Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.


# Supporting Information

## Bifunctional NiFe LDH as a piezoelectric nanogenerator and asymmetric pseudo supercapacitor

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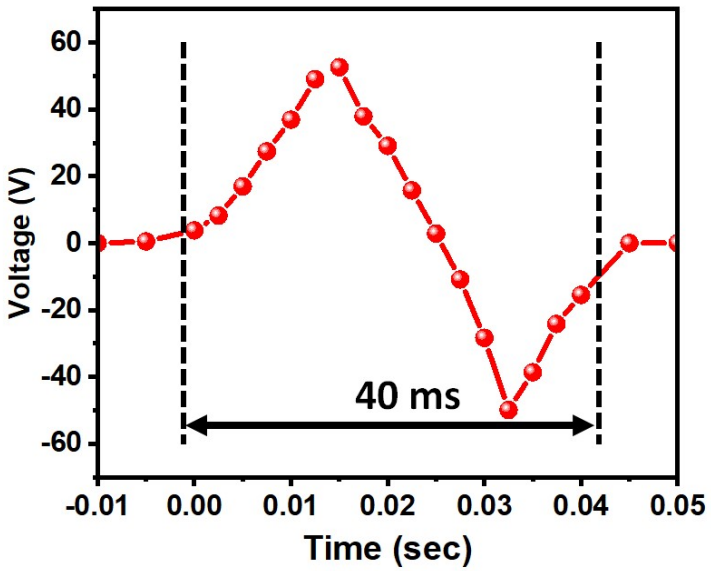


**Figure S1.** The response time of NiFe LDH nanogenerator

## S2. Experimental Section

### S2.1. Material

Nickel nitrate hexahydrate ($Ni(NO_3)_3.6H_2O$, CAS 13478-00-7, 99.9%), iron nitrate nonahydrate ($Fe(NO_3)_3.9H_2O$, CAS 7782-61-8, 98%), urea ($CO(NH_2)_2$, CAS 57-13-6, 99%),

sodium citrate ($Na_3C_6H_5O_7$, CAS 6132-04-3, 99.5%), ethanol ($CH_3CH_2OH$, CAS 64-17-5, 96%), potassium hydroxide (KOH, CAS 1310-58-3, 90%), hydrochloric acid (HCl, CAS 7647-01-0, 37%), polyvinyl alcohol (PVA, CAS 25213-24-5), acetylene black, Platinum (Pt; 99.999%; Sigma Aldrich) and polydimethylsiloxane (PDMS; Sylgard 184, Dow corning), poly(vinylidene fluoride) (PVDF, CAS 24937-79-9), N-methyl-2-pyrrolidone (NMP, CAS 872-50-4, 99.5%), polytetrafluoroethylene (PTFE, 60%) were procured from Sigma-Aldrich. De-ionized (DI) water was collected from the Millipore system (Resistivity: 18.3 MΩ) and used. Silver paste was used to make contacts and Cu wires were used to make connections.

**S2.2. Instrumentation**

X-ray diffraction (XRD, X'pert PRO, Cu Kα radiation, 0.15406 nm) was used to study the brucite-like layered crystal structure of NiFe LDH nanostructure. The microstructures of the synthesized materials were observed using a Field-emission scanning electron microscope (FESEM, ZEISS Ultra-55). Raman analysis was performed using a Renishaw spectrometer to study the functional groups present in the NiFe LDH nanostructure. The conductivity of Pt electrode and piezoelectric output current ($I_{SC}$) of piezoelectric nanogenerator was recorded using current source meter (SMU 2450, Keithley USA). The oscilloscope was used to measure the output voltage of the nanogenerator (DSO3062A; Agilent Technologies, USA). A functional generator governed dynamic shaker was adopted to regulate the constant vertical force on the piezoelectric nanogenerator (The Model Shop, USA). All the electrochemical characterization was performed on CHI 660E electrochemical workstation. Piezoelectric Force Microscope (Cypher AFM, Asylum Research, Santa Barbara, CA, USA) is used to study the piezoelectric properties of NiFe LDH nanostructure. Titanium/Iridium (5/20) coated Silicon material tip was used to scan the NIFe LDH nanostructure.All the experiments were performed under identical condition at room temperature of 30°C and humidity of 50% at laboratory ambience.

