Band-gap narrowing and electrochemical properties in N-doped and reduced anodic TiO2 nanotube arrays

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A B S T R A C T
Electrochemical activity of TiO2 nanotube arrays (NTAs) is restricted by a wide band gap of TiO2. To overcome this restriction, we considered systematic research on two effective methods of doping of TiO2 NTAs such as the N-doping and electrochemical reductive doping and predicting the proper application of them. Band gap narrowing was occurred from 3.16 eV for undoped TiO2 NTAs to 2.9 and 2.7 eV at N-doped and self-doped TiO2 ones respectively. The electrochemical responses of the TiO2 NTAs before and after doping were examined by cyclic Voltammetry (CV) curve. To understand the electrochemical behavior of the undoped and doped TiO2 NTAs, electrochemical impedance spectroscopy (EIS) was used and three equivalent circuit models were also built. The results showed that the undoped TiO2 NTAs is not strictly capacitive but a small quantity of N in TiO2 remarkably decreases the surface resistance of TiO2 electrode. In contrast, self-doped TiO2 NTAs resistance is reduced to very negligible contents of 0.0001322 \Omega cm^2, that not only self-doped sample becomes to completely capacitive but also, it leads to the semiconductor nature of TiO2 NTAs transforms to semi-metallic one, and the two orders of enhancement in capacitance of blue TiO2 NTAs are very astonishing and it has outstanding potential for applications like supercapacitors as the electrochemical response of the self-doped TiO2 NTA sample was found to be a content of about 7 mF cm^2 that it is improved about 20 times compared with undoped one. Furthermore, it was found that doping of TiO2 NTAs with nitrogen atoms increases the carrier density about 2.82 \times 10^{21} and self-doped TiO2 NTAs show the higher carrier density about 1.14 \times 10^{25} compared with N-doped NTAs. These finding help to understand the mechanism of doping in two different methods and select the best one in relevant applications.

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1. Introduction

Electrochemical anodization of titanium is one of the best methods to synthesis TiO2 NTAs due to easily adjust of the characteristics of TiO2 NTAs like the wall thickness, the tube diameter and length by varying the anodization parameters. Hence TiO2 NTAs have attracted notable recent attention because of plain fabrication, large specific surface area and highly ordered structures [1–3]. Because of these significant features of TiO2 NTAs, they have been extensively employed in various applications including supercapacitors [4], lithium/sodium ion batteries [5], solar cells [6], photocatalysts [7] and hydrogen production through water splitting systems [8].

The semiconductor nature of pristine TiO2, with a band gap energy of 3.0–3.2 eV, makes TiO2 an inefficient material for solar light application due to harvesting light in TiO2 photoanode is limited only to the UV region of the spectrum. On the other hand, narrowing the band gap of TiO2 leads to harvest a larger portion of sunlight near visible region [9]. For this deal, many strategies have been used up to now including doping with metal elements [10,11], applying anion dopants nitrogen or carbon [12,13], thermal treatments [14], and electrochemical reduction [15]. The great deal of attention has been devoted towards disadvantages of these strategies and it has been under debate up to now.

Some research results showed that doping element impurities introducing charge carrier trapping and recombination sites, hence it induces a degrading effect on photochemical activity [11,16]. The methods base on dopant-free TiO2 materials with a band gap
matches the visible light energy had emerged to reduce degrading effects, for example highly ordered dopant-free TiO2 NTAs through manipulating the band gap with applying microstructural strains [17] and reduced TiO2 NTAs through introducing the oxygen vacancies [1]. However, misunderstanding remains around the advantages and disadvantages of both methods of the doped TiO2 NTAs and reduced TiO2 NTAs (as free-dopant TiO2 NTAs) and the mechanism of doping levels is not sufficiently clear. Furthermore, to date, it is still controversial which doping method is beneficial to the photocatalytic processes.

Doped TiO2 photo-catalyst exhibits strong visible light photocatalytic activity as compared to pristine TiO2. Simple doping methods are used to modify the wide band gap of TiO2, which requires ultraviolet irradiation for photocatalytic activation. Because only a small fraction (8%) of the sun’s energy belongs to UV light compared to visible light (45%), any shift in the optical response of TiO2 from the UV to the visible spectral range will have a deep positive effect on the photocatalytic efficiency of the material [18]. Among the metal and non-metal elements as dopants, it was shown that the anionic dopant ions (non-metal elements) induced the desired band gap narrowing of TiO2 because in the metal element doping, the metal centers act as electron traps, also extensive preparation of transition-metal doped TiO2 and thermal instability of its limit their applications [19,20]. Substitutional doping of nitrogen was found to be most productive because the band gap narrowing acquires by mixing the N p states and O 2p states [18].

The implantation of N impurity into TiO2 crystal lattice leads to introduce the localized states at the top of the valence band. Some characteristic features of nitrogen atoms compared to oxygen ones, like comparable size, small ionization energy and high stability lead to incorporate of N into the TiO2 lattice structure. N-doped TiO2 material has been synthesized so far for various modified applications. These methods are classified to two categories: wet chemical methods such as, hydrothermal treatment [21], sol–gel processes [22], spray pyrolysis [23] and some dry powder method like implantation techniques [23], high temperature sintering under a nitrogen containing atmosphere [24], and sputtering [25].

