

## Supporting Information for

### Self-assembling solid-state hydrogen source for drylands

#### photocatalytic hydrogen production

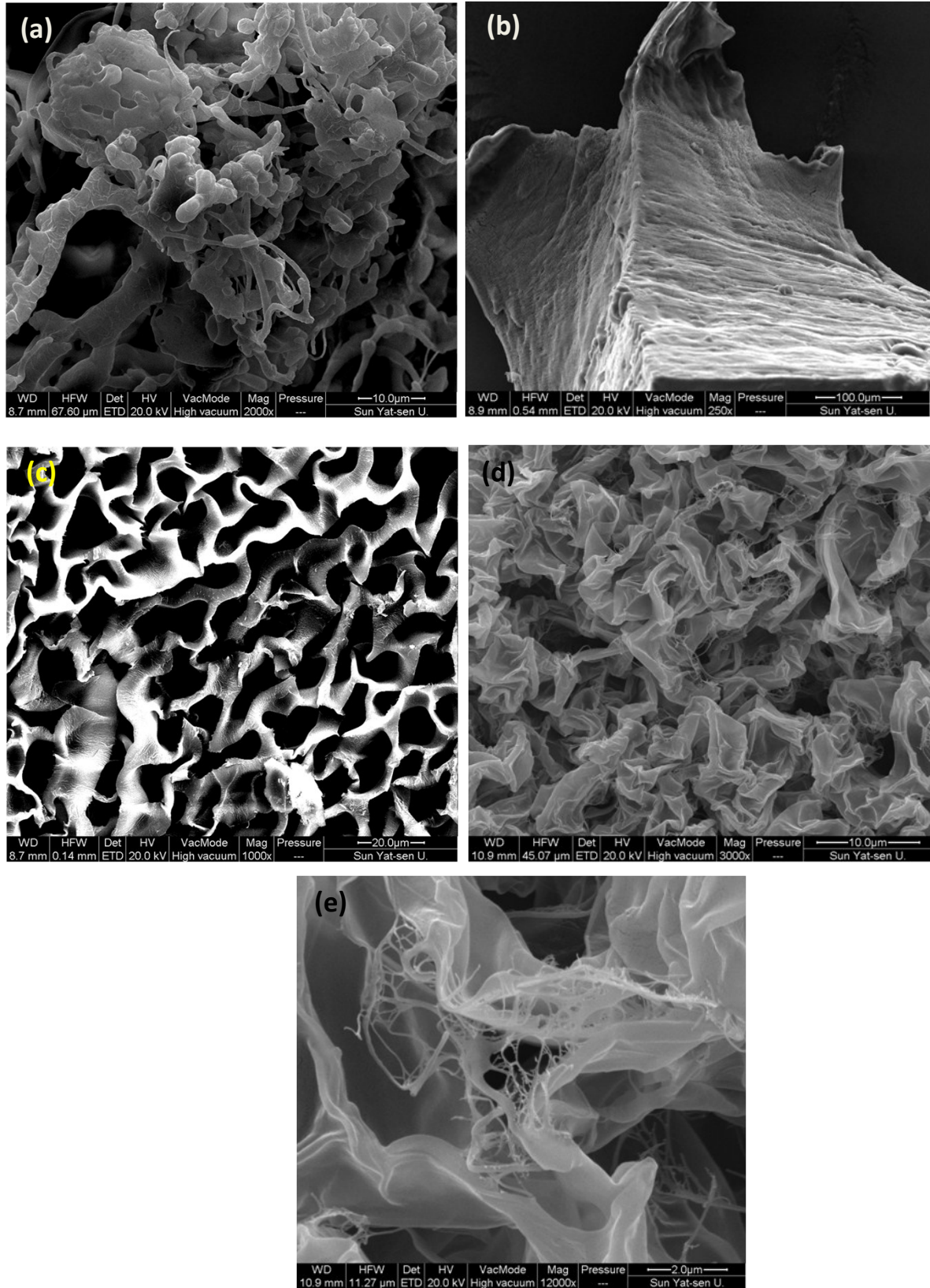
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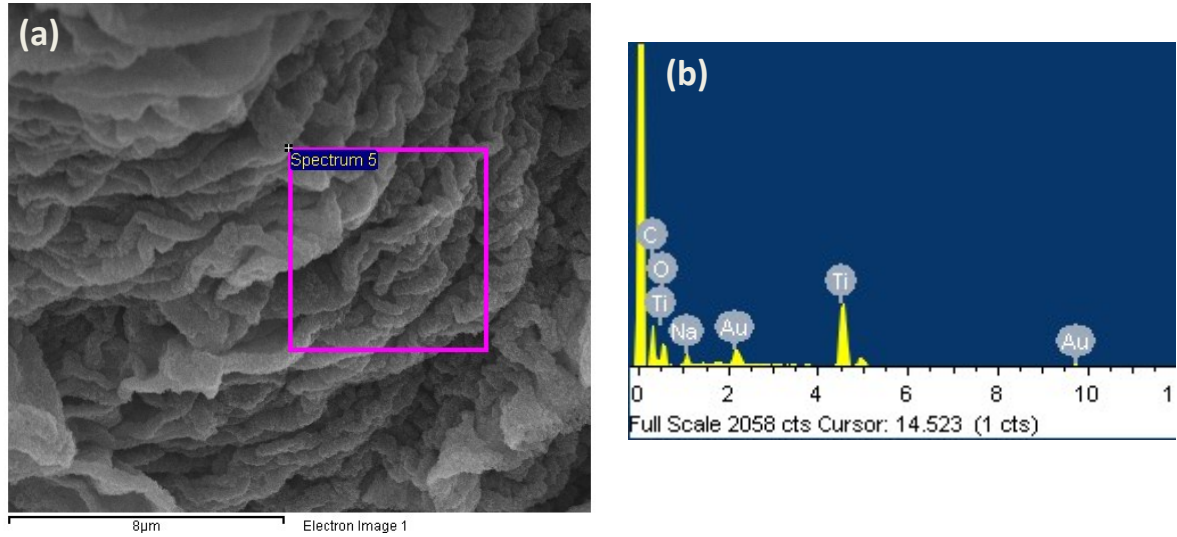
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**Fig. S1.** SEM images of AAC soaked in water for **(a)** 5 h. **(b)** 16 h. **(c)** 27 h. **(d-e)** SEM images of AAC hydrogel after repeated water absorption and water release for six times.



