Scalable fabrication of printed Zn//MnO₂ planar micro-batteries with high volumetric energy density and exceptional safety

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ABSTRACT

The rapid development of printed and microscale electronics imminently requires compatible micro-batteries (MBs) with high performance, applicable scalability, and exceptional safety, but faces great challenges from the ever-reported stacked geometry. Herein the first printed planar prototype of aqueous-based, high-safety Zn//MnO₂ MBs, with outstanding performance, aesthetic diversity, flexibility and modularization, is demonstrated, based on interdigital patterns of Zn ink as anode and MnO₂ ink as cathode, with high-conducting graphene ink as a metal-free current collector, fabricated by an industrially scalable screen-printing technique. The planar separator-free Zn//MnO₂ MBs, tested in neutral aqueous electrolyte, deliver a high volumetric capacity of 19.3 mAh/cm³ (corresponding to 393 mAh/g) at 7.5 mA/cm², and notable volumetric energy density of 17.3 mWh/cm³, outperforming lithium thin-film batteries (≤10 mWh/cm³). Furthermore, our Zn//MnO₂ MBs present long-term cyclability having a high capacity retention of 83.9% after 1300 cycles at 5 C, which is superior to stacked Zn//MnO₂ batteries previously reported. Also, Zn//MnO₂ planar MBs exhibit exceptional flexibility without observable capacity decay under serious deformation, and remarkably serial and parallel integration of constructing bipolar cells with high voltage and capacity output. Therefore, low-cost, environmentally benign Zn//MnO₂ MBs with in-plane geometry possess huge potential as high-energy, safe, scalable and flexible microscale power sources for direction integration with printed electronics.

Keywords: low cost, printed, planar, Zn//MnO₂ micro-batteries, metal-free current collectors

INTRODUCTION

The emerging smart printed electronics with the integrated features of exceptional flexibility, thinness, light weight, and miniaturization have significantly inspired the relentless pursuit of low-cost, safe and environmentally benign printed microscale energy-storage devices with high performance [1–5]. Lithium thin-film micro-batteries (MBs) with energy density of 10 mWh/cm³ are the most popular microscale power sources for various microsystems. However, most reported MBs are usually constructed in a non-planar stacked geometry, resulting in bulky volume, limited flexibility, and inconvenient serial and parallel connection via metal interconnects. Also, such MBs are generally fabricated by complicated manufacture processes, e.g. the photolithographic technique, and present unsatisfactory safety issues with flammable organic electrolytes. To overcome this, aqueous-based printed MBs with a separator-free planar geometry is acknowledged as a highly competitive class of microscale power sources due to the intrinsic non-flammability, high ionic conductivity of aqueous electrolytes [5,6], and great advances of planar device geometry with extremely short ion-diffusion pathways [7,8]. It is noteworthy that the printed planar MBs are highly favorable for direct integration of printed electronics on a single substrate, simultaneously combining the characteristics of outstanding flexibility, designable shapes, adjustable sizes, and space-saving connections.
So far, various printing techniques have been developed for fabricating traditional stacked batteries [9–12], such as lithium ion batteries by 3D printing [11], Zn–Ag batteries by inkjet printing [13], and Zn–air batteries by screen printing [14]. Also, great progress has been made with planar lithium thin-film MBs [15], lithium-ion MBs [16], Zn//Ag2O [3], Zn//LiMn2O4 [17], Zn//LiFePO4 [17], 3D MBs [18–20], and micro-supercapacitors [21–24] through the development of various microfabrication techniques, such as photolithography [25], electrodeposition [26], spraying [9,27], laser scribing [28], mask-assisted filtration [16], inkjet printing [10], roll-to-roll printing [29], and 3D printing [11,12]. In particular, screen printing can effectively control the precise pattern design with adjustable rheology of the inks, and is very promising for large-scale application [29]. Besides, screen printing is recognized as a cost-effective, easy-processing, and mass-production methodology for the fast construction of MBs, having precise control over the performance, flexibility, and integration with printed microelectronics. To address the cost effectiveness and safety issues, aqueous rechargeable Zn//MnO2 batteries, characterized by high abundance, low cost, non-toxicity and safety of both Zn and MnO2, as well as high output voltage of 0.9–1.8 V in aqueous electrolyte and high capacity of 820 mAh/g [30–32], are rising as one of the most compelling candidates [33–36]. Nevertheless, low-cost and scalable fabrication of aqueous-based Zn//MnO2 planar MBs with multiple innovative form factors of high performance, flexibility, and integration still remains challenging.