N-doped TiO2 powder photocatalysis has a major problem as recycling from the solution following the chemical reaction and it leads agglomeration of the particle into larger size and also reduce the performance of photocatalyst during the cycle. In contrast, nanotubes compensate these issues due to their high sedimentation rate and high specific surface area. Furthermore, nanotubes have a higher surface to volume ratio, high interfacial charge carrier transfer rate, and better reduction in the electron-hole pair recombination rate, which favors for enhanced photocatalytic efficiency [26]. They have a less active area in comparison to nanoparticle, but the main advantage of them is that they provide the strength cannel for electrons and holes to go through it. The micron size of them provides suitable layer for efficient light scattering in visible range of the spectrum.

As-prepared TiO2 NTAs, which were fabricated by anodization, could be treated and annealed in the presence of NH3 gas [27] or immersed in NH3–H2O solution followed by annealing in a muffle furnace for 2 h to obtain crystalline phase N-doped TiO2 NTAs electrode [28].

The important structural characteristic of N-doped TiO2 NTAs are wall-thickness and length. The wall thickness reduced the chance of photo-induced holes and electrons recombination rate and considerably increased the carrier diffusion length. It was found about another factor, length, that increase of N-doped TiO2 NTAs length obviously enhanced the photocatalytic performance due to the high surface area [29].

It was found that N-doped TiO2 photoanodes in DSSCs increased the solar to current conversion efficiency, because they harvested more visible-light and extended electron lifetime from the excited sensitizing dyes on the surface of TiO2 [30]. N-doping increased the dye absorption and enhanced the photoelectron concentration which improved electron lifetime and resistance of the electron transport within photoelectrode. Furthermore, N-doping effects of absorption in the visible-light region due to the red shift in absorption edge. Expansion in crystal lattice dimensions and decrease in surface resistance of TiO2 electrode leads N-doping in TiO2 crystal lattice to extend the absorbance spectra into the visible region [31,32].

A detailed study of photovoltaic performance in dye-sensitized N-doped TiO2 solar cells showed that the flat band potential was shifted to the negative value which resulted in the improvement of the open circuit voltage for DSSCs [33].

Reductive doping is one of the simplest ways of increasing the electrical properties of TiO2 nanostructures. This kind of doping could be performed through two ways: thermal treatment in the H2 atmosphere [34] and electrochemical reduction [35]. Reductive doping changes the stoichiometry or the intrinsic defect concentrations of the semiconductor. In thermal treatment in H2 atmosphere, neutral hydrogen atoms act as the reducing agent. Also, they intercalate into the TiO2 lattice and behave as mobile donor sites [35]. In contrast, electrochemical reductive doping has a different mechanism. In this process, Ti4+ is reduced to Ti3+ by electron transfer from the cathode. Protons from the electrolyte are adsorbed or intercalated into the TiO2 electrode simultaneously and protons act as counter ions to complete a charge compensation [36]. The correct voltage should be selected for electrochemical process to avoid excessive hydrogen evolution. The excessive hydrogen evolution may lead to surface fracturing [37].

Herein, we present systematic research on the N-doping and electrochemical reductive doping of TiO2 NTAs. In the N-doping method, the simplest way of doping was selected, and in electrochemical reductive doping correct voltage was chosen by investigation of the mechanism of the process. Then, TiO2 NTAs interface changes of in contact with electrolyte were surveyed by electrochemical impedance and corresponding equivalent circuits. At the electrode/electrolyte interface, TiO2 NTAs as pristine, N-doped and reduced showed completely different in that the charge transfer process so, each of these TiO2 NTAs should be used in different application to present their benefits. Hence, various tests, such as EIS, LSV and CV are carried out to explain what has happened in pristine, N-doped and reduced TiO2 NTAs. The reaction mechanisms for each of doping processes to the best of our knowledge, scarcely reported in the literature.

2. Experimental

Two-step anodic oxidation of polished Ti was used to obtain the highly oriented TiO2 nanotubes. For this purpose, commercially available high pure titanium sheets (Gr. 2, 99.7%, 0.5 mm) were employed in all experiments. The sheets were cut into 1 × 2 cm² and then ground on sand papers from 120 down to grade 1200. Then, they were mechanically polished using 0.05 μm Al2O3 powder. After polishing, the samples were degreased ultrasonically in acetone and ethanol for 15 and 10 min, respectively. The samples then were used as a anode in anodization process. The anodizing electrolyte consisted of ethylene glycol (C2H4O2), 0.15 M NH4F and 3 vol% DI water. The anodization was carried out using a two-electrode cylindrical configuration consisting of Ti as the anode and stainless steel with diameters of 60 mm as the cathode. The anodization cell was operated at a cell voltage of 60 V and temperature of 30 °C for 4 h. The solution was rigorously agitated using a magnetic stirrer during anodization. For the two-step anodizing
treatment, the titanium oxide layer formed in the first step was ultrasonically removed with deionized water, then, the second step of anodic oxidation was carried out under the same condition as used in the first step. After anodization process, the as-prepared samples were dried in oven at 80 °C for 20 min to avoid cracking in the anneal stage. Annealing was performed at 480 °C for 1 h under ambient atmosphere and the samples were left in furnace to cool down. The as-prepared samples that annealed at 480 °C, as called pristine.

