Electronic Supplementary Information

Electronic Structure Manipulation of Graphene Dots for Effective Hydrogen Evolution from Photocatalytic Water Decomposition

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Supporting information for:

(1) TEM images of A-GODs and A-SGODs;

(2) Full-range XPS spectra of GO-dots without hydrothermal NH_3 treatment;

(3) C 1s XPS spectra of GO-dots without hydrothermal NH_3 treatment;

(4) N 1s and S 2s XPS spectra of GO-dots without hydrothermal NH_3 treatment;

(5) Quantitative XPS data of GO-dots without hydrothermal NH_3 treatment;

(6) Possible quaternary N formation mechanism;

(7) PL spectra of GO-dots;

(8) UPS analysis of GO-dots;

(9) Activity variation of A-SNGODs in H_2 production under visible irradiation for 144 h.

1. TEM images of A-GODs and A-SGODs

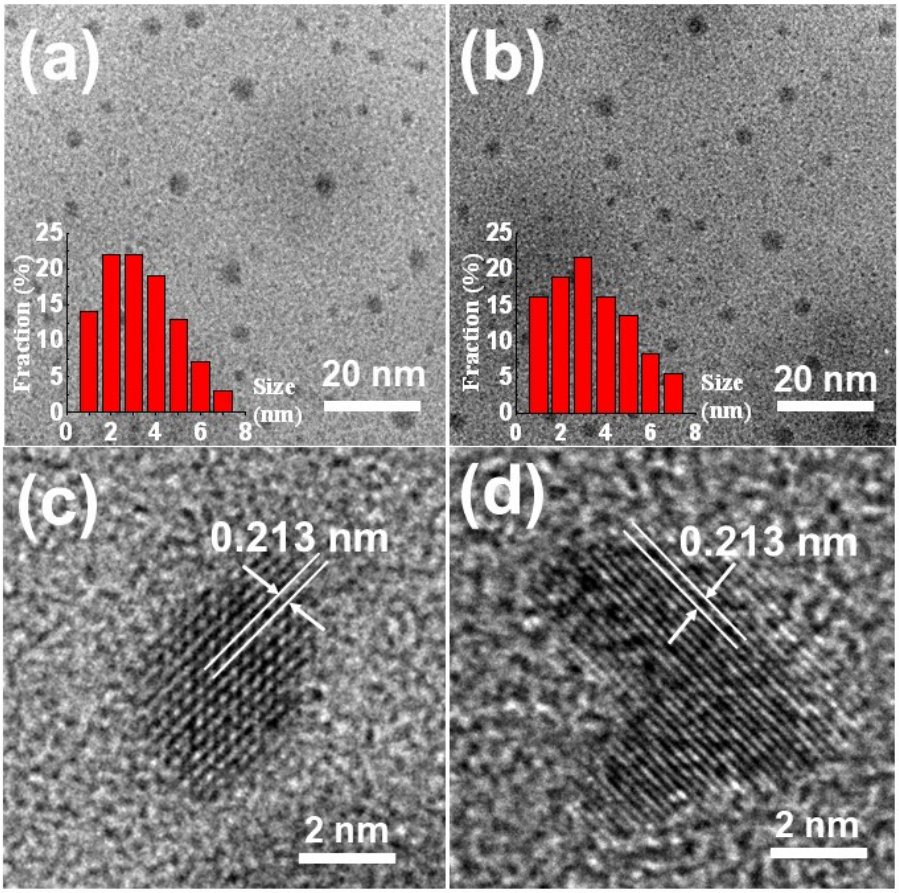


Fig. S1 TEM images of (a) A-GODs and (b) A-SGODs, with the insets showing the size-distribution histograms. HRTEM images of the (c) A-GOD and (d) A-SGOD particles, showing lattice fringes with a spacing of 0.213 nm, which corresponds to the graphene $\{1\,\bar{1}00\}$ d-spacing.

