Electronic Supplementary Material (ESI) for ChemComm.
This journal is © The Royal Society of Chemistry 2020

One-step synthesis of Ta_3N_5 nanorod photoanode from Ta plate and NH_4Cl powder for photoelectrochemical water oxidation

Yao Xiang,[ab] Boyang Zhang,[ab] Jintao Liu,[ab] Shanshan Chen,[c] Takashi Hisatomi,[c] Kazunari Domen,[cd] and Guijun Ma*[a]

a. School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, China

b. University of Chinese Academy of Sciences, Beijing 100049, China

c. Research Initiative for Supra-Materials, Shinshu University, 4-17-1 Wakasato, Nagano-shi, Nagano 380-8553, Japan

d. Office of University Professors, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

Contents

Supporting Information

Experimental section

Preparation of Ta_3N_5/Ta

A metal tantalum sheet (The Nilaco company) with an area of 25 × 7.5 mm^2 and a thickness of 0.1 mm was taken as a Ta precursor. NH_4Cl was used to provide nitrogen source for nitridation reaction. Before experiment, the NH_4Cl powder was dehydrated by heating in a muffle furnace at 473 K for 2 h in air. The tantalum sheet was sequentially cleaned in acetone, ethanol, and ultrapure water under sonication and dried in nitrogen stream. In a typical procedure, the tantalum metal sheet and 15 mg of NH_4Cl powder were put into a quartz tube (ϕ8 mm). Then, the tube was sealed by flame after evacuating to an approximate pressure of 1.3 Pa. The length of the filled tube was around 80 mm equaling to an inner volume of 4 cm^3. The samples were heated via a two-step temperature program with maintaining at 673–733 K for 2 h in the first step and 1023–1063 K for 2 h in the second one, and finally cooled down to room temperature naturally. The heating rate is 2.5 K min^{-1}. The obtained Ta_3N_5/Ta thin films were washed with ultra-pure water before usage.

Surface modification with $Co(OH)_x$ and $Ni(OH)_x$ on Ta_3N_5 film

Before the PEC measurement, $Co(OH)_x$ and $Ni(OH)_x$ were deposited sequentially on the prepared Ta_3N_5/Ta film as oxygen evolution catalysts. For the $Co(OH)_x$ deposition, the

Ta_3N_5/Ta samples were immersed in an aqueous solution containing 0.2 M $CoSO_4$ and 6.28 mM $NH_3 \cdot H_2O$ for 30 min, and then washed with copious deionized water. The $Ni(OH)_x$ layer was loaded over the above $Co(OH)_x/Ta_3N_5$/Ta through a electrodeposition route, in which 0.025 M $NiSO_4$ solution was used as an electrolyte in an undivided cell. An applied potential of 1.16 V vs Ag/AgCl was held until the charge passed through the outer circuit reached about 25 mC cm^{-2}.

Materials characterization

The morphologies of the samples were examined using a field-emission scanning electron microscope (SEM, JEOL JSM-7800F Prime) with an energy dispersive spectrometer (EDS) detector. The crystal structures of samples were investigated by X-ray diffraction (XRD, Bruker D8 Advance) with Cu Kα radiation.

PEC measurements of Ta_3N_5/Ta photoelectrodes

The PEC tests were conducted in a three-electrode system with a potentiostat (Gamry, Interface 1000T) under simulated AM 1.5G solar light irradiation (100 $mW \cdot cm^{-2}$, SAN-EI ELECTRIC, Class AAA Solar simulator). The fabricated Ta_3N_5, a platinum wire, and a Ag/AgCl (saturated potassium chloride) were used as working, counter and reference electrodes, respectively. Unless otherwise noted, 0.5 M $Na_2B_4O_7$ aqueous solution with pH adjusted to 13 by adding NaOH was used as an electrolyte after saturation with Ar gas

for 10 min. The measured potentials were converted to V vs RHE ($E_{RHE} = E_{Ag/AgCl} +$ 0.244 V + 0.059 V × pH). The photocurrent was measured by linear sweep voltammetry with a scan rate of 10 mV s^{-1}. The light was irradiated from the front side of electrodes for all cases. Incident photon-to-current efficiency (IPCE) was measured under monochromatic light irradiation, provided by a tungsten lamp equipped with a monochromator. The light intensity was obtained using a calibrated Si photodiode.

