



FABRICATION OF ELECTROSPUN NANOFIBERS OF TERNARY COMPOSITE POLYPYRROLE-CNT-MnO₂

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Abstract

Recently the ternary composite of conducting polymers, carbon based materials and metal oxides have gained the interest due to its enhanced and improved properties useful for various applications. In this paper we report the synthesis of ternary powder and the fabrication of the ternary composite electrospun nanofibers so as to use them in device application. Ternary composites of conducting polymer polypyrrole (PPY) and CNT-MnO₂ have been synthesized by *in-situ* chemical polymerization. Electrospun nanofibers of ternary composite were fabricated by using polystyrene as carrier polymer. Analytical techniques such as FTIR, UV-VIS, and XRD are used to characterize the synthesized ternary composites. The ternary composite showed good interaction based on the shift to longer wavelengths in the electronic transition, indicating the interaction between PPY and CNT-MnO₂ as observed in their UV-VIS and FTIR spectra of powder as well as fibers. Crystallinity of MnO₂ in ternary composite was confirmed from XRD results. The SEM images of synthesized ternary composites reveal dispersion of polymer over CNT and the SEM images of fiber indicates the diameter of fibers in the range of 100- 300nm.

Keywords: Conducting polymers, Polypyrrole, CNT, MnO₂, Electrospun nanofibers.

1. Introduction

Nanotechnology due to its tremendous potential and scope in various applications has become an active field of research as when well established materials are synthesized in nanoscale they often emerge with astonishing and improved properties. Moreover if the composites of the materials are synthesized even better and satisfying results are obtained. There are mainly four types of nanostructures: zero, one, two and three dimension structures. Among them, one-dimensional (1D)



nanostructures have been the focus of quite extensive studies worldwide, partially because of their unique physical and chemical properties. Compared to the other three dimensions, the first characteristic of 1D nanostructure is its smaller dimension structure and high aspect ratio, which could efficiently transport electrical carriers along one controllable direction, thus are highly suitable for moving charges in intergrated nanoscale systems. The second characteristic of 1D nanostructure is its device function, which can be exploited as device elements in many kinds of nanodevices [1]. 1D nanomaterials can be prepared by many methods such as template-directed methods, vapor-phase methods, interface synthesis techniques, solvothermal synthesis, solution-phase growth controlled by capping reagents, nanolithography and self-assembly. However, each of these methods has limitations, such as material restrictions, high cost, and high process complexity. [2] Electrospinning is a broadly used technology for electrostatic fiber formation which utilizes electrical forces to produce polymer fibers with diameters ranging from 2 nm to several micrometers using polymer solutions of both natural and synthetic polymers has seen a tremendous increase in research and commercial attention over the past decade This process offers unique capabilities for producing novel natural nanofibers and fabrics with controllable pore structure. Since the beginning of this century, researchers all over the world have been re-examining the electrospinning process. This process of electrospinning has gained much attention in the last decade not only due to its versatility in spinning a wide variety of polymeric fibers but also due to its ability to consistently produce fibers in the submicron range consistently that is otherwise difficult to achieve by using standard mechanical fiber-spinning technologies techniques . With smaller pores and higher surface areathan regular fibers, electrospun fibers have been successfully applied in various fields, such as, nanocatalysis, tissue engineering scaffolds, protective clothing, filtration, biomedical, pharmaceutical,



optical electronics, healthcare, biotechnology, defense and security, and environmental engineering [3]. Recently the electrospun nanofiber of polymer blends and polymer nanocomposite have attracted the attention of researchers due to its wide application in field of environment protection, catalyst, biomedical, enzyme carriers, solar cells, sensors and energy storage devices [4]. Researchers are engaged in exploring the multifunctional nanocomposite which can show improved and reliable properties and for that widely studied materials are the carbon based materials, metal oxides and polymers. In present work, we have made an attempt to synthesize the ternary composite of polypyrrole, CNT and MnO_2 by in-situ chemical oxidative method and that was fabricated into nanofiber by electrospinning.

