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Chang Kyu Jeong; Jae Hyun Han; Haribabu Palneedi; Hyewon Park; Geon-Tae Hwang; Boyoung Joung; Seong-Gon Kim; Hong Ju Shin; Il-Suk Kang; Jungho Ryu; Keon Jae Lee



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# Comprehensive biocompatibility of nontoxic and high-output flexible energy harvester using lead-free piezoceramic thin film

Chang Kyu Jeong,<sup>1,a,b,c</sup> Jae Hyun Han,<sup>2,a</sup> Haribabu Palneedi,<sup>3</sup> Hyewon Park,<sup>4</sup> Geon-Tae Hwang,<sup>3</sup> Boyoung Joung,<sup>4</sup> Seong-Gon Kim,<sup>5</sup> Hong Ju Shin,<sup>6</sup> Il-Suk Kang,<sup>7</sup> Jungho Ryu,<sup>3,c</sup> and Keon Jae Lee<sup>2,c</sup>

<sup>1</sup>Department of Materials Science and Engineering, College of Earth and Mineral Sciences, The Pennsylvania State University, University Park, Pennsylvania 16802, USA

<sup>2</sup>Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 34141, South Korea

<sup>3</sup>Functional Ceramics Group, Korea Institute of Materials Science (KIMS), Changwon, Gyeongnam 51508, South Korea

<sup>4</sup>Division of Cardiology, Severance Cardiovascular Hospital, Yonsei University Health System, Yonsei University College of Medicine, Seoul 03722, South Korea

<sup>5</sup>Department of Oral and Maxillofacial Surgery, Gangneung-Wonju National University Dental Hospital, College of Dentistry, Gangneung-Wonju National University, Gangneung, Gangwon 25457, South Korea

<sup>6</sup>Department of Thoracic and Cardiovascular Surgery, Chungbuk National University Hospital, College of Medicine, Chungbuk National University, Cheongju, Chungbuk 28644, South Korea

<sup>7</sup>Department of Nanostructure Technology, National Nanofab Center, Daejeon 34141, South Korea

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Flexible piezoelectric energy harvesters have been regarded as an overarching candidate for achieving self-powered electronic systems for environmental sensors and biomedical devices using the self-sufficient electrical energy. In this research, we realize a flexible high-output and lead-free piezoelectric energy harvester by using the aerosol deposition method and the laser lift-off process. We also investigated the comprehensive biocompatibility of the lead-free piezoceramic device using *ex-vivo* ionic elution and *in vivo* bioimplantation, as well as *in vitro* cell proliferation and histologic inspection. The fabricated LiNbO<sub>3</sub>-doped (K,Na)NbO<sub>3</sub> (KNN) thin film-based flexible energy harvester exhibited an outstanding piezoresponse, and average output performance of an open-circuit voltage of ~130 V and a short-circuit current of ~1.3  $\mu$ A under normal bending and release deformation, which is the best record among previously reported flexible lead-free piezoelectric energy harvesters. Although both the KNN and Pb(Zr,Ti)O<sub>3</sub> (PZT) devices showed short-term biocompatibility in cellular and histological studies, excessive Pb toxic ions were eluted from the PZT in human serum and tap water. Moreover, the KNN-based flexible energy harvester was implanted into a porcine chest and generated up to ~5 V and 700 nA from the heartbeat motion, comparable to the output of previously reported lead-based flexible energy harvesters. This work can compellingly serve to advance the development of piezoelectric energy harvesting for actual and practical biocompatible self-powered biomedical applications beyond restrictions of lead-based materials in long-term physiological and clinical aspects. © 2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). [<http://dx.doi.org/10.1063/1.4976803>]

<sup>a</sup>C. K. Jeong and J. H. Han contributed equally to this work.

<sup>b</sup>This research was started while C. K. Jeong was at KAIST Institute for NanoCentury, Daejeon 34141, South Korea.

