2017

Research Update: Hybrid energy devices combining nanogenerators and energy storage systems for self-charging capability

Jeonghun Kim
University of Wollongong, jhkim@uow.edu.au

Ju-Hyuck Lee
University of Wollongong

Jaewoo Lee
University of Wollongong, jl863@uowmail.edu.au

Yusuke Yamauchi
University of Wollongong, *National Institute for Materials Science*, yusuke@uow.edu.au

Chang-Ho Choi
Defence Science and Technology Organisation

See next page for additional authors

Publication Details

Kim, J., Lee, J., Lee, J., Yamauchi, Y., Choi, C. & Kim, J. (2017). Research Update: Hybrid energy devices combining nanogenerators and energy storage systems for self-charging capability. APL Materials, 5 (7), 073804-1-073804-12.

Research Update: Hybrid energy devices combining nanogenerators and energy storage systems for self-charging capability

Abstract

The past decade has been especially creative for nanogenerators as energy harvesting devices utilizing both piezoelectric and triboelectric properties. Most recently, self-charging power units using both nanogenerators and energy storage systems have begun to be investigated for portable and wearable electronics to be used in our daily lives. This review focuses on these hybrid devices with self-charging combined with energy harvesting storage systems based on the most recent reports. In this research update, we will describe the materials, device structures, integration, applications, and research progress up to the present on hybrid devices.

Publication Details

Kim, J., Lee, J., Lee, J., Yamauchi, Y., Choi, C. & Kim, J. (2017). Research Update: Hybrid energy devices combining nanogenerators and energy storage systems for self-charging capability. APL Materials, 5 (7), 073804-1-073804-12.

Authors

Jeonghun Kim, Ju-Hyuck Lee, Jaewoo Lee, Yusuke Yamauchi, Chang-Ho Choi, and Jung Ho Kim

Research Update: Hybrid energy devices combining nanogenerators and energy storage systems for self-charging capability

Jeonghun Kim, Ju-Hyuck Lee, Jaewoo Lee, Yusuke Yamauchi, Chang Ho Choi, and Jung Ho Kim

Citation: APL Materials **5**, 073804 (2017); doi: 10.1063/1.4979718
View online: http://dx.doi.org/10.1063/1.4979718
View Table of Contents: http://aip.scitation.org/toc/apm/5/7
Published by the American Institute of Physics

Research Update: Hybrid energy devices combining nanogenerators and energy storage systems for self-charging capability

Jeonghun Kim,[1,a] Ju-Hyuck Lee,[1,a] Jaewoo Lee,[1] Yusuke Yamauchi,[1,2] Chang Ho Choi,[3] and Jung Ho Kim[1,b]
[1]*Institute for Superconducting and Electronic Materials (ISEM), Australian Institute for Innovative Materials (AIIM), University of Wollongong, North Wollongong, NSW 2500, Australia*
[2]*International Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan*
[3]*Defence Science and Technology Group, 507 Lorimer Street, Fisherman's Bend, VIC 3207, Australia*

(Received 31 January 2017; accepted 15 March 2017; published online 1 May 2017)

The past decade has been especially creative for nanogenerators as energy harvesting devices utilizing both piezoelectric and triboelectric properties. Most recently, self-charging power units using both nanogenerators and energy storage systems have begun to be investigated for portable and wearable electronics to be used in our daily lives. This review focuses on these hybrid devices with self-charging combined with energy harvesting storage systems based on the most recent reports. In this research update, we will describe the materials, device structures, integration, applications, and research progress up to the present on hybrid devices.
[http://dx.doi.org/10.1063/1.4979718]

I. INTRODUCTION

The harvesting, storage, and utilization of energy are becoming a worldwide issue due to the energy crisis, environmental pollution, and the fast development of electronics for our daily life.[1–3] It is very urgent to find sustainable and renewable energy sources because of shortages of fossil fuels and rapid increases in our energy consumption.[4,5] In fact, there are considerable wasted energies in our environment, such as wind energy,[6] and thermal,[7] tide,[8,9] solar,[10,11] and various forms of mechanical energy. Among these energy sources, mechanical energy would be the most widely distributed energy form, existing all over our living environment including the human body (Fig. 1).[12]

Researchers have developed nanogenerators with piezoelectric and triboelectric properties that can be used to convert mechanical energy into electricity, which are effective devices to harvest low-frequency mechanical energy.[13–24] As well-known, the nanogenerator device and its material have the advantages of high output, simple design, low cost, flexibility, thin device packages, light weight, and excellent harmony with other materials and devices.[25,26] To date, the development of device structures,[27] materials,[28] systems,[29] and micro- and nano-technology[30] has been intensively investigated for improving the performance and achieving new applications of nanogenerators.[31,32] Nevertheless, nanogenerators have a fatal drawback: to be used for practical electronics, they need to generate continuous power, although a nanogenerator can generate instantaneous or pulsed power (i.e., alternating current) when it takes mechanical energy as an input. Otherwise, conventional energy storage systems (ESSs) with high power density, long cycle lifetime, and high capacitance, such as

[a]J. Kim and J.-H. Lee contributed equally to this work.
[b]Author to whom correspondence should be addressed. Electronic mail: jhk@uow.edu.au

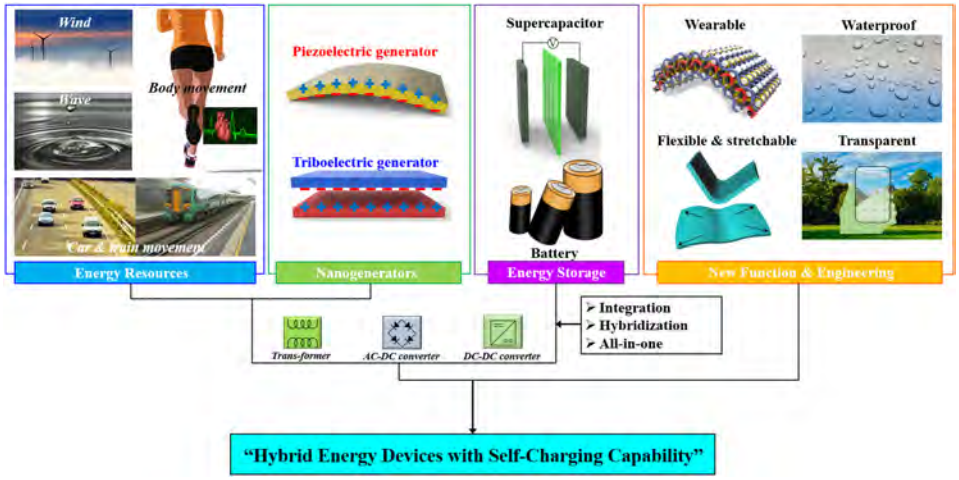

FIG. 1. Recent developments in hybrid devices based on nanogenerators and energy storage systems through integration, hybridization, and all-in-one designs for self-charging energy systems for future electronics.

supercapacitors[23–38] and batteries,[39–42] can supply continuous power to operate the electronics.[43,44] To overcome this critical problem of currently developed nanogenerators, the utilization of ESSs with nanogenerators should be essential for practical use in the future.

Based on this background, researchers have tried to integrate nanogenerators and ESSs to efficiently utilize the generated electricity for portable electronic devices such as mobile phones, tablets, bendable displays, portable electronic paper, wearable personal multimedia devices, and some medical devices.[45,46] Very recently, within the last one and a half years, many researchers have tried to fabricate and reported hybrid devices containing nanogenerators and ESSs that were developed via simple integration (circuit connection), hybridization of materials and systems, and all-in-one device design (Fig. 1). Here, we summarize the most recent research results on hybrid devices with self-charging capability and introduce their materials, concepts, and progress.

