



Fully packaged paper heater systems with remote and selective ignition capabilities for nanoscale energetic materials

Nam-Su Jang^{a,1}, Sung-Hun Ha^{a,1}, Soo-Ho Jung^b, Soo Hyung Kim^{a,c}, Hye Moon Lee^{b,**}, Jong-Man Kim^{a,c,*}

^a Department of Nano Fusion Technology and BK21 Plus Nano Convergence Technology Division, Pusan National University, Busan, 46241, Republic of Korea

^b Powder & Ceramics Division, Korea Institute of Materials Science, Changwon, 51508, Republic of Korea

^c Department of Nanoenergy Engineering, Pusan National University, Busan, 46241, Republic of Korea

ARTICLE INFO

Article history:

Received 23 October 2018

Received in revised form

23 December 2018

Accepted 14 January 2019

Available online 15 January 2019

Keywords:

Nanoscale energetic materials

Aluminum-doped paper

Low-voltage ignition

Flexible heater chips

Multifunctional thermal igniters

Remote/selective ignition system

ABSTRACT

Development of low-voltage driven multifunctional thermal igniters for nanoscale energetic materials (nEMs) is important for extending the application of nEMs to various thermal engineering fields. In this study, highly flexible heater chips capable of generating a sufficient amount of heat to ignite nEMs at a low voltage are demonstrated by incorporating a patterned aluminum-doped paper (AP) with polymeric substrates. A combination of automatic paper cutting and single-step ultraviolet polymer curing techniques helps in the fabrication of various designs of flexible AP heater chips in a simple and low-cost manner. Based on the AP heater chips, three models of flexible thermal igniters are designed to develop new functions such as selective ignition and sequential ignition in a single chip and successfully operated at low voltages. Two types of compact ignition systems are fabricated by fully integrating the arrayed AP igniters, circuit modules, and portable batteries in a three-dimensional printed single package and on a flexible circuit board. The systems are successfully demonstrated to ignite nEMs wirelessly and selectively with a smartphone.

© 2019 Elsevier B.V. All rights reserved.

1. Introduction

Composite nanoscale energetic materials (nEMs) comprising nanoscale fuel and oxidizer materials can rapidly convert stored chemical energy into thermal and mechanical energies (i.e., heat and pressure) upon ignition, exhibiting significantly higher reactivities and energy densities than those of microscale counterparts. Therefore, nEMs have recently attracted significant attention in numerous potential applications, including propellants, explosives, and pyrotechnics [1–8]. However, the current studies on nEMs are focused mainly on engineering of material systems to optimize the combustion and explosion characteristics.

Appropriate techniques for an efficient ignition of nEMs are required for device applications of nEMs in various thermal engi-

neering fields. Among diverse ignition strategies, electrothermal ignition has been the most widely used in various civilian and military applications [9–16]. This is predominantly attributed to considerable advances in micromachining technologies, which can significantly miniaturize thermal igniters by enabling fabrication of heating devices with patterned thin-film metal [9–13] and polysilicon wires [14–16] at the microscale.

The micromachined heaters (MHs) typically exhibit stable electrothermal performances coupled with fast response capabilities. In addition, it is feasible to integrate them in a compact system owing to the small footprint. Furthermore, MHs can be easily designed in an arrayed form and thereby can ignite EMs independently, yielding multiple ignitions in a single chip [17–24]. However, there are some critical challenges of MHs, which might hinder their use in practical applications. The fabrication of MHs is quite complex, expensive, and time-consuming owing to the multi-step process (e.g., lithography, heating material deposition, and patterning) and requirement for high-vacuum deposition equipment (e.g., evaporation, sputtering, and low-pressure chemical vapor deposition) [9–24]. In addition, most MHs might inevitably require a bulky complex power supply module as they are usually operated at high voltages, typically higher than a few tens of volts, to generate sufficient amount of heat to ignite the nEMs.

* Corresponding author at: Department of Nano Fusion Technology and BK21 Plus Nano Convergence Technology Division, Pusan National University, Busan, 46241, Republic of Korea.

** Corresponding author.

E-mail addresses: hyelee@kims.re.kr (H.M. Lee), jongkim@pusan.ac.kr (J.-M. Kim).

¹ These authors contributed equally to this work as a co-first author.

Recently, our group reported a new class of metal-doped paper heaters [25]. Unlike the conventional MHs, the paper-based heaters could be prepared by a wet chemical deposition process in a simple and cost-effective manner; furthermore they were capable of igniting nEMs at very low input voltages of 1 V. Based on the excellent electrothermal performance in conjunction with the simple fabrication, the paper heaters could be easily integrated with a wireless switching circuit and portable batteries in a single package to construct a compact remote ignition system. Nevertheless, the remote system was limited to only a single ignition of nEMs, as the paper heaters are not compatible with traditional microfabrication techniques owing to the stand-alone architectures of conductive papers; therefore, they are difficult to implement in an array on a single chip.

In this work, we present a simple, yet efficient fabrication route to flexible heater chips based on an aluminum-doped paper (AP). Three designs of AP heater chips (single, arrayed, and sequential models) are easily fabricated by combining computer-controlled paper cutting and one-step ultraviolet (UV) polymer curing processes. The proposed simple and cost-effective heater chip fabrication approach enables to demonstrate low-voltage-driven thermal igniters and develop new functions such as selective ignition and sequential ignition of nEMs.

The arrayed AP igniters are integrated with electrical circuit and portable battery modules in a three-dimensional (3D) printed compact package and even on a flexible circuit board. Based on the fully packaged ignition systems, nEMs can be ignited wirelessly and selectively with a smartphone.

2. Experimental details

2.1. Synthesis of aluminum-doped paper (AP)

Solution processable AP was prepared by a simple chemical deposition process according to a previously reported procedure [25–27]. Briefly, a blank paper sheet comprising a cellulose fiber network was catalytically treated by immersing it in a mixed solution of 5 vol% titanium isopropoxide ($\text{Ti}(\text{O}-i\text{-Pr})_4$) and 95 vol% dibutyl ether ($\text{O}(\text{C}_4\text{H}_9)_2$). After drying under an inert atmosphere, the catalyst-treated paper sheet was immersed in an aluminum (Al) precursor composite solution of $\text{AlH}_3\{\text{O}(\text{C}_4\text{H}_9)_2\}$. During this process, Al decomposed from $\text{AlH}_3\{\text{O}(\text{C}_4\text{H}_9)_2\}$ is nucleated and grown on all of the surfaces of the cellulose fibers in the paper sheet.

2.2. Fabrication of flexible AP heater chips

In order to fabricate flexible AP heater chips, first, the synthesized AP was attached to an adhesive supporting mat and patterned into various heater designs using a computer-controlled cutting plotter (Cameo, Silhouette). Next, unwanted portions of the AP were easily detached from the supporting mat with weak adhesion enough only to fix the AP during patterning. A liquid UV-curable resin (NOA 68, Norland Products) was then spin-coated on the prepared AP patterns at 500 rpm for 30 s and selectively cured by irradiating UV light only to the intended area with the aid of a photomask. The UV-curing process was performed in a UV chamber (MT-UV-A 17, Minuta Technology) under an intensity of 20 mW/cm^2 for 10 min. The uncured NOA parts were then chemically etched in an acetone solution, and the sample was thoroughly rinsed with deionized (DI) water and dried with nitrogen blow. Finally, the devices were prepared by carefully detaching them from the supporting mat. Three different models of the flexible AP heater chips (single, arrayed, and sequential models) were designed and fabricated.

