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PVDF nanofibers composite containing core-shell (ZnO@ZIF-8) for use in smart textile applications

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ABSTRACT

Currently, electronic textiles (E-textiles) have gained tremendous attention. In recent years, there has been significant interest in metal-organic frameworks (MOFs), which are emerging porous materials and have gained immense interest in recent years. In this study, we successfully synthesized a core-shell zinc oxide @ zeolite imidazolate framework-8 (ZnO@ZIF-8) composite and used it to fabricate electrospun polyvinylidene fluoride (PVDF) nanofibrous composites. Nanofibers were produced using an electrospinning machine. We analyzed the synthesized (ZnO@ZIF-8) powder and PVDF and PVDF/(ZnO@ZIF-8) nanofibrous composite using field emission scanning electron microscopy and X-ray diffraction techniques to investigate their morphological and crystallographic structures. The results demonstrated the successful fabrication of uniform and bead-free nanofibers. The incorporation of (ZnO@ZIF-8) composite particles into the PVDF polymer solution resulted in an increased β-phase content in the fabricated PVDF/(ZnO@ZIF-8) nanofibrous composite compared to the pristine PVDF nanofibrous composite. The nanofibrous mat has various applications, including E-Textiles, flexible sensors, energy scavenging, smart textiles, wearable devices, and energy harvesting.

I. INTRODUCTION

Recently, Electronic textiles (E-textiles) based on piezoelectric properties have gained tremendous attention based on the piezoelectric effect with the ability to convert mechanical energy into electricity and vice versa. poly vinylidene fluoride (PVDF) as a Polymeric Piezoelectric Materials (PPM) have many advantages over Ceramics Piezoelectric Materials (CPM) such as flexibility, low processing cost, biocompatibility, high chemical resistance and other properties. To improve the piezoelectric performance of PVDF for sensor application, the amount of electroactive crystalline phases, specially the β-phase with the largest spontaneous polarization, should be enhanced [1-5].

Various studies showed that the incorporation of piezoelectric nano materials was found to be efficient for improving the piezoelectric properties of PVDF-based nanofibrous mat. Examples include nano-clay [6], zinc oxide (ZnO) particle [7], Co-doped ZnO [8], Metal Organic Frameworks (MOFs) [9] and TiO_2 [10] which their piezoelectric enhancing effect has been shown, recently.

Recently, porous crystalline materials consisting of organic ligands and metal ions, called Metal-organic frameworks (MOFs), linked through coordination bonds have been attended. These nanostructures have attracted a lot of interest in a wide range of applications [11-14] Due to their superior unique structural features including high porosity, tunable pore size, specific surface area and versatile performance. [15, 16]. Zeolitic imidazolate

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frameworks (ZIFs) are a category of MOFs with the same structures to zeolites. They have are built upon 4-connected nets of tetrahedral units, wherein metal ions, such as Zn^{2+} or Co^{2+}, are linked through N atoms in diatopic imidazolate anions. Between the ZIFs, Zeolite Imidazolate Framework-8(ZIF-8), which is a type of albite zeolite with a nanoporous structure, is a regular representative of ZIFs [17].

Electrospinning is a simple, scalable, and widely used technique for fabricating nanofibers, it has been Multipurpose and used for several applications [18, 19]. Owing to the high voltage which will be applied to the electrospinning solution, caused the $-CF_2/-CH_2$ molecules to align. Molecular $-CF_2/-CH_2$ dipoles tend to be aligned [19]. According to this case, no additional polarization process is needed to increase the β phase value of PVDF nanofibers [1]. For example, Hasanzadeh et al. [1] produce PVDF nanofiber containing Graphene-ZnO. Their result show an increase in the β phase value of PVDF nanofiber containing the above composite from 51.08% for pristine PVDF nanofiber to 62.36%. In another research, Hadavi Moghadam et al. [2] fabricate a piezoelectric sensor based on PVDF nanofiber containing MOFs, exactly UIO-66, according to the XRD and FTIR results amount of the β crystalline phase is enhanced in the presence of MOF during electrospinning from 64% for raw PVDF to 67% for PVDF-5 wt % MOF. In this work, the synthesis and characteristics of (ZnO@ZIF-8) composite and PVDF, PVDF/(ZnO@ZIF-8) nanofibers were studied.

