Electrodeposition polyaniline nanofiber on the PEDOT:PSS-coated SiNWs for high performance supercapacitors

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Abstract: In this article, a novel silicon-based electrode was designed with the facile solution methods. With the modification of highly conductive PEDOT:PSS layer on the SiNWs by the spin-coated method (SiNWs-PSS), three-dimensional (3D) porous network polyaniline nanofibers (PANI) film was uniformly electrodeposited on the silicon surface (SiNWs-PSS@PANI). The sheet resistances of the PEDOT:PSS layer with different surfactants as well as the deposition time of the PANI were investigated. After optimization, the fabricated SiNWs-PSS@PANI electrode displayed high capacitance about 301.71 mF cm$^{-2}$ at the current density of 1mA cm$^{-2}$, which enhanced $\sim$29 fold comparing to 10.18 mF cm$^{-2}$ of electrode without the PEDOT:PSS layer between the SiNWs and PANI (SiNWs@PANI), outperforming most values of the reported silicon-based electrodes. The electrode designed in this paper provides a new idea to fabricate high-performance of silicon-based micro-supercapacitors with the simple and low-temperature method.

Keywords: SiNWs; Micro-supercapacitors; Electrodeposition; Polyaniline; PEDOT:PSS
1. Introduction

Due to the emergence and rapid development in the on-chip devices and portable micro-electronics, more efforts have been made to design and manufacture miniaturized energy storage devices[1-3]. In this regard, micro-batteries and micro-supercapacitors (MSCs) are a typical representative of some miniaturized energy storage devices, which play a crucial role in storing and managing the energy they obtained[2, 4]. For micro-batteries, they suffer from poor rate performance and limited cycle life[5]. Meanwhile MSCs have aroused tremendous interests and widely explorations, owing to their small size, fast charge/discharge property, good retention rate and high power density[6-9]. However, the low energy density of MSCs resulting from the low capacitance still restricts its practical applications. As known, the energy density is proportional to the capacitance \( E = \frac{1}{2}CV^2 \)[10]. Hence, various efficient strategies have been developed to improve areal capacitance of MSCs.

With the abundant source and relatively mature preparation technology of silicon materials, silicon-based electrodes have been investigated with particular attention to their use as the future on-chip MSCs. Compared with silicon wafer, three-dimensional (3D) silicon structure prepared on silicon substrate has larger specific surface area to load more active components. Many efforts have been dedicated to the 3D architectures for MSC electrode applications, such as silicon nanowires (SiNWs)[11-13], silicon nanotrees (SiNTrs)[14] and silicon nanorods (SiNRs)[15]. Among them, SiNWs with large surface/volume ratio are usually prepared via Chemical Vapor Deposition (CVD) or Metal-assisted Chemical Etching (MACE) methods[12, 16, 17]. The latter procedure is relatively simple and low cost[18]. However, the energy density of the pristine 3D silicon structure devices is very low, only \( \sim 440 \ \mu \text{F cm}^{-2} \), which is hard to drive small electronic components, limiting practical application[19]. Additionally, the surface of the pristine silicon structure is susceptible to oxidation or corrosion in aqueous solution, resulting a decline in stability. To overcome these issues, it is urgent to develop the 3D silicon-based device with high energy density and excellent stability.
During the past, carbon-based materials (glucose-derived porous carbon[20], ultrathin carbon sheath[21], diamond[10, 22] or graphene nanosheets[23]) have been used as the decorating materials on SiNWs for the purposes of gaining long cycle life and high energy density. Within this context, Kumar et al[24] prepared sucrose derived carbon coated silicon nanowires (SDCC-SiNWs) by drop casting. The resulting SDCC-SiNWs supercapacitor showed an areal capacitance of 3.3 mF cm⁻². Aradilla et al[10] reported a MSC device based on diamond-coated SiNWs electrodes, exhibiting outstanding cycling stability with a capacitance retention of 70% after 2×10⁶ cycles. Nevertheless, the use of expensive technologies, such as CVD and atomic layer deposition (ALD), in the preparation process as well as the high temperature (≥500 °C) may limit their integration on a chip or widespread application. Modification of SiNWs by conductive polymers[25, 26] and metal oxides[27, 28] has also been reported. Moulai et al[29] modified SiNWs with MnO₂ to obtain hybrid electrode with an areal capacitance of 21.296 mF cm⁻² at the scan rate of 10 mV s⁻¹. A Poly(3,4-ethylenedioxythiophene) PEDOT coating on the surface of SiNWs was successfully fabricated via electrochemical deposition and the resulting hybrid supercapacitor device delivered a specific energy of 10 W h kg⁻¹ at a cell voltage of 1.5 V[30].

