

1 Electron Competitive Migration Regulating for Dual Maxima of Water Photolysis

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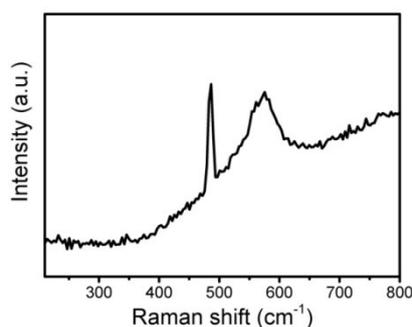
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7 **Supporting information**

8 **Raman shift:**



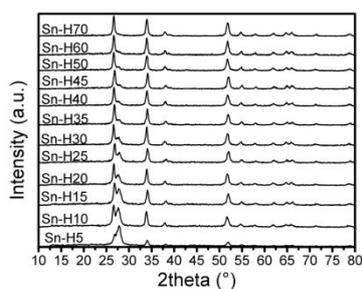
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10 **Figure S1.** Raman shift of SnO₂ quantum dots (SnO₂-SH) prepared after hydrothermal reactions at 200 °C.

11 The Raman signal at 486 cm⁻¹ is ascribed to E_g mode, and the low symmetric peak of 574 cm⁻¹ to

12 the oxygen vacancy and local disorder in SnO₂ lattice, as proposed elsewhere¹.

13 **XRD patterns:**

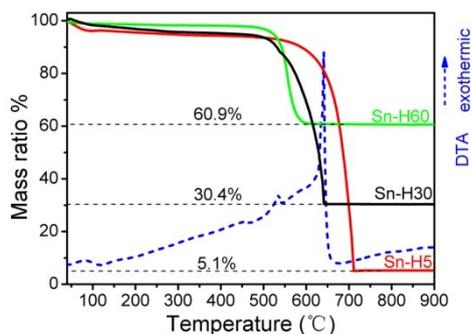


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15 **Figure S2.** XRD patterns of the as-prepared Sn-H_x hybrids.

1 The overlapped peaks in the range of 15-30 degrees could be distinguished to be associated with
2 (110) diffraction of SnO₂ and (002) peak of g-C₃N₄, and the diffraction intensity from SnO₂-AD
3 became increased with increasing the mass ratio of SnO₂-AD.

4 **T_g & DTA:**

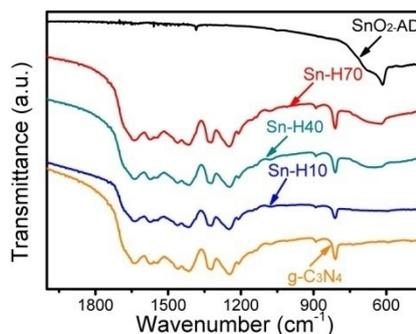


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6 **Figure S3.** TG curves of the selected hybrids and DTA curve of hybrid Sn-H30.

7 The selected samples have weight losses of about 95%, 70% and 40%, respectively, and two
8 exothermic peaks of Sn-H30 at 530 °C and 640 °C are caused by thermal decomposition of g-C₃N₄.

9 **FT-IR:**



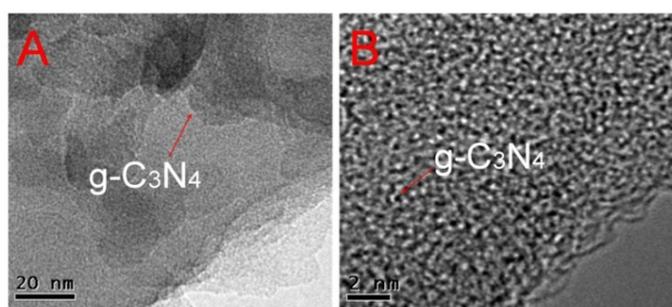
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11 **Figure S4.** FT-IR transmittance spectra of the as-prepared SnO₂-AD, g-C₃N₄ and selected Sn-Hx hybrids.

12 For the as-prepared SnO₂-AD, a wide and strong absorption signal appeared at 614 cm⁻¹, which is
13 due to the anti-symmetric Sn-O-Sn stretching mode of SnO₂ nanoparticles¹. The peak at 810 cm⁻¹
14 was resulted from the triazine ring, the peaks at 1246 and 1320 cm⁻¹ correspond to C-N stretching,
15 and the peaks at 1413, 1460, 1563, and 1641 cm⁻¹ could be assigned to the typical stretching

1 vibration modes of heptazine-derived repeating units². Typically, the peak intensity of 614 cm⁻¹
2 due to Sn-O-Sn stretching vibrations became stronger as the SnO₂ mass ratio increase from 10%
3 to 70%.

