Defect engineering of MnO₂ nanosheets by substitutional doping for printable solid-state micro-supercapacitors

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Abstract
Printed flexible energy storage devices such as micro-supercapacitors require high electrochemical performance for practical applications. Here, we report a high volumetric energy density of up to 1.13 × 10⁻¹⁰ Wh cm⁻³ at a power density of 0.11 W cm⁻³ by inkjet printing of Fe-doped MnO₂ nanosheets inks as active materials on polyimide substrates. The enhancement results from atomic-level substitutional doping of 3d metal ions (Co, Fe, Ni) in sub-nanometer thick 2D MnO₂ nanosheets. Substitutional doping introduces new electronic states near the Fermi level, thereby enhancing the electronic conductivity and contributing to the formation of redox-active 3d surface states. Fe-doped MnO₂ showed the best performance in terms of specific areal and volumetric capacitance. Our finding suggests that the rational doping at atomic scale shows great promise for achieving high energy and power density flexible energy storage devices.

1. Introduction

Two-dimensional (2D) materials have attracted great attention for supercapacitors (SCs) because of their unique physical and chemical properties induced by the dimensional reduction [1–3]. Specifically, 2D nanosheets with a few atomic-layer thickness and large specific surface area can expose nearly all its atoms as surface sites for charge storage, which facilitates the ion diffusion and the charge storage and transfer processes. Recently, various nanosheets have been explored for SCs, including graphene [4], black phosphorus [5], metal dichalcogenides [6], layer double hydroxides [1], transition metal carbides [7], and transition metal oxides (TMOs) [8,9]. Among these, TMOs are known as pseudocapacitive phases with high theoretical specific capacitance, and are thus promising electrode materials for SCs. From the TMO phases, 2D manganese dioxide nanosheets have been attracting interest due to the earth abundance of Mn, low toxicity and particularly their ultrathin nanosheets in SCs is limited by poor electronic conductivity. One of the strategies to improve the electronic conductivity and electrochemical performance of MnO₂ electrodes is to combine it with highly conductive materials such as graphene, carbon nanotubes or carbon fibers [14]. An alternative strategy is defect engineering, i.e. foreign element doping to enhance the intrinsic electronic conductivity and increase the concentration of redox-active sites [15–17]. Thus far, defect engineering has not resulted in notable improvement in electrochemical performance. Transition metal cations like Fe³⁺, Co²⁺ and Ni²⁺ are known to be stable in the framework of birnessite [18–20], but their effect on the electronic conductivity of MnO₂ nanosheets is still unknown.

Micro-supercapacitors (MSCs) which feature rapid power delivery, on-chip integration and miniaturized device size, are promising energy storage devices for small flexible electronic devices [21–24]. Versatile fabrication techniques have been utilized to directly deposit materials on different substrates to fabricate interdigitated electrode patterns for MSCs, such as laser scribing, electrochemical deposition, conversion reaction and inkjet printing [25]. While the laser scribing technique suffers from high cost, the electrochemical deposition and conversion reactions are restricted by the shapes of current collectors. Inkjet printing, which is a digital, non-contact, and high resolution deposition technique, does not require an intermediate carrier for deposition on a wide range of substrates such as silicon, glass, paper or flexible polymers [26–29]. However, preparation of printable functional inks remain a significant challenge for printed electronics.

In this work, we report inkjet-printed 2D MnO₂ nanosheet-based...
micro-supercapacitors with very high volumetric energy densities of up to 1.13 × 10⁻³ Wh cm⁻³ at a power density of 0.11 W cm⁻³. The excellent performance could be accomplished by atomic-level substitutional doping of 3d metal ions (Co, Fe, Ni) into 2D MnO₂ nanosheets by a facile bottom-up method, which introduced new electronic states near the Fermi level, thereby enhancing the electronic conductivity within the nanosheets and contributing to the formation of redox-active 3d surface states. Stable water-based inks were prepared without toxic solvents and were based on the surfactant-templated self-assembly of MnO₂ nanosheets in water. Three-electrode measurements were conducted on inkjet-printed undoped MnO₂, and on Fe, Co and Ni-doped MnO₂ nanosheet thin films. The influence of substitutional doping on band structure and the excellent performance of Fe doping in particular was explained using first principles calculations, which demonstrates that substitutional doping can largely improve the electrochemical performance of 2D oxide materials.

