Supporting Information

Enhanced water splitting activity for M-doped Ta_3N_5 (M = Na, K, Rb, Cs)

Yuya Kado[a], Chong-Yong Lee[a], Kiyoung Lee[a], Julian Müller[b], Matthias Moll[c], Erdmann Spiecker[b] and Patrik Schmuki[a]*

[a]Department of Materials Science and Engineering, University of Erlangen-Nuremberg,
Martensstrasse 7, D-91058 Erlangen, Germany
E-mail: (schmuki@ww.uni-erlangen.de)

[b]Department of Materials Science, Center for Nanoanalysis and Electron Microscopy (CENEM), University of Erlangen-Nuremberg, Cauerstrasse 6, 91058 Erlangen (Germany)

[C]Department of Inorganic Chemistry, University of Erlangen-Nuremberg,
Egerlandstrasse 1, D-91058 Erlangen, Germany

*Corresponding author

Phone: +49-9131-852-7575 Fax: +49-9131-852-7582

Email: schmuki@ww.uni-erlangen.de

Experimental

Tantalum foils (99.9% purity, Advent Research Material Ltd.) were degreased by sonicating in acetone, isopropanol and methanol for several minutes, followed by rinsing with distilled water and drying in a nitrogen stream. Samples were anodized in a mixture of glycerol and ethylene glycol (95:5 vol%) containing 0.2 M NH_4F and 0.15 M $(NH_4)_2SO_4$ at 30 V for 1 h [1]. Electrochemical anodization was carried out in a two electrode arrangement with a platinum foil as a counter electrode using a high-voltage potentiostat system (VSP 2653HE, VOLTCRAFT). The distance between the working and the counter electrode was adjusted to 1 cm. Thermal treatment was performed in a quartz tube in a flux of nitrogen (100 ml min^{-1}) or ammonia (50 ml min^{-1}). The furnace was heated up after nitrogen purging for 15 min, or nitrogen and ammonia purging, respectively, for 15 min. In order to produce alkaline metal doped Ta_3N_5, two step annealing was carried out; the oxide layers were converted to nitrides by annealing in NH_3 at 800°C for 1 h and then a certain concentration of alkaline metal solution was dropped on the sample followed by reannealing in NH_3 at 800°C for 3 h. The second step is used for doping with alkaline metals and for crystallization. Undoped samples were also prepared as references by annealing in NH_3 at 800°C for 1 h and then 3 h without any alkaline solutions. The treated samples were cooled down to room temperature under nitrogen flow before contact to ambient air. The structure and morphology of the samples were identified by a X-ray diffractometer (X'pert-MPD PW3040, Phillips) using CuKα radiation and a scanning electron microscope (FE-SEM, S4800, Hitachi), respectively. The TEM investigations were carried out using a Titan^3 80–300 microscope equipped with an image-side C_s-corrector. For the EDX analysis an EDAX detector attached to the Titan column was employed. Impedance measurements were performed using IM6 Zahner impedance unit in a three-electrode setup with an Ag/AgCl electrode as a reference electrode and platinum foil as a counter electrode in an electrolyte containing 0.1 mM $[Fe(CN)_6]^{3-}$ and 0.1 M $[Fe(CN)_6]^{4-}$.

Chemical characterization was carried out by X-ray photoelectron spectroscopy (PHI 5600, Physical Electronics) using AlKα monochromatized radiation. Ar^+ sputtering was carried out to eliminate contaminations on the surface. One cycle is able to sputter approximately 1.1 nm of the layer. Binding energies were referenced to the O1s peak at 531 eV.

