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

Supporting Information

Solar water splitting by Ta_3N_5 photoanode synthesized via a simple metal-organic-precursor decomposition process

Sung Gyu Han[a,b], *Sang Youn Chae*[a,c], *Si Young Lee* [a,e], *Byoung Koun Min*[a,d] , *and Yun Jeong Hwang**[a,e]

a. Clean Energy Research Center, Korea Institute of Science and Technology, Seoul 02792, Republic of Korea

b. Department of Physics, College of Science, Korea University, Seoul 02841, Republic of Korea.

c. Department of Chemistry, College of Science, Korea University, Seoul 02841, Republic of Korea.

d. Green School, Korea University, Seoul 02841, Republic of Korea

e. Division of Energy and Environmental Technology, KIST School, Korea University of Science and Technology, Seoul 02792, Republic of Korea

Corresponding Author

yjhwang@kist.re.kr

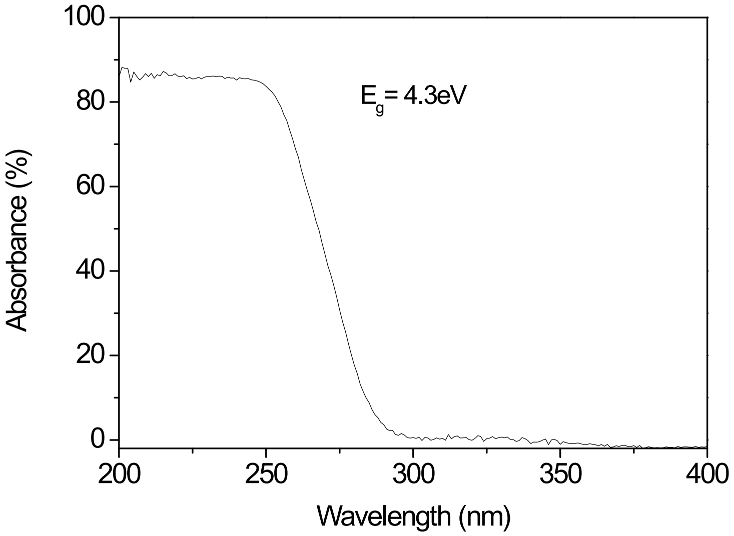

Figure S1. UV-vis spectroscopy of the deposited film on a quartz plate before the ammonia treatment. The tantalum precursor solution was spin coated on the quartz substrate, and it was annealed at 400°C in air for 1hour to prepare tantalum oxide as described in the experimental method. The measured UV-vis spectra shows only UV region absorption due to large bandgap of tantalum oxide.

