Electronic Supplemental Information

Activation of particulate Ta_3N_5 water-oxidation photoanode with GaN hole-blocking layer

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Contents

Details of the experimental procedures

Synthesis of particulate Ta_3N_5 and preparation of Ta_3N_5 film on glass substrate

Ta_3N_5 was synthesized according to the previous literature (M. Higashi *et al.*, *Energy Environ. Sci.*, 2011, **4**, 4138). Ta_2O_5 (99.99%, Rare metallic Co., LTD.) was subjected to nitridation at 850 ºC for 15 h under NH_3 (> 99.9995%, Sumitomo Seika Chemicals Co., LTD.) flow (500 mL·min^{-1}) in a vertical tubular furnace. The XRD pattern, the SEM image, and the UV-vis DRS spectrum (Fig. S1) of the obtained Ta_3N_5 indicate the synthesis of Ta_3N_5. 50 mg of Ta_3N_5 was added in 1mL of 2-propanol, and ultra-sonicated for 1 h to form the dispersion of Ta_3N_5. The dispersion was dropped on glass substrate (GS). After the drying of the solvent, GS/Ta_3N_5 was obtained.

Deposition of GaN for GS/Ta_3N_5 by using plasma-enhanced chemical paper deposition (PCVD)

Trimethylgallium (TMG; > 99.999% Ube Industries, Ltd.) at 3.5 ºC was carried into the deposition camber with N_2 flow (6 mL·min^{-1}). Radio Frequency plasma was conducted at 1000 W with the additional N_2 flow (20 mL·min^{-1}). GaN was deposited for 5 min under 21 to 22 Pa of the working pressure. The obtained laminated sample was denoted as GS/Ta_3N_5/GaN.

Deposition of Ta and Ti for GS/Ta_3N_5/GaN by radio frequency magnetron sputtering, and peeling from glass substrate

A Ta metal was deposited at a substrate temperature of 350 ºC for 5 min. Subsequently, a Ti metal was deposited at a substrate temperature of 200 ºC for 3 h. The RF power for Ta and Ti was conducted at 100 W and 200 W, respectively. The procedure led to the formation of the laminated structure of GS/ Ta_3N_5/GaN/Ta/Ti.

GS was peeled from GS/ Ta_3N_5/GaN/Ta/Ti, and the obtained substance was washed in water under ultrasonication to form Ta_3N_5/GaN/Ta/Ti.

Modification of Ta_3N_5/GaN/Ta/Ti with ferrihydrite and Co_3O_4

Ferrihydrite (Fh) as a hole trap layer and following Co_3O_4 as an oxygen evolution catalyst were deposited for Ta_3N_5/GaN/Ta/Ti according to the previous report (G. J. Liu *et al.*, *Angew. Chem. Int. Ed.*, 2014, **53**, 7295). Ta_3N_5/GaN/Ta/Ti was dipped into a solution containing 0.05 M $Fe(NO_3)_3$ (99.9%, Wako Pure Chemical Industries., Ltd.) and 0.375 M $NaNO_3$ (> 99.9%, Kanto Kagaku Chemical Co., Inc.), and the dipped electrode was heated at 100 ºC for 8 min to deposit ferrihydrite (Fh/Ta_3N_5/GaN/Ta/Ti).

28% NH_3 aqueous solution (0.35 mL, Kanto Kagaku Chemical Co., Inc.) was added dropwise into 0.04 M cobalt acetate ($(CH_3COO)_2Co\cdot 4H_2O$, 99.9%, Wako Pure

Chemical Industries., Ltd.) ethanol solution (25 mL). Ta_3N_5/GaN/Ta/Ti was transferred into the mixture, and treated solvothermally at 120 ºC for 1 h to modify Co_3O_4 on the electrode. The electrode after the solvothermal reaction is denoted as Co_3O_4/Fh/Ta_3N_5/GaN/Ta/Ti.

