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# **Influence of Surface Chemistry and Point Defects in TiN based Electrodes on Electrochemical Capacitive Storage Activity**

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## **ABSTRACT**

The effect of surface chemistry of reactive sputtered TiN electrodes in the electrochemical capacitors (ECs) was investigated. The TiN films were produced on vertically aligned carbon nanotubes. X-ray photoelectron spectroscopy analysis revealed surface defects generation with no effect on morphology. Cyclic voltammetry experiments were performed in aqueous 0.5 M K<sub>2</sub>SO<sub>4</sub> solution and 1 M Et<sub>4</sub>NBF<sub>4</sub> ((tetraethylammonium tetrafluoroborate)) organic electrolyte. The presence of oxygen vacancies and Ti interstitials on the top surface layer lead to enhanced electrochemical capacitive charge storage. Such findings open the way to design nitride films with optimized surface chemistry for use in the ECs.

**Keywords:** Titanium nitride; surface defects; electrochemical capacitor; XPS; Cyclic voltammetry

It is a well-known fact that the specific capacitance of electrochemical capacitors (ECs) is an electrochemical surface-confined process and, therefore, both the surface area and surface chemistry of the active material determine its capacitance value. Although research efforts are focused at surface area enhancement for super-capacitor development, the effect of surface chemistry of different active materials including oxides, nitrides and carbides remains relatively less explored [1-3]. Indeed, understanding the effect of surface chemistry is important in order to develop high performance materials for ECs.

Recently, transition metal nitrides (TMNs) are attracting attention for their use in electrochemical capacitors or micro-supercapacitors because of their good electrical conductivity, chemical inertness and thermal stability [4-10]. Among these TMNs, titanium nitride (TiN) [5-7] has been explored extensively due to its high electrochemical stability, good power density as well as interesting specific capacitance. Previously, we reported the effect of surface modification of TiN films through vacuum annealing in order to improve the specific capacitance [10].

In this communication, we provide an evidence that presence of surface defects on the TiN film electrodes are responsible for the electrochemical storage. In case of defect-free TiN electrodes or with very low defect density on the surface, high surface area TiN becomes inactive for electrochemical capacitive charge storage.

The carbon nanotubes (CNT) were grown over amorphous carbon (a-C)/Si substrate via microwave plasma-enhanced chemical-vapor deposition process using in acetylene and ammonia mixture with a  $\text{NH}_3/\text{C}_2\text{H}_2$  ratio of 0.2. The chamber pressure, microwave power, temperature and time were maintained at 0.2 Pa, 120 W, 600 °C and 60 min, respectively. More details of the CNT growth procedure are described elsewhere [11].

Following vertically aligned CNT array growth, titanium nitride (TiN) films were produced through reactive direct-current (DC) plasma sputter deposition. The details of the sputtering system can be found elsewhere [10]. The TiN films were deposited under different conditions of applied power and plasma gas mixture in order to induce different surface chemistries. In one case, the argon (Ar) and nitrogen ( $\text{N}_2$ ) gas volumetric flow ratio was maintained at 18:2 (sccm) at 120 W power. The sample was designated as TiN1-CNT. The other sample referred to as TiN2-CNT was obtained when the respective values of Ar: $\text{N}_2$  and P values were 20:1 and 80 W. In both samples, the TiN film thickness was kept to be ~100 nm as determined from the reference samples that used flat, polished silicon wafers as substrates.

The surface and cross-section of the TiN@CNT electrodes were examined under scanning electron microscope (SEM; JEOL JSM 7600F) by operating at 5 kV. The phase analysis was performed by means of X-ray diffraction (XRD) studies using a Siemens D5000 diffractometer with  $\text{CuK}\alpha 1$  monochromatic radiation in the Bragg Brentano configuration. The surface analysis was carried out through XPS measurements on a Kratos Axis Ultra apparatus. The high-resolution spectra were recorded using  $\text{AlK}\alpha$  (1486.6 eV) beam at 20 eV pass energy and 0.9 eV energy resolution. Any charge energy shift in the binding energy (BE) was compensated by setting the C 1s line of the contamination peak to 284.4 eV. For both TiN1-CNT and TiN2-CNT, the XPS measurements were performed ex-situ with the samples stored in the same environment for similar time periods.

