A complete three-dimensionally nanostructured asymmetric supercapacitor with high operating voltage window based on PPy and MnO₂

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Abstract
The development of novel functional nanostructures and the implementation of an asymmetric cell design are the key challenges to increase the electrochemical performance of aqueous based supercapacitors. In this manuscript complex three-dimensional electrode materials are nano-engineered based on free-standing open-ended core/shell nanotube arrays with tailored functions. Both the negative and positive electrode materials are designed and nanostructured individually, using an innovative material combination of Polypyrrole (PPy) and manganese oxide (MnO₂). This asymmetric cell design increases the possible operating potential window to 1.7 V, which is a major leap to enhance the specific energy of supercapacitors. The prepared device exhibits a high specific energy of 27.2 Wh kg⁻¹ and a high specific power 24.8 kW kg⁻¹.

Introduction
The ongoing technological advances in areas such as electric mobility, consumer electronics, wireless sensor networks, and energy harvesting set new demands for energy storage and energy management systems [1-3]. The next generation of high performance energy and power devices requires a strongly enhanced electrochemical performance as well as operating safety, limited environmental impact, and economical viability [4]. In order to fulfill these aims a crucial role is addressed to supercapacitors because of the superior power delivery and cycling life compared to those of lithium ion batteries. Today, the main challenge is to increase the specific energy of supercapacitors without sacrificing specific power.

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The specific energy of supercapacitors can be improved by maximizing the specific capacitance \( c \) and/or maximizing the operating potential window \( V \) according to the following equation: \[ E = \frac{1}{2}CV^2 \] (1)

In order to achieve an enhanced specific energy, three major strategies can be distinguished. (i) The implementation of new electrode materials that possess higher specific capacitance compared to commercially utilized carbon based materials, such as metal oxides \([6-12]\), conductive polymers \([13]\), and metal nitrides \([14]\). (ii) The development of novel functional nanostructures and material compositions. This mainly includes complex core/shell nanostructures that combine the advantage of two materials (i.e., core and shell) \([15-21]\). Such designs provide a fast electron transport through the core and a well utilization of the active electrode material in the shell. (iii) The realization of high-voltage supercapacitors operating in aqueous electrolytes \([22]\). Previously, asymmetric supercapacitors that use different electrode materials for the negative and positive electrode have drawn much attention \([23]\). Such configurations circumvent the main limitation of aqueous based supercapacitors and extend the operating voltage window beyond the thermodynamic limit of \( \sim 1.2 \) V to operating voltages as high as \( \sim 2 \) V \([24]\). Especially the combination of various carbon based negative and different \( \text{MnO}_2 \) based positive electrode structures were studied intensively \([5,25-28]\). However, other promising materials with complementary potential windows to \( \text{MnO}_2 \), in particular conductive polymers, are only insufficiently investigated as negative electrode materials in asymmetric supercapacitors. Thereby conductive polymers possess higher specific capacitance values compared to carbon materials and thus offer great potential to further increase the specific energy of supercapacitors \([29]\). The combination of asymmetric supercapacitors that utilize negative and positive electrode materials with complementary operating potential windows and the use of advanced functional electrode materials, such as optimized high aspect ratio core/shell structures are highly promising to enhance the electrochemical performance of the next generation of supercapacitors. However, until now supercapacitors with three-dimensionally nano-engineered negative and positive electrodes based on different materials have not been reported. In order to take full advantage of both the nanostructured electrode surface and the increased operating potential window due to the asymmetry of the electrodes nature, innovative supercapacitor configurations need to be developed.

Here, we report an all new asymmetric supercapacitor based on highly ordered free-standing three-dimensional (3D) core/shell nanotube arrays of \( \text{SnO}_2/\text{Polyaniline} \) (PPy) and \( \text{SnO}_2/\text{MnO}_2 \) as negative and positive electrode material, respectively (Figure 1). The utilized fabrication process allows a precise control of many structural parameters and is based on anodic aluminum oxide (AAO) nano-templates, \([30]\) atomic layer deposition (ALD) to synthesize free-standing \( \text{SnO}_2 \) nanotube (NT) arrays, and a conformal coating of PPy and \( \text{MnO}_2 \) by electrochemical deposition. Very importantly, the completely new cell-configuration of the nano-engineered 3D PPy//\( \text{MnO}_2 \) asymmetric supercapacitor can operated at 1.7 V and shows an outstanding electrochemical performance with obtained specific energy and specific power values that are among the highest reported.