2. Experimental

2.1 Materials and methods

The chemicals used in the preparation of ternary composite were all purchased from Merck. The monomer pyrrole was purchased from Sigma Aldrich and was distilled prior to use. High purity MWCNT of diameter 30-40 nm prepared by chemical vapour deposition techniques was made available from NPL, New Delhi, India. Other supplement chemicals were of AR grade and used as received. The formation of ternary composite was confirmed by FTIR measured on Bruker Alpha model and absorbance spectra in UV-VIS range was measured on Shimadzu UV-1800 spectrophotometer. The XRD measurement was performed on Philips PW1710 automatic X-ray diffractometer using Cu-K α wavelength ($\lambda=1.54059 \text{ \AA}$). The SEM images were taken by JEOL Model JSM - 6390LV having magnification $5 \times$ to $300,000 \times$ (Both in High and Low Vacuum Modes).



2.2 Fabrication of ternary composite electrospun nanofibers

As the MWCNT are not dispersed easily and cannot be mixed with polymer matrix they were chemically treated in the acid solution containing H_2SO_4 and HNO_3 in 3:1 ration in 40ml distilled water. The above solution containing certain amount of CNT was sonicated for 3 hrs at $50^\circ C$. After 3 hrs of sonication, the solution was centrifuged and filtered, washed with distilled water and vacuum dried at $80^\circ C$ overnight [5].

The ternary composite of conducting polymer polypyrrole (PPY) and CNT- MnO_2 was synthesized by *in-situ* chemical polymerization. To prepare this ternary composite in aqueous solution containing 0.25M Sodium Dodecyl Sulphate, Monomer pyrrole 0.75M was added and CNT's were suspended in this monomer solution. This solution containing CNT and monomer was sonicated for 30min to facilitate proper dispersion of CNT's and for more absorbance of monomer on walls of CNT's so that when oxidant is added dropwise it will provide a better polymerization and growth of polymer on the walls of CNT. To form a ternary composite containing MnO_2 , 0.75M $KMnO_4$ solution was used as an oxidant and was added drop wise in the continuously stirring solution of monomer and CNT. The stirring continued for 3hrs and later the solution was kept overnight and next day it was filtered and washed up till the filtrate was colorless. The obtained precipitate of ternary composite was vacuum dried at $80^\circ C$. The ternary composite in powder form was dissolved in NMP and to make the viscous solution polystyrene (PS) was dissolved in THF was vigorously stirred and heated simultaneously for 12 hrs. The solutions of PS and ternary composite were mixed and again stirred for 3 hrs to make a homogenous solution. Electrospun fibers of the ternary composite were produced by electrospinning prepared solution at a potential of 20 kV using a 10 ml syringe with a metal needle, which kept at a distance of 15cm from aluminum collecting drum covered with an

aluminum foil. The flow rate was adjusted to be 0.2 ml/hour using a syringe pump. Prepared electrospun fibers were collected on aluminum foil wrapped on rotary drum as collect to obtain well aligned nanofibers. The schematic diagram for alignment of nanofibers using drum as collector is shown in figure 1.

3. Results and discussion

The chemical structure of ternary composite of PPY-CNT-MnO₂ was confirmed by FT-IR spectra as shown in Fig 2. Moreover, the characteristic absorption bands in the 1200–1400 cm⁻¹ correspond to the C N stretching band of an aromatic amine. The broad band at 3396 cm⁻¹ is mainly caused by the N-H stretching. The other important IR bands observed at 2813 cm⁻¹ and 2656 cm⁻¹ which are due to the C H stretching vibrations and strong peak at 761 cm⁻¹ is due to the C H bending, which are the nanotube backbone vibrations [6]. The above bands indicate that PPY chains are formed in the ternary composite with the slight change in the peak values which may be attributed due to presence of CNT and MnO₂ [7]. The peak at 1069 cm⁻¹ was assigned to the C N stretching mode. The peaks at 1545 and 1480 cm⁻¹ were assigned to the fundamental PPY ring vibration [8]. But for the ternary composite these peaks were shifted to the peaks having value 1657 and 1467cm⁻¹ which indicates the shift of peaks at higher wave number. In addition, the bands in the regions from 400 to 800 cm⁻¹ can be assigned to Mn-O stretching vibrations, further indicating the existence of MnO₂ in the ternary composite [9].