All the photocurrent measurements were done in three electrode configuration using an Ag/AgCl electrode as a reference electrode and a counter electrode of platinum foil. Photocurrent spectra were acquired at an applied potential of 0.1 V vs. Ag/AgCl in 0.1 mM $[Fe(CN)_6]^{3-}$ and 0.1 M $[Fe(CN)_6]^{4-}$ recorded with 10 nm steps in the range of 300-800 nm using an Oriel 6365 150 W Xe-lamp equipped with a Oriel Cornerstone 7400 1/8 m monochromator. The obtained photocurrents were normalized to light intensity. Water splitting performance was examined in 0.1 mM $[Fe(CN)_6]^{3-}$ and 0.1 M $[Fe(CN)_6]^{4-}$ under AM 1.5 illumination. Inert electrolyte of 0.1 M Na_2SO_4 (pH 11.0) is also being employed. The light intensity was calibrated to be 100 mW cm^{-2} using the crystalline silicon solar cell. The transient was recorded in the chopped light irradiation.

Analysis of hydrogen gas was carried out by Shimadzu GC 17A and GCMS 2010S equipped with TCD and capillary columns: Supelco vocol 60m x 0.75 mm (GC 17A) and Restek molsieve 5A 30m x 0.53 mm (GCMS 2010S). Typical sample volumes of 100 up to 500 μl were injected by gastight Hamilton syringes. GC conditions: isothermic column temperature 70°C; temperature of injector and TCD-detector: 220°C; flow rates of N_2 carrier gas 24 ml/min. Certified gas mixtures Supelco No 501670 and 501697 were used to establish calibration curves for hydrogen and oxygen. The efficiency of H_2 evolution was calculated by the amount of H_2 detected and the theoretical value estimated from the total quantity of charges during electrolysis.

[1] W. Wei, J.M. Macak, N.K. Shrestha, P. Schmuki, J. Electrochem. Soc., 2009, 156, K104.

Table S1. IPCE at 500 nm and the estimated band gap of M-doped Ta_3N_5 (M = Na, K, Rb, Cs) prepared by annealing with 10 μl of 0.5M alkaline metal hydroxide solutions.

	Pure Ta_3N_5	Na-Ta_3N_5	K-Ta_3N_5	Rb-Ta_3N_5	Cs-Ta_3N_5
IPCE at 500 nm / %	0.8	8.0	9.5	9.0	9.4
Band gap / eV	2.0	1.8	1.7	1.7	1.8

