A Versatile Three-Dimensional Virus-Based Template for Dye-Sensitized Solar Cells with Improved Electron Transport and Light Harvesting

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Supplementary Information

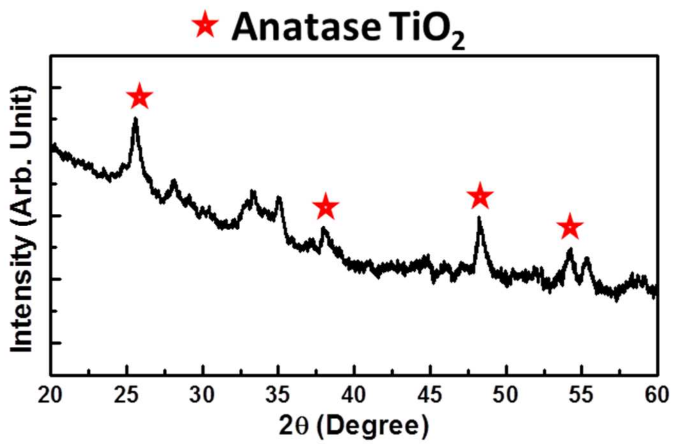

Figure S1. XRD analysis of the TiO_2 nanocrystallites after the hydrolysis of $TiCl_4$.

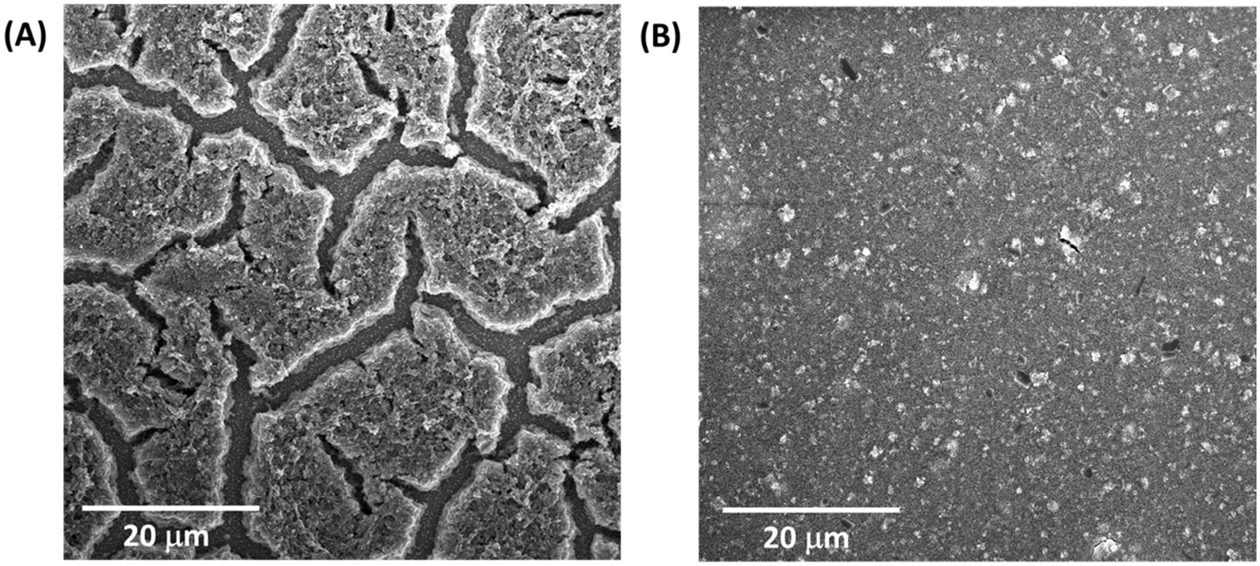

Figure S2. SEM images of the annealed virus-templated photoanodes (A) without (B) with the TiO_2 nucleation by $(NH_4)_2TiF_6/H_3BO_3$ solution.

