Supporting Information


Highly-Efficient Capillary Photoelectrochemical Water Splitting Using Cellulose Nanofiber-Templated TiO₂ Photoanodes

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Figure S1. XRD spectrum of fibrous TiO₂ nanotubes after annealing, confirming its anatase phase.
Figure S2. Schematic illustration (a) and a photo (b) of capillary PEC setup.
Figure S3. Calculated efficiencies versus bias voltages for capillary and in-electrolyte PEC setups using cellulose-templated TiO$_2$ photoanodes annealed in O$_2$ atmosphere. (a) Under Xe lamp illumination. (b) Under AM 1.5 G illumination.
Figure S4. Stability test of capillary PEC setup under 0.3V (vs. SCE) bias for 12 hours.

Figure S5. Illumination intensity decreases as a function of electrolyte (1M KOH) thickness that light passes through. The linear relation is consistent with the Beer–Lambert law.
S6: Analysis of pH-relationship

(1) Relationship between the Fermi level of the redox couple and their concentrations

\[ E_{F,\text{redox}} = E_{\text{redox}}^0 + kT \ln \left( \frac{[\text{Red}]}{[\text{Ox}]} \right) \]

where \( E_{\text{redox}}^0 \) is the standard redox potential of the redox couple.\(^{[1]}\)

For \( 4\text{OH}^- \rightarrow 2\text{H}_2\text{O} + \text{O}_2 + 4e^- \)

\([\text{Red}] = [\text{OH}^-], [\text{Ox}] = [\text{O}_2] = P_{\text{O}_2}\)

At pH = 14,

\[ E_{F,\text{redox}}^1 = E_{\text{redox}}^0 + kT \ln \left( \frac{1}{P_{\text{O}_2}} \right) \]

Also, \([\text{OH}^-] = 10^{-14}/[\text{H}^+]\]

At new pH value,

\[ E_{F,\text{redox}}^2 = E_{\text{redox}}^0 + kT \ln \left( \frac{10^{-14}}{P_{\text{O}_2}[\text{H}^+]} \right) \]

Thus, the potential change of the redox couple between new pH solution and pH=14 solution is:

\[ \Delta \varphi = E_{F,\text{redox}}^2 - E_{F,\text{redox}}^1 = kT \ln \left( \frac{10^{-14}}{[\text{H}^+]} \right) = \frac{kT}{\ln e} (pH - 14) = 0.059(pH - 14) \]

(2) Relationship between the Fermi level of the semiconductor and the number of accumulated holes

From interrupted \( J-V \) curve (black curves in the insets of Fig. 3) and the corresponding continuous \( J-V \) curve (red curves in the insets of Fig. 3), the area between them represents the number of accumulated holes at the semiconductor surface. Read data \((V_0, J_0)\) at \( t_0 \) and \((V_1, J_1)\) at \( t_1 \) on the black curve.

Based on the RC circuit model:

\[ I(t) = I_0 e^{-\frac{t}{\tau}} = \frac{dQ(t)}{dt} \]

\[ Q_0 = CV_0 \]
\[ I_0 = V_0/R = Q_0/RC \]

Thus,
\[ I(t) = (Q_0/RC)e^{-t/\tau_0} \]

Let \( t=t_1-t_0 \) where \( t \) can be achieved by \( (V_1-V_0)/S \), \( S \) is the scan speed = 0.05V/s.

Put \((J_0, 0)\) and \((J_1, t)\) into the equation to obtain the value of \( Q_0 \) (C cm\(^2\)).

For in-electrolyte PEC setup and capillary PEC setup, the average \( Q_0/e \) value were obtained as 8.24\(\times\)10\(^{12}\) (cm\(^2\)) and 3.43\(\times\)10\(^{12}\) (cm\(^2\)).