2. Experimental section

2.1. Synthesis of Fe, Co and Ni-doped MnO₂ nanosheets

In a typical synthesis, 20 mL of a mixed aqueous solution of 0.6 M tetrabutylammonium hydroxide (TB₄NOH, 40 wt% H₂O, Alfa Aesar) and 3 wt% H₂O₂ (30 wt% H₂O₂, Aldrich) was added to 10 mL of 0.3 M aqueous solution consisting of FeCl₃ (Fluka) and MnCl₂·4H₂O (Sigma-Aldrich) in a molar ratio of 0.05 (0.05 = Fe/(Fe + Mn)) within 15 s of mixing. FeCl₃·4H₂O (Acros Organics) and NiCl₂·6H₂O (Alfa Aesar) were used to prepare Co–MnO₂ and Ni–MnO₂ nanosheets at same molar ratio of 0.05. The resulting dark brown solution was stirred vigorously overnight in the ambient atmosphere at room temperature. The obtained solution was centrifuged using a Sigma 14 centrifuge at 1000 g for 20 min to remove unreacted metal ions (Co, Fe, Ni) into 2D MnO₂ nanosheets ink; the precipitate was washed by propylene glycol (Sigma-Aldrich): water by mass, 0.06 mg mL⁻¹ Triton X-100 and 6 vol% ethylene glycol (Merck) were added into PEDOT: PSS (3.0-4.0%, Sigma Aldrich) ink, 2 vol% Triton X-100 and 6 vol% ethylene glycol (Merck) were added into PEDOT: PSS solution.

2.2. Ink preparation

To prepare printable Fe, Co and Ni-doped MnO₂ nanosheets ink, the collected precipitate was re-dispersed in a printable solvent consisting of 1:10 propylene glycol (Sigma-Aldrich): water by mass, 0.06 mg mL⁻¹ Triton X-100 (Sigma-Aldrich). To estimate the concentration of resultant printable inks, the optical absorbance was measured by PerkinElmer UV/VIS/NIR spectrometer Lambda 950S from 800 to 2000 nm wavelength. Concentrations were extracted using Lambert-Beer law A/I = αC1l, where A is the absorbance, I = 1 cm is the cell length, C is the concentration of resultant inks and the absorption coefficient α is 1.13 × 10⁶ mol⁻¹ dm³ cm⁻¹. All inks were diluted to the same concentration for inkjet printing. To prepare printable poly (3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT: PSS) (3.0-4.0%, Sigma Aldrich) ink, 2 vol% Triton X-100 and 6 vol% ethylene glycol (Merck) were added into PEDOT: PSS solution.

2.3. Inkjet printing

A Dimatix DMP-2800 inkjet printer (Fujifilm Dimatix) equipped with a 16-nozzle cartridge and typical droplet volume of 10 pl was used to print all patterns. To fabricate electrodes for three-electrode measurements, Fe, Co, Ni-doped and pristine 5%MnO₂ nanosheets inks were printed at 50 °C with 20 µm drop spacing on polycrystalline substrate in 5 layers, followed by drying at 50 °C for 2 h. Then, 2 layers of PEDOT: PSS film were printed at room temperature with 20 µm drop spacing on top of all MnO₂ samples followed by annealing at 120 °C for 15 min.

2.4. Fabrication of micro-supercapacitors

All inks were inkjet printed in 5 layers at 20 µm drop spacing on a 120 µm thick flexible polyimide substrates at 50 °C. Then, 2 layers of PEDOT: PSS were printed at 20 µm drop spacing on top of the all MnO₂ nanosheets thin films, followed by thermal annealing at 120 °C for 15 min. The prepared PEDOT: PSS/nanosheets films were used as electrodes for symmetrical MSCs. The PVA/LiCl gel electrolyte was prepared by mixing 1 g PVA (Mw 85000–124000, Aldrich), 2.13 g LiCl (Alfa Aesar) and 10 mL DI water thoroughly at 85 °C under vigorous stirring. To complete the fabrication of MSC, the gel electrolyte was deposited on the electrodes area of MSC, and was dried overnight at room temperature.

