

Preparation of Titanium nitride nanomaterials for electrode and application in energy storage

Srinibas Mandal, *Department of Basic Science, Aryan Institute of Engineering & Technology, Bhubaneswar*

Itishree Swain, *Department of Basic Science, Raajdhani Engineering College, Bhubaneswar*

ABSTRACT:

The Titanium nitride was made by the carbamide and titanate chloride precursors. XRD results indicate that the precursor ratio N:Ti 3:1 leads to higher crystallinity. SEM and EDX demonstrated that Ti and N elements were distributed uniformly with the ratio of 1:1. The TiN used as the electrode material

for supercapacitor was also studied. The specific capacities were changed from 407 F.g^{-1} to 385 F.g^{-1} , 364 F.g^{-1} and 312 F.g^{-1} , when the current densities were changed from 1 A.g^{-1} to 2 A.g^{-1} , 5 A.g^{-1} and 10 A.g^{-1} , respectively. Chronopotentiometry tests showed high coulombic efficiency. Cycling performance of the TiN electrode was evaluated by CV at a scanning rate of 50 mV.s^{-1} for 20,000 cycles and

there was about 9.8% loss. These results indicate that TiN is a promising electrode material for the supercapacitors.

KEYWORDS: Energy storage Nanomaterials Anode Titanium nitride Supercapacitors

I. INTRODUCTION

Electrochemical supercapacitor (SC) is one of the important energy storage devices which have the advantages of safety, high power density, environmental friendliness and conveniences, and thus they show tremendous advances in complementing lithium-ion batteries [1–5]. As part of a significant field of electrochemical energy storage, they bridge the gap between conventional capacitors and batteries in various areas [4,5]. Therefore, the electrodes are the core of the SCs for their electrochemical performances such as the power density, life cycles [6–9].

In order to improve electrochemical performances, some strategies can be used by increasing the specific surface area. Electrodes made from nanomaterials are attracted intensive attention which can facilitate the charge transfer during an electrochemical process [8–11]. Doping with heteroatom is another frequently employed method to modify the properties of functional materials, which can enhance the intrinsic conductivity of electrodes as well as to improve the capacitive performance [12–14]. More recently, the introduction of heteroatoms (e.g., B, N, P and S doping) into electrode materials has been demonstrated as the novel and effective method to improve the capacitance [12,14–17].

Previous literatures reported transition-metal-based electrode materials (Ir, Mn, Ni, V, Ti or Co) serving as promising electrode materials through various approaches in the preparation [11,16–21]. Among these available electrode materials, Titanium is one of the favorable candidates for application in SCs due to their low cost, great reversibility, and high specific capacitance [16,17]. As the confinement of electronic states and the tendency to occupy the sites in the crystals, doping Ti-based nanostructures may lead to new phenomena not found in bulk materials [16,19–21].

In this work, we propose a thermal approach to incorporate N element into Ti to make nanocrystals which resulted in higher crystallinity with the ideal ratio. The effects of N doping on Ti, morphology, and electrochemical properties of TiN nanocrystals are investigated. The results provide new insights into establishing a doping model in SCs.

II. EXPERIMENTS

Preparation of the Titanium nitride

Different amount of carbamide powder (i.e., N precursor 1.8 g, 5.4 g) were weighted and added into the single neck flask and then 15 mL of chloroform was added to make the solutions. 3.6 mL of Titanate chloride (TiCl_4) (i.e., Ti precursor) was then added into the flask as well (The N:Ti ratio was 1:1 and 3:1, respectively). And the solution was transferred to the Mortar overnight before it was moved to the high temperature tube furnace. The temperature was increased to $800 \text{ }^\circ\text{C}$ with a heating rate of $5 \text{ }^\circ\text{C.min}^{-1}$ under nitrogen atmosphere

