

Supporting Information for
**Nitrogen fixation by alkali and alkaline earth metal hydrides
assisted by plasma**

Han Wu,^{a,b†} Kai Ma,^{a,b†} Jiaqi Wen,^{a,b} Liang Yang,^c Yeqin Guan,^{a,b} Qianru Wang,^{a,b} Wenbo Gao,^{a,b} Jianping Guo^{a,b,*}, Ping Chen^{a,b}

^a. *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China.*

^b. *Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China.*

^c. *Key Laboratory of Chemical Lasers, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China.*

† These two authors contribute equally to this work.

Corresponding Author E-mail: guojianping@dicp.ac.cn

1. Experimental section

1.1 Chemical reagents

LiH (Sigma-Aldrich, 90%), MgH₂ (Alfa Aesar, 98%), and CaH₂ (Sigma-Aldrich, 97%) were used as supplied. KH (Aladdin, 30wt% dispersion in mineral oil) was washed for several times by dry cyclohexane to remove the mineral oil before use. BaH₂ was prepared following reported procedures from the literature.¹ To prevent air or moisture contamination, all sample loadings and handlings were carried out in a glove box filled with purified argon. Ar (99.999%), N₂ (99.999%), and H₂ (99.999%) were obtained from Dalian Special Gas Co., Ltd.

1.2 Characterization

Fourier transform infrared (FTIR) measurements were conducted on a Bruker Tensor II unit in transmittance mode or DRIFT mode with a scan resolution of 4 cm⁻¹ and an accumulation of 32 scans each time.

XRD patterns were recorded on a PANalytical X'pert diffractometer using a homemade sample cell covered with KAPTON film to avoid air or moisture contamination.

The scanning electron microscopy (SEM) images were recorded using JSM-7800F.

Electron paramagnetic resonance (EPR) measurements were conducted on Bruker A200 spectrometer using sealed sample tube to avoid air exposure.

The discharge power was calculated by Lissajous method: an external capacitor was applied to measure the charge for discharge power calculation; The applied voltage $V(t)$ of the DBD was measured by a high voltage probe (Tektronix P6015A), the charge is measured across a capacitor ($C_m=470$ pF) connected in series with the reactor (between the grounded electrode and the ground).² All electrical signals were sampled by a four-channel digital oscilloscope (Tektronix, MDO 3054). The discharge power (P) was calculated with the following equations:

$$Q_m(t) = C_m V_m(t)$$

$$I_m(t) = C_m \frac{dV_m(t)}{dt}$$

$$P = \frac{1}{T} \int_0^T V_{(t)} C_m \frac{dV_m(t)}{dt}$$

$$P = \frac{1}{T} \oint V_{(t)} Q_m = fS$$

Where Q_m is the charge on the capacitor, V_m is the voltage across the capacitor, C_m is the capacitor capacitance, and I_m is the current through the capacitor, $V_{(t)}$ is the instantaneous values of the applied voltage across the reactor, f is discharge frequency and S is the area inside the closed Lissajous curve.

2. Performance evaluation of chemical looping ammonia synthesis

1) Plasma-assisted dinitrogen fixation

The plasma-assisted dinitrogen fixation experiments were conducted in a packed-bed dielectric barrier discharge (DBD) reactor without external heating and at atmospheric pressure. The reactor consists of a quartz tube with an inner diameter of 10 mm and a wall thickness of 1 mm. A stainless steel rod with a diameter of 6 mm is inserted along the center of the quartz tube to act as the inner electrode. The DBD was generated in the reactor using a high voltage AC power source with a frequency of 10 kHz (CTP-2000K). The flow rate of N_2 or Ar was controlled using mass flow controllers (Beijing Sevenstar Flow Co.). The flow rate of N_2 or Ar was set at 30 ml min^{-1} . Typically, the as-prepared alkali or alkaline earth metal hydride samples (ca. 30 mg) were packed into the reactor discharge zone and different voltages (8-12 kV) were applied. The possible reaction products during the N_2 fixation process were monitored with an on-line mass spectrometer (MS, Hiden HPR20).

