

Electronic Supplementary Information

Z-scheme photocatalytic hydrogen production over WO₃/g-C₃N₄ composite photocatalysts

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Experimental section

Preparation of WO₃/g-C₃N₄ composite photocatalysts

All chemicals used in this study were of analytical grade and were used without further purification. The commercially available WO₃ nanoparticles were obtained from Aldrich and were used here. g-C₃N₄ powder was prepared by direct heating urea (Nacalai tesque) at 500 °C in an muffle furnace for 2 h in an alumina crucible with a cover at a heating rate of 20 °C/min; the further heat treatment was performed at 520 °C for 2 h. After cooling to room temperature, the product was then collected and ground into powder. The synthesis of WO₃/g-C₃N₄ composite photocatalysts was as follows: various amounts of WO₃ with a suitable amount of g-C₃N₄ were added into an agate mortar and ground for 30 min using a pestle. The resulting mixture was calcined at 450 °C for 4 h at a ramp rate of 20 °C/min in an alumina crucible with a cover. The obtained samples were ground into powder.

Characterization

The powder X-ray diffractometer (XRD, RIGAKU Ultima IV, sample horizontal type) was used in order to record the diffraction patterns of photocatalysts employing Cu K α radiation. The fourier transform infrared spectra (FTIR) of the samples were recorded using a SPECTRUM 100 FTIR spectrometer (Perkin Elmer) equipped with an ATR assembly. X-ray photoelectron spectroscopy (XPS) measurements were carried out with a PHI Quantera SXM photoelectron spectrometer using Al K α radiation. A Hitachi S-4000 scanning electron microscope (SEM) and a JEOL JEM-1011 transmission electron microscope (TEM) were employed to observe the morphologies of the samples. High resolution TEM (HRTEM) observation was conducted using a Hitachi H-9000 TEM. The UV–visible diffuse reflectance spectra (DRS) of the photocatalysts were recorded using a Shimadzu UV-2450 spectrophotometer equipped with an integral sphere assembly. Photoluminescence (PL) spectra of oxide powders were measured at room temperature

using a Shimadzu RF-5300PC system equipped with solid sample holder.

Photocatalytic H₂ production

The pyrex column vessel reactor (inner volume: 123 mL) was used for the photocatalytic H₂ production from aqueous solution (40 mL) containing 10 vol% triethanolamine (TEA, Kishida Chemicals) as a sacrificial donor. 2 wt% Pt loaded on the surface of the photocatalyst by the in situ photodeposition method using H₂PtCl₆ (Wako Pure Chemicals). Before irradiation, N₂ gas was bubbled into the reaction solution for 30 min to remove a dissolved O₂. Typically, 40 mg of the photocatalyst were added into the reaction solution. The top of the reactor was tightly closed by a silicon rubber. A 300 W Xe lamp (MAX-303, Asahi Spectra) was applied as an artificial solar light source, which was positioned on the side of the photoreactor. In the case of visible light (>420 nm) irradiation, a UV cutoff filter (L-42, HOYA) was used. The photocatalysts were continuously dispersed in the aqueous TEA solution by a magnetic stirrer during the light irradiation. The photocatalytic reaction was performed at room temperature. The concentration of H₂ production from the aqueous TEA solution was analyzed by gas chromatography (GL Sciences, GC-3200) with thermal conductivity detector (TCD). The stainless column (4 m length, 2.17 mm i.d.) packed with Molecular Sieve 5A was used for the separation. The carrier gas was high purity Ar gas. The temperature conditions of GC were 50 °C for injection, column and detector. The apparent quantum efficiency (AQY) was estimated by using the equation: $AQY (\%) = (2 \times H/I) \times 100$, where H and I represent the numbers of evolved H₂ molecules and incident photons, respectively. The number of incident photons was measured using a calibrated Si photodiode. To estimate the AQY, a LED 405 nm lamp (Optocode) was applied as a light source.