From a variety of polymers, polyaniline (PANI) is extensively studied due to its low cost of aniline monomer, easy synthesis in aqueous media and high pseudo-capacitance. It is noted that the theoretical capacitance of pure PANI in the potential range of −0.2 ~ 0.8 V is 740 F g⁻¹[31]. However, only few reports about PANI applied for silicon-based MSCs. Li, et al[32] prepared the graphene@SiNWs electrode combined with pseudocapacitive polyaniline coating, which showed a large specific capacitance of 185 mF cm⁻². Liu, et al[33] synthesized coral-like polyaniline over the surfaces of aligned SiNWs via an in-situ polymerization method. The as-prepared electrode exhibited an areal capacitance of ~95 mF cm⁻² at a scan rate of 10 mV s⁻¹. However, the areal capacitance of the SiNWs/PANI hybrid electrode still needs to be further improved. Upon investigation, it was found that the interface between the inorganic silicon substrate and the surface modification material has a
significant effect on the capacitance and stability of the supercapacitor[34]. For instance, Zhou et al[35] have grafted poly(3,4-ethylenedioxythiophene) (PEDOT) to the surface of SiNWs and loaded polypyrrole (PPy) nanolayers. The results showed that the areal capacitance of the SiNWs/PEDOT@PPy composite electrode can be increased by 2.31 times by growing PEDOT as a surface modifier.

Hence, in this study, Poly(3,4-ethylenedioxythiophene): poly (styrene sulfonate) (PEDOT:PSS) with low cost and significant electrical conductivity is decorated between the SiNWs and PANI by the spin-coated method. The sheet resistances of the PEDOT:PSS layer with different surfactants as well as the electrodeposition time of PANI were investigated. After optimization, the resultant SiNWs-PSS@PANI electrode displayed amazing high areal capacitance about 301.71 mF cm\(^{-2}\) at the current density of 1 mA cm\(^{-2}\), much higher than that 10.18 mF cm\(^{-2}\) of SiNWs@PANI electrode.

2. Experimental section

2.1 Materials and reagents

Highly-doped n-type silicon (100) wafers (5-7 Ω cm) were purchased from Suzhou Crystal Silicon Electronic & Technology Co., Ltd. and used as the substrate for SiNWs growth. Phosphorus pentachloride (PCl\(_5\)) was purchased from Alfer. PEDOT:PSS solution (Clevios PH 1000) was purchased from Heraeus and used to modify silicon substrate surface. Hydrofluoric acid (HF>40%), silver nitrate (AgNO\(_3\)), hydrochloric acid (HCl, 36%~38%), nitric acid (HNO\(_3\), 65%~68%), Triton X-100, sodium sulfate (Na\(_2\)SO\(_4\)), 3-glycidoxypropyltrimethoxydsilane (GOPS) and tetraethoxysilane (TEOS) were provided by Sinopharm Chemical Reagent Co., Ltd. Chlorobenzene, multiwalled carbon nanotubes (CNT) and aniline (AN) was purchased from Aladdin Industrial Corporation (Shanghai, China). All the commercial reagents and solvents were used without further purification.