<sup>c</sup>Authors to whom correspondence should be addressed. Electronic addresses: [ckyujeong@gmail.com](mailto:ckyujeong@gmail.com); [jhyu@kims.re.kr](mailto:jhyu@kims.re.kr); and [keonlee@kaist.ac.kr](mailto:keonlee@kaist.ac.kr)

Piezoelectric devices have been regarded as plausible mechanical energy harvesting concepts due to simple structures and environmental stability without concerns about abrasion, humidity, and bulky heaviness.<sup>1–10</sup> Moreover, flexible energy harvesters (nanogenerators) can be easily fabricated using piezoelectric materials, and they are prospective candidates for realizing self-powered flexible electronics.<sup>11–14</sup> In that pursuit, many researchers have demonstrated high-performance flexible energy harvesters using representative lead-based piezoelectric materials, e.g.,  $\text{Pb}(\text{Zr,Ti})\text{O}_3$  (PZT),<sup>11,12,14,15</sup> even for wearable/bioimplantable applications.<sup>16–20</sup>

Although the lead-based materials have excellent piezoelectric properties, they should not be utilized in ecological/biological applications due to their toxicity, a legacy of the acknowledged Pb-related poisoning.<sup>21–23</sup> Several researchers have reported that PZT might be used for biological and *in vivo* applications, but these reports were only based on cell viability or histology over short-term periods,<sup>18,24,25</sup> which cannot guarantee actual biocompatibility for long-term periods or repeated exposures.<sup>26</sup> Pb causes severe chronic poisoning and pain with long-term exposure (years-to-decades), even when accumulated in small traces.<sup>27,28</sup> Additionally, compounds containing Pb, e.g., lead oxides, are also classified as hazardous materials because they have been implicated in diverse diseases, including tumors.<sup>29,30</sup> For instance, there is very famous and unequivocal historical evidence that widespread Pb usage in the Roman Empire, and the popular lead cosmetics of the Middle Ages, over long periods of time contributed to critical social decline.<sup>31–33</sup>

For these reasons, US Food & Drug Administration (FDA), Centers for Disease Control & Prevention (CDC), and Restriction of Hazardous Substances Directive (RoHS) have issued negative findings regarding lead-related materials and devices.<sup>34–37</sup>

Piezoelectric polymers (e.g., polyvinylidene fluoride (PVDF)) are alternative materials for piezoelectric-bionic applications because they are soft and flexible as previously reported bioimplantations,<sup>38,39</sup> but they have relatively weak chemical/mechanical resistivity, and mediocre piezoelectric coupling compared to piezoelectric ceramics.<sup>40</sup> Recently, numerous researchers have investigated high-performance lead-free piezoelectric ceramics with perovskite-crystalline structures such as  $\text{BaTiO}_3$ ,<sup>41,42</sup>  $(\text{Bi,Na})\text{TiO}_3$ ,<sup>43</sup> and  $\text{BiFeO}_3$ -based ceramics.<sup>44</sup> Although they are alternatives to lead-based piezoceramics, there are diverse shortcomings, such as the low Curie points, the poor piezoelectric coefficients, and the serious leakage levels. By contrast,  $(\text{K,Na})\text{NbO}_3$  (KNN)-based piezoceramics have attracted attention as replacements for lead-based ceramics because of their large piezoelectricity and high Curie temperature with good doping tunability.<sup>45–52</sup>

Nevertheless, the deposition or post-crystallization of KNN-based materials involves difficult processing due to the loss of vaporizable alkaline compositions and slow deposition rates.<sup>53,54</sup> Recently, our group developed a new deposition method, aerosol deposition method (ADM), which is a gas-deposition process that uses as-synthesized particles directly with an accelerated gas to build colloidal aerosol flows.<sup>54–56</sup>

