Journal of Colloid and Interface Science 478 (2016) 172–180

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

Regular Article

# Continuous wet-process growth of ZnO nanoarrays for wire-shaped photoanode of dye-sensitized solar cell

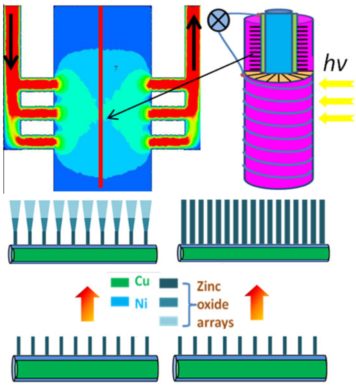
Pan Tao[a,b], Wanwan Guo[b], Jun Du[b], Changyuan Tao[b], Shenglan Qing[a,*], Xing Fan[a,b,*]

[a] State Key Laboratory of Coal Mine Disaster Dynamics and Control, Chongqing University, 400030 Chongqing, PR China
[b] College of Chemistry and Chemical Engineering, Chongqing University, 400030 Chongqing, PR China

## HIGHLIGHTS

- Well-aligned ZnO nanoarrays were grown on flexible wires via continuous wet process.
- The as-grown ZnO nanowires have finely-controlled length and uniform thickness.
- The micro flow field affects both the morphology and the pattern of the nanoarray.
- Photoanodes from the continuous reactor exhibited better photovoltaic performance.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

*Article history:*
Received 7 April 2016
Revised 29 May 2016
Accepted 2 June 2016
Available online 3 June 2016

*Keywords:*
Continuous reactor
ZnO nanoarray
Wire-shaped dye-sensitized solar cells
Wet process

## ABSTRACT

Well-aligned ZnO nanorod arrays have been grown on metal-plated polymer fiber via a mild wet process in a newly-designed continuous reactor, aiming to provide wire-shaped photoanodes for wearable dye-sensitized solar cells. The growth conditions were systematically optimized with the help of computational flow-field simulation. The flow field in the reactor will not only affect the morphology of the ZnO nanorod\nanowire but also affect the pattern distribution of nanoarray on the electrode surface. Unlike the sectional structure from the traditional batch-type reactor, ZnO nanorods with finely-controlled length and uniform morphology could be grown from the continuous reactor. After optimization, the wire-shaped ZnO-type photoanode grown from the continuous reactor exhibited better photovoltaic performance than that from the traditional batch-type reactor.

## 1. Introduction

Semiconductive zinc oxide materials have attracted great interest because of their important roles in nano-electronic and opto-electronic devices, including light-emitting diodes, field-effect transistors, optical sensors, and solar cells [1–6]. Well-aligned ZnO nanowires or nanorods with different patterns have been deposited on various types of conductive electrode substrate and successfully enhanced the optoelectronic performance, which promoted more interests on the synthesis of ZnO nanoarrays [5–8]. Different synthesis strategies have been developed, including chemical vapor deposition, physical vapor deposition, electrochemical growth, hydrothermal growth, and template-based methods [9–13]. Among them, wet-process methods, such as hydrothermal growth, are well-investigated owing to their low

---

[*] Corresponding authors at: College of Chemistry and Chemical Engineering, Chongqing University, 400030 Chongqing, PR China (X. Fan).

*E-mail address:* foxcqdx@cqu.edu.cn (X. Fan).

http://dx.doi.org/10.1016/j.jcis.2016.06.007
0021-9797/

cost, high efficiency, wide adoptability, and industrial scalability [12–16].

New challenges have been proposed based on the recent development of wearable electronics [17], such as better flexibility and lower cost. Optoelectronic devices have been fabricated on different flexible substrates, including polymer sheets, metal mesh, or even carbon/metal wires [18]. In particular, weaving using wire-shaped devices as building blocks is an attractive strategy for fabricating wearable electric devices [19]. Taking advantages of the flexibility of the fiber, electronic devices can be made into any shaped as required. Thus, flexible solar cells in a shape of wire or mesh have been developing rapidly in recent years. To fabricate highly efficient wire-shaped solar cells, semiconductive nano oxides, such as ZnO [19,20], were assembled on conductive wire substrates. Comparing with other conductive wires, metal-plated polymer wire is of special interest, because of its high conductivity, high flexibility, low weight and low cost, simultaneously [19,21]. However, assembling well-aligned ZnO nano arrays on thin wires with high surface curvature is difficult. For one thing, the direction of nanowires changes from parallel alignment to radial alignment. For another thing, micro-turbulent flow around the wire complicates the interaction on the solution/substrate interface, resulting in enlarged defects [22]. Furthermore, most studies on wet-process growth of longer oxide nanowire were based on repeated batch-type hydrothermal reaction [23,24]. To provide better optimization for the device structure, the ZnO growth process should be finely controlled continuously, aiming to synthesize well-aligned array of nanowires with continuously-adjustable length and morphology.

