



## Study on supercapacitance performance of TiO<sub>2</sub> nanotube arrays modified by non-metal doping and Polyaniline electrodeposition methods

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Received: 20 February 2021; Accepted: 29 April 2021

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### ABSTRACT

Highly ordered TiO<sub>2</sub> nanotube arrays were synthesized by a two-step anodizing method. Providing unidirectional path for electron transfer, led TiO<sub>2</sub> nanotubes to have excellent electrical and capacitive properties. But these properties can be improved by effective methods such as non-metallic doping or by a conductive polymer. For this purpose, nitrogen and hydrogen doping methods and electrical deposition of polyaniline were used simultaneously to prepare the polyaniline-TiO<sub>2</sub>, polyaniline/N-TiO<sub>2</sub>, and polyaniline/H-TiO<sub>2</sub> nanotube arrays samples. To evaluate the electrochemical and capacitive properties in more detail, cyclic voltammetry, electrochemical impedance spectroscopy, Mott-Schottky, and galvanostatic charge-discharge tests were performed. The results showed that the composite of TiO<sub>2</sub> doped with hydrogen and deposited with polyaniline nanowires had the highest capacitance (5666 μF.Cm<sup>-2</sup>) at the current density of 100 μA/cm<sup>2</sup>, approximately 4.5 times more than polyaniline/TiO<sub>2</sub> sample. It also has the lowest charge transfer resistance (0.008 Ωcm<sup>2</sup>) and the highest charge carrier density (1.63×10<sup>24</sup>cm<sup>-3</sup>). Increasing the density of charge carriers and decreasing the electrical resistance can be attributed to the fact that the hydrogen doping, the presence of oxygen vacancies, and conductive polymer can increase the rate of separation of the charge carriers and decrease their recombination rate. Therefore, the electron transfer rate and the electric current increase.

**Keywords:** TiO<sub>2</sub> nanotube arrays, Non-metal doping, Polyaniline, EIS, Capacitive performance.

### 1. Introduction

Electrochemical energy storage is one of the most important candidates for resolving the non-renewable energy crisis. As a result, attention has shifted to renewable-energy storage devices, including supercapacitors [1]. Supercapacitors (or electrochemical capacitors) have advantages such as high power density, fast charge-discharge capability, and long cycling life [2]. According to the storage mechanism, supercapacitors can be classified into two groups. The first group is electric double-layer

capacitors, which include materials such as carbon materials (carbon nanotubes, graphene, etc.). The next group is pseudocapacitor, which includes materials such as oxides of intermediate metals (such as TiO<sub>2</sub>, RuO<sub>2</sub> oxide, etc.) and conductive polymers (polyaniline and polypyrrole, etc.) [3]. The charge in the pseudocapacitors often stores through rapid and reversible oxidation-reduction reactions. Whereas in electric double-layer capacitors, the charge storage is based on the electrostatic charge penetration and its accumulation at the interface

between the electrode and the electrolyte [2, 4]. One of the most important and effective components of superconductors is the electrode. The properties of the materials used in the electrodes of the supercapacitors greatly influence the performance of the supercapacitors. Therefore, over the past years, extensive researches have been done to optimize and increase the efficiency of electrode materials [5, 6]. Among the various metal oxides, titanium oxide is one of the most suitable materials for supercapacitor electrodes due to its mechanical strength, environmental stability, excellent charge transfer properties, and low synthesis cost. Among the different morphologies of titanium oxide, nanotube arrays have been further studied for providing one-way and direct paths for electron transfer [7]. Although  $\text{TiO}_2$  nanotubes have excellent electrochemical properties, due to their semiconductive nature and wide bandgap, they have poor electrical conductivity and capacitive behavior without any modification. Therefore, different methods such as heat treatment, metal or non-metal doping, decoration with noble metal particles, and synthesis of nanocomposites with electronically active materials such as conductive polymer can increase the capacitance of  $\text{TiO}_2$  nanotubes [8, 9]. Among these methods, non-metallic doping, especially nitrogen and hydrogen, is a facile and effective method. By the non-metallic element doping, electron donor states are created in the titanium oxide bandgap. Hence charge carriers density and electrical conductivity of titanium oxide are increased [10, 11]. Wu et al. used a simple hydrogenation doping method to significantly improve the electronic conductivity and the capacitive performance of  $\text{TiO}_2$  nanotube electrodes. These electrodes treated by the electrochemical hydrogenation doping. The modified electrodes display a high average specific capacitance of  $20.08 \text{ mF}\cdot\text{cm}^{-2}$  at a current density of  $0.05 \text{ mA cm}^{-2}$ ,  $\sim 20$  times more than the pristine  $\text{TiO}_2$  nanotube electrodes [12]. In another study, Samsudin et al. in order to modification of the TNTs, applied a fast and facile electrochemical reduction method. R-TNTs that prepared at 5V for 30 s had a specific capacitance of  $11.12 \text{ mF}\cdot\text{cm}^{-2}$  at a current density of  $20 \mu\text{A}\cdot\text{cm}^{-2}$  [13]. Among conductive polymers, polyaniline (PANI) has received much attention due to its unique properties such as different oxidation modes, environmental stability, and good electron activity. Polyaniline has three different forms depending

