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Preferential Growth of Long ZnO Nanowire Array and Its Application in Dye-Sensitized Solar Cells

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A liquid-phase chemical process for preferential growth of long ZnO nanowires has been developed. The process effectively suppresses homogeneous nucleation and prevents formation of ZnO particles in the bulk solution while allowing rapid growth of ZnO nanowires on seeded substrates. With this process, ZnO nanowires on seeded substrates can grow at an initial rate over 10 times faster than that in the previous process with bulk ZnO precipitation and nanowires of more than 30 μm can be readily obtained within 10 h. The ultralong ZnO nanowires enable fabrication of dye-sensitized solar cells (DSCs) with up to 33 μm thick sensitizing films (the thickest in the literatures) while maintaining high electron collection efficiency, which results in greatly improved performance compared to previously reported ZnO nanowire-based DSCs.

Introduction

Vertically aligned ZnO nanowire arrays have recently attracted considerable interest because of their one-dimensional structure and unique properties. A great number of novel applications in optics, optoelectronics, catalysis, sensing, and energy conversion have been demonstrated.^{1,2} For example, in the field of energy conversion, nanowire dye-sensitized solar cells (DSCs) have been fabricated based on the fast electron transport in single crystalline ZnO nanowires;^{3–7} nanogenerators utilizing the piezoelectric and semiconducting properties of ZnO nanowire arrays have also been reported.⁸

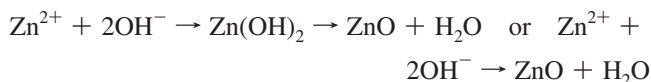
ZnO nanowires have been synthesized via gas-phase reactions^{3,6,8} and liquid-phase deposition (LPD).^{4,5,7,9–11} Compared to the gas-phase approaches, LPD approaches have the advantages of low growth temperature, low cost, and ease in scale-up. They have been used in fabrication of DSCs,^{4,5,7} light-emitting diodes,¹² and energy harvesting nanosystems.¹³ A major drawback of the liquid-phase approaches, however, is that ZnO forms both on the seeded substrates and in the bulk solution simultaneously. The formation of ZnO in the bulk solution results in rapid depletion of reactants and thus slows down the growth rate of wires on the substrates. In addition, the substrates are easily contaminated by the ZnO precipitated out of the bulk solution, degrading the device performance. To obtain long wires, the substrates must be repeatedly introduced into fresh solution baths every several hours, which makes the synthesis time-consuming.^{4,5,10} For example, growing wires of 15 μm long may require 50 h.⁴ In practice, growing high-quality ZnO nanowires longer than 10 μm by previously reported LPD approaches has been challenging. This frustrates many efforts for device development. For example, in nanowire-based DSCs, long wires are needed to increase the internal surface area for light-sensitizing dye adsorption. Therefore, a feasible process for growth of long ZnO nanowires is of significant interest.

Here, we report a new liquid-phase chemical process for rapidly growing arrays of ultralong ZnO nanowires solely on seeded substrates. This process prevents homogeneous nucleation and hence formation of ZnO particles in the bulk solution, while allowing the growth of ZnO nanowires at pre-existing

nuclei on seeded substrates. ZnO nanowires longer than 30 μm can be readily obtained with a growth rate as high as 4 $\mu\text{m}/\text{h}$. The ultralong ZnO nanowires enable fabrication of dye-sensitized solar cells (DSCs) with up to 33 μm thick sensitizing films (the thickest in the literatures) while maintaining high electron collection efficiency, which results in greatly improved performance compared to previously reported ZnO nanowire-based DSCs.

Experimental Section

ZnO Nanowire Synthesis Schemes. In typical LPD approaches, ZnO nanowires are synthesized based on the following reaction:



where hexamethylenetetramine (HMTA), NaOH, or NH_4OH may be used as the hydroxide source. In the reaction mixture, there is a high degree of supersaturation with respect to ZnO or $\text{Zn}(\text{OH})_2$, which consequently induces the formation of ZnO solid in the bulk solution through homogeneous nucleation as well as on the surface of pre-existing nuclei.