and kept the temperature for 4 h

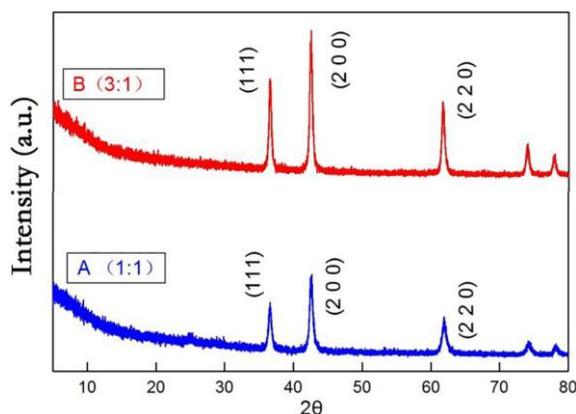


Fig. 1. XRD patterns of the Titanium nitride in N:Ti precursor's ratio 1:1 (A) and 3:1 (B).

before it was cooled to room temperature. Then the samples were ball milled into nanoscale for the electrodes.

The preparation of the electrodes

The conductive carbon black, TiN powder and PVDF were weighed as the mass ratio of 1:8:1, and then the mixture was transferred into the mortar to crush them till well dispersed. Then absolute ethanol was added into the mortar to make the slurry using the pestle. Then the mud was cast onto the Ni mesh in the vacuum oven at 60 °C for 4 h, before the tableting press under 3 MPa to make the testing electrodes.

Electrochemical performance tests

Briefly, the as-prepared electrode was put into the solution of KOH (1 mol.L⁻¹) and then cyclic voltammetry (CV) was measured using an electrochemical workstation (CHI, 440A) at room temperature. The scan rate for CV measurement was 5–50 mV.s⁻¹. The chronopotentiometry tests were conducted in the voltage range

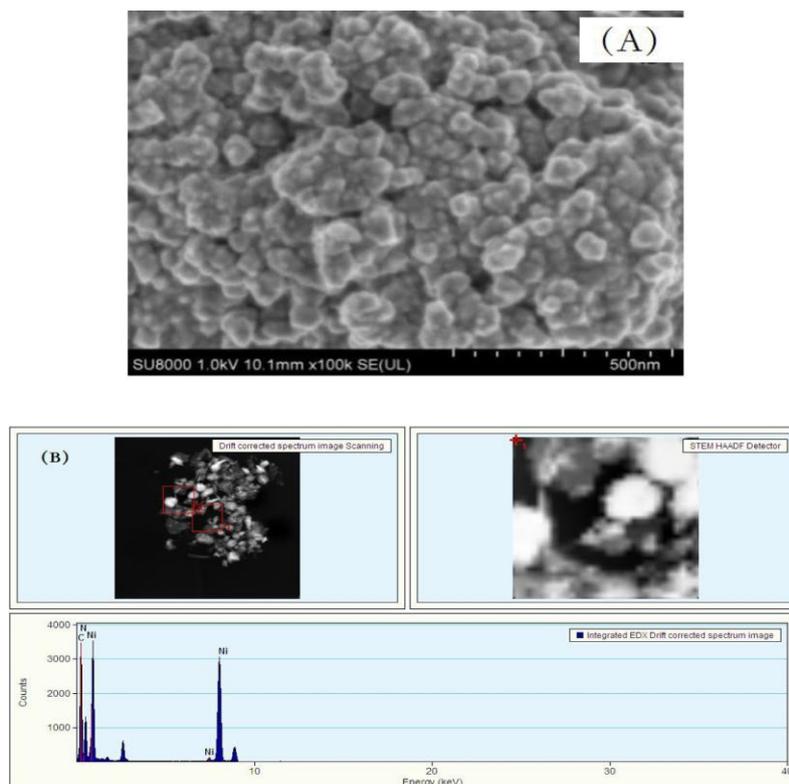


Fig. 2. SEM observation (A) and EDX spectrum (B) of the TiN samples.

