INDIAN JOURNAL OF SCIENCE AND TECHNOLOGY

RESEARCH ARTICLE

Electrochemical Fabrication and Characterization of a Gold-Polyaniline /Multi-walled Carbon Nanotubes/Manganese Dioxide Composite Electrode

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OPEN ACCESS

Received: 01.08.2021

Accepted: 13.11.2021

Published: 29.11.2021

Citation: Panda B, Dash SK (2021) Electrochemical Fabrication and Characterization of a Gold-Polyaniline /Multi-walled Carbon Nanotubes/Manganese Dioxide Composite Electrode. Indian Journal of Science and Technology 14(40): 3007-3013. https://doi.org/10.17485/IJST/v14i40.1420

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Funding: None

Competing Interests: None

Published By Indian Society for Education and Environment (iSee)

ISSN
Print: 0974-6846
Electronic: 0974-5645

Abstract

Objectives: Electrochemical fabrication and characterization of a gold-polyaniline/multi-walled carbon nanotubes/manganese dioxide (Au-PANI/MWCNT/MnO_2) composite electrode. **Methods:** The MnO_2 nanoparticles (NPs) were prepared by heating 1% $Mn(NO_3)_2.4H_2O$ at 100 ^{0}C for 24 h and characterized by using Fourier transform infrared spectroscopy (FTIR) and Ultraviolet/visible (UV/Vis) spectrophotometry. The size and shape of the NPs were determined from the transmission electron microscopic image. MWCNTs were functionalized with carboxyl groups on their sidewalls by sonicating in H_2SO_4:HNO_3 (3:1, v/v) for 12 h at 40 kHz. The functionalization was further confirmed through UV/Vis spectrophotometry. The working Au surface was first activated and then electropolymerized by using 50 μl of 0.005% $C_6H_5NH_2$ in 01 N HCl followed by electrodeposition with 0.1% each of the c-MWCNTs and manganese oxide NPs through 20 cycles of cyclic voltammetry (-0.2-0.9 mV) at the rate of 20 mV/s. The Au-PANI/MWCNT/MnO_2 composite was then characterized by using FTIR spectra and scanning electron microscopy. **Findings:** An Au-PANI/MWCNT/MnO_2 composite electrode was fabricated and characterized. **Novelty:** The nanocomposite electrode was designed by using screen printed electrode, which is very simple to construct, portable, and economic. The composite can be used to design a sensors or sensor array in future.

Keywords: Electrochemical Fabrication; Manganese Dioxide; Multi-walled Carbon Nanotubes; Nanocomposite Synthesis; Screen Printed Electrodes

1 Introduction

Biosensors are nowadays used as an important tool in medical diagnostics, environmental sample analysis, molecular biotoxicity evaluation, explosive tracking [1–3], and so on. Due to their simplicity, economic value, specificity, and sensitivity, these nanodevices are rapidly replacing other molecular detection methods. Sensitivity of a sensor mainly rely on the immobilized molecules, and nanocomposites can help for efficient immobilization [4,5]. A Nanocomposite, can be synthesized by using intercalation [6], templet

synthesis[7], ball milling[8], three-dimensional printing[9] or other methods with electropolymerization being simple, stable, and common[10]. Several studies have employed Using polyaniline (PANI) as a linker and Au NPs or Au electrode to fabricate nanocmposites.

Liu et al., (2012), used a chemical technique to prepare Au/PANI nanofiber composite for the reduction of O_2 [11]. At 0 ^{0}C, Aniline in $CHCl_3$ was combined with $(NH_4)_2S_2O_8$, and HCl for 12 h then added to $HAuCl_4$ of comparable concentration for 6 h at room temperature (RT). LI and her group created a nanocomposite by combining 4-aminothiophenol and multi-walled carbon nanotube (MWCNT) with aniline and potassium peroxydisulfate in HCl for 12 h at RT. Au@Pt core-shell NPswere coated onto the composite after it had been washed and dried[12]. Although the sensitivity and LOD of the method are satisfactory, the fabrication procedure involves multiple chemicals so also the synthesis of Au@Pt core-shell NP is quite hectic. Similarly, multiple investigations have reported fabrication of MWCNT-PANI composites. Sivakkumar et al., (2007), used interfacial polymerization to design a nanocomposite to use in supercapacitors[13]. Another such PANI/MWCNT-based ammonia sensor was developed by Maity et al., (2020)[14] while, Zhou et al., (2018) electrochemically fabricated PANI/MWCNT composite onto expanded graphite for improving the performance of supercapacitors[15]. Razak et al., (2009) suggested a PANI/MWCNT-MnO_2 ternary nanocomposite by coating MnO_2-filled MWCNTs with PANI in HCl. The composite showed significant electrical conductance[16]. In two separate studies in 2014, Vilian et al. developed a simple strategy for fabricating MWCNT onto glassy carbon electrode followed by electrochemical conjugation with MnO_2 NPs[17,18]. Another ternary composite electrode was fabricated by Iqbal et al., (2020) by using PANI, MnO_2, and CNT. They synthesized MnO_2 nanorods through hydrothermal approach. PANI@CNT was prepared by oxidative polymerization and subsequently polymerized onto MnO_2 nanorods[19]. However, hydrothermal method is time-consuming and requires a high temperature. Tran and coworkers[20] recently, developed an electrochemical impedance DNA sensor based on the MWCNT/MnO_2/PANI nanowire composite.

