

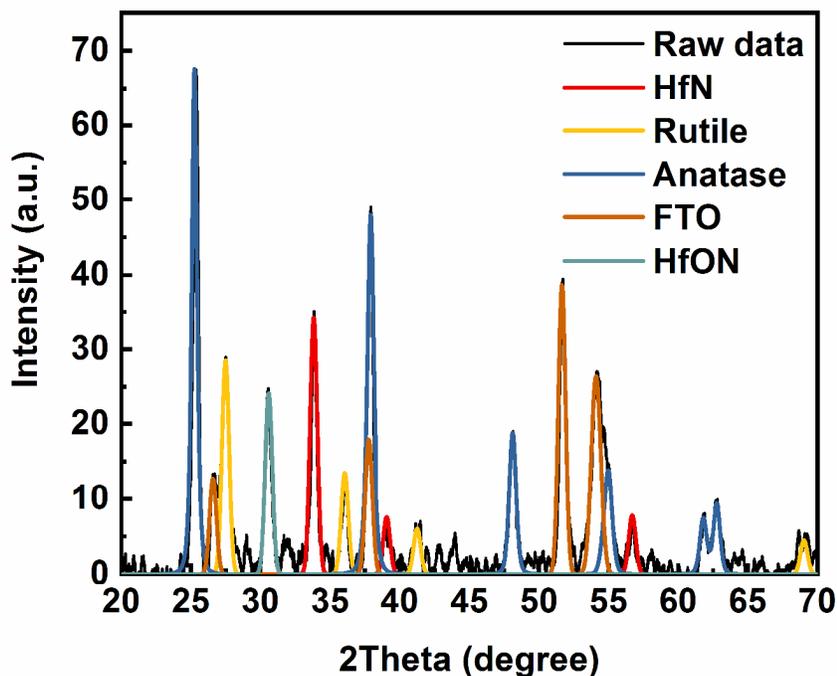
# Supporting Information

## TiO<sub>2</sub>-HfN Radial Heterojunction: Hot Carrier Photoanode for Sunlight-Driven Water-Splitting

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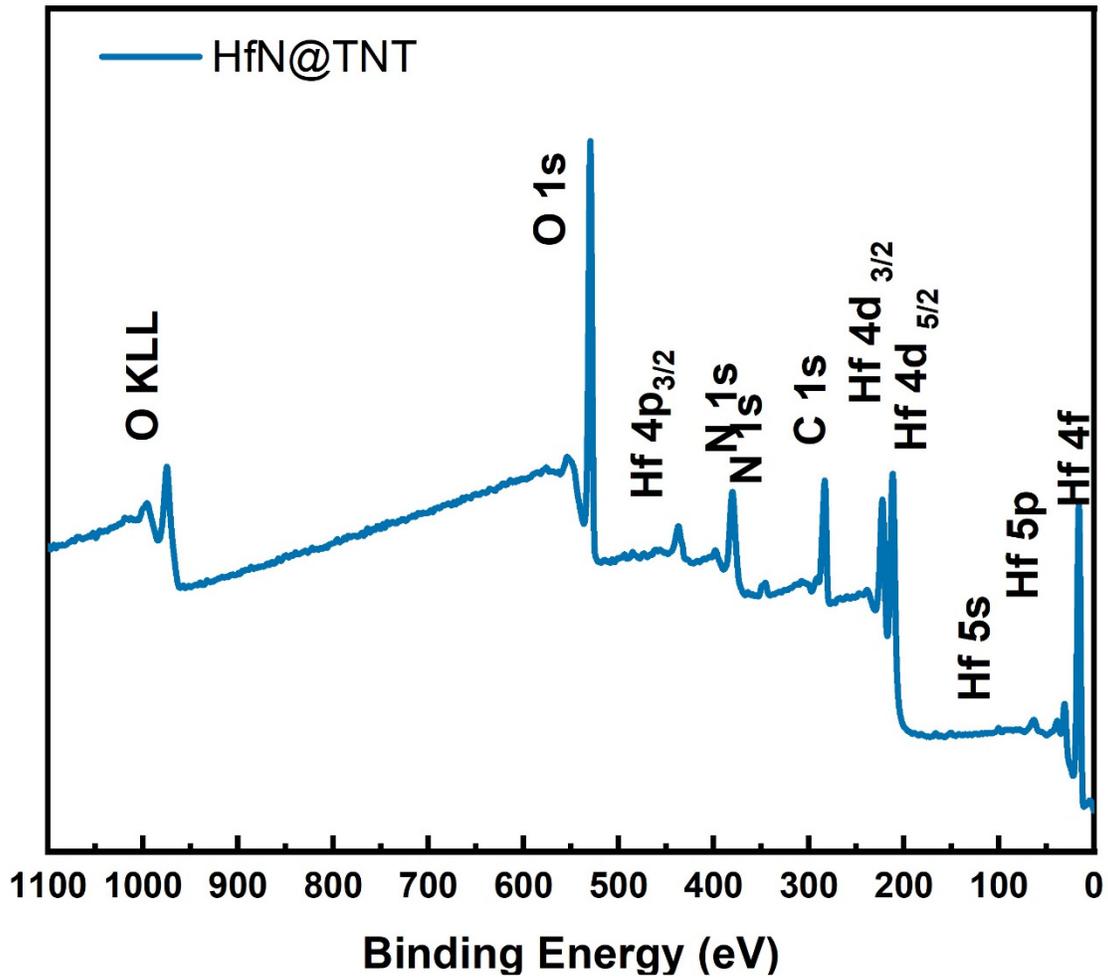
### Additional information on materials characterization and electromagnetic simulations