2.3. Preparation of nEM solution

Commercially available Al nanoparticles (NPs) and copper oxide (CuO) NPs (both 100 nm in diameter) were purchased from NTbase and used in this study as a fuel metal and oxidizer, respectively. In order to prepare Al/CuO nEMs, the Al and CuO NPs were added together in an ethanol solution at a fixed weight ratio of $\text{Al}:\text{CuO} = 3:7$. The NPs in the solution were then homogeneously mixed in an ultrasonic bath operating at a power of 200 W and frequency of 40 kHz for 5 min. The ethanol was then entirely evaporated in a convection oven at 80°C for 30 min, leaving well-mixed Al/CuO nEMs. Finally, the nEM solution was prepared by dispersing the Al/CuO powders in DI water at a concentration of 50 mg/mL for a drop-coating process.

2.4. Fabrication of remote and selective ignition (RSI) systems

The RSI system was constructed by assembling the ignition, electrical circuit, and battery parts in a single plastic package comprising two containers and lid. Each part of the plastic package was fabricated using a 3D printing system (Bonbot3-H4, LEEJO) based on a fused deposition modeling mechanism.

A single-board microcontroller (Arduino Nano), Bluetooth module (HC-06), solid-state relays (AQW212, Panasonic), and rechargeable lithium polymer batteries (MP503048-PCM, Max-power) were integrated and interfaced to each other inside the plastic containers. The AP igniter was fixed onto the top of the plastic lid using custom-made connectors, and electrically connected to the circuit and battery parts. The control board was programmed using the open-source Arduino Software (IDE).

The flexible RSI system was fabricated by directly mounting the system parts in parallel on a flexible circuit board and electrically interfacing them to each other.

2.5. Characterization

The morphologies of the AP and Al/CuO nEMs were investigated in detail using a field-emission scanning electron microscope (FESEM; Supra 40 V P, ZEISS). An energy-dispersive X-ray spectrometer (EDS) equipped in the SEM was used to analyze the chemical composition of the synthesized AP. The initial resistance of the AP heater chips was measured using a digital multimeter (U1235B, Keysight Technologies). The composition of the Al/CuO nEMs was analyzed using X-ray diffraction (XRD; X'Pert³, Malvern Panalytical).

The sheet resistance (R_s) of the AP was evaluated by a two-probe method. Briefly, the resistance (R) of the AP was measured using a digital multimeter; R_s was then calculated by $R_s = R \times (w/l)$, where w and l are the width and length of the tested AP, respectively.

For a static bending test, a bending deformation was applied to the flexible AP heater chip both outward and inward using a custom-made mechanical jig while observing the corresponding change in the R using a digital multimeter. The cyclic bending test was carried out by repeatedly bending the AP heater chip 1000 times using a programmable motorized stage (JSV-H100, JISC). The R of the device was intermittently measured during the test using a digital multimeter.

A thermal imaging camera (T630sc, FLIR) capable of measuring a temperature up to 660°C was used to investigate the electrothermal performances of the AP heater chips. The input voltage for heater operation was applied using a direct current power supply (K1205, Vupower).

All of the digital images of the AP, AP heater chips, AP igniters, and RSI systems were obtained using a camera module equipped in a smartphone.

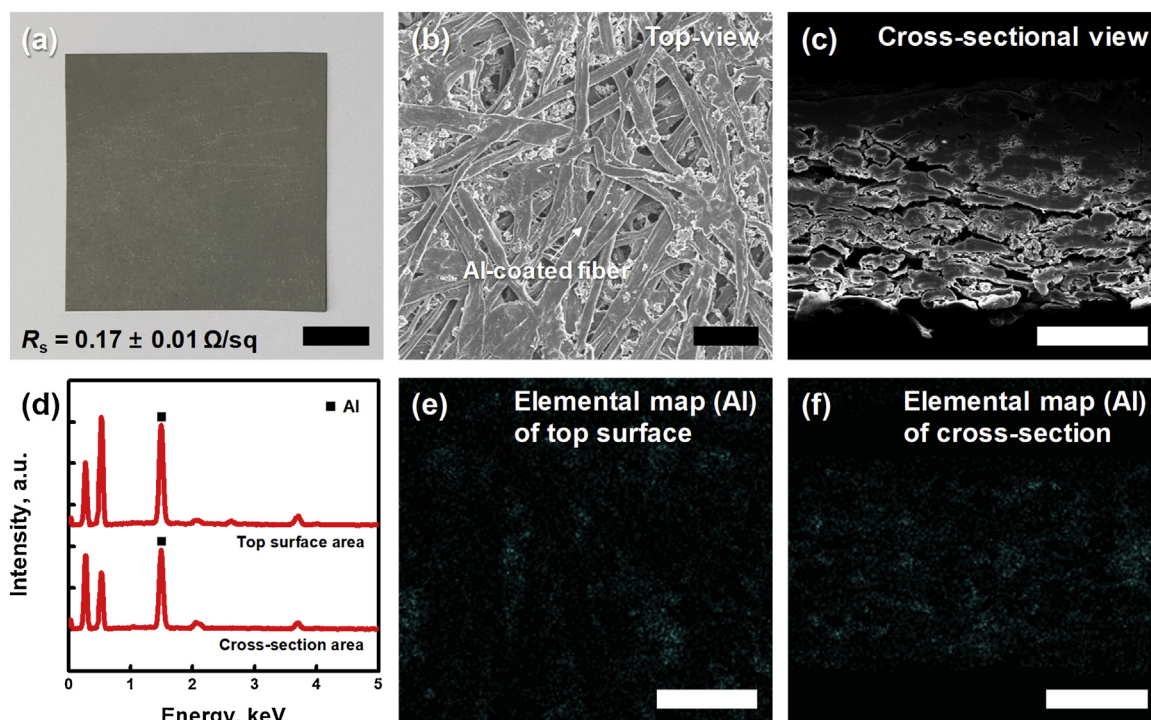


Fig. 1. Aluminum-doped paper (AP). (a) digital image of the AP synthesized by a wet chemical process (scale bar: 20 mm), (b) top-view and (c) cross-sectional SEM images of the AP (scale bars: 50 μm), and (d) EDS spectra of the AP and corresponding Al elemental maps for (e) top and (f) cross-section regions of the AP (scale bars: 50 μm).

3. Results and discussion

Highly conductive APs were prepared by a wet chemical deposition process in a simple and cost-effective manner. Fig. 1(a) shows a digital image of the AP synthesized from an $80 \times 80 \text{ mm}^2$ pristine paper sheet, which suggests that the simple process can be potentially extended to a large-area synthesis of conductive papers owing to the solution processability. The top-view SEM image in Fig. 1(b) shows a typical surface morphology of the synthesized AP, which cellulose fibers in the paper sheet are entirely covered by Al. Furthermore, Al features were well formed even inside the paper, as shown in the cross-sectional SEM image in Fig. 1(c), probably as the chemical solutions for Al synthesis (catalyst and Al precursor) can easily penetrate the porous paper during the deposition process. This enables Al features to conformally grow on all of the surfaces of the cellulose fibers in the paper, making the pristine paper highly conductive. Owing to the unique morphology, the AP exhibited an average sheet resistance as low as $0.17 \Omega/\text{sq}$, which reveals the possibility for low-voltage operation of the resulting AP heaters.

In order to quantitatively demonstrate the presence of Al features in the paper sheet, a chemical composition analysis was performed on both top surface and cross-section regions of the AP using EDS, as shown in Fig. 1(d). A strong Al peak around 1.5 keV was clearly observed at both top surface and cross-section regions. In addition, the elemental maps for Al in Fig. 1(e) and (f) confirm that Al features were deposited quite uniformly inside as well as on the top surface of the paper sheet.

The flexible AP heater chips were fabricated by patterning the AP into various heater designs and then incorporating them with a polymer substrate through a one-step UV-curing process, as schematically illustrated in Fig. 2(a). Fig. 2(b) shows a digital image of the fabricated single AP heater, which represents the highly flexible nature of the AP heater chips. The single heater chip was designed to have a heating strip with two probing electrodes at both ends in a monolithic fashion. In particular, the substrate part

underneath the heating strip was entirely removed, keeping the two probing electrodes embedded in the polymer substrate. This should significantly help to enhance the electrothermal performance of the device by minimizing the heat conduction loss to the substrate while ensuring the mechanical robustness. It is worth noting that the holes underneath the heating strips can be photolithographically patterned without affecting the simplicity in the overall device fabrication.

