Supplementary Material (ESI) for Journal of Materials Chemistry This journal is (c) The Royal Society of Chemistry 2010 **Supporting Information**

The solvothermal treatment was carried out at 150 °C for 10 h with different $SnCl_2$ concentrations of 0.001 M, 0.005 M, and 0.02 M. The 0.001 M sample is a very dense film without obvious holes on the surface, while the 0.005 M and 0.02 M samples show a porous structure with a decreased tube diameter, although the surface of the 0.02 M sample is more compact. The reason why a dense film formed in the 0.001 M sample is not clear, but repeated experiments show the same results. This may be because the lower Sn^{2+} concentration affects the solution wettability to the TiO₂ substrate surface, so the equilibrium between the nucleation speed and the crystal growth speed is different from the case with higher Sn^{2+} concentrations, with corresponding effects on the morphology.



Fig. S1 FESEM images of: (a) TiO₂ nano-array substrate; SnO₂/TiO₂ samples with different SnCl₂ precursor concentrations: (b) 0.001 M, (c) 0.005 M, (d) 0.02 M.

Supplementary Material (ESI) for Journal of Materials Chemistry This journal is (c) The Royal Society of Chemistry 2010



Fig. S2. FESEM images of SnO₂/TiO₂ samples at different magnifications with reaction times of 2 h (a,b); 5 h (c,d). Reaction was at 150 °C with 0.005 M SnCl₂.



Fig. S3. EDS results on 0.5 h SnO₂/TiO₂ sample: (a) Ti distribution; (b) Sn distribution; (c) EDS spectrum of sample.

Supplementary Material (ESI) for Journal of Materials Chemistry This journal is (a) The Poyal Society of Chemistry 2010



Fig. S4. EDS spectra corresponding to TEM images in Figure 3: (a) whole area of Figure 3(a), (b) region 1, (c) region 2, and (d) region 3. Platinum and gallium were used for the holder to prepare the TEM sample for the cross-sectional images, so their peaks are present in Figure S4. The C and Cu peaks are from the copper grid.



Fig. S5 (a) Cycling performance of 10 h SnO₂ / 200 nm or 2000 nm TiO₂ samples in different voltage ranges at current density of 20 μA cm⁻²; (b) galvanostatic curves of 0.5 h SnO₂/TiO₂ sample at different current densities.

Supplementary Material (ESI) for Journal of Materials Chemistry This journal is (c) The Royal Society of Chemistry 2010



Fig. S6 (a) TEM image of $0.5 \text{ h } \text{SnO}_2/\text{TiO}_2$ electrode after 5 cycles, (b) high resolution image.