical, without the use of any additional surfactant or capping agents. The only use of pure zinc electrodes as a precursor material favors high purity, easy and a less time-consuming purification process. Further, the current demonstrated method can also be used for the synthesis of other wide range of metal oxide nanomaterials and their conjugates. Moreover, due to high surface area to volume ratio of zinc oxide NFs and its conjugate with MWNTs, they can be used as an electrode material for development of sensors, for sensing of analytes such as gas molecules, heavy metal ions and biomolecules. Their application in remediation of water resources can also be explored where the properties of both the counterparts of nano-conjugates i.e. ZnO NFs and MWNT can be exploited.

References
[1] Wang R, Xin J H, Tao X M and Daoud W A 2004 ZnO Nanorods grown on cotton fabrics at low temperature Chemical Physics Letters 398 250-5
[2] Prasad T N V K V, Sudhakar P, Sreenivasulu Y, Latha P, Munaswamy V, Reddy K R, Sreeprasad T S, Sajanlal P R and Pradeep T 2012 Effect of Nanoscale Zinc Oxide Particles on the Germination, Growth and Yield of Peanut Journal of Plant Nutrition 35 905-27
[3] Chaudhry Q, Scotter M, Blackburn J, Ross B, Boxall A, Castle L, Aitken R and Watkins R 2008 Applications and implications of nanotechnologies for the food sector Food additives & contaminants. Part A, Chemistry, analysis, control, exposure & risk assessment 25 241-58
[4] Lu P J, Huang S C, Chen Y P, Chiuheh L C and Shih D Y 2015 Analysis of titanium dioxide and zinc oxide nanoparticles in cosmetics Journal of food and drug analysis 23 587-94

[5] Hanley C, Layne J, Punnoose A, Reddy K M, Coombs I, Coombs A, Feris K and Wingett D 2008 Preferential killing of cancer cells and activated human T cells using ZnO nanoparticles Nanotechnology 19 295103

[6] Rasmussen J W, Martinez E, Louka P and Wingett D G 2010 Zinc oxide nanoparticles for selective destruction of tumor cells and potential for drug delivery applications Expert opinion on drug delivery 7 1063-77

[7] Boruah B D and Misra A 2016 Conjugated assembly of colloidal zinc oxide quantum dots and multiwalled carbon nanotubes for an excellent photosensitive ultraviolet photodetector Nanotechnology 27 35204

[8] Paul K B, Singh V, Vanjari S R K and Singh S G 2017 One step biofunctionalized electrosprun multiwalled carbon nanotubes embedded zinc oxide nanowire interface for highly sensitive detection of carcinoma antigen-125 Biosensors & bioelectronics 88 144-52

[9] Paul K B, Panigrahi A K, Singh V and Singh S G 2017 A multi-walled carbon nanotube-zinc oxide nanofiber based flexible chemiresistive biosensor for malaria biomarker detection The Analyst 142 2128-35

[10] Kaur R, Paul A K and Deep A 2014 Conjugation of chlorinated carbon nanotubes with quantum dots for electronic applications Materials Letters 117 165-7

[11] Jiang L and Gao L 2005 Fabrication and characterization of ZnO-coated multi-walled carbon nanotubes with enhanced photocatalytic activity Materials Chemistry and Physics 91 313-6

[12] Baby T T and Ramaprabhu S 2011 Non-enzymatic amperometric glucose biosensor from zinc oxide nanoparticles decorated multi-walled carbon nanotubes Journal of nanoscience and nanotechnology 11 4684-91

[13] Potirak P, Pcharapa W and Techitdheera W 2013 Microwave-assisted synthesis of ZnO/MWCNT hybrid nanocomposites and their alcohol-sensing properties Journal of Experimental Nanoscience 9 96-105

[14] Gupta B K, Grover V, Gupta G and Shanker V 2010 Highly efficient luminescence from hybrid structures of ZnO/multi-walled carbon nanotubes for high performance display applications Nanotechnology 21 475701

[15] Li X L, Li C, Zhang Y, Chu D P, Milne W I and Fan H J 2010 Atomic Layer Deposition of ZnO on Multi-walled Carbon Nanotubes and Its Use for Synthesis of CNT-ZnO Heterostructures Nanoscale research letters 5 1836-40

[16] Jay Chithra M, Sathyra M and Pushpanathan K 2015 Effect of pH on Crystal Size and Photoluminescence Property of ZnO Nanoparticles Prepared by Chemical Precipitation Method Acta Metallurgica Sinica (English Letters) 28 394-404

[17] Huq M M, Hsieh C-T and Ho C-Y 2016 Preparation of carbon nanotube-activated carbon hybrid electrodes by electrophoretic deposition for supercapacitor applications Diamond and Related Materials 62 58-64

[18] Feng J M and Dai Y J 2013 Water-assisted growth of graphene on carbon nanotubes by the chemical vapor deposition method Nanoscale 5 4422-6

[19] Cai Q, Gao Y, Gao T, Lan S, Simalou O, Zhou X, Zhang Y, Harnoode C, Gao G and Dong A 2016 Insight into Biological Effects of Zinc Oxide Nanoflowers on Bacteria: Why Morphology Matters ACS applied materials & interfaces 8 10109-20

[20] Sankara Reddy B, Venkatramana Reddy S and Koteswara Reddy N 2013 Physical and magnetic properties of (Co, Ag) doped ZnO nanoparticles Journal of Materials Science: Materials in Electronics 24 5204-10

[21] Zhang Z, Zhao Y, Sun L, Liu D, Shen J, Zhou W, Luo Q, Jin A, Yang H, Gu C and Xie S 2009 Growth and electrical properties of zinc oxide nanowires Journal of nanoscience and nanotechnology 9 1119-22

[22] Chen D, Ai S, Liang Z and Wei F 2016 Preparation and photocatalytic properties of zinc oxide nanoparticles by microwave-assisted ball milling Ceramics International 42 3692-6

[23] Kumar A, Singh K and Pandey O P 2014 One Step Synthesis and Growth Mechanism of Carbon Nanotubes Journal of Materials Science & Technology 30 112-6

[24] Li X, Qin Y, Picraux S T and Guo Z-X 2011 Noncovalent assembly of carbon nanotube-inorganic hybrids Journal of Materials Chemistry 21 7527

[25] Carter C B and Norton M G 2007 Ceramic Materials: Springer)
[26] Shi S and Hwang J-Y 2003 Microwave-assisted wet chemical synthesis: advantages, significance, and steps to industrialization *Journal of Minerals and Materials Characterization and Engineering* 02 101-10

[27] Gan Y X, Jayatissa A H, Yu Z, Chen X and Li M 2020 Hydrothermal Synthesis of Nanomaterials *Journal of Nanomaterials* 2020 1-3

[28] Johnson R W, Hultqvist A and Bent S F 2014 A brief review of atomic layer deposition: from fundamentals to applications *Materials Today* 17 236-46

[29] Rane A V, Kanny K, Abitha V K and Thomas S 2018 Methods for Synthesis of Nanoparticles and Fabrication of Nanocomposites 121-39