

Investigating the effect of variation of TiO₂ nanoparticle concentration on the performance of nylon/TiO₂ nanocomposite-based teng

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This study explored the impact of varying concentrations of TiO₂ NPs on the performance of TENGs made from nylon/TiO₂ NCs. The TENGs were constructed using nylon films as one triboelectric material and polysiloxane (PS) as the other. Electrical measurements were performed to assess the TENGs' output parameters, such as open-circuit voltage and short-circuit current, with different TiO₂ concentrations (1%, 3%, and 5%). The findings revealed that increasing the TiO₂ concentration initially enhances the TENG's performance. For example, TENGs based on 1% TiO₂ NCs achieved maximum voltage and current values of 41.38 V and 2.5 μA, respectively, which are higher than those of ordinary nylon TENGs (30.36 V and 1.82 μA). This improvement is due to the increased dielectric constant of the NC material, which enhances charge storage capacity and boosts the TENG's output. However, when the TiO₂ concentration is further increased (e.g., to 5%), the TENG's performance begins to decline. This drop is caused by the agglomeration of TiO₂ NPs on the nylon surface, which reduces the active contact area between the nylon and PS films, weakening the triboelectric effect. Similar patterns were observed in TENGs with 3% and 5% TiO₂ concentrations, where excessive TiO₂ led to a decrease in output power due to uneven nanoparticle distribution.

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1. Introduction

In pursuing sustainable energy solutions, triboelectric nanogenerators (TENGs) have emerged as a promising technology for harvesting mechanical energy from various environmental sources. TENGs convert mechanical energy, such as vibrations, motions, and other kinetic energy into electrical energy through the triboelectric effect [1]. This phenomenon occurs when two different materials come into contact and are subsequently separated, generating electrical charges [2]. Given their ability to harness energy from ubiquitous sources, TENGs hold tremendous potential for powering small electronic devices and sensors and contributing to larger-scale energy systems [3,4]. Among the materials explored for TENG applications, polymer-based nanocomposites (NCs) have gained significant attention due to their tunable properties and enhanced performance [5]. Polymers' inherent flexibility, durability, and processability make them ideal candidates for creating TENGs adaptable to various environments and conditions [6,7]. When polymers are combined with nanoparticles (NPs), the resulting NCs can exhibit improved dielectric properties, increased surface area, and enhanced charge transfer capabilities, all of which are critical for boosting the efficiency

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of TENGs [8]. Nylon, a well-known polymer, has shown particular promise in TENGs due to its mechanical strength, flexibility, and ease of fabrication [9]. Nylon's chemical structure allows for effective interaction with various types of NPs, enabling the creation of composite materials with tailored properties. When integrated with NPs like titanium dioxide (TiO_2), Nylon's potential is further amplified. TiO_2 NPs are known for their excellent dielectric properties [10,11], high surface area, and chemical stability, making them an ideal additive for enhancing the triboelectric performance of Nylon-based composites [12].

The combination of Nylon and TiO_2 in NCs offers a versatile platform for TENG development. By varying the concentration of TiO_2 NPs within the nylon matrix, researchers can systematically tune the electrical and mechanical properties of the resulting NC. This customization is essential for optimizing the performance of TENGs, as the concentration of NPs directly influences factors such as charge density, surface roughness, and dielectric constant. Through careful design and experimentation, nylon/ TiO_2 NCs can be engineered to maximize energy conversion efficiency, providing a powerful tool for the development of next-generation energy harvesting devices. Researchers have leveraged these advantageous properties by incorporating nylon/ TiO_2 NCs directly into the active layers of TENGs [12]. The combination of Nylon and TiO_2 in these NCs offers a versatile platform for TENG development. By varying the concentration of TiO_2 NPs within the nylon matrix, the researchers were able to systematically tune the electrical and mechanical properties of the resulting NC, thereby optimizing the performance of the TENG. This concentration directly influences factors such as charge density, surface roughness, and dielectric constant, which are essential for maximizing the energy conversion efficiency of the TENG. As a result, the nylon/ TiO_2 NCs have demonstrated considerable potential in enhancing the overall effectiveness of TENGs, providing a powerful tool for the development of next-generation energy harvesting devices.

