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# Application of a novel 3D nano-network structure for Ag-modified TiO<sub>2</sub> film electrode with enhanced electrochemical performance



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## ABSTRACT

A series of anatase TiO<sub>2</sub> nanowires (TiO<sub>2</sub>-NWs) and Ag-modified TiO<sub>2</sub> nanowires (TiO<sub>2</sub>@Ag-NWs) film electrodes with hierarchical 3D nano-network structure are successfully synthesized via a facile hydrothermal process followed by the traditional silver mirror reaction. Successful modification of silver nanoparticles onto the TiO<sub>2</sub>-NWs surface is confirmed by X-ray diffraction, scanning electron microscope, transmission electron microscopy with energy-dispersive X-ray analysis, and inductively coupled plasma technique. The electrochemical performances of the TiO<sub>2</sub>-NWs and TiO<sub>2</sub>@Ag-NWs film electrodes are also investigated in this work. Compared with the pristine TiO<sub>2</sub>-NWs, the TiO<sub>2</sub>@Ag-NWs nanomaterial exhibits a higher rate capability and better reversibility. At charge/discharge rates of 50, 100, 200, 400, 800, 1600 and 3350 mA/g, the discharge capacities of the TiO<sub>2</sub>@Ag-NWs electrodes are 237, 219, 198, 179, 159, 139 and 120 mAh/g, respectively. After 120 cycles at 200 mA/g, its capacity retention was as high as 99.1% with little capacity fading.

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#### 1. Introduction

Rechargeable Li-ion batteries as a new generation of green, nonpollution chemical energy storage device are widely used in portable electronic apparatus and vehicles due to their highlights, such as large specific capacity, long cycle life, low self-discharge rate and no memory effect. However, the anode materials for Li-ion batteries are one of the key factors to constrain its whole performance. Currently, the graphitic carbon is commonly-used as anode materials due to the advantages of low cost, high abundance and outstanding kinetics [1,2]. However, there are still two defects that seriously limit its practical applications for high power batteries: one is volume expansion and shrinkage during Liion intercalation and extraction that causes the graphite particles gradully cracking, which leads to the resulting particles exfoliation from current collector such as Cu foil and thereby decreasing battery capacity [3]; and another is the safety issue including the potential dangers of explosion and fire, which mainly arises from lithium dendrite formation during the overcharge process owing to a low Li-intercalation potential of the graphite anode

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http://dx.doi.org/10.1016/j.electacta.2015.05.076 0013-4686/© 2015 Elsevier Ltd. All rights reserved. approaching 0V (vs  $Li^{+}/Li$ ) [4]. Therefore, searching for new electrode materials to meet these requirements becomes critical for large-scale battery development.

Compared with the current graphitic carbon anode materials, anatase TiO<sub>2</sub> has been extensively studied during the past decade [1] and found to be one of the potential candidates as a kind of lithium ion host materials because it is a high-capacity material with low cost, non-toxicity and environmental friendliness [1,5,6]. Moreover, anatase  $TiO_2$  exhibits a relatively high lithium ion insertion/extraction voltage (> 1.0 V vs Li<sup>+</sup>/Li), which is obviously higher than the operating voltage of graphitic anodes, thereby the formation of SEI and electroplating of lithium can be avoided [7– 11]. Besides, anatase TiO<sub>2</sub> possesses excellent reversibility and Liion mobility in the charge/discharge process, which is attributed to its structural stability during the lithium ion insertion/extraction process [8]. These features render it a promising anode material for large-scale and long-life energy storage batteries. However, bulk anatase TiO<sub>2</sub> normally possesses a practical specific capacity of 168 mAh/g [12,13], which is about half of the theoretical capacity of  $TiO_2$  materials (335 mAh/g). In addition,  $TiO_2$  has a poor electronic conductivity [7], approximately  $10^{-10}$  S cm<sup>-1</sup> attributing to empty Ti 3d-states with a band gap energy of  $\sim$ 3 eV [14], which may restrict its rate performance for high power batteries. To date, two main approaches have been reported for improving TiO<sub>2</sub> electrochemical performance: one is to synthesize nanostructural TiO<sub>2</sub>

Recently, one-dimensional nanostructural TiO<sub>2</sub>-based materials with high morphological specificity, such as nanowires, nanotubes, nanoribbons and nanofibers have attracted wide attention because of their unique microstructure and promising functions [10.11.21–23]. Peng et al. reported a template-free and seedless method to grow large arrays of TiO<sub>2</sub> nanoplates and nanowires and continuous network films directly from metal Ti (instead of TiO<sub>2</sub> powder) on the surface of Ti under alkaline hydrothermal conditions [22]. Liao et al. have successfully prepared a new type of hierarchical anatase TiO<sub>2</sub> nanowire arrays via a two-step hydrothermal procedure [23]. Meanwhile, a number of modification methods have been developed to improve electrochemical performance of TiO<sub>2</sub>. For example, Rahman et al. have successfully utilized the traditional silver mirror reaction to coat silver particles onto the anatase TiO<sub>2</sub> nanoribbons/ nanotubes (TiO<sub>2</sub>-NRTs) surface and prominently improved the TiO<sub>2</sub>-NRTs rate capability and cycle durability [6]. Park et al. reported the utility of anatase-TiO<sub>2</sub> by the carbon coating to improve the kinetics of TiO<sub>2</sub> toward fast lithium ion insertion/ extraction [24].

