Nonstoichiometry-Induced Enhancement of Electrochemical Capacitance in Anodic TiO2 Nanotubes with Controlled Pore Diameter

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Supporting Information

ABSTRACT: We report the fabrication of self-organized titania (TiO2) nanotubes (TNTs) with controlled pore diameters (140–20 nm) by anodization for the application of electrochemical capacitor electrodes. The areal capacitances obtained for 140 nm TNTs as 0.23/0.13 mF cm\(^{-2}\) at a scan rate of 1/5 mV s\(^{-1}\) and it is enhanced to 5.5/2.9 mF cm\(^{-2}\) (at the same scan rates) by controlling the pore diameter to 20 nm. In this study, role of pore diameter in the capacitance behavior of TNTs is explained on the basis of effective surface area and presence of oxygen vacancies/titanium interstitials. With a decrease in the pore diameter, the surface area-to-volume ratio (and hence, active surface sites) increases, which leads to greater dissociation of Ti\(^{4+}\) into Ti\(^{3+}\) under high temperature annealing and thus brings more nonstoichiometric defects like Ti\(^{3+}\) interstitials and oxygen deficiency within the lower dimensional TNTs. This manifests higher charge conductivity and greater electrochemical performance of TNTs with lower diameters. The simplicity of anodization method and the excellent electrochemical properties make these vertical TNTs as an alternative candidate for use in energy storage applications.

1. INTRODUCTION

Supercapacitors are being increasingly explored as a feasible charge storage technology in recent years.\(^1\)\(^{–}\)\(^6\) On the basis of the mechanism of charge storage, supercapacitors can be categorized into three general groups: (i) nonfaradic supercapacitors (electric double layer capacitors-EDLCs)\(^7\) that are based on electrostatic charge diffusion and accumulation at the electrode/electrolyte interface, (ii) faradic supercapacitors (pseudocapacitors)\(^8\) that are dominated by faradaic reactions on electrode materials,\(^9\)\(^,\)\(^10\) and (iii) hybrid supercapacitors.\(^11\) Additionally, the specific capacitance for both storage mechanisms can be enhanced by using a material with a high specific surface area, such as nanostructured conducting polymer and metal oxides porous or carbonaceous materials.\(^12\)\(^–\)\(^14\) Thus, understanding the surface and interface characteristics is critical for improving the performance of supercapacitors.

Nanostructured materials have significant role in the field of electrochemical capacitors due to the combination of nanoscale features with a highly defined geometry and high surface area. Over the past decade, TiO\(_2\) has been considered as a supercapacitor electrode material because of its semiconducting properties and chemical stability.\(^15\)\(^–\)\(^19\) Self-organized titania (TiO\(_2\)) nanotubes (TNTs) have been explored for use as binder-free supercapacitor electrodes.\(^18\)\(^,\)\(^20\) This nanostructured TNT surfaces have been fabricated using the optimized electrochemical anodization process using metallic titanium (Ti) foil as the substrate in fluoride containing electrolytes.\(^19\)\(^–\)\(^21\) Electrochemical anodization method offers suitably back-contacted nanotube layers on the substrate, which can be employed directly as an electrochemical device.\(^15\)\(^,\)\(^16\) Ideally, Ti foil is used directly as a current collector, which provides direct and uninterrupted charge transport pathways, while TiO\(_2\) nanotubes provide the active area for charge storage activity.\(^19\) The TNT structures also form surface electrical fields and reduce recombination by confining the injected electrons to the central zone of the tubes which is observed in dye-sensitized solar cell (DSSCs) applications.\(^19\)\(^,\)\(^22\) Vertically oriented TNTs have attracted much attention in charging storage systems because of their capacity to offer high surface area and greatly improved electron transfer pathways in comparison to nonoriented structures, which favor higher charge propagation in active materials.\(^19\)\(^–\)\(^21\),\(^23\)

