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# **Silicon nanowire-hydrogenated TiO<sub>2</sub> core-shell arrays for stable electrochemical micro-supercapacitors**

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## **Abstract**

In this paper, we fabricated silicon nanowire-TiO<sub>2</sub> core-shell arrays in a two-step process. First, silicon nanowire arrays (SiNW) were prepared in HF/AgNO<sub>3</sub> aqueous solution using metal-assisted chemical etching of bulk silicon. Then, atomic layer deposition (ALD) technique was applied to coat a 20 nm thin shell TiO<sub>2</sub> film. The TiO<sub>2</sub>/SiNW substrates were afterward annealed at 400 °C in hydrogen atmosphere for 4 h and tested as electrode materials for electrochemical micro-supercapacitors. The electrochemical features of the constructed H-TiO<sub>2</sub>/SiNW electrode were assessed in an aqueous 1 M Na<sub>2</sub>SO<sub>4</sub> electrolyte solution and revealed that the specific capacitance increased six times compared to non-annealed TiO<sub>2</sub>/SiNW and 20-fold compared to a reference SiNW electrode under the same operating conditions. Importantly, H-TiO<sub>2</sub>/SiNW also displayed a high stability over 30,000 cycles at 0.1 mA cm<sup>-2</sup> with an overall decrease of 19% of the initial capacitance. The hydrogen treatment increased the density of hydroxyl group and enhanced the carrier density on TiO<sub>2</sub> surface improving the capacitive properties of H-TiO<sub>2</sub>/SiNW.

**Keywords:** *Silicon nanowires; TiO<sub>2</sub> thin film; hydrogenation; micro-supercapacitor, high stability*

## 1. Introduction

Today, interest in energy saving, electric and hybrid vehicles and the quest for efficiency and multi-functionality in micro-systems make the research on electrochemical energy storage a field in full expansion [1, 2].

In particular, miniaturized versions of electrochemical supercapacitors (called micro-supercapacitors) that can be easily integrated into microelectronic circuits attracted more attention in recent years [3-5]. Increasing the specific surface area and chemical stability of electrodes is the current research strategy to improve their performances in terms of storage capacity, life cycle, energy and power densities [6, 7]. In this case, it appears that nanostructured materials and in particular nanowires are the most suitable for the supercapacitor electrode realization, due to their high developed surface area and quasi-ideal electric double layer [8-11].

Silicon nanowires (SiNW) are one of these semiconductor nanostructures investigated as potential electrode material in energy storage/release devices like electrochemical supercapacitors [12] and batteries [13-15]. The focus on Si-based electrodes is essentially governed by the well-established microfabrication technology, which holds great promise in the area of integrated storage devices. In addition, large surface areas can be achieved through nanostructuring of bulk Si using different routes e.g. reactive ion etching (RIE), chemical vapor deposition growth, and metal-assisted chemical etching (MACE) [13, 15]. The latter approach, used in our work, is a simple and effective wet chemical approach to produce a nanowire array from bulk Si avoiding the use of vacuum environment.

Even though, SiNW arrays feature high developed surface area, their direct utilization as electrodes is restricted by their chemical instability in aqueous and basic solutions [9,11]. In fact, oxide formation and dissolution limit their long-term operation and real-world potential application. Therefore, coating of these nanowires with organic and non-organic materials

was commonly applied to overcome this hurdle. In this context, coating SiNW arrays with transition metal oxides (NiO, MnO<sub>2</sub>, ZnO/Al<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub>) not only enhances the stability, but it also increases the specific capacity since they are battery-type or pseudo-capacitive materials [16-18]. Other coatings based on thin diamond [19, 20] and carbon [8, 21] films were also applied to enhance the capacitive performance of the SiNW electrodes.

TiO<sub>2</sub>, one of these transition metal oxides, is the subject of extensive academic and technological research, owing to its specific properties: non-toxic, abundant, inexpensive and chemically stable [22]. Despite its capacity is lower than that of other capacitive materials like RuO<sub>2</sub>, NiO or conductive polymer nanostructures, it was broadly investigated as electrode material for electrochemical supercapacitors [23]. Investigation of the capacity of TiO<sub>2</sub> nanotubes revealed significantly high values (911  $\mu\text{F cm}^{-1}$  at 1  $\text{mV s}^{-1}$ ) [24], and this value was improved upon hydrogenation treatment [25, 26]. Also, TiO<sub>2</sub> as a transition metal oxide has been applied in perovskite devices [27, 28].

SiNW coated with TiO<sub>2</sub> (SiNW/TiO<sub>2</sub>) were described in some reports. Konstantinou *et al.* used three processes to coat SiNW electrodes with TiO<sub>2</sub> thin film: TiCl<sub>4</sub> treatment method, dip coating path and hydrothermal method [29]. The highest surface capacity (386  $\mu\text{F cm}^{-2}$ ) was achieved based on the galvanostatic charge-discharge (GCD) technique at  $3.7 \times 10^{-5}$  A in [Bmim][NTf<sub>2</sub>] ionic liquid [29]. Besides, spin coating of TiO<sub>2</sub> on SiNW attained a specific capacity of 3.55  $\text{mF cm}^{-2}$  at 0.1  $\text{mA cm}^{-2}$  with a retention of 68.8% after 1,000 galvanostatic charge-discharge cycles [30].

Atomic layer deposition (ALD) is a technique able to afford compliant coatings on various substrates with a very precise control over the coating thickness [31]. Memarz *et al.* demonstrated that SiNW battery anode coated with TiO<sub>2</sub> by ALD featured a remarkable improvement in its performances, as compared to the non-coated one [32]. Although, TiO<sub>2</sub>-coated electrodes achieved enhanced capacitive properties, their specific capacitance values

were significantly lower than those recorded using other metal oxides [24, 33, 34], most likely due to the limited electrochemical performance and reduced electrical conductivity of TiO<sub>2</sub> [35, 36].

One way to address these limitations is through hydrogenation, which is capable to modify effectively the material's properties. Indeed, it has been shown its great ability in TiO<sub>2</sub> nanocrystals for introducing significant structural changes and improvement in their optical, electronic, photocatalytic, lithium-ion storage capability and field emission [37].

Based on above results, we applied the ALD method to coat a thin TiO<sub>2</sub> layer on SiNW, prepared by Ag-assisted chemical etching, and subsequent thermal annealing at 400 °C for 4 h in hydrogen atmosphere. The effect of the H-TiO<sub>2</sub> coating on the capacitive behavior of the SiNW electrode was studied in 1M Na<sub>2</sub>SO<sub>4</sub> aqueous electrolyte. The specific capacitance of H-TiO<sub>2</sub>/SiNW was enhanced six times as compared to non-annealed one and 20-fold compared to a reference SiNW (4.5 μm) electrode under the same operating conditions. Furthermore, the hydrogenation of TiO<sub>2</sub> thin film deposited on SiNW led to good reversibility and stability over 30,000 galvanostatic charge-discharge cycles.

