Supporting Information

Internal Field Engineering of WO$_3$ by ion channel migration with Enhanced Photocatalytic Oxygen Evolution Ability

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Sample Preparation for pristine m- WO_3, $T-Na_5W_{14}O_{44}$ and $T-Na_2W_4O_{13}$

• Pristine m-WO_3 was prepared by thermal decomposition method. The white APT powder was calcined at 500°C for 4hours in a static atmosphere of air, and then was rapidly cooled to room temperature.

• Pristine $T-Na_5W_{14}O_{44}$ and $T-Na_2W_4O_{13}$ was prepared using a hydrothermal method. In a typical procedure, 9.8955g $Na_2WO_4 \cdot 2H_2O$ was dissolved in 30ml deionized water. Then, 3mol/L HCl was slowly dropped into the solution with vigorous stirring, until the pH of the mixture was adjusted to 3.0. Finally, the transparent solution was transferred into a 100ml Teflon-lined stainless steel autoclave, and sealed, heated in an oven at 160 °C for 3h. The obtained white powder was washed five times with distilled water, and dried in a vacuum oven at 60 °C for 24h, which then calcined at 400°C and 500°C for two hours to get the pristine $T-Na_5W_{14}O_{44}$ and $T-Na_2W_4O_{13}$, respectively.

• **Apparent Quantum efficiency (AQE) calculation**

The apparent quantum efficiency (AQE) of Na/WO_3-500° for solar water oxidation was evaluated by calculating the percentage of energy conversion of incident photon. The AQE measurement for O_2 evolution is carried out according to a standard experimental procedure. The reaction solution containing the photocatalyst and sacrificial agent was irradiated by monochromatic light (λ=420 nm). The incident light intensity was tested to be 29.00 mW·cm^{-2} using a PL-MW2000 light power meter (Beijing Perfectlight Technology Co, LTD.) and the light irradiation area was 19.63 cm^2. The hole consumption rate can be calculated based on the evolution rate of

O_2 in the initial one hour irradiation, which was 41.9umol·h^{-1}. Therefore, the AQE can be estimated according to the following equation:

$$AQE(\%) = \frac{hole\ consumption\ rate}{incident\ photon\ rate} \times 100\%$$

$$= \frac{4 \times O_2 generating\ rate}{incident\ photo\ rate} \times 100\%$$

$$= \frac{4 \times 6.02 \times 10^{23} \times 41.9 \times 10^{-6}}{29.00 \times 10^{-3} \times 19.63 \times 420 \times 3600 \times 10^{-9} \Big/ 6.626 \times 10^{-34} \times 3 \times 10^8}$$

