Supporting Information

Linker-Controlled Polymeric Photocatalyst for Highly Efficient Hydrogen Evolution from Water

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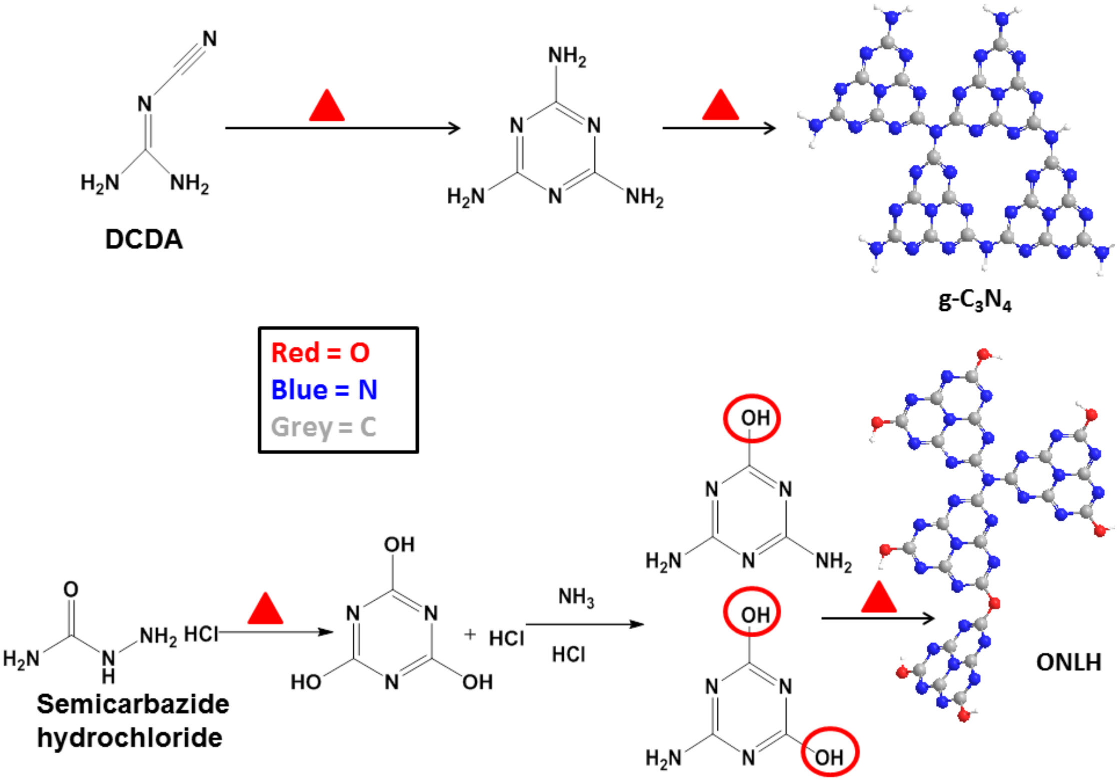
Computational results

The initial g-C_3N_4 structure, consisting of infinite 1D chains of linked heptazines, was based on the characterization study.[1] Density-functional theory calculations were done, as described in the Computational Method section of the main text. The optimized g-C_3N_4 structure (Figure 1a) has the lattice parameters a = 12.62 Å, b = 16.48 Å, c = 3.64 Å, α = 92.2°, β = 56.1°, γ = 90.0° (AB stacking); the interlayer distance is 3.07 Å. The stoichiometry of this structure, $C_3N_{4.5}H_{1.5}$, is very close to the experimental g-C_3N_4 stoichiometry ($C_3N_{4.5}O_{0.1}H_{1.6}$). The band gap was calculated to be 3.18 eV; the ~0.5 eV overestimate compared to the experiment is caused by the use of the B3LYP functional (cf. a recent review[2] found the mean absolute error of 0.47 eV for band gaps calculated with B3LYP), and because the calculated gap is the fundamental gap rather than the optical gap and does not include excitonic effects.