Herein, we demonstrate a high-performance KNN-based flexible piezoelectric energy harvester (f-PEH) using the ADM with the laser lift-off (LLO) process and investigate overall biocompatibility features (Fig. 1). This lead-free f-PEH produces high generating-output of  $\sim 130$  V and  $\sim 1.3$   $\mu\text{A}$  from bending motions; these values reach  $\sim 170$  V and  $\sim 5.5$   $\mu\text{A}$  using random finger flicks. Our developed f-PEH represents the best performance of lead-free f-PEHs, and it is even comparable to previously reported lead-based f-PEHs. We also conducted experiments of cell viability and histological stability to show the short-term biocompatibility of both KNN and PZT. To prove the comprehensive biocompatibility of piezoceramics, general elution tests detecting dissolved ions were additionally performed to foresee long-term toxicity. Finally, we confirmed the electrical output of our high-performance nontoxic f-PEH in *in vivo* circumstance, conformally sutured and deformed on a porcine heart, to show its bioimplantable feasibility.

Fig. 2(a) shows the fabrication of the KNN-based f-PEH device using the ADM and LLO. As shown in the scanning electron microscopy (SEM) image of Fig. 2(b), we synthesized  $0.058\text{LiNbO}_3$ - $0.942(\text{K}_{0.480}\text{Na}_{0.535})\text{NbO}_3$  (L-KNN) using the solid-state method for excellent piezoelectricity.<sup>49,57</sup> The tunneling electron microscopy (TEM) image and the fast-Fourier transformation (FFT) indicate the perovskite L-KNN particles (the right panel of Fig. 2(b)).<sup>58</sup> After granulation of the particles to ensure high efficiency in the ADM, the powders were blended with  $\text{O}_2$  gas to build aerosol flows to be directed onto a sapphire wafer. The aerosol flow was accelerated and ejected from a nozzle (Fig. 2(a)),

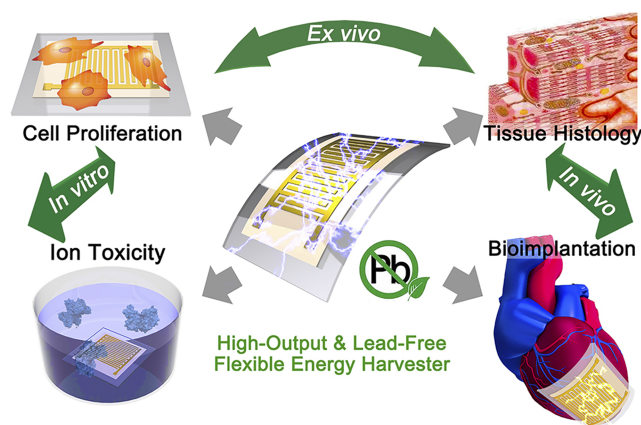


FIG. 1. Scheme illustrating the biocompatibility of our high-output lead-free KNN-based f-PEH.

and consequently, a dense L-KNN thin film was deposited by the mechanical collision of the granule spray in vacuum (GSV),<sup>56</sup> with  $\sim 2.7 \mu\text{m}$  thickness (Fig. 2(c)) after following post-annealing ( $800^\circ\text{C}$ , 1 h). SEM and atomic force microscopy (AFM) images of the as-deposited L-KNN film are also shown in Fig. S1.

To transfer the L-KNN film onto a flexible plastic sheet ( $\sim 125 \mu\text{m}$  thickness), the LLO process was applied to the lead-free piezoelectric film on the sapphire using a XeCl-pulsed excimer laser (Fig. 2(a)). In contrast to sapphire, the L-KNN film absorbs the incident energy since the KNN-based ceramic band-gap energy is lower than the laser photonic energy,<sup>59,60</sup> and this results in melting-dissociation of L-KNN at the interface, followed by the transfer of the L-KNN film from sapphire to the pre-attached flexible plastics (the right panel of Fig. 2(c)). More detailed conditions of the ADM and LLO processes are delineated in our previous reports.<sup>11,54–56</sup>

