

Supporting Information

Hydrogen Storage in a sandwich structure by assemble of BNs and MOFs

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A. Experimental Details

Materials. Zirconium (IV) chloride ($ZrCl_4$, 99.5 wt%), 4-[3,5-bis(4-carboxyphenyl)phenyl]benzoic acid (H_3BTB , 98 wt%) and formic acid ($HCOOH$, 99 %) were obtained from Innochem Technology Co., Ltd (Beijing, China). Boron oxide (B_2O_3 , 99 wt%) was obtained from Sigma Aldrich Chemical Co (Shanghai, China). Guanidine Hydrochloride (CH_5ClN_3 , 99 wt%) was obtained from Aladdin Biochemical Technology Co., Ltd (Beijing, China). Sodium chloride ($NaCl$, 99.5 wt%) and anhydrous methanol (CH_3OH) were obtained from Tianjin Xinbote Chemical Co., Ltd. Water with a resistivity of $18\text{ M}\Omega\cdot\text{cm}^{-1}$ was prepared using a Millipore Milli-Q system and used in all experiments.

Synthetic procedure for h-BN nanosheets.

h-BN nanosheets were prepared according to the referred literature¹. B_2O_3 and CH_5ClN_3 with the mole ratio of 1:30 were dissolved in the mixture of CH_3OH (25 mL) and DI water (25 mL) followed by stirring at 80 °C until the white powder dissolved completely to form a transparent solution. Then the solution is recrystallized resulting in a white powder. The white powder of the precursor was transferred to the mortar for gently grinding, and then the white powder was put into the tube furnace. First, argon is introduced for 30 min, and the gas atmosphere in the tube is completely replaced with argon. After the impurity gas is discharged, the argon introduction rate is adjusted to 60 mL/min, and the temperature rises to 900 °C at a heating rate of 5 °C/min and keeping for 120 min. Then it is naturally cooled to room temperature. The product was transferred to the sample bottle and dried for storage, named h-BN

nanosheets.

Synthetic procedure for NUS-8 (Zr) nanosheets.

NUS-8 (Zr) nanosheets were prepared according to the referred literature². $ZrCl_4$ and H_3BTB with the mass ratio of 1:1 were dissolved in the mixture of DMF (15 mL), DI water (2 mL) and anhydrous CH_3OH (2 mL) followed by 24 h incubation at 120 °C under stirring through bottom-up hydrothermal methods. The NUS-8 (Zr) suspension was obtained after the transparent solution changing to milky white gel. After repeating the centrifugation/redispersion cycle for 5 times in DMF, the solvent was replaced with DI water soaking for 24 hours to activate the prepared solid powder. Then, repeating the centrifugation/redispersion cycle for several times in anhydrous ethanol and DMF, the NUS-8 (Zr) nanosheets suspension was obtained. Notably, DMF was replaced regularly to keep the fresh NUS-8 (Zr) nanosheets suspension.

Synthetic procedure for NUS-8/BN hybrids.

As-prepared h-BN nanosheets were exfoliated by ultrasound for 360 min in 500 mL DMF. The as-prepared NUS-8 (Zr) nanosheets suspension was added into the as-prepared h-BN nanosheets with the mass ratio of 1:1, 1:2, 1:3 and 1:4 under the ultrasound treatment for 360 min through layer by layer self-assembly. After the finish of ultrasound, the DMF suspension is filtered using a vacuum water pump. The resulting solid powder is loaded into a sample bottle and heated in an oil bath at 120 °C to obtain the final product, named NUS-8/BN-X, where X=1, 2, 3, and 4, respectively, representing a mass ratio of 1:1, 1:2, 1:3, and 1:4 for NUS-8 nanosheets and BN nanosheets, respectively.

Characterization.

