Supporting Information

Ultrahigh-loading single-site Zn catalyst for efficient and ambient hydrogen generation from silanes

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Experimental sections

Materials

All the solvents and chemicals were available from suppliers and used as received without any further purification unless specially stated.

Zinc oxide (ZnO, 99%), 2-methylimidazole (98%), *N,N*-dimethylformamid (99.5%), ammonium nitrate (NH_4NO_3, 99%), methanol (MeOH, 99.7%), ethanol (EtOH, 99.5%), isopropyl alcohol (99.7%), Zinc chloride ($ZnCl_2$, 98%), zinc sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$, 99%), zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 99%), and melamine (99%) were purchased from Aladdin. Phenylsilane (97%), dimethylsilane (97%), p-tolylsilane (97%), and 1,4-disilabutane (97%) were obtained from Shanghai Meryer CO., LTD. Carbon black was supplied by Sigma-Aldrich.

Synthesis

ZIF-8 [1]: typically, $Zn(NO_3)_2 \cdot 6H_2O$ (4 mmol, 1.19 g) was dissolved in MeOH (30 mL) under the ultrasound for 15 min to form a clear solution in 250 mL beaker. Then, a solution of 2-methylimidazole (16 mmol, 1.31 g) in MeOH (15 mL) was added to 250 mL beaker and stirred for 1 h carefully. Subsequently, the mixture was transferred into 100 mL Teflon-line stainless-steel autoclaves and then kept at 120 °C for 4 h. The product was centrifuged, washed with DMF and MeOH, and finally dried at 70 °C overnight under vacuum.

ZIF-8-BM [2]: Typically, ZnO (12 mmol, 0.98 g), 2-methylimidazole (48 mmol, 3.91 g) were mixed in a mortar for 2 min. Then the solid was averagely added into four 100 mL agate ball milling jars. Every jar was added with 15 mg ammonium nitrate, 450 μL DMF, and several agate grinding balls. Subsequently, the agate jars were placed in a planetary ball mill (QM3SP2), and the mixture was milled for 2 h at 500 rpm.

Afterward, the milled mixture was scraped out and dried at 70 ℃ overnight under vacuum to obtain the ZIF-8-BM.

Zn_1-N-C: Typically, the above material ZIF-8-BM was placed in a temperature-programmable tube furnace (OTF-1200X) and subjected to the following thermal treatments in 100 mL/min N_2 flow (from room temperature (25 °C) to a final pyrolysis temperature (700 °C) at a heating rate of 5 °C min^{-1}, and kept at 700 °C for 3 h). After cooling down to room temperature, the single-site Zn catalyst (Zn_1-N-C) was obtained.

The scale-up procedure of Zn_1-N-C (25 grams) was similar as that of Zn_1-N-C except the milling time (10 hours) and the weight of the raw materials (25 times heavier).

N-C: melamine (1.0 g), carbon black (1.0 g) were mixed in a mortar for 2 min. Then the solid and several agate grinding balls were transferred into an agate ball milling jar. Subsequently, the jar was placed in a planetary ball mill, and the mixture was milled for 24 h at 500 rpm. After the ball milling, the mixture was scraped out and pyrolysis at 700 ℃ for 1 h to obtain the N-C.

Characterization

XRD patterns were recorded on a Bruker D8 Advanced diffractometer. SEM and EDX were operated on Thermal Field Emission Enviromental SEM EDS EBSD Quanta 400F. TEM and STEM images were obtained on FEI Tecnai G2 F30 operated at an electron acceleration voltage of 300 kV. AC HAADF-STEM images were obtained on a JEM-ARM200F TEM using an electron acceleration voltage at 200 kV. Element contents were determined by Vario EL cube EA instrument and PerkinElmer OPTIMA 8000DV ICP-OES instrument. XPS measurements were carried out on an

ESCALab250 XPS system. X-ray absorption spectroscopy (XAS) measurements were conducted on BL14W beamline at the Shanghai Synchrotron Radiation Facility (SSRF) and 1W1B beamline at the Beijing Synchrotron Radiation Facility (BSRF).