In this work, we describe a facile template-free route to fabricate anatase  $TiO_2$  nanowires ( $TiO_2$ -NWs) with hierarchical 3D nano-network structure growing directly on Ti substrate followed by uniformly modifying silver nanoparticles on the surface of  $TiO_2$ -NWs through the traditional silver mirror reaction (Fig. 1). Firstly,  $H_2Ti_3O_7$  with 3D nano-network structure growing directly on Ti substrate was obtained via an alkaline hydrothermal process followed by an ion-exchange process. Then, an annealing treatment in air at 400 °C was utilized to convert the  $H_2Ti_3O_7$  into anatase  $TiO_2$ -NWs. Finally, silver nanoparticles were modified

onto the surface of the TiO<sub>2</sub>-NWs through the traditional silver mirror reaction to obtain the TiO<sub>2</sub>@Ag-NWs film electrode. The novel 3D nano-network structure of TiO<sub>2</sub>@Ag-NWs film electrode possesses large specific space and high porosity, which facilitate the fast Li<sup>+</sup> transfer and the quick electrolyte absorption. And the electronic conductivity of TiO<sub>2</sub>@Ag-NWs is significantly improved by uniform surface modification of Ag nanoparticles via the silver mirror reaction, and resultantly enables TiO<sub>2</sub>@Ag-NWs electrode to be of the remarkable rate capability and cycling performance. When used as anodes for LIBs without any conductive agents and binders, the as-synthesized Ag-modified TiO<sub>2</sub> nanowires show an excellent rate capability and a significantly enhanced cycling performance.

#### 2. Experimental Section

# 2.1. Preparation of TiO<sub>2</sub>-NWs electrode on Ti substrates

In a typical hydrothermal procedure [22,23], a piece of commercial Ti substrates (99.5% in purity) with the thickness of 0.05 mm was used as the Ti source and the substrate, which is ultrasonically washed with ethanol and acetone for 30 min in sequence. The dried Ti substrate was transferred into the 100 mL Teflon-lined stainless steel autoclave and was kept vertical. Then 10 mL ethanol and 80 mL of 0.5 M NaOH solution were added into the autoclave, respectively. The sealed autoclave was heated to 220 °C with a heating rate of 3 °C/min and maintained at 220 °C for 16 h. After the autoclave was cooled naturally to room temperature, the obtained precursor was taken out. At this point, the precursor had lost its metallic luster and turned to be light blue. After washing with deionized water several times, the precursor was immersed into 100 mL of 0.1 M HCl for 6 h to achieve ion exchange of Na<sup>+</sup> into H<sup>+</sup> [25], followed by washing several times



Fig. 1. Schematic illustration for the fabrication of the TiO2-NWs and TiO2@Ag-NWs.

and dried in air at room temperature. Finally, the as-prepared hydrogen titanate was placed into a muffle furnace, heated to 400 °C with a temperature ramp of 3 °C/min and calcined in air atmosphere at 400 °C for 4 h. When the sample cools to room temperature, the pristine  $TiO_2$ -NWs electrode grown on Ti substrates was obtained.

#### 2.2. Preparation of TiO<sub>2</sub>@Ag-NWs film electrode

The traditional silver mirror reaction was utilized to deposit Ag nanoparticles onto the surfaces of the TiO<sub>2</sub>-NWs [5,6]. Typically, the above obtained pristine TiO<sub>2</sub>-NWs was set at the bottom of an 1 L beaker. Meanwhile, 85 mg of AgNO<sub>3</sub> powder was dissolved in 100 mL deionized water at room temperature followed by adding into the beaker, then 100 mL of 5 mM NaOH solution was added dropwisely to the solution with an ultrasonic dispersion giving a brown precipitate. Subsequently, concentrated (10 M) ammonia solution was added dropwisely into the mixed solution under vigorous ultrasonic dispersion until the brown precipitate dissolved completely. A colorless solution was therefore obtained on the basis of the following reaction [26]:

$$Ag^{+} + NH_{3} \rightleftharpoons Ag(NH_{3})^{+}$$
(1)

$$Ag(NH_3)^+ + NH_3 \rightleftharpoons Ag(NH_3)_2^+$$
<sup>(2)</sup>

Then, 100 mL of 10 mM glucose solution was then added dropwisely to the mixture with an ultrasonic dispersion and reacted for 3 h at room temperature. The following reaction [26] took place:

$$\begin{split} & 2[\text{Ag}(\text{NH}_3)_2]^+ + 2\text{OH}^- + \text{R} - \text{CHO} = 2\text{Ag} \downarrow + 3\text{NH}_3 \\ & \uparrow + \text{R} - \text{COO}^- + \text{H}_2\text{O} + \text{NH}_4^+ \end{split}$$

When the reaction finished, the product was taken out and washed with deionized water and ethanol for several times in turn, and then dried in a vacuum oven at  $60 \degree C$  for 12 h to obtain the TiO<sub>2</sub>@Ag-NWs film electrode.

#### 2.3. Materials characterizations

Powder X-ray diffraction (XRD) patterns were collected on a Rigaku MiniFlex600 X'pert (D8 Advance, Japan) diffractometer using Cu K $\alpha$  radiation ( $\lambda$  = 1.5405 Å). Morphologies and structure of the samples were examined with a field emission scanning electron microcopy (SEM, LEO 1530, HITACHI S-4800) and high resolution transmission electron microcopy (HRTEM, JEM-2100). Elemental mappings and corresponding area's Energy Dispersive Spectrum (EDS) were conducted using an energy dispersive X-ray (EDX) device attached to a LEO 1530, HITACHI S-4800 SEM. The elemental contents (Ti, Ag) of the TiO2@Ag-NWs material were detected by inductively coupled plasma (ICP) technique. For TEM, the scratched TiO<sub>2</sub>@Ag-NWs material from the Ti substrate were redispersed ultrasonically in ethanol solution and then dropped onto the surface of bronze nets. No metal coating treatment was performed on the samples before characterization by electron microscopy.