II. NANOGENERATORS

Basically, the nanogenerator can be divided into representative two devices depending on piezoelectric and triboelectric properties, called the piezoelectric nanogenerator (PENG) and triboelectric nanogenerator (TENG), respectively. The first demonstrated nanogenerator was the PENG using a ZnO nanowire (NW),[47] which was operated by the piezoelectric property. The formation of a piezoelectric potential or piezopotential was arisen from the breakage of central symmetry in the ZnO crystal structure by external force. In detail, the ZnO crystal with wurtzite structure has a stacked structure of tetrahedrally coordinated O^{2-} and Zn^{2+} along the *c*-axis (Figs. 2(a)–2(i)). The structure is deformed while an external force is applied. Therefore, the charge centers of the cations and anions are isolated and an electric dipole is formed, resulting in the generation of a piezopotential. The ZnO-based PENGs have been developed as various types, as shown in Fig. 2(a).[13,48–50] This basic principle and the model of power generation apply to other PENGs based on various piezoelectric materials, such as lead zirconate titanate (PZT),[51–53] $BaTiO_3$ (BTO),[54] poly(vinylidene fluoride) (PVDF),[55–58] and various two-dimensional (2D) materials (i.e., MoS_2)[59–61] (Figs. 2(b)–2(d)). Material selection and structural design are the key factors for the development of PENGs, which are based on the coupling of piezoelectric materials and flexible substrates.

The all-polymer-based flexible TENG based on triboelectrification and electrostatic induction was invented in 2012,[21] which could convert mechanical energy into electricity. Interestingly, triboelectrification can be found everywhere in the surrounding environment and in most common materials used every day in our daily lives. In detail, the working mechanism of TENGs can be

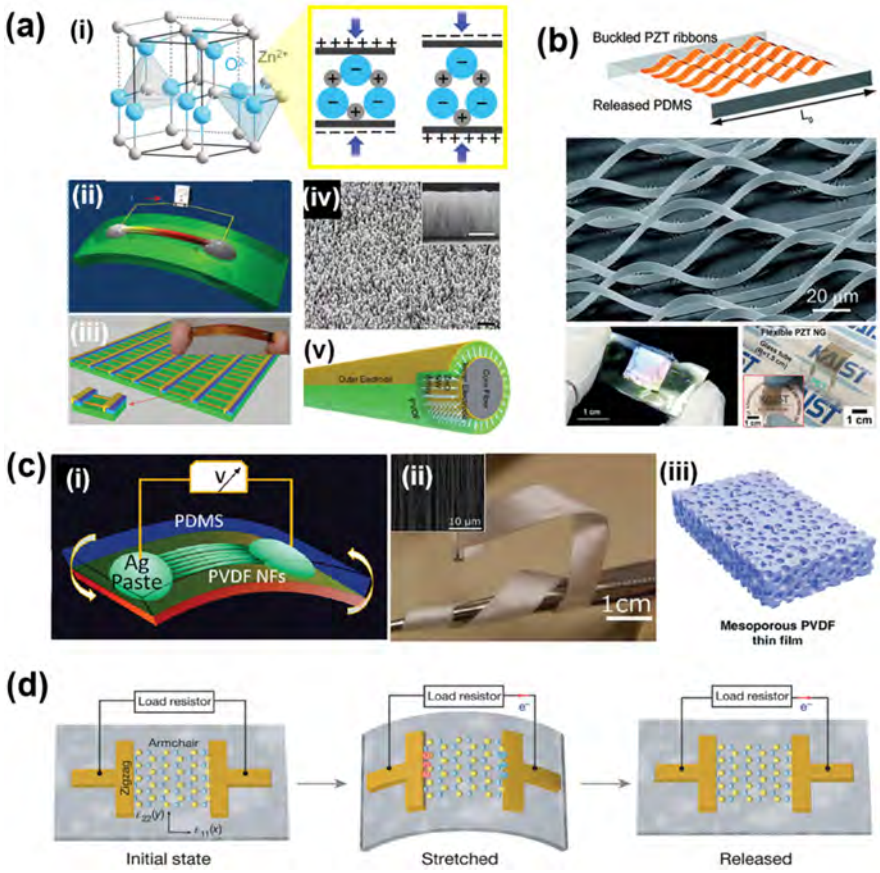

FIG. 2. *Piezoelectric and triboelectric nanogenerators, and energy storage systems* (*ESSs*). Piezoelectric materials: (a) piezoelectric property of ZnO and examples [(i) atomic model of the wurtzite-structured ZnO and its piezoelectric properties, (ii) single nanowire, (iii) lateral-nanowire-array, (iv) vertical ZnO NWs, v: structure of a hybrid fiber NG consisting of ZnO NWs and PVDF film] Reprinted with permission from R. S. Yang, Y. Qin, L. M. Dai, and Z. L. Wang, Nat. Nanotechnol. **4**, 34 (2009). Copyright 2009 Nature Publishing Group. Ref. 13 and Reprinted with permission from Z. L. Wang and J. H. Song, Science **312**, 242 (2006). Copyright 2006 The American Association for the Advancement of Science. Reprinted with permission from S. Xu, Y. Qin, C. Xu, Y. Wei, R. Yang, and Z. L. Wang, Nat. Nanotechnol. **5**, 366 (2010). Copyright 2010 Nature Publishing Group. Reprinted with permission from M. Lee, C. Y. Chen, S. Wang, S. N. Cha, Y. J. Park, J. M. Kim, L. J. Chou, and Z. L. Wang, Adv. Mater. **24**, 1759 (2012). Copyright 2012 John Wiley and Sons. Reprinted with permission from D. Choi, M.-Y. Choi, W. M. Choi, H.-J. Shin, H.-K. Park, J.-S. Seo, J. Park, S.-M. Yoon, S. J. Chae, Y. H. Lee, S.-W. Kim, J.-Y. Choi, S. Y. Lee, and J. M. Kim, Adv. Mater. **22**, 2187 (2010). Copyright 2010 John Wiley and Sons. Refs. 47–50; (b) PZT Reprinted with permission from Y. Qi, N. T. Jafferis, K. Lyons, C. M. Lee, H. Ahmad, and M. C. McAlpine, Nano Lett. **10**, 524 (2010). Copyright 2010 American Chemical Society. Reprinted with permission from Y. Qi, J. Kim, T. D. Nguyen, B. Lisko, P. K. Purohit, and M. C. McAlpine, Nano Lett. **11**, 1331 (2011). Copyright 2011 American Chemical Society. Reprinted with permission from K. I. Park, J. H. Son, G. T. Hwang, C. K. Jeong, J. Ryu, M. Koo, I. Choi, S. H. Lee, M. Byun, Z. L. Wang, and K. J. Lee, Adv. Mater. **26**, 2514 (2014). Copyright 2014 John Wiley and Sons. Refs. 51–53; (c) PVDF [(i) PVDF nanofibers (NFs), (ii) free-standing film of highly aligned piezoelectric fibers, (iii) mesoporous PVDF film] Reprinted with permission from B. J. Hansen, Y. Liu, R. S. Yang, and Z. L. Wang, ACS Nano **4**, 3647 (2010). Copyright 2010 American Chemical Society. Reprinted with permission from L. Persano, C. Dagdeviren, Y. W. Su, Y. H. Zhang, S. Girardo, D. Pisignano, Y. G. Huang, and J. A. Rogers, Nat. Commun. **4**, 1633 (2013). Copyright 2013 Nature Publishing Group. Reprinted with permission from Y. C. Mao, P. Zhao, G. McConohy, H. Yang, Y. X. Tong, and X. D. Wang, Adv. Energy Mater. **4**, 1301624 (2014). Copyright 2014 John Wiley and Sons. Reprinted with permission from J.-H. Lee, K. Y. Lee, B. Kumar, B. T. Tien, N.-E. Lee, and S.-W. Kim, Energy Environ. Sci. **6**, 169 (2013). Copyright 2013 Royal Society of Chemistry. Refs. 55–58; and (d) 2D materials (i.e., MoS_2) Reprinted with permission from W. Z. Wu, L. Wang, Y. L. Li, F. Zhang, L. Lin, S. M. Niu, D. Chenet, X. Zhang, Y. F. Hao, T. F. Heinz, J. Hone, and Z. L. Wang, Nature **514**, 470 (2014). Copyright 2014 Nature Publishing Group. Ref. 59. (e) Working principle of the TENG Reprinted with permission from G. Zhu, C. Pan, W. Guo, C.-Y. Chen, Y. Zhou, R. Yu, and Z. L. Wang, Nano Lett. **12**, 4960 (2012). Copyright 2012 American Chemical Society. Ref. 62. (f) Representative energy storage systems (ESSs): the supercapacitor and rechargeable battery with their future new functions for application with nanogenerators (i.e., flexible, textile, stretchable, etc.).