$$= 2.33\%$$
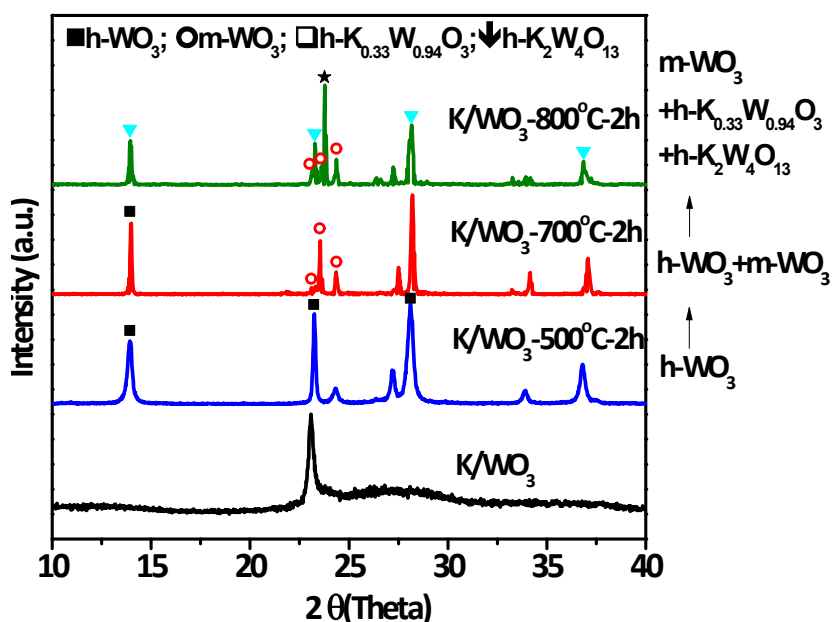
Figure S1 XRD patterns of different samples prepared by calcination of K/WO$_3$ at different temperatures, where ■= hexagonal, O= monoclinic WO$_3$, ▼Hexagonal K$_{0.33}$W$_{0.94}$O$_3$, ★= Hexagonal K$_2$W$_4$O$_{13}$ crystal structure.
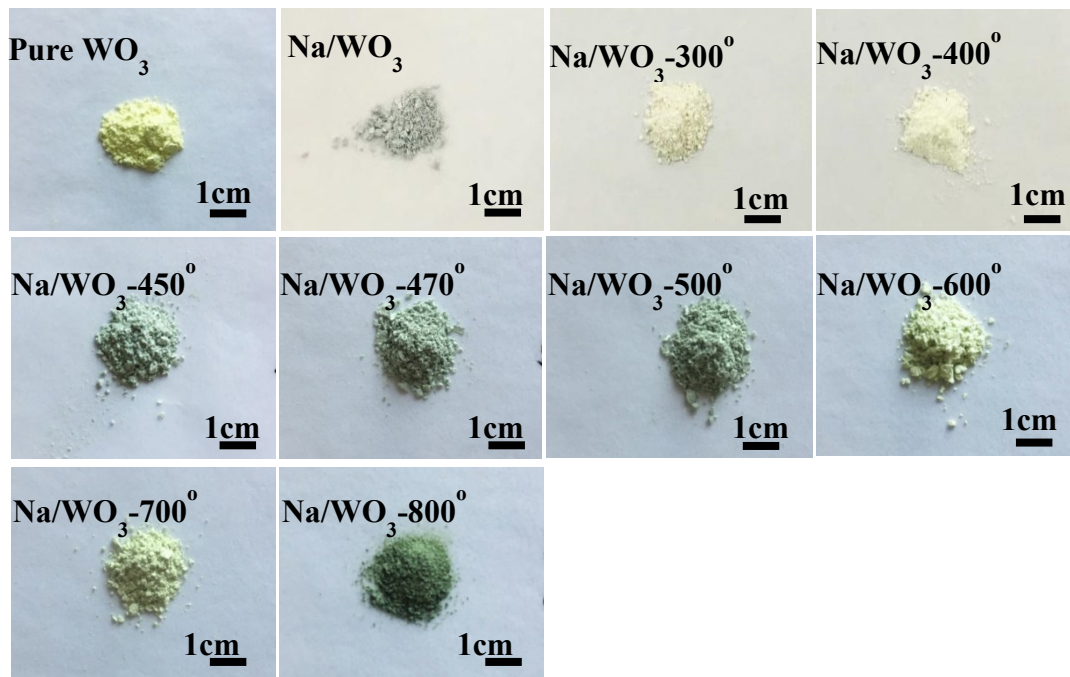
Figure S2 Sample pictures of pure WO_3, Na/WO_3, and Na/WO_3-T.
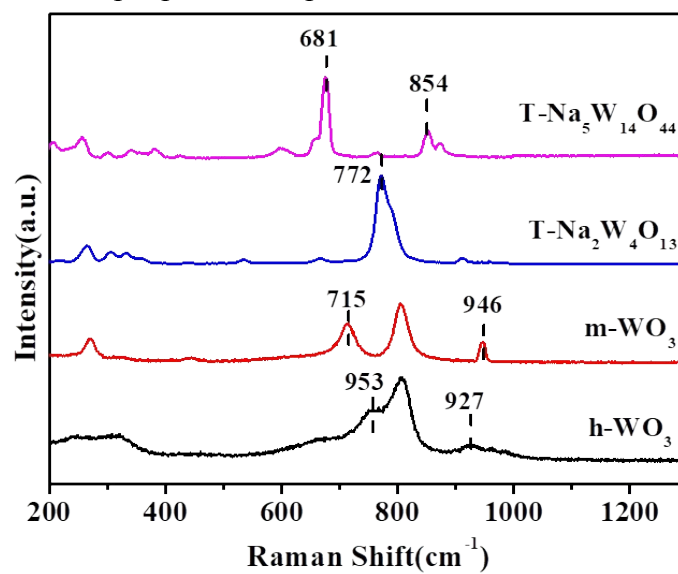
Figure S3 Vis-Raman spectra (Laser line 532nm) of pure phases: h-WO_3, m- WO_3, T-$Na_5W_{14}O_{44}$ and T-$Na_2W_4O_{13}$
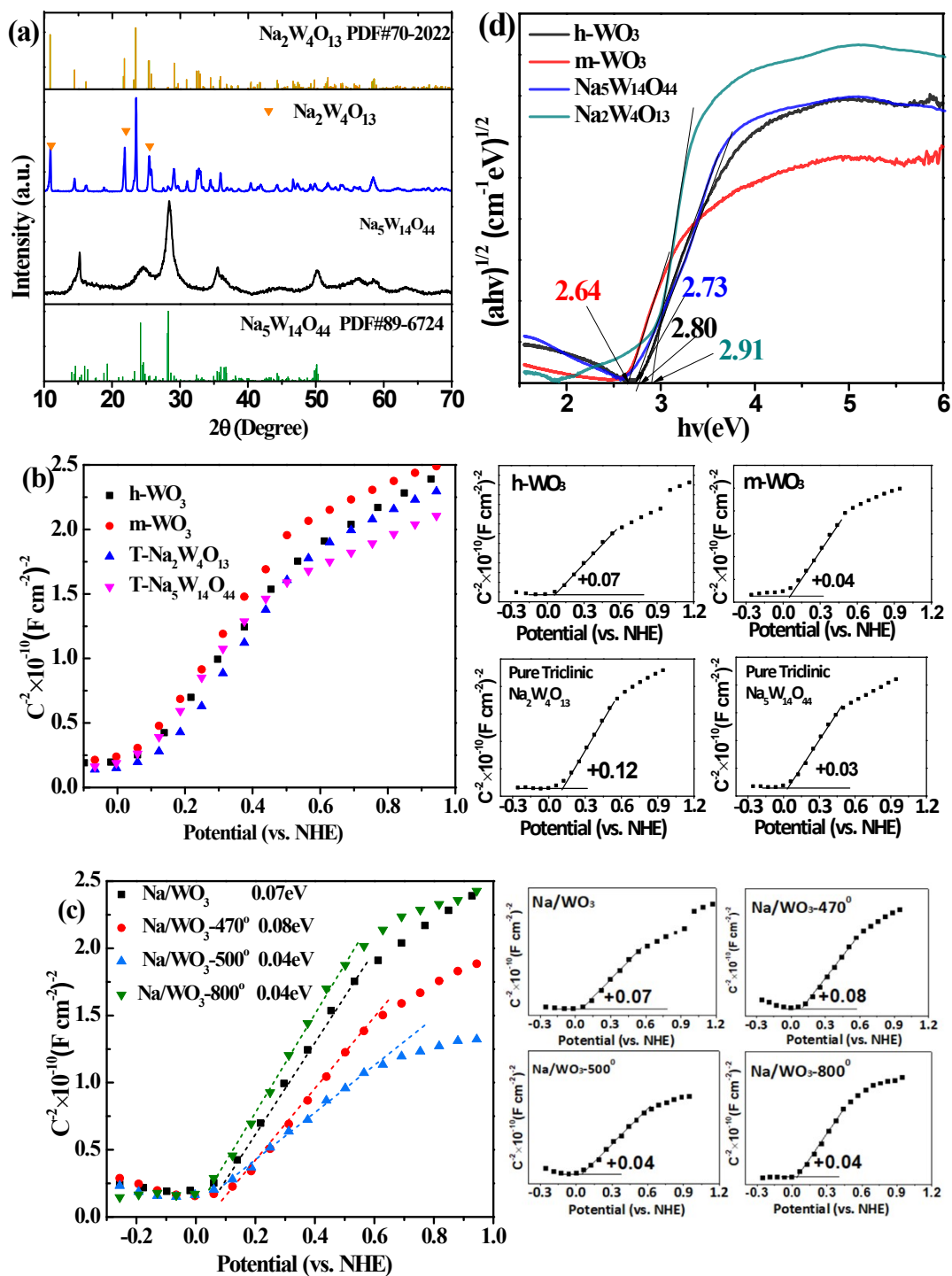
Figure S4 (a) XRD of prepared T-Na$_5$W$_{14}$O$_{44}$ and T-Na$_2$W$_4$O$_{13}$ using the modified solid state synthesis method in sample preparation section. (b) Mott-Schottky curves of h-WO$_3$, m-WO$_3$, pure T-Na$_2$W$_4$O$_{13}$ and pure T-Na$_5$W$_{14}$O$_{44}$, The extrapolation of the C^{-2} *vs.* E curves on the *x* intercepts give the E$_{FB}$ of +0.07eV(*vs.* NHE) for h-WO$_3$, +0.04eV for m-WO$_3$, +0.12 eV for T-Na$_2$W$_4$O$_{13}$, and +0.03 eV for T-Na$_5$W$_{14}$O$_{44}$,