**S2.3. Synthesis of NiFe LDH nanostructure**

A molar weight percent ratio of Ni/Fe = 3:1 has been employed to synthesize NiFe LDH nanostructure using hydrothermal synthesis. 250 mL DI water solution was made using 1.5 M $Ni(NO_3)_3.6H_2O$ and 0.5 M Fe $(NO_3)_3.9H_2O$. Separate DI solution of 1.5 M $Ni(NO_3)_3.6H_2O$ and 0.5 M Fe $(NO_3)_3.9H_2O$ was also made and kept for stirring for 30 min. Both the solutions were

mixed by maintaining a constant pH of 11 in ambient temperature. The resulting suspension was mechanically agitated for 1 h at room temperature for proper mixing and then transferred to an autoclave with a Teflon coating to synthesize a well crystalline nanostructure. The precipitate produced after the hydrothermal treatment was filtered and washed multiple times with DI water to eliminate excess soluble ions until the filtrate pH was 7. The powder was dried overnight at 60$^{o}$C, yielding a product that ranged in color from green to greenish-brown, depending on the hydrothermal treatment settings.

**S2.4. Fabrication of Platinum electrode on PET substrate**

Platinum (Pt) metal was deposited over the flexible PET substrate using the thermal evaporation technique. Pt pellets were thermally evaporated by a tungsten coil in a high-pressure vacuum chamber of $10^{-6}$ Torr. The evaporation rate was maintained at 2 nm/s for 30 secs to obtain a highly transparent and flexible conductive electrode on a PET substrate with uniform thickness.

**S2.5. Fabrication of NiFe LDH: PDMS nanogenerator**

Initially, the homogenous mixture of PDMS polymer and NiFe LDH was coated over ITO/PET substrate using the spin coater technique at 500 rpm for 45 sec. The different weight percent of NiFe LDH (2 wt.%, 5 wt.%, 10 wt.%, 15 wt.%) PDMS composite film was deposited on the ITO/PET substrate. These composite films were mechanically placed under a Pt-coated PET counter electrode to fabricate a piezoelectric nanogenerator. The same device was fabricated using PDMS polymer (without filler) for the comparative studies.

**S2.6. Fabrication of asymmetric flexible supercapacitor (AFSC)**

An asymmetric electrode was fabricated with NiFe-LDH and biomass-derived AC as positive and negative electrodes respectively. The choice of PVA-KOH as the electrolytic medium is due to its high activation energy and flexibility. The flexible electrolytic substrate was prepared by soaking PVA overnight into a 6 M KOH solution. VA-KOH electrolyte was placed between the positive and negative electrodes and connections were made using silver paste. The AFSC was encapsulated using PDMS polymer to avoid leakage.

## S2.7. Electrochemical Measurements of the Supercapacitor

At ambient temperature, the electrochemical characteristics of the AFSC were investigated. In a two-electrode setup, electrochemical characterization comprising cyclic voltammetry (CV) and galvanostatic-charge discharge studies (GCD) were carried out. With an alternating current perturbation amplitude of 10 mV and a frequency range of 100 kHz to 0.01 Hz, electrochemical impedance spectroscopy (EIS) was performed. In the potential range of 0 to 1 V, CV studies were performed at different scan speeds ranging from 10 to 100 $mVs^{-1}$. The electrode's GCD property was evaluated at various current densities with a cut-off voltage ranging from 0 to 1 V, and specific capacitance, energy density, power density per area were determined (calculations given in electronic supplementary information). The stability of the electrodes was evaluated using the GCD techniques of about 10,000 charge-discharge cycles period. A battery test system was used to determine the cycle life (Neware BTS4000 series). AFSCs were created using NiFe LDH as the positive electrode and biomass-derived activated carbon (AC) as the negative electrode, respectively. 6 M KOH was used as the electrolyte.