## **2. Experimental section**

### **2.1.1. Preparation of TiO<sub>2</sub>/SiNW**

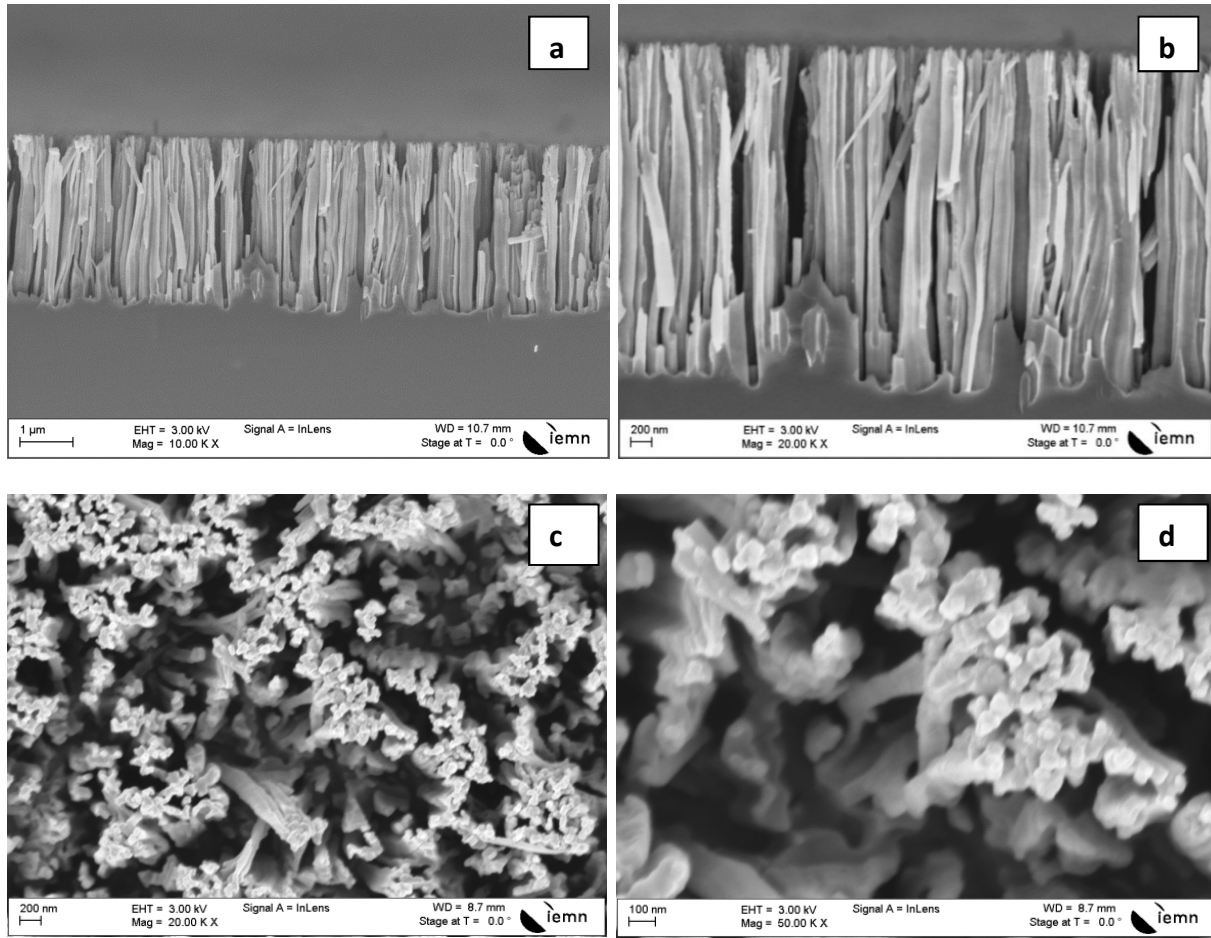
TiO<sub>2</sub> thin coatings were produced by ALD using TiCl<sub>4</sub> (titanium source), H<sub>2</sub>O vapor (oxygen source), and nitrogen as the purge gas. The deposition was conducted at 260°C and 2.8 mbars using a pulse duration of 250 ms for both precursors separated by 2 s of N<sub>2</sub> purge. The thickness of TiO<sub>2</sub> is function of the number of cycles and was determined by ellipsometry on flat Si surface (placed alongside with SiNW substrates in the reaction chamber). We set all experimental ALD parameters to obtain TiO<sub>2</sub> thickness of 20 nm.

### **2.1.2. Hydrogenation process**

The TiO<sub>2</sub>/SiNW were subsequently annealed under hydrogen atmosphere (named here after as H-TiO<sub>2</sub>/SiNW) and the other in the open air (designed as air-TiO<sub>2</sub>/SiNW) both at 400 °C for 4 h. The hydrogenation time at the maximum temperature was 4 h per sample and the hydrogen flow was started 30 min before the thermal programming and continued until the sample attained room temperature. The total duration of the hydrogen flow was about 10 h.

### 3. Results and discussion

**Figure S1** illustrates the scanning electron microscopy (SEM) micrographs of SiNW arrays produced by silicon dissolution in an aqueous solution of HF/AgNO<sub>3</sub> at 55°C for 30 min. The nanowires network forms bundles on the top surface due to inhomogeneous dissolution caused by Ag particles random distribution or van der Waals forces between the nanowires during the process of drying [38]. The cross-section observations revealed that a large quantity of nanowires well-aligned and perpendicular to the surface were obtained [39]. As it can be seen in **Figure S1b**, the wires are about 4.5 μm in length with different diameters. SEM images of a SiNW substrate ALD-coated with a TiO<sub>2</sub> thin film are depicted in **Figure 1**. **Fig. 1a** and **b** show that a thin film of TiO<sub>2</sub> was coated conformally on SiNW. The top view SEM images (**Fig. 1c,d**) confirmed that the TiO<sub>2</sub> layer was deposited in a uniform and conformal manner on the silicon nanowires. A TiO<sub>2</sub> film thickness of 20 nm was optimal to obtain high specific capacity and high cycling lifetime

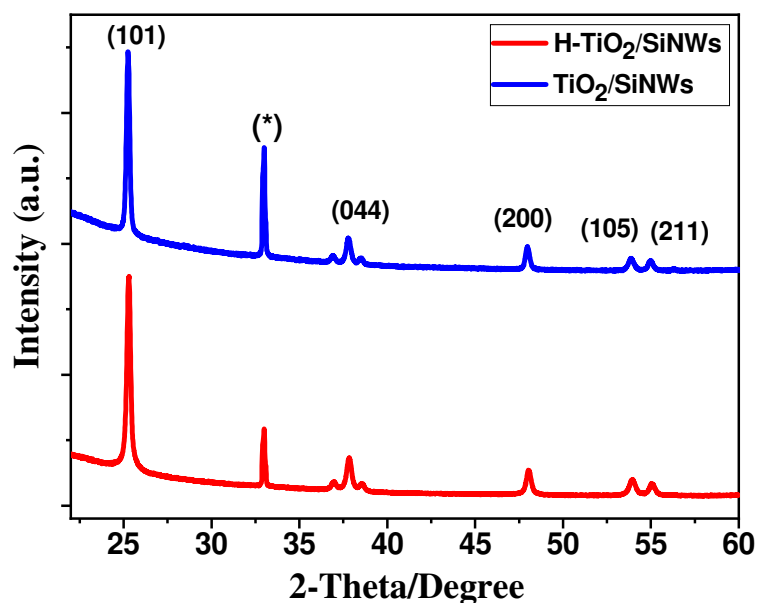


**Figure 1:** Cross-section (a,b) and top-view (c,d) SEM micrographs of SiNW arrays coated with 20 nm of TiO<sub>2</sub> by ALD.

To check if there is a change in the crystalline phase of TiO<sub>2</sub> after thermal hydrogenation, X-ray diffraction (XRD) patterns of TiO<sub>2</sub>/SiNW and H-TiO<sub>2</sub>/SiNW (400°C) were recorded. **Figure 2** displays the two diffractograms that present the same peaks at  $2\theta$  angles of 25.3°, 37.84°, 48.07°, 53.95° and 55.10° corresponding respectively to the (101), (044), (200), (105) and (211) diffraction planes. This indicates that the deposited TiO<sub>2</sub> phase is anatase (JCPDF No.21-1272) and that the thermal hydrogenation did not impact the TiO<sub>2</sub> crystalline structure [23, 40]. In addition to a slight decrease of the TiO<sub>2</sub> peak intensity after hydrogenation at high temperature, a small increase of the Full Width at High Half Maximum (FWHM) was observed, due most likely to increased defect density in TiO<sub>2</sub> structure, in accordance with

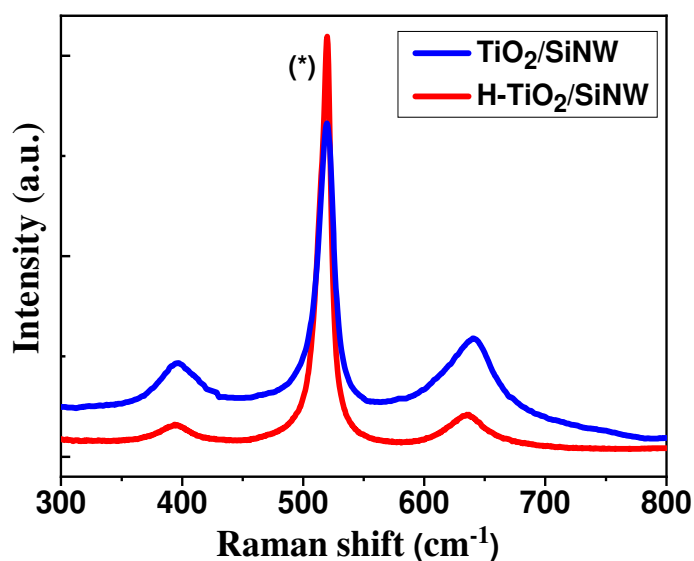


reference [40]. Note that the peak at  $33^\circ$  is due to the  $\lambda$ -half contamination of the (400) (200) diffraction plan of the silicon substrate.