2.2. Synthesis of SiNWs

SiNWs were prepared by a metal-assisted chemical etching (MACE) method[36]. The cleaned silicon wafers were firstly immersed in etching solution (5 M HF/0.02 M
AgNO₃) for 60 min to be etched, and followed by repeatedly rinsed with deionized water. A concentrated HNO₃ solution was used to soak the silicon wafers for at least 1 hour. To remove native oxide layers, the silicon wafers were put into a 5% HF solution for about 10 min. Subsequently, the SiNWs were quickly immersed in a saturated solution of PCl₅ in chlorobenzene in an oil bath and kept for 2 hours at 115 °C to obtain the treated SiNWs[37].

2.3. Synthesis of SiNWs-PSS

The PEDOT:PSS solution was employed with 0.1 wt% Triton X-100 and 0.3 wt% GOPS or TEOS to enhance the uniform and adhesion between PEDOT:PSS layer and the silicon substrate. The mixed solution was spin-coated on the SiNWs substrate at 2000 rpm for 60 s and annealed in vacuum at 150 °C for 15 min. The process was repeated for two times. After the annealing process, the as-prepared substrate was immersed in concentrated sulfuric acid for 5min. The samples are labeled as GOPS, TEOS, GOPS-SA and TEOS-SA, respectively. For comparison, the sample was also fabricated with the solution only added Triton X-100.

2.4. Synthesis of SiNWs-PSS@PANI

The PANI film was prepared on the silicon substrate by electrodeposition in a typical two-electrode system, where the SiNWs-PSS substrate and a Pt sheet were employed as the working electrode and the counter electrode, respectively. Electrodeposition is carried out at a constant voltage of 2V. The electrolyte consisted of AN (0.3 M) and HCl (1M). During electrodeposition, the area of the working electrode extending into the electrolyte was 1 cm × 1 cm. The electrodes with different electrodeposition time of 5, 10, 15, 20 and 25 min were labeled as T5, T10, T15, T20 and T25 respectively. As comparing, the PANI was also electrodeposited on the pristine SiNWs substrate with the silver as the rear contact for 20 min (SiNWs@PANI-T20).

To enhance the charge transfer as well as current collection of the electrode, another PEDOT:PSS layer was spin-coated above the PANI. For further increasing the capacity of the electrode, the top PEDOT:PSS layer was doped with CNT, where the as-prepared PEDOT:PSS solution was mixed with 6 mg mL⁻¹ CNT solution in the
volume ratio of 1:3. The electrodes fabricated without the top PEDOT:PSS layer, with the top PEDOT:PSS layer and with the PEDOT:PSS layed doped CNT was named as non-PSS, PSS and CNT doped PSS, respectively.

2.5. Fabrication of symmetric supercapacitors

A symmetric two electrode configuration was used to study the behavior of the SiNWs-PSS@PANI as supercapacitor electrodes under operating conditions. The electrochemical performance of the device was tested in 1M Na$_2$SO$_4$, and the total geometric area of the active surface was 1 cm $\times$ 1 cm.

2.6. Material characterization and electrochemical measurement

The sheet resistances of the samples spin-coated on the planar silicon were measured by the four-probe method. The cross-section and 45 tilt angle morphology of these composite electrodes were characterized by using a field emission scanning electron microscope (FESEM, NovaNano450) equipped with element Mapping. The microstructure images were investigated using transmission electron microscope (TEM, JEM-2100 (HR)). Raman spectra were recorded using a DXR Raman microscope with 532 nm laser. Fourier transform infrared spectrometry analyzer (FTIR, Nicolet iS10) was used to study molecular structures and chemical bonds of PANI. X-ray diffractometer (XRD, D8 ADVANCE) was used to further investigate the microstructure and composition of electrodeposited polyaniline.