Generally, titania capacitors resembles to conventional EDLCs, which act by a nonfaradic mechanism with a very low specific capacitance of 10–40 μF cm\(^{-2}\) in the process of
charge—discharge. It has been typically suggested that TiO₂ only contributes a very low nonfaradic capacitance and almost no faradic capacitance in terms of the mechanism of charging.Recently, many research studies have been conducted to improve the electrical conductivity of TNTs by a thermal treatment for inducing surface defects such as oxygen vacancies and reduction of Ti⁴⁺ to Ti³⁺. Also by changing the crystallinity (anatase-rutile), doping with nonmetals, hydrogenated processes and by making nanocomposites with electroactive materials has been reported to achieve the improved capacitive behavior. Annealing is a simple method to get better electrical conductivity and improvement of the electrochemical capacitance. Luet al. reported largest specific capacitance of 3.24 mF cm⁻² at a scan rate of 100 mV s⁻¹ by hydrogenation of TNTs. The hydrogenated TiO₂ electrodes were obtained by calcination of anodic TiO₂ nanotube arrays in hydrogen atmosphere at high temperatures. It is widely believed that bare titania, due to high electric resistance and low specific surface area, shows low electrochemical capacitance. However, it has been reported that decreasing the particle size of TiO₂ to less than 10 nm results in pseudocapacitive behavior of the resultant material, allowing for an increase in the capacitance of anatase of up to 90–120 μF cm⁻². It is well-known that high surface area, interconnectivity and high conductivity of the active materials will enhance the capacitive properties. Generally, the specific capacitance depends not only on the specific surface area of the materials, but also on other parameters, such as the pore size, pore density etc. This article reports the effect of pore diameter of TNTs on the electrochemical capacitance under various scan rates. Controlled pore diameters (20–140 nm) are fabricated via optimizing the anodization parameters which includes the anodization voltage, time, ratio of ethylene glycol (EG) and HF electrolyte. In energy storage applications such as batteries and supercapacitors, electrochemical properties of titania particles mostly depend on the size of the particles rather than the phases. However, in this study, crystallinity of TNT's is analyzed by X-ray photoelectron spectroscopy (XPS), Raman spectra, etc. The results of XPS and Raman revealed that presence of Ti³⁺ and oxygen vacancies depending upon the diameter of TNTs. The effect of pore diameter and surface area (from AFM results) on capacitance is also studied. To the best of authors’ knowledge, there are no reports in the literature regarding the variation of capacitance with pore diameter of TNTs with a detailed explanation using weight fraction of anatase/effective surface area/titanium interstitials-oxygen vacancies. Additionally, a possible mechanism for capacitance...
is provided based on the pore size, surface area of TNTs, and electrolyte ion size.

2. EXPERIMENTAL SECTION

2.1. Materials. Titanium plate (99% purity, 2 mm thick, Sigma-Aldrich), platinum plate (99% purity, 2 mm thick, Sigma-Aldrich), hydrofluoric acid (48%, Sigma-Aldrich), ethylene glycol (99.8% purity, Sigma-Aldrich), acetonitrile (95%, DUKSAN pure chemicals co. Ltd., Korea), and a dc power supply (EP-5001, PNCYS, Korea) were used for the sample preparations. Deionized (DI) water with a resistivity of 18.2 MΩ·cm was used throughout the experiment.

2.2. Fabrication of TiO₂ Nanotubes (TNTs). The electrochemical anodization was carried out on commercially purchased titanium plates (14 mm² area) acting as the anode, with platinum plate as the cathode connected to a regulated dc power supply (PNCYS, EP-5001). The electrolyte system used for the study was a 0.5 wt % hydrofluoric acid (HF) containing ethylene glycol (EG). Here, different volume ratios (1:1, 1:5, 1:10) of 0.5 wt % HF:EG have been used at two different anodization voltages (viz. 20 and 40 V) to tune the pore diameters (∼140–20 nm) of TNTs. Among the different anodization conditions systematic change in pore diameters with good uniformity were selected to perform the electrochemical capacitance studies. Generally, as-synthesized TiO₂ is amorphous, which confines its application in various fields. So, to improve the crystallinity and capacitance, the as-prepared TNTs were air-annealed at 600 °C for 1 h in a conventional box furnace (Lind Berg Blue M 10 kA, 120/24 V).

2.3. Characterization of TNTs and Device Performance. Surface morphology and dimensional characteristics of TNTs were carried out using Field Emission Scanning Electron Microscopy (FE-SEM, HITACHI, S-4800, Japan). Crystallinity of the TNT samples was analyzed using X-ray diffraction (XRD, PANalytical Xpert Pro, USA). Raman spectroscopy (HORIBA Scientific, Xplora plus-France) measurements were carried out using Raman spectroscopy with laser excitation of 532 nm. X-ray photoelectron spectroscopy (XPS) measurements were performed using a spectrometer (K-ALPHA, Thermo Scientific, U.K.) with a pass energy of 30.00 eV. Atomic force microscopy (AFM) imaging and surface roughness/specific surface area measurements were carried out using Digital Instruments (Nanoscope IIIa, USA) Scanning Probe Microscope Controller.

Electrochemical measurements were carried out in 1 M aqueous potassium chloride (KCl) solution. A typical three-electrode experimental cell equipped with TNTs as the working electrode, a platinum plate as the counter electrode, and an Ag/AgCl (KCl saturated) as the reference electrode for measuring the electrochemical properties of working electrode. An electrochemical workstation (CHI 760E, CH Instruments, Inc.) consisting of cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) was employed to study the specific capacitance/electrical resistance of the electrodes. CV was conducted over a voltage range of −0.8 to +0.1 V at various scan rates (1, 5, 10, 20, 50, 100, 200, and 500 mV s⁻¹) for all TNT samples. EIS measurements were performed between 100 kHz and 1 Hz under a constant potential of −0.2 V using a 5 mV rms sinusoidal modulation.