Owing to the fabrication simplicity, the electrical properties of the AP heater chips can be easily controlled by modulating the dimensions of the device. Fig. 2(c) shows the R of the single AP heater chip as a function of the strip width. The device with the strip width of 1 mm and length of 10 mm exhibited a low R of $0.97 \pm 0.04 \Omega$ owing to the high inherent conductivity of the AP. The R tended to gradually decrease with the increase in the strip width at a fixed length; a very low R of $0.21 \pm 0.02 \Omega$ was obtained at the width of 5 mm.

The AP heater chips should be fairly robust even under mechanical deformations so that the devices can be employed as a flexible igniter. In order to investigate this characteristic, the single AP heater chip was subjected to both outward and inward bending deformations. Fig. 2(d) shows the relative resistance change ($\Delta R/R_0$) of the device bent at various bending radius (r_b) values. The electrical performance of the device was found to be highly reliable so that $\Delta R/R_0$ was smaller than 1.3%, even at a small r_b of 2 mm, regardless of the bending direction. This can be attributed to the stable architecture of the AP coated entirely with Al features, even inside. The similar $\Delta R/R_0$ profiles of the device upon bending outward and inward probably originate from the suspended structure of the heating strip, which is not supported by the substrate. Fig. 2(e) shows the normalized resistance (R/R_0) of the single AP heater chip in response to 1000 bending cycles at $r_b = 5 \text{ mm}$. The R of the device was maintained almost constant with insignificant deviations, smaller than 0.8% with respect to the initial value, during the cyclic bending test, reflecting the considerable long-term electrical stability.

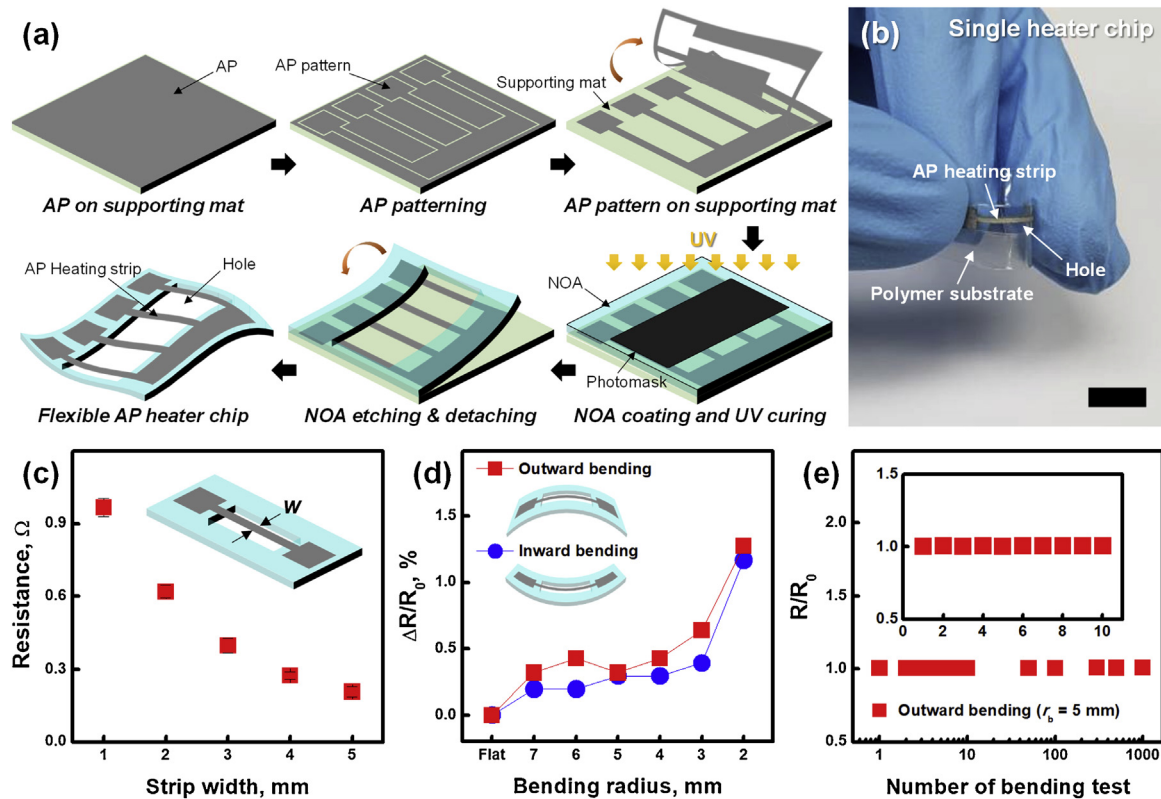


Fig. 2. Flexible AP heater chip incorporated with a polymer substrate. (a) schematic illustration of the fabrication process, (b) digital image of the fabricated single AP heater chip (scale bar: 10 mm), (c) initial resistance of the single AP heater chip as a function of the conductor width with respect to a fixed length, (d) relative resistance change ($\Delta R/R_0$) of the single heater chip under outward and inward bendings at various bending radii, and (e) normalized resistance (R/R_0) of the single heater chip under repeated bending tests for up to 1000 cycles at $r_b = 5$ mm (inset: magnified plot for up to 10 cycles).

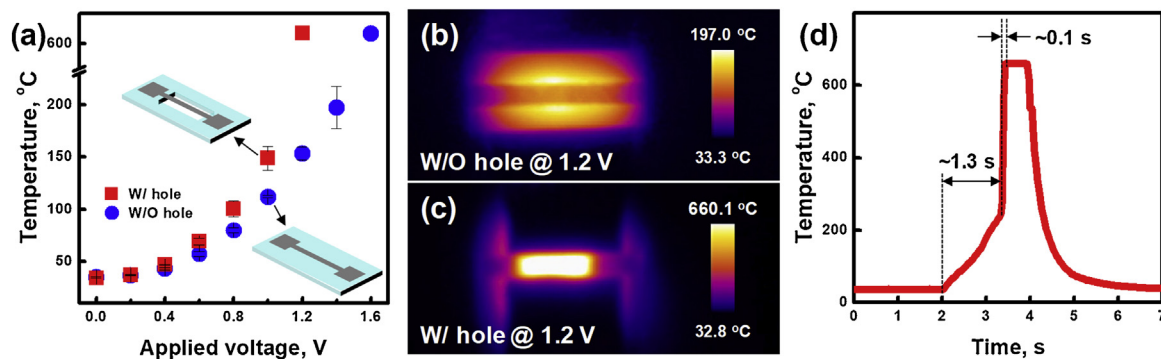


Fig. 3. Electrothermal performance of the single AP heater chip. (a) temperature of the device as a function of the applied input voltage, thermal camera images of the devices (b) without and (c) with the hole underneath the heating strip with an input voltage of 1.2 V, and (d) time-dependent temperature of the device under a step voltage of 1.2 V, indicating the fast electrothermal response.

The electrothermal performance of the AP heater chips was characterized using a thermal imaging camera. Fig. 3(a) shows the steady-state temperature (T) of the single heater chip in response to the input voltage increased by 0.2 V every 5 s. The T of the device gradually increased proportionally to the applied voltage up to 1 V owing to the Joule heating effect, followed by a sudden increase at 1.2 V beyond the measurable temperature limit (T_L 660 °C) of the equipment used in this study. In particular, the ignition temperature of the Al/CuO nEMs was estimated to be lower than 600 °C by differential scanning calorimetry analysis, as shown in Fig. S1 in the Supporting Information (SI). This suggests that the AP heaters can provide a sufficient energy to thermally ignite the nEMs even at low voltages. The sudden increase in the T is attributed to the

sufficient amount of heat generated immediately after the paper material was ignited.

