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ORIGINAL PAPER

# Spray pyrolysis-deposited $TiO_2$ thin films as high-performance lithium ion battery anodes

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## Abstract

Focusing on additive-free electrodes, thin films are of typical interest as electrodes for lithium ion battery application. Herein, we report the fabrication of $TiO_2$ thin films by spray pyrolysis deposition technique. X-ray diffraction and transmission electron microscopic analysis confirms the formation of anatase $TiO_2$. Electrochemical evaluation of these sub-micron $TiO_2$ thin films exhibits high-rate performance and long cycling stability. At 1C rate (1C = 335 mA/g), the electrode delivered discharge capacity of 247 mAh/g allowing about 0.74 lithium into the structure. The electrodes also delivered specific capacities of 122 and 72 mAh/g at 10 and 30C rates, respectively. Without conductive additives, this excellent performance can be attributed to the nanosize effect of $TiO_2$ particles combined with the uniform porous architecture of the electrode. Upon cycling at high rates (10 and 30C), the electrode exhibited excellent cycling stability and retention, specifically only < 0.6% capacity loss per cycle over 2500 cycles.

**Keywords** Anodes · Li-ion batteries · Electrochemical characterizations · Spinel · Thin-films

## Introduction

Thin-film battery research were receiving momentous attention due to its wide spread applications ranging from RFID tags, sensors, medical devices, and micro batteries [1, 2]. This is principally due to benefit associated with the formation of additive-free electrode minimizing dead mass and maximizing utilization of entire active electrode [3]. Fabrication process for such thin-film electrodes ranges from dip-coating [4], spray pyrolysis process [3], ink-jet printing [5], physical vapor deposition [6], and chemical vapor deposition [7]. Numerous transition metal oxides, insertion-based lithium-containing compounds, and alloying electrodes were deposited by the aforementioned processes [8–10]. Among the transition metal oxides, $TiO_2$ is an interesting negative electrode for lithium ion battery applications. Out of the different polymorphs of $TiO_2$, anatase phase synthesized at low temperature emerges as an anode material with a high theoretical capacity (335 mAh/g), fairly less volume expansion (3–4%), and better lithium kinetics [11]. Yet, the innate problem of the materials is in its kinetic limitation allowing only 0.5 Li into the lattice. This can easily be tackled by nanostructuring thus reducing the diffusion lengths and improving the practical capacity values [12].

$TiO_2$ thin films as battery electrodes are well investigated through different fabrication techniques [3, 13, 14]. However, the intricate processes parameters and the requirement of sophisticated equipment with high vacuum conditions complicate the fabrication processes, posing serious challenges to the scale-up of the films. In order to address the aforementioned issues here, we demonstrate the fabrication and electrochemical characterization of $TiO_2$ thin films through a simple and scalable spray pyrolysis deposition technique. The process involves the atomization of a colloidal sol solution and deposition of the same onto a heated substrate. Since the sol was synthesized prior, control in $TiO_2$ particle size can easily be achieved. Further, the spraying process does not need any high vacuum condition and can be carried at low temperature conditions. The same technique can be utilized to fabricate well-compacted films over large area demonstrating the potential of

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same to be extended to large scale applications as well. An added advantage is in its capacity to tune film thickness (even up to 100 s of microns) by varying the duration of deposition [3]. In this work, we report the high-rate electrochemical performance of additive/binder less $TiO_2$ thin films for lithium ion battery applications. The SPD-$TiO_2$ film crystallized in anatase phase was observed to have interlinked nanosized $TiO_2$ particles forming a porous electrode structure which attributes to the excellent electrochemical and cycling performances. The same rendered high-specific capacity of 274 mAh/g at 1C and ≤ 0.6% capacity loss per cycle for over 2500 cycles at both 10 and 30C rate.

## Materials and methods

Titanium isopropoxide, ethanol, Triton-X 100, and acetic acid were purchased from Sigma-Aldrich. Stainless steel substrate (SS 316 with 0.1 mm thick) used for deposition was obtained from MTI (USA). The synthesis and spray pyrolysis deposition has been described by Haridas et al. [3]. Prior to deposition, a colloidal technique was carried out to synthesis $TiO_2$ nanoparticles wherein 10 ml titanium isoproxide dissolved in mixture of 15 ml isopropanol and 1.5 ml acetic acid was allowed to precipitate by passing steam. The resulting thick mass was diluted with distilled water and allowed to stir until formation of a proper dispersion. Later stabilization of the colloidal mass was done through a hydrothermal technique maintaining the solution at 180 °C for 3 h. Further, 10 ml of this solution was diluted with 10 ml isopropyl alcohol, 2.5 ml of acetic acid, and 3 drops of Triton-X 100 and used as such for spray deposition. Optimized spraying conditions to obtain films of 0.7 mg/cm$^2$ loadings were temperature 110 °C, flow rate 6 ml/min, and post annealing at 400 °C for 3 h in air.