**Figure 2.** X-ray diffractograms of  $\text{TiO}_2/\text{SiNW}$  and  $\text{H-TiO}_2/\text{SiNW}$  samples.

To study in more detail the effect of the hydrogenation process on the phase structure, the  $\text{TiO}_2/\text{SiNW}$  and  $\text{H-TiO}_2/\text{SiNW}$  samples were characterized by Raman spectroscopy. The Raman plots are depicted in **Figure 3** and both comprise Raman bands at  $397\text{ cm}^{-1}$  ( $\text{B1g}$ ) and  $640\text{ cm}^{-1}$  ( $\text{Eg}$ ), characteristic of  $\text{TiO}_2$  anatase. The width at mid-height of these two peaks were  $36.05$ ,  $33.69\text{ cm}^{-1}$  and  $33.47$ ,  $27.87\text{ cm}^{-1}$  respectively for the  $\text{TiO}_2/\text{SiNW}$  and  $\text{H-TiO}_2/\text{SiNW}$  samples. This means that the anatase phase is maintained after hydrogenation treatment, in accordance with XRD results. The Raman peaks of the  $\text{H-TiO}_2/\text{SiNW}$  sample are negatively offset and widen as compared to those of  $\text{TiO}_2/\text{SiNW}$ , which suggests an increase in the amount of vacant oxygen [41]. The feature at  $520\text{ cm}^{-1}$  (\*) is ascribed to the silicon substrate, its high intensity dominated the expected peak at  $515\text{ cm}^{-1}$  ( $\text{Eg}$ ), another characteristic peak of  $\text{TiO}_2$  anatase which was not visible [42].

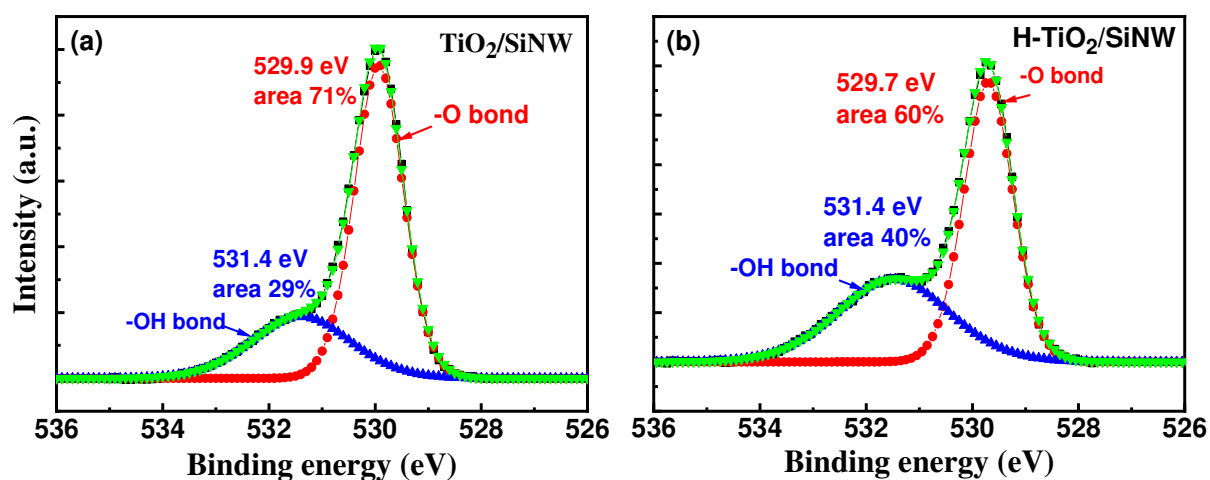


**Figure 3.** Raman plots of TiO<sub>2</sub>/SiNW (blue) and H-TiO<sub>2</sub>/SiNW (red) samples.

In order to determine surface chemical bonds, XPS data was acquired on the TiO<sub>2</sub>/SiNW and H-TiO<sub>2</sub>/SiNW substrates. The XPS survey profiles of TiO<sub>2</sub>/SiNW and H-TiO<sub>2</sub>/SiNW treated at 400 °C are comparable (see **Figure S2**). They both comprise Ti and O peaks characteristic of TiO<sub>2</sub> along with carbon signal originating from surface contamination during sample preparation and handling. The results infer that the hydrogenation process did not incorporate impurities into the TiO<sub>2</sub> lattice of H-TiO<sub>2</sub>/SiNW.

**Figure S3** displays the Ti<sub>2p</sub> wide XPS scans of TiO<sub>2</sub>/SiNW and H-TiO<sub>2</sub>/SiNW. Both comprise peaks at 458.5 and 464.5 eV assigned respectively to Ti<sub>2p3/2</sub> and Ti<sub>2p1/2</sub>, which are consistent with the typical values for TiO<sub>2</sub> [42-44]. **Figure 4a** and **b** depicts the O<sub>1s</sub> plots of TiO<sub>2</sub>/SiNW and H-TiO<sub>2</sub>/SiNW. Both spectra can be deconvoluted with two bands at around 530 eV (Ti–O–Ti species) and 531 eV (–OH groups). The –OH peak intensity in the O<sub>1s</sub> XPS spectrum increased after hydrogenation treatment, indicating the TiO<sub>2</sub> surface generated more surface hydroxyl groups [23]. The O peak remains the same meaning that the TiO<sub>2</sub> structure was not altered [45-47]. The result correlates well with the literature data [23], suggesting that hydrogen reacts with oxygen in TiO<sub>2</sub>, resulting in defect formation in the system [47].

The valence band (VB) edge positions were determined to study the impact of the hydrogenation process on TiO<sub>2</sub> electron band structure. The VB positions of TiO<sub>2</sub>/SiNW and H-TiO<sub>2</sub>/SiNW were deduced from the XPS spectra (**Figure S4**). The comparison between **Figure S4a** and **b** reveals a blue-shift of the VB edge from 1.27 to 1.12 eV after hydrogenation treatment in accordance with the literature [40, 44, 45, 47]; this could be related to hydrogen reaction with oxygen on TiO<sub>2</sub> surface in accordance with XPS results



quoted above.

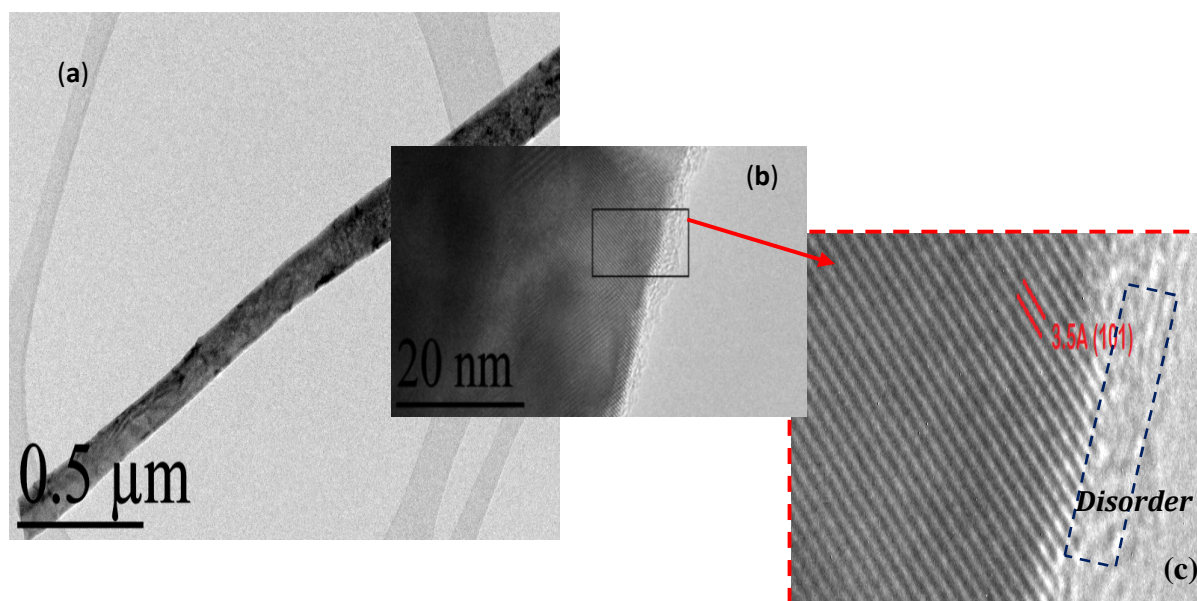
**Figure 4.** O<sub>1s</sub> XPS high-resolution profiles of (a) TiO<sub>2</sub>/SiNW and (b) H-TiO<sub>2</sub>/SiNW surfaces.

