Supporting Information for

# Covalent grafting of molecular catalysts on $C_3N_xH_y$ as robust, efficient and well-defined photocatalysts for solar fuel synthesis

Christopher D. Windle,[†] Alexander Wieczorek,[‡] Lunqiao Xiong,[†] Michael Sachs,[‡] Carlota Bozal-Ginesta,[‡] Hy-ojung Cha,[‡] Jeremy K. Cockcroft,[§] James Durrant[‡] and Junwang Tang[*,†]

[†] Department of Chemical Engineering, UCL Torrington Place, London, WC1E 7JE, UK

[‡]Department of Chemistry and Centre for Plastic Electronics, Imperial College London, White City Campus, London, W12 0BZ, United Kingdom

[§]Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ, UK

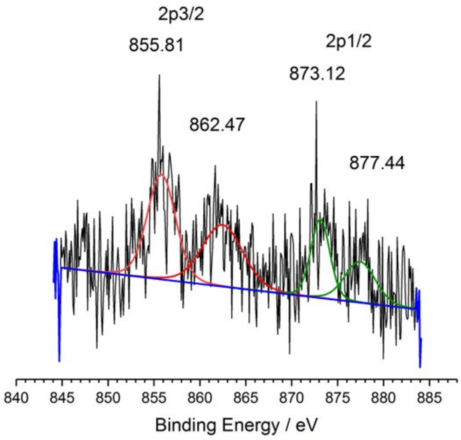


Figure S1. XPS of $CN_{urea}$-**Ni(abt)$_2$** after 24 h irradiation (λ > 420 nm, 10% TEOA, pH = 11)

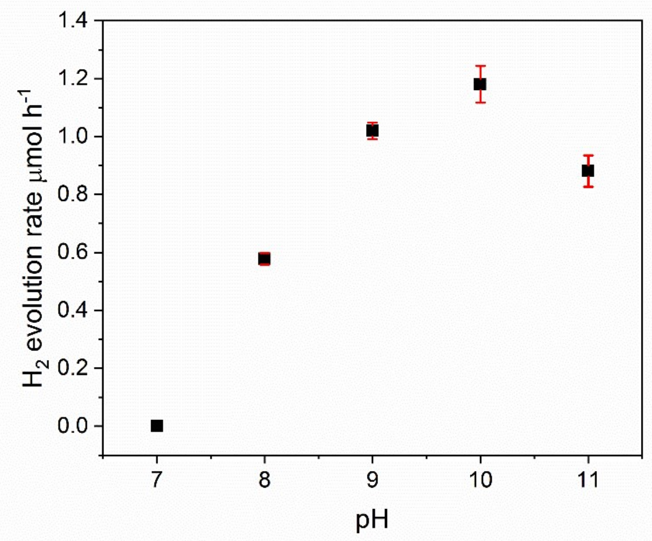


Figure S2. Effect of the pH of $CN_{urea}$-Ni(abt)$_2$ suspension on the rate of photocatalytic $H_2$ evolution in $H_2O$ with 10% TEOA (pH = 11) and visible irradiation (λ > 420 nm) (adjusted by $H_2SO_4$).

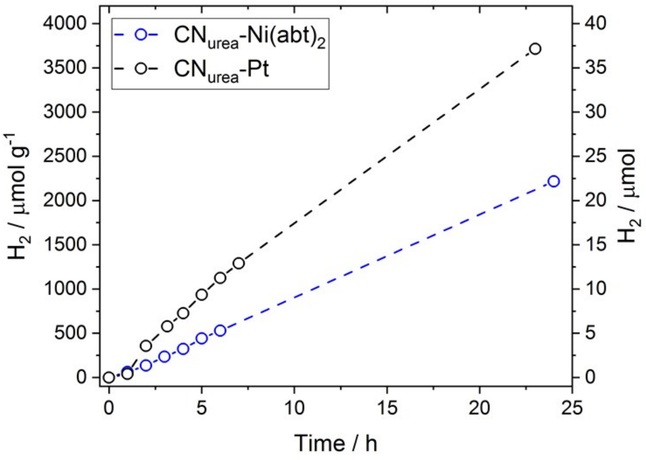
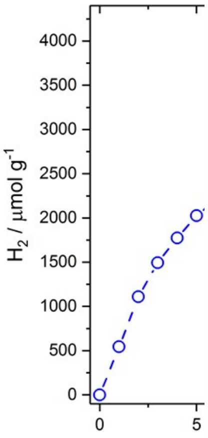