2. Full-range XPS spectra of GO-dots without hydrothermal NH_3 treatment

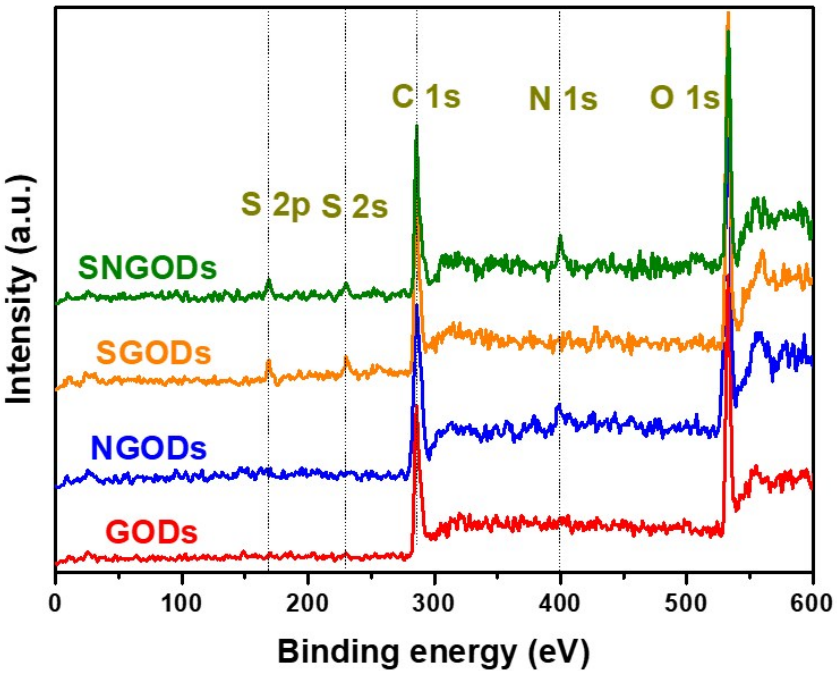


Fig. S2 Full-range XPS spectra of GODs, NGODs, SGODs, and SNGODs.

