Supporting Information

Merging Single Atom Dispersed Silver and Carbon Nitride to a Joint Electronic System via Co-Polymerization with Silver Tricyanomethanide

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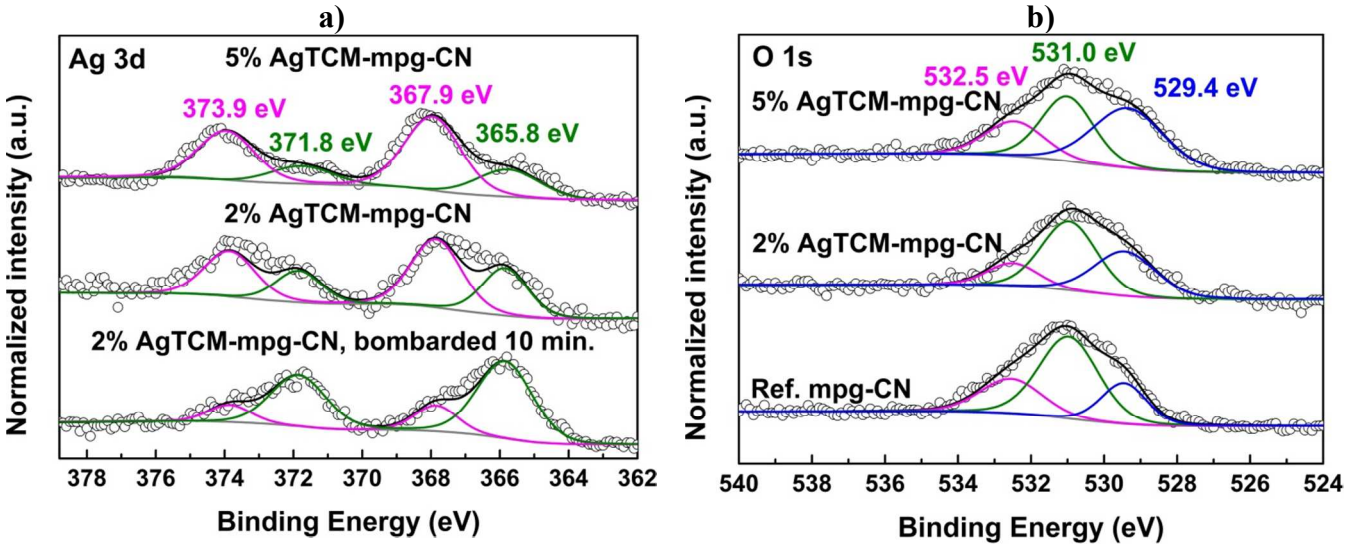
Table S1. Elemental composition of the reference mesoporous graphitic carbon nitride (ref. mpg-CN) and AgTCM-doped mpg-CN products. C, N, and H content were determined by elemental analysis (EA), while Ag and O content were estimated by EDS and XPS measurements.

Product	**C[(a)] (wt.%)**	**N[(a)] (wt.%)**	**H[(a)] (wt.%)**	**C/N (wt.)**	**Ag[(b)] (wt.%)**	**Ag[(c)] (wt.%)**	**Ag[(d)] (wt.%)**	**O[(d)] (wt.%)**
ref. mpg-CN	33.38	55.88	2.59	0.60	-	-	-	4.48
1% AgTCM-mpg-CN	31.85	53.27	2.59	0.60	0.74	0.76	n.a.[(e)]	n.a.[(e)]
2% AgTCM-mpg-CN	31.83	52.63	2.59	0.60	1.45	1.45	1.32	2.97
3.5% AgTCM-mpg-CN	31.23	51.49	2.63	0.61	2.48	2.95	n.a.[(e)]	n.a.[(e)]
5% AgTCM-mpg-CN	31.06	49.6	2.50	0.63	3.46	3.35	3.48	5.25
10% AgTCM-mpg-CN	31.32	48.84	2.38	0.64	6.44	6.09	n.a.[(e)]	n.a.[(e)]