For the N-doped TiO2 NTAs, the as prepared samples were immersed in 1 M NH3·H2O solution for 15 h and annealed in a furnace under an ambient atmosphere for 2 h to obtain N-doped TiO2 NTA electrode with crystalline phase. The as-prepared TiO2 NTAs after annealing (as anatase TiO2 NTAs) were exposed to electrochemical reductive doping in a three-electrode electrochemical system with an electrochemical work station (SAMAS500 ElectroAnalyzer System) at ambient temperature. TiO2 NTAs and a platinum sheet (1.5 × 3 cm²) were used as the working electrode and counter electrode, respectively. A saturated calomel electrode (SCE) was placed as reference electrode.

A saturated calomel electrode (SCE) was placed as reference electrodes in the supporting electrolyte of an aqueous solution of 0.5 M Na2SO4. The potentiostatic cathodic reduction was carried out by potentiostatic cathodic polarization at different potentials of −1.2, −1.4 and −1.6 V for the polarization period of 10 min. The samples were then dried in oven at 80 °C for 20 min.

The electrochemical response of the TiO2 NTAs before and after doping was investigated by cyclic Voltammetry (CV), galvanostatic charge-discharge tests, and electrochemical impedance spectroscopy (EIS) studies in a conventional three-electrode cell employing an electrochemical workstation (AUTOLAB) and as the same as that described for the reductive doping experiment in the supporting electrolyte of 0.5 M Na2SO4. All EIS tests were performed at an open circuit voltage and the frequency range was 100 kHz to 0.01 Hz with a 10 mV rms sinusoidal modulation. Mott—Schottky curves of reduced TiO2 NTAs were measured at 1000 Hz under different applied DC potentials between −0.1 to 0.9 V with a step potential of 0.05 V.

The surface morphology of the synthesized TiO2 NTAs before and after doping were characterized by field emission scanning electron microscopy (FE-SEM; MIRA3 FEG-SEM, Tescan). Chemical composition of metal oxide samples was studied by X-ray photoemission spectroscopy. XPS studies were carried out by SPECS EA 300 equipped with Al monochromatic anode.

The diffuse reflectance of the samples was measured using an Avantes spectrophotometer (model: AvaLight-DHS). A BaSO4 reference was used to provide a nominal 100% reflectance measurement. The Kubelka-Munk model has been generally used for determining the band gap from diffuse reflectance data of TiO2 NTA samples [17].

3. Results and discussion

Fig. 1 shows the CV curve, which was recorded for the pristine TiO2 nanotube sample. Selection of the correct constant voltage should be used to avoid excessive H2 evolution during the cathodic polarization. At higher voltages, excessive hydrogen evolution leads to surface fracturing of layers. Furthermore, it should be considered that the onset potential of H2 evolving shifts with a change in the pH of the solution [1]. From Fig. 1, it could be seen that the apparent peak at −1.55 V (vs SCE) results from the reduction of Ti4+ to Ti3+ ions. Thereby, the high density of Ti3+ states causes low resistances and the increase in current was occurred. Along with the reduction, charge compensation via proton or other small cations inside the electrolyte could be possible. Further increase in more negative voltage of −1.65 V (vs SCE) shows the hydrogen evolution initiation which the reaction of 2H+ + 2e− → H2 could be occurring.

According to the results of Zhou and co-worker [4], besides the proton injection theory, the trap theory also explains the charging–discharging of TiO2 via a trapping–detrapping process in TiO2 bulk or surface. Thereby, it could be expected the behavior of the trapping–detrapping process of electrons by trap sites. In our results, also the existence of traps is emerged as cathodic capacitance peak (an increase of the negative current density in the Voltammetry pattern) around −0.02 V. It could be explained that the traps will catch free electrons, so a cathodic capacitance peak would be formed at around the flatband potential (Vfb), because depletion of conduction band electrons in TiO2 nanomaterials occurred at applied potentials positive of Vfb, because depletion of conduction band electrons in TiO2 nanomaterials occurred at applied potentials positive of Vfb, because depletion of conduction band electrons in the conduction band, hence filling of the trap should appear at around Vfb potential. After depletion of conduction band electrons, the negative current density gets increased due to the enhancement of conductivity [4]. From Fig. 1 it could be concluded that peak at +0.02 V followed by an increase of negative current at −0.1 V is due to the filling of traps. Because, as seen later,
the measurement of $V_{fb}$ from Mott-Schottky curve shows a value of about +0.04 V for the pristine TiO$_2$ nanotubes. As the proved results [4], the intercalation of protons or other small cations in nanostructured TiO$_2$ takes place at potentials significantly negative of $V_{fb}$.

During the synthesis process, the color of oxide is changed as seen in Fig. 2. The as-anodized TiO$_2$ NTAs had gray color. When they were exposed to heat up to 80 $^\circ$C in the oven, the gray color was switched to brown. After annealing at higher temperatures like 480 $^\circ$C, the brown was changed to light gray. When the light gray anatase TiO$_2$ NTAs were placed in an electrolyte during cathodic polarization, electrochromic switching was occurring and the light gray was changed to blue one. Our results showed that even after drying of the blue TiO$_2$ NTAs at 80 $^\circ$C, they kept the blue color. In our cathodic polarization potentials ($-1.2$ to $-1.6$ V), the reduction of TiO$_2$ NTAs was observed not to be reversible and after heating up to 80 $^\circ$C, stability of the samples were obtained. It is noteworthy that in the potential ranges of $-1.2$ to $-1.6$ V, the oxygen vacancies that formed in the self-doped TiO$_2$ NTAs intercalate to the TiO$_2$ lattice much vigorous, and H$^+$ intercalation, even in more negative ones H$_2$ evolution, break down Ti–O bonds, thereby the irreversible process could be expected.