2.5. Electrochemical characterisation

All electrochemical characterizations were done on an Autolab workstation (PGSTAT128 N). The printed thin film electrodes were measured in 0.5 M Na₂SO₄ (ABCR GmbH) and 5 M LiCl solution in a three-electrode configuration with Ag/AgCl (3 M KCl) electrode (Metrohm) and platinum wire as the reference and counter electrodes, respectively. The all-solid-state MSC was characterized in a two-electrode configuration. Cyclic voltammetry was performed at a scan rate of 5–50 mV s⁻¹; galvanostatic charge-discharge curves were measured at current densities from 10 to 100 μA cm⁻². Electrochemical impedance spectroscopy was performed by applying an AC voltage of 10 mV amplitude in the frequency range from 0.1 Hz to 10 kHz. The high frequency impedance characteristics were interpreted in terms of a R₁(R₂Q) equivalent circuit, where R₁ represents the series resistance of the nanosheet based electrode, R₂ its charge transfer resistance, and Q a constant phase element.

2.6. First principles calculations

The first principles calculations were carried out within the framework of density functional theory (DFT) using the projector augmented wave (PAW) method [30] and a plane-wave basis set with a cut-off energy of 500 eV as implemented in the VASP code [31,32]. In this paper, exchange and correlation effects were described in the local spin density approximation (LSDA) as parameterized by Perdew and Zunger [33] with an on-site Coulomb interaction U added onto d orbitals [34]. The effective Coulomb term Ueff of 3.2 eV, 3.6 eV and 2.8 eV were chosen for Mn, Fe, Co, and Ni 3d orbitals, respectively [35]. Monolayers of MnO₂ periodically repeated in the c direction were separated by more than 20 Å of vacuum to minimize the interaction. The atomic positions were relaxed using a 5 × 4 × 1 Γ-centered k-point mesh until the forces on each ion were smaller than 0.01 eV Å⁻¹. Spin-polarized calculations were performed with a denser mesh corresponding to 8 × 8 × 1 k-points.

2.7. Characterisation

Powder X-ray diffraction (XRD) was performed on a Bruker diffractometer (D8 Advance) with Cu Kα radiation (λ = 0.15405 nm). Thin film XRD was measured by a PANalytical X'Pert Pro with Cu Kα radiation (λ = 0.15405 nm). AFM (Veeco Dimension Icon) was conducted in standard tapping mode. The AFM data were analyzed by Gwydion (version 2.47) software. Image-corrected TEM was performed by model Titan 80–300 ST (300 kV) with energy dispersive X-ray spectroscopy (EDS) capability. X-ray photoelectron spectroscopy (XPS) was conducted by an Omicron Nanotechnology GmbH (Oxford Instruments) surface analysis system with a photon energy of 1486.7 eV (Al Kα X-ray source) with a scanning step size of 0.1 eV. The pass energy was set to 20 eV. The spectra were corrected using the binding energy of C 1s of the carbon residual on nanosheets as a reference. High resolution scanning electron
microscopy and EDS analyze (HRSEM; Zeiss MERLIN) were performed to acquire information of printed Fe, Co and Ni-doped MnO₂ films. Fe-, Co- and Ni-doped MnO₂ Raman spectra were recorded on a micro-Raman spectrometer (LabRAM ARAMIS, Horiba-Jobin Yvon, Germany) using a 633 nm laser. Undoped MnO₂ Raman spectra was recorded on a laser-scanning confocal Raman microspectrometer by Krypton laser (Innova 90-K; Coherent, Santa Clara, CA, λexc 647.1 nm).

The specific areal capacitance \( C_A \) of film electrodes was calculated from the GCD curves by using Equation (1):

\[
C_A = \frac{\left[ I / \left( \frac{dV}{dt} \right) \right]}{A_{\text{electrode}}} \tag{1}
\]

where \( I \) is the discharge current, \( \frac{dV}{dt} \) is the slope of discharge curve, and \( A_{\text{electrode}} \) refers to the area of the film electrode.