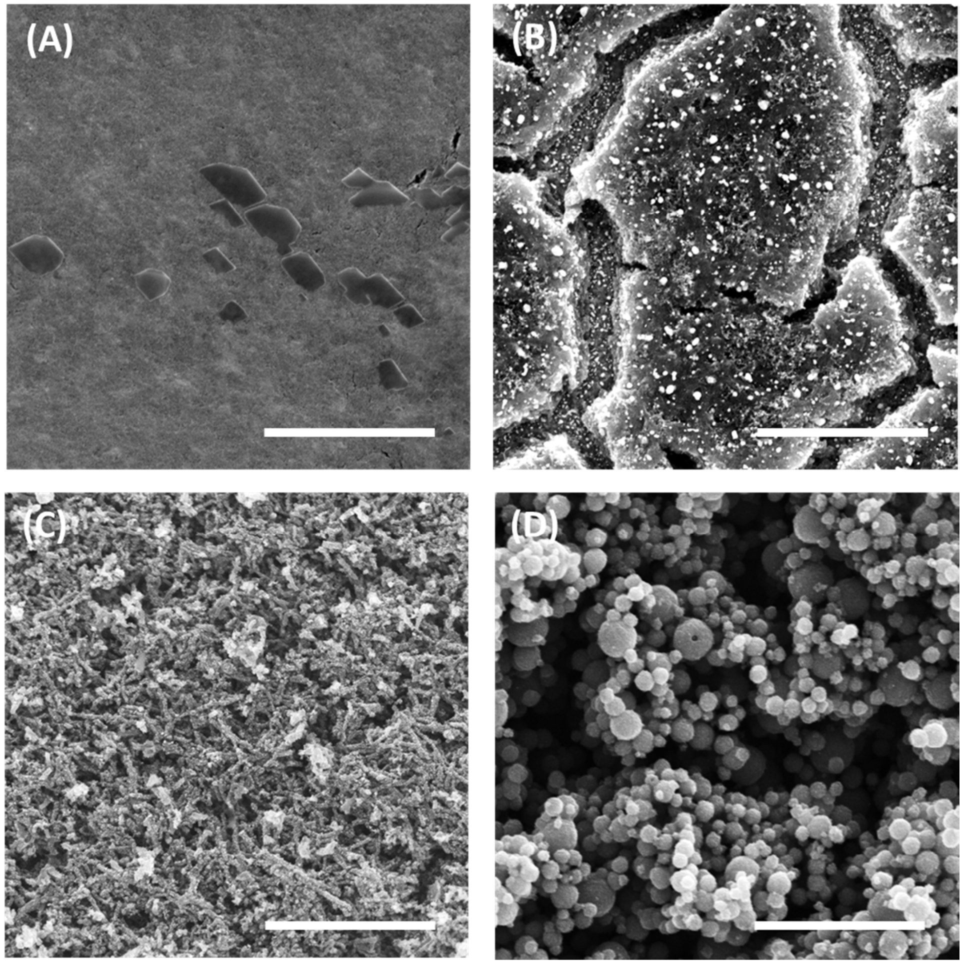

Figure S3. SEM images of the annealed virus-templated photoanodes nucleated in different concentration of the $TiCl_4$ solution. (A) 0.04 M. (B) 0.1 M. (C) 0.2 M. (D) 0.4 M. All of the films are also nucleated with $(NH_4)_2TiF_6/H_3BO_3$ solution subsequently. The scale bar is 4 μm.

Calculation of Diffusion Length (L_n) from Electrochemical Impedance Spectra (EIS)

The electron diffusion length, L_n, can be calculated from $L_n = L \times (R_{REC}/R_T)^{1/2}$, where L is the film thickness, R_{REC} is electron recombination resistance, and R_T is electron transport resistance. R_{REC} and R_T were obtained by fitting the measured electrochemical impedance spectra to the transmission line model (shown in **Figure S5**) with the Z-view software (v3.2b, Scribner Associates Inc). The transmission line component (Z_{TiO2} in **Figure S5**) in an equivalent circuit is often used to represent the interface resistance and capacitance for a porous structure, which is the case for the photoanodes of DSSCs. During fitting the electrochemical impedance spectra to the transmission line model, the resistance and capacitance at the substrate/TiO_2 interface, and the substrate/electrolyte interface were assumed negligible due to good contact between substrate and TiO_2 and blocking layer of TiO_2. In **Figure S4**, electrochemical impedance spectra from each of three types of DSSCs, measured at 625 mV, are shown in symbols. The fitted results are shown as solid lines. For more detailed information about fitting electrochemical impedance spectra to the transmission line model and extracting electron diffusion length from fitted electrochemical impedance spectra, refer references.[1-5]

