

# Selective local nitrogen doping in TiO<sub>2</sub> electrode for enhancing photoelectrochemical water splitting

Junyu Cao<sup>1</sup>, Yuanjian Zhang<sup>2</sup>, Hua Tong<sup>1,3</sup>, Peng Li<sup>1,2,4</sup>, Tetsuya Kako<sup>1</sup>, Jinhua Ye<sup>1,2,3,4</sup>

<sup>1</sup> Environmental Remediation Materials Unit, Catalytic Materials Group, National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki, Japan

<sup>2</sup> International Center for Materials Nanoarchitectonics, National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba, Ibaraki, Japan

<sup>3</sup> TU–NIMS Joint Research Center, School of Materials Science and Engineering, Tianjin University, 92 Weijin Road, Nankai District, Tianjin 300072, P. R. China

<sup>4</sup> Department of Chemistry, Graduate School of Science, Hokkaido University, Sapporo, Japan

## Supporting Information

### Experimental process

Pulsed laser deposition method was adopted to fabricate local or uniformly nitrogen-doped TiO<sub>2</sub> thin films and TiO<sub>2</sub> thin film (four thin films including (a) inner N-doped TiO<sub>2</sub>, (b) outer N-doped TiO<sub>2</sub>, (c) uniformly N-doped TiO<sub>2</sub>, and (d) pure TiO<sub>2</sub>). Pellet of rutile TiO<sub>2</sub> was utilized as the target and Sn doped Indium-oxide-coated glass sheet (ITO) was used as the substrate. The TiO<sub>2</sub> pellet and ITO were set in the PLD machine (ST-PLD; Pascal co., Japan), and the distance between the pellet and the ITO was set to be 5 cm. After that, the film-preparation chamber of the PLD machine was evacuated to 0.001 Pa, and then pure O<sub>2</sub> or N<sub>2</sub> was introduced into the chamber until the pressure became 4 Pa. After ITO substrate was heated to 550°C, the

TiO<sub>2</sub> target was irradiated by the laser pulse (355 nm in wavelength) emitted from a Nd:YAG laser. After the deposition, the substrate temperature (550°C) was still kept for 1 h in the presence of O<sub>2</sub> (9.6×10<sup>4</sup> Pa) for the post-heat treatment of the samples.

The TiO<sub>2</sub> thin film was fabricated by 1 h of deposition in O<sub>2</sub>, while uniformly nitrogen-doped TiO<sub>2</sub> thin film was fabricated by 1 h of deposition in N<sub>2</sub>. Outer nitrogen-doped TiO<sub>2</sub> thin film was fabricated by 0.5 h of deposition in O<sub>2</sub> firstly and then 0.5 h of deposition in N<sub>2</sub>. Inner nitrogen-doped TiO<sub>2</sub> thin film was fabricated by 0.5 h of deposition in N<sub>2</sub> firstly and then 0.5 h of deposition in O<sub>2</sub>.

Chemical compositions of the prepared thin films were evaluated with a field-emission scanning electron microscope (JSM-6701F, JEOL Co., Japan) operated at an accelerating voltage of 15 kV and an energy dispersive X-ray spectroscopy (EDS) system (EX-230, JEOL) and a transmission electron microscope (2100F, JEOL Co., Japan). Photocurrent densities were measured with an electrochemical station (ALS/CH model 650A) using three-electrode mode. Platinum and Ag/AgCl electrode were used as the counter electrode and reference electrode, respectively. In the photoelectrochemical measurement, the photo-electrodes were illuminated with the light from the side of the electrolyte/film interface in aqueous NaOH solution (1 M) through a

quartz window. AM 1.5 Solar simulator (PEC-L01, Pecell Co., Japan) was utilized as the light sources. The hydrogen and oxygen generation of the prepared thin film was also measured using the water splitting system. With the connection to electrochemical station, the PEC water splitting cell (local N-doped TiO<sub>2</sub> electrode as working electrode, Pt as counter electrode, Ag/AgCl as reference electrode, and 1 M NaOH as electrolyte) was put in a glass cell, which was connected with a closed gas circulation system. The generated H<sub>2</sub> and O<sub>2</sub> was in-situ analyzed with a TCD gas chromatograph (Shimadzu GC-8AIT, argon carrier). A 300-W Xe arc lamp (ILC Technology, CERMAX LX-300) was used as the light source.