[(a)] Elemental analysis; [(b)] nominal values; [(c)] energy-dispersive X-ray analysis; [(d)] X-ray photoelectron spectroscopy; [(e)] not analyzed.



c)

Contribution	ref. mpg-CN	2%-AgTCM-mpg-CN	5%-AgTCM-mpg-CN
C 1s			
1: 288.4 eV	59.57 %	46.61 %	45.18 %
2: 286.5 eV	19.66 %	36.57 %	21.98 %
3: 284.8 eV	10.96 %	10.15 %	19.50 %
4: 282.5 eV	9.81 %	6.67 %	13.34 %
N 1s			
1: 400.8 eV	14.88 %	11.94 %	15.18 %
2: 399.6 eV	14.10 %	14.31 %	21.55 %
3: 398.4 eV	60.10 %	45.57 %	33.55 %
4: 396.6 eV	10.92 %	28.17 %	29.72 %
O 1s			
1: 532.5 eV	24.26 %	11.74 %	21.04 %
2: 531.0 eV	54.68 %	51.26 %	34.84 %
3: 529.4 eV	21.05 %	37.00 %	44.12 %

Figure S1. Ag3d XPS spectra of 2%-AgTCM-mpg-CN, 5%-AgTCM-mpg-CN and 2%-AgTCM-mpg-CN after 10 minutes of Ar bombardment (a); O1s XPS spectra of mpg-CN, 2%-AgTCM-mpg-CN and 5%-AgTCM-mpg-CN (b); relative content of various C, N, O contributions in the samples (c).