Catalytic Performance Test

As shown in Fig. S1, the volume of hydrogen generation was measured by the methods of drainage at room temperature.[3] 10 mg catalyst was charged into the reaction tube, and 1 mmol silane and 1 mL alcohol solution was added into the constant pressure dropping funnel, and the glass plug was tightly plugged. (For reactions with water, 50 uL water and 1 mL acetone were first mixed as an alternative solvent of alcohols) Then, the reaction tube was connected with the rubber tube, the burette valve was closed, the burette was filled with water and buckled into a beaker with a small amount of water, and the burette piston was opened, then we recorded the liquid level scale (V_0). The device was further kept for 10-15 min to check leaking. If the liquid level in the burette did not change within 15 min, the air tightness of the device would be available for experiments. Subsequently, the initial liquid level before reaction and the finial liquid level after reaction were recorded as V_0 and V't, respectively, thus the corresponding volume of the resulting hydrogen gas (V_t) was calculated by $V_t = V_0 - V'_t$.

After reaction, the burette was moved up and down to eliminate the influence of its internal and external pressure difference by keeping the two liquid levels same.

The H_2 yield was evaluated by Eq. S1:

$$H_2 \text{ Yield} = \frac{V_t \times M_s}{24.5 \times \text{n} \times m_s} \times 100\% \qquad \text{Eq. S1}$$

where, V_t was the corresponding gas production volume (L); m_s was the mass of the silane (g); the molar volume of gas at room temperature is 24.5 L/mol; n was the number of the Si–H; M_s was the molar mass of silane (g/mol), respectively.

Within <20% H_2 yield, the TOF of the catalyst was determined by Eq. S2:

$$TOF = \frac{V_t \times M_c}{24.5 \times \omega \times m_c \times t} \quad \text{Eq. S2}$$

where, V_t was the corresponding gas production volume (L) at *t* time (h); the molar volume of gas at room temperature was 24.5 L/mol; ω was the metal loading in the catalyst; m_c was the mass of the catalyst; M_c was the molar mass of Zn (g/mol), respectively.

After the reaction, directly added with 1 mmol of silane into the constant pressure dropping funnel to test the recycle performance.

In addition, hydrogen storage capacity (HSC) was evaluated by Eq. S3:

$$\text{HSC} = \frac{n \times 2}{M_s + \text{n} \times \text{M}} \times 100\% \quad \text{Eq. S3}$$

where, n was the number of the Si–H; Ms was the molar mass of silane (g/mol), respectively; M was the molar mass of corresponding alcohol or water (g/mol).

