Supplementary Material (ESI) for Chemical Communications

Supporting Information

Nitrogen Doped Titania Nanosheets Towards Visible Light Response

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Experimental Section

Layered titanate precursor of $Cs_{0.68}Ti_{1.83}O_4$ was prepared according to a procedure previously reported. [1] Nitrogen doping in layered titanate was conducted by calcining the white $Cs_{0.68}Ti_{1.83}O_4$ powder at 750 ^oC in ammonia atmosphere for 2 hrs, resulting in nitrogen doped $Cs_{0.68}Ti_{1.83}O_{4-x}N_x$ powder with a bright yellow color. Its protonated form of $H_{0.68}Ti_{1.83}O_{4-x}N_x$ was prepared by ion-exchange of $Cs_{0.68}Ti_{1.83}O_{4-x}N_x$ with H^+ in 1 mol·dm^{-3} HCl solution for three days. The resulting yellow $H_{0.68}Ti_{1.83}O_{4-x}N_x$ (1.2g) sample was dispersed in a tetrabutylammonium hydroxide (TBAOH) solution (300 cm^3, 0.2 mol·dm^{-3}) and was shaken for more than 7 days at room temperature to exfoliate into a yellow colloidal suspension of $Ti_{0.91}O_{2-x}N_x$ nanosheets. To make a thin film photoelectrode, $Ti_{0.91}O_{2-x}N_x$ nanosheets were deposited on pre-treated quartz glass, silicon wafer, or ITO glass substrates via the electrostatic (layer-by-layer) LBL self-assembly method reported previously. [17] The substrate was first dipped in a polyethyleneimine (PEI) solution (0.125 wt%, pH = 9) for 20 min and then rinsed thoroughly with distilled water. Subsequently, the PEI coated substrate was immersed into the colloidal suspension of $Ti_{0.91}O_{2-x}N_x$ nanosheets (0.08 g·dm^{-3}, pH = 9) for 20 min, followed by rinsing in water and drying in nitrogen gas flow. Deposition of (PEI/$Ti_{0.91}O_{2-x}N_x$) was repeated to reach desirable layer numbers for the fabrication of multilayer thin film.

Measurements of photoelectrochemical water-splitting process were conducted in a quartz cell in a three-electrode system with a Pt foil and Ag/AgCl electrode as counterpart electrode and reference electrode, respectively. The electrolyte was 0.1

$mol \cdot dm^{-3}$ NaOH solution. Visible light irradiation in the range of 420 nm to 770 nm was supplied by a Xe lamp with the filter glasses. Photocurrent was recorded with the Solartron 1480 Multistat electrochemical measurement unit.

