Electronic Supplementary Information

S-doped C$_3$N$_5$ derived from thiadiazole for efficient photocatalytic hydrogen evolution

Xinwei Guan,[a] Mohammed Fawaz,[a] Ranjini Sarkar,[b] Chun-Ho Lin,[c] Zhixuan Li,[a] Zhihao Lei,[a] Nithinraj Panangattu Dharmarajan,[a] Prashant Kumar,[a] Xiangwei Zhang,[a] Jae-Hun Yang,[a] Long Hu,[c] Tom Wu,[c,d] Sudip Chakraborty,[b] Jiabao Yi,*[a] and Ajayan Vinu*[a]

[a.] Global Innovative Centre for Advanced Nanomaterials, School of Engineering, College of Engineering, Science and Environment, The University of Newcastle, Callaghan, NSW, 2308 Australia
E-mail: jiabao.yi@newcastle.edu.au; ajayan.vinu@newcastle.edu.au.

[b.] Materials Theory for Energy Scavenging (MATES) Lab, Harish-Chandra Research Institute (HRI) Allahabad, HBNI, Chhatnag Road, Jhunsi, Prayagraj (Allahabad), 211019 India

[c.] School of Materials Science and Engineering, University of New South Wales (UNSW), Sydney, NSW, 2052 Australia

[d.] Department of Applied Physics, The Hong Kong Polytechnic University, Hung Hom, Hong Kong, 999077 P. R. China

Experimental Section

Materials Synthesis:

5-ATDA (C$_2$H$_3$N$_3$S$_2$) (purity 95%), hydrogen hexachloroplatinate (IV) solution (H$_2$PtCl, 8 wt% in H$_2$O), and n-butanol (CH$_3$(CH$_2$)$_3$OH, 99.8%) were purchased from Sigma-Aldrich and ACS reagent grade. All the chemicals were used without further purification. The SCNs and different precursors-based g-CN were prepared by a simple calcination method under different temperatures. In brief, 3 g of precursors were directly calcined in a tube furnace with a nitrogen flow. The obtained bulk samples were well-grounded before measurements.

Characterization:

XRD patterns were characterized by a Panalytical Empyrean X-ray diffractometer equipped with Cu-Kα radiation (λ = 1.5418 Å) and Galipix Detector at 40 kV and 40 mA. SEM images were recorded by the JEOL JSM-7900F, and TEM analysis was taken by the JEOL JEM-2100F. FT-IR data were measured by a Perkin Elmer Frontier FTIR/NIR spectrometer by a KBr disk method. XPS measurements were conducted by a VG ESCALAB MK2 system with

monochromatized Al Kα radiation under a pressure of 5.0×10^{-7} Pa. NEXAFS spectra were carried out from the Soft X-ray Spectroscopy Beamline at the Australian Synchrotron. The beamline has a hemispherical electron analyzer and a microchannel plate detector to measure the total and partial electron yield simultaneously. The PL spectra measurements were performed at room temperature using a custom laser PL spectroscopy system (Crystal Laser, Model BLC-050-405). The laser pulse width was 130 fs, and the repetition rate was 100 MHz. The excitation wavelength for both PL and TRPL measurements is 370 nm. UV-Vis spectra were conducted by the Perkin Elmer Lambda 365 UV/VIS. Perkin Elmer EA 2400 Elemental Analyzer determined the samples' quantification of C, N, and S. For measuring porous textures, all samples were firstly degassed under 10^{-3} Torr vacuum at 200 °C for twelve hours and then conducted the N_2 adsorption-desorption isotherm analysis at liquid nitrogen temperature by ASAP 2040. Parameters like specific surface area, total pore volume, and pore size were systematically recorded. The thermogravimetric analysis was conducted by the Perkin Elmer STA 8000 with a ramping rate of 10 °C min^{-1} and an N_2 flow rate of 20 mL min^{-1}.

Photoelectrochemical cell preparation and method:

50 mg of carbon nitride powder mixed with 50 µl of 10 wt% Nafion solution and a few drops of ethanol and grounded in an agate mortar to form a uniform paste. A 1 cm^2 electrode is prepared by masking an FTO-coated glass substrate with scotch tape (3 sides) and subsequently applying a thin layer of prepared carbon nitride paste by the doctor blade technique. The prepared electrode is dried at room temperature. After peeling the scotch tape, the exposed FTO surface is coated with epoxy resin to get the working electrode.