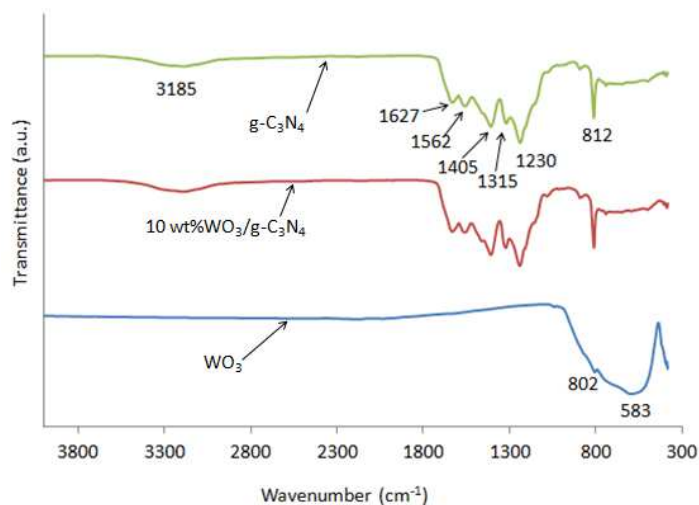


Fig. S1. FTIR spectra of g-C₃N₄, WO₃ and 10 wt% WO₃/g-C₃N₄ composite photocatalysts.

For the pure g-C₃N₄, the peaks at 1627 cm⁻¹ could be attributed to C-N stretching vibration modes, while those at 1230, 1315, 1405 and 1562 cm⁻¹ could be assigned to aromatic C-N breathing modes.^{S1} The sharp band at 812 cm⁻¹ and the broad bands at around 3200 cm⁻¹ were indicative of the breathing mode of the triazine units and the N-H stretching vibration modes, respectively.^{S2} For the pure WO₃, the broad peak around 320-850 cm⁻¹ was clearly observed, which corresponds to O-W-O and W-O-W stretching vibration modes in WO₃.^{S3} On the other hand, the broad peak could not be observed in the 10 wt% WO₃/g-C₃N₄ composite sample, which would be due to the low content of WO₃ and the existence of g-C₃N₄.^{S4}

