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:

\[
\text{IPCE} = 1240 \times \frac{I_{\text{light}}}{\lambda \times P} \times 100\% \tag{1}
\]

where \( \lambda \) (nm) is the wavelength of the monochromatic irradiation, \( I_{\text{light}} \) (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 \( \text{Ta}_3\text{N}_5 \) 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$_3$N$_5$/Ta/Ti on Si substrates with Ta$_3$N$_5$ film thicknesses of (a) 570, (b) 1120, and (c) 1620 nm.
Fig. S2. XPS spectra of Ta₃N₅/Si (black lines), Ta₃N₅/Ta/Ti after the thin film transfer process (red lines), and transferred Ta₃N₅/Ta/Ti after surface etching by a HF/HNO₃/H₂O (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 Ta₃N₅ near the surface of a Ta₃N₅/Ta/Ti photoelectrode.
Fig. S4. Mott–Schottky (M–S) plot obtained from Ta$_3$N$_5$(570 nm)/Ta/Ti without Co(OH)$_x$ cocatalyst. The linearly fitted M–S plot indicates that the flat band potential for the Ta$_3$N$_5$/Ta/Ti is 0.02 V vs. RHE, which is consistent with the previously reported value for Ta$_3$N$_5$ photoanodes.$^{1,2}$
Fig. S5. IPCE spectrum for the Co(OH)$_2$/Ta$_2$N$_5$(570 nm)/Ta/Ti photoanode measured at 1.23 V vs. RHE.
Fig. S6. Top-view SEM images of a Co(OH)$_x$/Ta$_3$N$_5$(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$_3$N$_5$ films modified with various interfacial layers between the Ta$_3$N$_5$ and Ta layers. (a) Ta$_3$N$_5$/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$_3$N$_5$ thin film on the Si substrate. (b) Ta$_3$N$_5$/CdS/Ta/Ti. A thin layer of CdS (approximately 60 nm) is deposited on top of the as-prepared Ta$_3$N$_5$/Si sample using chemical bath deposition (CBD), employing a previously reported method.$^3$ After depositing the modified contact layers on the Ta$_3$N$_5$/Si samples, the Ta$_3$N$_5$ 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 Ta₃N₅/Ta/Ti and Ta₃N₅/NbNx/Ta/Ti photoelectrodes at different electrode potentials.
Table S1 Work functions of various polycrystalline metals.\textsuperscript{4}

<table>
<thead>
<tr>
<th>Metal (Polycrystalline)</th>
<th>Work function (eV)</th>
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<tbody>
<tr>
<td>Ta</td>
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<tr>
<td>Nb</td>
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<td>Ti</td>
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<tr>
<td>Zr</td>
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<td>Mg</td>
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References