Optical band gap was also estimated by using the Kubelka-Munk [K-M or F(R)] method (&SI for details). The determined values from diffuse reflectance spectra revealed that the band gap was blue shifted from 3.03 eV to 2.82 eV when TiO<sub>2</sub>/SiNW sample was hydrogenated (**Figure S5**). A comparable shift was found after hydrogenation of TiO<sub>2</sub> [40, 44-47] and was assigned to the formation of more hydroxyl groups on the H-TiO<sub>2</sub> surface.

The structure of H-TiO<sub>2</sub>/SiNW was studied by transmission electron microscopy (TEM), **Figure 5a**. An individual silicon nanowire uniformly coated by TiO<sub>2</sub> thin film with a diameter of about 130 nm could be evidenced. In **Figure 5c** is exhibited a zoom of selected area of the

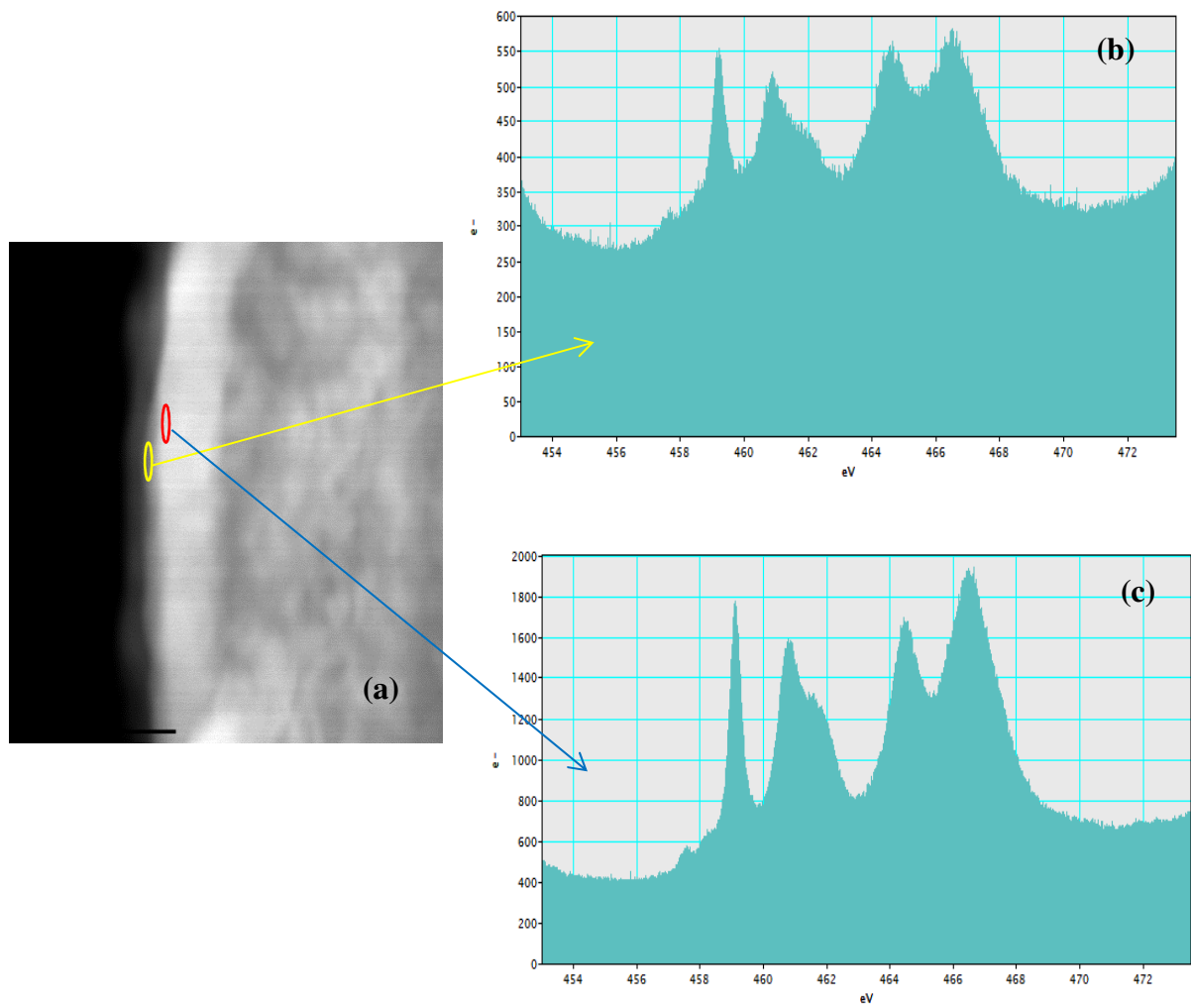
image **b**, where a spacing of 3.5 Å between adjacent planes, assigned to anatase TiO<sub>2</sub> (101), is clearly visible. This value correlates well with the expected TiO<sub>2</sub> interlayer distance [39]. In addition, a thin amorphous layer near the crystalline surface is also evident, which is in accordance with previous reports on hydrogenated TiO<sub>2</sub> [37, 48].

We can see also, in supplementary information (**Figure S6**), a chemical analysis of the image area of 20 nm TiO<sub>2</sub> layer, the concentration is very close to TiO<sub>2</sub> (27% Ti – 70% O).

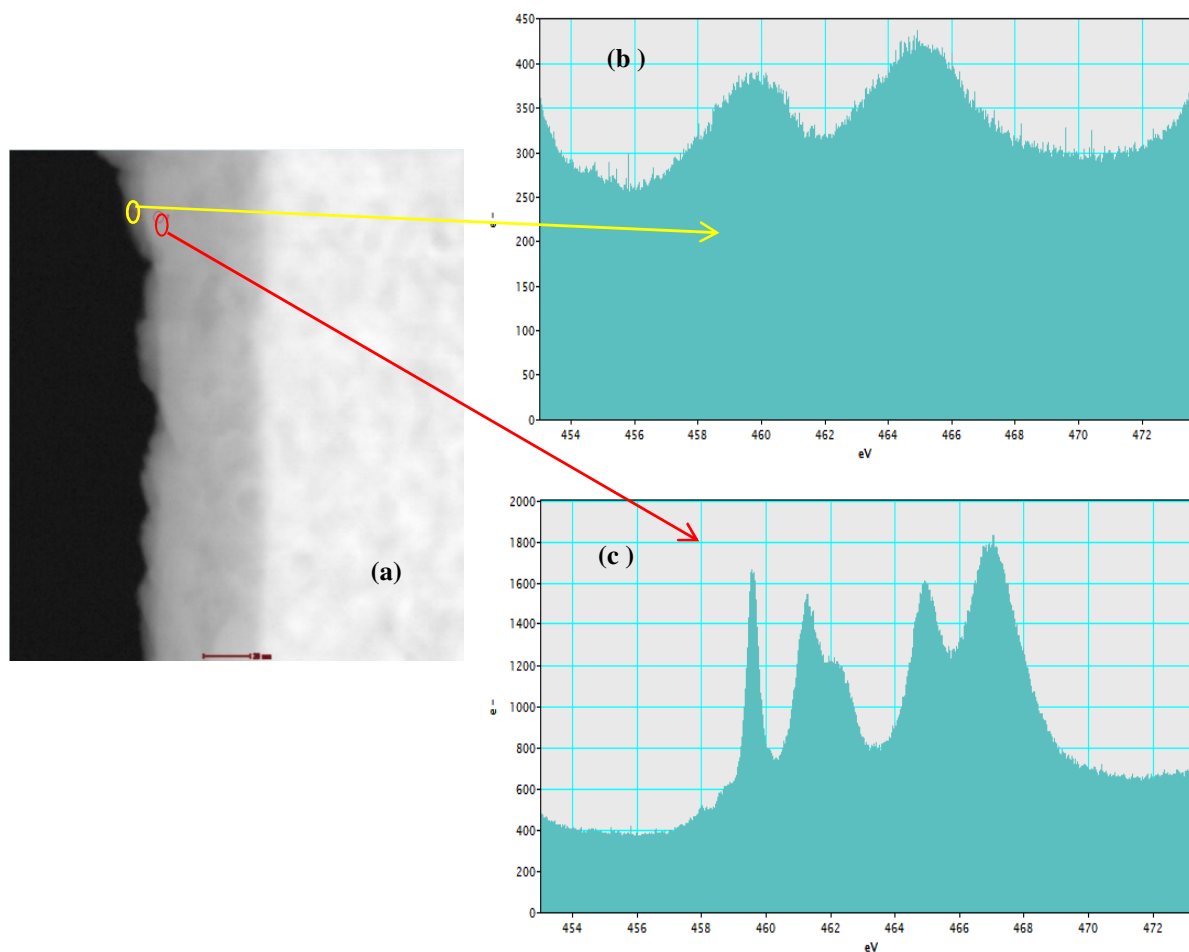


**Figure 5.** (a) Scanning transmission electron microscopy (STEM) of an individual H-TiO<sub>2</sub>/SiNW; HR-TEM micrographs at low (b) and high (c) resolution. The thickness of TiO<sub>2</sub> is 20 nm.