Our key idea for growing long ZnO nanowires solely on seeded substrates is to suppress the homogeneous nucleation while maintaining the growth of pre-existing nuclei. Given that homogeneous nucleation is favored by a high degree of supersaturation, decreasing the degree of supersaturation will suppress the homogeneous nucleation process. On the other hand, ZnO seed crystals with diameters of 5–20 nm can be formed on the substrates prior to growth stage by a seeding procedure.¹¹ The growth of ZnO wires on the seeded substrates can thus proceed without undergoing three-dimensional nucleation stage. Also, compared to homogeneous nucleation, crystal growth rate depends on the supersaturation to the power of a smaller number.¹⁴ Therefore, it is expected that moderately decreasing the degree of supersaturation would not significantly affect the growth rate of ZnO nanowires on the seeded substrates while suppressing formation of ZnO particles in the bulk solution.

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We have introduced ammonium hydroxide to the system. Ammonium hydroxide forms complexes with the zinc ions, $\text{Zn}^{2+} + n\text{NH}_3 \leftrightarrow \text{Zn}(\text{NH}_3)_n^{2+}$, where $n = 1, 2, 3$, or 4. The complexes also serve as a buffer for Zn^{2+} ; it continuously supplies Zn^{2+} while lowering the degree of supersaturation of the reaction system. The use of ammonium hydroxide substantially suppresses ZnO homogeneous nucleation. However, by using ammonium hydroxide alone to effectively prevent formation of ZnO in the liquid phase, a high concentration of ammonium hydroxide is required, which also results in very slow growth of the wires on the seeded substrate due to excessively low degree of supersaturation.

To solve the problem, we have used polyethyleneimine (PEI) to further suppress the homogeneous nucleation process. We found that in the presence of both PEI and ammonium hydroxide, formation of ZnO in the bulk solution can be effectively prevented while ZnO wires still grow on the seeded substrate at a reasonably high growth rate. A plausible explanation is the following. PEI preferentially adsorbs to certain crystal faces of ZnO clusters and inhibits further crystal growth along these faces.^{4,10} In the homogeneous nucleation case, the ZnO clusters initially formed due to thermal fluctuation is so small that the polymer chain of PEI adsorbed to certain crystal faces is long enough to cover other faces and, as a result, the steric hindrance of the PEI chain inhibits the crystal growth along all faces. Consequently, the clusters have a very small chance to grow to the critical size that thermodynamically favors the growth of crystals. On the seeded substrates, however, the pre-existing seeds are large enough (5–20 nm) that despite PEI adsorption to certain crystal faces, the growing faces remain exposed to the reactants. Therefore, growth of ZnO nanowires can normally occur on the seeded substrates. The significance of this discovery is that ZnO nanowires now may grow on seeded substrates without precipitation in the bulk solution at a reasonable degree of supersaturation through coupled use of ammonium hydroxide and PEI.

Growth of Long ZnO Nanowires. The following describes our specific experimental procedure for rapid growth of long ZnO nanowires. It started with seeding indium-doped tin oxide (ITO) glass substrates with ZnO nanocrystals. ITO substrate of area 6.25 cm² was first cleaned by sonication in a mixture of acetone and ethanol, followed by treatment in an ultraviolet ozone cleaner. The substrate was then spin coated with 5 mM zinc acetate solution in ethanol followed by thermal treatment at 300 °C for 20 min. Thermal decomposition of zinc acetate formed ZnO nanocrystals on the substrate as seeds for subsequent ZnO wire growth. The growth solution consists of 0.025–0.050 M zinc nitrate, 0.0125–0.025 M hexamethylenetetramine (HMTA), 0.005 M PEI (end-capped, molecular weight 800 g/mol LS, Aldrich), and 0.35–0.45 M ammonium hydroxide. The seeded substrate was then placed in 30 mL of the growth solution. The container was covered and then placed in a water bath that has been preheated to 87–88 °C to start the growth of ZnO wires. It takes about 10 min for the growth solution to reach 87–88 °C. The pH of the growth solution before and after the processes was measured to be 9.2 and 9.3, respectively. The resulting arrays were rinsed with DI water and calcined in air at 450 °C for 30 min to remove any residual organics.

