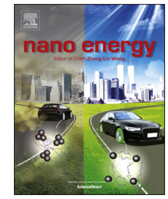
Nano Energy 49 (2018) 7–13

Contents lists available at ScienceDirect

Nano Energy

journal homepage: www.elsevier.com/locate/nanoen



Full paper

Lead iodide nanosheets for piezoelectric energy conversion and strain sensing

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ARTICLE INFO

Keywords:
Two-Dimensional
Piezoelectricity
Self-powered
Nanogenerator
Strain sensor

ABSTRACT

Flexible piezoelectric devices are attractive for energy conversion and strain sensing applications, including in the area of wearable electronics and self-powered sensors. Here, we report a piezoelectric nanogenerator/strain sensor based on lead (II) iodide (PbI_2) nanosheets with the shape of two-dimensional (2D) structures, of which the piezoelectricity is not affected by the number of layers. A typical 2D piezoelectric device fabricated with 3 layers PbI_2 nanosheets has recorded peak values of open-circuit voltage, short-circuit current and loading power as 29.4 mV, 20 pA, and 0.12 pW, respectively, and also possess good charging and integration capabilities. Moreover, these devices can be applied as self-powered strain sensors, with high sensitivity and excellent stability. As such, this study provides new knowledge and strategy for flexible energy harvesting or strain sensing devices based on 2D structures.

1. Introduction

Harvesting ambient mechanical energy or sensing the mechanical signals based on nanomaterials for self-powered and flexible systems can provide potentially revolutionary advancements in energy technologies [1–6]. Piezoelectric nanogenerators/sensors, which can be fabricated using nanowires with none-centrosymmetric structure (such as ZnO [6,7] and GaN [8]) or polarization domains ($BaTiO_3$ [9], $PbZr_xTi_{1-x}O_3$ [10] and P(VDF-TrFE), [11,12] *etc.*), have been widely demonstrated for applications in wearable electronics, implantable devices, wireless transmitters, *etc* [13–16]. Compared to one-dimensional (1D) nanowires, two-dimensional (2D) piezoelectric nanomaterials such as molybdenum sulfide (MoS_2) [17–20], hexagonal boron nitride (h-BN) [21,22], and tungsten diselenide (WSe_2) [21] might have the morphological advantages in constructing flexible nanogenerators. Reports have shown that only monolayered MoS_2 and h-BN, or a specifically stacked bilayer form of WSe_2, exhibit significant piezoelectricity [17,23]. However, precise fabrication of monolayers or specific bilayer 2D nanomaterials with traditional methods such as chemical vapor deposition (CVD) or recrystallization is still challenging [24,25].

In this work, we have demonstrated that lead (II) iodide (PbI_2) nanosheets fabricated with a recrystallization method have the piezoelectricity which is not affected by the numbers of layer. The PbI_2 nanosheets have been used to construct flexible 2D piezoelectric devices by depositing gold (Au) electrodes on both sides of the hexagonal nanosheets. Mechanical compression and subsequent relaxation process changes the dipole moments within PbI_2 nanosheets to generate piezoelectric potentials. The preliminary tests show peak open-circuit voltage and short-circuit current reaching 29.4 mV and 20.9 pA, respectively, with loading power and energy conversion efficiency of 0.12 pW and about 3.2%. Moreover, the electrical energy generated by the nanogenerator is accumulated *via* a capacitor and can be enhanced by integration. As a self-powered strain sensor (gauge factors from about 10–25), this 2D piezoelectric device demonstrates strain detection ranging from 0.137% to 0.339% and stable working period of 4500 cycles.

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https://doi.org/10.1016/j.nanoen.2018.04.029
Received 7 February 2018; Received in revised form 29 March 2018; Accepted 10 April 2018
Available online 11 April 2018
2211-2855/