3. RESULTS AND DISCUSSION

3.1. SEM Analysis. Figure 1 represents the SEM images of different pore diameters of TiO₂ nanotube surfaces prepared under optimized conditions of anodization (as shown in Table 1). The insets are showing the lateral view images of corresponding surfaces. All the dimensional measurements were carried out using SEM micrographs and are shown in Table 1. Figure S1 represents the pore diameter size distribution of TNTs. The nanotubular length of all samples was ∼1.3 μm by adjusting the anodization time. By tuning the anodization parameters, 20, 35, 80, and 140 nm average pore diameters of TNTs are formed and termed as TNT-20, TNT-35, TNT-80, and TNT-140, respectively.

3.2. XRD Measurements. Figure 2(a) represents the XRD pattern of different pore diameters (TNT-20, TNT-35, TNT-80, and TNT-140 nm) of TNTs which is air-annealed at 600 °C for 1 h. Annealing leads to the formation of a mixture of anatase and rutile phases. The relative weight percentage of anatase phase in TNT samples were also calculated from the Spurr and Myers equation, eq 1:

\[ f = 1/[1 + 1.265(I_R/I_A)] \]  

(1)

Here, f is the weight fraction of anatase, while \( I_R \) and \( I_A \) denote the rutile (110) and anatase (101) reflection intensities. The calculated percentage of anatase phase for different TNTs from eqn 1 is plotted in Figure 2b. The 20 nm diameter TNTs showed ∼48% of anatase weight fraction and with increasing pore diameter of TNTs, the anatase weight fraction increases as ∼54%, ∼62%, and ∼66% for 35, 80, and 140 pore diameters of TNTs, respectively. Annealing or calcination is the widely used process for anatase–rutile transformation and also to generate defects in TiO₂ phases. It has been reported that with gradual increase in the annealing temperature from 400 °C to more than 1000 °C, the titania phase gradually transforms from a pure anatase phase to a pure rutile phase via an intermediate anatase–rutile mixed phase. This anatase-to-rutile phase transformation occurs due to a nucleation and growth process, during which rutile nuclei form at the surface (grain boundary) of the anatase crystallites and (or) within the grains of anatase and grow in size by consuming the surrounding anatase, which is mainly due to the fact that rutile is more thermally stable than anatase. Hence it becomes apparent that, in either case, higher surface-to-volume ratio provides larger nucleation sites for rutile, and therefore, nanostructured titania produces higher rutile phase at lower annealing temperature than the bulk counterparts. In the current case, 20 nm TNT depicts
higher active surface area (detailed in section 3.5), and gradually decreases with increasing nanotube diameter. Therefore, 20 nm TNT provides maximum nucleation sites for rutile, and hence, under identical annealing temperature, 20 nm TNT shows highest rutile fraction (∼52%), and gradually decreases to ∼34% for 140 nm TNT. Also, as stated earlier, annealing/calcination of titania results in the formation of some structural defects, such as the partial reduction of $\text{Ti}^{4+}$ to $\text{Ti}^{3+}$ and oxygen vacancies inside the $\text{TiO}_2$ phase, as discussed below.

