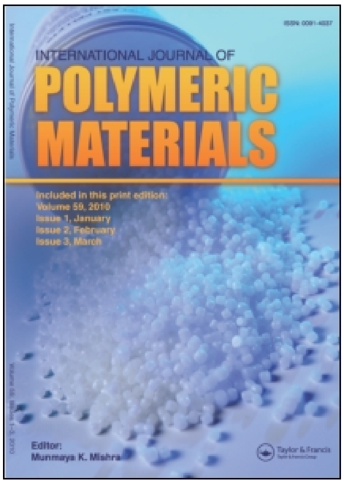

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Synthesis and Substrate-Aided Alignment of Porphyrinated Poly(ethylene oxide) (PEO) Electrospun Nanofibers

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Aligned and unaligned vanadium (IV) oxide meso-tetraphenyl porphine (VMP)/polyethylene oxide (PEO) hybrid nanofibers have been successfully synthesized by electrospinning technique. The nanofibers were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), atomic force microscopy (AFM),

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optical microscopy and scanning electron microscopy (SEM). The SEM and AFM analyses of the morphology showed that the nanofibers are cylindrical with diameters ranging from 400–700 nm. The AFM analysis also confirmed that the aligned nanofibers deposited on a small metallic spring are smoother than the unaligned ones deposited on FTO. FTIR analysis showed that the polar environment provided by the phenyl groups of VMP molecules modified the chemical configuration of PEO molecules, and XRD studies indicated that the VMP molecules were homogeneously distributed within the PEO matrix.

Keywords electrospinning, nanofibers, PEO, porphine

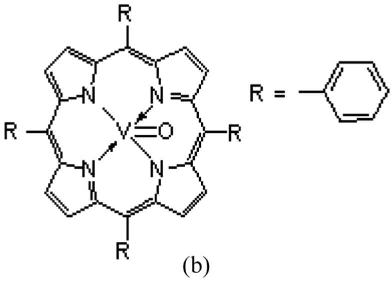
INTRODUCTION

Porphyrins and other tetrapyrroles (such as chlorophylls) have been attractive building blocks (tectons) for functional organic nanostructures [1] for decades due to their robustness and diverse photophysical and chemical properties that make them useful for applications in catalysis sensors [2], molecular electronics [3], interactions with biological systems [4], enzyme mimics for catalysis [5], light-emitting and energy/electron-transfer materials [6] and solar energy conversion [1]. Furthermore, synthetic porphyrins and their metalloporphyrin derivatives are also known to form functional nanostructures with enhanced optical and electronic properties [7] in the form of nanotubes [8,9], nanofibers [10,11] by ionic self-assembly and/or self-metallization approaches, nanospheres by coordination polymerization technique [12] or nanosheets by re-precipitation method. Nonetheless, most of these porphyrin-based nanostructures are in less useful forms like nanoparticles, sheets, or fractal objects [13,14].

On the other hand, one-dimensional (1-D) nanostructured materials, such as nanofibers, nanowires or nanorods, have attracted much attention in recent years because of their desirable and enhanced characteristics when compared to their bulk counterparts. These unique characteristics of 1-D nanostructural materials, which are due to their large surface area-to-volume ratio [15,16], have given them great potential applications in the fields of sensors [17], catalysts [18], photonics [19] and medicine [20]. As a result of this great attention to 1-D nanostructural materials in recent times, the moribund technique of electrospinning has been revived [21,22,23]. Electrospinning is a versatile, simple and economical technique of synthesizing nanofibers of diverse polymeric materials. It makes use of very high electric voltage (usually 5 kV or higher) which is applied to a polymeric solution or melt. This applied voltage generates electrostatic force which deforms the droplet of polymer solution or melt at the end of a capillary tip to a cone shape known as a Taylor cone. As the electrostatic force overcomes the surface tension of the deformed droplet, a jet is formed which is subsequently stretched and extended through spiraling loop under the electric field. The nanofibers are eventually deposited as

$$-[-CH_2-CH_2-O-]_n-$$

(a)



(b)

Figure 1: Chemical structures of (a) PEO and (b) VMP molecules.

randomly oriented mesh on the collector. Though this technique proves to be simple but controlled, production of aligned nanofibers on a substrate remains a major challenge because the disordered structures of these nanofibers are problematic for use in device fabrication in such areas as microelectronics and photonics [24,25]. Several approaches have been considered for the zalignments of the electrospun nanofibers, such as collecting fibers by parallel electrodes [26], over two fixed points [27] and a rotating drum [28].