According to results from Fig. 1, with considering the potentials of reduction of Ti$^{4+}$ to Ti$^{3+}$ and H$_2$ evolution, the as-prepared arrays underwent a cathodic polarization process at suitable negative potential from $-1.2$, $-1.4$ and $-1.6$ V using aqueous electrolyte to achieve self-doped TiO$_2$ NTAs. Fig. 3a reveals the dependence of current on time at different cathodic potentials $-1.2$, $-1.4$ and $-1.6$ V vs. SCE. According to the macroscopic observations, electrochromic effect (evolution the blue color at samples) in all three samples was occurred and the color of samples was changed to blue. Electrochromic effect is related to the formation of oxygen vacancy states of Titania generally localized with energies of 0.8–1.2 eV below the conduction band [38]. As seen in Fig. 3a, a large current of 12 mA cm$^{-2}$ was yielded immediately after the TiO$_2$ NTAs were switched on, and then rapidly decreased to a stable value. The current was enhanced by raising the cathodic potential. Increasing the current at higher potentials like $-1.6$ V is not only related to the reduction of Ti$^{4+}$ to Ti$^{3+}$ but also to the reduction of H$^+$ to H$_2$. With formation of Ti$^{3+}$ defects below the conduction band, pristine TNAs that is nearly insulating are converted into a beneficial highly conductive state. On the other hand, after reducing of Ti$^{4+}$ to Ti$^{3+}$ and increasing density of Ti$^{3+}$ dopant states, the pristine semiconductor behaves as metallic. The electrochemical reduction is initiated at the bottom of the TNA and then rapidly extends to the whole internal surface. It is started by simultaneous injection of electrons and protons into TiO$_2$ crystallites from Ti and water. Because the electron which injected to TiO$_2$ unsettles the charge equilibrium, positively-charged protons are also injected into TiO$_2$ crystallites. The overall reduction reaction involving injected electrons and protons are seen in Eq. (1):

$$2n e^- + 2nH^+ + TiO_2 \rightarrow TiO_2{n} + nH_2O \quad (1)$$

Reducing ability of electrochemically injected electrons leads to producing Ti$^{3+}$ states (or the oxygen vacancy states) and they are energetically localized below the conduction band. Hence, from the valence band top to the oxygen vacancy states more than $-2.2$ eV energy is required. In order to perform an effective electrochemical reduction, injected electrons should have energy about $-2.2$ eV, so applied cathodic potentials should be high enough to meet this energy requirement [39].

In order to determine the capacitive properties of reduced TiO$_2$ NTAs (blue TiO$_2$ NTAs) and to evaluate the effect of reducing process on the electrochemical properties of TiO$_2$ NTAs, the pristine and the blue TiO$_2$ NTAs reduced at different potentials are investigated by CV measurements in 0.5 M Na$_2$SO$_4$ solution. Fig. 3a and b shows current-time and CV curves of these electrodes at a scan rate of 100 mV s$^{-1}$ respectively. From Fig. 3b, The CV curve of the pristine with almost triangular shape is consistent with semiconducting manner and shows a strong dependence of current density on potential, while rectangular shape characteristic of blue TiO$_2$ NTAs shows semi-metallic behavior of the sample. As seen later, from EIS curves, the pristine with the n-type semiconductor
properties has high resistances at more positive potentials, hence high resistances currents decreases the current density and a slope is formed in a CV curve at positive potentials. Also, the CV curves of blue TiO₂ NTAs at −1.2, −1.4 and −1.6 are shown in Fig. 3b. The −1.2 V blue TiO₂ NTAs still slightly preserved the dependence of current density on potential, thereby it could have high resistance with the low density of Ti³⁺ states. By increasing the voltage up to −1.4 V, the current was enhanced, but more increase in voltage up to −1.6, the current was decreased. As seen in Fig. 1, at voltages higher than −1.55 V, H₂ evolution and surface fracturing caused by excessive hydrogen evolution was occurring in the sample and it leads to current was decreased along the CV rectangular curve. Doping level can be estimated according to the amount of charge passed during the electrochemical reductive process, hence according to the above electrochemical data, we can choose suitable voltage for electrochemical reductive doping of TiO₂ NTAs as −1.4 V.

For comparing the catalytic activity of the pristine TNAs and the blue TNAs reduced at −1.4 V, the samples were evaluated by CV test at three electrode system in 0.5 M Na₂SO₄ solution. Fig. 3c shows the CV curves of these electrodes at a scan rate of 100 mV s⁻¹. The CV curve of pristine TiO₂ NTAs shows a strong dependence of current density on potential with almost triangular shape. The N-doped sample also was examined by CV test and it reveals the manner same as the pristine ones. Because after N-doping, the semiconductor behavior of TiO₂ NTAs preserved. But, the blue TNAs highly reduced at −1.4 V exhibit an almost rectangular shape characteristic of electrical double-layer capacitance.