2) Thermal hydrogenation to ammonia

Thermal hydrogenation of fixed N in alkali or alkaline earth metal hydride samples to ammonia were conducted in the same DBD reactor. The reactor was heated by a furnace in a H_2 flow (30 ml min^{-1}) from room temperature to $450 \text{ }^\circ\text{C}$ with a ramping rate of $10 \text{ }^\circ\text{C min}^{-1}$. The exhaust gases were analyzed by either an on-line mass spectrometer (Hiden HPR20) or a conductivity meter (Mettler Toledo Sevenmulti). To quantify the amount of ammonia, the ammonia produced was trapped in a dilute sulfuric acid solution and the proton conductivity was recorded with time by a conductivity meter. The amount of NH_3 produced in the thermal hydrogenation process can be obtained from the decrease of proton conductivity. This conductivity method has been widely applied in ammonia synthesis rate

measurements.³

The principle of this method is shown below. When NH_3 was fed into a diluted H_2SO_4 solution, the reaction ($\text{NH}_3 + \text{H}^+ \rightarrow \text{NH}_4^+$) takes place. Due to the smaller limiting ionic conductivities of NH_4^+ than that of H^+ in water, the conductivity of solution will decrease. And the conductivity decreasing ($\Delta\kappa$) is proportional to the amount of ammonia (Δn_{NH_3}), i.e., $\Delta n_{\text{NH}_3} = a\Delta\kappa + b$. The coefficient a is defined as the ratio of amount of ammonia and conductivity change. The a value can be obtained by calibrating the ammonia synthesis rate over a reference catalyst (e.g., Ru/MgO) at its equilibrium conversion.⁴

3) Hydrolysis to ammonia

For certain samples, the thermal hydrogenation of fixed N to NH_3 under low temperatures is difficult. In these cases, hydrolysis of fixed N to NH_3 was conducted. The hydrolysis runs were carried out in a fixed-bed reactor connected to a conductivity meter to measure the amount of ammonia produced under room temperature. Water vapor entered the reactor and reacted with the sample to produce ammonia.

3. Supplementary Figures

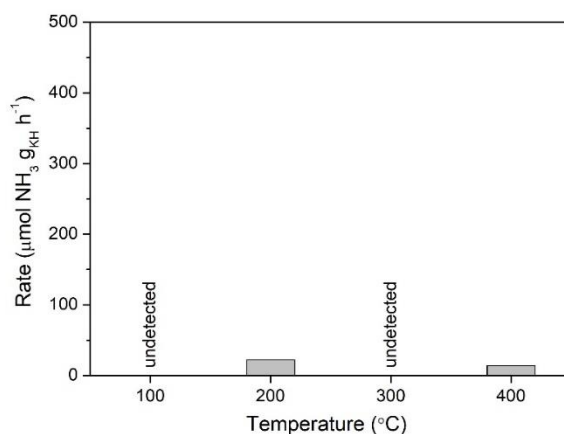


Figure S1 Thermal chemical looping NH_3 production rates as a function of temperature mediated by KH. The pressures of N_2 and H_2 are both fixed at 1 bar. The flow rate of N_2 or H_2 is 30 ml min^{-1} . The time of nitridation or hydrogenation steps is 30 min. Negligible amounts of ammonia were detected experimentally from KH.

