Electronic Supplementary Material (ESI) for Chemical Science.

Supplementary Information

Thin film transfer for the fabrication of tantalum nitride photoelectrodes with controllable layered structures for water splitting

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Experimental Section

Monochromatic irradiation (full width at half wavelength: 10 nm) from a Xe lamp (MAX-302, Asahi Spectra) was used to measure the incident photon-to-current conversion efficiency (IPCE). The IPCE values were calculated using the equation:

$$\mathrm{IPCE} = 1240 \times I_{\mathrm{light}} / (\lambda \times P) \times 100\% \qquad (1)$$

where λ (nm) is the wavelength of the monochromatic irradiation, I_{light} (mA cm^{-2}) is the photocurrent density, and P (mW cm^{-2}) is the incident photon flux for the monochromatic irradiation. The flat band potential for Ta_3N_5 photoanode in a 0.5 M KPi electrolyte was determined by the Mott−Schottky (M−S) method using a potentiostat-frequency response analyser (METEK, VersaSTAT3-200) at a frequency of 1000 Hz and an AC amplitude of 10 mV. After fitting the M−S plots, the flat band potential was derived from the intersection with the potential axis in each plot.

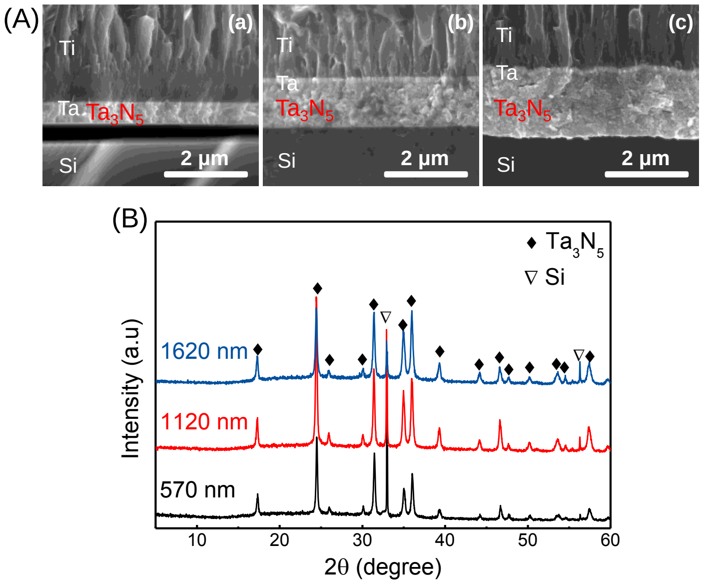

Fig. S1. (A) Cross-sectional SEM images and (B) XRD patterns for Ta_3N_5/Ta/Ti on Si substrates with Ta_3N_5 film thicknesses of (a) 570, (b) 1120, and (c) 1620 nm.