Herein we report a cost-effective and industrially applicable screen-printing strategy for fast and scalable production of rechargeable Zn//MnO2 planar MBs, featuring high performance, superior flexibility, scalable applicability, and high safety. The Zn//MnO2 planar MBs, free of separators, were manufactured by directly printing the zinc ink as the anode (thickness of 6.4 μm) and γ-MnO2 ink as the cathode (thickness of 9.8 μm), high-quality graphene ink as metal-free current collectors, working in environmentally benign neutral aqueous electrolytes of 2 M ZnSO4 and 0.5 M MnSO4. Benefiting from the suitable rheological properties of the inks and high electrical conductivity of microelectrodes (463 S/m for zinc anode, and 339 S/m for MnO2 cathode), the as-fabricated Zn//MnO2 MBs showed outstanding volumetric capacity of 19.3 mAh/cm3 at 7.5 mA/cm3 (393 mAh/g at 154 mA/g), high energy density of 17.4 mWh/cm³, long-term cycling stability (~83.9% after 1300 times at 5 C), designable shape, extraordinary flexibility, outstanding serial and parallel modular-ization for boosting the capacity and voltage output. Therefore, taking such impressive performance into account, our Zn//MnO2 MBs fabricated with screen-printing technology could potentially meet the stringent requirements of high performance, environmental friendliness, low cost, easy scalability, and high safety for printed electronics [37].

RESULTS AND DISCUSSION

The screen-printing fabrication of the interdigital Zn//MnO2 planar MBs is schematically illustrated in Fig. 1a–h. Firstly, highly stable and conductive graphene ink with appropriate rheological properties was printed on the substrates, e.g. flexible polyethylene terephthalate (PET), cloth, A4 paper, and even rigid glass (Fig. 1i–k), through a screen-printed process to form the interdigital planar patterns as metal-free current collectors, with a typical thickness of 1.4 μm, and exceptional electrical conductivity of 2.3 × 104 S/m (Fig. S1a, Supporting Information). Secondly, the anodic four fingers of asymmetric interdigital microelectrodes were deposited by extruding Zn-based ink (33.3 wt% Zn microparticles) (Fig. 2a, Figs S2a and S3a, b, Supporting Information) through the screen on one side of the four graphene current collectors. Thirdly, the cathodic four fingers were manufactured by screen-printing γ-MnO2-based ink (18.8 wt% MnO2 nanoparticles) (Fig. 2b, Figs S2b, S3c, d, and S4, Supporting Information) on the other side of the four graphene-based current collectors. Notably, all inks possessed typical thixotropic behavior, showing a decreasing viscosity with increasing shear rate, staying below 1 Pa·s from 10 to 8000 s⁻¹ (Fig. S5a–c, Supporting Information), which is highly important for precisely patterning microelectrodes [37,38]. The screen-printed Zn-based anode and MnO2-based cathode (SEM, Fig. S6, Supporting Information), with a typical thickness of 6.4 and 9.8 μm (Fig. 2c–f), exhibited high electrical conductivity of ~320 and ~450 S/m (Fig. S1b–c, Supporting Information), respectively. It is noted that the as-fabricated Zn//MnO2 planar MBs, free of both the separator and metal current collectors, exhibited extremely short ion-diffusion distances [39–42], and robust flexibility without film fracture and delamination from the substrate under various bending states (Fig. 2g–m) [8]. Furthermore, our screen-printing technique is highly simple, effective and scalable for low-cost production of flexible and seamlessly integrated Zn//MnO2 MBs with designable shapes and complex planar geometries, such as individual (Fig. 2g, j) and multiple parallel interdigital MBs via connection in series and in parallel (Fig. 2i, k), our institute logo MBs (Fig. 2h),
Figure 1. Fabrication of printed Zn//MnO$_2$ planar MBs. (a–d) Schematic of screen-printing fabrication of printed Zn//MnO$_2$ MBs: (a) the blank PET substrate, (b) the printed graphene current collectors, (c) the printed MnO$_2$ cathode and (d) the printed Zn anode. (e–h) Optical photographs showing the stepwise printing fabrication of Zn//MnO$_2$ MBs: (e) the blank PET substrate, (f) the graphene current collectors, (g) the printed MnO$_2$ cathode and (h) the printed Zn anode on interdigital graphene fingers. (i–k) Zn//MnO$_2$ MBs printed onto different substrates, including (i) cloth, (j) A4 paper, and (k) glass.