### Materials and methods

\( \text{SnO}_2 \) substructure: the free-standing \( \text{SnO}_2 \) NT array was fabricated by AAO templates and ALD. The AAO template was synthesized using a two step-anodization process \([31,33]\) from a 99.999% pure aluminum foil at 40 V in 0.2 M oxalic acid with a second anodization time of 15 min, including a post-etching in 5 wt% phosphoric acid for 15 min at 30°C to increase the AAO pore size to 60 nm. Such AAO templates were then coated by \( \text{SnO}_2 \) nanotubes in a PicoSun ALD reactor according to the following process. The ALD cycle was based on 1 s pulse and 4 s purge for the \( \text{Tin(IV)chloride} (\text{SnCl}_4) \) precursor and 2 s pulse and 8 s purge for \( \text{H}_2\text{O} \) at 250°C. This cycle was repeated for 1500 times. Afterwards, the backside of the \( \text{SnO}_2 \) covered AAO was supported by a 100 nm gold layer by physical vapor deposition, the aluminum base was removed in a saturated copper chloride solution, and the remaining AAO template was etched by a 5 wt% sodium hydroxide solution in a two-step process. First, a pre-etching of 20 min was applied to liberate the \( \text{SnO}_2 \) NT top parts, which were then removed by scratching the surface of the sample with a sharp scalpel. Second, the remaining AAO template was dissolved entirely in the same etching solution for 120 min, gaining a free-standing \( \text{SnO}_2 \) NT array (see supplementary video).

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Positive and negative electrode: the positive electrode was fabricated by electrochemical deposition of \( \text{MnO}_2 \) onto the \( \text{SnO}_2 \) NT array from a solution containing 0.1 M manganese acetate (\( \text{Mn(Ac)}_2 \)) and 0.1 M sodium sulfate (\( \text{Na}_2\text{SO}_4 \)) at 1 V versus a Ag/AgCl reference electrode. A Pt foil was used as a counter electrode. The electrochemical performance of the fabricated \( \text{SnO}_2/\text{MnO}_2 \) core/shell positive electrode was investigated in a three-electrode cell containing a 1 M \( \text{Na}_2\text{SO}_4 \) electrolyte, a Ag/AgCl reference electrode, and a Pt foils as the counter electrode. The electrodes performance was studied in a potential window from 0–0.9 V.
The SnO2/PPy core/shell negative electrode material was synthesized by electrochemical polymerization of PPy onto SnO2 NT arrays from a solution containing 0.1 M pyrrole monomer (98%) and 0.2 M oxalic acid at 0.8 V versus Ag/AgCl. The electrochemical performance was investigated in an identical setup as described for the positive electrode in a potential window from −0.8 to 0 V versus Ag/AgCl. The specific capacitances of the SnO2/PPy and SnO2/MnO2 core/shell NT arrays were calculated for various current densities from the gradient of the associated discharge curve according to the following equation:

$$c_{+/+} = \frac{l}{(\Delta V/\Delta t) \times m_{+/+}} \quad (2)$$

with $m_{+/+}$ being the negative and positive active electrode masses derived from the charge flown during the electrochemical deposition process.