3. C 1s XPS spectra of GO-dots without hydrothermal NH_3 treatment

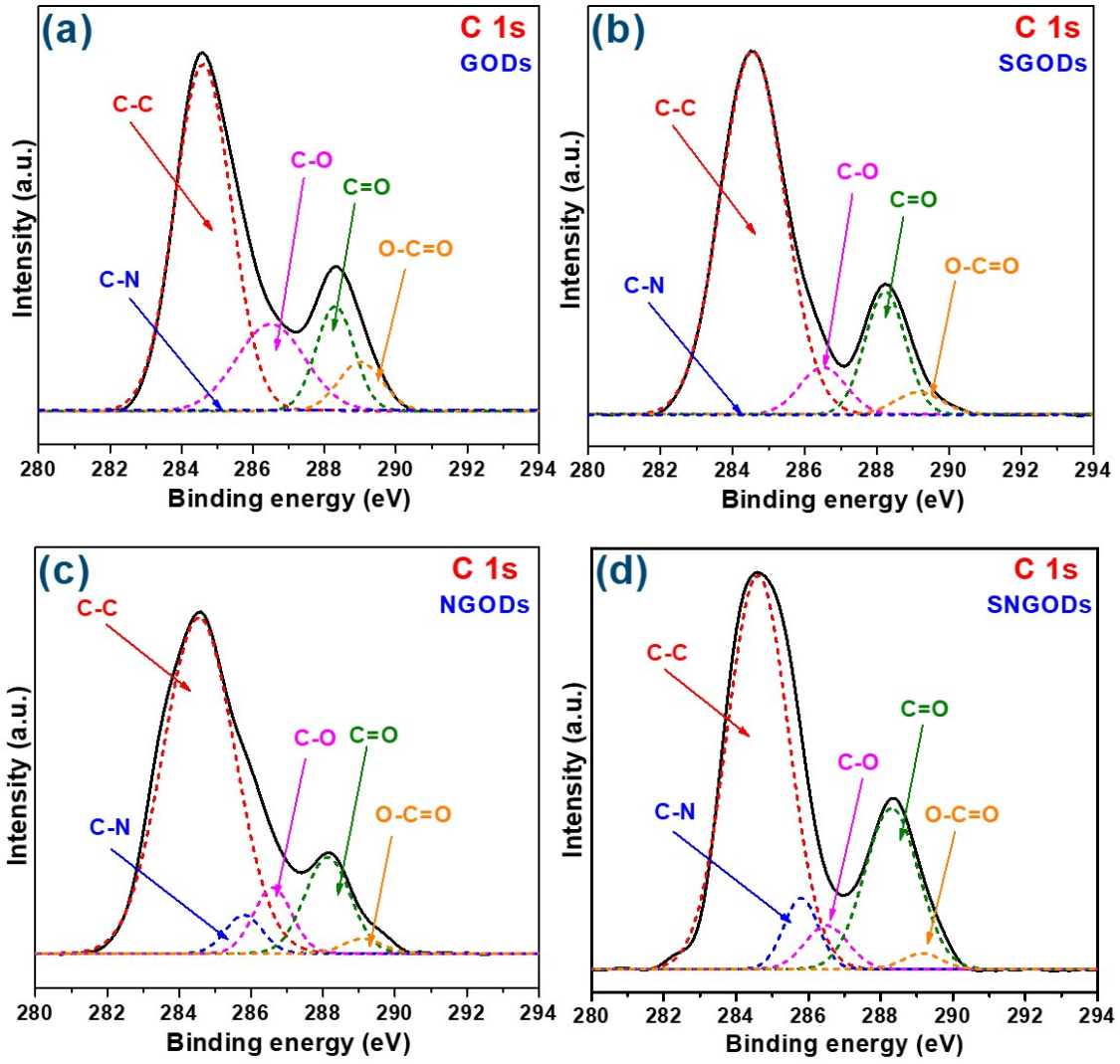


Fig. S3 C 1s XPS spectra: (a) GODs; (b) SGODs; (c) NGODs; (d) SNGODs.

