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Tunable preparation of chrysanthemum-like titanium nitride as flexible electrode materials for ultrafast-charging/discharging and excellent stable supercapacitors

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HIGHLIGHTS

- The TiN preserves the nanostructure of CL-TiO_2 very well during nitridation.
- The CL-TiN possesses special porous structure and high degree of nitridation.
- The CL-TiN/GCE shows good capacitive property even at high scan rate of $10\ V\ s^{-1}$.
- The FSS-SC based CL-TiN shows extraordinary cycling stability and flexibility.

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ABSTRACT

A novel chrysanthemum-like titanium nitride (CL-TiN) has been synthesized through hydrothermal method combining reduction and nitridation treatment. The morphology of CL-TiN can be successfully obtained by strict controlling heating rates. The CL-TiN is characterized as microspherical structure with an average diameter of 2 μm and is assembled from two-dimensional leaf-like nanorods with a width of 200 nm and a length of 500 nm. The CL-TiN is employed to construct supercapacitors and exhibits excellent capacitive performance due to efficient ion diffusion as well as good structural stability. The specific capacitance of the CL-TiN in a three-electrode system is $23.35\ F\ g^{-1}$ at a current density of $1.0\ A\ g^{-1}$. Importantly, the capacitance retention still maintains 90.0% after 10 000 cycles at a scan rate of $0.1\ V\ s^{-1}$. Furthermore, a symmetric flexible-solid-state supercapacitor (FSS-SC) based on CL-TiN nanostructures with Na_2SO_4/carboxymethyl cellulose (CMC) gel as electrolyte is assembled. The supercapacitor shows excellent volumetric capacitance ($7.48\ F\ cm^{-3}$ at $0.05\ A\ cm^{-3}$), high energy density ($0.34\ mW\ h\ cm^{-3}$) and ultrafast-charging/discharging performance. The cycling stability is remarkable with a capacitance increase of about 36.7% after 20 000 cycles. This work could give a promising guidance for designing and fabricating ultrafast-charging/discharging and excellent stable supercapacitors.

1. Introduction

With the rapid increase of portable/wearable electronics demands, high performance flexible and lightweight power sources have been intensively studied and developed in recent years [1]. Supercapacitors (SCs) are explored as a kind of potential energy storage devices to bridge the gap between conventional electrostatic capacitors and rechargeable batteries due to their fast charge/discharge rates, considerable power/energy density and long cycling lifetime [2,3]. According to the charge storage mechanism, SCs can be generally classified into two types. One is pseudocapacitors, which store charges on the electrode surface via fast faradaic reactions. The pseudocapacitors are widely based on transition metal oxides and conducting polymers which usually suffer from poor conductivity and general kinetic irreversibility [4,5]. The other is electric double-layer capacitors (EDLCs), which store charges at the electrode–electrolyte interface via adsorption and desorption of electrolyte ions and no faradaic reactions [6,7]. In this model, the common electrode materials are based on carbon materials and the pore size distribution and effective surface area of the materials influence strongly the capacitance [8]. In addition,

