Advances in Ink-Jet Printing of MnO₂-Nanosheet Based Pseudocapacitors

Johan E. ten Elshof* and Yang Wang*

An overview of recent progress in the development of 2D manganese oxide nanosheet-based pseudocapacitors is provided, with emphasis on underlying methods and strategies. 2D manganese oxide nanosheets are sheet-like monocrystallites of ≈ 0.5 nm thickness and lateral dimensions of 50–5000 nm. MnO₂ nanosheets are synthesized in the form of colloids, which can be readily utilized in wet-chemical processes like ink-jet printing. The synthetic strategies to make 2D δ -MnO₂ nanosheets by bottom-up and top-down approaches are discussed, and the relationship between the ionic defect structure of δ -MnO₂ nanosheets and their pseudocapacitance is explained. The basic principles and experimental challenges of ink-jet printing of 2D materials at high resolution, and the development of 2D nanosheet-based inks are discussed, with emphasis on δ -MnO₂, graphene, and graphene oxide. The fabrication and performance of δ -MnO₂ nanosheet derived pseudocapacitors, including ink-jet printed flexible microsupercapacitors, is described. The relationship between the electrode thickness and layer architecture and the specific capacitance is explained.

for small-sized supercapacitors in electrical appliances, autonomous devices, and flexible electronics will increase further. In order to enable the fabrication of such high-performance flexible micro-supercapacitor (MSC) devices on large scale at low cost, it is necessary to develop new scalable, versatile, solution-based methods and printing techniques.

Supercapacitors can be divided into two main classes, i.e., electrochemical double layer (EDL) capacitors and pseudocapacitors.^[1] The energy density of EDL capacitors is limited to the charge that can be stored in the so-called electrochemical double layer that is present in the electrolyte near the electrode surfaces. EDL capacitors typically employ metallic or graphitic electrodes. Pseudocapacitors also make use of fast and reversible faradaic reactions at the electrode surface. This requires the use of specific materials with

1. Introduction

The rapid penetration of portable consumer electronics and autonomous devices in our society has led to a growing need for small-scale electrochemical storage (EES) devices to provide them with energy. The currently dominant energy sources are rechargeable Li ion batteries, which have a high energy density. They are powering almost all forms of consumer electronics and electric vehicles. The energy density of supercapacitors is considerably smaller, but supercapacitors are appreciated for their high power density, long cycle life and safe operation. Supercapacitors are particularly useful in applications where a large amount of electrical energy needs to be stored or delivered quickly. Supercapacitor technology is developing quickly because of their increasing need in the ongoing electrification of our society. Next to their use in electrical vehicles, especially buses that have to stop frequently where charging facilities can be provided, energy storage based exclusively on ultracapacitors becomes viable. It can also be foreseen that the need

a high concentration of surface redox sites. Since the EDL effect is also operative in pseudocapacitors, they can achieve significantly higher energy densities than EDL capacitors can. The best pseudocapacitive materials are transition metal oxides. In particular, hydrous RuO₂, MnO₂, V₂O₅, several spinel phases and lamellar transition metal hydroxides can exhibit very high specific capacitances.^[2]

One of the most promising families of materials for pseudocapacitors are the manganese oxide phases.^[3] Manganese oxide is abundantly present on Earth. It has a low toxicity and is an environmentally nonharmful element. It can crystallize in a number of polymorphs and morphologies. Manganese oxide is being used on large scale in Li ion batteries, however it also exhibits a very large pseudocapacitance.^[4] The electrochemical properties of MnO₂ based electrodes are determined by their crystal structure, morphology, conductivity, mass loading, and the type of electrolyte used. Faradaic surface charge storage is accomplished by adsorption and desorption of protons or alkali cations from the electrolyte. One of the main disadvantages of MnO₂ is its low conductivity, which limits the pseudocapacitive redox reactions to the surface and near-surface layers. Careful engineering of the crystal structure and electrode morphology of MnO₂ based electrodes is therefore of crucial importance to maximize their energy density and performance. A thin sheet-like crystal shape is advantageous in this respect, since it provides a high specific surface area, in the extreme limit all atoms are (near-)surface atoms. Research on such 2D materials for supercapacitor technology has exploded over the

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The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/smt.201800318>.

DOI: 10.1002/smt.201800318

past few years.^[5] One of the manganese oxide polymorphs consists of such 2D building blocks, namely the layered δ -phase, also known as birnessite. As discussed in the next section, there are synthetic strategies with which individual 2D MnO_2 building blocks can be isolated from birnessite crystals, or be synthesized directly from solution. Since the specific capacitance scales with surface area, very high capacitances can in principle be reached with these building blocks. Their single-crystalline nature and lateral dimensions in the micrometer-range and their high aspect ratios, typically in the range of 100–5000, allow the formation of percolative oxide networks via which electrons can be transported to the back electrode over large distances, even when the volume fraction of nanosheets would be limited.^[6] The sheet structure can also be hybridized with more conductive components, e.g., graphene and derivatives thereof, or carbon nanorods. Nanosheets are mechanically flexible due to their thinness even though they are oxides. This makes them bendable, and allows them to be applied in thin film form in flexible and wearable electronic applications.

Due to its simple, versatile and low-cost features, ink jet printing (IJP) shows great potential for fabrication of supercapacitor with any desired configuration, e.g., interdigitated, asymmetric, etc. Since nanosheets are typically obtained in the form of homogeneous aqueous colloidal solutions, these colloids can serve as starting point for the formulation of water-based inks that are suitable for IJP small devices on arbitrary substrates.^[7] We have been working on the development of ink-jet printed MnO_2 -based pseudocapacitors from such 2D building blocks. In the present contribution, we discuss and emphasize the underlying experimental strategies and methodologies used in research toward the realization and characterization of such devices. The procedures for obtaining various forms of MnO_2 nanosheets, and their structure-property relationships with respect to pseudocapacitance are summarized in Section 2. The principles of ink jet printing of δ - MnO_2 nanosheets and the optimization of 2D inks for IJP are discussed in Section 3. As 2D MnO_2 is likely to be used in conjunction with the electronically more conductive 2D phases graphene and graphene oxide, these 2D materials are also included in the discussion in Section 3. The current state of the art in δ - MnO_2 nanosheet derived pseudocapacitors and (ink-jet printed) MSCs in a broader context is described in Section 4. In the final Section 5, some general conclusions are drawn and a future outlook is given.