We wanted to construct an Au-PANI/c-MWCNT/MnO_2 composite with a different conjugation than those previously described. The composite will provide significant surface area for efficient molecular immobilization and high electrical conductance. This on the other hand will impart high sensitivity if used to construct a sensor. We intended to make the composite by using a two-step electrochemical fabrication technique that is quick, simple, stable, and can allow broad types of molecules. We have used screen-printed gold electrode (SPGE) in this study, such that the composite electrode is easy-to-construct, economic, and may be used to build a sensor or sensor array.

2 Materials and Methods

2.1 Chemicals and reagents

Aniline ($C_6H_5NH_2$), acetic acid (CH_3COOH), dimethylformamide (DMF), hydrochloric acid (HCl), manganese nitrate [$Mn(NO_3)_2.4H_2O$], sodium acetate [$(CH_3COO)Na$], sodium dihydrogen ortho-phosphate (NaH_2PO_4), di-sodium hydrogen orthophosphate (Na_2HPO_4), sodium chloride (NaCl) were procured from SRL, India. MWCNT (diameter 7-15 nm, length 0.5-10 μm, purity >99 %) was purchased from Sigma Aldrich, USA. All other chemicals used were of analytical grade. SPGE (gold: working and counter; silver: reference) were procured from DropSens, Spain.

2.2 Apparatus required

Laboratory incubator (MIC), Modern Industrial Corporation, India, weighing balance (PGB 200), Wensar India, pH meter, EUTECH Instruments, India, Fourier transform infrared spectrophotometer (FTIR; BX-59333) Perkin-Elmer, USA, MiliQ water plant, Milipore, India, scanning electron microscope (SEM; EVO 40), Carl Zeiss, Germany, UV/Vis spectrophotometer, Perkin-Elmer, USA, potentiostat/galvanostat (FRA2 μAutolab type iii), Metrohm, India, Ultrasonic bath sonicator, PCi analytics, India, transmission electron microscope (TEM), TECNAI 200 kV TEM (Fei, Electron Optics), centrifuge (REMI R-24, magnetic stirrer (2 MLH), -20 ^{0}C Freezer (Quick freezer), REMI India, spinwin (MC-00), spinix, Tarsons India, were used to carry out the work. The plasticwares and glasswares were obtained from Tarsons and Borosil, respectively and sterilized before use.

2.3 Synthesis of MnO_2 NPs and Carboxyl functionalization of MWCNT

A simple approach reported by Najafpour et al., (2012)[21] was employed with minor changes for the synthesis of MnO_2 NPs. In an incubator, 5 ml of MiliQ water containing 1% $Mn(NO_3)_2.4H_2O$ was heated at 100 ^{0}C for 24 h before being washed with MiliQ water. The particles were then dried at 100 ^{0}C and stored at 4 ^{0}C. FTIR spectroscopy and UV/Vis spectrophotometry were used for the characterization of the NPs whereas, size and shape of the NPs were determined through TEM imaging.

Following our prior work, the MWCNTs were functionalized with carboxyl groups on their sidewalls [22]. The nanotubes (1.2 mg/ml) were sonicated for 12 h at 40 kHz in H_2SO_4:HNO_3 (3:1, v/v) and centrifuged at 8,000×g for 10 min at room temperature (RT). The particles were then rinsed repeatedly in MiliQ water to neutralize the pH. Subsequently, the particles were suspended in double the volume of DMF:H_2O (1:1, v/v) and stored at 4 ^{0}C for future use. UV/Vis spectra of the nanotubes for equal concentrations (1.2 mg/ml) were acquired both before and after the sonication to confirm the functionalization [23].

