Effect of Addition of Polyaniline on Polyethylene Oxide and Polyvinyl Alcohol for the Fabrication of Nanorods

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ABSTRACT: For the first time, the fabrication of novel nanorods by the addition of polyaniline (PANI) to polyethylene oxide (PEO) and polyvinyl alcohol (PVA) polymers through electrospinning method is investigated. Field emission scanning electron microscopy observations reveal the formation of nanofibers and nanorods having diameters in the range of 26.87–139.90 nm and 64.11–122.40 nm, respectively, and lengths in the range of 542.10 nm to 1.32 μm. Photoluminescence (PL) analysis shows the presence of peaks which are characteristic of isotactic polymers (363–412, 529–691 nm), 412–529 nm for PVA/PEO and 363–691 nm for PVA/PEO/PANI. PL spectra also show peak bonding at a wavelength of 552 nm. Manufacture of nanorods by electrospinning method gives better options for controlling the diameter and length of nanorods.

1. INTRODUCTION

A polymer is a macromolecule composed of multirepeating subunits, and because of their properties, both synthetic and natural polymers have a ubiquitous role in everyday life. Because of the presence of the reactive −NH− groups within its chain, polyaniline (PANI) is considered as one of the most attractive conduction polymers and is used in many applications such as sensors, batteries, super capacitors, electronic devices, and corrosion protection in organic coatings. It possesses good chemical and physical properties, high environmental stability, low cost, good electrical conductivity (p-type), facile fabrication, flexibility, light weight, and potential of chemical and electrochemical syntheses, where conductivity of PANI is a very important parameter. In addition, it is difficult to cast PANI as a free-standing film or deposit as a thin film onto a substrate, so PANI is usually mixed with polyvinyl alcohol (PVA)/polyethylene oxide (PEO). PANI is an organic conduction polymer that has been known for more than 100 years. Recently, research on PANI has proven that it is one of the conductive polymers (CPs), whose conductivity can be increased by doping hydrogen acids during polymerization. Many previous studies have dealt with the effect of adding PANI. Deshmukh et al. found that EDET-PANI/single-walled nanotube (SWNT) composite is suitable for Cu(II) ion determination. They used the CP (PANI) and found that using a PANI layer for PANI/SWNTs on a metal sensor surface increased the transfer speed of the electrical signal through carbon nanotubes. They succeeded in further modification by ethylenediaminetetraacetic acid with electrochemical synthesis of PANI/SWNT nanocomposite. Deshmukh et al. synthesized an electrochromic PANI film on indium tin oxide (ITO)-coated glass substrates using potential cycling; they noted the electrochromic and electrochemical responses by PANI/ITO toward Cu(II) ions through aqueous solutions. Popov et al. deposited the PANI–poly(3,4-ethylenedioxythiophene (PEDOT) film electrochemically on glass with an ITO electrode using various techniques. Through deposition of PANI and by the presence of PEDOT using electrochemical technique, the conductivity of the formed PANI–PEDOT film improved with a short response time of the sensor. Subsequently, the sensor was used to determine pH, and CO2 sensors that are sensitive to pH were fabricated. Turemis et al. indicated through photoluminescence (PL) measurements that ZnO/PANI nanocomposites are good candidates at room temperature to determine acetic acid. The PL results and measurements of composites exposed that increasing the sample concentration led to decreased PL. ZnO/PANI sensors showed good sensitivity to acetic acid in the range 1–13 ppm, with suitable recovery and response times for monitoring of acetic acid.
were obtained using the electrospinning method. Electrospinning method is a straightforward nonmechanical method used for the fabrication of long polymer fibers discovered in air since the 1930s.23 PEO is soluble in water with the idealized formula \( \text{C}_n\text{H}_{4n+2}\text{O}_{n+1} \), as can be seen in Figure 1b. PEO features such as thickening, stickiness, water retention, and film formation can be used in a variety of applications, such as mining paper, pharmaceuticals, and cleaning products. In addition to being cast for providing high processing flexibility, PEO has many applications in the bulk and in solution to prepare porous materials and systems of hybrid and controlling of drug delivery. PEO is not particularly hazardous and has been used since the 1970s in Canadian newsprint mills because of its shear history and other applications based on high-yield pulps.