### 3.3. Raman Characterizations.

Phase changes of all annealed samples were further analyzed by Raman spectroscopy (Figure 3a). The Raman bands located at ∼$156 \text{ cm}^{-1}$ ($E_g$), ∼$211 \text{ cm}^{-1}$ ($E_g$), ∼$405 \text{ cm}^{-1}$ ($A_g + B_{1g}$), and $637 \text{ cm}^{-1}$ ($E_g$) are attributed to anatase peaks and ∼$237 \text{ cm}^{-1}$ ($B_{1g}$), ∼$447 \text{ cm}^{-1}$ ($E_g + A_{1g}$), and ∼$610 \text{ cm}^{-1}$ ($A_{1g}$) to peaks for rutile phase (corresponding Raman-active modes are given in the brackets). The strongest $E_g$ mode at ∼$156 \text{ cm}^{-1}$ arising from the external vibration of the anatase structure is well resolved, which indicates that an anatase phase was formed in the annealed TNTs and the long-range order was fairly formed. These results are consistent with the XRD spectra as shown in Figure 2a. Comparing the Raman spectra of four different pore diameters of TNTs, it becomes apparent that the Raman bands shift with respect to a change in the pore diameter. For example, the lowest $E_g$ mode of anatase at ∼$156 \text{ cm}^{-1}$ of TNT-140 gradually shifts toward ∼$161 \text{ cm}^{-1}$ in TNT-20 sample. Also the line width (full-width-at-half-maxima, fwhm) increases and intensity decreases accordingly (as shown in Figure 3b). The corresponding quantitative values are plotted in Figure S2(a) of the Supporting Information. The change in the position and shape of the Raman peaks is attributed to several factors like nonstoichiometric defect, induced disorder via minor phases, pressure, phonon confinement, strain, nonhomogeneity of the size distribution etc. Among these factors, phonon confinement due to grain size effect and stress are argued to be least effective for the Raman line shift of heat-treated nanostructured $\text{TiO}_2$. In any case, for nanotubular structures (as in the current case), grain size effect is always least influential. Also the size-strain analysis from the XRD data depicts negligible strain and crystallite size variations within TNTs with different pore diameters. Therefore, the observed change in the line position and shape of the Raman-active lowest anatase $E_g$ peak (at $156 \text{ cm}^{-1}$) is considered to be due to oxygen nonstoichiometry, as XPS analyses clearly reveal an increase in the oxygen deficiency as a decreasing function of the nanotube diameter (discussed in section 3.4). That means that TNT-20 has the highest oxygen deficiency and also shows the maximum blue-shift of the line position, maximum increment in the line width (fwhm), and minimum line intensity. As the oxygen nonstoichiometry decreases according to the following trend: TNT-20 > TNT-35 > TNT-80 > TNT-140 (discussed later in details), the blue-shift of the line position and the line width also decrease according to the above trend (cf. Figure S2a) and as expected, the line intensity varies in the reverse
trend (cf. Figure 3b). On the other hand, the rutile $447 \text{ cm}^{-1}$ peak is blue-shifted with increase in the pore diameter (i.e., with decrease in the nonstoichiometry) (cf. Figure S2b). The trend in the line width of this peak is not analyzed mainly because of the asymmetric nature of this peak to produce unreliable data. All the above trends are consistent with the literature, indicating the signature of increasing oxygen deficiency as a decreasing function of the pore diameter of the TNTs. This trend is apparently because of higher active surface area in the lower dimensional TNTs (as shown later in the AFM Figure 4. Ti 2p XPS spectra of TNTs (a) 20, (b) 35, (c) 80, and (d) 140 nm pore diameters.

Figure 5. O 1s XPS spectra of TNTs (a) 20, (b) 35, (c) 80, and (d) 140 nm pore diameters.
**Table 2. Various XPS Data of O and Ti Species within Different TNT Samples**

<table>
<thead>
<tr>
<th>electronic level</th>
<th>Ti 2p</th>
<th>sample</th>
<th>TNT-20</th>
<th>TNT-35</th>
<th>TNT-80</th>
<th>TNT-140</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti^{4+} 2p_{3/2}</td>
<td>BE (eV)</td>
<td>457.4</td>
<td>457.5</td>
<td>457.4</td>
<td>457.5</td>
<td></td>
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<tr>
<td></td>
<td>fwhm (eV)</td>
<td>0.84</td>
<td>0.85</td>
<td>0.85</td>
<td>0.85</td>
<td></td>
</tr>
<tr>
<td></td>
<td>area (%)</td>
<td>64.5</td>
<td>64.5</td>
<td>64.1</td>
<td>64.5</td>
<td></td>
</tr>
<tr>
<td>Ti^{4+} 2p_{1/2}</td>
<td>BE (eV)</td>
<td>463.1</td>
<td>463.2</td>
<td>463.4</td>
<td>463.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>fwhm (eV)</td>
<td>1.75</td>
<td>1.76</td>
<td>1.77</td>
<td>1.76</td>
<td></td>
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<tr>
<td></td>
<td>area (%)</td>
<td>35.5</td>
<td>35.5</td>
<td>35.9</td>
<td>35.5</td>
<td></td>
</tr>
<tr>
<td>Ti^{3+} 2p_{3/2}</td>
<td>BE (eV)</td>
<td>458.7</td>
<td>458.7</td>
<td>458.6</td>
<td>458.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>fwhm (eV)</td>
<td>0.92</td>
<td>0.83</td>
<td>0.98</td>
<td>0.83</td>
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<tr>
<td></td>
<td>area (%)</td>
<td>5.4</td>
<td>5.3</td>
<td>6.0</td>
<td>5.3</td>
<td></td>
</tr>
<tr>
<td>Ti^{3+} 2p_{1/2}</td>
<td>BE (eV)</td>
<td>462.7</td>
<td>462.6</td>
<td>462.8</td>
<td>462.5</td>
<td></td>
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<td></td>
<td>fwhm (eV)</td>
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<td>1.10</td>
<td>0.86</td>
<td>1.03</td>
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<td></td>
<td>area (%)</td>
<td>9.0</td>
<td>6.0</td>
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<td>2.0</td>
<td></td>
</tr>
<tr>
<td>O 1s</td>
<td>Ti−O</td>
<td>BE (eV)</td>
<td>530.5</td>
<td>530.5</td>
<td>530.6</td>
<td>530.5</td>
</tr>
<tr>
<td></td>
<td>fwhm (eV)</td>
<td>0.86</td>
<td>0.83</td>
<td>0.9</td>
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<tr>
<td></td>
<td>area (%)</td>
<td>27.1</td>
<td>29.9</td>
<td>38.8</td>
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<tr>
<td>oxygen deficiency</td>
<td>Ti−O</td>
<td>BE (eV)</td>
<td>531.5</td>
<td>531.5</td>
<td>531.5</td>
<td>531.5</td>
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<td>fwhm (eV)</td>
<td>1.49</td>
<td>1.46</td>
<td>1.46</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>area (%)</td>
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<td>26.3</td>
<td>22.0</td>
<td>19.3</td>
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</tr>
<tr>
<td>Ti−OH</td>
<td>BE (eV)</td>
<td>532.2</td>
<td>532.2</td>
<td>532.8</td>
<td>532.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>fwhm (eV)</td>
<td>2.98</td>
<td>2.97</td>
<td>2.76</td>
<td>3.05</td>
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<tr>
<td></td>
<td>area (%)</td>
<td>45.5</td>
<td>43.7</td>
<td>41.9</td>
<td>38.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O/Ti ratio</td>
<td>1.44</td>
<td>1.52</td>
<td>1.82</td>
<td>1.89</td>
<td></td>
</tr>
</tbody>
</table>

