## **Supporting information**

## Decoration of CdS nanoparticle on dense and multi-edge sodium titanate nanorods to form a highly efficient and stable photoanode with great enhancement in PEC performance

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## Characterization and equipment

X-ray diffraction patterns were obtained by XRD spectroscopy (Bruker D8Advance) with monochromatic Cu K $\alpha$  radiation ( $\lambda$ =1.5406 Å) in the 2 $\theta$  range of 2–80° at room temperature (RT). The morphologies of different photoanodes were evaluated with the scanning electron microscopy (SEM), Model Quanta 250 FEG (Field Emission Gun), and transmission electron microscopy (JEM-2100F). Raman spectra were recorded using a labRam HR micro-Raman spectrophotometery (Bruker, model: Senteraa 2009, Germany) with a 785 nm laser line as an excitation source at RT. The chemical states of the elements in the samples were investigated using X-ray photoelectron spectroscopy (XPS) data recorded by Thermo Scientific Sigma Probe spectrometer with a monochromatic AlK $\alpha$  source (photon energy 1486.6 eV), a spot size of 400  $\mu$ m, pass energy of 200 eV, and an energy step size of 1.0 eV. The UV–vis absorbance spectra were taken by Unico UV-2100 spectrophotometer. The spectra were recorded at RT in the air within the range of 200–800 nm. The photoluminescence (PL) spectra were obtained by Shimadzu

RF-1501 spectrofluorophotometery at an emission wavelength of 350 nm and a range of 200-800 nm.

## Hydrogen and Oxygen Evolution Measurement:

For gas evolution measurement, a tight closed cell is used, which is sealed by rubber plugs and parafilm. Photoanode was as a working electrode, Pt wire as the counter electrode, and the RHE as a reference electrode. Before starting the water splitting reaction, the 0.5 M Na<sub>2</sub>SO<sub>3</sub> electrolyte which its pH adjusted to 9, purged via nitrogen gas. The produced hydrogen and oxygen gas amounts were measured using the gas chromatography (GC) system (YL Instrument, 6500GC System). The evolved gas was evaluated every 30 min for 2 h reaction at 1V (vs. RHE). The gas samples were injected in the GC, and the resulting peak areas (Area H<sub>2</sub>, Area O<sub>2</sub>) were recorded. The calibration curve was obtained by injecting 1-5% hydrogen and oxygen gases in the nitrogen balanced gas.

The evolved hydrogen-oxygen gases were calculated according to the following formula:

$$H_{2}(O_{2})\mu mol.cm^{-2} = \left[\frac{Area \ of \ H_{2}peak}{Slope \ of \ calibration \ curve}\right] \times [Head \ space \ volume] \times (\frac{1mol}{24.2 \ L})$$



Fig. 1. XRD patterns of Ti foil



Fig. 2. valance band edge for pure NTO and CdS



Fig. 3. growth of CdS on the top side of NTO nanorods

It can be observed that most of CdS particles coated the top surface of nanorods, rather than the side surface.



Fig. 4. Cross-sectional SEM images of NTO/CdS12



Fig. 5. long time photocurrent stability of NTO/CdS12 photoanode

$$\frac{1}{C^2} = \frac{2}{\varepsilon \varepsilon_0 A^2 e N_D} (V - V_{fb} - \frac{K_B T}{e})$$
(1)

$$Slope = \frac{2}{\varepsilon \varepsilon_0 A^2 e N_D} \rightarrow N_D = \frac{2}{\varepsilon \varepsilon_0 A^2 e(Slope)}$$
(2)

$$\operatorname{int} ercept = V_{fb} + \frac{K_B T}{e} \rightarrow V_{fb} = \operatorname{int} ercept - \frac{K_B T}{e}$$
(3)

Where, C is the capacitance of the space charge layers, *e* is the electron charge ( $1.60 \times 10^{-19}$  C), *\varepsilon* is the dielectric constant of the Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> (3.9),  $\varepsilon_0$  is the vacuum permittivity ( $8.854 \times 10^{-14}$  F/cm), N<sub>D</sub> is the donor density (cm<sup>-3</sup>), and k<sub>B</sub> is the Boltzmann constant ( $1.38 \times 10^{-23}$  J. K<sup>-1</sup>).

The donor concentration can be measured from the slope of the Mott-Schottky plot, and  $V_{fb}$  is obtained as the value of the x-intercept (See Table 1 and Fig.10c). Accordingly, the smaller slope of the electrode represents a higher  $N_D$ .