on the degree of oxidation. The leucoemeraldine base refers to the fully reduced polyaniline state. Whereas emeraldine base is a half-oxidized form, and pernigraniline is completely oxidized. The only conductive form of polyaniline is emeraldine salt, which is obtained by doping or protonation of the base. These forms of polyaniline are easily converted. Transitions between different forms of polyaniline are accompanied by changes in color and conductivity [14, 15]. Polyaniline is obtained by chemical or electrochemical polymerization of aniline. The electrochemical polymerization method is desirable because the polymer is directly deposited on the electrode surface and facilitates analysis. This method has other advantages than the chemical method, such as control of the thickness of the polymer deposition, low cost, and no need for a catalyst [16]. Xiao et al. prepared polyaniline/ $\text{TiO}_2$  nanotube arrays composite electrodes by depositing polyaniline on  $\text{TiO}_2$  nanotube arrays through the cyclic voltammetry method. The areal capacitance of the composite electrode fabricated in ethanol solvent is  $6.25 \text{ mF}\cdot\text{cm}^{-2}$  at the scan rate of  $50 \text{ mV/s}$  [17]. EIS and Mott-Schottky tests are two powerful and valuable tools for studying the electrochemical properties of materials, including  $\text{TiO}_2$  nanotube arrays as a supercapacitor electrode. In previous articles, these tests, especially Mott-Schottky, have either not been performed or a brief explanation has been provided. Also, similar works have investigated the properties of titanium oxide nanotubes doped with non-metallic elements such as nitrogen (N- $\text{TiO}_2$  NTAs) and hydrogen (H- $\text{TiO}_2$  NTAs) or polyaniline/ $\text{TiO}_2$  NTAs. While the electrochemical properties and capacitive performance of the Polyaniline/N- $\text{TiO}_2$  NTAs and polyaniline/H- $\text{TiO}_2$  NTAs have not been fully investigated [13, 17-21]. In this paper, we tried to examine the electrochemical properties of samples in more detail using these tests. Due to the simultaneous effect of hydrogenation doping (creating of oxygen vacancy) and PANI electrodeposition (PANI/H- $\text{TiO}_2$  NTs electrode), the result of Mott-Schottky indicates that most charge carrier density ( $1.63 \times 10^{24} \text{ cm}^{-3}$ ) and the least charging transfer resistance ( $0.008 \Omega\cdot\text{cm}^2$ ). In this study, the two-step anodic oxidation method was used for the synthesis of well-aligned  $\text{TiO}_2$  nanotubes. To compare the effect of different dopants, the samples were doped once with nitrogen by immersion in ammonia and once again, using the two-electrode system,

the samples were doped with hydrogen. Finally, the polyaniline nanowires were deposited on the nanotubes by electrochemical polymerization. Cyclic voltammetry, electrochemical impedance spectroscopy, Mott-Schottky, and galvanostatic charge-discharge performed to evaluate the electrochemical properties and supercapacitive performance of the samples.

## 2. Materials and Methods

### 2.1 Preparation of TiO<sub>2</sub> nanotube arrays

In this study, for sample preparing, grade 2 titanium sheet with 99.7% purity and 0.5 mm thickness was cut into 1×2 cm pieces. To achieve regular and smooth nanotubes at anodizing, the substrate must be smooth and clear. For this purpose, the samples were first sanded with sandpaper from 220 to 2000 mesh and then polished with 0.5 μm alumina powder to achieve mirror-like surfaces. Then the samples were subjected to ultrasonic irradiation in acetone and ethanol for 15 min, respectively. Finally, the samples were washed with distilled water and thoroughly dried. The TiO<sub>2</sub> nanotube arrays were synthesized by the anodizing method. Anodizing was performed on a two-electrode system in which the prepared Ti sheet was used as the anode and the stainless steel sheet used as the cathode. The intermediate distance between two electrodes was 2 cm, and the electrolyte temperature was 28 °C. The anodizing electrolyte contained ethylene glycol, 0.15 M NH<sub>4</sub>F, and 3% vol deionized water. The first anodizing was performed at 2h at a voltage of 60V. To obtain more regular and better adhesion to the substrate, the oxide layer formed by the first anodizing was ultrasonically removed in distilled water from the substrate. The second anodizing was then carried out in the same solution and condition and time of 3h. Finally, the samples were washed with distilled water and ethanol to remove residual organic electrolytes. To remove residual debris on the top surface of the nanotubes, the samples were ultrasonicated for 30 s in 50 nm alumina powder slurry and washed again with distilled water.

### 2.2 Preparation of N-TiO<sub>2</sub> and H-TiO<sub>2</sub> NTAs

The nanotubes prepared by anodizing were exposed to nitrogen doping. They were immersed in 2 M NH<sub>3</sub>·H<sub>2</sub>O solution for 15 h and then washed with deionized water and dried. Subsequently, because the primary nanotubes were amorphous, the doped samples (N-TiO<sub>2</sub>) were annealed

at 500 ° C for 4 h at a rate of 2.1 °C / min to obtain the crystalline structure in the ambient atmosphere. For hydrogenation of TiO<sub>2</sub> nanotubes, the samples were first annealed at 500 °C. The electrochemical hydrogenation of the nanotubes was then performed on a two-electrode system in 0.5M Na<sub>2</sub>SO<sub>4</sub> solution. TiO<sub>2</sub> nanotube arrays had been used as cathode and graphite electrode as anode. Between the two electrodes, a 5 V voltage was applied for 30 seconds. During the process, hydrogen and oxygen were evolutioned on the cathode (TiO<sub>2</sub> nanotubes) and anode (graphite) surface, respectively. The doped samples (H-TiO<sub>2</sub>) washed with deionized water and dried.

### 2.3 Preparation of PANI/N-TiO<sub>2</sub> and PANI/H-TiO<sub>2</sub> NTAs nanocomposites

The electrical deposition of polyaniline was performed on TiO<sub>2</sub>, N-TiO<sub>2</sub> and, H-TiO<sub>2</sub> NTs samples in the three-electrode system. In this system, the saturated calomel electrode (SCE), platinum sheet and, the prepared samples were used as a reference, counter and working electrodes, respectively. The aqueous base electrolyte contained 0.5 M sulfuric acid + 0.1 M aniline monomer. Electrochemical polymerization was performed by cyclic voltammetry from -0.7 to 1V voltage at a scan rate of 200 mV/s for 30 cycles. After that, the samples rinsed with deionized water and dried. The color of the samples changed to green after the electrodeposition of polyaniline.

