Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Modulating the interaction between gold and TiO_2 nanowires for enhanced solar driven photoelectrocatalytic hydrogen generation

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S1. Crystalline structure

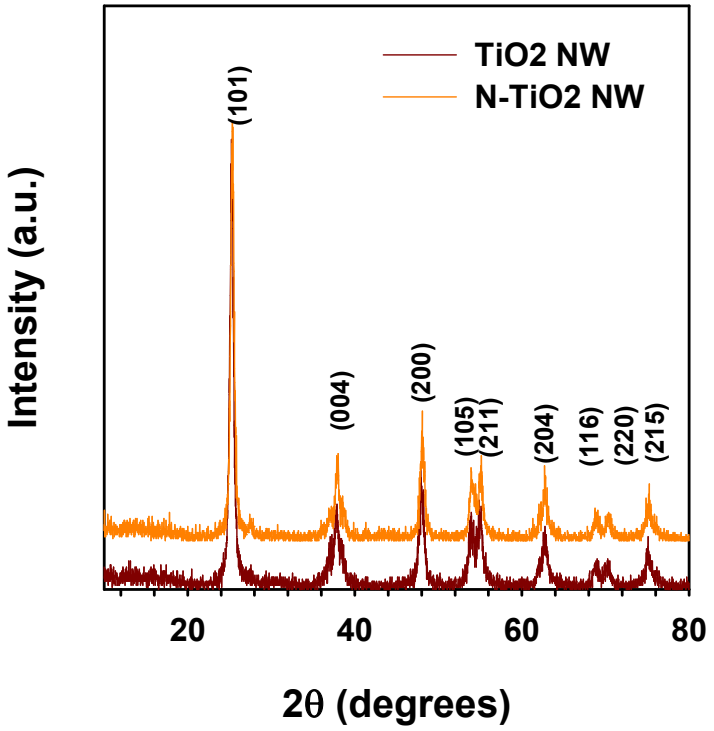

Figure S1. X ray diffraction spectra of pristine TiO_2-NWs and N-TiO_2-NWs.

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 CuKα 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 ~ $2\theta = 25.3°$ 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

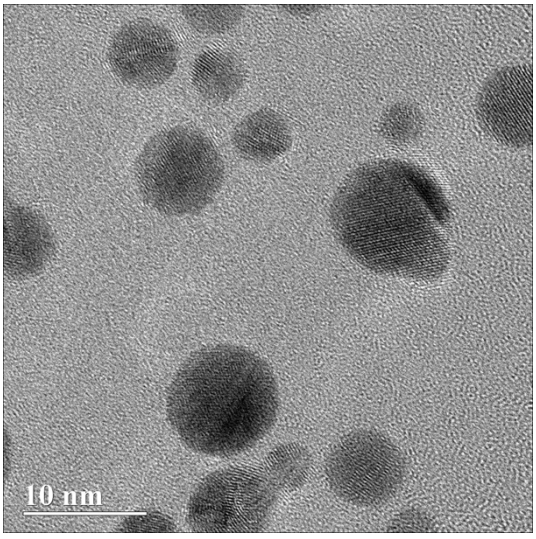

Figure S2. High resolution transmission electron image of Au nanoparticles.