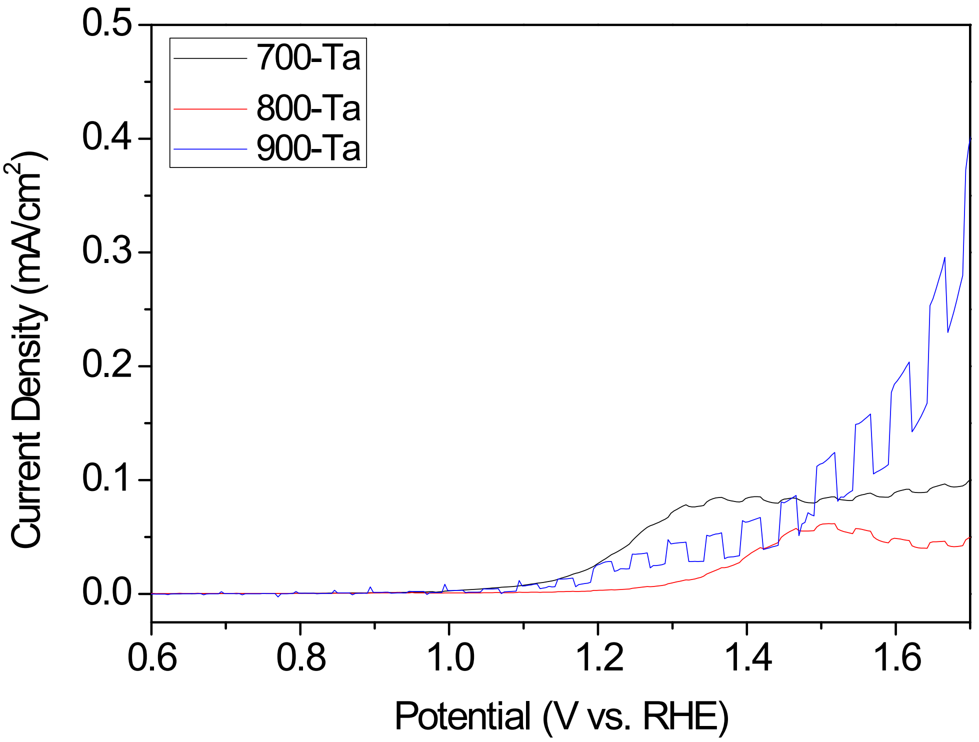

Figure S2. Photocurrent density-potential curves of the control Ta foil samples prepared by the same air annealing and ammonia annealing processes without spin-coating of the precursor solution, and the annealing temperature in ammonia varies from 700, 800, and 900 ^{o}C denoted as 700-Ta, 800-Ta, and 900-Ta. The measured current densities were small compared to those of Ta_3N_5 photoanodes indicating the contribution by the bottom Ta substrate was negligible, and the photocurrents of the Ta_3N_5 are mainly originated from the deposited thin film layer.

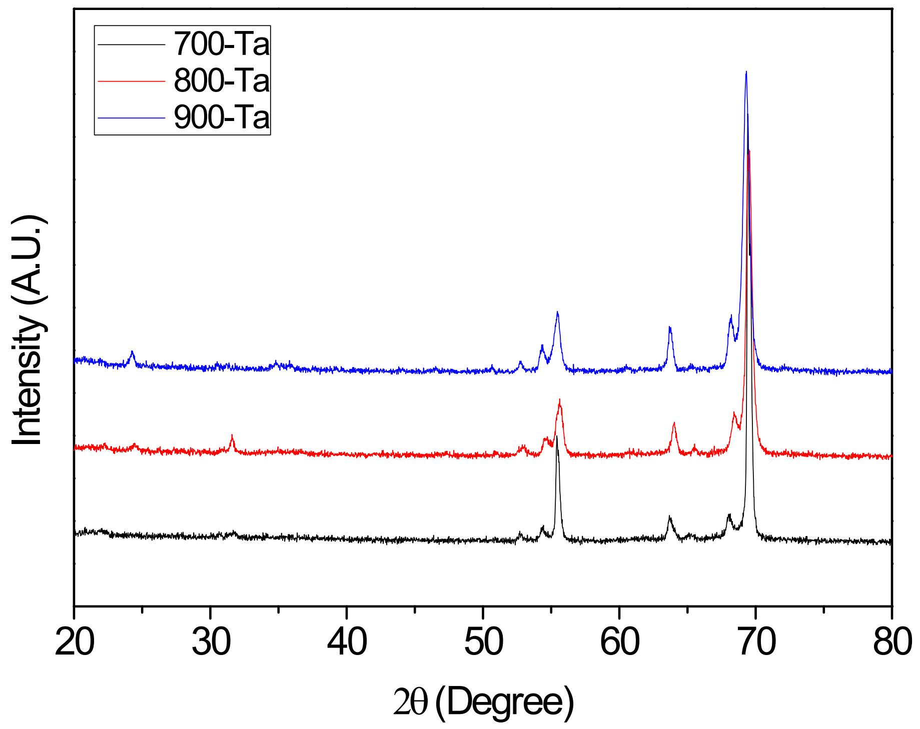

Figure S3. XRD patterns of 700-Ta, 800-Ta, and 900-Ta showing strong metallic Ta patterns. The absence of the Ta_3N_5 patterns compared to 700-, 800-, and 900-Ta_3N_5 samples indicates the crystalline Ta_3N_5 thin film is formed by using Ta source from the precursor solution through the preparation processes in this work.