Thin-film X-ray diffraction analysis was conducted in Rigaku (Ultimate IV Japan) diffractometer with scan rate of 1°/min. Surface and cross sectional images were performed in FEI Nova NanoSEM while transmission electron microscopic imaging were carried out in transmission electron microscopic (TEM) Technai FEI-G$^2$. Surface analyses were done using XPS Kratos (Axis Ultra UK) with Al-K$\alpha$ as X-ray source. Obtained annealed films were used as such for cell fabrication in Swagelok setup with lithium metal as reference/counter electrode and 1 M $LiPF_6$ (EC/DMC = 1:1) as electrolyte. All electrochemical measurements were conducted in battery cycler Arbin (BT 2000) in 1 ≤ V ≤ 3 potential window.

## Results and discussions

Annealing the SPD-$TiO_2$ films at 400 C results in crystallization of the sample in anatase phase. Figure 1 shows the thin-film XRD pattern of the SPD-$TiO_2$ film deposited on stainless steel substrate. This is in concurrence with data available in literature with 100% intensity peak indexed to (101) of anatase $TiO_2$ [11, 12, 15].

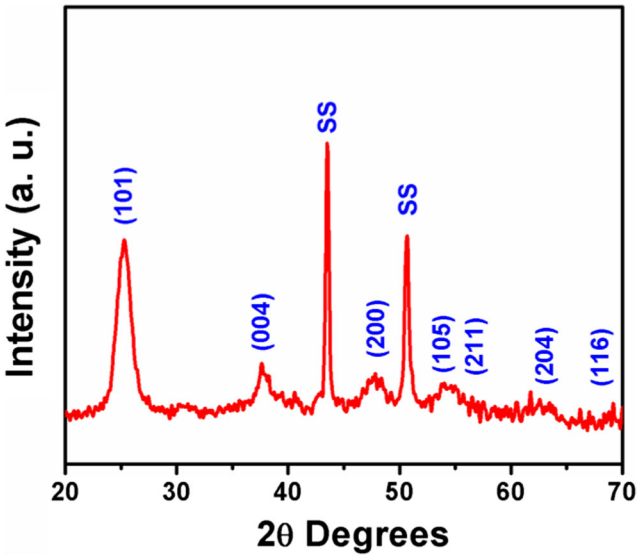


**Fig. 1** Thin-film XRD pattern of the spray pyrolysis-deposited $TiO_2$ film

Scanning electron microscopy images depicted in Fig. 2a shows the surface image of the as-deposited film. As can be visualized, the films were composed of interconnected $TiO_2$ nanoparticles with pores in-between. It is well established that such porous films favor better electrolyte access throughout the entire film leading to better lithium ion transport [3, 16]. Porous nature of the film can even be confirmed from cross-sectional image shown in Fig. 2b, and the imaging was done by spraying the $TiO_2$ colloidal solution on silicon substrate. The sample was then cleaved to get a clear image of the cross-section of SPD-$TiO_2$ film. Spray pyrolysis deposition was optimized in order to obtain an electrode active loading of 0.7 mg/cm$^2$ which was observed to have a thickness of around 3 μm.

TEM image of the colloidal $TiO_2$ nanoparticles used for SPD deposition are shown in Fig. 3a. TEM image shows uniformly sized nanoparticles of average 12–15 nm in size, while HRTEM image (Fig. 3b) shows crystalline particles of lattice spacing 0.35 nm which corresponds to (101) plane of anatase phase of $TiO_2$.

XPS spectra of the SPD electrode are presented in Fig. 4. Figure 4a displays the survey spectra and the absence of any parasitic signals except that of Ti, O, and C confirm the purity of the sample. Curve fitting the high-resolution Ti 2p spectra (Fig. 4b) shows Ti in $4^+$ oxidation state which was confirmed from the Ti $2p_{3/2}$ and Ti $2p_{½}$ binding energies and from the spin-orbit separation value of 5.7 eV [17, 18]. Deconvoluting the high-resolution O 1 s spectrum (Fig. 4c) results in two curves peaking at around 529.4 and 531.2 eV. Former can be related to the presence of lattice oxygen Ti-O while later one with lesser intensity to adsorbed hydroxyl ions [19].