The electrochemical measurements were performed in two different electrolytes namely an aqueous solution of 0.5 M  $\text{K}_2\text{SO}_4$  and an organic solution of 1.0 M  $\text{Et}_4\text{NBF}_4$  (tetraethylammonium tetrafluoroborate) in HPLC grade acetonitrile. The high purity chemicals procured from Alfa Aesar were used without any further purification. For electrochemical characterization, a cell in three-electrode configuration was used with Ag/AgCl and a platinum gauze as reference and counter electrodes, respectively. The measurements were recorded using a VMP 3 multi potentiostat-galvanostat (Biologic, France) with EC-Lab software for monitoring. The surface area of the working electrode was defined by means of a Teflon TM cell holder. For cycling voltammetry studies, ten cyclic voltammograms (CVs) were obtained prior to those presented in this work in order to ensure that the CV data were representative of each electrode.

The top view and cross section of the TiN film deposited on to the vertically aligned CNTs were examined under SEM, as shown in Fig. 1. Since there was no noticeable difference in morphologies of the two TiN electrodes although the sputter deposition conditions were different, only the SEM results for the TiN1-CNT electrode are presented. The microstructures revealed that the TiN nanostructures anchored to the outer surfaces of the individual CNTs at their tips and length segments near their top ends, thus causing an increase in the outer diameter of the CNTs by few tens of nanometers. The XRD patterns (Fig.1c) confirm the presence of TiN phase (JCPDS file: 87-0633) in both samples with diffraction peaks at  $36.7^\circ$  and  $42.5^\circ$  assigned to the (111) and (200) crystallographic orientations [5, 8]. In case of TiN2-CNT electrode, a slight shift to higher  $2\theta$  values by  $0.1^\circ$  in the diffraction peaks was noticed that may be attributed to the stress effect within the TiN deposit [12]. The CNT exhibit presence of the diffraction peaks at  $2\theta$  values of  $25.9^\circ$  and  $42.7^\circ$  that correspond to the (002) and (100) graphite reflections (JCPDS No. 01-0646), respectively. However, in

our case, the vertically aligned CNTs have an average length of about 2  $\mu\text{m}$  and a relatively low area density of  $10^9 \text{ cm}^{-2}$ . Therefore, it is difficult to evidence the CNT diffraction peaks using X-Ray diffraction. The peak at  $44.5^\circ$  is attributed to fcc Ni phase [11] that was used as catalyst for CNT growth. The other weak diffraction peaks present in all the three samples maybe ascribed to the substrate.

The XPS deconvolution of the Ti 2p core level high resolution spectra for the TiN1-CNT and TiN2-CNT electrodes are represented in Fig. 2a and Fig. 2d, respectively. The peak deconvolutions show that the TiN1-CNT exhibit major components mixture of Ti–N–O, Ti–N and Ti–O chemical bonds. The intense peak located at 458.2 eV can be related to Ti  $2p_{3/2}$  and can be assigned to  $\text{TiO}_2$  ( $\text{Ti}^{4+}$  oxidation state) while the weak peak at lower binding energies ( $\sim 454.6 \text{ eV}$ ) can be assigned to TiN [13, 14]. Between these two peaks, there are two other peaks that can be attributed to the oxynitride ( $\text{TiO}_x\text{N}_y$ ) and  $\text{Ti}_2\text{O}_3$  which have an oxidation state between those of TiN and  $\text{TiO}_2$  [13, 14]. According to literature, one doublet can be related to Ti ( $\text{Ti}^{3+}$  oxidation state) in  $\text{Ti}_2\text{O}_3$ . The  $\text{Ti}^{3+}$  oxidation state is usually attributed to the defects in  $\text{TiO}_2$  [15, 16]. In case of Ti 2p core level spectrum of TiN2-CNT electrode (Fig. 2d), there is no peak related to  $\text{Ti}_2\text{O}_3$  suggesting that the  $\text{TiO}_x$  layer that built up on the TiN surface has very few or no defects at all. The amount of  $\text{Ti}_2\text{O}_3$  is related to the number of oxygen vacancies generated due to nitrogen doping of  $\text{TiO}_x$  layer at the top surface of TiN. The absence of  $\text{Ti}_2\text{O}_3$  phase ( $\text{Ti}^{3+}$ ) may be accounted for the low density or absence of oxygen vacancies in the  $\text{TiO}_x$  layer of this electrode. On the other hand,  $\beta\text{-N}$  (the nitrogen that substitutes oxygen in the  $\text{TiO}_x$  layer) introduces these oxygen vacancies, as reported in our previous work [5].