For comparison, the device without hole was also tested, as shown in Fig. 3(a). The device without hole exhibited a similar thermal response to that of the device with a hole. However, the device with the hole exhibited a higher T for a given voltage, reaching above the T_L at a lower voltage, compared to the device without hole. This occurred as the heat conduction loss to the substrate was significantly reduced by entirely etching the substrate part under the heating strip. The effect of the hole on the reduction in the heat loss was more precisely investigated using a thermal imaging camera. Fig. 3(b) and (c) show thermal images of the devices with and without hole under the same input voltage of 1.2 V. The device

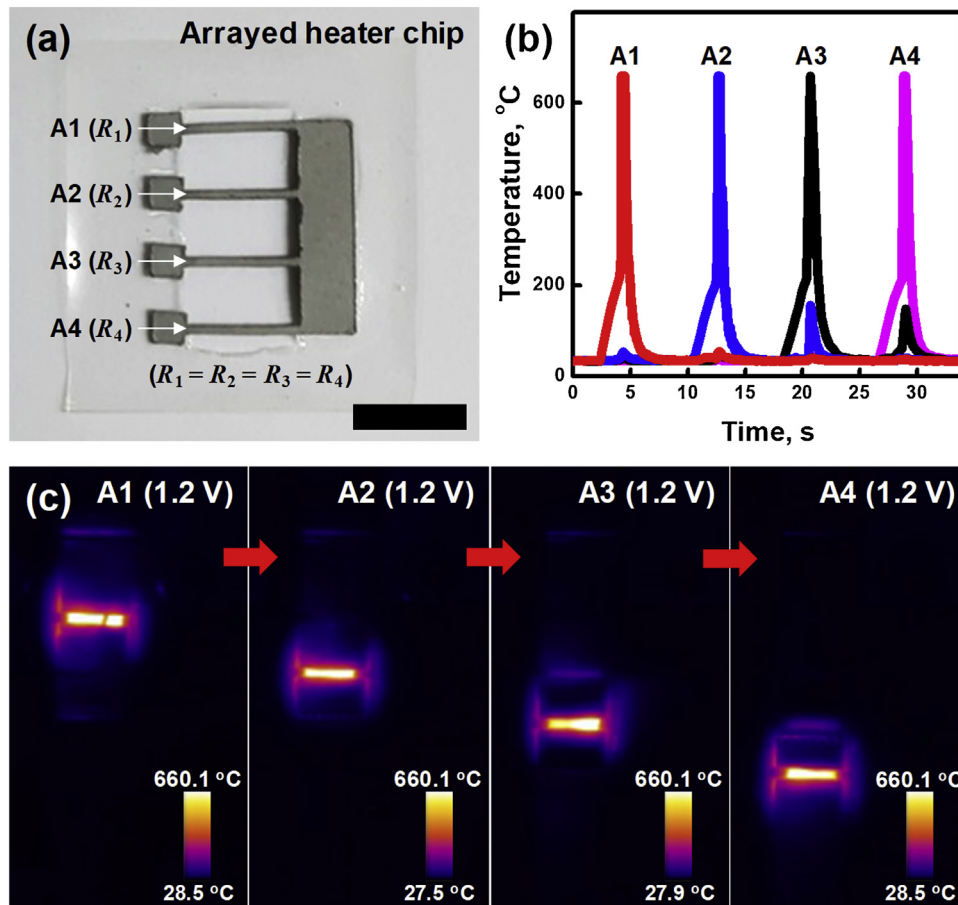


Fig. 4. Arrayed AP heater chip. (a) digital image of the fabricated device (scale bar: 10 mm), and (b) time-dependent temperature profiles of the four heating strips (A1–A4) powered independently by an input voltage of 1.2 V (A1 → A2 → A3 → A4 in turn) in the device and (c) corresponding thermal camera images.

without hole exhibited a blurred spatial temperature distribution (Fig. 3(b)). This implies that a considerable amount of heat was transferred to the substrate part in contact with the heating strip and spread throughout the substrate through heat conduction. On the other hand, the heat was highly concentrated on the suspended heating strip in the device with the hole even at the same voltage (Fig. 3(c)), yielding a lower power consumption than that of the device without hole.

Fig. 3(d) shows a typical time-dependent temperature profile of the single AP heater chip in response to the applied voltage of 1.2 V, representing a relatively fast thermal response. The T of the device increased to ~ 244 °C, close to the ignition point of the paper material (typically smaller than 250 °C) within ~ 1.3 s after the input voltage was applied at 2 s. The T then rapidly increased above T_L within ~ 0.1 s due to the heat generated upon ignition of the paper material. When the paper material was completely burned, the heating strip easily broke and the T of the device instantly decreased due to the electrical disconnection.

Based on the proposed strategy for incorporation of AP conductors with polymer substrates, the single heater design could be easily extended to an arrayed heater chip, as shown in Fig. 4(a). The device consists of four identical heating strips (denoted as A1–A4 hereafter; $R_1 = R_2 = R_3 = R_4$), each with an individual electrode and common ground, which can enable multiple ignitions in a single chip by individually operating each heating strip with the same input voltage.

Fig. 4(b) shows the time-dependent temperature profiles of the four heating strips powered independently by an input voltage of 1.2 V in the arrayed AP heater chip. When the input voltage was

applied to A1, the T of A1 increased with a similar trend to that of the single AP heater chip in Fig. 3(d), while the others (A2–A4) did not exhibit a significant temperature increase. This process was repeated for A2, A3, and A4 operating them independently at the same input voltage. Corresponding thermal camera images are presented in Fig. 4(c). The highest T above the T_L was observed only in the activated heating strip, which provides the potential for multiple and selective ignitions of nEMs in a chip. It is worth noting that a high-density array of heating strips can be implemented in a chip by simply optimizing the device design.

In addition, a new class of AP heater chip was demonstrated, which can be sequentially operated with a single input voltage, as shown in Fig. 5(a). The sequential AP heater chip was designed so that three heating strips with different R values (denoted as S1–S3 hereafter) were connected in parallel. The R of the heating strips was simply controlled by differentiating the lengths ($R_1 < R_2 < R_3$). When a single input voltage is applied to the device, the resulting electrical current (i) is divided into the three heating strips in inverse proportion to the R value of each strip (i.e., $i_1 > i_2 > i_3$). Consequently, the highest temperature can be obtained from the heating strip capable of carrying the highest i (i.e., with the lowest R) at the fixed input voltage according to the Joule's law related to the thermal power $P = i^2 R$. Therefore, the T of the shortest heating strip can most rapidly reach the T_L ; this strip can be broken first after being burned up due to the ignition of the paper material. This process occurs sequentially with time until the heating strip with the highest R in the device is burned up.

Fig. 5(b) shows the time-dependent temperature profiles of the three parallel heating strips in response to the applied voltage of

