

HIGH ASPECT RATIO-TITANIUM DIOXIDE-STABILIZED ZINC OXIDE NANOWIRES FOR PHOTOCATALYTIC HYDROGEN GAS HARVESTER

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ABSTRACT

We present a Titanium Dioxide (TiO₂)/Zinc Oxide (ZnO) nanowire array based on a fabrication process using hybrid hydrothermal/atomic layer deposition (ALD) for use as a solar-powered hydrogen gas (H₂) harvester. Three advancements have been accomplished in this work: (1) high aspect ratio TiO₂ nanowires (over 8μm), (2) improved stability over bare ZnO Nanowires during photocatalysis, and (3) excellent onset voltage (bias voltage needed) to split water into H₂ and O₂ gas. As such, this process opens up new class of micro/nano fabrication process for making efficient photocatalytic gas harvesting systems.

INTRODUCTION

There has been growing interest in the field of hydrogen production through photoelectrochemical (PEC) water splitting because of its potential to passively convert solar energy into hydrogen gas more effectively than electrolysis by photovoltaics (PV) [1]. After Fujishima and Honda's first report of water splitting using an n-type TiO₂ electrode [2], numerous studies have been conducted to achieve stable and efficient PEC systems using materials responsive to solar spectrum [3-5]. However, the state-of-art devices show three major drawbacks: (1) low conversion efficiency due to recombination and poor quality of materials; (2) high onset voltages (requiring a voltage bias to begin red/ox of water); and (3) poor material stability in the photocatalytic process [6]. Thus, subsequent research focused on either stabilization layers or increasing

conversion efficiencies [7]. In this research, we report high aspect-ratio, TiO₂-stabilized ZnO nanowires that show chemical stability in aqueous solutions during the photocatalysis. Furthermore, our PEC devices show excellent onset voltage due to enhanced charge separation, which is induced by the geometry of our devices: by increasing the aspect ratio, travel distance of the minority carriers into the solution is limited.

CONCEPT

Figure 1 shows the conceptual schematic of photocatalytic H₂ gas harvesting system. In this research, we introduced the high aspect ratio TiO₂ nanowires with a TiO₂-coated stabilizing active layer for improved stability during photocatalysis and increased hydrogen production at low bias potentials. The photocatalytic H₂ gas harvesting system consists of a photoelectrode and a counter electrode submerged in an aqueous electrolyte solution. In the photoelectrode, light absorption generates electron-hole pairs promote electrons from the valence band to the conduction band. A Schottky barrier is formed at the photoelectrode-electrolyte interface. With properly chosen electrolyte solution (potential) and photoelectrode (Fermi level), minority carriers move into the electrolyte and begin reduction/oxidation (depending on whether the photoelectrode is p- or n-type) of water. Majority carriers oxidize/reduce water at the counter electrode-electrolyte interface. Figure 2 shows the energy band diagram for photocatalytic system using an n-type, TiO₂ photoanode.

