



Diameter-dependent electrochemical supercapacitive properties of anodized titanium oxide nanotubes

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Electrochemical supercapacitors of titanium dioxide nanotubes (NTs) of various diameters were synthesized from ethylene glycol (EG), polyethylene glycol (PEG) and diethylene glycol (DEG) reagents using anodization process. NTs prepared from the EG were 100 (± 20) nm whereas those obtained from PEG and DEG were 200 (± 50) and 300 (± 50) nm, respectively. Due to a diameter difference followed by charge transfer resistance, NTs obtained from EG, PEG and DEG demonstrated 14.39, 21.81, and 26.12 F g⁻¹ specific capacitances, respectively.
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Anodization is an electrochemical process where protective or decorative oxide nanostructured layer is obtained over the surface of metal itself. The morphology of anodized metal oxide depends upon several parameters. The anodic voltage and solution concentration are essentially important for obtaining well-aligned nanotubes (NTs) of titanium oxide (TiO₂) [1–3]. This is a general method, applicable for several nanostructures including NTs of TiO₂, [4] and nanowires, nanotubes, etc., of copper oxide, [5] can be obtained. Due to high specific surface area, they are applicable in dye-sensitized solar cells, [6] electrochromic devices, [7] and gas sensors, etc. [8–13]. In area of energy storage devices, demand for potential new materials is increasing day-by-day. Electrochemical supercapacitor (ES) is considered a promising device for energy storage that can store the charges that exist between electrode/electrolyte interfaces. Accordingly, based on

energy storage mechanism, ES is divided into two types; (1) electrochemical double layer capacitors (EDLCs) where the charge separation takes place at the electrode/electrolyte interface, and (2) pseudocapacitors where the fast Faradaic redox reactions take place at the surface of active electrode materials. The ES appeared as an excellent character in high power density, long cycle life, small size, inexpensive, and good reversibility which can be utilized in industrial applications such as lightweight electronic fuses, backup power for calculators, and in electric vehicles for surge-power delivery, etc. [14]. The metal oxide electrode is one of the important elements in ES. In addition to specific surface area, catalytic activity and chemical states of ES electrode are also important while estimating specific capacitance (SC) [15]. Three major types of active material electrodes including transition metal oxides, carbon, and conducting polymers, etc., are known for this application [16]. The ability and available surface area for fast redox reaction of ruthenium oxide between electrode/electrolyte interfaces have contributed higher power and energy densities. Due to its high cost and toxicity scientists and industrialists are worried for the direct use as the electrode material for SC application [17]. TiO₂, one of transition metal oxides, can be used as active electrode material in electrochemical energy storage [18–20]. Low electronic conductivity and high resistance limit its use in EDLC [20–22].

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Various TiO₂ nanostructures are obtained using a process of anodization previously [23,24]. Usually order, length, and diameter of TiO₂ NTs can be controlled with adjusting experimental conditions like electrolyte, applied potential/current, temperature, etc. Synthesis of porous titania from ethylene glycol (EG) with 0.38 wt.% of ammonium fluoride (NH₄F) and 1.79 wt.% of water at 20 °C within the potential range of 30–70 V using anodization process is known [23]. Increase in NT mouth diameter from 59 to 72 nm depends upon the voltage applied. With glycerol and different concentrations of water (0%, 20%, 50%, and 70%) at a constant concentration of NH₄F, TiO₂ mouths with different diameters were obtained. Without water, the NTs were clear and circular. The morphology of NTs with different concentrations of water was irregular, i.e., circular shape was not maintained [24]. Diethylene glycol (DEG) with NH₄F electrolyte and water can increase the conductivity of electrolyte and the morphology of NTs was pyramidal, separated and pore diameter was ~120 nm [25]. There are many methods used for the synthesis of TiO₂ NTs. Due to change of physical and chemical properties, each method produces NTs with different lengths and diameters [26]. ES of TiO₂ was obtained using solvothermal reaction whose SC was 17.7 F g⁻¹ [27]. ES of TiO₂ NTs and nanopowder developed from EG, NH₄F, and de-ionized water have demonstrated the SC values as high as 911 and 181 μF cm⁻², respectively [28].

In this work, ESs of TiO₂ NTs composed of different diameters were developed using a process of room-temperature anodization from different electrolytic solutions viz. EG, and polyethylene glycol (PEG) and DEG. These NTs were characterized for their morphologies and structures using field-emission scanning electron microscopy (FE-SEM) images and X-ray diffraction (XRD) patterns. Effect of TiO₂ NT-diameter on SC performance is investigated using cyclic voltammetry (CV), charge–discharge and electrochemical impedance spectra (EIS) measurements.