II. EXPERIMENTAL METHOD / TEORETICAL METHOD

2.1 Materials

Zinc oxide (ZnO, 99.0%), 2-methylimidazole (2-MIM) and, ($Zn(NO_3)_2.6H_2O$, 98%) were obtained from Merck Co. (Germany), Poly(vinylidene fluoride) (PVDF) (Mw =350,000 g/mol) was obtained from Kynar Co. (USA) and N,N-dimethylformamide (DMF, Mw=73.09 g/mol, 99.0%) was obtained from Neutron Pharmachemical Co. (Iran) and used without any further purification.

2.2 Synthesis of ZnO@ZIF-8

Core–shell ZnO@ZIF-8 composite was synthesized by a modified method that described by Zhan et al. [20]. In a typical experiment, 0.164 g 2-methylimidazole (2-MIM) was dissolved in 15 mL N, N-dimethylformamide (DMF), and the solution was pre-heated at 70 °C. After that, 0.140 g of ZnO powder was added into 5 ml deionized water and stirred for 15 minutes then ZnO suspension wasadded to the pre-heated solution. After that, three drops of anionic soap were added to the above mixture for the emulsifying role. Then the mixed suspension was heated at 70 °C with stirring for 5 h. The ZIF-8 powder was synthesized as in the previous works with a slight change [11-14].

2.3 Synthesis of ZnO@ZIF-8

A 25 wt % solution of PVDF in DMF was prepared and then stirred for 12 h at 50 °C. Different percent of composites (1,3,5,10 wt %) was added to the prepared solution, followed by another 12 h stirring and finally sonicated for 20 min to obtain a homogenous mixture. PVDF/(ZnO@ZIF-8) nanofibers fabrication done by an horizontal electrospinning machine (Nano-Azma, Iran). Table 1 shows the electrospinning solutions condition.

The mixture solutions were filled into 5mL syringes (22-gauge needle). The flow rate of the device was 0.2 mL/h. A DC high-voltage power supply (25 kV) was applied between grounded collector (12 cm spinning distance) and the needle tip. A rotating drum (2000 RPM) with traverse mode used to collect the nanofibrous mat. The electrospinning process was done at 28% relative humidity and 27 °C temperature for 4 h. The parameters of electrospinning were obtained based on a series of trial-and-error experiments.

Table 1. Electrospinning conditions of PVDF/(ZnO@ZIF-8) nanofibrous mat

Composite amount *(wt%)*	**Applied voltage** *(kV)*	**Spinning distance** *(cm)*	**Volume flow rate** *(mL/h)*	**Drum speed** *(rpm)*
0	25	12	0.2	2000
1	25	12	0.2	2000
3	25	12	0.2	2000
5	25	12	0.2	2000
10	25	12	0.2	2000

2.4 Characterizations

The morphology of fabricated composite and nanofibers were studied by field-emission scanning electron microscopy (FESEM) (MIRA III, TESCAN). measuring the diameter of nanofibers done by Digimizer software . in FESEM images to determine the diameter distribution. crystalline characteristics of the synthesized composite and nanofibers were evaluated by X-ray diffraction (XRD).

III. RESULTS AND DISCUSSIONS

3.1 Characteristics of (ZnO@ZIF-8) Composite

The formation of a layer of perfect ZIF-8 shell over the core is a vital step in the fabrication of a core–shell ZIF-8 based structure. Generally, the core had to be modified with some organic groups or ZIF-8 seeds to facilitate the formation of ZIF-8 over the core. As shown in Figure 1, the surface of the ZnO core was closely packed with hexahedron ZIF-8 nanocrystals, showing that a layer of ZIF-8 shells had grown well on the core.