2. Synthesis and Structure of δ - MnO_2 Nanosheets

Birnessite ($\text{Na}_4\text{Mn}_{14}\text{O}_{27} \cdot 7\text{H}_2\text{O}$), also known as δ - MnO_2 is the layered manganese oxide parent compound from which 2D MnO_2 nanosheets can be derived. Its crystal structure consists of a stack of one-unit-cell thick $\text{MnO}_2^{\delta-}$ layers with charge-compensating Na^+ (or K^+) cations sandwiched between them, see **Figure 1a**. The MnO_2 layers consist of edge-sharing MnO_6 octahedra. Birnessite has a single hydration layer and the MnO_2 - MnO_2 interlayer spacing is 0.7 nm. The layers are negatively charged due to the presence of Mn^{3+} in the lattice.

Synthetic birnessite is usually prepared in water by oxidation of aqueous Mn^{2+} using oxidants such as molecular oxygen,

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H_2O_2 or $\text{S}_2\text{O}_8^{2-}$.^[8] For example, $\text{Mn}(\text{OH})_2$ (pyrochroite) is first oxidized to β - MnOOH before gradually transforming into MnO_6 octahedra. The average oxidation state of Mn in birnessite ranges between 3.40 and 3.99. Because of the sheets' negative charges, it is possible to intercalate (hydrated) alkali cations and form layered compounds. Since H^+ and K^+ are competitive in aqueous solution, high pH favors formation of the layered K_xMnO_2 phase.^[9] For the exfoliation route discussed in below, the precursor birnessite phase K_xMnO_2 is made by solid state reaction, e.g., at 1073 K involving stoichiometric amounts of Mn_2O_3 and KOH under O_2 flow.^[10] Other precipitation pathways involve stoichiometric conversion of $\text{Mn}(\text{OH})_2$ in aqueous NaOH by redox reaction with $\text{Mg}(\text{MnO}_4)_2$ or $\text{KMnO}_4/\text{MgCl}_2$,^[11] and the reduction of MnO_4^- by alcohols in basic media.^[12]

2.1. MnO_2 Nanosheets by Bottom-Up Synthesis

The mechanism that leads to MnO_2 sheet formation as described above can be utilized to synthesize unilamellar sheets of MnO_2 (**Figure 1b**), provided that the subsequent stacking of nanosheets due to electrostatic interactions between $\text{MnO}_2^{\delta-}$ and Na^+ or K^+ cations is prevented. Thus, the key to nanosheet stabilization is the absence of hard cations. Furthermore, to achieve well-shaped and well-dispersed MnO_2 sheets that will stay in solution, the precipitation reaction is slowed

down by the use of chelating agents. For instance, thin lamellae of δ - MnO_2 of less than 10 nm thickness can be made by mixing Mn^{2+} and EDTA (disodium dihydrogen ethylenediaminetetraacetate) in NaOH solution.^[18] Truly monolayer nanosheets can be made by oxidizing MnCl_2 with H_2O_2 in the presence of tetramethylammonium hydroxide (TMAOH).^[19] The hydroxide anions guarantee high pH, and TMA^+ acts as charge-compensating cationic species for the MnO_2 nanosheets. The resulting colloidal solution consists of unilamellar MnO_2 sheets with lateral sheet sizes of 50–150 nm. This size range is very suitable for ink jet printing applications, which requires components at least ≈ 2 orders of magnitude smaller than the printer nozzle. Air-drying of the colloids,^[19] or slow ageing and gelation at 25–85 °C,^[20] results in the solid hybrid phase $(\text{TMA})_x\text{MnO}_2$, with $x = 0.2$ –0.51.

An alternative chemical reduction route to unilamellar δ - MnO_2 colloids has also been reported, see Figure 1c.^[13] The key component is sodium dodecyl sulfate ($\text{C}_{12}\text{H}_{25}\text{SO}_4\text{H}$; SDS) that functions both as structure-directing agent and as source for dodecanol, the reductant of MnO_4^- . First, some dodecanol is formed by hydrolysis of the SDS anion, i.e., $\text{C}_{12}\text{H}_{25}\text{SO}_4^- + \text{H}_2\text{O} \rightarrow \text{C}_{12}\text{H}_{25}\text{OH} + \text{H}^+ + \text{SO}_4^{2-}$. Dodecanol then reacts with

MnO_4^- via: $3\text{C}_{12}\text{H}_{25}\text{OH} + 4\text{MnO}_4^- + \text{H}^+ \rightarrow 3\text{C}_{11}\text{H}_{23}\text{COOH} + 4\text{MnO}_2 + 5\text{H}_2\text{O}$. The structure-directing function of SDS is thought to be its self-assembly into thin lamellae in water, onto which MnO_4^- is subsequently reduced to form single-layer MnO_2 sheets. The presence of nanosheet colloids in a solution can be demonstrated by the Tyndall effect (Figure 1d). On the nanoscale, transmission electron microscopy (TEM) and atomic force microscopy (AFM) are typically used to obtain more direct proof of the presence of nanosheets, as illustrated by TEM and AFM images of bottom-up synthesized MnO_2 nanosheets in Figure 1e,f.

