Extending Visible-Light Photocatalytic Solar-to-Hydrogen Production with Phenyl-Modified Carbon Nitride

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Solar-driven hydrogen production demands photocatalysts that both harvest visible light and convert the absorbed photons into fuel with high efficiency. Graphitic carbon nitride (g-C_3N_4, g-CN) is an attractive metal-free,2D layered-structured visible-light photocatalyst [1], but its relatively wide band gap (~2.6 eV) and fast electron–hole recombination limit solar hydrogen production. Molecular phenyl modification mitigates both: thermal condensation of the precursor 2,4-diamino-6-phenyl-1,3,5-triazine (DPT) yields phenyl-modified carbon nitride (PhCN), in which incorporated phenyl groups extend π-conjugation, narrow the band gap to ~2.0 eV and strongly red-shift the optical absorption. PhCN is best known for its intense, red-shifted photoluminescence, which has made it a bright green phosphor for solid-state lighting [2,3]; its potential as a hydrogen-evolution photocatalyst, however, has remained largely unexplored, which is the focus of this work.

As a first step, we optimised the photocatalytic hydrogen-production setup by tuning the platinum cocatalyst deposition environment. Pt is essential to drive the hydrogen-evolution reaction, yet in the common in-situ protocol, cocatalyst formation and proton reduction proceed simultaneously and on similar timescales, so the measured activity convolutes the intrinsic response of the support with that of the still-forming Pt interface. We therefore decoupled the two steps using *ex-situ* Pt photodeposition [4], depositing Pt without a sacrificial agent, in triethanolamine (TEOA) and in methanol. Methanol gave the highest and most reproducible activity (order MeOH > no-SA > TEOA), because TEOA strongly complexes the $[PtCl_6]^{2-}$ precursor and suppresses its photoreduction to metallic Pt [5]. Using this optimised methanol protocol, bulk g-CN and PhCN were prepared with closely matched crystallinity and surface area, so that activity differences reflect electronic structure and the Pt–support interface rather than texture. PhCN consistently outperformed g-CN. ICP-MS showed that the most active PhCN–Pt(MeOH) carried the *lowest* Pt loading (~0.41 wt%, versus ~0.83 wt% for g-CN), while HAADF-STEM/TEM revealed that methanol produces smaller, more uniformly dispersed Pt nanoparticles (≈1.2 nm) rather than the larger aggregates formed without a sacrificial agent. Activity is therefore governed by Pt dispersion and interfacial quality, not by the absolute amount of metal.

Building on this, the bulk PhCN was subjected to solvent-assisted hydrothermal post-treatment, with methanol again identified as the optimal solvent: it partially exfoliates PhCN, increasing surface accessibility through functionalized edges and stabilising surface defects. Steady-state photoluminescence (PL) and photoluminescence-excitation (PLE) measurements show reduced emission and modified excitation pathways for the exfoliated material, consistent with suppressed charge recombination, which translates directly into a hydrogen-evolution rate roughly four times that of bulk PhCN under the solar simulator. The central result is the comparison of apparent quantum efficiency (AQE) for the three single-component photocatalysts, bulk g-CN, bulk PhCN and methanol hydrothermally-exfoliated PhCN under monochromatic LEDs at 365, 470, 520 and 590 nm. The AQE rises systematically from g-CN to bulk PhCN to exfoliated PhCN at every wavelength: 8.12 → 14.4 → 20.9 % at 365 nm, 0.7 → 2.7 → 8.2 % at 470 nm and 0.02 → 0.19 → 1.7 % at 520 nm, as shown in Figure 1. Strikingly, at 590 nm, both bulk samples are inactive, whereas hydrothermally-exfoliated PhCN still evolves hydrogen (AQE ~0.08 %). This near-red-edge activity for photocatalytic H_2 production deep

in the long-wavelength visible region is rarely reported for a single-component carbon nitride and represents the key advance of this work, establishing methanol hydrothermally-exfoliated PhCN as an efficient, low-Pt, single-component visible-light photocatalyst for hydrogen production.

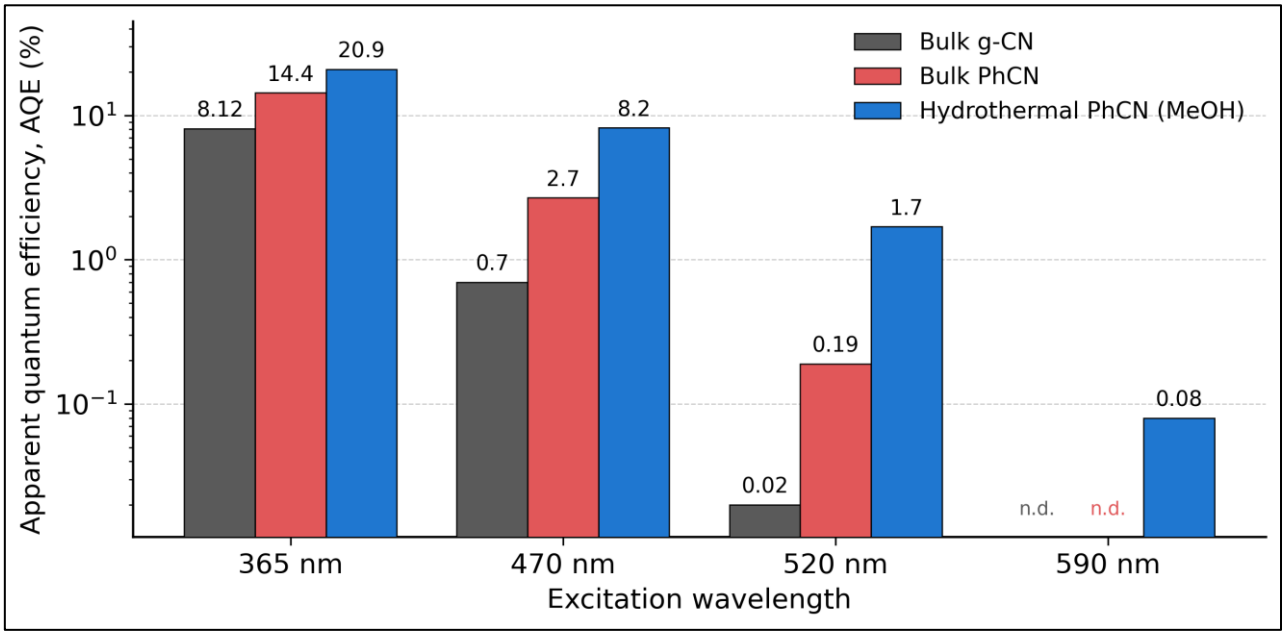

Figure 1 – Apparent quantum efficiency (AQE, log scale) for photocatalytic H_2 evolution by the three single-component photocatalysts — bulk g-CN, bulk PhCN and methanol hydrothermally-exfoliated PhCN — under 365, 470, 520 and 590 nm monochromatic LEDs (Pt photodeposited in methanol). At 590 nm, only the exfoliated PhCN is active; n.d. = no measurable activity.

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