## 2.4. Electrochemical performance characterization

The TiO<sub>2</sub>-NWs and TiO<sub>2</sub>@Ag-NWs grown on Ti substrates were directly used as film electrodes for electrochemical characterization. And the specific capacity of TiO<sub>2</sub>-NWs electrode is calculated by the mass of TiO<sub>2</sub>, while for TiO<sub>2</sub>@Ag-NWs, is calculated by both the weights of TiO<sub>2</sub> and Ag nanoparticles, respectively. CR2016type coin cells for lithium battery were assembled in an argonfilled glove box with Li metal foil (China Energy Lithium CO., LTD.) as the counter and reference electrode, one layer of Celgard 2400 (Celgard, Inc. USA) as the separator, and  $LiPF_6(1 \text{ mol}/L)$  dissolved in a 1:1:1 (V:V:V) mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) as the electrolyte. Galvanostatic charge/discharge experiments were performed at different current densities between 1.0 and 3.0 V (vs Li<sup>+</sup>/Li) using an Arbin cell test instrument (BT2000, College Station, Texas, USA) at room temperature. The electrochemical impedance spectra (EIS) of the unmodified and Ag-modified TiO<sub>2</sub>-NWs film electrodes at an open-circuit potential (OCP) of  $\sim$ 3.0V, the discharge plateau voltage of  $\sim$ 1.75 V and the full charge stage of  $\sim$ 3.0 V (vs Li<sup>+</sup>/Li) cycled 10 th later at 200 mA/g were measured in the frequency range of 10 mHz-100 kHz using two-electrode coin cells with Li metal as the counter electrode via an Autolab PGSTAT 101 cell test instrument. A four-point probe meter (SX1934 (SZ-82) digital fourprobe testing instrument) was also used to investigate the sheet resistances of TiO<sub>2</sub>-NWs and TiO<sub>2</sub>@Ag-NWs film electrodes in this work

To calculate the mass (m) of the TiO<sub>2</sub>-NWs active materials and the weight of the Ag nanoparticles in the electrodes, we weighed the original weight (m<sub>0</sub>) of the prepared TiO<sub>2</sub>-NWs grown on Ti substrate in advance. Then, the prepared TiO<sub>2</sub>-NWs active materials grown on one side of Ti substrate were scratched off the Ti substrate by a scraping knife, and then the weight  $(m_1)$ , which includes the residue TiO<sub>2</sub>-NWs active materials grown on the other side of Ti substrate and Ti substrates, was measured. Herein, the mass of the TiO<sub>2</sub>-NWs active materials is given by  $m = m_0 - m_1$ . The mass (M) of the TiO<sub>2</sub>@Ag-NWs active materials and the weight (M<sub>A</sub>) of Ag nanoparticles in the electrodes were calculated as mentioned above from the original weight  $(M_0)$  of the  $TiO_2@Ag-NWs$  grown on Ti substrate, and the weight  $(M_1)$ including the residue TiO<sub>2</sub>@Ag-NWs active materials grown on the other side of Ti substrate and Ti substrates, respectively. All the TiO<sub>2</sub>-NWs prepared in the same condition and without any treatment before the silver mirror reaction, so, the mass of the TiO<sub>2</sub>@Ag-NWs active materials and the weight of Ag nanoparticles in the electrodes are given by  $M = M_0 - M_1$  and  $M_A = M - m$ , respectively.

#### 3. Results and Discussion

The crystal structure and morphologies of the as-prepared TiO<sub>2</sub>-NWs and TiO<sub>2</sub>@Ag-NWs were characterized by X-ray diffraction, scanning electron microscopy and transmission electron microscopy. Fig. 2 shows the XRD parterns of the unmodified and Ag-modified TiO2-NWs. For the unmodified TiO<sub>2</sub>-NWs, all the diffraction peaks position at  $2\theta = 25.4^{\circ}$ ,  $37.8^{\circ}$ , 48.1°, 62.8°, 76.2° are agreed well with the anatase phase of  $TiO_2$ (JCPDS No. 89-4921) [9,22], except that these diffraction positions at  $2\theta = 40.2^{\circ}$ , 53.0°, 70.6° belong to the current collector, metal tatinium (JCPDS No. 89-2762). After the silver mirror reaction, the intensities of the anatase TiO<sub>2</sub> and tatinium diffraction peaks become relatively weaker, and the new series of diffraction peak positions at  $2\theta = 38.1^{\circ}$ ,  $44.3^{\circ}$ ,  $64.4^{\circ}$ ,  $77.4^{\circ}$ , which consistented well with the cubic phase of silver (JCPDS No. 87-0717), can be clearly observed in the XRD patterns of Ag-modified TiO<sub>2</sub>-NWs. It's obvious that Ag in Ag-modified TiO<sub>2</sub>-NWs existed really in the form of metal silver and there is not any negative impact on the crystal phase of the TiO<sub>2</sub>-NWs during the traditional silver mirror reaction [5,6].