**Fig. S2. (a)** SEM image of composite AAC/ Pt/TiO<sub>2</sub>. **(b)** Corresponding EDX spectrum. **(c)** Corresponding elemental analysis.



(c)

Element	Weight %	Atomic %
C K	30.83	48.58
O K	32.27	38.18
Na K	3.15	2.60
Ti K	24.73	9.77
Au M	9.02	0.87
Totals	100.00	

**Fig. S3.** (a-b) TEM image of Pt/TiO<sub>2</sub>. (c) TEM image of the NiB products, the inset is the corresponding SAED image of NiB. (d) XRD pattern of NiB. (e) Low-powered TEM image of NiB/CdS. (f) High-powered TEM image of NiB/CdS.

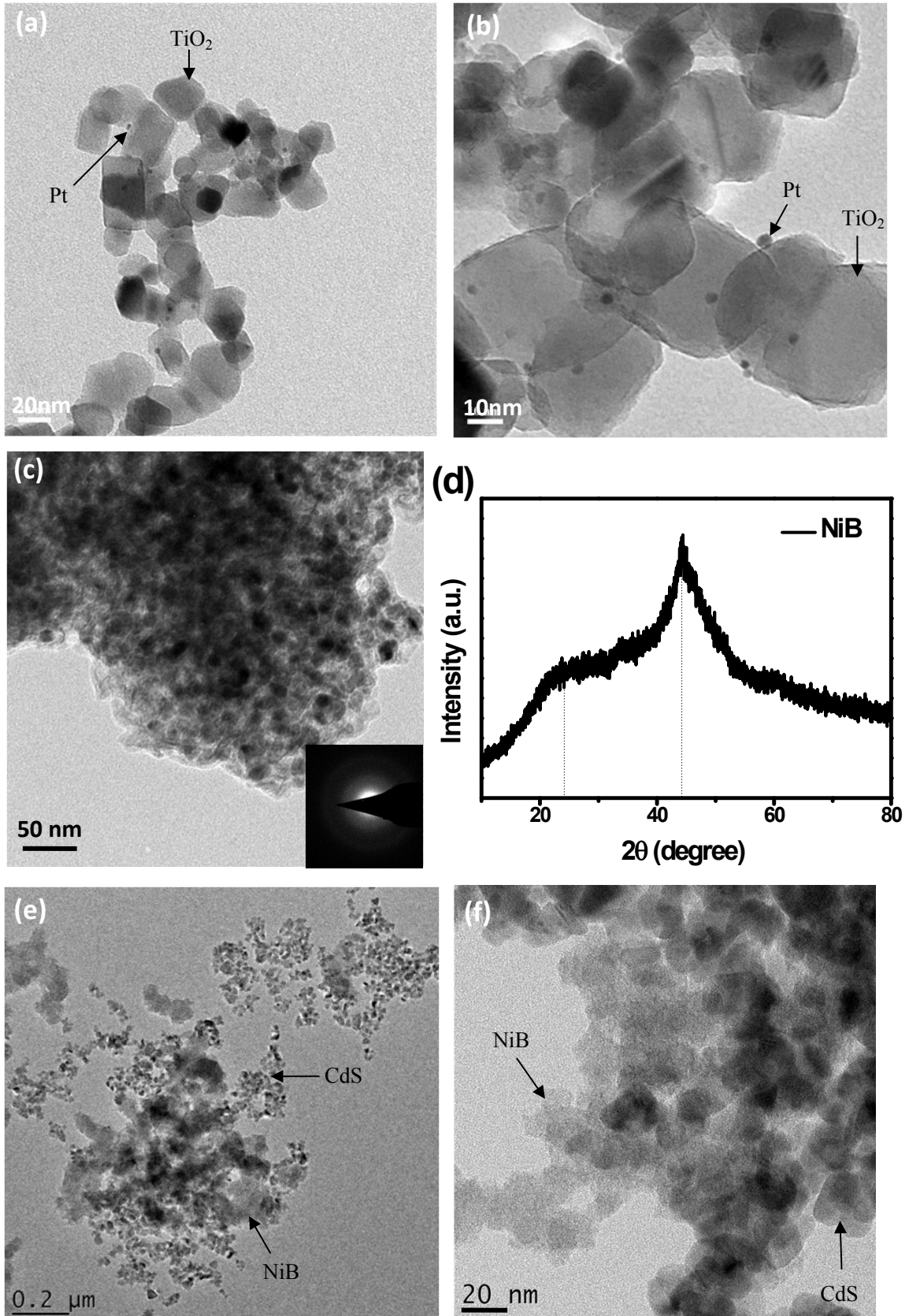
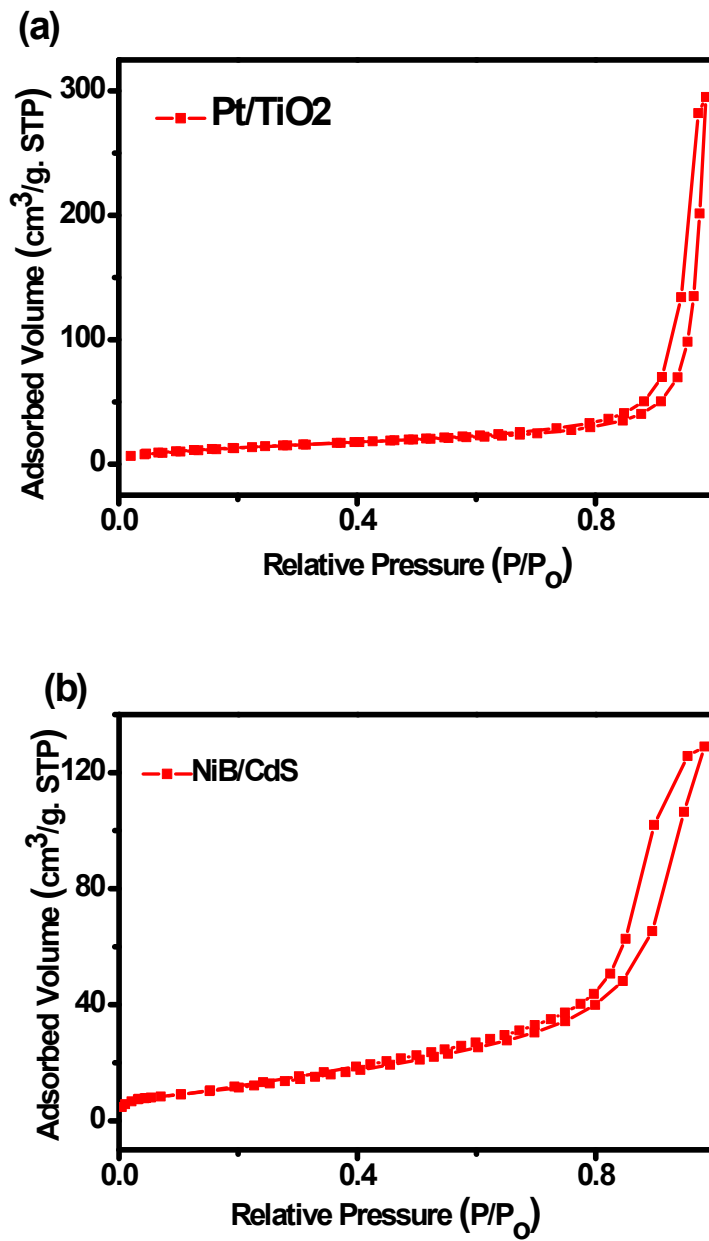