The morphology and microstructure of obtained h-BNs, NUS-8 (Zr) nanosheets and NUS-8/BNs hybrids were observed with field emission scanning electron microscopy (SEM, Hitachi SU8010) and transmission electron microscopy (TEM, JEOLJEM-2100PLUS). The chemical compositions of the as-prepared nanosheets and hybrids were investigated using an energy dispersive spectrometer (EDS) attached to the Hitachi SU8010 TEM. Fourier Transform infrared (FT-IR) spectra

were acquired using a Nicolet Impact 410 Fourier transform infrared spectrometer. Powder X-ray diffraction (XRD) patterns were collected on a Rigaku Smart Lab powder diffraction, in which data were collected from 15 to 60 ° at a scan rate of 10 °/min. Nitrogen sorption isotherms were measured by using a Quantachrome Autosorb-iQ2 analyzer at 77 K. Prior to nitrogen sorption isotherm measurement, the samples were dried in vacuum ($\sim 1 \times 10^{-5}$ Torr) at room temperature for 1 h, at 100 °C for 12 h. Hydrogen adsorption isotherms were measured by using a JW-TB400 analyzer at 77 K and 87 K. Prior to hydrogen adsorption performance measurement, the samples (100mg) were dried in vacuum ($\sim 1 \times 10^{-5}$ Torr) at room temperature for 1 h, at 100 °C for 12 h.

B. Supplementary Materials

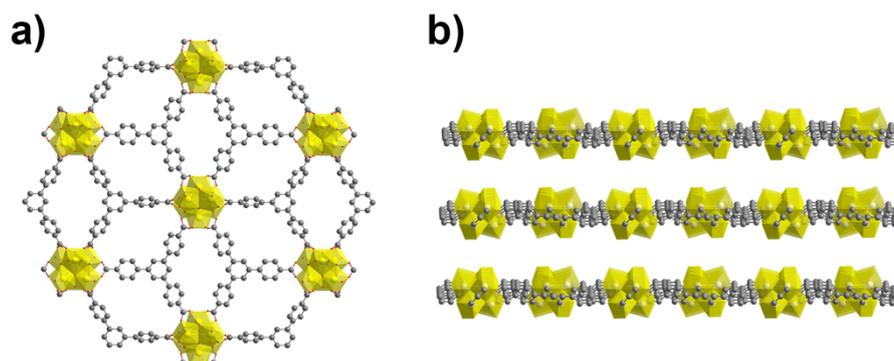


Figure S1. Schematic illustration of the crystal structure of NUS-8 (Zr) nanosheets.

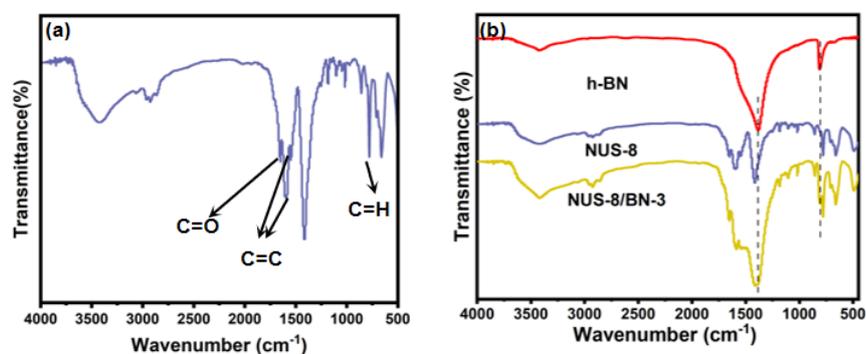


Figure S2. (a) The FT-IR spectrum of NUS-8 (Zr) nanosheets. (b) The FT-IR spectrum of h-BNs (red curve), NUS-8 (Zr) nanosheets (blue curve) and NUS-8/BNs hybrids (yellow curve).

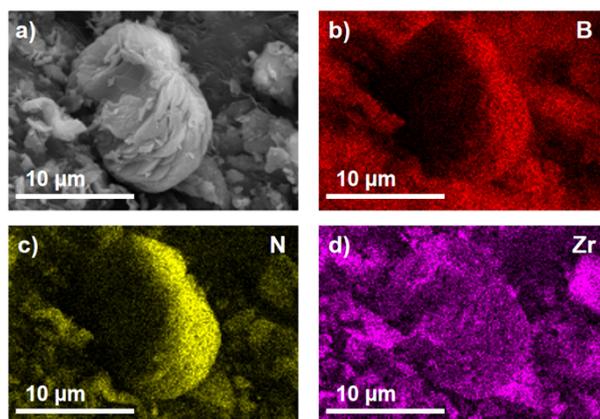


Figure S3. (a-d) The EDS elemental mapping images of the as-prepared NUS-8/BNs.

