

Developing Piezophototronic Materials for a Lab-on-a-Chip and Wearable Electronic Systems

A newly developed smart and soft material, composed of photoconductive nano particles and a piezoelectric polymer, is designed for three-way piezo-phototronic applications.

The utilization of ferroelectric properties of polymers has attracted much interest because of their flexibility, which enables portable electro-mechanical applications, such as tactile sensors, non-volatile memories and actuators. Moreover, piezoelectric polymers facilitate mass production, and are compatible with standard moulding and lamination.

To design this newly-developed three-way piezo-phototronic system, shown in Fig. 1, Wen-Ching Ko (Industrial Technology Research Institute) and his Ph.D. adviser Prof. Chih-Kung Lee (National Taiwan University) examined the piezo-phototronic effect. They developed a technique to apply a piezopotential to modulate the carrier activities and to adjust the performance of opto-electronic devices.¹

To improve the sensitivity and light emission of piezo-phototronics, it is important to understand the underlying mechanisms. Can the photo-

sensitive carrier activities tune the piezo-electric property? Can a local piezopotential control bulk piezo-tronic devices? What are the kinetics?

E-Wen Huang (National Chiao Tung University), Wei-Tsung Chuang (NSRRC), and Yu-Hsiang Hsu (National Taiwan University) developed a new method to answer the aforementioned questions.²

They applied, *in situ*, X-ray diffraction experiments at **BL01C2** for SWLS - X-ray powder diffraction and **BL13A1** for SW60 - X-ray scattering. The team works closely with Chung-Kai Chang of **BL01C2** and Ming-Tao Lee of **BL13A1**.

The major diffraction signals corresponding to photoconductive nano particles and piezoelectric polymer, respectively, are identified with greater energy at **BL01C2**. The advanced detector of **BL13A1** enables the team to resolve timely the kinetics.

They systematically investigated the micro-structural-photon responses of this piezo-phototronic material subjected to external voltages at a lattice level. Figure 2(a) shows a conceptual experimental setup. Their results reveal the correlation

between microstructure and bulk performance.

The team demonstrated that the bulk photon-induced piezoelectric responses under illumination are nearly twice those in conditions without light energy. The direct comparisons are shown in Fig. 3(a) for P(VDF-TrFE) without TiOPc and Fig. 3(b) for (VDF-TrFE) with TiOPc, respectively. In Fig. 3, the two ordinate axes show lattice information on the left and bulk responses on the right. The blue stars denote the lattice strain on the *b*-axis; the red stars indicate the results of bulk strain (d_{33}). The solid and empty stars are data measured with and without illumination, respectively.

Qualitatively, in Fig. 3(a), both bulk and lattice strains of samples without TiOPc are not influenced by illumination with visible light. In Fig. 3(b), in contrast there is a significant effect on subjecting to visible illumination in both lattice and bulk levels. Further, both bulk and lattice strains of P(VDF-TrFE) without TiOPc are greater than those of P(VDF-TrFE) with TiOPc.

The bulk piezoelectric responses of P(VDF-TrFE) with TiOPc are decreased on the addition of TiOPc nano-particles, which implies a weaker piezoelectric effect, but, when this sample is illuminated, the bulk piezoelectric responses of P(VDF-TrFE) with TiOPc become twice those without light. The lattice responses shown in Fig. 3(b) (solid ● vs. empty ○ blue circles) are much greater than that of the bulk responses, d_{33} , (solid ● vs. empty ○ red circles) subjected to

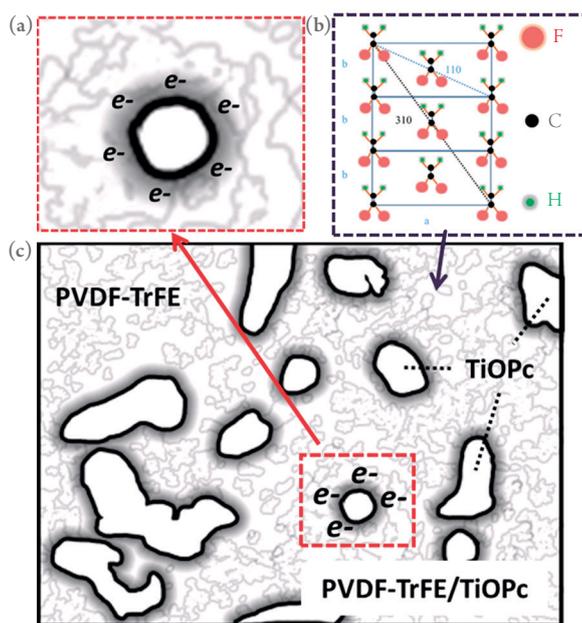


Fig. 1: Conceptual ideas to blend (a) photo-conductive nano titanium oxide (TiOPc) particles with (b) semi-crystalline poly(vinylidene fluoride-co-trifluoroethylene) piezoelectric polymer (PVDF-TrFE) for (c) PVDF-TrFE + TiOPc composite. [Reproduced from Ref. 2]