Photoelectrochemical measurement, Mott-Schottky measurement, and electrochemical impedance spectroscopy (EIS) were measured in a three-electrode system where FTO-supported CN film, Platinum spring electrode, and Ag/AgCl (3M KCl) act as a working electrode, counter electrode and the reference electrode respectively, in a 0.2 M Na_2SO_4

electrolyte solution and recorded using a CHI-Potentiostat. PEC measurements in a three-electrode configuration are carried out after purging argon gas for 20 minutes under the illumination of a 300 W Xenon lamp ($\lambda > 400$ nm) at 0 V (vs Ag/AgCl), where the light beam is irradiated on the glass side of the working electrode. The material's photocurrent density curve (chronoamperometry) is measured by illuminating the photoelectrode at regular intervals of 20 seconds. For Mott-Schottky, the potential range of – 0.3 V to 1 V (vs. Ag/AgCl) was used. Electrochemical Impedance Spectra (EIS) measurements were recorded by sweeping the frequency from 10 KHz to 10 mHz with a 10 mV AC excitation signal using the same electrochemical configuration.

Photocatalytic HER:

The photocatalytic reactions of SCNs were conducted in a top-irradiated Pyrex reactor, which is connected to the closed gas circulation and evacuation system. In typical experiments, 100 mg of the SCN samples were dispersed in 100 mL of 10-vol% TEOA aqueous solution with continuing magnetic stirring. To thoroughly remove the air in the system, Ar gas was passed into the system and evacuated multiple times, with a final pressure of around 40 Torr. Afterwards, simulated solar light with one sun power was illuminated on the reactor using the Newport Class ABB solar simulator with 450 W Xe lamp and 1.5 G air-mass filter. The evolved H_2 gas was analyzed by an in-situ auto-injection system periodically, which is composed of a gas chromatograph (PerkinElmer Clarus 580).

Computational methodology:

Plane-wave pseudopotential (PW-PP) based DFT calculations are carried out using Quantum Espresso package.[1] GGA-PBE functional[2] is employed with ultrasoft pseudopotential (USPP)[3] considering the plane-wave cut-off energy of 50 Ry (680 eV), and 3 × 3 × 1 and 15 × 15 × 1 k-grid points for geometry optimization and electronic structure calculations. The convergence threshold of energy and force was set to 1.36×10^{-5} eV and

0.025 eV/Å (which is 2.15×10^{-4} eV/Å per atom for SCN-9 and 1.61×10^{-4} eV/Å per atom for SCN-12), respectively.
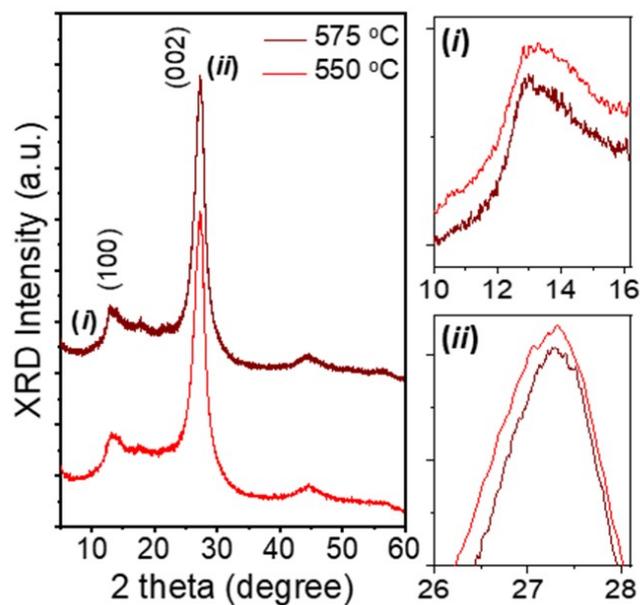
Fig. S1. Powder XRD patterns of SCN-550 and SCN-575. The enlarged (100) and (002) reflection peaks indicate a crystallinity reduction when enhancing the calcination temperature to 575 °C.

Table S1. Elemental composition of SCNs obtained from CHNS analysis (wt%).