Regardless of the increased rates, it was observed that the polarization did not virtually increase at high discharge rates. Importantly, our MBs presented exceptionally high capacity at the different rates. It was revealed that the discharge capacity varies from 18.4 (5th cycle), 14.2 (15th cycle), 9.8 (25th cycle) to 7.7 (35th cycle) mAh/cm$^3$ with increasing rates from 0.5, 1, 3 to 5 C, respectively (Fig. 3b). Notably, the capacity thus readily returned to 9.6 (45th cycle), 13.6 (55th cycle) and 19.3 (65th cycle) mAh/cm$^3$ when the rates go back to 3, 1, and 0.5 C, respectively (Fig. 3b).

The long-term cycling stability of Zn//MnO$_2$ MBs is one of the most important performance metrics for actual applications. Through the elaborate screening of cathodic MnO$_2$ and anodic zinc powder, selection of aqueous electrolytes (ZnSO$_4$ + MnSO$_4$), processing of highly stable and conducting inks, and usage of metal-free graphene current collectors, together with advanced planar geometry with a shorter ion-diffusion pathway and free of separator, and a sophisticated screen-printing technique, synergistically working together, the resulting Zn//MnO$_2$ MBs showed remarkably satisfactory cycling performance (Fig. 3c, d, g). It is disclosed that the Zn//MnO$_2$ planar MBs displayed an impressive capacity of 15 mAh/cm$^3$ over 100 cycles at a low current density of 1 C. In sharp contrast, the stacked Zn//MnO$_2$ MBs based on sandwich-like Zn foil and MnO$_2$ electrode with a thickness of ~200 μm, prepared by conventional blade coating (MnO$_2$: acetylene black: polyvinylidene fluoride...
Figure 2. Characterization and shape diversity of printed Zn//MnO$_2$ planar MBs: SEM images of (a) Zn anode and (b) MnO$_2$ cathode; (c) 2D pseudo-color view and (d) 3D view of MnO$_2$ microelectrode finger on PET substrate, showing the microelectrode thickness of $\sim 9.8$ $\mu$m; (e) 2D pseudo-color view and (f) 3D view of Zn microelectrode finger on PET substrate, showing the microelectrode thickness of 6.4 $\mu$m; photographs of flexible Zn//MnO$_2$ MBs with various shape diversity, including (g) individual interdigital structure, (h) ‘DICP’ logo-based Zn//MnO$_2$ MBs, and (i) an energy-storage pack of Zn//MnO$_2$ MBs connected in a tandem fashion of 5 series $\times$ 3 parallel; photographs of shape-designable Zn//MnO$_2$ MBs under different bending states, including (j) an individual interdigital Zn//MnO$_2$ MB, (k) tandem energy-storage packs via self-connection of (g) interdigital Zn//MnO$_2$ MBs in 5 series $\times$ 3 parallel bent at 180$^\circ$, (l) four concentric-circle-shape, and (m) five linear-shape Zn//MnO$_2$ MBs in series, under flat and bending (180$^\circ$) states.

