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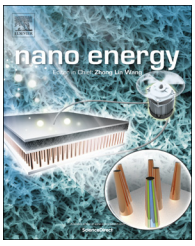

RAPID COMMUNICATION

# Hierarchical nanocomposite electrodes based on titanium nitride and carbon nanotubes for micro-supercapacitors

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**Abstract**
Electrochemical capacitors that can store high density of electrical energy with fast power delivering and long operating life time are important for many challenging applications. Tremendous research efforts aim at developing electrodes which gather the advantages of both electrochemical double layer capacitors (high power density, long cycling life) and pseudo-capacitors (high energy density). Here we highlight the design of hierarchically composite electrodes consisting of porous and nanostructured TiN grown on vertically aligned CNTs as high-performance electrode for micro-supercapacitors. The electrodes, which are deposited on silicon substrates, exhibit an areal capacitance as high as 18.3 mF $cm^{-2}$ at 1 V $s^{-1}$ that can be further enhanced by increasing the TiN layer thickness. Furthermore, this capacitance is maintained over 20,000 cycles. We propose that such high performance originates from the high surface area of the electrodes having a nanoporous structure, as well as to their specific surface chemistry, which contains large amount of oxygen vacancies as a result of nitrogen self-doping of anatase which forms at the TiN surface.


## Introduction

The rapidly growing applications and miniaturization of conventional electronic devices to microelectronics and microsystems makes conventional capacitors insufficient to

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supply enough energy during electrical powering. In order to satisfy such continuous demand, a new concept has emerged for developing and integrating (at the micro-scale) electrochemical energy storage devices holding higher energy density in the form of packed films [1-8]. Micro-supercapacitors are an attractive solution because they can provide a volumetric energy density which is ~100 times higher than that of conventional dielectric capacitors [5-7], while still operating for longer time and delivering higher power density than lithium-microbatteries [4,9]. Carbon based materials (referred to as EDLCs) [1-3] are considered as one of the most promising electrodes for micro-supercapacitors, due to their fast power delivering and outstanding cycling stability. But these materials exhibit low energy density compared to micro-batteries [1-4]. Therefore, for more challenging applications, research efforts are focusing to enhance the energy density of EDLC electrode materials while maintaining their cycling stability and power capability. For this purpose, nanostructured carbon materials with high surface area and tunable pores size, such as carbon nanotubes (CNTs) [5], carbide-derived carbon [6] or nanoporous carbon [7] electrodes, have been envisioned for micro-supercapacitors. Pseudocapacitive materials such as polypyrrole [10], $RuO_2$ [11,12] and $MnO_2$ [13,14] have shown much higher storage capacity than carbons in micro-device designs. However, charge storage occurs in these compounds via surface or sub-surface redox reaction which is detrimental to their cycling life. Furthermore, the relatively moderate electronic conductivity of pseudocapacitive materials drastically limits their power density compared to carbon based electrodes. Nanostructured materials with high conductivity and large surface area, including CNTs [15-17], graphene [18,19] and porous gold [20] have been used as template for pseudocapacitive materials deposition, in order to enhance their power density while keeping high energy density. Nevertheless, in most cases this approach finds a limitation when more pseudocapacitive material is loaded. The challenge is not only to develop electrochemical capacitor (EC) electrodes which can deliver high energy density under high power density, but also to propose materials that can sustain long term cycling, thus providing a long operating life time to the corresponding device. TiN is a low cost transition metal nitride with remarkable properties [21-24] such as good electronic conductivity and good stability in alkaline solutions. It is commonly reported as catalyst support in fuel[21] cells and as counter electrode in DSSC [22]. TiN powder has recently attracted some interest as active material for EC applications [23,24], but it has been poorly investigated because of its moderate specific capacitance and poor cycling ability [23,24]. The recent reports have only focused on using nanostructured TiN with good electrical conductivity as a template to enhance pseudocapacitive performance [25]. Up to now, the potentiality of TiN nanostructured films for micro-supercapacitors applications was not highlighted although TiN is widely used in the field of semiconductor technology [26]. In the present work, we demonstrate a high performance nanostructured electrodes based on TiN deposited on CNTs which fulfills this challenge, i.e., electrodes with an areal capacitance similar to pseudocapacitors [15-17], a promising cycling life (up to 20,000 cycles) and a power density comparable to those of EDLCs [5-7].

The nanostructured TiN/CNTs composite films have been fabricated by reactive DC-sputtering of TiN on vertically aligned CNT template leading to hierarchical electrodes with fancy 3D architectures. The properties of these 3D nanostructures were maintained even when more TiN was loaded with an increase of energy storage, and preserving high power delivery and long term cycling stability. Moreover, the electrodes have shown such high performance in mild aqueous electrolyte with neutral pH. Herein, light is shed on the mechanism behind the observed high capacitive storage of nanostructured TiN films. It is proposed that both the high surface area and surface chemistry of the electrode contribute to the enhancement of capacitive storage. More specifically, the oxidized top surface of titanium nitride nanostructure contains a large amount of oxygen vacancies, which are substantially responsible for the observed high capacitive storage.

## Experimental

### Fabrication of vertically aligned TiN coated CNTs electrodes

A very thin buffer layer (~ 10 nm thick) of amorphous carbon film (a-C) acting as a conducting barrier film against impurity diffusion was deposited on (100) oriented n-type monocrystalline silicon substrate by ionized physical vapor deposition (IPVD) system. Afterwards, nickel nanopacticles catalysts (~ 50 nm in diameter) were electrochemically deposited on the a-C film using nickel nitrate solution, prior to CNT growth step. The CNTs were grown by microwave plasma-enhanced chemical-vapor deposition in acetylene plasma diluted in ammonia with a $NH_3/C_2H_2$ ratio of 0.2, at a pressure of 0.2 Pa and microwave power of 120 W. The substrate temperature was kept at 600 °C and the growth time was fixed at 60 min. More experimental details of CNT growth are already reported elsewhere [27]. Next titanium nitride (TiN) was deposited directly on the as prepared CNTs/a-C/Si substrates by reactive DC sputtering (at power density of 10.7 W/cm$^2$) in a sputter machine which is equipped with a turbo molecular pumping system that allows achieving a base pressure of less than $10^{-7}$ mbar in the vacuum chamber. Pure argon (99.99%) and nitrogen (99.99%) were used as sputtering and reactive gases respectively. The target was a titanium metal of purity 99.6%. The reactive sputtering was carried out without intentional substrate heating. The resulting composite nanostructured electrodes are referred to 100 nm, 500 nm and 1200 nm TiN according to the thickness measured on flat silicon substrates acting as reference samples to calibrate our deposition process.

### Characterizations

The samples were characterized by Scanning Electron Microscopy (SEM) performed on a JEOL JSM 7600F apparatus and Transmission Electron Microscopy (TEM; H9000-NAR) operating at 300 kV. For TEM characterization, samples were scratched with a diamond tip and collected on a TEM copper grid covered with a thin holey carbon film. Micro-Raman was performed with a Horiba Jobin Yvon LabRam HR system