respectively.(c) Mott-Schottky curves of Na/WO$_3$ (h-WO$_3$) and Na/WO$_3$-T, measured in Na$_2$SO$_4$ solution (0.5M, pH ca. 7.0). (d)Tauc plot of the h-WO$_3$, m-WO$_3$, Pure T-Na$_5$W$_{14}$O$_{44}$ and Pure T-Na$_2$W$_4$O$_{13}$.
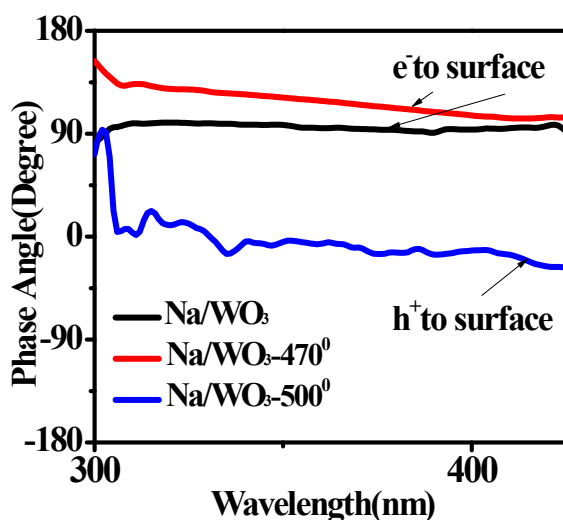