Fig. 3 shows SEM images of the as-prepared  $TiO_2$ -NWs and  $TiO_2@Ag$ -NWs, the corresponding elemental mapping images and energy dispersive X-ray spectrum of the  $TiO_2@Ag$ -NWs. As shown



Fig. 2. XRD patterns of TiO<sub>2</sub>-NWs and TiO<sub>2</sub>@Ag-NWs.

in Fig.  $3a \sim c$ , the as-prepared samples show a 3D nano-network stucture, composed of lots of nondirectional, homogeneous 1D nanowires with a column diameter of 60~70 nm and length of several micrometers. The special 3D nano-network stucture could be expected to provide short pathways for Li<sup>+</sup> diffusion, large specific space to facilitate the fast transfer of Li<sup>+</sup> and the facile electrolyte infiltration throughout the thin film electrode. After the silver mirror reaction, we can clearly see that 3D nano-network stucture can keep in the primary shape (Fig. 3d~e) and silver nanoparticles with a diameter of 10~30 nm are uniformly adhered to the surface of TiO<sub>2</sub>-NWs (Fig. 3f, Fig. S1a~c). From Fig. S1a~c, we can see the synthetic method of Ag modification makes the Ag nanoparticles liable to deposite not only on the single TiO<sub>2</sub>-NW but also on the joint of TiO<sub>2</sub>-NWs. Finally the integrated and uniform conductive network can be formed. Meanwhile, the detailed local elemental composition and distribution of the synthesized TiO<sub>2</sub>@Ag-NWs were further analyzed by energy dispersive X-ray spectrum and scanning transmission electron microscopy. The distribution of silver shown in Fig. 3g gives a direct proof of the uniform surface modification of Ag element on TiO<sub>2</sub>-NWs. Furthermore, a presence of the Ag element in the TiO<sub>2</sub>@Ag-NWs electrode can also be obviously observed in Fig. 3j. These above obtained results undoubtedly indicate that the uniform surface modification of Ag element on TiO<sub>2</sub> materials via the silver mirror reaction would be successful and effective.

The distribution of crystalline silver nanoparticles within the  $TiO_2$ -NWs were further characterized by transmission electron microscope. Fig. 4 exhibits a typical TEM images of the Agmodified  $TiO_2$ -NWs, along with corresponding area's energy dispersive X-ray spectrum. Obviously, it shows that the size of these uniform nanoparticles adhered to the surface of the nanowires (Fig. 4a~b) are about 10~30 nm, which consists well with the obtained SEM results (Fig. 3f). As shown in Fig. 4c, the

(101) crystal planes of Anatase TiO<sub>2</sub> nanowires with the interplanar distance of 0.352 nm [5] and the (111) crystal planes of Ag with the interplanar distance of 0.236 nm [27] can be clearly found. Only two different kinds of particles can be seen in the TEM image, which is consistent with the XRD results (except current collector Ti substrates diffraction peaks located at  $2\theta = 40.4^{\circ}$ , 53.1°, 70.7°). In addition, according to the energy dispersive X-ray spectrum results (Fig. 4d $\sim$ e), we could find that major element compositions of the nanoparticles and nanowires are Ag and Ti. O. respectively. In order to further investigate the modified content of silver on the TiO<sub>2</sub>@Ag-NWs electrode, the scratched TiO<sub>2</sub>@Ag-NWs material from the Ti substrate were dissolved in acid solution and measured via inductively coupled plasma method. According to the measured results (Table 1), the mass ratio of Ag and Ti are determined to be 5.20 wt% and 56.88 wt%, respectively. The above results undoubtly prove that silver modification of TiO<sub>2</sub>-NWs via the silver mirror reaction is feasible. And when used as anodes for lithium half-cells, the TiO<sub>2</sub>-NWs chemically modified with Ag nanoparticles exhibit an enhanced rate performance and cycle stability (discussed later).

The electrochemical performance of unmodified and Agmodified TiO<sub>2</sub>-NWs was measured by galvanostatic charge/ discharge mesurement. Fig. 5a and b show the charge/discharge curves of unmodified and Ag-modified TiO2-NWs cycled at 200 mA/g ( $\approx$ 0.6C, 1C = 335 mA/g), respectively. There are distinct potential plateaus observed at  $\approx$ 1.75 and 2.0V (vs Li<sup>+</sup>/Li) during discharging (Li<sup>+</sup> insertion) and charging (Li<sup>+</sup> extraction) the electrodes with unmodified and Ag-modified TiO2-NWs. The discharge curves of TiO<sub>2</sub>-NWs (Fig. 5a), corresponding to Li<sup>+</sup> insertion process, can be divided into three consecutive potential regions [7,15,28]. The first potential region is marked by a steep voltage decrease from the open-circuit potential (OCP) to 1.75 V (vs Li<sup>+</sup>/Li) forming a solid solution phase, which is attributed to Li insertion into the  $I4_1/amd$  tetragonal anatase lattice (Li<sub>x</sub>TiO<sub>2</sub>) without the nucleation of other phases [28,29]. The second potential region is the discharge plateau region at  $\approx$ 1.75 V (vs Li<sup>+</sup>/ Li), indicating a two-phase reaction between the Li-poor tetragonal anatase  $Li_xTiO_2$  and orthorhombic  $Li_{0.5}TiO_2$  phases [7,28,29]. A long slope-like potential region is observed from 1.75 V to 1.0 V (vs Li<sup>+</sup>/ Li), which represents the non-faradaic process in which the interfacial Li<sup>+</sup> insertion storage is similar to the capacitive behavior of nanomaterials [16]. This interfacial Li<sup>+</sup> insertion storage contributes to the additional pseudocapacitive lithium inserted into the surface layer of the TiO<sub>2</sub>-NWs, forming the Li-rich I4<sub>1</sub>/amd tetragonal lattice (Li<sub>0.5+x</sub>TiO<sub>2</sub>), as observed in many other nano-TiO<sub>2</sub> materials [7,20,30,31]. It is clearly seen that the capacity of the long slope-like region is the main contribution to the capacity of TiO<sub>2</sub>-NWs and is also larger than that reported by other research groups, which is probably due to its larger surface area and specific structure. From the inset of Fig. 5a, it can be clearly seen that the color of the sample electrodes changed from light blue to dark gray followed by the silver mirror reaction treatment. As shown in Fig. 5b, the discharge/charge curves of Ag-modified TiO<sub>2</sub>-NWs are similar to unmodified TiO<sub>2</sub>-NWs without any other charge/ discharge plateaus occurred, suggesting that Ag nanoparticles without any electrochemical activity just play a role of improving the TiO<sub>2</sub>-NWs electrode electrical conductivity and could not change the electrochemical properties of TiO<sub>2</sub>-NWs electrodes. Besides, as the Fig. S2 shown, it is remarkable that the diffraction peaks of anatase TiO<sub>2</sub> lattice deviate to lower angle forming orthorhombic Li<sub>0.5</sub>TiO<sub>2</sub> phase after lithium intercalation. However, Ag nanoparticles in both the pristine and lithiated samples are existed in the form of metal silver, and the intensity of the Ag nanoparticles diffraction peaks in the lithiated sample is similar to the pristine sample with almost no changes even after cycling. This result would further support that Ag nanoparticles would not be