Characterization

The crystal structure and optical properties of Ta_3N_5 were investigated by X-ray diffraction (Rigaku, MiniFlex300) with CuKα radiation (λ = 1.5418 nm) at 30 kV and 10 mA and by UV-visible diffuse reflectance spectroscopy (JASCO, V-670) with an integrating sphere at r.t., respectively. Scanning electron microscopy (SEM) images were obtained by Hitachi SU-8020. Scanning transmission electron microscopy (STEM) images was measured by JEOL JEM-2800. STEM-EDS was performed using an X-MAX 100TLE SDD detector (Oxford Instruments).

Photoelectrochemical measurement

The laminated electrodes were glued to a glass plate with a piece of carbon0contained adhesive tape, and the metal layer connected to a copper wire with indium solder. The unnecessary part was covered with epoxy resin.

The electrodes fixed on glass were measured with a three-electrode system by using a potentiostat (Hokuto Denko, HSV-110 for *I-E* curves, and Princeton Applied Research, VersaSTAT 3 for *I-t* curves and Mott-Schottky plots) An Ag/AgCl (in saturated KCl aqueous solution) electrode and a Pt wire were used as a reference electrode and a counter electrode, respectively. The potential against the reference electrode ($E_{Ag/AgCl}$) was converted into a potential with respect to reversible hydrogen electrode (E_{RHE}) by using an equation shown below.

$$E_{RHE} = E_{Ag/AgCl} + 0.199\ V + 0.0592 \times pH$$

PEC measurements were performed in an aqueous solution of potassium phosphate (0.2 M, pH 13) under a simulated AM 1.5G (San-EI Electric, XES-40S). The time courses of the photocurrent from the photoanode were recorded at 1.0 V *vs.* RHE with a CrO_x-coated Pt mesh as a counter electrode, while the amounts of the evolved gases were evaluated by micro-gas chromatography.

Half-cell solar-to-hydrogen (HC-STH) conversion efficiency was calculated from *I-E* curves of the photoanode by using an equation shown below.

$$\text{HC-STH}(\%) = J \times (1.23\text{-}V) \times 100 / P$$

where J is the photocurrent density, V is the potential *vs.* RHE of the electrode, and P is the intensity of the irradiated light (simulated AM1.5G (100 mW·cm^{-2})).

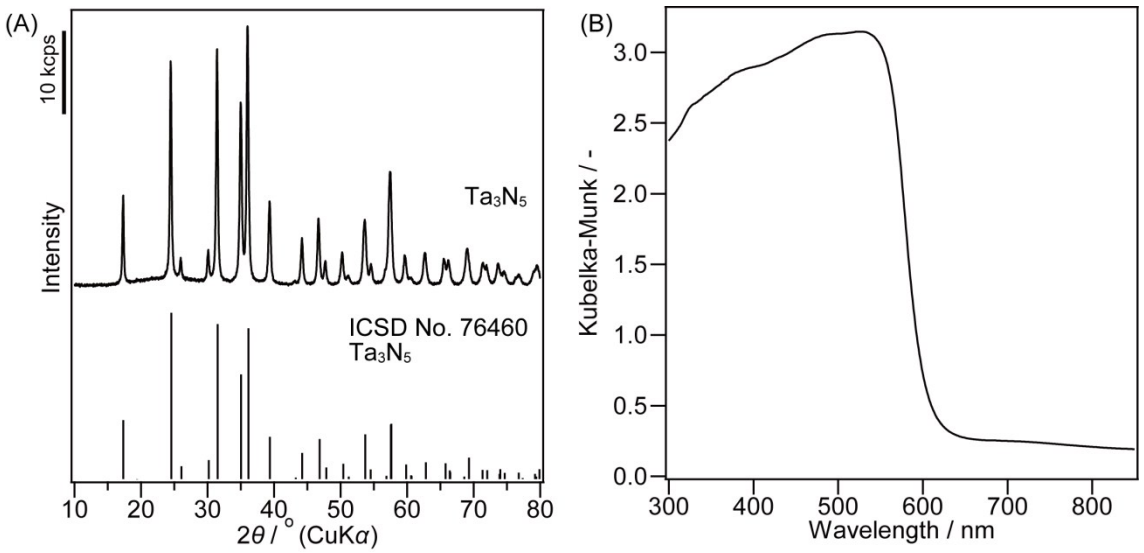

Fig. S1 (A) XPD pattern and (B) UV-vis-DRS spectrum of Ta_3N_5.