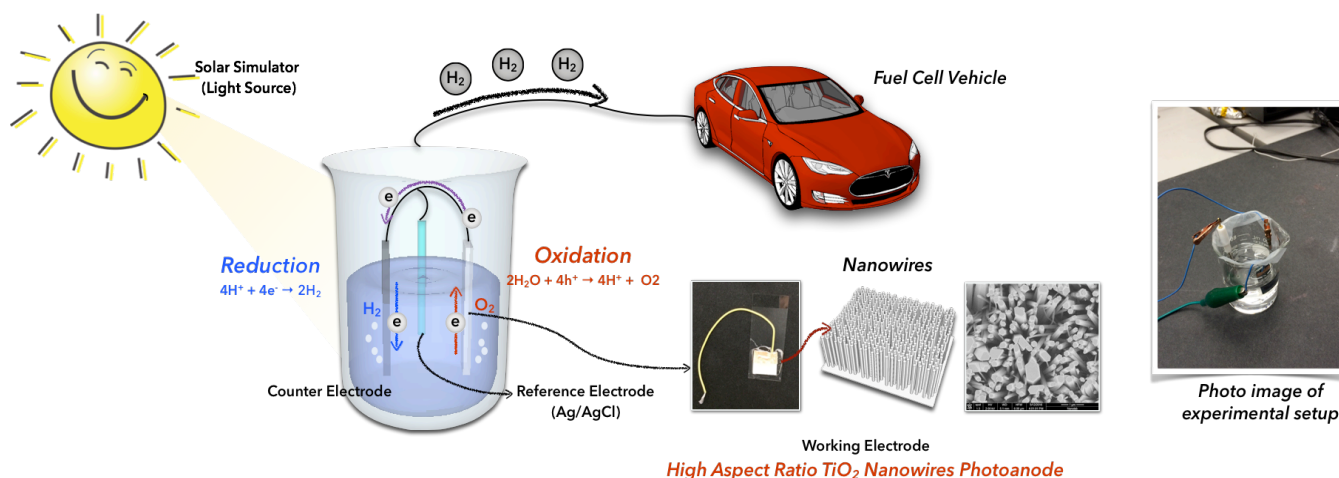


Figure 1: Conceptual illustration of a photocatalytic system. Light induces electron-hole pair generation at the photoanode, oxidizing water to produce hydrogen ions and oxygen gas. The generated electrons reduce the hydrogen ions at the photocathode producing hydrogen gas.

Efficient, low-cost, and scalable PEC water splitting systems have some limited photoelectrode selections. Photoelectrodes must have a suitable band structure for absorbing as much solar energy as possible. The minimum band gap for photoelectrode materials is determined by the required Gibbs free energy (1.23 eV) for water splitting plus thermodynamic losses (0.3eV~0.4eV) and overpotentials for driving chemical reactions (0.4eV~0.6eV) [8, 9, 10]. Consequently, the energy band gap should be higher than 1.9 eV for ensuring sufficiently fast energetics. However, photoelectrode band gaps must also encompass the water reduction (0.0 V) and oxidation (-1.23 V) potentials for the redox half-reactions at the electrode-electrolyte interface. Hence the ideal value of the energy band gap of the photoabsorber material should be placed between 1.9 eV and 3.2 eV while encompassing redox half-reaction potentials.

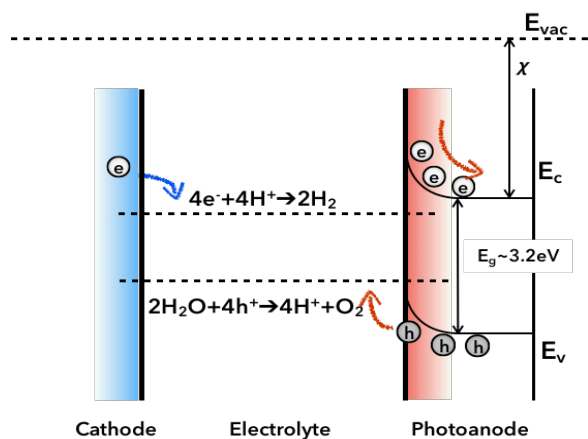


Figure 2: Band position and band bending of TiO₂ at the interface between semiconductor and electrolyte.

Photoelectrode materials with sufficient band structure can suffer from poor photo-conversion efficiency due to recombination and poor light absorption, among other

factors. However, nanowires have been shown to have three distinct advantages in increasing photo-conversion efficiency. (1) by increasing the specific surface area, sites to perform half-reactions have increased. The extended surface area not only enhances light absorption, but also enhances charge transfer kinetics at the photoelectrode-electrolyte interface. (2) Nanowires can improve photo-conversion efficiency by enhancing light trapping. Multiple reflections of the incident light in the nanowire forest increase the probability of light absorption. (3) By using one-dimensional structures, the travel distance of photo-generated minority carriers is limited, thus increasing charge separation and water oxidation efficiency.

