

Chapter 2

Film Deposition on a Wire/Fiber via In Situ Joule Heating Process

As argued in Chap. 1, photovoltaic performance of thin-film solar cells is highly relied on the quality of multilayer functional films and their interfaces. Thanks to extensive researches on planar thin-film solar cells, film deposition technologies on planar substrates via vacuum processes, such as sputtering, thermal evaporation, epitaxial growth, etc., as well as solution processes such as spin-coating, printing, blading, etc., have been well established. Depositing films on high-curvature wire/fiber substrates via these technologies was tried, but few successes were achieved with poor device performance due to poor film and interface quality. Unique device architecture as well as film deposition technologies compatible with wire/fiber substrates are urgently desirable for fiber solar cells.

In this chapter, I will demonstrate a novel film deposition technology on a conducting wire/fiber via in situ Joule heating process, which has below advantages: rapid film deposition with high film quality, high reproducibility, capability to deposit multilayer functional layers of thin-film solar cells, low energy consuming by confining heating on wire/fiber substrates, compatible with large-scale production process, such as roll-to-roll and cup-to-cup process. I will demonstrate this process by depositing multiply functional thin films, to fabricate fiber working electrodes for fiber dye-sensitized solar cells (DSSCs).

For fiber DSSCs, the fiber working electrode, consisting of a dense TiO_2 layer, a sensitized mesoporous TiO_2 layer, and a hole-transport layer on a fiber/wire substrate, plays a critical role in light-harvesting, exciton separation, and charge carrier transport process. In Zou's pioneering work, functional TiO_2 and CuI (hole-transport materials) precursor solutions were manually drop-coated on a stainless steel or Ti wire and then annealing at high temperature with external heating sources, such as hotplates, furnaces, or IR lamps [1, 2]. However, it is very challenge to control the film qualities via those methods, and both device performance and reproducibility are rather poor. Considering unique requirements for fiber working electrodes for fiber DSSCs, I will introduce a homemade automatic Joule-heating film-depositing system, optimize the critical processing parameters, and demonstrate several strategies to improve film qualities as well as device

performance. Besides, scalable high-quality fiber working electrodes will provide a platform to research on other components and working mechanism of fiber DSSCs.

2.1 Setup of Joule Heating on-a-Wire Film-Depositing Systems

Considering cylinder shape of fiber substrates, our setup consists of four parts: a driving system, which draws the fiber along the axial direction and rotates it along the axial direction, simultaneously; a high power current supply, which interconnects with a conducting fiber substrate, generates Joule heat on the fiber; a precursor source, which can be in gas state or in solution state; a ambient chamber to guarantee all processing in a required environment, such as vacuum, active or inert gas protection. When the fiber was heated up to a setting temperature, it is drawn and rotated through precursor sources, which will physically or chemically decompose and uniformly deposit on the surface of the fiber to a desirable film thickness.

In order to calibrate the temperature-heating current relationship of fiber substrates, a Ti wire (with resistivity of $0.42 \mu\Omega\text{m}$ and diameter of $250 \mu\text{m}$) is wound around a thermocouple, and the measured data was consistent with theoretical relationship ($T \sim I^2$), yet overestimation of temperature is expected due to crowded arrangement of Ti wires. To estimate more accurate temperature, thermal expansion of Ti wire was measured, and the temperature is calculated with as known linear thermal expansion coefficient value of Ti. We found that typical annealing temperature of 450°C for DSSC fabrication can be achieved by applying a current of 1.3 A.

With heating current of 1.3 A (estimated temperature 450°C) for 15 min., Silver-shining Ti wire turns to yellow-to-purple color if supplying oxygen or air gas as precursor, indicating Ti was oxidized to TiO_x , and a dense thin film was formed, which is similar to TiO_x dense layers via annealing Ti wire in a furnace oxidizes. The thickness of this dense film is around several to tens of nanometers according to previous work on planar substrate, but further thickness measurement of this film on Ti wire was failed due to the limitation of our characterization facility.