Both Raman spectra before and after the LLO clearly manifest the tetragonal/orthorhombic symmetries of L-KNN maintained during the LLO process,<sup>58</sup> and high crystallinity was confirmed by X-ray diffraction (XRD) patterns (Figs. S2(a) and S2(b)). The chemical composition of the L-KNN film was also retained during the LLO transfer, as demonstrated in the X-ray photoelectron spectroscopy (XPS) (Fig. S2(c)), revealing the advantage of ADM for depositing vaporizable-elemental films. The optical microscope image in Fig. S2(d) shows the overall surface morphology of the transferred L-KNN thin film after the LLO, including slightly overlapping square-shaped laser tracks (beam size  $\sim 625 \mu\text{m} \times 625 \mu\text{m}$ ). As shown in Fig. S2(d) and Fig. S3, the more the laser shots were overlapped, the more bubble-like nanoscale ridged agglomerates arose on the laser-irradiated surface. This topographical phenomenon results from laser-induced local melting/dissociation during the short energy-duration irradiation of the pulsed laser ( $< 30 \text{ ns}$ ).<sup>11,61</sup> In the LLO process, namely, there was neither mechanical damage nor chemical degradation for the transfer of the entire area of the L-KNN film onto the flexible polymer sheet.

Fig. 3(a) shows a lead-free f-PEH device made from the KNN-based film. The gold interdigitated electrodes (IDEs), with a  $200 \mu\text{m}$  gap-and-width pitch, were fabricated by photolithography. The bottom inset of Fig. 3(a) provides the results of a three-dimensional (3D) finite element analysis (FEA) simulation, with confirmed physics,<sup>46,49,57,62,63</sup> which indicates the efficient piezopotential of the L-KNN between a pair of IDEs when subjected to bending with a bending radius of  $\sim 1.8 \text{ cm}$  (tensile strain of  $\sim 0.25\%$ , rate of  $\sim 2.2\% \text{ s}^{-1}$ , and frequency of  $\sim 0.4 \text{ Hz}$ ). The polarization-electric field (P-E) curve of the L-KNN film energy harvester also exhibited definite ferroelectric behavior (Fig. S4(a)), comparable to that of a previously reported AD-formed PZT film, considering different thickness factors.<sup>55</sup>

As displayed in the second downward peak of Fig. 3(b), the KNN-based f-PEH generated maximum signals up to  $140 \text{ V}$  and  $1.8 \mu\text{A}$  during reciprocating bending/unbending with a strain of  $\sim 0.25\%$ . The produced electrical energy was definitively ascribed to the piezoelectric effect of the L-KNN film, as verified by a polarity switching with forward/reverse connections (Fig. S4(b)). Our lead-free