The X-ray diffraction (XRD) patterns of ZIF-8, ZnO, and ZnO@ZIF-8 powders are depicted in Figure 2. XRD analysis plays a crucial role in characterizing the crystalline structure and crystallographic planes present in the synthesized powders. ZnO crystals exhibited characteristic peaks at 2θ values of 31.8°, 34.5°, 36.42°, 47.5°, 56.6°, 62.8°, and 69.1°, corresponding to the (100), (002), (101), (102), (110), (103), (200), (112), and (201) planes, respectively. On the other hand, the XRD pattern of ZIF-8 demonstrated a crystalline structure with distinct peaks at 2θ values of 7.3°, 10.3°, 12.8°, 16.5°, 18.1°, 19.7°, 22.2°, 24.6°, 25.7°, 26.8°, 28.9°, and 29.8°, corresponding to the (011), (002), (112), (013), (222), (123), (114), (233), (224), (134), (125), and (044) planes, respectively. These findings are consistent with previously reported works [11, 12, 14] which provide valuable insights into the crystalline characteristics of ZIF-8. Importantly, the XRD pattern of the ZnO@ZIF-8 composite revealed the presence of characteristic peaks corresponding to both ZIF-8 and ZnO. This observation confirms the successful formation of the desired core-shell structure, as reported in similar studies [21, 22]. The agreement between the experimental results and previous findings strengthens the validity and reliability of the synthesized materials. Overall, the XRD analysis provides valuable information on the crystalline properties and crystallographic planes

of the synthesized powders, supporting the successful synthesis of ZIF-8 and the formation of the core-shell structure in the ZnO@ZIF-8 composite.