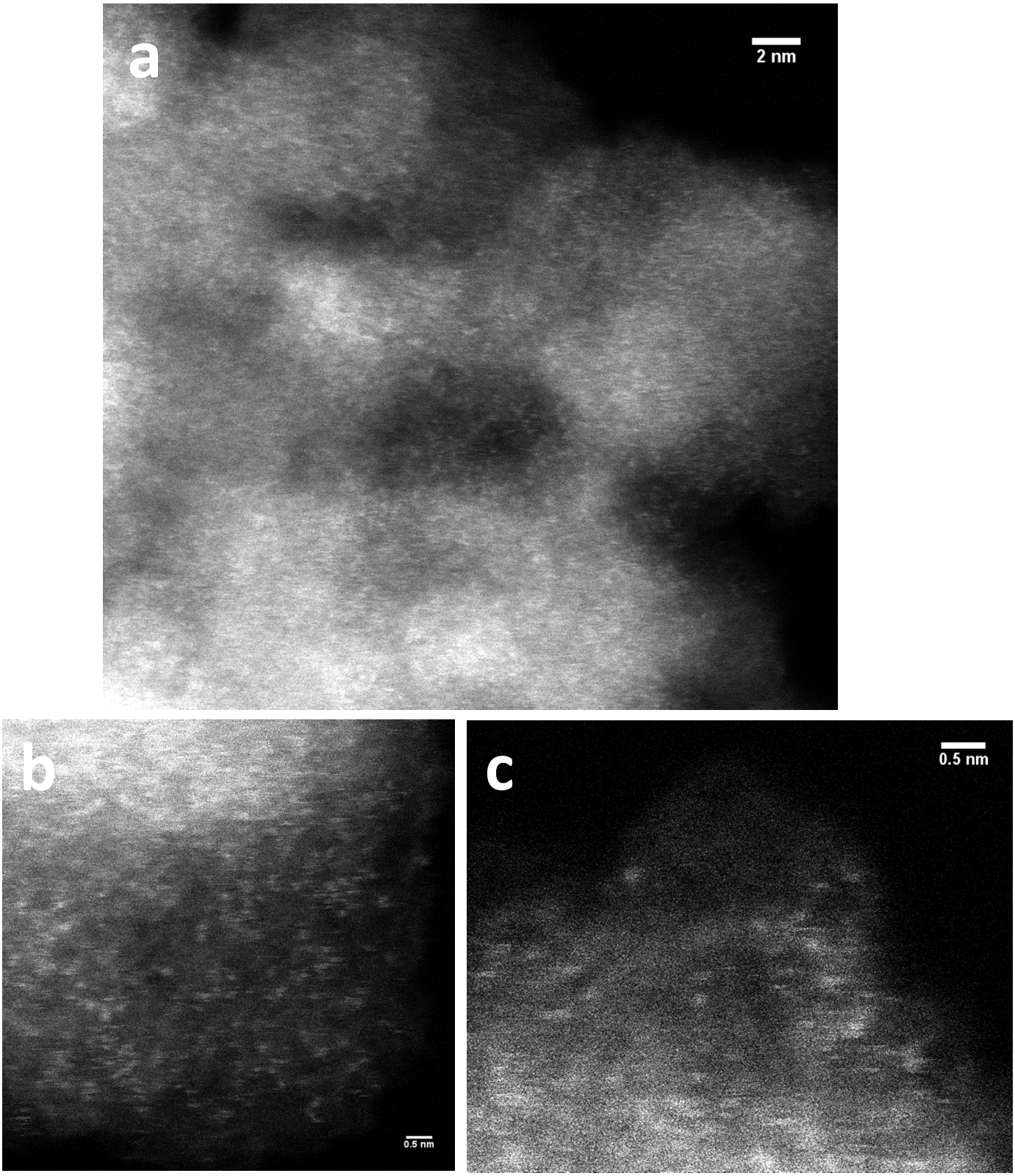


Figure S2. Aberration-corrected STEM images of the 1 wt.%-AgTCM-mpg-CN, showing isolated single Ag atoms distributed across the mpg-CN support (a-c); (b) shows a larger field of view around the region shown in Figure 3a of the main manuscript.