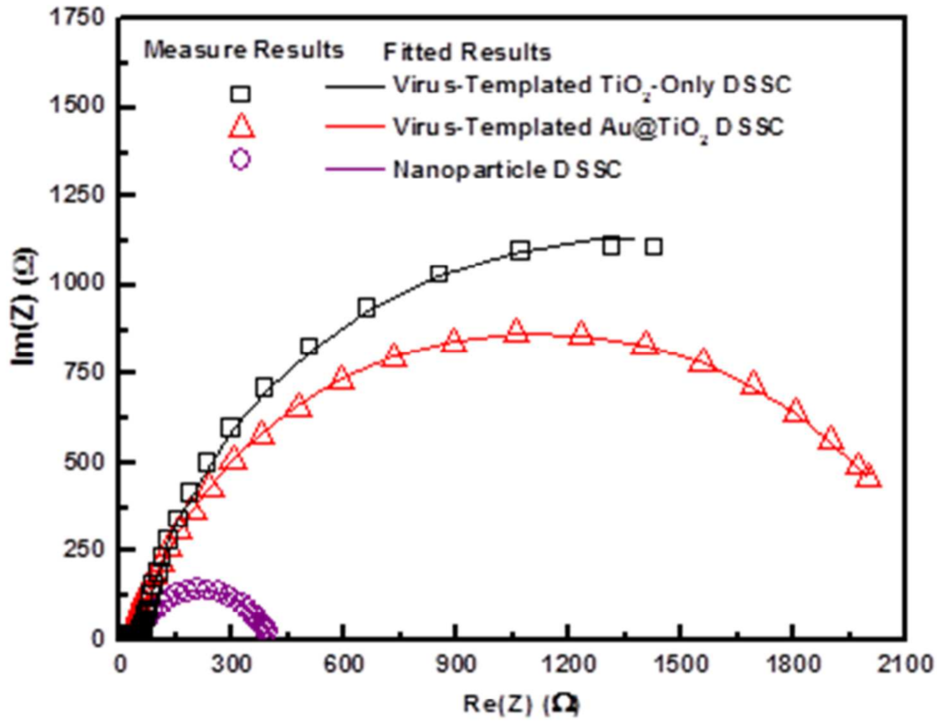

Figure S4. Nyquist diagrams of the EIS obtained under dark condition for different devices at 625 mV. Both data and fitted lines are shown.

Experimental data are presented by symbols, and fitted results using the equivalent circuit in **Figure S4** are shown as solid lines. The bias applied to all the devices during measurement is 625 mV. For the virus-templated TiO_2-only DSSCs, $R_{REC} = 2212.2$, $R_T = 31.4$, thus $L_n/L = 8.4$; for the virus-templated Au@TiO_2 DSSCs, $R_{REC} = 2646.9$, $R_T = 51.9$, thus $L_n/L = 7.1$; for nanoparticle DSSCs, $R_{REC} = 330$, $R_T = 105$, thus $L_n/L = 1.8$.

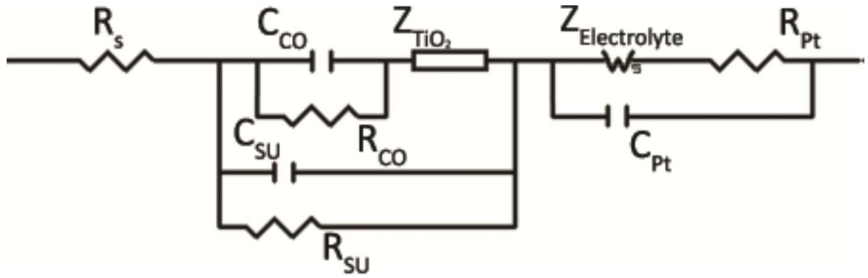

Figure S5. Equivalent circuit impedance model (transmission model) of DSSCs. R_s: Ohmic series resistance of the cell. R_{CO} and C_{CO}: Contact resistance and capacitance at the interface between the conducting substrate and the TiO_2 photoanode film. R_{SU} and C_{SU}: Charge transfer resistance and double layer capacitance at the substrate/electrolyte interface. R_{Pt} and C_{Pt}: Charge transfer resistance and double layer capacitance at the counter electrode-electrolyte interface. Z_{TiO2}: transmission line impedance of the TiO_2 photoanode film consisting of the elements R_T (resistivity of electron transport in the photoanode film), R_{REC} (charge recombination resistance at the TiO_2/dye/electrolyte interface), and C_μ (chemical capacitance of the photoanode film). $Z_{Electrolyte}$: mass transport impedance at the counter electrode.