2.4 Electrochemical fabrication of the nanocomposite

As described in our earlier article [24], the working surface of the SPGE was first activated with H_2SO_4:H_2O_2 (1:1, v/v) and then rinsed with MiliQ water, followed by 70% ethanol before drying at RT. After that, 50 μl of 0.005% $C_6H_5NH_2$ in 01 N HCl was electropolymerized onto the working surface (area: 0.126 cm^2) by 20 cycles of CV (-0.2 - 0.9 mV) at a rate of 20 mV/s [25]. The Au/polyaniline (Au-PANI) electrode was then washed with 50 mM phosphate buffer, 0.9 % NaCl (PBS), pH 7.0±0.2 followed by 50 mM acetate buffer, pH 5.2±0.2 before drying at RT. Following that, 20 cycles of CV (-0.2 - 0.9 mV) at the rate of 20 mV/s were used to electrodeposit 0.1% each of the c-MWCNTs and manganese oxide NPs onto Au-PANI surface in 50 mM acetate buffer, pH 5.2±0 [26] [Figure 1]. Subsequently, the Au-PANI/MWCNT/MnO_2 nanocomposite electrode was washed with 50 mM acetate buffer, pH 5.2±0.2, MiliQ water, and 80% C_2H_5OH followed by air dying at RT. The surface topography of the bare Au, Au-PANI, and Au-PANI/MWCNT/MnO_2 composite electrodes was studied using SEM imaging. For further characterization, the FTIR spectra for both Au and Au-PANI/MWCNT/ MnO_2 composite electrodes were obtained.

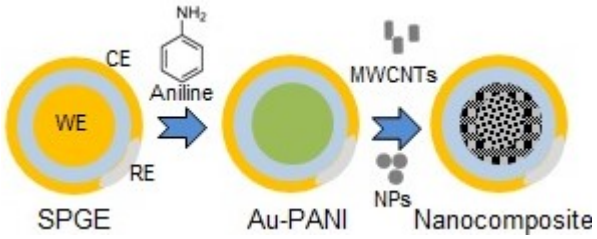

Fig 1. Schematic presentation of the fabrication of Au-PANI/MWCNT/MnO_2 composite electrode

3 Results and Discussion

3.1 Synthesis of MnO_2 NPs and functionalization of MWCNT

After heating the $Mn(NO_3)_2.4H_2O$ solution at 100 ^{0}C for 24 h, a black precipitate formed which was washed and dried at 100 ^{0}C to result in black NPs. The FTIR spectra of the NPs revealed a broad peak at 3066.82 cm^{-1} may be corresponding to the H-O-H stretching vibration, indicating towards the hydrate nature of the particles [27]. The band at 1078.21, 1398.39, and 1670.35 cm^{-1} might have been contributed by the bending vibrations of O-H combined to Mn [28]. The absorption bands at 415.88 and 567.07 cm^{-1} may be attributed to the O-Mn-O stretching [29] [Figure 2a]. In the UV/Vis study, the particles produced an absorption peak (λ_{max}) at 315 nm, which may be corelated to the surface plasmon resonance of the manganese oxide (O→Mn) NPs [30] [Figure 2b]. The results obtained with FTIR and UV/Vis study confirmed the NP thus synthesized to be MnO_2. Shape of the MnO_2 NPs thus synthesized were found to be roughly spherical under TEM [Figure 2c] by using ImageJ software analysis. Further, average size (μ) and standard deviation (σ) of the NPs were found to be 40.92 nm ±0.63, and 3.74, respectively [31] [Figure 2d]. The UV/Vis spectra of the MWCNT before sonication showed no specific λ_{max} in between 190-320 nm whereas, after sonication for 12 h, two clear and distinguished peaks appeared at 209 and 265 nm [Figure 2e], might be indicating towards the O=C-O-H functionalization [32].