Fig. S4. BET of (a) Pt/TiO<sub>2</sub>, (b) NiB/CdS.



### S5. Calculation of STH

The STH were evaluated by using AM 1.5G (irradiation area is 10.18 cm<sup>2</sup> and the light power density is 100 mW/cm<sup>2</sup>) solar simulator as the light source with 5 mg Pt/TiO<sub>2</sub>. After 5h of illumination, 365 μmol H<sub>2</sub> was detected by GC. The total input solar energy was  $E_{solar} = 5 \times 3600 \times 10.18 \times 100 \times 10^{-3} = 18324 J$ . The energy generated by water splitting is

$$E_F = 365 \times 10^{-6} \times 6.02 \times 10^{23} \times 2.46 \times 1.609 \times 10^{-19} = 86.97 J, \text{ 2.46 eV is}$$

the free energy of water splitting.

$$STH = \frac{\text{Energy of generation of hydrogen by water splitting}}{\text{Solar energy irradiating the reaction cell}} \times 100\%$$
$$= \frac{E_F}{E_{solar}} \times 100\% = \frac{86.97}{18324} \times 100\% = 0.475\%$$

## **S6. The interaction of Pt/TiO<sub>2</sub> and NiB/CdS during the catalysis of H<sub>2</sub>O.**

In the case of Pt/TiO<sub>2</sub> photocatalyst, generally, Pt was used as co-catalyst which plays a role as electron trap to prevent the electron–hole combination. Consequently, photo-excited electrons and holes were driven to react with adsorbed agent, leading to the photocatalytic reaction.<sup>1</sup> That is, after photoexcitation, free electrons and trapped electrons exist in the bulk of TiO<sub>2</sub>. These electrons can be quickly transferred to the Pt particles and consumed by reduction reaction.<sup>2</sup>

