



# Designing micro/nano hybrid TNT@ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> composites for high performance supercapacitors

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## ARTICLE INFO

### Article history:

Received 27 May 2020

Received in revised form 28 July 2020

Accepted 15 August 2020

### Keywords:

Titania nanotube

Anodization

$\alpha$ -Fe<sub>2</sub>O<sub>3</sub>

Micro/nano-hybrid

Hydrothermal

Supercapacitor

## ABSTRACT

In the present work, we demonstrate the supercapacitor applications of titania nanotube @ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> composites (TNT@ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) synthesized via successive anodization–hydrothermal methods. The structure and morphology of the composites were studied through XRD and SEM analyses and the electrochemical properties were studied through CV, GCD and EIS analyses. The hybrid composite, TNT-Fe4 exhibited highest supercapacitor performance with a capacitance of 157.32 mFcm<sup>-2</sup> at a scan rate of 5 mVs<sup>-1</sup> owing to the unique micro/nano hybrid architecture of the composite, comprising of a hierarchical layered Fe<sub>2</sub>O<sub>3</sub> coating on titania nanotubes. The asymmetric supercapacitor fabricated with the composite electrode together with activated carbon showed an excellent capacitance of 142.86 mFcm<sup>-2</sup> with an energy density of 38.88  $\mu$ Whcm<sup>-2</sup> at 0.2 mAcms<sup>-1</sup>. The high rate capability and outstanding cyclic stability of the composite validate the potential application of the device in charge-storage systems.

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## 1. Introduction

The development of alternative energy sources such as hydropower, nuclear, wind and solar energy has paramount significance in the light of increased energy demand [1]. The maximum use of these less controllable and un-predictable renewable energy demands economically viable and environmental friendly energy storage and conversion systems. Compared with traditional energy storage systems, supercapacitors are the promising candidates by virtue of high power density, long cycle life, high efficiency, wide range of operating temperature, faster charge–discharge rate and long shelf life. Based on the charge storage mechanism, electrochemical capacitors are generally classified into two basic types, electric double layer capacitors (EDLC) and pseudocapacitors [2]. Even though there are commercial supercapacitors that utilize carbon based EDLC materials, their low energy density limits their applications in electric vehicles, solar power plants, etc. Pseudocapacitors with very high specific capacitance and energy density have potential in resolving these issues. Even though many efforts have been made to design novel pseudocapacitor materials like conducting polymers [3,4], metal

sulfides [5–7], metal nitrides [8,9], metal hydroxides [10,11], etc., Among different electrode materials, metal oxides are gaining much attention owing to their fast and efficient faradaic reactions and better cyclic stability [12–17].

Diverse metal oxides such as RuO<sub>2</sub> [18–20], MnO<sub>2</sub> [21–23], Nb<sub>2</sub>O<sub>5</sub> [24–27], V<sub>2</sub>O<sub>5</sub> [28–30], etc. and their combinations with other metal oxides or carbon nanostructures are being extensively studied as prospective electrode materials for different pseudocapacitor designs. However, it is a major challenge to overcome their low electrical conductivity and cyclic stability as compared to carbon based electrode materials while also addressing other issues like high cost, toxicity, slow electrochemical kinetics and poor structural stability. For instance, although RuO<sub>2</sub> is the most studied metal oxide system which would deliver very good capacitance value, its high cost and environmental toxicity restricts its wide applications [20]. MnO<sub>2</sub>, being another well-explored material for its easy availability and nontoxic nature suffers from poor electronic conductivity and partial dissolution into the electrolyte during cycling ensuing capacitance degradation [21]. Similarly, regardless of their ultra-high theoretical capacitance, low cost, eco-friendliness and ease of fabrication; the low electrochemical utilization and unstable crystal structure of Nb<sub>2</sub>O<sub>5</sub> and V<sub>2</sub>O<sub>5</sub> respectively makes them incompetent [31]. Hence, it would be highly advisable to choose a system that is cheap and environmentally friendly and to improvise their properties in terms of cyclic stability and conductivity to scale up

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