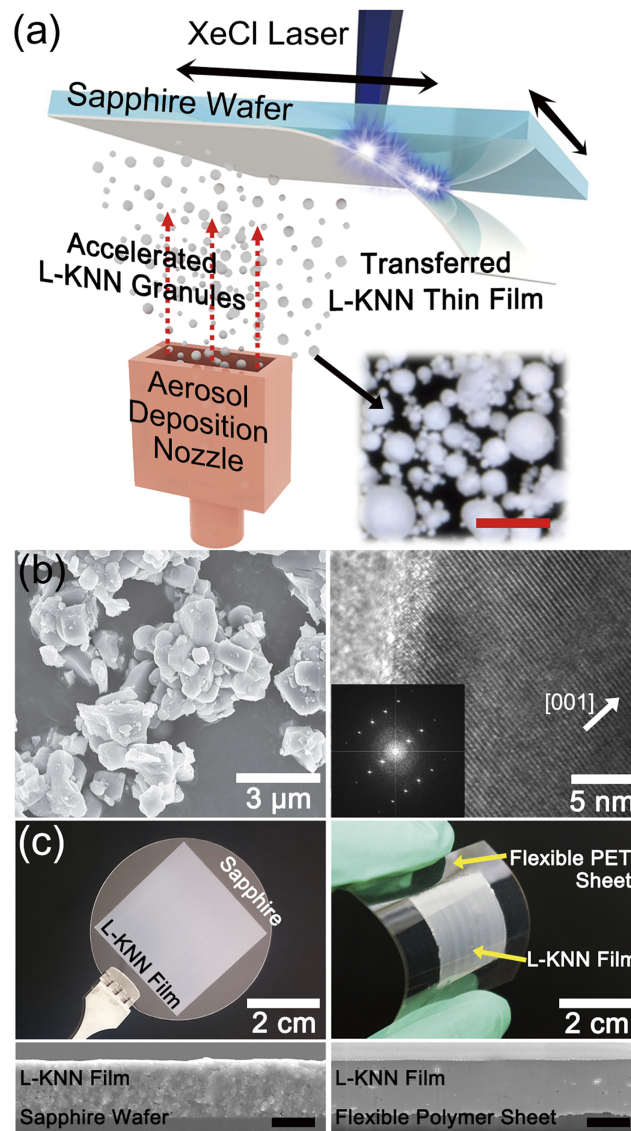


FIG. 2. (a) Schematics of the ADM and LLO. Inset: SEM image of L-KNN granules (scale bar:  $100\ \mu\text{m}$ ). (b) SEM image (left), and high-resolution TEM image and FFT pattern (right) of a L-KNN particle. (c) Photographs of the as-deposited L-KNN film on a sapphire wafer (left) and the L-KNN film transferred onto a flexible PET (right); bottom figures are cross-sectional SEM images (scale bars:  $2\ \mu\text{m}$ ).

energy harvester also showed good mechanical endurance during the durability test with over 6000 cycles and 1 week-strained status (Fig. S4(c)). There is no mechanical crack after repetitive bending (Fig. S5). The voltage output through the circuit load gradually augmented with ascending resistance in the gross (Fig. S4(d)). From changing circuit resistance, a maximum instantaneous power of  $\sim 30\ \mu\text{W}$  was elicited at  $\sim 150\ \text{M}\Omega$ . Although this matching impedance was too high to be compared with conventional electronic components, due to the high internal resistance of the IDE-type piezoelectric devices,<sup>64</sup> our result demonstrates that lead-free piezoceramics can replace lead-based piezoelectric energy harvesters, even for mechanically flexible manner. Furthermore, the KNN-based f-PEH produced even higher output with finger flicking (time interval of  $\sim 4\ \text{s}$ , approximately), up to  $\sim 170\ \text{V}$  and  $\sim 5.5\ \mu\text{A}$ , and operated 40 light-emitting diodes (LEDs) with diverse colors (Fig. S4(d)).

Fig. 3(c) is a plot depicting the output performance levels of previously reported representative f-PEHs including both lead-based and lead-free (KNN-based) piezoceramic devices, compared to this study. Recently, Kim *et al.* reported a KNN thin film f-PEH using direct sputtering deposition

