Chemical Communications C2CC35610D

Electronic Supplementary Information

Hierarchical nanotubular titanium nitride derived from natural cellulose substance and its electrochemical properties

Xiaoyan Liu, Yanhua Zhang, Tao Wu and Jianguo Huang*

Department of Chemistry, Zhejiang University, Hangzhou, Zhejiang 310027, China
E-mail: jghuang@zju.edu.cn

Experimental Details

Reagents. Titanium *n*-butoxide [$Ti(O^nBu)_4$, TBT], acetylene black and magnesium granules (98%) were purchased from Aldrich Chemicals. All the other chemicals were guaranteed reagents and used as-received without further purification. Milli-Q water (resistivity, 18.2 MΩ cm) was used in all related cases.

Preparation of the hierarchical nanotubular titanium nitride. To fabricate the hierarchical nanotubular titanium nitiride, titania replicas of the initial filter paper was firstly prepared. In a typical procedure, certain pieces of filter paper were dipped into prepared titania gel (ethanol : TBT : concentrated HCl solution = 100 g : 7 g : 5 g) for 3 h followed by thorough rinsing with Milli-Q water and dried at 65 °C overnight. The as-prepared titania/filter paper composite was then subjected to calcination in air at 600 °C for 5 h at a heating rate of 2 °C min^{-1} to remove the original filter paper, and eventually led to the formation of titania replicas of filter paper composed of titania nanotubes with wall thickness of *ca.* 55 nm.

Magnesiothermic reduction of the prepared titania replicas of filter paper mentioned above was carried out in a homemade stainless steel autoclave. The titania replicas of filter paper and magnesium granules were separately spread evenly within two different steel boats and placed in the autoclave. The molar ratio of magnesium granules and titania replicas of filter paper was 2.5 : 1. The excess of magnesium granules can promote the reduction completely proceed. After filled with nitrogen gas, the autoclave was sealed into a vertical tube furnace and heated to 1200 °C at a heating rate of 2 °C min^{-1} for 3 h and allowed to cool to room temperature in the flowing N_2 atmosphere to avoid oxidation. The raw product was then collected and treated with 2.0 M HCl aqueous solution for 6 h to selectively dissolve the by-product magnesia.

Electrochemical measurements. The working electrode was prepared by mixing 80% of the hierarchical nanotubular titanium nitride with 20% acetylene black in an agate mortar until a homogeneous black powder was obtained. The resulting mixture was wetted by anhydrous ethanol and pressed onto a foam nickel plate at 15 MPa. The prepared electrode was then allowed to dry in air. The weight of the each electrode was about 10 mg and the geometric surface area of the electrode was about 1 cm^2.

All the electrochemical measurements were performed in a glass electrochemistry cell with a three-electrode system in 1 M KOH electrolyte. Pt sheet (2 × 2 cm^2) was used as a counter electrode and saturated calomel electrode (SCE) as a reference electrode. The cyclic voltammetry (CV) measurements were performed with a potential window ranging from −1.2 V to 0.2 V at different scan rates in the range of 10 mV s^{-1} to 80 mV s^{-1}. The electrochemical impedance spectroscopic (EIS) tests were run on from 10 kHz to 100 MHz with an alternate current amplitude of 5 mV. Galvanostatic charge/discharge analyses were taken between −1.2 V and 0.2 V at different current densities.

The specific capacitance of the nanotubular titanium nitride was calculated according to the equation:

$$C = \frac{\int (Id\varphi)}{2mv\Delta V}$$

where m is the mass of the electrode, and I, v, ΔV, φ are the average current of charge and discharge, scan rate, potential difference and potential range, respectively.

The specific capacitance of the TiN is calculated by the equation:

$$C = \frac{I\Delta t}{m\Delta V}$$

where I represents the average current of charge and discharge, and m, ΔV and Δt are the mass of the electrode, voltage and time, respectively.

Characterizations. To prepare the specimens for SEM and TEM observations, a small piece of the sample was suspended in ethanol (1.0 mL) by ultrasonication until homogeneous suspension was obtained. The suspension was dropped onto silicon wafer for SEM observation or onto carbon coated copper mesh grid for TEM observation, and the specimens were dried in air. SEM images were obtained on a Carl Zeiss Ultra 55 field-emission scanning electron microscopy at an acceleration voltage of 3.0 kV, and the specimen was sputtered with platinum to reduce charging. TEM observations were performed on a JEM-200CX instrument at an acceleration voltage of 160 kV and HRTEM observations were performed on JEOL JEM-2010 electron microscope operating at an acceleration voltage of 200 kV. The X-ray diffraction (XRD) analyses were carried out on an X'Pert PRO diffractometer with Cu Kα radiation (λ = 0.15418 nm). Nitrogen adsorption and desorption isotherms were acquired at 77 K on a Micromeritics ASAP 2020 accelerated surface area and porosimetry analyzer. The linear part of the Brunauer-Emmett-Teller (BET) equation was used for the specific surface area determination. The surface composition of the hierarchical nanotubular titanium nitride was determined by X-ray photoelectron spectrometer (XPS, VG ESCALAB Mark II, UK). The electrochemical properties of the electrode was evaluated by cyclic voltammetry (CV) using a CHI 600C instrument (CHI Instrument Inc.), electrochemical impedance spectroscopic (EIS) measurements were performed on a M273 potentiostat (Princeton Applied Research, USA) combined with a M5210 lockin amplifier (Signal Recovery, USA), and galvanostatic charge/discharge measurements were conducted using a BT-2000 battery test equipment (Arbin Instrument, USA).