The amount of evolved oxygen was determined through operation in a three electrode system with a potentiostat (Interface 1000T, Gamry) at a potential of 1.0 V vs RHE in a closed configuration, in which the produced gases were analyzed by an online gas chromatograph (Agilent Technologies Inc., 490 Micro GC) using a thermal conductivity detector (TCD).

Analysis of the products

After the calcination of the quartz tube containing Ta metal plate and NH_4Cl powder, the products were characterized using a Fourier-transform infrared (FTIR) instrument before the quartz tube was opened. The FTIR spectra were obtained in a transmission mode with a VERTEX 70 spectrometer by averaging 64 scans at a resolution of 2 cm^{-2}. After that, the quartz tube was placed inside a soft plastic tube with Ar gas continuously flowing from one end and purging into 100 ml water at the other end. After the quartz tube was broken inside the plastic tube, the pH of the water was decreased owing to dissolution of HCl. The amount of HCl was calculated based on the change of the pH value. In a similar operation, the amount of hydrogen and nitrogen in the quartz tube were detected by connecting the

plastic tube to a gas chromatograph (GC). In this case, the HCl was trapped by a 1M NaOH solution before the sampling using a GC. The experimental data are summarized in Table S1.

Summarization of the processes of synthesizing Ta_3N_5

Table S2 summarizes several methods typically applied to synthesizing Ta_3N_5 photoanodes. In the early research, Ta_3N_5 electrodes were fabricated by physically stacking the particle precursor on a conductive substrate (such as FTO) using paste or electrophoretic deposition (EPD), etc.[1] The high resistance between particle/particle and particle/substrate seriously inhibited the charge transport on Ta_3N_5. Abe and coworkers found that a post-necking treatment resulted in improvement of the photocurrent of Ta_3N_5 electrode due to the facilitation of electron transport between electrode particles (entry 1). After that, a more efficient particle transfer (PT) method (entry 2) was developed, by which a mono-particle layer of Ta_3N_5 was directly embedded in a metal substrate to improve the conductivity.[2] Both entry 1 and 2 are *ex situ* method that is the preparation and deposition of Ta_3N_5 particles are separated. An *in situ* growth of Ta_3N_5 is generally supposed to further improve the conductivity. In this case, by employing a Ta-containing conductive substrate as the precursor of nitridation, the Ta_3N_5 particles are chemically bonded to the substrate in a molecular-level (entry 3 to 9).[3] As shown in table 1, the photocurrent obtained from the *in situ* growth method is averagely higher than the *ex situ* one. At present, the top two currents produced over Ta_3N_5 photoanode were reported from entry 4 and 7.[4,7] Except the conductivity, morphology is another key factor in determining the activity through affecting light absorbance, bulk charge transfer efficiency, and number of reactive surface

sites, etc. Of those works related to the morphology design, TaO_x nanotube and nanorod precursors were prepared by a widely applied anodization (entry 5 and 6) or a recently-reported magnetron glancing angle deposition (entry 7) technique.[5,6,7] After high-temperature nitridation in NH_3 flow, the nanostructures of the 1D TaO_x precursor were kept in the Ta_3N_5 product. From entry 1 to 7, it can be found that the use of TaO_x precursor necessitates the use of NH_3 and the multi-step operation during preparation of Ta_3N_5. Li's group reported a carbonate-assisted one-step synthesis of Ta_3N_5 films (entry 8).[8] This method enabled the direct synthesis of high-oxidation-state metal nitride films from metal precursors under ammonia flow, and the prepared Ta_3N_5 electrode exhibited promising water splitting performance. In case of using TaO_x as precursor, the temperatures for synthesizing Ta_3N_5 are generally higher than 1100 K so as to break down the Ta-O bond. Compared with the previous reports, our work (entry 9) is featured with one- step, *in situ*, low-temperature (*ca.* 200 K lower than before) and none-NH_3 synthesis of nanostructured Ta_3N_5 photoanode.