4. N 1s and S 2s XPS spectra of GO-dots without hydrothermal NH_3 treatment

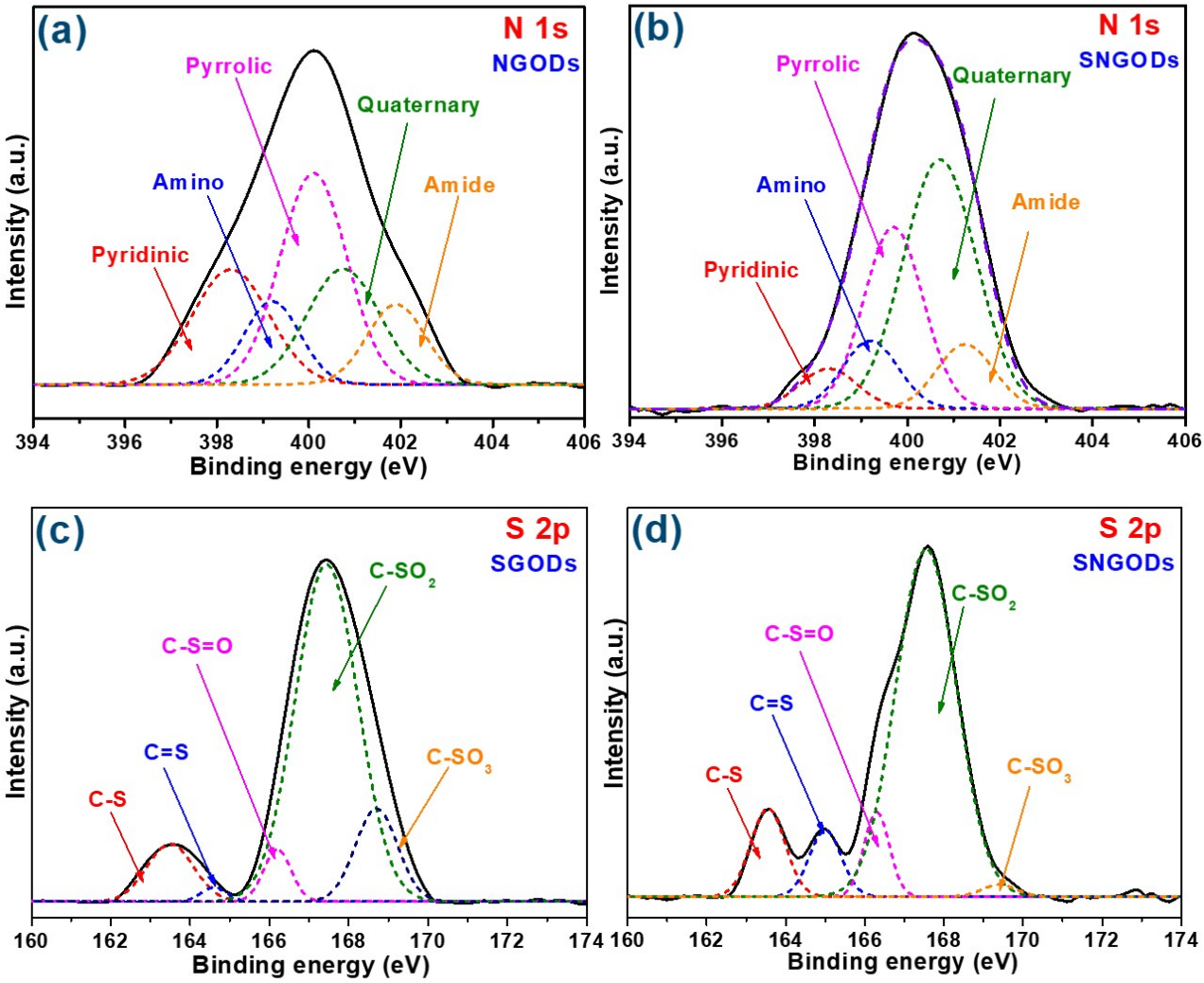


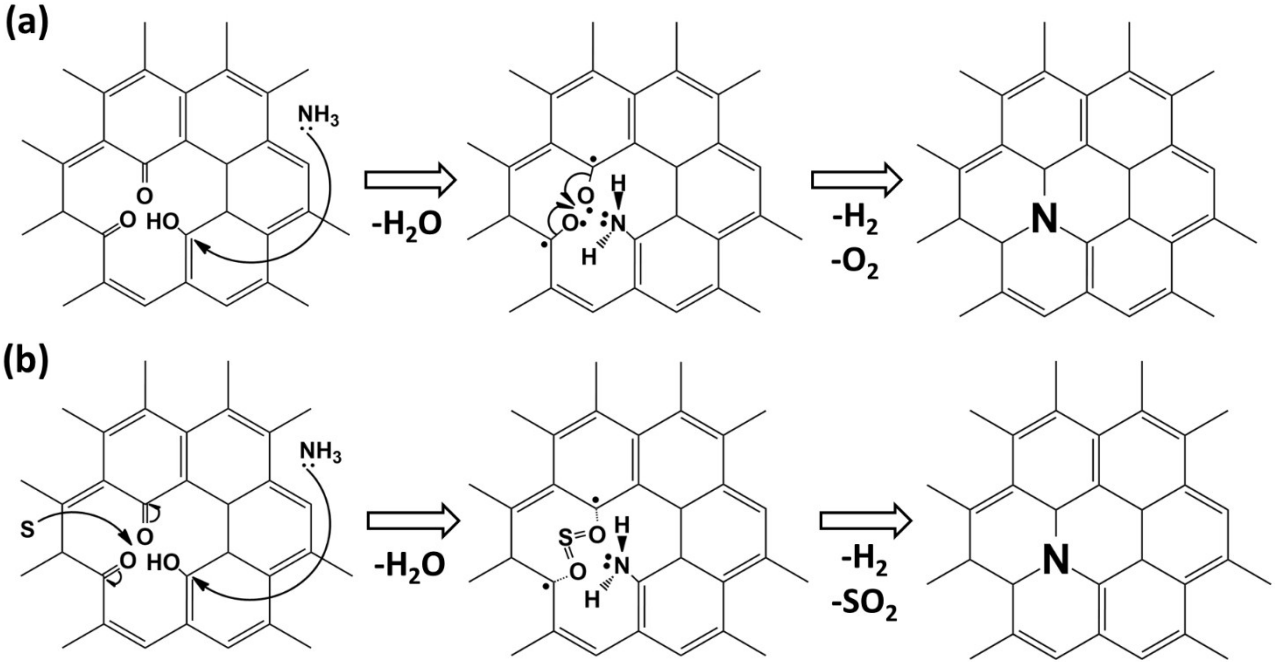
Fig. S4 N 1s XPS spectra: (a) NGODs; (b) SNGODs. S 2p XPS spectra: (c) SGODs; (d) SNGODs.