**Fig. 3.** SEM images of the as-prepared  $TiO_2$ -NWs ( $a \sim c$ ) and  $TiO_2@Ag$ -NWs ( $d \sim f$ ); The corresponding elemental mapping images of silver (g), titanium (h), oxygen (i), and EDX spectra of the  $TiO_2@Ag$ -NWs (j) in the selected area (pink rectangle in (d)).

involved in the electrochemical reaction with  $Li^+$  in the  $TiO_2@Ag$ -NWs electrode and have any negative impact on the structure of  $Li_{0.5}TiO_2$  during the charge-discharge cycling. Compared with the  $TiO_2$ -NWs, the capacity retention of the Ag modified  $TiO_2$ -NWs is higher, suggesting that the  $TiO_2@Ag$ -NWs electrodes can exhibit higher reversibility towards lithium intercalation/deintercalation without any negative impact on the electrochemical performance of  $TiO_2$ -NWs electrode and enhanced electrochemical storage of lithium than the  $TiO_2$ -NWs electrode without Ag modification. The initial discharge capacity and the first coulombic efficiency of TiO<sub>2</sub>-NWs electrodes are 324.5 mAh/g and 66.3%, while for TiO<sub>2</sub>@Ag-NWs electrodes, are 351.2 mAh/g and 63.9%, respectively. The discharge capacity for the first cycle is higher than the theoretical capacity for both electrodes. This behavior may be ascribed to surface phenomena such as the irreversible decomposition of electrolyte accompanying the formation of the solid electrolyte interface (SEI) [17], a shorter diffusion length for both the electron and Li<sup>+</sup> and a larger electrode/electrolyte contact area



Fig. 4. (a, b) TEM and (c) HRTEM images of TiO<sub>2</sub>@Ag-NWs, (d, e) the corresponding EDX spectra from selected area in (b).

#### Table 1

Elemental contents (in weight percent) of Ag and Ti in the Ag-modified  $TiO_2$ -NWs samples obtained via ICP testing method.

Element	Measured results (ug/mL)	Calculated results (wt%)
Ti	3.94	56.88
Ag	0.36	5.20

of TiO<sub>2</sub>-NWs compared with traditional bulk TiO<sub>2</sub> materials [7,20,30], which facilitates the Li<sup>+</sup> insertion and extraction. Whereas, the irreversible capacity could be attributed to the inability to remove all the lithium ions that are inserted in the first discharge and the formation of SEI film which has been demonstrated by P.G. Bruce et al. [32]. The lower first coulombic efficiency of TiO<sub>2</sub>@Ag-NWs electrode may be attributed to the activation of TiO<sub>2</sub>@Ag-NWs electrode by several cycles and the increased specific surface area [33], however, the cycle and rate performance of the TiO<sub>2</sub>@Ag-NWs electrode are remarkably better than that of TiO<sub>2</sub>-NWs electrode at the subsequent cycles (Fig.  $5e \sim f$ ). Fig. 5c and d exhibit the normalized discharge curves of TiO<sub>2</sub>-NWs and TiO<sub>2</sub>@Ag-NWs electrodes at 200 mA/g, respectively. It can be found that the discharge plateaus of 1st, 2nd, 10th for TiO<sub>2</sub>-NWs are 1.74 V, 1.76 V, and 1.77 V (vs  $Li^+/Li$ ), while for  $TiO_2$ @Ag-NWs electrodes, are 1.72 V, 1.74 V, and 1.77 V (vs Li<sup>+</sup>/Li), respectively. The discharge plateau of TiO<sub>2</sub>@Ag-NWs electrodes is lower in the first two cycles, which indicates that the polarization of TiO<sub>2</sub>@Ag-NWs electrode is greater than TiO<sub>2</sub>-NWs and it needs to be activated after several cycles, and becomes similar 10 cycles later. Besides, Ag nanoparticles occupied part of the surface of the TiO<sub>2</sub>-NWs (Fig. 4a~b) may cause some channel-blocking point defects and effect the lithium ion diffusion channel [34] followed by leading to lower specific capacity. These explain why the first coulombic efficiency of TiO<sub>2</sub>@Ag-NWs electrode is lower than the unmodified TiO<sub>2</sub>-NWs.