PEA with the idealized formula \( \text{[C}_n\text{H}_{4n}\text{O}]_n \), is also called polyethanol; its structure is shown in Figure 1c. PVA has the following features: adhesive and emulsifying properties; resistant to oil, grease, and solvents; highly transparent; and flexible. In addition, it has high aroma barrier and oxygen properties; however, these properties depend on humidity (i.e., more water is absorbed with higher humidity). Water as a plasticizer will work to reduce the tensile strength with increasing tear strength and elongation. PVA biodegrades slowly and is nontoxic; solutions up to 5% PVA are nontoxic to fishes.24

Lian and Ye25 investigated the impact of PEO on the structure and property of the gel. The subatomic PEO chains with relatively high crystalline nature and the subatomic weight may restrain the activity chains of PVA, bringing about the increasing transition temperature \( T_m \) of PVA and addition of mechanical properties of the PVA hydrogel. Hence, expanding the amount of PEO results in an expanded equipoise proportion of PVA/PEO hydrogel films, bringing about the development of a permeable micro-structure with expanded pore size and slim water retention limit. Avci et al.26 prepared PEO/PVA nanofibers using the electrospinning method, and the results proved that 2.793% Li in a solution of PEO/PVA showed the impact of bacteriostatic action on Escherichia coli and impact of bactericidal action against Staphylococcus aureus.

Dispenza et al.27 used oxidative chemical polymerization with either PVA or chitosan as polymeric stabilizers in water and reported noted emissive demeanor of two PANI nanoparticle systems fabricated for the first time. They investigated that increasing the pH of the suspending medium from acidic to alkaline (PVA/PANI) or neutral (chitosan/PANI) could not lead to emission from PANI nanoparticles. Reciprocally, PANI nanorods fabricated under the same conditions, but with added poly(N-vinyl pyrrolidone) (PVP), are not emissive at any pH. The polymeric surfactant is the main factor in controlling the morphology and properties of the PANI dispersions obtained. Chitosan polymer is highly effective in controlling the particle size of PANI and the size distribution with the chosen conditions. Counter to PVP and PVA, the disadvantage of chitosan is its limited water solubility.28,29 Li et al.30 used the measurement of four-terminal resistance based on the same doping method and observed good conductivity of the nanofibers compared to PANI/PEO thin film. Decreasing the concentration through decreasing the molecular weight to 0.10 wt % (less than 5,000,000 wt) leads to improved conductivity of the mixed polymers; a better morphology of the homogeneous nanofibers was obtained. The authors used electrospinning PANI/PEO nanofibers to detect poisonous NH3 sensors showing high performance such as a good response time of 6 s with reuse in sub-6 min as cycle time. The use of micro/nanomanufacturing technology with low cost and good processing characteristics makes possible unification with other systems and devices, especially electronic ones. Mostafaei and Zolriasatein31 demonstrated that PANI filled with ZnO nanorods was prepared by the chemical oxidative method, and the results showed that the interaction between ZnO and PANI is based on the structured bonding of hydrogen and the electrostatic interaction. The structural bonding of hydrogen and the electrostatic interaction between acid of camphorsulfonic-capped ZnO nanorods and PANI play a main role in the fabrication of PANI/ZnO nanocomposite. The conductivity of the PANI film was found to be higher than that of the PANI/ZnO nanocomposite film; the reason was attributed to the interface formation between oxygen of ZnO nanorods and hydrogen of PANI.

Until lately, the field of electrically CPs contained materials with practically no processability. Recently, it was found that monomers based on aniline, pyrroles, and thiophenes can be manufactured and polymerized to materials with high molecular weight. Careful controlling of substituents that make CPs is possible.32 CP nanowires and nanotubes can be fabricated by various methods, such as electrospinning method; chemical methods such as soft and hard physical template-guided synthesis (interfacial and reverse emulsion polymerizations); and lithography methods. These nanostructures have a good potential in applications and fundamental research in molecular electronics or nanoelectronics, nanodevices and systems, medicine, bionanotechnology, and nanocomposite materials.33 Multilayers of polymer solar cells (PSCs) and dye-sensitized solar cells can be fabricated using electrospinning. Advantages and disadvantages of different devices arise according to their structure; bulk heterojunction and inverted types result in the best solar cells. The electrospinning method will be appropriate to fabricate the active layer in bulk heterojunctions.34,35 The formation of nanorod-like morphology could enable the manufacturing of inexpensive and easily scalable optoelectronic devices. The critical aspect ratio (rod length/rod diameter) is an important parameter and is
considered as a key factor in revealing enhanced properties, leading to high-efficiency solar cells, light-emitting diodes, and photodetectors. In this study, novel nanorod-based PVA/PEO/PANI composites have been fabricated via electrospinning method, where both the diameter and length (aspect ratio) of the nanorods can be controlled by optimizing the parameters of electrospinning and polymers.

