Piezoelectricity

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Piezoelectricity in Two-Dimensional Materials

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Two-dimensional (2D) materials, such as graphene and transition-metal dichalcogenides (TMDs), have attracted a great deal of attention owing to their fascinating properties, which arise from their 2D morphology and ultrathin thickness, and a wide range of potential applications, for example, in (opto)electronics, clean energy production, chemical and biosensors, bioimaging, catalysis, and water remediation.[1,2]

2D materials embody the spontaneous breakdown of 3D symmetry commonly perceived for bulk materials. Among the thirty-two 3D crystal classes, twenty-one are non-centrosymmetric. In other words, in these specific crystal classes, we cannot find a point through which a spatial inversion operation leaves the structure invariant. In contrast, there are only four 2D crystal classes, that is, oblique, rectangular, cubic, and hexagonal. It is also important to note that even for the same material composition, the inversion symmetry can be preserved in the 3D form, but broken in the 2D one.[3]

It has been known for more than one century that most of the non-centrosymmetric materials exhibit a piezoelectric effect or the emergence of charges and voltages upon the application of an external mechanical pressure (Figure 1).[4,5] In fact, piezoelectricity is a prevalent phenomenon existing in a wide range of natural and synthetic materials, including quartz crystals, ferroelectric ceramics, poly(vinylidene fluoride) polymers, and even silk and bone. Piezoelectric sensors and actuators can be found in various applications, ranging from ultrasonic nozzles, cigarette lighters, and microbalances to scanning probe microscopes.

A new twist to this old story is the prediction of ferroelectricity in 2D TMD monolayers by Reed et al. using density functional calculations.[3] In a recent experimental study by Wang, Hone and co-workers,[6] the stretching of 2D MoS_2 flakes with odd numbers of layers was indeed found to produce a piezoelectric voltage and a current output (Figure 2). A single-layer MoS_2 device under 0.53% strain generates a voltage of 15 mV and a current of 20 pA, which

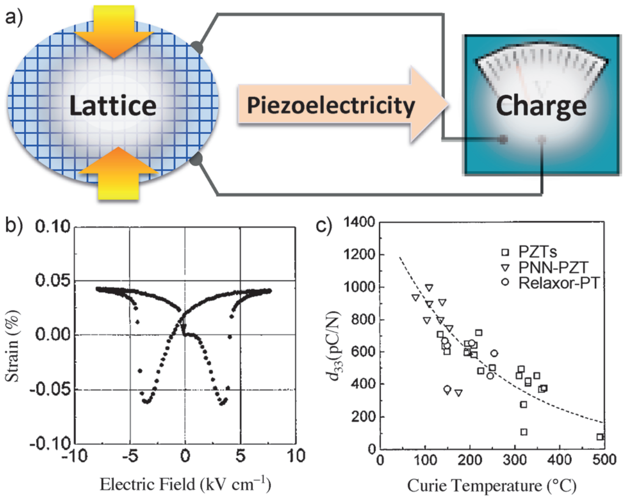

Figure 1. a) The piezoelectric effect: A lattice deformation produces charge and voltage outputs. b) Dependence of the strain on the electric field for a $Pb(Zn_{1/3}Nb_{2/3})O_3$ crystal. c) The piezoelectric coefficient as a function of the transition temperature for selected piezoelectric ceramics. PZT = $Pb(Zr_xTi_{1-x})O_3$. Parts of the Figure were reproduced with permission from Ref. [5].

are significant values considering the atomically thin nature of the 2D flakes. However, this was not the first time that piezoelectricity was observed for low-dimensional materials. In 2006, Wang and Song reported the construction of piezoelectric nanogenerators based on 1D ZnO nanowire arrays.[7] In the following years, more efforts were directed towards building large-scale self-powered energy systems to either harvest or sense vibrational forces from body motions, for example.[8] In a work led by McAlpine, ultrathin piezoelectric ribbons of lead zirconate titanate ($Pb(Zr_xTi_{1-x})O_3$, PZT) were transformed into macroscopic, flexible, and biocompatible rubber substrates.[9] Most recently, the device concept of piezotronics was extended to the arena of 2D materials, which further demonstrated the feasibility of array integration to enhance the performance of energy conversion materials.[6]

It is a consensus in the community that selecting the metal material and tailoring the procedure of contact preparation are critical for the fabrication of high-performance devices based on 2D materials. When the devices involve heterojunctions, the measurements reflect not only the intrinsic properties of the 2D materials, but also the extrinsic proper-

