Supplementary Information

ZIF-8 Immobilized Ni(0) Nanoparticles: Highly Effective Catalysts for Hydrogen Generation from Hydrolysis of Ammonia Borane

Pei-Zhou Li,[a,b] Kengo Aranishi,[a] and Qiang Xu*[a,b]

[a]*National Institute of Advanced Industrial Science and Technology (AIST), Ikeda, Osaka 563-8577, Japan. Fax: +81-72-751-9629; Tel: +81-72-751-9562; E-mail: q.xu@aist.go.jp*
[b]*Graduate School of Engineering, Kobe University, Nada Ku, Kobe, Hyogo 657-8501, Japan.*

Experimental section

General experimental information: All the reagents and solvents employed were commercially available and used without further purification: zinc(II) nitrate tetrahydrate ($Zn(NO_3)_2 \cdot 4H_2O$, 98%, Merck), 2-methylimidazole (>97.0%, TCI), aqueous ammonia (28%, Wako), ammonia borane (AB, NH_3BH_3, 97%, JSC Aviabor), bis(cyclopentadienyl)nickel(II) (nickelocene, 99%, Azmax). Powder X-ray diffraction (XRD) measurements were performed on a Rigaku 2000 diffractometer at 40 kV and 40 mA for Cu Kα radiation (λ = 1.5406 Å). The nitrogen sorption isotherms were measured on an automatic volumetric adsorption equipment (Belsorp mini II). X-ray photoelectron spectroscopic (XPS) analyses were carried out on a Shimadzu ESCA-3400 X-ray photoelectron spectrometer. The Ni content of each sample was analyzed by means of an inductively coupled plasma (ICP) spectrometer (Rigaku, CIROS-120EOP). Transmission electron microscope (TEM, FEI TECNAI G2) equipped with energy dispersed X-ray detector (EDS) was applied for the detailed microstructure and composition information for the prepared samples.

Preparation of Ni@ZIF-8: ZIF-8 was synthesized according to the literature.[1] The sample of ZIF-8 used for loading Ni nanoparticles was pretreated as follows: As-synthesized ZIF-8 was washed by distilled water and methanol for 3 times, immersed in methanol at ambient temperature for 48 h, and dried by heating at 120 °C for over 6 h under vacuum, and then the white powder of ZIF-8 was obtained.

Chemical vapor deposition (CVD) method[2,3] for the preparation of ZIF-8 immobilized Ni NPs: In a typical synthesis, the samples of pretreated ZIF-8 (100 mg, 0.26 mmol) and $Ni(cp)_2$ (200 mg, 1.05 mmol) in separate small glass vessels were placed together in a Schlenk tube. After evacuating for 30 min at room temperature, the reaction tube was sealed under static vacuum and heated to 110 °C for 24 h, and then the intermediate sample of ZIF-8-loaded $Ni(cp)_2$ ($CVD\text{-}Ni(cp)_2$@ZIF-8, ~205 mg) in dark brown was obtained. Then the sample of $CVD\text{-}Ni(cp)_2$@ZIF-8 was treated in a H_2/Ar flow (50 mol% H_2, 50 mL·min^{-1}) at 300 ºC for 3 h to yield black CVD-Ni@ZIF-8 (**1a**, ~125 mg, 19.0 wt% Ni loading based on ICP result and yield = 37.7 % based on Ni). Other samples of ZIF-8 immobilized Ni(0) catalysts with the CVD method

were prepared in the similar procedure except for the starting $Ni(cp)_2$/ZIF-8 weight ratios. For **1b** (obtained ~121 mg, 16.7 wt% Ni loading based on ICP result and yield = 64.5 % based on Ni), the weight ratio of starting materials (ZIF-8/$Ni(cp)_2$) was 100 mg/100 mg and the yield of **3b** was ~190 mg. For **1c** (obtained ~110 mg, 8.6 wt% Ni loading based on ICP result and yield = 60.6 % based on Ni), the weight ratio of starting materials (ZIF-8/$Ni(cp)_2$) was 50 mg/100 mg and the yield of **3c** was ~145 mg.

Chemical liquid deposition (CLD) method[4,5] for the preparation of ZIF-8 immobilized Ni NPs: In a typical synthesis, the sample of pretreated ZIF-8 (70 mg, 0.18 mmol) in 10 mL of methanol was mixed with $Ni(cp)_2$ (100 mg, 0.53 mmol) in 10 mL of diethylether. After vigorous stirring for 3 h, removing the solvents by natural evaporation for about 24 h at room temperature and evacuating at 60 ^oC for 4 h, the intermediate sample of ZIF-8-loaded $Ni(cp)_2$ (CLD-$Ni(cp)_2$@ZIF-8, ~160 mg) in dark brown was obtained. Then the sample of CLD-$Ni(cp)_2$@ZIF-8 was treated in a H_2/Ar flow (50 mol% H_2, 50 mL·min^{-1}) at 300 ºC for 3 h to yield black CLD-Ni@ZIF-8 (**2a**, ~91 mg, 22.0 wt% Ni loading based on ICP result and yield = 63.5 % based on Ni). Other ZIF-8 immobilized Ni(0) catalysts with the CLD method were prepared in the similar procedure except for the $Ni(cp)_2$/ZIF-8 weight ratios. For **2b** (obtained ~94 mg, 14.3 wt% Ni loading based on ICP result and yield = 66.1 % based on Ni), the weight ratio of starting materials (ZIF-8/$Ni(cp)_2$) was 80 mg/65 mg and the yield of **4b** was ~142 mg. For **1c** (obtained ~99 mg, 8.4 wt% Ni loading based on ICP result and yield = 80.5 % based on Ni), the weight ratio of starting materials (ZIF-8/$Ni(cp)_2$) was 90 mg/33 mg and the yield of **4c** was ~121 mg.

It should be noted that some percents of $Ni(cp)_2$, as a volatile molecule, can vaporize and be taken away by the H_2/Ar gas flow during the reduction process at 300 ºC and the ICP measurement is needed for getting the accurate amount of Ni loading for each prepared sample.

The stability of host ZIF-8 framework: The prepared samples of CVD-/CLD-$Ni(cp)_2$@ZIF-8 and CVD-/CLD-Ni@ZIF-8 before and after hydrolysis of AB were characterized by powder XRD measurements. In powder XRD patterns for all the samples (See Fig. S1-S4), even for the samples of CVD-/CLD-Ni@ZIF-8 after the hydrolysis of AB (See Fig. S5-S6), the main reflection peaks in the range of 2θ = 5-30 deg were consistent very well with those of pristine ZIF-8, indicating that the framework of ZIF-8 is stable and maintains very well in the whole process of catalyst preparation and AB hydrolysis.