The UV-VIS absorption spectra of ternary composite of PPY/CNT-MnO₂ in dimethylsulfoxide (DMSO) are shown in Fig. 3. It shows the characteristics band for the polaronic transition around 420 nm and the peak around 294 nm represents the π - π^* electron orbital transition along the backbone of the polymer chain. As CNTs-MnO₂ were incorporated with polymer, the characteristic peak assigned to the polaron- π^* transition of polymer chain shifted to longer wavelengths, indicating the interaction between quinoid rings and MWCNTs. The π - π^* transition of polymer in the nanocomposites was also shifted to longer wavelengths

[7]. The MnO_2 filling shows its presence by a strong peak in visible range in the ternary composite [9].

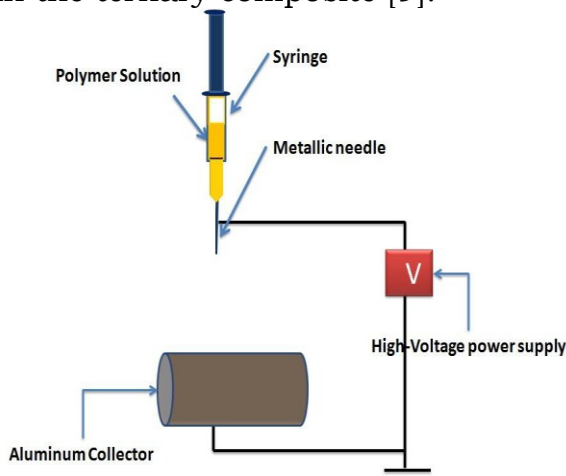


Fig. 1: Schematic diagram of electrospinning

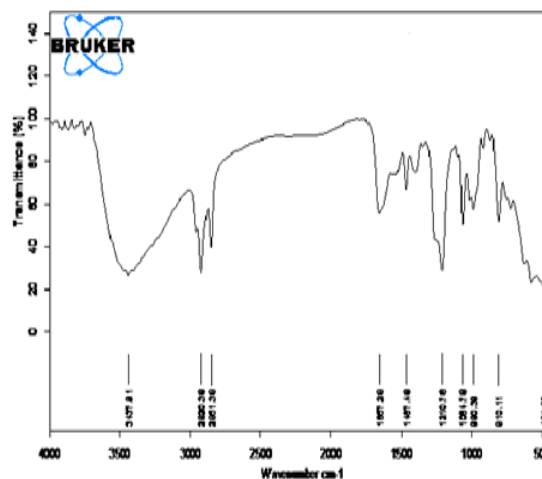


Fig 2: FTIR spectrum of PPY/CNT-MnO₂

To know the crystallinity of the MnO_2 in the ternary composite, XRD analysis was made and the resultant XRD pattern for PPY/CNT- MnO_2 is shown in Fig. 4. diffraction peaks around 37° and 66° can be readily indexed to amorphous monoclinic birnessite (JCPDS 18-0802). The peaks around 37.5° and 66.7° endorsed the presence of MnO_2 . Similar, weak, broad signals, which correspond to MnO_2 have also been observed by other authors and have suggested that the MnO_2 is in poor nanocrystallinity [10,11].