2.2. MnO_2 Nanosheets by Exfoliation

The second main synthesis route to unilamellar MnO_2 sheets in colloidal form is by delaminating preformed Na- or K-birnessite crystals into their constituent 2D structural motifs.^[21] This process is applicable to many layered oxides, including titanates,^[22] niobates,^[23] tungstates,^[24] and ruthenates.^[25] The exfoliation process consists of two steps. Starting with K_xMnO_2 , the first step involves replacing the intercalant alkali atoms by

Figure 1. a) Crystal structure of birnessite. Purple planes are MnO_2 nanosheets, spheres indicate alkali cations. Concentration of alkalis varies with Mn oxidation state; b) top view of MnO_2 nanosheet; c) bottom-up synthesis of MnO_2 nanosheets in water: SDS self-assembly into thin lamellae, where MnO_4^- is reduced to single-layer MnO_2 . Reproduced with permission.^[13] Copyright 2015, Wiley-VCH; d) MnO_2 nanosheet solution (12 mg L^{-1}) exhibiting the Tyndall effect. Reproduced with permission.^[10] Copyright 2003, American Chemical Society; e) TEM image of wrinkled MnO_2 nanosheets, and f) AFM image showing MnO_2 nanosheets made by bottom-up synthesis. Adapted with permission.^[14] Copyright 2018, Elsevier; g) SEM image of protonated birnessite crystal (top) and its exfoliated MnO_2 nanosheets (bottom). Reproduced with permission.^[15] Copyright 2004, American Chemical Society; h) relative abundances of TBA-intercalated protonated birnessite, exfoliated MnO_2 nanosheets, and restacked/osmotically swollen state as function of TBA^+/H^+ ratio. Reproduced with permission.^[10] Copyright 2003, American Chemical Society; i) Mechanism of sheet exfoliation and restacking: 1) mixing protonated layered oxide with TAAOH, 2) annihilation of protons by OH^- , 3) formation of nanosheets, 4) restacking into swollen state at high TAA^+/H^+ ratio. Reproduced with permission.^[16] Copyright 2015, Wiley-VCH; j) Schematic of strained MnO_2 nanosheet with Mn^{4+} vacancies in the 2D crystallite, and surface Mn^{3+} ions (indicated in green) residing above the crystallite plane. Oxygen ions surrounding surface Mn^{3+} have been omitted for the sake of clarity. Image based on CIF data available from ref. [17].

protons in an ion exchange process, see Figure 1g (top) for a scanning electron microscopy (SEM) image.^[15] This is done by soaking the parent oxide in a HCl solution for 3–10 days, often including repeated replacement of the acid solution within this period. Ion exchange of $K_{0.45}MnO_2$ in HCl solution carried out in this way yielded $H_{0.13}MnO_2$,^[10] i.e., a layered manganese oxide phase with a Mn oxidation state of 3.87. The latter value determines the charge density of the MnO_2 platelet, and with that the cation concentration in the interlayer region. Thus, the Mn oxidation state determines the crystal binding energy of the layered oxide to a large extent. A value of 3.87 indicates that the electrostatic energy that stabilizes the crystal structure is relatively small. In the second step of the exfoliation process, H_xMnO_2 is reacted with a tetraalkylammonium (TAA) hydroxide, where alkyl = $-C_nH_{2n+1}$ ($n = 1-4$).^[26] The intercalated protons are annihilated by acid-base reaction with OH^- .^[16] Ultimately, all protons are replaced by TAA^+ . Depending on the TAA^+/H^+ ratio, several things can happen, often simultaneously,^[10,26] as shown in Figure 1h. At low TAA^+/H^+ ratio, TAA^+ is intercalated, yielding a $(TAA)_xMnO_2$ layered hybrid structure. At higher ratios TAA^+/H^+ , MnO_2 sheets delaminate from the parent crystals and form nanosheets in solution. This is the preferred form for further development of 2D nanosheet ink. At TAA^+/H^+ ratios > 10 , the layered hybrid structure remains topotactically intact but osmotic swelling of the parent crystals occurs. The exfoliation process is schematically depicted in Figure 1i. For efficient exfoliation, intermediate TAA^+/H^+ ratios typically in the region unity or slightly higher, are preferable. As Figure 1h illustrates, a post-synthesis separation step in which colloidal exfoliated sheets are separated from intercalated or swollen material, is always necessary, irrespective of the actual TAA^+/H^+ ratio. The separation is usually based on the fact that exfoliated material remains colloidally dispersed, while hybrid intercalated and swollen material is much heavier and can be filtered from solution using a membrane, or settles spontaneously under gravitational force. In general, tetrabutylammonium (TBA^+) is a better dispersant for oxide nanosheets than short-chain TMA^+ .^[27] A practical issue associated with making nanosheets via exfoliation is that the final concentration of sheets in the dispersion is not known and needs post-synthesis analysis.^[28]

It is also possible to prepare stable nanosheet dispersions in nonpolar solvents.^[29] In this case the ionic sheets are first dispersed by replacing Na^+ by protonated alkylamines $C_nH_{2n+1}-NH_3^+$ ($n = 10-18$) in water via ion exchange at pH 7. Then the solution is air-dried, and the resulting precipitate is redispersed in toluene, and centrifuged. The resulting toluene-based supernatant contains only alkyl-grafted MnO_2 nanosheets. The exfoliation process is facilitated by the weakened electrostatic interactions between nanosheets and intercalants due to the spacer effect of the bulky alkyl chains, and the high solubility of C_nH_{2n+1} -coated nanoparticles in nonpolar solvents.

2.3. Structure of MnO_2 Nanosheets

There are two essential differences between manganese oxide nanosheets synthesized by bottom-up and top-down methods.

The bottom-up syntheses are done at room temperature in water starting from molecular precursors, while the exfoliation process employs layered crystals that were obtained after prolonged exposure to elevated temperatures, i.e., >1000 °C. Due to thermal crystallization and equilibration, the (point) defect concentrations in exfoliated nanosheets are close to the thermodynamic equilibrium values, i.e., smaller than as expected in self-assembled nanosheets. Second, crystallite growth at high temperatures yields larger birnessite crystallites (micrometer range) than low temperature precipitation methods do. Exfoliated nanosheets can thus have substantially larger diameters (>1 μm)^[15] (Figure 1g) than MnO_2 sheets obtained by self-assembly (<150 nm) (Figure 1f).^[19] Both types can be used to fabricate pseudocapacitors, although the size of nanosheets for ink jetting should not exceed 5% of the nozzle diameter, and ideally they should be smaller than 2%.^[30] An effective route to decrease the size of exfoliated nanosheets is by milling synthetic birnessite powder prior to proton exchange and exfoliation. The colloidal nanosheets are also very sensitive to fracture due to shear forces in the fluid, and the sizes of nanosheets obtained in practice are often a factor of 5–10 smaller in diameter than the diameter of the parent crystals.