N_2 adsorption examination: N_2 adsorption examinations were carried out for the samples of ZIF-8, CVD-/CLD-$Ni(cp)_2$@ZIF-8, and CVD-/CLD-Ni@ZIF-8. Before the measurements, the samples of ZIF-8 and CVD-/CLD-Ni@ZIF-8 were pretreated by evacuating for 2 h at 120 ºC, and the samples of CVD-/CLD-$Ni(cp)_2$@ZIF-8 were pretreated by evacuating for 2 h at room temperature. As shown below (Fig. S7-S10), the surface area decreased obviously after $Ni(cp)_2$ loading, while the reduction of $Ni(cp)_2$ by H_2 resulted in increase of surface area. The BET surface area of ZIF-8 was 1443 m^2/g. The BET surface areas were 872, 881, and 1147 m^2/g for the

CVD-Ni(cp)$_2$@ZIF-8 samples **1a**, **1b**, and **1c**, and 621, 650, and 836 m^2/g for the corresponding intermediate CVD-Ni(cp)$_2$@ZIF-8 samples **3a**, **3b**, and **3c**, respectively. The BET surface areas were 856, 1060, and 1258 m^2/g for the CLD-Ni(cp)$_2$@ZIF-8 samples **2a**, **2b**, and **2c**, and 467, 689, and 943 m^2/g for the corresponding intermediate CLD-Ni(cp)$_2$@ZIF-8 samples **4a**, **4b**, and **4c**, respectively.

Catalytic activity characterization: The hydrolysis of AB can be briefly expressed as the formula: $NH_3BH_3 + 2H_2O = NH_4^+ + BO_2^- + 3H_2$.[6] The catalytic reactions were carried out at room temperature using a two-necked round bottom flask.[6,7] One neck of the flask is connected to a gas burette to monitor the volume of gas evolution, and the other is used for introducing the reactants into the flask. The catalytic hydrogen generation from hydrolysis of AB was initiated by mixing the aqueous suspension of Ni@ZIF-8 (10 mg in 1 mL of H_2O) and aqueous AB (63.5 mg in 1 mL of H_2O) in the flask. Fig. S11 and S12 show hydrogen generation from AB catalyzed by the synthesized CVD-Ni@ZIF-8 and CLD-Ni@ZIF-8 with different Ni loadings. The catalytic activity of the samples prepared in the same method is nearly proportional to Ni loading.

Durability/stability of Ni@ZIF-8 catalysts: After the hydrogen generation reaction was completed, another equivalent of AB (63.5 mg) was added into the reaction system and the released gas was monitored by the gas burette. As shown in Fig. S13 for **1a**, and S14 for **2a**, even after 5 runs of hydrolysis, no significant decrease in activity was observed for both catalysts, indicating the Ni@ZIF-8 samples have high durability/stability in the hydrogen generation from hydrolysis of AB under ambient atmosphere.

X-ray photoelectron spectroscopic (XPS) analyses: XPS measurements were carried out on a Shimadzu ESCA-3400 X-ray photoelectron spectrometer using an Mg Kα source (10 kV, 10 mA). The Ar sputtering was carried out under the conditions of background vacuum of 3.4×10^{-6} Pa, sputtering acceleration voltage of 0.5 kV and sputtering current of 10 mA (See Fig. S15 for **1a**, S16 for **2a**).

Inductively coupled plasma (ICP) analyses: ICP measurements were performed to determine the loadings of metals in the samples and the results are shown in Table S1.

Table S1. ICP analyses for the samples.

Sample	Zn content (%)	Ni content (%)
1a	18.8	19.0
1b	19.7	16.7
1c	22.1	8.6
2a	18.3	22.0
2b	23.5	14.3
2c	25.6	8.4

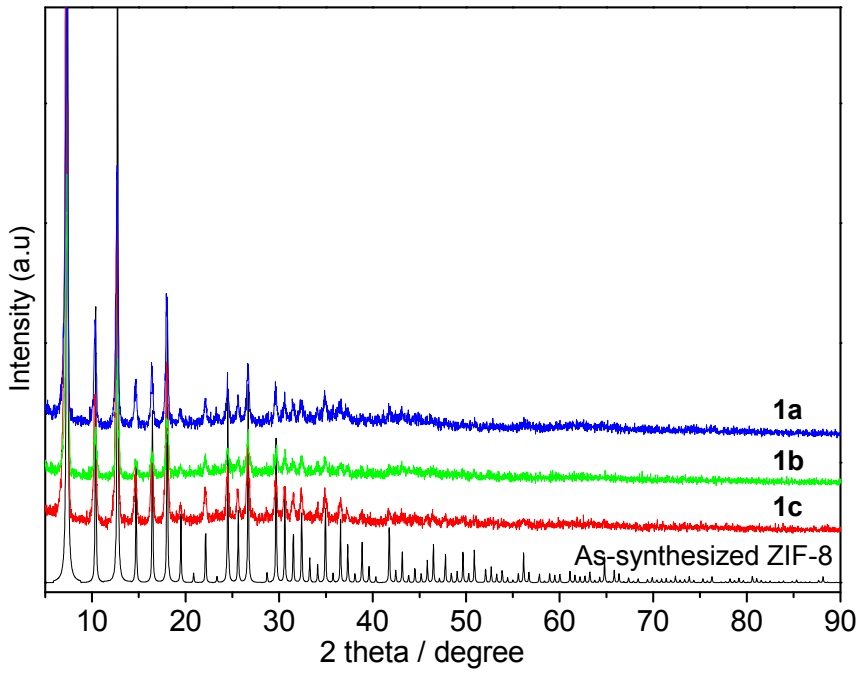

Fig. S1. Powder XRD patterns of CVD-Ni@ZIF-8 with different Ni loadings (1**a-c**).

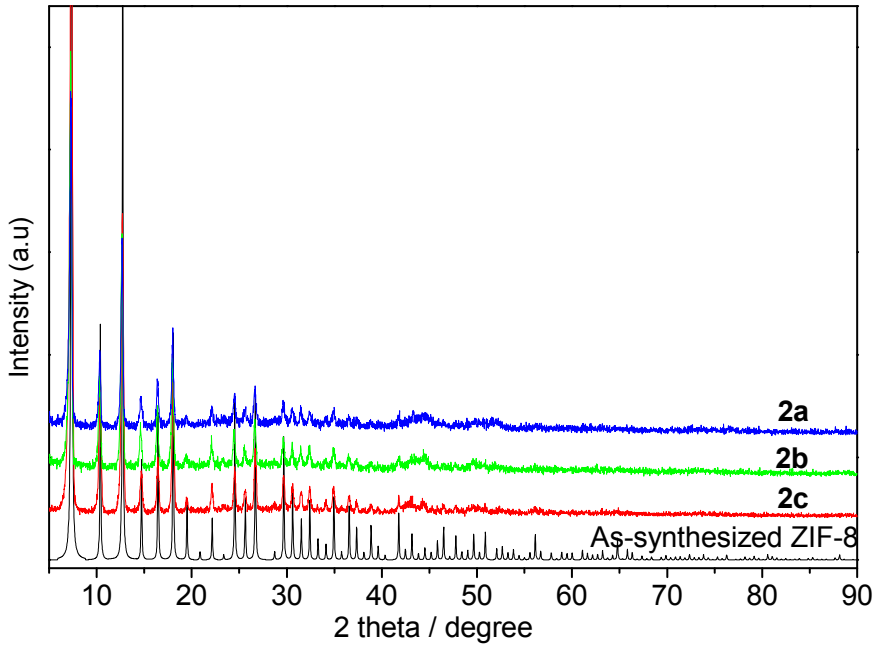

Fig. S2. Powder XRD patterns of CLD-Ni@ZIF-8 with different Ni loadings (2**a-c**).