*With respect to the entire Ti 2p curve. *With respect to the entire O 1s curve.

**Analytical Considerations,** which tends to induce more oxygen vacancies via the reduction of Ti^{4+} to Ti^{3+} at the surface of the titania nanotubes. Also the considerable difference in the lower Raman E_{g} peak intensity between the standard value (∼147 cm⁻¹)⁵² and the current samples (∼156–161 cm⁻¹) is probably due to the breakdown of long-range translational crystal symmetry manifested by the nonstoichiometric defects within the as-synthesized TNTs.⁵³

### 3.4. XPS Analysis

X-ray photoelectron spectroscopy (XPS) is used to analyze the Ti 2p and O 1s valence environment in TNTs with pore diameters. Figure 4 and 5 represents the high resolution XPS spectra of Ti 2p and O 1s photoelectrons. All the binding energies (BEs) obtained in the XPS analysis are calibrated using the C 1s peak at binding energy 284.5 eV as the reference. Deconvolution and curve fitting of spectra were performed using CasaXPS Gaussian–Lorentzian peak shape. The BEs, FWHMs, and relative percentage (area under the curves) of all the peaks are furnished in Table 2. The BEs of Ti 2p located at ∼457.1 and ∼457.4 are assigned to Ti^{4+} 2p_{1/2} and Ti^{4+} 2p_{3/2} states of photoelectrons.⁵⁴ The energy difference between these two peaks is around 5.7–5.8 eV, which is consistent with the values reported in the literature for Ti (IV).⁵⁶ After deconvolution, two sub peaks appeared at BEs ∼458.7 and ∼462.7 eV, which are assigned to Ti^{4+} 2p_{3/2} and Ti^{3+} 2p_{1/2}, respectively.⁵⁶ The presence of this lesser oxidation states of Ti ions indicates the formation of higher percentage of loosely bound Ti^{3+}−O bonds against stronger Ti^{4+}−O bonds, which enhances the charge transfer process between anions and cations and, thus improves the electrochemical performance of TNTs.⁵⁶ Also this less oxidized Ti^{3+} states manifest higher oxygen deficiencies within the TNTs, as corroborated by Raman measurements shown earlier. A closer look of the XPS data reveals that the percentage of Ti^{3+} states against the total Ti states (Ti^{4+} + Ti^{3+}) increases with the decrease in the pore diameter, as shown in Figure S3. This is because of the higher surface-to-volume ratio (shown later in AFM analyses) of the lower-dimensional TNTs to manifest higher reduction of Ti^{4+} to Ti^{3+} at the surface of the titania nanotubes.⁵⁰

