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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_2SO_4 solution and 1 M Et4NBF4 ((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.

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 is 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 an acetylene and ammonia mixture with a NH_3/C_2H_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 (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: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.

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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 CuKα1 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 AlKα (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 K_2SO_4 and an organic solution of 1.0 M Et_4NBF_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° and 42.5° assigned to the (111) and (200) crystallographic orientations [5,8]. In case of TiN2-CNT electrode, a slight shift to higher 2θ values by 0.1° 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 2θ values of 25.9° and 42.7° 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 μm and a relatively low area density of 10^9 cm^{-2}. Therefore, it is difficult to evidence the CNT diffraction peaks using X-ray diffraction. The peak at 44.5° 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 d, respectively. The peak deconvolutions show that the TiN1-CNT exhibits 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 TiO_2 (Ti^{4+} oxidation state) while the weak peak at lower binding energy (~454.6 eV) can be assigned to TiN [13,14]. Between these two peaks, there are two other peaks that can be attributed to the oxynitride (TiO_xN_y) and Ti_2O_3 which have an oxidation state between those of TiN and TiO_2 [13,14]. According to literature, one doublet can be related to Ti (Ti^{3+} oxidation state) in Ti_2O_3. The Ti^{3+} oxidation state is usually attributed to the defects in TiO_2 [15,16]. In case of Ti 2p core level spectrum of TiN2-CNT electrode (Fig. 2d), there is no peak related to Ti_2O_3 suggesting that the TiO_x layer that built up on the TiN surface has very few or no defects at all. The amount of Ti_2O_3 is related to the number of oxygen vacancies generated due to nitrogen doping of TiO_x layer at the top surface of TiN. The absence of Ti_2O_3 phase (Ti^{3+}) may be accounted for the low density or absence of oxygen vacancies in the TiO_x layer of this electrode. On the other hand, β-N (the nitrogen that substitutes oxygen in the TiO_x layer) introduces these oxygen vacancies, as reported in the previous works [5,17].

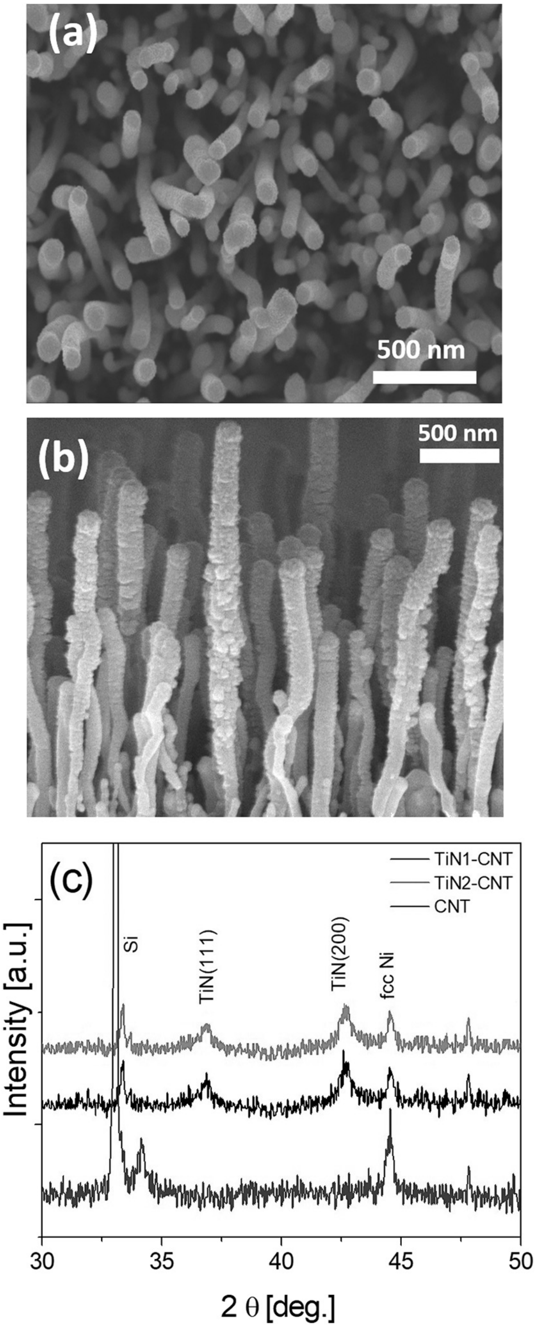

Fig. 1. Vertically aligned CNT array coated with a 100-nm TiN film used as electrode: (a, b) SEM microstructures revealing surface and cross-section growth morphologies, and (c) X-ray diffraction patterns of the two samples and CNT without TiN deposit.

In order to confirm the absence of defects 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 e. 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 (TiN_xO_y) and nitrogen oxygen adsorbed species ($NO_x =$ NO or NO_2) or Ti-NO_x [19–20] compounds at the surface. The intense