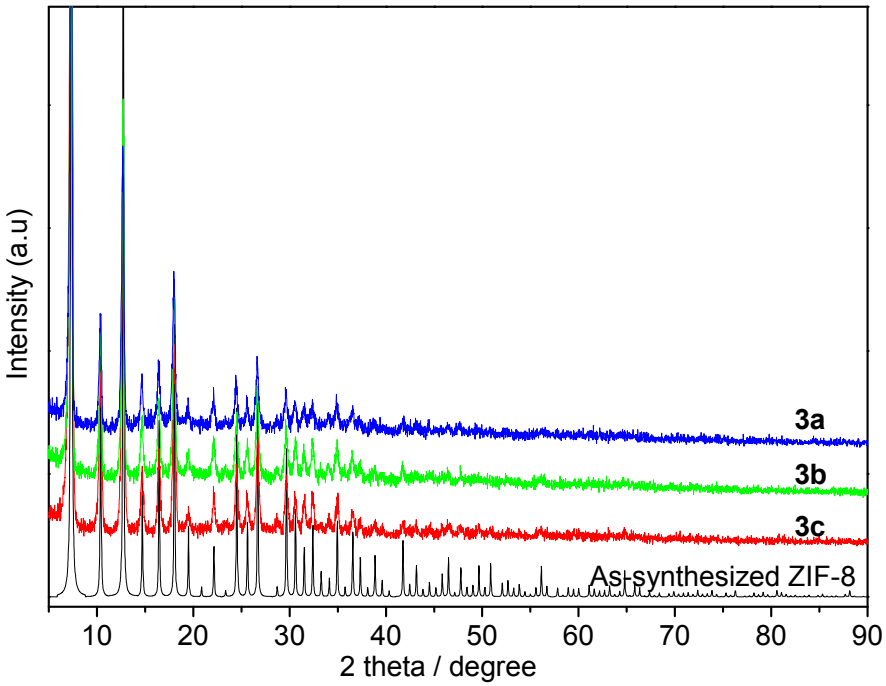

Fig. S3. Powder XRD patterns of CVD-Ni(cp)$_2$@ZIF-8 prepared with different Ni(cp)$_2$/ZIF-8 weight ratios (**3a-c**).

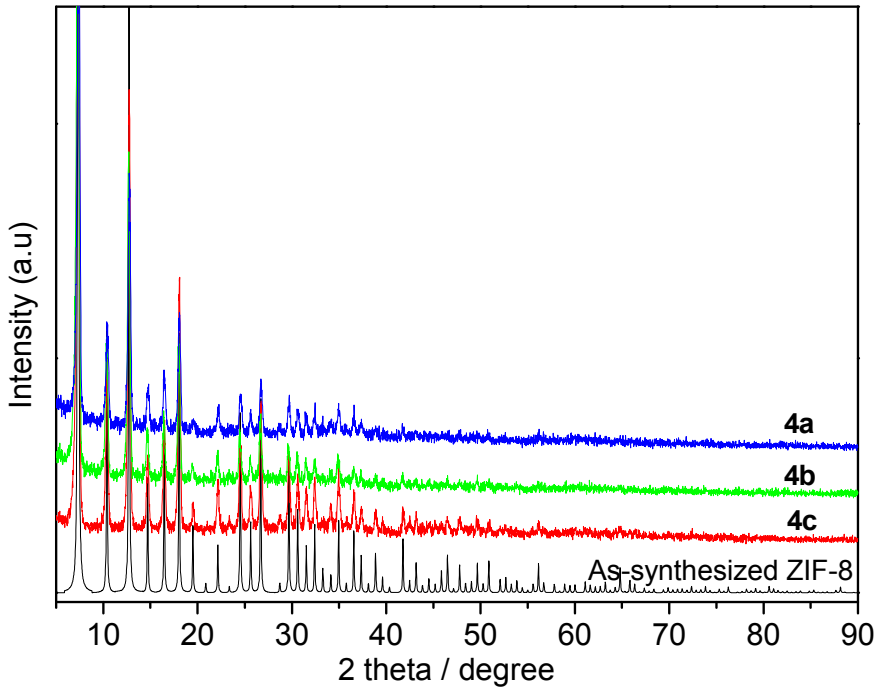

Fig. S4. Powder XRD patterns of CLD-Ni(cp)$_2$@ZIF-8 prepared with different Ni(cp)$_2$/ZIF-8 weight ratios (**4a-c**).

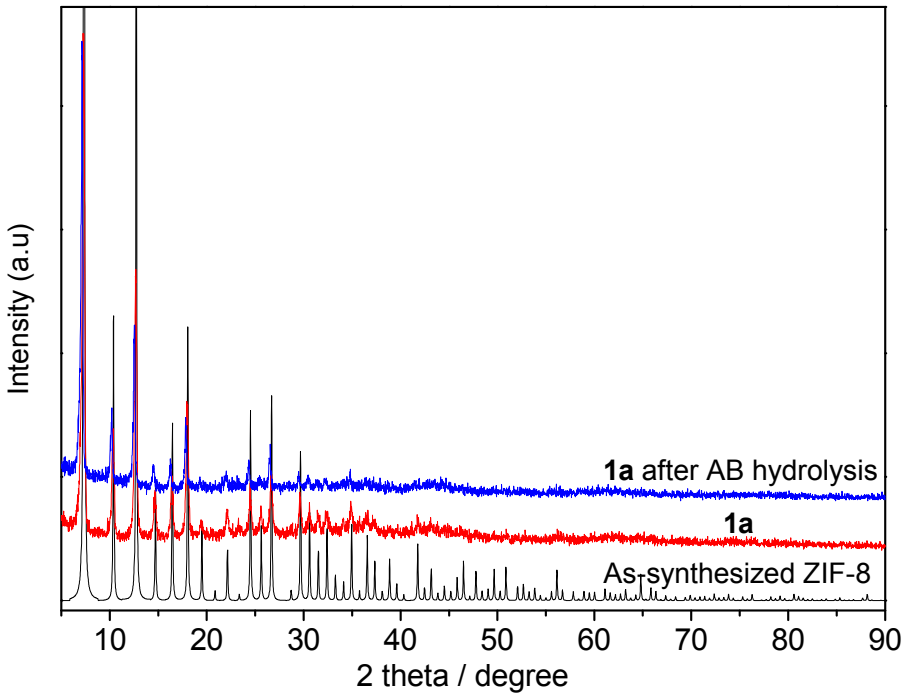

Fig. S5. Powder XRD of CVD-Ni@ZIF-8 (**1a**) before and after the catalytic hydrolysis of AB.