$\Delta = 8:1:1$), only showed about 4 mAh/cm$^3$ after 100 cycles at 1 C (Fig. 3d), which definitely identify the superior performance of the Zn//MnO$_2$ planar MBs. Importantly, the definite discharge voltage platform of the GCD profiles was still well maintained (Fig. 3e), further demonstrating the outstanding structural stability of microelectrodes. In addition, the GCD profiles show that the capacity of planar MBs (15 mAh/cm$^3$) is much higher than stacked MBs (4 mAh/cm$^3$). Electrochemical impedance spectroscopy (EIS) revealed that the slope of Zn//MnO$_2$ planar MBs is much higher than the stacked cell at low frequencies (Fig. 3f, Fig. S8), indicative of the faster ion diffusion in the thinner microelectrodes of planar MBs. Furthermore, our Zn//MnO$_2$ MBs displayed exceptional long-term cycling stability, with a capacity retention of 83.9% even at a high rate of 5 C after 1300 cycles (Fig. 3g), outperforming most reported Zn//MnO$_2$ batteries, such as Zn//$\beta$-MnO$_2$ (75% retention after 200 cycles) [30], Zn//MnO$_2$@poly(3,4-ethylendioxythiophene) (83.7% retention after 300 cycles) [33], yarn Zn//MnO$_2$ (98.5% retention after 500 cycles) [43], and Zn//MnO$_2$ (81.5% retention after 1000 cycles) [27]. The capacity decay was mainly attributed to the slow dissolution and disruption of the MnO$_2$ cathode, the volume changes of microelectrodes owing to the large size of Zn$^{2+}$ insertion/extraction, and the concomitant stresses on account of the irreversible side reaction [44]. Also, the capacity fluctuation of Zn//MnO$_2$ MBs was mainly caused by the slow and non-uniform permeation of aqueous electrolyte into the electrodes during the cycling process. Several factors working together contributed to the outstanding electrochemical performance. First, metal-free graphene current collectors can significantly enhance the electrical conductivity of microelectrodes, and remarkably improve the rate capability of Zn//MnO$_2$ MBs. Secondly, compared with $\alpha$-MnO$_2$ [45], the cathode of $\gamma$-MnO$_2$ with the mixed tunnels of
Figure 3. Electrochemical performance of printed Zn//MnO$_2$ planar MBs: (a) the GCD profiles, and (b) rate capability of Zn//MnO$_2$ MBs obtained from 0.5 C to 5 C; (c) the 1st, 40th, 90th, 100th GCD profiles, measured at a low rate of 1 C (15 mA/cm$^2$); (d) cycling stabilities of printed Zn//MnO$_2$ MBs with planar and sandwich-like stacked geometries, measured at a rate of 1 C; (e) the GCD profiles of the planar and stacked Zn//MnO$_2$ MBs; (f) EIS normalized to 1 of the planar and stacked Zn//MnO$_2$ MBs; (g) long-term cycling stability of Zn//MnO$_2$ planar MBs over 1300 cycles at a high rate of 5 C.

(1 \times 1)$ and $(1 \times 2)$, is favorable for the Zn$^{2+}$ ion intercalation/deintercalation in Zn//MnO$_2$ MBs, and also highly active to the proton, following the so-called two-step pathways in a mild electrolyte. Thirdly, the aqueous electrolyte containing Zn$^{2+}$ with a Mn$^{2+}$ additive has a high ionic conductivity of \(>1.0 \text{ S/cm}\), three orders of magnitude higher than organic electrolytes (\(10^{-3} \text{ S/cm}\)) \[46,47\], thereby greatly hindering the pulverization and dissolution of MnO$_2$ and effectively improving the cyclability \[48\]. Last but not least, the polymer-assisted stable and conductive inks could substantially prevent the enormous volume change and the concomitant huge stress, thus contributing to the superior cyclability. As a result, the specific capacity and long-term cyclability of our Zn//MnO$_2$ MBs are much better than those reported Zn//MnO$_2$ batteries (Tables S1 and S2).

To properly understand the charge storage mechanism of Zn//MnO$_2$ MBs, we further examined the cyclic voltammetry (CV) curves tested at different scan rates (Fig. 4a). It is evident that the two pair redox peaks (1.6 vs. 1.35 V, and 1.52 vs. 1.22 V) of the CV curves became gradually broader with increasing scan rate, but their shapes stayed almost consistent (Fig. 4a). To obtain an insight into the intrinsic mechanism of Zn//MnO$_2$ MBs, we further analyzed the CV curves using the classic kinetics equations \[49,50\], \(i = a v^b\) (or \(\log i = \log a + b \log v\)), where the current \(i\) obeys a power-rule relationship with the scan rate \(v\). Both \(a\) and \(b\) are adjustable parameters. The value \(b = 0.5\) indicates
Kinetics analysis of ion intercalation of printed Zn//MnO₂ planar MBs: (a) CV curves of Zn//MnO₂ MBs obtained at various scan rates (v) from 0.1 to 0.4 mV/s; (b) plots of log (i) versus log (v) curves of cathodic and anodic peaks.

A diffusion-controlled insertion process, while a b value of 1.0 represents a surface capacitive process. In terms of this regulation, it is calculated that, for our Zn//MnO₂ MBs, the b values of four peaks are 0.875 (peak 1) and 0.987 (peak 2), respectively (Fig. 4b), indicating that the electrochemical kinetics of Zn//MnO₂ MBs mainly involved the surface capacitive process, accompanied by the diffusion-controlled intercalation process to some extent, contributing to the superior performance [1].