In this study, we present a novel methodology for fabricating TENGs utilizing nylon/ TiO_2 NCs as the active material. The fabrication process employs advanced spray coating technology, which allows for the precise and uniform deposition of the NC films onto substrates. Our investigation focuses on understanding the influence of TiO_2 NP concentration within the nylon matrix on the overall performance of the TENG. By systematically varying the TiO_2 concentration, we aim to explore its effects on key parameters such as surface morphology, dielectric properties, and energy conversion efficiency. This approach not only provides insights into optimizing the material composition for enhanced TENG performance but also demonstrates the scalability and effectiveness of spray coating as a fabrication technique for high-performance energy harvesting devices.

2. Materials and experiment

2.1. Materials

To fabricate the nylon/ TiO_2 NCs, we utilized titanium dioxide NPs (rutile phase, particle size 10–30 nm) sourced from SkySpring Nanomaterials, Inc. The NPs were dispersed in ethanol (Riolux, a hygienic agent, rectified 96% ethyl alcohol). Our selection of materials for the TENGs was guided by cost-effectiveness and commercial availability. As triboelectric pairs, we used silicone rubber (RTV2, a mold casting material commonly used for home decoration) and nylon derived from nylon socks (composition: 90% nylon and 10% other polymers, with a thread diameter of 43 μm). Aluminum foil (Pratikon, with a thickness of 16 μm) served as the metal electrode in the device.

2.2. Preparation of nanocomposite triboelectric materials and TENGs

As shown in Figure 1 NC materials based on TiO_2 NPs with nylon as the polymer matrix have been developed for the first time using spray coating technology. To initiate the synthesis of NCs with different TiO_2 concentrations (1, 3, and 5 wt%), we mixed 20 mL of ethanol with 0.2, 0.6, and 1 g of TiO_2 NPs. This mixture was stirred using a magnetic stirrer for 15 minutes at room temperature. The nanoparticle dispersion was further homogenized for each of the three TiO_2 concentrations using the sonochemical synthesis method for one minute. Nylon has adhered to Al

foil using double-sided tape. Nylon films, measuring 4×4 cm, were cut from these nylon/Al foil samples. The TiO_2 solutions, prepared in three different concentrations, were then applied to the surface of the nylon films using a spray coating method. All samples were left to dry at room temperature for one day. For the preparation of PS samples, which were used as the complementary triboelectric material, 12.50 g of PS was mixed with 1.3 mL of a cross-linking agent and stirred for 15 minutes. To create thin PS layers, this solid solution was applied to pre-prepared Al foil using the drop-casting method. The PS samples were also dried at room temperature for one day. The following day, parts measuring 4×4 cm were cut from the dried PS layers, and these samples were used as the triboelectric material.

2.3. Characterization of nylon/ TiO_2 NCs films

The structural analysis of the nylon/ TiO_2 NC films was conducted using a Rigaku Mini Flex 600 X-ray diffractometer (XRD). The analysis employed Ni-filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.54060 \text{ \AA}$) with a step width of 0.1 degrees and a scan speed of 5 degrees per minute, covering a 2θ range from 10° to 90° . Elemental composition and distribution were assessed through energy-dispersive X-ray (EDX) analysis using an X-Max spectrometer. Additionally, the surface morphology of the NC films was examined with a Scanning Electron Microscope (SEM), specifically the Vega model from Tescan.

2.4. Measurement of TENG's performance

To investigate the impact of TiO_2 NPs on the output performance of TENGs, we compared ordinary nylon with nylon NCs containing TiO_2 NPs on their surface. PS was used as the complementary triboelectric material in the TENGs. For the TENG fabrication, 4×4 cm samples were cut from both the nylon and PS films. The prototypes were assembled by placing the nylon film and the PS film together, with a 60 mm gap between them. The output performance of these TENGs was measured using a digital multimeter (DMM6500 6-1/2 Digital Multimeter, Keithley). Testing was conducted at a contact-separation frequency of 2 Hz, with the temperature and relative humidity maintained at 28°C and 58%, respectively.

