Modulating the interaction between gold and TiO$_2$ nanowires for enhanced solar driven photoelectrocatalytic hydrogen generation

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S1. Crystalline structure

**Figure S1.** X ray diffraction spectra of pristine TiO$_2$-NWs and N-TiO$_2$-NWs.

The crystalline phases of the pristine TiO$_2$-NWs and N-TiO$_2$-NWs were studied by X-ray diffraction (XRD) using a diffractometer (Rigagu Denki Japan) with CuK$_\alpha$ radiation. The d-spacing of the crystallite lattice and full-width half maximum of the peaks were analyzed by PDXL-2 software. Fig. S1 shows the XRD results of TiO$_2$-NWs and N-TiO$_2$-NWs electrodes prepared on FTO substrate. The predominant diffraction peak is observed at $\sim 2\theta = 25.3^\circ$ in Fig. S1 belongs to the (101) reflection of anatase TiO$_2$ and there is no rutile peaks observed. No change in phase was observed due to the nitridation.
S2. TEM analysis of Au nanoparticle

**Figure S2.** High resolution transmission electron image of Au nanoparticles.
**Figure S3.** (a) Ultraviolet photoelectron spectra (UPS) of TiO$_2$-NWs and N-TiO$_2$-NWs electrodes and (b) zoomed view of low binding energy region.

The UPS spectra taken with photon energy using He I source ($h\nu = 21.2$ eV): full valence band, with 0 eV binding energy corresponding to the Fermi level. The valence band maximum is estimated from linear extrapolation from the band edge to binding energy axis as is shown in inset of Fig.S4 inset.$^1$ The VBM position is found to be $\sim 3.26$ eV and $\sim 2.69$ eV for TiO$_2$ and N-TiO$_2$, respectively. This implies that N doping carriers are creating sub-band or defects above the VB of TiO$_2$. 

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$^1$ Reference should be provided for further reading.
Figure S4. Schematic energetic structure of pristine and nitrogen doped TiO$_2$ decorated with Au nanoparticles for photocatalytic water oxidation process.

Reference:

S5. Durability test

Figure S5. Chronoamperometry plots (J-T) of pristine and Au NPs coated TiO$_2$ nanowire electrodes (Note that Au NPs were coated from 0.34×10$^{-7}$ M concentration stock solution). The applied potential was 1 V vs RHE.
Figure S6. IPCE spectra of TiO$_2$ and TiO$_2$-Au electrodes. The aqueous 0.5M Na$_2$SO$_4$ electrolyte is used for measurements. The IPCE data is recorded at 1.2 V vs (Ag/AgCl) applied potential.