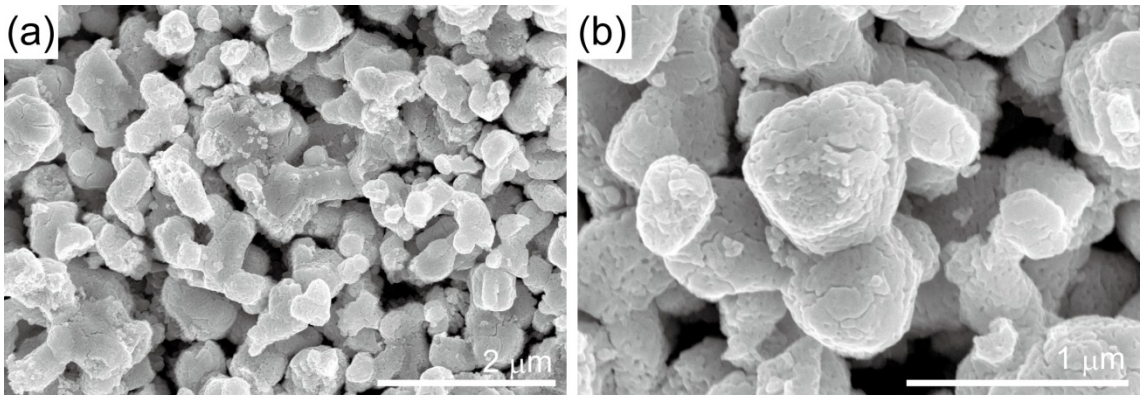

Fig. S2 SEM images of particulate Ta_3N_5.

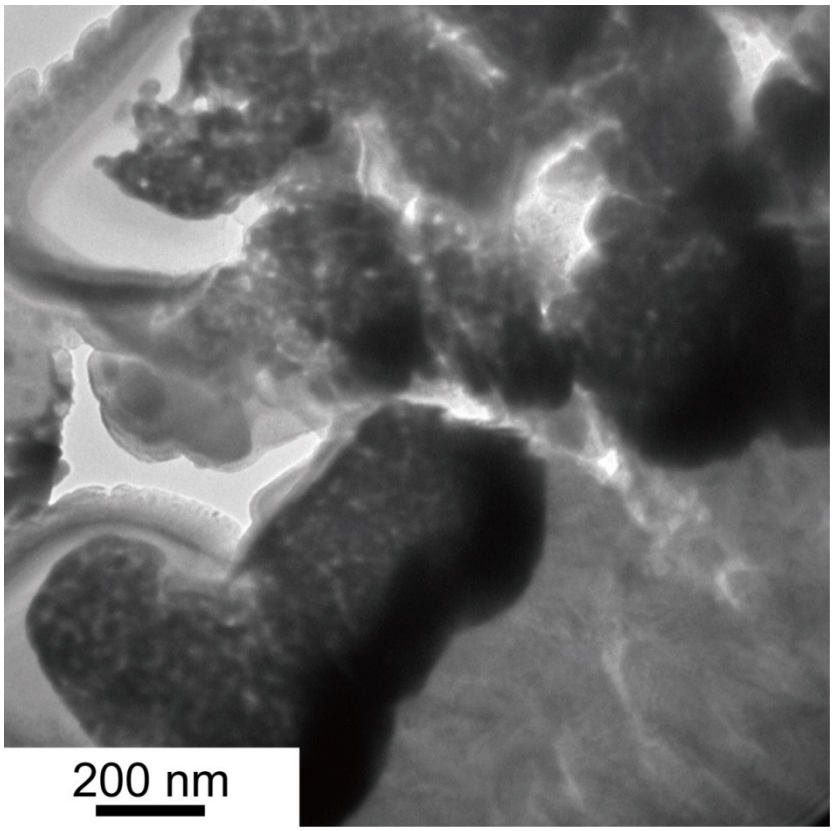

Fig. S3 High Resolution (HR) TEM image of the cross section of Ta_3N_5/Ta/Ti.