5. Quantitative XPS data of GO-dots without hydrothermal NH_3 treatment

Table S1 Atomic ratios (O 1s)/(C 1s), (N 1s)/(C 1s), (S 2p/C 1s), and (S 2s/C 1s) determined from the full-range XPS spectra (Fig. S2), carbon bonding compositions determined from the C 1s XPS spectra (Fig. S3), nitrogen functionality compositions determined from the N 1s XPS spectra (Fig. S4(a,b)), and sulfur functionality compositions determined from the S 2p (2s) XPS spectra (Fig. S4(c,d))for GODs, SGODs, NGODs, and SNGODs.

	Atomic ratio	Carbon bonding composition (%)				
	O 1s / C 1s	C–C	C–N	C–O	C =O	O–C=O
GODs	64	62	—	19	13	6.8
SGODs	59	74	—	7.0	16	3.3
NGODs	58	70	4.2	8.5	16	1.8
SNGODs	59	64	6.5	5.0	23	1.6
	Atomic ratio	Nitrogen functionality composition (% of C 1s)				
	N 1s / C 1s	Pyridine	Amino	Pyrrolic	Quaternary	Amide
NGODs	6.37	1.41	0.62	2.36	1.35	0.62
SNGODs	7.68	0.45	0.75	2.24	3.51	0.73
	Atomic ratio	Sulfur functionality composition (% of C1s)				
	S 2p / C 1s (S 2s/C 1s)	C-S-C	C=S	C-S=O	C-SO2	C-SO3
SGODs	5.9 (5.6)	0.55	0.12	0.26	4.2	0.48
SNGODs	6.2 (6.1)	0.68	0.48	0.48	4.7	0.09

6. Possible quaternary N formation mechanism



Scheme S1 The possible mechanisms for the formation of quaternary N on the GO surface under annealing ammonia treatment: (a) annealing without sulfur; (b) annealing with sulfur. The presence of sulfur facilitates the formation of the quaternary N groups.