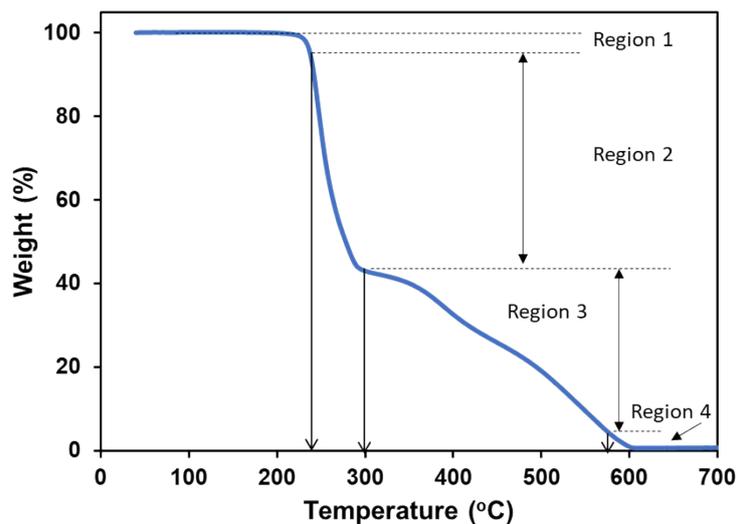| Samples	N(%)	C (%)	H(%)	S (%)	C:N:S
SCN-350	60.45	30.51	2.61	3.59	$C_3N_{5.09}S_{0.13}$
SCN-450	60.07	32.44	2.20	1.53	$C_3N_{4.76}S_{0.05}$
SCN-500	59.94	33.27	2.08	0.35	$C_3N_{4.63}S_{0.011}$
SCN-550	59.59	33.43	2.01	0.35	$C_3N_{4.58}S_{0.01}$
SCN-575	59.55	33.47	1.87	0.09	$C_3N_{4.57}S_{0.003}$

Fig. S2. TGA curve of 5-ATDT. A small weight loss between 30 and 237 °C corresponds to the removal of the water adsorbed (region 1). The melting point of 5-ATDT is 237 °C, and it is decomposed to CH_4N_2S and $N\equiv C\text{-}SH$ after melting in region 2 (Fig. 2). Finally, the carbon nitrides are completely decomposed at 600 °C.
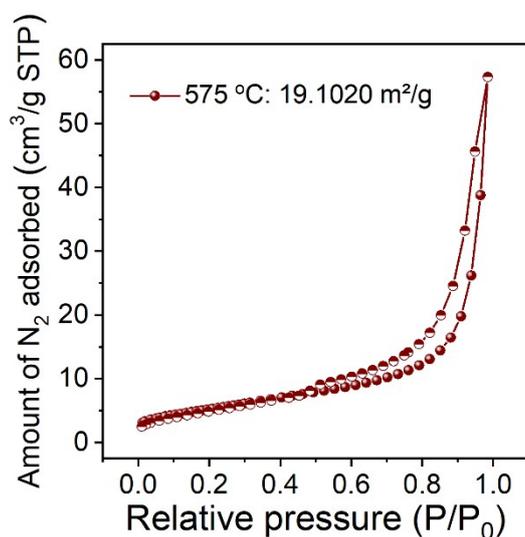

Fig. S3. N_2 adsorption-desorption isotherms of SCN-575. Compared to SCN-550, the specific surface area of SCN-575 is almost double due to partial material vaporization and H_2S release during the carbonation process.

Table S2. N-N, C-N, C-S, and N-S bond lengths within the SCNs monolayer.