X-ray diffractograms were collected to investigate the phase structure and crystalline nature of the samples. The deconvolution of X-ray diffraction pattern is presented in Figure S1 exhibiting peaks corresponding to HfN (JCPDS#33-0592), HfON (JCPDS#89-8346), anatase TiO<sub>2</sub> (JCPDS#21-1272), rutile TiO<sub>2</sub> (JCPDS#21-1276), and FTO (JCPDS#41-1445).



**Figure S1.** X-ray diffractogram of HfN-TNT sample, illustrating material components by separating signals.

## X-ray photoelectron spectroscopy (XPS)

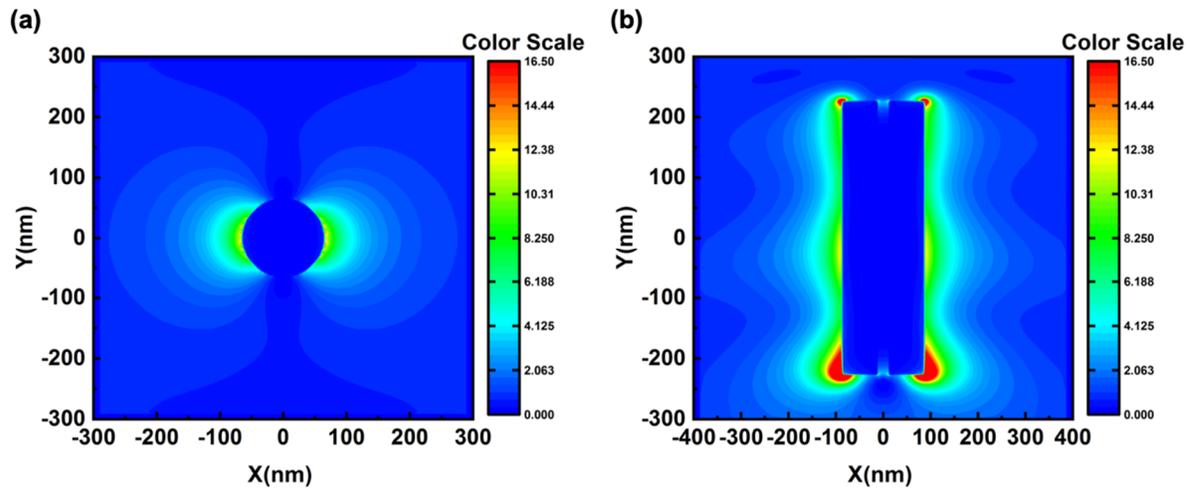


**Figure S2.** XPS survey scan of HfN-TNT sample

### Simulation of electric field

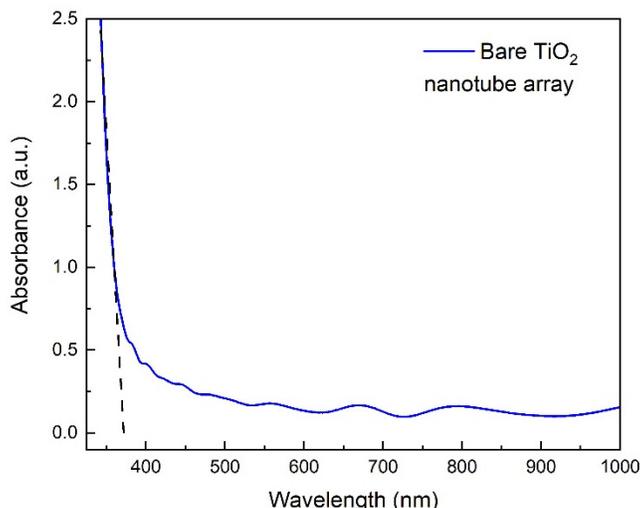
Optical properties of the HfN-TNT structures were investigated using Lumerical FDTD simulation software. The composite structures were simulated with reference to experimental SEM and TEM images obtained and spanned TiO<sub>2</sub> nanotubes of inner diameter 50 nm and outer diameter of 100 nm. The nanotubes are 700 nm in length and are coated by a 20 nm thick layer of HfN. The coating is conformal in nature and is simulated by encasing the nanotube in a HfN cylindrical block.