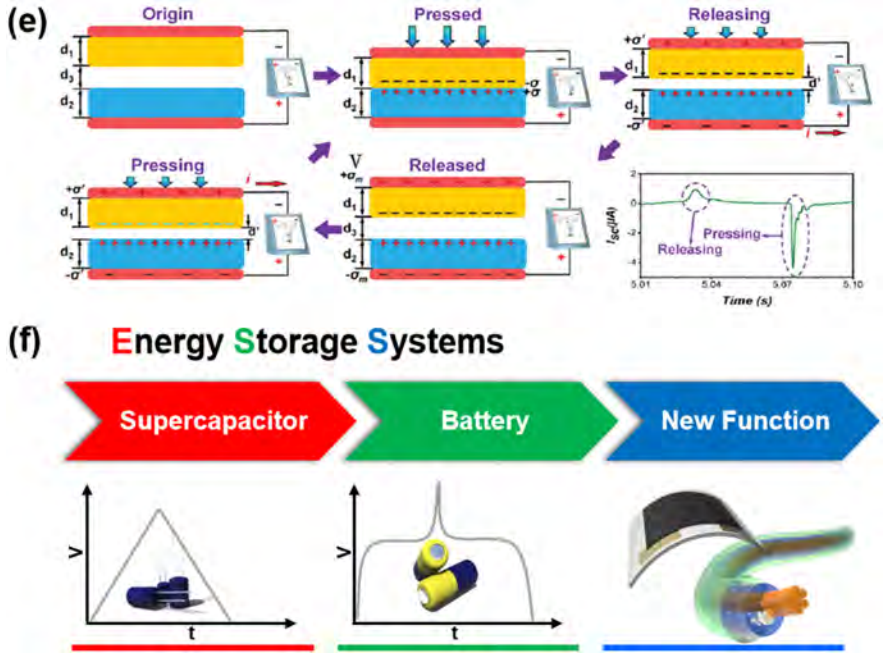

FIG. 2. *(Continued.)*

explained as shown in Fig. 2(e). When the TENG is pressed by external energy, the two materials come into contact. Because of their different electron-attracting abilities, electrons could be transferred from one material to the other. Then, there are net negative charges on the surface of the layer with a strong electron attracting ability and net positive charges on the opposite layer.[22,62] When the two materials are isolated, the tribo-charges in the interfacial regions are separated. This can generate an electrical potential in the interfacial region and electrons in the attached induction electrodes can be driven to flow from one side to the other. In this process, electrons continue flowing until the TENG is fully released. At this stage, both the induced potential difference and the amount of transferred charges can be obtained as their maximum values. When the two materials approach, the potential difference decreases and the electrons flow back. Therefore, the entire process generates an alternating current pulse output. In order to provide stable power using nanogenerators, ESSs such as supercapacitors and rechargeable batteries are essential for future electronic devices (Fig. 2(f)). Thus, the selection of the materials, structural design, and circuit connections in designs for hybridizing ESSs and nanogenerators should be properly considered and designed because most nanogenerators have thin, lightweight, flexible substrates, and require bendable, and stretchable device formation.[63] In addition, wired and textile ESSs and other new functions are required according to the developments of advanced nanogenerators with higher output power and new application in future.

III. INTEGRATION OF NANOGENERATORS AND ESSs

To test the efficient charging of the battery for hybrid devices, recently, researchers have studied how to integrate the TENGs with lithium-ion batteries (LIBs) using a rectifier. In 2016, Pu *et al.* demonstrated efficient charging of LIBs by a rotating TENG with pulsed output current, as shown in Fig. 3(a).[64] Fast Li-ion extraction from the typical electrode materials $LiFePO_4$ and $Li_4Ti_5O_{12}$ was achieved by the TENG at a rotation speed of 250 rpm. The estimated coulombic efficiency of the TENG charging and the following 0.5 C discharging can be higher than 90%, comparable with constant current charging. Interestingly, improvement of the power utilization efficiency (up to 72.4%) in transferring power from the TENG to the $LiFePO_4$-$Li_4Ti_5O_{12}$ full battery was achieved by optimizing the coil ratio of a transformer. High efficiency was achieved when the impedance of the TENG was

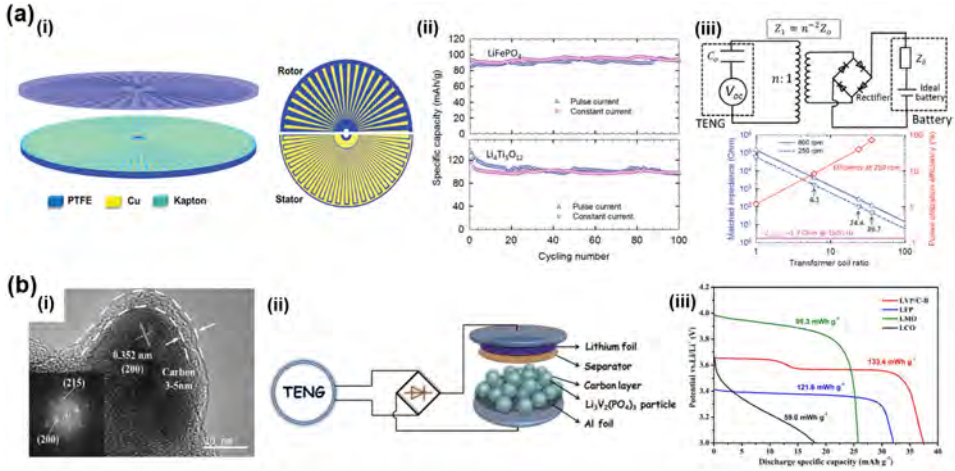

FIG. 3. *Hybrid devices based on integration of TENG and battery*. (a) Charging of LIB with pulsed output current from rotating TENG [(i) scheme of the rotating TENG, (ii) comparison of cycling performances of $LiFePO_4$ (at 160 mA g^{-1}) and $Li_4Ti_5O_{12}$ (at 350 mA g^{-1}), both with Li-metal as counter electrode, charged by pulsed and constant current, (iii) equivalent circuit for battery charging by the TENG with the aid of a transformer and a rectifier (upper) and The effect of the transformer coil ratio on matched impedances of the TENG, and the power utilization efficiency of the TENG at 250 rpm when charging an LFP–LTO full cell (lower)] Reprinted with permission from X. Pu, M. Liu, L. Li, C. Zhang, Y. Pang, C. Jiang, L. Shao, W. Hu, and Z. L. Wang, Adv. Sci. **3**, 1500255 (2016). Copyright 2016 Author(s), licensed under a Creative Commons Attribution 3.0 Unported License. Ref. 64. (b) Charging of LIB with pulsed energy from traditional TENG. [(i) TEM image of synthesized cathode material LVP/C-B, (ii) scheme of hybrid device, (iii) discharge curves at 1 C of different cathode materials, which have been charged with pulsed electricity generated by TENG for 3 min] Reprinted with permission from X. Nan, C. Zhang, C. Liu, M. Liu, Z. L. Wang, and G. Cao, ACS Appl. Mater. Interfaces **8**, 862 (2016). Copyright 2016 American Chemical Society. Ref. 65.

reduced to close to that of the battery cell. In addition, they showed that a 1 h charging of a commercial LIB by the rotating TENG (600 rpm, 36.7 transformer coil ratio) can exhibit a discharge capacity of 130 mAh.