### 2.4 Characterization

The surface morphologies of PANI/TiO<sub>2</sub> NTs, PANI/N-TiO<sub>2</sub> NTs and, PANI/H-TiO<sub>2</sub> NTs were characterized by a field emission scanning electron microscope (FE-SEM, MIRA3 TESCAN) at an acceleration voltage of 10 kV. The crystallization of the prepared samples were determined by X-ray diffractometer (XRD, D-5000 Siemens with Cu Kα radiation). The FTIR spectrum was recorded over a wavenumber range of 400-4000 cm<sup>-1</sup> (FTIR-8400S.SHIMADZU). Cyclic Voltammetry (CV), electrochemical impedance spectroscopy (EIS), Mott-Schottky and Galvanostatic charge-discharge (GCD) were used to examine the electrochemical properties and capacitive performance using an electrochemical workstation (Wonatech, ZIVE SP1). The electrochemical tests were performed in a three-electrode system composed of the sample as the working electrode, the Pt sheet as the counter electrode, and the SCE as the reference electrode.

The electrolyte of electrochemical tests were conducted in 0.5M H<sub>2</sub>SO<sub>4</sub>. The frequency range was selected between 100 kHz to 0.01Hz with a 10mV amplitude for the EIS test. The Mott–Schottky method was performed at a single frequency of 1000Hz and a potential between -0.1 to 0.9V with a step potential of 0.05V to study the donor density on the electrode surface.

### 3. Results and discussion

Fig.1a depicts the top view of the FESEM image of TiO<sub>2</sub> nanotube arrays. As the result of two-step anodization, Well-ordered and uniform nanotubes with open top surface are synthesized. TiO<sub>2</sub> nanotubes have an inner diameter of approximately 129 nm and a wall thickness of 27-34 nm. Fig.1b shows the EDS spectrum of TiO<sub>2</sub> nanotube arrays. TiO<sub>2</sub> nanotubes contain the elements of Ti, O, N and C. The top view of the FESEM image of PANI/TiO<sub>2</sub> nanotube composite was presented in Fig.1c. As seen in Fig.1c, irregular PANI nanowires are formed on the top surface of TiO<sub>2</sub> nanotubes. Nonetheless, the regular morphology of TiO<sub>2</sub> nanotubes was maintained. Fig.1d shows the

EDS spectrum of PANI/TiO<sub>2</sub> nanotubes. Samples contain the elements of Ti, O, N, C and, S. High content of the Carbon element in the sample indicates that PANI nanowires have deposited successfully on the top surface of TiO<sub>2</sub> nanotubes. Electrochemical polymerization by CV method was used for Polyaniline deposition. Fig.2a shows CV curves recorded in cycles of 1,5,10,15,20,25 and 30 at scan rate of 200 mV/s. Redox peaks of aniline polymerization appeared in the CV voltammograms, indicating the existence of PANI. As shown in Fig.2a, when cycle number increases, anodic peak current (oxidation) also increases. In contrast, cathodic peak potential (reduction) slightly shifted toward a negative potential and oxidation potential shifted toward a positive potential. These results demonstrate facility of aniline electropolymerization and increase electropolymerization rate. As can see from Fig.2b, first anodic peak at potential 0.2 V corresponds with the transformation of Leucoemeraldine base (fully reduced form) to Emeraldine salt (half reduced form). Another anodic peak at potential 0.8 V refers to the transformation of Emeraldine

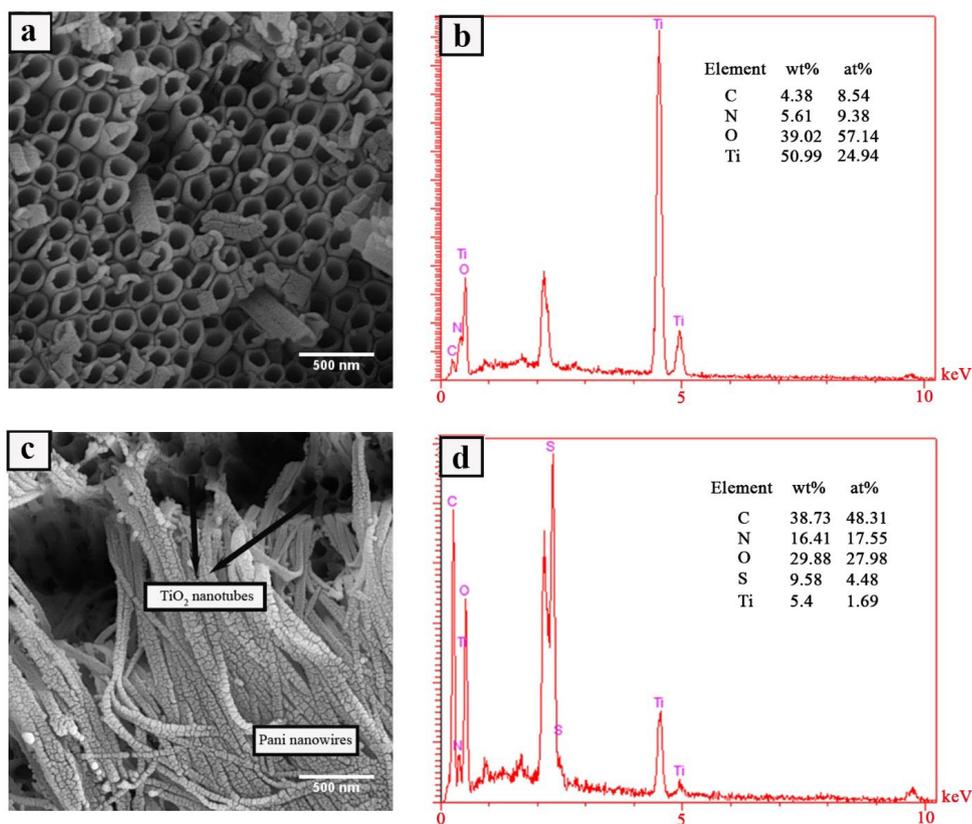


Fig. 1- Top view of FESEM images and EDS spectra of TiO<sub>2</sub> NTAs (a,b), PANI/TiO<sub>2</sub> NTAs (c,d).