Electrochemical measurements were accomplished by employing a CHI760E electrochemical workstation (CH Instruments Inc., Shanghai, China). The cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS) measurements were conducted at room temperature. CV curves were performed between -0.1 and 0.9 V using different scan rates (10~100 mV s$^{-1}$) and GCD curves were performed between -0.3 and 0.7 V using different current densities (1~5 mA cm$^{-2}$). The EIS tests were investigated by using a sinusoidal signal of 10mV amplitude at open circuit potential and a frequency ranging from 100 kHz to 0.01 Hz. Under 3-electrode system, the electrochemical performance of single electrode was investigated, where Pt plate as counter electrode, Ag/AgCl as reference electrode and the as-prepared silicon-based electrode as the working electrode. Each
The electrode area was 1 cm × 1 cm. All electrochemical experiments are conducted in 1 M Na₂SO₄.

The areal capacitance Ca (mF cm⁻²) based on CV curve was calculated according to the equation (1):

\[ C_a = \frac{\int_a^b i(V)dV}{2A\Delta V} \]  \hspace{1cm} (1)

The areal capacitance Cs (mF cm⁻²) based on GCD was according to the equation (2):

\[ C_s = \frac{1000I\Delta t}{A\Delta V} \]  \hspace{1cm} (2)

Where \( \int_a^b i(V)dV \) was the integrated area of the CV curve, \( \Delta V \) (V) was the potential window, A (cm²) was the electrode area, \( v \) (V s⁻¹) was the scan rate, I (A) referred to the applied discharge current and \( \Delta t \) (s) was the discharge time.

The energy and power densities of the micro-supercapacitor were calculated according to the following equations:

\[ E = \frac{1}{2} \times C_{\text{device}} \frac{(\Delta V)^2}{3600} \]  \hspace{1cm} (3)

\[ P = \frac{E}{\Delta t} \times 3600 \]  \hspace{1cm} (4)

Where E (mWh cm⁻²) was the energy density, P (mW cm⁻²) was the power density, \( C_{\text{device}} \) (mF cm⁻²) was the whole areal capacitance of the device, \( \Delta V \) (V) was the potential window and \( \Delta t \) (s) was the discharge time.

3. Results and Discussion

3.1 Modification of SiNWs

The morphology images of different silicon substrates are shown in Fig. 1. From Fig. 1a, high-density and ordered SiNWs are distributed vertically on the silicon substrate with the MACH method. In the literature, the density of SiNWs can be significantly reduced by dipping the substrate into a saturated solution of PCl₅ in chlorobenzene[37]. As shown in Fig. 1b, after being immersed in PCl₅ solution for 2 hours, the space between the nanowires is largely increased, which is beneficial for the subsequently decoration of polymers. Additionally, the nanowires are reduced
from ~3.10 to 2.52 μm. It is known that PANI can be synthesized on the conductive substrate by electrodeposition method, however, as shown in Fig. 1c, there is only few PANI formed on the naked silicon substrate with Ag as the rear contact, even the electrodeposition time attaining to 10 min.