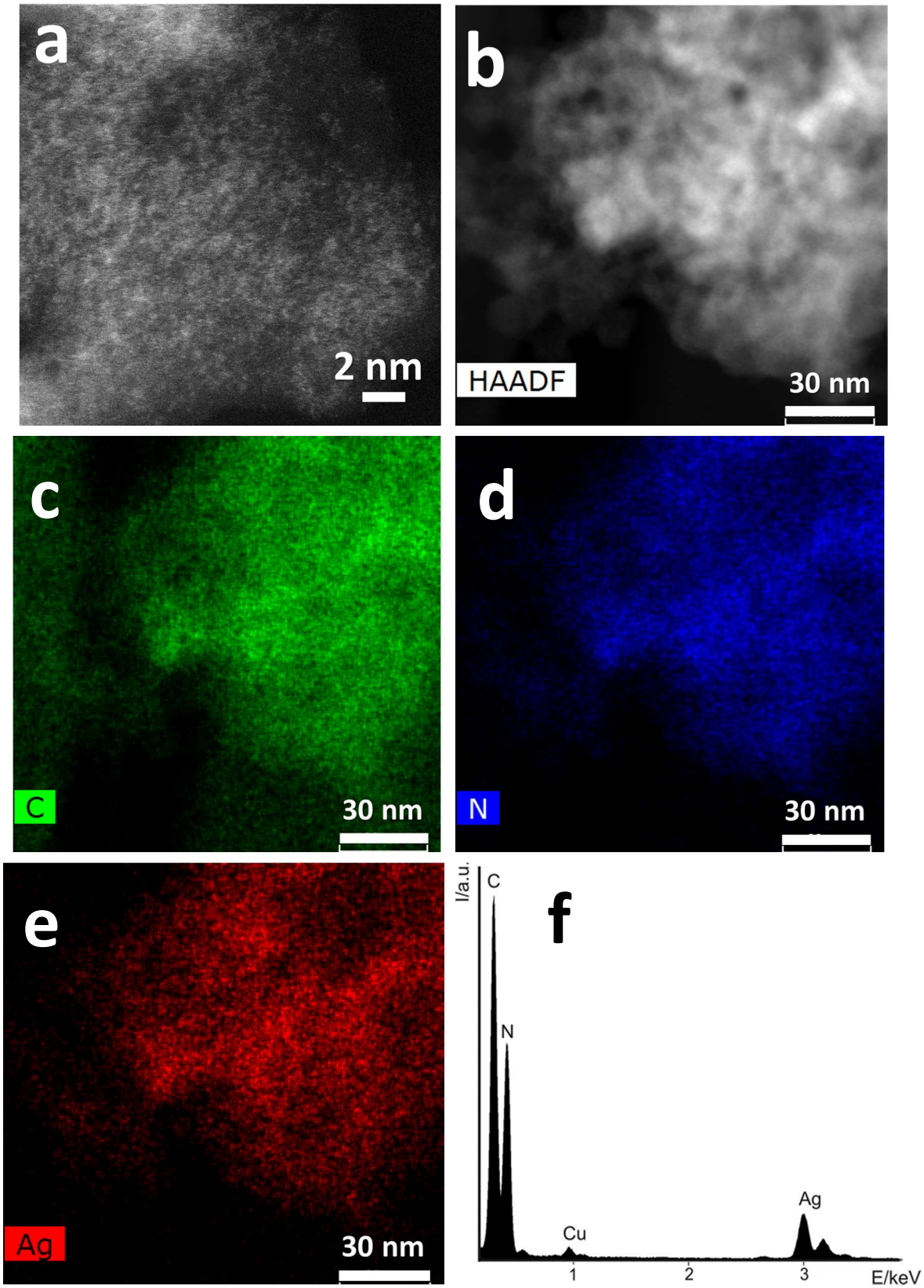
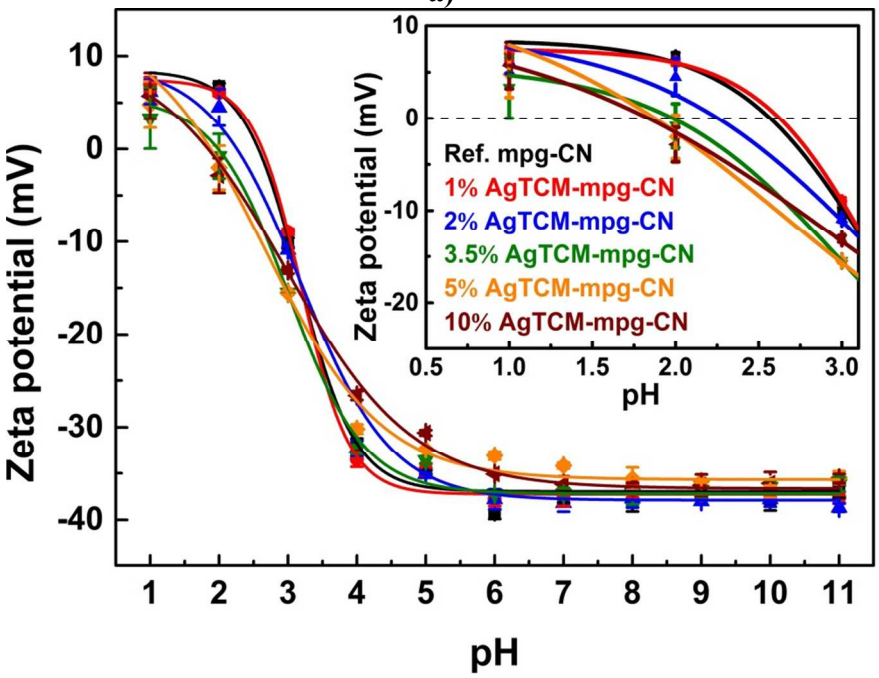