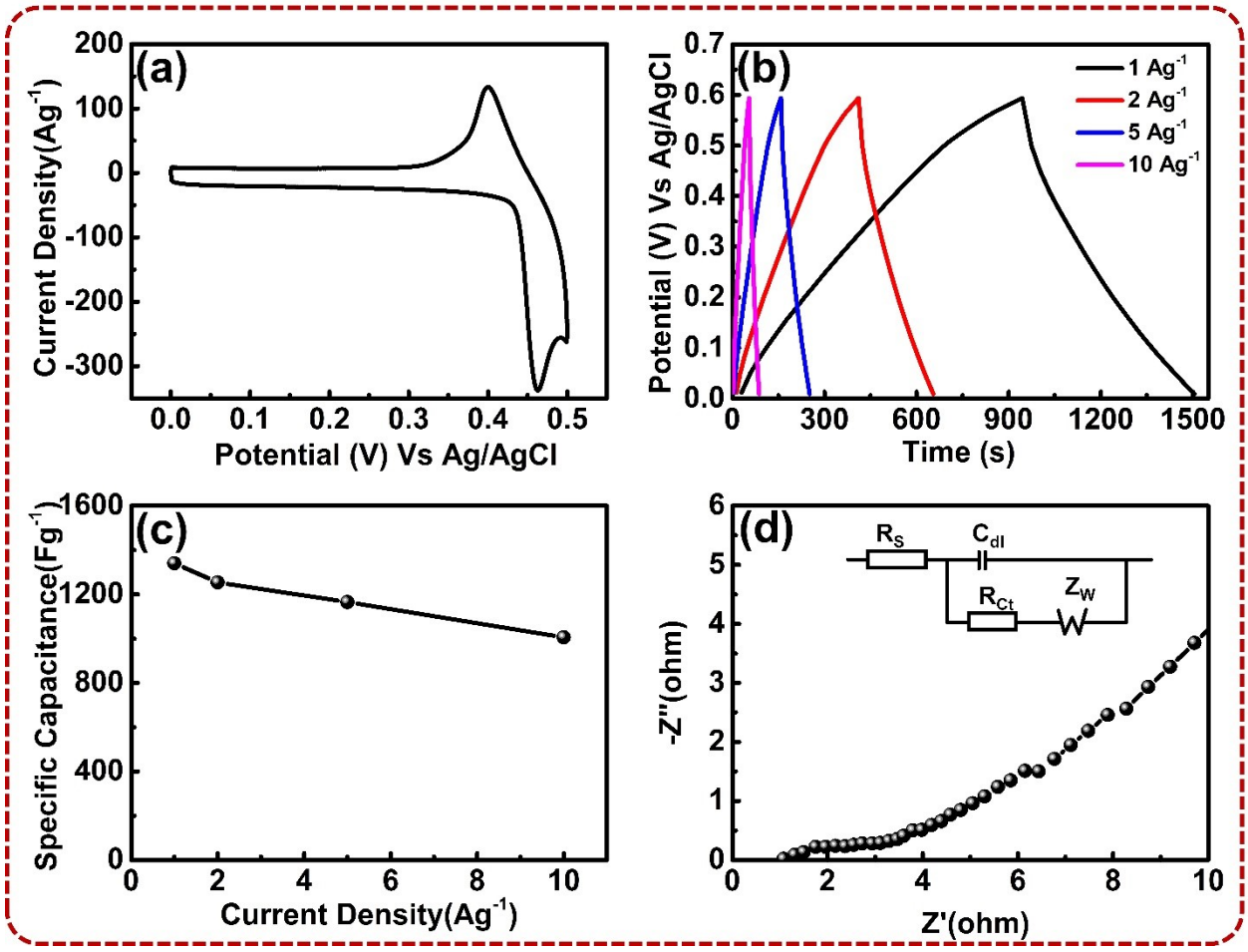


**Figure S2.** Electrochemical capacitive properties of NiFe-LDH composites tested using a three-electrode system in 6M KOH solution. **(a)** CV curve at 10 mVs-1, **(b)** GCD curves at different current densities, **(c)** rate performances at different current densities, **(d)** Nyquist plot measured at frequency range between 0.01 and 10 5 Hz, inset: corresponding equivalent circuit.