To model ONLH, several structures were considered, with oxygen atoms replacing NH groups either in linkers, or in terminal –NH_2 groups, or in heptazine rings (the latter were high in energy). Among the structures with –O– linkers and –OH terminals, one structure, with –O– linkers present in only one of the two chains in the unit cell, has the band gap noticeably reduced compared to g-C_3N_4: 2.84 eV compared to 3.18 eV for g-C_3N_4. The structure is shown in Figure 2b (a 2×2 extension of the unit cell). The stoichiometry, $C_3N_{4.3}O_{0.3}H_{1.3}$, is close to the experimental ONLH-600 stoichiometry ($C_3N_{4.3}O_{0.5}H_{1.8}$). The lattice parameters for this structure are a = 12.62 Å, b = 16.54 Å, c = 3.57 Å, α = 80.7°, β = 60.2°, γ = 89.8° (approximately AB stacking), very similar to the g-C_3N_4 structure; the interlayer distance (3.09 Å) is very slightly larger than in g-C_3N_4 – in good agreement with the PXRD results. However, while the g-C_3N_4 structure is planar, the layers in the oxygen-linked structure are not entirely planar and show a wave pattern, caused by bending of the C-O-C linker bond; this nonplanarity is consistent with the experimental indication of disorder in the ONLH structure.

The density of states of ONLH projected on C, N and O atoms in the two chains (Figure 1c) shows that the top of the valence band (VB) and the bottom of the conduction band (CB) are dominated by the NH-linked and O-linked chains, respectively, while oxygen atoms make negligible contributions to the VB and CB. The calculated infrared absorption spectra for g-C_3N_4 and ONLH (Figure S2) show that the intensity of absorption is reduced in ONLH compared to g-C_3N_4, both in the N-H and C-N stretch regions, and the peaks are somewhat broadened – both in agreement with experimental FT-IR spectra.



Scheme S 1. Proposed mechanism of the reaction paths for the formation of polymeric g-C_3N_4 and ONLH.

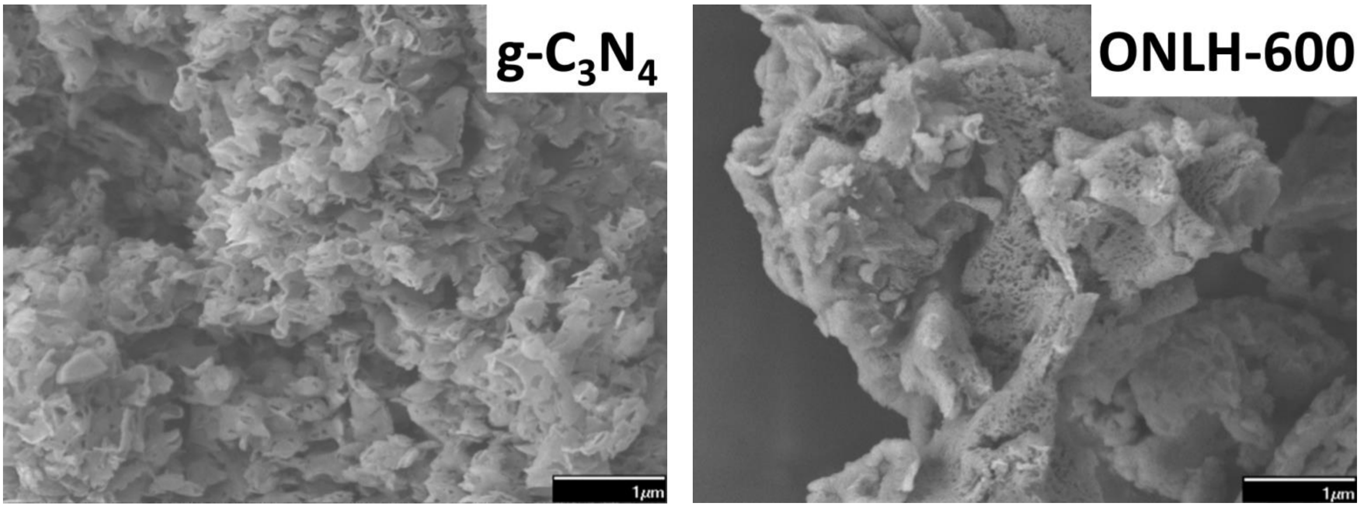


Fig. S1. SEM images of g-C_3N_4 and ONLH-600. Both are porous and sheet-like materials.