As elaborated in Li. *et al's* work,<sup>3</sup> Photoluminescence (PL) spectroscopy and Room-temperature EPR spectra have both explained the interaction of NiB/CdS. PL spectroscopy is a physical process that helps to identify the electronic structure of samples. Using laser-excitation at a wavelength of 325 nm, the fluorescence emissions were notably quenched after loading NiB as the cocatalyst, indicating that photoinduced electrons can transfer from CdS to NiB. This transferal suppresses electron-hole recombination and improves the photocatalytic activity. Moreover, room-temperature EPR spectra were recorded to test electron-electron interaction between CdS and NiB. The spectra of NiB/CdS showed well-resolved six-coordinate “EPR-silent” Ni<sup>2+</sup> complexes. These complexes may have arisen from the fact that Ni<sup>2+</sup> can exist in many coordination environments (e.g. tetrahedral or octahedral) and often exhibits complicated intermolecular electron–electron interactions that arise from spin–orbit and spin–spin coupling. CdS and NiB alone exhibited no signal, indicating that electrons were transferred from CdS to NiB.

The presence of cocatalysts Pt and NiB resulted in powerful trapping electrons ability and highly adsorption of protons.

### **References**

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## **S7. The magnetic property of Ni in the NiB and its effects on the catalytic performance.**

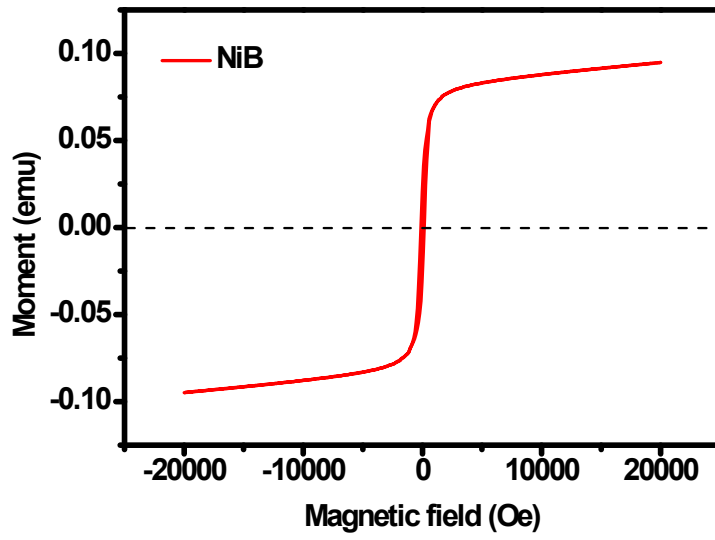
Magnetic Property Measurement System (MPMS XL-7) from Quantum Design is employed to measure the magnetic property of the as-synthesized amorphous NiB and catalyst NiB/CdS, both as a function of magnetic field  $M(H)$  at 300 K. The mass of NiB and NiB/CdS is 21.9 mg and 50.5 mg, respectively. As shown in Fig.S7 (a), the coercivity force was almost ignored at 300 K, which indicate that NiB was superparamagnetic and the saturation magnetization  $M_s$  was calculated about 3.74 emu/g, which is relatively small.<sup>1,2</sup> After combined with CdS, the magnetic became even smaller, as shown in Fig.S7 (b), has paramagnetic behavior, which can be contributed to the relatively low content of NiB in NiB/CdS. Actually, according to Zhang. *et al's* work,<sup>2</sup> the photo-catalyst with the larger  $M_s$  value has stronger Hall effects on the photo-generated electrons. Higher Lorentz force could slow down the migration speed of electrons and aggravate the deflection of electrons from their original transfer path, however, only an appropriate magnetic nature can effectively enhance the electron-transfer rate and promote the reaction of water electrolysis. Stated thus, the magnetic property of Ni in the NiB has little effect on the NiB/CdS's catalytic performance.