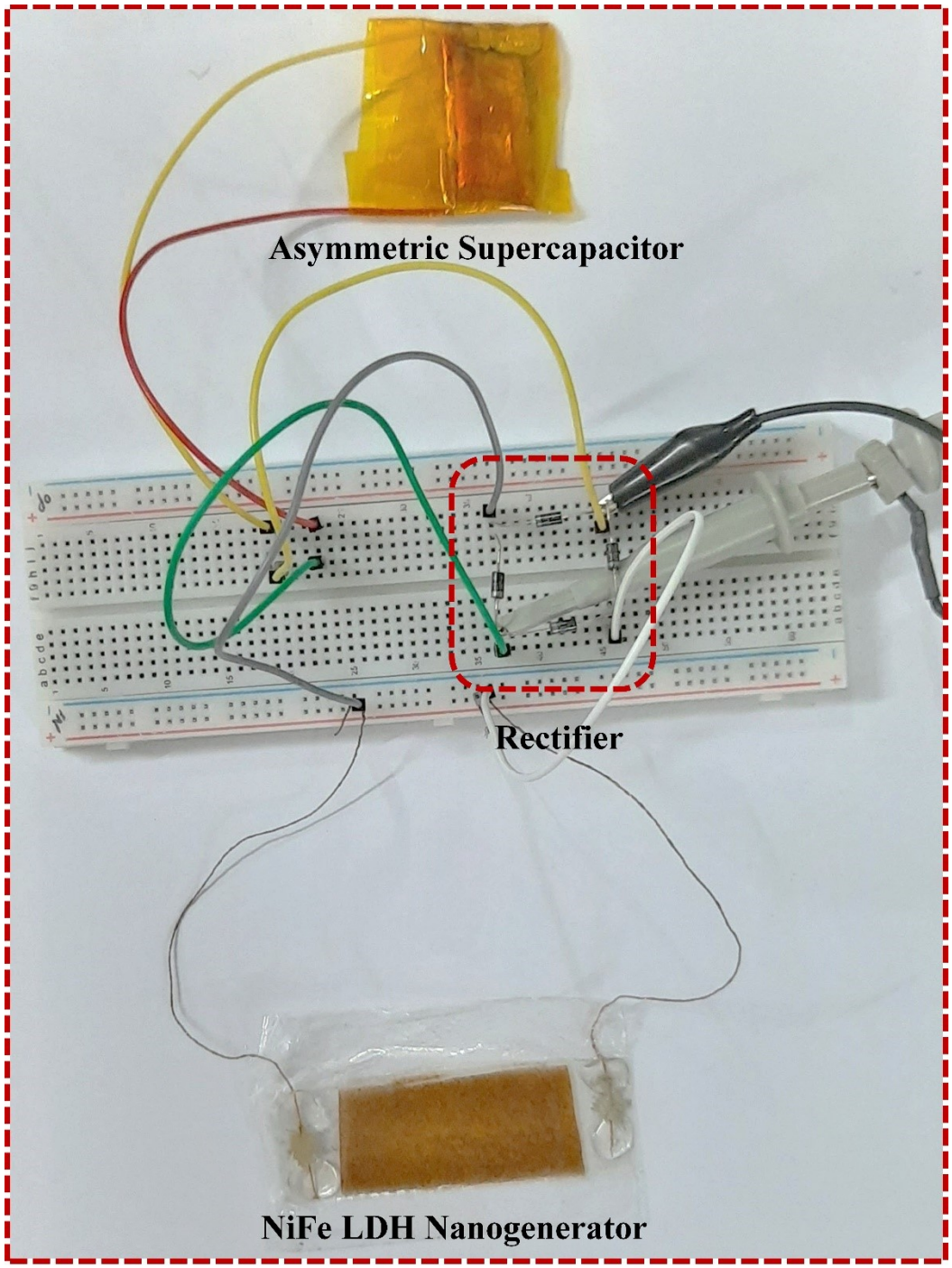


**Figure S3.** Charging of Supercapacitor powered by NiFe LDH nanogenerator.

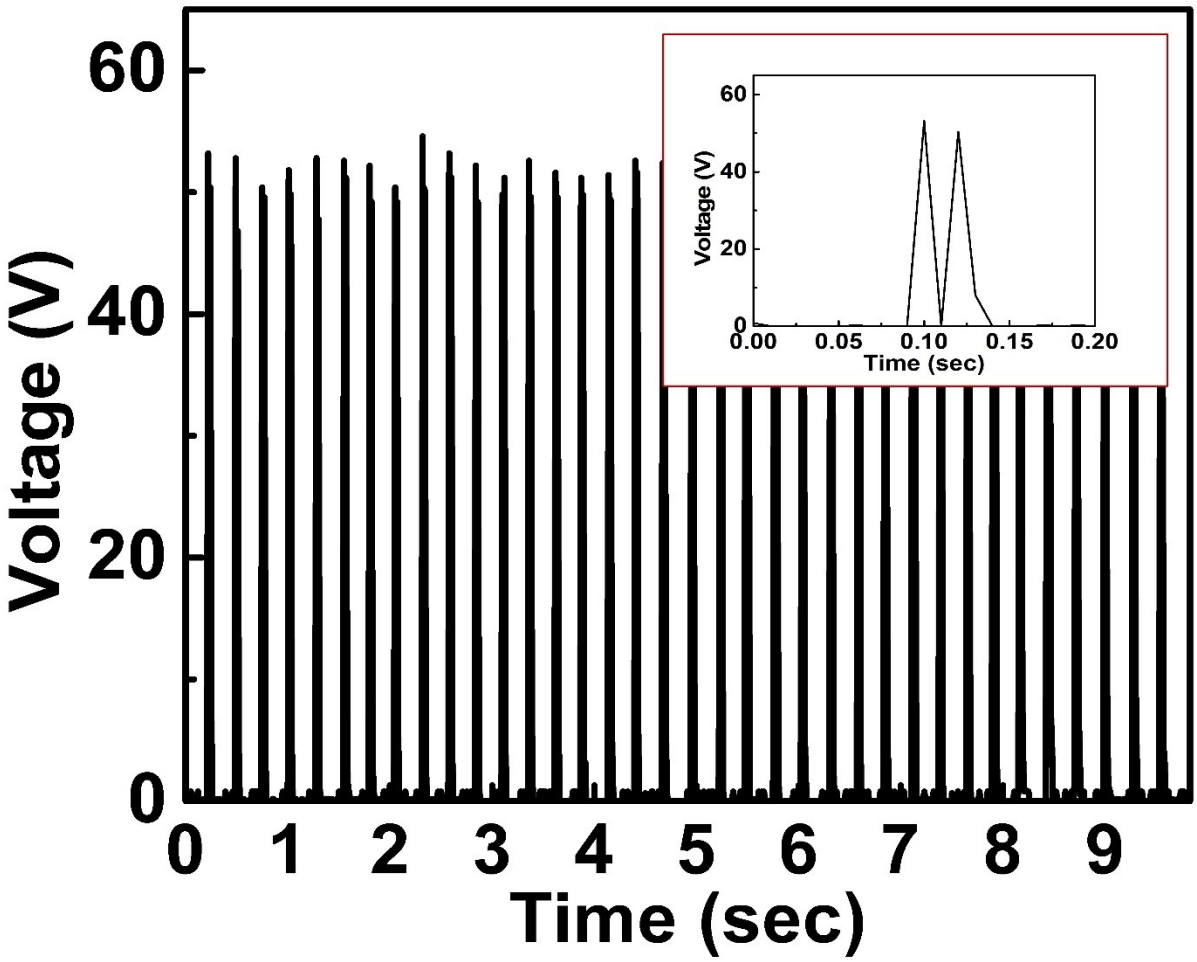


**Figure S4.** Rectified output of NiFe LDH at 0.15 kgf compression force.

## S5. Calculation of cost per self-charged power system:

a) **Calculation for piezoelectric Nanogenerator**

1. Price of ITO coated PET substrate (6 x 3) $cm^2$ = $ 0.104
2. Cost of chemical utilized per device = $ 0.816
3. Overhead Charges (8%) = $ 0.08

b) **Calculation of pH sensor**

1. Price of PET substrate (4 x 2) $cm^2$ = $ 0.052
2. Cost of chemical utilized per device = $ 0.404
3. Overhead Charges (8%) = $ 0.04

Total Cost = $ (1 + 0.496) = $ 1.964 = ~$ 1.496

Section S6.