The defect structure of MnO_2 nanosheets on atomic level is crucial for the pseudocapacitance of the sheets, since surface defects can function as surface redox sites.^[31] Three main known imperfections in MnO_2 nanosheets are: 1) the presence of Mn^{4+} vacancies in the nanosheet layer, 2) the presence of Mn^{3+} , and 3) the curling of monolayers as a result of the 2D weakened interlayer interactions caused by the high concentration of defects.^[17] A considerable fraction of Mn^{3+} ions occupy positions above the plane of the MnO_2 nanosheet, and the combination of Mn^{4+} vacancies in the layer and Mn^{3+} ions above the layer have been referred to as “surface Frenkel defects.”^[31] Mn^{3+} ions are also present in the MnO_6 octahedra in the plane of the sheet (see Figure 1j). The concentration of Mn^{4+} vacancies and out-of-plane Mn^{3+} surface sites increases with decreasing pH, up to 19% Mn^{4+} vacancies and 21% surface Mn^{3+} sites at pH 3 for redox-precipitated MnO_2 .^[17] This value is close to the value of 26.5 at% Mn^{4+} vacancies in exfoliated MnO_2 at pH 2.^[31]

Despite the high Mn^{3+} concentration and the reasonably small band gap of δ - MnO_2 nanosheets of 2.23 eV,^[32] stacks and precipitates of MnO_2 nanosheets are poorly conductive,^[33] i.e., electron mobility is low, which is a serious drawback for their potential application in pseudocapacitors. The simplest solution to improve conductivity is to disperse a conductive second phase, such as Ag nanoparticles,^[34] graphene^[35] or reduced graphene oxide.^[36] Another, hardly explored strategy to increase conductivity is via substitution in the MnO_2 host lattice. Transition metal cations that are known to be stable in the framework of birnessite are Fe^{3+} , Co^{2+} , and Ni^{2+} ,^[37] but their effect on electronic conductivity is unknown. Ru has been doped up to 10 at% into birnessite, and the resulting composite made from exfoliated and restacked $Mn_{1-x}Ru_xO_2$ nanosheets ($x = 0.05-0.10$) had lower ohmic resistances than comparable MnO_2 sheets.^[38] Phase-pure RuO_2 nanosheets show a very high conductivity compared to all other oxide nanosheets,^[39] implying that electron transfer between nanosheets is also rapid.

3. Ink-Jet Printing of 2D Materials

Inkjet printing has been attracting considerable attention because of its digital, noncontact and high resolution features that can be used to deposit various functional materials like organic materials,^[40] inorganic nanomaterials^[41] and 2D nanomaterials^[7b,42] onto different substrates such as paper,^[43] glass^[44] and flexible polymeric substrates.^[45] The printing process consists of jetting droplets from a nozzle under driving pressure, followed by impaction and deposition of droplets on a substrate. The morphology of printed patterns depends on the printing apparatus, ink formulation, substrate interface properties, and post-treatment process. Thus far, inkjet printing has been used to fabricate electronic devices like field effect transistors,^[46] solar cells,^[47] organic light-emitting diodes,^[48] and electrochemical energy storage devices.^[14]

3.1. Principles of Inkjet Printing

Depending on the printing mechanism, an inkjet printer can be operated in two different modes: continuous inkjet (CIJ) and drop-on-demand (DOD) printing, as shown in **Figure 2a**. The CIJ mode is a process in which a continuous stream of droplets is jetted by the printer head nozzles. The jetted droplets are then subjected to an electrostatic field, which directs them toward the substrate. All undesired droplets are directed to a recycling system. The DOD mode is a process in which droplets are jetted only when desired. They are deposited onto a substrate in a pre-designed pattern. Because the recycling system may contaminate the ink, the CIJ mode is not used very often. DOD mode printers are the majority inkjet printers for printed electronics manufacturing. Thermal and piezoelectric actuations are the two main actuation mechanisms of a DOD inkjet printer. In the thermal process, a resistive element is activated that forms a gas bubble inside the reservoir, leading to ejection of a droplet via the nozzle. As this point, the resistive element is turned off and the vacuum draws new ink to refill the reservoir. In the piezoelectric process, a voltage pulse is applied to the piezoelectric reservoir walls, which creates a mechanical pressure. The pressure squeezes the functional ink through the nozzle onto the substrate. When the voltage pulse is switched off, the vacuum created by reservoir walls will draw new ink into the reservoir.

Inkjet printing has several advantages: 1) As a digital printing technique, it does not need a physical mask. Therefore, inkjet printing is highly flexible with respect to pattern design. 2) As a noncontact process, the printer head does not need to contact the substrate physically, which helps to avoid contaminations. 3) Inkjet printing systems can be varied easily from small sized device fabrication systems to large-scale production equipment. However, due to the strict requirements of the inkjet printer, the biggest challenge is to prepare printable inks with proper physical properties like viscosity and surface tension.

3.2. Ink Formulation Engineering

Dispersions of nanosheets produced by the synthesis methods described in Section 2 can be used to prepare printable inks.

However, the nanosheet dispersion itself cannot serve directly as an ink. To prepare printable nanosheet-based inks, additives such as surfactants and/or thickeners are added to optimize the physical properties of the inks and improve their storage stability. It has been found that the average lateral sizes and size distributions of nanosheets are important parameters in the preparation of printable ink formulations. For inkjet printing electrochemical energy storage devices, the average lateral nanosheet size needs to be optimized to get the best electrochemical performance.

Other key issues in inkjet printing are ink formulation and morphology optimization of ink-jet printed patterns, and the avoidance of nozzle clogging. Ink formulation optimization is an efficient way to control droplet formation, and the morphology of printed patterns. Ink surface tension (γ) and dynamic viscosity (η) are the main two rheological parameters that need to be optimized to get printable and reproducible inks. Inks with surface tensions within the optimum range can be inkjet printed: too low surface tensions would lead to spontaneous ink dripping from the nozzles, while too high values make jetting impossible.^[52] The dynamic viscosity affects the shape, size and velocity of the ejected droplets and is a crucial physical parameter of the ink.^[53] The ideal dynamic viscosity range varies with the type of inkjet printer. Ideally, a Newtonian fluid with a constant viscosity/shear rate relationship is preferred for inkjet printing.