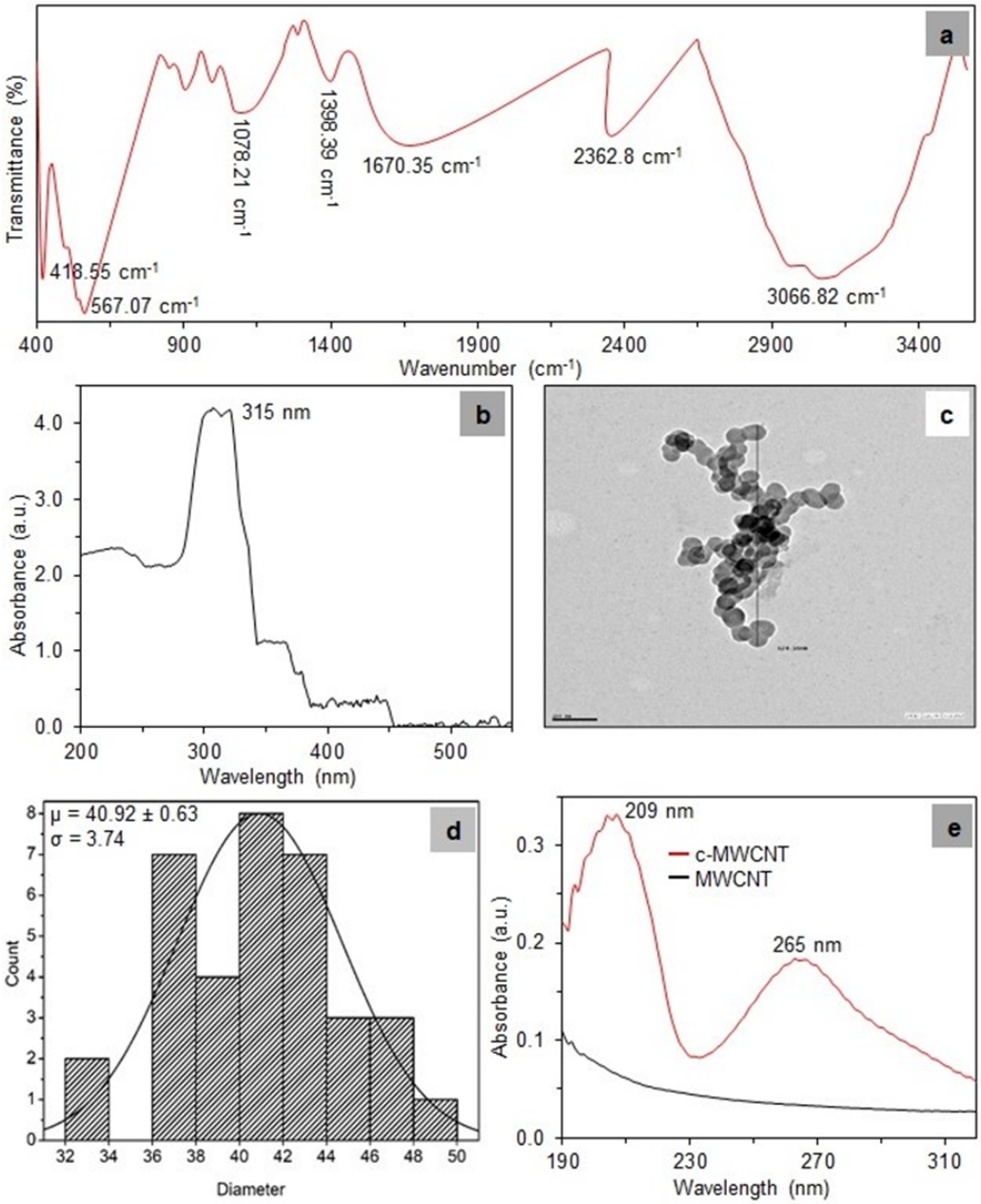

Fig 2. (a) FTIR spectra, (b) UV/Vis spectra, (c) TEM image, and (d) histogram for the size distribution of the MnO_2 NPs, (e) UV/Vis spectra of MWCNT and c-MWCNT

3.2 Fabrication of the nanocomposite

The multi-layer coating [Figure 3a] of the working Au electrode with PANI, changed the surface into green[33] while electrodeposition of the c-MWCNT [Figure 3b] and MnO_2 NPs rechanged the surface into black[34]. With increasing scan repeat, both CV cathodic (I_{pa}) and anodic (I_{pa}) peaks of electrodeposition increased. The I_p value of Au-PANI/MWCNT/MnO_2 nanocomposite electrode was higher than that of Au-PANI electrode [Figure 3b inset] indicating that the former has higher immobilization surface area[25]. As a result, a sensor if synthesized by using this nanocomposite will impart a higher sensitivity through enhancing the immobilization efficiency.

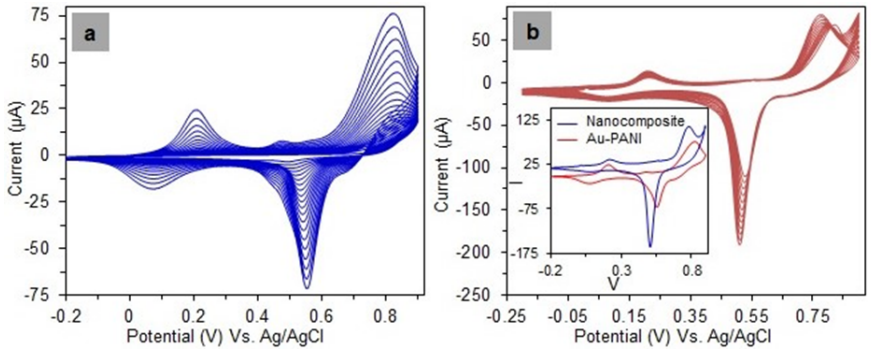

Fig 3. Cyclicvoltammogram of (a) electropolymerization of $C_6H_5NH_2$ onto Au electrode of SPGE, (b) electrodeposition of c-MWCNT and MnO_2 NPs, (inset) Au-PANI and Au-PANI/MWCNT/MnO_2 composite electrodes