The obtained peak voltage was lesser than that of the NiFe:PDMS device. This could be attributed to the poor deposition of pristine NiFe LDH along the device. When NiFe LDH was coated over the ITO substrate, the nanoparticles tend to form aggregates on the substrate resulting in poor performance of the device. However, upon uniform dispersion of NiFe LDH in PDMS device, the peak output voltage was obtained as 53 V. Due to the interfacial or a Maxwell-Wagner-Sillars polarization observed on the crossing point in heterogeneous materials, the dielectric constant increases which leads to the very high output voltage of 53 V upon application of a 0.05 kgf pressure.

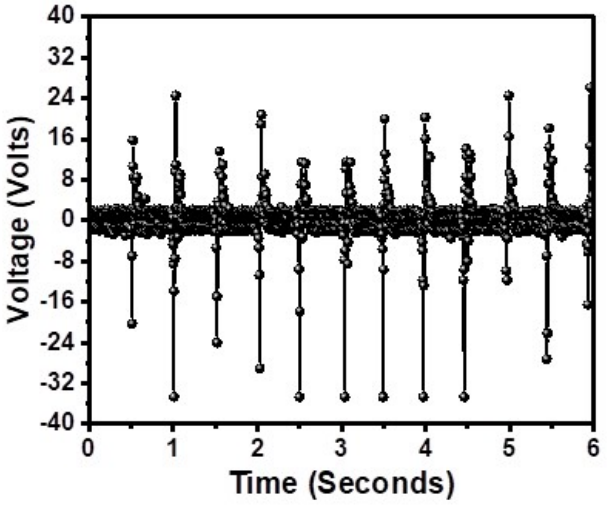


Figure 4. The output voltage of NiFe LDH based nanogenerator under a vertical compression force of 0.05 kgf.