Bonds	Bond length (Å)	
	Within unit A ($C_3N_{4.8}$)	Within unit B ($C_3N_{4.2}S_{0.06}$)
N8-N5	1.40	-
N5-N7	1.42	-
N5-C4	1.40	-
S-C4	-	1.88
S-N7	-	2.02
N7-C2	1.31	1.27
C2-N6	1.36	1.38
N6-C1	1.32	1.31
C1-N4	1.35	1.35
N4-C3	1.33	1.33
C3-N1	1.37	1.39
N1-C4	1.36	1.35
C4-N3	1.31	1.29
C3-N2	1.33	1.34
N2-C5	1.35	1.33
C5-N3	1.36	1.37
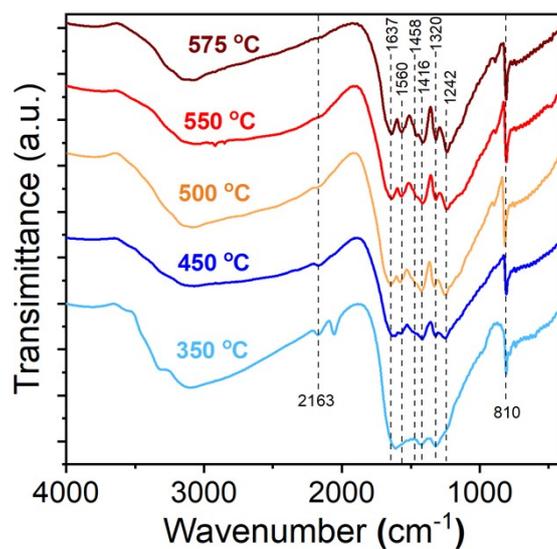
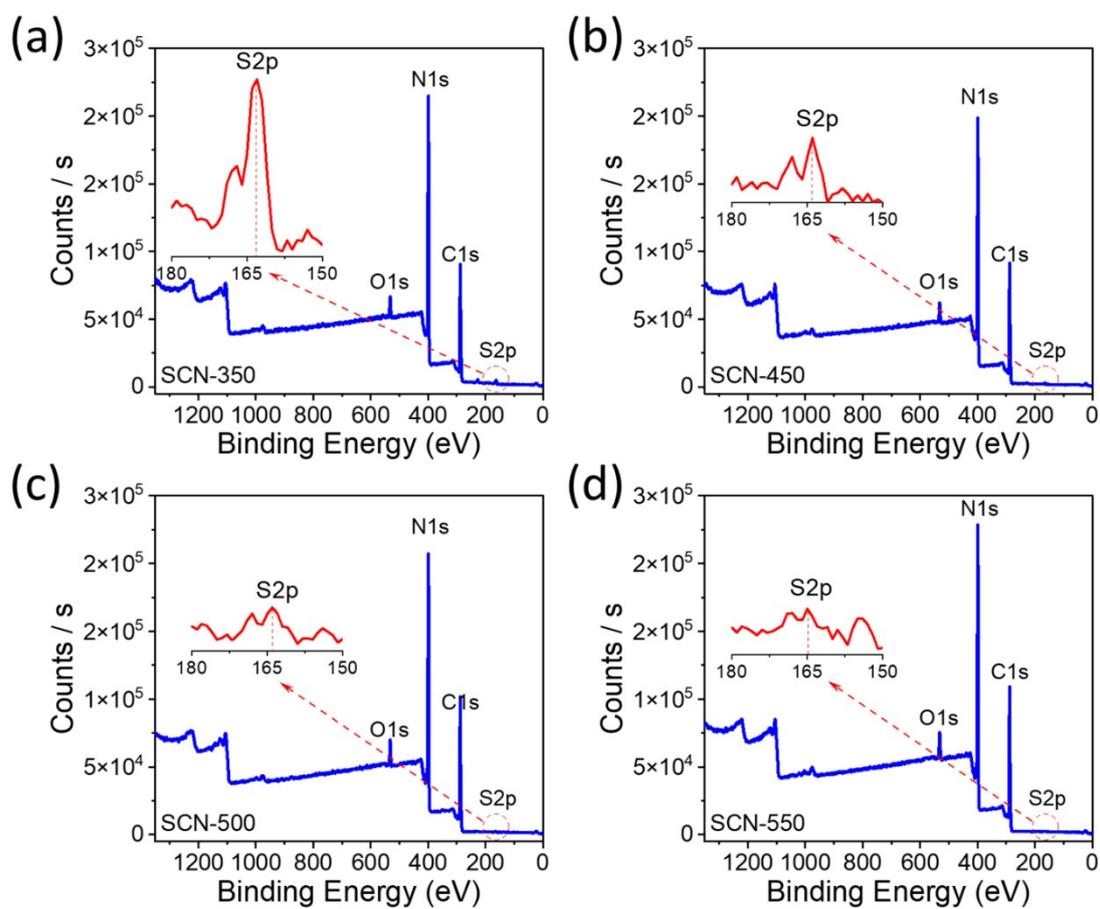**Fig. S4.** FT-IR spectra of SCN samples calcinated at different temperatures.