Considering the potential applications of porphyrin nanostructures in electronic and photonic devices, it is desirable to fabricate porphyrins into well-aligned and highly ordered 1-D architectures [1,6]. However, electrospinning of nanofibers from porphyrin-containing polymers has not received much attention [29]. In this work, well-aligned and bead-free hybrid nanofibers of vanadium (IV) oxide mesotetraphenyl porphine (VMP)/poly(ethylene oxide) (PEO) (chemical structures shown in Figure 1) were successfully electrospun on a small metallic spring.

EXPERIMENTAL

0.025 g of VMP (Sigma-Aldrich) was dissolved in 35.0 g of $CHCl_3$ and stirred vigorously for 20 min, after which 0.80 g of PEO Sigma-Aldrich) was then added. Then the final solution was stirred for another 48 h on a magnetic stirrer to ensure complete dissolution of PEO.

The electrospinning of VMP/PEO hybrid fibers was carried out using the set-up as shown in Figure 2. The solutions obtained were loaded into a glass pasteur pipette. The diameter of the tip of the pipette was 1 mm. The electric field was provided by a high voltage (HV) power supply that can generate DC voltages up to 20 kV. A copper wire was inserted into the pipette to act as the electrode for charging the polymer solution. A grounded aluminium foil target

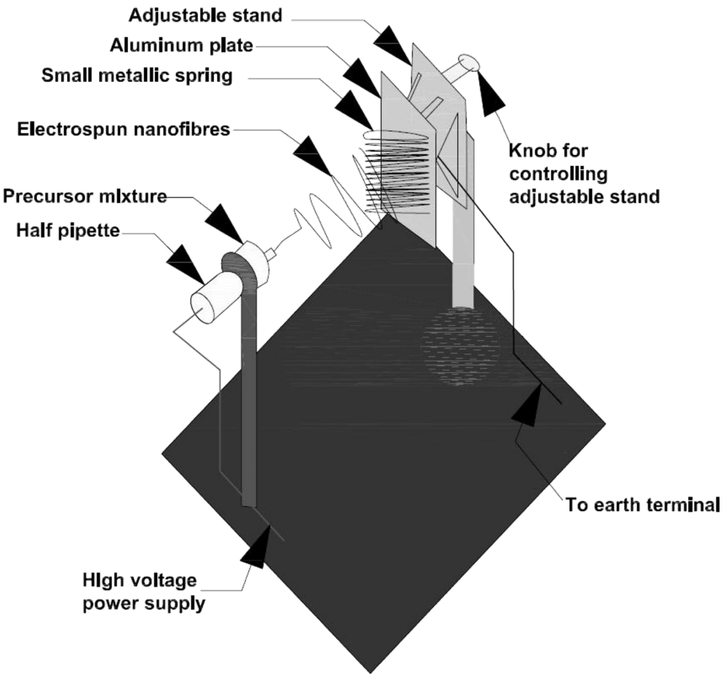


Figure 2: Simple schematic drawing of single-nozzle electrospinning set-up used in this work.

was placed opposite and almost perpendicular to the tip of the pipette on which fluorine-doped tin oxide (FTO) and a small metallic spring (perpendicular to target) as substrate for the deposition of the fibers. The stationary grounded target distance from the charged capillary tip was varied from 5 to 20 cm. We successfully deposited fibers at 15 cm for 5 kV.

Atomic force microscopy (AFM) measurements were carried out with a Nanoscope III (Digital Instruments, Inc., Santa Barbara, CA, USA) in tapping mode with etched Si probe. Fourier transform infrared (FTIR) spectra were obtained using a Perkin Elmer Pragon 1000PC FTIR spectrometer. Optical microscopy was performed on the electrospun nanofibers using a polarized optical compound microscope Nikon Eclipsen 90i/80i. For higher magnifications and detailed morphology of the fibers, samples were mounted onto scanning electron microscope (SEM) plates and examined using a Vega Tescan scanning electron microscope.

RESULTS AND DISCUSSION

Optical Microscopy and Scanning Electron Microscopy

Figure 3 is an optical image of hybrid nanofibers of red-colored VMP/PEO electrospun on a small metallic spring. The red color of the nanofibers was due