The aim of this study was to obtain a novel structure by electrospinning and hence a greater ability to control the diameter and length of the nanorod structure to improve the performance of solar cells and sensors. The parameters of electrospinning are able to control the diameter and length of the nanorods better than other methods of deposition because it is easier to control the deposition and thickness of the film.

We studied the impact of addition of PANI to the mixture PEO/PVA in changing the microstructure and thus the properties of the obtained nanocomposites. PVA was characterized with a high adhesion degree, transparency, and good solubility in water, and hence it is a very suitable choice to be mixed with PANI that has a too weak adhesion as a thin film. In addition, PEO has great impact in improving the conformation and hence is the best choice to be a suitable compound with the selected polymers in this study.

2. EXPERIMENTAL SECTION

2.1. Sample Preparation. PEO with a molecular weight (Mw) of 600,000, PVA with a Mw of 22,000 (alcoholysis degree 87–89%), and PANI with Mw > 15,000 were purchased from Sigma-Aldrich. A solution of PANI was dissolved in 1.4 wt % chloroform, which was then magnetically stirred for 6 h at room temperature. A solution of 5 g of PEO was dissolved in distilled water for 2 h at 60 °C by stirring. A solution of PVA (15 wt %) was dissolved in distilled water for 4 h at 80 °C by stirring. After that, using the above polymeric solutions, the two mixtures were prepared:

(1) A mixture of PVA and PEO (1:1) was stirred at room temperature for 18 h. The symmetric solution was transferred to a 5 mL plastic syringe with a needle (27 g). The syringe to syringe pump was placed, and a high voltage supply up to 15 kV was connected between the collector plate and the needle. The setup used to fabricate nanofibers via electrospinning was optimized: the distance between the needle and the collector is 9 cm, the flow rate is 5 mL/h, and the high voltage is 12 kV. After completion of deposition, the nanofibers were removed from the Al foil and then dried in air.

(2) A mixture of PVA, PEO, and PANI (4:4:1) was stirred at room temperature for 24 h. The conditions used to produce PVA/PEO/PANI nanorods via electrospinning were similar.

2.2. Characterization Techniques. A high-resolution X-ray PANalytical X’Pert PRO diffractometer equipped with Cu Kα radiation (λ = 1.5418 Å) was used to check the crystalline quality and growth orientation of the obtained nanostructures. Morphological observations were performed using field emission scanning electron microscopy (FESEM, Carl Zeiss, Leo-Supra 50VP). Micro-PL measurements were carried out at room temperature using HeCd laser with an excitation source of 325 nm. The viscosity of the solutions was measured by a rotational Visco Basic Plus L viscometer in the range 20–2,000,000 cP and speed 0.3–100 rpm (C/Constitucio—Barcelona—Spain).

3. RESULTS AND DISCUSSION

3.1. Solution Characterization. The viscosity values of PVA/PEO and PVA/PEO/PANI are 2300 and 2700 cP, respectively, see Table 1. The difference between the viscosities can be attributed to the polymeric structure and molecular weight of each individual polymer as well as the type of solvents. These polymers have an average molecular weight of 22,000, 600,000, and >15,000 according to the manufacturers. Further, there are parameters which have an effect on the polymer chain and thus on viscosity, including factors controlling the polymer–solvent interaction. Moreover, the surface tension of solutions exhibited similar values for PVA, PEO, and PANI, which is due to low concentration and difference in surface tension of the solvent and polymer.