3. Results and discussion

Nylon was selected for its positive triboelectric properties, while PS was chosen for its negative triboelectric properties. The TiO_2 NPs were effectively dispersed in ethanol using magnetic stirring and sonication, as demonstrated in Fig. 1(a). The TiO_2 solution remained stable throughout the experiment.

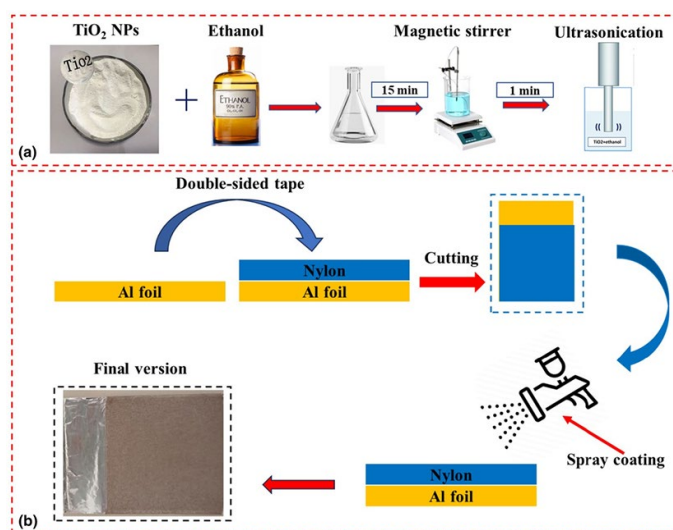


Fig. 1. Preparation of nylon/ TiO_2 NC films.

Three nylon films with different TiO_2 concentrations were prepared, as illustrated in Fig. 1(b). Each of these films was sprayed with the TiO_2 solution at different spraying times, while a fourth nylon film was left untreated for comparison.

The XRD results of nylon/ TiO_2 NC films are shown in Figure 2. So, the spectra presented here are those of ordinary nylon, a nylon film immersed in 3wt% TiO_2 solution, and nylon films with TiO_2 nanoparticles sprayed 5 and 15 times, respectively. These results are consistent with previous studies in the scientific literature [13,14], and in this study, the same characteristic peaks of TiO_2 NPs were also observed. From the graphs shown in Figure 2, the crystal faces with the Miller indices (110), (101), (210) and (211) formed in the case of the NC prove that the TiO_2 NPs were on the surface of the nylon layers as shown in the diffraction angles $2\theta = 27.44^\circ$, 36.44° , 44.07° and 54.61° obtained from the analysis of the XRD results. This result confirms the presence of TiO_2 NPs on the nylon films sprayed with TiO_2 nanoparticles. The peaks observed at the diffraction angle $2\theta = 28.79^\circ$ were identified from the literature [15] as corresponding to the nylon layer.