The specific areal capacitance \( C_{A,\text{device}} \) and volumetric capacitance \( C_{V,\text{device}} \) of the MSC devices were also calculated from the GCD curves according to equations (2) and (3), respectively

\[
C_{A,\text{device}} = \frac{\left[ I / \left( \frac{dV}{dt} \right) \right]}{A_{\text{device}}} \tag{2}
\]

\[
C_{V,\text{device}} = \left[ \frac{1}{2} \frac{I}{V_{\text{device}}} \right] \frac{dV}{dt} \tag{3}
\]

where \( A_{\text{device}} \) refers to the total area of the device including the electrodes and the gap between the electrodes, \( V_{\text{device}} \) refers to the total volume of the device, including the volume of the electrodes and the gap between the electrodes.

The volumetric energy densities \( E_V, \text{Wh cm}^{-3} \) and power densities \( P_V, \text{W cm}^{-3} \) were calculated from equations (4) and (5)

\[
E_V = C_{V,\text{device}} V^2 / (2 \times 3600) \tag{4}
\]

\[
P_V = 3600 \times E_V / \Delta t \tag{5}
\]

where \( \Delta t \) refers to discharge time.
3. Results and discussion

3.1. Nanosheets characterizations

The crystal structures and phase information of the Fe, Co and Ni-doped MnO₂ nanosheets (Referred to as Fe–MnO₂, Co–MnO₂ and Ni–MnO₂, respectively) were acquired from powder X-ray diffraction (XRD) of freeze-dried samples as shown in Fig. 1a. All the patterns show the reflections of (00l) series that indicate the laminar and ultrathin features of the prepared samples. Two asymmetrical in-plane (100) and (110) reflections at 2θ = 36° and 65° are observed in all samples, indicating a hexagonal unit cell and the layered birentiss-type structure in Fe, Co and Ni-doped MnO₂ nanosheets [36]. The small differences between the (002) diffraction peak angles can be explained by small variations in the spacings between nanosheets in different restacked 2D structures. Element mappings from energy-dispersive spectroscopy (EDS) show homogeneous spatial distributions of Fe (Fig. 1b), Co and Ni (Fig. S1, Supporting Information) in the basal plane of MnO₂ and the incorporation of foreign atoms into the MnO₂ nanosheet lattice. The solubility of Fe, Co and Ni in the MnO₂ nanosheet crystal structure can be attributed to the similar ionic radius, oxidation state and electronegativity.

The thickness of nanosheets, deposited on silicon substrates by the Langmuir-Blodgett (LB) method [37], as determined by atomic force microscopy (AFM), showed average thicknesses of 1.0–1.8 nm for Fe–MnO₂ (Fig. 1c), Co–MnO₂ and Ni–MnO₂ (Fig. S2, Supporting Information), respectively, in accordance with the reported AFM thicknesses of MnO₂ nanosheets in our previous report [38]. The variation in thickness and difference with the crystallographic thickness, which is 0.52 nm based on its atomic architecture, is attributed to hydration and the presence of organic ions, i.e., TBA⁺ on both sides of the nanosheets [36,39]. The lateral sizes of Fe, Co and Ni-doped MnO₂ nanosheets estimated from AFM images indicate that the majority of nanosheets have lateral sizes between 50 and 150 nm, 40–120 nm and 40–140 nm for Fe, Co and Ni-doped MnO₂ nanosheets, respectively (Fig. S3, Supporting Information), which are suitable dimensions for ink jetting [10].