Next to surface tension and dynamic viscosity, another issue in ink formulation concerns the ejection of stable droplets without any satellite droplets or tails that might decrease the resolution of the printed patterns. The droplet jetting behavior can be evaluated by the parameter Z , the dimensionless inverse Ohnesorge (Oh) number

$$Z = \frac{(\alpha \rho \gamma)^{1/2}}{\eta} \quad (1)$$

where α is the nozzle diameter, and ρ is the density of the fluid. By considering single droplet formability, position accuracy, and maximum allowable jetting frequency, Jiang et al. demonstrated the optimal range of Z to be between 4 and 14.^[54] However, Z values outside this range have also shown to result in stable jetting behavior. For example, Hsiao et al. reported a Z value as low as 1 for photoresist ink.^[55] Much higher values than 14 are also possible. Stable ink jetting has been reported for ethylene glycol-water ink ($Z = 35.5$),^[56] glycerol-water ink ($Z = 68.5$),^[57] as well as for stable water-based inks with a Z value around 19.^[14] As illustrated in **Figure 2b**, stable printing without any satellite droplets can be confirmed by time-resolved optical images of droplet formation. Finally, rapid evaporation of solvents near the nozzle is known to lead to blocking of the nozzle. This phenomenon may be suppressed by using cosolvents that dry relatively slowly.

3.3. Printed Pattern Morphology Optimization

The quality of printed patterns influences the performance of printed devices. Nonuniform deposition of solids can lead to a decrease of the resolution of printed patterns and device

Figure 2. a) Schematic of CIJ (left) and DoD (right) inkjet printing; b) optical image of ink droplet formation versus time. The scale bar is 50 μm ; c) droplet drying process excess surfactant and d) with optimized surfactant concentration. Reproduced with permission.^[14] Copyright 2018, Elsevier; e) optical image of dried graphene film with coffee-ring effect and f) uniformly deposited droplet. Reproduced with permission.^[44] Copyright 2013, Wiley-VCH. g) Optical micrograph of final distributions of ellipsoidal (left) and spherical (right) particles after evaporation. Reprinted with permission.^[49] Copyright 2011, Springer Nature; h) Width of the “coffee-ring” (w) normalized by droplet radius (R) as a function of lateral size of GO flakes. Reproduced with permission.^[50] Copyright 2017, Wiley-VCH; i) Optical images of printed lines at varying droplet spacing. The scale bar is 100 μm . Reproduced with permission.^[14] Copyright 2018, Elsevier; j) Droplet morphology map of drying droplets defined by substrate temperature and mean flake size. Reproduced with permission.^[50] Copyright 2017, Wiley-VCH; k) Optical micrograph of inkjet printed graphene droplet on O_2 plasma-cleaned (left), pristine (middle) and HMDS-coated (right) Si/SiO_2 substrate, and l) AFM images of printed graphene stripes on pristine (left), O_2 plasma-cleaned (middle), and HMDS-coated (right) Si/SiO_2 substrate. Reproduced with permission.^[46b] Copyright 2012, American Chemical Society; m) sheet resistance as a function of thickness of printed graphene lines on Si/SiO_2 substrate before and after annealing. Reproduced with permission.^[51] Copyright 2017, Springer Nature.

performance. Recently, a water-based $\delta\text{-MnO}_2$ nanosheet ink was developed using propylene glycol to increase the viscosity of water, and Triton X-100 to decrease the surface tension.^[14] The excess of Triton X-100 tended to unpin the contact line of the printed droplet and shrink the droplet size, leading to non-uniform distribution of $\delta\text{-MnO}_2$ nanosheets, as illustrated in Figure 2c. By carefully optimizing the concentration of Triton X-100 to ensure the pinning of the contact line of the printed droplet during drying, $\delta\text{-MnO}_2$ nanosheets were uniformly deposited on the substrate due to recirculating Marangoni flow, as shown in Figure 2d.

The undesired coffee-ring effect is a common phenomenon in inkjet printing. The general strategy to prevent it is to modify the physical properties of the ink by adding specific agents. Li et al. reported mixing low and high contact angle solvents together with polymers to suppress the coffee-ring effect.^[44] Due to the fast evaporation of ethanol, the interface between the remaining terpeneol and polymer-modified surface showed poor wetting, which led to nonuniform deposition of solids

(Figure 2e). However, when the substrate temperature was increased, the surface energy between solid and liquid decreased while terpeneol evaporated faster than at room temperature. The combination of these two factors resulted in more uniform deposition of solids, as illustrated in Figure 2f. *N*-methylpyrrolidone (NMP) can also be used as solvent for graphene ink to reduce coffee-ring effect owing to its higher boiling point ($\approx 202^\circ\text{C}$) and heat of vaporization (54.5 kJ mol^{-1}) than water.^[46b] Alternatively, when toxic solvents such as NMP are to be avoided, certain mixed solvents, e.g., consisting of isopropyl alcohol (IPA) and polyvinylpyrrolidone (PVP), can be used.^[58] IPA with its low boiling point (82.6°C) and low toxicity is widely used in commercial functional inks. To prevent the precipitation of graphene in IPA ink, PVP can be added to stabilize the graphene dispersion.

The shape of the suspended particles can also be exploited to optimize the morphology of patterns and reduce the coffee-ring effect.^[49] As shown in Figure 2g, ellipsoidally shaped particles have been uniformly deposited. In contrast, spherical particles

were deposited nonuniformly, although the chemical composition and the capillary flows were the same in both cases. It was demonstrated that strong interparticle capillary interactions were present between the ellipsoidal particles. These strong long-ranged interactions lead to the formation of loosely packed or arrested structures that prevented the suspended ellipsoidal particles from moving to the droplet edge, and ensure uniform deposition after evaporation.

It has also been shown that the morphology of printed graphene oxide (GO) droplets is influenced by the flake size.^[50] As shown in Figure 2h, the width of the coffee-ring normalized by the droplet radius as a measure of the mean diameter of GO shows a gradual transition from the coffee-ring structure to uniform deposition. So printed GO droplets present a coffee-ring structure when the mean diameter of the GO flakes is below a critical size, while GO flakes with a larger mean diameter do not show the coffee-ring effect.