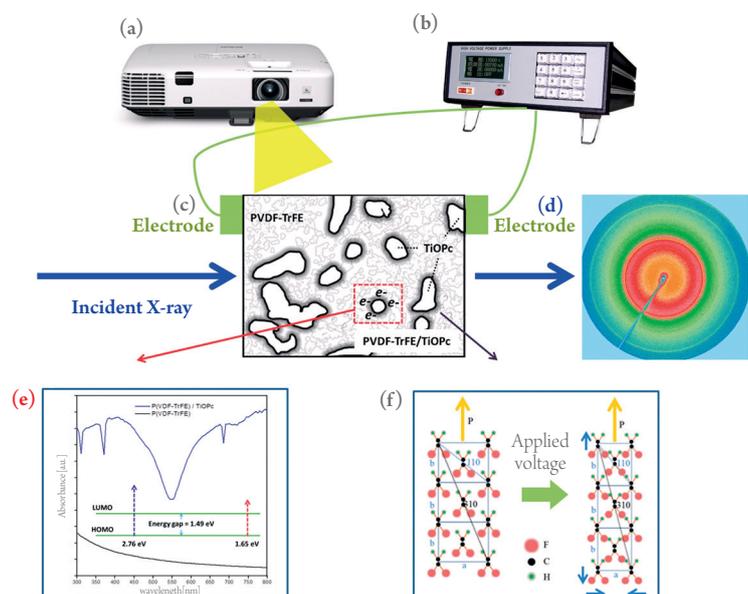


Fig. 2: X-ray diffraction experiments *in situ*: (a) visible light source; (b) power supply; (c) illuminated sample; (d) diffraction rings; (e) light-modulating TiOPc light absorbance spectra; (f) distortion of PVDF-TrFE lattice corresponding to piezoelectricity. [Reproduced from Ref. 2]

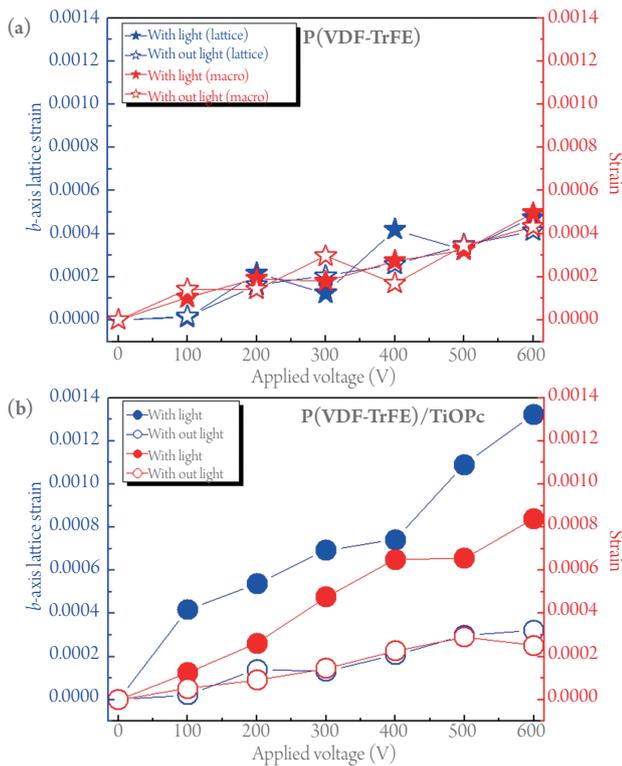


Fig. 3: (a) Macro with light (★), macro without light (☆), *b*-axis lattice with light (●), and *b*-axis lattice without light (○) strain evolution of P(VDF-TrFE) subjected to an applied voltage; (b) macro with light (●), macro without light (○), *b*-axis lattice with light (●), and *b*-axis lattice without light (○) strain evolution of P(VDF-TrFE)/TiOPc subjected to an applied voltage. [Reproduced from Ref. 2]

illumination. The reason is that a bulk specimen containing TiOPc has no piezoelectric effect.