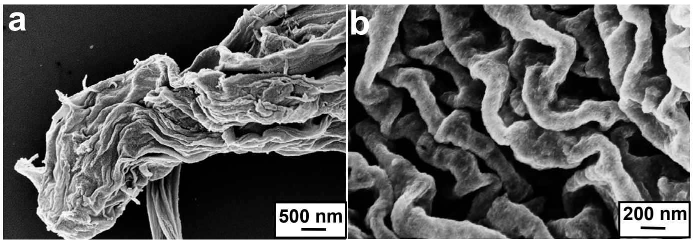

Fig. S1 (a) SEM image of the titania replicas of filter paper; (b) magnified SEM image of the material.

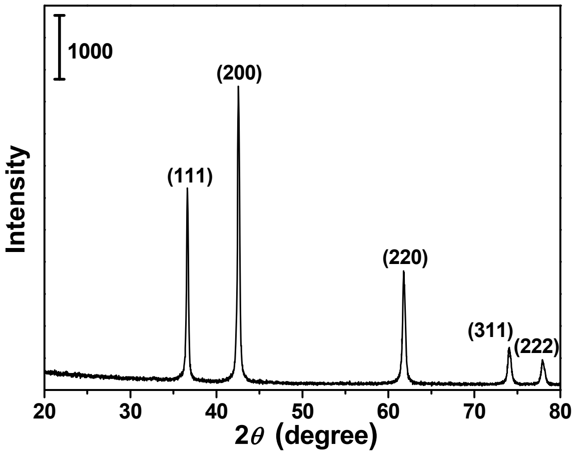

Fig. S2 XRD pattern of the hierarchical nanotubular titanium nitride. The XRD measurements confirmed the removal of the by-product MgO by treating the raw product with aqueous HCl. Five prominent diffraction peaks positioned at $2\theta = 36.63°$, 42.55°, 61.78°, 74.06° and 77.92° are observed in the XRD pattern of the resulting nanotubular TiN, which are ascribed to the (111), (200), (220), (311) and (222) planes, respectively; matching well with the face-centered cubic lattice of TiN phase (PDF #87-0629).

