Supporting Information

Enhanced photocatalytic performance at Au/N-TiO₂ hollow nanowire array by combinatorial light scattering and reduced recombination

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S1. Crystalline structure



Figure S1. X ray diffraction spectra of pristine TiO₂-NWs and N-TiO₂-NWs.

The crystalline phases of the pristine TiO₂-NWs and N-TiO₂-NWs were studied by X-ray diffraction (XRD) using a diffractometer (Rigagu Denki Japan) with CuK α 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 TiO₂-NWs and N-TiO₂-NWs electrodes prepared on FTO substrate. The predominant diffraction peak is observed at ~ $2\theta = 25.3^{\circ}$ in Fig. S1 belongs to the (101) reflection of anatase TiO₂ and there is no rutile peaks observed. No change in phase was observed due to the nitridation.

S2. Chemical environment



Figure S3. XPS N1s core spectra of pristine TiO₂-NWs and N-TiO₂-NWs.

The surface nitrogen doping at TiO₂-NWs is verified with X ray photoelectron spectra (XPS). The XPS studies were performed using an angular resolved electron analyzer with a monochromatic Al K α source (model Theta Probe, Thermo Fisher Scientific). The emitted electrons were detected at the angles between 23° and 83°. The resultant N1s core spectra of TiO₂-NWs and N-TiO₂-NWs are compared in Fig. S2. The presence of nitrogen carriers at N-TiO₂-NWs is ensured from the peak at ~395.6. It is reported that N 1s peak observed at <397 eV implies that the nitrogen carriers are chemisorbed on TiO₂ surface instead of substitutional Ti–N bond formation.

S3. Elemental mapping



Figure S3. Elemental mapping of Au/N-TiO₂-NWs measured along the yellow line indicated in the high magnification TEM image.

<u>S4. Ultraviolet photoelectron spectroscopy</u>



Figure S4. (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 (hv = 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 TiO₂ and N-TiO₂, respectively. This implies that N doping carriers are creating sub-band or defects above the VB of TiO₂.

Reference:

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