PEDOT:PSS is commercially used as a buffer layer between the electrode and the active materials in energy storage devices[38]. Here, to form the uniform PANI on the SiNWs, PEDOT:PSS layer is spin-coated on the SiNWs. As shown in Fig. 1d, the formed PEDOT:PSS layer is tightly wrapped around the surface of SiNWs, forming a intimate core-shell structure. To increase the connection between the SiNWs and PEDOT:PSS, the surfactants of GOPS and TEOS were added to the PEDOT:PSS solution, respectively. After annealing, that the prepared layer is also immersed in concentrated sulfuric acid for 5min. The sheet resistances of the synthesized PEDOT:PSS layers is measured by four-probe method on planar silicon and summarized in Table 1. It can be found that the sheet resistance of TX-100 is 252.2Ω cm/□. After adding the surfactants of GOPS and TEOS, the resistance values decrease to 57.4 Ω cm/□ and 68.2 Ω cm/□, respectively. It is know that with the dipping treatment in acid solution, the conductivity of the PEDOT:PSS can be enhanced. Interestingly, when TEOS sample is treated with sulfuric acid, its resistance increases to 90.2 cm/□, while GOPS-SA shows the lowest 45.48 Ω cm/□. Therefore, we choose GOPS as the surfactant with sulfuric acid treatment. EIS measurement is also carried out to investigate the ion diffusion and charge transfer resistance of the SiNWs-PSS electrodes with different treatment. In general, Nyquist plot composed of three characteristic regions: (i) Intercept to real axis Z′(Ω) at high frequency region gives series resistance (R_s);(ii) Semicircle represent charge transfer resistance (R_ct)[39]; (iii) Straight line in low frequency region shows capacitive behavior of electrode. As indicated in Fig. S1, both the obtained R_s and R_ct of GOPS-SA sample is much smaller comparing to others, illustrating that the GOPS-SA has the lowest sheet resistance. The result of EIS is consistent with that from the four-probe measurements (Table 1). Fig. 1e and f shows that PANI is successfully synthesized on the surface of SiNWs-PSS. It can be found that the PANI is homogeneously and fully covered on
the substrate. The fibers are intertwined with each other, forming the 3D porous polymer network.

**Table 1** The sheet resistance of the PEDOT:PSS layers prepared with different surfactants

| Surfactant | TX-100 (%) | GOPS (%) | TEOS (%) | Sulfuric acid treatment | Sheet resistance (Ω cm/□) |
|------------|------------|----------|----------|-------------------------|--------------------------|
| TX-100     | 0.1        | 0        | 0        | ×                       | 252.2                    |
| GOPS       | 0.1        | 0.3      | 0        | ×                       | 57.4                     |
| TEOS       | 0.1        | 0        | 0.3      | ×                       | 68.2                     |
| GOPS-SA    | 0.1        | 0.3      | 0        | ✓                       | 45.48                    |
| TEOS-SA    | 0.1        | 0        | 0.3      | ✓                       | 90.4                     |

**Fig. 1** SEM images of different silicon substrates. **a** SiNWs synthesized with MACE method for 60 min, **b** SiNWs treated by PCl₅ solution for 2h. Insets are cross-section corresponding images. **c** PANI electrodeposited on the pristine SiNWs substrate using the Ag as the rear electrode for 10 min, the inset shows the image at high
magnification, d SiNWs-PSS. Inset is cross-section image, e and f different magnification images of SiNWs-PSS@PANI with the deposition time of 5 min.

To further characterize micromorphology and molecular structure of the electrodeposited PANI, TEM, FITR, Raman and XRD measurements were carried out. As shown in Fig. 2a, there are many particles distributed on the surface of polyaniline nanowires, which results in the rough surface of PANI, increasing the contact area with the electrolyte. The diameter of the PANI is ~100 nm. Fig. 2b shows the FTIR spectrum of synthesized PANI, it can be seen a series of characteristic peaks including C=C stretching vibration of benzenoid units at 1486 cm\(^{-1}\) and 1562 cm\(^{-1}\) of PANI are presented [40, 41], which makes clear that the PANI is in semi-oxidation state, illustrating that the SiNWs-PSS@PANI has excellent electronic conductivity. The bands at 1298 cm\(^{-1}\) and 1240 cm\(^{-1}\) are attributed to C-N stretching vibration of secondary aromatic amino structures [42]. The main characteristic band at 791 cm\(^{-1}\) is ascribed to the aromatic N-H stretching vibration of the secondary aromatic amine bending vibration [43]. Furthermore, the two main band at 876 cm\(^{-1}\) and 1121 cm\(^{-1}\) are ascribed to the out-of-plane bending vibration of C–H within the 1,4-disubstituted aromatic ring and the stretching vibration of C-N of the secondary aromatic amine structures bending vibration, respectively [44]. Raman spectra of the PANI is shown in Fig. 2c. The two typical characteristic peaks of PANI are at 1590 and 1340 cm\(^{-1}\), which are corresponded to C-C stretching of benzenoid structure and C-N stretching of quinoid structure of PANI [43]. The characteristic peak at 1490 cm\(^{-1}\) is ascribed to C=C stretching of quinoid structure of PANI [40]. Fig. 2d provides the XRD patterns of PANI to evaluate the crystallinity phase purity. The three samples show an amorphous background in their XRD patterns because polyaniline is incomplete crystalline. The crystallinity and coherence length of the pure PANI polymer chain orientation can be analyzed by the diffraction peaks at 20 values of 21.4° and 25.4° [45-47]. The diffraction peaks at 21.4° and 25.4° are attributed to the vertical and parallel periodicity of the PANI polymer chain, respectively [41]. The results of
FTIR, Raman and XRD demonstrated that PANI were successfully electrodeposited on the SiNWs-PSS substrate.