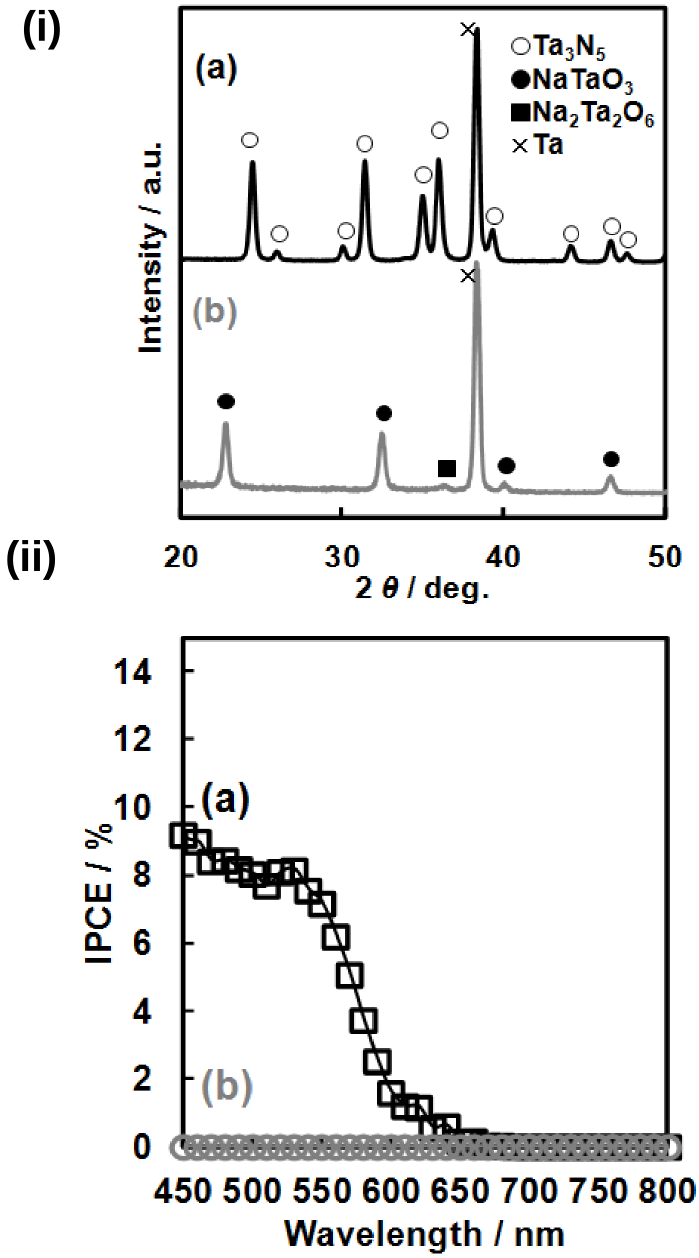


Figure S1. (i) XRD patterns (○Ta_3N_5, ●$NaTaO_3$, ■$Na_2Ta_2O_6$, ×Ta) and (ii) IPCE spectra at 0.1 V vs. Ag/AgCl taken in a solution containing 0.1 mM $[Fe(CN)_6]^{3-}$ and 0.1 M $[Fe(CN)_6]^{4-}$ for samples of a thickness approximately 5 μm annealed at 800°C for 1 hour and then 3 hours with 10 μl of a 0.5 M sodium hydroxide solution in (a) NH_3 and (b) N_2 atmosphere.

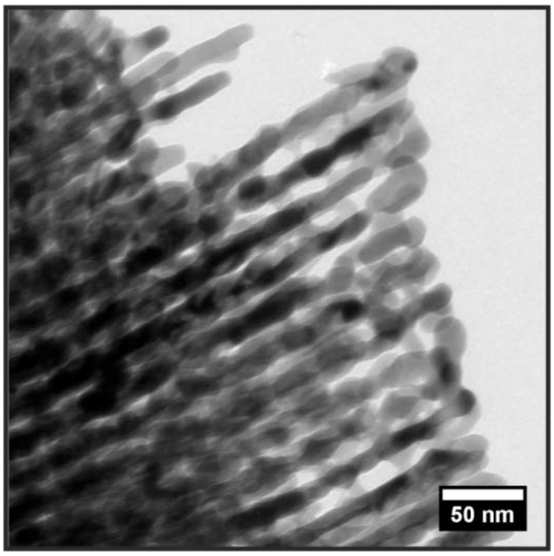


Figure S2. TEM bright field image of an undoped Ta_3N_5 sample.

An example of a bright field image of an undoped Ta_3N_5 sample is given in figure S2. The lamellar structure of the sample with a spacing of about 20 nm can be seen.

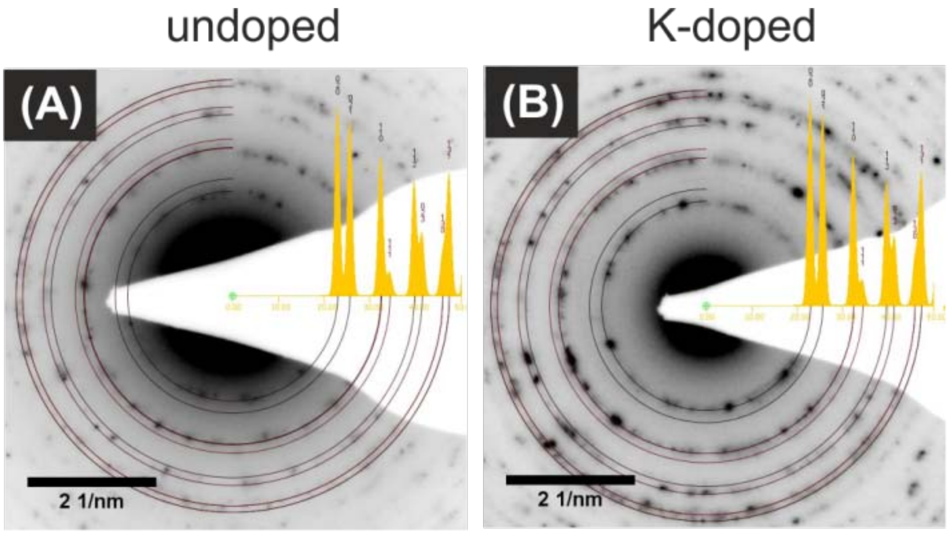


Figure S3. (a) and (b) are the diffraction pattern of an undoped and K-doped sample. Also shown is the simulated ring pattern of Ta_3N_5.