Titanium sheets of 0.25 mm thick and 99.5% purity were purchased from Korea. EG, PEG and DEG solvents were purchased and used without any further purification. Titanium sheets of 1 × 1 cm² dimensions were ultrasonically cleaned before anodization process in distilled water, ethanol, and acetone for 10 min separately and then dried in an oven before use. The anodization process was carried out on the titanium foil, as the anode, in the presence of platinum electrode (1.5 × 1.5 cm²), as the cathode. All the operating parameters were constant during the process of anodization, i.e., 60 V-applied voltage, 15 h-anodization time for EG, PEG, DEG (designated with the same names) solvents. The concentrations of NH₄F and water were fixed to 0.3 and 4 wt.%, respectively, and the distance between anode and cathode was 2 cm. The oxide layer formed on the titanium substrate with EG was gray whereas, in PEG and DEG electrolytes, surfaces were light and dark sky-blue, indicating the presence of anodizing electrolyte plays a significant role during TiO₂ NT growth process. After anodization, all the Ti foils with TiO₂ NTs were cleaned with distilled water and left for drying in the air, before use. Hitachi S-4200 FE-SEM was used for knowing change in the surface morphology as a function solvent used. The XRD patterns were obtained on Rigaku D/MAX 2500 V, Cu Kα, λ = 1.5418 Å X-ray diffractometer for the phase confirmation. The electrochemical characterizations such as CV, charge–discharge and EIS measurements were operated in 1 M NaOH. For EIS measurement, an Impedance Analyzer

(COMPACTSTATE: IVIUM Technologies) in a frequency range of 0.01 Hz to 1.5 MHz was preferred with 50 mV amplitude.

Figure 1(a–d) presents surface morphologies and XRD patterns of TiO₂ NTs, obtained onto Ti-substrate after 15 h anodization, from EG, PEG, and DEG solvents. All FE-SEM images were scanned at the same magnification, i.e., 100,000×. Although, operating conditions were the same, developed architectures and evolved morphologies are different from one another, indicating an importance of solvent in a growth process. The TiO₂ NTs, obtained from the EG solvent (Figure 1a), are smaller in diameter, obviously more in number (within scanned area) than NTs obtained from the PEG and DEG solvents. Secondly, NTs of EG are regular and cross-linked to one another whereas NTs, obtained from PEG and DEG are higher in diameters, off-course fewer in number, and well-separated from one another. The EG-based TiO₂ NTs are nearly circular, which are considerably diminished in the cases of DEG and PEG. For PEG case, they are perpendicular to Ti-substrate, i.e., upright-standing whereas, for DEG case, mouth diameters of NTs seem to be closed (Figure 1b and c). Secondly, EG-based NTs are debris-free, whereas DEG and PEG-based NTs are composed of few free-circular rings, of same dimensions, at their mouths. There is no and/or little free-space between NTs obtained from the EG and PEG solvents which is considerable, due to bending nature, in the case of DEG. The average diameters of NTs obtained from EG, PEG and DEG solvents are 100 (±20), 200 (±50) and 300 (±50) nm, respectively. Figure 1(d) presents XRD patterns of TiO₂ NTs, obtained from EG, DEG and PEG solvents. For reference XRD pattern of non-anodized Ti-sheet is also given. Ti-sheet reveals XRD peaks at around 38.3°, 40.1°, 52.9° and 70.6°, which are common in all NTs. Peaks marked with # sign belong to TiO₂ in accordance with JCPDS file 46-1237. The diffraction peaks that appeared at 44.45°, 63.03°, and 76.28°, for TiO₂ NTs prepared from DEG are of (601), (421), and (005) planes, respectively. The diffraction peaks of TiO₂ NTs produced from PEG at 54.17°, 62.95°, 76.28°, 77.45°, and 82.30° can be indexed to

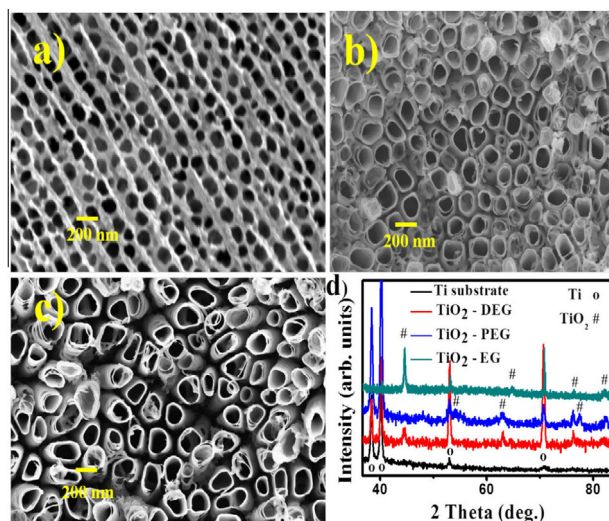


Figure 1. (a–c) Top-view FE-SEM images of anodized TiO₂ NTs from EG, PEG, and DEG solvents, and (d) XRD patterns of pristine Ti-substrate with TiO₂ NTs of different diameters.

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