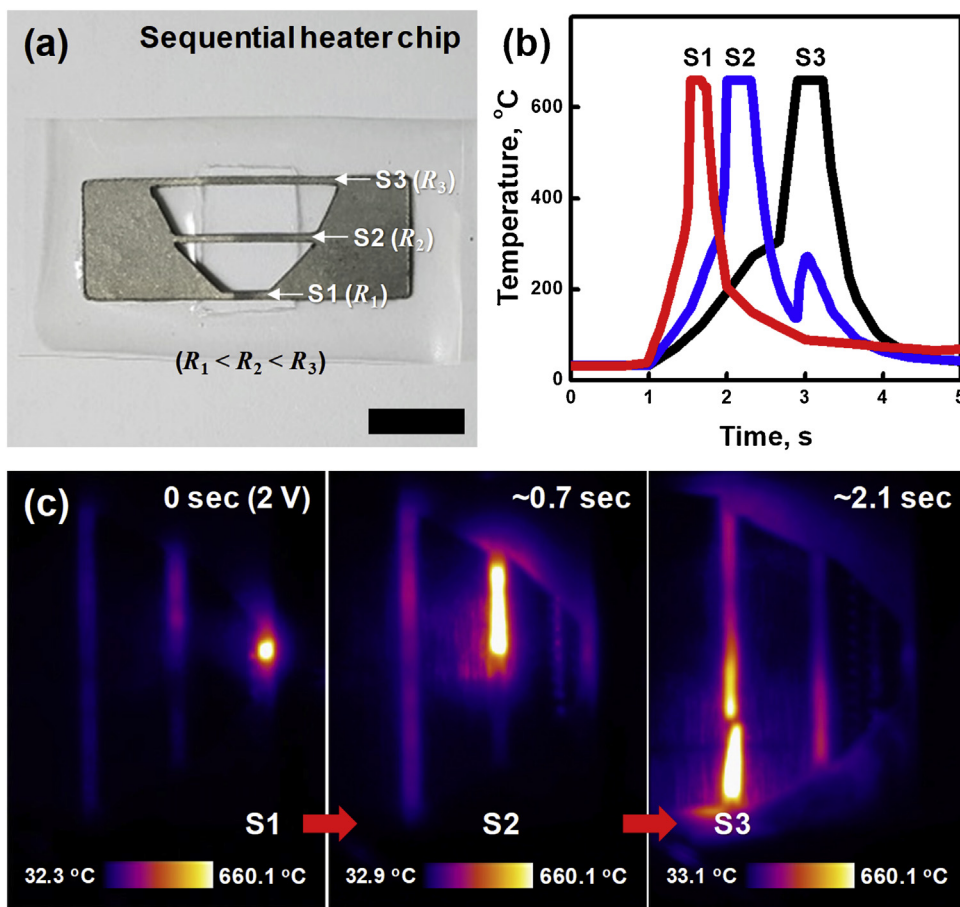


Fig. 5. Sequential AP heater chip. (a) digital image of the fabricated device (scale bar: 10 mm), and (b) time-dependent temperature profiles of the three parallel heating strips (S1–S3) in response to the applied voltage of 2 V in the device and (c) corresponding thermal camera images.

2 V in the sequential AP heater chip. In this case, the lengths of S1, S2, and S3 were designed to be 5, 15, and 20 mm, respectively, with a fixed width of 1 mm. At a fixed input voltage, the slopes of the T -time profiles (i.e., heating rates) of the heating strips exhibited clear differences from each other until the paper material was ignited. The slope decreased in the order of S1, S2, and S3, which eventually led to the sequential burning in that order. This occurs as a higher efficiency of transducing the electrical energy into Joule heat is achievable when a higher power is applied to a heater [28–30].

The corresponding serial thermal camera images of the device at the moments when each heating strip reached the highest T are shown in Fig. 5(c), which clearly shows that S1 with the lowest R was burned first due to the highest heating rate, while S2 and S3 maintained significantly lower T than the ignition point of the paper material at that time (rightmost in Fig. 5(c)). S2 and S3 were then burned sequentially within 0.7 s and 2.1 s after S1 was burned, respectively. This confirms that the sequential operation of the device is possible by designing each heating strip in parallel connection to have different R and thereby to have different heating rate with a fixed input voltage. Furthermore, this suggests that the time interval and order of the sequential operation can also be easily modulated by controlling the device geometry. The unique working principle of the sequential heater chip can be used to develop a new class of thermal igniter capable of sequential ignition for nEMs.

The flexible AP igniters were prepared by simply depositing nEMs on the suspended heating strips using a simple drop-coating process, as schematically illustrated in Fig. 6(a). It is important to note that the coating process was conducted immediately after dis-

persing the Al/CuO powders in DI water to avoid any unforeseen oxidation process. In particular, the coating volume of the nEM solution was fixed (1 μ L) to provide reproducible ignition characteristics of the nEMs on the same devices. The SEM images in Fig. 6(b) show the nEM thin film deposited on the heating strip, indicating that the Al/CuO powders and AP are in good contact with each other. In addition, the XRD spectrum in Fig. S2 in the SI shows clear diffraction peaks for Al and CuO, indicating that the nEMs are composed of relatively pure Al and CuO NPs.

The ignition and explosion properties of the AP igniters were investigated by monitoring the devices in response to the applied voltage in real time using a digital camera. Fig. 6(c) shows digital images of the single AP igniter in the initial and ignited states. The nEMs on the device exploded immediately after an input voltage of 1.2 V was applied to the device. This occurred as the nEM powders composed of Al and CuO NPs are highly reactive and the single AP heater chip could generate a sufficient amount of heat ($> 660^\circ\text{C}$ at 1.2 V) to thermally ignite the nEMs, as confirmed in Fig. 3. The intimate contact between the nEMs and AP is also likely to contribute to the stable and prompt explosion of the nEMs upon ignition by promoting the efficient heat transfer. However, the ignition properties of the nEMs can be strongly dependent on temperature and relative humidity conditions. It is believed that the aging effect of the AP igniters can be reduced by coating the Al/CuO powders with functional polymer binders [31].

Fig. 6(d) shows digital images of the arrayed AP igniter when an input voltage of 1.2 V was applied independently to each single igniter. Owing to the ability of the arrayed heater chip to independently operate each heating strip in the device, the selective