Furthermore TEM diffraction patterns of the undoped and K-doped Ta_3N_5 samples are shown (figure S3 (a) and (b)). No significant difference between the two different patterns can be found indicating no structural change due to the K-doping. From the ring pattern it can be stated that no other phase than the Ta_3N_5 is present which is also confirmed by the simulated pattern in figure S3.

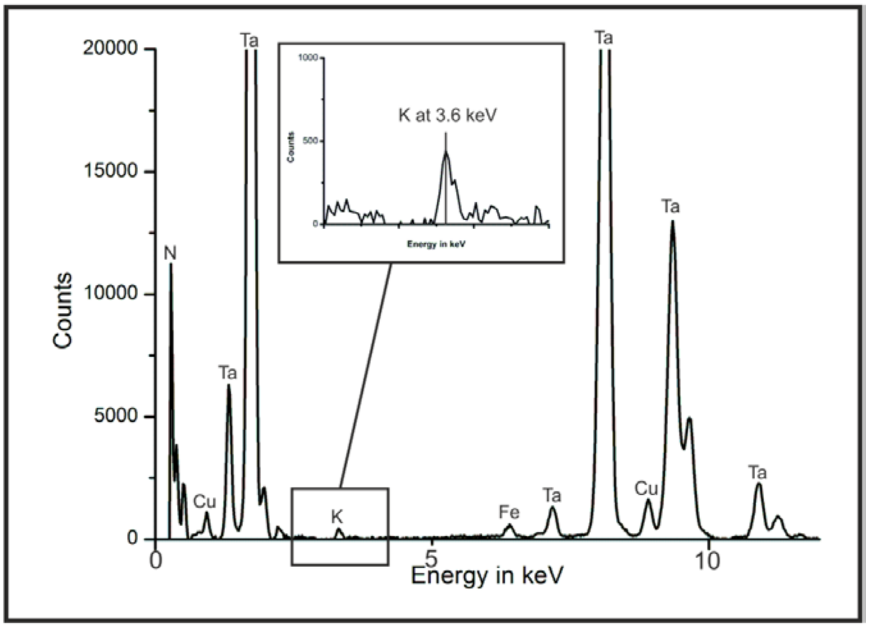
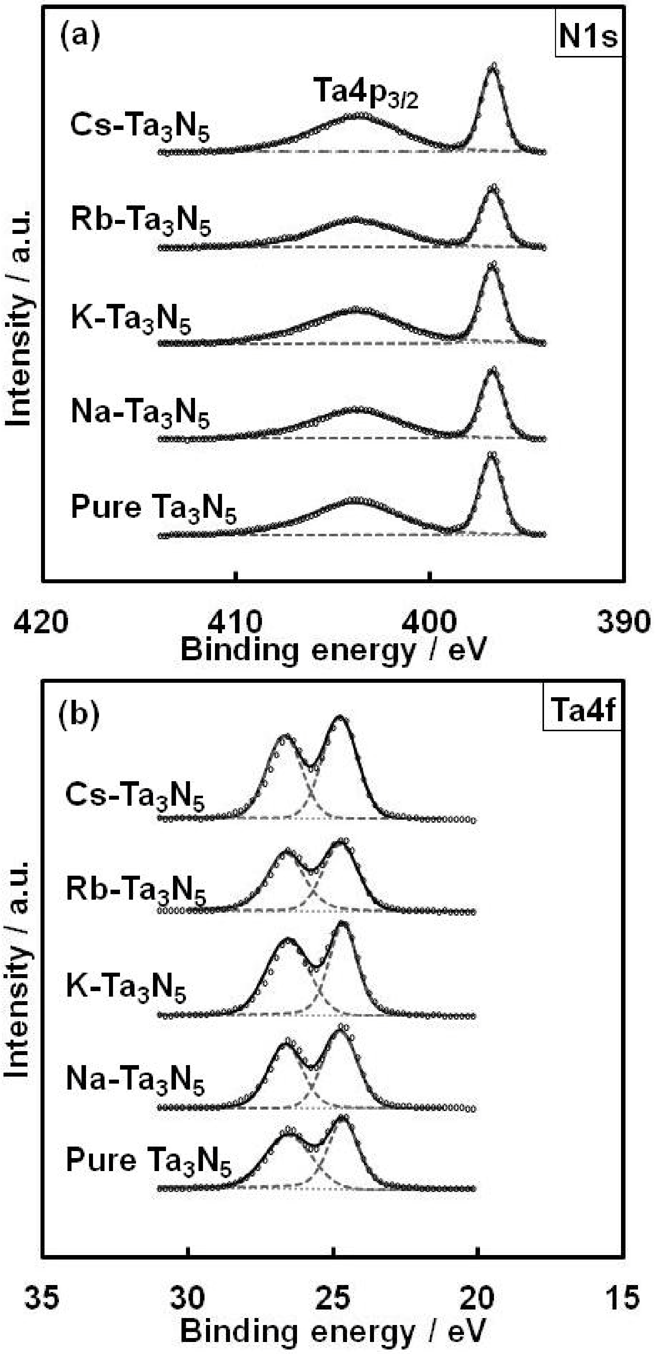