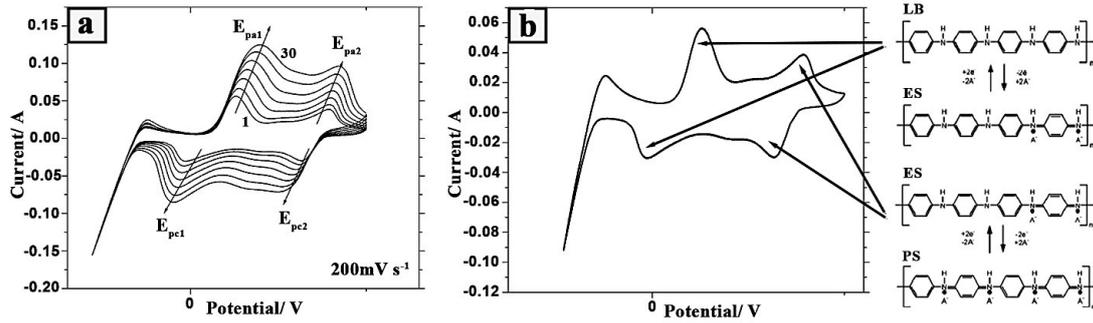


Fig. 2- curves of electrochemical polymerization of aniline by CV method at scan rate of 200 mV/s (a) and characteristic peaks in cyclic voltammograms of electrochemical polymerization (b).

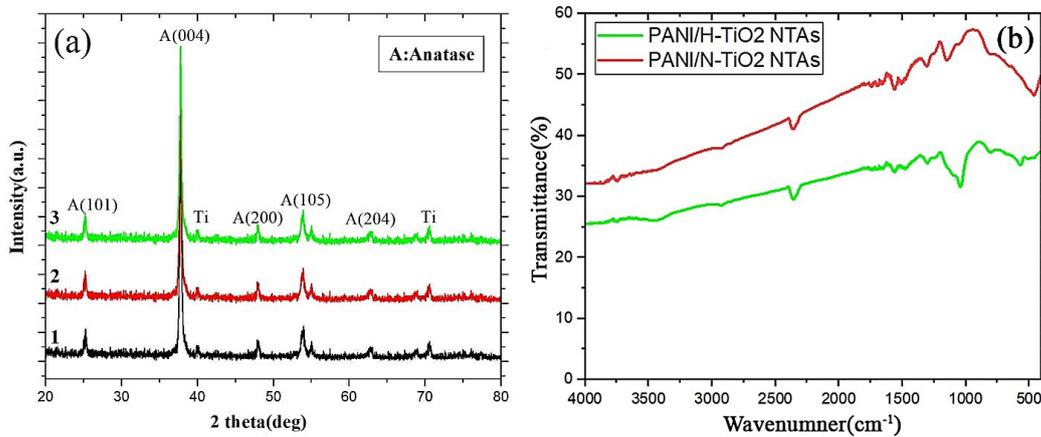


Fig. 3- (a) XRD patterns of 1: PANI/TiO<sub>2</sub> NTs, 2: PANI/N-TiO<sub>2</sub> NTs, 3: PANI/H-TiO<sub>2</sub> NTs and (b) FTIR spectra of PANI/N-TiO<sub>2</sub> NTs, PANI/H-TiO<sub>2</sub> NTs.

salt to the Pernigraniline base (fully oxidized) [22].

The XRD patterns of PANI/TiO<sub>2</sub>, PANI/N-TiO<sub>2</sub>, and PANI/H-TiO<sub>2</sub> NTs samples are illustrated in Fig.3a. The peaks at 25.3°, 37.8°, 48°, 54.2°, and 63° correspond to the (101), (004), (200), (105) and (204) diffraction peaks that can be attributed to Anatase TiO<sub>2</sub> (JCPD:21-1272). It can be deduced that the position and intensity of Anatase peaks didn't change due to non-metal doping and PANI electrodeposition. Therefore hydrogenation and nitrogen doping, as well as PANI electrodeposition, didn't affect the crystal structure of TiO<sub>2</sub> nanotubes [19].

Fig.3b shows the FTIR spectrum of PANI/N-TiO<sub>2</sub> and PANI/H-TiO<sub>2</sub> NTs. FTIR analysis was conducted to investigate the structural information of these samples and to confirm the formation of polyaniline and the doping of nitrogen and hydrogen. Several characteristic peaks are appeared on the FTIR spectra of samples at a wavenumber of 400-4000 cm<sup>-1</sup>. The broad peak from 400 to 800 cm<sup>-1</sup> and 3200 to 3600 cm<sup>-1</sup> are assigned to Ti-O-Ti

stretching vibration and O-H stretching vibration on TiO<sub>2</sub> nanotubes, respectively. After immersing of TiO<sub>2</sub> NTAs in NH<sub>3</sub>.H<sub>2</sub>O solution, the new peak around 1451 cm<sup>-1</sup> is related to N-Ti-O stretching vibration [11]. Electrochemical hydrogenation doping of TiO<sub>2</sub> NTAs cause shift the absorption band of Ti-O-Ti [23]. After the electrodeposition of PANI, the main characteristic bands of PANI are attributed as follows: The band at 3440 cm<sup>-1</sup> is due to the N-H stretching mode. The peaks at 1490 cm<sup>-1</sup> and 1475 cm<sup>-1</sup> correspond to C=C stretching vibration in the benzenoid ring of PANI/N-TiO<sub>2</sub> and PANI/H-TiO<sub>2</sub>, , respectively. The peaks at 1566 cm<sup>-1</sup> and 1564 cm<sup>-1</sup> correspond to C=C stretching vibration in the quinoid phenyl ring of PANI/N-TiO<sub>2</sub> and PANI/H-TiO<sub>2</sub> NTAs, respectively. For PANI/N-TiO<sub>2</sub> NTAs, the peaks at 1305 cm<sup>-1</sup> and 1240 cm<sup>-1</sup> are related to the C-N stretching vibration of the benzenoid unit. While, For PANI/H-TiO<sub>2</sub> NTAs, the peaks at 1307 cm<sup>-1</sup> and 1242 cm<sup>-1</sup> are related to the C-N stretching vibration of the benzenoid unit. The peak at 800 cm<sup>-1</sup> is attributed to