**Figure 6** depicts a STEM and the corresponding electron energy loss spectroscopy (EELS) plots recorded from the surface of hydrogenated TiO<sub>2</sub>/SiNW; obvious changes in shape and position, shifting to lower energies, were observed as compared to the EELS acquired in the bulk TiO<sub>2</sub> in **Figure 6c**. This indicates that the surface shell around TiO<sub>2</sub> comprises hydroxyl species ascribed to diffusion of H atoms into the anatase TiO<sub>2</sub> [49]; this was not evidenced on the non-hydrogenated TiO<sub>2</sub>/SiNW surface in **Figure 7** where the EELS spectra state the same in the shell (**Figure 7b**) and bulk (**Figure 7c**).

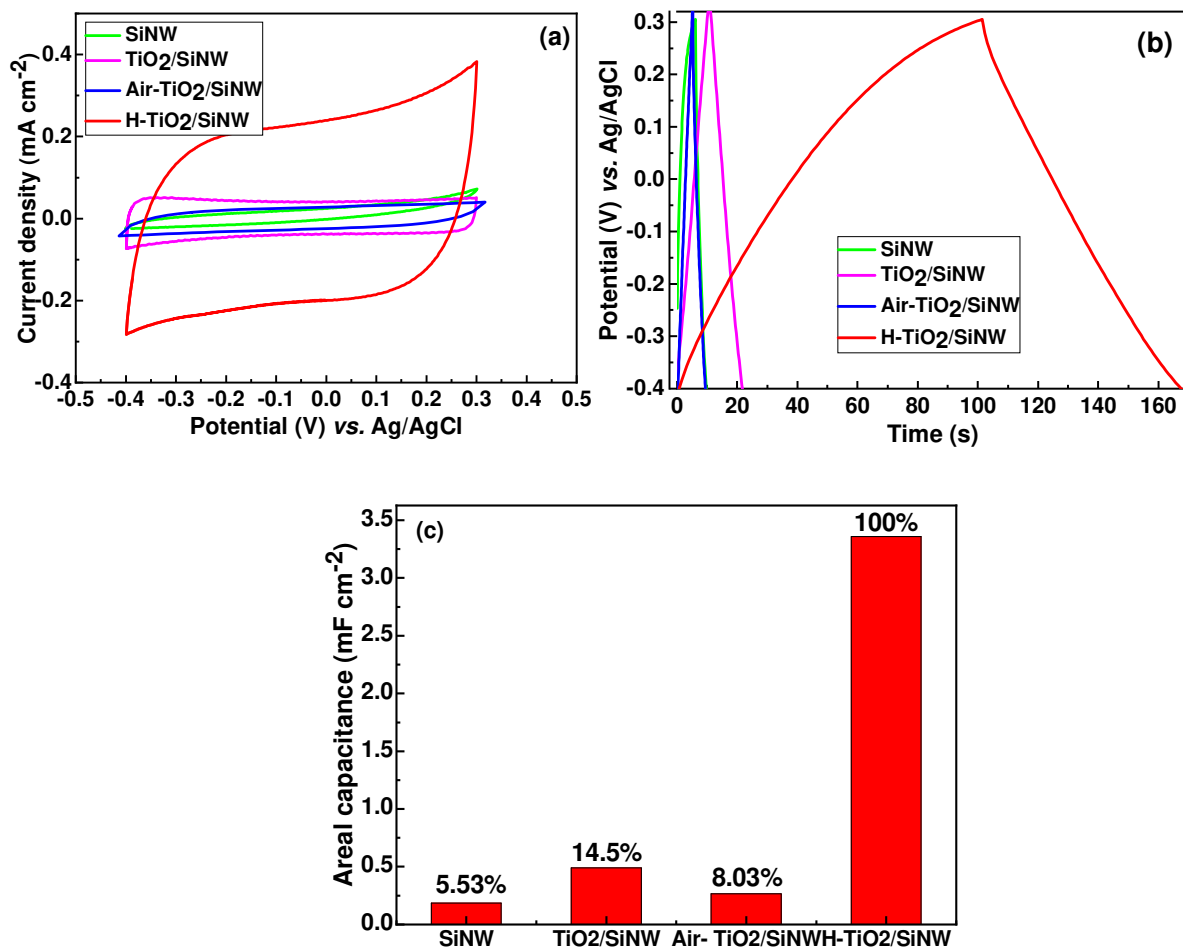


**Figure 6.** (a) STEM-HAADF image of TiO<sub>2</sub>/SiNW surface; EELS spectra of (b) the extreme surface (less than 3 nm) and (c) 15 nm below the surface of TiO<sub>2</sub>.



**Figure 7.** (a) STEM-HAADF image of H-TiO<sub>2</sub>/SiNW surface; EELS spectra of (a) extreme surface (less than 3 nm) ~~Ti-reduced~~ and (c) 15 nm below the surface of TiO<sub>2</sub>.

The fabricated electrodes are characterized in a 3-electrodes electrochemical cell by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) in aqueous 1 M Na<sub>2</sub>SO<sub>4</sub> solution using Ag/AgCl reference and platinum counter electrodes. **Figure 8a** displays the CV profiles of the uncoated SiNW, TiO<sub>2</sub>/SiNW, air-TiO<sub>2</sub>/SiNW and H-TiO<sub>2</sub>/SiNW electrodes acquired at 100 mV s<sup>-1</sup>. The plots feature a quasi-rectangular typical shape ascribed to the formation of an electric double layer at the electrode-electrolyte interface without any obvious redox peaks. It is obvious that H-TiO<sub>2</sub>/SiNW attained largest current than SiNW, TiO<sub>2</sub>/SiNW and air-TiO<sub>2</sub>/SiNW electrodes [21].



**Figure 8.** (a) CV plots of different electrodes collected at  $100 \text{ mV s}^{-1}$  in a potential range from  $-0.4$  to  $+0.3\text{V}$ , (b) GCD profiles recorded at  $0.035 \text{ mA cm}^{-2}$ , (c) Areal capacitance of different electrodes acquired at  $100 \text{ mV s}^{-1}$ .

The specific capacitance was determined from the CV plots using equation (1):

$$C = \frac{\int j dV}{2 \times V \times r} \quad (1)$$

C is the areal capacitance, j denotes the current density, V corresponds to the potential window, r represents the scan rate.

Additionally, the specific capacitance of the samples was determined from the GCD plots using equation (2):

$$C = j \frac{dt}{dV} \quad (2)$$

$dt$  denotes the time of discharge,  $dV$  represents the potential range,  $j$  corresponds to the current density.

The specific capacitance values are given in **Table 1**. The SiNW, TiO<sub>2</sub>/SiNW and air-TiO<sub>2</sub>/SiNW electrodes achieved specific capacities of 0.186, 0.489 and 0.265 mF cm<sup>-2</sup>, respectively at 0.035 mA cm<sup>-2</sup>. These values are comparatively smaller than that recorded for H-TiO<sub>2</sub>/SiNW electrodes (3.36 mF cm<sup>-2</sup>) under otherwise identical experimental conditions. The effect of annealing under hydrogen atmosphere is highlighted by the 6-fold enhancement of the capacitance value, in comparison to that of the sample annealed in air at the same temperature i.e. air-TiO<sub>2</sub>/SiNW electrode. This improvement in energy storage capacity could be ascribed to improved conductivity, increased hydroxyl groups on the TiO<sub>2</sub> surface, and/or generation of oxygen vacancies. Comparable results have been reported by several research groups for TiO<sub>2</sub> nanotubes thermally annealed under hydrogen atmosphere [23], thermally annealed in air followed by chemical reduction using NaBH<sub>4</sub> [50], or through electrochemical hydrogen doping by water electrolysis [51].