Fig. 4 shows the high-resolution XPS spectrum of N 1s for N-doped TiO₂ NTAs and O 1s and Ti 2p for pristine, N-doped and blue TiO₂ NTAs. XPS measurements were used to identify the chemical states of N atoms in N-doped TiO₂ NTAs. As the Fig. 4, the N 1s peak was deconvoluted into three peaks at 394.18, 396.78 and 399.11 eV. The XPS analysis of the state of nitrogen in N-doped TiO₂ NTAs thin films widely surveyed by Ronero and co-workers [40]. On the basis of previous works, at around 395 eV, nitrogen triple bonds to Ti as TiN [40], which in this case, some oxygen sites of TiO₂ lattice were substituted by nitrogen. In around 400 eV, (i.e., around 397 and 399 at Fig. 4) nitrogen bonds to oxygen and titanium in a defective lattice site. In this situation, structures of the type Ti–N–O–⋅⋅⋅–Ti or Ti–O–N–Ti could be formed [40]. Also, from high-resolution XPS spectra for the Ti 2p and O 1s regions shown in Fig. 4 could be concluded that the binding energies of Ti 2p and O 1s are shifted to lower energies. These negative shifts is because of presence of Ti³⁺ and oxygen vacancies compared to pristine one.

Fig. 5 compares surface uniformity and roughness of the pristine, N-doped and blue TiO₂ NTAs. All samples were evaluated by FESEM after annealing process, so the nanotubes are covered in some regions with oxides on top surfaces. As seen in Fig. 5, the surface features of the pristine, N-doped and blue TiO₂ NTAs show no obvious changes. Different processes which were performed on as prepared TiO₂ NTAs, such as annealing at 480 °C for 1 h to form pristine, NH₃ treat of as-anodized and then annealing at 480 °C for 2 h to form N-doped and electrochemical reducing of pristine TiO₂ NTAs at −1.4 V for 10 min to form blue TiO₂ NTAs, only changed the electronic and defect levels of samples and it has no obvious effect on surface roughness, morphology and tube size of nanotubes. The length of the nanotubes is about 28 μm and it is proper to TiO₂ photo-induced applications.

Fig. 6 shows the diffuse reflectance spectra for pristine, N-doped and blue TiO₂ NTAs and Tauc plots of their reflectance data. A procedure known as Tauc model was used to determine the band gap of TiO₂ nanotubes grown on Ti substrate from diffuse reflectance spectrum according to:

\[
\frac{(h \nu)^{1/n}}{\alpha} = A(h \nu - E_g)
\]

where, h is Plank's constant, ν is the frequency of vibration, α is absorption coefficient, E_g is band gap, A is the proportional constant and n depends on the band structure of the sample is 2 for indirect allowed transition (n = 2), due to TiO₂ in amorphous and anatase phase exhibits indirect electron transfer [41]. Diffuse reflectance spectrum data could be converted according to the Kubelka-Munk function according to F(R) = (1−R)²/2R, where R is the reflectance of samples and F(r) is proportional to the absorption coefficient (α). Using the Kubelka-Munk function, (hνF(R))¹/² was plotted against hν. A line is drawn tangent to the point of intersection of the tangent line and the horizontal axis is the band gap E_g value [17]. Diffuse reflection from solids is generally not due to surface roughness. The most general mechanism by which a surface gives diffuse reflection does not involve exactly the surface; most of the light is contributed by scattering centers beneath the surface [42].

Thereby, Kubelka-Munk Function is a well-known method for converting reflectance to transmittance or absorbance. As the Tauc plots of Fig. 6a, it is interesting to observe that doped TiO₂ nanotubes reveals a significant reduction in the energy band gap. From Fig. 6a, it could be seen that the diffuse reflectance spectra shows a broad absorption at wavelengths around 400–700 nm which is probably caused by the trapped charge carriers or the absorption of incident light by nanotube arrays band gap, as similar to our previous reports [17]. The blue TiO₂ NTA has the maximum absorption because of semi-metallic property and the N-doped TiO₂ NTAs also have higher absorption as compared to pristine, because dopant states reduce the band gap.
The results from the Tauc plots (Figs. 6b, c, d and Table 1) clearly indicate that N and oxygen vacancies were incorporated in TiO$_2$ lattice to extend the absorption to a longer wavelength range [43]. As TiO$_2$ is an indirect band-gap semiconductor, the red-shift due to N doping is substantial in comparison to the 3.2 eV theoretical band gap of anatase TiO$_2$ (and 3.16 calculated in this report for pristine), and would improve the UV/Vis photocatalytic activity. From the results, narrowing the band gap while doping, leads to reducing the band gap from 3.16 eV (with band tailing 2.2 eV) for pristine to 2.9 eV (with band tailing 1.8 eV) and 2.7 eV (without band tailing) for N-doped and blue TiO$_2$ NTAs respectively, therefore the absorption wavelength was shifted from 390 nm to around 430 and 460 nm, so it was shifted to inset of the visible region. It seems to the lack of band tailing in blue sample is attributed to semi-metallic property of blue TiO$_2$ NTA that the bands slide each other.