Figure S5 Phase angle curves of Na/WO$_3$-T. Signal in the first or fourth quadrant (-90° ~+90°) means photoinduced holes transferred to the surface of photocatalysts under the irradiation, in second or third quadrant (+90° ~+180°, -90° ~-180°) photoinduced electrons transfered to surface.
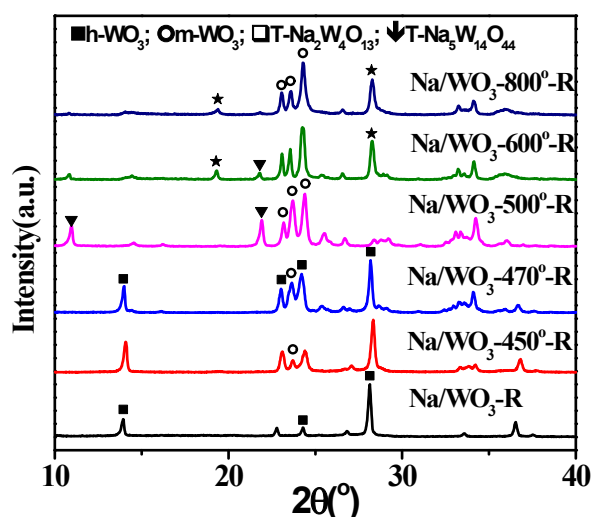