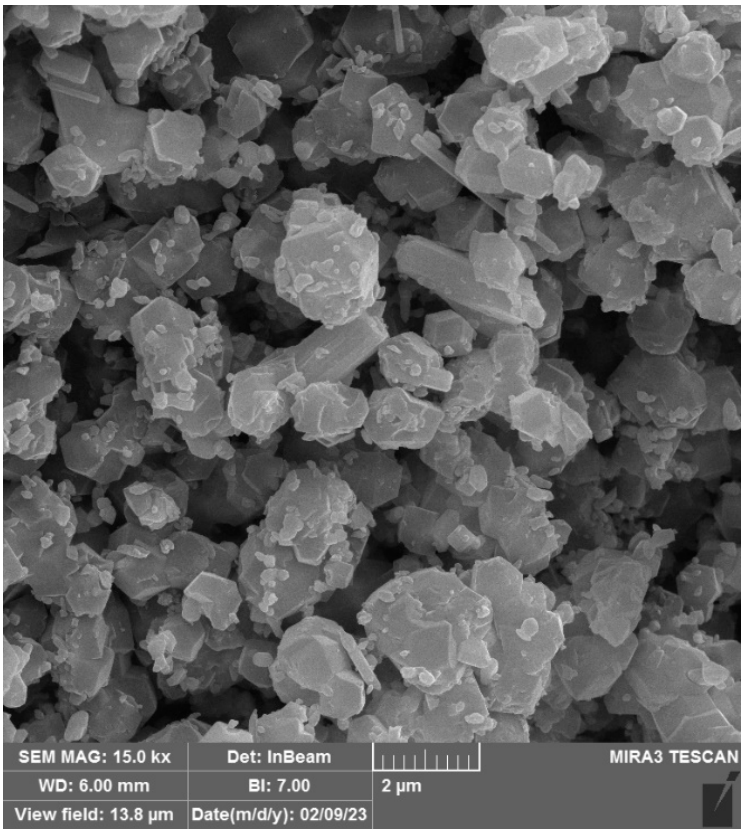

Figure 1. FESEM image of (ZnO@ZIF-8) composite

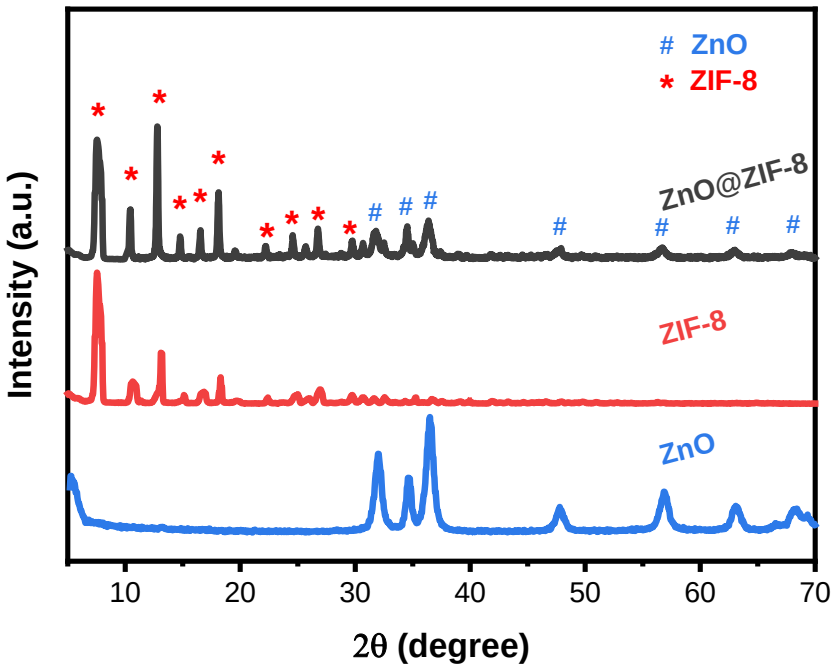

Figure 2. X-ray diffraction pattern of ZnO, ZIF-8 and (ZnO@ZIF-8) powders

3.2 Size and Morphology of Nanofibers

Figure 3 shows the PVDF and PVDF/(ZnO@ZIF-8)-10% electrospun nanofibrous mat surface morphology and diameter distribution. Both of the nanofibers show a uniform diameter distribution and an interconnected network of random fibers with smooth surfaces. Figure 3a the PVDF nanofibers exhibited a bead-free uniform morphology with an average diameter of 253 nm. According to Figure 3b by the addition of composite crystals to the PVDF nanofibers, the surface of the nanofibers, is wrapped with a layer of composite particles. Furthermore, the 10 wt% of composite in the PVDF solution reduced the average diameter of nanofibers to ~233 nm. Figure 3c and Figure 3d shows the normal distribution that in the raw PVDF sample, the dispersion of the data is more than that of the PVDF/(ZnO@ZIF-8)-10% sample.

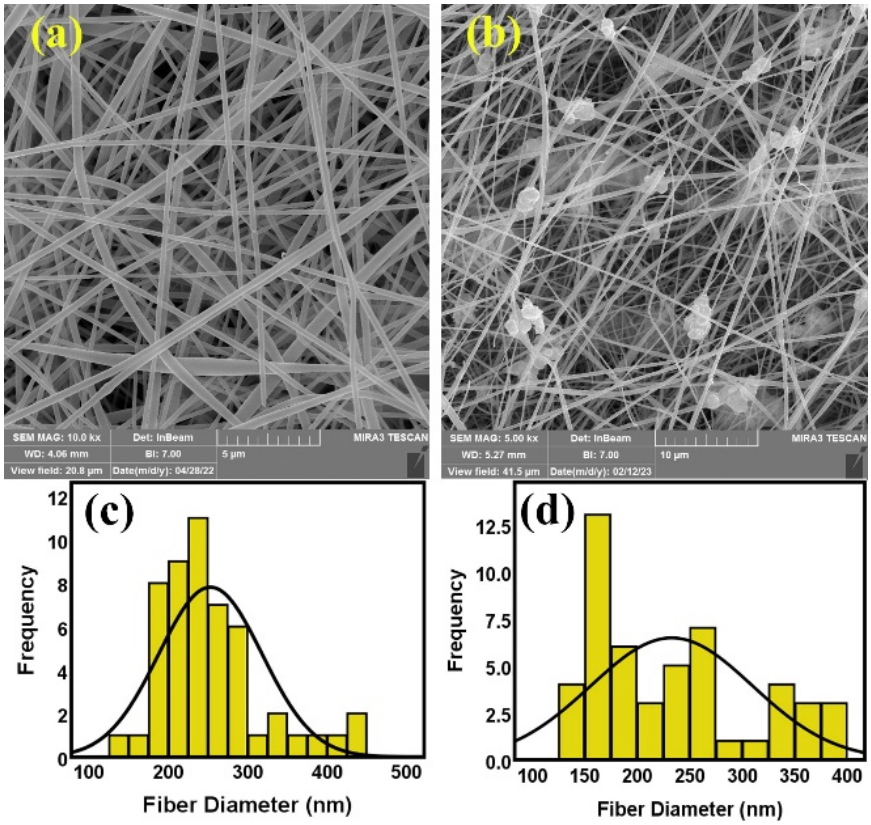

Figure 3. FESEM image and diameter distribution histogram of (a,c) PVDF and (b,d) PVDF/(ZnO@ZIF-8) nanofibers, Respectively

3.3 Phase Analysis

Both of the nanofibrous specimens exhibit the main diffraction peaks of PVDF at 18.8° and 20.5°, which correspond to the α and β-phases, respectively [23]. Figure 4 that refers to XRD analysis of PVDF/(ZnO@ZIF-8) nanofibrous specimen, shows main diffraction peaks signed as * and #, which are in good agreement with MOF and ZnO, respectively.