Figure S4. EDX-measurement of the K-doped sample.

Additionally the EDX data of the K-doped sample is shown including an inset of an enlarged view of the energy spectrum of K (figure S4). The spectrum was acquired in 900 seconds to ensure good reliability of the measurement. The potassium is clearly visible in the inset and was quantified to be around 1-2 at. % corresponding well to the expected doping ion concentration. In contrast, no K could be found in the undoped sample (not shown).


(a)
N1s
Ta4p3/2
Cs-Ta3N5
Rb-Ta3N5
K-Ta3N5
Na-Ta3N5
Pure Ta3N5
Intensity / a.u.
420
410
400
390
Binding energy / eV
(b)
Ta4f
Cs-Ta3N5
Rb-Ta3N5
K-Ta3N5
Na-Ta3N5
Pure Ta3N5
Intensity / a.u.
35
30
25
20
15
Binding energy / eV

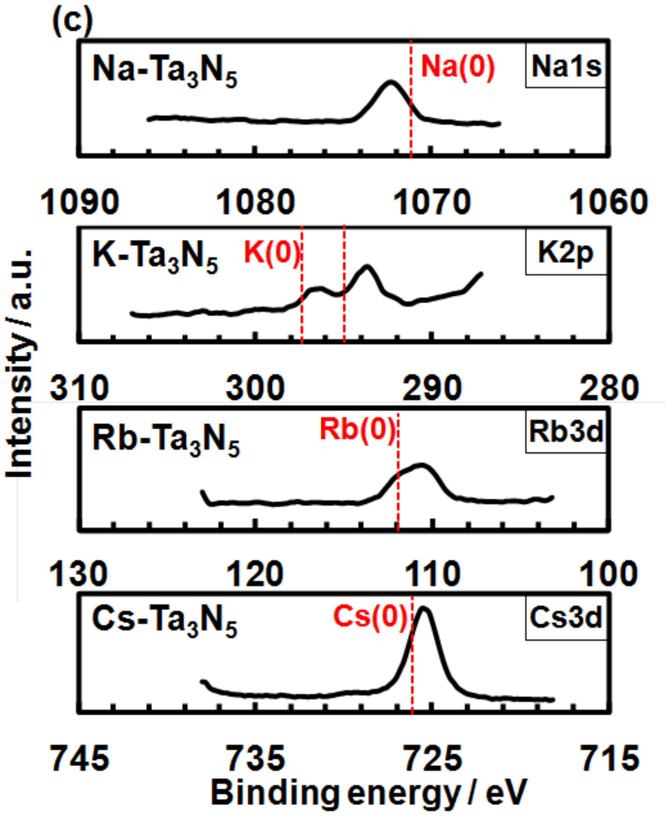