X-ray photoelectron spectroscopy (XPS) scans in Figs. S4a–e (Supporting Information) reveal the presence of Fe, Co and Ni elements in Fe, Co and Ni-doped MnO₂, respectively, which is consistent with the EDS mapping data. The high resolution spectrum of Fe 2p shows two binding energy (BE) peaks that can be assigned to Fe 2p½ and Fe 2p½, respectively (Fig. 1d). The BE difference of 13.7 eV indicates the presence of Fe³⁺ [40]. The high resolution spectrum of Co 2p shows two BE peaks at 781.3 and 797.5 eV that can be assigned to Co 2p½ and Co 2p½, respectively (Fig. 1e), indicating the existence of Co⁴⁺ [41]. The high resolution Ni 2p spectrum in Fig. 1f shows two BE peaks that are Ni 2p½ at 855.1 and Ni 2p½ at 872.8 eV, and two broad satellites peaks which can be assigned to Ni⁵⁺ [42]. The high resolution XPS of Mn 2p shows spin-orbit doublet corresponding to the Mn 2p½ and Mn 2p½ states (Fig. S4d, Supporting Information) which can be used to roughly determine the oxidation state of Mn. However, due to the complex oxidation and spin states in the Mn 2p spectrum, the splitting of Mn 3s peaks is normally used as a probe to determine the oxidation state of Mn, as shown in Fig. 1g. The ∆E values are 4.8 eV for pristine δ-MnO₂ nanosheets, 5.2 eV for Fe–MnO₂ nanosheets, 5.3 eV for Co–MnO₂ nanosheets and 5.0 eV for Ni–MnO₂ nanosheets, indicating the coexistence of Mn⁵⁺ and Mn³⁺ in Fe, Co and Ni-doped MnO₂ nanosheets. In order to maintain charge neutrality, it is likely that oxygen vacancies were also present in the structure, and these have been shown to occur in MnO₂ nanosheets [43]. Furthermore, the Raman spectra in Fig. S5 (Supporting Information) confirm that undoped and doped MnO₂ nanosheets have their characteristic peaks at similar positions, indicating that the structure of MnO₂ was maintained upon doping.

3.2. Formulation of water-based printable nanosheets inks

Water-based inks were developed following the protocol reported in our previous work [38]. The ink formulation was optimized to have optimal rheological properties for inkjet printing. The surface tension and viscosity of water-based inks were 46 mN m⁻¹ and 1.7 mPa s, respectively. As an example, the good quality viscoelastic properties and stability of the Fe–MnO₂ ink is illustrated by the stroboscopic images of ink droplet formation versus time; no satellite droplets can be seen (Fig. S6, Supporting Information). Top-view SEM images of inkjet-printed Fe (Fig. 1h), Co and Ni-doped MnO₂ nanosheets (Fig. S7, Supporting Information) films on silicon substrates indicate uniform deposition of nanosheets and good film continuity across a large surface area. The surface roughness of printed films by AFM at different length scales (Fig. S8, Supporting Information) showed similar root mean square (RMS) values. The scan area does not have a large influence on the RMS roughness values, which indicates highly uniform printed nanosheet films. The x-ray diffractograms (XRD) of all films in Fig. 1i show (00l) series reflections at 2θ = 5.3°, 10.7°, 15.9°, 21.6° and 27.1°, originating from the (001), (002), (003), (004) and (005) reflections, respectively. The presence of higher order basal peaks indicates highly c-oriented and laminar features with a layer spacing of 1.6 nm. This distance is large enough to facilitate ion diffusion between the interdigitated electrodes of MSCs. The doping concentrations were estimated by EDS and were found to be about 5.3%, 5.3% and 4.7% for Fe, Co and Ni-doped MnO₂ nanosheets, respectively (Fig. S9, Supporting Information), in accordance with the nominal element compositions targeted during synthesis.

3.3. Three-electrode measurement of printed electrodes

Thin film electrodes fabricated by printing poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT: PSS)/MnO₂ nanosheet films were studied in a three-electrode electrochemical setup. The cyclic voltammetry (CV) curves of Fe, Co and Ni-doped MnO₂ electrodes at a scan rate of 5 mV s⁻¹ in Fig. 2a show broad redox peaks that contribute more capacitance than the corresponding undoped δ-MnO₂ electrode in the potential window from 0 to 1 V (versus Ag/AgCl), as demonstrated by the area integrated within the current-potential curves. The electrochemical activity of the Fe–MnO₂ electrode is clearly much larger than that of the Co–MnO₂, Ni–MnO₂ and pristine δ-MnO₂ electrodes. Notably, the pair of redox peaks of Fe–MnO₂ at 0.72 and 0.46 V provide more redox-active sites than pure MnO₂, arising from the pseudocapacitance generated by the faradic redox reactions of mixed valent MnO₂ and doped Fe³⁺, which was also confirmed in a 5 M LiCl electrolyte (Fig. S10, Supporting Information) [44]. The governing surface redox reactions are as follows:

\[
\text{MnO}_2 + \text{Na}^+ + e^- \rightarrow \text{MnOONa}. \quad (6)
\]

\[
\text{Fe(III)} + e^- \rightarrow \text{Fe(II)} \quad (7)
\]