TiO₂ is an intrinsically n-type semiconductor material with an energy band gap of 3.2 eV [10]. Its band edge positions straddle water redox potentials as shown in Figure 2. Moreover, the TiO₂ production is cheap, scalable, while TiO₂ is chemically stable in aqueous solution. However, the state-of-art TiO₂ usages are plagued by lower photocurrent due to poor light absorption and previous work on texturizing TiO₂ weren't able to produce high aspect ratio TiO₂ nanowires. Instead, undesirable compact layers are observed at the bottom of the wire arrays [11]. In this work, we fabricate high aspect ratio TiO₂ nanowire arrays using a hybrid hydrothermal/atomic layer deposition (ALD) process. After growing the high aspect ratio ZnO nanowires using the hydrothermal methods, a uniform coating of TiO₂ was applied by ALD.

EXPERIMENT

Figure 3 illustrates the fabrication process of high aspect ratio TiO₂/ZnO nanowires. ZnO nanowire growth begins with the deposition of a ZnO quantum dot seed layer onto n-type Si (100) wafers. After several iterations of spin-casting, the wafer is annealed at 350°C for 30 min to ensure seed layer adhesion onto the wafer.

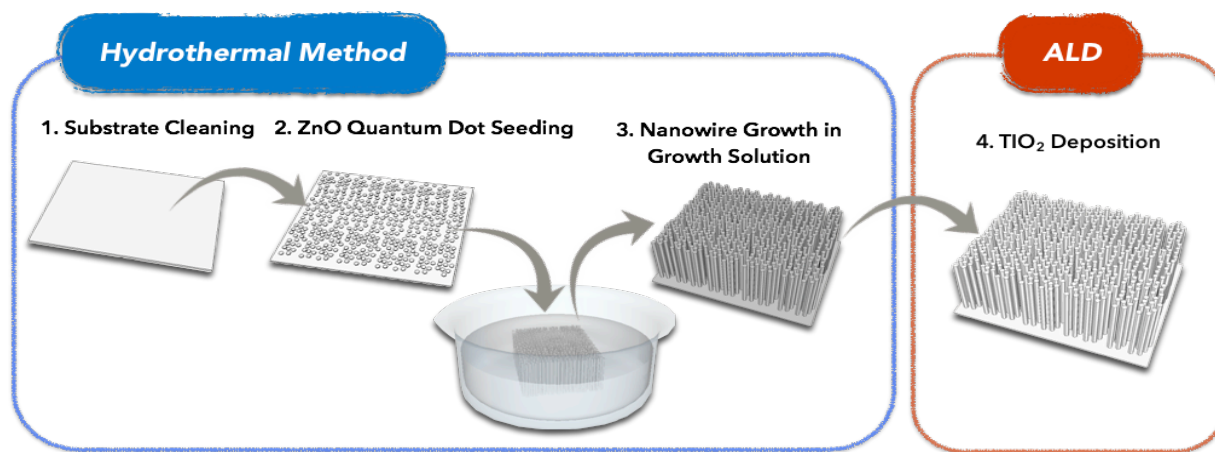


Figure 3: First, a seed layer is deposited and rinsed several times, forming a quantum dot network on the substrate. Then the substrate is submerged into a Zn-rich growth solution and heated to grow single crystalline ZnO nanowires. Finally, TiO₂ deposited using atomic layer deposition.

Afterwards, hydrothermal ZnO growth was carried out using a growth solution at 90°C for 8 hrs. The wafer was removed from the solution and cleaned with deionized water. After drying the samples, uniform deposition of TiO₂ over ZnO nanowires was performed using ALD. In the ALD process, gaseous precursors are flowed onto the substrate in a systematic and cyclic manner to create a self-limiting reaction—one layer of TiO₂ is deposited per cycle. The ZnO nanowire array was coated by 800 cycles of thermally grown ALD TiO₂ at a process temperature of 250°C, using Tetrakis(dimethylamido)titanium and H₂O as the Titanium and Oxygen precursors, respectively.

RESULTS AND DISCUSSION

A field emission scanning electron microscopy (FESEM) was used for verifying the surface morphology of nanowires before and after ALD processing. A transmission electron microscopy (TEM) was analyzed for characterizing the single nanowire. Figure 4, SEM images of both the bare ZnO nanowires and TiO₂-coated ZnO, show the ZnO nanowires are highly ordered and polygonal in shape, indicating single-crystalline nature, and grow up to 10 μm in height. Figure 4(B) reveals that ALD processed TiO₂ coating over the ZnO nanowires has good uniformity and conformity.