Figure S3. Photocatalytic hydrogen production by $CN_{urea}$-Ni(abt)$_2$ compared with $CN_{urea}$ with Pt loaded. The $H_2$ evolution rate on $CN_{urea}$-Ni(abt)$_2$ is 60% of that on Pt-CN while the turnover frequency of $CN_{Urea}$-Ni(abt)$_2$ is 9.2 $h^{-1}$, is 6.9 $h^{-1}$ on Pt loaded CN under the same condition. All in $H_2O$ with 10% TEOA (pH = 11) and visible irradiation ($\lambda > 420$ nm).. Similar amount of Pt was loaded on $CN_{urea}$ by photodeposition, using full-arc of a 300 W Xenon light source and methanol as sacrificial agent. TOFs are calculated by the equation below:

$$TOF = (moles\ of\ desired\ product\ formed)/(moles\ of\ active\ centers * reaction\ time)$$

Catalyst loading amounts for CN-Ni(abt)$_2$ and CN-Pt are 0.1 µmoles and 0.23 µmoles respectively.



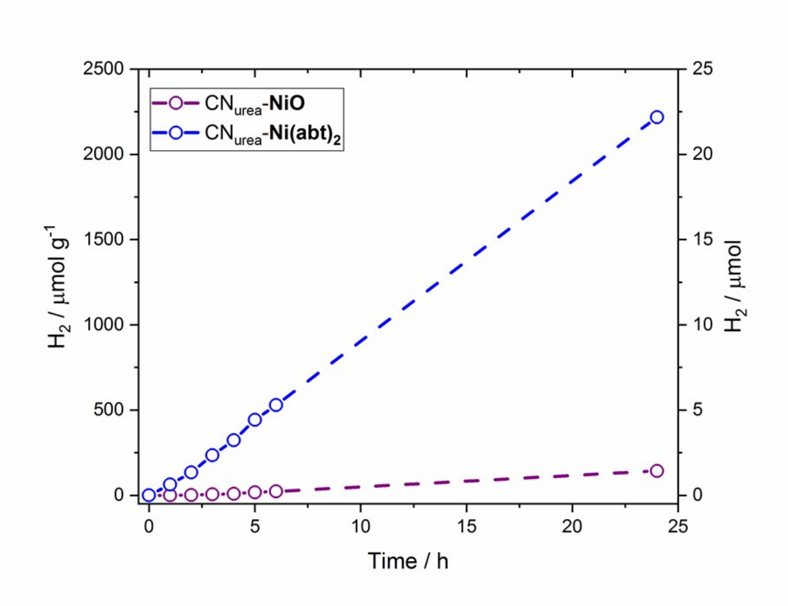


Figure S4. $CN_{urea}$-Ni(abt)$_2$ with $\lambda > 320$ nm

Figure S5. Photocatalytic hydrogen production by $CN_{urea}$-Ni(abt)$_2$ and $CN_{urea}$ loaded with NiO in $H_2O$ with 10% TEOA (pH = 11) and visible irradiation ($\lambda > 420$ nm).