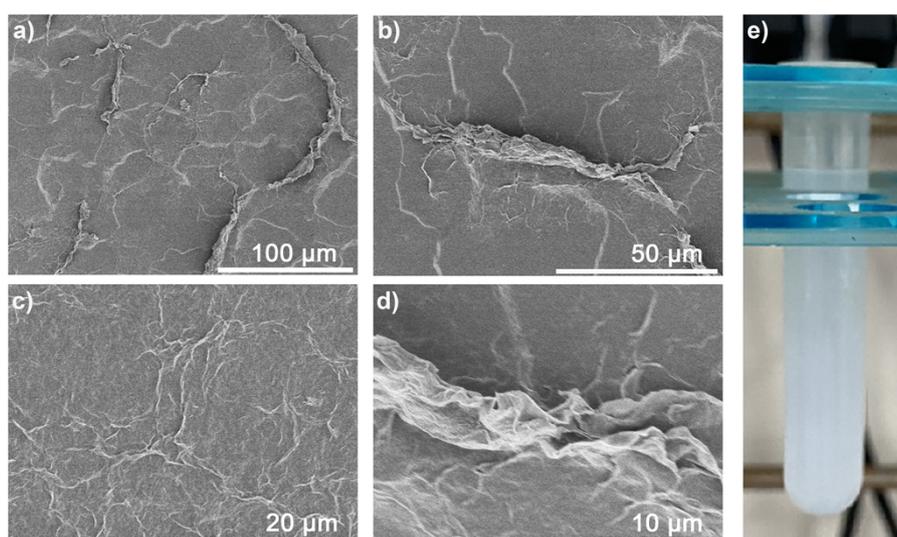


Figure S4. (a-d) The SEM images of the as-prepared NUS-8 (Zr) nanosheets. (e) Photograph of NUS-8 (Zr) nanosheets sol after letting it stand still for 180 days.

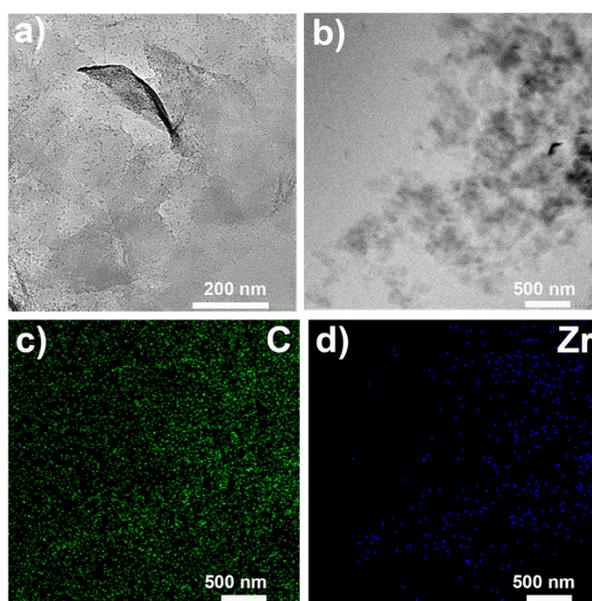


Figure S5. TEM (a-b) and EDS (c-d) elemental mapping images of as-prepared NUS-8 (Zr) nanosheets.

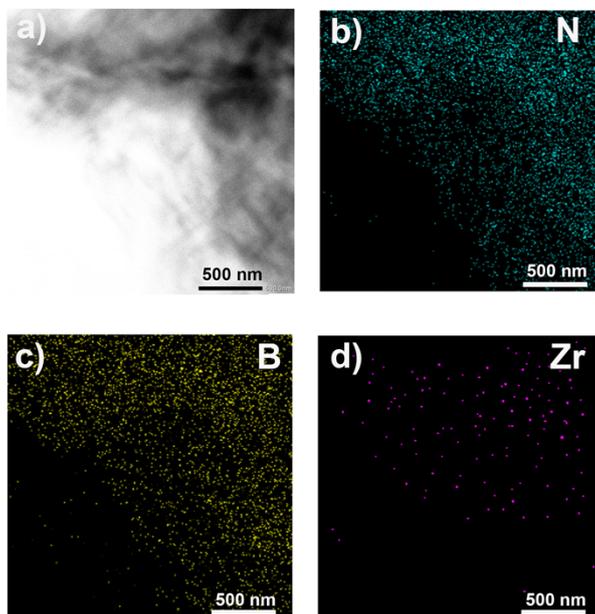


Figure S6. TEM (a) and EDS (b-d) elemental mapping images of as-prepared NUS-8/BNs hybrids.

