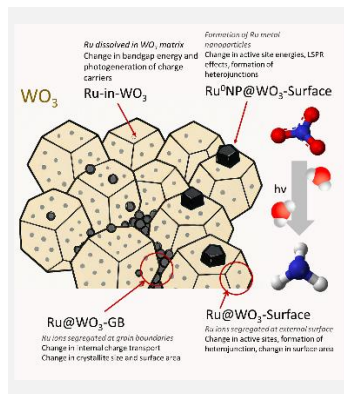




Ru-Doped WO₃ Photocatalysts Prepared by the Pechini Method for Nitrate Photoreduction

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WO₃ is an n-type semiconductor ($E_g \sim 2.6$ eV) with visible-light absorption suitable for photocatalytic ammonia production. Ru-doped WO₃ powders (0.1, 1.0, 5.0, 10.0 mol% Ru) were synthesised by the Pechini method and calcined at 350 degrees C. XRD with Rietveld refinement confirmed phase-pure monoclinic WO₃ with no secondary RuO₂. XPS showed a systematic W-4f binding-energy downshift with increasing Ru, consistent with W(VI) to W(V) reduction and oxygen vacancy formation. BET surface area and SSA/GBA ratio peaked at 1-5 mol% Ru. Undoped WO₃ produced ~ 2.0 $\mu\text{mol/L}$ NH₃ from NO₃⁻ photoreduction under UVC irradiation; Ru-doped samples are expected to improve this through enhanced adsorption at oxygen-vacancy sites.

Introduction

Ammonia is a cornerstone chemical for fertilisers and a potential hydrogen carrier, yet industrial Haber-Bosch synthesis emits 1-1.6 t CO₂ per tonne and accounts for $\sim 1\%$ of global CO₂ emissions [1]. Photocatalytic nitrogen reduction reactions (NxRR) using solar irradiation represent a sustainable decentralised alternative [2].

Tungsten trioxide (WO₃) has a monoclinic crystal structure (P21/n), a bandgap of ~ 2.6 eV enabling visible-light absorption up to ~ 480 nm, excellent photochemical stability, and a conduction band edge suitable for multi-electron reductions [3]. These properties make WO₃ a strong NxRR catalyst candidate, although its relatively positive conduction band potential necessitates co-catalysts to promote nitrogen activation (Figure 1). Ruthenium is a well-established co-catalyst for this purpose: small Ru clusters lower the N triple bond N dissociation barrier via electron back-donation into the π^* orbital, and Ru provides favourable end-on N-binding geometry [4].

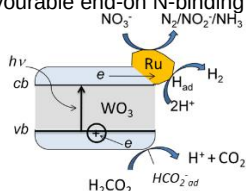


Figure 1. Photocatalytic NxRR with Ru/WO₃

Despite the promise of Ru/WO₃, a systematic study correlating Ru concentration with structural modifications (oxygen vacancies, grain size, phase purity), electronic structure (XPS binding energy shifts), surface basicity and photocatalytic NH₃ yields is lacking. This work addresses this gap with a series of Ru-doped WO₃ powders (0-10 mol% Ru)

synthesised by the Pechini polymeric-precursor method, providing full physicochemical characterisation and preliminary photocatalytic NxRR data.

Material and Methods

Synthesis by Pechini method. WCl₆ was dissolved in concentrated HNO₃(aq) at 0 °C; citric acid (CA) and ethylene glycol (EG) were added at CA:total metal:EG = 3:1:12 (molar). RuI₃ was added at 0.1, 1.0, 5.0 and 10.0 mol% relative to total W+Ru. The mixture was heated at 90 °C until a transparent resin formed. This resin was burned at 350 °C for 4 h and calcined at the same temperature for 15 h in air.

Characterisation. (a) Powder XRD (Cu K α , 2-80 degrees 2theta, step 0.02 degrees, 2 s/step) with Rietveld refinement in GSAS-II (monoclinic WO₃ P21/n, ICDD 43-1035). (b) XPS (Al K α monochromatic, pass energy 20 eV; C 1s = 284.8 eV charge reference); W 4f (30-45 eV) and Ru 3d (275-295 eV) spectra deconvoluted with Shirley backgrounds. (c) N₂ physisorption at -196 °C (Micromeritics); BET specific surface area (SSA) and grain boundary area (GBA = 6/(pD)) to give SSA/GBA ratio. (d) ICP-OES for W and Ru concentrations. (e) DRIFTS: CO₂ adsorption at 25 °C, 5 min, then He purge; difference spectra for surface basicity quantification.

Photocatalytic tests. UV-C batch reactor (254 nm, Osram HNS 15 W), 1.0 g/L catalyst, 1.0 g/L KNO₃ as N source, 0.2% formic acid as hole scavenger, N₂ purge, 25 °C; NH₃ quantified by Berthelot colorimetry (670 nm). An extended Langmuir-type kinetic model with NH₃ formation (k_f), product inhibition (k_i) and volatilisation (k_{loss}) was fitted to [NH₃] vs. time profiles by non-linear least squares.