DSC Fabrication and Characterization. To fabricate DSCs, the ZnO nanowire arrays were limited to about 0.5 cm² by removing extra wires with a blade. The films were immersed in 0.5 mM (Bu₄N)₂[Ru(4,4'-(COOH)-2,2'-bipyridine)₂(NCS)₂] (N719 dye) in ethanol for 1 h. A 60 μm thick hot melt sealing

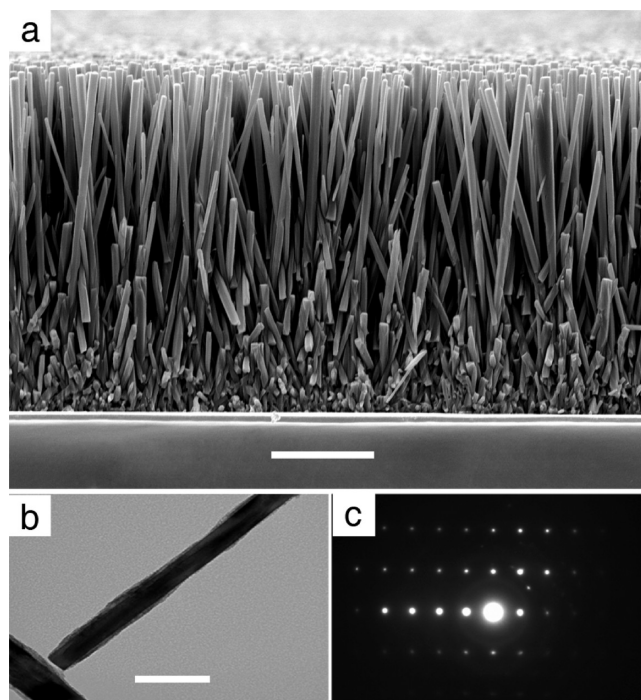


Figure 1. (a) Cross-section SEM image of ZnO nanowire arrays grown for 7 h from a single solution bath. Scale bar, 5 μm. (b) TEM image of a ZnO nanowire; scale bar, 500 nm. (c) Electron diffraction pattern of the ZnO nanowire.

foil (SX1162-60, Solaronix) frame with one side left open was sandwiched between the sensitized films and a platinized ITO electrode. A solution consisting of 0.1 M LiI, 0.1 M I₂, 0.5 M tert-butylpyridine, and 0.6 M tetrabutylammonium iodide in acetonitrile was introduced into the cell from the opening of the sealing frame. The opening was immediately sealed with silicone. The electrolyte that was introduced is about 0.003 cm³ and is in contact with about 0.5 cm² anode. The counter electrode has about the same area as the anode. Then, cells were immediately tested under 100 mW/cm² AM 1.5G simulated sunlight (Model 67005, Oriel), and the *J*–*V* curve was recorded using Reference 600 Potentiostat (Gamry Instruments). Monochromatic illumination was achieved through M 77250 monochromator (Oriel). The accurate anode area was obtained by applying image processing software to a scanned anode image. Current density was calculated based on the anode area. Electrical contacts were made with alligator clips. Dye loading and light-harvesting efficiency (LHE) were quantified on a USB2000 Spectrometer (Ocean Optics) by measuring the absorbance of N719, which was desorbed from the films by using 0.01 M NaOH. Light absorption enhancement due to light scattering within the nanowire arrays may be neglected because of the slow regeneration rate of dye molecules from their excited states relative to light traveling speed between wires.

Results and Discussion

Preferential Growth of Long ZnO Nanowires. With coupled use of ammonium hydroxide and PEI, formation of ZnO in the bulk solution and hence depletion of reactants are prevented, up to 17 μm ZnO nanowires can be grown without replenishing or refreshing the reaction solution. Figure 1a shows a cross-section scanning electron microscopy (SEM) image of ZnO nanowire arrays grown for 7 h from a single solution bath. The wires are ~17 μm long and 150–300 nm in diameter. TEM

