

## Supplement files

### Materials and methods

#### Chemicals and materials

$K_{10}P_2W_{17}O_{61} \cdot nH_2O$  ( $P_2W_{17}$ ) was prepared according to the literature method and identified by IR spectra (Figure S1), UV-vis absorption spectra (Figure S2) and cyclic voltammetry (Figure S3).

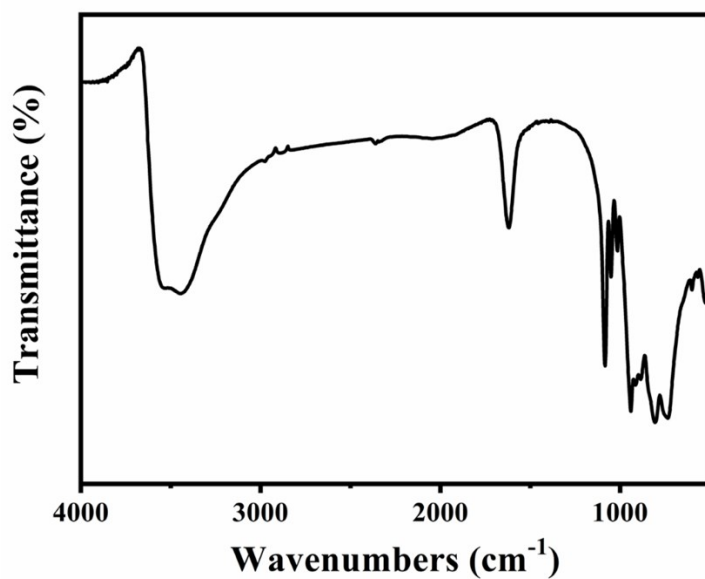


Figure S1. The IR spectra of  $K_{10}P_2W_{17}O_{61} \cdot nH_2O$

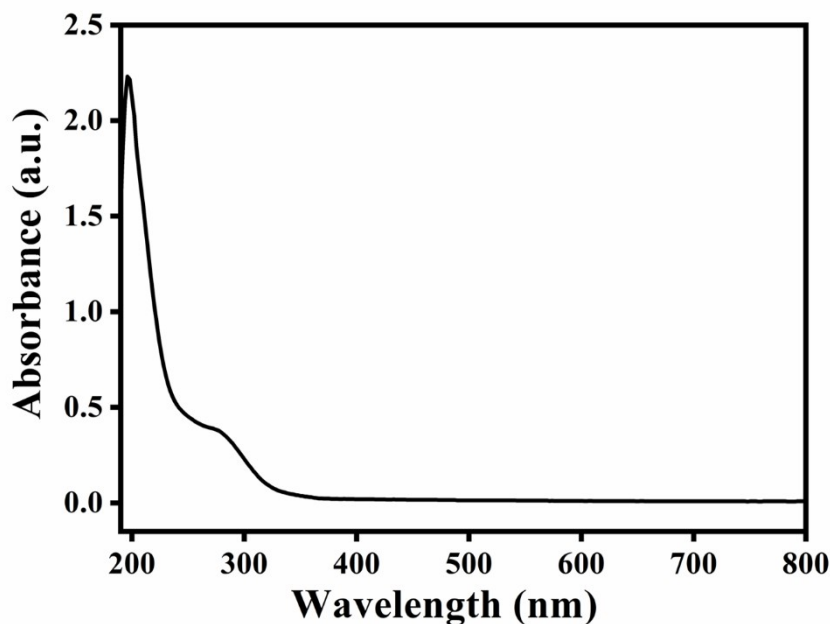


Figure S2. The UV-vis spectra of  $K_{10}P_2W_{17}O_{61} \cdot nH_2O$

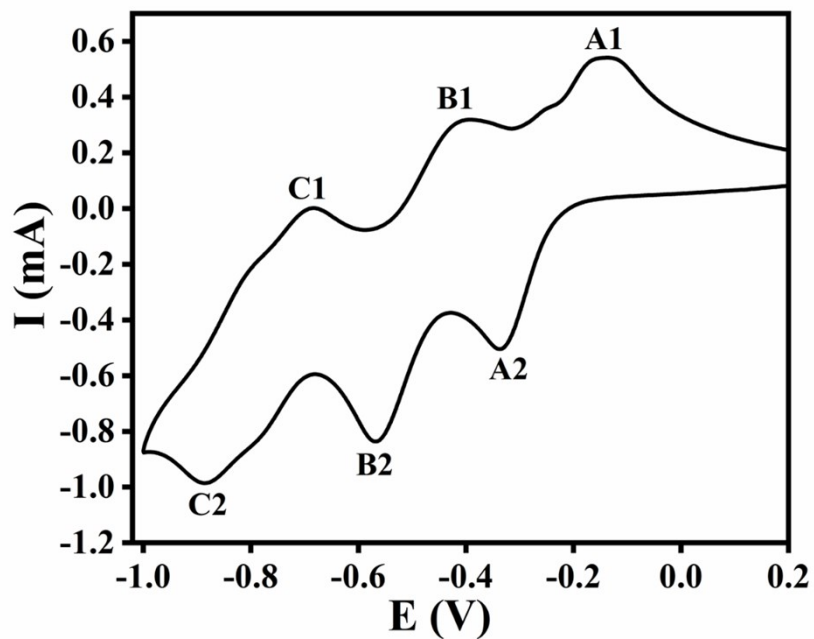


Figure S3. CV curve of  $K_{10}P_2W_{17}O_{61} \cdot nH_2O$  in HOAc-NaOAc solution (pH = 3.5).