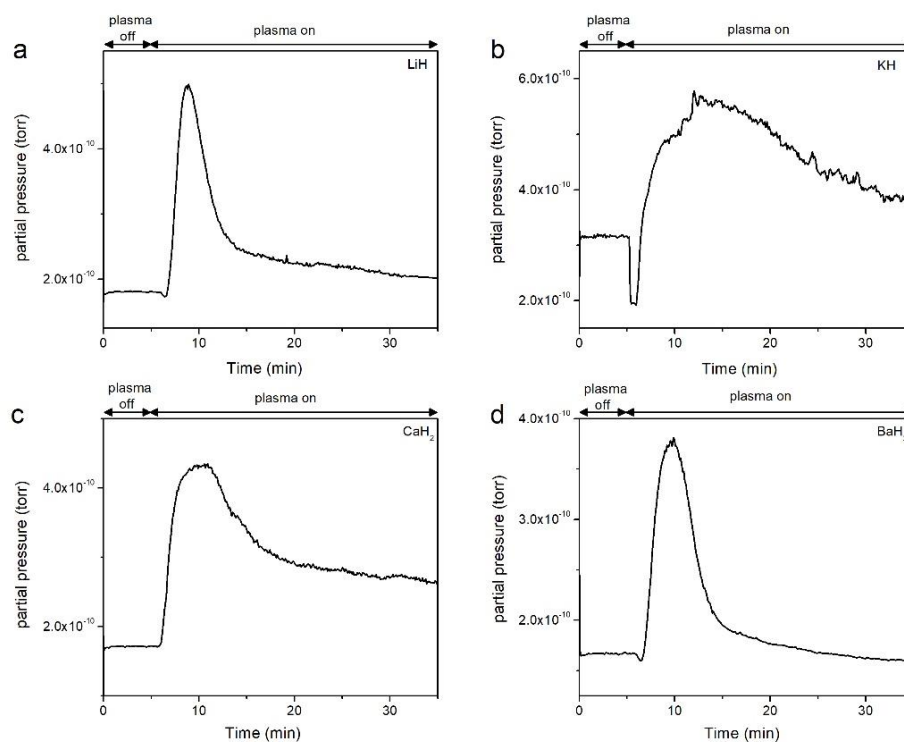


Figure S2 Time courses of H_2 MS signal ($m/z=2$) for LiH (a), KH (b), CaH_2 (c), and BaH_2 (d) samples under argon plasma. The plasma power is ca. 8 W.

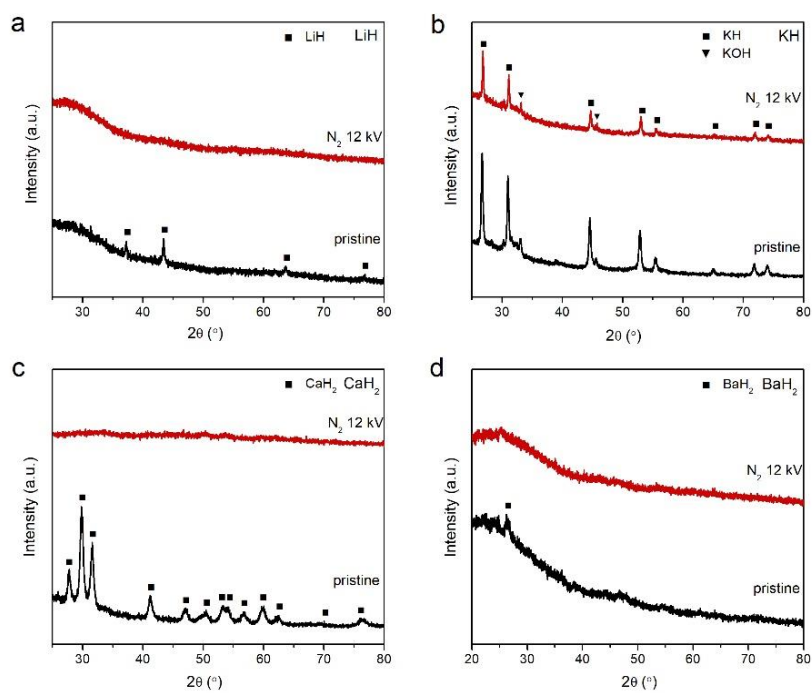


Figure S3 XRD patterns for the pristine alkali and alkaline earth metal hydrides and the samples collected after nitrogen plasma treatment. Voltage is 12 kV.