the stretching vibration of the C-C and C-H bonds in benzenoid ring. As a result, the presence of main peaks of polyaniline in the spectrums confirms the formation of polyaniline on the surface of titanium oxide nanotubes. However, due to the interaction of polyaniline with samples of titanium oxide nanotubes doped with nitrogen and hydrogen, the characteristic peaks of the samples are shifted [24, 25].

Fig.4a displays cyclic voltammetry curves of PANI/TiO<sub>2</sub>, PANI/N-TiO<sub>2</sub>, and PANI/H-TiO<sub>2</sub> NTs at a scan rate of 50 mV/s. As the figure shows, the current density of PANI/H-TiO<sub>2</sub> NTs is the highest, and the integrated inner area of the curve is the largest; therefore it is expected to enhance capacitance performance of PANI/H-TiO<sub>2</sub> NTs composite. To investigate the claim, the capacitance of samples calculated through the following equation and CV curves [26].

$$C_s = \left( \int IdV \right) / vSV \quad (1)$$

Where C<sub>s</sub> is the areal capacitance (mF/cm<sup>2</sup>), I is

the current (A), v is the scan rate (V/s), V is the potential (V), and S is the surface area of the working electrode (cm<sup>2</sup>). The areal capacitance calculated for PANI/TiO<sub>2</sub>, PANI/N-TiO<sub>2</sub>, and PANI/H-TiO<sub>2</sub> NTs are 150, 223, and 287 mF/cm<sup>2</sup>, respectively. These results indicate that hydrogenation doping and PANI electrodeposition can increase both conductivity and charge carriers. Nitrogenation also increases capacitance, but the effect of Hydrogenation is greater due to increased electron transfer rate. CV curves were recorded at different scan rates (10-200 mV/s) for PANI/H-TiO<sub>2</sub> NTs (Fig.4b). As seen in Figure, The shape of curves are retained with scan rate increases, so it exhibits good capacitance. Besides, with an increase of scan rate, oxidation peaks toward positive potentials, and reduction peaks toward negative potentials are shifted, showing good reversibility of PANI/H-TiO<sub>2</sub> NTs. The areal capacitance of samples in terms of the scan rate is presented in Fig.4c. The areal capacitance of samples is decreased with increasing the scan rate. The areal capacitance of PANI/H-TiO<sub>2</sub> NTs is decreased from 395 mF/cm<sup>2</sup> to 242 mF/cm<sup>2</sup>

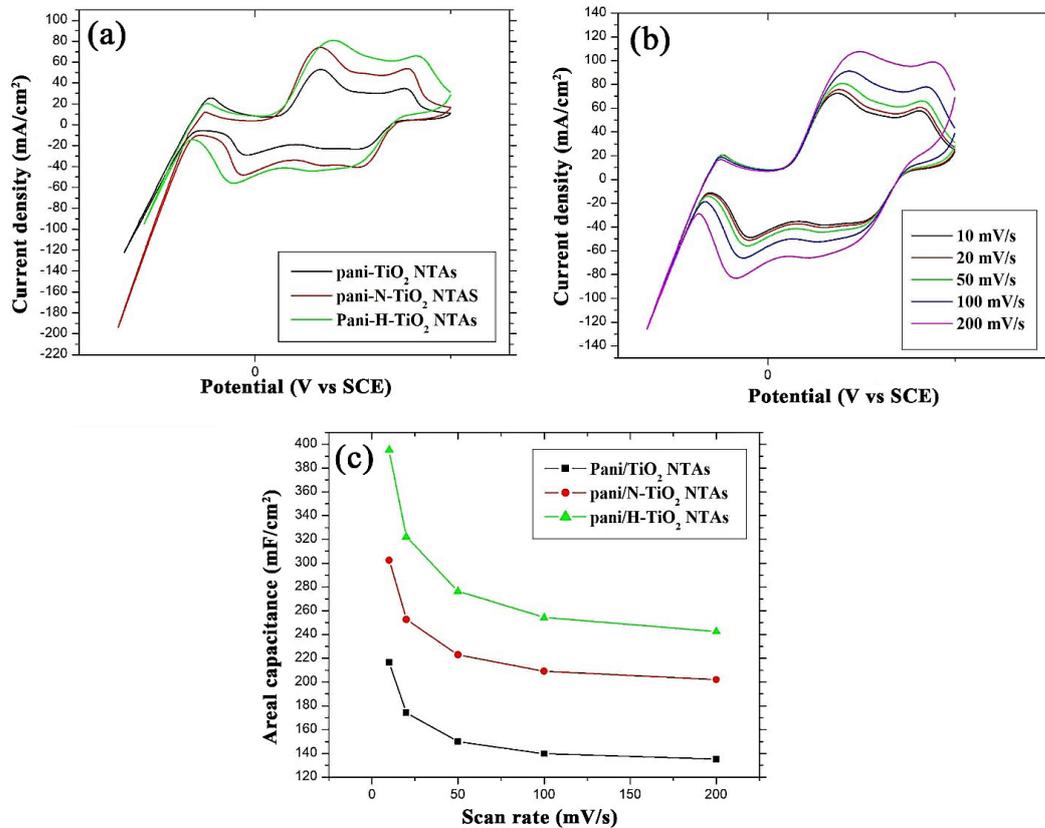


Fig. 4- CV curves of PANI/TiO<sub>2</sub>, PANI/N-TiO<sub>2</sub>, and PANI/H-TiO<sub>2</sub> NTs at the scan rate of 50 mV/s (a), CV curves of PANI/H-TiO<sub>2</sub> NTs recorded at different scan rate from 10 to 200 mV/s (b), the areal capacitance of samples in terms of different scan rate (c).

cm<sup>2</sup> with increasing the scan rate from 10 to 200 mV/s. 61.3% of the initial capacitance remained. At the same scan rate, the areal capacitance of PANI/H-TiO<sub>2</sub> NTs is higher than other samples. Modification processes such as hydrogen doping accompanied by PANI electrodeposition cause improve charge carriers transport significantly, so enhance electrical conductivity [21].