After switching the precursors to TiO_2 colloids (Degussa P25: acetylacetonate: water 2 g: 0.4 mL: 2 mL), we tried to deposit a mesoporous TiO_2 film on a Ti wire. As shown in Fig. 2.1, the as-prepared mesoporous TiO_2 film was uniformly coated on the Ti wire, which is much smoother than the film used to be deposited with an external IR lamp heating. Besides, we found that stability of current/precursor supply and fiber driving rate is critical to obtain a uniform film. Thus, including optimizing hardware of our setup, critical processing parameters, such as current, coating rate, rotating rate as well as colloid components were optimized as below in order to obtain high-quality fiber electrodes, which will be further evaluated by comparing the photovoltaic performance of assembled all-solid-state fiber DSSCs (Ti wire/dense TiO_x /mesoporous TiO_2 /N719/CuI/Au wire).

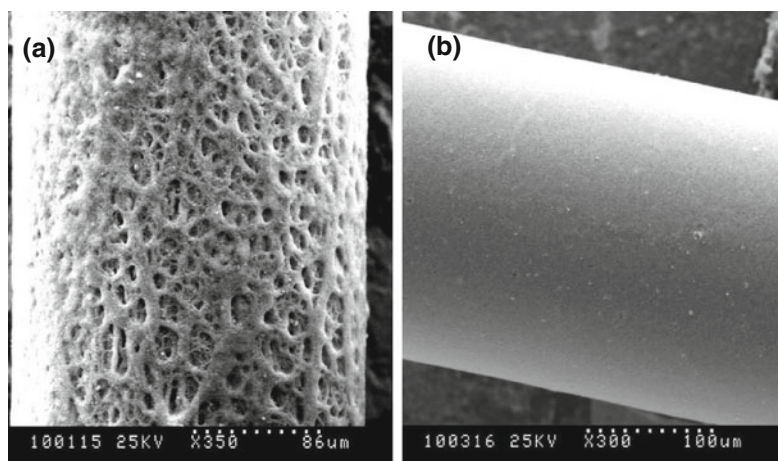


Fig. 2.1 SEM images of TiO₂ mesoporous film on Ti wire deposited via IR lamp heating (a) and Joule heating (b)

2.2 Optimization of TiO₂ Mesoporous Film Deposition

2.2.1 Heating Current

The heating current is chosen according to the required temperature of physical process or chemical reaction for film deposition. Compared with dense TiO₂ film via in situ oxidation reaction, mesoporous TiO₂ film that required much low temperature was deposited by drying TiO₂ nanocrystals colloids. We found that when coating at high heating current (≥ 0.9 A), TiO₂ nanocrystals colloids were unstable and the adhesion of as-coated TiO₂ film was very poor due to fast solvent evaporation and decomposition of organic additives at high temperature. Film quality is improved when decreasing heating current, while much longer time or repeating times of coating process was required to achieve the same film thickness. The heating current was optimized at 0.7 A to achieve best film quality, such as adhesion, uniformity, thickness of the film.

These fiber electrodes were sensitized and then assembled to all-solid-state fiber DSSC (device architecture: Ti/TiO₂ dense layer/TiO₂ mesoporous layer/N3 or N719/CuI/Au wire). Notably, the as-coated mesoporous TiO₂ film had to be annealed at high temperature (at 450 °C) either in a furnace or our system (at 1.3 A or above) before dye sensitization in order to get rid of organic additives. Figure 2.2 shows typical current–voltage (J–V) curve of our fiber DSSCs prepared at different heating currents under a calibrated solar simulator (100 mW/cm², AM 1.5) or dark environment. Calculated from J–V curve, the preliminary efficiency was in the range of 0.5–0.9%, which is comparable or even higher than the best value reported before. The optimized heating current at 0.7 A gave best device performance.