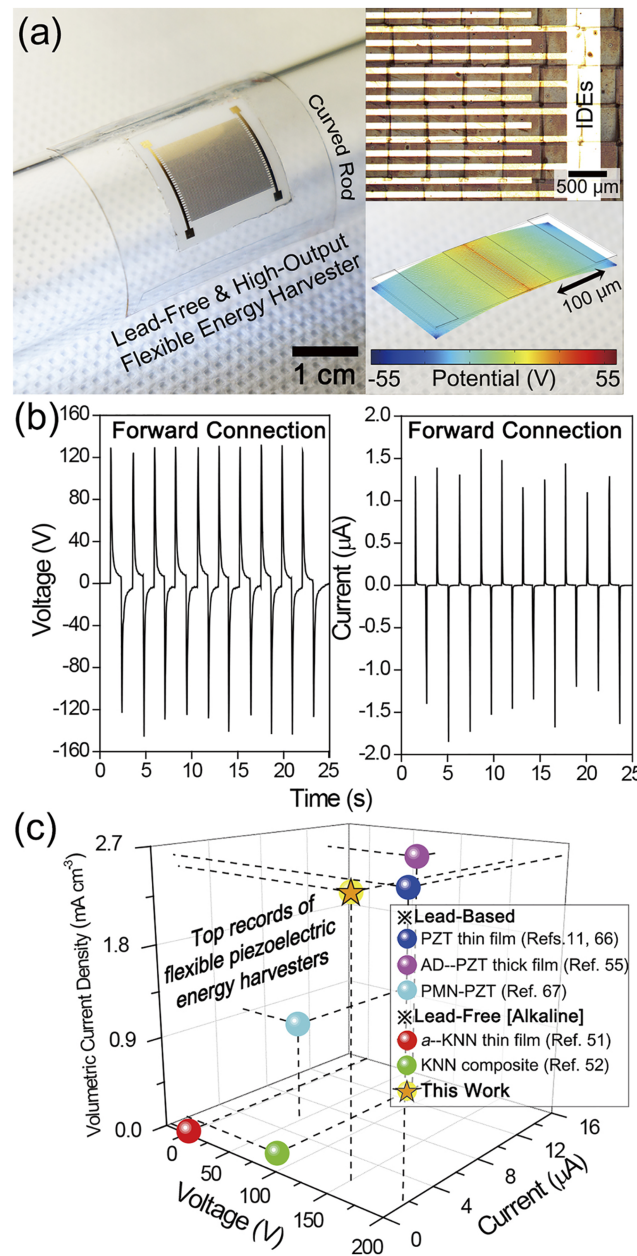


FIG. 3. (a) Photograph of the L-KNN film f-PEH. Insets: optical micrograph of partial IDEs (top) and 3D-FEA simulation of f-PEH. (b) Voltage and current from the lead-free f-PEH. (c) Comparison between this study and previous studies.

onto flexible plastics, but the output was low since it could not be crystallized (amorphous KNN, a-KNN) below 300  $^{\circ}\text{C}$ .<sup>51</sup> Although Gao *et al.* fabricated a decent-performance flexible nanogenerator using patterned/aligned KNN-elastomer composites, the device was too thick ( $\sim 200 \mu\text{m}$ ) to achieve efficient mechanical flexibility and high output density.<sup>52</sup> On the contrary, our AD-formed KNN f-PEH device is strikingly superior to these representative previous reports of flexible lead-free generators. The high performance in this work is even comparable to that of prior high-performance lead-based f-PEHs made by sol-gel PZT films,<sup>11,65</sup> AD-formed PZT thick film,<sup>55</sup> and solid-grown  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ -PZT (PMN-PZT) thick film<sup>66</sup> with IDEs under similar deformations. This remarkable output performance of our lead-free f-PEH stems from the high-quality and dense AD-formed L-KNN piezoceramic thin film.

We subsequently performed cell growth and tissue implant experiments using both AD-formed KNN and PZT films to study cytotoxicity and histotoxicity. Figs. 4(a) and 4(b) present the results of cell viability tests of human embryonic kidney (HEK)-293 cells well cultured on KNN and PZT devices like control groups (Fig. S6), respectively, which shows that neither of the piezoceramics are cytotoxic for short-term periods. No species or cell specificity was observed, as evident from H9C2 cell line (rat's cardiomyocyte) also well proliferating on both ceramics, on a par with the control group (Fig. S6).

Cell attachability on both KNN and PZT films was evaluated by culturing the MG-63 (human osteosarcoma) cell. The osteocyte adhered well to both the piezoceramic surfaces without significant biological degradation (Figs. S7(a) and S7(b)). Based on the diverse cell growth, average cell proliferation ratios were calculated for both KNN and PZT devices, which determined that the cells well lived in all cases (Fig. S7(c)). The right panels of Figs. 4(a) and 4(b) show the optical micrographs of rat's muscular tissue after implanting both piezoceramics into the living rat's thigh for one week, showing no serious histological inflammation, similar to the control tests (Figs. S7(d) and S7(e)).