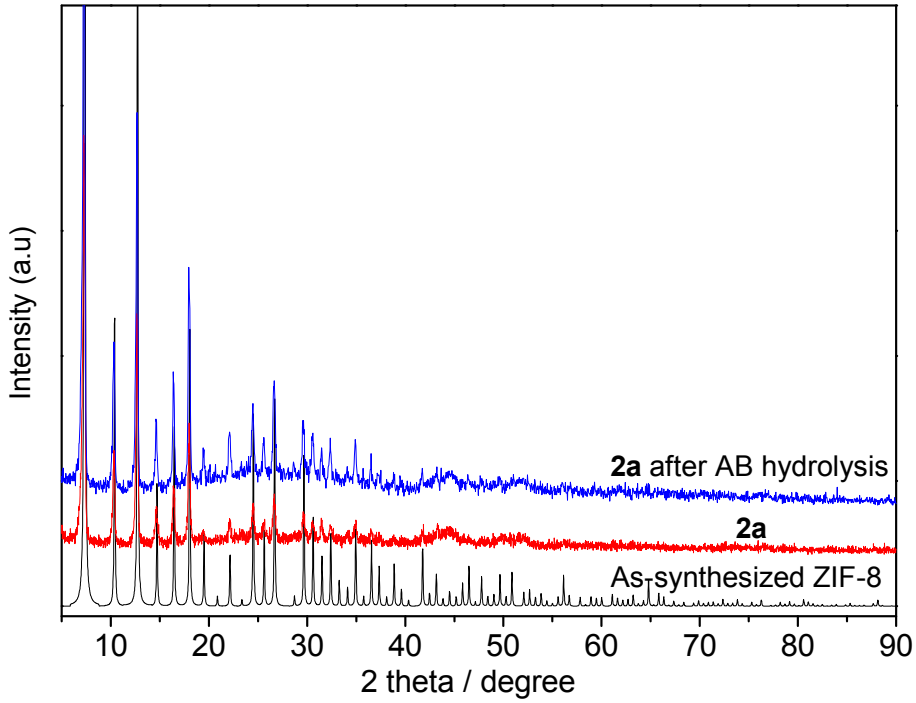

Fig. S6. Powder XRD of CLD-Ni@ZIF-8 (**2a**) before and after the catalytic hydrolysis of AB.

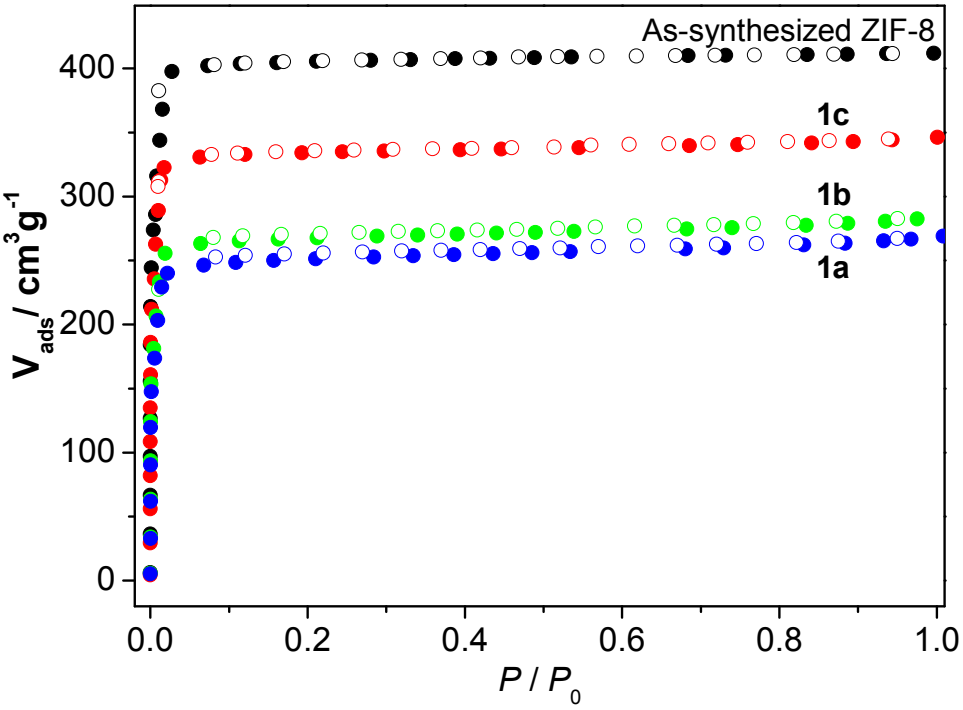

Fig. S7. N_2 adsorption of the CVD-Ni@ZIF-8 samples with different Ni loadings (**1a-c**).

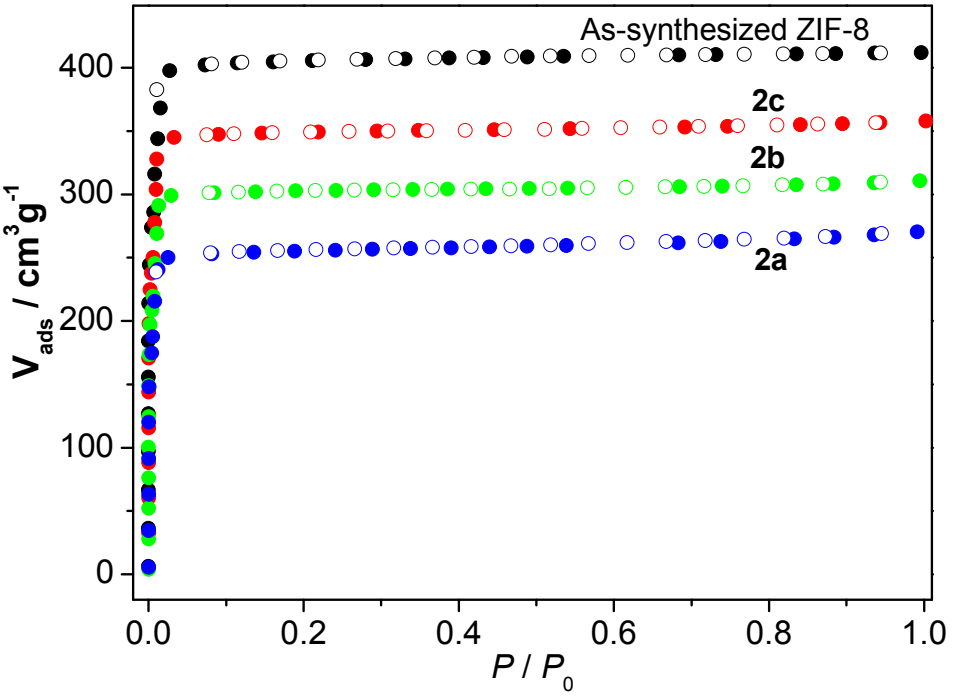

Fig. S8. N_2 adsorption of the CLD-Ni@ZIF-8 samples with different Ni loadings (**2a-c**).