The mass loading of different samples: NW- $P_2W_{17}$  is 0.0401g, FTO- $P_2W_{17}$  is 0.0144g, FTO- $TiO_2$  is 0.0257g.

## Results and discussion

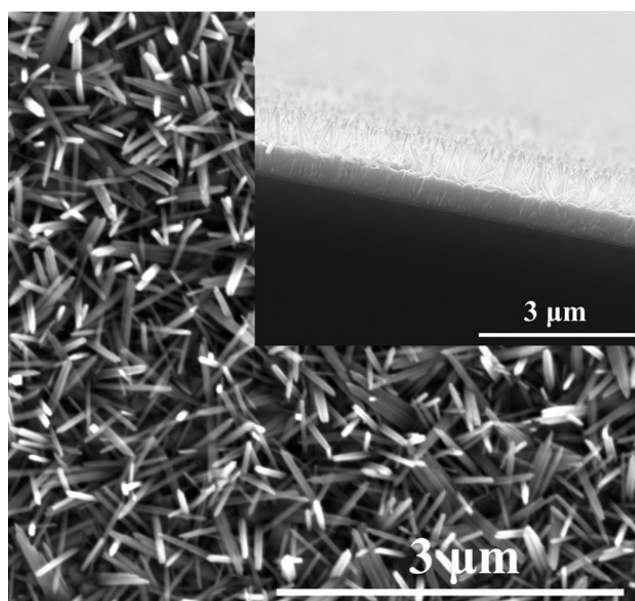


Figure S4. The SEM images of  $TiO_2$  NW (inset: the cross-sectional images of prepared films)

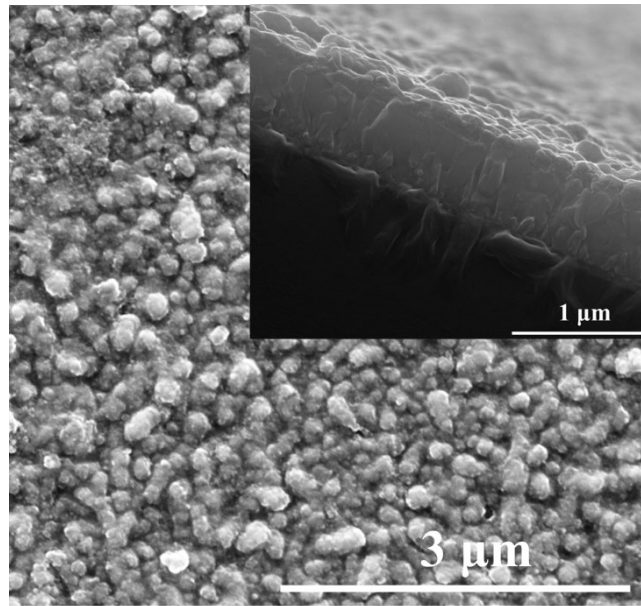


Figure S5. The SEM images of FTO-P<sub>2</sub>W<sub>17</sub> (inset: the cross-sectional images of prepared films)

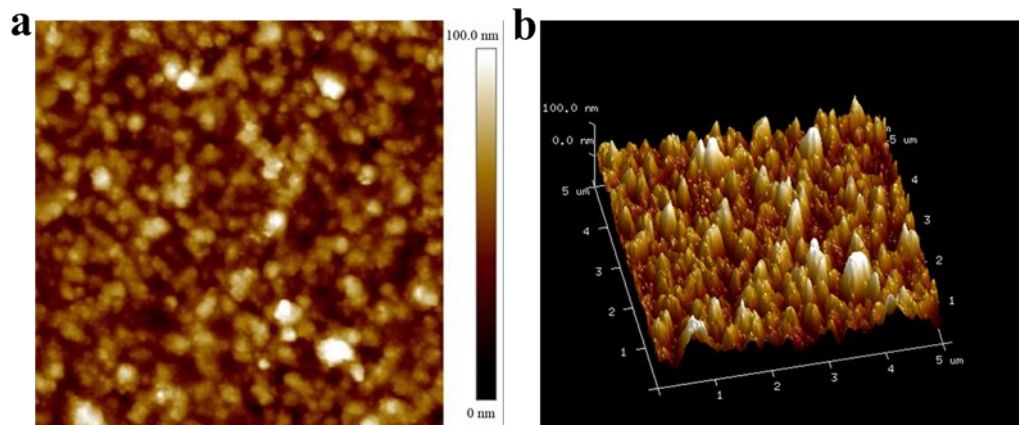


Figure S6. 2D AFM images of (a) FTO-P<sub>2</sub>W<sub>17</sub> and 3D AFM images of (b) FTO-P<sub>2</sub>W<sub>17</sub>