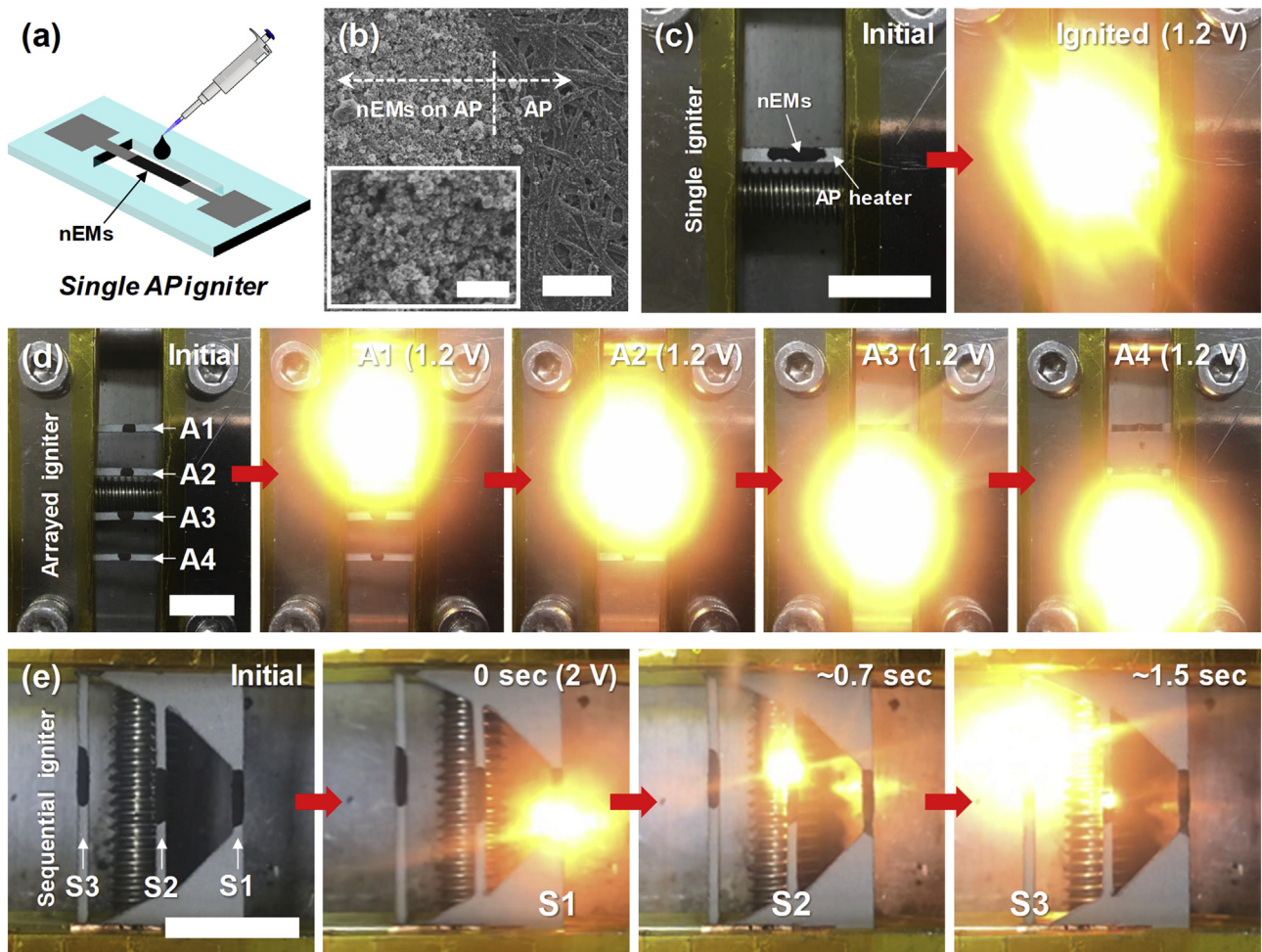


Fig. 6. AP heater chips as a flexible nEM igniter. (a) schematic illustration of the single AP igniter prepared by drop-coating of the nEM solution, (b) SEM images of the Al/CuO nEMs coated on the top surface of the single heater (scale bar: 100 μm) (inset: magnified SEM image of the nEMs (scale bar: 10 μm)), and digital images of the (c) single igniter in response to the applied voltage of 1.2 V, (d) arrayed AP igniter at operation of each single igniter in the device individually with an input voltage of 1.2 V (A1 $\rightarrow$ A2 $\rightarrow$ A3 $\rightarrow$ A4 in turn), and (e) sequential AP igniter at the moment when each single igniter in the device was ignited with a fixed input voltage of 2 V (scale bars: 10 mm).

ignition of the nEMs was facilitated with the arrayed igniter. In particular, all of the single igniters in the device exhibited similar ignition and explosion characteristics of the nEMs to each other. This is of significance, particularly in the development of multi-arrayed igniters toward practical applications.

Fig. 6(e) shows serial digital images of the sequential AP igniter when an input voltage of 2 V was applied to the probing electrodes shared by three parallel single igniters. The explosion of the nEMs occurred in succession from the shortest single igniter in the device, as the AP heating strip with the lowest R can most rapidly generate a sufficient amount of heat to ignite the nEMs for a given input voltage owing to the inverse relationship between the R and heating rate, as confirmed in Fig. 5.

In order to demonstrate a compact system that can ignite nEMs in a wireless and selective manner, three-layered system parts (ignition, circuit, and battery parts) were integrated in a 3D printed plastic package, as schematically illustrated in Fig. 7(a). In the top layer, the AP igniter was fixed onto a plastic lid using the electrical connectors. The circuit part with a microcontroller, Bluetooth, and relay modules was located in the middle layer and connected electrically to the ignition part to send a command signal to ignite the nEMs. In the bottom layer, two lithium polymer batteries were placed, connected to the ignition and circuit parts to power them up for their wireless operations. Fig. 7(b) shows digital images of the fabricated RSI system and each system part. All of the system

parts were fully integrated in a single package with dimensions of $90 \times 60 \times 40 \text{ mm}^3$.

Fig. 7(c) shows digital images of the RSI system with the arrayed igniter under the wireless operation using a smartphone in real time. In this case, the corresponding close-up digital images of the arrayed igniter during the system operation were obtained from a camera module installed in another smartphone (inset in Fig. 7(c)). The RSI system could be successfully operated using a smartphone. Briefly, the input signal generated by a smartphone is transmitted wirelessly to the microcontroller through Bluetooth. The microcontroller then sends a specific command signal to a target relay to electrically connect the allocated heating strip and battery, and thereby thermally ignite the nEMs on the strip. The wireless ignition of the nEMs in the arrayed igniter could be selectively controlled according to the smartphone operation, as shown in Fig. 7(c).

As a proof-of-concept for flexible RSI systems, the three system parts were integrated in parallel on a flexible circuit board with dimensions of $130 \times 50 \text{ mm}^2$, as shown in Fig. 8(a). The mechanically flexible architecture of the fabricated system is also presented in Fig. 8(b). In order to evaluate the practicality as a flexible ignition system, the fabricated RSI system was remotely operated with a smartphone after attaching it onto a curved surface while monitoring the overall process in real time using a digital camera module, as shown in Fig. 8(c). Similar to the results in Fig. 7(c), upon selection

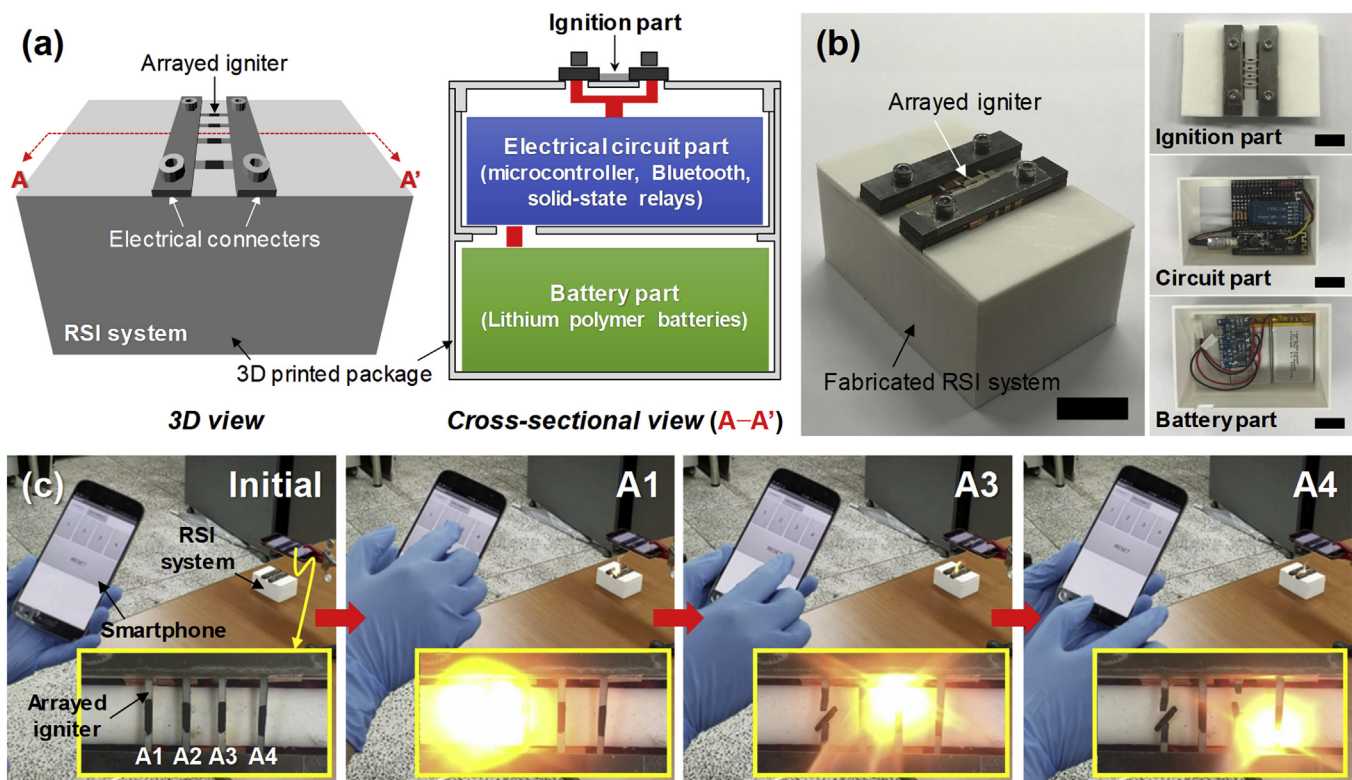


Fig. 7. Remote and selective ignition (RSI) system for nEMs. (a) schematic illustrations of the RSI system fully integrated in the 3D printed plastic package, (b) digital images of the fabricated RSI system and each system part (scale bars: 20 mm), and (c) digital images of the RSI system during remote and selective ignition with a smartphone (A1 → A3 → A4 in turn) (inset: corresponding top-view digital images of the arrayed AP igniter upon ignition).