Asymmetric supercapacitor: The negative SnO2/PPy and positive SnO2/MnO2 core/shell electrode materials were assembled into two-electrode Swagelok-type cells forming an asymmetric supercapacitor labeled as PPy//MnO2 (negative electrode//positive electrode). The electrodes were separated by a porous membrane and a 1 M Na2SO4 solution was used as an electrolyte. The cells were operated at a potential window of 1.7 V. Thereby the active electrode materials, the specific capacitances of the respective electrode material, and $\Delta U_{+/+}$ the respective operating potential (0.8 V for negative and 0.9 V for positive electrode). The specific energy is calculated according to:

$$E = \frac{1}{2} \times c_{asy} \times V^2 \quad (4)$$

with $V$ being the voltage after the potential drop and $c_{asy}$ being the specific capacitance of the asymmetric supercapacitor cell measured from the discharge curve gradient of the charge/discharge profiles according to:

$$c_{asy} = \frac{l}{(\Delta V/\Delta t) \times m} \quad (5)$$

where $l$ is the discharge current and $m$ is mass of the active electrode materials. The specific power is calculated from the specific energy divided by the discharge time ($t_{\text{discharge}}$) according to:

$$P_{\text{real}} = \frac{E}{t_{\text{discharge}}} \quad (6)$$

All electrochemical measurements were performed on a Bio-Logic VSP electrochemical work station at 20 °C.

Results and discussion

The fabrication of the asymmetric PPy//MnO2 supercapacitor is based on free-standing SnO2 nanotube arrays that are fabricated by using AAO nano-template structures and atomic layer deposition (see supplementary video for the details of the fabrication process). The synthesized SnO2 nanotube arrays serve as a fundamental substructure to fabricate (via conformal electrochemical polymerization and deposition) both 3D SnO2/PPy and SnO2/MnO2 core/shell nanotube arrays for the use as negative and positive electrode materials, respectively (Figure 1). The implementation of the two different electrodes into one single supercapacitor defines the asymmetric device nature and enables the highly desired increase in operating potential window. We want to emphasize that the developed fabrication process for both electrodes is highly reproducible, which ensures a well repeatable electrochemical performance.

Negative electrode

The PPy based negative electrode is fabricated by potentiostatic electrochemical polymerization of pyrrole monomer at 0.8 V vs Ag/AgCl onto a SnO2 nanotube array. The structure and the core/shell nature of the 3D SnO2/PPy nanotube array are investigated by SEM and TEM measurements. Figure 2a displays a top-view and cross-section SEM image of a bare free-standing SnO2 nanotube array (diameter ~60 nm), showing the high structural regularity, the top-opened nanotube nature, and the vertical alignment of adjacent nanotubes (length ~1.8 μm). These unique structural features make this high aspect ratio material an ideal substructure for fabricating 3D core/shell materials for supercapacitor applications. A representative top-view and cross-section view of a PPy covered SnO2 nanotube array is presented in Figure 2b, showing the conformal coating of PPy and the high porosity of the structure. The TEM inset of a single SnO2/PPy nanotube in Figure 2c outlines the well conformal coating, which is supported by the observed morphology change during electrochemical polymerization of PPy on the surface of bare SnO2 nanotubes, as compared by SEM cross-section images in Figure 2d. The formation of a core/shell structure is further verified by EDX line-scans and reveals the material distribution across the tubular structure. Figure 2e presents the Sn L line scan profile across two parallel SnO2/PPy nanotubes, showing signal peaks located at the wall positions of the SnO2 NTs, which proves the nanotubular nature of SnO2. The C K spectrum in Figure 2f indicates an increased carbon concentration across the nanotubes, originating most likely from the PPy shell.

The electrochemical performance of the SnO2/PPy core/shell nanotube array as a negative electrode in supercapacitor devices is investigated by cyclic voltammetry (CV) and galvanostatic charge/discharge measurements. The electrochemical measurements were performed in a three-electrode configuration (platinum foil as counter electrode; Ag/AgCl reference electrode) in a water-based 1 M Na2SO4 electrolyte from −0.8 to 0 V vs Ag/AgCl. The CV curves in Figure 3a are recorded at different scan rates in the range from 2-50 mV s−1. The shape of the CV profiles reassembles the expected shape for a pseudocapacitive material to great extent and is of reversible nature, indicating a well capacitive behavior. The charge/discharge curves in Figure 3b are measured at various current densities to investigate the...
specific capacitance and the rate capability of the core/shell structure as a negative supercapacitor electrode. The specific capacitance \((c)\) is calculated from the gradient of the discharge curve according to Eq. (2) (Eqs. 2-6 are listed in the Materials and methods section) and achieves a maximum of \(260 \text{ F g}^{-1}\) at \(1 \text{ A g}^{-1}\) and remains high \(189 \text{ F g}^{-1}\) at \(50 \text{ A g}^{-1}\), assigning the core/shell structure a good rate capability (Figure S2). Hence, this PPy based core/shell nanotube array is a promising candidate as a negative electrode material in supercapacitors.