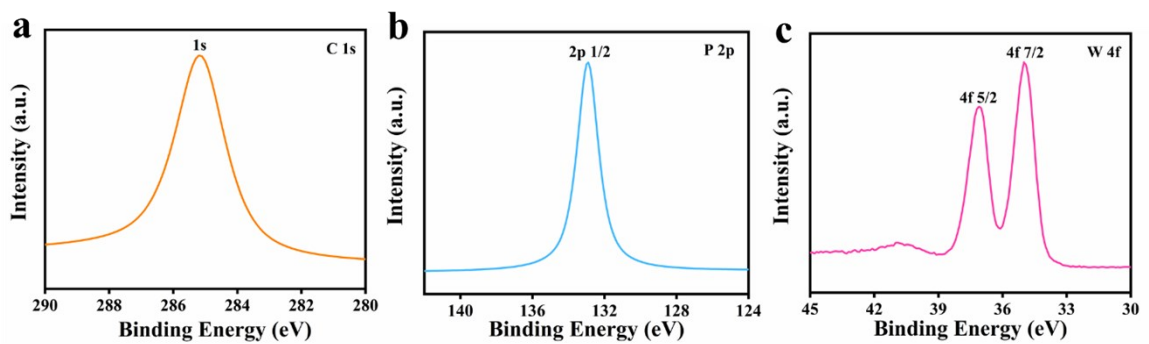


Figure S7. High-resolution XPS spectra for C1s(a), P2p (b) and W 4f (c) of FTO-P<sub>2</sub>W<sub>17</sub> film.

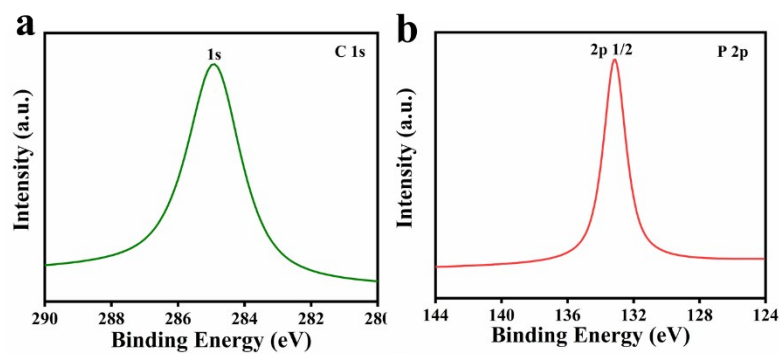


Figure S8. High-resolution XPS spectra for C 1s (a) and P 2p (b) of NW-P<sub>2</sub>W<sub>17</sub> film.

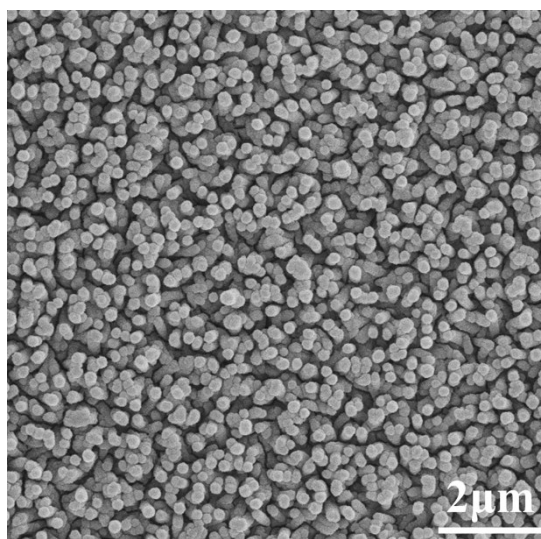


Figure S9. The SEM of NW-P<sub>2</sub>W<sub>17</sub> film after cycle stability test.

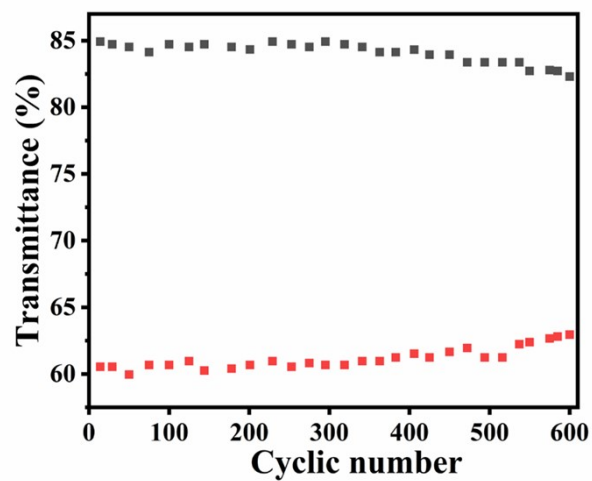


Figure S10. Cycle stability of FTO-P<sub>2</sub>W<sub>17</sub> film at 600 nm under square wave potentials of -1.5 V and +1.5 V.