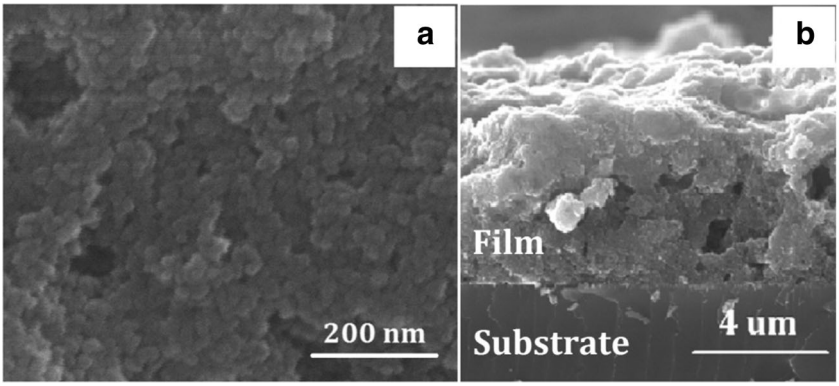


**Fig. 2** **a** Surface SEM image of the deposited $TiO_2$ film. **b** Cross-sectional image showing porous in-between

## Electrochemical characterizations

Electrochemical performance of SPD-$TiO_2$ thin-film electrodes are presented in Fig. 5. Figure 5a shows the charge-discharge profile of SPD-$TiO_2$ films at three different C-rates (1C = 335 mAh/g) from 3 to 1 V voltage window. As can be seen, the electrode showed typical anatase $TiO_2$ profile with discharge plateau at 1.7 V and charge at 2.1 at 1C rate, and the electrode was capable of rendering first discharge capacity of 247 mAh/g. The nanosized $TiO_2$ particles facilitate the lithiation of more than 0.5 Li into the lattice which is kinetically restricted in bulk particles. At 3C rate, the electrode delivered discharge capacity of 175 mAh/g and charge capacity of 149 mAh/g. Upon increasing the C-rate to 10C, the electrode was observed to have slightly polarized voltage profiles yet delivering 122 and 115 mAh/g as discharge and charge capacity, respectively.

Further, to understand the high rate and cycling stability of SPD-$TiO_2$ electrodes, we have cycled electrodes at 10 and 30C rates for 2500 cycles. Figure 5b shows 10C charge-discharge profiles at different cycle numbers, wherein the initial cycle capacity was observed to be 122 mAh/g and with a Coulombic efficiency of 94% refer Fig. 6a. Subsequently, the Coulombic efficiency value increases and attains almost 99.2 and 99.7% at 10 and 30C respectively till the end of 2500 cycles. This capacity/retention values are better than several reports on $TiO_2$ nanostructures [20, 21]. The SPD-$TiO_2$ electrode displayed negligible capacity loss per cycle (0.6%) while maintaining a capacity of 106 mAh/g at the end of 2500 cycles. Both 10 and 30C long cycling performance is depicted in Fig. 5c. The electrode was capable of rendering excellent cycling stability even at a high rate of 30C. Even after 2500 cycles, the electrode retained 95.6% of its initial capacity indicating the electrodes potential for high-power, long-life applications. As a comparison, we have investigated the electrochemical performance of synthesized $TiO_2$ nanoparticles casted via the conventional slurry casting method with mass ratio 70:20:10 (active material: conductive carbon: PVdF). From the electrochemical results (Fig. 6b), it is confirmed that even with a high amount of conductive carbon (20%) in the composite electrode was able to deliver similar yet slightly less capacity at 10C rate. This improved performance emerges from the deposition of nanosized $TiO_2$ particles as interconnected porous film through spray pyrolysis deposition leading to better electrolyte percolation and kinetics. It may be noted that the SPD technique is capable of fabricating additive-free electrodes in large scale and with high rate of deposition. Thus, the excellent performance of $TiO_2$ thin films fabricated via SPD technique validates the advantages of having additive-free, high energy density electrodes for lithium ion batteries, which can even be extended to other electrode materials.