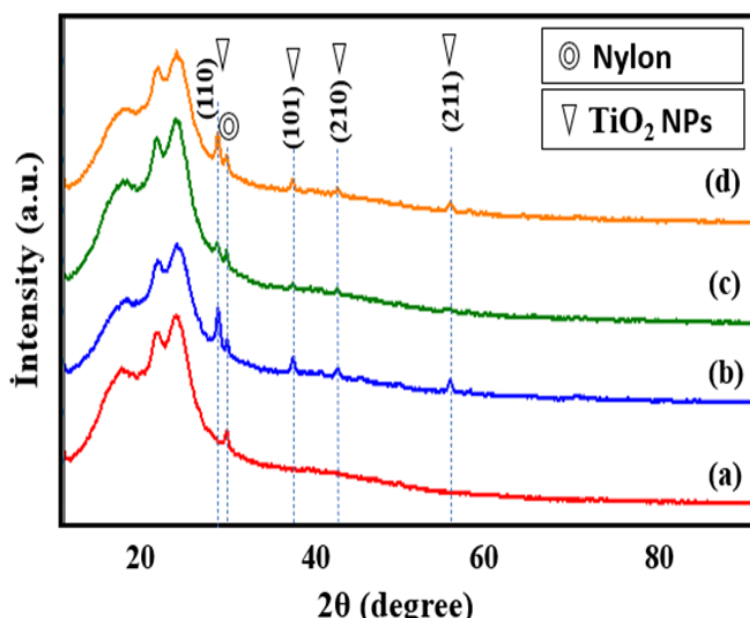


Fig. 2. XRD pattern of nylon/ TiO_2 NCs: plain nylon (a), immersed in 3wt% TiO_2 solution (b), sprayed 5 times (c) and 15 times (d).

Figure 3 shows the results of EDX analysis conducted on ordinary, 5-times sprayed, 15-times sprayed, and dipped nylon films.

The EDX results indicate that the amount of TiO_2 NPs deposited on the nylon surface increases with the number of spraying cycles. In the case of the nylon sample sprayed 5 times, the atomic share of Ti was 0.54%, while for the sample sprayed 15 times, it increased to 0.85%. Finally, this value further increased to 2.57% for the dipped nylon sample. These findings demonstrate that varying amounts of TiO_2 NPs are deposited on the nylon films depending on the number of spraying cycles, with the highest deposition observed in the dipped nylon sample.

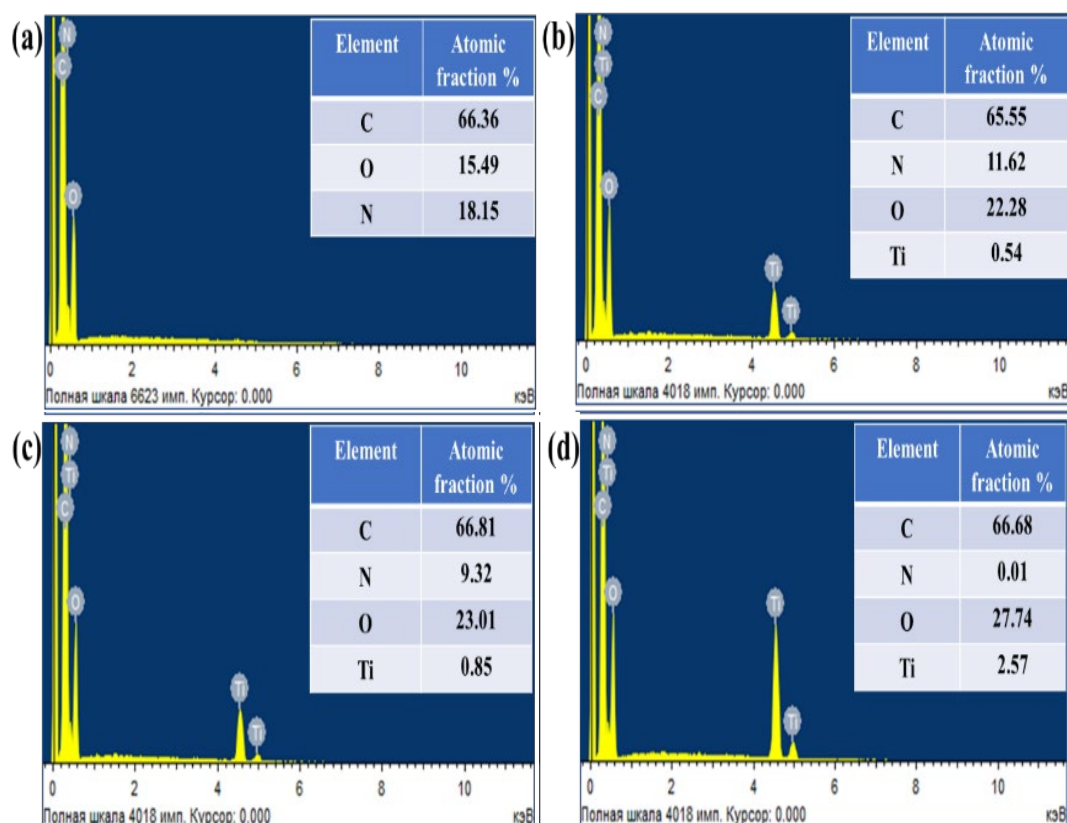


Fig. 3. EDX results of samples: (a) ordinary nylon; (b) 5 times and (c) 15 times sprayed nylon/TiO₂ NCs and (d) dipped in TiO₂ NPs solution.