In fact, the energy conversion efficiency is very important when the generated output power is stored in ESSs. Nan *et al.* prepared the cathodic material $Li_3V_2(PO_4)_3$/C and compared the storage efficiency with most popular cathodic materials: $LiCoO_2$, $LiFePO_4$, and $LiMn_2O_4$ (Fig. 3(b)).[65] They simply prepared the integrated hybrid device using a radial-arrayed rotary TENG and coin cell type batteries containing different cathodic materials. The $Li_3V_2(PO_4)_3$/C nanocomposite possessed a discharge capacity of 128 mAh g^{-1} at 1 C, which is very close to the theoretical capacity of $Li_3V_2(PO_4)_3$ (133 mAh g^{-1} in the potential range of 3.0-4.3 V vs. Li/Li^+). The capacity retention was up to 90% after cycling for 1000 times at a rate of 5 C, corresponding to a capacity fading of 0.01% per cycle. The $Li_3V_2(PO_4)_3$/C composite showed outstanding energy conversion efficiency when it was charged by a large high frequency current produced by the TENG, far better than for any other known cathode materials, including $LiCoO_2$ (66.1%), $LiFePO_4$ (74.4%), and $LiMn_2O_4$ (73.6%). These results show that the selection of electrode materials is important for efficient charging in hybrid devices.

IV. ALL-IN-ONE HYBRID DEVICES AND INTEGRATING NEW FUNCTIONALITIES

The term "all-in-one hybrid device" means that a single device has both an energy harvesting nanogenerator and an ESS in the device without complicated connections. The all-in-one hybrid device design has many advantages for compact, simple, and portable devices, but more efforts are needed to fabricate the devices because of the problem of matching device and material characteristics, such as flexibility, coatings, compositions, electrochemical properties, etc., between the nanogenerator and the ESS. Very recently, researchers have reported and suggested new concepts for all-in-one devices.

In 2016, Wang *et al.* reported a new nano-energy cell (NEC) that uses high density piezoelectric nanowires to harvest mechanical energy and has a large electrolyte (phosphoric acid/polyvinylalcohol (H_3PO_4/PVA) gel electrolyte)-nanowire interface to store electricity in the all-in-one system consisting of a PENG and an electric double-layer supercapacitor (EDLC), as shown Fig. 4(a).[66] The device achieved a continuous output current for over 90 s, and the mechanical-electric energy conversion efficiency of the NEC was over 10 times higher than that of the PENG without increasing the device volume or reducing the efficiency. Interestingly, Ramadoss *et al.* made an all-in-one device from a PENG and a pseudocapacitor based on PVDF-ZnO and MnO_2, respectively (Fig. 4(b)).[67] The device exhibited self-charging capability under palm impact (aluminum-foil-based device to 110 mV over 300 s; fabric-based device to 45 mV over 300 s). As shown in Fig. 4(c), most recently, Song *et al.* demonstrated an integrated sandwich-shaped, self-charging power unit (SCPU) with a wrinkled poly(dimethyl siloxane) (PDMS) based TENG and a carbon nanotube (CNT)/paper-based solid-state EDLC.[68] During vibrations, the device can be utilized to simultaneously harvest and store the mechanical energy as electrochemical energy, and it could be charged to 900 mV in 3 h under the compressive stress at 8 Hz. This study showed that their developed novel all-in-one device is a promising candidate for flexible electronics and wearable devices.

Another strand of important research progress in all-in-one hybrid devices can be explained as achieving new functions, such as devices that are stretchable, bendable, twistable, waterproof, and

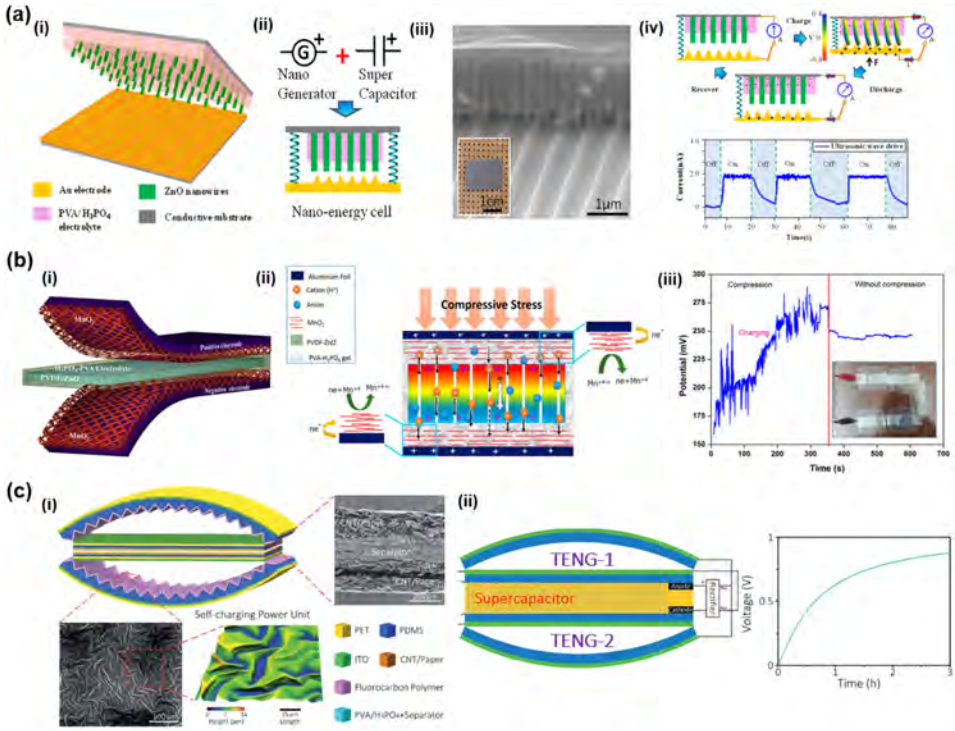

FIG. 4. *All-in-one hybrid device containing nanogenerators and ESSs*. (a) Nano energy cell with piezoelectric nanogenerator and EDLC dual functions [(i) schematic illustration of the structure of the device, (ii) working mechanism and cross-section, (iii) cross section in scanning electron microscope (SEM) image of the as-fabricated device, (iv) the mechanism and performance] Reprinted with permission from F. Wang, C. Jiang, C. Tang, S. Bi, Q. Wang, D. Du, and J. Song, Nano Energy **21**, 209 (2016). Copyright 2016 Elsevier. Ref. 66. (b) Hybrid device with a piezoelectric nanogenerator and a pseudocapacitor based on metal oxide [(i) schematic diagram of the fabricated device (ii) working mechanism of the device driven by mechanical deformation, (iii) self-charging performance of serially connected devices] Reprinted with permission from A. Ramadoss, B. Saravanakumar, S. W. Lee, Y.-S. Kim, S. J. Kim, and Z. L. Wang, ACS Nano **9**, 4337 (2015). Copyright 2015 American Chemical Society. Ref. 67. (c) Flexible hybrid device based on EDLC and triboelectric nanogenerator [(i) device structure showing integration of sandwich-shaped and self-charging power unit, (ii) working mechanism and circuit (left) and charging curve of the SC charged by sandwich-shaped TENGs at the compressive stress of 8 Hz. (right)] Reprinted with permission from Y. Song, X. Cheng, H. Chen, J. Huang, X. Chen, M. Han, Z. Su, B. Meng, Z. Song, and H. Zhang, J. Mater. Chem. A **4**, 14298 (2016). Copyright 2016 Royal Society of Chemistry. Ref. 68.