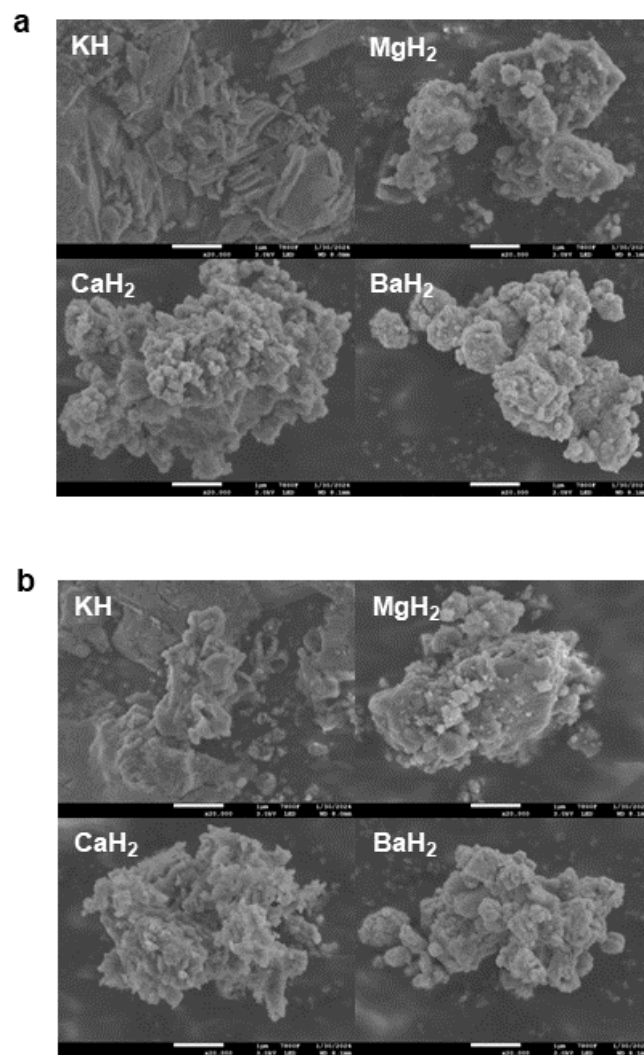


Figure S4 SEM images of pristine (a) and nitrogen plasma-treated (b) hydride samples.

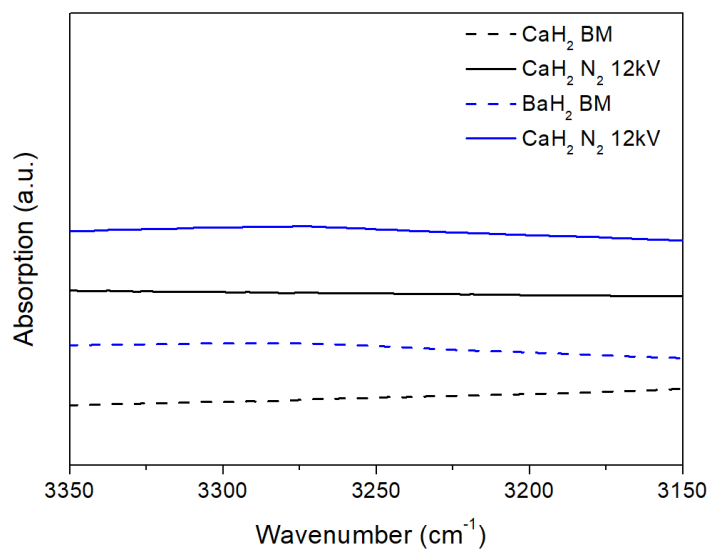


Figure S5 FTIR spectra for the CaH₂ and BaH₂ samples collected after nitrogen plasma treatment. There are no significant N-H vibrations on these samples.

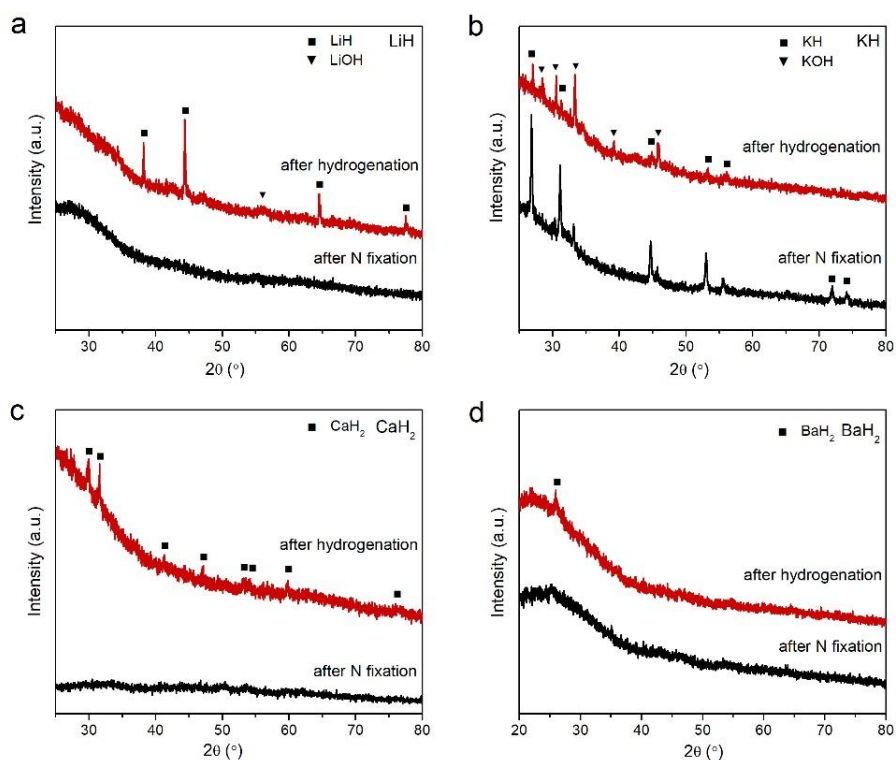


Figure S6 XRD patterns for samples collected after thermal hydrogenation tests. The formation of KOH is probably due to contamination of the sample by oxygen or moisture during the handling and the reaction process.