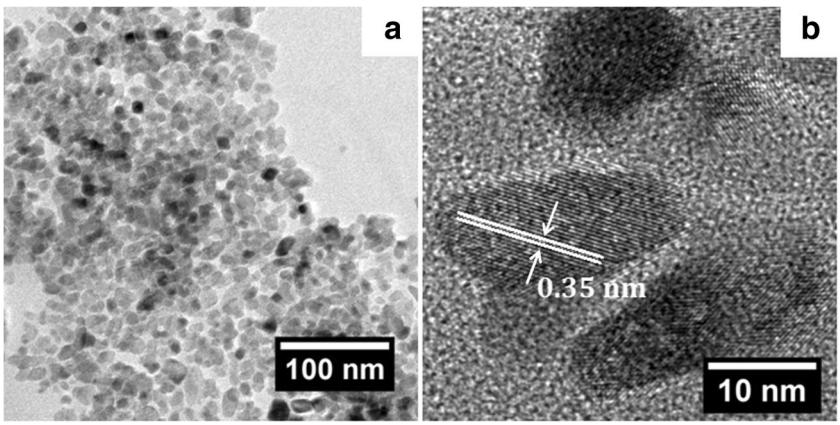


**Fig. 3** **a** Low magnification TEM image of the $TiO_2$ particles. **b** High-resolution image showing crystalline particles

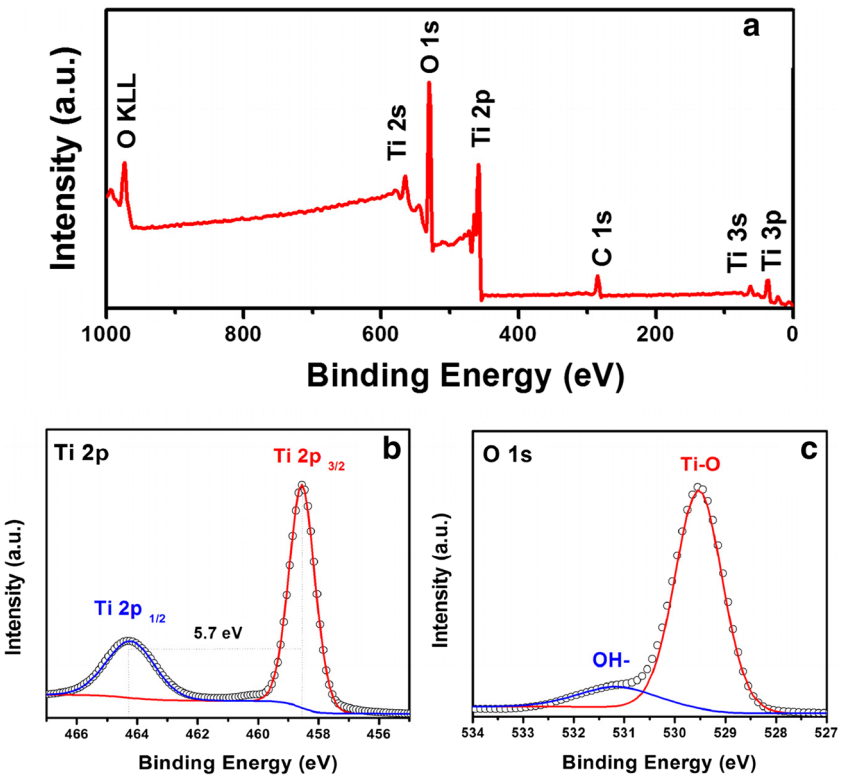


**Fig. 4** XPS spectra of the spray pyrolysis-deposited $TiO_2$ film **a** survey scan, **b** Ti 2p high-resolution spectra, and (**c**) O 1 s spectra