7. PL spectra of GO-dots

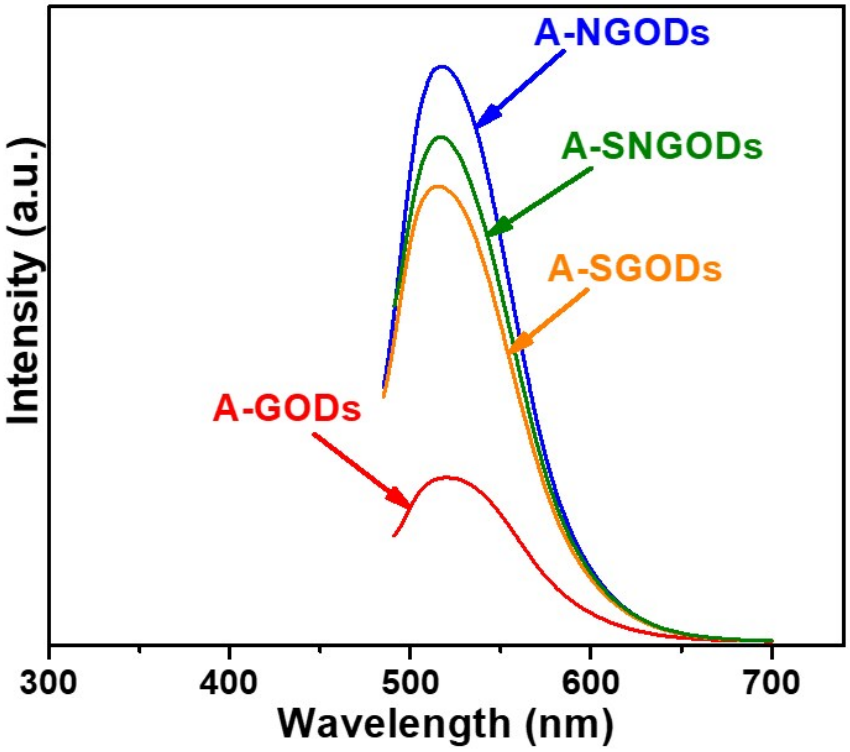


Fig. S5 The photoluminescence spectra of the aqueous solutions of AGODs, A-SGODs, A-NGODs, and A-SNGODs excited at 470 nm.