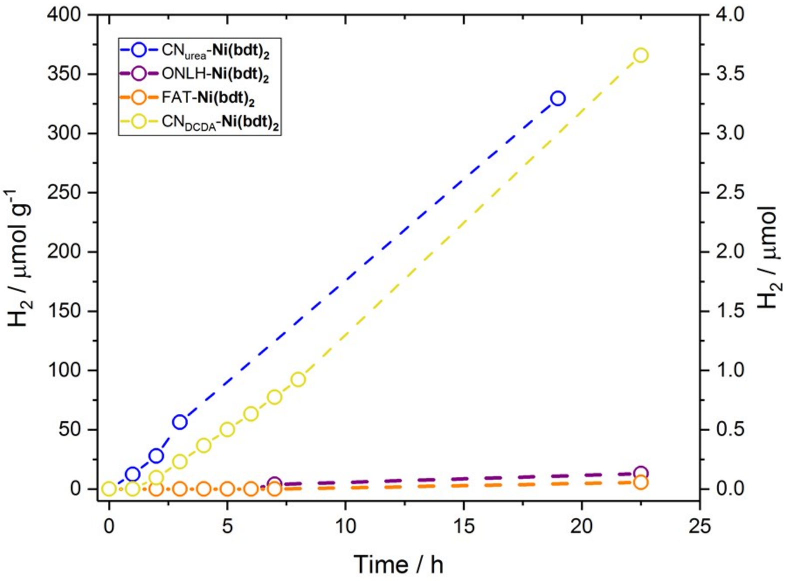


Figure S6. $H_2$ evolution of Ni(bdt)$_2$ hybrid materials (10% TEOA in $H_2O$, $\lambda > 420$ nm, pH = 11). Considering the estimated potentials of conduction bands, it is clear that $CN_{urea}$ and $CN_{DCDA}$ could be reduced to transfer electrons to both catalysts (Ni(abt)$_2$ and Ni(bdt)$_2$). For Ni(abt)$_2$, there is a significantly greater driving force for electron transfer from $CN_{urea}$ and $CN_{DCDA}$. When the driving force is so sufficient, the degree of polymerization determines hydrogen-evolution rates from water. Higher polymerization degree in $CN_{urea}$ resulted to better migration of charger carriers to active sites. Therefore, $H_2$ evolution rate for $CN_{urea}$-Ni(abt)$_2$ is significantly higher than that of $CN_{DCDA}$-Ni(abt)$_2$. In the case of Ni(bdt)$_2$, driving force is so moderate that the polymerization degree could not make a big difference. Hence the rates for $CN_{urea}$-Ni(abt)$_2$ and $CN_{DCDA}$-Ni(abt)$_2$ are similar.

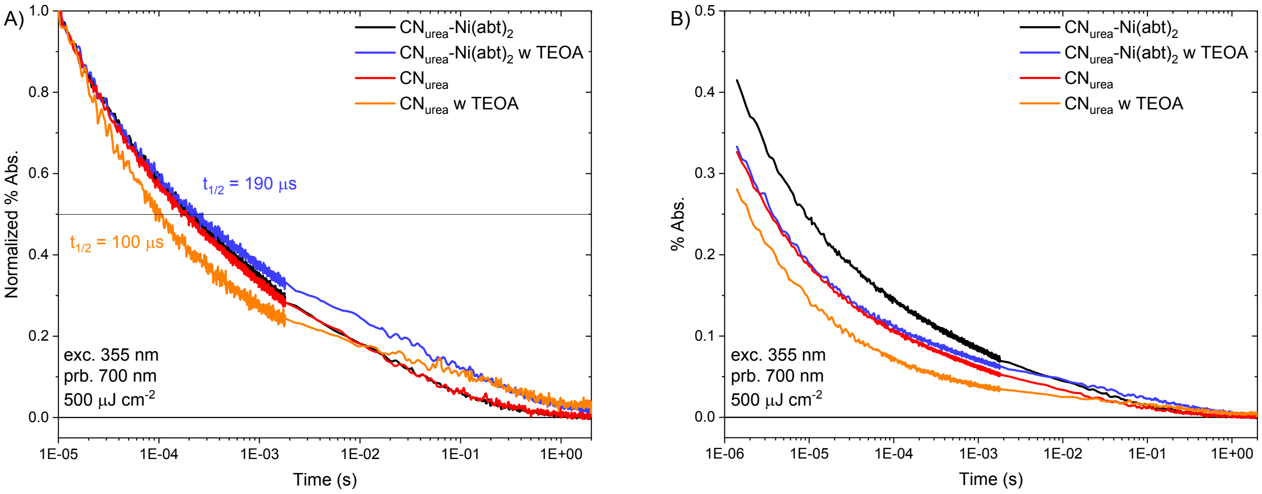


Figure S7. A) Normalized kinetics at a probe wavelength of 700 nm with half time ($t_{1/2}$) of decays in TEOA containing solvents. B) Raw traces at the same probe wavelength.