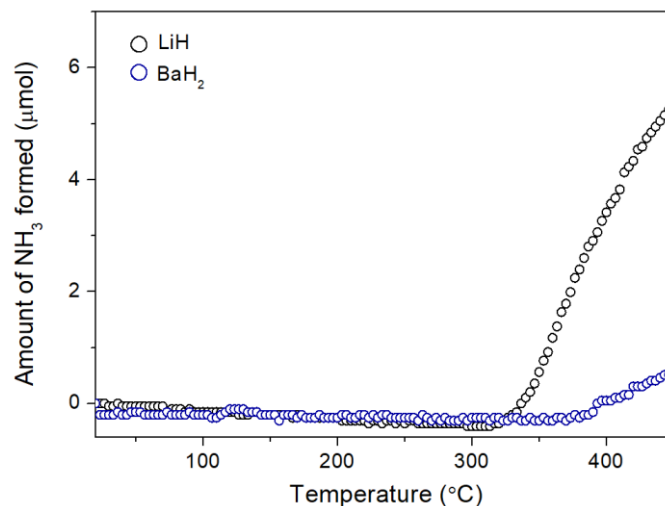


Figure S7 Temperature-programmed hydrogenation (TPH) profiles of conductivity decrease during the hydrogenation of the nitrogen plasma-treated LiH and BaH₂ samples. Sample masses of LiH and BaH₂ are 10 and 30 mg, respectively. P_{H₂} is 1 bar. H₂ flow rate is 30 mL min⁻¹.

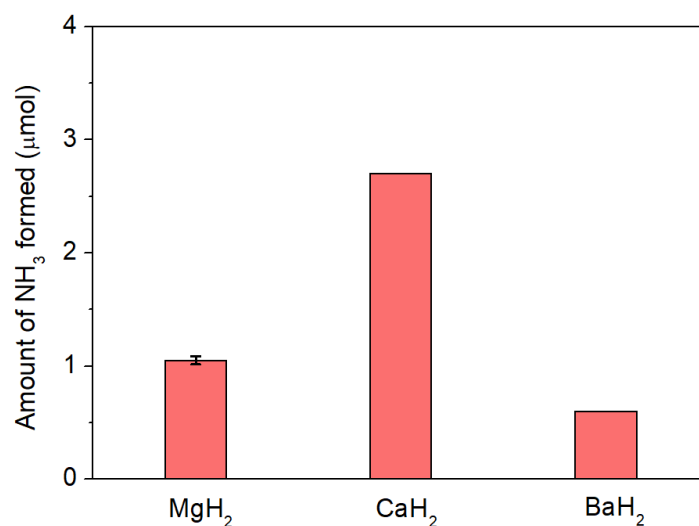


Figure S8 The amounts of fixed nitrogen by nitrogen plasma-treated MgH₂, CaH₂, and BaH₂ samples determined by hydrolysis reaction, respectively. Error bars represent the standard deviation from three independent measurements.

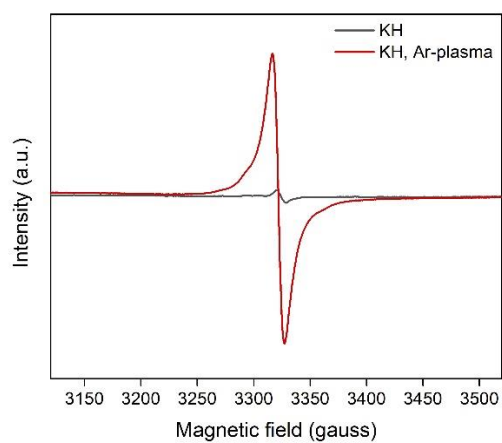


Figure S9 Room-temperature EPR spectra of the pristine KH and the sample collected after Ar plasma treatment.