![TEM image of electrodeposited polyaniline nanofibers](image1)

**Fig. 2** a TEM image of electrodeposited polyaniline nanofibers, b FTIR spectra of PANI, c Raman spectra of PANI and d XRD patterns of PANI.

### 3.2 Top PEDOT:PSS layer doped with CNT

To reduce the sheet resistance of the electrode, another PEDOT:PSS layer was spin-coated over the PANI. As shown in Fig. S2, due to the porous structure of PANI, the S element is uniformly distributed over the entire cross-section of the SiNWs-PSS@PANI, suggesting that the PEDOT:PSS layer is fully infiltrated into the active materials. To further improve capacity of the electrode, the top PEDOT:PSS layer is mixed with CNT, whose diameter of the CNT is about 5-10 nm and the length is between 1 μm to 5 μm. In this case, CNT acts as a conductive link, which not only provides the best one-dimensional ion transport channel, but also significantly improve the capacitance and stability of the composite electrode on account of the synergistic effect[48]. The electrochemical behavior of non-PSS, PSS and CNT doped PSS electrodes is examined by CV and GCD measurements using a three-electrode configuration. **Fig. 3a** displays the CV curves of the electrodes recorded at the same
scan rate of 50 mV s\(^{-1}\) in 1 M Na\(_2\)SO\(_4\) electrolyte. It can be seen that the CNT doped PSS electrode has larger integral area and stronger peak current, indicating higher area capacitance. The calculated areal capacitance of CNT doped PSS electrode is 43.59 mF cm\(^{-2}\), higher than 31.76 mF cm\(^{-2}\) of PSS electrode and 23.72 mF cm\(^{-2}\) of non-PSS electrode.

In Fig. 3b, all the GCD curves of the electrodes at 1 mA cm\(^{-2}\) show a slight deviation from the triangular shape due to the Faradaic reactions from the Faradaic charge storage mechanism. The corresponding calculated areal capacitance from the GCD is presented in Fig.3c. It can be seen that the CNT doped PSS electrode displays the highest areal capacitance of electrode is 76.09 mF cm\(^{-2}\). The variation of the areal capacitance with different scan rates and current densities is displayed in Fig. 3d and e, respectively. Upon increasing the current density up to 5 mA cm\(^{-2}\), a small gradual degradation of the capacitance is observed. The reason is that the ions and charges in the electrolyte cannot be diffused and transferred to the electrode adequately at a large current density. However, even at high current density of 5 mA cm\(^{-2}\), CNT doped PSS electrode still shows an areal capacitance of 32.51 mF cm\(^{-2}\). The GCD results are line with the CV results. By analyzing the Nyquist diagram (Fig. 3f), the Rct is calculated to be about 54.9, 50.6 and 20.8 Ω for non-PSS, PSS and CNT doped PSS electrode, respectively, indicating that the highly conductive layers doped with CNT can obviously reduce the charge transfer resistance. All the CV, GCD and EIS results confirm that the top PEDOT:PSS layer can promote charge transfer and collection of the electrode, improving its the capacity, which can be further enhanced by doping the PEDOT:PSS with CNT. In the next section, all the SiNWs-PSS@PANI electrodes is fabricated with the top PEDOT:PSS layer mixed with CNT.
Electrochemical performance of the SiNWs-PSS@PANI electrodes with different top layer. 

