Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information (ESI)

Stable solar-driven water splitting by anodic ZnO nanotubular semiconducting photoanodes

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- **Synthesis of ZnO nanowires, hierarchical and nanotubes**

ZnO nanowire arrays were synthesized via the anodization of Zn foil at room temperature (approximately 22 °C). Prior to anodization, pure Zinc foil samples (1.5 cm × 1.0 cm × 0.25 mm) were ultrasonically cleaned with acetone, ethanol and finally rinsed with distilled water. The anodization was carried out in an electrochemical cell with platinum foil as the counter electrode and Zinc foil as the working electrode, electrolyte was $KHCO_3$for 30 minutes, 10 V. After anodization, the samples were rinsed thoroughly with acetone and distilled water. ZnO nanowires samples (Figure S1) dried at 65 ^{o}C for 45 min and annealed in air for 1 h at 250 °C with heating rates of 1 °C/min. Finally, the sample was stored in a vacuum desecrator cabinet for further characterizations.

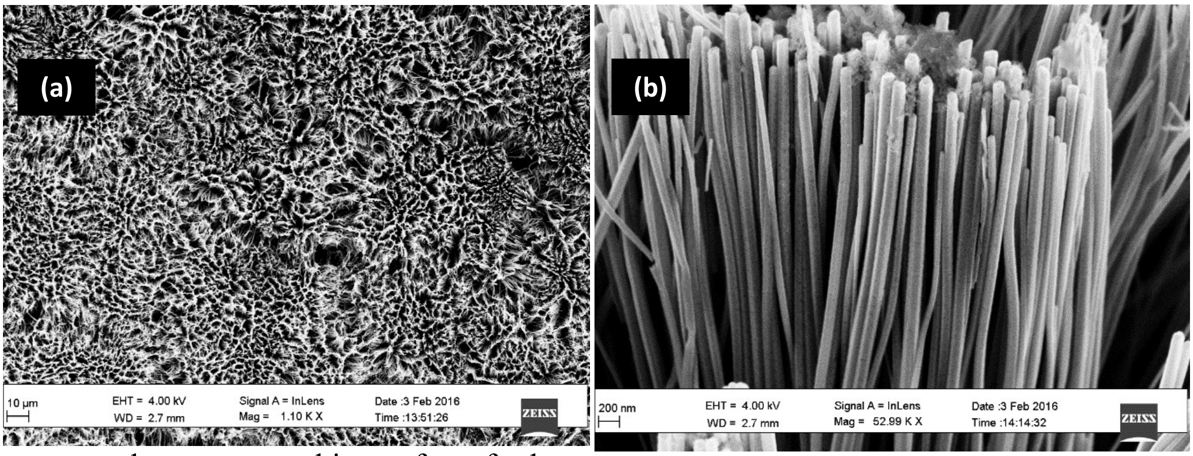
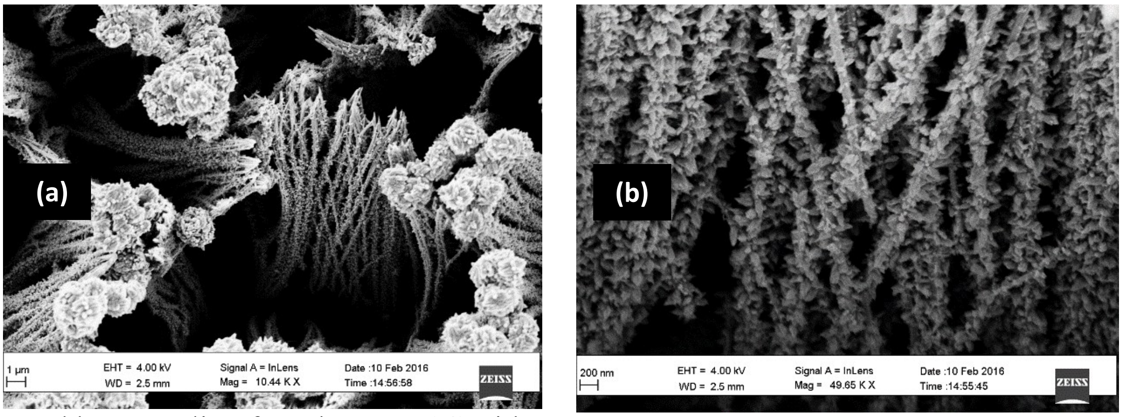


Figure S1: FESEM (a) Top and (b) cross-sectional views of the ZnO nanowires fabricated in an aqueous electrolyte containing 50 mM $KHCO_3$.

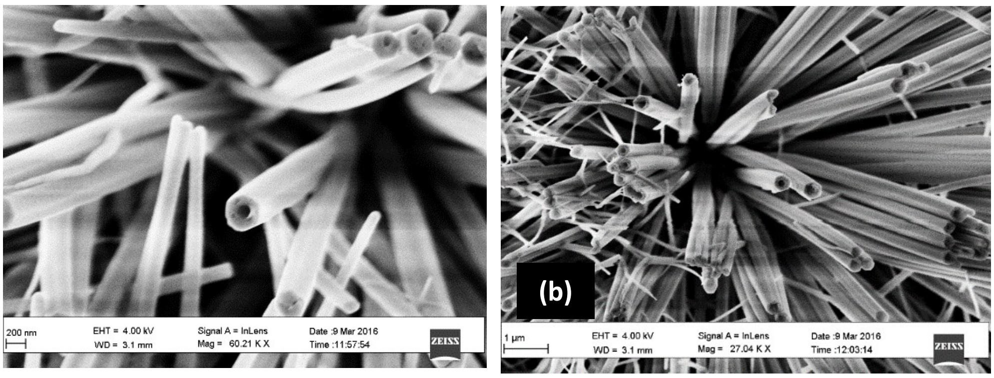
It was found that through a simple post-treatment, an interesting hierarchical structure (nanoparticles decorated on nanowire) was obtained (Figure S2). This treatment involved leaving the nanowires film (1.6 gm) in a sealed vial of (100 ml) deionized water for 24 h,



followed by annealing for 1 h at 250 °C with heating and cooling rates of 1 °C/min. A further peculiarity in the anodization was also observed in the form of hierarchical growth.