From the above biocompatibility tests with cellular/histological approaches, it appears that lead-based piezoceramics like PZT, as well as alkaline-based lead-free piezoceramics like KNN, are biocompatible, as contended by several engineers.<sup>18,24</sup> However, these highly localized and short-term approaches cannot ensure actual biocompatibility over long-term periods, with genotoxic, metabolic, and clinical systems.<sup>26–30</sup> First, generally, heavy metal ion uptake-related symptoms do not occur directly or rapidly during a temporary exposure.<sup>26,31–35</sup> Second, cell proliferation/adhesion are not seriously affected by surficial compositions, other than surficial topographies.<sup>67–69</sup> In addition, histological inflammation and infection do not easily occur with sterilized extraneous objects without the involvement of germs, viruses, or macroscopic stabs.

The best way to realistically examine biocompatibility is with long-term follow up surveys to reveal chronological trends in body fluids and clinical effects after implanting devices into the body; but this is very hard to perform at the laboratory level. *In lieu* of the actual long-term diagnostic analyses, therefore, we studied the dissolution of PZT and L-KNN films in not only human serum but also tap water, using an inductively coupled plasma mass spectrometer (ICP-MS) to investigate heavy metal ion concentrations eluted from the devices. The temperatures of the human serum and tap water were maintained at about 36.5 °C and 25 °C, respectively, agitated by shaking and stirring, to create close to real conditions. We selected Nb and Pb ions as the primary elements for this ion detection test of KNN and PZT, respectively. Note that Nb is basically considered to be a nontoxic element<sup>70</sup> although there is a report about the harmfulness of Nb dust,<sup>71</sup> which is not the chemical maleficence of Nb. The left panel of Fig. 5 highlights that the eluted Pb concentration from the PZT is about three orders of magnitude higher than the Nb concentration from the KNN in both serum

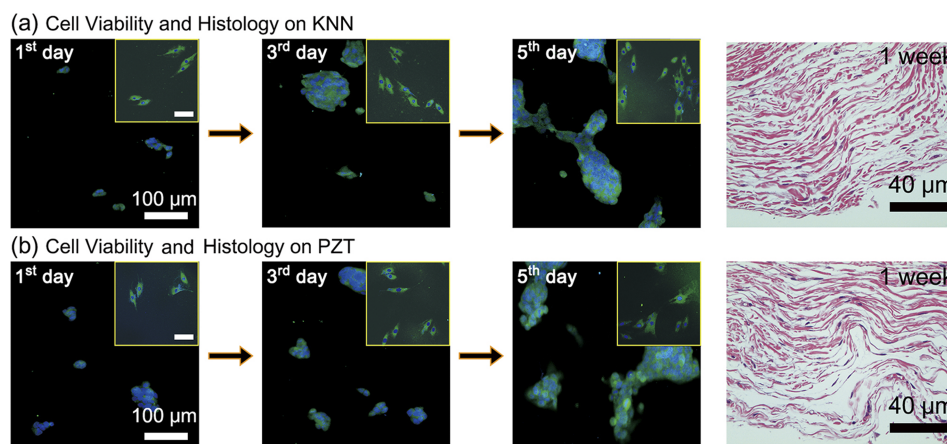


FIG. 4. Fluorescent confocal images of HEK-293 cells cultured on and histological image after implantation of (a) L-KNN and (b) PZT films. Insets: Confocal images of H9C2 cells.