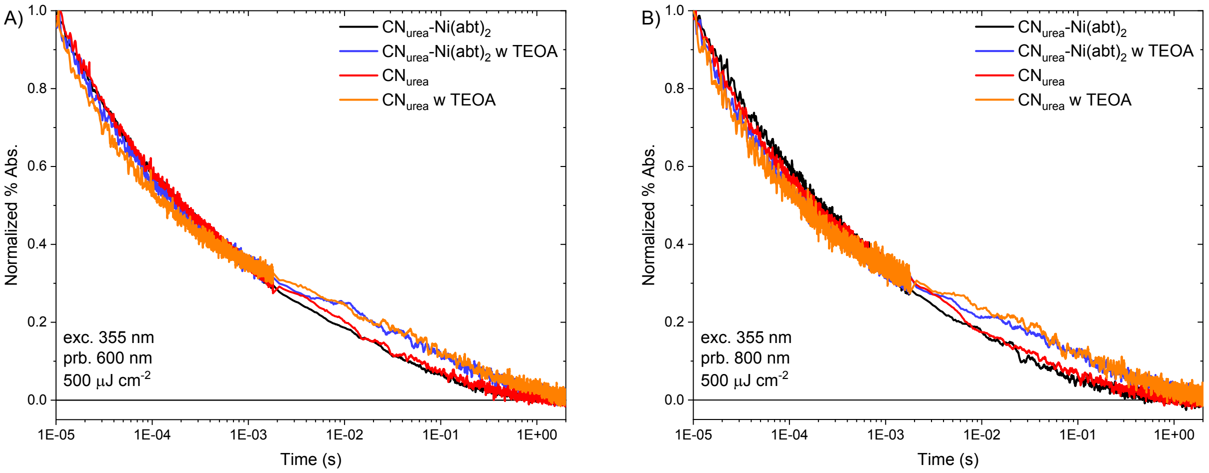


Figure S8. Normalized kinetics of investigated samples probed at A) 600 nm and B) 800 nm.

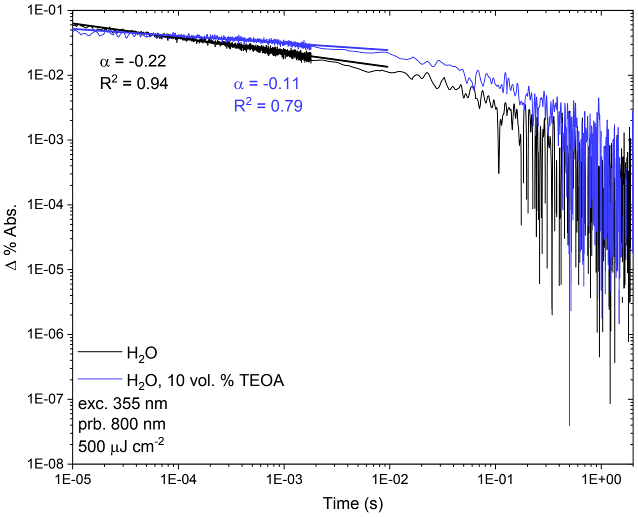


Figure S9. Fit parameter for an assumed power-law decay ($A \propto t^{-\alpha}$) of the estimated co-catalyst kinetics from $CN_{urea}$ and $CN_{urea}$-**Ni(abt)$_2$** in both solvent conditions, probed at 700 nm.

Table S1. Crystal data and structure refinement for **Ni(abtCl)$_2$**

| | |
|---|---|
| Identification code | exp_1401 |
| Empirical formula | $C_{12}H_8Cl_2N_2NiS_2$ |
| Formula weight | 373.93 |
| Temperature / K | 150 |
| Crystal system | monoclinic |
| Space group | $C2/c$ |
| $a$ / Å | 29.8655(12) |
| $b$ / Å | 3.81961(14) |
| $c$ / Å | 11.3728(3) |
| $\alpha$ / ° | 90 |
| $\beta$ / ° | 96.147(3) |
| $\gamma$ / ° | 90 |
| Volume / Å$^3$ | 1289.88(8) |
| $Z$ | 4 |
| $\rho_{calc}$ / g cm$^{-3}$ | 1.926 |
| $\mu$ / mm$^{-1}$ | 8.872 |
| $F$(000) | 752.0 |
| Crystal size / mm$^3$ | 0.101 × 0.059 × 0.015 |
| Radiation | Cu Kα ($\lambda$ = 1.54184 Å) |
| 2θ range for data collection / ° | 11.922 to 146.092 |
| Index ranges | $-32 \leq h \leq 36$, $-4 \leq k \leq 4$, $-13 \leq l \leq 13$ |
| Reflections collected | 3847 |
| Independent reflections | 1267 [$R_{\mathrm{int}} = 0.0209$, $R_{\mathrm{sigma}} = 0.0181$] |
| Data/restraints/parameters | 1267/0/104 |
| Goodness-of-fit on $F^2$ | 1.132 |
| Final $R$ indexes [$I \geq 2\sigma(I)$] | $R_1 = 0.0340$, $wR_2 = 0.0924$ |
| Final $R$ indexes [all data] | $R_1 = 0.0354$, $wR_2 = 0.0935$ |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.40/−0.47 |