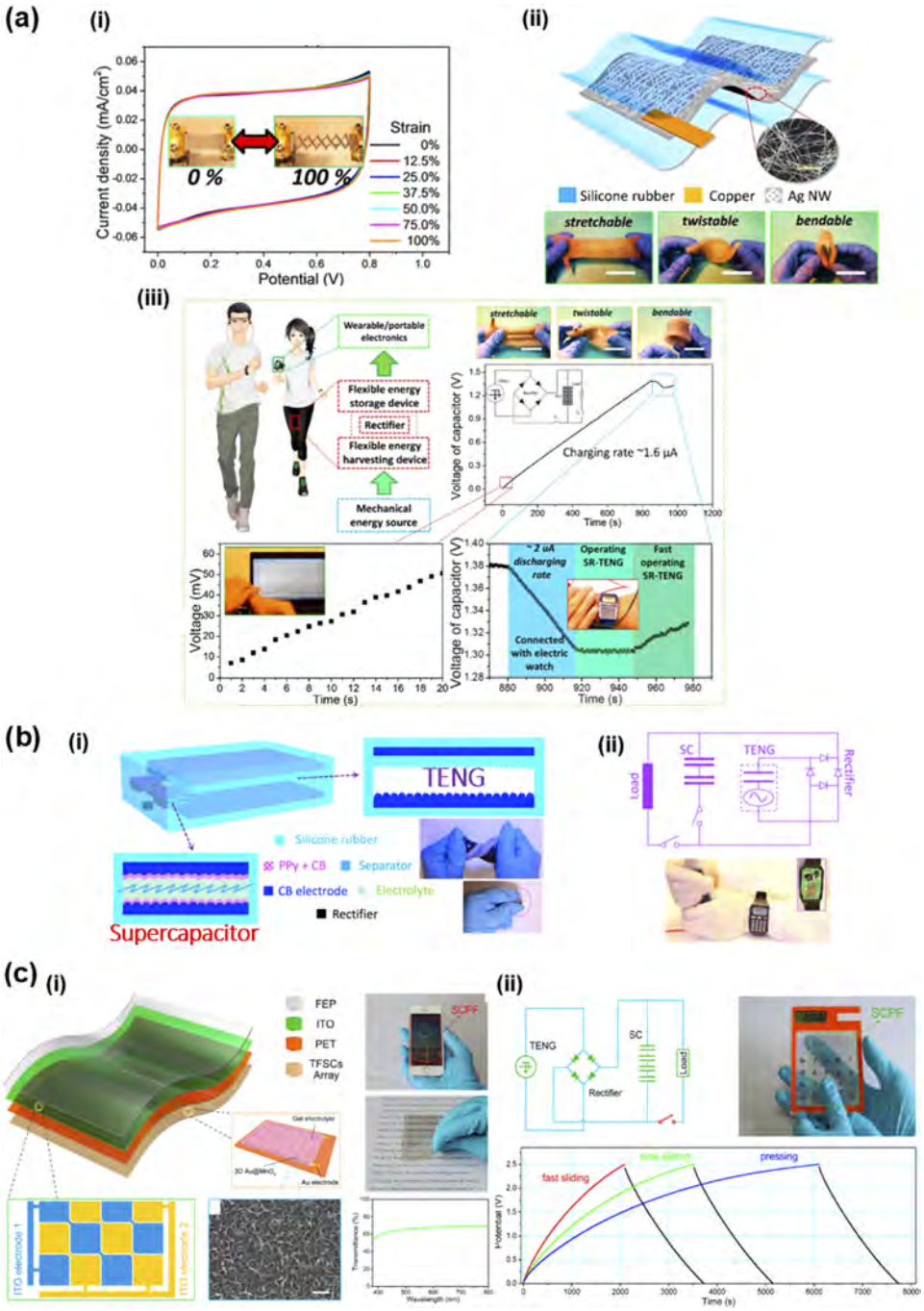

FIG. 5. All-in-one hybrid devices with new functions. (a) Shape-adaptive self-charging power package [(i) CV curves of the kirigami paper-supercapacitor under change in mechanical strain from 0% to 100%, (ii) structural scheme of the silicone rubber based flexible triboelectric nanogenerator, (iii) application of the all-in-one shape-adaptive self-charging power package in conventional wearable electronics] Reprinted with permission from H. Guo, M.-H. Yeh, Y.-C. Lai, Y. Zi, C. Wu, Z. Wen, C. Hu, and Z. L. Wang, ACS Nano **10**, 10580 (2016). Copyright 2016 American Chemical Society. Ref. 69. (b) Stretchable and waterproof self-charging power systems [(i) schematic diagram showing the detailed structure of the power system, (ii) circuit diagram of the power system with a load and electric watch driven by the self-charging power system] Reprinted with permission from F. Yi, J. Wang, X. Wang, S. Niu, S. Li, Q. Liao, Y. Xu, Z. You, Y. Zhang, and Z. L. Wang, ACS Nano **10**, 6519 (2016). Copyright 2016 American Chemical Society. Ref. 70. (c) Transparent and flexible self-charging power film [(i) structural design of the transparent and flexible device, (ii) performance of the transparent and flexible device] Reprinted with permission from J. Luo, W. Tang, F. R. Fan, C. Liu, Y. Pang, G. Cao, and Z. L. Wang, ACS Nano **10**, 8078 (2016). Copyright 2016 American Chemical Society. Ref. 71.

transparent. Within 1 year, several interesting research programs have been reported as follows. Guo *et al.* reported the concept of an all-in-one shape-adaptive self-charging power package based on a TENG and EDLC that has been simultaneously demonstrated for harvesting body motion energy to sustainably drive wearable/portable electronics Fig. 5(a).[69] By utilizing the kirigami architecture, an ultra-stretchable kirigami paper-based supercapacitor with 100% stretchability and specific capacitance of ~1 mF cm^{-2} and ~12 F g^{-1} was designed and fabricated, which showed good capacitance and superior mechanical stability for application as a super-flexible energy storage device. By utilizing silicone rubber and Ag nanowires, an ultra-stretchable and shape-adaptive TENG was fabricated with an output of ~160 nC per half working cycle and open-circuit voltage of ~250 V in the 100% stretching state. By assembling the kirigami-EDLC into the TENG with a full-wave rectifier, an all-in-one shape adaptive device was achieved for harvesting the energy from hand flapping and continually powering an electric watch. As shown in Fig. 5(b), Yi *et al.* also developed a soft, stretchable, and waterproof all-in-one device based on a TENG and an enclosed polypyrrole-based pseudocapacitor.[70] The fabricated device was washable and waterproof due to the outer surface of the device. This creative concept demonstrated a promising route to develop stretchable and wearable energy harvesters and power sources for stretchable and wearable electronics. A transparent and flexible self-charging power film with a TENG and pseudocapacitor was developed by Luo *et al.*, as shown in Fig. 5(c).[71] By embedding a grid-like indium tin oxide (ITO) electrode in a fluorinated ethylene propylene (FEP) film, mechanical energy can be harvested from both contact and sliding. To store the scattered energy, all-solid-state transparent and flexible supercapacitors based on Au@MnO_2 nanocomposites were fabricated and directly connected to the TENG. This approach showed the strong potential that the transparent and flexible all-in-one device would be applicable to future portable, wearable, and smart electronics.

V. WEARABLE DEVICES CONSISTING OF ESSs AND NANOGENERATORS

Recently, wearable electronics, such as smart phones, smart watches, healthcare sensors, smart glasses, etc., have been developed and become an important part of our lives.[72] To utilize these electronics, wearable energy devices are consequently required. Conventional ESSs (batteries and supercapacitors) require frequent and inconvenient charging, however. Therefore, wearable self-charging power devices that combine energy-harvesting and energy-storage technologies could be potential solutions.

Pu *et al.* reported wearable hybrid devices combining nanogenerators with a supercapacitor[73] and a flexible battery,[74] respectively. As shown in Fig. 6(a), they reported the facile and scalable fabrication of an all solid-state flexible yarn supercapacitor and its integration with a TENG cloth for a self-charging power textile.[73] A conformal Ni layer and reduced graphene oxide (rGO) film were successively coated on the surfaces of common polyester yarns (with the product denoted as rGO-Ni-yarn). The resulting symmetric yarn supercapacitor achieved both high capacitance (13.0 mF cm^{-1}, 72.1 mF cm^{-2}) and stable cycling performance (96% for 10 000 cycles). Moreover, stable performance was observed for 1000 cycles of 180° bending. This result is valuable because they were the first to demonstrate a textile self-charging power system by the yarn supercapacitors with a TENG cloth. In addition, this cost-effective and industrially scalable approach to yarn supercapacitors and self-charging power textiles paves the way to wearable electronics. To fabricate wearable a TENG-battery self-charging power textile, a flexible battery will be essential. Fig. 6(b) shows a wearable power unit integrating a whole-textile TENG-cloth and a flexible LIB belt.[74] Insulating polyester fabrics were transformed into conductive ones with an electroless plating of a conformal Ni film, and they were then utilized both as electrodes in the TENG-cloth and as current collectors in the LIB belt. The TENG-cloth demonstrated its capability of converting the mechanical energy of various types of human motion into electricity, and the LIB belt showed good electrochemical performance, even when it was severely folded at 180° for 30 times. Importantly, the LIB belt was charged by the TENG-cloth for 3 cycles, and it powered a heartbeat meter strap capable of remote communication with a smart phone, verifying the viability of the whole wearable and self-charging power unit for future wearable smart electronics.