Figure S3. Aberration-corrected STEM image (a) and low magnification STEM image (b) along with C (c), N (d), and Ag EDS mapping (e) of 10 wt.%-AgTCM-mpg-CN. EDS spectrum extracted from the map data. The Cu peak is due to the material of the TEM grid (f).

a)



b)

Samples	Isoelectric point
Ref. mpg-CN	2.56
1% AgTCM-mpg-CN	2.62
2% AgTCM-mpg-CN	2.26
3.5% AgTCM-mpg-CN	1.98
5% AgTCM-mpg-CN	1.87
10% AgTCM-mpg-CN	1.83

Figure S4. Measured Zeta-potentials (plotted with the corresponding error bars) of the reference mpg-CN and AgTCM-doped products at different pH (a), estimated values of isoelectric points (b).

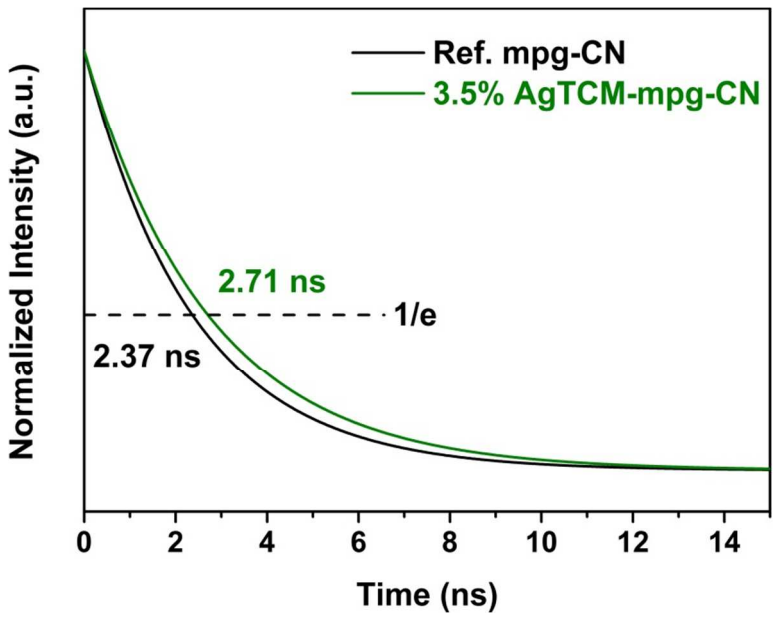
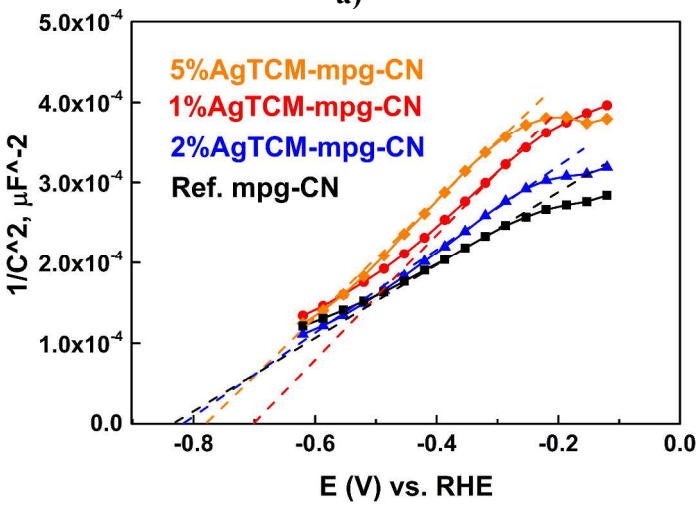


Figure S5. Time-resolved photoluminescence spectra of mpg-CN and 3.5%-AgTCM-mpg-CN. The samples were excited at 420 nm and the emission at 525 nm was collected.

a)



b)

Product	CB, eV (RHE)	VB, eV (RHE)	E_{BG}, eV
mpg-CN	-0.83	1.95	2.78
1%AgTCM-mpg-CN	-0.70	2.09	2.79
2%AgTCM-mpg-CN	-0.82	1.97	2.79
5%AgTCM-mpg-CN	-0.78	1.95	2.73

Figure S6. Mott-Schottky plots (a) and band positions (b) of ref. mpg-CN and selected AgTCM-doped products. All the values in tables are referred to the electrochemical scale of the reversible hydrogen electrode ($H^+ + e^- \leftrightarrow ½H_2$, E0=0,00 V RHE).