| polymers | viscosity (cP) | surface tension (mN/m) |
|----------|---------------|------------------------|
| PVA      | 1700          | 37.3                   |
| PEO      | 18,500        | 43                     |
| PANI     | 960           | 26.6                   |
| PVA/PEO  | 2300          | 39.4                   |
| PVA/PEO/PANI | 2700      | 31                     |

Table 1. Viscosity and Surface Tension of PVA, PEO, PANI, PVA/PEO, and PVA/PEO/PANI

3.2. FESEM Observations. Electrospinning PVA/PEO composite nanofibers were stabilized to overcome the disintegration in water. Figure 2a shows the formation of fiber with an average diameter ranging from 26.87 to 139.90 nm; in addition, the fibers have smooth surfaces and are interconnected forming a network-type of microstructure. Different parameters are responsible for the morphology of PVA/PEO such as the type of acid dopant and oxidants. On the other hand, electrospinning showed an irregular microstructure with variable diameter of PVA and PEO fibers. Image analysis also confirms the formation of clear fibers, where PEO plays a key role in improving the quality of the obtained morphology. Through formation of fibers using electrospinning, a solution jet is affected by humidity and temperature. The high voltage that is applied on the solutions of the polymer is considered accountable for the stretching of the fiber and ultimately for the distribution of the fiber diameter. The surrounding air has an effect on the jet’s transmission, thus affecting the distribution of the fiber diameters. Figure 2b shows the formation of nanorods of PVA/PEO/PANI. Higher magnification reveals that the nanorods have diameters and lengths in the range of 64.11–122.40 nm and 542.10 nm–1.32 μm, respectively. The surface of the nanorods looks smooth as well. The relationship of the end facet size with the diameter presumably causes a decrease of the polydispersity of the rods.
and an increase of the ratio. The proposed growth mechanism is based on the evolution of morphologies for PVA/PEO/PANI nanorods. Chemical properties of PANI polymerization combined with the effects of electrospinning deposition play primary roles in formation of nanorods and sphere-shaped structuring of the micelles to the complexing more molecules of aniline with selenious acid when the selenious acid to aniline ratio is greater than 1, where a few freely diffusing molecules of aniline in the SELA-ANI micelle form PANI nanorods. The PANI nanorods were obtained by combining the initiator solution with rod-like micelles.\(^42\)

Essentially, anisotropic crystal growth is mainly required to form nanorods, which is generally achieved when the free energy of the surface has different crystallographic planes. The relationship between the growth speed of a crystalline plane \((hkl)\) in the normal direction and the interplane spacing is inverse; consequently, it helps in getting the optimum shape of the hexagonal structure of PVA/PEO/PANI. During the polymerization, the micelles are big spheres by accretion\(^43\) or tubes/rods during extension\(^44\) depending on the work conditions. The experiments showed that the occurrence of the extension procedure judges the morphology of PANI. The micelle size plays a main role on the size of the nanostructures; hence, samples of PANI doped with various inorganic acids have various diameters. Self-assembly is a process used to achieve this are when the unimers shaping the micelles are prevented at the temperature in which the micelles are found, insoluble in the solvent of the micelle or if core shaping is to achieve this are when the unimers shaping the micelles are further, addition of the surfactant and change in concentration affect the diameter of the PANI nanostructure.

Kinetically frozen process is a process in which polymer micelles do not have the feature of relaxation. Two conditions to achieve this are when the unimers shaping the micelles are insoluble in the solvent of the micelle or if core shaping is prevented at the temperature in which the micelles are found, which retains the shape when the conditions are achieved.\(^45\)\(^,\)\(^46\)

Further, certain morphologies are formed based on the lack of relaxation processes;\(^47\)\(^,\)\(^48\) kinetically frozen micelles make them particularly interesting for the development of long-circulating drug delivery.\(^49\)

In addition to that mentioned above, mechanisms of PANI nanorods using electrosprinning have been studied. PVA/PEO and PVA/PEO/PANI composites were deposited by the same parameters, where they differed in viscosity and surface tension. Although the solution jet traveling toward the collector intermittently because of a high voltage was not enough to extend the jet, it helped with growth of the micelles during mixing of polymers to form the nanorods. Intermittently jets occurred when PANI was added to PVA/PEO using the same parameters used for the formation PVA/PEO nanofibers. This chipping occurred during the deposition process, where the viscosity and surface tension changed when added to PANI, which led to getting cut up as in a process of spraying. When the deposition was continued for a sufficient time, the longitudinal growth continued to form nanofibers; note that many studies confirmed fabricating nanorods by the spray technique.\(^50\)\(^,\)\(^51\)