**Table 1:** Areal capacitance of the prepared working electrodes in 1 M Na<sub>2</sub>SO<sub>4</sub> deduced from the CV and GCD measurements.

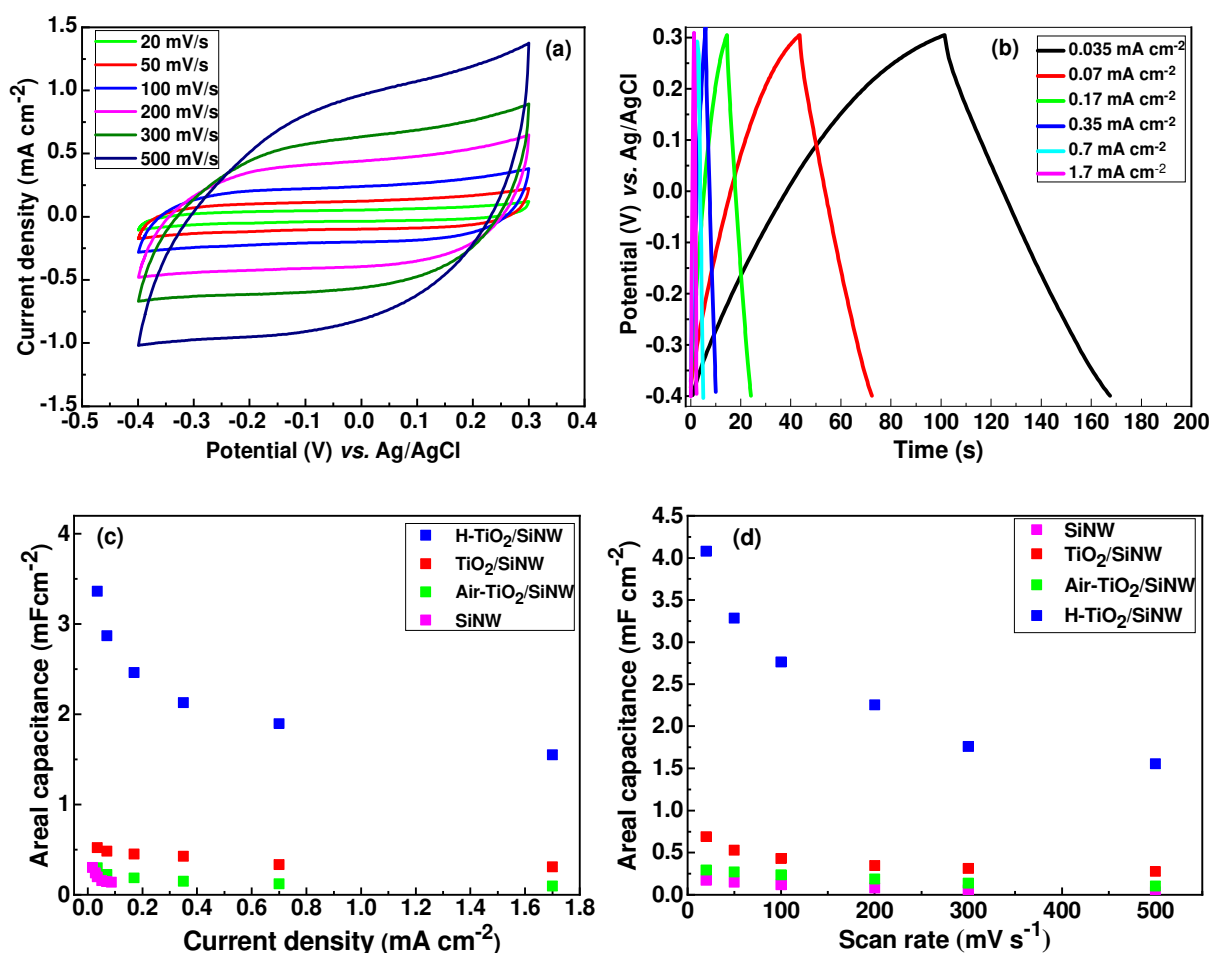
Working electrode	Technique used to calculate Areal capacitance (mFcm <sup>-2</sup> )	
	CV Scan rate=100 mVs <sup>-1</sup>	GCD $J= 0.035 \text{ mA cm}^{-2}$
SiNW	0.137	0.186
TiO <sub>2</sub> /SiNW	0.434	0.489
Air-TiO <sub>2</sub> /SiNW	0.227	0.265
H-TiO <sub>2</sub> /SiNW	2.76	3.36



This areal capacitance is much larger than the literature data recorded for rGO-SiNW ( $240 \mu\text{F cm}^{-2}$  at  $0.01 \text{ mA cm}^{-2}$ ) [52],  $\text{HNO}_3$ -oxidized *p*-type SiNWs ( $404 \mu\text{F cm}^{-2}$  at  $50 \text{ mV s}^{-1}$ ) [53] and the best areal capacitance of  $386 \mu\text{F cm}^{-2}$  recorded for  $\text{TiO}_2$ -coated SiNW array electrode in [Bmim][NTF2] at  $3.7 \times 10^{-5} \text{ A}$  [29]. Our result is also better than that recorded for carbon-coated SiNW electrode ( $105 \mu\text{F cm}^{-2}$  at  $1 \text{ V s}^{-1}$  using cyclic voltammetry) [54], Si-NR/TiN electrode ( $1.08 \text{ mF cm}^{-2}$  at  $100 \text{ mV cm}^{-2}$ ) [55], and diamond-coated SiNW ( $1.55 \text{ mF cm}^{-2}$ ) using a cell voltage of  $4 \text{ V}$  [20]. The value is comparable to that reported for  $\text{TiO}_2$ -coated SiNW using spin coating [30]. A comparison table between the works already performed on  $\text{TiO}_2$  electrode is given in the **supplementary information**.

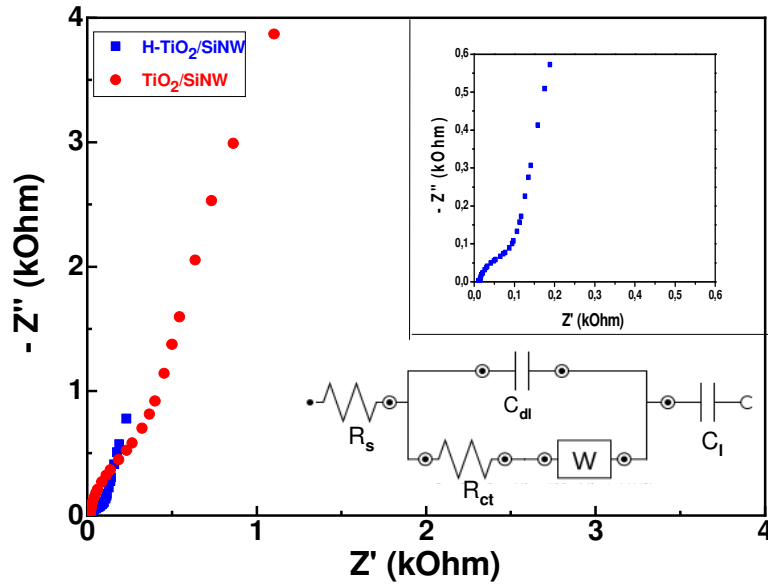
The CV profiles of H- $\text{TiO}_2$ /SiNW electrodes acquired at various scan rates showed nearly rectangular shape (**Figure 9a**). The improved capacitive behavior and high-rate capability of H- $\text{TiO}_2$ /SiNW electrodes were proved by the unchanged shape upon changing the scan rate from 20 to  $500 \text{ mV s}^{-1}$ . The GCD plots of H- $\text{TiO}_2$ /SiNW electrodes are depicted in **Figure 9b**. All curves displayed an almost ideal triangular shape, suggesting a good capacitive behavior in full accordance with the CV measurements. The areal capacitance values of untreated SiNW,  $\text{TiO}_2$ /SiNW, air- $\text{TiO}_2$ /SiNW and H- $\text{TiO}_2$ /SiNW electrodes recorded at different scan rates and current densities are compared respectively in **Figure 9c** and **d**. Upon increasing the scan rate and current density, a decline in the capacitance was evident; this behavior might be ascribed to restricted accessibility of parts of the surface to the electrolyte at high scan and charging-discharging rates. In fact, electrolyte ions diffusion into the electrode internal structure and pores is hindered at high scan rate and the interaction between the electrode surface and electrolyte becomes ineffective, thereby, the specific capacitance declines. This contrasts with low scan rates, where ions have sufficient time to diffuse deeply into pores, leading to enhanced specific capacitance. In addition, it is evident that the H- $\text{TiO}_2$ /SiNW

electrode features the highest capacitance followed by  $\text{TiO}_2/\text{SiNW}$  and air- $\text{TiO}_2/\text{SiNW}$ ; such a behavior can be related to the enhancement of  $\text{TiO}_2$  electrical conductivity upon hydrogenation [19]. The calculated areal capacitance of H- $\text{TiO}_2/\text{SiNW}$  at a high scan rate ( $500 \text{ mV s}^{-1}$ ) was  $1.56 \text{ mF cm}^{-2}$ , which correlates with a capacitance retention of almost 61% as compared to the value recorded at  $20 \text{ mV s}^{-1}$ . The power loss was most likely due to reduced electrical conductivity ( $0.009\text{--}0.01 \text{ } \Omega \text{ cm}$ ) of the doped silicon substrate particularly at high scan rate [19].