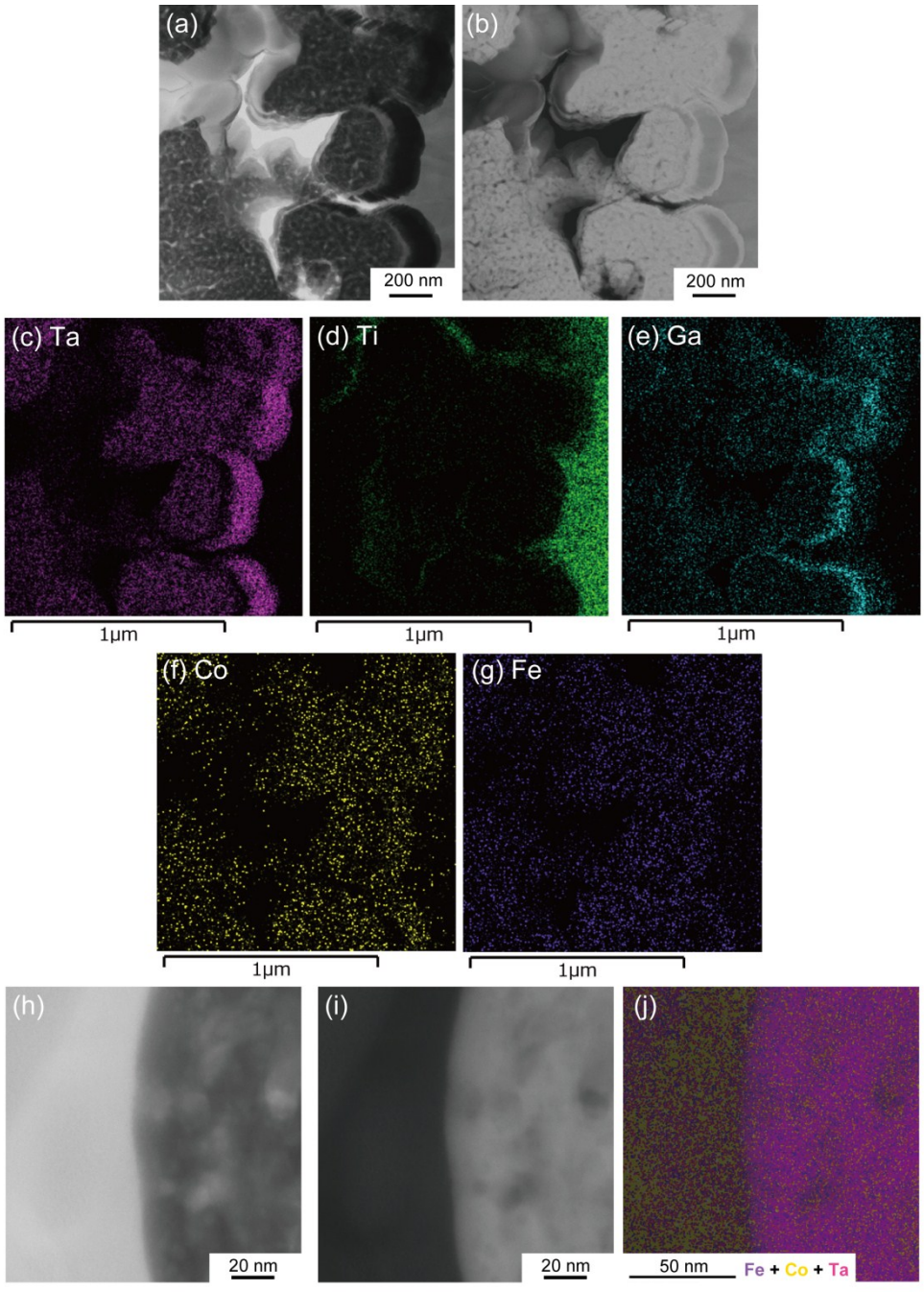

Fig. S4 (a) Bright- and (b) dark-field STEM images, and simultaneously-conducted STEM-EDS mappings of (c) Ta, (d) Ti, (e) Ga, (f) Co, and (g) Fe species of Co_3O_4/Fh/Ta_3N_5/GaN/Ta/Ti. (h) Bright-field and (i) dark-field STEM images, and (j) simultaneously-conducted STEM-EDS mapping.