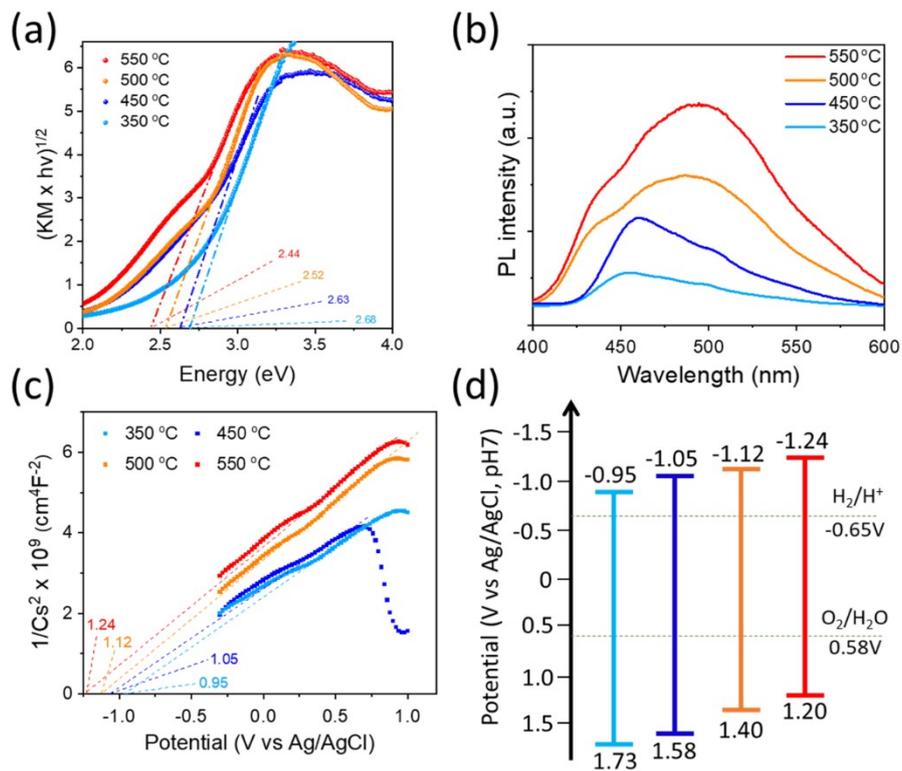**Fig. S5.** Elemental survey scan of SCNs.

Fig. S6. a) Kubelka-Munk plots of SCNs derived from the UV-vis spectra. b) PL plots of SCNs. c) Mott-Schottky plots measured at 2700 Hz and d) their electronic band gap structures.

Table S3. Lifetimes of SCN samples.

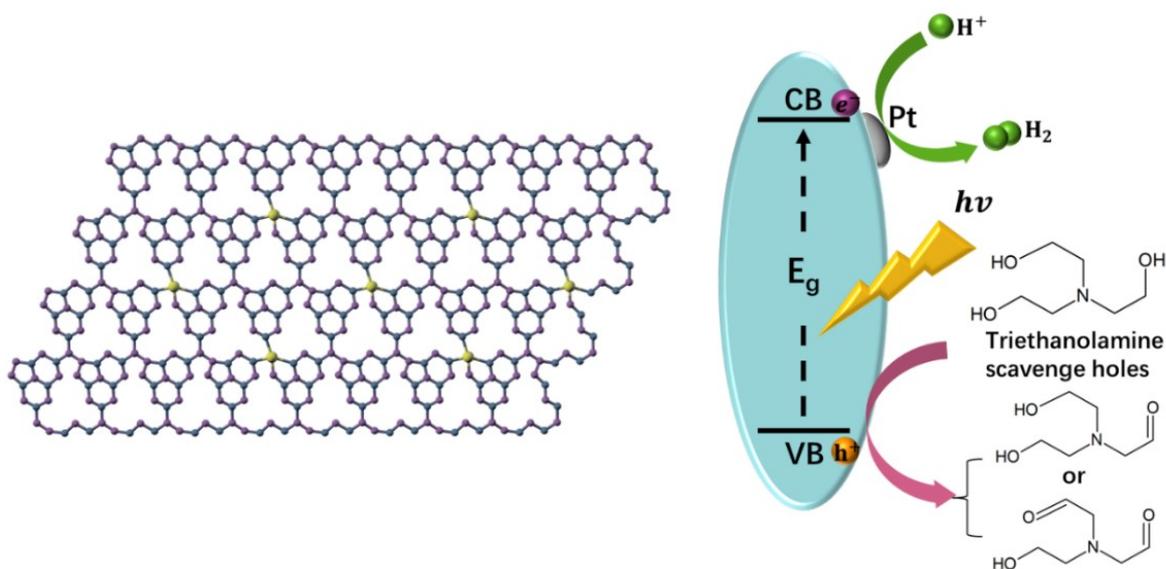|	τ_1 (ns)	A_1	τ_2 (ns)	A_2	$\tau_{average}$ (ns)
SCN-350	1.3	0.5131	4.7	0.5089	2.99301
SCN-450	2.2	0.7177	8.5	0.2888	4.00769
SCN-500	5.7	0.8309	23.1	0.2057	9.15281
SCN-550	7.1	0.8229	28.5	0.2217	11.64182
SCN-575	6.2	0.8096	26.3	0.2213	10.5148

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Fig. S7. The mechanism of photocatalytic H_2 evolution reaction in SCNs.