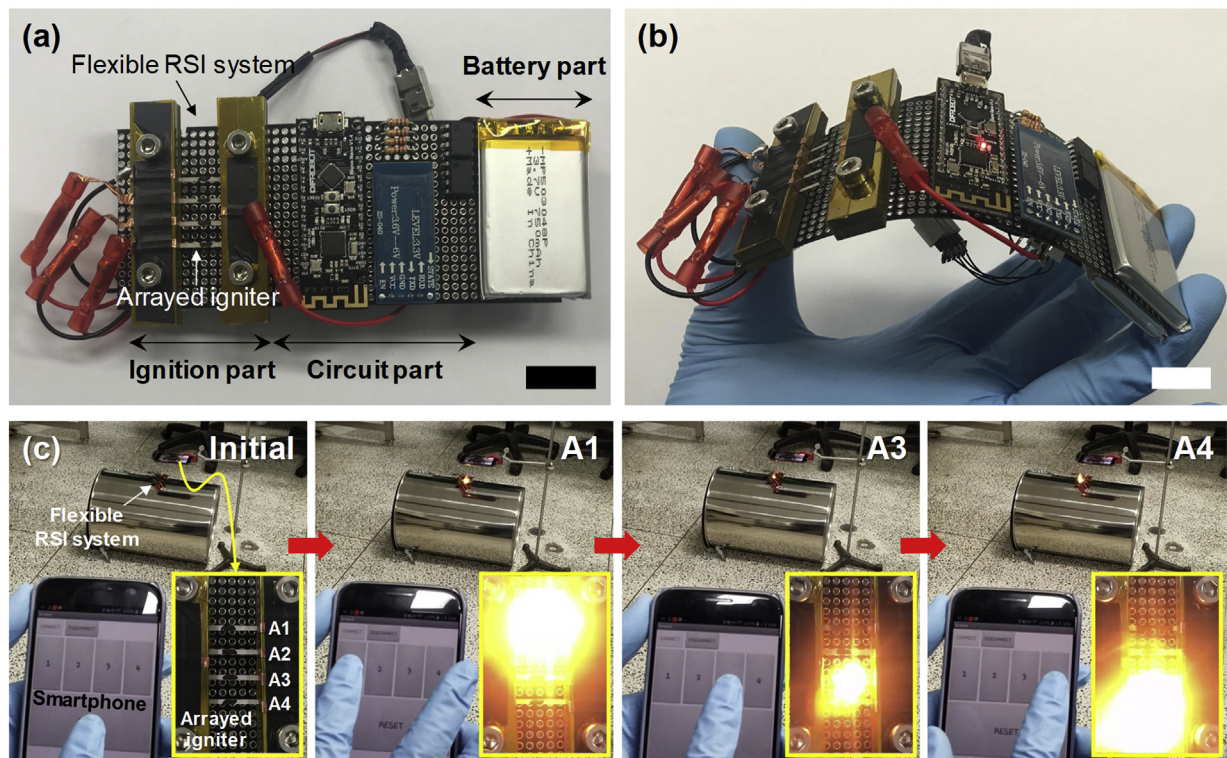


Fig. 8. Flexible RSI system for nEMs. Digital images of the fabricated flexible RSI system fully integrated on a flexible circuit board in the (a) initial and (b) bent states (scale bars: 20 mm), and (c) digital images of the flexible RSI system attached on a curved surface during a remote and selective operation with a smartphone (A1 → A3 → A4 in turn) (inset: corresponding top-view digital images of the arrayed AP igniter upon ignition).

of a certain button on a smartphone, the nEMs on the corresponding heating strip were ignited remotely and selectively, demonstrating the feasibility for use in flexible applications.

The observations confirm that the proposed AP heater-chip-based thermal nEM igniters are highly feasible for implementation in compact ignition systems and can be used in many applications in various civilian and military fields owing to the diverse advantages including the simple and low-cost fabrication, low-voltage ignition capability, mechanical flexibility, and multifunctionality.

4. Conclusions

In summary, flexible AP heater-chip-based low-voltage nEM igniters and their integration to compact systems with remote and selective ignition capabilities were presented. The AP was synthesized using a simple chemical deposition process in an entirely solution processed manner. For the fabrication of the flexible AP heater chips, the AP was patterned into three heater geometries (single, arrayed, and sequential models) using a cutting plotter. The patterned AP was then embedded in a polymer substrate while suspending the heating strips through the selective UV polymer curing process. The overall device fabrication was simple, fast, and cost-effective.

By depositing the nEMs on the heating strips in the AP heater chips using a simple drop-coating method, three designs of flexible AP igniters were fabricated: single, arrayed, and sequential devices. The single AP igniter could induce nEM explosion at an input voltage of only 1.2 V, significantly lower than those of the conventional MHs. Through a design optimization of the device, the arrayed and sequential AP igniters could provide unique functions of selective ignition and serial ignition of the nEMs at low voltages, respectively.

The integration of the arrayed AP igniter with the circuit and battery modules in the 3D single package demonstrated the potential for development of a compact system with remote and selective ignition capabilities for nEMs. In addition, the flexible RSI system was fabricated by fully integrating the system components on the flexible circuit board. The systems were successfully demonstrated to ignite the nEMs wirelessly and selectively using a smartphone. We believe that the proposed approach is very promising for use in various civilian and military applications.

Acknowledgements

This work was supported by the Civil and Military Technology Cooperation Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science and ICT (No. 2013M3C1A9055407). This work was also supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (No. NRF-2018R1A2A2A05018201).

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.sna.2019.01.016>.