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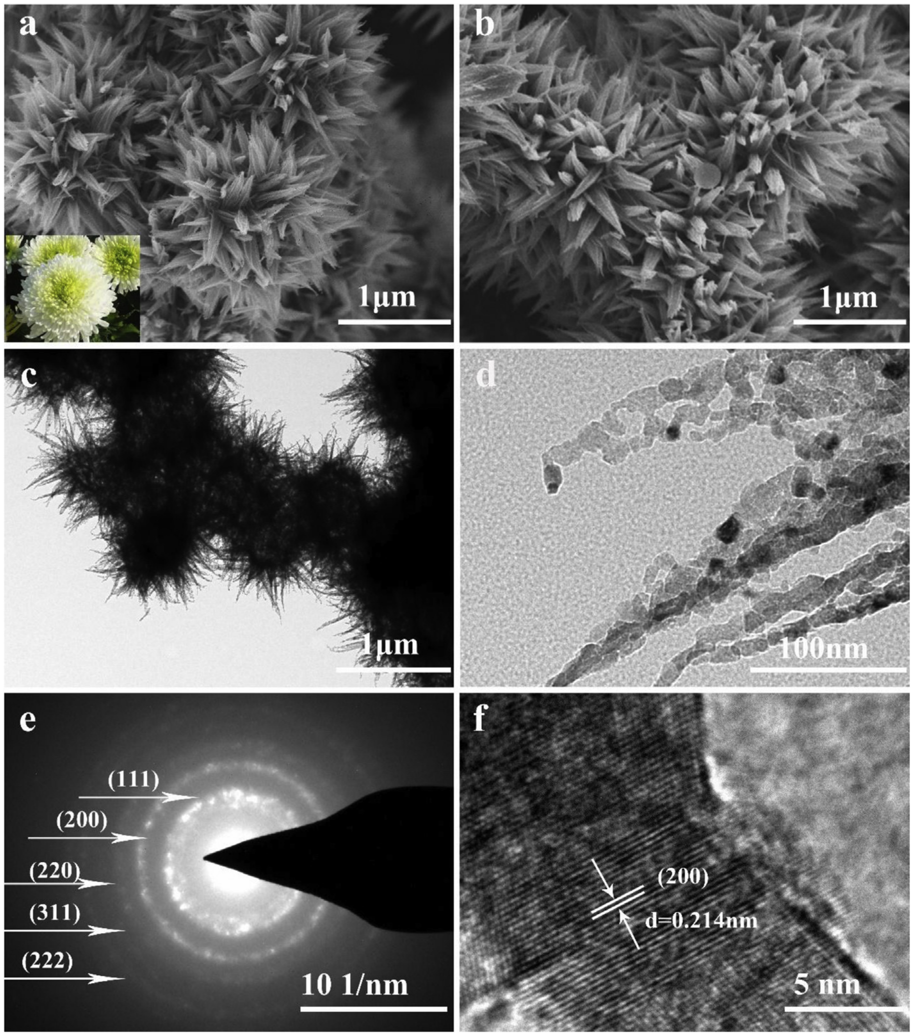

Fig. 1. (a) SEM image of the CL-TiO_2 sample and the inset is the photo of chrysanthemum, (b) SEM image of the CL-TiN, (c, d) TEM images of CL-TiN, (e) SAED pattern of CL-TiN, (f) HRTEM image of CL-TiN.

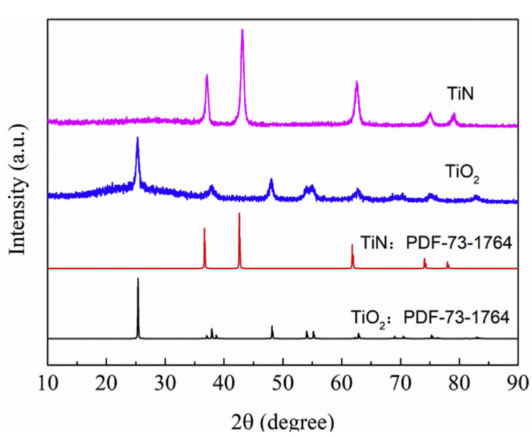

Fig. 2. XRD patterns of CL-TiO_2 and CL-TiN.

the power density and charging/discharging rate are determined by ion and electron transport kinetics within the electrode particles [9,10]. In a word, each type has its own advantages and disadvantages. As we all know, whatever type of SCs, electrode materials are considered to be the key factor affecting the capacitive performance. The design and exploration of new nanostructured materials as EDLCs may be an effective way to improve charging/discharging rate and electrochemical stability.

As a typical transition metal nitride, titanium nitride (TiN) has attracted great interest as a new class of electrode materials for high-performance SCs due to its excellent electrical conductivity (4×10^3 and $5.55 \times 10^4\,S\,cm^{-1}$) and mechanical stability [11,12]. Different methods have been adapted to synthesize various nanostructured TiN including corn-like [13], cauliflower [14], nanotube [6,15], nanogrid [16] and nanoparticles [17], to construct SCs. The general synthetic strategy to obtain TiN is through a two-step method, in which TiO_2 is firstly fabricated and then nitrogenized into TiN. TiO_2 with different morphologies has been prepared by various methods, such as hydrothermal/solvothermal methods, sol-gel methods and surfactant-assisted methods [18,19]. However, the main challenge is to maintain the inherent morphology of TiO_2 nanostructures during the formation of TiN process at high temperature, especially, the porous structure, because the partial breakdown of the TiO_2 nanostructures could not be avoided during reduction and nitridation [20,21]. Furthermore, the TiN electrode has poor electrochemical stability due to the irreversible electrochemical oxidation reaction in aqueous solution [5]. To solve above issues, carbon coatings were used to modify TiN [5,11]. However, the fabrication process is complicate and hinders its further practical applications. Recently, Lu et al. reported the solid-state polymer electrolyte could greatly enhance the stability of the TiN nanowires [22]. In addition, Wang et al. demonstrated hierarchically structured chrysanthemum-like TiO_2 materials shortened the distances for both