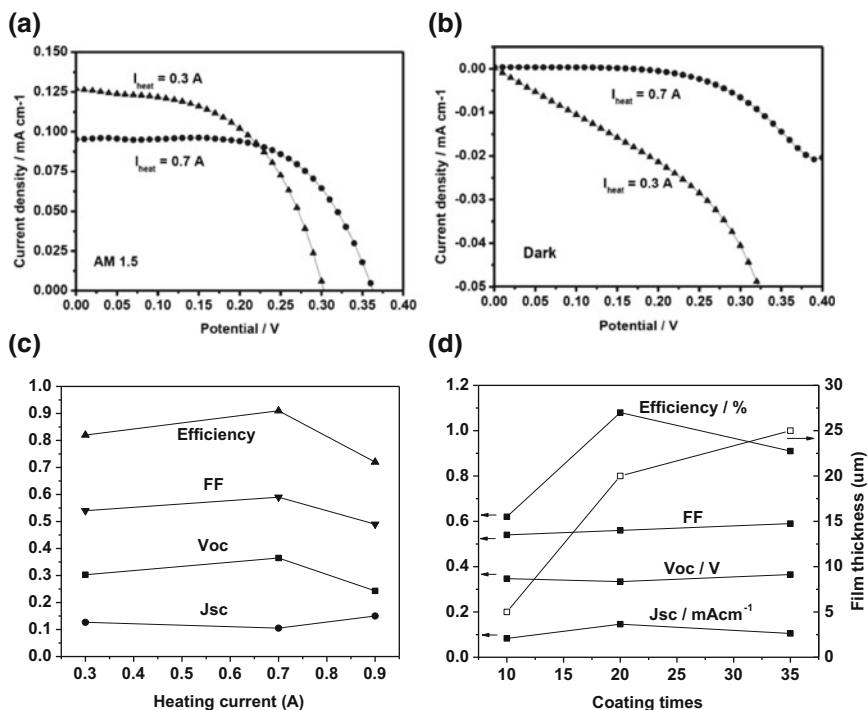


Fig. 2.2 Photovoltaic performance of all-solid-state fiber DSSCs fabricated at varied heating currents and coating times

Notably, the projected area of the working electrode was used to calculate efficiency through this entire thesis, unless otherwise specified.

2.2.2 Coating Times

In addition to heating current, film thickness can be controlled by repeating the coating process. With the same heating current (0.7 A), film thickness can be increased to 25 μm if the coating process is repeated up to 30 times, and the film uniformity was maintained. However, some small cracks were found if the film thickness was continued to increase with coating times.

Compared with three TiO₂ film thicknesses (5, 20 and 25 μm), short-circuit current density and efficiency of as-prepared all-solid-state fiber DSSCs first increased and then decreased with the increase of film thickness. The short-circuit current of DSSCs highly depends on the thickness of mesoporous TiO₂ films, which determined the loading amount of dyes. For thinner TiO₂ film, limited dye sensitizers absorbed on TiO₂ nanocrystals were limited, which cannot efficiently harvest incidental light.

On the other hand, the loss of photogenerated carriers during transporting through thick TiO₂ film before being collected by Ti wire was much more serious. After optimization, the device with thickness of 20 μm showed best performance.

2.2.3 Drawing Rate and Rotating Rate

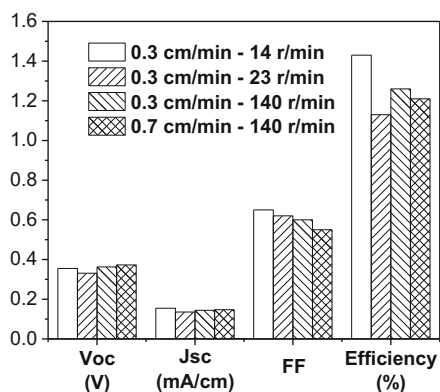
Compare with planar substrate, one feature of the fibers/wires is their high-curvature axial-symmetric shape, which requires more effort to control the film uniformity along both radical and axial directions during film deposition. Rotating the fibers/wires along the axial direction during drawing was used to create almost identical coating condition for the whole fibers/wires. Rotating with a rate of 14 r/min. is enough to guarantee good device performance (efficiency 1.43%), which was much higher than other reported devices.