Figure 5 represents the XPS spectra of O 1s states with different pore diameters. The binding energy at ∼530.5 eV can be assigned to the oxygen bound to Ti^{4+} ions in TNTs and the oxygen anions (O^{2−}) are in the lattice (Ti−O−Ti).²⁸,⁵⁷ The peak located at ∼531.5 eV is attributed to oxygen vacancies.⁵⁷ Generally, for an ideal fully oxidized, defect-free TiO₂ surface, all the surface Ti cations are supposed to be in the +4 oxidation state and having a 5-fold coordination to the oxygen anions. Heating the surface to high temperatures induces desorption of surface oxygen, producing oxygen vacancies.²⁵,⁶⁰,⁶¹ Apparently, low-dimensional nanostructures with higher surface area-to-volume ratio would induce more oxygen deficiency within the nanomaterial, and due to this reason, the 20 nm TNTs in the current case showed highest percentage of O-deficiency (27.4%) and gradually reduced with increase in the pore diameter under identical annealing temperature (cf. Figure S3). A schematic diagram is presented in Figure S4, which depicts the effect of higher active surface area in lower dimensional TNTs to induce higher oxygen vacancies and Ti^{4+} interstitials. Similarly, as stated earlier (detailed in section 3.2), 20 nm TNT provides maximum nucleation sites for rutile, and hence, under identical annealing temperature, 20 nm TNT shows highest rutile fraction (∼52%), and gradually decreases to ∼34% for 140 nm TNT. The oxygen vacancies created inside the TNT structures will help to increase the capacitance due to increase in the TiO₂ conductivity via an increase in the carrier concentration⁵⁵ according to the following defect equilibria:²³ MexicanAmericanScientifics
where $O_0^X$, $V_0^{2+}$, $T_i$, $V_i$ and $e$ denote lattice oxygen, oxygen vacancy, lattice Ti, interstitial Ti and electron, respectively. Superscripts $X$, $-$ and $+$ denote effective neutral, negative, and positive charge states, respectively. Because of the highest oxygen deficiency being within TNT-20 sample, it shows better electrochemical properties against other samples, as shown in section 3.6.

The O 1s BEs at ~532.2 eV are assigned to surface adsorbed hydroxyl or water molecules from atmospheric contaminations during sample preparations and handling. The high percentage of Ti–OH concentration (~38–45%, cf. Table 2) clearly depicts the higher OH$^-$-terminated surfaces in the current samples, which also increase with the decrease in the pore diameter, apparently because of the higher surface adsorption sites in the lower dimensional TNTs. Because of the higher percentage of this surface “titanol” group, the hydrophilicity of the samples also increases, which in turn increases the electrochemical performance under aqueous electrolyte. Finally, the elemental composition of the samples, obtained from the XPS survey spectra, clearly shows higher oxygen deficiency at lower dimensional TNTs. For example, O/Ti ratio for TNT-140 (1.89, closer to the stoichiometric value of 2) decreases gradually to 1.44 (more nonstoichiometry) for TNT-20, thus corroborating the Raman and high-resolution XPS measurements.

### 3.5. AFM Analysis

The AFM images of TNT surfaces are represented in Figure 6. The observed surface roughness and calculated relative percentage of increase in effective surface area with respect to 140 nm pore diameter sample (TNT-140) are tabulated in Table 3. TNTs of 20 nm pore diameter show maximum (~88.24%) of effective surface area as well as maximum surface roughness (~18 nm), both of which produce

![AFM micrographs of TNTs with different pore diameters](image)

**Table 3. Surface Roughness, Relative Increase of Effective Surface Area (with Respect to) 140 nm of TNTs and Specific Capacitance of Different TNT Samples**

<table>
<thead>
<tr>
<th>pore diameter of TNTs (nm)</th>
<th>surface roughness $R_s$ (nm)</th>
<th>relative increase of effective surface area with respect to TNT-140 (%)</th>
<th>specific capacitance at 1 mV/s$^{-1}$ scan rate (mF cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>140 ± 3</td>
<td>10 ± 1</td>
<td>0</td>
<td>0.23</td>
</tr>
<tr>
<td>80 ± 4</td>
<td>13 ± 2</td>
<td>49.55</td>
<td>0.68</td>
</tr>
<tr>
<td>35 ± 3</td>
<td>16 ± 2</td>
<td>62.15</td>
<td>1.14</td>
</tr>
<tr>
<td>20 ± 4</td>
<td>18 ± 1</td>
<td>88.24</td>
<td>5.51</td>
</tr>
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</table>
highest active surface sites for improved electrochemical performance. It is well-known that high surface area of the active materials will enhance the capacitive properties. However, only the surface of the pores that the ions can access will contribute to the double layer capacitance of the EDLCs. Since the electrical energy stored in EDLCs are given by the separation of charged species in the electrical double layer across the electrode/electrolyte interface, the performance of the EDLCs depend strongly on the electrolyte and the specific surface area of the electrode materials.