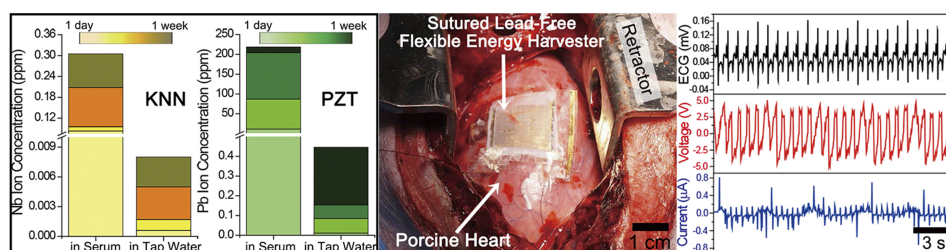


FIG. 5. Concentration of Nb and Pb ions eluted from L-KNN and PZT films (left). *In vivo* L-KNN film f-PEH sutured on a porcine heart (middle). Original porcine electrocardiogram (ECG), *in vivo* generated energy harvesting voltage and current (right). Note that the peak deviation in current was due to the individually different periodic movements of ECG.

and water cases. The Pb levels in those fluids are not acceptable, certainly according to many official reports and policies concerning biocompatibility.<sup>34–37,72,73</sup>

These dissolution results are reasonable because lead oxides are readily soluble in aqueous conditions,<sup>74</sup> while niobium oxides are theoretically insoluble.<sup>75</sup> Note that the amount of dissolution in human serum was much higher than the amount in water owing to enhanced corrosive interactions with proteins.<sup>76,77</sup> Control tests conducted without devices are plotted in the [supplementary material](#) (Fig. S8).

Although the elution test is an *ex vivo* experiment, it definitely shows the Pb-dissolution of lead-based piezoceramic film which can induce vulnerable/oxidative damage in biosynthetic and metabolic pathways, possibly causing long-term symptoms like carcinogenesis.<sup>21–23,26–30,72,73,78</sup> To further directly inspect the chronological/clinical effects of bioimplanted piezoceramics, we are currently conducting biochemistry studies and long-term epidemiologic investigations using canine/porcine models.

We finally demonstrated the *in vivo* implantation of our lead-free piezoelectric energy harvester into a porcine chest. As given in Fig. 5 (the middle panel), the KNN-based nontoxic high-output f-PEH was intimately fixed to the living porcine heart by suturing. Our lead-free f-PEH converted the continuous heartbeat biomechanical energy into electrical energy of up to 5 V and 700 nA (Fig. 5, the right panel), which comparable to *in vivo* PZT-ribbons-array f-PEH.<sup>18</sup> Our result is the first to show the bioimplantation of a lead-free f-PEH with high performance in a large-animal model.

To sum up, a high-performance lead-free f-PEH was accomplished using a flexible KNN-based piezoceramic film enabled by the ADM and LLO processing. The lead-free f-PEH generated ~130 V and ~1.3  $\mu$ A with regular bending and 170 V and 5.5  $\mu$ A with random flicking, which is the best output performance among previously reported lead-free f-PEHs. This result is even comparable to up-to-date lead-based flexible piezoelectric generators. Both AD-formed KNN and PZT showed good short-term biocompatibility as determined by cell and histological studies. Because these approaches do not provide proper information for clinicians, however, we additionally performed ion elution tests of KNN and PZT in both human serum and tap water to chase dissolved heavy metal ions, which can affect physiological phenomena, even in infinitesimal amounts, with long-term accumulation. The resulting concentration of eluted noxious Pb ions measured in the test was meaningful for evaluating the hazardous potential of lead-based piezoceramics for medical/environmental devices. Although the elution test is an indirect approach for determining clinical toxicity, it can provide crucial information about poisoning related to long-term bio-/eco-compatibility. Finally, we confirmed the bioimplantation of our KNN-based f-PEH using a large-animal model. By harnessing the movement of living porcine heart, the sutured nontoxic high-output f-PEH produced electricity of up to 5 V and 700 nA. This work demonstrates the promise of high-performance lead-free piezoelectric energy harvesting for biocompatible and ecofriendly applications, as notable alternatives to lead-based piezoceramics.

See [supplementary material](#) for additional information referred in the text.

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