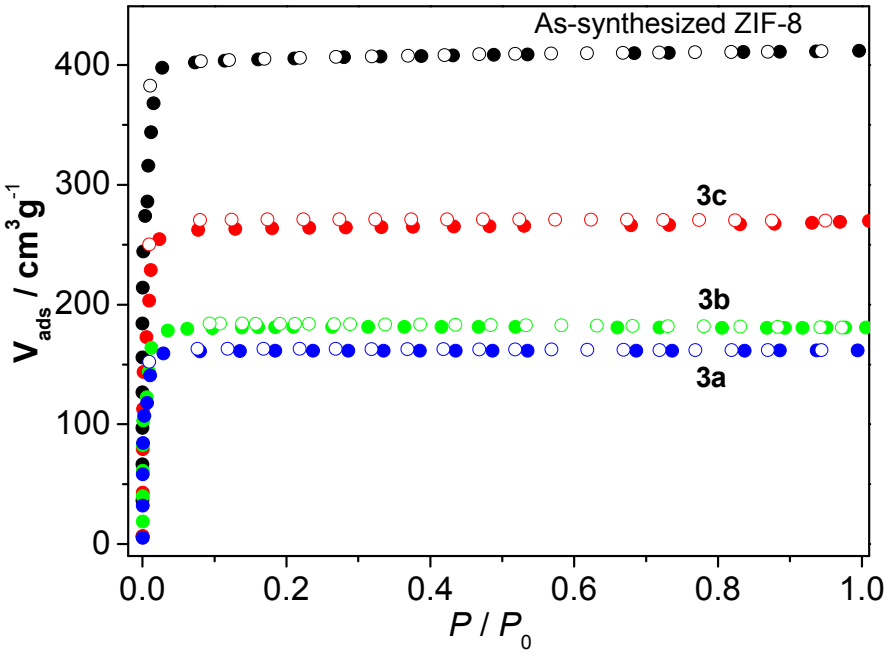

Fig. S9. N_2 adsorption of the CVD-Ni(cp)$_2$@ZIF-8 samples with different Ni(cp)$_2$/ZIF-8 weight ratios (**3a-c**).

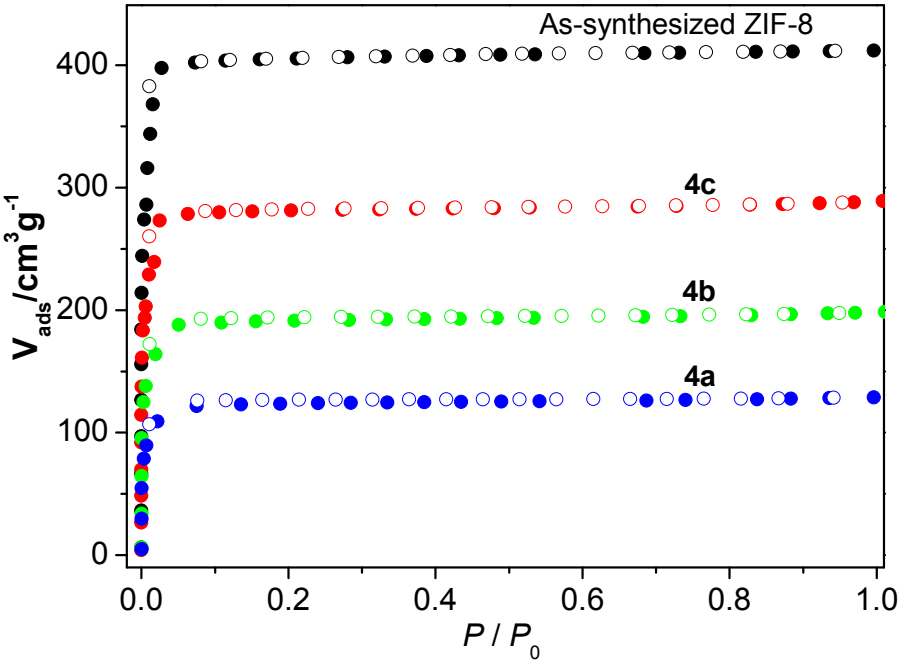

Fig. S10. N_2 adsorption of the CLD-Ni(cp)$_2$@ZIF-8 samples with different Ni(cp)$_2$/ZIF-8 weight ratios (**4a-c**).

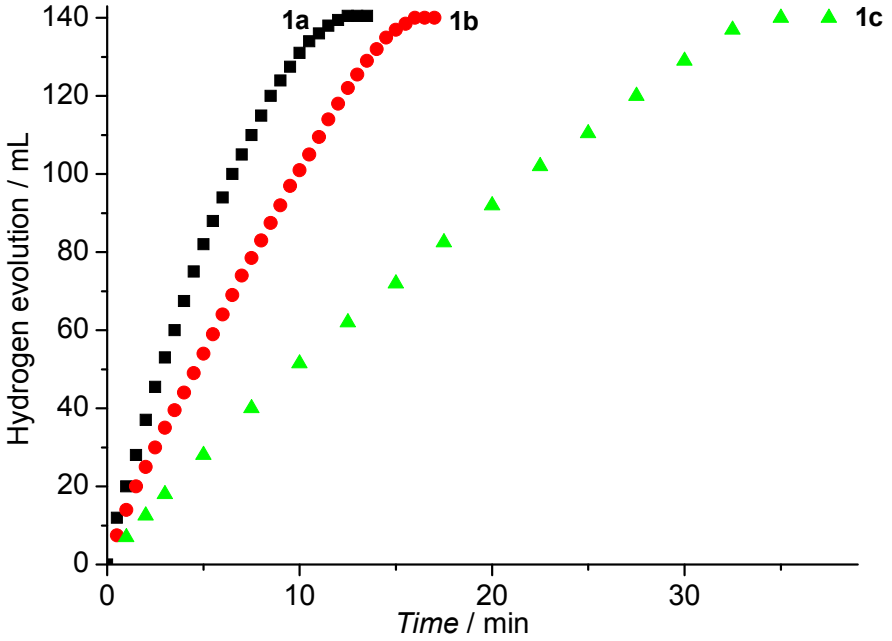

Fig. S11. Catalytic activity of CVD-Ni@ZIF-8 with different Ni loadings for hydrogen generation from hydrolysis of AB.