The higher specific capacitance of the Fe-doped MnO₂ electrode compared with Co and Ni-doped MnO₂ is confirmed by the galvanostatic charge/discharge (GCD) curves between 0 and 1 V at varying current densities (Fig. 2b–c, Fig. S11, Supporting Information). The potential does not show a linear change with time, indicating a faradic redox reaction during charging and discharging. The bare PEDOT: PSS film showed a smaller current response than the electrodes, indicating the negligible contribution of PEDOT: PSS to the overall capacitance. The areal capacitances of all samples are shown in Fig. 2d. At current density of 0.1 mA cm⁻², the areal capacitance is 39 mF cm⁻² for Fe–MnO₂ electrode, 22 mF cm⁻² for Co–MnO₂ electrode, 24 mF cm⁻² for Ni–MnO₂ electrode and 12 mF cm⁻² for the pristine δ-MnO₂ electrode. Electrochemical impedance spectroscopy (EIS) was employed to study the series resistance and charge transfer resistance of all electrodes, as shown in Fig. S12 (Supporting Information). All doped MnO₂ electrodes...
exhibited lower series resistance (indicated by the real axis value at high frequency intercept) and lower charge transfer resistance (indicated by the radii of the semicircle in the high frequency region) than undoped MnO₂ electrode. Specifically, Fe–MnO₂ electrode showed the lowest series resistance and charge transfer resistance of all samples (Table S1, Supporting Information). These experimental data clearly demonstrate that substitutional doping improves both the electronic conductivity of the MnO₂ nanosheets, as well as their electron transfer kinetics.

### 3.4. First principles calculations

First principles calculations were carried out to gain further insight into the effect of aliovalent doping on the electronic properties of MnO₂ nanosheets. The band structures are shown in Fig. S13 (Supporting Information). The model structure used here, a 2D 4x5 MnO₂ supercell with one dopant atom at its center, may be simplified with respect to the real defect structure of doped MnO₂, but it does provide qualitative insight into the general trends of foreign element doping on the band structure of (doped) MnO₂. The partial density of state (PDOS) of pristine δ-MnO₂ nanosheets shown in Fig. 3a indicates semiconducting behavior with a band gap of 2.16 eV, which is in good agreement with the reported experimental band gap of 2.23 eV [45]. By introducing 5% Fe doping, occupied and unoccupied impurity states emerge in the fundamental band gap so that the chemical potential is increased, which effectively decreases the band gap and increases the mobile charge carrier density (Fig. 3b). Only empty impurity states form in the band gap for Ni and Co doped systems (Fig. 3c–d) and these do not contribute much to the carrier density as illustrated in Fig. 2. The origin of the difference lies in the competition of crystal field splitting and spin interaction effects with the radii of the semicircle in the high frequency region) than undoped MnO₂ electrode. Specifically, Fe–MnO₂ electrode showed the lowest series resistance and charge transfer resistance of all samples (Table S1, Supporting Information). These experimental data clearly demonstrate that substitutional doping improves both the electronic conductivity of the MnO₂ nanosheets, as well as their electron transfer kinetics.

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compositions is smaller than that of undoped MnO$_2$ (2.14 eV).

3.5. Electrochemical performance of printed MSCs

A symmetrical MSC with interdigitated Fe–MnO$_2$ nanosheet-based electrodes was printed on a polyimide substrate, and CV and galvanostatic charge-discharge measurements were conducted. The CV curves at scan rates between 5 and 50 mV s$^{-1}$ (Fig. 4a) are confirmed in the GCD curves (Fig. 4b). The CV curves in Fig. 4a are qualitative match with three-electrode measurements in Fig. 2a. The possible reasons for the Faradaic character in Fig. 4a are the lower ions mobility in gel electrolyte compare with liquid electrolyte and polarizations effect. The areal capacitances and volumetric capacitances calculated from the GCD curves (Fig. 4c) showed that the highest areal and volumetric capacitances are 1.2 mF cm$^{-2}$ and 9.2 F cm$^{-3}$ at a current density of 30 $\mu$A cm$^{-2}$, respectively. Notably, the surface area used for the calculation of the capacitance includes the area and the gap between the electrodes, while the volume in the calculation included the volume of the electrodes and the spatial gap between the electrodes.