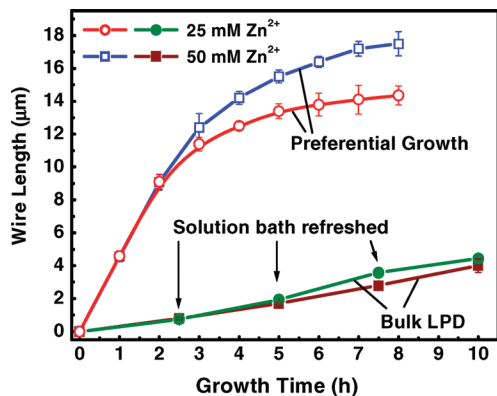


Figure 2. Comparison of wire growth by using the preferential growth process developed in this study and the bulk liquid-phase deposition method reported in the literature. The wire length is plotted as a function of growth time at different growth conditions.

characterization (Figure 1b,c) indicates that the ZnO wires are single-crystalline.

As a comparison, we have also synthesized ZnO nanowires by a previous LPD method as reported in the literature,^{4,5,9–11} where ZnO forms both in the bulk solution and on the seeded substrate. Figure 2 compares the lengths of the wires grown for varied periods of time by our method and the previous method under two different Zn²⁺ concentrations (50 and 25 mM, respectively). It is evident that ZnO wires grow much faster with our method. The growth rate is as high as 4.5 μm/h in the first 2 h. Afterward, it gradually slows down and eventually levels off upon consumption of the reactants after about 8 h. In contrast, using the previous method, the wires grow at a rate of about only 0.4 μm/h and the substrates must be introduced into new solution baths every 2.5 h due to the depletion of Zn²⁺ caused by the formation of ZnO in the bulk solution. The advantage of our method is more apparent when the dependence of growth rate on Zn²⁺ concentration is examined. Upon increasing the Zn²⁺ concentration from 25 to 50 mM with our method, the wire grows longer and it takes longer time to deplete the reactants; with the previous method, however, the wire grows even slightly slower because more concentrated Zn²⁺ results in more rapid bulk precipitation and thus faster depletion of the reactants.

Another advantage of our method is the prevention of the sample surfaces from contamination by particles floating in the solution that would otherwise be formed. Figure 3 shows top view SEM images of the ZnO nanowire array shown in Figure 1. It can be seen that the top surface is completely free of particles. This is in apparent contrast to the sample obtained by the previous method, where ZnO particles formed in the bulk solution are seen all over the sample surfaces (see Supporting Information Figure S1). In addition, after the growth process with our method, we measured the UV absorption spectrum of the growth solution and observed no absorption below 400 nm wavelength, indicating that no ZnO particles were suspended in the bulk solution. The growth solution remained as clear as it appeared before the growth process.

Because of the high growth rate and little sample contamination, our method is particularly useful for growing ultralong ZnO nanowires. By introducing the substrates into fresh solution baths every 3.5 h, we have synthesized arrays of ZnO wires up to 33 μm long, shown in Figure 4a–e. Currently there has not been an effective way to completely stop the lateral growth of the wires. When the wires grow beyond a certain limit, ~30

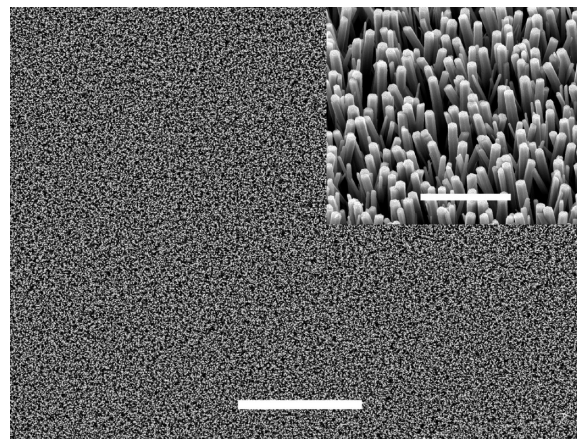


Figure 3. Top view SEM images of ZnO nanowire arrays grown for 7 h using the preferential growth process. Scale bar, 50 μm. Inset, scale bar, 5 μm.

μm in our case, they start to fuse with each other at the root. We are currently developing methods to solve this problem.