The Nyquist plots of PANI/TiO<sub>2</sub>, PANI/N-

TiO<sub>2</sub>, and PANI/H-TiO<sub>2</sub> NTs have been shown in Fig.5a-c. As seen from Figure, the plots contain two semicircles that one is in the high frequency, and the other is in the low-frequency region. The enlarged high-frequency segment has been shown in the inset of the figure. In this electrochemical system, we considered two interfaces between electrolyte/PANI nanowires and between PANI nanowires/TiO<sub>2</sub> nanotubes. Therefore, the equivalent circuit

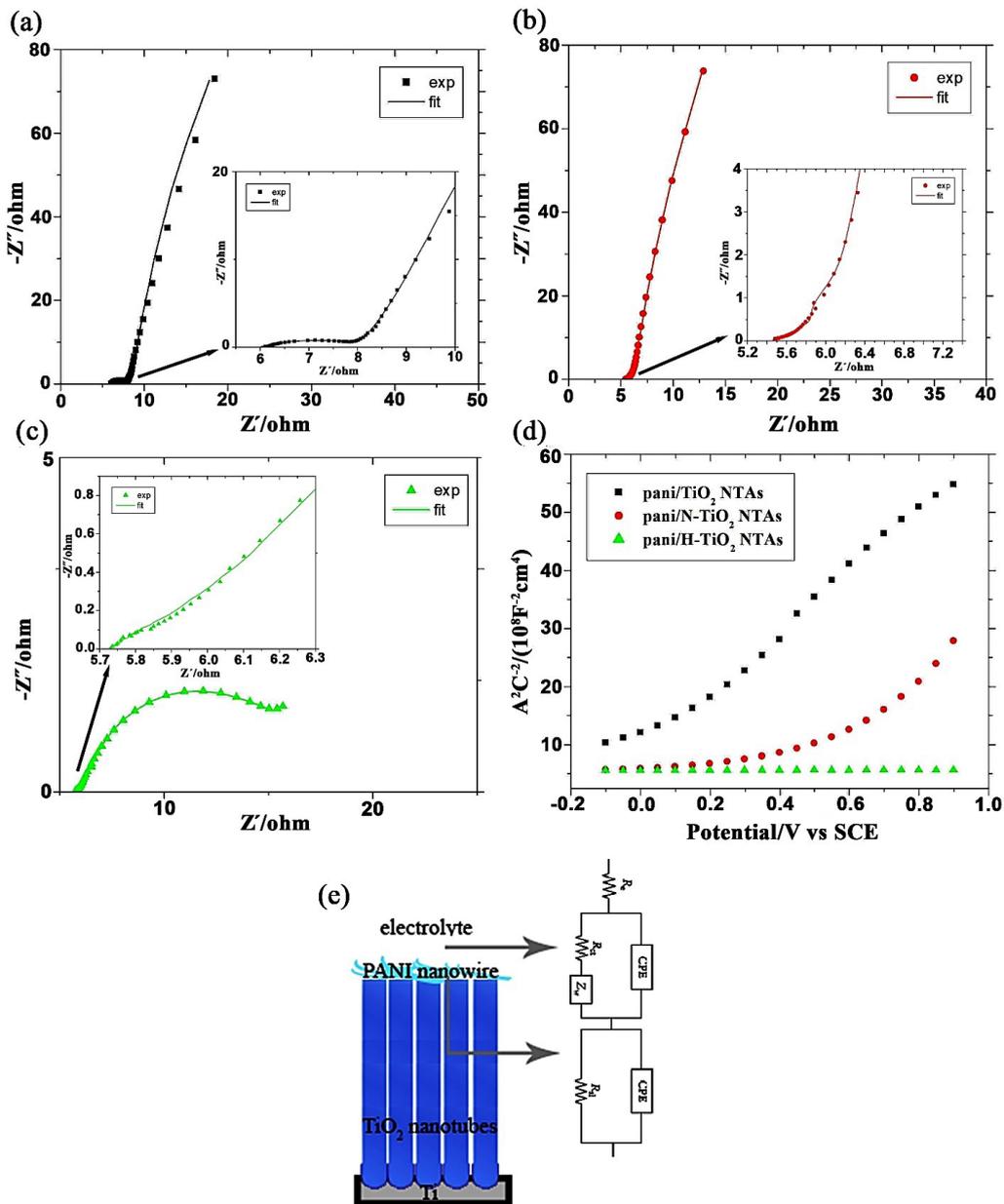


Fig. 5- The Nyquist plots of PANI/TiO<sub>2</sub> (a), PANI/N-TiO<sub>2</sub> (b), PANI/H-TiO<sub>2</sub> NTs (c) in a frequency range of 100 kHz-10 MHz with 10mV amplitude in a 0.5M H<sub>2</sub>SO<sub>4</sub> solution, the Mott-Schottky plot of electrodes in a frequency of 1000Hz with a potential range of -0.1V to 0.9 V (d) and electrical equivalent circuit for impedance spectra fitting (e).