The morphology of printed patterns must also be optimized in terms of droplet spacing between neighboring droplets and substrate temperature during printing. The ideal droplet spacing for inkjet printing is such that the merging of neighboring droplets does neither lead to overlap, nor to isolated droplets. Figure 2i illustrates the relationship between the morphology of printed lines and the droplet spacing.^[14] The morphology can be seen to vary from bulging, which is caused by the overlap of droplets, to uniform deposition as the droplet spacing increases from 15 to 40 μm . A further increase of the droplet spacing to 45 μm leads to a disconnected line, as the droplets become too far apart to be able to merge. The influence of substrate temperature on droplet morphology is illustrated in Figure 2j.^[50] For mean GO flake sizes below 1 μm , the coffee-ring effect was observed in dried droplets with substrate temperatures between 20 and 60 $^{\circ}\text{C}$. By increasing the mean GO flake size, a transition region from coffee-ring to indistinct coffee-ring structure was observed with increasing substrate temperature. Upon increasing the mean GO flake size further, droplets were deposited uniformly without coffee-ring effect.

The morphology of inkjet printed patterns is also affected by the nature of the substrate interface. The wetting of a substrate, which can be defined in terms of contact angle and typically involving terms as hydrophilicity and hydrophobicity, is related to the surface energy and morphology. The wetting process can be described by Young's equation

$$\gamma_{sv} = \gamma_{si} + \gamma_{iv} \cos \theta \quad (2)$$

where γ_{sv} , γ_{si} , and γ_{iv} are the interface surface energies between the solid surface (s), the vapor (v), and the ink (i), and θ is the contact angle. Different contact angles represent different wetting properties. Small contact angles, $\theta \ll 90^{\circ}$ indicate good wetting of the ink on the substrate, meaning that the ink is able to form a continuous layer. Large angles, $\theta \gg 90^{\circ}$ indicate poor wetting of the ink, meaning that the ink tends to break up into discontinuous patches. However, a good wetting property with an appropriate contact angle is crucial for functional printing. For instance, the surface energy and contact angle need to be balanced carefully to achieve high resolution printed patterns. High surface tension solvents like NMP and water usually show poor wetting on common substrates. To address this issue,

Torrisi et al. investigated the morphology of printed graphene patterns on SiO_2 substrates with different surface treatment methods.^[46b] As shown in Figure 2k, printed graphene droplets on pristine SiO_2 substrates showed a coffee-ring structure. The authors then modified the Si substrate in two ways, namely by hexamethyldisilazane (HMDS) coating and by O_2 plasma cleaning. The same type of droplet was able to spread more uniformly on the HMDS-coated SiO_2 substrate than on the O_2 plasma-cleaned one. The high γ_{sv} and small θ results in very rapid droplet spreading on O_2 plasma-cleaned substrates. In contrast, the HMDS-coated substrate has a lower γ_{sv} and higher θ , which reduces the wettability and results in more uniform deposition. As shown in Figure 2l, the AFM images of printed lines on the HMDS-coated substrate indeed show more uniformity than the other two images.

As discussed in Section 3.2, additives like surfactants often need to be added to printable nanosheet-based inks. For example, organic quaternary ammonium ions typically surround nanosheets to prevent their aggregation and precipitation. These additives do not help to improve the electrochemical performance of devices. A post-treatment is thus necessary to improve the electrical properties of printed electrodes.^[33] Thermal annealing is a process in which solvent residues are evaporated and additives are removed. For example, McManus et al. demonstrated that thermal annealing removed surfactant and lowered the resistance of printed graphene lines on Si/ SiO_2 substrate.^[51] As illustrated in Figure 2m, the sheet resistance of printed graphene lines decreased by one order of magnitude after thermal annealing at 300 $^{\circ}\text{C}$ under N_2 atmosphere. Unfortunately, this annealing process can only be applied to thermally stable substrates, e.g., Si/ SiO_2 , quartz or polyimide. The MSC based on printed graphene electrodes and silver current collectors fabricated by Li et al. also needed high temperature thermal annealing after printing.^[44] In this case annealing was done at 375 $^{\circ}\text{C}$ for 1 h to remove the polymer from the printed graphene electrodes and sinter the silver nanoparticles. A MSC based on printed graphene serving as electrodes and current collectors on polyimide prepared by Hiram et al. was annealed at 350 $^{\circ}\text{C}$ for 4 h to remove all organic solvents.^[59] The same principle can be applied to metal dichalcogenide nanosheet based devices. For example, to remove ethyl cellulose from printed MoS_2 nanosheet electrodes, the device was annealed at 450 $^{\circ}\text{C}$ for 1 h.^[60] This was done in N_2 atmosphere to protect MoS_2 from being oxidized.

4. $\delta\text{-MnO}_2$ Nanosheet-Based Pseudocapacitors and Ink-Jet Printed Microdevices

Pseudocapacitive charge storage of manganese oxides in aqueous electrolytes occurs by reduction of Mn^{4+} to Mn^{3+} and adsorption of an alkali ion or proton, e.g.,

where A = Li, Na, K. Full reduction ($x = 1$) of Mn would correspond in theory to a specific capacitance of 1233 F g^{-1} , assuming a 0.9 V voltage window.^[2a] However, since the electronic conductivity of layered manganese oxides is small (10^{-5} to $10^{-6} \text{ S cm}^{-1}$

for Na-birnessite^[61], charge can only be stored in a very thin layer near the MnO₂ surface. This emphasizes the importance of 2D nanosheets, since nanosheets consist entirely of near-surface Mn atoms. For most practical purposes, nanosheets have to be organized into thicker electrode structures in order to achieve useful capacitances. The simplest way of assembling nanosheets is by reassembling them from colloidal solution, for example, via precipitation by bringing them into contact with (hard) cations (**Figure 3a**),^[62] or by simply drying the solution or the ink. In stacks of MnO₂ nanosheets electrical charge can be stored via three mechanisms: i) the electrochemical double layer, ii) a surface redox reaction, and iii) (de)intercalation.^[63] The nanosheets need to be assembled into functional electrode architectures in such a way that all nanosheets remain easily accessible to diffusing and adsorbing alkali ions from the electrolyte. For example, the natural 0.7 nm spacing of Na-birnessite^[64] can be increased by replacing the alkalis by other larger (organic) cations. Restacked MnO₂ nanosheet multilayers with poly-diallyl-dimethyl-ammonium (PDDA⁺) in the intergaleries yielded 0.92 and 1.54 nm for single-layer^[65] and bilayer