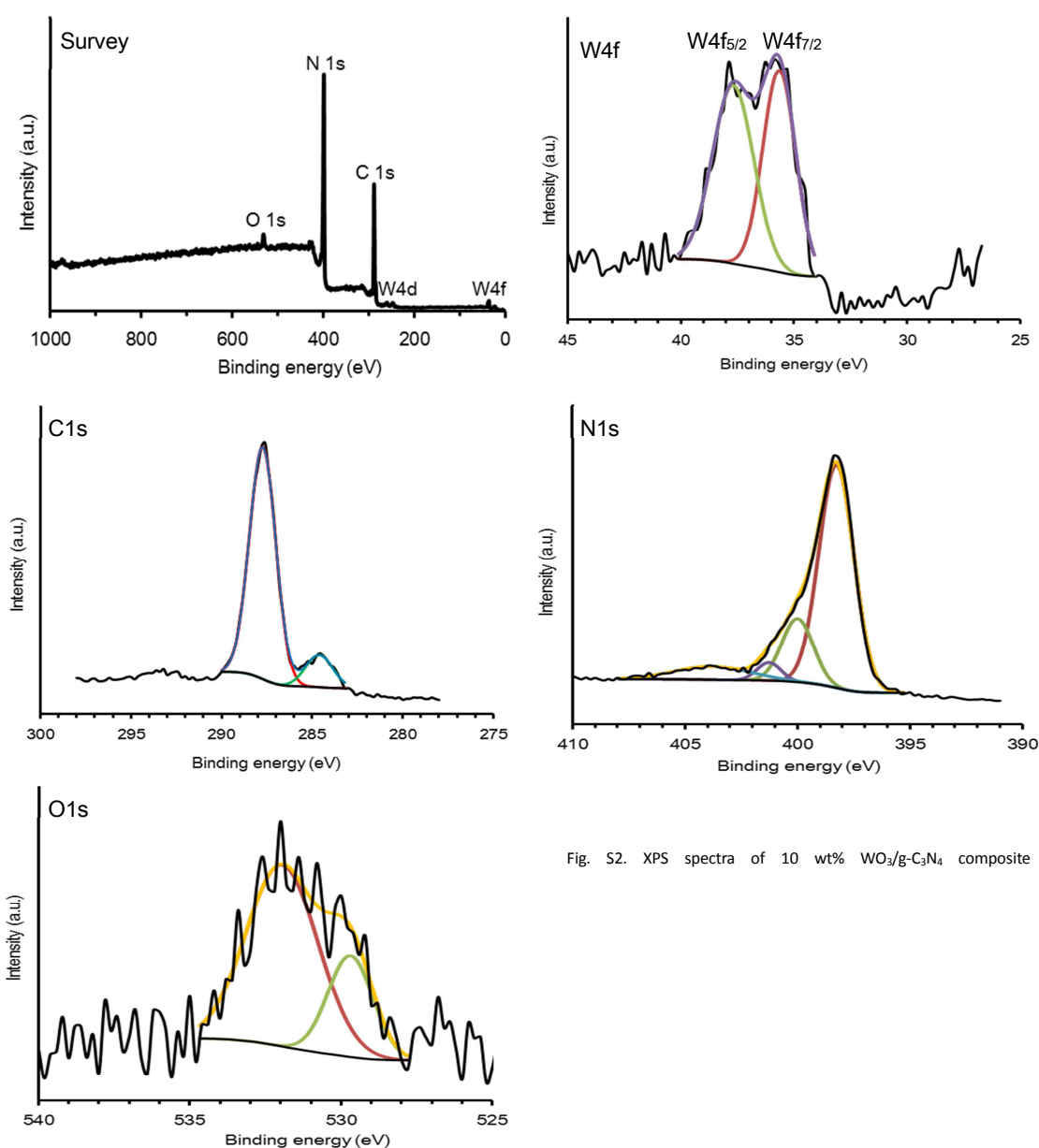


Fig. S2. XPS spectra of 10 wt% $\text{WO}_3/\text{g-C}_3\text{N}_4$ composite

It was clearly seen that only W, O, C and N elements were detected in the XPS survey spectrum. No peaks for other elements were found, indicating that the 10 wt% $\text{WO}_3/\text{g-C}_3\text{N}_4$ composite is primarily composed of W, O, C and N elements. The W 4f XPS spectra displayed two peaks at 35.6 and 37.7 eV that could be attributed to W 4f_{7/2} and 4f_{5/2}, respectively. These values were ascribed to the W⁶⁺ state in oxides and are consistent with reported values.^{S5} The O1s peak centered at 529.7 eV is associated with the O²⁻ in the WO_3 . The other O1s peak at 531.9 eV is associated with the presence of an -OH group or a water molecule on the surface of the 10 wt% $\text{WO}_3/\text{g-C}_3\text{N}_4$ composite photocatalyst.^{S6} It can be seen from C1s spectrum that the 10 wt% $\text{WO}_3/\text{g-C}_3\text{N}_4$ showed the two C 1s peaks located at 284.6 and 287.7 eV. The former is ascribed to the adventitious hydrocarbon from the XPS instrument itself and defect-containing sp²-hybridized carbon atoms present in graphitic domains, while the latter one is assigned to C-N-C coordination.^{S7} In the N1s spectrum several binding energies could be separated including triazine rings (C-N-C, 398.4 eV), tertiary nitrogen (N-(C)₃, 400.1 eV), amino functions (N-H, 401.6 eV) and the charge effects (403.8 eV).^{S7}