The bright- and dark-field STEM images (Fig. S4a and b), and the corresponding STEM-EDS mappings (Fig. S4c-g) show almost the same laminated structure as that of Ta_3N_5/GaN/Ta/Ti, and the presence of Co and Fe species over the electrode surface. In the STEM images (Fig. S4h,i), we cannot find any particulate derived from Co and Fe species on the Ta_3N_5 particles in spite of the presence of the species as shown by the STEM-EDS mappings (Fig. S4f,g,j). It means that the particle sizes of the deposited Co_3O_4 and ferrihydrite are very small. The small sizes should not prevent the efficiency of the light-absorption of Ta_3N_5.

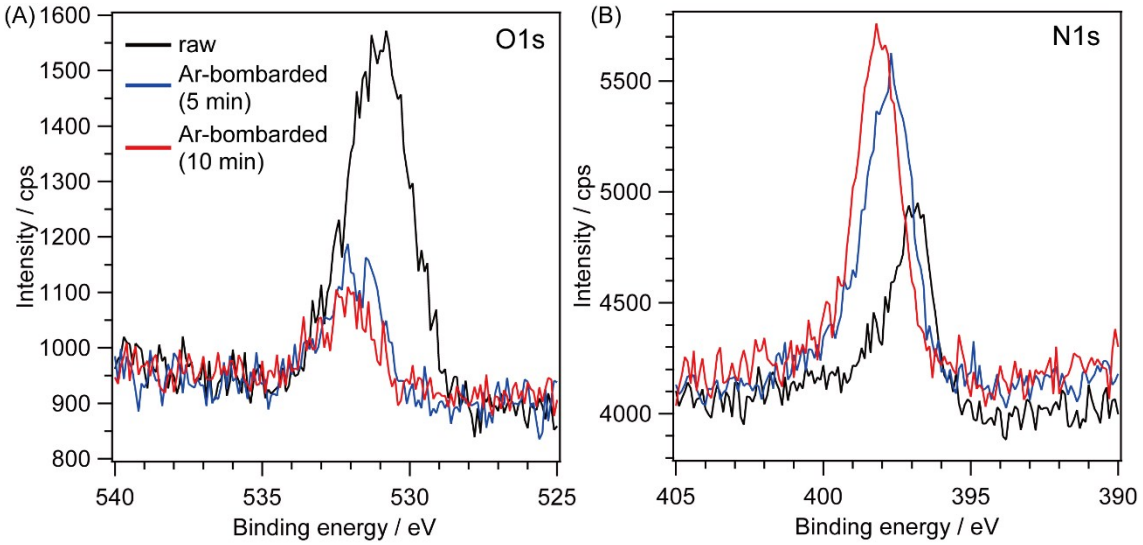

Fig. S5 XPS spectra of (a) O 1s and (b) N 1s of the GaN layer. The black curves were recorded before Ar bombardment. The blue and red curves were recorded after Ar-bombardment for 5 min and 10 min, respectively.

The XPS spectrum of GaN layer before Ar bombardment shows the presence of oxygen on the surface. As the sample was bombarded, the oxygen content drastically decreased, indicating oxygen was a minor species within the GaN layer.