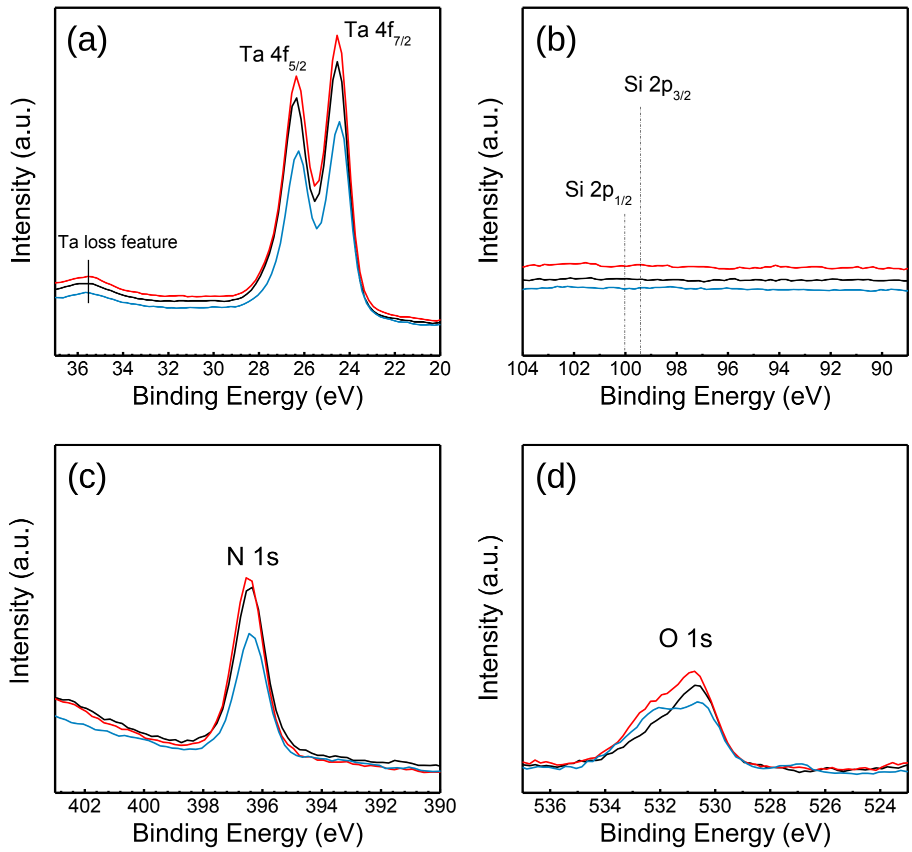

Fig. S2. XPS spectra of Ta_3N_5/Si (black lines), Ta_3N_5/Ta/Ti after the thin film transfer process (red lines), and transferred Ta_3N_5/Ta/Ti after surface etching by a $HF/HNO_3/H_2O$ (1:2:7, v/v) solution (blue lines): (a) Ta 4f, (b) Si 2p, (c) N 1s, and (d) O 1s.

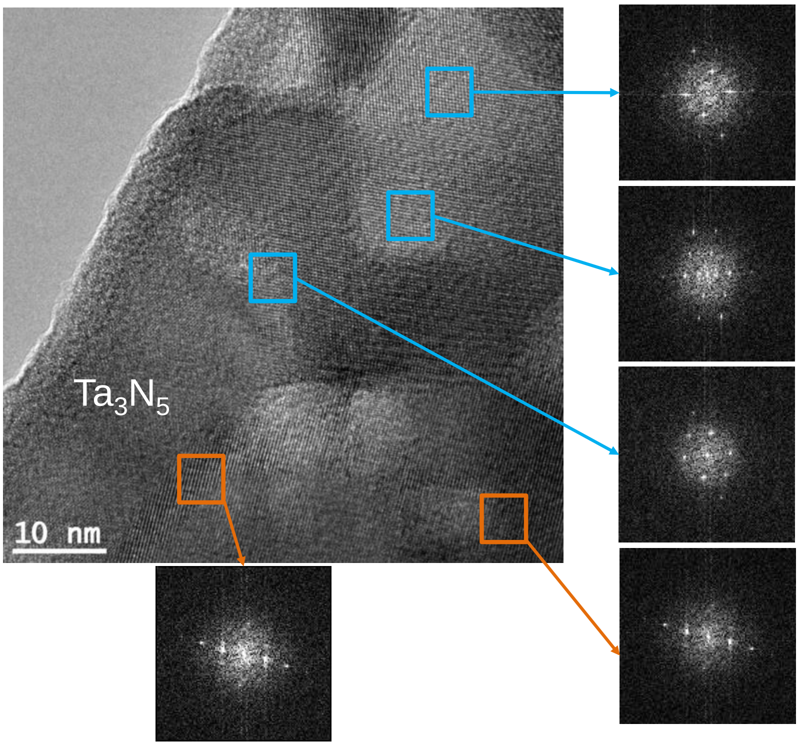

Fig. S3. TEM FFT diffraction patterns of Ta_3N_5 near the surface of a Ta_3N_5/Ta/Ti photoelectrode.