Table 1- Fit parameters of the equivalent circuit for the Nyquist plots shown in Fig.5

Element	PANI/TiO <sub>2</sub> NTs	PANI/N-TiO <sub>2</sub> NTs	PANI/H-TiO <sub>2</sub> NTs
R <sub>s</sub> (Ω.cm <sup>2</sup> )	6.12	5.45	5.73
CPE <sub>dl</sub> -T(mF.cm <sup>-2</sup> )	0.136	0.219	0.303
CPE <sub>dl</sub> -P(mF.cm <sup>-2</sup> )	0.82	0.16	0.74
R <sub>ct</sub> (Ωcm <sup>2</sup> )	1.9	0.02	0.008
W-R(Ω.cm <sup>2</sup> )	3.55	1.29	0.31
W-T(S.s <sup>-0.5</sup> )	0.004	0.03	0.06
W-P	0.39	0.72	0.19
CPE <sub>c</sub> -T(mF.cm <sup>-2</sup> )	0.002	0.005	0.006
CPE <sub>c</sub> -P(mF.cm <sup>-2</sup> )	0.99	0.97	0.95
R <sub>c</sub> (Ωcm <sup>2</sup> )	35.93	23.45	7.108

of Fig.5e was used to fit the electrochemical impedance data with ZView software, and the fitting results are presented in Table1. R<sub>s</sub> is the solution, and connections resistance, R<sub>ct</sub> related to charging transfer resistance and CPE<sub>dl</sub> is the double layer capacitance in between electrode/electrolyte interface. The phenomenon of ions diffusion in the interface of electrode and electrolyte are illustrated with the Warburg element. The low-frequency semicircle is related to the interface between PANI nanowires and TiO<sub>2</sub> nanotubes. As can be inferred from the Fig.5 and Table.1, the charge transfer resistance of the interface in PANI/H-TiO<sub>2</sub> NTs is the least; indicating increase in the rate of separation and transfer of charges. As the result, the electric current increases. In addition, Warburg resistance and contact resistance are much lower and CPE<sub>dl</sub> is higher for PANI/H-TiO<sub>2</sub> NTs [21]. To further investigation of the electrochemical properties of the samples as a supercapacitor electrode, Mott-Schottky plots recorded at a frequency of 1000 Hz (Fig.5d). The following formula calculates the carrier density (N<sub>D</sub>).

$$\frac{1}{C_{sc}^2} = \frac{2}{\epsilon\epsilon_0 e N_D} \left( E - E_{fb} - \frac{KT}{e} \right) \quad (2)$$

Where ε is the dielectric constant of the semiconductor (for anatase: 31), ε<sub>0</sub> is vacuum permittivity (8.854 × 10<sup>-14</sup> F/cm), e is the electron charge (1.602 × 10<sup>-19</sup> C), E is applied potential, K is the Boltzmann constant, T is the absolute temperature, N<sub>D</sub> displays the donor density and C<sub>sc</sub> designates the capacitance of the space charge [27]. As can be inferred from the Fig.5 and Table.2, the N<sub>D</sub> for PANI/H-TiO<sub>2</sub> NTs is much higher than PANI/N-TiO<sub>2</sub> and PANI/TiO<sub>2</sub>. The result of Mott-Schottky indicates that charge carrier density and rate of charge transfer were enhanced. All these results prove that the PANI/H-TiO<sub>2</sub> NTs electrode has better capacitive performance due to

Table 2- Parameters of Mott-Schottky plot

Sample	N <sub>D</sub> (cm <sup>-3</sup> )	E <sub>b</sub> (V)
PANI/TiO <sub>2</sub> NTs	7.9×10 <sup>20</sup> cm <sup>-3</sup>	0.05
PANI/N-TiO <sub>2</sub> NTs	1.45×10 <sup>21</sup> cm <sup>-3</sup>	0.5
PANI/H-TiO <sub>2</sub> NTs	1.63×10 <sup>24</sup> cm <sup>-3</sup>	-

the simultaneous effect of hydrogenation doping and PANI electrodeposition which, increase the capacitance.

The galvanostatic charge-discharge test assesses the capacitive performance of electrodes. Fig.6a shows the charge-discharge curves of electrodes at the current density of 100μA/cm<sup>2</sup>. As shown in Figure, curves of potential in terms of time during the charge-discharge process have a slightly non-linear shape that indicates a reversible and fast Faradic process. Areal capacitance is calculated by the following formula [28].

$$C_s = I\Delta t / S\Delta V \quad (3)$$

Where C<sub>s</sub> is the areal capacitance (μA/cm<sup>2</sup>), I is the constant current during discharge (A), ΔT is the discharge duration (s), ΔV is the potential window (V), and S is the surface area of the electrode (cm<sup>2</sup>). The areal capacitance of PANI/TiO<sub>2</sub>, PANI/N-TiO<sub>2</sub>, and PANI/H-TiO<sub>2</sub> NTs are 1250, 1417, and 5666 μF/cm<sup>2</sup>, respectively. It can be inferred from the increased capacitance that its reason is the existence of Nitrogen and Hydrogen dopants. Non-metal doping is an easy and inexpensive method that helps rapid charge transfer and enhances the charge carriers and reduces the recombination rate. So the electrical current and consequently capacitance will enhance. The effect of Hydrogen doping is greater than Nitrogen doping because it facilitates the faster transfer of charge and increases the electrical current, due to interstitial hydrogen ions and oxygen vacancy [29]. However, nitrogen is also known to be an effective doping agent because