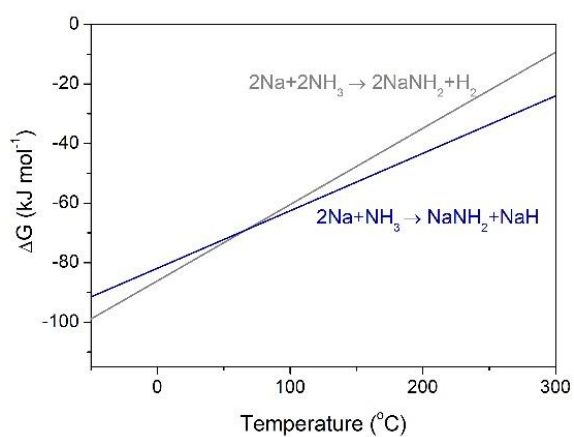


Figure S10 Temperature dependences of ΔG for reactions of Na and NH_3 to form different products. The enthalpies of NaH and NaNH_2 are taken from the literature.⁵ The entropies of solids are not considered.

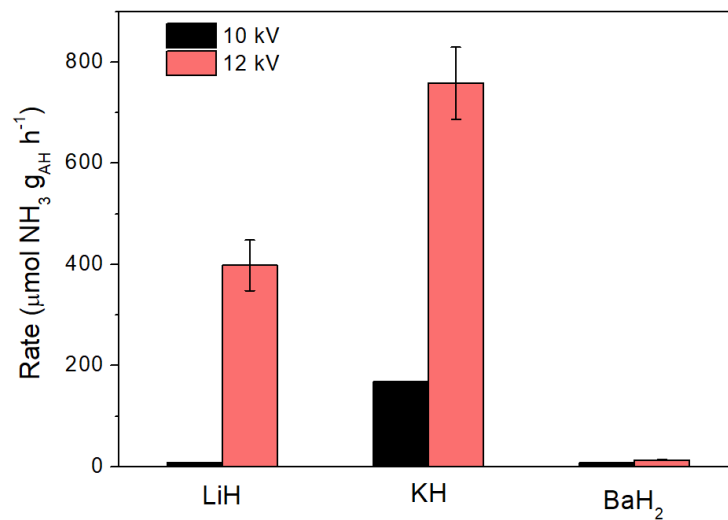


Figure S11 Voltage-dependent ammonia production rates of LiH, KH, and BaH₂. Error bars represent the standard deviation from three independent measurements.

Table S1 The lattice energies for a series of alkali and alkaline earth metal hydrides.⁶

Metal hydride	Lattice energy (kJ/mol)
LiH	858
NaH	782
KH	699
MgH ₂	2791
CaH ₂	2410
BaH ₂	2171

References

1. Y. Q. Guan, C. W. Liu, Q. R. Wang, W. B. Gao, H. A. Hansen, J. P. Guo, T. Vegge and P. Chen, *Angew. Chem. Int. Ed.*, 2022, e202205805.
2. R. X. Wang, Y. W. Yang, S. B. Chen, H. Jiang and P. Martin, *IEEE Trans. Plasma Sci.*, 2021, **49**, 2210-2216.
3. a) R. Kojima, K. Aika, *Appl. Catal. A* 2001, **218**, 121; b) D. McKay, D. H. Gregory, J. S. J. Hargreaves, S. M. Hunter, X. Sun, *Chem. Commun.* 2007, **29**, 3051; c) W. Gao, J. Guo, P. Wang, Q. Wang, F. Chang, Q. Pei, W. Zhang, L. Liu, P. Chen, *Nat. Energy* 2018, **3**, 1067.
4. H. Wu, L. Yang, J. Wen, Y. Xu, Y. Cai, W. Gao, Q. Wang, Y. Guan, S. Feng, H. Cao, T. He, L. Liu, S. Zhang, J. Guo and P. Chen, *Adv. Energy Mater.*, 2023, **13**, e2300722.
5. F. Chang, Y. Q. Guan, X. H. Chang, J. P. Guo, P. K. Wang, W. B. Gao, G. T. Wu, J. Zheng, X. G. Li and P. Chen, *J. Am. Chem. Soc.*, 2018, **140**, 14799-14806.
6. S. Harder, *Chem. Commun.*, 2012, **48**, 11165-11177.