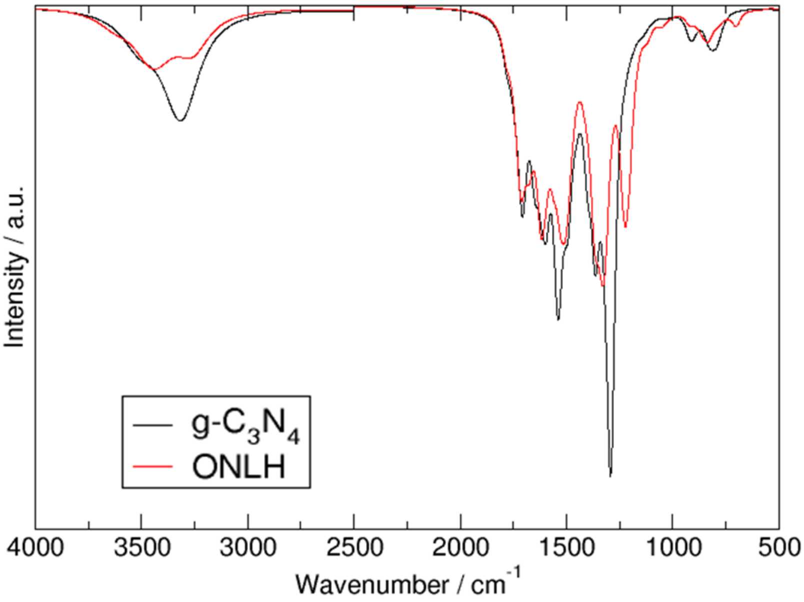


Fig. S2. Calculated IR spectra of ONLH and g-C_3N_4, with the low-frequency region (below 2500 cm^{-1}) broadened with the Lorentzian parameter 50 cm^{-1}, and the high-frequency region (above 2500cm^{-1}) broadened with Lorentzian parameter 200 cm^{-1}. The large broadening for the N-H stretch region is probably due to a variety of arrangements available to the NH_2, NH and OH groups, while the C-N framework is more rigid.