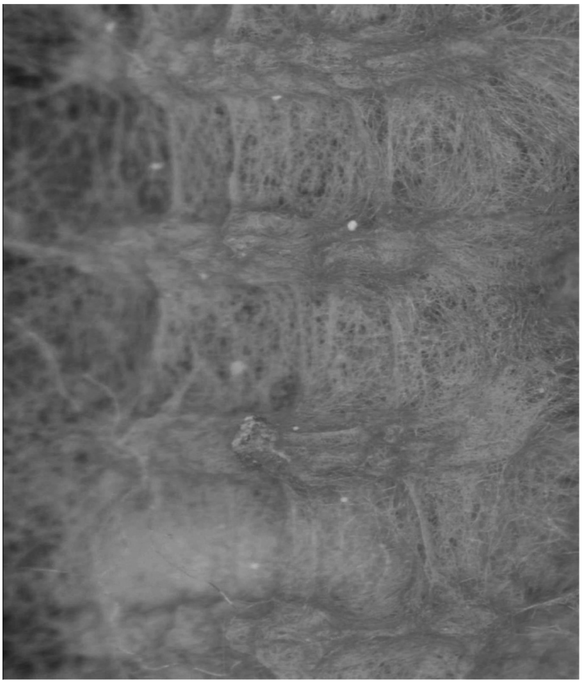


Figure 3: Optical micrograph of VMP/PEO hybrid nanofibers on a small metallic spring.

to the presence of VMP which is a metallo-porphyrin derivative. Figures 4(a) and 4(b) show the SEM micrographs of randomly deposited VMP/PEO fibers on FTO, while Figures 5(a) and 5(b) show well-aligned deposited VMP/PEO fibers on a small metallic spring at both 5 kV. As could be observed in the micrographs, the nanofibers are uniform in their overall morphology and are bead-free with cylindrical structure in all the samples.

Atomic Force Microscopy (AFM)

The surface topography of VMP/PEO hybrid nanofibers deposited on the substrates was studied by tapping mode atomic force microscopy (AFM) as shown in Figure 6. It could be observed that the VMP/PEO hybrid nanofibers have a uniform and nearly smooth surface. The surface roughness average, Ra (the most commonly used surface roughness parameter), was calculated using Nanoscope III software. The Ra of the unaligned and aligned nanofibers was calculated to be 75.4 and 34.2 nm, respectively. This confirmed that the aligned nanofiber roughness is smoother than the unaligned. In this work, the nanofiber diameters were also measured to be in the range of 400–700 nm according to the procedure suggested by Demir et al. [30] using AFM.

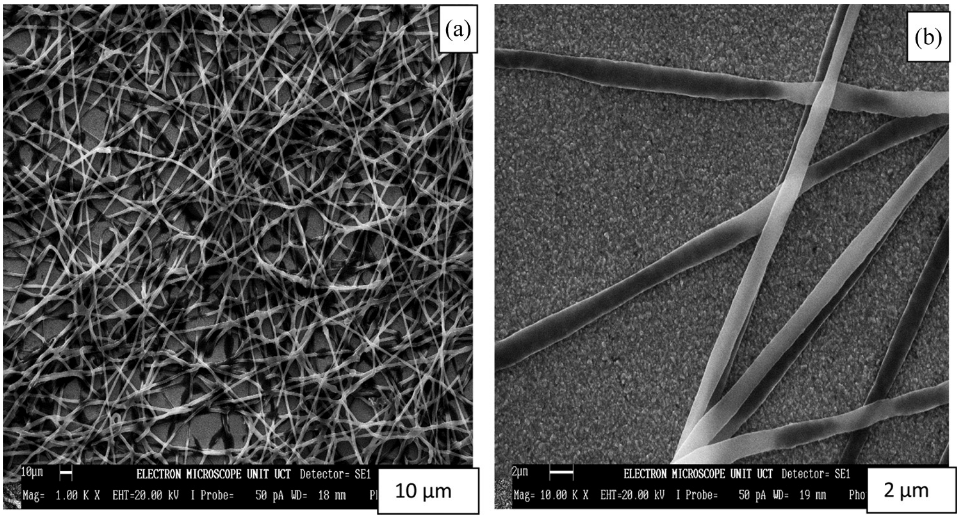


Figure 4: SEM micrographs of unaligned VMP/PEO nanofibers deposited on FTO at 5 kV for (a) 1000 and (b) 10000 magnifications.