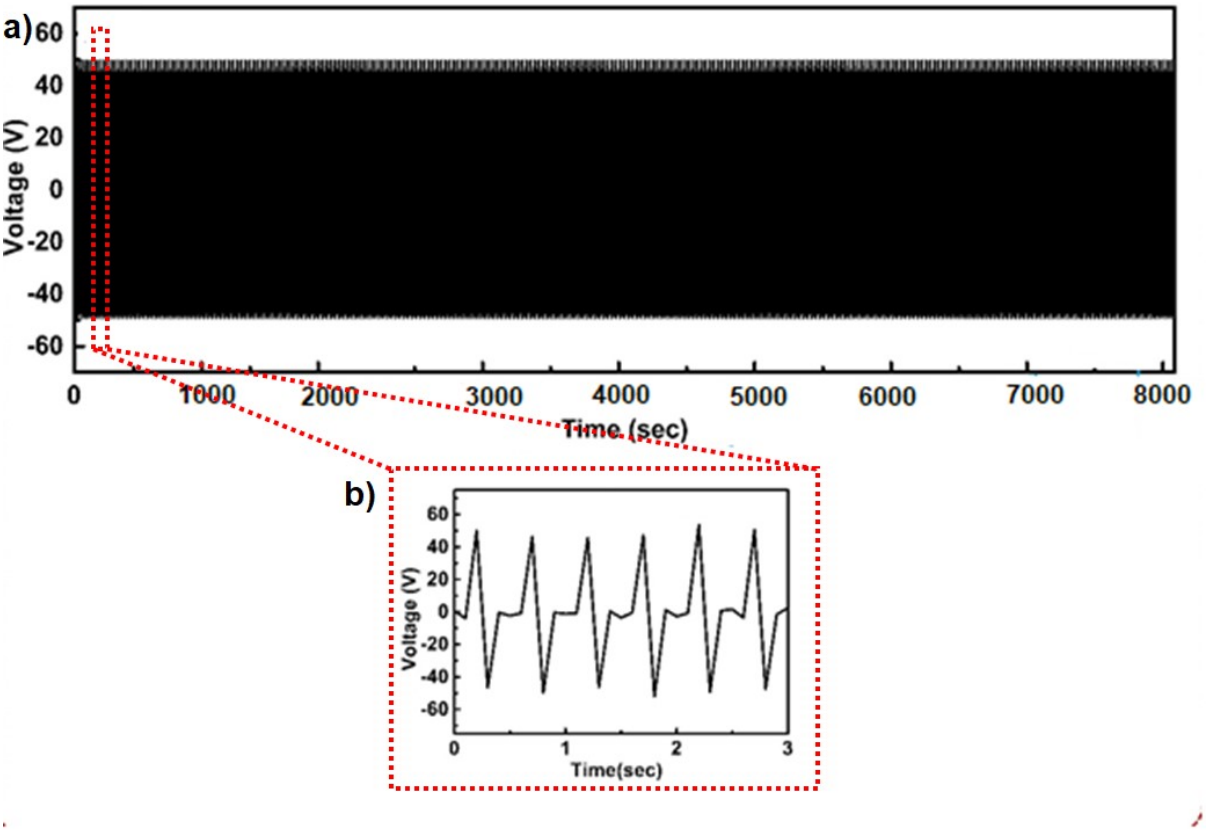


Figure S7. a) Stability test of NiFe: PDMS nanogenerator for 8000 cycles, b) The enlarged view of the cyclic tests.

**S8. Integration of NiFe-LDH nanogenerator and NiFe LDH Supercapacitor**

Further, the charging of ASC was performed using NiFe LDH nanogenerator and the schematic is shown in **Figure 6(h)** and the real image is shown in **Figure S4.** From the results, it is proved that the LDH materials could be an effective approach in achieving high energy density while retaining power density. The output generated for the nanogenerator was rectified using the full-wave rectifier and the rectified DC voltage **(Figure S3)** was utilized to charge the ASC. A very fast charging curve of up to 0.8 V sec was observed over a continuous tapping for 100 secs as shown in **Figure 6(i).** The integrated self-powered system that works by charging the ASC using a piezoelectric hybrid nanogenerator was demonstrated, which has huge potential in smart wearable electronics devices. The cost for fabrication of the self-powered unit comprising of piezoelectric nanogenerator (6 cm x 3 cm) and a supercapacitor (4 cm x 2 cm) was calculated to be ~$1.5 (**details in S5**) thus making it a low-cost platform.

S9. The performances of emerging supramolecular materials based TENG

| S.No. | Method used | Materials used | Application |
|---|---|---|---|
| 1 | Spin coating | Sulfonic-acid-terminated polystyrene and poly (2-vinyl pyridine) ($P_2VP$) | TENG |
| 2 | Conventional ion exchange process | Poly(lipoic acid)-based conductive self-healable organohydrogel | TENG |
| 3 | Wet processing | amine-terminated poly(ethylene oxide) added sulfonic-acid-terminated poly(styrene) and poly(2-vinylpyridine) | TENG |

Recently, supramolecular routes are employed for fabricating TENG based on an alkali-metal-bound porous film, where the alkali metal ions are readily switched among one another to generate voltage. Sulfonic-acid-terminated polystyrene and poly (2-vinyl pyridine) (P2VP) have been used for fabricating a TENG [1]. This wide-range triboelectric tuning can be achieved simply by a conventional ion exchange process in a reversible manner, thereby allowing reversible control of the output performance in a single device platform [2]. Further, an electrode gel was prepared by mixing poly(lipoic acid) with supramolecular crosslinkers of Fe3+ and phytic acid (PA), and the conductive polymer poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) to fabricate a triboelectric nanogenerator [3].

References:

[1]. Park, C., Song, G., Cho, S.M., Chung, J., Lee, Y., Kim, E.H., Kim, M., Lee, S., Huh, J. and Park, C., 2017. Supramolecular-assembled Nanoporous film with switchable metal salts for a triboelectric Nanogenerator. Advanced Functional Materials, 27(27), p.1701367.

[2]. Khan, A., Ginnaram, S., Wu, C.H., Lu, H.W., Pu, Y.F., Wu, J.I., Gupta, D., Lai, Y.C. and Lin, H.C., 2021. Fully self-healable, highly stretchable, and anti-freezing supramolecular gels for energy-harvesting triboelectric nanogenerator and self-powered wearable electronics. Nano Energy, 90, p.106525.

[3]. Park, C., Koo, M., Song, G., Cho, S.M., Kang, H.S., Park, T.H., Kim, E.H. and Park, C., 2020. Surface-conformal triboelectric nanopores via supramolecular ternary polymer assembly. ACS nano, 14(1), pp.755-766.