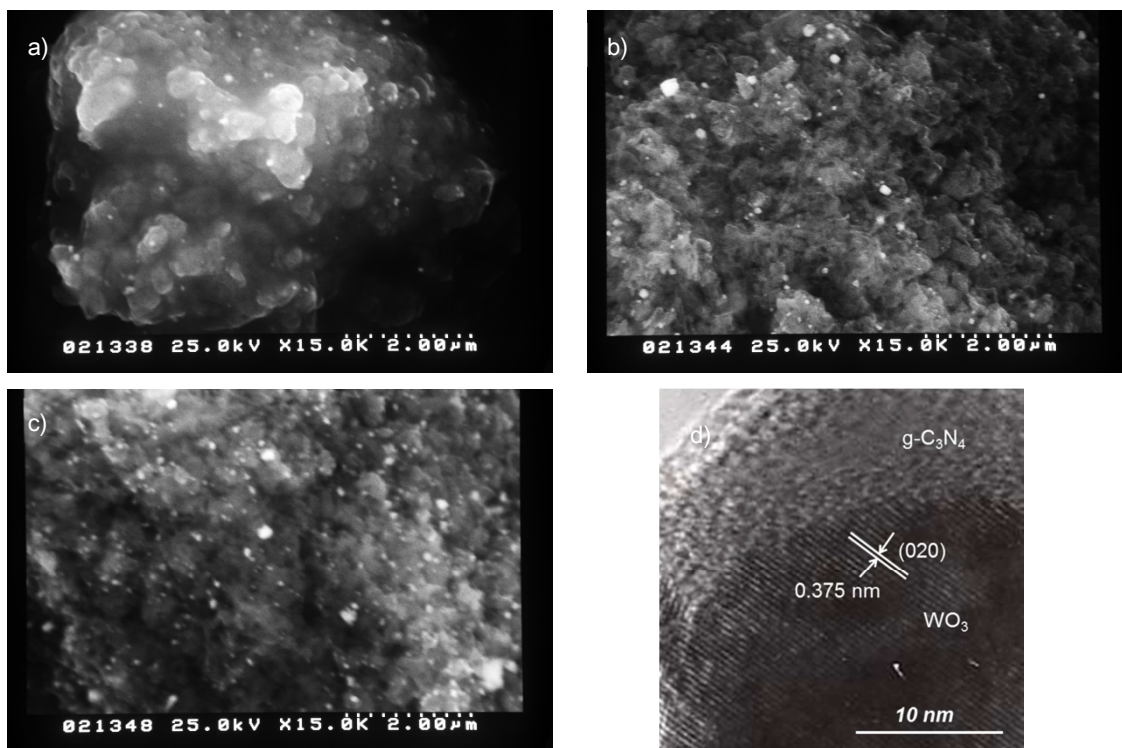


Fig. S3. SEM images of a) 5 wt%, b) 15 wt%, c) 30 wt% $\text{WO}_3/\text{g-C}_3\text{N}_4$, and d) HRTEM image of 10 wt% $\text{WO}_3/\text{g-C}_3\text{N}_4$ composite photocatalysts.