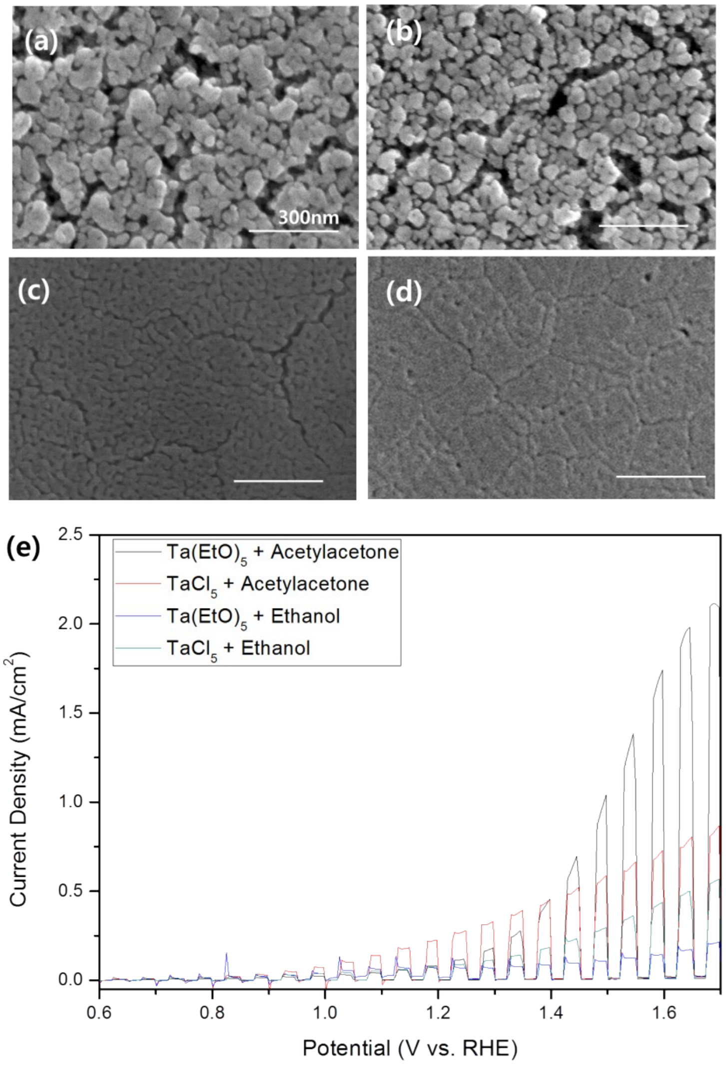

Figure S4. SEM images of Ta_3N_5 thin film prepared from different precursor solutions: (a) $Ta(EtO)_5$ + Acetyl acetone, (b) $TaCl_5$ + Acetyl acetone, (c) $Ta(EtO)_5$ + Ethanol, and (d) $TaCl_5$ +Ethanol. (e) Effect of the precursor solution on the PEC activity of the Ta_3N_5 photoanodes.