Figure S2: (a), (b) SEM images of ZnO hierarchical (nanoparticles decorated on nanowires) structure fabricated in an aqueous electrolyte containing $KHCO_3$ by simple post treatment in water.

ZnO nanotubes were obtained by anodizing pure zinc foils of size (1.5 cm × 1 cm × 0.25 mm). Before anodization, samples cleaned with water, isopropanol and acetone and dried under nitrogen stream. The anodization was performed in two-electrode electrochemical cell using zinc as the anode and platinum as the cathode. Initial experiments were done using an aqueous solution of 50 mM



$KHCO_3$ as electrolyte. In this case, the anodization was initially done at 10 V followed by a second anodization at 5 V for 10 minutes (Figure S3).

(a)

Figure S3: SEM images of ZnO nanotube/nanowire mixed structure fabricated in an aqueous electrolyte containing only $KHCO_3$

After optimization of the experimental conditions, the second anodization was eliminated and a single anodization was performed at 10 V at room temperature in an electrolyte consisting of 50 mM $NaHCO_3$ and 30 mM Na_2CO_3 in water for 10 minutes. (Figure S4). The results indicated that the nanotubes were formed by two processes, the nanowire growth and etching and hence, it is different from anodic nanotube or nanoporous structure formation in many materials such as titanium or aluminum.

Although it is unclear how the etching starts selectively from the top of the amorphous nanowires, we believe that this is due to the anisotropic nature provided by the shape and local crystallinity in nanowires. Typically, the etching was found to start from the top when the wire diameter reached about 100 nm and this is consistent with the results published by other groups on ZnO nanowire etching. As the nanowire growth continues, the etching takes place rapidly along the length of the wire to the bottom as directed by electric field or freshly formed etch kinks. Meanwhile, the diameter and length of the tube increases due to mass transport from the bottom. At equilibrium, the mass transport makes the nanotube grow further in length while the etching at the bottom continues so that the tubular structure is maintained. The nanowires that do not acquire enough lateral size through mass transport to create the conditions required for etching remain as nanowires. [1-3]

Figure S4: SEM images of zinc oxide nanotubes
fabricated in an aqueous electrolyte containing both Na_2CO_3 and $NaHCO_3$

In Summary:

- Nanowires: lower voltage and concentration leads to thicker, denser and lower diameter nanowires.
- Hierarchical structure: water post treatment is the main step responsible for developing this structure.
- Nanotubes: the two-step anodization yields best results when lowering the second voltage to about 50 % of the first-step voltage.
- Nanotubes: one-step anodization in mixed electrolyte resulted from etching process of CO_3^- species.

References

1. D. O. Miles *et al*, J. Mater. Chem. A, 2015, **3**, 17569-17577.
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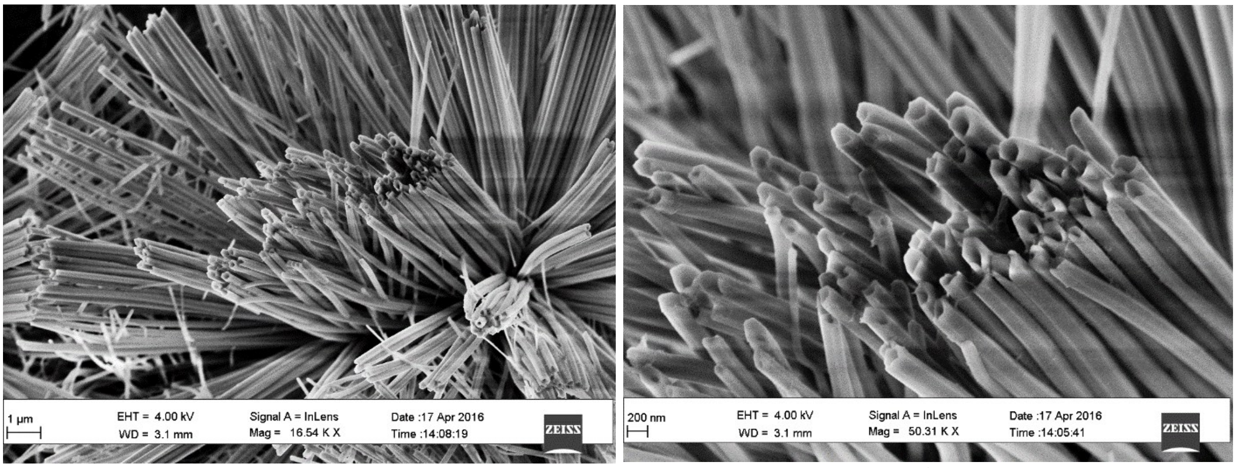

3. B. E. Conway and D. C. W. Kannangara, J. Electrochem. Soc.1987, **134**, 906–918