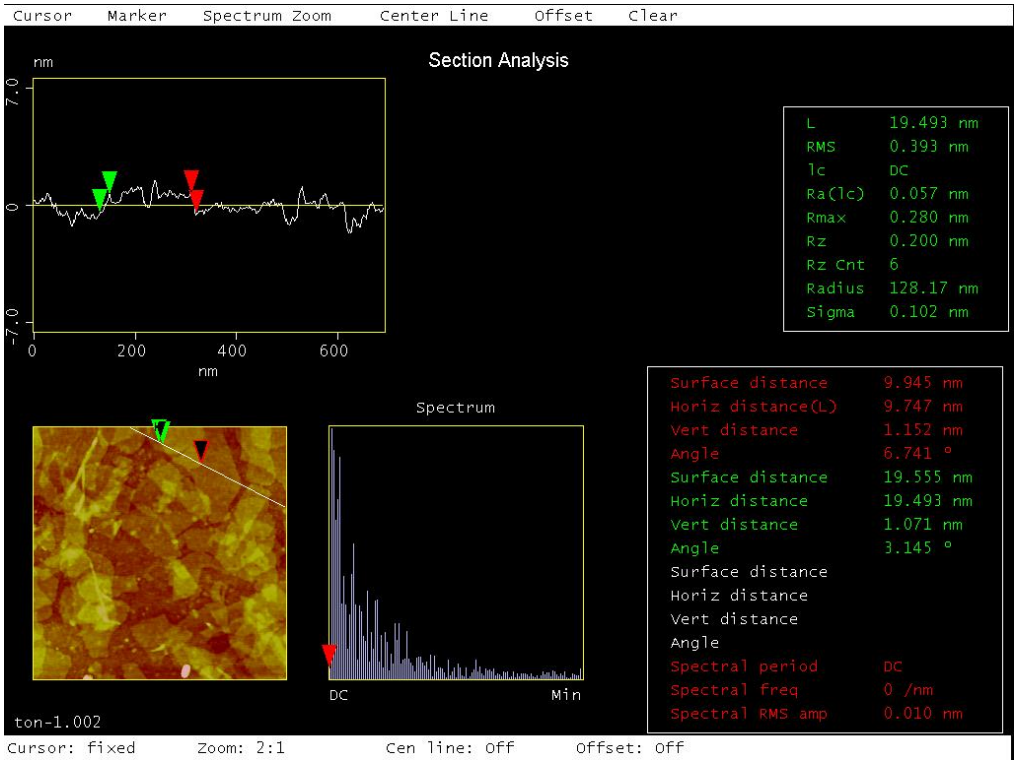


Fig. S1 The thickness measurement in AFM image of $Ti_{0.91}O_{2-x}N_x$ nanosheets on Si wafer.

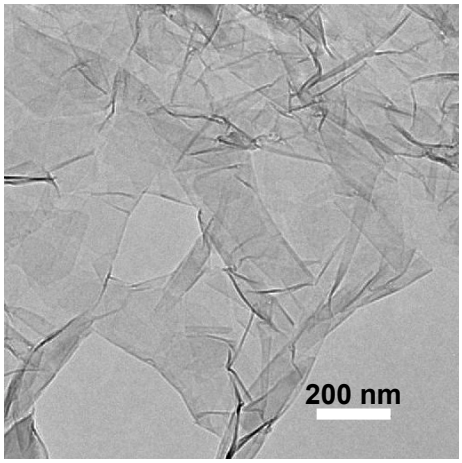


Fig. S2 TEM image of exfoliated $Ti_{0.91}O_{2-x}N_x$ nanosheets loaded on copper grid.