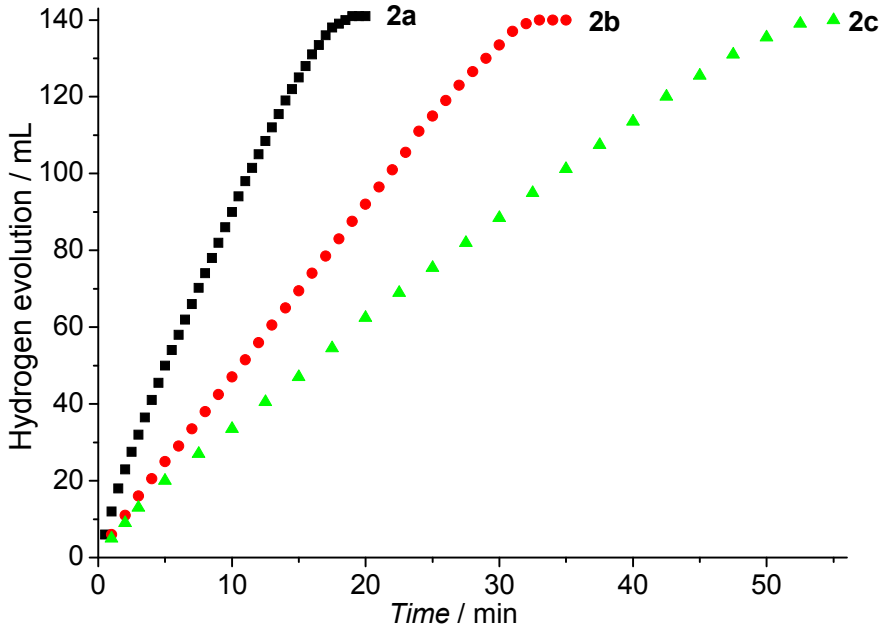

Fig. S12. Catalytic activity of CLD-Ni@ZIF-8 with different Ni loadings for hydrogen generation from hydrolysis of AB.

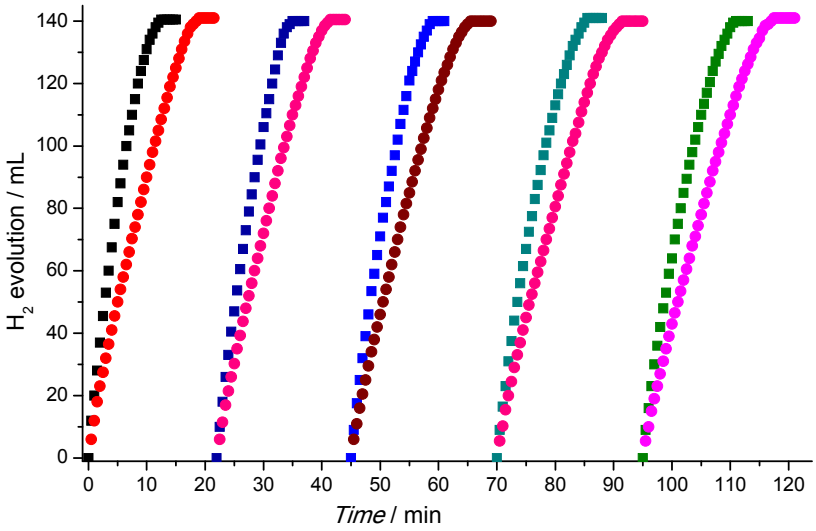

Fig. S13. Durability/stability characterization of CVD-Ni@ZIF-8 (**1a**, square) and CLD-Ni@ZIF-8 (**2a**, circle) in five runs for hydrogen generation from hydrolysis of AB.

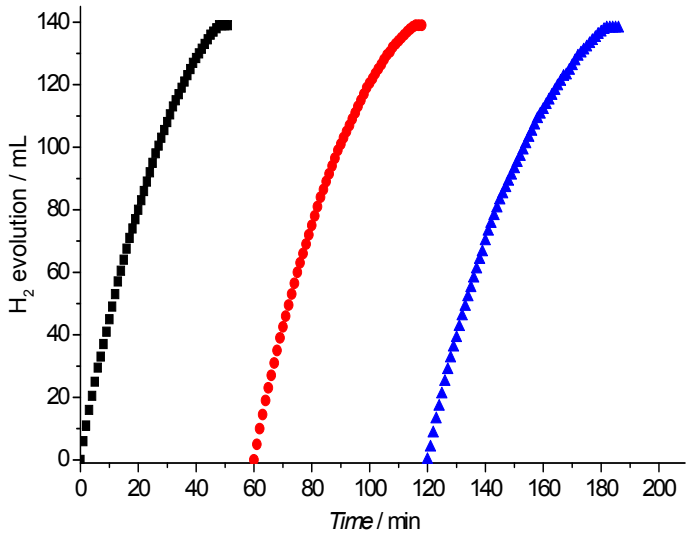

Fig. S14. Catalytic activity and durability/stability characterization of Ni NPs prepared without ZIF-8 as support for hydrogen generation from hydrolysis of AB in three runs.

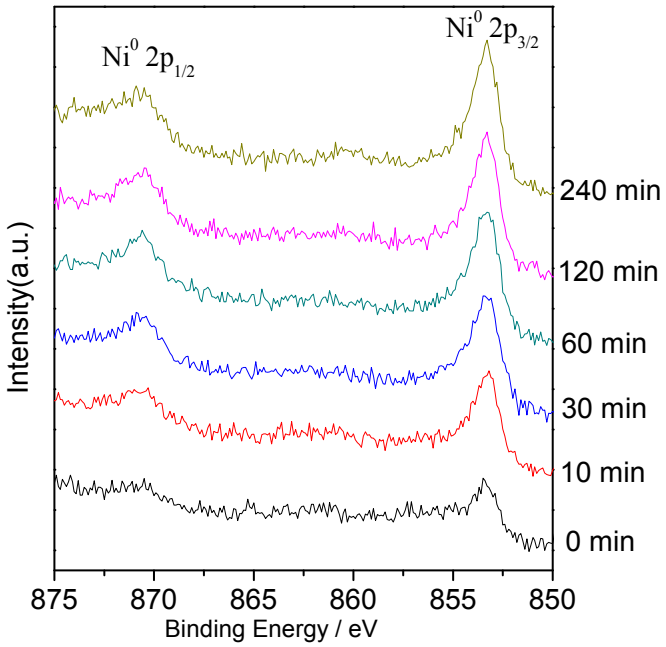

Fig. S15. XPS profiles of CVD-Ni@ZIF-8 (**1a**) before and after periodic Ar sputtering (10 - 240 min).