**Figure 9.** (a) CV plots of H- $\text{TiO}_2/\text{SiNW}$  acquired at different scan rates (potential range: -0.4 to +0.3 V), (b) GCD plots recorded for H- $\text{TiO}_2/\text{SiNW}$  at different current densities, (c) Areal capacitance of all electrodes *versus* scan rate, (d) Areal capacitance of all electrodes *versus* current density.

EIS was applied to examine the electrode/electrolyte interface and gain a better understanding on the electrochemical behavior and electrode kinetics. **Figure 10** depicts the Nyquist curves of H-TiO<sub>2</sub>/SiNW and TiO<sub>2</sub>/SiNW electrodes in 1M Na<sub>2</sub>SO<sub>4</sub> within 100 mHz – 100 kHz frequency range at open circuit potential. The inset corresponds to the enlarged high frequency region for H-TiO<sub>2</sub>/SiNW electrode. The plot comprises two main features: a single semicircular arc in the high frequency domain (inset) and a straight line in the low frequency region. The diameter of the semicircular in the middle section of Z' axis corresponds to the charge transfer resistance ( $R_{ct}$ ) of the electrode. Moreover, the straight line (low frequency domain) infers that the charge storage capability of H-TiO<sub>2</sub>/SiNW electrode is governed by rapid ion diffusion pathway. In addition, EIS analysis allowed to assess the evolution of the resistance before and after hydrogenation; the equivalent circuit is depicted in the inset of **Figure 10** ( $R_{ct}$ ,  $R_s$ ,  $C_{dl}$ ,  $W_o$ , and  $C_l$  are the charge-transfer resistance, internal resistance, double-layer capacitance, Warburg element, and limit capacitance, respectively). The  $R_s$  and  $R_{ct}$  values are dramatically reduced from initial 12.21 and 625.82  $\Omega$  to 10.47 and 90.13  $\Omega$  after hydrogenation, respectively, owing to improved electrical conductivity along with decreased ion diffusion resistance, as evidenced by the steeper line at low frequencies. Nyquist curves of TiO<sub>2</sub> and H-TiO<sub>2</sub> nanotube electrodes in [56] present the same decreasing trend after hydrogenation. Also, in our results, the high value of  $R_{ct}$  for the non-hydrogenated TiO<sub>2</sub>/SiNW suggests a poor electrical conductivity of TiO<sub>2</sub> deposited thin film.



**Figure 10.** Nyquist plot in the 0.1 Hz to  $5 \times 10^5$  Hz frequency range. Inset displays the enlarged region at high frequency for H-TiO<sub>2</sub>/SiNW electrode.

Furthermore, EIS was also commonly applied to assess the capacitive behavior of electrochemical micro-supercapacitors. Using equation (3), the imaginary part of the complex capacitance versus frequency can be determined [10]:

$$C''(\omega) = \frac{Z'(\omega)}{\omega |Z(\omega)|^2} \quad (3)$$

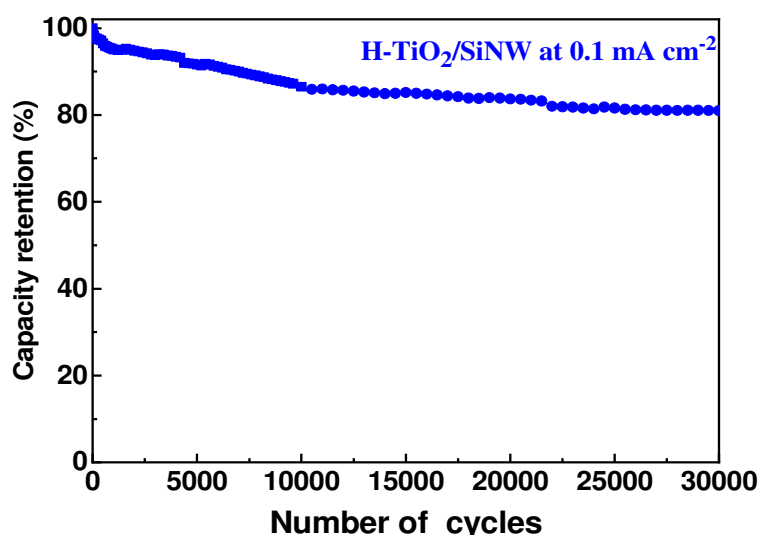
where  $C''(\omega)$  denotes the imaginary part of the capacitance,  $Z'(\omega)$  corresponds to the real part of the impedance,  $Z(\omega)$  is the impedance and  $\omega = 2\pi f$  ( $f$  is the frequency).

**Figure S7** exhibits the plot of  $C''$  versus frequency for the H-TiO<sub>2</sub>/SiNW electrode. In addition, the relaxation time constant ( $\tau_0$ ), defined as the minimum time necessary to discharge all the energy from a supercapacitor with at least 50% efficiency, can be derived from this spectrum [10]. From the curve in **Figure S7**, a time constant of 2.05 ms was determined using the relation ( $\tau_0 = 1/f_0$ ). The rapid frequency response of 0.5 Hz was ascribed to the porous architecture of the electrode, which provides full access to the electrolyte ions,

allowing a faster rate of diffusion. This value is lower than that reported for electrochemical micro-supercapacitors based on SiNW electrodes (e.g. values 3.51 ms) [10].

High-performance electrochemical supercapacitors are commonly characterized by enhanced cycling stability. The H-TiO<sub>2</sub>/SiNW stability was assessed by GCD for 30,000 cycles. The percentage of capacitance retention *versus* cycle number is exhibited in **Figure 11**. The electrode retained ~81% of its original specific capacitance after complete 30,000 cycles at 0.1 mA cm<sup>-2</sup> in the -0.4 to +0.3 V potential window in 1 M Na<sub>2</sub>SO<sub>4</sub>. The result proved the good stability of the electrode after 30,000 cycles.

