

## フッ素添加 DLC 膜を用いた高出力・高耐久性摩擦発電機の開発

## Triboelectric nanogenerators with enhanced output and durability based on fluorinated DLC films

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Triboelectric nanogenerators (TENG), a disruptive technology that can convert mechanical energy into electricity based on contact electrification and electrostatic induction [1], have attracted significant attention because of their self-powering ability, low cost, simple structure, and ease of fabrication [2]. Although significant progress has been made over the past decade, the durability of TENG is still unsatisfactory because most dielectric materials for TENGs are organic polymers, which are very easy to wear during the working process. To solve this problem, in this study, we proposed a strategy to use fluorine-doped diamond-like carbon films deposited by a plasma-based coating technology as durable and high-performance electronegative materials for TENG. Both the tribological and triboelectric properties of the F-DLC films were systematically investigated. The optimal fluorine-doped diamond-like carbon (F-DLC) film with excellent tribological and triboelectric properties was obtained by varying the fluorine doping content.

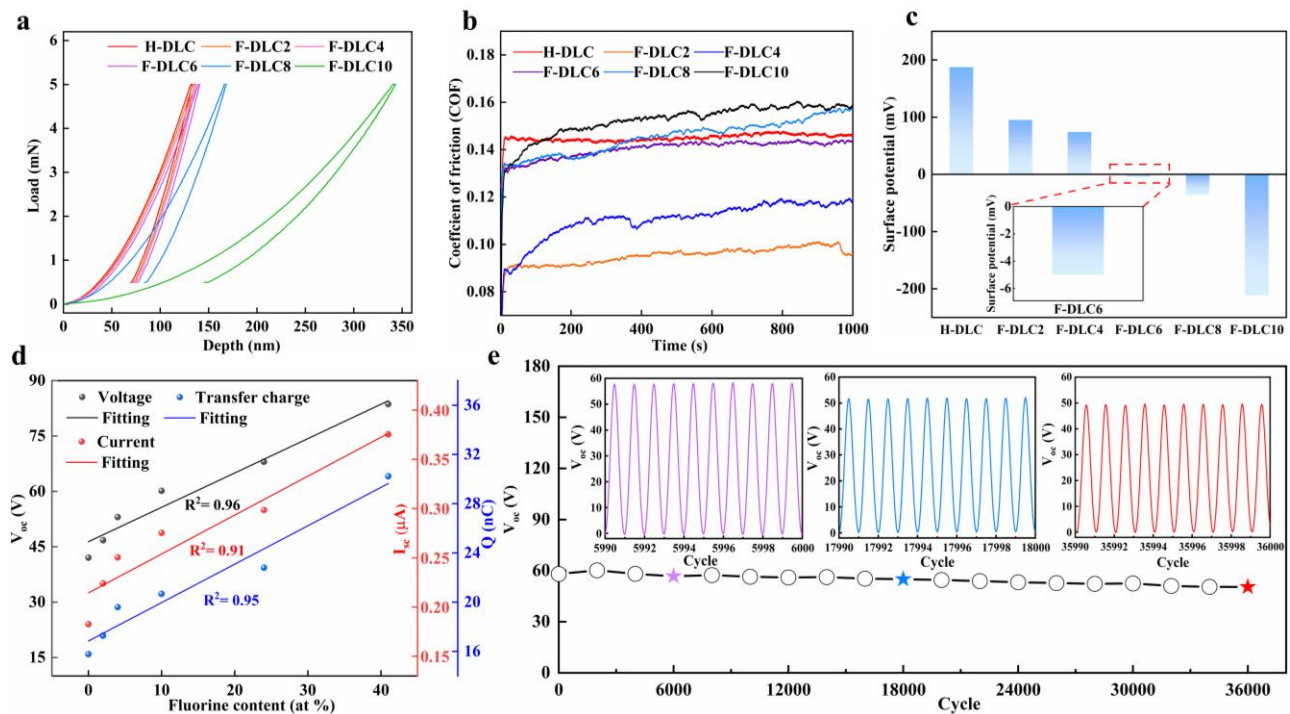
F-DLC films were deposited on Al and Si substrates by bipolar-type plasma based ion implantation and deposition (PBII&D) [3]. A gas mixture of toluene ( $C_6H_5CH_3$ ) and hexafluorobenzene (HFB,  $C_6F_6$ ) was used as the source gas. F-DLC films with different F contents were deposited by changing the mixture ratio of toluene and HFB to determine the F-DLC film with the best performance. For comparison, a hydrogenated DLC (H-DLC) film without F-doping was prepared using only toluene as the precursor gas. The F-DLC films with different HFB ratios are denoted as F-DLC2, F-DLC4, F-DLC6, F-DLC8, and F-DLC10, as shown in **Table 1**.

The physical and triboelectric properties of the F-DLC films were characterized by nanoindentation, Kelvin probe force microscope, and ball-on-disk tribometer as shown in **Figure 1**. Although the hardness and Young's modulus decreased with increasing F content, the mechanical properties of the DLC films did not degrade significantly when doped with a small amount of fluorine (F-DLC2-6). However, when the doped fluorine reached a high level (F-DLC8 and F-DLC10), a significant decline in

**Table 1.** The parameters deposited F-DLC and H-DLC films.

Sample name	Toluene (sccm)	HFB (sccm)	HFB Ratio	F content (at.%)	Film thickness ( $\mu\text{m}$ )
H-DLC	10	0	0	0	1.9
F-DLC2	8	2	20%	2	1.8
F-DLC4	6	4	40%	4	1.8
F-DLC6	4	6	60%	10	1.9
F-DLC8	2	8	80%	24	2.0
F-DLC10	0	10	100%	41	2.1

the mechanical properties was observed. Regarding the tribological properties, the F-DLC2 film exhibited the lowest COF (0.09) compared to that of H-DLC (0.14). The COF of the F-DLC films gradually increased to that of the H-DLC films as the fluorine content increased. These results indicate that a small amount of fluorine doping can improve the tribological properties of DLC films, whereas excessive doping can be detrimental. For the surface potential, after F doping, the surface potential of the DLC films changed from positive to negative, indicating a polarity transfer from electropositive to electronegative with a stronger electron-withdrawing capability. Therefore, the voltage, current, and charge transfer were proportional to the fluorine content. However, despite its excellent electrical performance, the F-DLC10 film is not suitable for practical applications because of its poor mechanical and tribological properties caused by excessive F doping. By comprehensively considering the various properties of the DLC films, it is suggested that F-DLC6 is the optimal film because of its excellent mechanical properties, enhanced tribological properties, and good triboelectric performance. The as-designed F-DLC6-based TENG exhibited stable electrical output after 36,000 cycles of dry reciprocating motion under a velocity of 2 Hz and a pressure of 12.5 kPa, featuring three inserts that illustrate the enlarged VOC in different stages. The VOC decreased from 58 to 50 V (13.8%).



**Figure 1.** The physical and triboelectric properties of the F-DLC films. (a) Nanoindentation results for H-DLC and F-DLC films. (b) Coefficients of friction obtained from ball-on-disk tribotests with nylon. (c) Surface potential of H-DLC and F-DLC films with an enlarged insert for F-DLC6. (d) Relationship between the fluorine content (x at.%) and voltage ( $V = 0.93x + 46$ ), current ( $I = 0.004x + 0.21$ ) and transfer charge ( $Q = 0.31x + 17$ ) with nylon. (e) TENG durability for at least 36,000 cycles under 2 Hz and 12.5 kPa.

## References

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