The surface morphology of nylon/TiO₂ nanocomposites was examined using scanning electron microscopy (SEM), as shown in Figure 4. Figure 4(a) displays the SEM image of a standard nylon surface, revealing that nylon has a network structure with closely connected fibers. Figures 4(b), 4(c), and 4(d) show SEM images of nylon layers with different TiO₂ treatments: ordinary nylon, nylon sprayed with TiO₂ solution 5 times, and nylon sprayed with TiO₂ solution 15 times, respectively. Figure 4(e) depicts nylon layers immersed in TiO₂ solution, all at a magnification of approximately 10,000x. With an increasing amount of TiO₂ solution applied to the nylon films, whether through spraying or immersion, the distribution of TiO₂ nanoparticles on the nylon fibers becomes more apparent. For the 5 and 15 times sprayed and dipped samples, TiO₂ nanoparticles are dispersed on the surface of the nylon fibers. Due to their small size, individual nanoparticles cannot be distinctly resolved. The images clearly show that as the number of sprayings increases, the density of TiO₂ on the nylon fibers also increases, and more spherical particles are observed forming on the surface.

To investigate the impact of varying concentrations of TiO₂ nanoparticles on the output parameters of TENGs, nylon films measuring 4 x 4 cm were cut, and TENGs were fabricated using PS as the complementary triboelectric material. Electrical measurements of the TENGs based on nylon/TiO₂ NCs were conducted. Figure 5 presents the graphs showing the average open-circuit voltage and short-circuit current intensity of TENGs made from 1%, 3%, and 5% nylon nanocomposite layers as a function of the number of spray coatings applied.

In figures 5(a) and 5(b), it is evident that TENGs fabricated with nylon/TiO₂ NCs exhibit higher open-circuit voltage and short-circuit current values compared to those made from ordinary nylon. Specifically, the maximum voltage and current intensity values for TENGs made with ordinary nylon were determined to be 30.36 V and 1.82 μA, respectively. In the case of five times spray coatings, these values increased to 33.38 V and 2.03 μA, respectively. As the TiO₂ concentration increased to 1% and the number of spray coatings increased, the output parameters of

the NCs-based TENGs further improved, reaching 41.38 V and 2.5 μ A for voltage and current, respectively. The output parameters of the NCs-based TENG increased to 41.38 V and 2.5 μ A for voltage and current intensity as the TiO₂ content increased to 1% (with more spray coatings). This enhancement in the TENG's output is attributed to the increased dielectric constant of the NC material, which occurs as the concentration of TiO₂ NPs within the NC rises. As the proportion of NHs on the surface increases, the charge storage capacity of the NC also improves [12].