We followed the method of Huang *et al.*³ to estimate the effective dielectric evolution based on the lattice response; the normalized dielectric values are shown in Fig. 4. A lattice-level decay was found during the initial stage of charging, which differs from a linearly increased bulk strain subjected to an applied voltage.

These experimental findings allow us to tune and to control a piezopotential-induced strain for bio-related applications. With further improvement in the composite fabrication, the piezo-phototronic effect can be tailored. In view

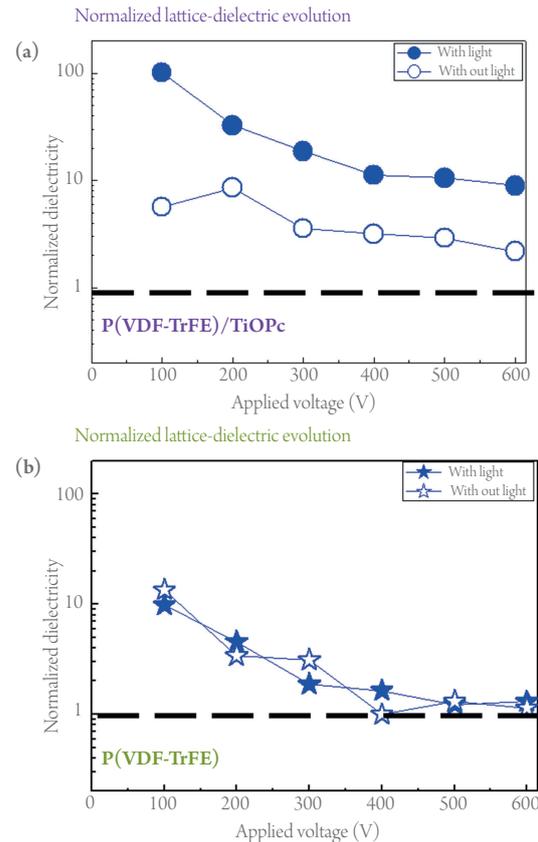


Fig. 4: Normalized lattice-dielectric evolution subjected to applied voltage: (a) P(VDF-TrFE) with TiOPc with light (●) and without light (○); (b) P(VDF-TrFE) without TiOPc with light (★) and without light (☆). [Reproduced from Ref. 2]

of the flexible soft piezo-phototronics, the present results demonstrate the potential of composites in this new class for photon-modulated piezoelectronics. (Reported by We-Tsung Chuang)

This report features the work of E-Wen Huang, Yu-Hsiang Hsu, Wei-Tsung Chuang, Wen-Ching Ko, Chih-Kung Lee and their co-workers published in *Adv. Mater.* **27**, 7728 (2015).

References

1. W.-C. Chang, A.-B. Wang, C.-K. Lee, H.-L. Chen, W.-C. Ko, and C.-T. Lin, *Ferroelectrics* **446**, 9 (2013).
2. E. Huang, Y.-H. Hsu, W.-T. Chuang, W.-C. Ko, C.-K. Chang, C.-K. Lee, W.-C. Chang, T.-K. Liao, and H. C. Thong, *Adv. Mater.* **27**, 7728 (2015).
3. C. Huang, Q. M. Zhang, and J. Su, *Appl. Phys. Lett.* **82**, 3502 (2003).

How Do Spinning Processes Affect Nano-Scale Silk Properties in Nutritiously Stressed Spiders?

Spider major ampullate (MA) silk has exceptional strength (gram-for-gram greater than steel), extensibility, and toughness (gram-for-gram greater than Kevlar®). It is produced within an aqueous solution at room temperature and is biocompatible. Hence the commercialization of a biomimic system to spin fibers that resemble the natural properties of MA silk is the "holy grail of

bioengineering".

It is known that the expressed ratio of two proteins (spidroins), called Major ampullate Spidroin 1 (MaSp1) and Major ampullate Spidroin 2 (MaSp2), can influence MA silk mechanical properties, and the spidroins expressed can vary according to a spider's nutritional uptake. For

instance, spiders on protein poor diets generally downregulate their expression of MaSp2. The reason for this is thought to be because MaSp2 is more metabolically expensive to synthesize than MaSp1. However, because of the complexities of silk spinning, changes in MaSp1 and/or MaSp2 expression alone are not necessarily enough to influence MA silk mechanical properties.¹ Thus