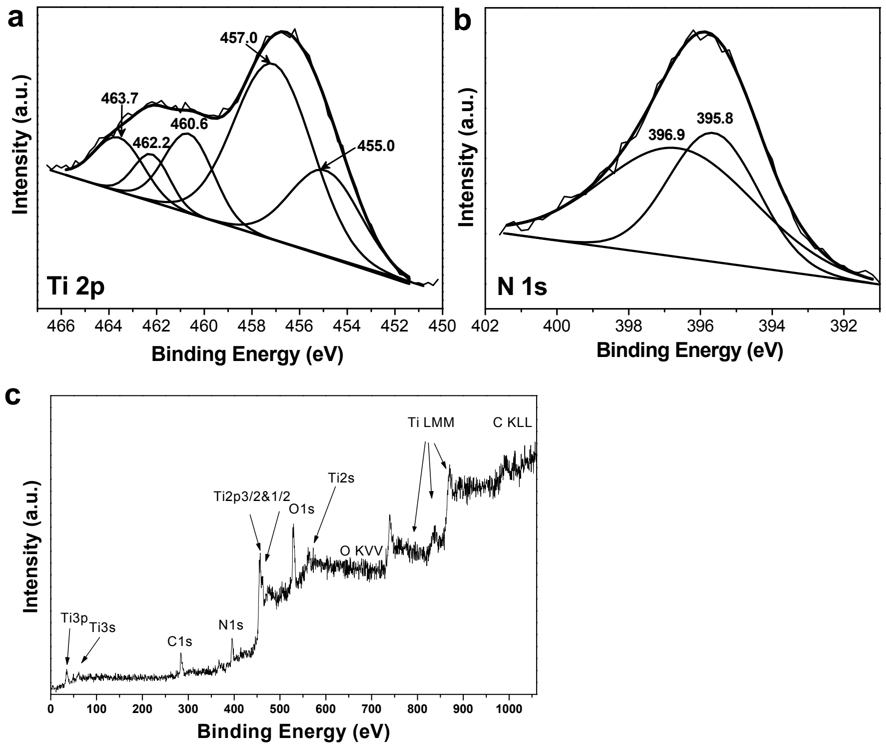

Fig. S3 X-ray photoelectron spectra (XPS) of the hierarchical nanotubular titanium nitride. (a) Ti (2p) region; (b) N (1s) region; (c) the whole spectrum. In the XPS spectrum, the deconvolution of the complex Ti 2p bands yields major peaks in each doublet (Ti $2p_{3/2}$ and Ti $2p_{1/2}$) (panel a). The peaks at 455.0 eV (Ti $2p_{3/2}$) and 460.6 eV (Ti $2p_{1/2}$) are ascribed to TiN phase, the peaks at 457.0 eV (Ti $2p_{3/2}$) and 462.2 eV (Ti $2p_{1/2}$) are corresponding to TiO_xN_y phase, and the peak at 463.7 eV (Ti $2p_{1/2}$) is assigned to TiO_2 phase.[1,2] The corresponding N 1s bands (panel b) with peak at 396.9 eV is due to TiN,[1,2b,c] and the peak at 395.8 eV is attributed to nitrogen in the bulk oxynitride[1,3] or atomic β-N.[2b,4]

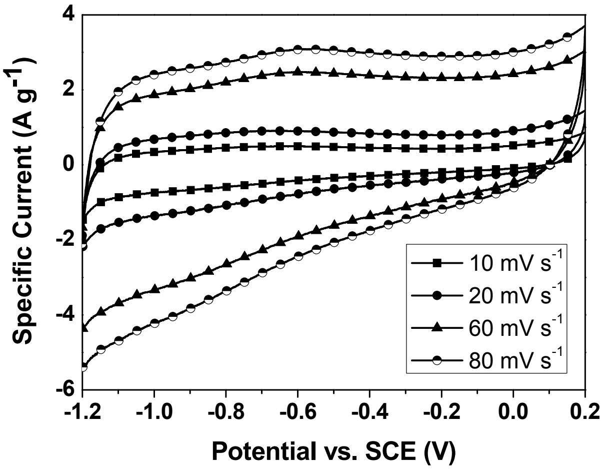

Fig. S4 Cyclic voltammograms of the hierarchical nanotubular titanium nitride at various scan rates ranging from −1.2 V to 0.2 V.

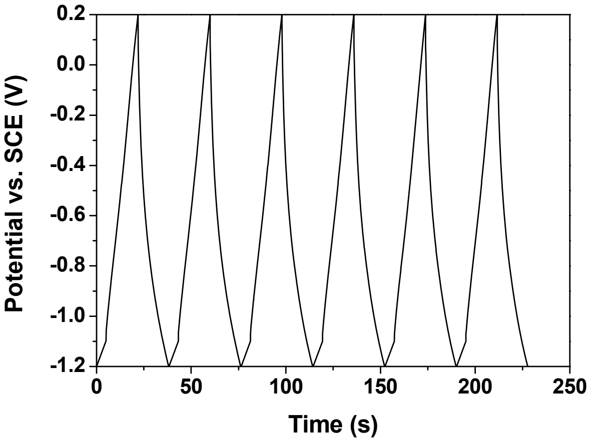

Fig. S5 Charge–discharge curves of the hierarchical nanotubular titanium nitride electrode at a current density of 2.16 A g^{-1} in 1 M KOH electrolyte.

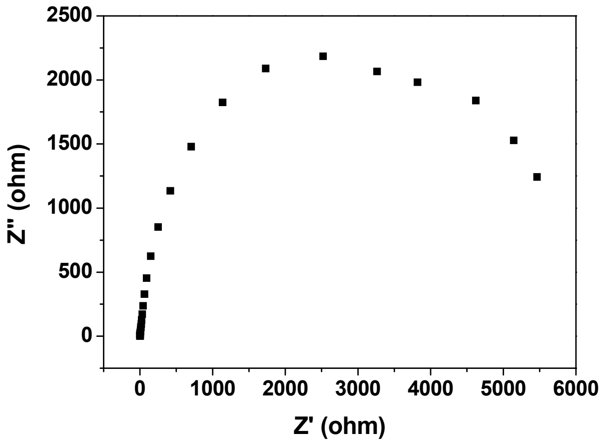

Fig. S6 Nyquist plot of the foam nickel plate electrode.

References:

1 M. Drygaś, C. Czosnek, R. T. Paine and J. F. Janik, *Chem. Mater.*, 2006, **18**, 3122–3129.

2 (*a*) Y. Qiu and L. Gao, *J. Phys. Chem. B*, 2005, **109**, 19732–19740; (*b*) M. M. O. Thotiyl, T. R. Kumar and S. Sampath, *J. Phys. Chem. C*, 2010, **114**, 17934–17941; (*c*) N. Jiang, H. J. Zhang, S. N. Bao, Y. G. Shen and Z. F. Zhou, *Phys. B*, 2004, **352**, 118–126.

3 H. Höchst, R. D. Bringans, P. Steiner and T. Wolf, *Phys. Rev. B*, 1982, **25**, 7183–7191.

4 (*a*) R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki and Y. Taga, *Science*, 2001, **293**, 269–271; (*b*) N. C. Saha and H. G. Tompkins, *J. Appl. Phys.*, 1992, **72**, 3072–3079.