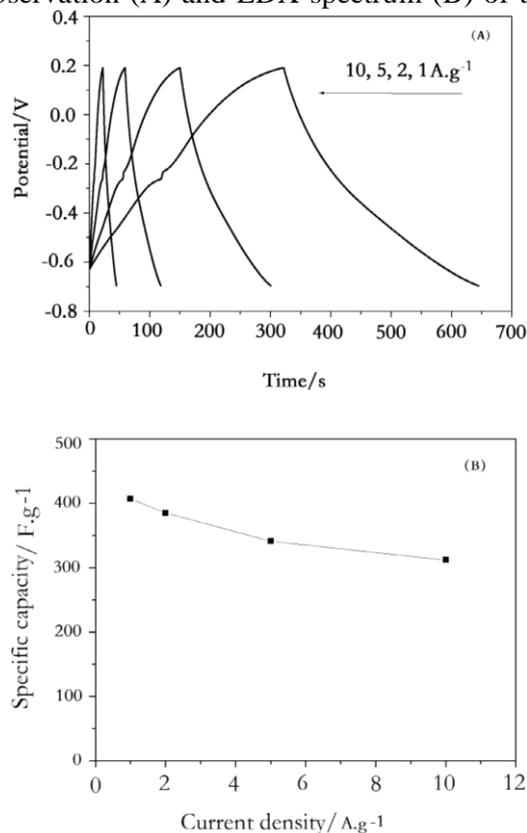


Fig. 3. CV curves of the TiN electrode at different scanning rates (A), chronopotentiometry curves (B) and corresponding capacity as a function of current density (C).

- from 0.6 V to 0.2 V with current density of 1 A.g⁻¹, 2 A.g⁻¹, 5 A.g⁻¹ and 10 A.g⁻¹. A Pt wire and an Hg/HgO electrode were used as counter and reference electrodes, respectively.

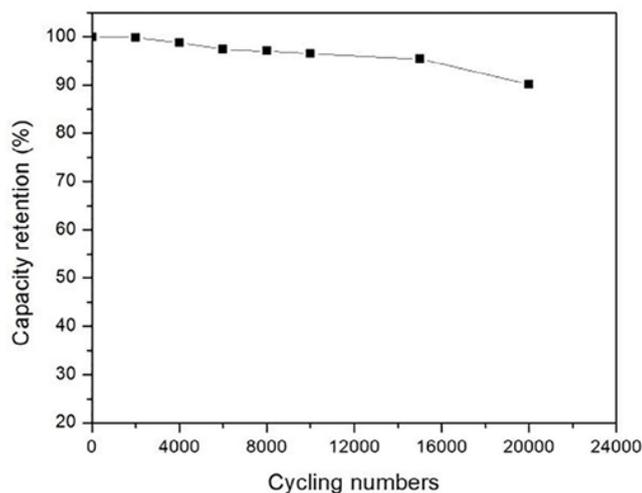


Fig. 4. Capacity as a function of the cycling numbers at the scanning rate of 50 mV.s^{-1} .

III. RESULTS AND DISCUSSION

In order to demonstrate the precursor ratio effects on the crystallization of the TiN samples, XRD analysis was carried out. Fig. 1 shows the XRD patterns of the TiN samples in the precursor's ratio of 1:1 and 3:1. From the results we can see that the diffraction peaks of the both samples were consistent. The degree of the diffraction peaks are 37° (111), 43° (200) and 63° (220) which are consistent with the standard diffraction peaks of the cube crystal TiN [18,19–22]. But for the ratio of 3:1 (N:Ti) (Fig. 1, B), the intensity are stronger than that of the 1:1 (Fig. 1, A) which indicates that the precursor ratio N:Ti 3:1 leads to higher crystallinity than 1:1. The results prove that the as-prepared TiN samples are of high purity and good degree of crystallization.

Fig. 2 (A) shows the as-prepared TiN morphology under SEM observation. From the SEM we can see that the TiN particles are in nanoscale, and the particle sizes are in the range from 50 nm to 100 nm. Further Energy-dispersive X-ray spectroscopy (EDX) results (Fig. 2 B) shows that as-synthesized resultant contains N and Ti elements. Further N and Ti elements mapping showed that there were strong signals which indicate the N and Ti elements are distributed uniformly that the sample has good purity and crystallization, with the ratio of 1:1.