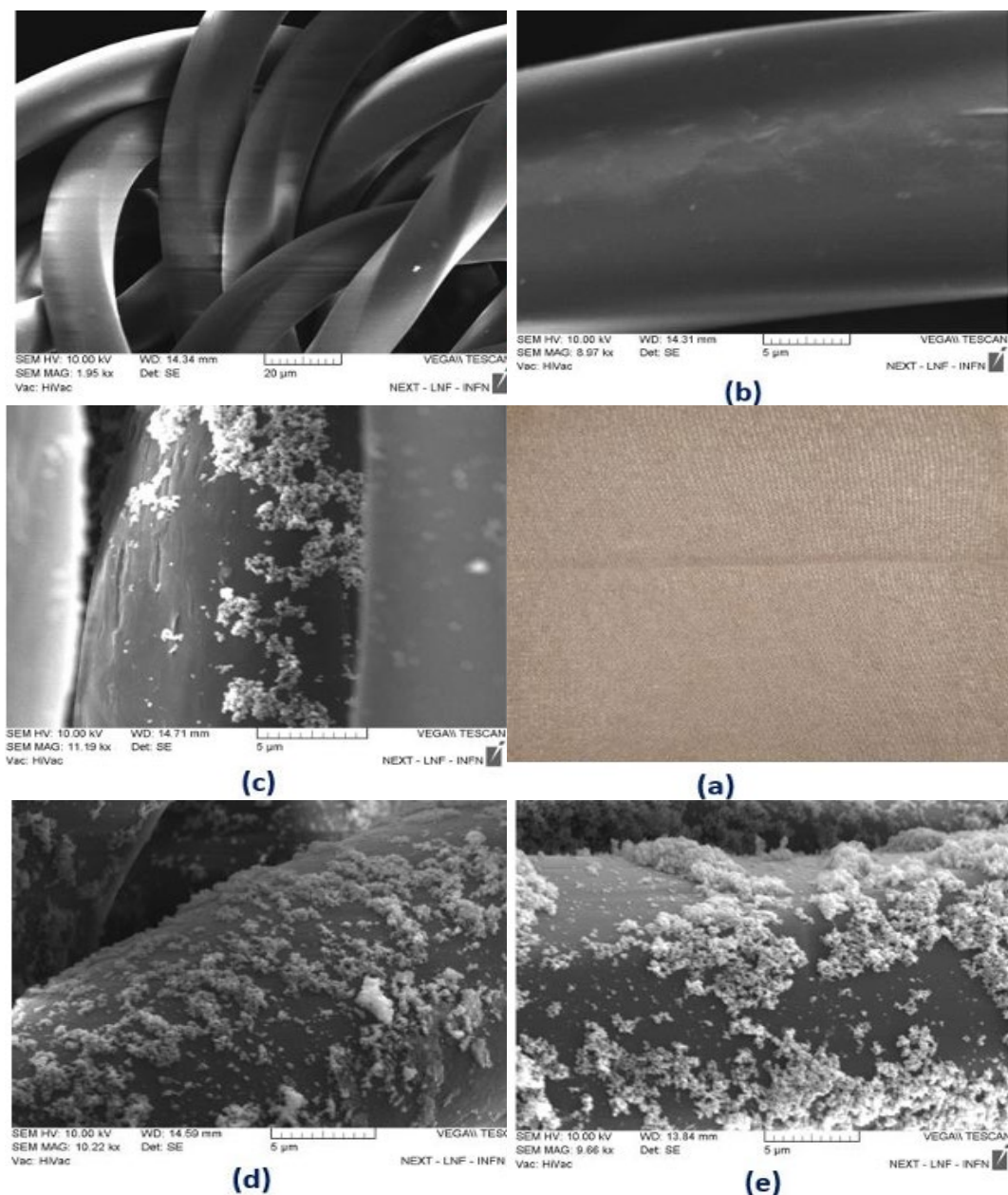


Fig. 4. SEM images of nylon films. (a) A piece of nylon SEM images of the nylon films at 2000X and the ordinary nylon (b) the ordinary nylon at 10000X, (c) the nylon/TiO₂ NCs sprayed 5 times with 3wt% TiO₂ NP solution at 10000X, (d) the nylon/TiO₂ NCs sprayed 15 times with 3wt% TiO₂ solution at 10000X, (e) the nylon film soaked in 3wt% TiO₂ NP solution.