3.6. Electrochemical Performance. In general, the cyclic voltammetry (CV) method is used to characterize the capacitive behavior of the electrode materials. Cyclic voltammetry tests of TNT samples were carried out at potentials between −0.8 to +0.1 V in 1 M aqueous electrolyte of KCl solution. The CV responses of the different pore diameters of TNT (140, 80, 35, 20) samples at a scan rate of 1, 5, 10, 20, 50, 100, 200, and 500 mV s$^{-1}$ are shown in Figure 7a−d. It is noted that the shape of the CV curves are rectangular-like pattern and they have significantly changed with the increase of scan rate, even up to 500 mV s$^{-1}$. There is no redox peaks observed, therefore the nanotubes show electrical double layer capacitance behavior. In particular, the CV for TNT-20 sample shown in Figure 7d shows a symmetrical and nearly rectangular shape for all scan rates from 50 to 500 mV s$^{-1}$. This indicates that the process is highly reversible and the nanotubes capacitance behavior is based on the electrical double layer principle.

The specific capacitance ($C_s$) of the electrodes was calculated from eqn 3.

$$C_s = 1/A. \nu (V_2 - V_1) \int_{V_1}^{V_2} I(V) \, dV$$

(3)

where $C_s$ is the specific capacitance measured in the potential range of $(V_2 - V_1)$, $\nu$ is the scan rate (mV s$^{-1}$), $A$ is the area (cm$^2$) of the working electrode and $I(V)$ is the response current. The calculated specific capacitance of TNT samples are plotted against the scan rate and shown in Figure 8. The $C_s$ for pore diameters of 140, 80, 35, and 20 nm at a scan rate of 1 mV s$^{-1}$ is 0.23, 0.68, 1.14, and 5.51 mF cm$^{-2}$ (Table 3), respectively. The specific capacitance value decreases with increasing scan rate due to the diffusion limitations in the nanotube channels. The highest $C_s$ value of 5.51 mF cm$^{-2}$ is obtained for 20 nm diameter TNT sample at a scan rate of 1 mV s$^{-1}$. The cyclic voltammograms reveals a significant increase in capacitance with decreasing the pore diameter of TNTs. The $C_s$ result clearly shows the effect of nanotubular pore diameters.
on the enhancement of specific capacitance of the TNTs. The vertically oriented TNTs prepared by anodization showed enhanced capacitance properties by providing a direct pathway for electron transfer and this TNTs which were directly grown on conductive Ti metallic substrate provides an intrinsically high surface area of these nanostructured materials and ensures the exploitation of electrode materials with higher specific capacitance. Also, annealing at 600 °C helps to generate Ti\(^{3+}\) interstitials and oxygen vacancies which further leads to higher charge/ionic transfer (TNT-80, 35 20 nm), and subsequently results in improved capacitance values.

Electrochemical double layer capacitors (EDLCs) store energy at the electrolyte/electrode interface through reversible ion adsorption onto the electrode surface, thus charging the so-called “double layer capacitance”; no faradaic (redox) reaction is involved in the charge storage mechanism. Figure 9a shows a schematic diagram of the electric double layer structure showing the arrangement of solvated anions and cations near the electrode/electrolyte interface. Figure 9b shows the electric circuit representation of an electric double layer capacitance, where \(\Phi_{\text{surf}}(t)\) is the time-dependent surface potential of the electrode, \(R_{\text{elec}}\) is the electrode resistance, \(C_{\text{stern}}\) is the Stern layer and \(C_{\text{diff}}\) is the diffuse layer specific capacitances in series, respectively. Solvated cations can migrate and are adsorbed to the electrode surface due to electrostatic forces. The Stern layer/compact layer contains immobile ions which are strongly adsorbed to the electrode surface. There are no free charges within the Stern layer, whereas the diffuse layer is situated outside the Stern layer where ions are mobile under the coupled influence of electrostatic forces and diffusion. Since the compact layers of ions residing on adjacent electrode walls contribute considerably to the capacitance, the effective surface area of the electrode and solvated electrolyte’s...
ion size become the key parameters to control the overall specific capacitance.\textsuperscript{66,67} Although the size of solvated ion (K\textsuperscript{+}, Cl\textsuperscript{-}) is on the angstrom level\textsuperscript{68} which is substantially smaller than the pore sizes of TNTs, the present study, the imposed compact ion layers from adjacent pore walls and the effective surface area of the TNT electrode affects the double-layer formation and plays a significant role in the capacitance enhancement. Also, the roughness of the surface will provide the active surface sites which further increase the capacitance per unit electrode area, as the capacitance is directly proportional to the surface area and inversely proportional to the charge separation. Parts c–e of Figure 9 represent the variation of surface roughness, effective surface area, and capacitance (at 1 mV s\textsuperscript{-1}) with pore diameter of TNTs based on the results furnished in Table 3. Evidently, the effective surface area and the surface roughness increase with the decrease in the pore diameter, which leads to the increase in the specific capacitance as a decreasing function of the TNT pore diameters. Therefore, the better electrochemical performance shown by the 20 nm TNT samples over the other TNT electrodes is the combined effect of several physicochemical properties which include (i) high oxygen vacancy that induces high carrier concentration and charge conductivity, (ii) high interstitial Ti\textsuperscript{3+} ions that creates more loosely bound Ti\textsuperscript{3+} − O bonds for better charge transfer, (iii) high surface “titanol” groups to increase the hydrophilicity of the sample surface to enhance interfacial properties for better electrochemical performance under aqueous electrolyte, (iv) high surface roughness that provides large active surface sites and competes with the Debye length\textsuperscript{69} to favorably control the capacitance per unit electrode area,\textsuperscript{70} and (v) high effective surface area that tends to closely align the electrochemical double layer parallel to the surface at every point to enhance the overall capacitance.