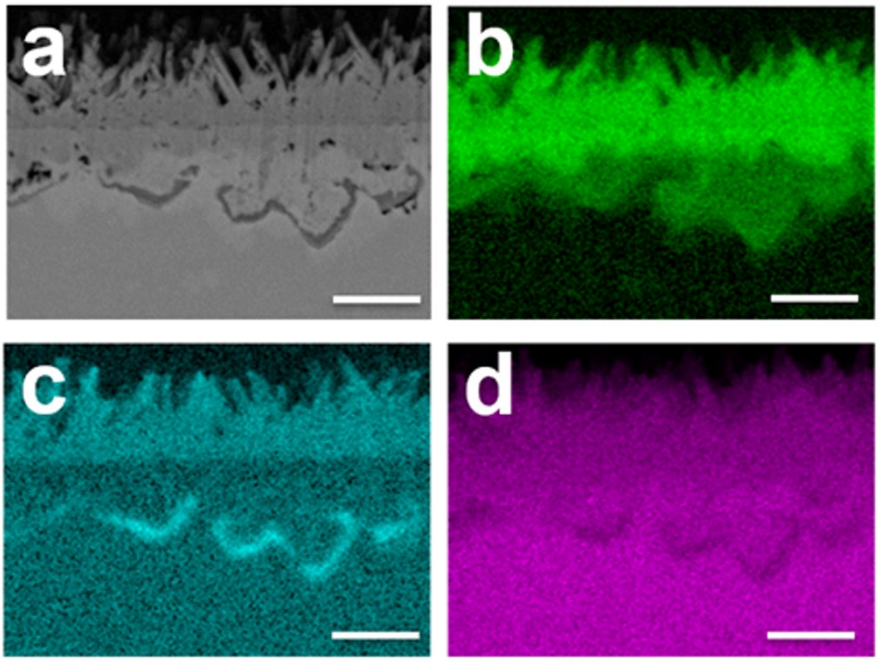

Figure S1. EDS elemental mapping images of a cross-section of the Ta_3N_5/Ta sample. The scale bars are 500 nm. **a)** BSE image, **b)** N K series, **c)** O K series, **d)** Ta K series.

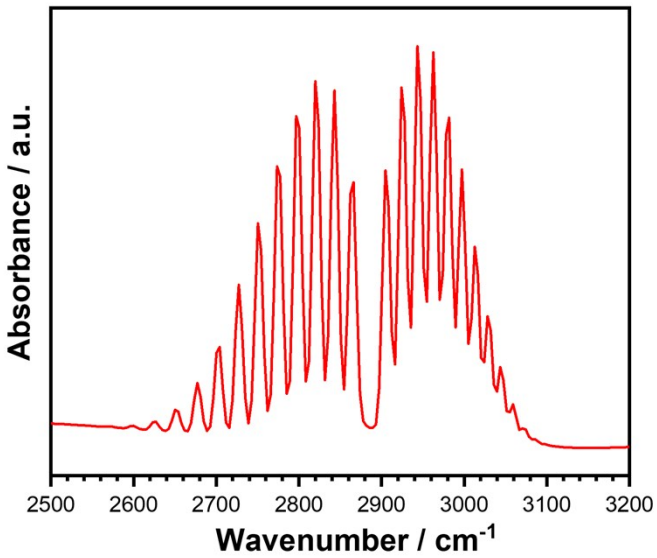

Figure S2. FTIR spectra of the products in the quartz tube after reaction. The absorption peaks were assigned to gaseous HCl species.