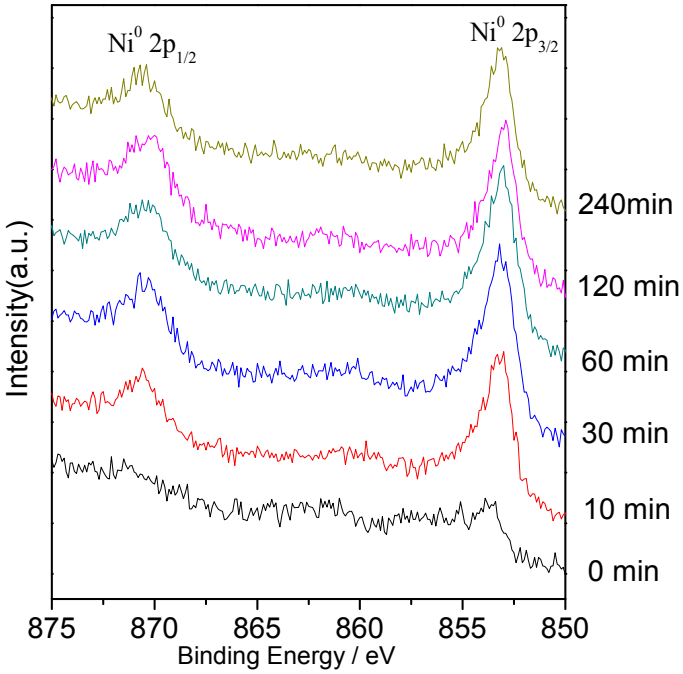

Fig. S16. XPS profiles of CLD-Ni@ZIF-8 (**2a**) before and after periodic Ar sputtering (10 - 240 min).

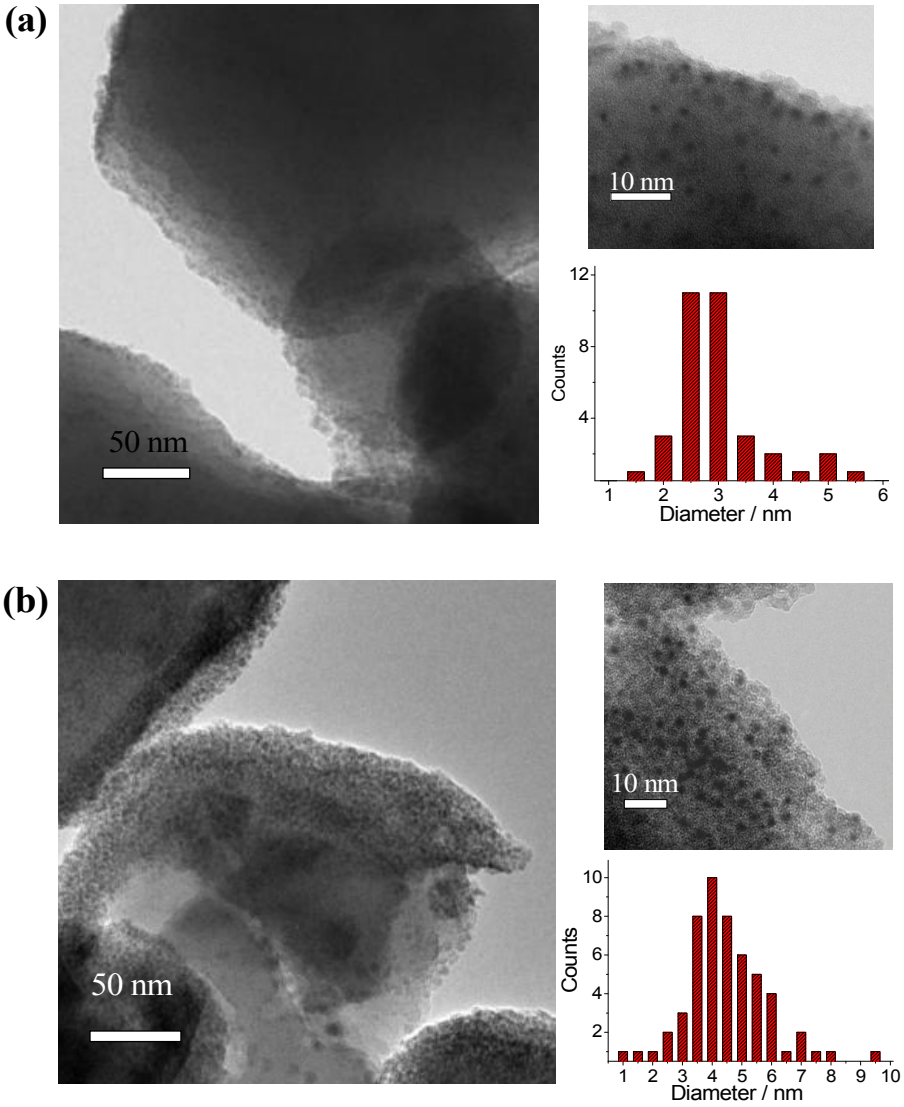

Fig. S17. Bright-field TEM images of (a) CVD-Ni@ZIF-8 (**1a**) and (b) CLD-Ni@ZIF-8 (**2a**), and the corresponding particle size distributions of Ni NPs in **1a** and **2a**.