3.6.1. EIS Measurements. Electrochemical impedance spectroscopy (EIS) is a powerful technique and widely used to study porous electrodes. It gives an information about the internal resistance of the electrode material and the resistance between the electrode and the electrolyte.\textsuperscript{71} Figure 10 compares the Nyquist plots of TNT samples with pore diameters 140–20 nm. The high frequency regions of the spectra are shown as the inset. The high frequency region corresponds to the charge transfer limiting process and is ascribed to the double-layer capacitance (C\textsubscript{dl}) in parallel with the charge transfer resistance (R\textsubscript{ct}) at the contact interface structure between electrode surface and electrolyte solution.\textsuperscript{72} The linear part in the low frequency region is related to the Warburg resistance (diffusive resistance) of the electrolyte into the interior of the electrode surface and an ion diffusion/transport into the electrode surface.\textsuperscript{64} A slight semicircular arc was observed in TNT-140 and TNT-80, indicating a charge transfer limiting process, which is usually the result of a parallel combination of internal resistance and capacitance.\textsuperscript{23} However, no such semicircular arc was observed for the samples TNT-35 and TNT-20, which corresponds to good charge transfer of the working electrode and indicates that there is no electrical resistance. These results reveal that the TNT samples with a particular heating regime results in improved electrical conductivity of TNT and therefore high charge propagation in TNT.

4. CONCLUSIONS
TiO\textsubscript{2} nanotubes (TNTs) with different pore diameters (140, 80, 35, and 20 nm) are fabricated on the surfaces of metallic Ti by controlling the electrochemical anodization parameters. The samples are annealed @ 600 °C, 1 h and used as an electrochemical supercapacitor electrode. The capacitance value increases with decreasing pore diameters (140–20 nm) and maximum aerial capacitances of 5.5 mF cm\textsuperscript{-2} at a scan rate of 1 mV s\textsuperscript{-1} is obtained in 20 nm TNTs. The XPS analysis shows that presence of titanium interstitials (Ti\textsuperscript{3+}) and oxygen vacancies increases with the decrease in the pore diameter, and manifested by the higher surface area-to-volume ratio of the lower dimensional TNTs. With a decrease in the pore diameter, the surface area-to-volume ratio (and hence, active surface sites) increases, which leads to higher temperature-induced desorption of surface oxygen to produce higher oxygen vacancies and greater dissociation of Ti\textsuperscript{4+} into Ti\textsuperscript{3+} under high temperature annealing. Hence 20 nm TNTs showed maximum nonstoichiometric defects like Ti\textsuperscript{3+} interstitials and oxygen vacancies under annealing. This establishes higher charge conductivity/electrochemical performance of TNTs with smaller diameters. Raman spectra analysis revealed that the values of lowest anatase E\textsubscript{g} and rutile peaks shift with respect to a change in the TNT pore diameter, which is attributed to the induction of higher oxygen vacancies in the lower dimensional TNTs, which further helps to improve the electrochemical capacitance in this sample. The AFM results corroborated this by revealing that the effective surface area increases with decreasing pore diameter and 20 nm TNTs showed a maximum effective surface area (~88.24\% increase, with respect to the 140 nm TNTs) and highest average surface roughness (~18 nm), which provided an improved capacitance values in 20 nm TNTs compared 140, 80, and 35 nm TNTs. These results demonstrated that vertically aligned TNTs have many advantages such as high surface area, increased number of delocalized carriers and an improved charge transport properties compared to the spherical nanoparticles. Therefore, it can be concluded that the high surface area and highly active surface site will enhance the ion diffusion, charge transfer and capacitance values.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b01171.
variation of nanotube’s pore diameter size distribution, shift of Raman peak at anatase and rutile peak with pore diameter of titanat nanotubes, variation of $Ti^+/Ti$ ratio, oxygen vacancy, and $O/Ti$ ratio, and schematic diagram depicting the desorption of surface oxygen under annealing in higher and smaller pore diameter of nanotubes (PDF)

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**Notes**

The authors declare no competing financial interest.

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