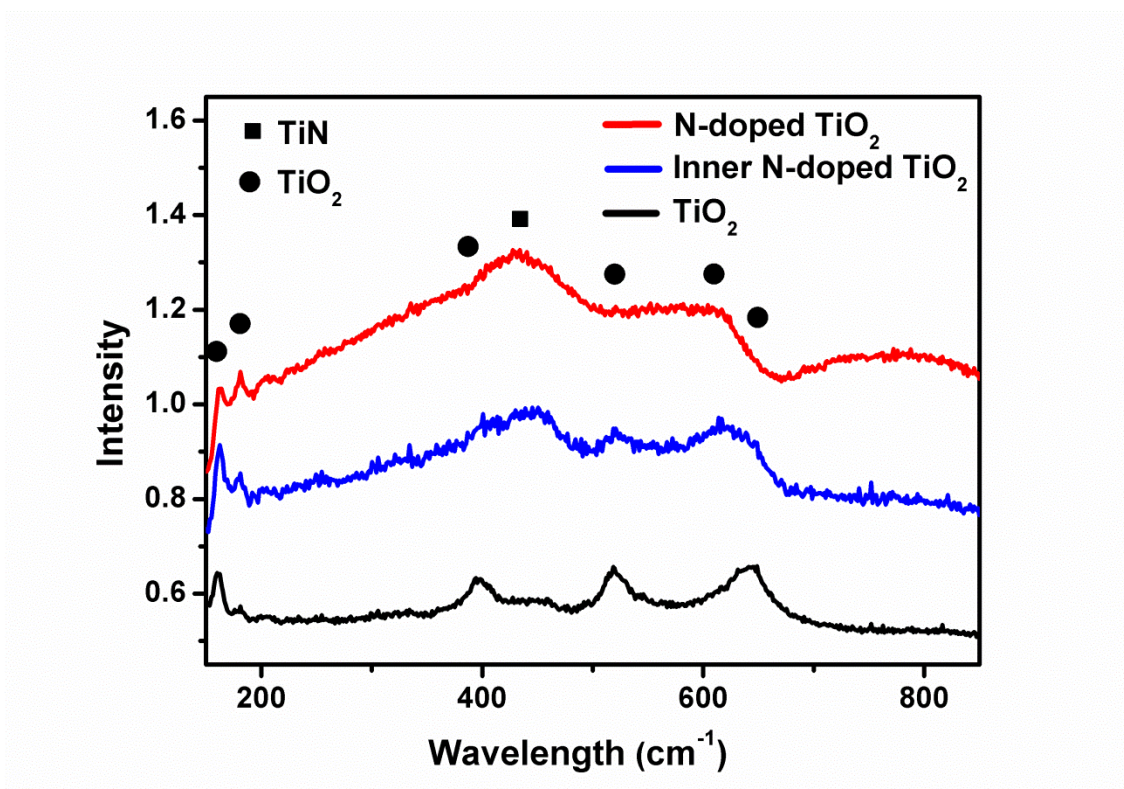


Fig. S1 Raman spectra of uniformly N-doped TiO<sub>2</sub> thin film, inner N-doped TiO<sub>2</sub> thin film, and TiO<sub>2</sub> thin film. The Raman peaks marched to the previous results of TiO<sub>2</sub> and N-doped TiO<sub>2</sub> electrodes prepared by PLD method.<sup>1-2</sup>