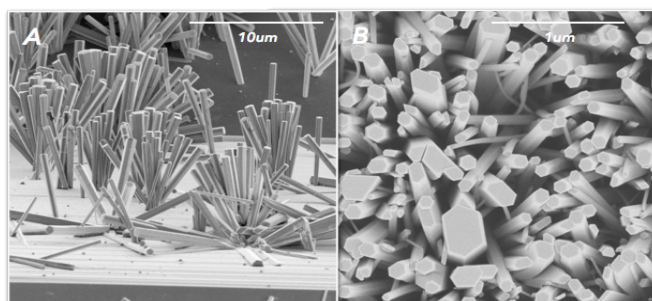


Figure 4: SEM image of (a) zinc oxide nanowires (ZnO NWs) by using hydrothermal growth method; (b) uniformly coated TiO₂ on ZnO NWs using Atomic Layer Deposition (ALD).

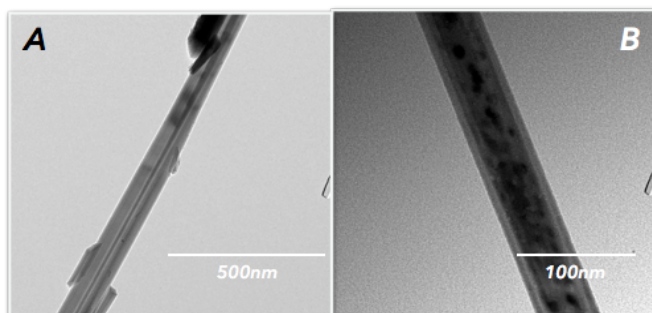


Figure 5: TEM image of (a) ZnO NW grown by using hydrothermal method; (b) TiO₂ coated ZnO NW using ALD

Figure 5 shows the TEM characterization of a single nanowire removed from the array. Figure 5(A) is the image of a single nanowire of ZnO before ALD process and Figure 5(B) shows a TiO₂ coated ZnO nanowire and indicates the

conformal coverage of the TiO₂ onto ZnO.

The phase structure of hydrothermally grown ZnO nanowires was characterized using powder X-ray diffraction (XRD). Figure 6 displays the X-ray diffraction peaks indicate the excellent crystalline nature for the sample and hexagonal wurtzite ZnO phase. (JCPDS card No. 36-1451)

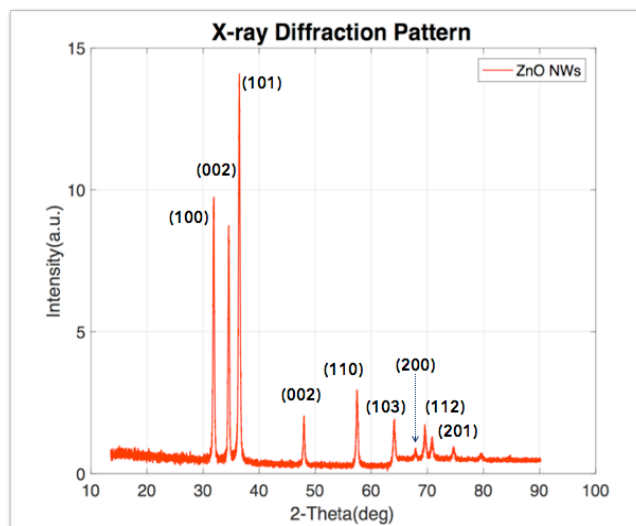


Figure 6: X-ray Diffraction pattern of ZnO nanowires.

Photocurrent testing of ZnO and TiO₂-coated ZnO nanowires was carried out in a 0.5M H₂SO₄ solution using a three electrodes setup with Platinum counter electrode and Ag/AgCl reference electrode.