To meet the demands of future flexible and integrated microelectronics, developing flexible and integrated Zn//MnO₂ MBs is urgently required. To highlight this feature, we examined CV curves of Zn//MnO₂ MBs under varying bending angles from 0 to 180° at a scan rate of 1 mV/s (Fig. 5a). Apparently, it is confirmed that all the CV curves with typical battery behavior are well overlapped (Fig. 5b), along with an extraordinary capacity retention of almost 100% even when bent at 180° (Fig. 5c), suggestive of highly stable flexibility. This is attributed to the advance of the separator-free planar geometry of Zn//MnO₂ MBs built on one substrate, which can greatly enhance the intimate contact between the microelectrodes and flexible PET substrate, without involving the multiple interfacial delamination of stacked MBs [17].

Furthermore, the integrated Zn//MnO₂ MBs were constructed via connection of multiple cells in series and in parallel (Fig. 5d), free of metal-based interconnects. It is worth noting that, from the GCD profiles, Zn//MnO₂ MBs connected in series displayed analogical electrochemical properties, and simultaneously a stepwise increase of output voltage from 1.3 V for a single cell to 2.6 V for two cells and 3.9 V for three cells (Fig. 5e), suggestive of exceptional performance uniformity. Moreover, in a parallel fashion, the volumetric capacity of the integrated Zn//MnO₂ MBs connected from one to three cells increased progressively, while the output voltage stayed almost unchanged (Fig. 5f). Notably, a tandem pack of two serially connected Zn//MnO₂ MBs can readily power a light-emitting diode (LED) for a significantly long time under the flexible state, and light up a display screen of our institute ‘DICP’ logo, manifesting the enormous potential of our integrated Zn//MnO₂ MBs (Fig. 5g, h).

The volumetric energy density and power density are also important performance metrics to evaluate microscale energy-storage devices; therefore, a Ragone plot is shown to compare our Zn//MnO₂ planar MBs with other miniaturized energy-storage devices (Fig. 5i). Encouragingly, our printed Zn//MnO₂ MBs could output a maximum volumetric energy density of 17.3 mWh/cm³ at a power density of 150 mW/cm³. This energy density is much higher than the commercially available supercapacitors (SC: 1 mWh/cm³), Zn-ion microsupercapacitors (Zn-MSC: 11.81 mWh/cm³) [2], and lithium thin-film battery (10 mWh/cm³) [51], ZnO//NiO (11 mWh/cm³) [52], and NiO//Fe₃O₄ (1.83 mWh/cm³) [53]. In addition, the power density of the Zn//MnO₂ MBs is 150 mW/cm³, three orders of magnitude higher than a lithium thin-film battery (0.08 mW/cm³). Therefore, our printed Zn//MnO₂ MBs not only manifest the merits of green, low-cost, scalable, and safe characteristics, but also possess high volumetric energy and power densities, making them suitable for numerous potential applications in miniaturized and printed electronics.

**CONCLUSIONS**

In summary, we have demonstrated the cost-effective and scalable fabrication of rechargeable printed Zn//MnO₂ planar MBs, with intriguing features of scalability, environmental benignity, high safety and metal-free current collectors, possessing high volumetric energy density, excellent rate capability and long-life cycling durability. Significantly, our printed Zn//MnO₂ MBs could be designed with various planar configurations, simultaneously representing designable artistic shapes, impressive flexibility, and remarkable modularization of building bipolar cells with high voltage and capacity output. More importantly, taking into the full considerations of low-cost and safe Zn, earth-abundant MnO₂, environmentally benign neutral aqueous electrolyte, and inexpensive screen-printing technology, our strategy of constructing printed Zn//MnO₂ MBs holds great potential as next-generation microscale power sources in various wearable, flexible, miniaturized and printed electronics [18].
Figure 5. Exceptional flexibility and integration of Zn//MnO$_2$ planar MBs. (a) Photographs, (b) CV curves, and (c) capacity retention of Zn//MnO$_2$ MBs tested under different bending angles. (d) Schematic illustration of the integrated Zn//MnO$_2$ MBs connecting three cells in series (top) and in parallel (bottom). (e, f) GCD profiles of the integrated Zn//MnO$_2$ MBs connected in series (e) and in parallel (f) from 1 to 3 cells. (g, h) Photographs of two serially connected Zn//MnO$_2$ MBs, lighting up a LED (g), and powering a display of our institute ‘DICP’ logo (h) in a flexible state. (i) Ragone plot of Zn//MnO$_2$ MBs compared with other microscale energy-storage devices (AC: active carbon, CNTs: carbon nanotubes).