The accurate energy level band diagram derived from combined XPS and DRS measurement results is shown in Fig. 7 for three different samples. As the Fig. 7, the bandgap of TiO$_2$ nanotubes exhibits red-shift and overlaps with the visible spectrum photon energy by narrowing the band gap. As the literatures, defect bandgap states are often observed at about 0.8 below E$_F$ for TiO$_2$ [44].

According to earlier reports, although doping of TiO$_2$ successfully extends its photo response to visible light, the resulting materials demonstrate mixed photocatalytic activities, as beyond a minimal concentration, the doped ions serve as recombination centers in the photogenerated electron–hole pairs [45]. Usually, the reduction in band gap can be attributed to the presence of a defect band of ionized acceptors. Although the observed red-shift is advantageous, with applying self-doping as called the reduced TiO$_2$ NTAs, the band gap was reduced even more.

To explore the nature of interfacial behavior and different doping level of samples, electrochemical impedance measurements for different samples of pristine, N-doped and reduced TiO$_2$ NTAs were performed at an open circuit voltage (30, 60 and 60 mV for pristine, N-doped and blue TiO$_2$ NTAs respectively). Fig. 8 shows EIS data and the equivalent circuit when the samples were placed in contact with electrolyte. Rs represents the resistance of the solution between the work electrode and reference electrode. On the inside of nanotubes, the impedance of the interfacial reaction described as capacitive component and a series combination of Faraday resistance and Warburg impedance due to diffusion is the controlling step at the interface. The capacitive element can be replaced by a constant-phase element due to the complex nature of the interfacial reaction.

According to Fig. 8, it could be generally seen that Nyquist plots reveal a line at 45° at high frequencies followed by a vertical line at low frequencies. The slope of vertically part is different in various samples. The straight line at 45° indicates that the real and imaginary parts of the impedance are identical. At high frequencies, the AC signal cannot penetrate to the bottom of the pore because of the IR drop and very low impedance of the pore walls. On the other hand, at low frequencies, the AC signal can penetrate to the bottom of the pore and the measured capacitance corresponds to the total capacitance of the pore walls [46].

For practical application, diffusion is as finite-length linear
where the diffusion layer corresponds to the layer thickness. From two kinds of finite-length diffusion (transmissive and reflective boundary), transmissive boundary is in the case of steady-state concentration gradient in the membrane and reflective boundary is observed for the cases that the membrane is impermeable. In transmissive boundary a semicircle is obtained because a DC current can flow \[ 46 \].

From inset of Fig. 8a, in the pristine TNAs, close to an arc shape is seen at the very high-frequency region due to the parallel combination of resistance and capacitive element \[ 1 \]. It could be concluded that transmissive boundary is not shown because the plot not included the complete arc region and the sample is not strictly capacitive. Hence the reflective boundary finite-length diffusion could be considered in our samples. In reflective, the mass transfer impedance displays a straight line at 45°/sqrt(C) at high frequencies because the penetration length of the ac signal is smaller than the layer thickness and at lower frequencies the imaginary part goes to infinity as the constant current cannot flow. In such cases, a so-called generalized finite-length Warburg element was used for reflective geometry. The physical interpretation is related to nonuniform diffusion or multiple paths in the system \[ 47 \].

Because of nonuniform diffusion it could be considered the constant phase element (CPE) in the system. In the mid- and low frequency regions, generalized Warburg impedance could be seen as linear nature of Nyquist plot. Also, Fig. 8b shows bode and phase

Fig. 6. a) diffuse reflectance spectra for pristine, N-doped and blue TiO2 NTAs. Calculated Tauc plots showing band gap of b) pristine, c) N-doped and d) blue TiO2 NTAs. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Table 1
Calculated energy band gaps of pristine, N-doped and blue TiO2 NTAs using Tauc plots of diffuse reflectance spectra.

<table>
<thead>
<tr>
<th>sample</th>
<th>Step 1 condition</th>
<th>Step 2 condition</th>
<th>Step 3 condition</th>
<th>Energy band gap (eV)</th>
</tr>
</thead>
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<tr>
<td>pristine TiO2 NTAs</td>
<td>Two-step anodizing</td>
<td>Annealing at 480</td>
<td></td>
<td>3.16</td>
</tr>
<tr>
<td>N-doped TiO2 NTAs</td>
<td>Two-step anodizing</td>
<td>NH3 treating</td>
<td>Annealing at 480</td>
<td>2.93</td>
</tr>
<tr>
<td>blue TiO2 NTAs</td>
<td>Two-step anodizing</td>
<td>Annealing at 480</td>
<td>Cathodic polarization</td>
<td>2.73</td>
</tr>
</tbody>
</table>

Fig. 7. Energy band diagrams of undoped (pristine), N-doped and reduced (blue) TiO2 NTAs and comparison of the visible light spectrum with the related energy bandgap. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)
plots of the pristine TiO$_2$ sample. Fig. 8c and d also shows EIS data of N-doped TiO$_2$ NTAs. The effect of the N doping on the kinetics of electrochemical processes could be interpreted from the data. Previous results showed a small quantity of N in TiO$_2$ remarkably decreases the surface resistance of TiO$_2$ electrode [31]. Table 2 shows the resistance of the electrode. From the Table 2, the interface charge transfer resistance (Rct) decreased with intercalating of N into TiO$_2$ structure. Regarding the fact that introduction of N atom is more beneficial to the separation of the photoinduced carriers (e$^-$ - h$^+$), so it leads to enhance the electron life time and retard the recombination reaction. Therefore, the N-doped TiO$_2$ NTAs displays greater separation efficiency of photogenerated electron–hole pairs.

Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pristine</th>
<th>N-doped</th>
<th>Blue</th>
</tr>
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<tbody>
<tr>
<td>Rs ($\Omega \cdot \text{cm}^2$)</td>
<td>9.316</td>
<td>7.123</td>
<td>10.34</td>
</tr>
<tr>
<td>CPE1-T (mFsp/C$\Omega$ cm$^2$)</td>
<td>7.203 x 10$^{-5}$</td>
<td>4.8638 x 10$^{-4}$</td>
<td>6.1987 x 10$^{-3}$</td>
</tr>
<tr>
<td>CPE1-P</td>
<td>0.74163</td>
<td>0.58426</td>
<td>0.85439</td>
</tr>
<tr>
<td>Rct ($\Omega$ cm$^2$)</td>
<td>39.67</td>
<td>11.53</td>
<td>0.0001322</td>
</tr>
<tr>
<td>W-R ($\Omega$ cm$^2$)</td>
<td>732.9</td>
<td>304.3</td>
<td>60.88</td>
</tr>
<tr>
<td>W-P</td>
<td>0.96593</td>
<td>1.041</td>
<td>0.276</td>
</tr>
<tr>
<td>W-P</td>
<td>0.42318</td>
<td>0.41757</td>
<td>0.58477</td>
</tr>
<tr>
<td>R1 ($\Omega$ cm$^2$)</td>
<td>–</td>
<td>–</td>
<td>475.7</td>
</tr>
<tr>
<td>Cl (mFsp/C$\Omega$ cm$^2$)</td>
<td>–</td>
<td>–</td>
<td>0.062511</td>
</tr>
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pairs and faster charge transfer than that of the pristine TiO2 NTAs electrode at the solid—liquid interface.

Researches showed that by decreasing the resistance, electron is easy to be transferred to the underlying TiO2, hence electron injection is enhanced and photo-application of the electrode is improved [31]. Also, the N-doped nanotube array electrode displayed greater separation of photogenerated electron—hole pairs and faster charge transfer than that of the pure TiO2 nanotube film at the solid—liquid interface [48]. In our results, also it could be seen that N-doping reduced resistance of electron transfer. But the important issue is about Nyquist plots of N-doped TiO2 NTAs compared with the pristine ones. As Fig. 8c and d, although the Nyquist plot is similar to the pristine, the arc shape at the very high-frequency region is slightly depressed. Hence the capacitive property of the N-doped sample is better than the pristine one. In the N-doped sample, also the reflective boundary finite-length diffusion is considered.

Fig. 8e and f reveals EIS data of reduced TiO2 NTAs as blue sample. As it could be seen from the Figs., the arc shape at the very high-frequency region was disappeared and the vertical line at low frequencies inclined to perpendicular direct and therefore an R–Cpore connection in series should be added to equivalent circuit that means the AC signal can penetrate to the bottom of the pore. At low frequencies the imaginary parts go to infinity and the electrode displays its capacitive behavior [46].

From Table 2 the Rct resistance was reduced to very negligible contents of 0.0001322 Ocm$^{-2}$. We could say that physically inter-operation of this phenomena is related to the transforming semiconductor nature of pristine TiO2 NTAs to semi-metallic nature of blue TiO2 NTAs. In the case of blue TiO2 NTAs, the oxygen vacancy levels reduced the band gap between the conduction and valence bands, and the finite-length diffusion becomes completely capacitive. In this situation, R1 shows the resistance of the electrons which penetrate into layer thickness. As Table 2, the Rct value was diminished to 0.0001322 Ocm$^{-2}$ because reducing process significantly improve the electron transport conditions of the TiO2 NTAs [49]. Also, from Table 2, the two orders of enhancement in capacitance are very astonishing and it could be concluded that the blue TiO2 NTAs has outstanding potential for applications like batteries and supercapacitors.

Fig. 9a shows CV curves were recorded at different scan rates of 5–200 mV s$^{-1}$. These curves show the capacitive performance of the blue TiO2 NTA sample. From Fig. 9a, a nearly ideal capacitive shape of the curves remain even at high scan rate of 200 mV s$^{-1}$. Fig. 9b shows the charge–discharge curves of the pristine, N-doped and blue TiO2 NTA samples collected at a current density of 50 µA cm$^{-2}$. As shown in Fig. 9b, the charge–discharge curves of the blue TiO2 NTAs are symmetric that it reveals excellent capacitive behavior. Fig. 9c reveals capacitances of the samples derived from the charge–discharge curves measured at different current densities according to the following equation:

$$C_A = \frac{I \times \Delta t}{\Delta V \times S}$$

where $C_A$ is the areal capacitance, $I$ is the constant current during discharge segment, $\Delta t$ is the discharge duration, $\Delta V$ is the potential window and $S$ is the working electrode surface area. As the Fig. 9c, the blue TiO2 NTA sample has the highest capacitance of about 7 mF cm$^{-2}$. Hence, the capacitance of blue TiO2 NTA is improved about 20 times compared with pristine one. It is necessary to mention that the blue TiO2 NTA sample could be reached to remarkable enhancement in capacitance as compared to previous researches [4,50].