FTIR Spectra Analysis

Figure 7 showed FTIR spectra of pure PEO powder, VMP powder and VMP/PEO nanofibers. The bands of PEO molecules around 1460 and 1348 cm^{-1} are ascribed to the vibrations of $-CH_2-$ group, likewise, the bands about 1100 and 960 cm^{-1} are due to C-O group asymmetric stretching

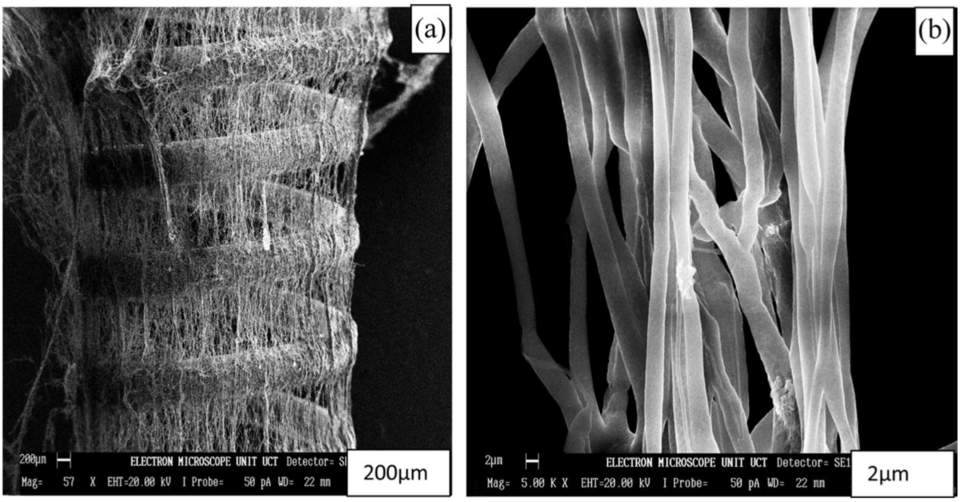


Figure 5: SEM micrographs of aligned VMP/PEO nanofibers deposited on a small metallic spring at 5 kV for (a) 57 and (b) 5000 magnifications.

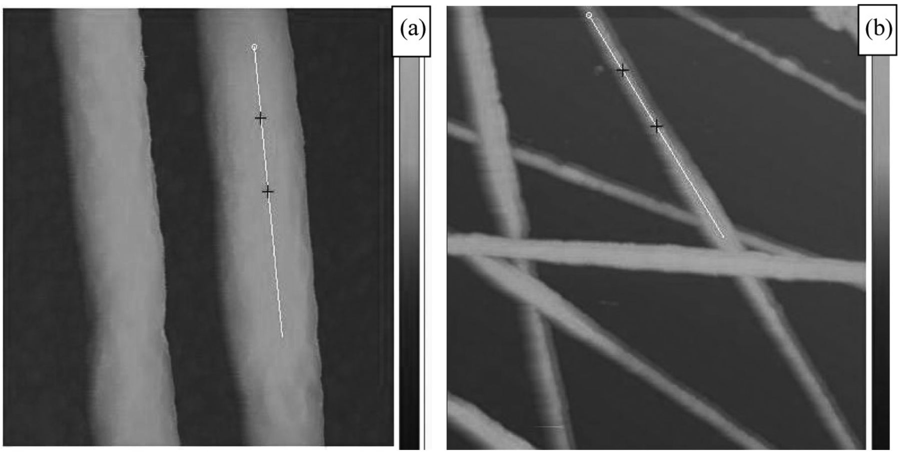


Figure 6: AFM images of VMP/PEO hybrid nanofibers depicting the line for the calculation of roughness along (a) aligned and (b) unaligned nanofibers.

vibrations [31], and the strong band near 2885 cm^{-1} is attributed to the symmetric and asymmetric C-H stretching [32]. Also, the spectra showed medium stretching vibration bands at 1593 and 1480 cm^{-1} attributed to C=C of the phenyl groups of VMP molecules. It also showed one weak in-plane and two sharp ring torsion bending vibration bands at 1170, 1070, and 1000 cm^{-1} attributed to =C-H of the phenyl groups of VMP molecules. Being

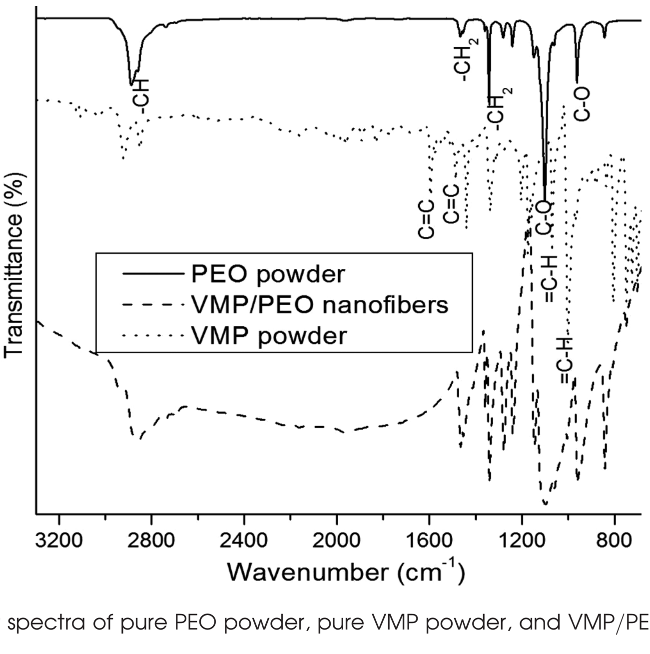


Figure 7: FTIR spectra of pure PEO powder, pure VMP powder, and VMP/PEO hybrid nanofibers.