In order to confirm the absence of defect on the surface of TiN2-CNT electrodes, one can compare the N 1s core level spectra of both electrodes, as shown in Fig. 2b and Fig. 2e. The deconvoluted N 1s peak of TiN1-CNT electrode contains four peaks (Fig. 2b). The peak located in the 396.1–396.9 eV range can be attributed to titanium nitride in agreement with Ref [18]. Two or three other peaks at higher energies can be resolved and may result from superposition of peaks corresponding to the oxynitride ( $\text{TiN}_x\text{O}_y$ ) and nitrogen-oxygen adsorbed species ( $\text{NO}_x = \text{NO}$  or  $\text{NO}_2$ ) or  $\text{Ti-NO}_x$  [19-20] compounds at the surface. The intense peak at lower energy side (395.2–395.9 eV) is attributed to  $\beta\text{-N}$  which is associated with oxygen substitution by nitrogen in the  $\text{TiO}_x$  layer. The peak related to  $\beta\text{-N}$  does not appear in the deconvoluted N 1s spectrum of TiN2-CNTs (Fig. 2e). As mentioned above, this kind of substituted nitrogen atoms are believed to create oxygen vacancies. Therefore, the

lack of  $\beta$ -N species at the surface of TiN2-CNTs sample is in a good agreement with the absence of  $\text{Ti}_2\text{O}_3$  band on the electrode surface.

Another way to examine the presence of defects on the surface of  $\text{TiO}_x$  layer is by looking at the valence band ( $V_B$ ). In Fig. 2c and 2f are presented the  $V_B$  of TiN1-CNT and TiN2-CNT electrodes, respectively. In case of TiN1-CNT electrode (Fig. 2e), the band located at about 0.84 eV can be assigned to Ti 3d ( $\text{Ti}^{+3}$ ) defect states related to oxygen vacancies or Ti interstitial defects in  $\text{TiO}_2$  [21-23]. In contrast, the case of the XPS band characteristic of the Ti 3d ( $\text{Ti}^{+3}$ ) defect states located at 0.84 eV [20] is absent from the surface of TiN2-CNT electrode (Fig. 2c), thus indicating the lack of oxygen vacancies and/or Ti interstitial defects in  $\text{TiO}_2$ . Again, this is in a good agreement with absence of the bands assigned to the  $\text{Ti}_2\text{O}_3$  bonding and  $\beta$ -N arising from substitutional-insertion nitrogen doping on the surface of this electrode. Therefore, the detailed XPS analysis of the TiN2-CNT electrode demonstrates prevalence of very low defects density on the surface of this electrode. Based on our previous works, such different surface chemistry should have an impact on the electrochemical capacitive storage of such materials [5, 8, 10]. It is noteworthy that the oxide layers at the TiN surface may be a by-product that is formed during film deposition and/or aging as it is not possible to avoid oxidation of the surface of transition metal nitrides once they are exposed to air.

In order to assess the surface chemistry effect on the electrochemical behaviour of the two electrodes, cyclic voltammetry (CV) was used to investigate the electrochemical behavior of the two samples in different types of electrolytes. The cyclic voltammograms of the TiN1-CNT electrode after testing in 0.5 M  $\text{K}_2\text{SO}_4$  aqueous solution and 1.0 M  $\text{Net}_4\text{BF}_4$  organic electrolyte at  $200 \text{ mV.s}^{-1}$  are showcased in Fig. 3a and Fig. 3b, , respectively. The CV exhibits a near symmetrical rectangular shape in 0.5 M  $\text{K}_2\text{SO}_4$  electrolyte solution that indicates quasi-ideal capacitive behavior. On the other hand, the capacitive current was found to decrease in 1 M  $\text{Net}_4\text{BF}_4$  organic electrolyte because of the absence of protons in this kind of electrolyte, as discussed earlier [5]. In contrast with this behavior, the CVs for the TiN2-CNT electrode (Fig. 4 c, d) exhibit a completely distorted shape and a very low capacitive current in both electrolytic solutions. This indicates that the TiN2-CNT film does not store as much charges as TiN1-CNT sample even it exhibits the same high surface area. The absence or scarcity of point defects on the surface as qualitatively determined from XPS analyses (absence of  $\beta$ -N,  $\text{Ti}_2\text{O}_3$  phase and  $\text{Ti}^{+3}$  d band) may account for this trend. The electrical double layer (EDL) capacitance of the TiN2-CNT electrode in 0.5 M  $\text{K}_2\text{SO}_4$  aqueous electrolyte in the 0 to 0.15 V

vs Ag/AgCl potential window was calculated to be  $10 \mu\text{F}\cdot\text{cm}^{-2}$  which is a standard EDL capacitance value for carbon based electrodes. Furthermore, it seems that hydrogen evolution reaction is promoted in this electrolyte since it occurs below 0 V vs Ag/AgCl. The oxidation current at more positive potentials can be related to oxidation processes occurring at the TiN surface. Further research is required to investigate the nature of these electrochemical processes, as this is outside the scope of this communication.