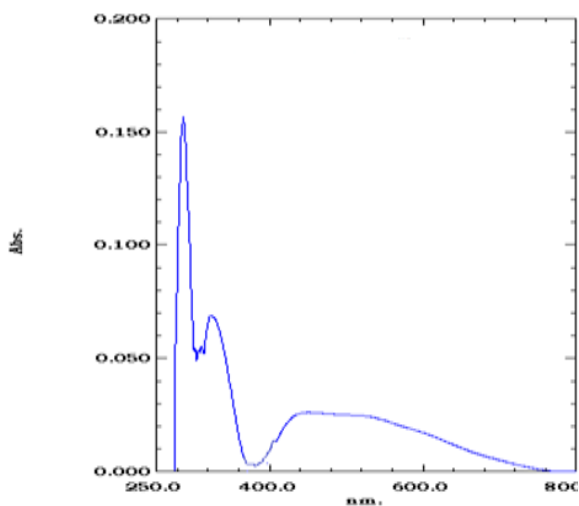


Fig 3: UV-VIS spectra of PPY/CNT-MnO₂

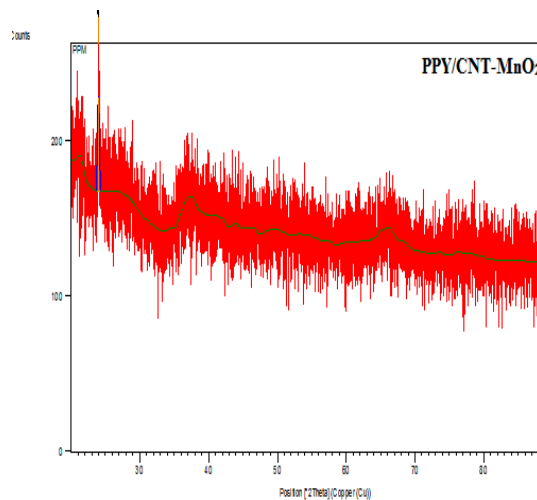


Fig 4: XRD pattern of PPY/CNT-MnO₂

The SEM image of ternary composite hardly shows presence of CNT in the material which reveals that the CNT's are well coated with the MnO_2 and polymers as shown in Fig. 5(a). The continuous well aligned nanofibers of ternary composite with the diameter in the range of 250 – 430 nm as shown in Fig. 5(b). The present composite material appears to have uniform distribution of these three individual components and it also bears pores on the surface. One dimensional ternary composite materials are useful in biosensor, supercapacitor, e-textiles etc. due to their large aspect ratio and porosity apart from high surface to volume ratio.

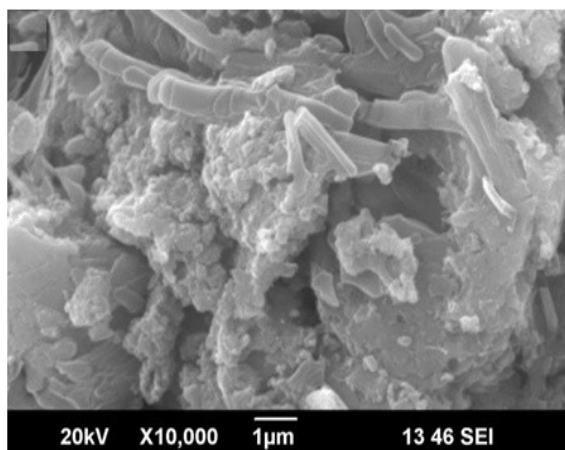


Fig 5(a): SEM image of PPY/CNT-
 MnO_2

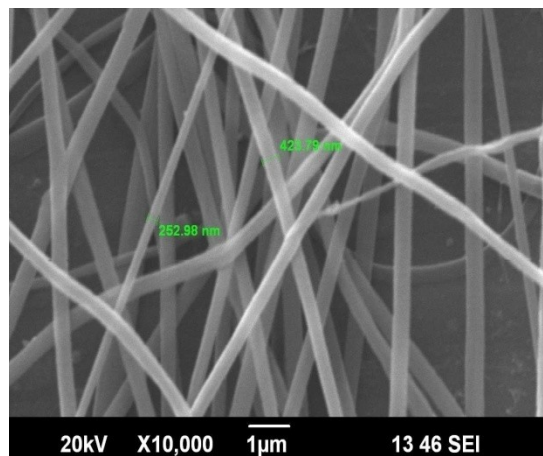


Fig 5(b): SEM image of PPY/CNT-
 MnO_2 nanofibers

4. Conclusion

The ternary composite of PPY-CNT- MnO_2 was successfully prepared by in-situ chemical oxidation method. The SEM images of the ternary composite reveals that the composite material appears to have uniform distribution of these three individual components and it also bears pores on the surface. The formation of ternary composite was confirmed by FTIR, UV-VIS and XRD. The uniform and aligned fibrous structure of ternary composite of PPY-CNT- MnO_2 with the diameter less than 500 nm were fabricated successfully by electrospinning technique.



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