S3. Ultraviolet photoelectron spectroscopy

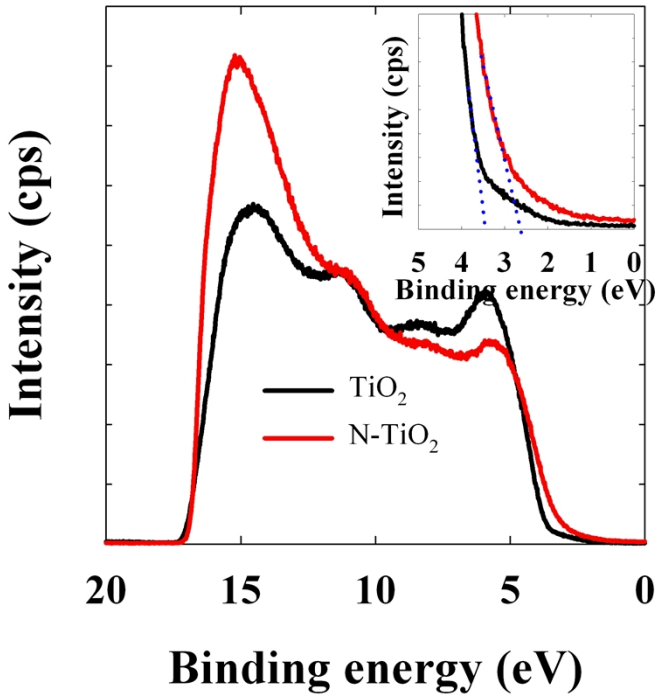

Figure S3. (a) Ultraviolet photoelectron spectra (UPS) of TiO_2-NWs and N-TiO_2-NWs electrodes and (b) zoomed view of low binding energy region.

The UPS spectra taken with photon energy using He I source (hυ = 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 ~3.26 eV and ~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.

S4. Energetic structure

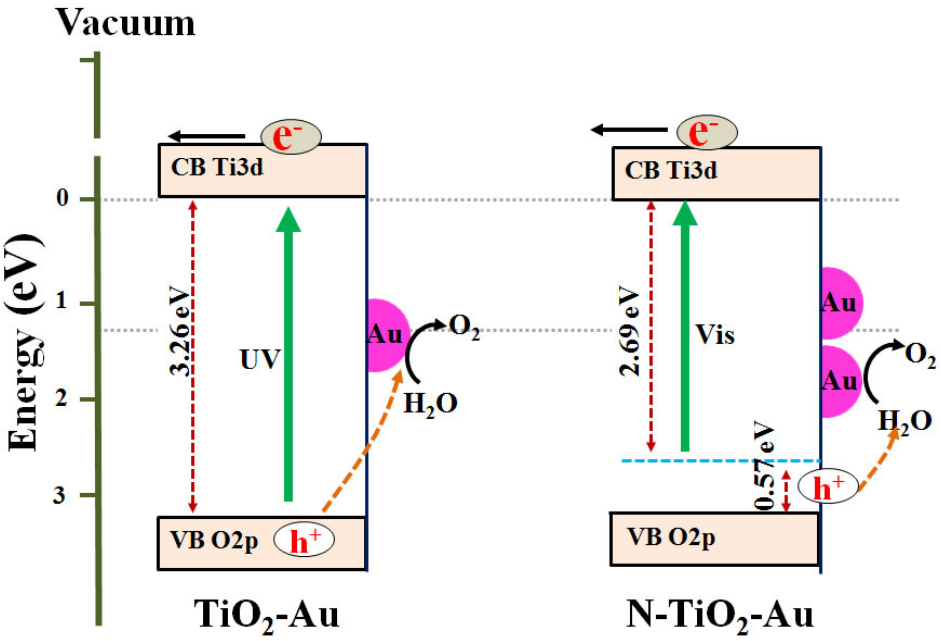

Figure S4. Schematic energetic structure of pristine and nitrogen doped TiO_2 decorated with Au nanoparticles for photocatalytic water oxidation process.

Reference:

1. B. Carlson, K. Leschkies, E. S. Aydil and X. Y. Zhu, *The Journal of Physical Chemistry C*, 2008, **112**, 8419-8423.

S5. Durability test

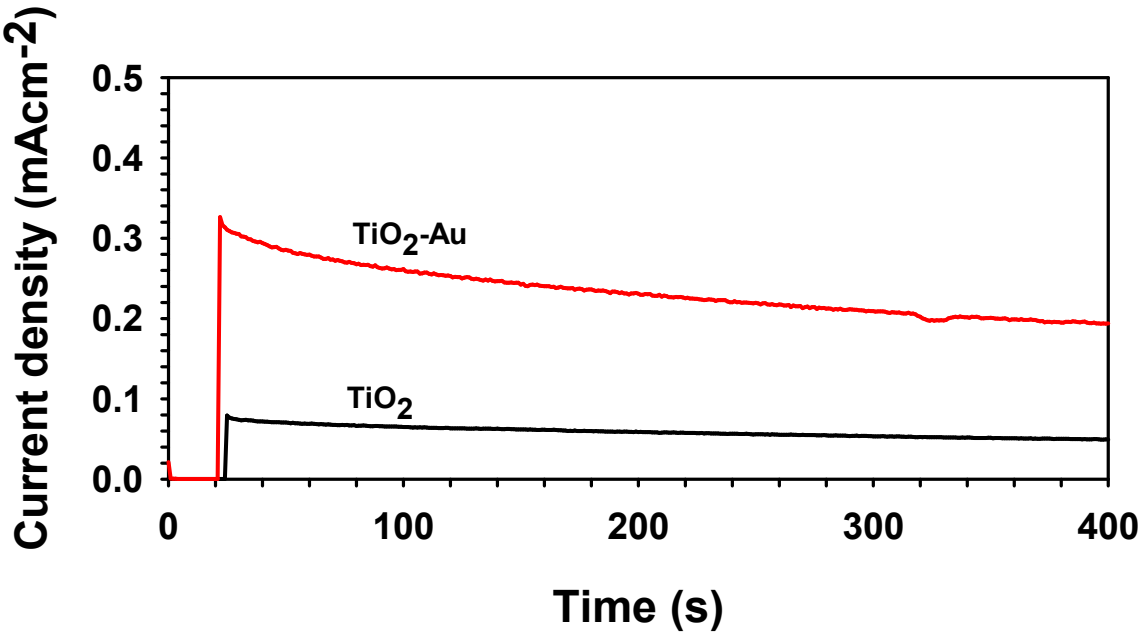

Figure S5. Chronoamperometry plots (J-T) of pristine and Au NPs coated TiO_2 nanowire electrodes (Note that Au NPs were coated from 0.34×10^{-7} M concentration stock solution). The applied potential was 1 V vs RHE.

S6. IPCE

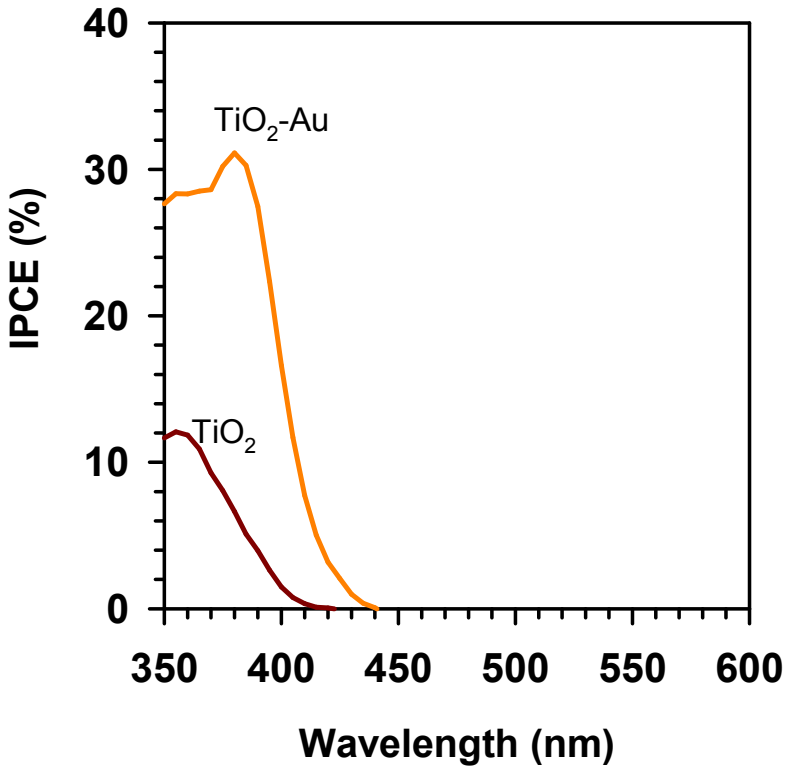

Figure S6. IPCE spectra of TiO_2 and TiO_2-Au electrodes. The aqueous 0.5M Na_2SO_4 electrolyte is used for measurements. The IPCE data is recorded at 1.2 V Vs (Ag/AgCl) applied potential.