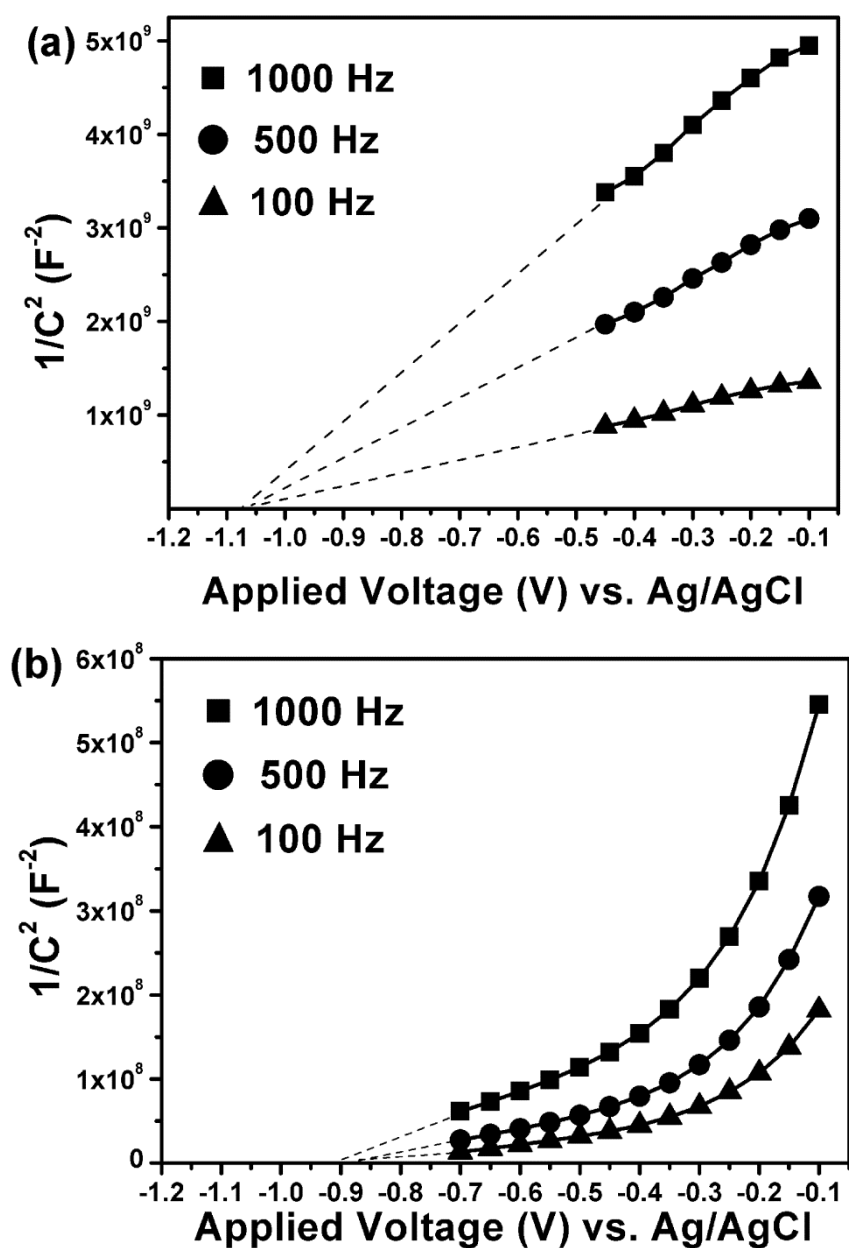


Fig.S2 (a) Mott-Schottky plots of  $TiO_2$  electrode at frequencies of 100, 500, 1000 Hz; (b) Mott-Schottky plots of N-doped  $TiO_2$  electrode at

frequencies of 100, 500, 1000 Hz.

The carrier densities were calculated using the following equation<sup>3</sup>:

$$N = \frac{2C^2}{e\epsilon\epsilon_0A^2} \times (E - E_{fb} - kT/e)$$

Here,  $N$  carrier density,  $C$  electrode capacitance,  $\epsilon$  dielectric constant (set as 120)<sup>3</sup>,  $\epsilon_0$  permittivity of vacuum,  $E$  applied potential,  $E_{fb}$  flatband potential,  $e$  electron charge,  $A$  electrode area and the roughness factors set as 2.

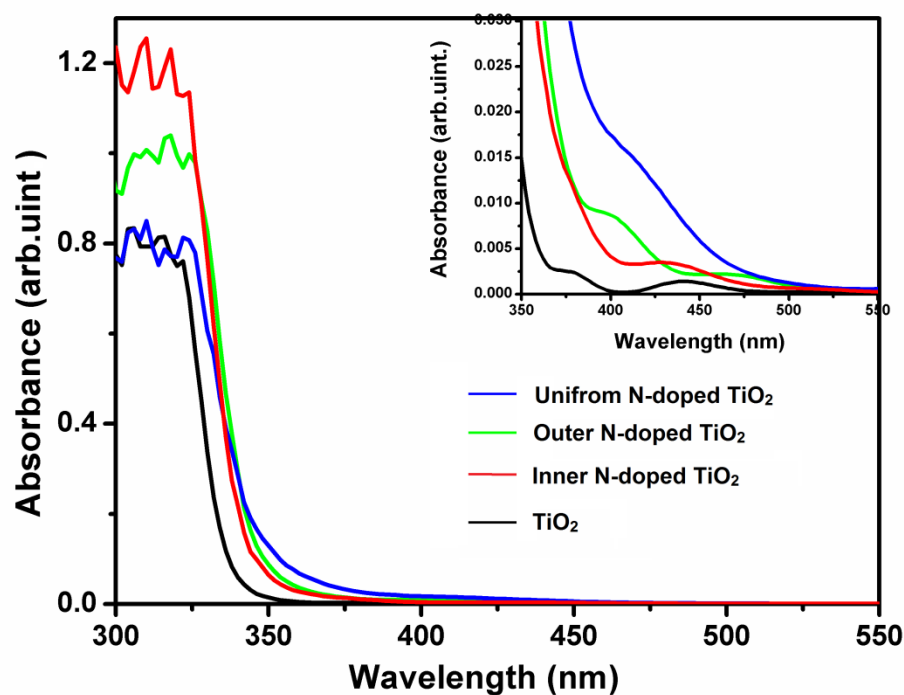


Fig. S3 the UV-vis absorbance of the as-prepared four samples. The inset shows the UV-vis absorbance in the region of 350 nm- 550 nm.

Reference:

- [1]. M. Ivanda, S. Music, M. Gotic. *Journal of Molecular Structure*. **1999**, 480-481, 645.
- [2]. U. Koslowski, K. Ellmer, H. Tributsch et al. *J. Vac. Sci. Technol. A*. **2006**, 24, 2199.
- [3]. L. Kavan and M. Gratzel. *Electrochimica Acta*. 1995, 40, 643.