Table S4. The evolution rate of H_2 of SCNs in the photocatalytic water splitting reaction.

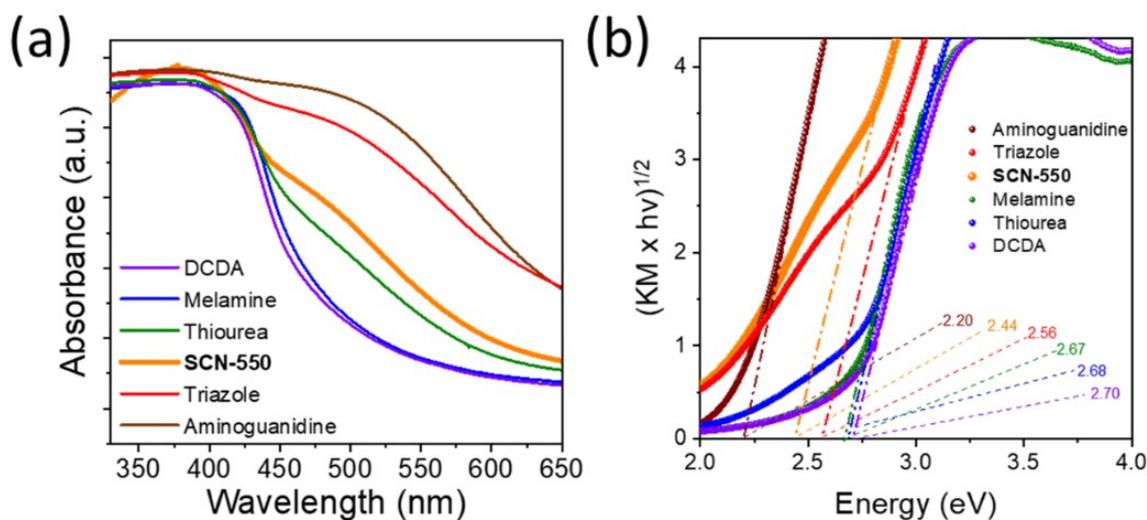|	H_2 evolution rate (μmol h^{-1} g^{-1})	Amount of evolved H_2 in 5 hours (μmol h^{-1} g^{-1})
SCN-350	0	0
SCN-450	6.53	25.4
SCN-500	26.7	111.2
SCN-550	48.6	188
SCN-575	38.7	164.6

Fig. S8. a) UV–Vis spectra and b) the derived bandgaps of carbon nitrides derived from different precursors. From Fig. S8a, SCN-550 has an absorption bump in the range above 450 nm, and the bandgap of SCN-550 is also smaller than other precursors except for aminoguanidine. Therefore, SCN-550 can absorb more visible photons compared to other precursors.
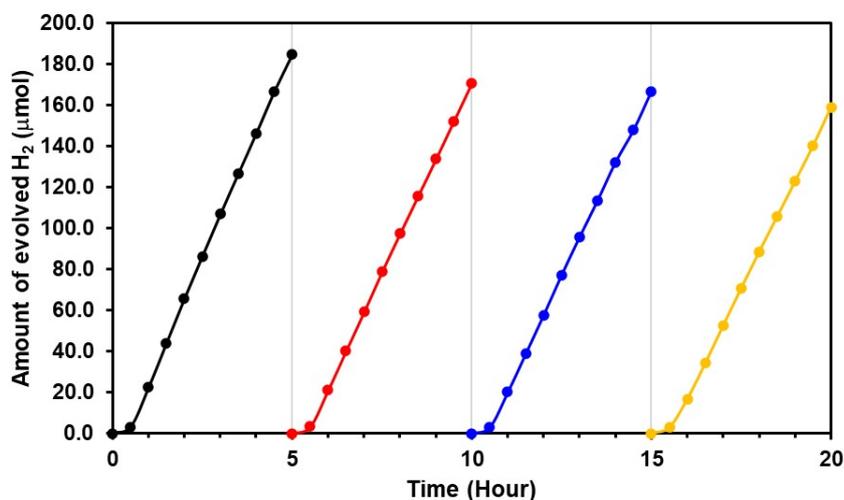

Fig. S9. The long-term stability test of SCN-550 for 20 hours with evacuation every 5 hours.

Reference:
[1]   P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, *J. Phys. Condens. Matter.* **2009**, *21*, 395502.
[2]   J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865.
[3]   D. Vanderbilt, *Phys. Rev. B* **1990**, *41*, 7892.