In our experiments, the thickness of the TiO\(_2\) nanotube film was \( \sim \)10 \( \mu \)m. Therefore, the concentrations of trapped holes were approximately 8.24\(\times\)10\(^{15}\) (cm\(^{-3}\)) and 3.43\(\times\)10\(^{15}\) (cm\(^{-3}\)) for in-electrolyte and capillary setups, respectively.

The current spikes diminish at higher potential as a larger proportion of holes have sufficient potential to oxidize water.\(^{[2]}\) Previous research also revealed that the magnitude of the current spikes decreases with increasing positive bias. This effect was explained by bending of the favored band due to positive potentials.\(^{[3]}\) Therefore, understanding the difference between the number of accumulated holes for the two PEC setups is equivalent to investigating the difference of band shifting using the following equations:

\[ E_i - E_{f_1} = kT \ln \left( \frac{N_1}{N_i} \right) \]

\[ E_i - E_{f_2} = kT \ln \left( \frac{N_2}{N_i} \right) \]

\( N_i \) is the carrier concentration in TiO\(_2\) photoanodes; \( N_2 = N_i + \Delta N \), where \( \Delta N \) (>0) is the change of hole concentration determined from \( J-V \) curves (\( \Delta N \sim 5\times10^{15} \text{ cm}^{-3} \)). Typically, for \( n \)-type TiO\(_2\), \( N_i = \sim 10^{17} \text{ (cm}^{-3} \) ). Thus,

\[ \Delta \phi_2 = E_{f_1} - E_{f_2} = kT \ln \left( \frac{N_2}{N_1} \right) = kT \ln \left( 1 + \frac{\Delta N}{N_i} \right) \]

(3) **Relationship between pH and accumulated charges.**

The water oxidation reaction occurs when the over potential between semiconductor and electrolyte is met. Assume the value of over potential does not change in our TiO\(_2\)-KOH system and in the two PEC setups, the TiO\(_2\) nanotube photoanodes did not change. Thus, the calculated potential difference for the semiconductor described in section 2 is actually the potential difference for KOH solution.

Let \( \Delta \phi_1 = \Delta \phi_2 \), we have:
\[ 0.059(pH - 14) = kT \ln \left(1 + \frac{\Delta N}{N_1}\right) \]

For \(N_1 \sim 10^{17}, \Delta N \sim 5 \times 10^{15}, kT \sim 0.025\text{eV}\)

Then, \(pH \approx 14.02\)

To confirm the pH effect, PEC measurement was performed within an electrolyte with a pH value of 14.02 using the in-electrolyte setup. As shown in Figure S6, no initial current spikes were observed.

**Figure S6.** \(J-V\) characteristics of cellulose-templated TiO\(_2\) photoanodes measured under interrupted illumination using in-electrolyte PEC setup, where the pH value of electrolyte was 14.02. Inset is enlarged top regions of one \(J_{ph}\) cycle showing the flatness of initial current.
**Figure S7.** (a) TEM image of fibrous TiO$_2$ nanotubes obtained after 600 °C 24 hours annealing in vacuum. (b) TEM image showing TiO$_2$ wall with uniform thickness. (c) HRTEM image of TiO$_2$ wall showing good crystallinity.
Figure S8. EDS spectra of fibrous TiO$_2$ nanotube samples after 600 °C annealing for 24 hours under the environment of O$_2$ atmosphere (a) vacuum (b). The observed average elemental content of carbon (atom %) was 5.713% for TiO$_2$ annealed in O$_2$ atmosphere; and 10.025% for TiO$_2$ annealed in vacuum. The “Si” peak and “Sn” peaks came from the FTO glass substrate.
**Figure S9.** (a) Calculated efficiencies of “black” cellulose-templated TiO₂ photoanode measured using capillary and in-electrolyte PEC setups under Xe lamp illumination. (b, c) Calculated efficiencies of cellulose-templated TiO₂ photoanodes annealed in vacuum (black curves) and in oxygen (red curves) measured with UV cutoff filter (c) and AM 1.5 G filter (d). All the curves were measured using capillary PEC setup.

**References:**