- **a** CV curves at the scan rate of 50 mV s$^{-1}$
- **b** GCD measurement at the current density of 1 mA cm$^{-2}$
- **c** areal capacitances at the current density of 1 mA cm$^{-2}$
- **d** areal capacitance at different scan rates
- **e** areal capacitance at different current densities
- **f** Nyquist impedance plots at the open circuit voltage.

**Fig. 3** The electrodeposition time is 5 min.

### 3.3 Electrodeposition time of PANI

With the extension of deposition time, the load of active material increases, which can increase the electrode capacitance. However, there is an adverse effect on the diffusion of electrolyte ions due to the increase of ion diffusion resistance when the active layer becomes thicker[49]. Therefore, there is an optimal electrodeposition time. The electrochemical performance of the electrode with different deposition time is described in **Fig. 4**. As a comparison, PANI electrodeposited on the naked silicon substrate using the Ag as the rear electrode for 20 min is also investigated. **Fig. 4a** shows the CV measurement under the scan rate of 50 mV s$^{-1}$, The T20 electrode exhibits the larger CV curve area than those of other electrodes. The GCD curves of the electrodes at the current density of 1 mA cm$^{-2}$ as well as the corresponding calculated areal capacitance values are shown in **Fig. 4b** and **c**, respectively. Distinctly, the T20 electrode has the longest discharge time and displays high areal
capacitance about 301.71 mF cm$^{-2}$, showing that 20 min is the optimized deposition
time. Obviously, as shown in Fig.4c, at the same deposition time of 20 min, the
electrode of PANI decorated on the naked SiNWs (SiNWs@PANI) is only 10.18 mF
cm$^{-2}$, much smaller than those of the electrodes with PEDOT:PSS layer. The reason
can be ascribed to the load of the PANI. As shown in Fig. S4, even the
electrodeposition time extends to 20 min, few polyaniline nanofibers are deposited on
naked SiNWs substrate. Meanwhile, the high density intertwining PANI is
homogeneously deposited on the SiNWs-PSS substrate. Thus, we can conclude that
the PEDOT: PSS layer spin-coated on the SiNWs could increase the contact between
the SiNWs and PANI, benefiting large load of PANI uniformly deposited on SiNWs

Fig. 4d and e show the CV curves and GCD curves of the T20 electrode at
different scan rates and current densities, respectively. It is noted that even at the
largest CV current density of 100 mv s$^{-1}$ and the highest current density of 5 mA cm$^{-2}$,
the CV and GCD curves has slight changes, indicating high electron and electrolyte
ion mobility in the electrode. At high current density of 5 mA cm$^{-2}$, the T20 electrode
still can attains an areal capacitance of 116.74 mF cm$^{-2}$. Additiontionaly, the obtained
T20 electrode exhibited reliable stable cyclability with a capacitance retention of
77.4% of the initial value after 1000 cycles (Fig. 4f).