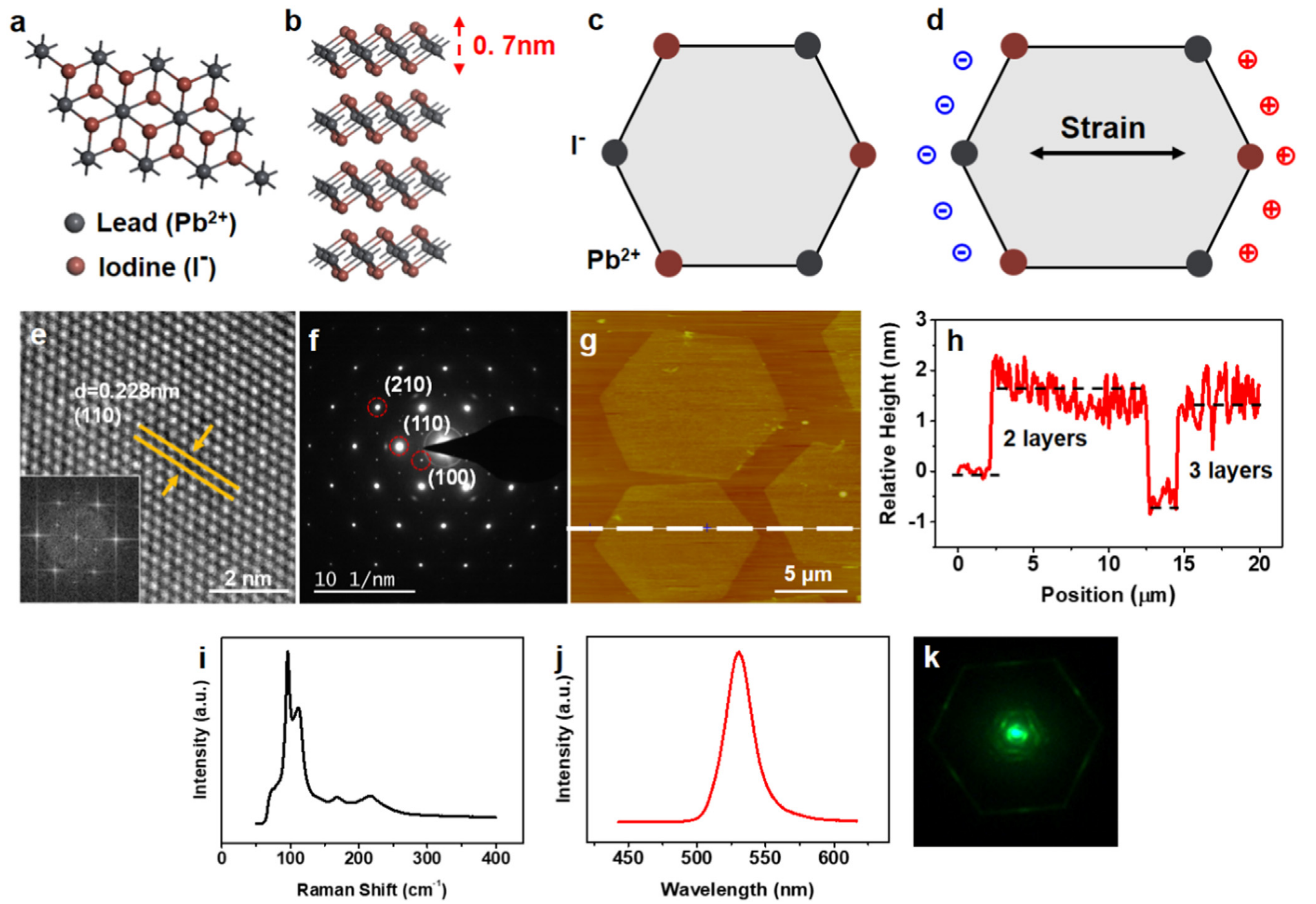

Fig. 1. Fabrication and piezoelectricity of PbI_2 nanosheets. Schematic diagram showing the crystal structure in (a) monolayer and (b) multilayer PbI_2 nanosheets. (c) There is no dipole moment in the initial state, and (d) the dipole moment arises under an applied strain. (e) High resolution TEM image of a PbI_2 nanosheet and the corresponding FFT image (inset in the left-bottom corner). (f) SAED pattern of a PbI_2 nanosheet. (g) AFM image of PbI_2 nanosheets. (h) Relative altitudes along the white lines in (g). (i) Raman measurement result for a PbI_2 nanosheet under 532 nm laser excitation. (j) Fluorescence measurement result and (k) image of a PbI_2 nanosheet using 800 nm femtosecond laser (30 fs, 80 MHz).

2. Results and discussion

2.1. Fabrication and piezoelectricity of PbI2 nanosheets

Fig. 1**a and b** are the schematic diagrams for the defect-free atomic structure of monolayer and multilayer PbI_2 nanosheets, respectively. Lead ions (Pb^{2+}) and iodide ions (I^-) can bond with each other in an ordered fashion to form a hexagonal structure. As shown in Fig. 1**c**, each side of the hexagonal structure has the same lattice in the absence of strain. The positive charges are centralized around Pb^{2+} and the negative charges are centralized about I^-, resulting in dipole moments of zero within the PbI_2 nanosheet. When a mechanical strain is applied along the horizontal direction (Fig. 1**d**), the shape of the hexagonal structure is stretched. As a result, non-zero dipole moments along the strain direction are produced and a corresponding piezoelectric potential is generated.

For multilayer PbI_2 nanosheets (Fig. 1**b**), the thickness of each layer is about 0.7 nm. Most importantly, the orientation of the alternating layers is the same, in contrast with traditional 2D piezoelectric materials such as MoS_2 and h-BN [17]. Because of the opposite orientation of alternating layers in MoS_2 and h-BN, the directions of the dipoles generated by each layer are in the opposite directions with each other. Thus, only structures with an odd number of layers exhibit piezoelectricity (Fig. S1). The piezoelectricity of PbI_2 nanosheets is not affected by the number of constituent layers, implying easier implementations of 2D mechanical-electrical transducer by using PbI_2 nanosheets.

Experimentally, high quality PbI_2 nanosheets are fabricated with a simple recrystallization method (details in the *Experimental Section*), with Scanning Electron Microscope (SEM) and photo shown in Fig. S2. The size of the nanosheet is about tens of micrometers. The high-resolution Transmission Electron Microscope (TEM) image of a PbI_2 nanosheet and the corresponding Fast Fourier Transformation (FFT) image provided in Fig. 1**e** confirm the [110] preferred crystallographic orientation. Moreover, the Selective Area Electron Diffraction (SAED) pattern also clearly depicts the preferential orientation, as detailed in Fig. 1**f**. The center pole represents the (110) direction and the nearest two poles are defined as the (100) and (210) directions. The number of layers of PbI_2 nanosheets fabricated using this process are typically two or three, as determined from the Atomic Force Microscope (AFM) measurement results (Fig. 1**g and h)**.

A PbI_2 nanosheet is excited with a 536 nm laser, and the corresponding Raman spectra is shown in Fig. 1**i**. The sample has characteristic peaks at about 96 and 112 cm^{-1}, which are assigned to the A_{1g} and E_{2u} vibration modes of an ultrathin PbI_2 nanosheet [26], respectively. Furthermore, the PbI_2 nanosheets exhibit strong photoluminescence centered at 500 nm under the excitation by an 800 nm femtosecond laser at room temperature, confirming the high quality of our ultrathin PbI_2 nanosheets, as indicated in Fig. 1**j and k**.