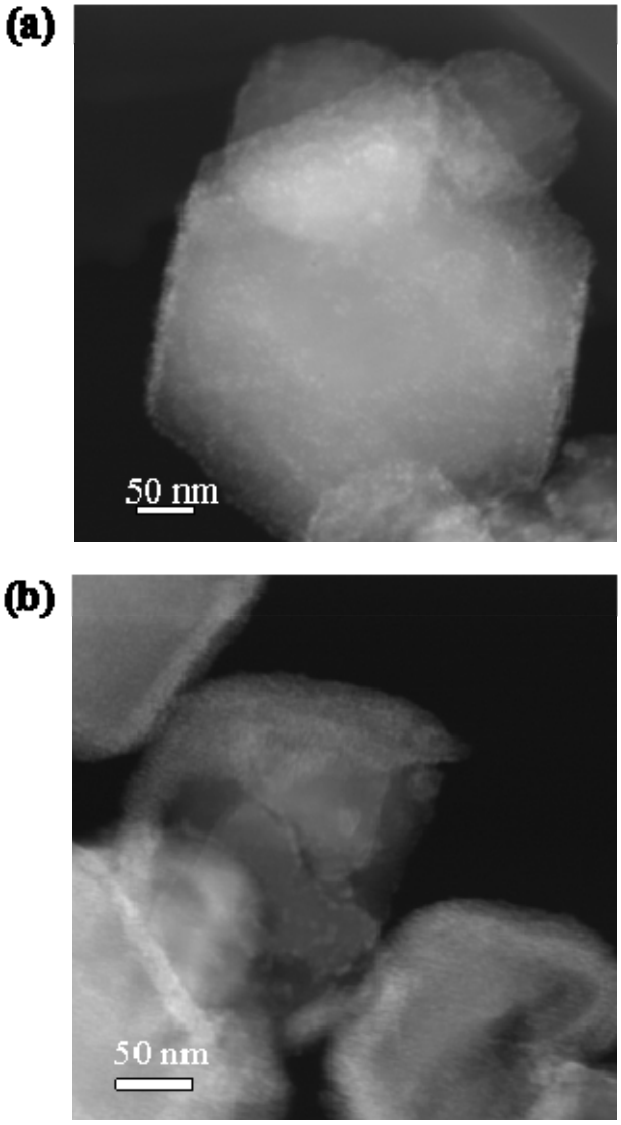

Fig. S18. The high-angle annular dark-field scanning TEM (HAADF-STEM) images of (a) CVD-Ni@ZIF-8 (**1a**) and (b) CLD-Ni@ZIF-8 (**2a**).

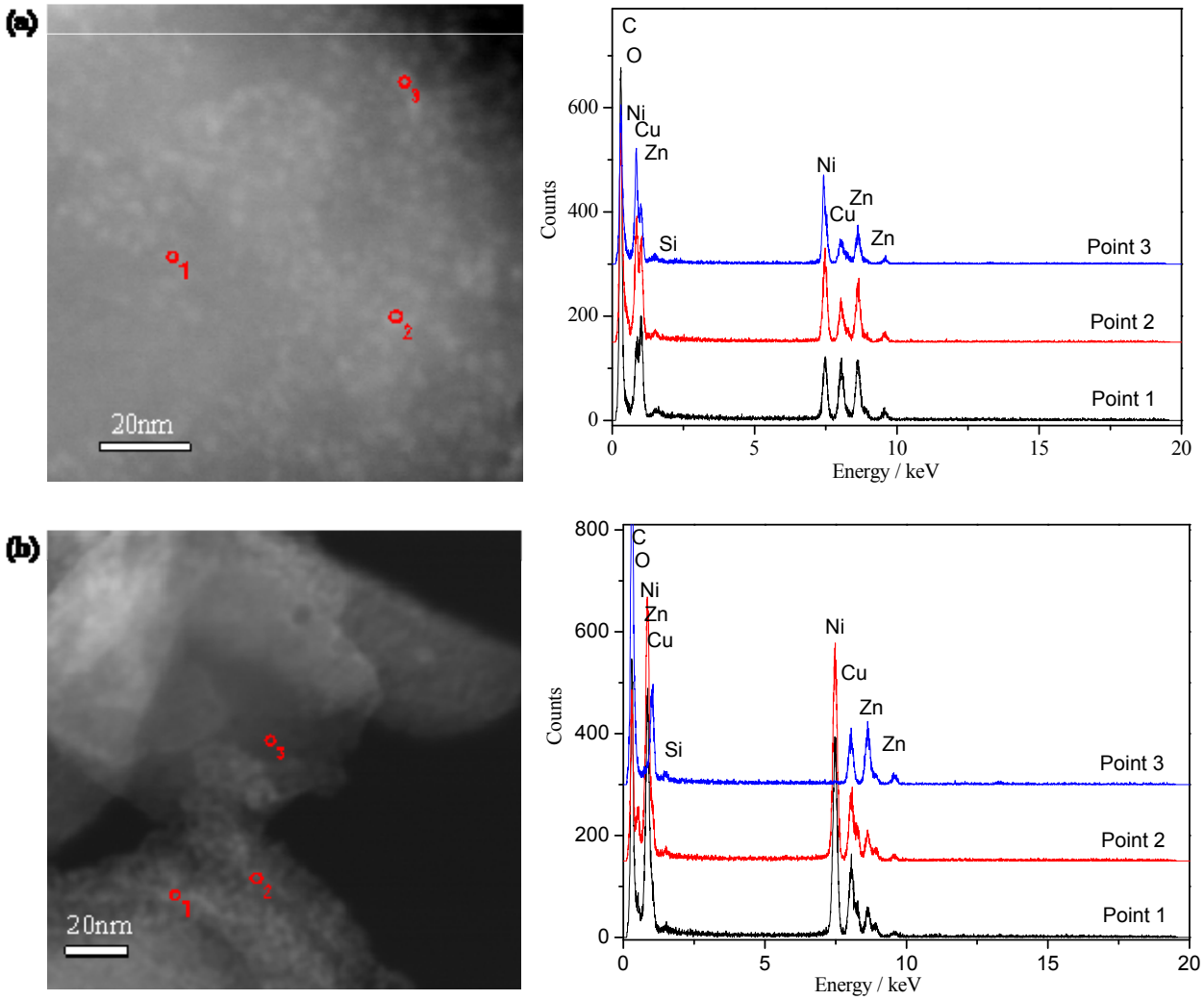

Fig. S19. HAADF-STEM images and corresponding EDS spectra of (a) CVD-Ni@ZIF-8 (**1a**) and (b) CLD-Ni@ZIF-8 (**2a**).

References:

1 X.-C. Huang, Y.-Y. Lin, J.-P. Zhang and X.-M. Chen, *Angew. Chem. Int. Ed.*, **2006**, *45*, 1557.

2 S. Hermes, M. K. Schröter, R. Schmid, L. Khodeir, M. Muhler, A. Tissler, R. W. Fischer and R. A. Fischer, *Angew. Chem. Int. Ed.*, **2005**, *44*, 6237.

3 Y. K. Park, S. B. Choi, H. J. Nam, D.-Y. Jung, H. C. Ahn, K. Choi, H. Furukawa and J. Kim, *Chem. Commun.*, **2010**, *46*, 3086.

4 H.-L. Jiang, T. Akita, T. Ishida, M. Haruta and Q. Xu, *J. Am. Chem. Soc.*, **2011**, *133*, 1304.

5 X. Gu, Z.-H. Lu, H.-L. Jiang and Q. Xu, *J. Am. Chem. Soc.*, **2011**, *133*, 11822.

6 M. Chandra and Q. Xu, *J. Power Sources*, **2006**, *156*, 190.

7 J.-M. Yan, X.-B. Zhang, T. Akita, M. Haruta, and Q. Xu, *J. Am. Chem. Soc.*, **2010**, *132*, 5326.