Compared to other silicon-based ultracapacitors that have been reported (Table
S1), such as PEDOT@SiNWs (115 mF cm$^{-2}$ at 0.5 mA cm$^{-2}$)[26], SiNTRs/PPy (14 mF
cm$^{-2}$ at 1mA cm$^{-2}$)[25], SiNWs/PEDOT@PPy (106 mF cm$^{-2}$ at 0.5 mA cm$^{-2}$)[35], this
work provides a feasible way to improve the areal capacitance of silicon/polymer-based supercapacitors. The superior performance of this ternary
architecture can be attributed to the following factors: (i) SiNWs with a large specific
surface area provide a large contact area with the electrolyte. (ii) the doped PEDOT:
PSS layer provides a highly conductive surface; Therefore, the diffusion and transfer
of active ions can be accelerated. (iii) Electrodeposited PANI has an ideal
pseudocapacitance behavior and makes a significant contribution to the improvement
of areal capacitance. (iv) the presence of CNT not only improves the electrical
conductivity of the electrode, but also improves the rate performance.
Fig. 4  a CV curves at a scan rate of 50 mV s\(^{-1}\), b GCD curves at 1 mA cm\(^{-2}\), c areal capacitance of different electrodeposition time extracted from the GCD curves, d CV curves at various scan rates, e GCD curves at different current densities and f Cyclic stability at 100 mV s\(^{-1}\) of the electrode.

3.4 Electrochemical properties of symmetric supercapacitor device

In order to explore the possibility of practical application of the prepared ternary electrode material, we assembled a symmetric ultracapacitor. Fig. 5a shows the schematic diagram of a symmetric supercapacitor based on SiNWs-PSS@PANI electrodes. Fig. 5b illustrates the CV curves of the symmetrical supercapacitor within a potential window of 1 V at different scan rates. Quasi-rectangular CV curves indicate the ideal capacitive behavior of the assembled device. Fig. 5c shows the GCD curves of the symmetric supercapacitor at different current densities from 1 to 5 mA cm\(^{-2}\) in 1 M Na\(_2\)SO\(_4\) electrolyte. Based on the GCD curves, the calculated areal capacitance of the device reaches to 169.58 mF cm\(^{-2}\) at 1 mA cm\(^{-2}\). Even at a high current density of 5 mA cm\(^{-2}\), it still remains 65.37 mF cm\(^{-2}\)(Fig. 5d).

Energy density and power density are two important factors for the supercapacitor, since they represent its overall energy transfer capacity. In our work, the assembled SiNWs-PSS@PANI electrode-based symmetric device delivers the
highest energy density of 0.023 mWh cm\(^{-2}\), with a power density of 0.279 mW cm\(^{-2}\) at a lower current density of 1 mA cm\(^{-2}\). Even at the high power density of 2.832 mW cm\(^{-2}\), the device delivers a high energy density of 0.009 mWh cm\(^{-2}\), confirming the best capabilities of the fabricated device. These values are considerably higher than those of the symmetric silicon-based supercapacitors. For instance, Li et al.\cite{50} reported an energy density of 15.1 μWh cm\(^{-2}\) for a GNW/RuO\(_x\) based hybrid MSC. Zhou et al.\cite{35} synthesized SiNWs/PEDOT@PPy composite device, whose energy density was 0.0146 mWh cm\(^{-2}\) at the power density of 0.375 mW cm\(^{-2}\).

**Fig. 5**

(a) Schematic diagram of a symmetric supercapacitor based on SiNWs-PSS@PANI electrodes, (b) CV curves at various scan rates, (c) GCD curves at...
different current densities, d areal capacitance at different current densities and e Ragone plots of MSCs with other reported values for comparison.

4. Conclusions

In summary, a ternary electrode of SiNWs-PSS@PANI was successfully fabricated via a simple and low-temperature method, which exhibited an amazing areal capacitance of 301.71 mF cm\(^{-2}\) at a current density of 1 mA cm\(^{-2}\), exceeding most values of the reported Si-based electrodes. Additionally, the obtained SiNWs-PSS@PANI electrode exhibited a reliable stable cyclability with 77.4% capacitance retention after 1000 cycles. The device assembled with symmetrical ternary electrode exhibited a high capacitance of 169.58 mF cm\(^{-2}\) in a wide potential of 1 V. All the preliminary results demonstrate that high capacitive performance of Si-based MSCs could be fabricated by the simple and low-cost approach.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at XXXX.

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