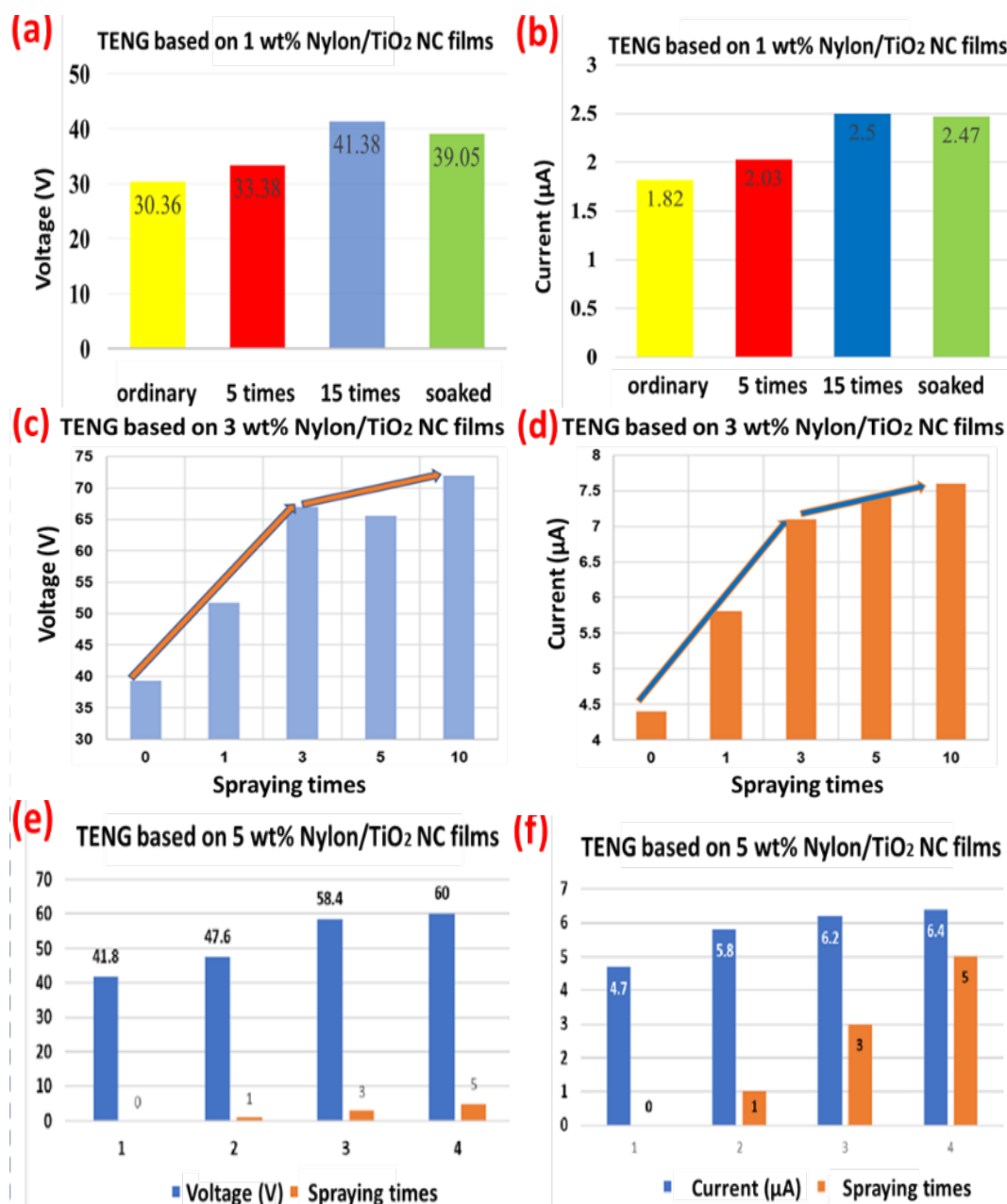


Fig. 5. Voltage graphs of the TENGs based on 1, 3, and 5 wt% Nylon/TiO₂ NC films.