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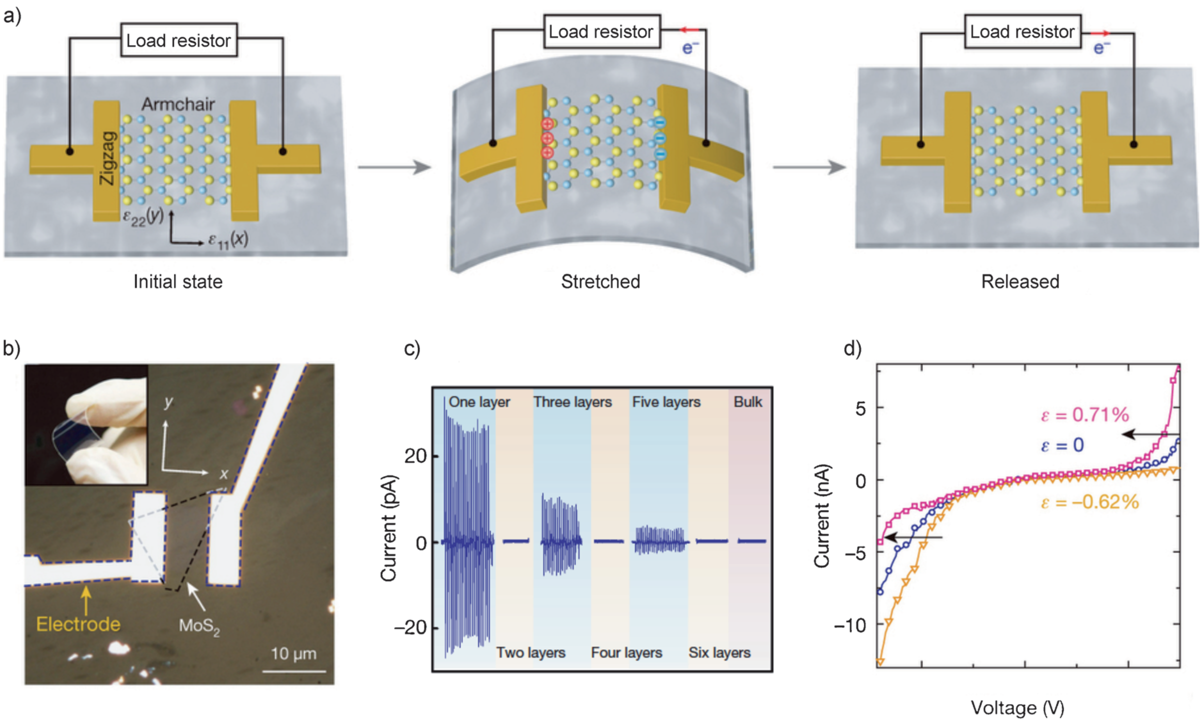

Figure 2. a) Operation of a single-layer MoS_2 piezoelectric device, where the strain and charges are coupled at the zigzag edges of the MoS_2 flake. b) Structure and photograph of the flexible single-layer MoS_2 device. c) Piezoelectric output of single-layer MoS_2 devices as a function of the number of atomic layers in the MoS_2 flakes. d) Asymmetric modulation of the carrier transport by applying a strain for a single-layer MoS_2 device, showing the expected piezotronic effect. Figure reproduced with permission from Ref. [6].

ties of the semiconductor–metal interfaces. In the work by Wu et al., palladium was used as the electrode material in the two-terminal MoS_2 based piezotronic devices,[6] which rises the question as to how the ferroelectricity and the properties of the Schottky barriers are correlated. In the future, experiments will need to be done with electrode-free techniques, such as piezo-force microscopy, which is commonly used to probe piezoelectricity and electromechanical energy conversion on the nanoscale.

In many aspects, thoroughly elucidating the properties of 2D materials is a new and challenging task for materials scientists. In 3D piezoelectric devices, the piezoelectric coefficient is directly proportional to the polarization, the electrostrictive coefficient, and the dielectric constant. These fundamental parameters, however, are often unknown for 2D materials or even require new definitions as a result of the reduced dimensionality. Furthermore, piezoelectric materials should display a converse piezoelectric effect, where the application of an electric field leads to mechanical deformation. If 2D MoS_2 flakes also possess this property, they will be the material of choice to make the thinnest actuators for nanoelectromechanical systems (NEMS) to date.

The perspectives of incorporating 2D materials in functional devices look brighter than ever. There are urgent needs to benchmark the properties of available 2D materials, such as the recently discovered piezoelectricity,[6] against conventional material choices. At the moment, the mechanical-to-electrical energy conversion efficiency of MoS_2 devices is merely 5% and thus one order of magnitude smaller than that of PZT cantilevers. Compared to MoS_2, other 2D materials, such as $MoTe_2$ and WTe_2, may feature a larger piezoelectric effect.[3] Likewise, optimizing the device architecture, tailoring the interface properties, and improving the operation reliability remain to be great challenges on the road ahead.

The discovery of piezoelectricity in 2D materials represents another milestone towards embedding such exciting low-dimensional materials into future disruptive technologies. Mechanical motions, such as bending, stretching, and twisting are found everywhere in our daily life, and piezoelectric 2D materials may facilitate the sensing of these motions and the harvesting of their energies in miniature devices that are made of atomically thin flakes. Piezoelectricity is not a novel concept, but the MoS_2 device exhibits very high gauge factors and an even better performance than commercial strain sensors. We are very optimistic that endeavors in 2D materials will allow other novel properties that are not observed for the three-dimensional bulk counterparts to be revealed, transform the existing technologies, and create new ones in the future.

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