PDDA⁺,^[66] respectively. Such additives can also be used in IJP inks. Obviously, these spacers also occupy some space by themselves, thereby partly counteracting the advantages of wider interlayer spacings. For examples, the use of 7+ charged large aluminum polyoxocations with a diameter of 0.86 nm, of which only few are needed to counterbalance the negative charge of the MnO₂ sheets, did not result in any significant gallery widening. The reason is that the polyoxocation concentration in the intergallery space was so low that it could not stabilize the easily bendable nanosheet structure in between.^[67] On the other hand, the use of the large but not so highly charged organic cation TMA⁺ as intercalant between restacked MnO₂ nanosheet electrodes with a spacing of 0.92 nm showed specific capacitances of 180 F g⁻¹ at 0.5 A g⁻¹, which is substantially higher than found for birnessite.^[64]

In general, the specific capacitance increases with decreasing electrode thickness. For ultrathin nanosheet films of MnO₂, specific capacitances of up to 860–1180 F g⁻¹ have been reported.^[13,70] In most cases, the reported specific capacitances are considerably lower, 150–700 F g⁻¹, depending on layer

Figure 3. a) Schematic process of exfoliation of protonated layered MnO₂, followed by restacking by precipitation with Li⁺. Reproduced with permission.^[68] Copyright 2003, American Chemical Society; b) Specific capacitance and c) charge transfer resistance of restacked MnO₂ electrodes at pH 2 and pH 4, and comparison with protonated layered MnO₂ before exfoliation. Reproduced with permission.^[31] Copyright 2017, Nature Publishing Group; d) CV curves and e) capacitance retention of i) Li-MnO₂, ii) Li-Mn_{0.95}Ru_{0.05}O₂ and iii) Li-Mn_{0.9}Ru_{0.1}O₂ nanocomposites. Reproduced with permission.^[38] Copyright 2014, Wiley-VCH; f) schematic depicting the functionalization of graphene oxide by PDDA⁺, followed by coprecipitation with MO₂. Reproduced with permission.^[36] Copyright 2011, American Chemical Society; g) schematic of mask-assisted fabrication of all-solid-state planar graphene-MnO₂ microsupercapacitor (MSC), and optical images of flat and bent MSCs. Reproduced with permission.^[69] Copyright 2018, Elsevier.

architecture, thickness, charging rates, and the other electrode components.^[62,71] A correlation between the capacitance and the concentration of surface Frenkel defects (see Section 2) and the Mn^{3+} concentration has also been established. The Mn^{4+} vacancies provide intercalation sites for cations like Na^+ . On the other hand, Mn^{3+} can participate in polaron hopping conduction, thus improving electrical conductivity and charge transfer.^[31] The concentration of such defects is related to the conditions during electrode formation, in particular the pH of the solution (or ink) has been identified as an important factor. The positive effect of increasing the defect concentration is illustrated by Figure 3b,c, where the specific capacitance and charge transfer resistance of three systems are compared. Clearly, a low pH is beneficial for increasing the specific capacitance.

There are few reports of the influence of homogeneous doping of foreign elements in the MnO_2 matrix on specific capacitance, e.g., Ru and Co.^[37c,38] Although RuO_2 is known to exhibit extremely high capacitances $> 1000 \text{ F g}^{-1}$, the addition of 5–10 at% Ru to MnO_2 has a predominantly positive effect only on the electrical conductivity of the MnO_2 matrix (Figure 3d,e). The increase of specific capacitance in $\text{Mn}_{1-x}\text{Co}_x\text{O}_2$ ($x = 0.2\text{--}0.5$) nanosheets upon Co doping is also more likely the result of conductivity improvement rather than an increased concentration of surface redox sites.

In virtually all pseudocapacitors, conductive phases such as carbon black or graphene, and a polymeric binder, e.g., polyvinylidene fluoride (PVDF), are mixed with MnO_2 in order to provide electronic pathways between the back electrode and the redox-active MnO_2 phase. Obviously, the sheet architecture of graphene is very suitable in combination with MnO_2 nanosheets to achieve intimate contact between a redox-active and an electronically conductive phase. But the hydrophobic nature of graphene prevents intimate contact with the hydrophilic manganese oxide phase. Hence, graphene is partially oxidized into more polar graphene oxide (or its derivative reduced graphene oxide) in order to mix well with oxidic nanosheets. Since both compositions are negatively charged in water, an adhesion promotor such as PDDA⁺ may be added to promote the interaction between the two phases (Figure 3f).^[36,72] Alternatively, a direct precipitation route involving positively charged DMF-exfoliated graphene and anionic MnO_2 can be pursued,^[35] although this strategy may work less well when IJP from solutions is used to form the electrode. Coprecipitation of graphene oxide and manganese oxide by addition of ions such as Li^+ has also been employed, and in this way specific surface areas of $70\text{--}100 \text{ m}^2 \text{ g}^{-1}$ have been achieved.^[73] Other conductivity promoters such as Ag nanoparticles,^[34] polyaniline,^[74] and RuO_2 ^[75] have also been demonstrated. Graphene can also be used, as was recently shown by an all-solid-state microsupercapacitor based on an interdigitated electrode structure made from exfoliated graphene, and subsequently covered by a MnO_2 nanosheet film (see Figure 3g).^[69]

MSCs as a new class of energy storage devices are highly promising for integration on chips or flexible substrates for embedded microsystems.^[76] The two main architectures of MSCs are the thin film stacked configuration (Figure 4a) and the in-plane interdigitated configuration (Figure 4b). In the stacked configuration MSC, nanosheets are stacked onto

current collectors that face each other, thereby increasing the path length for the transport of electrolyte ions across the nanosheets. In contrast, in-plane interdigitated configuration MSCs where stacked nanosheets electrodes lie side by side in the same plane, offer several advantages over stacked MSCs. Due to the fact that the electrodes are exposed to the electrolyte, the in-plane geometry increases the accessibility of the active electrode materials and favors faster electrolyte ion transport along the basal plane of the nanosheets. As a result, the power density is enhanced. The in-plane MSCs also allow high frequency response because of the small interspace between the finger electrode arrays. Furthermore, the in-plane configuration makes it easy to integrate MSCs into microdevices.