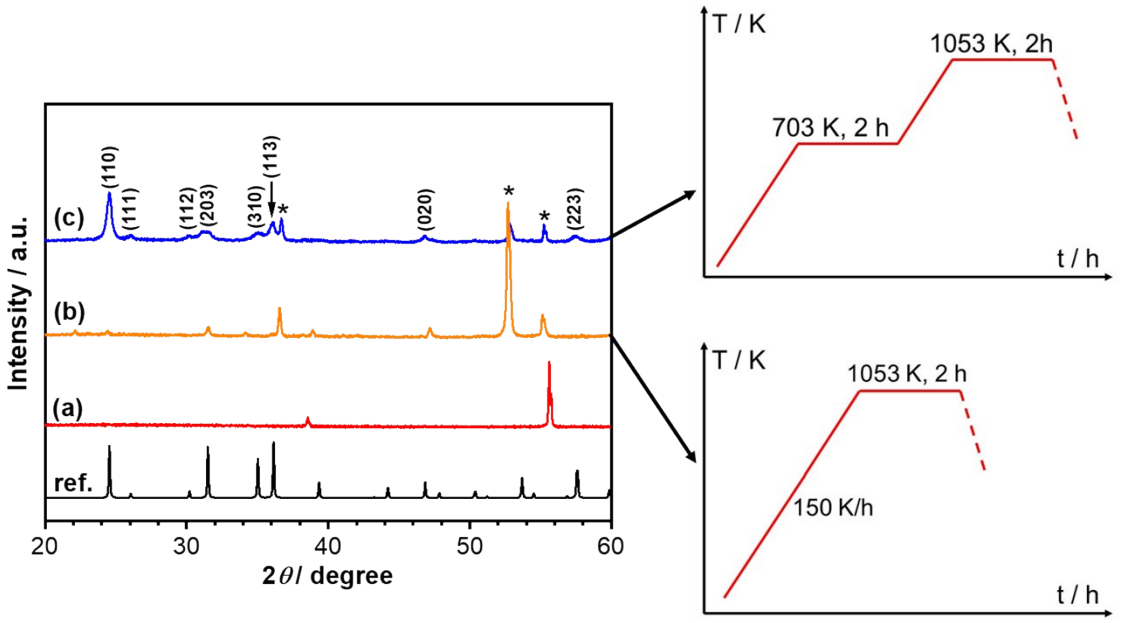

Figure S3. Left: XRD patterns of **(a)** Ta plate and the samples prepared by reaction of Ta plate and NH_4Cl powder in vacuo at **(b)** 1053 and **(c)** 703-1053 K. Ta_3N_5 peaks are indexed. Asterisks represent the TaN*x* signals. Right: the temperature programs for preparation of sample **(b)** and **(c)**.

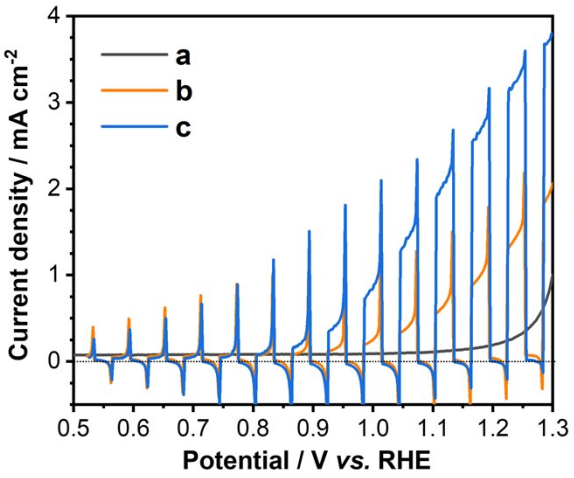

Figure S4. Current-potential curves for (a) pristine Ta_3N_5, (b) $Co(OH)_x/Ta_3N_5$ and (c) $Ni(OH)_x/Co(OH)_x/Ta_3N_5$ photoanodes under AM 1.5G simulated solar light in 0.5 M $Na_2B_4O_7$ aqueous solution (pH = 13). The Ta_3N_5 photoanode was prepared with the temperature program of 703-1053 K.

Table S1. The amount of precursors and the constituents detected after the reaction of synthesizing Ta_3N_5 from Ta and NH_4Cl.