High drawing rate with acceptable film quality is desirable for fast film/device fabrication. The efficiency was almost same when increasing drawing rate from 0.30 to 0.74 cm/min. Notably, TiO₂ colloid droplet in a small container of our setup was disturbed if drawing too fast, which may be avoided by reasonable designs of containers or spraying colloids (Fig. 2.3).

2.2.4 TiO₂ Colloids

As reported in previous work, the film quality of mesoporous TiO₂ and device performance of planar DSSCs are highly relied on TiO₂ colloids, such as TiO₂ nanocrystals, solvents, additives, etc. For solid-state DSSCs, porosity and nanostructures of TiO₂ film have to be reasonably designed in order to improve the interfacial contact between TiO₂ and hole-transport materials, which is less likely to

Fig. 2.3 Photovoltaic parameters of all-solid-state fiber DSSCs fabricated at varied drawing rates and rotating rates



be filled into the pores in the TiO_2 films than liquid-state electrolytes. We tried to use polystyrene beads (dia. 100–500 nm) as self-sacrificed templates to tune the porosity of TiO_2 films. However, polystyrene aggregates were observed when directly dispersing unmodified polystyrene nanobeads powder into our TiO_2 colloids (P25/acetylacetonate/water) due to their high hydrophobic properties. PEO was used as surfactant to disperse polystyrene beads in water or ethanol before mixing with TiO_2 colloids, but the stability did not improve as expected due to low binding interaction of PEO on polystyrene beads. Thus, we synthesized highly stable aqueous polystyrene colloids with monodispersed particle size by emulsion polymerization, which were mixed with TiO_2 colloid with different volume ratio. The mixed colloids with polystyrene/ TiO_2 ratio from 0.05 to 0.6 are stable enough to be processed by our Joule-heating film deposition process, while aggregation was observed when ratio is higher than 0.6.

This modified TiO_2 colloids were deposited on Ti wire with TiO_2 dense films, and then polymer templates were removed via high-temperature annealing, before assembled to all-solid-state fiber DSSCs, leading to improved efficiency. The details on film deposition, device fabrication, and characterization with this mixed colloids could be found elsewhere [3], if readers are interested.

2.2.5 Surface Modification

In order to further improve film quality, TiO_2 mesoporous film was surface functionalized with metal oxides. The as-prepared Ti wire with TiO_2 mesoporous layers was soaked in four metal ions aqueous solutions, TiCl_4 , $\text{Zn}(\text{NO}_3)_2$, $\text{Zn}(\text{Ac})_2$, and $\text{Mg}(\text{Ac})_2$, which were then decomposed to corresponding metal oxides (TiO_2 , ZnO , and MgO) via another high-temperature annealing.

Surface modification by ZnO , which has better electronic mobility than TiO_2 , was found to improve the open-circuit voltage and thus efficiency (to 1%) of all-solid-state fiber DSSCs. Compared to $\text{Zn}(\text{Ac})_2$ precursor, $\text{Zn}(\text{NO}_3)_2$ showed better results, which indicates the counter anions also play a significantly role in the surface modification due to different solubility and hydrolysis properties (Fig. 2.4).

It is reported that MgO can passivate the surface traps within mesoporous films and surpass the recombination process of injected electrons in TiO_2 back to dyes or hole-transport layers. However, we failed to see any improvement of photovoltaic performance, which probably due to not optimized processing parameters, such as anion types, concentration, processing temperature and time, etc.

Among three metal oxides, TiO_2 was found to be most effective to improve the photovoltaic performance, where open-circuit voltage, short-circuit current, filled factor as well as efficiency were increased simultaneously. This additional TiO_2 modification improved film quality by passivating surface traps of mesoporous TiO_2 films. Besides, a layer of fine TiO_2 nanoparticles with diameter less than 5 nm formed on P25 TiO_2 nanoparticles observed by SEM, which increased surface area of TiO_2 mesoporous film and absorb more dyes.