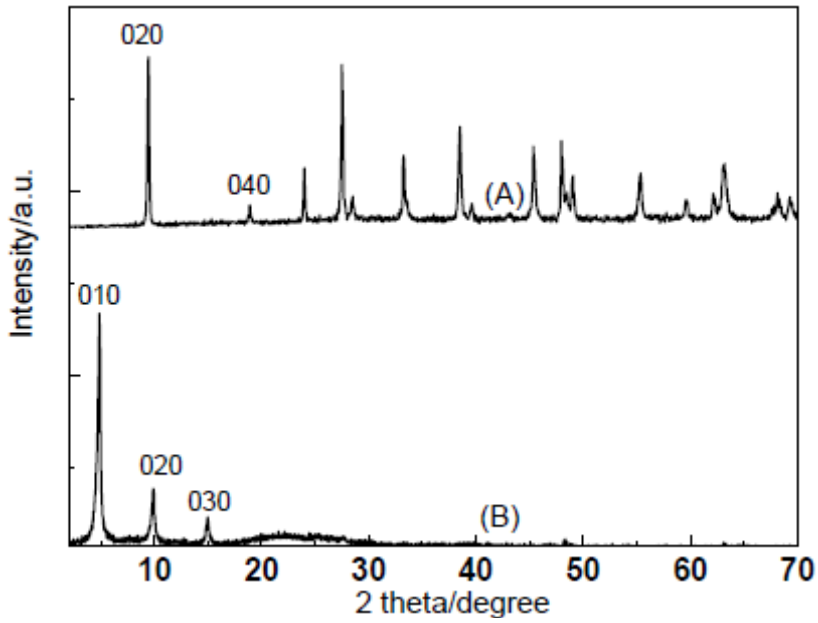
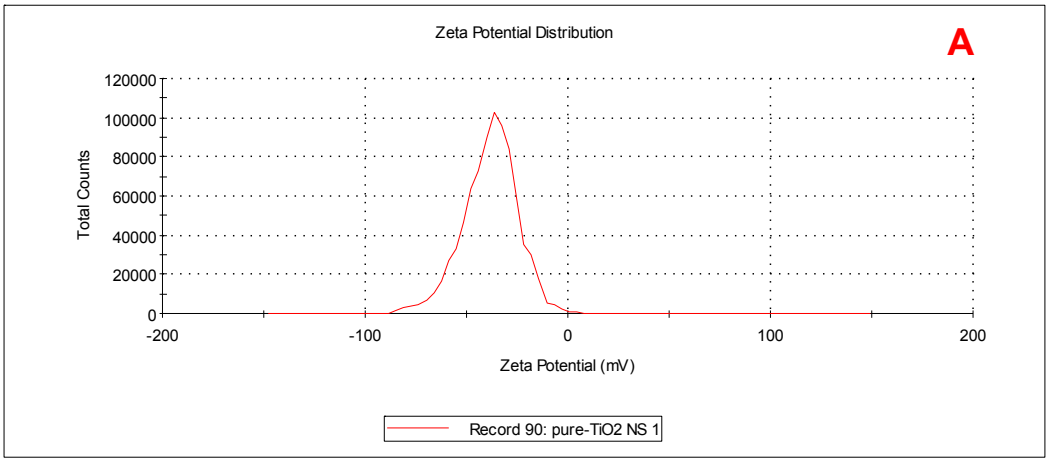


Fig. S3 XRD patterns of layered $H_{0.68}Ti_{1.83}O_{4-x}N_x$ (A) and restacked $Ti_{0.91}O_{2-x}N_x$ nanosheets.



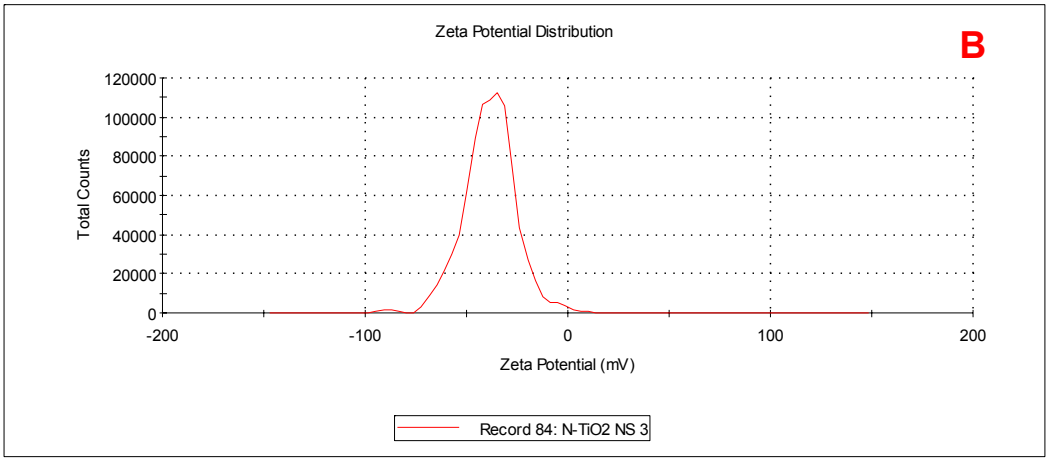


Fig. S4. Zeta-potential of $Ti_{0.91}O_2$ (A) and $Ti_{0.91}O_{2-x}N_x$ (B) nanosheets.