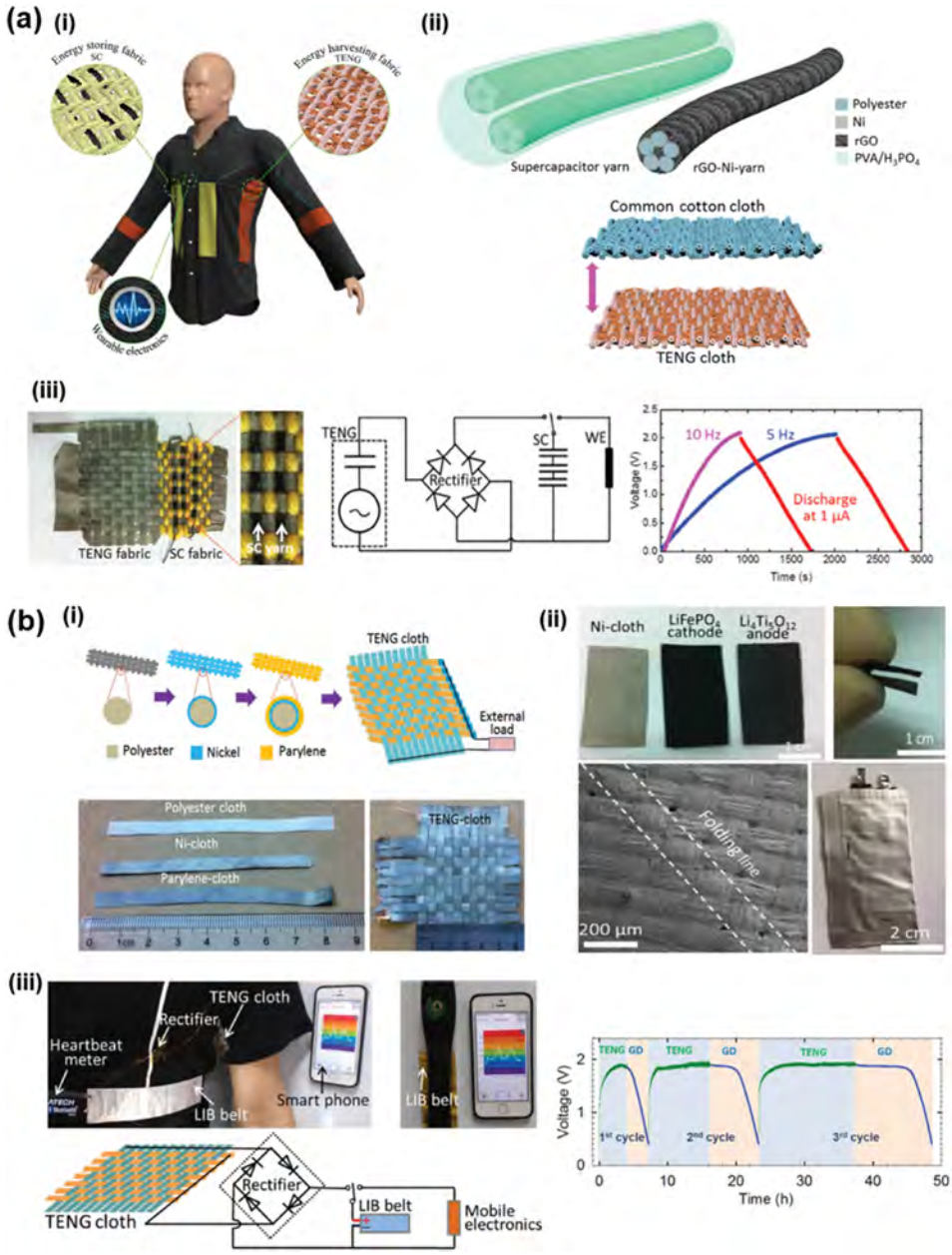

FIG. 6. *Wearable self-charging power textile based on flexible ESSs and fabric nanogenerators*. (a) Self-charging power textile based on EDLC and triboelectric nanogenerator [(i) scheme of a self-charging power textile, (ii) all-solid-state symmetric yarn supercapacitor (upper) and triboelectric nanogenerator cloth (lower), (iii) the fabricated self-charging power textile and performance] Reprinted with permission from X. Pu, L. Li, M. Liu, C. Jiang, C. Du, Z. Zhao, W. Hu, and Z. L. Wang, Adv. Mater. **28**, 98 (2016). Copyright 2016 John Wiley and Sons. Ref. 73. (b) Self-charging power unit integrating a textile triboelectric nanogenerator and a flexible lithium-ion battery [(i) fabrication of TENG-cloth, (ii) fabrication and performance of flexible LIB belt, (iii) self-charging power unit and performance] Reprinted with permission from X. Pu, L. Li, H. Song, C. Du, Z. Zhao, C. Jiang, G. Cao, W. Hu, and Z. L. Wang, Adv. Mater. **27**, 2472 (2015). Copyright 2015 John Wiley and Sons. Ref. 74.

VI. MULTI-FUNCTIONAL HYBRID SELF-POWERED WEARABLE DEVICES

Very recently, Wen *et al.* reported a multi-functional hybridized self-charging power textile system designed to simultaneously collect outdoor sunshine and random body motion energy by a dye-sensitized solar cell (DSSC) and a TENG, respectively, and then storing the energy in a fiber-shaped supercapacitor (Fig. 7).[75] A single fiber-DSSC unit showed an overall power conversion

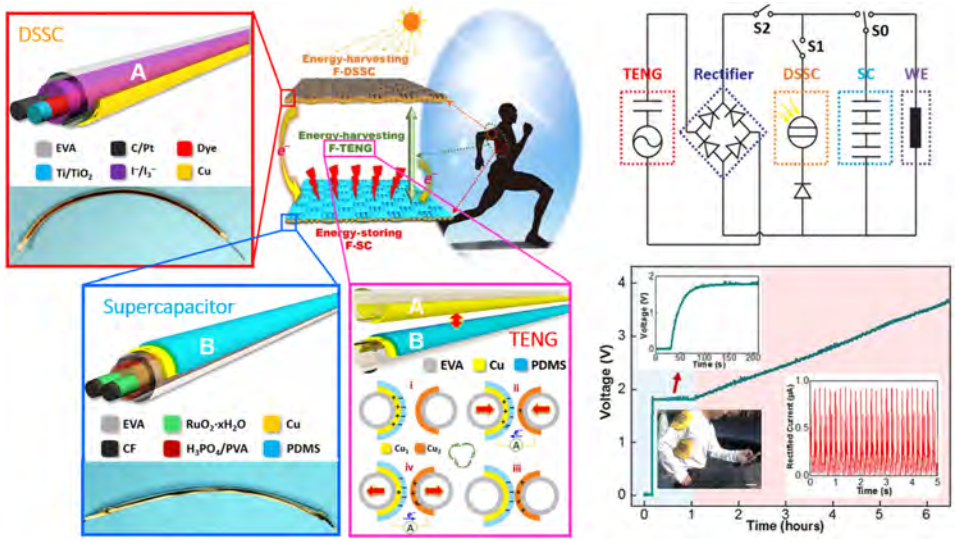

FIG. 7. *Multi-functional hybrid self-powered textile*. Self-powered textile for wearable electronics created by hybridizing fiber-shaped nanogenerators, solar cells, and supercapacitors (left). Circuit diagram of the self-charging powered textile for wearable electronics (top right). Charging curve of the fiber-DSSC and the fiber-TENG, where the light blue-shaded area corresponds to the charging curve of the fiber-DSSC and the light red-shaded area corresponds to the charging curve of the fiber–DSSC/fiber-TENG hybrid (bottom right). Reprinted with permission from Z. Wen, M.-H. Yeh, H. Guo, J. Wang, Y. Zi, W. Xu, J. Deng, L. Zhu, X. Wang, C. Hu, L. Zhu, X. Sun, and Z. L. Wang, Sci. Adv. **2**, e1600097 (2016). Copyright 2016 Author(s), licensed under a Creative Commons Attribution 3.0 Unported License. Ref. 75.