3.3 Characterization

Figure 4a, b, and c depicts the SEM images of the Au, Au-PANI, and Au-PANI/MWCNT/MnO_2 nanocomposite electrode. The first had a smooth layer[35], whereas the second one showed a clear and distinct uniform layer that may be attributed to the PANI layer[36]. Porous tubular intercrossed network-like structures impregnated with spherical granules was seen in the final electrode. MWCNTs may be responsible for the network, whereas granules may indicate MnO_2 NPs[36,37]. The functionalization was further confirmed through FTIR analysis. The FTIR spectrum of Au didn't showed any specific absorption peak while FTIR spectrum of the composite electrode revealed peaks at 33392.78, 2951.08 and 2355.08, 1651.06, 1172.72 and 1064.74, 852.32 and 588.29 cm^{-1}. The broad peak at 33392.78 cm^{-1} may correspond to the O-H stretching vibration of the surface -COOH functional groups[38,39] while the bands at 2951.08 and 2355.08 cm^{-1} could signal towards the asymmetric and symmetric methyl stretching, respectively on the defective regions of the MWCNTs[40]. The peak at 1651.06 cm^{-1} perhaps indicates for C-O bands of -COO^- functional groups on the sidewalls of MWCNTs[41] whilst, the band at 1172.72 and 1064.74 cm^{-1} may be attributed to Mn-O vibrations.[25] [Figure 4d]. The peaks at 852.32 and 588.29 may correspond to the C-C stretch of the MWCNTs[42].

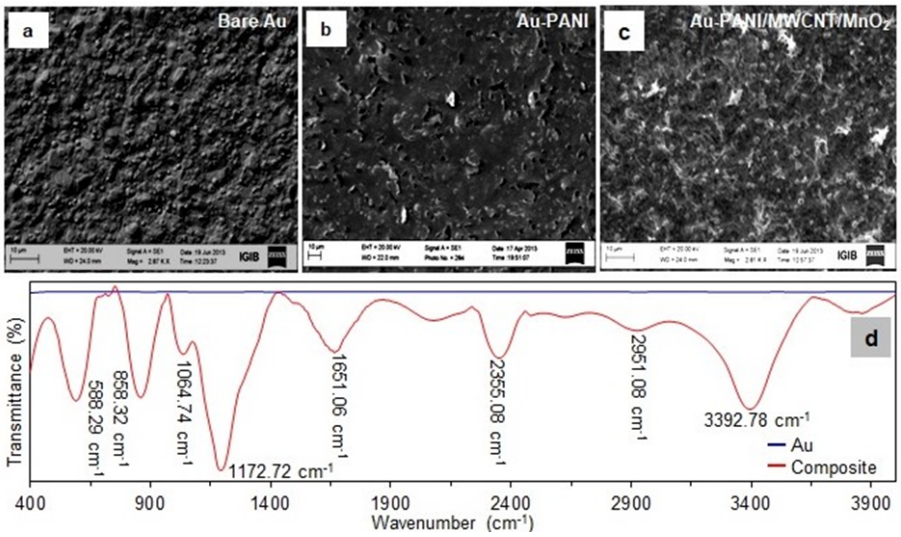

Fig 4. SEM image of (a) bare Au, (b) Au-PANI, and (c) Au-PANI/MWCNT/MnO_2 nanocomposite electrode, (d) FTIR spectra of Au and Au-PANI/MWCNT/MnO_2 electrodes

4 Conclusion

We have electrochemically polymerized aniline onto the Au surface of a SPGE followed by electrochemical deposition of MWCNT/MnO_2 to construct a nanocomposite electrode. Since SPGE is small electrode, therefore, the composite electrode fabricated by using this electrode can be used construct a sensor or sensor array easily. A portable potentiostat can be designed for onsite detection of an analyte by using the sensor. In addition, the current technique includes NM electro-polymerization, which is a simple and cost-effective method that may be used to immobilize a variety of molecules for the fabrication of electrochemical sensors. Furthermore, because electro-polymerization is a stable fabrication technique, the electrodes can be stored at 4-8 ^{0}C for more than six months. The antimicrobial properties of MnO_2 NMs as well as physicochemical resistance of both MnO_2 and c-MWCNTs, added to the electrode's stability. However, immobilization of biomolecules on the other hand, may change its stability, which will be calculated on real-time in future during the development of any sensor that uses it.