Electric field intensity profiles (at the resonant wavelength) were captured using near, and far-field profile and frequency monitors. Optical constants for TiO<sub>2</sub> and HfN were obtained via in-lab ellipsometry measurements and Palik. A light source of bandwidth range 350-1200 nm was incident upon the structures at a normal incidence from above. Lumerical's in-built refractive index monitor was utilized to confirm the structures were appropriately configured and modeled throughout the course of the simulation. Antisymmetric and symmetric boundary conditions were utilized to shorten simulation time. Relevant results pertaining to the electric field intensity profiles, were obtained at the resonant wavelength of 650 nm and viewed along different planes including the xy- and xz-planes.



**Figure S3.** Results of FDTD simulations of HfN-TNT showing electric field intensities for (a) xy plane and (b) xz plane at the resonant wavelength of 650 nm.

## UV-vis spectrum of bare (uncoated) TiO<sub>2</sub> nanotube arrays



**Figure S4.** Optical extinction spectrum of a bare TiO<sub>2</sub> nanotube array. The semiconductor band-edge occurs in the ultraviolet at  $\sim 3.25$  eV. Notice the interference fringes due to the constructive and destructive interference of light reflected from the top-surface (air/TiO<sub>2</sub> nanotube interface) and bottom surface (TiO<sub>2</sub> nanotube/FTO interface) of the nanotube array film respectively.

## H<sub>2</sub> generation

In order to validate the premise that the photocurrent is truly from photoelectrochemical water splitting, the hydrogen evolution experiment was conducted using a H-cell with a Pt counter electrode. Both oxygen and hydrogen were generated and collected in a photoelectrochemical H-cell. However, our pulse discharge detector (PDD) equipped gas chromatograph is significantly more sensitive and accurate for H<sub>2</sub> measurements. The sample was in 0.1 M KOH electrolyte with +0.6 V applied bias and illuminated under AM 1.5G solar simulated light for 1 hour. The evolved hydrogen was collected using a gas-tight syringe at the Pt counter electrode and analyzed by gas chromatography with a pulsed discharged detector. The generated hydrogen at the Pt counter was calculated to be 33.6  $\mu\text{mol h}^{-1}$ , which was calibrated by a standard gas mixture for quantitative analysis. Faradaic efficiency (FE%) was calculated to be 91.6% based on the equation below:

$$\text{FE}\% = \frac{\text{Observed hydrogen evolution}}{\text{Theoretical hydrogen evolution}} \times 100$$

$$= \frac{\textit{Observed hydrogen evolution}}{(J \times A \times T)/(2 \times e \times N_A)} \times 100$$

The observed hydrogen evolution is in moles,  $J$  is photocurrent density in  $\text{Acm}^{-2}$ ,  $A$  is the irradiated area in  $\text{cm}^2$ ,  $T$  is the photoelectrochemical water splitting time duration in seconds,  $e$  is the elementary electronic charge ( $1.602 \times 10^{-19}$  C), and  $N_A$  is Avogadro number ( $6.02 \times 10^{23} \text{ mol}^{-1}$ ).

## REFERENCES

- [1] S. Shinkai, K. Sasaki, Influence of Sputtering Parameters on the Formation Process of High-Quality and Low-Resistivity HfN Thin Film, Japanese Journal of Applied Physics, 38 (1999) 2097-2102.
- [2] P. Kumar, P. Kar, A.P. Manuel, S. Zeng, U.K. Thakur, K.M. Alam, Y. Zhang, R. Kisslinger, K. Cui, G.M. Bernard, V.K. Michaelis, K. Shankar, Noble Metal Free, Visible Light Driven Photocatalysis Using TiO<sub>2</sub> Nanotube Arrays Sensitized by P-Doped C<sub>3</sub>N<sub>4</sub> Quantum Dots, 8 (2020) 1901275.
- [3] E.D. Palik, Handbook of optical constants of solids, Academic press 1998.