As a digital printing technique, inkjet printing shows great potential for in-plane interdigitated MSC fabrication.^[45,77] Recently, Wang et al. reported an all-solid-state in-plane MSC based on inkjet printed $\delta\text{-MnO}_2$ nanosheet electrodes.^[14] To fabricate the MSC, $\delta\text{-MnO}_2$ ink was first inkjet printed on polyimide substrate as electrodes with 10 in-plane interdigitated fingers, followed by thermal annealing at 350°C for 1 h under N_2 atmosphere. Then, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) ink was printed on top of the annealed $\delta\text{-MnO}_2$ patterns, followed by thermal annealing at 120°C for 15 min. Finally, a PVA/LiCl gel electrolyte was deposited on the printed PEDOT:PSS/ $\delta\text{-MnO}_2$ electrode and dried at room temperature overnight (Figure 4b). To evaluate the electrochemical performance of these MSCs, galvanostatic charge–discharge measurements were carried out at different current densities as shown in Figure 4c. Figure 4d presents the volumetric capacitance of the MSC, based on the galvanostatic charge–discharge data. The MSC exhibited its highest volumetric capacitance of 2.4 F cm^{-3} at a current density of 0.05 A cm^{-3} , which corresponds with a surface area-normalized capacitance of 0.26 mF cm^{-2} . Cyclic voltammography curves recorded at different bending angles are shown in Figure 4e. The CV curves remain nearly unchanged even when the device is bent over 120° with a bending radius of about 1 cm. The MSC exhibits good mechanical flexibility indicating the potential for application in flexible electronics. Charge–discharge cycling measurements were performed at a current density of 0.2 A cm^{-3} . As shown in Figure 4f, a 22% drop in volumetric capacitance was observed after 3600 charge–discharge cycles, indicating good cycling performance.

Another interesting development for IJP concerns the use of paper as a substrate for device fabrication. The highly porous morphology of paper provides a very high specific surface area on which nanosheets can be dispersed very well, without the need for an extra binder.^[69] Indeed, a recently demonstrated commercial A4 paper-based MnO_2 supercapacitor showed a specific capacitance of 1035 F g^{-1} , and 99% retention of capacitance after $>10\,000$ cycles.^[78]

5. Conclusion and Outlook

With the increasing use of electronic devices in our society, the role of MSCs in emerging applications such as autonomous sensors, actuators and flexible consumer electronics is increasing rapidly. This growing demand of small-scale

Figure 4. a) Schematic of vertically stacked MSC configuration; b) schematic of in-plane interdigitated MSC configuration; c) CV curve, d) volumetric capacitance, e) CV curves of MSC under different bending angles at a scan rate of 20 mV s⁻¹, and f) cyclic stability measurement of MSC at a current density of 0.2 A cm⁻². Reproduced with permission.^[14] Copyright 2018, Elsevier.

rechargeable energy storage devices has spawned the search for new charge storage materials and novel fabrication methods to realize their scalable production. The use of the 2D form of manganese oxide offers one of the most practically viable alternatives for the fabrication of supercapacitor electrodes, since the material combines several preferable features: 1) manganese oxide phases have a high intrinsic pseudocapacitance, 2) the 2D sheet-like shape guarantees maximum specific surface area for ion adsorption and surface redox reactions, and maximum sheet flexibility, and 3) manganese oxides are known as Earth-abundant, nontoxic and environmentally friendly phases, unlike most other alternatives.

Unilamellar single-crystalline 2D MnO₂ nanosheets are made in colloidal form, and these colloids can form the basis of ink formulations for MnO₂ based pseudocapacitor devices using ink jet printing technology as discussed above. Both water- and solvent-based colloids have already been demonstrated. Although the process of printing 2D materials is still at an early stage of development, the IJP approach seems to be a viable and flexible method to fabricate MSC devices. IJP is ideal for realizing interdigitated structures. The gap between the electrodes can be carefully controlled, while the overlapping of 2D nanosheets guarantees that the electrodes have a well-connected percolative oxide microstructure, even when the electrodes are very thin. In the previous sections, we have summarized the developments and state of the art in 2D MnO₂ nanosheet based supercapacitors in general, and the ink jet printing of 2D MnO₂ based MSCs in particular. Studies on MnO₂ nanosheet based pseudocapacitors have demonstrated excellent performance and cycling stability under widely varying charging/discharging conditions. However, the measured specific capacitances can vary widely from one device to the other, ranging from about 150 to over 1000 F g⁻¹. The large differences are attributed to differences in the microstructure and 3D architecture of the electrodes, i.e., the way in which nanosheets are stacked in the electrode, the intergallery spacings (pore size)

between nanosheet layers, the total porosity, length of the ionic diffusion paths, and the overall electronic conductivity of the electrode.

In general, the specific capacitance has been shown to increase with decreasing electrode thickness due to the decreasing influence of diffusion resistance. On the other hand, thicker layers contribute more to the overall capacitance of the device, so a balance between these two opposing factors has to be established. The main current challenges are to maximize the electronic conductivity and pseudocapacitive properties of the nanosheets, to optimize the surface and pore structure of the electrodes, to facilitate the diffusion rate of ions and to maximize the surface area available for pseudocapacitive surface redox reactions using the IJP approach. Doping with suitable foreign elements such as Ru, and/or the combined use of (reduced) graphene oxide have already shown to be effective strategies to increase the conductivity and improve the specific capacitance, and further exploration of these approaches seems promising. Moreover, dopants have also been reported to enhance the quantum capacitance.^[79] Rational control over the electrode architecture and porosity presents a bigger challenge, since 2D sheets tend to form layered stacks, leading to relatively low porosity and long diffusion paths. However, also here it is expected that further optimization of the electrode architecture is very well possible and that this can ultimately lead to flexible MSCs with even higher capacitances and longer lifetimes.

Acknowledgements

The authors acknowledge the financial support of the China Scholarships Council program (CSC, No. 201608340058).

Conflict of Interest

The authors declare no conflict of interest.

Keywords

ink jet printing, manganese oxide, nanosheets, printed electronics, supercapacitors

Received: August 23, 2018
Revised: September 10, 2018
Published online:

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