Acknowledgement

The author would like to thank HOD, Zoology, B.U., for providing academic support and infrastructures to carry out the work.

References

1) Fapyane D, Berillo D, Marty JL, Revsbech NP. Urea Biosensor Based on a CO2 Microsensor. *ACS Omega*. 2020;5(42):27582–27590. Available from: https://dx.doi.org/10.1021/acsomega.0c04146.
2) Babapoor A, Hajimohammadi R, Jokar SM, Paar M. Biosensor Design for Detection of Mercury in Contaminated Soil Using Rhamnolipid Biosurfactant and Luminescent Bacteria. *Journal of Chemistry*. 2020;2020:1–8. Available from: https://dx.doi.org/10.1155/2020/9120959.
3) Paul M, Tscheuschner G, Herrmann S, Weller MG. Fast Detection of 2,4,6-Trinitrotoluene (TNT) at ppt Level by a Laser-Induced Immunofluorometric Biosensor. *Biosensors*. 2020;10(8):89. Available from: https://dx.doi.org/10.3390/bios10080089.
4) Yang T, Duncan TV. Challenges and potential solutions for nanosensors intended for use with foods. *Nature Nanotechnology*. 2021;16(3):251–265. Available from: https://dx.doi.org/10.1038/s41565-021-00867-7.
5) Saber NB, Mezni A, Alrooqi A, Altalhi T. A review of ternary nanostructures based noble metal/semiconductor for environmental and renewable energy applications. *Journal of Materials Research and Technology*. 2020;9(6):15233–15262. Available from: https://dx.doi.org/10.1016/j.jmrt.2020.10.090.
6) Fu S, Sun Z, Huang P, Li Y, Hu N. Some basic aspects of polymer nanocomposites: A critical review. *Nano Materials Science*. 2019;1(1):2–30. Available from: https://dx.doi.org/10.1016/j.nanoms.2019.02.006.
7) Bhatia P, Aman P, Akash S, Manoj KAG. A mini review: Polymer-matrix nanocomposites and its synthesis techniques. *AIP Conference Proceedings*. 2019;2142(1):150011. doi:10.1063/1.5122560.
8) Vinyas M, Athul SJ, Harursampath D, Loja M, Thoi TN. A comprehensive review on analysis of nanocomposites: from manufacturing to properties characterization. *Materials Research Express*. 2019;6(9):092002. Available from: https://dx.doi.org/10.1088/2053-1591/ab3175.
9) Silva M, Pinho IS, Covas JA, Alves NM, Paiva MC. 3D printing of graphene-based polymeric nanocomposites for biomedical applications. *Functional Composite Materials*. 2021;2(1):8–29. Available from: https://dx.doi.org/10.1186/s42252-021-00020-6.
10) Kolzunova L, Shchitovskaya E, Karpenko M. Polymethylolacrylamide/AuNPs Nanocomposites: Electrochemical Synthesis and Functional Characteristics. *Polymers*. 2021;13(14):2382. Available from: https://dx.doi.org/10.3390/polym13142382.
11) Liu S, Xu H, Ou J, Li Z, Yang S, Wang J. A feasible approach to the fabrication of gold/polyaniline nanofiber composites and its application as electrocatalyst for oxygen reduction. *Materials Chemistry and Physics*. 2012;132(2-3):500–504. Available from: https://dx.doi.org/10.1016/j.matchemphys.2011.11.060.
12) Li S, Zhou J, Noroozifar M, Kerman K. Gold-Platinum Core-Shell Nanoparticles with Thiolated Polyaniline and Multi-Walled Carbon Nanotubes for the Simultaneous Voltammetric Determination of Six Drug Molecules. *Chemosensors*. 2021;9(2):24. Available from: https://dx.doi.org/10.3390/chemosensors9020024.
13) Sivakkumar SR, Kim WJ, Choi JA, MacFarlane DR, Forsyth M, Kim DW. Electrochemical performance of polyaniline nanofibres and polyaniline/multi-walled carbon nanotube composite as an electrode material for aqueous redox supercapacitors. *Journal of Power Sources*. 2007;171(2):1062–1068. Available from: https://dx.doi.org/10.1016/j.jpowsour.2007.05.103.
14) Maity D, Manoharan M, Kumar RTR. Development of the PANI/MWCNT Nanocomposite-Based Fluorescent Sensor for Selective Detection of Aqueous Ammonia. *ACS Omega*. 2020;5(15):8414–8422. Available from: https://dx.doi.org/10.1021/acsomega.9b02885.
15) Zhou H, Zhi X, Zhai HJ. A facile approach to improve the electrochemical properties of polyaniline-carbon nanotube composite electrodes for highly flexible solid-state supercapacitors. *International Journal of Hydrogen Energy*. 2018;43(39):18339–18348. Available from: https://dx.doi.org/10.1016/j.ijhydene.2018.07.168.
16) Abd RSI, Latif AA, Sharif Z. Polymerisation of protonic polyaniline/multi-walled carbon nanotubes-manganese dioxide nanocomposites. *Journal of Physical Science*. 2009;20:27–34.
17) Vilian ATE, Chen SM, Lou BS. A simple strategy for the immobilization of catalase on multi-walled carbon nanotube/poly (l-lysine) biocomposite for the detection of H2O2 and iodate. *Biosensors and Bioelectronics*. 2014;61:639–647. Available from: https://dx.doi.org/10.1016/j.bios.2014.05.023.
18) Vilian ATE, Chen SM. Preparation of carbon nanotubes decorated with manganese dioxide nanoparticles for electrochemical determination of ferulic acid. *Microchimica Acta*. 2015;182(5-6):1103–1111. Available from: https://dx.doi.org/10.1007/s00604-014-1431-2.
19) Iqbal J, Ansari MO, Numan A, Wageh S, Al-Ghamdi A, Alam MG, et al. Hydrothermally Assisted Synthesis of Porous Polyaniline@Carbon Nanotubes–Manganese Dioxide Ternary Composite for Potential Application in Supercapattery. *Polymers*. 2020;12(12):2918. Available from: https://dx.doi.org/10.3390/polym12122918.
20) Tran LT, Tran HV, Tran T, Nguyen NT, Bui DV, Tran PQ, et al. A Highly Sensitive Electrochemical DNA Sensor Based on Nanostructured Electrode of Multi-Walled Carbon Nanotubes/Manganese Dioxide Nano-Flowers-like/Polyaniline Nanowires Nanocomposite. *Journal of The Electrochemical Society*. 2021;168(5):057518. Available from: https://dx.doi.org/10.1149/1945-7111/ac001b.