In addition, in such cases, there are reasons for the formation of “nanorods.” The interactions between PANI particles (probably PANI-ES—as prepared) and matrix polymers are rather low. Therefore, PANI particles remain aggregated, and the formation of rod-like agglomerates is a consequence of hydrodynamic field forces acting during the electrosprinning process.

### 3.3. X-ray Diffraction Analysis

Figure 3a shows the X-ray diffraction (XRD) pattern of PVA/PEO film deposited onto a glass substrate. Two diffraction peaks can be observed at 2\(\theta\) of 18.856 and 24.733\(^\circ\), which correspond to (101) and (111) reflections of the PVA and PEO phases, amorphous, and \(\beta = 90^\circ\) and either to a planar zigzag conformation or to a 72° helical conformation,\(^52\)\(^,\)\(^53\) with lattice parameters \(a = 6.9760\) Å, \(b = 8.6290\) Å, \(c = 10.4300\) Å, and \(\beta = 90^\circ\) crystal structures, respectively. Figure 3b shows the XRD pattern of the PVA/PEO/PANI thin film synthesized by interfacial polymerization and shows sharp and well-defined peaks. In addition, a new intense peak appears around 2\(\theta\) = 22°. The sharpness of peaks indicates the semicrystalline nature of PANI\(^54\) with improved crystallinity. The planes of benzimidazol and quinoxid rings of PANI chain are responsible for its crystalline nature. PANI nanofibers could be fabricated in large scale without undesired byproducts using the electrosprinning method.\(^55\) The peaks, characteristic of polymer–fiber crystallites, were observed, resulting in solvent-induced polymer crystallization. During the crystallization of fibers produced by electrosprinning, other factors contributed, besides the nature of the polymers, such as the rate of flow of the plane of the needle, where a slow flow rate is favored, leading to higher production of fibers by electrosprinning.

### 3.4. PL Characterization

Absorption of PL occurs among electrosprinning light-emitting nanofibers Figure 4. PL spectra show almost identical emissions: (i) peak around 412 and (ii) doublet around 529 nm. A strong PL resonance excitation appears within a wavelength range of 412–529 nm of PVA/PEO configuration. Consequently, the emission peaks occur in multiple overlap peaks but with higher intensity. This may be due to the many absorption states of diverse defects existent in PVA/PEO. A similar graph was also observed but with the existing of the PVA/PEO peak at a wavenumber of 412 nm. Broad emission bands occur within a range of 412–552 nm, when the excitation is increased. However, the emergence of clear peaks located at 363 and 691 nm after the addition of PANI can be noticed; their intensity is high in comparison with PVA/PEO, and the latter shows a peak with a very low intensity. The photons, the energy of which is consonant with the band gap between the bonding orbital and the antibonding orbital, will be absorbed as PANI was radiant by light. The morphology of the PANI film changes from nanofibers to...
nanorods with the stretch of deposition time, and the surface area increases in contrast; see Figure 2a,b. More photons are absorbed and for that reason, more holes will merge with the excited electrons to strengthen the luminous intensity. This shows that the luminous intensity of PVA/PEO/PANI films increase with the addition of PANI.

4. CONCLUSIONS

Novel nanorods are fabricated by the electrospinning method through the addition of PANI to PVA/PEO composites as shown in the FESEM image. We demonstrate for the first time that various nanostructures (nanofibers and nanorods) of the polymer blend can be produced using the electrospinning method by choosing an appropriate polymer and optimizing the process parameters. This novel method could be extended to other materials to fabricate a variety of nanomaterials having various morphologies and enhanced/novel properties offering potential technological applications. It will have an active role in the manufacture of PSCs as well as in the manufacture of organic light-emitting diodes.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge the support of the school of physics University Science Malaysia under grant FRGS no. 203/PFIZIK/6711349.

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