Precursors	Amount of substance (μmol)	The reaction products	Amount of substance (μmol)
Ta metal plate	1700 ± 100	HCl	140 ± 20
NH_4Cl powder	280 ± 15	H_2	220 ± 20
		N_2	65 ± 10
		Ta_3N_5	1 ± 0.1
		Residual NH_4Cl[a]	140 ± 20

([a]the amount was obtained by subtracting the amount of HCl from the NH_4Cl precursor)

Table S2 Synthesis processes of Ta_3N_5 photoanodes

Entry	Synthesis processes	Total steps	NH_3 flow ($mL\ min^{-1}$)	Temp. (k)	*In/ex situ*	J_{photo} ($mA\ cm^{-2}$)[e] at 1.23 V_{RHE}	Ref.
1[a]	$Ta_2O_5 \xrightarrow{NH_3} Ta_3N_5 \xrightarrow{EPD,\ necking} Ta_3N_5/FTO$	2	500	1123	*ex situ*	3	1
2[b]	$Ta_2O_5 \xrightarrow{NH_3} Ta_3N_5 \xrightarrow{PT} Ta_3N_5/Ta/Ti$	2	100	1173	*ex situ*	3.5	2
3	$Ta \xrightarrow{Sputter} TaO_x/Ta \xrightarrow{NH_3} Ta_3N_5/Ta$	2	100	1113	*in situ*	2	3
4	$Ta \xrightarrow{Hydrothermal} NaTaO_3/Ta \xrightarrow{NH_3} Ta_3N_5/Ta$	2	250	1223	*in situ*	12.1	4
5[c]	$Ta \xrightarrow{Anodization} Ta_2O_5$ nt/Ta $\xrightarrow{NH_3} Ta_3N_5$ nt/Ta	2	100	973	*in situ*	—	5
6[d]	$Ta \xrightarrow{Anodization} Ta_2O_5$ nr/Ta $\xrightarrow{NH_3} Ta_3N_5$ nr/Ta	4	10	1273	*in situ*	5	6
7[d]	$Ta \xrightarrow{Sputter} TaO_x$ nr/Ta $\xrightarrow{NH_3} Ta_3N_5$ nr/Ta	2	250	1253	*in situ*	9.95	7
8	$Ta \xrightarrow{CO_2 + NH_3} Ta_3N_5/Ta$	1	250	1173	*in situ*	8	8
9[d]	$Ta+NH_4Cl \xrightarrow{Vacuum\ heating} Ta_3N_5$ nr/Ta	1	No	953	*in situ*	3.2	This work

([a]EPD: Electrophoretic deposition, [b]PT: Particle transfer, [c]nt: Nanotube, [d]nr: Nanorod, [e]Under AM 1.5 solar simulator)

References

1 M. Higashi, K. Domen and R. Abe, *Energy Environ. Sci.*, 2011, **4**, 4138–4147.
2 C. Wang, T. Hisatomi, T. Minegishi, M. Nakabayashi, N. Shibata, M. Katayama and K. Domen, *Chem. Sci.*, 2016, **7**, 5821–5826.
3 D. Yokoyama, H. Hashiguchi, K. Maeda, T. Minegishi, T. Takata, R. Abe, J. Kubota and K. Domen, *Thin Solid Films*, 2011, **519**, 2087–2092.
4 G. Liu, S. Ye, P. Yan, F. Xiong, P. Fu, Z. Wang, Z. Chen, J. Shi and C. Li, *Energy Environ. Sci.*, 2016, **9**, 1327–1334.
5 X. Feng, T. Latempa, J. Basham, G. Mor, O. Varghese and C. Grimes, *Nano Lett.*, 2010, **10**, 948–952.
6 Y. Li, T. Takata, D. Cha, K. Takanabe, T. Minegishi, J. Kubota and K. Domen, *Adv. Mater.*, 2013, **25**, 125–131.
7 Y. Pihosh, T. Minegishi, V. Nandal, T. Higashi, M. Katayama, T. Yamada, Y. Sasaki, K. Seki, Y. Suzuki, M. Nakabayashi, M. Sugiyama and K. Domen, *Energy Environ. Sci.*, 2020, **13**, 1519–1530.
8 T. Fang, H. Huang, J. Feng, Y. Hu, Y. Guo, S. Zhang, Z. Li and Z. Zou, *Sci. Bull.*, 2018, **63**, 1404–1410.