References

- [1] D. Sundaram, V. Yang, R.A. Yetter, Metal-based nanoenergetic materials: synthesis, properties, and applications, *Prog. Energy Combust. Sci.* 61 (2017) 293–365.
- [2] X. Zhou, M. Torabi, J. Lu, R. Shen, K. Zhang, Nanostructured energetic composites: synthesis, ignition/combustion modeling, and applications, *ACS Appl. Mater. Interfaces* 6 (2014) 3058–3074.
- [3] C. Rossi, K. Zhang, D. Estève, P. Alphonse, P. Tailhades, C. Vahlas, Nanoenergetic materials for MEMS: a review, *J. Microelectromech. Syst.* 16 (2007) 919–931.
- [4] R.A. Yetter, G.A. Risha, S.F. Son, Metal particle combustion and nanotechnology, *Proc. Combust. Inst.* 32 (2009) 1819–1838.
- [5] E.L. Dreizin, Metal-based reactive nanomaterials, *Prog. Energy Combust. Sci.* 35 (2009) 141–167.
- [6] C. Rossi, Engineering of Al/CuO reactive multilayer thin films for tunable initiation and actuation, *Propellants Explos. Pyrotech.* 43 (2018), <http://dx.doi.org/10.1002/prep.201800045>.
- [7] Y. Shen, J. Xu, N. Li, J. Dai, C. Ru, Y. Ye, R. Shen, W. Zhang, A micro-initiator realized by in-situ synthesis of three-dimensional porous copper azide and its ignition performance, *Chem. Eng. J.* 326 (2017) 1116–1124.
- [8] J. Xu, Y. Tai, C. Ru, J. Dai, Y. Ye, R. Shen, P. Zhu, Tuning the ignition performance of a microchip initiator by integrating various Al/MoO₃ reactive multilayer films on a semiconductor bridge, *ACS Appl. Mater. Interfaces* 9 (2017) 5580–5589.
- [9] K. Zhang, C. Rossi, M. Petrantonio, N. Mauran, A nano initiator realized by integrating Al/CuO-based nanoenergetic materials with a Au/Pt/Cr microheater, *J. Microelectromech. Syst.* 17 (2008) 832–836.
- [10] J. Wang, X. Jiang, L. Zhang, Z. Qiao, B. Gao, G. Yang, H. Huang, Design and fabrication of energetic superlattice like-PTFE/Al with superior performance and application in functional micro-initiator, *Nano Energy* 12 (2015) 597–605.
- [11] K. Zhang, S.K. Chou, S.S. Ang, Investigation on the ignition of a MEMS solid propellant microthruster before propellant combustion, *J. Micromech. Microeng.* 17 (2007) 322–332.
- [12] J.Y. Ahn, S.B. Kim, J.H. Kim, N.S. Jang, D.H. Kim, H.W. Lee, J.M. Kim, S.H. Kim, A micro-chip initiator with controlled combustion reactivity realized by integrating Al/CuO nanothermite composites on a microhotplate platform, *J. Micromech. Microeng.* 26 (2016), 015002.
- [13] G. Taton, D. Lagrange, V. Conedera, L. Renaud, C. Rossi, Micro-chip initiator realized by integrating Al/CuO multilayer nanothermite on polymeric membrane, *J. Micromech. Microeng.* 23 (2013), 105009.
- [14] P. Pennarun, C. Rossi, D. Estève, D. Bourrier, Design, fabrication and characterization of a MEMS safe pyrotechnical igniter integrating arming, disarming and sterilization functions, *J. Micromech. Microeng.* 16 (2006) 92–100.
- [15] K. Zhang, Y. Yang, E.Y.B. Pun, R. Shen, Local and CMOS-compatible synthesis of CuO nanowires on a suspended microheater on a silicon substrate, *Nanotechnology* 21 (2010), 235602.
- [16] G.A.A. Rodríguez, S. Suhard, C. Rossi, D. Estève, P. Fau, S. Sabo-Etienne, A.F. Mingotaud, M. Mauzac, B. Chaudret, A microactuator based on the decomposition of an energetic material for disposable lab-on-chip applications: fabrication and test, *J. Micromech. Microeng.* 19 (2009), 015006.
- [17] J. Lee, K. Kim, S. Kwon, Design, fabrication, and testing of MEMS solid propellant thruster array chip on glass wafer, *Sens. Actuator A-Phys.* 157 (2010) 126–134.
- [18] J. Lee, T. Kim, MEMS solid propellant thruster array with micro membrane igniter, *Sens. Actuator A-Phys.* 190 (2013) 52–60.
- [19] Q. Shen, W.Z. Yuan, H. Li, J.B. Xie, H.L. Chang, Silicon-on-insulator-based microsolid propellant thruster array, *Micro Nano Lett.* 10 (2015) 258–262.
- [20] D. Seo, J. Lee, S. Kwon, The development of the micro-solid propellant thruster array with improved repeatability, *J. Micromech. Microeng.* 22 (2012), 094004.
- [21] H.-U. Oh, T.-G. Kim, S.-H. Han, J. Lee, Verification of MEMS fabrication process for the application of MEMS solid propellant thruster arrays in space through launch and on-orbit environment tests, *Acta Astronaut.* 131 (2017) 28–35.
- [22] C. Rossi, T.D. Conto, D. Estève, B. Larangot, Design, fabrication and modelling of MEMS-based microthrusters for space application, *Smart Mater. Struct.* 10 (2001) 1156–1162.
- [23] C. Rossi, B. Larangot, D. Lagrange, A. Chaalane, Final characterizations of MEMS-based pyrotechnical microthrusters, *Sens. Actuator A-Phys.* 131 (2005) 508–514.
- [24] C. Rossi, B. Larangot, P.-Q. Pham, D. Briand, N.F. de Rooij, M. Puig-Vidal, J. Samitier, Solid propellant microthrusters on silicon: design, modeling, fabrication, and testing, *J. Microelectromech. Syst.* 15 (2006) 1805–1815.
- [25] N.-S. Jang, S.-H. Ha, J.H. Kim, S.-H. Jung, S.H. Kim, H.M. Lee, J.-M. Kim, Low voltage ignition of nanoenergetic materials with a conductive paper heater for compact remote ignition system, *Combust. Flame* 173 (2016) 319–324.
- [26] H.M. Lee, H.B. Lee, D.S. Jung, J.-Y. Yun, S.H. Ko, S.B. Park, Solution processed aluminum paper for flexible electronics, *Langmuir* 28 (2012) 13127–13135.
- [27] H.M. Lee, S.-Y. Choi, A. Jung, S.H. Ko, Highly conductive aluminum textile and paper for flexible and wearable electronics, *Angew. Chem. Int. Ed.* 52 (2013) 7718–7723.
- [28] D. Sui, Y. Huang, L. Huang, J. Liang, Y. Ma, Y. Chen, Flexible and transparent electrothermal film heaters based on graphene materials, *Small* 7 (2011) 3186–3192.
- [29] T.-Y. Zhang, H.-M. Zhao, Z. Yang, Q. Wang, D.-Y. Wang, N.-Q. Deng, Y. Yang, T.-L. Ren, Improved electrothermal performance of custom-shaped micro heater based on anisotropic laser-reduced graphene oxide, *Appl. Phys. Lett.* 109 (2016), 151905.
- [30] T.Y. Kim, Y.W. Kim, H.S. Lee, H. Kim, W.S. Yang, K.S. Suh, Uniformly interconnected silver-nanowire networks for transparent film heaters, *Adv. Funct. Mater.* 23 (2013) 1250–1255.
- [31] K.J. Kim, M.H. Cho, J.H. Kim, S.H. Kim, Effect of paraffin wax on combustion properties and surface protection of Al/CuO-based nanoenergetic composite pellets, *Combust. Flame* 198 (2018) 169–175.

Biographies

Nam-Su Jang received the M.S. degree in Nano Fusion Technology from the Pusan National University (PNU), Republic of Korea, in 2014. He is currently working toward the pH.D. degree at PNU. His current research interests include synthesis and applications of functional nanomaterials, micromachined sensors, and flexible devices.

Sung-Hun Ha received the M.S. degree in Nano Fusion Technology from the Pusan National University (PNU), Republic of Korea, in 2016. He is currently working toward the pH.D. degree at PNU. His current research interests include synthesis and applications of functional nanomaterials, microfabrication, and flexible/stretchable sensors.

Soo-Ho Jung received the M.S. degree in Material Science and Engineering from the Korea Advanced Institute of Science and Technology, Republic of Korea, in 2014. In 2014, he joined the Korea Institute of Materials Science, where he is currently a senior researcher. His current research interests include synthesis and applications of multifunctional soft materials, and flexible/stretchable devices.

Prof. Soo Hyung Kim received the pH.D. degree in Mechanical Engineering from the University of Minnesota, USA, in 2003. In 2006, he joined the Pusan National University, where he is currently a Professor in Department of Nanoenergy Engineering. His current research interests include synthesis and characterization of nanostructured materials, and their applications to the fields of photovoltaic and electronic devices.

Dr. Hye Moon Lee received the pH.D. degree in Chemical Engineering from the Hiroshima University, Japan, in 2006. In 2006, he joined the Korea Institute of Materials Science, where he is currently a Principal Researcher. His current research interests include conductive ink and coating technology, and their application to electronics and environmental industries.

Prof. Jong-Man Kim received the pH.D. degree in Electrical Engineering and Computer Science from the Seoul National University, Republic of Korea, in 2007. In 2008, he joined the Pusan National University, where he is currently a Professor in Department of Nanoenergy Engineering. His current research interests include design, fabrication, and characterization of MEMS sensors and actuators, biomimetic engineering, synthesis and applications of functional nanomaterials, and flexible/stretchable electronics.