Results and Discussion

All diffractograms indexed exclusively to monoclinic WO₃ (P21/n); no RuO₂ diffraction peaks detected at any Ru loading, indicating amorphous Ru species or solid-solution substitution. Unit cell volume increased monotonically with Ru content (+0.12% at 10 mol% Ru vs. undoped), consistent with partial W(VI) ($r = 0.60$ Å) substitution by Ru(IV) ($r = 0.62$ Å). XPS of the samples (Figure 2) revealed systematic shifts in both W and Ru core levels with increasing dopant concentration. The W-4f_{7/2} binding energy decreased monotonically from 36.31 eV in undoped WO₃ to 36.02 eV at 10% Ru ($\Delta = -0.29$ eV), indicative of a progressive increase in electron density around tungsten and consistent with partial W⁶⁺ to W⁵⁺ reduction induced by charge compensation upon Ru incorporation. The Ru 3d_{5/2} component, undetectable below 1% Ru, emerged at 281.64 eV (1%) and shifted to 281.26 eV (10%), values lying ~0.5 eV above the RuO₂ reference (280.75 eV), suggesting that Ru is stabilised in a W-O-Ru coordination environment rather than forming a segregated ruthenium oxide phase. The convergence of Ru 3d_{5/2} toward the RuO₂ reference with increasing loading may reflect a gradual transition from dilute lattice substitution to surface RuO_x clustering at higher concentrations.

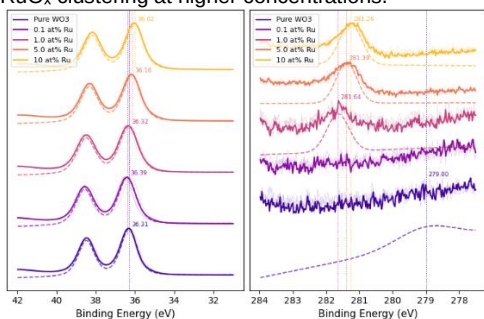


Figure 2. XPS spectra of W-4f (left) and Ru-3d (right)

BET surface area measurements reveal that the specific surface area (SSA) of WO₃ remains largely unchanged upon low Ru doping (48–50 m²/g from 0 to 5 mol% Ru), with a slight maximum of 50.5 m²/g

Conclusions

Ru-doped WO₃ photocatalysts (0.1-10 mol% Ru) synthesised by Pechini method were thoroughly characterised and their photocatalytic potential assessed. Key outcomes: (i) monoclinic WO₃ phase purity is maintained at all Ru loadings with no RuO₂ segregation detected by XRD; (ii) Ru incorporation drives W(VI) to W(V) reduction; (iii) BET surface area and SSA/GBA ratio are maximised at 1-5 mol% Ru, identifying this as the optimal concentration window; (iv) enhanced surface basicity (DRIFTS) at higher Ru loadings may improve nitrogen adsorption at defect sites; (v) undoped WO₃ establishes a NH₃ photoreduction baseline of ~2.0 umol/L which Ru-doped formulations are expected to exceed. WO₃ is confirmed as a viable photocatalyst platform for sustainable NxRR.

Acknowledgments

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References

- [1] A.J. Medford, M.C. Hatzell, *ACS Catal.* **7** (2017) 2624; [2] C. Smith et al., *Energy Environ. Sci.* **13** (2020) 331; [3] X.K. Doudrick et al., *Appl. Catal. B: Environ.* **136** (2013) 40; [4] T. Subramani, S.K. Nagarajan, *Inorg. Chem. Commun.* **142** (2022) 109709

at 1 mol% Ru, before decreasing markedly to 37.6 m²/g at 10 mol% Ru. The grain-boundary area (GBA) follows a similar trend, peaking near 36.8 m²/g at 5 mol% Ru and declining at 10 mol% Ru. Notably, the GBA/SSA ratio increases monotonically from 0.62 (pure) to 0.91 (10 mol% Ru), indicating that the grain-boundary contribution to the total surface grows progressively with doping. DRIFTS spectra in the 1200–1700 cm⁻¹ region show that bands near 1416 and 1625 cm⁻¹, present in all samples, intensify with Ru content; more significantly, samples at ≥5 mol% Ru develop a structured envelope of additional features spanning 1213–1690 cm⁻¹, encompassing positions characteristic of bridging carbonate (1393–1416 cm⁻¹), bidentate carbonate (1449–1458 cm⁻¹), and adsorbed bicarbonate/hydroxycarbonate species (1506–1540 cm⁻¹), suggesting a progressive increase in surface basicity and CO₂ adsorption capacity at higher Ru loadings.

Regarding the photosynthesis of NH₃, undoped WO₃ reached ~2.0 umol/L NH₃ from NO₃⁻ at 30 min (plateau). Extended Langmuir model fits ($R^2 > 0.96$) showed significant product inhibition ($k_i \gg 0$), limiting conversion at longer reaction times. Results for Ru-doped samples are pending; the SSA/GBA optimum and maximum oxygen vacancy density at 1-5 mol% Ru strongly suggest this window will deliver the best photocatalytic performance.

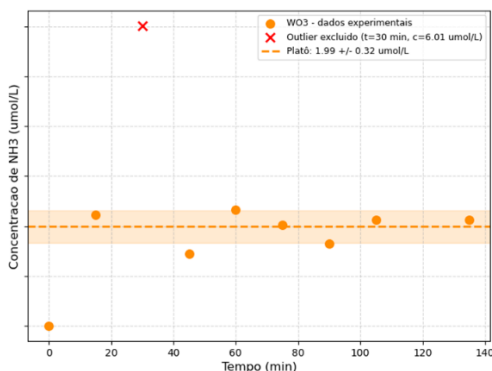


Figure 2. Ammonia formation over pure WO₃.