4 **Morphology of g-C₃N₄:**

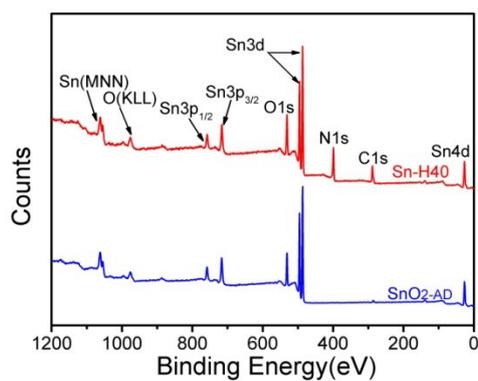


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Figure S5. TEM (A) and HR-TEM (B) images for as-prepared g-C₃N₄.

7 **Survey XPS spectra:**



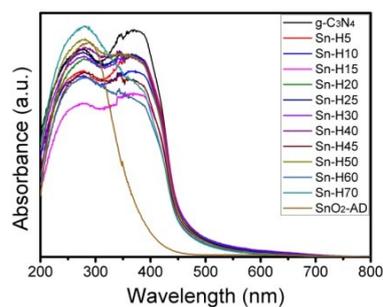
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Figure S6. Survey XPS spectra of as-prepared SnO₂-AD and Sn-H40 hybrid.

10 Compare with the survey XPS data for SnO₂-AD, Sn-H40 exhibits two additional photoelectron
11 peaks at 287.2 eV and 398.8 eV, respectively, which could be assigned to C1s and N1s from g-
12 C₃N₄.

13 **UV-vis spectra:**

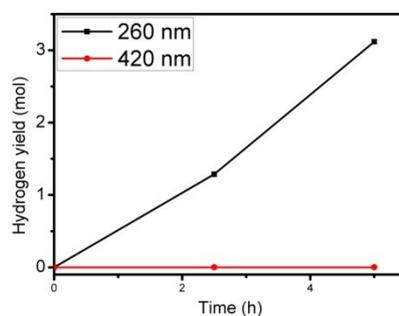


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Figure S7. UV-vis absorbance spectra of SnO₂, g-C₃N₄ and SnO₂/g-C₃N₄ hybrids.

3 **Photocatalytic test for water splitting:**



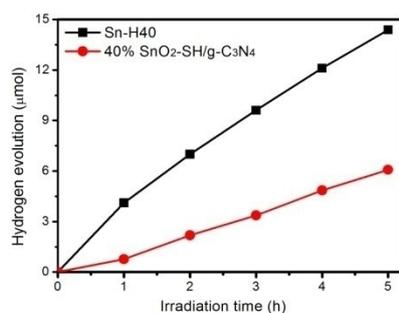
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5 **Figure S8.** Hydrogen yield from water splitting under visible light (420nm) irradiation for 5 hours of 100mg of as-
6 prepared defective SnO₂ under ultraviolet ($\lambda > 260$ nm) and visible ($\lambda > 420$ nm) light irradiation with 300W Xe lamp.

7 The activity of as-prepared SnO₂-AD in photo-splitting water is really poor to yield hydrogen of 3

8 μmol and 0 μmol after irradiation for 5h under the 260 nm and 420 nm light, which approved it

9 had appropriate energy band position as well as narrower gap (3.5 eV) than references value.

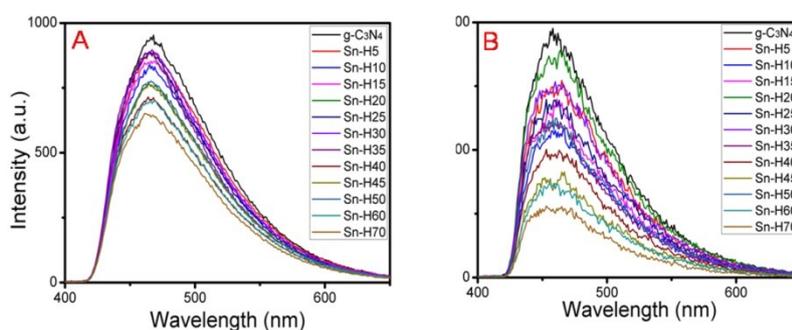


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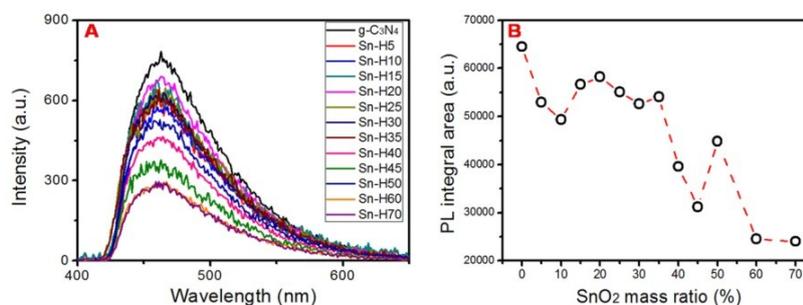
1 **Figure S9.** Comparison of the hydrogen evolution for SnO₂-SH/g-C₃N₄ hybrid in 40% SnO₂-SH mass ratio and
2 Sn-H40 irradiated by 420 nm light within 5 hours.