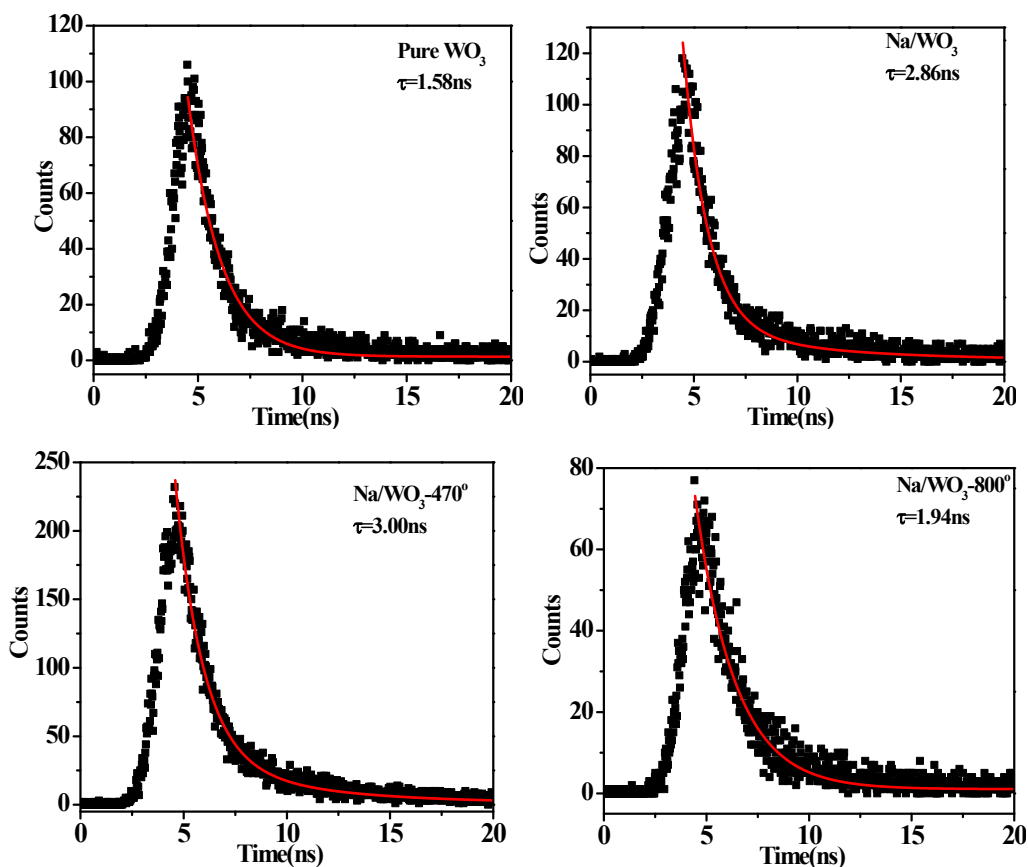Figure S6 XRD of the photocatalysts after 4 hours' photocatalytic reactions.

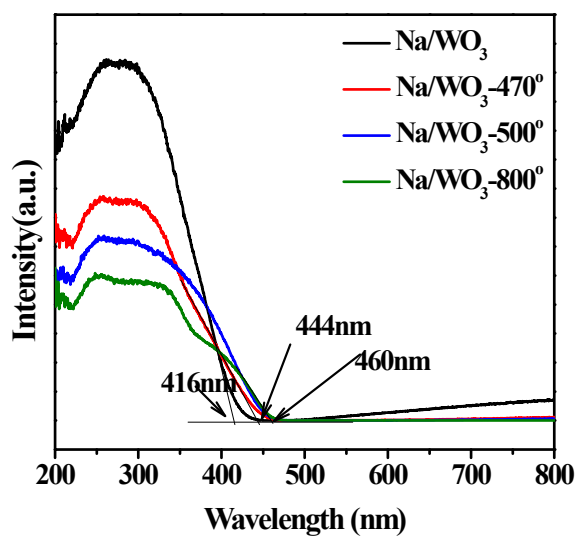Figure S7 Time-resolved photoluminescence spectroscopy for Pure WO_3, Na/WO_3, Na/WO_3-470°, and Na/WO_3-800°.

Figure S8 UV-vis DRS of Na/WO_3 and Na/WO_3-T and their absorption edges.