Supplementary Figures and Tables

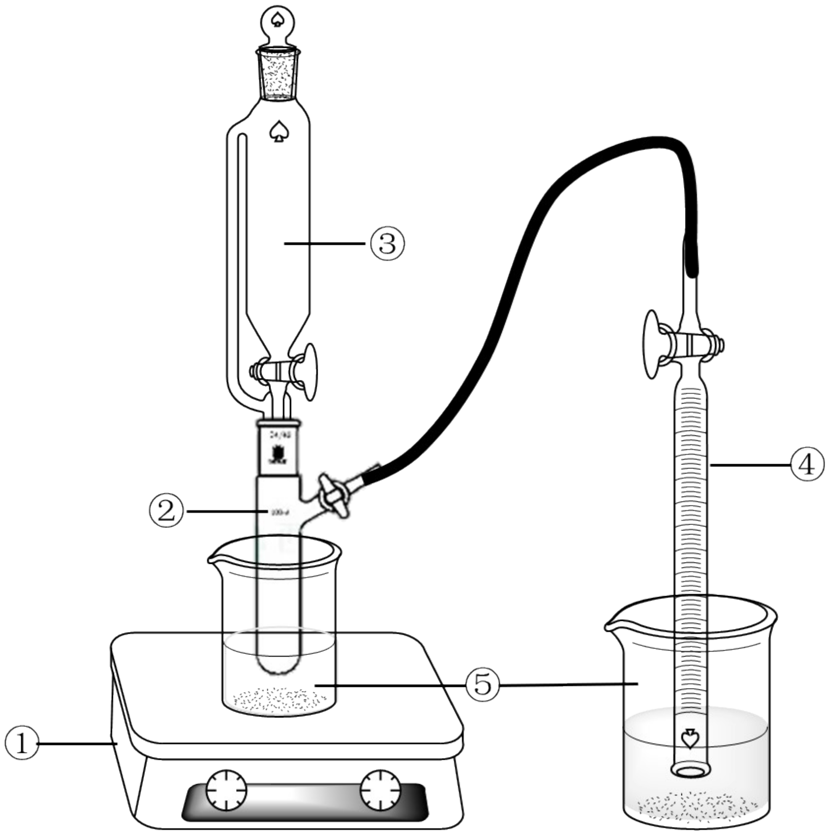

Fig. S1 Experimental facility. er—Magnetic stirrer，&—Reaction tube，●—Constant pressure dropping funnel，❍—burette，■—Beaker with water.

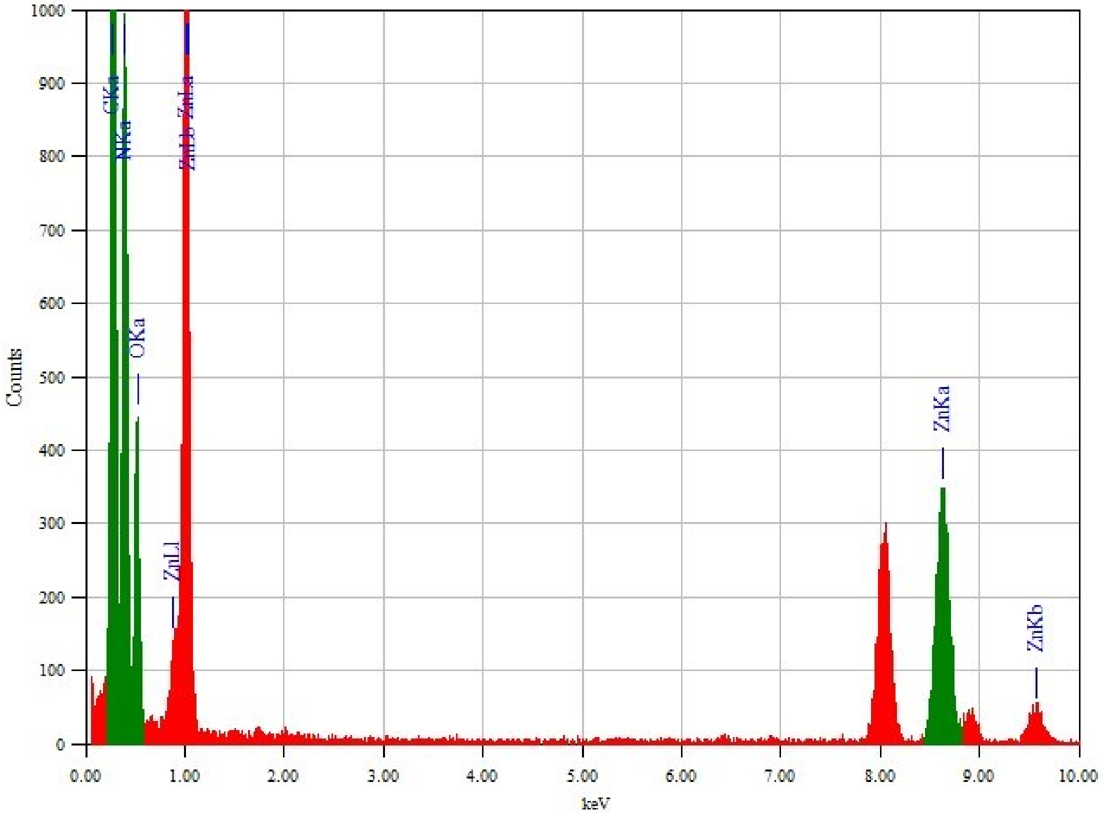

Fig. S2 Energy dispersive spectrum of Zn_1-N-C.