21) Najafpour MM, Rahimi F, Amini M, Nayeri S, Bagherzadeh M. A very simple method to synthesize nano-sized manganese oxide: an efficient catalyst for water oxidation and epoxidation of olefins. *Dalton Transactions*. 2012;41(36):11026. Available from: https://dx.doi.org/10.1039/c2dt30553d.
22) Dash SK, Sharma M, Khare S, Kumar A. Carbon-Mercaptooctadecane/Carboxylated Multi-walled Carbon Nanotubes Composite Based Genosensor for Detection of Bacterial Meningitis. *Indian Journal of Microbiology*. 2014;54(2):170–177. Available from: https://dx.doi.org/10.1007/s12088-013-0435-7. doi:10.1007/s12088-013-0435-7.
23) Dash SK, Sharma M, Kumar A, Khare S, Kumar A. Carbon composite-based DNA sensor for detection of bacterial meningitis caused by Neisseria meningitidis. *Journal of Solid State Electrochemistry*. 2014;18(10):2647–2659. Available from: https://dx.doi.org/10.1007/s10008-014-2525-9.
24) Dash SK, Sharma M, Khare S, Kumar A. rmpM Genosensor for Detection of Human Brain Bacterial Meningitis in Cerebrospinal Fluid. *Applied Biochemistry and Biotechnology*. 2013;171(1):198–208. Available from: https://dx.doi.org/10.1007/s12010-013-0339-3.
25) Yadav S, Kumar A, Pundir CS. Amperometric creatinine biosensor based on covalently coimmobilized enzymes onto carboxylated multiwalled carbon nanotubes/polyaniline composite film. *Analytical Biochemistry*. 2011;419(2):277–283. Available from: https://dx.doi.org/10.1016/j.ab.2011.07.032.
26) Devi R, Yadav S, Pundir CS. Amperometric determination of xanthine in fish meat by zinc oxide nanoparticle/chitosan/multiwalled carbon nanotube/polyaniline composite film bound xanthine oxidase. *The Analyst*. 2012;137(3):754–759. Available from: https://dx.doi.org/10.1039/c1an15838d.
27) Kumara BP, Karikkatb S. Synthesis, Characterization of Nano MnO2 and its Adsorption Characteristics Over an Azo Dye. *Research & Reviews: Journal of Material Sciences*. 2014;02(01). Available from: https://dx.doi.org/10.4172/2321-6212.1000116.
28) Moon SA, Salunke BK, Alkotaini B, Sathiyamoorthi E, Kim BS. Biological synthesis of manganese dioxide nanoparticles by Kalopanax pictus plant extract. *IET Nanobiotechnology*. 2015;9(4):220–225. Available from: https://dx.doi.org/10.1049/iet-nbt.2014.0051.
29) Racik KM, Guruprasad K, Mahendiran M, Madhavan J, Maiyalagan T, Raj MVA. Enhanced electrochemical performance of MnO2/NiO nanocomposite for supercapacitor electrode with excellent cycling stability. *Journal of Materials Science: Materials in Electronics*. 2019;30(5):5222–5232. Available from: https://dx.doi.org/10.1007/s10854-019-00821-3.
30) Saha RH, Yousuf MMA, Hasan SMAB. Poly(vinyl alcohol)-MnO2 nanocomposite films as UV-shielding materials. *Polymer Bulletin*. 2018;75(12):5629–5643. doi:10.1007/s00289-018-2355-5.
31) Rasmussen MK, Pedersen JN, Marie R. Size and surface charge characterization of nanoparticles with a salt gradient. *Nature Communications*. 2020;11(1). Available from: https://dx.doi.org/10.1038/s41467-020-15889-3.