### **References**

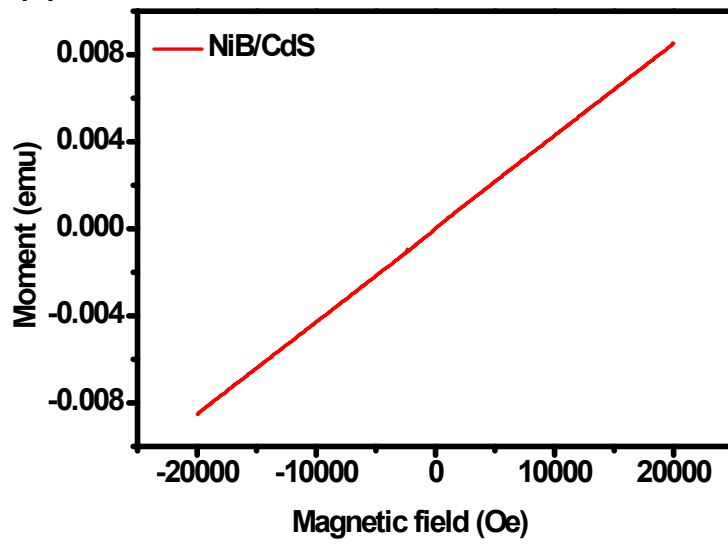
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(a)

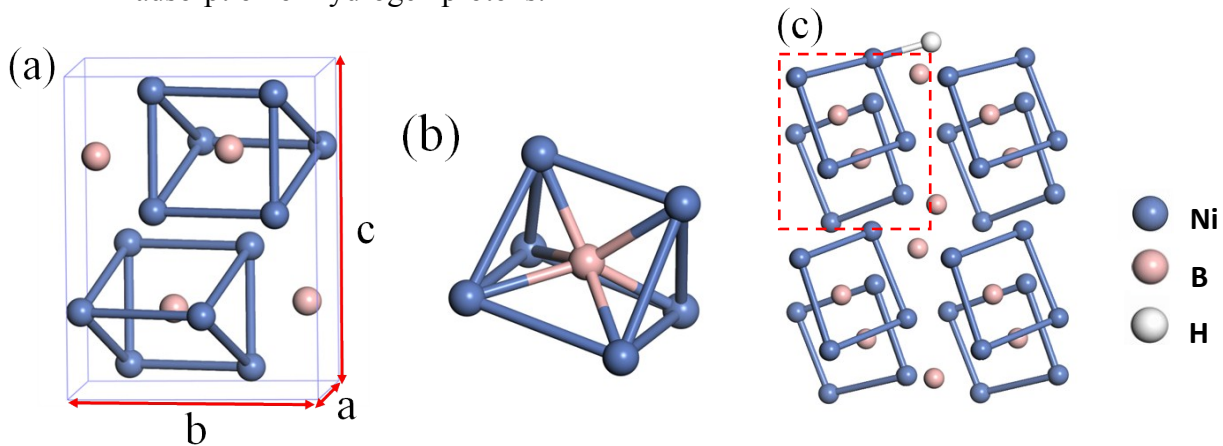


(b)



### S8. Active center of NiB/CdS for the H<sub>2</sub>O decomposition.

From Li. *et al*'s theoretical calculation work, we know that although the as-prepared nickel boride is amorphous (NiB), the amorphous shows short-range order and we can calculate the structure of Ni<sub>3</sub>B.<sup>1</sup> Analysis from the crystal structure, Ni<sub>3</sub>B has an orthorhombic structure and the structure's symmetry belongs to space group Pbnm.<sup>2</sup> As shown below, a unit cell contained 4 B atoms and 12 Ni atoms. The local environments around a B atom in Ni<sub>3</sub>B were a trigonal prism of 6 Ni atoms, that is NiB is a cage like structure with B atom as the center and Ni atoms exposed to the outside. Based on the above analysis, we think the active center of NiB/CdS for the H<sub>2</sub>O decomposition is the Ni atoms. Exposed nickel atoms have strong ability of adsorption of hydrogen protons.



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- 2 J. Ajao, S. Hamar-Thibault, J. Thibault-Desseaus, *J. Mater. Sci.*, 1989, **24**, 3647-3659.