To test the mechanical flexibility and ductility in conjunction with their electrochemical performance, the CV characteristic was measured at different bending angles (Fig. 5a). The CV curves remained unaffected when the devices with the device area of around 1.2 cm$^2$ (Fig. 5b) and electrodes thickness around 1.3 $\mu$m were bent with a bending radius of about 2 cm. The cross-sectional SEM image of a printed Fe–MnO$_2$ film and corresponding optical microscopy images of printed electrodes and the interspace between them are shown in Fig. S16 (Supporting Information). The MSC showed 86.7% capacitance retention after 300 bending cycles with bending radius of about 2 cm (Figs. 4d), and 78.7% capacitance retention after 5200 charge-discharge cycles without bending (Fig. 4e), indicating good cycling stability. The MSC reached the highest volumetric energy density ($E_V$) of 1.13 $\times$ 10$^{-3}$ Wh cm$^{-3}$ at a volumetric power density ($E_P$) of 0.11 W cm$^{-3}$, which is superior to the performance of MSCs based on inkjet-printed $\delta$-MnO$_2$ nanosheets (Fig. 4f) [38]. The $E_V$ of MSC is higher than commercial 3V/300 $\mu$F Al electrode capacitors [47], and the $E_P$ of our MSC is higher than that of a 4V/500 $\mu$Ah lithium thin film battery [47]. Although the 3V/300 $\mu$F Al electrode capacitors and 4V/500 $\mu$Ah lithium thin film battery show higher power density and energy density than our MSC, respectively, the Fe-doped MnO$_2$ based MSC demonstrated here is performing better when considering the combination of energy and power density. Moreover, the performance of printed Fe–MnO$_2$ nanosheet MSCs is comparable to or better than that of other devices based on MnO$_2$@carbon fibers [48], graphene [49], MnO$_2$@multiwalled carbon nanotube (MWCNT) [50], and boron-doped laser-induced graphene (B-LIG) [51]. The self-discharge rate of MSCs is a major issue for practical applications. During self-discharge, a small amount of leakage current could cause the voltage decay of a charged supercapacitor over time [52]. As shown in Fig. 5c, the MSC shows an ultra-small leakage current of <700 nA after 10 h, compared with 5 $\mu$A for commercial SCs [52]. Since most SCs are working in the range of $V_{\text{max}}$ to $\frac{1}{2} V_{\text{max}}$ [53], the self-discharge time for such a voltage drop is practically relevant. The Fe–MnO$_2$ MSC self-discharges from 1 V to 0.5 V in about 12 h (Fig. 5d), which is comparable with two commercial supercapacitors that show self-discharge rates of 8 h and 21 h [52], thus suggesting that the Fe–MnO$_2$ MSC is a promising candidate material for practical applications.
applications that require long lifetime and high reliability.

4. Conclusions

In summary, we have demonstrated atomic-level engineering of MnO₂ nanosheets by substitutional doping with Fe, Co and Ni atoms.
The theoretical calculations show that the excellent electrochemical behavior of Fe-doped MnO₂ nanosheets can be attributed to the new electronic states emerging near the Fermi level that increase the electronic conductivity and form additional surface redox sites. Owing to their excellent dispersibility in water, the Fe-, Co-, and Ni-MnO₂ nanosheets could be formulated directly in water-based stable inks. As best performing candidate among the tested compositions, Fe-MnO₂ nanosheet ink was used to fabricate all-solid-state flexible MSCs on polyimide substrates by inkjet printing technology. The printed MSC exhibited superior performance in terms of the combination of high energy density and high power density when compared to other state of the art concepts, and commercially available products on the market. In comparison with undoped 2D MnO₂ MSCs [38], both the power density and the energy density increased by a factor of more than 6. The printed Fe-MnO₂ MSC showed good cycling stability and good mechanical properties in terms of flexibility and ductility. Overall, both inkjet-printed all-solid-state MSCs and the proposed substitutional doping strategy hold great potential to develop next-generation high energy and high power energy storage devices for portable electronics and wearable electronics applications.

Declaration of competing interest

The authors declare no competing financial interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.nanoen.2019.104306.

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