METHODS
Preparation of Zn ink and MnO$_2$ ink
Polyurethane resin (99%, Henan DaKen Chemical Co., Ltd) was added into the dispersant of aromatic solvents (S150, 98%, Pengchen New Material Technology Co., Ltd) and ethylene glycol diglycidyl ether (99%, Hangzhou Dayangchem Co., Ltd). To fully dissolve the resin, the mixture was heated to 80°C for 2 h. Subsequently, graphene (Nanjing XF-NANO Materials Tech Co., Ltd), superfine graphite (Wuxi Hengtai Metal Material Co., Ltd), carbon black (90%, Zhengzhou Blue Ribbon Industry Co., Ltd) and MnO$_2$ powder (99.9%, Beijing DK Nano Technology Co. Ltd) were put into the above resin solution with an intense stirring of 1500 r/min for 30 min. After the resultant precursor was repeatedly ground under a three-roll grinder, MnO$_2$ ink was achieved. The mass proportion of polyurethane resin: graphene: superfine graphite: carbon black: MnO$_2$ powder is 3: 1: 1: 3: 2. The graphene conductive ink was prepared using the same reagent and procedure with graphene nanosheets (lateral size of 5–10 μm, 3–6 layers, Fig. S9), except with no addition of MnO$_2$. The Zn ink was made by uniformly mixing the as-prepared conductive ink and zinc powder (6–9 μm, 97.5%, Alfa Aesar) with a weight ratio of 2:1, when it was used.

Fabrication of Zn//MnO$_2$ MBs
Firstly, the highly conductive graphene ink was first printed on the PET, A4 paper, glass, or cloth substrates to form graphene-based current collectors and dried at 80°C in a vacuum box for 20 min.
until totally dry. Secondly, Zn-based ink via the same approach was overlapped as anode on one side of the graphene-based current collectors, while MnO₂-based ink was subsequently deposited as cathode on the other side of the graphene-based current collectors. Then, the screen-printed asymmetric microelectrodes of Zn//MnO₂ MBs were dried at 80 °C for 12 h. Afterwards, the neutral aqueous electrolyte of 2 M ZnSO₄ and 0.5 M MnSO₄ was slowly dropped onto the project area of the microelectrodes and packaged with Kapton tape. Finally, aqueous-based printed Zn//MnO₂ MBs were obtained. Note that the interdigital customized screen has eight fingers, with length of 12 mm, width of 1 mm and interspace of 1 mm (Fig. S10).

Materials characterization

The morphology, structure and composition of the active materials, graphene, the inks, and microelectrodes were analyzed using field-emission scanning electron microscopy (SEM, JSM-7800F), high-resolution transmission electron microscopy (HRTEM, JEM-2100), X-ray diffraction (XRD, X’pert Pro) (5–90°), four-point probe equipment (RTS-9), alpha step D-600, and thermogravimetric analysis (TGA, STA449F3) (measure data in atmosphere, 10°/min from 25 to 1000 °C).

Electrochemical measurement

The CV curves obtained at varying scan rates of 0.1–0.4 mV/s and EIS tested from 100 kHz to 0.01 Hz with an AC amplitude of 5 mV were conducted by an electrochemical workstation (CHI 760E), and the EIS tested from 100 kHz to 0.01 Hz with an AC amplitude of 0.4 mV/s and EIS tested from 100 kHz to 0.01 Hz. The morphology, structure and composition of the active materials, graphene, the inks, and microelectrodes were analyzed using field-emission scanning electron microscopy (SEM, JSM-7800F), high-resolution transmission electron microscopy (HRTEM, JEM-2100), X-ray diffraction (XRD, X’pert Pro) (5–90°), four-point probe equipment (RTS-9), alpha step D-600, and thermogravimetric analysis (TGA, STA449F3) (measure data in atmosphere, 10°/min from 25 to 1000 °C).

SUPPLEMENTARY DATA

Supplementary data are available at NSR online.

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