Supplementary Material

Charge Carrier Transfer in Ta3N5 Photoanodes Prepared by Different Methods for Solar Water Splitting

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Experimental

Preparation of Ta\textsubscript{3}N\textsubscript{5} photoanodes

The electrophoresis deposition method: The Ta\textsubscript{2}O\textsubscript{5} powder was nitrided at 850 °C for 15 h under a flow of ammonia gas (500 mL min\textsuperscript{-1}) to form Ta\textsubscript{3}N\textsubscript{5} powder. The Ta\textsubscript{3}N\textsubscript{5} powder was deposited on the Ta substrates to form Ta\textsubscript{3}N\textsubscript{5}/Ta films by electrophoresis deposition following previous method.\textsuperscript{[1]} And then the Ta\textsubscript{3}N\textsubscript{5}/Ta dropped with TaCl\textsubscript{5} methanol solution (10mM, 10uL) for five times. Finally, the dropped Ta\textsubscript{3}N\textsubscript{5}/Ta was heated at 500 °C for 30 min under a flow of ammonia gas (500 mL min\textsuperscript{-1}). The oxidation and nitridation of Ta foil method: Ta foils (1× 1.5× 0.02 cm\textsuperscript{3}) were cleaned in ethanol and acetone. The Ta foils were oxidized at 610 °C in air for 30 min, and then were nitrided at 850 °C for 8 h under a flow of ammonia gas (500 mL min\textsuperscript{-1}) to form Ta\textsubscript{3}N\textsubscript{5}/Ta films. An impregnation method was used for Co(OH)\textsubscript{x} loading on Ta\textsubscript{3}N\textsubscript{5}/Ta.\textsuperscript{[1]} Firstly, NaOH was added into an aqueous solution containing Co\textsuperscript{2+} ions to fabricate the colloidal Co(OH)\textsubscript{x} solution. Secondly, the Ta\textsubscript{3}N\textsubscript{5}/Ta were immersed into the Co(OH)\textsubscript{x} colloidal solution for 1 h at room temperature, and then washed by distilled water and dried in air.

Characterization of Ta\textsubscript{3}N\textsubscript{5} photoanodes

The crystal structures of the Ta\textsubscript{3}N\textsubscript{5} photoanodes were measured by X-ray diffraction (XRD, Rigaku, Ultima III). The film thickness was measured by a Dektak Series 150 Surface Profiler. The morphology and film thickness of Ta\textsubscript{3}N\textsubscript{5} photoanodes were examined with a scanning electron microscope (SEM, Nova NanoSEM 230 FEI Co). The electrochemical impedance spectra (EIS) of the Ta\textsubscript{3}N\textsubscript{5} photoanodes were measured by an electrochemical analyzer (Solartron 1260 + 1287) with a 10 mV amplitude perturbation and frequencies between 0.1 Hz ~ 1 MHz. The Co/Ta ratios of the samples were investigated by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250).

Photoelectrochemical and electrochemical measurement

Photoelectrochemical properties were measured in a three-electrode cell using an electrochemical analyzer (CHI-633C, Shanghai Chenhua). An aqueous solution of 1 M NaOH was employed as electrolyte. A 500W Xenon lamp and an AM1.5G sunlight simulator (100 mW cm\textsuperscript{-2}, oriel 92251A-1000) were used as light sources. A Ta\textsubscript{3}N\textsubscript{5}/Ta, a Pt foil and a saturated calomel electrode (SCE) were used as working electrode, counter electrode and reference electrode, respectively. The potentials of the working electrode were obtained by the formula

\[ V_{RHE} = V_{SCE} + 0.242V + 0.059 \times \text{pH}, \]  

(1)

Where \( V_{RHE} \) was the potential vs. a reversible hydrogen potential, \( V_{SCE} \) was the potential vs. SCE electrode, and pH was the pH value of electrolyte.

The incident photon-to-current efficiency (IPCE) was determined under irradiation light of different wavelength generated by monochromatic filters. The APCE was calculated as follow:

\[ \text{APCE} = 1240 \times \frac{I_{ph}}{P \times \lambda \times \eta_{abs}}, \]  

(2)

Where \( I_{ph} \) is the photocurrent density (uA cm\textsuperscript{-2}), \( P \) and \( \lambda \) are the incident light
intensity (uW cm$^{-2}$) and wavelength (nm), respectively, and $\eta_{abs}$ is the light harvesting efficiency. The incident light intensity was measured by a photometer (Newport, 840-C, USA).

Reference


Figure S1. XRD patterns of EPD Ta$_3$N$_5$ and ONTF Ta$_3$N$_5$.

Figure S2. The circuit to simulate the EIS data

Figure S3. (a) The photocurrent of Ta$_3$N$_5$ in 1M NaOH aqueous solution. (b) The photocurrent of Ta$_3$N$_5$ in 1M NaOH+H$_2$O$_2$ aqueous solution.
Figure S4. (a) The XRD data of ONTF Ta$_3$N$_5$ and polished ONTF Ta$_3$N$_5$. (b) The photocurrent of EPD Ta$_3$N$_5$ with Ta foil and polished ONTF Ta$_3$N$_5$ as substrates.

Figure S5. SEM images of Co(OH)$_x$ loaded Ta$_3$N$_5$ photoanodes prepared by EPD (a) and ONTF (b) methods. Maps of the Co signal intensity of Ta$_3$N$_5$ photoanodes prepared by EPD (c) and ONTF (d) methods after Co(OH)$_x$ loading.