3 To confirm the negative role of oxygen vacancies in SnO₂/g-C₃N₄ hybrids, the hybrid in 40%
4 mass ratio of SnO₂-SH was also tested under the similar experimental condition. Sn-H40 showed a
5 hydrogen yield of 14.4 μmol in 5 h. Comparatively, the hydrogen evolution of 40% SnO₂-SH/g-
6 C₃N₄ hybrid is just 6.1 μmol. Therefore, oxygen vacancies in SnO₂ act as the electron trap centres
7 and weaken the photocatalytic activity of hybrids in water splitting. Consequently, there should be a
8 competitive migration between conduction band and oxygen vacancy.

9 **PL spectra of samples:**

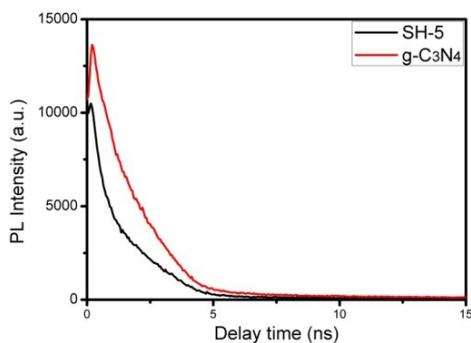


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11 **Figure S10.** (A) Solid state PL spectra under 390 nm excitation wavelength, and (B) aqueous environment PL
12 spectra of g-C₃N₄, SnO₂/g-C₃N₄ hybrids with same concentration under 390 nm excitation wavelength.



13
14 **Figure S11.** PL intensity spectra in triethanolamine solution environment of 1wt% Pt deposited g-C₃N₄, Sn-Hx;
15 and (B) PL integral areas of 1wt% Pt deposited Sn-Hx under 390 nm excitation wavelength.

1 After depositing 1wt% Pt for all samples, the variation trend of PL spectra integral areas in
 2 triethanolamine solution environment is the same as that of PL properties in pure water, which
 3 confirms that 1wt% deposition of Pt didn't change the PL properties trend in a very short period of
 4 time.



5
 6 **Figure S12.** Typical PL decays measured at 464 nm emission wavelengths corresponding to g-C₃N₄ and Sn-H5 in
 7 solid PL state.

8 Base on average PL lifetime formula given from reference³:

$$9 \quad \tau_{avg} = \frac{\sum_n \alpha_n \tau_n^2}{\sum_n \alpha_n \tau_n}$$

10 The average PL life for g-C₃N₄ and SH-5 is 6.8 ns and 6.4 ns, respectively. The shortened PL life
 11 indicates SnO₂-AD separated apart of free photo-generated charges from g-C₃N₄, and decreased
 12 the intrinsic radiative recombination of charges in g-C₃N₄.

13 **Table S1.** Photocatalytic activity of SnO₂-AD/g-C₃N₄ hybrids under visible light irradiation ($\lambda > 420$ nm).

SnO ₂ mass ratio	Integral area	Hydrogen yield	Hydrogen generation rate	P-H conversion efficiency
(%)	(a.u.)	(μmol)	($\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$)	($\mu\text{mol}\cdot\text{g}^{-1}_{\text{C}_3\text{N}_4}$)
0	33927	8.37	27.90	8.37
5	54511	13.45	44.82	14.15

10	66059	16.29	54.32	18.11
15	55427	13.67	45.57	16.08
20	50249	12.39	41.32	15.49
25%	43780	10.80	36.00	14.40
30	31358	7.74	25.78	11.05
35	40449	9.98	33.26	15.35
40	54230	13.38	44.59	22.29
45	52148	12.86	42.88	23.39
50	25258	6.23	20.77	12.46
60	13338	3.29	10.97	8.23
70	12885	3.18	10.59	10.59
100	0	0	0	0

1

2 The hydrogen yields were calculated by the following formula base on gas chromatograph
3 emendation:

4
$$x = \frac{S}{4054}$$

5 Where x represent the hydrogen yield and S represent integral area of gas chromatograph. Photon-

6 Hydrogen (P-H) conversion efficiency was calculated by equation:

7
$$y = \frac{x}{p}$$

8 Where y represent P-H conversion efficiency, x represent hydrogen yield, and p represent the mass
9 ratio of g-C₃N₄ in SnO₂/g-C₃N₄ Hybrids.

10 Reference

- 1 1 A. Das, V. Bonu, A. K. Prasad, D. Panda, S. Dhara and A. K. Tyagi, *J Mater Chem C*, 2014, 2, 164-171.
- 3 2 F. Dong, L. Wu, Y. Sun, M. Fu, Z. Wu and S. C. Lee, *J Mater Chem*, 2011, 21, 15171-15174.
- 4 3 S. Kumar, M. Jones, S. S. Lo and G. D. Scholes, *Small*, 2007, 3, 1633-1639.