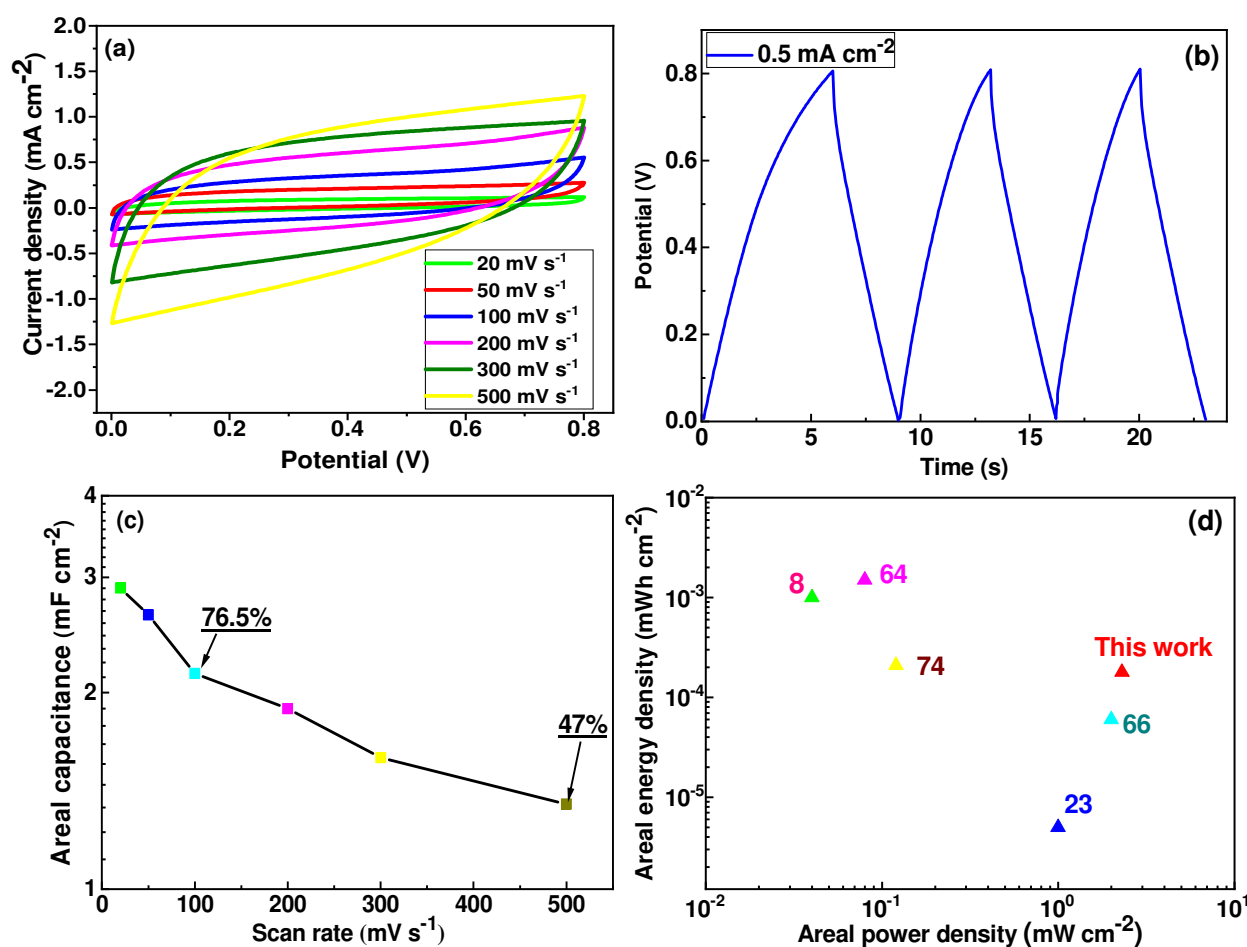
SEM imaging of the H-TiO<sub>2</sub>/SiNW after the stability test revealed a similar morphology, testifying the high stability of the electrode material under our experimental conditions (data not shown). Also, this could be a good indication that the storage is mainly by EDL mechanism since in this case during the charging/discharging cycles, there is not an alteration of the structure of the electrode at the interface.

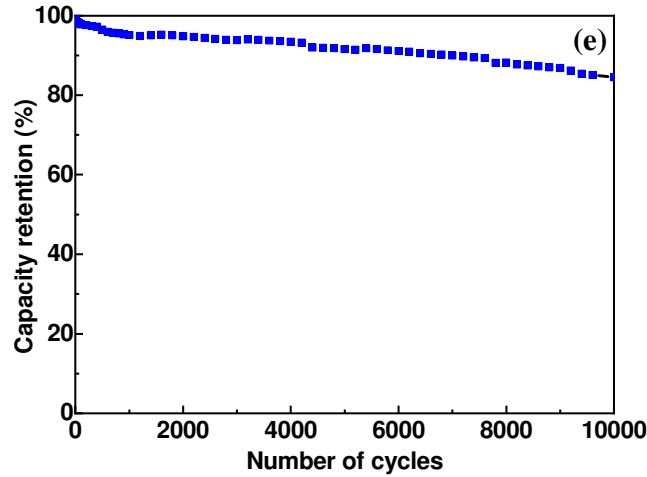


**Figure 11.** Life time testing of the H-TiO<sub>2</sub>/SiNW electrode in an aqueous 1M Na<sub>2</sub>SO<sub>4</sub> electrolyte.

## Symmetric electrochemical supercapacitor devices

Using a classical 2-electrode symmetric configuration cell (**Figure S8**), we tested our electrode for its potential application in energy storage devices [57]. Both the cathode and anode consisted of H-TiO<sub>2</sub>/SiNW core-shell electrodes and 1 M Na<sub>2</sub>SO<sub>4</sub> aqueous electrolyte. Interestingly, the device exhibited nearly rectangular CV plots (**Figure 12a**) and symmetrical triangular GCD profiles (**Figure 12b**), indicating the good capacitive performance. Upon increasing the scan rate from 0.02 to 0.1 mV s<sup>-1</sup>, the cell capacitance remained at 76.5% (decrease from 2.89 to 2.14 mF cm<sup>-2</sup>), **Figure 12c**. The specific capacitance was determined from the CV plots using Eq.1 multiplied by a factor 2 (the factor 2 is due to the two symmetric electrodes construction) [58]. In the same configuration, as in the case of CV measurements using 1 M Na<sub>2</sub>SO<sub>4</sub>, GCD experiments carried out at 0.5 mA cm<sup>-2</sup> allowed to determine a specific capacitance of 2.08 mF cm<sup>-2</sup>.





**Figure 12.** (a) CV curves of H-TiO<sub>2</sub>/SiNW symmetric electrochemical cell collected at various scan rates (potential window: -0.4 to +0.3 V), (b) GCD profiles of the device charged at 0.5 mA cm<sup>-2</sup>, (c) specific capacitance *versus* scan rate, (d) Ragone plot, (e) Capacitance retention percentage of the H-TiO<sub>2</sub>/SiNW symmetric electrochemical supercapacitor for 10,000 cycles at 0.5 mA cm<sup>-2</sup>.

The energy density was calculated from a two-electrode cell as an operating device using  $E = \frac{0.5}{3.6} C(dV)^2$ , where C and V correspond respectively the specific capacitance and potential window. Further, energy and power densities values of 0.179 μWhcm<sup>-2</sup> and 2.13 mWcm<sup>-2</sup> were determined from the GCD plots at 0.5 mAcm<sup>-2</sup>, respectively.

For comparison, **Figure 12d** summarizes the literature data on cell energy density and power density. **Figure 12e** depicts the cyclability test carried out at 0.5 mA cm<sup>-2</sup> up to 10,000 cycles, which showed retention of ~84.6% of the initial capacitance. Thus, the results reveal excellent capacitive feature of the H-TiO<sub>2</sub>/SiNW in this 2-electrode device configuration.

#### 4. Conclusion

In this paper, we compared electrochemical properties of silicon nanowires (SiNW) covered with a TiO<sub>2</sub> thin film. The TiO<sub>2</sub> layer was coated on the SiNW using atomic layer deposition (ALD), some samples of TiO<sub>2</sub>/SiNW were subjected to a hydrogen atmosphere annealing (H-TiO<sub>2</sub>/SiNW) and the others in the open air (air-TiO<sub>2</sub>/SiNW) both at 400 °C for

4 h. The effect of hydrogenation treatment on the specific capacitance of the TiO<sub>2</sub>/SiNW electrodes was investigated. Our results revealed that hydrogenation improved substantially the energy storage ability of H-TiO<sub>2</sub>/SiNW as electrode material for electrochemical supercapacitors. Indeed, after hydrogenation, H-TiO<sub>2</sub>/SiNW featured a specific capacity of 3.36 mF cm<sup>-2</sup> at 0.035 mA cm<sup>-2</sup> in 1 M Na<sub>2</sub>SO<sub>4</sub>, a value 6 times larger than that recorded for air-TiO<sub>2</sub>/SiNW electrode. The electrode maintained ~81% of its original specific capacitance after complete 30,000 cycles at 0.1 mA cm<sup>-2</sup> (potential window: -0.4 – +0.3 V) in 1 M Na<sub>2</sub>SO<sub>4</sub>. Furthermore, H-TiO<sub>2</sub>/SiNW//H-TiO<sub>2</sub>/SiNW symmetric supercapacitor device was assembled and exhibited energy and power densities of about 0.179 μWhcm<sup>-2</sup> and 2.13 mWcm<sup>-2</sup>, respectively, determined from the galvanostatic charge/discharge plots at 0.5 mA cm<sup>-2</sup> in 1 M Na<sub>2</sub>SO<sub>4</sub> with 84.6% retention of the original capacitance value after 10,000 cycles. The capacitance improvement of H-TiO<sub>2</sub>/SiNW can be ascribed to an increase of the density of hydroxyl groups and carrier density on TiO<sub>2</sub> surface. The results obtained in this work hold great promise for the application of ALD technique and hydrogenation for the design of high-performance electrode materials for energy storage.

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