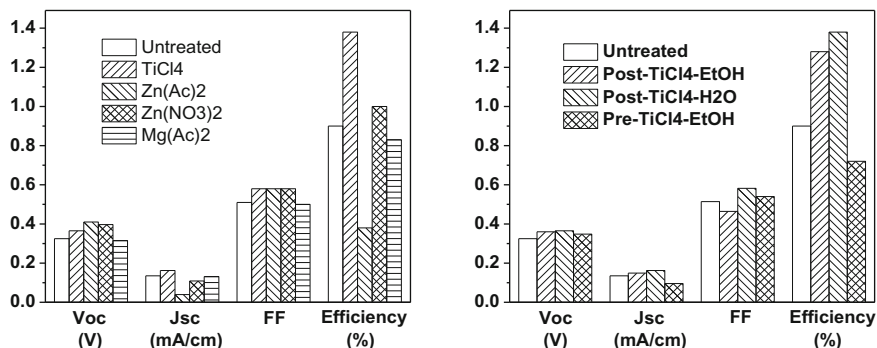


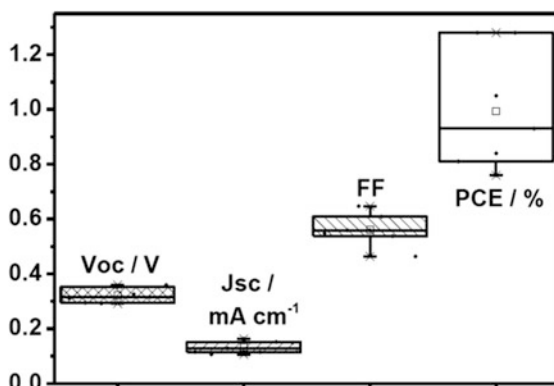
Fig. 2.4 Effect of posttreatment on photovoltaic parameters of all-solid-state fiber DSSCs

In order to optimize TiO₂ surface modification processing, we further investigated the effect of different solvents for metal ions solution. Although both TiO₂ precursors in ethanol and water were able to improve the device performance, aqueous solution showed slightly higher short-circuit current and filled factor. Moreover, it was found that surface modification immediately after depositing mesoporous films before first annealing process gave best device performance.

2.2.6 Reproducibility and Stability

After optimization, our film deposition processing has good reproducibility. The photovoltaic parameters of seven batch of all-solid-state fiber DSSCs fabricated with our method were statistic analyzed in Fig. 2.5, and average efficiency above 1% was achieved, which was the best result so far. The photovoltaic performance

Fig. 2.5 Statistic photovoltaic parameters of seven batch of all-solid-state fiber DSSCs



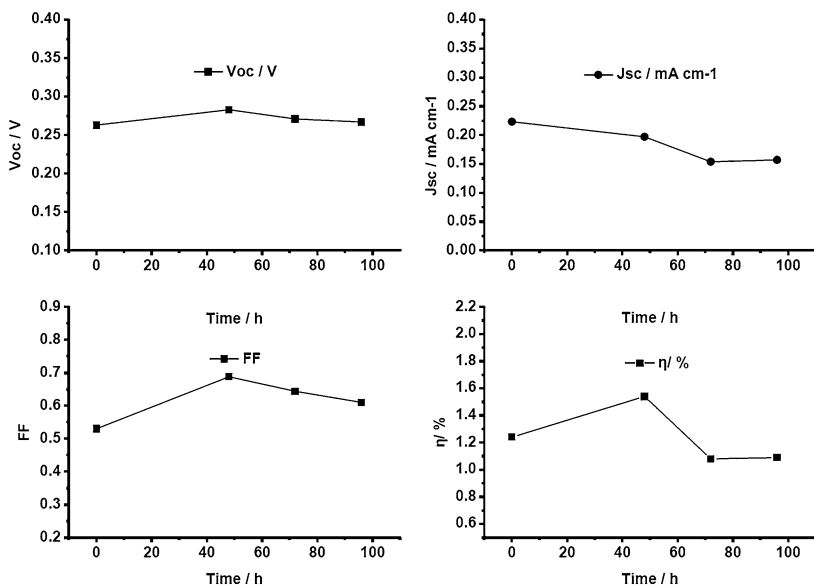


Fig. 2.6 Short-term stability of all-solid-state fiber DSSCs

can be highly enhanced by placing a white plastic foam board underneath of the device, and the apparent efficiency was as high as 2.97%.