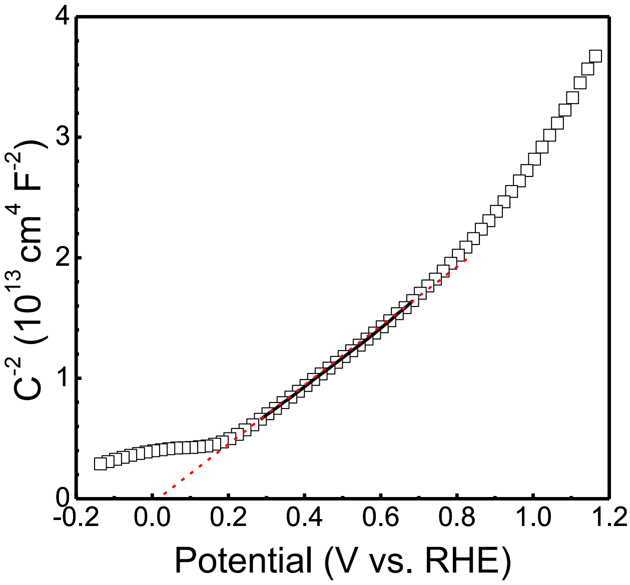

Fig. S4. Mott−Schottky (M−S) plot obtained from Ta_3N_5(570 nm)/Ta/Ti without $Co(OH)_x$ cocatalyst. The linearly fitted M−S plot indicates that the flat band potential for the Ta_3N_5/Ta/Ti is 0.02 V vs. RHE, which is consistent with the previously reported value for Ta_3N_5 photoanodes.[1, 2]

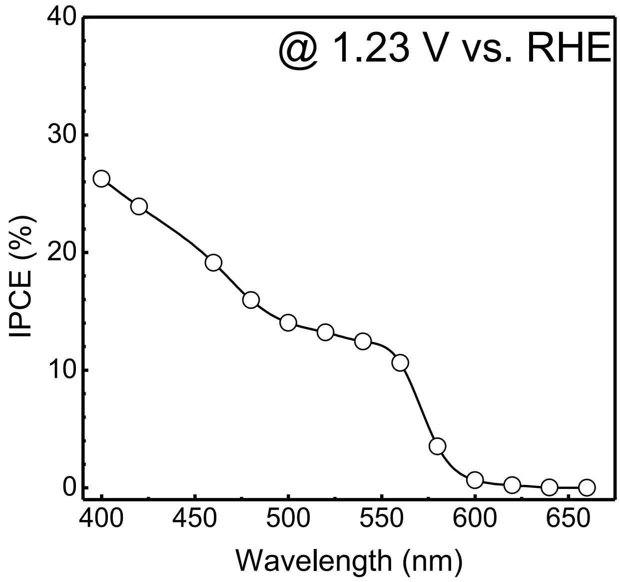

Fig. S5. IPCE spectrum for the $Co(OH)_x/Ta_3N_5$(570 nm)/Ta/Ti photoanode measured at 1.23 V vs. RHE.

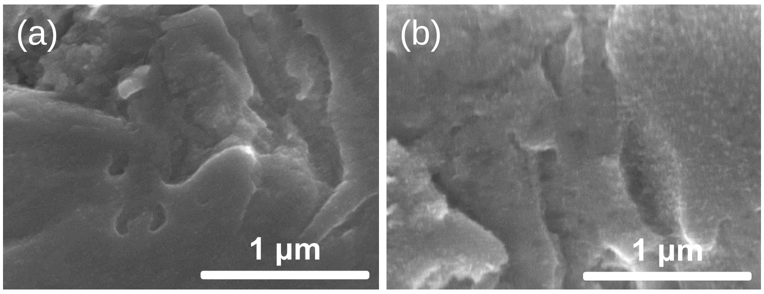

Fig. S6. Top-view SEM images of a $Co(OH)_x/Ta_3N_5$(570 nm)/Ta/Ti photoanodes (a) before and (b) after a static potential measurement at 1.23 V vs. RHE for 20 min.