efficiency of 5.64% and fiber-TENG can take advantage of human motions, such as jogging, to deliver an output current of up to 0.91 mA. The fiber-supercapacitor showed excellent pseudocapacitance of 1.9 mF cm^{-1} from $RuO_2 \cdot xH_2O$. Due to the properties all-fiber-shaped devices, this textile system can be easily woven into electronic textiles to fabricate smart clothes that can operate wearable electronic devices. These multi-functional hybrid self-powered devices will result in practical human benefits.

VII. SUMMARY AND OUTLOOK

In this review, we have introduced and updated the progress on hybrid devices based on the simple integration of nanogenerators and ESSs to achieve all-in-one systems, wearable designs, new functions, and multifunctional approaches. It is clear that the hybridized devices containing nanogenerators and ESSs are essential for smart electronics in the future. To develop and improve the new systems and performances of hybridized energy devices, further research efforts are needed on the design of devices, materials, integration, and better understanding of various energy harvesting and storage devices. Through this creative hybridization technology, it is expected that other energy harvesting devices using clean environmental energy sources will improve the harvesting capability of nanogenerators. In addition, we hope that superior energy-harvestable nanogenerators with excellent charging efficiency can be applied for integration with next-generation ESSs with high energy storage capability, such as the metal-air battery, Li-sulfur battery, Li-silicon battery, etc.

ACKNOWLEDGMENTS

This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF), funded by the Ministry of Education (No. 2016R1A6A3A03009359).

[1] C. Liu, F. Li, L. Ma, and H. Cheng, Adv. Mater. **22**, 28 (2010).
[2] A. I. Hochbaum, R. Chen, R. Delgado, D. Liang, W. E. Garnett, C. Najarian, M. A. Majumdar, and P. Yang, Nature **451**, 163 (2008).
[3] L. Hu, J. W. Choi, Y. Yang, S. Jeong, F. L. Mantia, L.-F. Cui, and Y. Cui, Proc. Natl. Acad. Sci. U. S. A. **106**, 21490 (2009).
[4] S. Chu and A. Majumdar, Nature **488**, 294 (2012).

[5] E. A. Rosa and T. Dietz, Nat. Clim. Change **2**, 581 (2012).
[6] Y. Wu, X. Zhong, X. Wang, Y. Yang, and Z. L. Wang, Nano Res. **11**, 1631 (2014).
[7] S. M. Yang, T. Lee, and C. A. Jeng, Sens. Actuators, A **153**, 244 (2009).
[8] G. Zhu, Y. Su, P. Bai, J. Chen, Q. Jing, W. Yang, and Z. L. Wang, ACS Nano **8**, 6031 (2014).
[9] J. Chen, J. Yang, Z. Li, X. Fan, Y. Zi, Q. Jing, and Z. L. Wang, ACS Nano **9**, 3324 (2015).
[10] B. Tian, X. Zheng, T. J. Kempa, Y. Fang, N. Yu, G. Yu, J. Huang, and C. M. Lieber, Nature **449**, 885 (2007).
[11] N. S. Lewis, Science **315**, 798 (2007).
[12] S. P. Beeby, M. J. Tudor, and N. M. White, Meas. Sci. Technol. **17**, R175 (2006).
[13] R. S. Yang, Y. Qin, L. M. Dai, and Z. L. Wang, Nat. Nanotechnol. **4**, 34 (2009).
[14] B. Saravanakumar, R. Mohan, K. Thiyagarajan, and S. J. Kim, RSC Adv. **3**, 16646 (2013).
[15] K. Y. Lee, D. Kim, J.-H. Lee, T. Y. Kim, M. K. Gupta, and S.-W. Kim, Adv. Funct. Mater. **24**, 37 (2014).
[16] K. Y. Lee, J. Chun, J.-H. Lee, K. N. Kim, N.-R. Kang, J.-Y. Kim, M. H. Kim, K.-S. Shin, M. K. Gupta, J. M. Baik, and S.-W. Kim, Adv. Mater. **29**, 5037 (2014).
[17] J.-H. Lee, H.-J. Yoon, T. Y. Kim, M. K. Gupta, J. H. Lee, W. Seung, H. Ryu, and S.-W. Kim, Adv. Funct. Mater. **25**, 3203 (2015).
[18] J.-H. Lee, H. Ryu, T.-Y. Kim, S.-S. Kwak, H.-J. Yoon, T.-H. Kim, W. Seung, and S.-W. Kim, Adv. Energy Mater. **5**, 1500704 (2015).
[19] Z. L. Wang, Sci. Am. **298**, 82 (2008).
[20] Z. L. Wang and W. Wu, Angew. Chem., Int. Ed. **51**, 11700 (2012).
[21] F. R. Fan, Z. Q. Tian, and Z. L. Wang, Nano Energy **1**, 328 (2012).
[22] Z. L. Wang, ACS Nano **7**, 9533 (2013).
[23] L. Lin, Y. Xie, S. Niu, S. Wang, P. Yang, and Z. L. Wang, ACS Nano **9**, 922 (2015).
[24] R. Zhou, G. Hu, R. Yu, C. Pan, and Z. L. Wang, Nano Energy **12**, 588 (2015).
[25] Y. Hu and Z. L. Wang, Nano Energy **14**, 3 (2015).
[26] X. Wang, J. Song, J. Liu, and Z. L. Wang, Science **316**, 102 (2007).
[27] J.-H. Lee, K. Y. Lee, M. K. Gupta, T. Y. Kim, D.-Y. Lee, J. Oh, C. Ryu, W. J. Yoo, C.-Y. Kang, S.-J. Yoon, J.-B. Yoo, and S.-W. Kim, Adv. Mater. **26**, 765 (2014).
[28] W. Seung, H.-J. Yoon, T. Y. Kim, H. Ryu, J. Kim, J.-H. Lee, J. H. Lee, S. Kim, Y. K. Park, Y. J. Park, and S.-W. Kim, Adv. Energy Mater. **7**, 1600988 (2017).
[29] J. Wang, Z. Wen, Y. Zi, L. Lin, C. Wu, H. Guo, Y. Xi, Y. Xu, and Z. L. Wang, Adv. Funct. Mater. **26**, 3542 (2016).
[30] J. Chen, Y. Huang, N. Zhang, H. Zou, R. Liu, C. Tao, X. Fan, and Z. L. Wang, Nat. Energy **1**, 16138 (2016).
[31] W. Seung, M. K. Gupta, K. Y. Lee, K.-S. Shin, J.-H. Lee, T. Y. Kim, S. Kim, J. Lin, J. H. Kim, and S.-W. Kim, ACS Nano **9**, 3501 (2015).
[32] U. Khan, T.-H. Kim, K. H. Lee, J.-H. Lee, H.-J. Yoon, R. Bhatia, I. Sameera, W. Seung, H. Ryu, C. Falconi, and S.-W. Kim, Nano Energy **17**, 356 (2015).
[33] R. R. Salunkhe, Y. V. Kaneti, J. Kim, J. H. Kim, and Y. Yamauchi, Acc. Chem. Res. **49**, 2796 (2016).
[34] J. Kim, C. Young, J. Lee, M.-S. Park, M. Shahabuddin, Y. Yamauchi, and J. H. Kim, Chem. Commun. **52**, 13016 (2016).
[35] Y. Wang, Y. Song, and Y. Xia, Chem. Soc. Rev. **45**, 5925 (2016).
[36] R. R. Salunkhe, J. Tang, N. Kobayashi, J. Kim, Y. Ide, S. Tominaka, J. H. Kim, and Y. Yamauchi, Chem. Sci. **7**, 5704 (2016).
[37] T. Han, M.-S. Park, J. Kim, J. H. Kim, and K. Kim, Chem. Sci. **7**, 1791 (2016).
[38] R. R. Salunkhe, J. Tang, Y. Kamachi, T. Nakato, J. H. Kim, and Y. Yamauchi, ACS Nano **9**, 6288 (2015).
[39] J. Lu, Z. Chen, Z. Ma, F. Pan, L. A. Curtiss, and K. Amine, Nat. Nanotechnol. **11**, 1031 (2016).
[40] E. Park, J. Kim, D. J. Chung, M.-S. Park, H. Kim, and J. H. Kim, ChemSusChem **9**, 2754 (2016).
[41] K.-N. Jung, J. Kim, Y. Yamauchi, M.-S. Park, J.-W. Lee, and J. H. Kim, J. Mater. Chem. A **4**, 14050 (2016).
[42] K. J. Kim, H. S. Lee, J. Kim, M.-S. Park, J. H. Kim, Y.-J. Kim, and M. Skyllas-Kazacos, ChemSusChem **9**, 1329 (2016).
[43] D. P. Dubal, O. Ayyad, V. Ruiz, and P. Gómez-Romero, Chem. Soc. Rev. **44**, 1777 (2015).
[44] J. Kim, J. Lee, J. You, M.-S. Park, M. S. A. Hossain, Y. Yamauchi, and J. H. Kim, Mater. Horiz. **3**, 517 (2016).
[45] X. Xue, W. Zang, P. Deng, Q. Wang, L. Xing, Y. Zhang, and Z. L. Wang, Nano Energy **13**, 414 (2015).
[46] J.-H. Lee, J. Kim, T. Y. Kim, M. S. A. Hossain, S.-W. Kim, and J. H. Kim, J. Mater. Chem. A **4**, 7983 (2016).
[47] Z. L. Wang and J. H. Song, Science **312**, 242 (2006).
[48] S. Xu, Y. Qin, C. Xu, Y. Wei, R. Yang, and Z. L. Wang, Nat. Nanotechnol. **5**, 366 (2010).
[49] M. Lee, C. Y. Chen, S. Wang, S. N. Cha, Y. J. Park, J. M. Kim, L. J. Chou, and Z. L. Wang, Adv. Mater. **24**, 1759 (2012).
[50] D. Choi, M.-Y. Choi, W. M. Choi, H.-J. Shin, H.-K. Park, J.-S. Seo, J. Park, S.-M. Yoon, S. J. Chae, Y. H. Lee, S.-W. Kim, J.-Y. Choi, S. Y. Lee, and J. M. Kim, Adv. Mater. **22**, 2187 (2010).
[51] Y. Qi, N. T. Jafferis, K. Lyons, C. M. Lee, H. Ahmad, and M. C. McAlpine, Nano Lett. **10**, 524 (2010).
[52] Y. Qi, J. Kim, T. D. Nguyen, B. Lisko, P. K. Purohit, and M. C. McAlpine, Nano Lett. **11**, 1331 (2011).
[53] K. I. Park, J. H. Son, G. T. Hwang, C. K. Jeong, J. Ryu, M. Koo, I. Choi, S. H. Lee, M. Byun, Z. L. Wang, and K. J. Lee, Adv. Mater. **26**, 2514 (2014).
[54] C. K. Jeong, I. Kim, K. I. Park, M. H. Oh, H. Paik, G. T. Hwang, K. No, Y. S. Nam, and K. J. Lee, ACS Nano **7**, 11016 (2013).
[55] B. J. Hansen, Y. Liu, R. S. Yang, and Z. L. Wang, ACS Nano **4**, 3647 (2010).
[56] L. Persano, C. Dagdeviren, Y. W. Su, Y. H. Zhang, S. Girardo, D. Pisignano, Y. G. Huang, and J. A. Rogers, Nat. Commun. **4**, 1633 (2013).
[57] Y. C. Mao, P. Zhao, G. McConohy, H. Yang, Y. X. Tong, and X. D. Wang, Adv. Energy Mater. **4**, 1301624 (2014).
[58] J.-H. Lee, K. Y. Lee, B. Kumar, B. T. Tien, N.-E. Lee, and S.-W. Kim, Energy Environ. Sci. **6**, 169 (2013).
[59] W. Z. Wu, L. Wang, Y. L. Li, F. Zhang, L. Lin, S. M. Niu, D. Chenet, X. Zhang, Y. F. Hao, T. F. Heinz, J. Hone, and Z. L. Wang, Nature **514**, 470 (2014).