Figure S5. (a) N1s and (b) Ta4f XPS spectra of the M-doped Ta_3N_5 (M = Na, K, Rb, Cs) and pure (undoped) Ta_3N_5 samples prepared by annealing with 10 µl of 0.5M alkaline metal hydroxide solutions. A solid line denotes fitting and dotted lines express deconvolution. (c) Na1s, K2p, Rb3d and Cs3d XPS spectra of the M-doped Ta_3N_5 samples (M = Na, K, Rb, Cs). Dotted lines denote the peak position of metallic states of each metal.

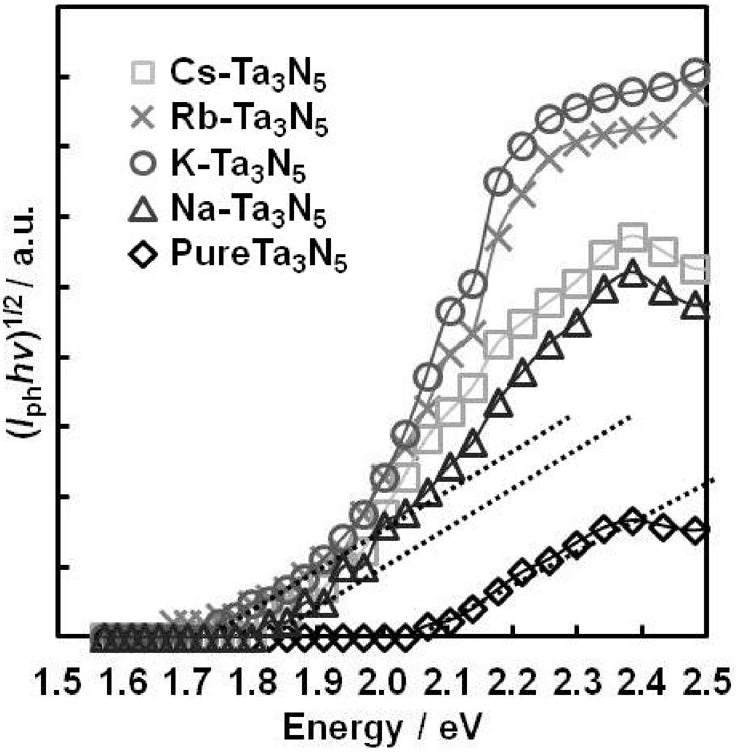


Figure S6. Band-gap determination plots for the M-doped Ta_3N_5 (M = Na, K, Rb, Cs) and pure Ta_3N_5 samples prepared by annealing with 10 μl of 0.5M alkaline metal hydroxide solutions.

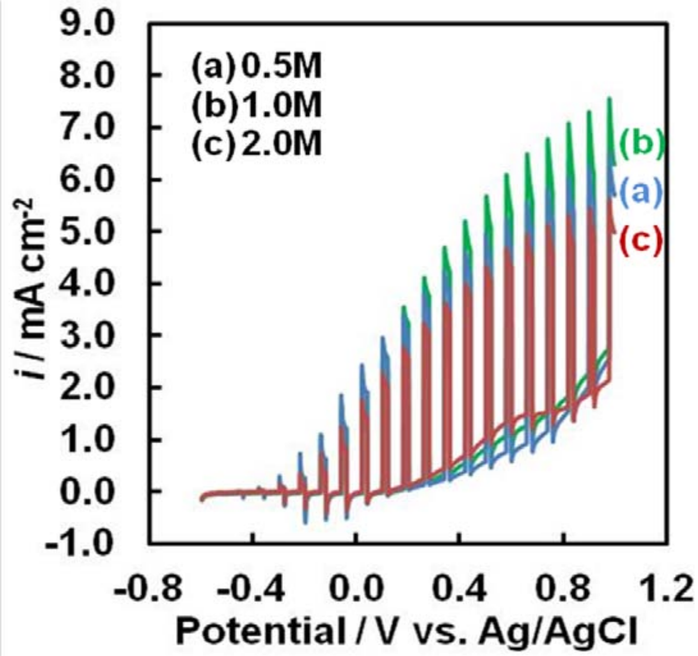


Figure S7. Photocurrent transients measurement performed in a solution containing 0.1 mM $[Fe(CN)_6]^{3-}$ and 0.1 M $[Fe(CN)_6]^{4-}$ under simulated sunlight AM 1.5 conditions for the K-doped samples prepared by different concentrations of KOH.