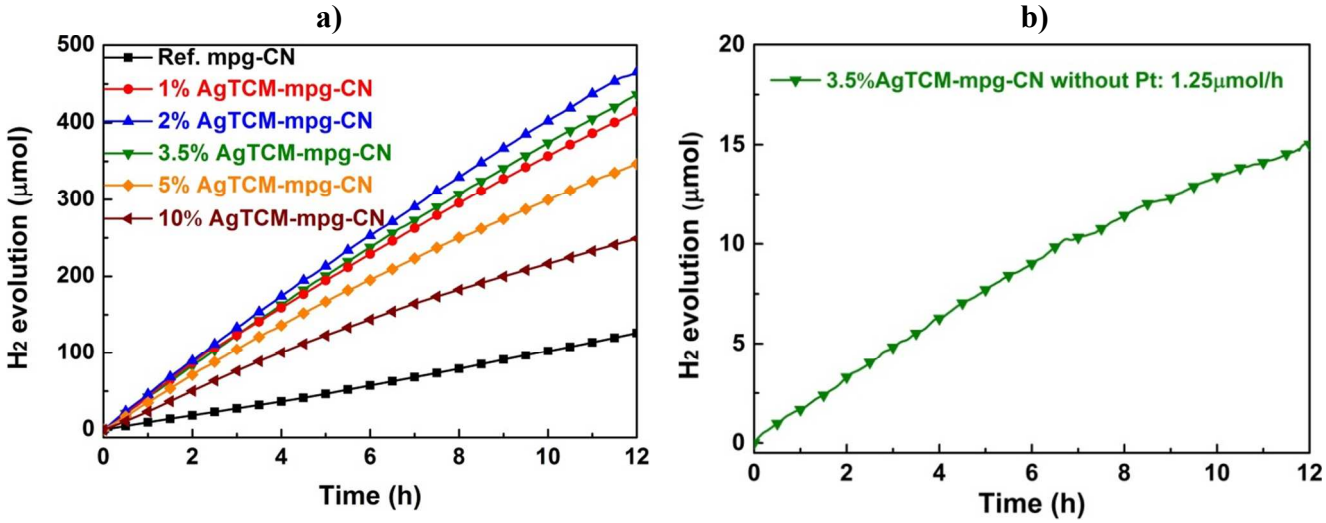


Figure S7. Time course of H_2 production upon irradiation with white light (50W LED array) in the presence of Pt and ref. mpg-CN or AgTCM-doped products (a); time course of H_2 evolution over 3.5% AgTCM-mpg-CN, without Pt-assistance (b).

Table S2. Composition and textural properties of the mpg-CN-based catalysts used for hydrogenation studies.

Product	**C[(a)] (wt.%)**	**N[(a)] (wt.%)**	**H[(a)] (wt.%)**	**C/N (wt.%)**	**Ag[(b)] (wt.%)**	**S_{BET}[(c)] (m^2/g)**	**Average particle size[(d)] (μm)**
AgTCM-mpg-CN	31.83	52.63	2.59	0.60	0.92	211	22.4 ± 0.4
Ag-SD-mpg-CN	33.1	56.3	2.48	0.59	0.91	34	18.3 ± 0.7
Ag-IR-mpg-CN	33.0	56.6	2.41	0.58	1.19	121	33.5 ± 1.9

[(a)] Elemental analysis; [(b)] energy-dispersive X-ray spectroscopy; [(c)] BET method; [(d)] laser diffraction.