Fig. 5e presents the specific discharge capacity and coulombic efficiency with respect to cycle number for the TiO<sub>2</sub>-NWs and TiO<sub>2</sub>@Ag-NWs electrodes at a current density of 200 mA/g. In terms of TiO<sub>2</sub>-NWs electrode, the second discharge capacity is 248.6 mAh/g and decreases to 204.0 mAh/g after 120 cycles with capacity retention of 82.1%. However, for TiO<sub>2</sub>@Ag-NWs electrode, it delivers 231.6 mAh/g (This value is calculated by both the weights of TiO<sub>2</sub> and Ag nanoparticles, while calculated by the weight of TiO<sub>2</sub>, is 244.3 mAh/g) with high capacity retention of 99.1% after 120 cycles, indicating the remarkable cycling stability of TiO<sub>2</sub>@Ag-NWs electrode. This further proves that Ag nanoparticles with high conductivity benefits TiO<sub>2</sub>-NWs materials. Fig. 5f shows the comparison of the rate capabilities between unmodified and Ag-modified TiO<sub>2</sub>-NWs electrodes at different current rates range from 50 mA/g to 3350 mA/g (All the data of the electrochemical performance are summarized as Table S3 and Table S4). It can be clearly found that the capacity of TiO<sub>2</sub>-NWs electrode decreases rapidly with the cycles and the increase of current density, but



**Fig. 5.** (a, b) Charge and discharge curves of TiO<sub>2</sub>-NWs and TiO<sub>2</sub>@Ag-NWs electrodes at a current density of 200 mA/g. (c, d) The normalized discharge curves of TiO<sub>2</sub>-NWs and TiO<sub>2</sub>@Ag-NWs electrodes at a current density of 200 mA/g. (e) Cycle performances for TiO<sub>2</sub>-NWs and TiO<sub>2</sub>@Ag-NWs electrodes at a current density of 200 mA/g. (f) Rate capabilities of TiO<sub>2</sub>-NWs and TiO<sub>2</sub>@Ag-NWs electrodes at a current density of 200 mA/g. (f) Rate

 $TiO_2@Ag-NWs$  electrode obviously exhibits a much higher storage capacity and much better rate capability than  $TiO_2-NWs$  electrode at the higher current rates. For example, at a current rate of 3350 mA/g, the specific capacity of  $TiO_2@Ag-NWs$  electrode is around 120 mAh/g, which is remarkably higher than the same rate capacity (86 mAh/g) of  $TiO_2-NWs$  electrode.

To further understand the distinctions of the unmodified and Ag-modified TiO<sub>2</sub>-NWs on the electrochemical performance, all the film electrodes were investigated by electrochemical impedance spectroscopy (EIS), four-point probe meter and cyclic voltammograms (CV). EIS may be considered as one of the most powerful tools to study the kinetic parameters of the electrode process [6,7,35]. Fig. 6a~c show the obtained EIS data and fitting results using an equivalent circuit of unmodified and Ag-modified TiO<sub>2</sub>-NWs film electrodes, which were measured at the open circuit potential (OCP) of  $\approx$ 3.0 V, the discharge plateau voltage of  $\approx$ 1.75 V, and the full charge stage of  $\approx$ 3.0 V (*vs* Li<sup>+</sup>/Li) after 10 cycles at 200 mA/g, respectively. And each plot consisted of one semicircle at higher frequency followed by a linear portion at lower frequency. The high-frequency semicircle is related to the charge transfer resistance, while the low frequency region of the

straight line is attributed to the Warburg impedance of long-range lithium ion diffusion.[31] In the equivalent circuit as shown in Fig. 6d, Rs represents the ohmic resistance of electrolyte, porous separator, conductor, active materials and so on, Rct represents the charge-transfer resistance at the active material interface, CPE represents the double-layer capacitance and passivation film capacitance, and Ws represents the Warburg impedance, respectively. A good agreement was observed between the impedance data and fitting results using the above mentioned equivalent circuit model (the error is less than 2%). The parameters obtained from the equivalent circuit are recorded in Table 2. Obviously, Agmodified TiO<sub>2</sub>-NWs electrode exhibits much lower charge-transfer resistance than that of unmodified TiO<sub>2</sub>-NWs electrode, meaning that the modification of Ag nanoparticles on the surface of TiO<sub>2</sub>-NWs can effectively improve the electronic conductivity. Table 3 shows the four-point probe meter testing results of TiO<sub>2</sub>-NWs and TiO<sub>2</sub>@Ag-NWs electrodes. Clearly, the sheet resistance of TiO<sub>2</sub>@Ag-NWs electrode  $((1.8 \pm 0.4) \times 10^2 \Omega/\Box)$  is eminently smaller than that of TiO<sub>2</sub>-NWs (>1.0 × 10<sup>5</sup>  $\Omega/\Box$ ), further indicating that the modification of Ag nanoparticles is beneficial to improve the electrical conductivity of TiO<sub>2</sub>-NWs and necessary.