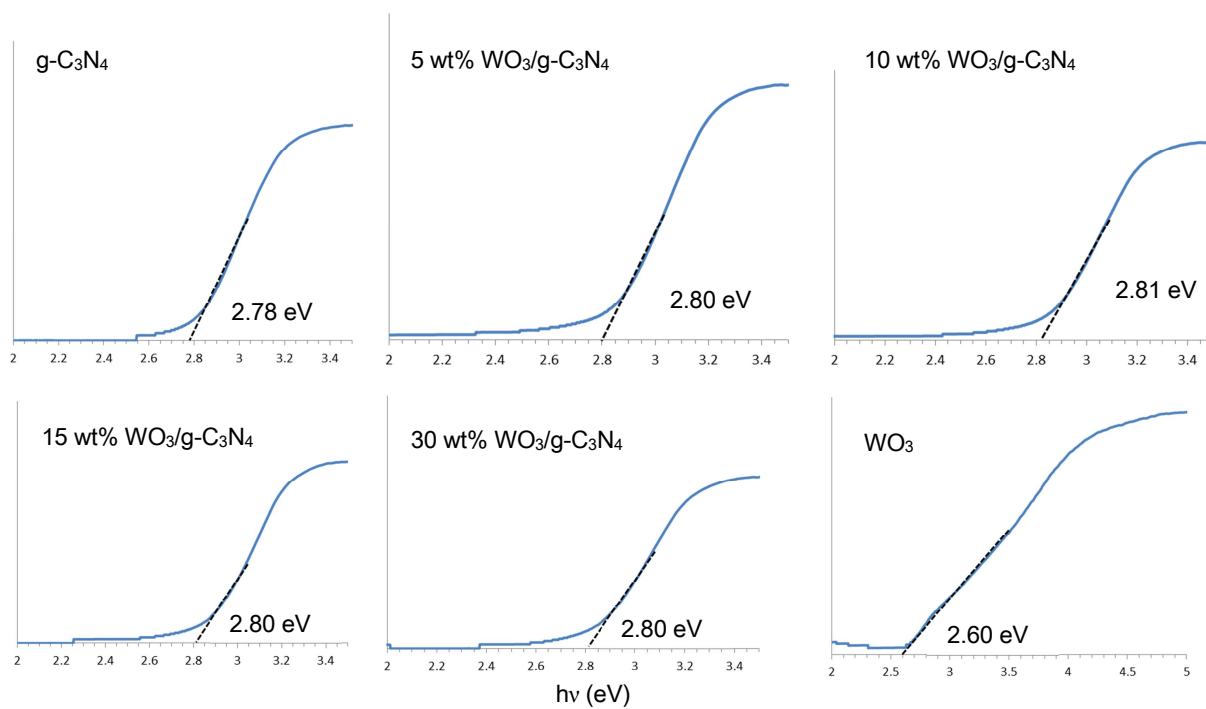


Fig. S4. Tauc plots of $\text{g-C}_3\text{N}_4$, WO_3 and $\text{WO}_3/\text{g-C}_3\text{N}_4$ composite photocatalysts.

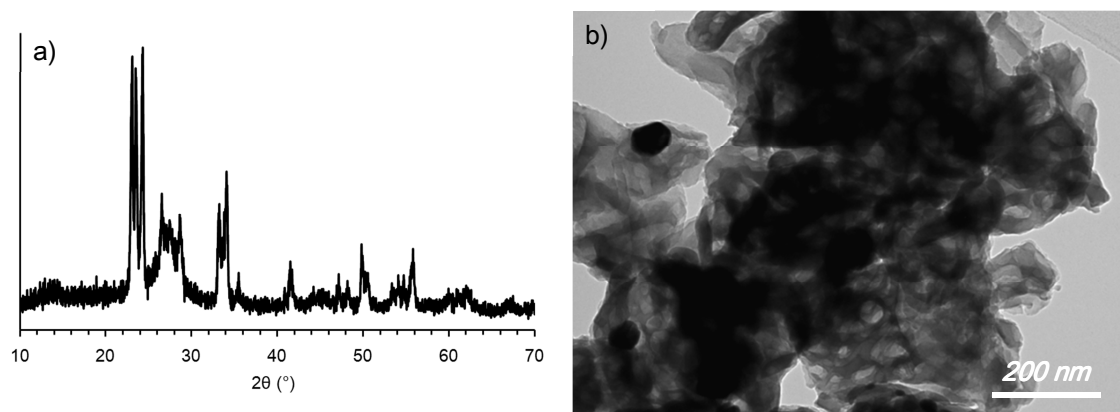


Fig. S5. a) XRD pattern and b) TEM image of 10 wt% $\text{WO}_3/\text{g-C}_3\text{N}_4$ composite after photocatalytic reaction.

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