Moreover, it is believed that the loss of electrochemical character of the TiN film as ECs electrode is not merely related to the absence of oxygen vacancies in the  $\text{TiO}_x$  layer at the top surface of this electrode. In fact, the absence of the  $\text{Ti}^{3+}$  d band (shown in Fig. 3b) can also indicate the absence of other types of defects such as interstitial Ti atoms, which in turn, can also have an impact on the electrochemical charge storage properties of the TiN2-CNT electrode. Therefore, it can be suggested that both type of defects i.e. oxygen vacancies and interstitial Ti in the top  $\text{TiO}_x$  layer formed at the TiN surface may contribute to the electrochemical charge storage in the TiN electrode. The research findings presented here highlight the role of surface defects in the TiN based electrodes towards electrochemical charge storage properties.

A very thin TiN film (100 nm thick) was produced over vertically aligned carbon nanotubes using two different deposition conditions to obtain EC electrodes with similar high surface area and surface morphology, albeit different surface chemistry. The electrode surface resulting from higher plasma power (120 W) and less degree of nitrogen gas dilution ( $\text{Ar:N}_2$  of 18:2) had point defects generated due to top layer oxidation. The surface chemistry of this electrode comprised of  $\beta\text{-N}$ ,  $\text{Ti}_2\text{O}_3$  as well as  $\text{Ti}^{3+}$  d as probed with X-ray photoelectron spectroscopy (XPS). Thus, XPS analyses confirm the presence of surface defects such as oxygen vacancies and Ti interstitials on the surface of this electrode. During EC measurements, such electrode exhibited the highest performance in terms of electrochemical charge storage in both aqueous and organic-based electrolytes. The TiN film deposited under a different set of processing conditions (80 W power,  $\text{Ar:N}_2$  of 1:20), however, indicated absence of  $\beta\text{-N}$ ,  $\text{Ti}_2\text{O}_3$  phases and the  $\text{Ti}^{3+}$  d band in the valence band as figured out from the XPS analysis. The lack of these chemical moieties may be ascribed to the absence of surface defects that led to the loss of capacitive/pseudo capacitive charge storage behavior. To the best to our knowledge, these findings are the first evidence of the effect of surface chemistry on the energy storage characteristics of transition metal nitrides. Our results highlight the effect of the surface defects on the electrochemical behavior of TiN thin films and pave the way to design enhanced nitride-based electrodes for electrochemical capacitors.