Table S1 Element content of Zn_1-N-C.

Catalyst	Zn (wt%) [a]	N (wt%) [b]	C (wt%) [b]	O (wt%) [b]
Zn_1-N-C	28.3	21.4	38.2	10.1
N-C	0	16.5	75.8	5.4

[a] Inductively coupled plasma optical emission spectrometry.
[b] Element analysis.

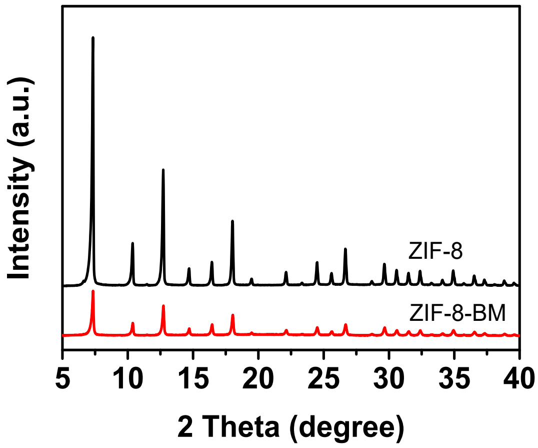

Fig. S3 XRD patterns of ZIF-8 and ZIF-8-BM.

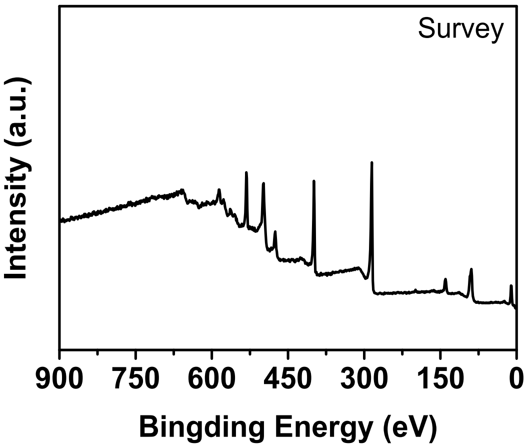

Fig. S4 XPS survey of Zn_1-N-C.

Table S2 EXAFS fitting parameters of the Zn_1-N-C（$S_0^2 = 0.90$）.

samples	path	C. N.[a]	R (Å) [b]	σ^2 ($\times 10^{-3}$ Å^2) [c]	ΔE (eV) [d]	R factor [e]
Zn_1-N-C	Zn-N/O	3.9±0.8	1.96±0.01	3.5±2.2	-0.7±2.5	0.02

[a] C. N.: coordination numbers;

[b] R: bond distance;

[c] σ^2: Debye-Waller factors;

[d] ΔE_0: the inner potential correction.

[e] R factor: goodness of fit.

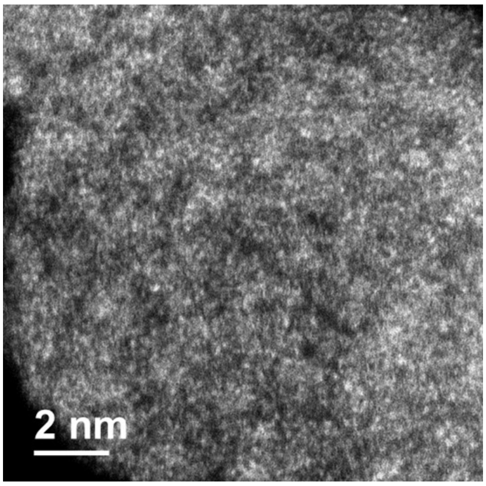

Fig. S5 AC HAADF-STEM image of Zn_1-N-C (25g).

References

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