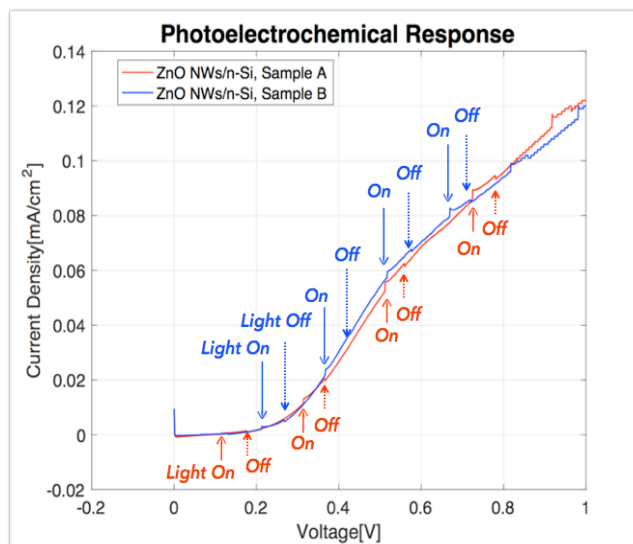


Figure 7: Photoelectrochemical response of ZnO using the hydrothermal method.

Figure 7 shows the chopped (alternating light off/on) current-potential (I-V) curves of hydrothermally-grown ZnO nano-array under a Xenon lamp (Asahi Catecl, AM 1.5). Photoelectrochemical response of the bare ZnO nano-array is mostly obscured by side reactions, causing peaking and

sharp increases in current and subsequently obscuring photocurrent.

In contrast, ALD TiO₂-coated ZnO nano-array shows significantly higher and more stable photocurrent as shown in Figure 8, suggesting that the hydrothermal growth method for ZnO results in impurities and instabilities that make the ZnO nanowire array unsuitable for use in photocatalytic water splitting. However, these instabilities have been shown to be stabilized by TiO₂.

Furthermore, in contrast to previous work on TiO₂, we are able to achieve tall, highly ordered TiO₂ arrays. By using ALD to deposit a thin coating of TiO₂, we have further limited the distance of travel for minority carriers, minimizing recombination and ensuring better charge separation. The favorable geometry and high quality coating with ALD allows us to achieve stable devices with excellent onset voltage, produce photocurrent at extremely low bias voltage.

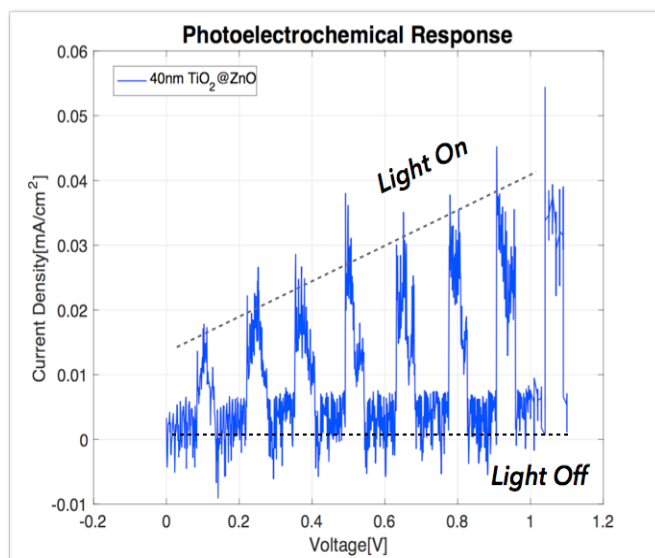


Figure 8. Photoelectrochemical response of TiO₂ coated ZnO NWs.

CONCLUSION

High aspect-ratio and vertically ordered TiO₂-stabilized ZnO nanowires as long as 10 μm and less than 50 nm in diameter were successfully synthesized for use as a solar-powered hydrogen (H₂) gas harvester. Hybrid hydrothermal/ALD processing was used to achieve high aspect ratio and high quality nanowire arrays. Surface morphology and phase structure were analyzed to confirm TiO₂-coated ZnO nanowires. Photoelectrochemical responses of synthesized nanowires were measured to investigate their performance as hydrogen gas harvesters. Nanowires with TiO₂ demonstrated improved stability over bare ZnO nanowires during photocatalysis and excellent bias voltage. Results show that favorable geometry and high quality nanowires not only enhanced chemical stability but also improved required bias voltage to yield photocurrent.

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