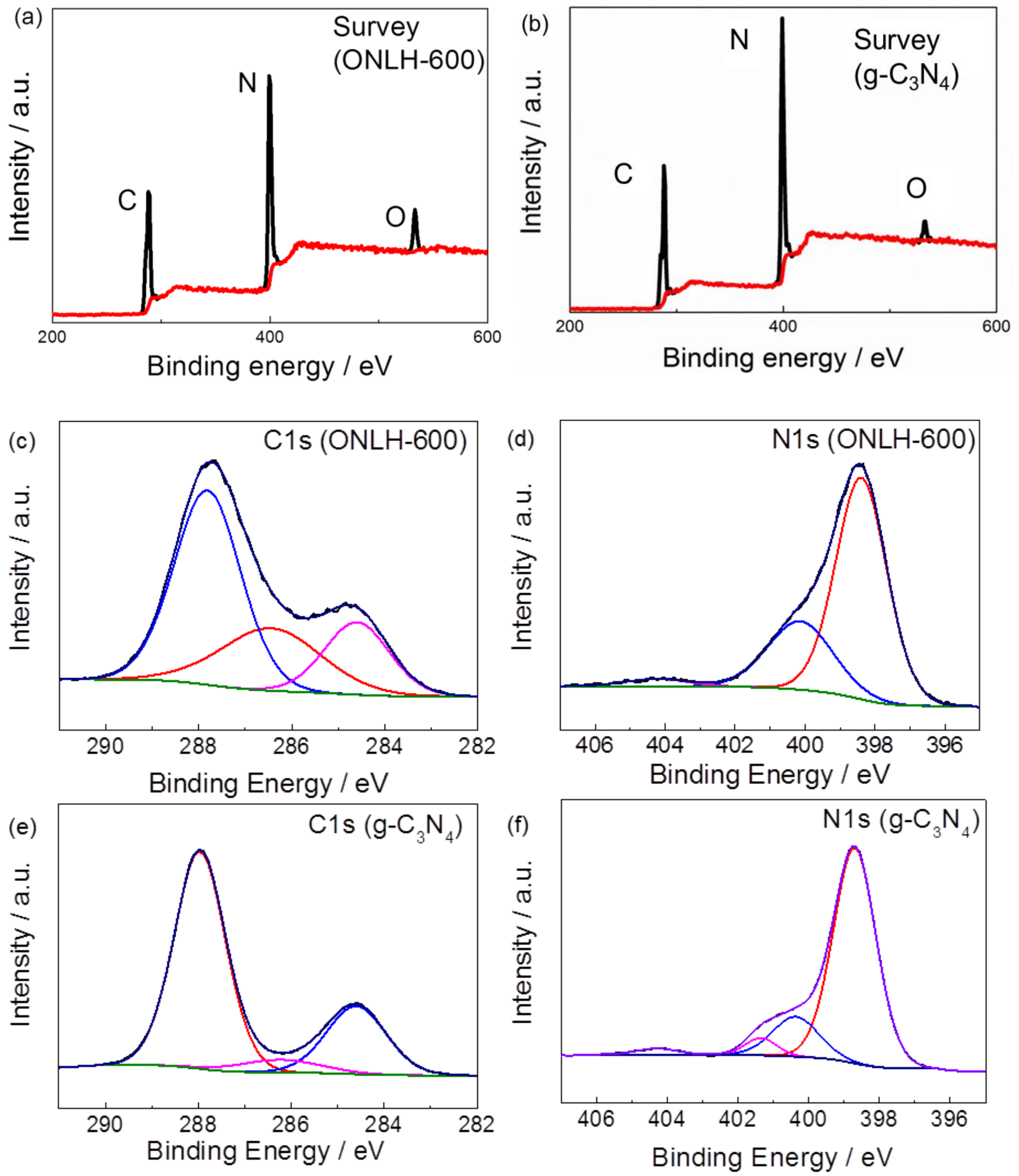


Fig. S3. XPS spectra: C1s and N1s spectra (a)-(d) and survey spectra (e-f) of ONLH-600 and g-C_3N_4.