Fabrication and Characterization of DSCs Fabricated with ZnO Nanowires. The capability in growing ultralong ZnO nanowires may enable significant device improvements. One particular example is the DSCs. One of the motivations for using long ZnO nanowires in DSCs is to be able to increase the sensitized film thickness while still maintaining high electron-collection efficiency (η_{cl}), so that more sunlight could be absorbed to boost DSC efficiency. Therefore, as a proof of concept, we fabricated DSCs with up to 33 μm thick sensitizing films (the thickest in the literatures) using the synthesized ultralong ZnO nanowires and characterized their performance as a function of the length of the nanowires.

J – V curves of DSCs made by using the 11–33 μm long ZnO nanowire are presented in Figure 5. The short circuit current (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF), and power conversion efficiency (η) are summarized in Table 1. As expected, increasing the length of the wires leads to significant increase in J_{sc} . When the wire length increases from 11 to 27 μm, J_{sc} increases from about 5.2 to 9.7 mA/cm². When the wire length further increases, J_{sc} starts to decrease. As we show in the next section of this article, the electron-collecting efficiency does not decline with film thickness, suggesting that the film thickness has not approached the electron diffusion length in ZnO nanowire DSCs. Therefore, we attribute the saturation of J_{sc} with film thickness to the widening and fusion of the wires at the root which results in loss of the surface area for dye adsorption. The power conversion efficiency gradually increases as a function of the wire length and reaches 2.1% as the film thickness increases to 33 μm.

High Electron-Collecting Efficiency of the Long ZnO Nanowire-Based Electrode. One intriguing question is whether the ultralong ZnO nanowires still maintain a high electron-collecting efficiency (η_{cl}), because this is the basic assumption for using ZnO nanowires in DSCs. To answer this question, we examined η_{cl} in the DSCs with varied lengths of nanowires. In DSCs, η_{cl} can be estimated using following equation:

$$\text{IPCE}(\lambda) = \text{LHE}(\lambda)\phi_{inj}\eta_{cl} \quad (1)$$

where (IPCE) is the incident-photon-to-current conversion efficiency, LHE is the light harvesting efficiency, and ϕ_{inj} is electron injection efficiency. The product of ϕ_{inj} and η_{cl} is referred to as internal quantum efficiency (IQE).