Device stability is another critical parameter for solar cells. Our devices showed slightly increase of efficiency to 1.54%, and was maintained at 90% of initial efficiency after 100 h (Fig. 2.6). Long-term stability was also confirmed, and the performance of the device encapsulated with a thin layer of PMMA maintained at 1.2% even after 2 years storage.

2.3 Capability of Depositing Multifunctional Layers on a Fiber/Wire

Our Joule-heating film deposition approach is capable to deposit other functional materials, such as hole-transport materials, as well as stack multilayers on a fiber/wire for fiber solar cells. For solid-state DSSCs, it is very challenging to deposit high-quality hole-transport layers on TiO₂ mesoporous layers, and their poor interfacial contact was usually blamed for the higher charge recombination and lower device performance, compared with liquid-state DSSCs.

We tried to deposit a CuI hole-transport layer on a Ti wire with the sensitized TiO₂ mesoporous film using the same CuI precursor solutions (30 mg/mL CuI,

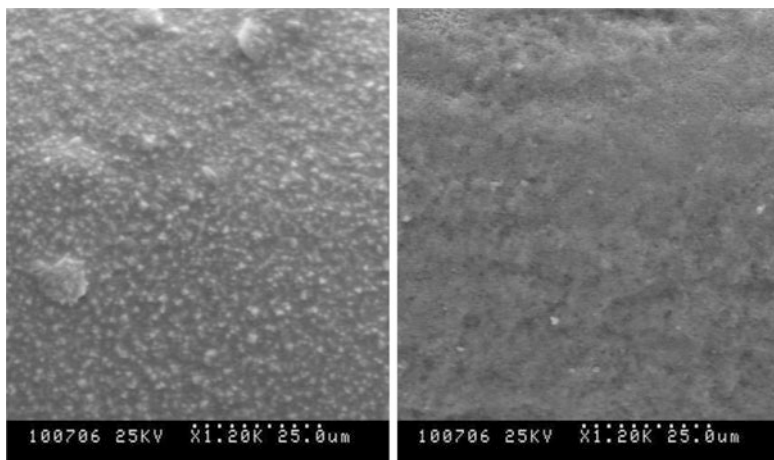


Fig. 2.7 SEM images of CuI films deposited by drop-casting (*left*) and Joule heating (*right*)

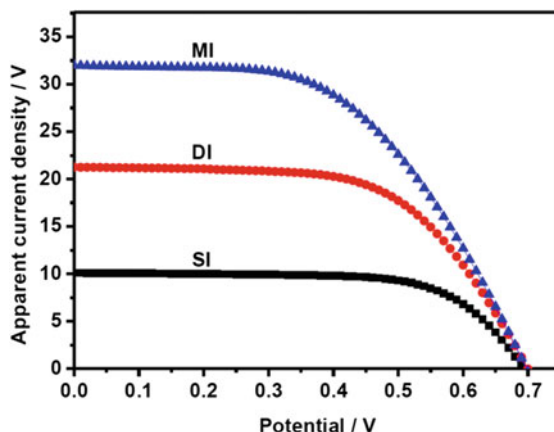
1.5 mg/mL 3-ethylimidazole thiocyanate in acetonitrile) previously optimized for fiber DSSCs by Zou's group. As a reference, CuI film was also prepared by drop-casting on a Ti wire with TiO₂ mesoporous layers on a hotplate at 100 °C in the N₂-filled glovebox. Figure 2.7 shows the typical morphologies of as-prepared CuI film prepared by above two methods. From SEM images, CuI film prepared by our methods was as uniform as that prepared by drop-casting methods, while the crystal size was much smaller. It indicates the fast crystalline process of CuI during solvent evaporation was significantly suppressed due to localized heating on the fiber/wire via our method. However, the fine CuI crystals were too loose to guarantee the electronic contact and mechanical strength, which required further optimization processing and posttreatment, such as annealing.