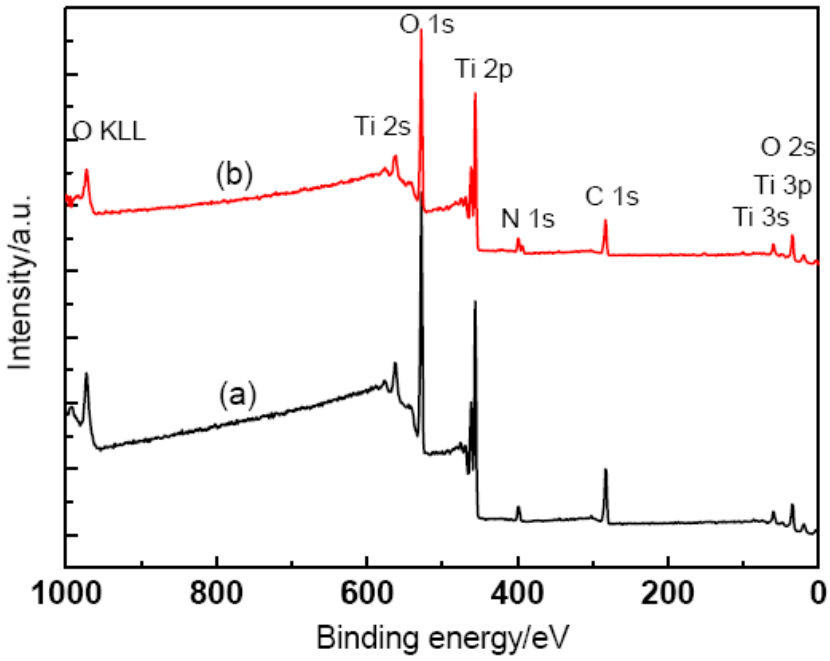


Fig. S5. XPS survey of $(PEI/Ti_{0.91}O_2)_{10}$ (a) and $(PEI/Ti_{0.91}O_{2-x}N_x)_{10}$ (b) nanosheets deposited on quartz substrates.

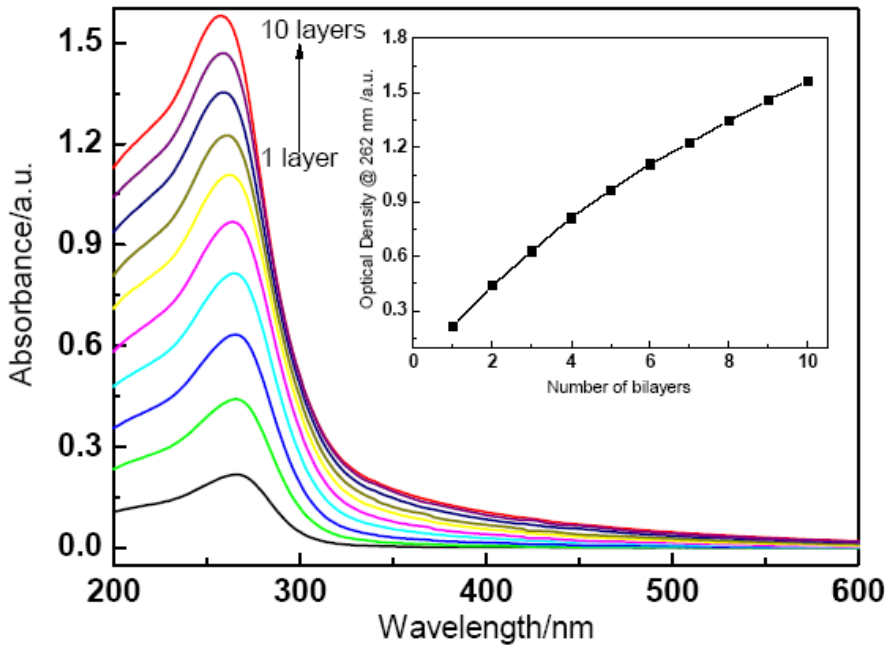


Fig. S6. UV-visible absorption spectra for multilayer films of $(PEI/ Ti_{0.91}O_2)_n$ on a quartz glass substrate. The inserted figure is the dependence of peak absorbance at 262 nm on the number of deposition cycles.