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Supporting Information

Passivation of Surface States by ALD-Grown TiO_2 Overlayers on Ta_3N_5 Anodes for Photoelectrochemical Water Oxidation

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Experimental Section

Preparation of Ta_3N_5 thin film photoanode

Ta foil (99.5%, Beijing Sunstone Tungsten Molybdenum Co., Ltd.) was fist annealed in a tube furnace under the flow of air at 600 ^{o}C for 30 min. Then the obtained Ta_2O_5 film was annealed in the tube furnace under the flow of NH_3 at 850 ^{o}C for 8 h. After the annealing, the surface of the obtained Ta_3N_5 thin film photoanode was cleaned with N_2 flow.

Atomic layer deposition (ALD) of TiO_2 overlayer: TiO_2 overlayer was deposited onto Ta_3N_5 thin film photoanode at 250 ^{o}C in a home-made ALD system using titanium (IV) isopropoxide (TTIP, 99.99%, Sigma-Aldrich Co. LLC.) and H_2O as precursors. The precursors were held at 55 °C and 25 ^{o}C respectively. One ALD cycle consists of TTIP dose for 0.06 s, N_2 purge for 10 s, H_2O dose for 0.2 s and N_2 purge for 10 s.

Characterization

The morphology and microstructure of the samples were characterized by field-emission scanning electron microscopy (S-4800, Hitachi). The crystal structure of the sample was investigated using an X-ray diffractometer (D/MAX-2500) with Cu Kα radiation (λ = 1.5416 Å) at 40 kV and 140 mA. X-ray photoelectron spectroscopy (XPS) analysis of the samples was carried out on a Physical Electronics PHI 1600 ESCA system with an Al Kα X-ray source (E = 1486.6 eV). The binding energy was calibrated using the C 1s photoelectron peak at 284.6 eV as the reference. The thickness of the TiO_2 overlayer was characterized by an M-2000 DI spectroscopic ellipsometer (J.A. Woollam Co., Inc.).

Electrochemical measurements

Electrochemical measurements of Ta_3N_5 NTAs electrodes were performed using a three-electrode configuration with the Ta_3N_5 NTAs as the working electrode; saturated Ag/AgCl as the reference electrode; and platinum foil (2×2 cm^2) as the counter electrode. A 1.0 M

NaOH (99% Tianjin Windship Chemistry Technological Co.) aqueous solution (pH 13.6) was used as the electrolyte which was purged with N_2 for 20 min to remove the oxygen before the measurements. Potentials *vs.* Ag/AgCl were converted into potentials *vs.* RHE according to the Nernst equation ($E_{RHE} = E_{Ag/AgCl} + 0.059pH + 0.196$). An electrochemical workstation (CompactStat.e20250, IVIUM) was used to measure the *J–V* curves and EIS. The *J–V* curves were measured with a scan rate of 20 mV s^{-1} under the irradiation of a 300 W xenon lamp (Beijing Perfectlight Technology Co. Lt, LS-SXE300CUV) equipped with an AM1.5G filter. The intensity of the light was adjusted to 100 mW cm^{-2}. Before the test, the electrode was encapsulated by epoxy and covered with a mask to expose 0.28 cm^2 surface area to the irradiation. EIS data were gathered at a bias of 1.0 V *vs.* RHE using a 25 mV amplitude perturbation of between 10,000 and 0.1 Hz under irradiation. Data were fitted using Zview software (Scribner Associates).