Fig. 3 (A) shows that chronopotentiometry curves of the TiN electrode supercapacitor at different current densities. Clearly, all the curves show good symmetry which indicates a high coulombic efficiency because of the highly reversible redox reactions on the charge/discharge process. When the current densities were changed from 1 A.g^{-1} to 2 A.g^{-1} , 5 A.g^{-1} and 10 A.g^{-1} , the specific capacities were changed from 407 F.g^{-1} to 385 F.g^{-1} , 364 F.g^{-1} and 312 F.g^{-1} , respectively (Fig. 3B).

Fig. 4 shows the cycling performance of the TiN electrode evaluated by CV tests at a scanning rate of 50 mV.s^{-1} for 20,000 cycles. As can be seen, specific capacity remains 90.2% of the initial capacitance even after 20,000 cycles. This is an indication of excellent kinetic reversibility associated with the TiN nanoparticles. The overall electrochemical studies strongly suggest that the resultant is the promising electrodes prepared via the thermal crystallization.

IV. CONCLUSIONS

The as-synthesized TiN has good purity and crystallization. The CV curves are closer to rectangle when reduce the scanning rates and it proves the TiN is an excellent supercapacitor electrode material with high coulombic efficiency and with long cycles of life. The TiN is a promising electrode material for the supercapacitors.

ACKNOWLEDGEMENT

This project was supported by the Scientific Research Initial funding for the advanced talent of Jiangnan University (08010001, 06750001), Basic Research Project of Wuhan City (2015011701011593), 4th Yellow Crane Talent Programme of Wuhan City (08010004), Hubei Province Innovative Young Research Team in Universities (T201318), The Key Project of Natural

Science Foundation of Hubei Province (2014CFA098).

REFERENCES

- [1]. Hu CG, Lv LX. *Chem Mater* 2015;27:5253–60.
- [2]. Liu F et al. *Results Phys* 2017;7:250–5.
- [3]. Lu P, Li C. *J Phys Chem C* 2014;118:896–903.
- [4]. Yan J, Cao YC, Liu F. *RSC Adv* 2016;6:113228.
- [5]. Liu X, Cao YC, et al. *Appl Surf Sci* 2017;394:183–9.
- [6]. Liang J, Bu LT, et al. *J Taiwan Inst Chem E* 2016;65:584–90.
- [7]. Jiang YZ, Li ZH, et al. *J Power Sources* 2016;320:13–9.
- [8]. Cheng Q, Tang S, et al. *Results Phys* 2017. <http://dx.doi.org/10.1016/j.rinp.2017.01.040>.
- [9]. Yang XQ, Li CF, et al. *J Power Sources* 2016;319:66–72.
- [10]. Zhang HT, Zhang L, et al. *J Power Sources* 2016;315:120–6.
- [11]. Liu XY, Chen H, et al. *Ceram Int* 2016;42(7):9227–33.
- [12]. Zhou J, Shen HL, et al. *Electrochim Acta* 2016;209:557–64.
- [13]. Hu J, Li MC, et al. *J Power Sources* 2015;294:120–7.
- [14]. Quan HY, Cheng BC, et al. *Electrochim Acta* 2016;210:557–66.
- [15]. Wu K, Liu QM. *Appl Surf Sci* 2016;79:132–9.
- [16]. Liu XL et al. *Mater Lett* 2017;187:15–9.
- [17]. Zheng LX, Dong YC, et al. *Electrochim Acta* 2016;203:257–64.
- [18]. Wang JM, Liu WG, et al. *Ceram Int* 2004;30:1921–2.
- [19]. Kawamura M, Abe Y, et al. *Thin Solid Films* 1996;287:115–9.
- [20]. Grigoras K, Keskinen J, et al. *Nano Energy* 2016;26:340–5.
- [21]. Ananthapadmanabhan PV. *J Alloys Compd* 1999;287:126–7.
- [22]. Liu N, Xu YD, et al. *J Eur Ceram Soc* 2002;22(13):2409–14.