**Fig. 6.** (a). AC impedance measurements of TiO<sub>2</sub>-NWs and TiO<sub>2</sub>@Ag-NWs electrodes at open-circuit potential of  $\approx$ 3.0 V (vs Li<sup>+</sup>/Li). (b) AC impedance measurements of TiO<sub>2</sub>-NWs and TiO<sub>2</sub>@Ag-NWs electrodes at discharge plateau of  $\approx$ 1.75 V (vs Li<sup>+</sup>/Li). (c) AC impedance measurements of TiO<sub>2</sub>-NWs and TiO<sub>2</sub>@Ag-NWs electrodes after 10 cycles (200 mA/g) at full charge stage  $\approx$ 3.0 V (vs Li<sup>+</sup>/Li). (d) The equivalent circuits for the EIS measurements.

#### Table 2

AC impedance parameters of TiO2-NWs and TiO2@Ag-NWs electrodes.

Sample	Rs $(\Omega)$	Error%	Rct $(\Omega)$	Error%
TiO <sub>2</sub> -NWs (OCP)	4.03	1.11	350.3	1.44
TiO <sub>2</sub> @Ag-NWs (OCP)	3.76	0.98	137.9	0.67
TiO <sub>2</sub> -NWs (1.75 V)	3.73	0.78	225.1	0.35
TiO <sub>2</sub> @Ag-NWs (1.75 V)	3.28	0.45	102.2	0.31
TiO <sub>2</sub> -NWs (after 10 cycles)	8.43	1.09	104.3	0.52
TiO <sub>2</sub> @Ag-NWs (after 10 cycles)	7.48	0.72	53.6	0.40

#### Table 3

Sheet resistances of TiO<sub>2</sub>-NWs and TiO<sub>2</sub>@Ag-NWs electrodes measured by the four-point probe testing method.

	TiO <sub>2</sub> -NWs	TiO <sub>2</sub> @Ag-NWs
Sheet resistance $(\Omega / \Box)$	$> 1.0  imes 10^5$	$(1.8\pm0.4)\times10^2$

Fig. 7a~b compares the representative cyclic voltammograms for unmodified and Ag-modified TiO2-NWs film electrodes at a scan rate of 0.1 mV/s. The area under the curves represents the total stored charges which arise from both faradaic and nonfaradaic processes [31]. It can be found that two couples of oxidationreduction peaks appear when the electrode potential scans from 1.0 to 3.0 V (vs Li<sup>+</sup>/Li). The cathodic/anodic peaks (named A-peaks), usually occurred at ca. 1.75 and 2.0V (vs Li<sup>+</sup>/Li), respectively, represent the solid-state lithium ion insertion/extraction behavior in the anatase TiO<sub>2</sub>-NWs lattice. And the other cathodic/anodic peaks (named S-peaks) occurred at ca. 1.55 and 1.65 V (vs Li<sup>+</sup>/Li), respectively, represent the (pseudo) capacitive lithium ion insertion/extraction process in the anatase TiO<sub>2</sub>-NWs lattice, which are consistent with previous reports [11,31]. This (pseudo) capacitive storage scales with surface area (or reverses particle size) of anatase TiO<sub>2</sub> [31]. For the as-prepared TiO<sub>2</sub>-NWs materials, the occurrence of S-peaks in the cyclic voltammograms, which is similar to the monoclinic  $TiO_2(B)$  [36,37], may be attributed to the effect of nanowire morphology [38] with a novel and open nanonetwork structure, which facilitates the Li<sup>+</sup> insertion and extraction. This lithium ion insertion process is written as the follow equation:

$$\Gamma iO_2 + xLi^+ + xe^{-} \underset{Charge}{\overset{Discharge}{\rightleftharpoons}} Li_x TiO_2$$
(4)

The lithium ion insertion coefficient, *x*, is normally found to be close to 0.5 for the anatase structure when it is at maximum accommodation [9,31,39,40] and corresponds to a specific capacity of 168 mAh/g. In comparison, both of the A-peaks shapes and current densities are similar, whereas, the S-peaks of  $TiO_2@Ag$ -NWs material are sharper and higher than  $TiO_2$ -NWs material, indicating that the silver modification can significantly improve the kinetics of  $TiO_2$ -NWs toward fast lithium ion insertion/ extraction and the specific capacity followed by the silver mirror reaction.

In order to further understand how the silver nanoparticles improve the kinetics of TiO2-NWs toward fast lithium ion insertion/extraction and the specific capacity, CV measurements at different scan rates were also tested as following. Fig.  $7c \sim d$ summarize the specific capacitance calculated from the integration of the CV curves at different scan rates. It can be found that the total amount of the stored charge in the TiO<sub>2</sub>-NWs and TiO<sub>2</sub>@Ag-NWs are strongly dependent on the sweep rate in the range between 0.1 and 5 mV/s. As the sweep rate decreases, the total amount of stored charge increases. This indicates that the full storage capacity has not been reached at the given sweep rates because of kinetic limitations associated with the diffusion of Li<sup>+</sup> through the TiO<sub>2</sub> [31]. In addition, all A-peaks of TiO<sub>2</sub>-NWs and TiO<sub>2</sub>@Ag-NWs gradually disappear with the sweep rate increase, and all TiO<sub>2</sub>@Ag-NWs S-peaks shapes are sharper than TiO<sub>2</sub>-NWs material, further indicating the silver nanoparticles are beneficial



**Fig. 7.** CV measurements of TiO<sub>2</sub>-NWs (a) and TiO<sub>2</sub>@Ag-NWs (b) at a scan rate of 0.1 mV/s. CV measurements of TiO<sub>2</sub>-NWs (c) and TiO<sub>2</sub>@Ag-NWs (d) at different scan rates. The linear fittings of S-peak current density versus square root of the scan rate for TiO<sub>2</sub>-NWs (e) and TiO<sub>2</sub>@Ag-NWs (f) electrodes, respectively.

to improve the rate performance of TiO<sub>2</sub>-NWs. From the images of Fig. 7e and f, the S-peak current density shows a linear relationship versus square root of the scan rate, suggesting that the reversible and diffusion-controlled characteristics of this redox reaction on both electrodes [41]. However, the current density measured for the Ag-modified TiO<sub>2</sub>-NWs electrode (Fig. 7d) is larger than the value of the unmodified TiO<sub>2</sub>-NWs (Fig. 7c). Apparently, the Ag-modified TiO<sub>2</sub>-NWs electrode has a higher activity than unmodified TiO<sub>2</sub>-NWs for this redox reaction.