**Positive electrode**

The positive electrode based on a SnO\(_2\)/MnO\(_2\) core/shell nanotube array is fabricated by potentiostatic electrochemical deposition of MnO\(_2\) onto a bare SnO\(_2\) nanotube array from a solution containing \(0.1 \text{ M Mn(Ac)}_2\) at \(1 \text{ V vs Ag/AgCl}\).
material in supercapacitors was investigated by CV and galvanostatic charge/discharge measurements. The measurements were performed using a three-electrode configuration in a potential window from 0-0.9 V vs Ag/AgCl in a water-based 1 M Na₂SO₄ electrolyte. Figure 4c presents the CV curves recorded at different scan rates. The profiles of the curves are rectangular and exhibit a mirror image characteristic to the x-axis and maintain this symmetry even at high scan rates, proving a good pseudocapacitive behavior. The specific capacitance \( C_{sp} \) of the SnO₂/MnO₂ core/shell material is calculated according to Eq. (2) and achieves excellent 910 F g\(^{-1}\) at 1 A g\(^{-1}\) and remaining 217 F g\(^{-1}\) at 50 A g\(^{-1}\) (see Figures S1 and S2 for charge/discharge curves and rate capability), making this core/shell structure an attractive material for the positive electrode in asymmetric supercapacitors.

**Asymmetric supercapacitor device**

The merge of 3D core/shell PPy based negative and MnO₂ based positive electrode materials into one single device offers a completely new path to enhance the electrochemical performance of supercapacitors. The 3D nanostructured tubular array increases the surface area of the electrodes drastically while the asymmetric nature of the electrode materials enables the expansion of the operating potential window, leading both to an increase in specific energy. Thereby the core/shell nature provides a well utilization of the active electrode materials and ensures a fast charge carrier transport through the electrode matrix, which is a key criterion to obtain high specific power, as shown by resent results [34]. Figure 5a outlines the working potential windows of each electrode individually and emphasizes the ideal combination of PPy as negative and MnO₂ as positive electrode materials. Both materials show pseudocapacitive behavior in complementary operating potential windows so that the integration of both electrodes into one supercapacitor is leading to the desired increase in operating cell voltage to 1.7 V. Owing to the asymmetric device configuration, PPy can serve as a negative electrode material, unlike in symmetric PPy systems where undoping and the formation of an isolating state of PPy under negative potentials hinders its usage in energy storage applications, as investigated by Béguin et al. [22]. The maximum operating potential window of the PPy//MnO₂ asymmetric configuration...
is investigated on the basis of CV measurements in the range from 0.9-1.7 V in a two-electrode cell configuration at 20 mV s\(^{-1}\) in a 1 M \(\text{Na}_2\text{SO}_4\) electrolyte, as shown in Figure 5b. The CV curves of the PPy//MnO\(_2\) supercapacitor exhibit a mirror-image current response on voltage reversal until 1.7 V, proving a good capacitive behavior and the superiority to symmetric MnO\(_2://\text{MnO}_2\) configurations (i.e., max. cell voltage 0.9 V). Thereby this configuration circumvents the main limitation of aqueous based supercapacitors, namely the dissociation of water at potentials higher than \(\sim 1.2\) V, because of high over-potentials for hydrogen and oxygen evolution at the negative and positive electrodes and extends the operating voltage window beyond the thermodynamic limit to 1.7 V [22,35].