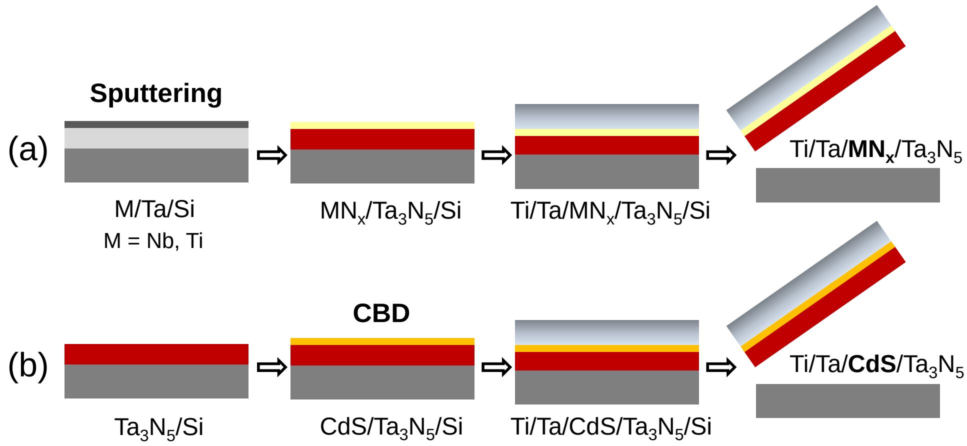

Fig. S7. Schematic of the procedure used to prepare Ta_3N_5 films modified with various interfacial layers between the Ta_3N_5 and Ta layers. (a) Ta_3N_5/MN_x/Ta/Ti (M = Nb, Ti). A metallic Nb (or Ti) film is initially deposited on the Ta/Si by sputtering. After oxidation (700 °C for 2 h) and nitridation (900 °C for 2 h in a 100 sccm NH_3 gas flow) of the M/Ta/Si (M = Nb, Ti) sample, a layer of NbN_x (or TiN_x) is formed on top of the Ta_3N_5 thin film on the Si substrate. (b) Ta_3N_5/CdS/Ta/Ti. A thin layer of CdS (approximately 60 nm) is deposited on top of the as-prepared Ta_3N_5/Si sample using chemical bath deposition (CBD), employing a previously reported method.[3] After depositing the modified contact layers on the Ta_3N_5/Si samples, the Ta_3N_5 photoelectrodes are prepared by following the identical transfer procedure shown in Fig. 1 in the main text.

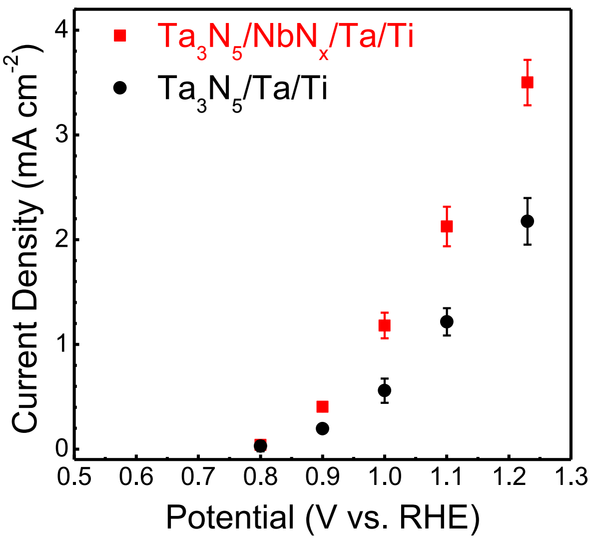

Fig. S8. Average photocurrent densities (n = 4, ±σ) of Ta_3N_5/Ta/Ti and Ta_3N_5/NbN_x/Ta/Ti photoelectrodes at different electrode potentials.

Table S1 Work functions of various polycrystalline metals.[4]

Metal (Polycrystalline)	Work function (eV)
Ta	4.25
Nb	4.30
Ti	4.33
Zr	4.05
Mg	3.66

References

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3. M. A. Contreras, M. J. Romero, B. To, F. Hasoon, R. Noufi, S. Ward, and K. Ramanathan, *Thin Solid Films*, 2002, **403**, 204-211.

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