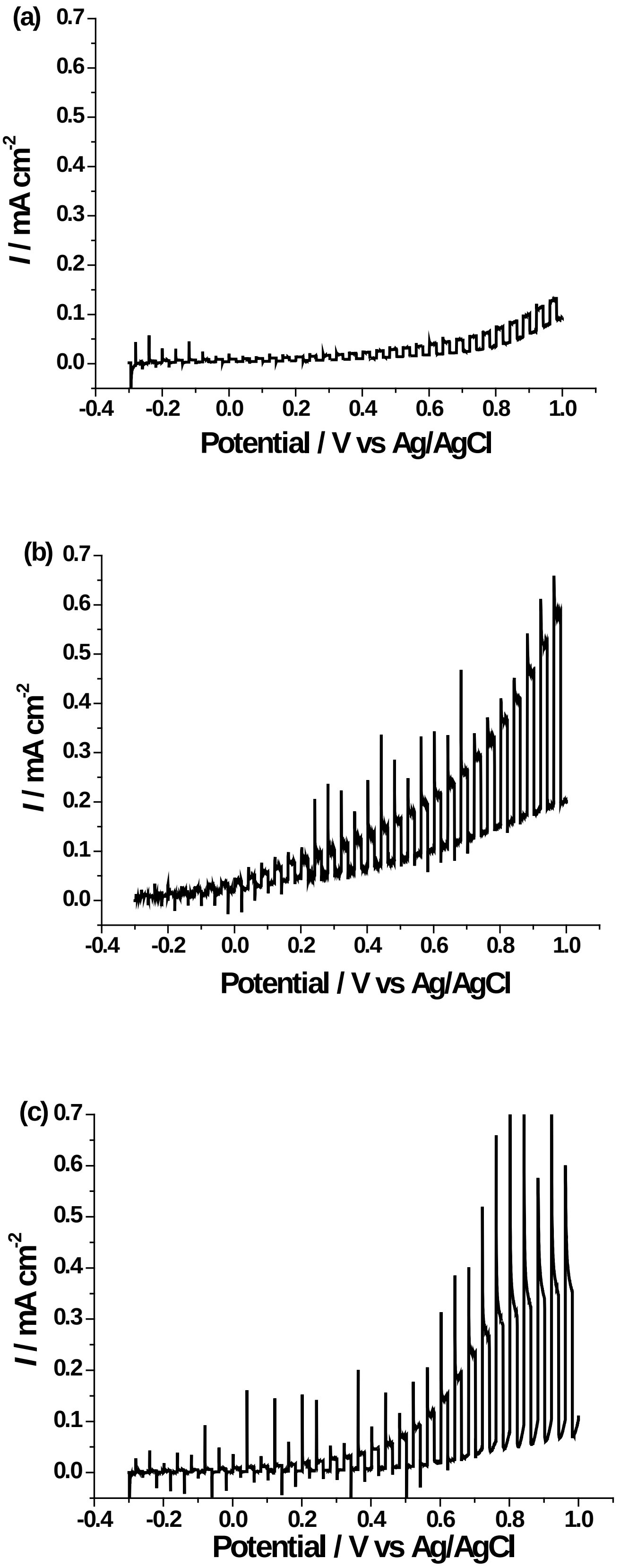


Figure S8. Chopped photocurrent measurements measured in a solution containing 0.1 M Na_2SO_4, pH 11.0 under simulated sunlight AM 1.5 conditions for the (a) undoped, (b) K-, and (c) Na-doped Ta_3N_5 samples.