32) Alizadeh ZH, Alireza Z, Akbar SA, Mohammad AA, Mojtaba F. Interaction of single and multi wall carbon nanotubes with the biological systems: tau protein and PC12 cells as targets. *Scientific Reports*. 2016;6(1):26508. doi:10.1038/srep26508.
33) Majumdar S, Mahanta D. Deposition of an ultra-thin polyaniline coating on a TiO2 surface by vapor phase polymerization for electrochemical glucose sensing and photocatalytic degradation. *RSC Advances*. 2020;10(30):17387–17395. Available from: https://dx.doi.org/10.1039/d0ra01571g.
34) Nguyen TT, Pham NT, Dinh TTM, Vu TT, Nguyen HS, Tran LD. Electrodeposition of Hydroxyapatite-Multiwalled Carbon Nanotube Nanocomposite on Ti6Al4V. *Advances in Polymer Technology*. 2020;2020:1–10. Available from: https://dx.doi.org/10.1155/2020/8639687.
35) Xiangmin M, Chung-Nga K, Kasipandi V, Zongbing L, Guanjun Y, Chung-Hang L, et al. Leung Chung-Hang, Ma Dik-Lung. A cyclometalated iridium(III) complex used as a conductor for the electrochemical sensing of IFN-γ. *Scientific Reports*. 2017;7(1). doi:10.1038/srep42740.
36) Anita G, Aleksandar P, Perica P, Aleksandar TD, Maurizio A. MWCNT/Polyaniline nanocomposites used for pH nanosensors of marine waters. In: Mariacristina C, Emilia DP, Emanuela EM, Gennaro G, Alessio M, Raffaella M, editors. Proceedings of the International Conference on Microplastic Pollution in the Mediterranean Sea. Springer. 2018;p. 231–239.
37) Girish G, Deepak D, Nilesh C, Jun-Young C, Pedro GR, Chan P. Lokhande Chandrakant D. Low-cost flexible supercapacitors with high-energy density based on nanostructured MnO2 and Fe2O3 thin films directly fabricated onto stainless steel. *Scientific Reports*. 2015;5(1). doi:10.1038/srep12454.
38) Stobinski L, Lesiak B, Kövér L, Tóth J, Biniak S, Trykowski G, et al. Multiwall carbon nanotubes purification and oxidation by nitric acid studied by the FTIR and electron spectroscopy methods. *Journal of Alloys and Compounds*. 2010;501(1):77–84. Available from: https://dx.doi.org/10.1016/j.jallcom.2010.04.032.
39) Amaral MTLD, Henrique CF, Barros MJP, Batista TD, Nelson D. Lemes Ana Paula. Effect of MWCNT functionalization on thermal and electrical properties of PHBV/MWCNT nanocomposites. *Journal of Materials Research*. 2015;30(1):55–65. doi:10.1557/jmr.2014.303.
40) Scheibe B, Borowiak-Palen E, Kalenczuk RJ. Oxidation and reduction of multiwalled carbon nanotubes — preparation and characterization. *Materials Characterization*. 2010;61(2):185–191. Available from: https://dx.doi.org/10.1016/j.matchar.2009.11.008.
41) Ali AM, Bakather O, Yehya T, Bassam AT. Abuilaiwi Faraj Ahmad, Fettouhi Mohamed B. Effect of carboxylic functional group functionalized on carbon nanotubes surface on the removal of lead from water. *Bioinorganic Chemistry and Applications*. 2010;2010(11):603978. doi:10.1155/2010/603978.
42) Panicker RM, Priya S. Fabrication of flexible conducting thin films of copper-MWCNT from multi-component aqueous suspension by electrodeposition. *Journal of Solid State Electrochemistry*. 2014;18(2):487–496. Available from: https://dx.doi.org/10.1007/s10008-013-2279-9.