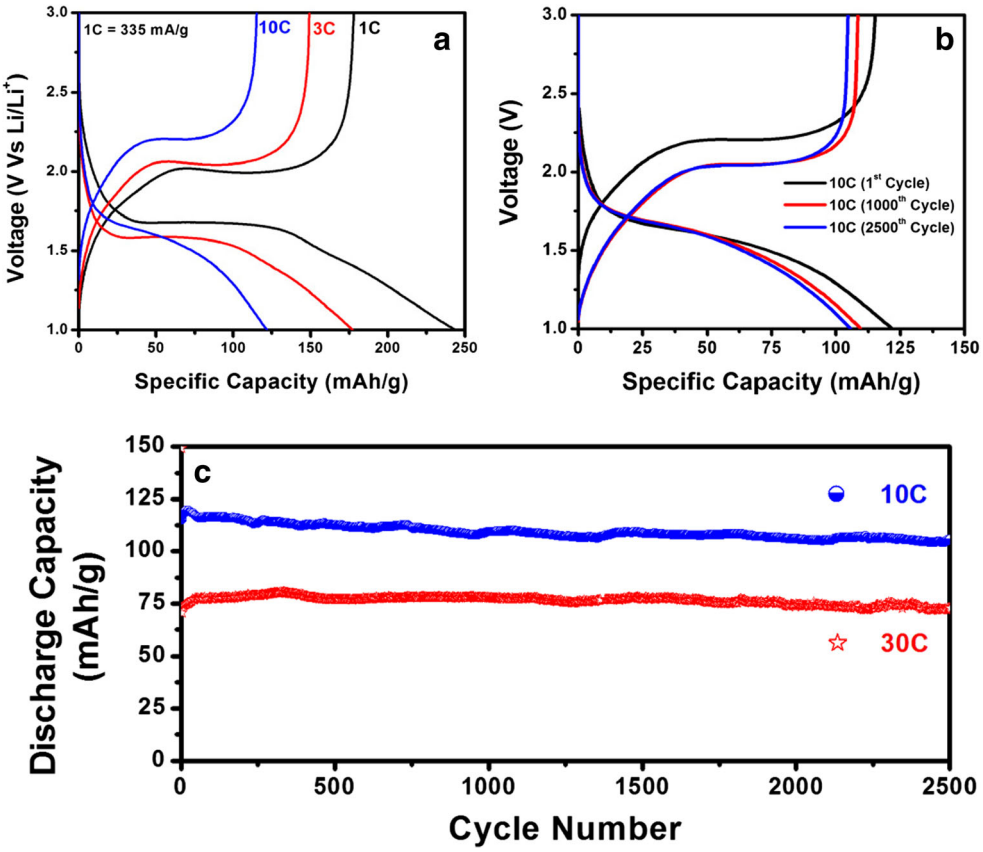


**Fig. 5** Electrochemical performance of SPD-$TiO_2$ electrode **a** charge-discharge profiles at different rates, **b** 10C cycling profiles at different cycle numbers, and **c** long cycling performance at 10 and 30C as indicated in legend

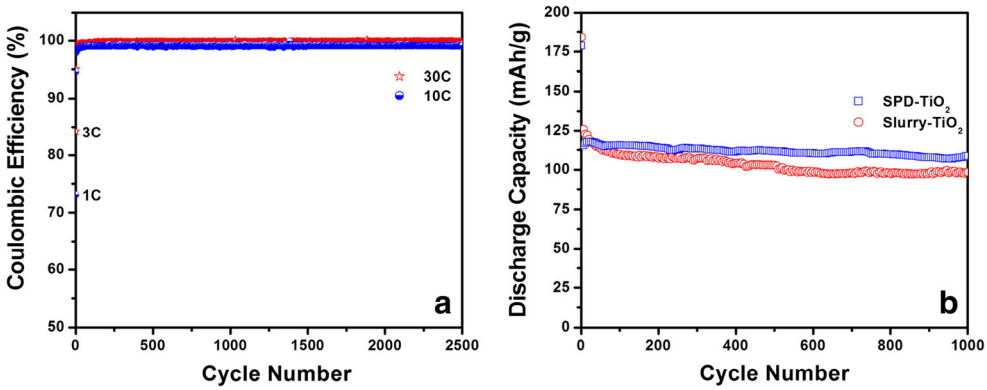


**Fig. 6** **a** Coulombic efficiency plot of the SPD-$TiO_2$ electrode at both 10 and 30C rate. **b** 10C cycling performance of SPD-$TiO_2$ and slurry-$TiO_2$ samples as indicated in legend

## Conclusions

In this report, we have demonstrated fabrication of additive-free $TiO_2$ thin films through spray pyrolysis deposition technique. Uniqueness of this technique is in its capability to fabricate large scale films of uniform and tunable thickness with excellent particle-particle electrical contact and good porosity. Since the particles are synthesized prior to deposition, control over the particle size is also feasible. Utilizing these additive-free electrodes as lithium ion battery electrodes, we have demonstrated excellent electrochemical performance in terms of its cycling stability (2500 cycles) and high-rate capability (30C). The electrode delivered 274 mAh/g at 1C rate while at high rates of both 10 and 30 C; the electrode delivered stable capacity with negligible loss (< 0.6% per cycle) for almost 2500 cycles. Our results ascertain spray pyrolysis deposition technique as an effective technique in fabricating additive-free thin-film electrodes and can be extended to 3D micro batteries, flexible energy storage, and conversion devices.

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### Compliance with ethical standards

**Conflicts of interest** The authors declare that they have no conflicts of interest.

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