Herein, the continuous growth of ZnO nano arrays on metal-plated polymer wire was investigated to provide wire-shaped photoanodes with well-aligned arrays of uniform and long ZnO nanorods for wearable dye-sensitized solar cells (DSSCs). The influence of flow-field and chemical conditions during the continuous reaction process were simulated and experimentally optimized. This new synthesis strategy for ZnO-type electrode is promising for applications in many area, such as optoelectronics, energy-harvesting, biology and catalysis.

## 2. Experimental

### 2.1. Methods and materials

Electro-plated polymer\Ni wires have been reported as a type of low-cost and industrial scalable electrode substrate for wire-shaped solar cell [25]. As a typical type of low-cost and light-weight polymer substrate, insulated polybutylene terephthalate wire (0.2 mm) was selected and was chemically plated with a layer of Cu [25] to make the wire conductive before electro-plating. As is previously reported, the energy level and redox potential of Cu is not suitable for applications in DSSC [21,25]. Therefore, Ni was then electroplated on the polymer\Cu wire from an aqueous $NiSO_4$ solution (0.76 M) [25,26]. After cleaning with deionized water and drying, a layer of ZnO nanoseeds was deposited on the Ni-plated substrate using dipping method. The substrate was first dipped into the aqueous solution of zinc acetate (0.5 M) and hexamethylenetetramine (0.5 M), and then dried on a hot-plate of 180 °C for 4 min. After repeating the above process for six times, the thickness of the nanoseeds layer reached to 700–800 nm.

The substrate with the ZnO nanoseed layer was then immersed into a continuous reactor. Same concentrations of hexamethylenetetramine solution and zinc acetate solution were then pumped into the reactor simultaneously by two constant flow pumps (HL-2, Shanghai Huxi, China). Before entering the reactor, the two flows were pre-heated and pre-mixed through a PTFE tube. The pre-mixed time was controlled by the length of the tube and flow rate of the solution. The solution inside the reactor was pumped out by another constant flow pump (HL-2, Shanghai Huxi, China) to maintain the solution inside the reactor. The whole reactors were bathed in hot oil to ensure a constant temperature. After the reaction, the electrode was cleaned via deionized water and dried in vacuum. Before testing, the as-prepared working electrodes were sensitized in the ethanol solution of N719 (Solaronix, Switzerland) for 20 h [27].

### 2.2. Characterization

The morphology of the electrode was characterized using field-emission scanning electron microscopy (FESEM, JEOL, JSM-7800F). The electrochemical impedance spectroscopy (EIS) was also implemented on the electrochemical working station. EIS analysis was conducted at a bias voltage of 0 V in the dark. The photoelectrochemical tests were conducted on an electrochemical working station (CHI660D, Shanghai Chenhua). The light source was an AM1.5 standard solar simulator (XES40, San-Ei Electric, Japan) at an intensity of 100 $mW/cm^2$. For evaluation of the photoanode, the wire-shaped electrode was directly assembled on a Pt foil (99.9%); the electrolyte consisted of lithium iodide (0.5 M), iodine (0.05 M), lithium perchlorate (0.05 M), and 4-*tert*-butylpyridine (0.5 M) in acetonitrile [28].

## 3. Results and discussion

### 3.1. Growth of nano-ZnO on wire substrate in a continuous reactor

The schematic structure of a typical wire-shaped DSSC is shown in Fig. 1a. The wire-type photoanode was fabricated by growing a layer of ZnO nanoarray on a light-weight and low-cost Ni-plated polymer wire as the substrate, as illustrated in Fig. 1a. The electrolyte penetrated into tiny gaps between ZnO nanowires to collect holes from the dye, which were then transferred to the counter electrode. With wire-shaped photoanode and counter electrode helically twisted together into a flexible wire device, the photoanode is accessible to light from any direction, so that, the electrodes do not need to be transparent, greatly extending the range of materials and lowering the cost. On one hand, the thin wire can be weaved into almost any shape. On the other hand, the alignment of nanoarray would be largely affected. Dye molecules adsorbed on well-aligned ZnO nanowires (Fig. 1b) are excited by photons, and then photogenerated carriers are injected into the conducting band of ZnO. The ZnO nanowires act as both the carrier channel and the electron acceptor. Thus, the structure of the ZnO nanowires is important to the photovoltaic performance of the photoanode.

The schematic diagram of the continuous reactor for the growth of ZnO nanoarrays is shown in Fig. 1c. Two solutions respectively containing zinc acetate and hexamethylenetetramine are pumped into a tube, and sent into the reactor after thorough mixing, and then warmed up. In the premixing process, the mixing status of the solution into the reactor could be regulated by the tube length and flow speed. A typical flow velocity distribution in the reactor simulated by FLUENT at a certain flow rate is shown in Fig. 1d. A direct observation on the structure of flow field distribution, either in the micro scale or large scale, is difficult from the technique point of view. Taking advantages of recent advances in fluid dynamics, simulation works have provided a convenient way to understand and predict what has happened to the micro flow-field, which would contribute a lot to the mechanism works and future process scaling-up. It shows that the flow field in the reactor is uneven. The fluid at the inlet spreads from the tubule to the reactor, resulting in a sudden drop in flow rate, and the flow pattern