8. UPS analysis of GO-dots

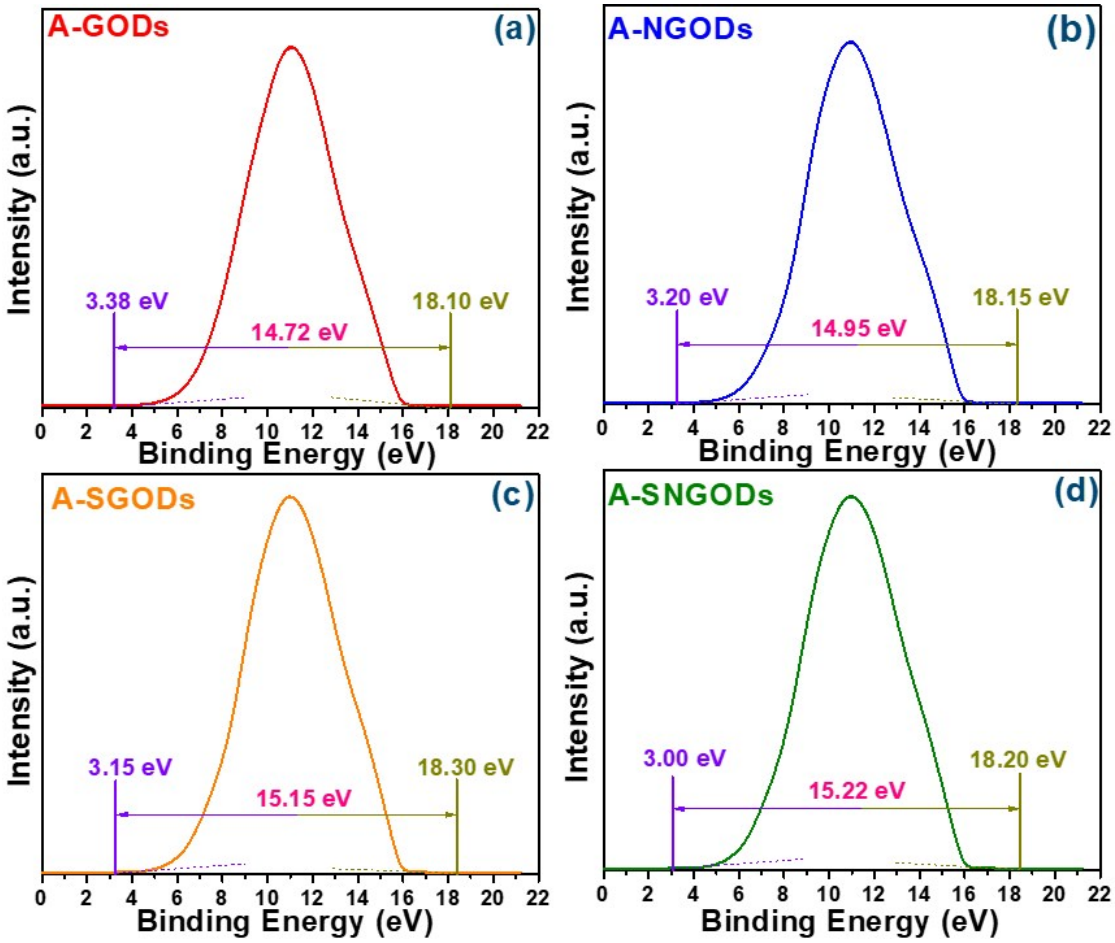


Fig. S6 UPS spectra of the photocatalysts: (a) A-GODs; (b) A-NGODs; (c) A-SGODs; (d) A-SNGODs. The VBM levels with respect to the Fermi levels were determined from the intercepts of the extrapolated straight lines (blue dashed line) on the abscissa at low binding energy. The intersections of the tangent (red dashed line) with the abscissa at high binding energy give the secondary electron onset binding energy. The UPS widths (black lines) can be determined by these two intercept binding energies, and the VBM levels can be calculated by subtracting these widths from the excitation energy (21.2 eV).

9. Activity variation of A-SNGODs in H_2 production under visible irradiation for 144 h

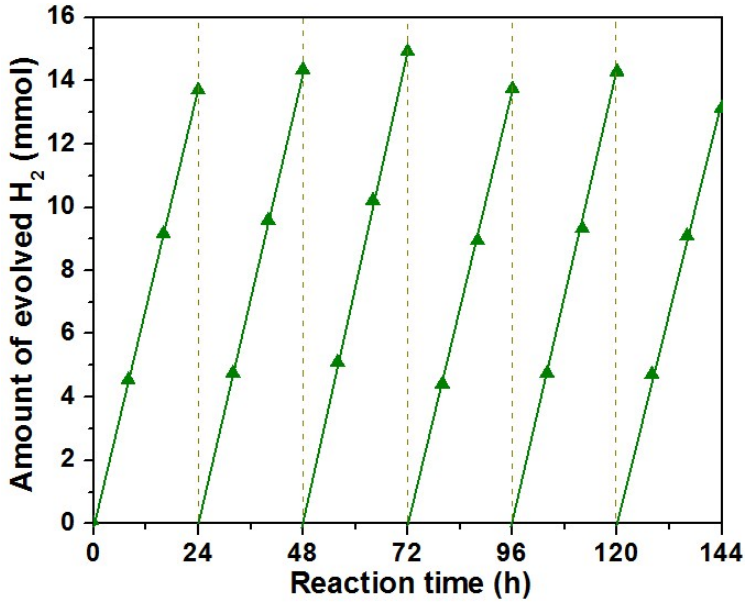


Fig. S7 Time course of H_2 production from the 10 vol% triethanolamine aqueous solution containing the 3 wt% Pt-deposited on 0.4 g A-SNGODs under visible light (420–800 nm) irradiation of intensity 38 mW cm^{-2} over a period of 144 h.