According to the capacitor model of the TENG, the triboelectric charges are closely related to the electrical capacitance of the device. However, a slight decrease in the output parameters of the NC-based TENG was observed with a further increase in the TiO₂ content. In this case, the open-circuit voltage and short-circuit current intensity of the TENG were measured at 39.05 V and 2.47 μ A, respectively. This decrease in output is explained by the excessive amount of TiO₂, which leads to agglomeration on the surface of the nylon layers, forming larger NPs, and nanoclusters causing an uneven distribution on the surface. This in turn causes the nylon to come into less contact with the PS, which ultimately reduces the output power of the TENG. In more detail, an agglomerated and unevenly distributed nanoparticle layer is formed on the surface of nylon fibers with increasing concentrations of TiO₂ NPs. This layer physically prevents direct contact between nylon and PS. As a result, this obstacle in the contact area limits the interaction of materials during triboelectric processes. TiO₂ is a ceramic material with relatively high electrical resistance. If the thickness of the TiO₂ layer increases in the case of the nanocomposite, it can act as an insulating effect that hinders

the flow of charge carriers between the nylon and PS surfaces. This insulating effect reduces the efficiency of charge transfer during triboelectric interactions.

From the voltage and electric current graphs of 3% nylon/TiO₂ NC-based TENGs shown in Figure 5(c) and (d), it was determined that the maximum voltage and current for the ordinary nylon-based TENG were 36.8 V and 4.4 μA, respectively. When a single layer of TiO₂ was sprayed onto the nylon surface, these values increased to 45.6 V and 5.7 μA. With three and five-times spray coatings, the voltage and current saw even greater increases, reaching 66.8 V and 65.4 V for voltage, and 7.1 μA and 7.4 μA for electric current, respectively. As shown, the output performance of the TENG improves with the increase in TiO₂ content. Finally, after ten times spray coatings, the maximum voltage and current intensity reached 72 V and 7.6 μA, respectively. This indicates that compared to ordinary nylon, the voltage and current of the NC-based TENG with ten times TiO₂ increased by nearly twofold on average. This enhancement in voltage and current is attributed to the high dielectric properties of TiO₂ NPs, demonstrating the high efficiency of using TiO₂-based NC materials in TENGs. However, as shown in Figure 5(c) and (d), the output parameters of the TENG initially increased rapidly due to the TiO₂-sprayed NC films compared to ordinary nylon. Yet, as the number of spray coatings increased from five to ten, the rate of increase slowed down. This can be explained by the growing amount of TiO₂ NPs on the nylon surface, which reduces the active contact area between the nylon and PS films. The NPs on the surface weaken the triboelectric effect between these two films, ultimately leading to a decrease in the TENG's output efficiency.

The research also revealed that a similar trend is observed in TENGs based on a 5% nylon/TiO₂ nanocomposite, as shown in Figure 5(e) and (f). Additionally, it was found that increasing the concentration of TiO₂ nanoparticles from 3% to 5% leads to a decrease in the TENG's output power compared to the 1% and 3% cases. This reduction is attributed to the negative triboelectric effect, specifically the decrease in the active contact area caused by the uneven distribution of nanoparticles on the nylon surface as their concentration increases.

Therefore, nylon/TiO₂ nanocomposite materials have proven to be effective triboelectric materials in TENGs. By adjusting the amount of filler, it is possible to control the TENG's efficiency by determining the optimal concentration.

4. Conclusion

Nylon/TiO₂ NCs are highly effective as triboelectric materials in TENGs, offering the potential for substantial performance improvements. The study reveals that optimizing TiO₂ concentration in the NC can significantly enhance the output performance of TENGs. Specifically, increasing TiO₂ concentration boosts the open-circuit voltage and short-circuit current of the TENGs due to the improved dielectric properties of the NC. However, careful optimization is essential. Excessive TiO₂ concentration can lead to problems such as NP agglomeration and uneven distribution on the nylon surface. These issues reduce the effective contact area between the nylon and PS films, weakening the triboelectric effect and diminishing the TENG's efficiency. Therefore, this research underscores the need for precise control of TiO₂ concentration to avoid these negative effects and achieve optimal TENG performance. It highlights the significant potential of TiO₂-based nanocomposites for creating high-efficiency TENGs, which are promising for advanced energy harvesting technologies.

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