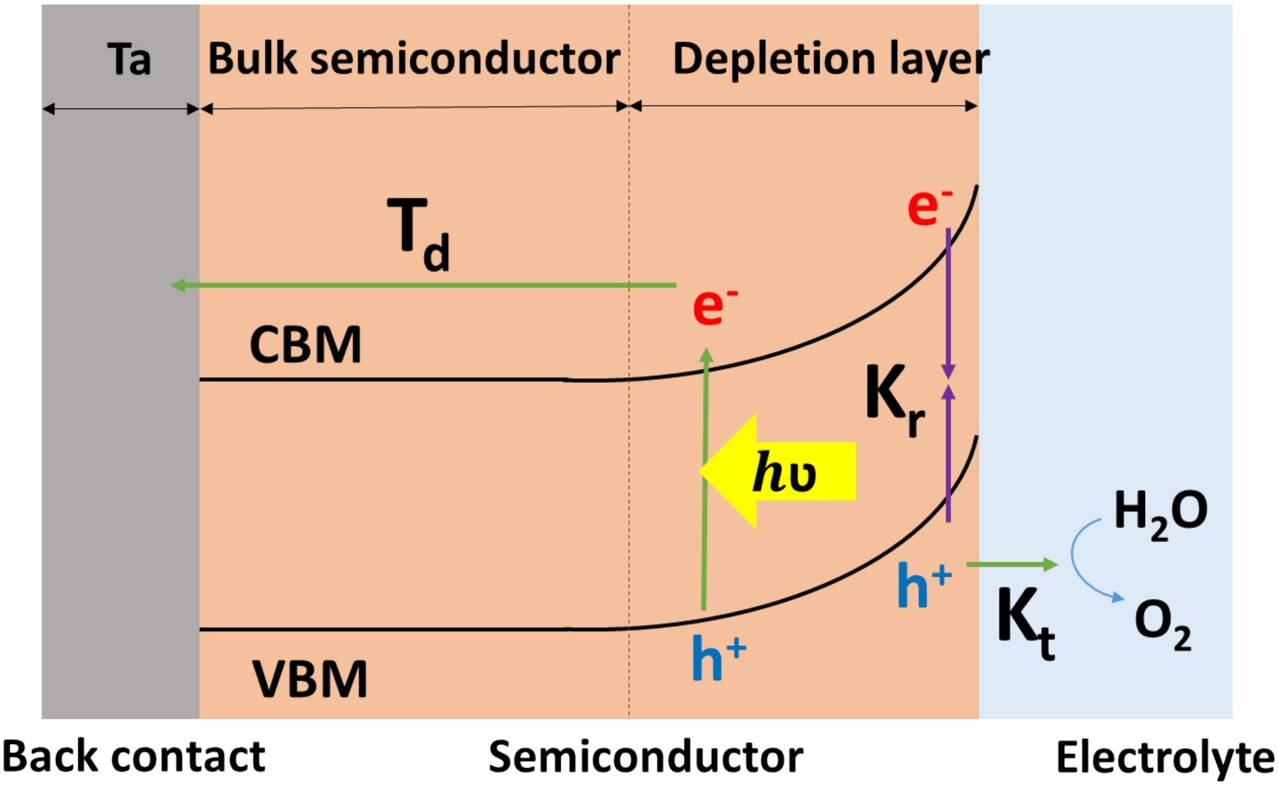

Figure S5. Schematic illustration of charge flow process and charge separation related parameters in a semiconductor photoanode.

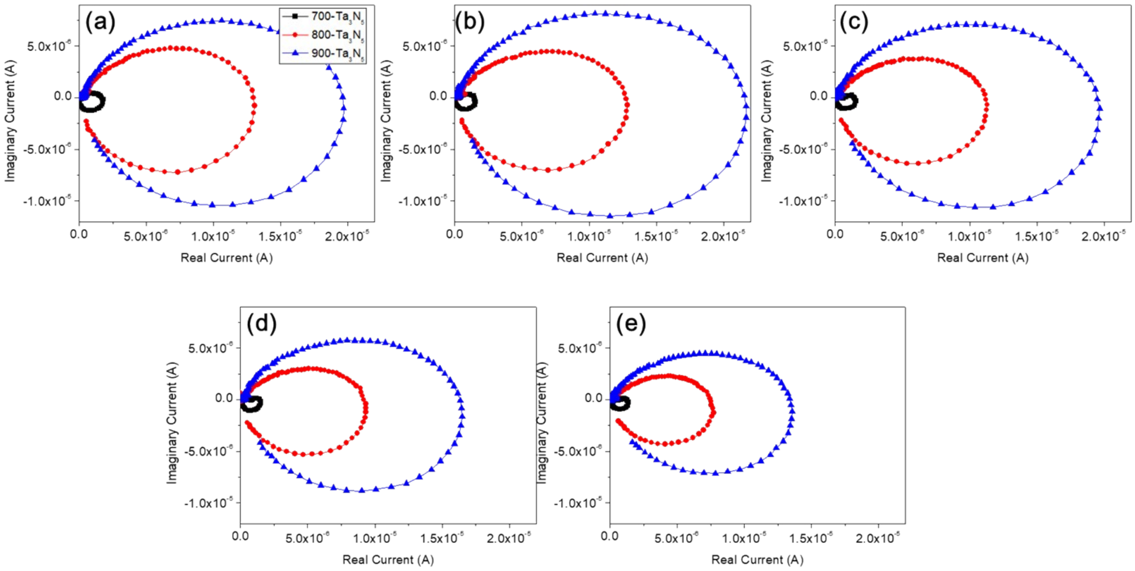

Figure S6. Nyquist plots of Ta_3N_5 photoanodes depending on the nitridation temperatures at various applied potentials; (a) 1.05 V, (b) 1.25 V, (c) 1.45 V, (d) 1.65 V and (e) 1.85 V vs. RHE measured in 1 M KOH aqueous solution.

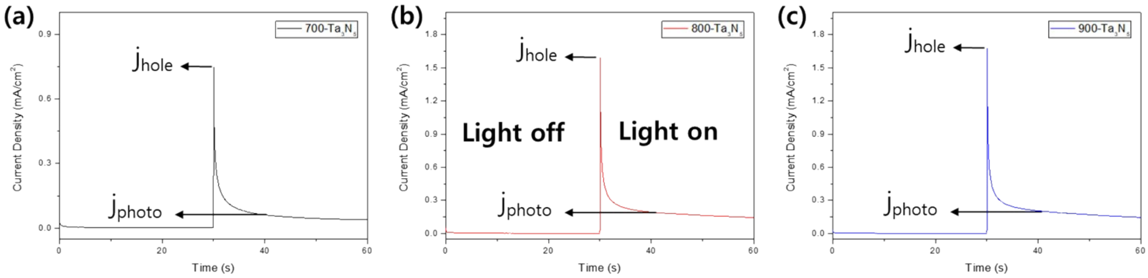

Figure S7. Current density versus elapsed time during IMPS measurement for each sample. j_{hole} and j_{photo} are marked in the I-t graph.

