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Fabrication of tungsten decorated titania nanotube arrays as electrode materials for supercapacitor applications

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ABSTRACT

Tungsten decorated titania (WT) nanotube arrays was fabricated by electrochemical anodizing followed by chemical bath deposition in combination with a pyrolysis process. Resulting WT nanotube arrays were studied as potential electrode materials for electrochemical double layer capacitor (supercapacitor) applications. The structural, morphological, and compositional characteristics of the resulting electrode materials were evaluated by using X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), and energy-dispersive X-ray (EDX) spectroscopy. Results showed that titania nanotube arrays (T) with an internal diameter of the tubes around 90–120 nm, an external diameter around 120–160 nm, wall thickness in the range of 30–60 nm and a length of 39 μm were grown on titanium substrate by electrochemical anodizing. Also tungsten particles are decorated mainly on the surface of the titania nanotube and to a less extent inside the nanotubes. The electrochemical behavior of WT electrodes was investigated by cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS) techniques in 1 M Na_2SO_4 aqueous electrolyte. The maximum capacitance obtained was 191 mF cm^{-2}. The good electrochemical performance was attributed to the anchoring function of tungsten and support of titania nanotube arrays. Therefore this electrode material can be used as a promising material in supercapacitor applications.

Introduction

With close attention paid to the world ecology and economy, people are observing the bountiful, low-cost, and clean energy from sun and wind which, in principle, should be able to satisfy the ever increasing and urgent demands. However, most of the renewable energy is intermittent and cannot meet the immediate needs for casual use, except for converting to electricity [1–3]. Electric double layer capacitors (EDLCs), also known as supercapacitors or ultracapacitors, offer a promising approach for fast storing the excess electrical energy and

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are gaining vast applications in different technology areas such as portable electronics, hybrid electric vehicles, and stand-by power systems [2–9]. The performance of these devices depends intimately on the physicochemical properties of their electrode materials. Therefore, it is urgent to develop excellent electrode materials [3,4].

Recently, one-dimensional (1D) nanostructured materials e.g. nanotubes (NTs) and nanowire arrays have attracted great attention for electrochemical energy storage systems [4]. Supercapacitors represent an emerging energy storage technology that offers high power density, long cycle life, short charging time, good safety, and so forth. Supercapacitors can be used either alone as a primary or as an auxiliary power source along with rechargeable batteries for high power applications such as load cranes and hybrid electric vehicles [10]. Over the past decade, self-organized oxide nanotube arrays have attracted a great deal of scientific and technological interest [11]. Ordered nanotube arrays could be grown successfully on some of valve metals such as Ti, Nb, Zr, Hf and even Fe by a simple optimized anodizing process [12–14]. In recent years, highly ordered TiO_2 nanotube arrays have attracted much attention as an active material for potential charge storage device owing to their high regulation, large surface area, excellent controllability, stability and simple fabrication method [15]. These findings reveal that, unlike carbon based materials and other metal oxides, TiO_2 capacitors exhibited the behavior of conventional EDLCs by a non-faradic mechanism with a very low specific capacitance. The poor capacitive behavior of TiO_2 was found to be mainly due to its low electrochemical activity and high ohmic resistance, originated from its semiconductor characteristics, thereby restricting its applications in the construction of high performance supercapacitors [2,15–17]. It is well known that electrical conductivity of TiO_2 can be significantly increased through introducing metal or nonmetal impurities or dopants into the oxide, which can generate donor or acceptor states in the band gap and thereby increase the concentration of charge carriers [18–21]. Consequently, numerous research efforts concerning the doping or modification of TiO_2 material have been reported [22]. Synthesis and electrochemical properties of oriented NiO–TiO_2 nanotubes as electrodes for supercapacitors were report by Kim et al. They found that changes in the morphology and crystal structure strongly influenced the electrochemical properties of the NT electrodes. Electrodes composed of NiO–TiO_2 nanotubes films annealed at 600 °C displayed pseudocapacitor behavior and stable long-term cycling performance [10]. Yang et al. prepared highly ordered mixed V_2O_5–TiO_2 nanotubes by self-organizing anodization of Ti–V alloys. These mixed nanotubes exhibited greatly enhanced capacitive properties compared with neat TiO_2 nanotubes [13]. Xie et al. prepared polypyrrole-titania nanotube by controlled electrochemical synthesis route for supercapacitor electrode material applications. This nanostructure with a high surface area and tubular channels contributed a short diffusion path and effective electron transfer path, led to the promoted reversible redox reaction in a charge/discharge process. The specific capacitance of this nanotube hybrid was 179 F/g in 1.0 M H_2SO_4 electrolyte solution [23]. Molybdenum oxide coated onto TiO_2 nanotubes (MoO_3-TN) by Guan et al. and these composites were used as an anode material for electrochemical supercapacitors. The results of their studies showed that MoO_3-coated TiO_2 nanotubes deliver significantly higher capacitance than bare TiO_2 nanotubes and MoO_3 films in KCl solutions [24]. Recently a composite electrode comprising of flower-like zinc sulfide/titania nanotube (ZnS/T-NT) were synthesized for supercapacitor application. The electrochemical studies of this composite electrode indicated that a high specific capacitance (226 F/g) can be achieved in the electrode together with high stability during large charging conditions [25]. Most recently, Ray et al. synthesized TiO_2 nanotube/cobalt sulfide (T-NT)/CoS composite material for supercapacitance applications and studied the electrochemical behavior these composite materials in four different electrolytes: 2 M KOH, 1 M Na_2SO_4, 1 M Na_2SO_3 and 2 M KCl. The specific capacitance values of these composites were 493, 427, 374, and 360 F/g for the Na_2SO_3, KCl, Na_2SO_4, and KOH electrolytes, respectively. Their study demonstrated the feasibility of T-NT/CoS electrode to be used as high performance supercapacitor material in various electrolytes [26]. However, it is worth noting that the most used methods were realized by using either expensive facilities or high processing temperatures or a long duration process. Therefore, a simple, facile, and inexpensive method of synthesizing doped TiO_2 nanotubes is quite desirable.

In this study, tungsten decorated titania nanotube arrays (WT) were fabricated via an efficient and easily accessible approach. The decoration of tungsten occurs homogenously and tungsten decorated titania nanotube films can be achieved by using chemical bath deposition (CBD) technique. This method makes it more favorable for the deposition on the outer layers of the tubes rather than their insides and provides a general way for any mesoporous or microporous substrate on which this type of selective deposition is desired. To the best of our knowledge, no previous report on the preparation of tungsten decorated titania nanotube arrays films by anodizing followed by chemical bath deposition is available. Also, quantitative study on the effect of the amount of tungsten in titania nanotube arrays (WT) on the electrochemical capacitance behavior of WT is lacking. In this paper, two-step process developed to prepare WT films. In the first step, titania nanotube arrays (T) were prepared by anodizing of titanium foils. Then tungsten was deposited on these nanotubes by chemical bath deposition. The morphology and structure were characterized by field emission scanning electron microscopy (FE-SEM), energy dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD) method. The effect of tungsten on the supercapacitor behavior of these was investigated by cyclic voltammetry (CV), galvanostatic charge–discharge (GCD) and electrochemical impedance spectroscopy (EIS) techniques.

Experimental

All chemicals were of analytical grade and used as received without further purification and/or treatment. All solutions were prepared with distilled water. Pieces of titanium metal sheet (99.99% purity, 1-mm thick) were cut into proper dimensions. Then obtained titanium electrodes were