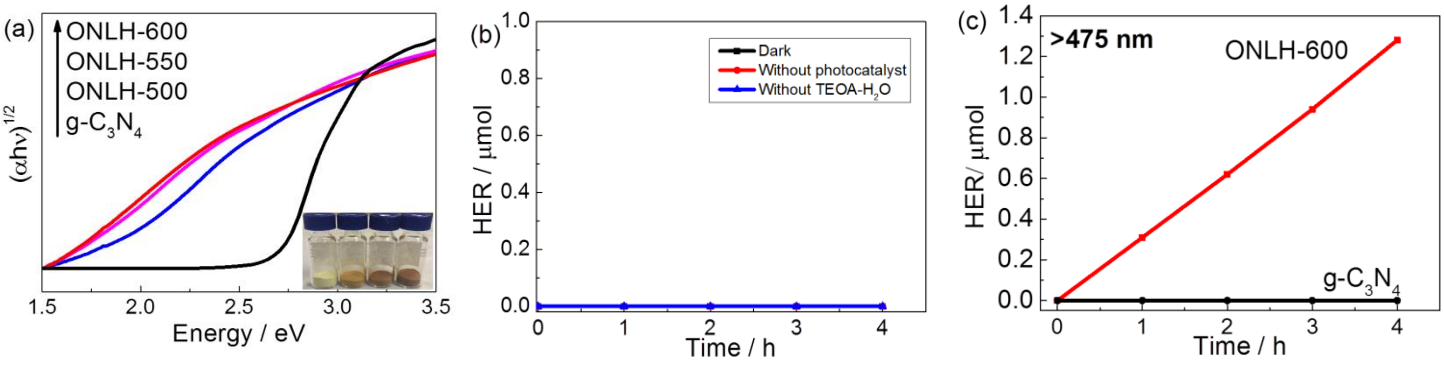


Fig. S4. (a) Tauc plot of ONLH samples. (b) Hydrogen evolution rate under control conditions (> 420 nm) of ONLH. No activity is detected under dark condition or without photocatalyst or without sacrificial regent. (c) Hydrogen evolution rate under control conditions (> 475 nm) of ONLH-600 and $g\text{-}C_3N_4$.

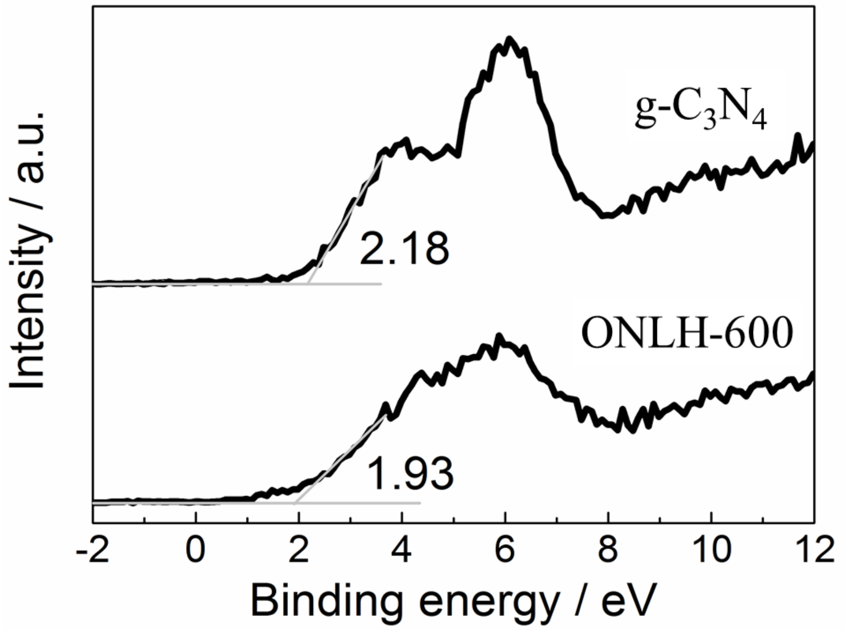


Fig. S5. Valence band (VB) XPS spectra of ONLH-600 and $g\text{-}C_3N_4$

Table S1. Comparison of apparent quantum yields at 420 nm of ONLH and recent reported polymer photocatalysts measured under 1 bar pressure.

Samples	AQY / %	Ref.
ONLH	10.3	This work
Planarized conjugated polymer photocatalyst	2.3	[3]
P-doped g-C_3N_4	5.8	[4]

Table S2. Comparison of the properties of foreign atom modified g-C_3N_4. The majority were measured under vacuum condition, while the P-doped material[4] and this work were measured at 1 bar atmosphere. The majority of the heteroatoms were doped into heptazine units, whilst this work selectively doped oxygen at the linker positions.

Method	Band Gap / eV	Abs. Edge / nm	HER > 420 nm /μmol(gh)-1	AQY at 420 nm / %	Reference
O-linker	1.55	800	337	10.3	This work
P-doped	2.55	487	650	5.8	[4]
N-doped (> 400 nm)	2.65	467	553	Not Given	[5]
I-doped	2.69	462	740	Not Given	[6]
O-doped	2.49	498	375	Not Given	[7]
B-doped	2.07	600	255	Not Given	[8]
F-doped (500 W)	2.63	472	140	Not Given	[9]
S-doped	2.85	436	750	Not Given	[10]

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