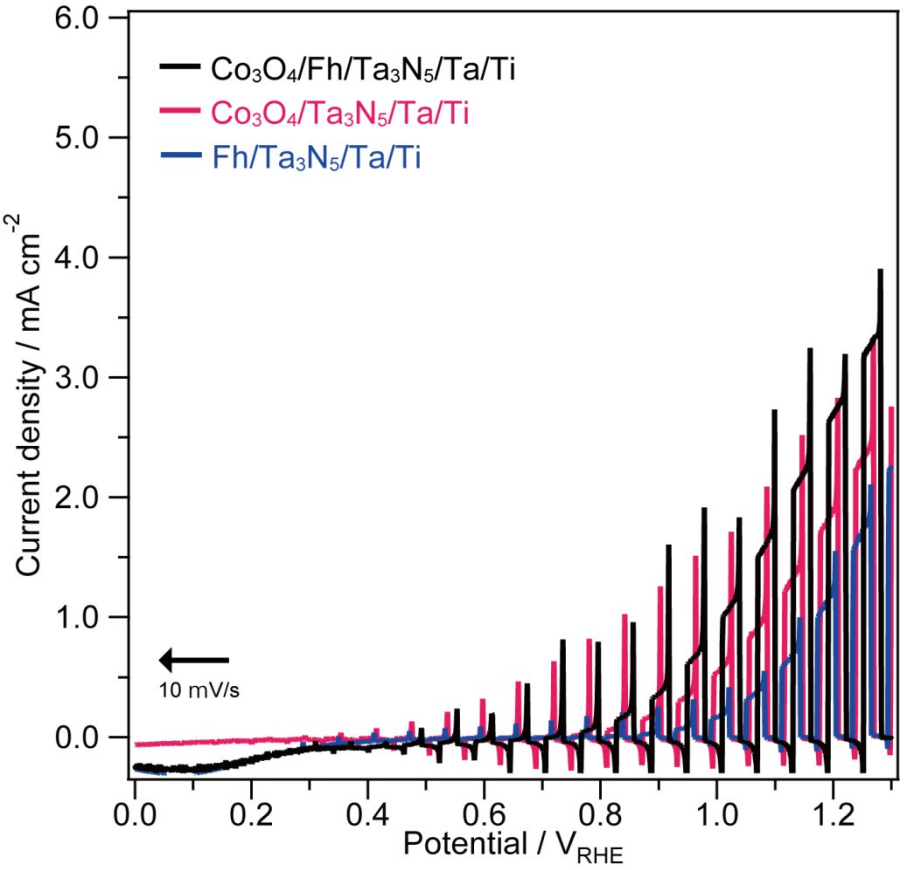

Fig. S6 *I-E* curves of $Fh/Ta_3N_5/Ta/Ti$, $Co_3O_4/Ta_3N_5/Ta/Ti$, and $Co_3O_4/Fh/Ta_3N_5/Ta/Ti$.

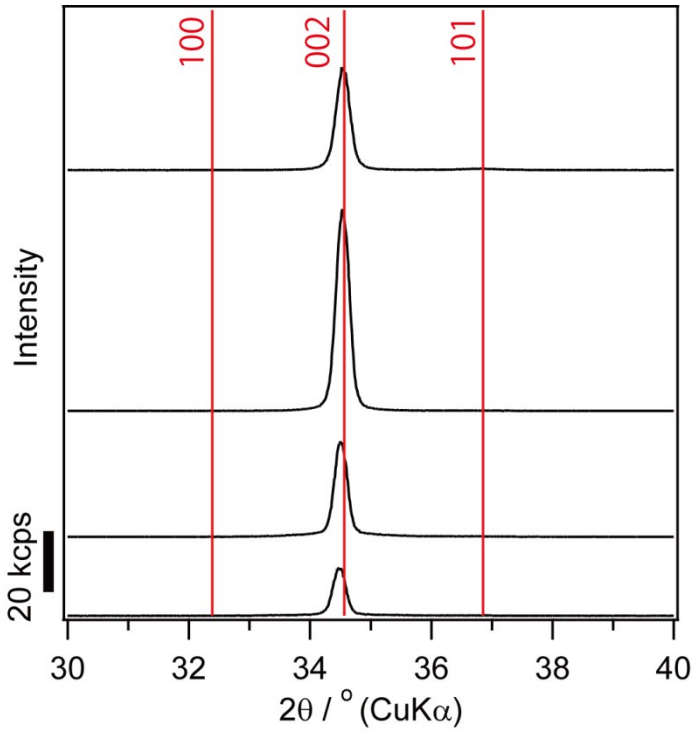

Fig. S7 XRD patterns of GaN deposited on sapphire (001) substrate for 20 min at (a) 300, (b) 400, (c) 500, and (d) 600 °C. The red lines show the position of GaN diffractions.