Table S1. T_d of Ta_3N_5 photoanodes at various applied potentials calculated from IMPS measurement

Applied potential (V_{RHE})	700-Ta_3N_5	800-Ta_3N_5	900-Ta_3N_5
1.05	1.18×10^{-5} s	1.64×10^{-5} s	1.32×10^{-5} s
1.25	1.18×10^{-5} s	1.64×10^{-5} s	1.47×10^{-5} s
1.45	1.18×10^{-5} s	1.32×10^{-5} s	1.47×10^{-5} s
1.65	1.06×10^{-5} s	1.18×10^{-5} s	1.18×10^{-5} s
1.85	1.18×10^{-5} s	1.06×10^{-5} s	1.06×10^{-5} s

Equation S1 Equations used for calculation of charge separation and charge injection efficiency characterized by photocurrent measurements w/wo scavengers.

$$\mathit{Charge\ separation\ efficiency} = \frac{\mathit{Photocurrent\ with\ hole\ scavanger}}{\mathit{maximum\ Photocurrent\ through\ absorbance}}$$

$$\mathit{Charge\ injection\ efficiency} = \frac{\mathit{Photocurrnet}}{\mathit{Photocurrent\ with\ hole\ scavanger}}$$

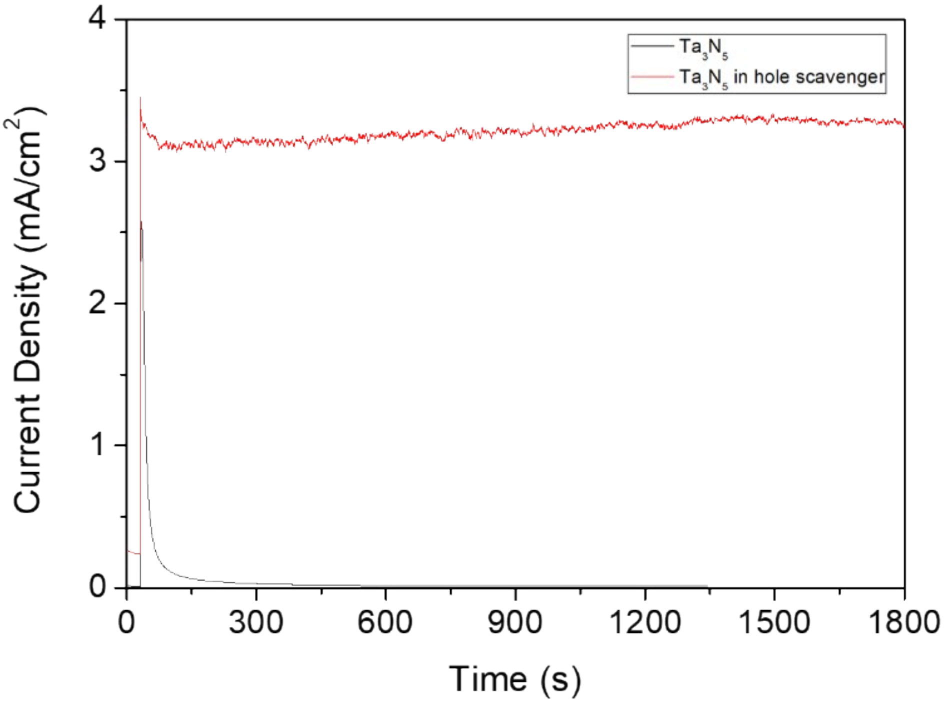

Figure S8. PEC Stability of 900_Ta_3N_5 measured at 1.6 V vs. RHE under 1 Sun condition measured in the 1M KOH (black), and in 0.1M $K_4[Fe(CN)_6]$ / 0.1M $K_3[Fe(CN)_6]$ / 1M KOH (red). The photocurrent of the Ta_3N_5 photoanode decreased in the absence of the scavenger, while stable photocurrent over 3 mA/cm^2 was obtained over 1800 sec in the case when the hole scavenger was added. This change in the stability indicates that the slow oxidation reaction causes significant loss in PEC activity as well as photochemical instability in Ta_3N_5. This result is also consistent with our conclusion that the most direct descriptor to Ta_3N_5 PEC activity is the charge injection efficiency on its surface compared with the other characteristics such as charge separation efficiency, charge transfer rate constant, charge recombination rate constant, or light absorption properties.