one of the polymers with a hydrophilic oxygen atom and hydrophobic ethylene group aligned alternatively, PEO interaction to its environment is in two different configurations. PEO has a zigzag configuration in a polar environment where it embeds most of its polar oxygen atoms in the PEO chains, while in the polar environment, the oxygen atoms are exposed to strong interaction with other species like the solvent molecule and other polar species in the solution [31].

Comparing the three spectra in Figure 6, one could observe that the PEO vibration band at 2885 cm^{-1} was broadened in the VMP/PEO hybrid nanofiber; the intensity of the band at 1460 cm^{-1} was increased and width broadened, and the band at 1348 cm^{-1} was only red-shifted to 1340 cm^{-1} in the nanofibers while the bands at 1100 and 960 cm^{-1} were convoluted into one band, which broadened from 1170 to 968 cm^{-1}. Similar observations had been reported by Sui et al. [31] and Tang et al. [33]. This observation suggested that there were some chemical interactions between PEO and VMP molecules which could be a result of the polar environment, provided by the phenyl group of VMP molecules in their solution, which makes the oxygen atoms of PEO stretch out which effectually modified its chemical configuration.

XRD

XRD studies were performed on the pure PEO, pure VMP and VMP/PEO nanofibers as shown in Figure 8. The XRD patterns showed that pure VMP

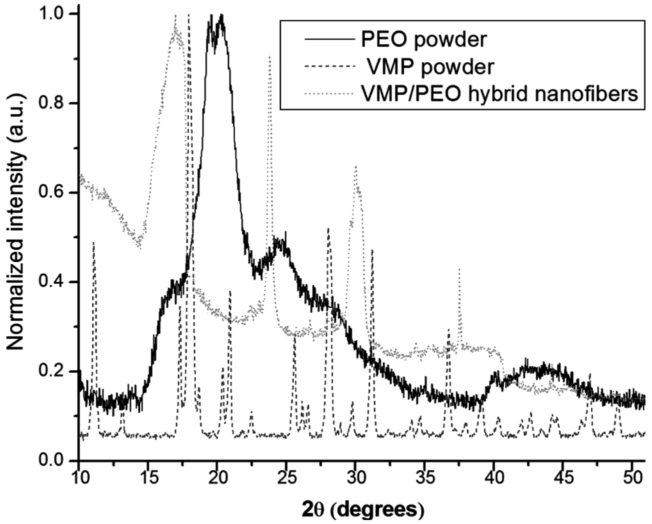


Figure 8: XRD patterns of pure PEO powder, pure VMP powder and VMP/PEO hybrid nanofibers.

is essentially crystalline while the PEO is semicrystalline. From the figure, pure PEO diffraction peaks are at $2\theta = 19.40^\circ$ and 24.15° which correspond to the PEO crystalline phase. This is in close agreement with the report of Yan et al. [34] and Uyar et al. [35]. The figure also shows that VMP major diffraction peaks were at 11.09, 17.98, 21.01, 28.00, 31.22, and 36.80°. However, in the XRD patterns of the hybrid nanofibers there were no distinct peaks of VMP which suggests that the VMP molecules were distributed homogenously in the hybrid [35], but the diffraction peaks of PEO were slightly shifted to 16.97° and 23.60°, respectively [34], and there were appearances of two new distinct peaks at 30.11° and 37.56°. This depicts interactions between VMP and PEO molecules as confirmed by the FTIR studies and these interactions increased the crystallinity of PEO molecules.

CONCLUSION

In this study, aligned VMP/PEO hybrid nanofibers were successfully prepared by simply depositing them on a small metallic spring via electrospinning technique. The morphology of the nanofibers has been characterized by SEM and AFM. The AFM analysis showed that the nanofibers are cylindrical in structure with their diameter ranging from 400–700 nm. The chemical interactions between the VMP and PEO molecules were studied by FTIR and XRD, which showed that the polar environment provided by the phenyl group of VMP molecules changed the PEO molecules' configuration and increased its crystallinity. The AFM analysis also confirmed that the aligned nanofibers deposited on a small metallic spring are smoother than the unaligned ones deposited on FTO.

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