The XRD pattern of the laminated electrodes showed no peak attributed to hexagonal GaN phase because of low crystallinity and very thin layer. For this, we deposited GaN on sapphire (001) substrate at the various temperatures for a longer time (20 min) under the same condition of the other factors. The order of their crystallinity should be coincident with that for thin GaN deposited on Ta_3N_5 particle. All the patterns shows only a peak attributed to 002 diffraction of hexagonal GaN, indicating oriented growth along (001) face of sapphire substrate. The intensity was altered by the deposition temperature. The GaN films deposited at 500 °C, which led to the highest photocurrent of the corresponding electrode, possessed highest intensity among them, indicating its highest crystallinity. The XRD pattern of GaN deposited at 300 °C, which led to the lowest photocurrent of the corresponding electrode, showed the 002 peak position was located at lower angle than its ideal position and the intensity was very low, suggesting very low crystallinity. Consequently, the crystallinity of GaN as a back contact should highly affects the photocurrent of the electrode.

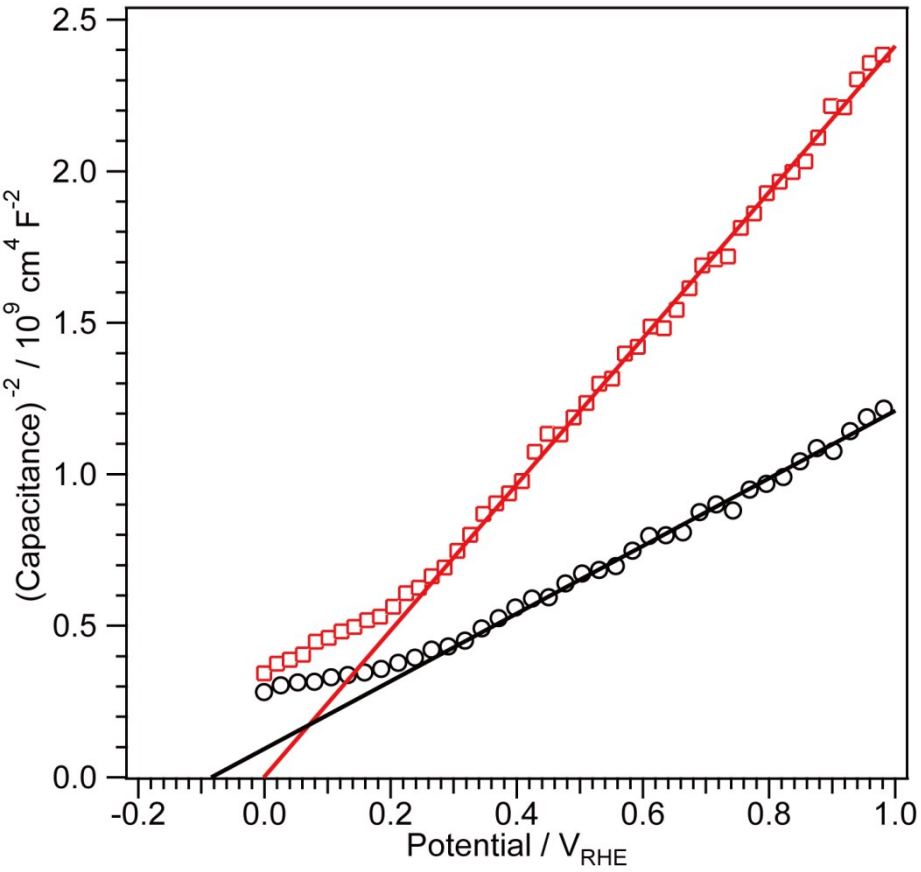

Fig. S8 Mott-Schottky plots at 100 Hz of Ta_3N_5/Ta/Ti (black) and Ta_3N_5/GaN/Ta/Ti with GaN deposited at 500 ºC. A 0.2 M K_2HPO_4 adjusted to pH 13 by adding KOH was used as an electrolyte.