To obtain more information about capacitive contributions to overall charge of Li-storage, cyclic voltammograms of the Li<sup>+</sup> insertion into  $TiO_2$ -NWs and  $TiO_2@Ag$ -NWs were analyzed in detail according to the mathematical deconvolution of cyclic voltammograms recently reported by Laskova [38] and Dunn et al. [31]. The peak current response at a fixed potential can be expressed by:

$$i(v) = k_1 \cdot v + k_2 \cdot v^{1/2} \tag{5}$$

where  $k_1\nu$  corresponds to the capacitive current contribution associated with the storage of Li<sup>+</sup> at the TiO<sub>2</sub>-NWs surface and also to the bulk faradaic pseudocapacitance. The second term  $k_2\nu^{1/2}$ corresponds to the diffusion-controlled current, which is attributed to the insertion of Li<sup>+</sup> in the bulk of anatase TiO<sub>2</sub>-NWs lattice [31,38]. According to the CV measurements at different scan rates shown in Fig. 7e~f, we randomly chose four groups data of two different points (Table S1) to calculate the coefficients k<sub>1</sub> and k<sub>2</sub>. It can be clearly seen that there is a small difference about the coefficient k<sub>2</sub> between TiO<sub>2</sub>-NWs and TiO<sub>2</sub>@Ag-NWs, however, the value of k<sub>1</sub> for TiO<sub>2</sub>@Ag-NWs is greater than that of TiO<sub>2</sub>-NWs (Table S2), conforming that modification of Ag nanoparticles is beneficial to improve the Li-storage of TiO<sub>2</sub>-NWs, especially the capacitive storage in TiO<sub>2</sub>-NWs, which is corresponding to the capacitive current contribution and the bulk faradaic pseudocapacitance.

In order to further verify the effect of Ag-modification on the electrochemical process of  $TiO_2@Ag-NWs$  electrode, XPS and SEM analysis have been carried out (see Fig. S3 and Fig. S4). From the C1s and O1s spectra in Fig. S3,  $R-OCO_2^-$  and/or  $CO_3^{2-}$ , C-O-C, C=O, C-O-H/Li groups are observed from 1.5 V and generate on a large scale at 0.8 V. It can be attributed to formation of SEI on the  $TiO_2@Ag-NWs$ , which is consistent well with the another reports about  $TiO_2$  electrodes [42], and indicates the Ag-modification has no effect on the SEI layer formation for  $TiO_2$  electrode. In the Ag3d spectra, there is only pure metal Ag peak for the  $TiO_2@Ag-NWs$ 

electrode during cycling, which further suggests that Ag-NPs show a good chemical stability during the charge-discharge process and could not take part in the SEI layer formation of TiO<sub>2</sub>@Ag-NWs electrode.

Fig. S4 exhibits the SEM images of the TiO<sub>2</sub>@Ag-NWs electrode after 20 cycles at a current density of 200 mA/g. It can be clearly seen that TiO<sub>2</sub>@Ag-NWs electrode can keep in the primary shape and structure with almost no changes after 20 charge-discharge cycles, further conforming that the stable 3D nano-network structure is one of reasons for improving the cell performance and cycle stability of TiO<sub>2</sub>@Ag-NWs electrode.

# 4. Conclusion

In summary, we have successfully synthesized anatase TiO<sub>2</sub>-NWs and TiO<sub>2</sub>@Ag-NWs via a facile hydrothermal process followed by the traditional silver mirror reaction. The 3D nanonetwork structure provide not only short pathways for Li<sup>+</sup> diffusion but also large surface area for interfacial Li<sup>+</sup> ion storage for TiO<sub>2</sub>-NWs electrode, and resultantly facilitates the fast Li<sup>+</sup> transfer and the electrolyte infiltration throughout the thin film electrode. Modification of silver nanoparticles further improves the electrochemical kinetics of the TiO<sub>2</sub>-NWs, which results in high rate capabilities and high cycle stabilities for lithium storage. At a rate of 10C, the TiO2@Ag-NWs film electrode exhibits a discharge capacity of 120 mAh/g, which is remarkably higher than the same rate capacity (86 mAh/g) of TiO<sub>2</sub>-NWs film electrode. In addition, after 120 cycles at 200 mA/g, the capacity retention is as high as 99.1% with nearly no capacity fading. The superior electrochemical performance of TiO<sub>2</sub>@Ag-NWs film electrode was attributed to the TiO<sub>2</sub>@Ag-NWs with a 3D nano-network structure and silver nanoparticles modification, which enabled faster ion transport and better electron conductivity. This surface modification is relatively simple and effective, and may be a useful approach to solve the problems of poor electronic conductivity and rate performance of TiO<sub>2</sub>. We believe that the traditional silver mirror reaction method could be applied in a wide range of fields and that TiO<sub>2</sub>@Ag-NWs could be a promising anode material for high power LIBs.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.electacta. 2015.05.076.

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