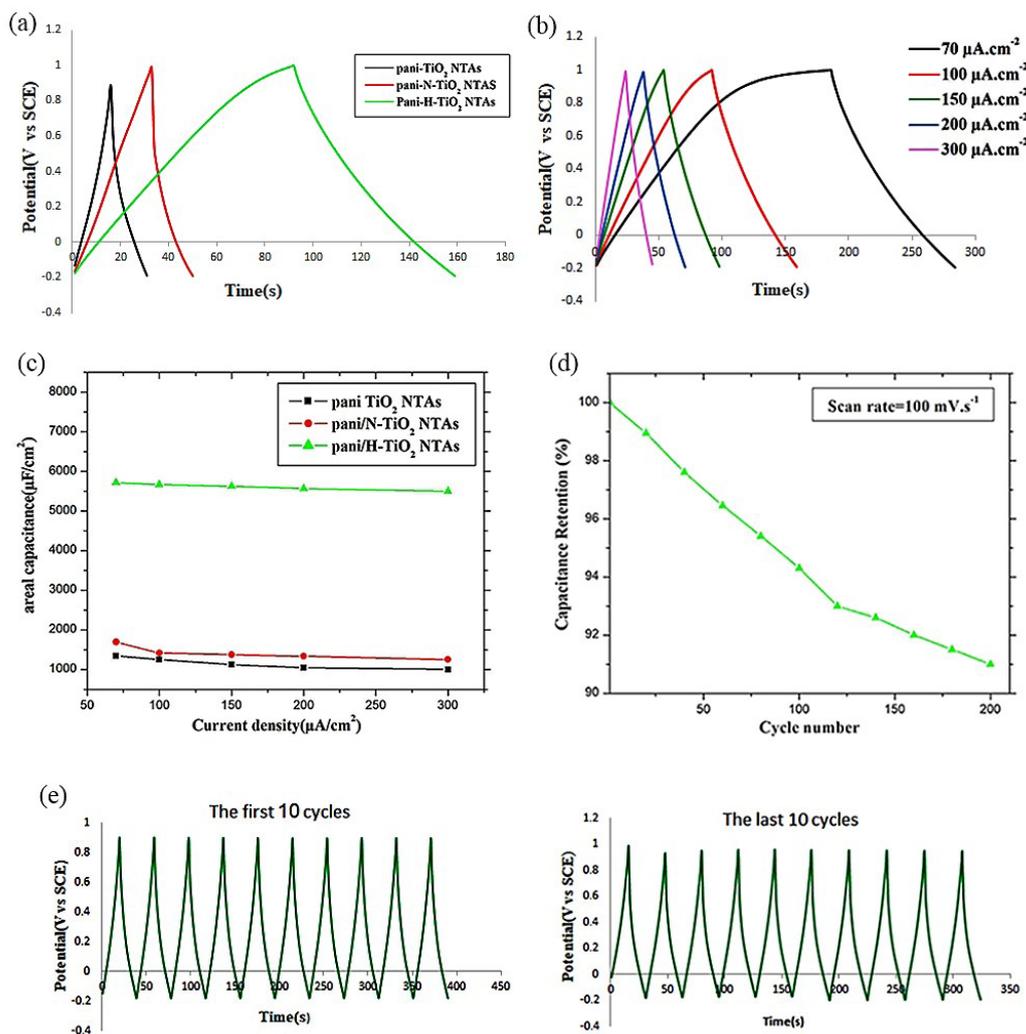


Fig. 6- Galvanostatic charge-discharge curves of prepared electrodes at a current density of  $100\mu\text{A}/\text{cm}^2$  (a), galvanostatic charge-discharge curves of PANI/H-TiO<sub>2</sub> NTs at different current density from 70 to  $300\mu\text{A}/\text{cm}^2$  (b), the areal capacitance in terms of current density for electrodes.

it exhibits better electrochemical and capacitive performance than non-doped samples [30]. The electrodeposition of conductive polymer such as Polyaniline on the surface of TiO<sub>2</sub> nanotubes is another useful and efficient method. PANI electrodeposition significantly improves electrical conductivity and capacitive performance. Fig.6b presents the charge-discharge curves of PANI/H-TiO<sub>2</sub> NTs at various current density from 70-300  $\mu\text{A}/\text{cm}^2$ . As the current density enhances from 70 to 300  $\mu\text{A}/\text{cm}^2$ , the areal capacitance of samples is slightly reduced (Fig.6c). In every current density, the areal capacitance of PANI/H-TiO<sub>2</sub> NTs is much higher than other samples. The capacitive stability test was performed on the optimal sample during 200 cycles. The first ten and the last ten

cycles, together with the capacitance retention, are shown in Fig.6d. As can be seen from figure.6d, its capacitive stability is not significant. Because the prepared electrode is a pseudocapacitor electrode, the pseudocapacitors have lower cyclic stability despite their high capacitance. It is worth mentioning that to increase the stability and cyclic life of the PANI/H-TiO<sub>2</sub> NTs electrode, it should be combined with an electric double-layer capacitor type to form a composite.

#### 4. Conclusion

Titanium oxide nanotubes are recognized as one of the most suitable candidates for capable electrochemical capacitors by providing direct and one-dimensional paths for fast charge transfer and

high surface area. But because of the semiconductor nature and the large energy band gap, it has to be composed of electronically active materials. In this paper, titanium nanotubes effectively doped with non-metallic elements (nitrogen and hydrogen). Then, to further increase the electrical conductivity, the polyaniline nanowires were electrically deposited on the doped nanotubes. The results showed that the composite of TiO<sub>2</sub> doped with hydrogen and deposited with polyaniline nanowires had the highest capacitance (5666 μF.Cm<sup>-2</sup>) at the current density of 100 μA/cm<sup>2</sup>, approximately 4.5 times more than PANI/TiO<sub>2</sub> sample (1250 μF.Cm<sup>-2</sup>). It also has the lowest charge transfer resistance (0.008 Ωcm<sup>2</sup>) and the highest charge carrier density (1.63×10<sup>24</sup>cm<sup>-3</sup>). Non-metal doping helps rapid charge transfer and enhances the charge carriers and reduces the recombination rate. So the electrical current and consequently capacitance will enhance. The effect of Hydrogen doping is more significant than Nitrogen doping because it facilitates the faster transfer of charge and increases the electrical current, due to interstitial hydrogen ions and oxygen vacancy.

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