It can be seen that the β-phase peak intensity (2θ = 20.5°) in the patterns for the PVDF/(ZnO@ZIF-8) nanofiber increased as the composite content was prolonged up to 10 wt.%. The incorporation of (ZnO@ZIF-8) composite into the PVDF nanofibers is deduced to be favorable for stretching the PVDF polymer chain and transforming the

α-phase into the β-phase. Moreover, both components of the composite (ZnO and ZIF-8) can be effective as a nucleation agent in increasing the β-phase of PVDF/(ZnO@ZIF-8) nanofiber because of their metallic component that is Zn^{+2} [24-26]. In comparison with other research conducted in this study, our results, like others, confirm the increase in the amount of β-phase from the XRD and FTIR results for the sample containing the composite compared to the raw sample.

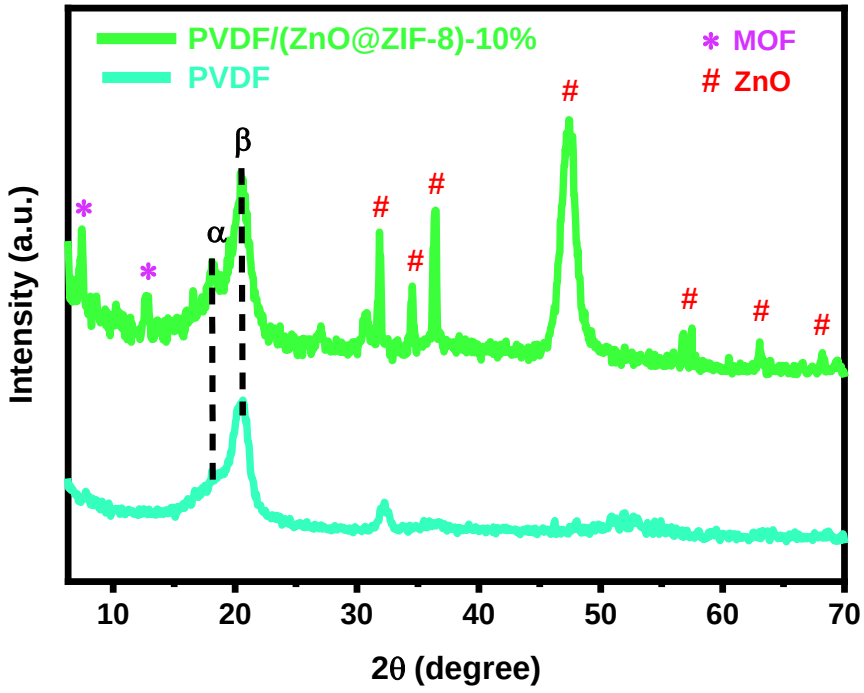

Figure 4. X-ray diffraction of PVDF and PVDF/(ZnO@ZIF-8)-10% nanofibers

IV. CONCLUSIONS

In this study, a successful synthesis of the core-shell (ZnO@ZIF-8) composite was achieved, and its characteristics were thoroughly investigated. Furthermore, electrospinning was employed to fabricate nanofibrous composites of polyvinylidene fluoride (PVDF) and PVDF/(ZnO@ZIF-8) with a composite loading of 10%. The analysis of the fabricated nanofibers revealed the production of uniform and bead-free structures. Moreover, the incorporation of the (ZnO@ZIF-8) composite into the PVDF polymer solution resulted in an increased amount of the β crystalline phase and a reduction in nanofiber diameter. These findings suggest that the composite addition enhances the crystalline properties of PVDF nanofibers and improves their structural characteristics. The fabricated nanofiber mat holds great potential for various applications, including E-Textiles, flexible sensors, and wearable devices. The uniformity and improved characteristics of the nanofibers make them suitable for these applications. Furthermore, based on the obtained results, it is anticipated that the incorporation of this composite can enhance the piezoelectric properties of PVDF nanofibers, opening up possibilities for their utilization in piezoelectric-based applications. Overall, this study successfully synthesized the core-shell (ZnO@ZIF-8) composite and demonstrated its positive impact on the fabrication and characteristics of PVDF nanofibers. The findings contribute to the development of functional nanofiber materials for various technological applications.

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