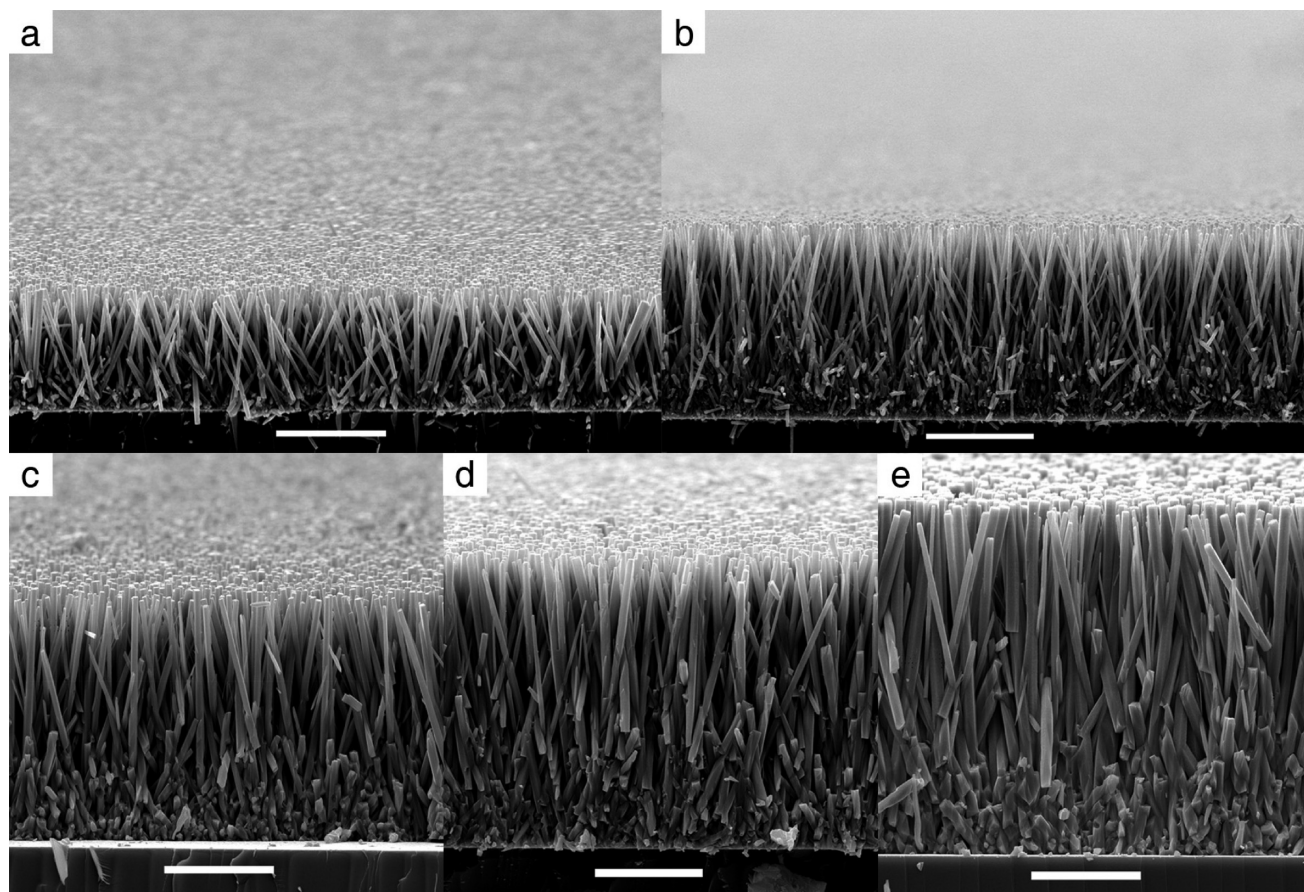


Figure 4. SEM images of arrays of ZnO nanowires in varied lengths. Scale bar, 10 μm . Wire length (a) 11 μm , (b) 17 μm , (c) 22 μm , (d) 27 μm , (e) 33 μm .

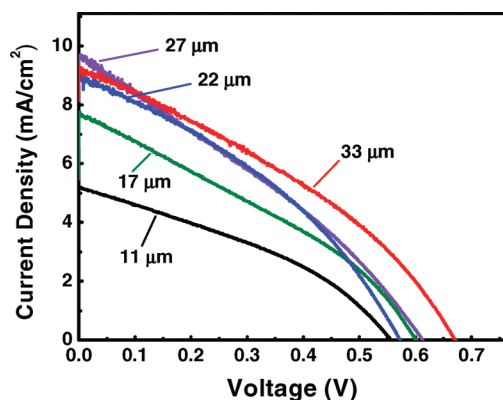


Figure 5. J – V characteristics of DSCs based on ZnO nanowire arrays of various lengths.

TABLE 1: Photovoltaic Performance Data of ZnO Nanowire-Based DSCs Derived from Figure 5

wire length (μm)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η (%)
11	5.2	0.556	0.357	1.0
17	7.7	0.601	0.319	1.5
22	9.0	0.573	0.320	1.8
27	9.7	0.613	0.305	1.8
33	9.3	0.672	0.341	2.1

Figure 6a,b shows IPCE and LHE, respectively, measured as a function of wavelength for DSCs with different lengths of nanowires from which IQE is calculated. The result of IQE for DSCs with varied length of nanowires is presented in Figure 6c. It is seen that IQE is almost independent of the wire length and remains at $\sim 80\%$ for all DSCs tested. If we assume a ϕ_{inj}

of 100%, η_{cl} is about 80%. In reality, ϕ_{inj} is less than 100% and, therefore, η_{cl} must be higher than 80%, which indicates efficient electron collection at the anodes of ZnO nanowires. It is worthy of noting that with ZnO nanowires, the IQE and hence the η_{cl} do not decline with increasing the wire length up to 33 μm . This is in contrast to nanoparticle-based DSCs, in which case η_{cl} decreases significantly as the film thickness exceeds 10–12 μm .¹⁵