Calculation of Electron Collection Efficiency (η_{COL}) from Electron Diffusion Length (L_n/L)

The electron collection efficiency is,[3]:

$$\eta_{COL} = \frac{\left[-L\alpha\cosh\left(\frac{d}{L}\right) + \sinh\left(\frac{d}{L}\right) + L\alpha e^{-\alpha d}\right] L\alpha}{(1 - e^{-\alpha d}) \cdot [1 - L^2\alpha^2]\cosh\left(\frac{d}{L}\right)}$$

where d is the thickness of the TiO_2 film, L is the electron diffusion length, and α is the extinction coefficient of dye sensitized TiO_2 film. (The notation is different from that we used in the manuscript: we used L for the thickness of the TiO_2 film and L_n for the electron diffusion length.) For the calculation, we assume αd equals to 1, indicating 90% of the incident light is absorbed. For the virus-templated TiO_2-only DSSCs, L/d = 8.4, η_{COL} = 99.6%; for the virus-templated Au@TiO_2 DSSCs, L/d = 7.1, η_{COL} =99.4%; for nanoparticle DSSCs, L/d = 1.8, η_{COL} = 92.0% (all L/d values were taken at a bias value of 625 mV, as shown in **Figure 4(A)** and **Table 1**).

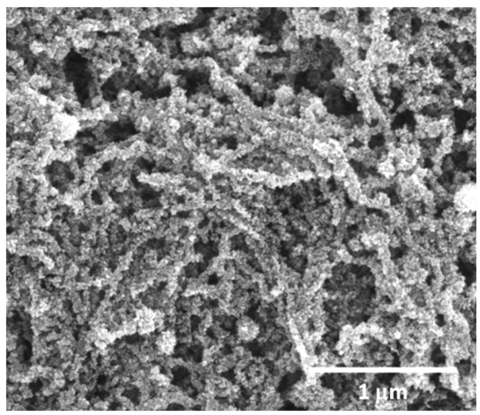

Figure S6. SEM image of the annealed virus-templated Au@TiO_2 photoanodes.

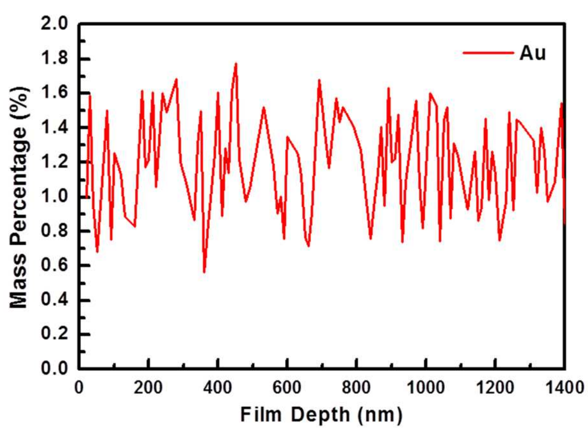

Figure S7. XPS measurement of the Au@TiO_2 virus-templated photoanode. The average concentration of AuNPs in the photoanodes is 1.03 wt%.

Supplementary References

1. Bisquert, J.; Fabregat-Santiago, F.; Mora-Seró, I. n.; Garcia-Belmonte, G.; Giménez, S., Electron Lifetime in Dye-Sensitized Solar Cells: Theory and Interpretation of Measurements. *J. Phys. Chem. C* **2009,** *113*, 17278-17290.
2. Bisquert, J.; Garcia-Belmonte, G.; Fabregat-Santiago, F.; Ferriols, N. S.; Bogdanoff, P.; Pereira, E. C., Doubling Exponent Models for the Analysis of Porous Film Electrodes by Impedance. Relaxation of TiO_2 Nanoporous in Aqueous Solution. *J. Phys. Chem. B* **2000,** *104*, 2287-2298.
3. Halme, J.; Vahermaa, P.; Miettunen, K.; Lund, P., Device Physics of Dye Solar Cells. *Adv. Mater.* **2010,** *22*, E210-E234.
4. Wang, M.; Chen, P.; Humphry-Baker, R.; Zakeeruddin, S. M.; Grätzel, M., The Influence of Charge Transport and Recombination on the Performance of Dye-Sensitized Solar Cells. *ChemPhysChem* **2009,** *10*, 290-299.
5. Wang, Q.; Ito, S.; Grätzel, M.; Fabregat-Santiago, F.; Mora-Seró, I.; Bisquert, J.; Bessho, T.; Imai, H., Characteristics of High Efficiency Dye-Sensitized Solar Cells. *J. Phys. Chem. B* **2006,** *110*, 25210-25221.