Very recently, Zou's group has also successfully deposited perovskite light absorbers on a titanium wire via this method, which was further assembled to fiber perovskite solar cells or memories with impressive performance.

2.4 Liquid-State Fiber DSSCs

As reviewed in Chap. 1, liquid-state planar DSSCs currently hold much high photovoltaic performance than all-solid-state ones. To pursuit possible maximum efficiency of fiber solar cells, the fiber working electrodes (Ti wire/TiO₂ dense layer/TiO₂ mesoporous layer/N719) were wounded with a platinum-coated carbon fibers, sealed in a glass capillary (dia. 0.9 mm) filled with liquid electrolyte

Fig. 2.8 J-V curves of liquid-state fiber DSSCs under normal illumination (SI, 100 mW/cm^2 , AM 1.5), Double-side illumination (DI), and light-concentrating condition (MI)



(containing 0.03 M I_2 , 0.5 M BMII , $1.5 \text{ vol.}\%$ tert-butylpyridine in acetonitrile), and then assemble to liquid-state DSSCs.

Under normal illumination condition, V_{oc} , J_{sc} , FF, and efficiency of this liquid-state fiber DSSCs were 0.69 V , 10.11 mA/cm^2 , 0.67 and 4.72% , respectively, which was significant higher than that of all-solid-state fiber DSSCs. Thanks to 3D light-harvesting capability, the J_{sc} and efficiency of the device were increased twice under double-side illumination by placing a white plastic foam underneath. The apparent efficiency could further be promoted to 11.8% with a microgroove concentrator, which confirmed high quality of fiber electrodes fabricated by our Joule-heating film deposition approach (Fig. 2.8).

2.5 Summary

This chapter introduced a novel film deposition approach on nonplanar fiber substrates utilizing in situ Joule heating. A prototype setup was demonstrated, and processing conditions were optimized to obtained high-quality fiber electrodes. When 1.3 A of electric current on applying Ti wire ($250 \text{ }\mu\text{m}$ in diameter and 35 cm in length) in air, a dense TiO_x film can be deposited. To deposit high-quality mesoporous TiO_2 film, the best parameters are 0.7 A of heating current, 0.3 cm/min of drawing rate, $14\text{--}140 \text{ r/min}$ of rotating rate, coating 20 times, and posttreating with TiCl_4 solution. The all-solid-state and liquid-state fiber DSSCs fabricated by this method reached 1.24 and 4.72% , respectively, exceeding previously reported devices fabricated manually (0.2 and 0.5% , respectively). Besides, this method had good reproducibility and was capable to be scaled up.

References

1. Fan X, Chu ZZ, Wang FZ, Zhang C, Chen L, Tang YW, Zou DC (2008) Wire-shaped flexible dye-sensitized solar cells. *Adv Mater* 20 (3):592–+. doi:[10.1002/adma.200701249](https://doi.org/10.1002/adma.200701249)
2. Fan X, Chu ZZ, Chen L, Zhang C, Wang FZ, Tang YW, Sun JL, Zou DC (2008) Fibrous flexible solid-type dye-sensitized solar cells without transparent conducting oxide. *Appl Phys Lett* 92(11). Artn 113510. doi:[10.1063/1.2891051](https://doi.org/10.1063/1.2891051)
3. Wang D, Hou S, Wu H, Zhang C, Chu Z, Zou D (2011) Fiber-shaped all-solid state dye sensitized solar cell with remarkably enhanced performance via substrate surface engineering and TiO₂ film modification. *J Mater Chem* 21(17):6383–6388. doi:[10.1039/c1jm00016k](https://doi.org/10.1039/c1jm00016k)

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