It should be noted that limitation of the length of the ZnO nanowires is primarily due to the fusion of wires at their root when the wires are very long. Therefore, further research is required to solve this problem so that even longer wires can be used to further improve the DSCs performance. In addition to being directly used in DSCs and quantum dot-sensitized solar cells,¹⁶ ZnO nanowire arrays have also been used as a template to fabricate ZnO–TiO₂ core–shell structure or TiO₂ nanotube arrays for DSCs.^{17,18} The TiO₂-based DSCs have higher FF and V_{oc} and hence may have a higher power conversion efficiency compared to ZnO-based cells.^{17,18} The ultralong ZnO nanowires may enable fabrication of ultralong ZnO–TiO₂ core–shell structures or TiO₂ nanotubes for DSCs. Research in these areas is currently under way in our lab.

Conclusion

In summary, we have developed a rapid and preferential process for growing ZnO nanowire arrays solely on seeded substrates without simultaneously forming ZnO precipitates in the bulk solution. This process allows rapid formation of high quality arrays of ultralong ZnO nanowires. With this process, ZnO wire can grow at a rate up to 4 $\mu\text{m}/\text{h}$, and more than 30 μm thick arrays can be

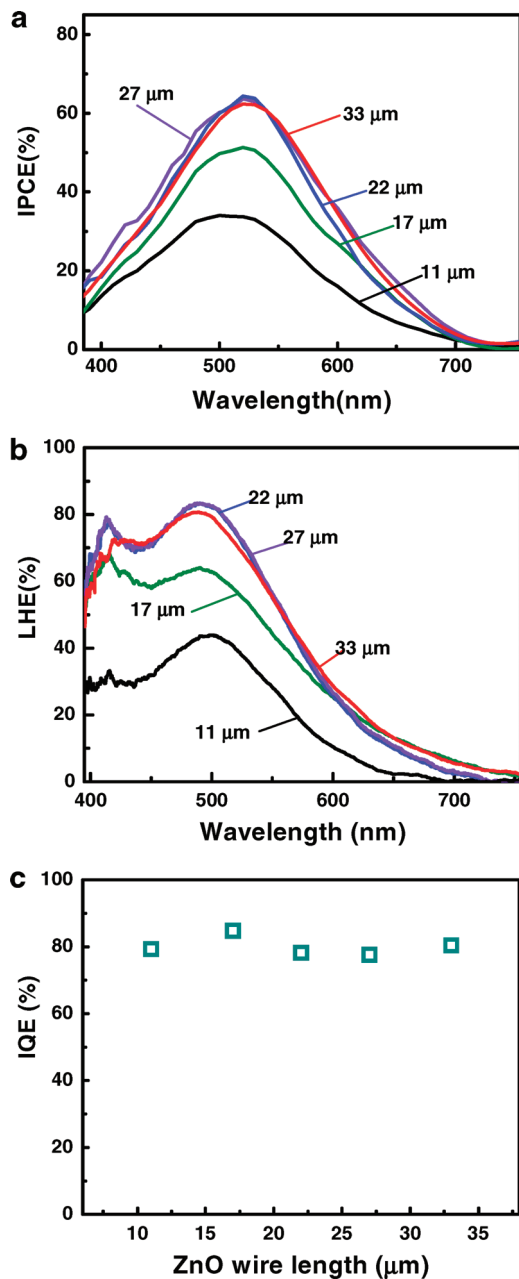


Figure 6. (a) IPCE, (b) LHE, and (c) IQE of DSCs based on ZnO nanowire arrays of various lengths.

readily achieved within 10 h. As a proof of concept, we have used these ultralong ZnO nanowires in DSCs and achieved significant efficiency improvement compared to previous ZnO nanowire-based DSCs simply by increasing the wire length. The ZnO nanowire-based DSCs retain a high electron collecting efficiency even when the sensitizing film is as thick as 33 μm. The capability of growing arrays of vertically aligned ultralong ZnO nanowires opens up new opportunities for improving energy conversion devices and other applications.

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Supporting Information Available: Top view SEM images of arrays of ZnO nanowires synthesized by bulk liquid phase deposition method reported in literature. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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