The electrochemical performance of the nanostructured PPy//MnO\(_2\) asymmetric supercapacitor is investigated in a two-electrode setup, using a 1 M \(\text{Na}_2\text{SO}_4\) aqueous electrolyte in a potential window of 1.7 V. Figure 6a presents the CV curves of a PPy//MnO\(_2\) device recorded at different potential scan rates. The shape of the curves outline that the charge storing characteristic of individual PPy and MnO\(_2\) based electrodes could be successfully transferred into a full asymmetric device. The CV curves exhibit a nearly symmetric and rectangular shape, which is maintained at high scan rates over the entire potential window of 1.7 V, proving the good capacitive behavior of this device. This result is further supported by the symmetric triangular shape of the galvanostatic charge/discharge profiles, as shown in Figure 6b. Thereby possesses the PPy//MnO\(_2\) asymmetric supercapacitor a high charge efficiency (>96%) and exhibits a good long-time cycling stability with a capacitance retention of over 80% after 2000 consecutive charge/discharge cycles (Figure 6c). As shown in Figure S3, the cycling stabilities of the individual PPy and MnO\(_2\) based electrodes, measured in a three-electrode configuration within their respective voltage windows, show comparable stability characteristics. Leakage current is a serious concern is supercapacitor applications. However, only very few publications report this value in their study. As shown in Figure S4. The leakage current of the reported device was determined to 57 \(\mu\)A after 30 min potential hold at 1.7 V, which is in the range of a reported CNT/PANI supercapacitor [36]. Most importantly, the 3D PPy//MnO\(_2\) core/shell asymmetric supercapacitor obtains specific energy and specific power values that are among the highest reported. The devices specific energy (\(E\)) is calculated from the associated charge/discharge curve in Figure 6b according to Eq. (4) while the real specific power (\(P_{\text{real}}\)) is derived by dividing the specific energy by the discharge time according to Eq. (6). The device exhibits a high specific energy of 27.2 Wh kg\(^{-1}\) at 0.85 kW kg\(^{-1}\) and remains excellent 7.8 Wh kg\(^{-1}\) at 24.8 kW kg\(^{-1}\), fulfilling the power target requirements (15 kW kg\(^{-1}\) based on the active electrode mass) of the Partnership for a New Generation of Vehicles (PNGV).
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Thereby this device exceeds the performance reported for other asymmetric supercapacitor devices, such as Fe$_2$O$_3//\text{MnO}_2$ [37,38] and PEDOT//MnO$_2$ [39] and can compete with the highest reported values for carbon//MnO$_2$ [25,35,38,40-46] and graphene//MnO$_2$ [17,31,32] asymmetric devices, as outlined in Figure 6c. Further the asymmetric PPy//MnO$_2$ supercapacitor outnumbers the electrochemical performance of aqueous devices based on symmetric configurations like MnO$_2$//MnO$_2$ [38,47] and carbon//carbon, [48-50] as well as a symmetric device based on as-prepared 3D SnO$_2$/MnO$_2$ electrodes. These results demonstrate that the electrochemical performance of supercapacitors can be successfully enhanced by introducing three-dimensionally structured electrodes in combination with an asymmetric cell design.

Conclusion

In summary, this work describes an innovative method for efficiently fabricating 3D core/shell nanotube arrays as negative and positive electrodes for supercapacitor applications. The implementation of an innovative PPy//MnO$_2$ asymmetric aqueous based supercapacitor has shown that the electrochemical performance of supercapacitors can be improved by introducing 3D core/shell nanostructures in combination with complementary energy storing materials. Considering the fact that many of the challenges that face the field of aqueous supercapacitors are related to difficulties associated with compound materials and operating potential window, the fabrication of asymmetric supercapacitors based on 3D core/shell nanotube arrays could dramatically accelerate the progress in this field and lead to energy storage devices that are safe to operate and have limited environmental impact.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.nanoen.2014.08.019.

Supplementary data and Supplementary Video are available from the Wiley Online Library or from the author.

References

[34] J. Yan, A. Sumboja, X. Wang, C. Fu, V. Kumar, P.S. Lee, Small 10 (2014) 3568-3578.