Conductive electrodes in contact with an electrolytic solution show accumulated charge at the electrode surface. In this situation, charge distribution occurs on the solution only. Because of semiconductor electrodes concentration of conductive species (electrons or holes) is much smaller than that in solution, redistribution of the space charge in electrode occurs at distances much larger than that in solution. Larger spaces lead smaller capacitance of the semiconductor electrodes [46]. Fig. 10 shows Mott–Schottky plots of the semiconductor pristine and N-doped and also semi-metallic blue TiO2 NTAs. From Fig. 10, it could be seen that there is a big difference in the donor density of the pristine and N-doped TiO2 NTAs with the blue ones. Mott–Schottky plots describe the reciprocal of the square of capacitance ($1/C^2$) against applying potential. According to the Mott–Schottky theory, the space charge capacitance $C_{sc}$ of a semiconductor is expressed as follows:

$$\frac{1}{C_{sc}^2} = \frac{2}{e\varepsilon_0\varepsilon N_D} \left( E - E_{fb} - \frac{kT}{e} \right)$$

where, $\varepsilon$ is the dielectric constant of the semiconductor, $\varepsilon_0$ is the dielectric permittivity of the vacuum, $e$ is the elementary electric charge, $k$ is the Boltzmann constant, $N_D$ is the donor density, and $kT/e = 0.0257 V$ at 25°C. The intercept to the X axis provides the flatband potential and allows establishing the semiconductor conduction band level with respect to the reference of potential. The slope of the plot also gives the donor density. Based on the recent research has been done by Santamaria et al. measuring capacitance in reverse bias mode provide information mostly on barrier layer [51]. Considering that the achieved data from Mott–Schottky widely provide information about the barrier layer,
however with some approximation it may be assumed that the same feature exists for tube walls. As before mentioned, flatband potentials from the Mott-Schottky curves of Fig. 10 could be estimated as +40 mV and −150 mV for the pristine and N-doped TiO2 nanotubes respectively. A positive slope of the samples indicates semiconductor behavior of n-type electrodes. As Fig. 10, the pristine and N-doped TiO2 samples show a strong capacity dependence on the voltage that it is normal for space charge layer controlled capacity of an n-type semiconductor [4]. In contrast, the blue TiO2 NTAs sample exhibit a weak dependence of capacitance on the applied voltage that it shows the blue sample has metallic behavior. In metallic behavior, a capacitance solely determined by the Helmholtz layer at the solid–liquid interface, hence a flatband potential cannot be expected. Furthermore, the carrier density (Nd) could be calculated from the slope of Mott-Schottky curves. From the curves, the donor densities are 4.55 × 10^{21}, 2.82 × 10^{21} for pristine and N-doped TiO2 NTAs, while the donor density of blue TiO2 NTAs is equal to 1.14 × 10^{22} and it is much higher than that of pristine and N-doped NTAs. It is concluded that the conductivity of undoped samples could be enhanced via doping processes.

4. Conclusion

Two-step anodized TiO2 NTAs were exposed to two various methods of doping to produce N-doped and self-doped TiO2 NTAs for improving the electrical properties. It found that reduction of Ti^{4+} to Ti^{3+} ions is occurring at −1.55 V (vs SCE) and the effective self-doped TiO2 NTAs could be achieved at 1.4 V via cathodic polarization. XPS results show the intercalation of nitrogen atoms in a defective lattice sites of TiO2 structure and also, the presence of oxygen vacancies lead to negative shift of binding energy in the both doped TiO2 NTAs. Therefore the N-doping and self-doping methods are comparable with each other in reducing the band gap, as DRS results prove the narrower band gap in doped NTAs as doped TiO2 ones respectively. EIS data and the equivalent circuit of the undoped and doped samples reveal that the undoped sample is not strictly capacitive but a small quantity of N in TiO2 remarkably decreases the surface resistance of TiO2 electrode. In contrast, self-doped TiO2 NTAs resistance is reduced to very negligible contents of 0.0001322 Ωcm−2, it becomes to completely capacitive and lead to semiconductor nature of TiO2 NTAs transforms to semi-metallic nature. The two orders of enhancement in capacitance of blue TiO2 NTAs are very astonishing and it has outstanding potential for applications like batteries and supercapacitors as the electrochemical response of the blue TiO2 NTAs sample was found to be about of 7 mFcm−2 that it is improved about 20 times compared with undoped one. It was found that N-doped and self-doped TiO2 NTAs show increasing in the carrier density about 2.82 × 10^{21} and 1.14 × 10^{22} respectively. All in all, From the CV, DRS and EIS results, it could be concluded that the blue TiO2 sample is proper to some type of applications such as supercapacitors, due to narrow band gap, semi-metallic property and astonishing capacitance, while the N-doped one is suitable to be considered as the photoanode of other ones like solar cell because of some semiconductor features such as larger charge carrier densities as well as proper band tailing around 1.8 eV.

Fig. 10. Mott–Schottky plots of the pristine, N-doped and blue TiO2 NTAs. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

References

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