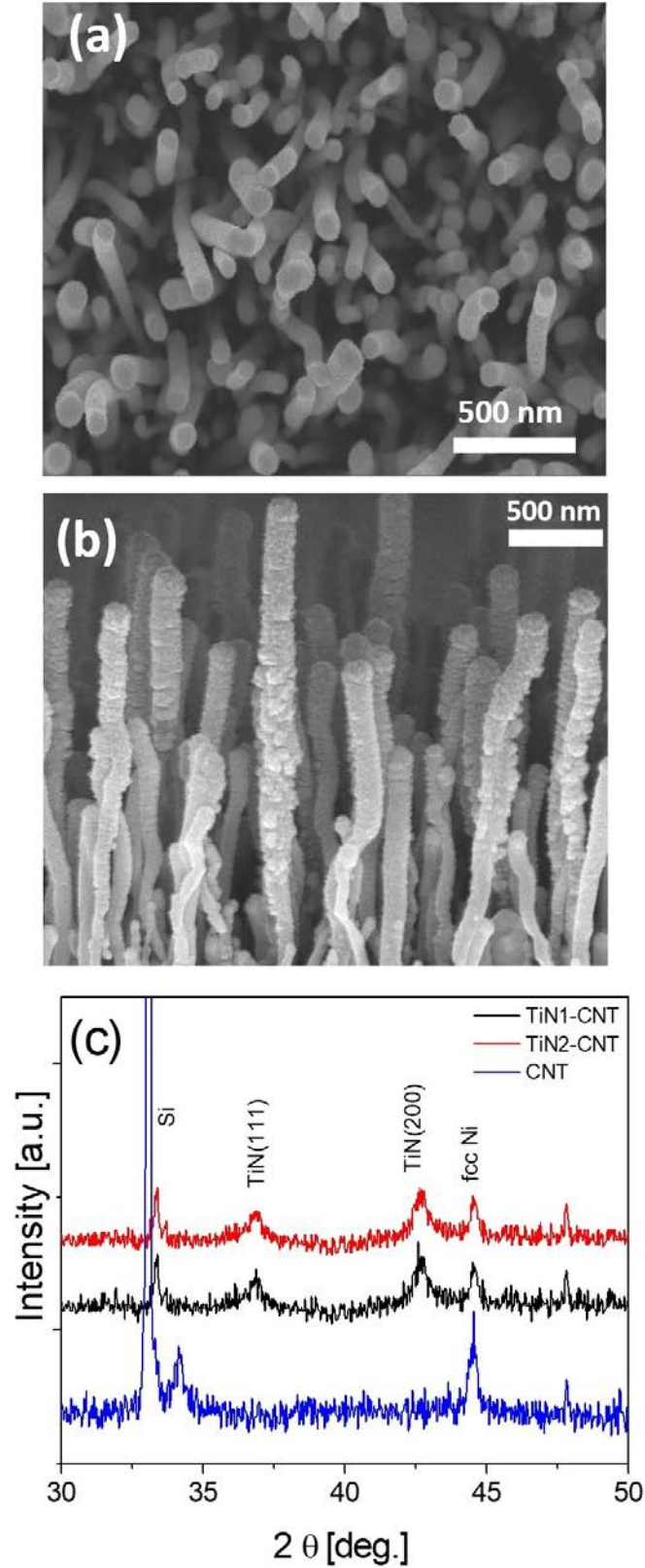


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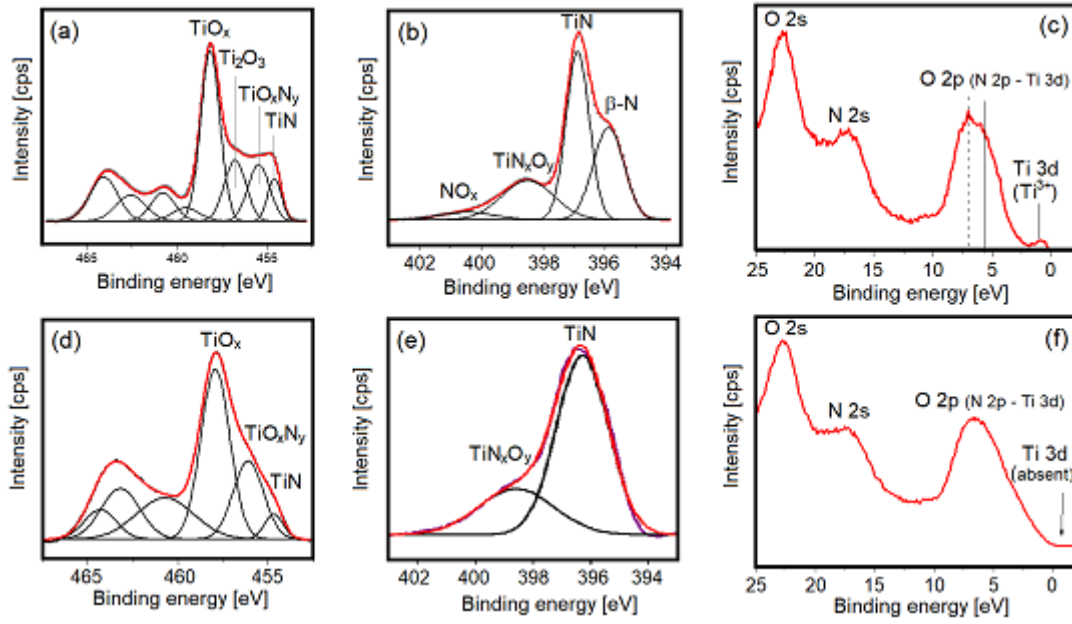
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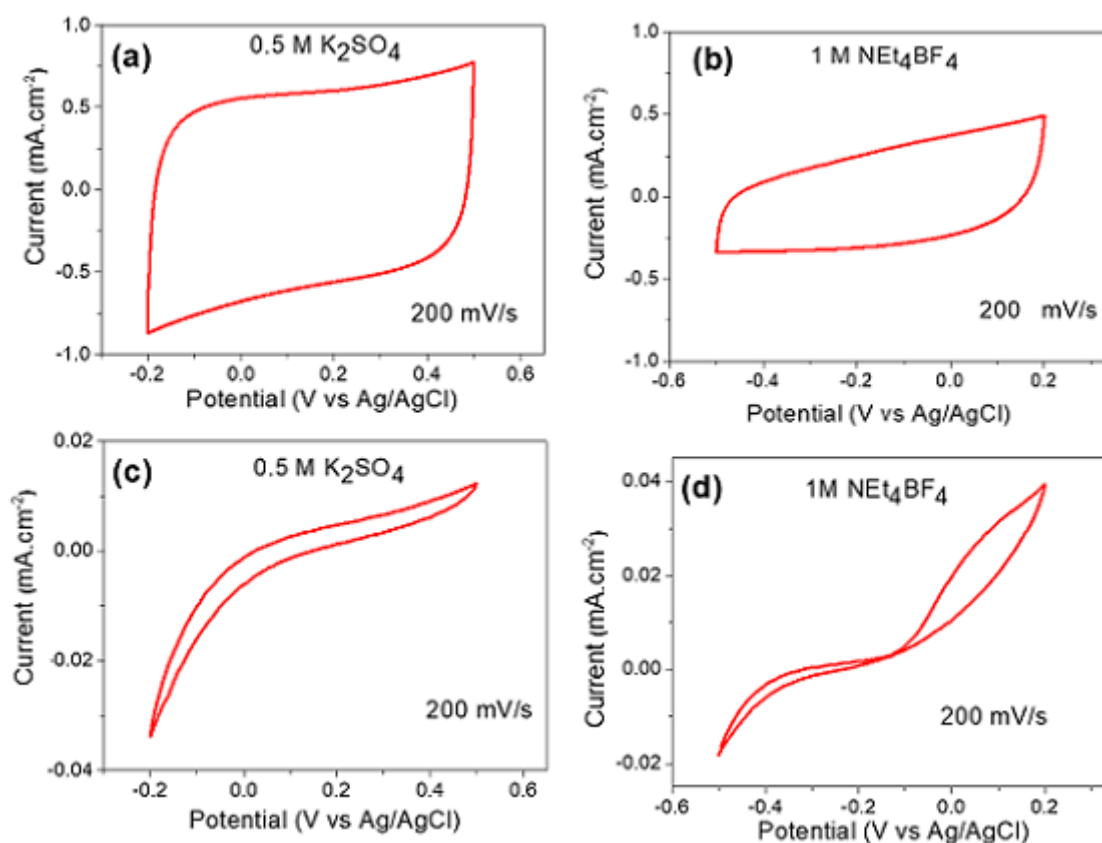
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**Fig. 1** Vertically aligned CNT array coated with a 100-nm TiN film used as electrode: (a, b) SEM microstructures revealing surface and cross-section growth morphologies, and (c) X-ray diffraction patterns of the two samples and CNT without TiN deposit.



**Fig. 2** XPS spectra of the two different TiN coated CNT electrodes: For TiN1-CNT electrode, high resolution, deconvoluted spectra for the (a) Ti 2p band, (b) N 1s band high resolution spectrum, and (c) XPS valence band are shown. For the TiN2-CNT sample, high resolution, deconvoluted spectra for the (d) Ti 2pband, (e) N 1s band high resolution spectrum, and (f) XPS valence band are presented.



**Fig. 3** Cyclic voltamograms of TiN/CNT-A electrode in (a) 0.5 M K<sub>2</sub>SO<sub>4</sub> aqueous electrolyte solution and (b) in 1 M Net<sub>4</sub>BF<sub>4</sub> organic electrolyte at a scan rate of 200 mV.s<sup>-1</sup>. Cyclic voltamogramms of TiN/CNT-B electrode in (a) 0.5 M K<sub>2</sub>SO<sub>4</sub> aqueous electrolyte solution and (b) in 1 M Net<sub>4</sub>BF<sub>4</sub> organic electrolyte at a scan rate of 200 mV.s<sup>-1</sup>.