Table S2. Comparison of carbon nitride – molecular catalyst systems for $H_2$ evolution.

| **Carbon Nitride Precursor** | **Catalyst** | **Solvent** | **Light source** | **Running time / h** | **$H_2$ rate / μmol $h^{-1}$** | **TON** | **TOF / $h^{-1}$** | **QY** | **Ref DOI** |
|---|---|---|---|---|---|---|---|---|---|
| Cyanamide | NiP | $H_2O$ | λ > 300 nm | 3 | 2.2 | 170 | 109 | 0.37% (365 nm) | 10.1002/anie.201406811 |
| | | | λ > 420 nm | 4 | 0.4 | 60 | 15 | 0.04% (460 nm) | |
| Urea | Cobaloxime-pyrene | $CH_3CN$-$H_2O$ 1/9 | λ > 400 nm<br>300 W Xe | 9 | 20 | 281 | 40 | | 10.1039/c4ra01413h |
| Dicyandiamide | Ni TEOA complex | $H_2O$ | λ > 400 nm<br>500 W Xe | 60 | 7 | 281 | 10 | 1.5% (400 nm) | 10.1002/cssc.201200490 |
| Melamine then KSCN | NiP | $H_2O$ | λ > 400 nm<br>100 mW $cm^{-2}$ | 24 | 0.8 | 200 | 12 | 15% (360 nm) | 10.1021/jacs.6b04325 |
| | | | AM 1.5 | 24 | 1.5 | 425 | 31 | | |
| Melamine then KSCN then graphene oxide | NiP | $H_2O$ | AM 1.5 | 4 | 6 | 360 | 116 | | 10.1021/acscatal.8b01969 |
| Melamine | Cobaloxime | $H_2O$ | 350 - 740 nm<br>300 W Xe | 8 | 2.6 | 4 | 0.5 | 0.62 (365 nm) | 10.1039/c3cp53350f |
| Urea | $Ni(abt)_2$ | $H_2O$ | λ > 420 nm<br>300 W Xe | 192 | 1.2 | 1360 | 9.2 | ~2.3% (365 nm)<br>~1.5% (400 nm)<br>0.7% (420 nm) | This work |
| | | | λ > 320 nm<br>300 W Xe | 24 | 5.7 | 422 | 54.3 | | |
| Semicarbazide hydrochloride | $Ni(abt)_2$ | $H_2O$ | λ > 475 nm<br>300 W Xe | 24 | 0.2 | 22 | 1.2 | | This work |

Table S3. Comparison of $H_2$ evolution rate for different carbon nitride – molecular catalysts in this work

| **Catalyst** | **$H_2$ rate / µmol $h^{-1}$** |
|---|---|
| $CN_{DCDA}$-**Ni(abt)$_2$** | 0.14 |
| FAT-**Ni(abt)$_2$** | 0.28 |
| ONLH-**Ni(abt)$_2$** | 0.34 |
| $CN_{urea}$-**Ni(abt)$_2$** | 0.92 |
| $CN_{urea}$-**Pt** | 1.55 |
| $CN_{DCDA}$-**Ni(bdt)$_2$** | 0.16 |
| FAT-**Ni(bdt)$_2$** | 0.002 |
| ONLH-**Ni(bdt)$_2$** | 0.005 |
| $CN_{urea}$-**Ni(bdt)$_2$** | 0.17 |

Reaction condition: 10 mg catalyst in a solution of $H_2O$ with 10% TEOA (50 mL) irradiated with a 300 W Xenon light source (Newport 66485-300XF-R1) equipped with a $\lambda > 420$ nm filters for 24 h.