[60] H. Y. Zhu, Y. Wang, J. Xiao, M. Liu, S. M. Xiong, Z. J. Wong, Z. L. Ye, Y. Ye, X. B. Yin, and X. Zhang, Nat. Nanotechnol. **10**, 151 (2015).
[61] S. K. Kim, R. Bhatia, T.-H. Kim, D. Seol, J. H. Kim, H. Kim, W. Seung, Y. Kim, Y. H. Lee, and S.-W. Kim, Nano Energy **22**, 483 (2016).
[62] G. Zhu, C. Pan, W. Guo, C.-Y. Chen, Y. Zhou, R. Yu, and Z. L. Wang, Nano Lett. **12**, 4960 (2012).
[63] S. Wang, Z. Lin, S. Niu, L. Lin, Y. Xie, K. C. Pradel, and Z. L. Wang, ACS Nano **7**, 11263 (2013).
[64] X. Pu, M. Liu, L. Li, C. Zhang, Y. Pang, C. Jiang, L. Shao, W. Hu, and Z. L. Wang, Adv. Sci. **3**, 1500255 (2016).
[65] X. Nan, C. Zhang, C. Liu, M. Liu, Z. L. Wang, and G. Cao, ACS Appl. Mater. Interfaces **8**, 862 (2016).
[66] F. Wang, C. Jiang, C. Tang, S. Bi, Q. Wang, D. Du, and J. Song, Nano Energy **21**, 209 (2016).
[67] A. Ramadoss, B. Saravanakumar, S. W. Lee, Y.-S. Kim, S. J. Kim, and Z. L. Wang, ACS Nano **9**, 4337 (2015).
[68] Y. Song, X. Cheng, H. Chen, J. Huang, X. Chen, M. Han, Z. Su, B. Meng, Z. Song, and H. Zhang, J. Mater. Chem. A **4**, 14298 (2016).
[69] H. Guo, M.-H. Yeh, Y.-C. Lai, Y. Zi, C. Wu, Z. Wen, C. Hu, and Z. L. Wang, ACS Nano **10**, 10580 (2016).
[70] F. Yi, J. Wang, X. Wang, S. Niu, S. Li, Q. Liao, Y. Xu, Z. You, Y. Zhang, and Z. L. Wang, ACS Nano **10**, 6519 (2016).
[71] J. Luo, W. Tang, F. R. Fan, C. Liu, Y. Pang, G. Cao, and Z. L. Wang, ACS Nano **10**, 8078 (2016).
[72] X. Wang, X. Lu, B. Liu, D. Chen, Y. Tong, and G. Shen, Adv. Mater. **26**, 4763 (2014).
[73] X. Pu, L. Li, M. Liu, C. Jiang, C. Du, Z. Zhao, W. Hu, and Z. L. Wang, Adv. Mater. **28**, 98 (2016).
[74] X. Pu, L. Li, H. Song, C. Du, Z. Zhao, C. Jiang, G. Cao, W. Hu, and Z. L. Wang, Adv. Mater. **27**, 2472 (2015).
[75] Z. Wen, M.-H. Yeh, H. Guo, J. Wang, Y. Zi, W. Xu, J. Deng, L. Zhu, X. Wang, C. Hu, L. Zhu, X. Sun, and Z. L. Wang, Sci. Adv. **2**, e1600097 (2016).