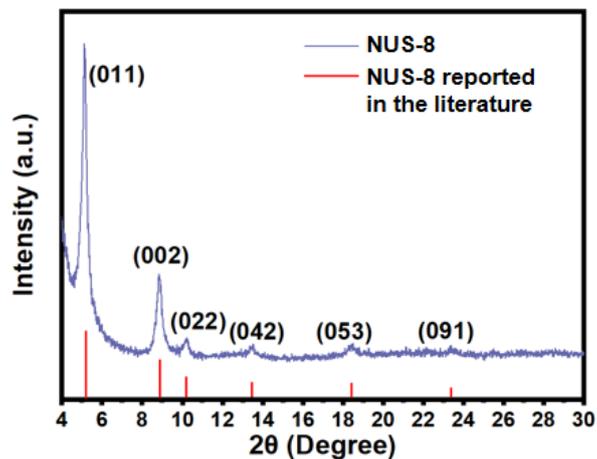


Figure S7. The XRD patterns of the as-prepared NUS-8 (Zr) nanosheets.

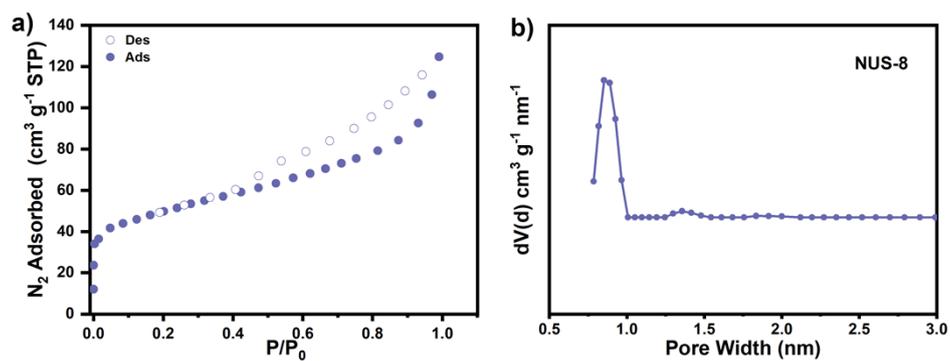


Figure S8. Nitrogen sorption isotherms (a) and pore size distribution profiles (b) of as-prepared NUS-8 (Zr) nanosheets.

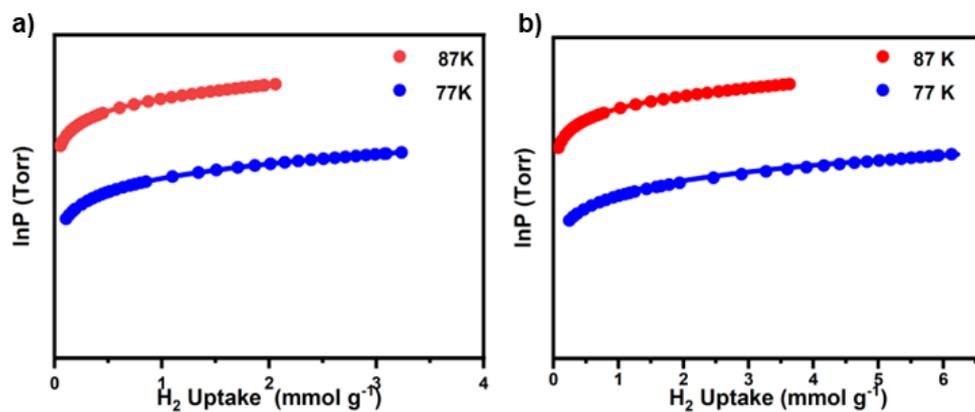


Figure S9. H₂ adsorption nonlinear fitting curve of (a) h-BN nanosheets and (b) NUS-8/BN-3 hybrids.

Table S1. The specific surface area and total pore volume of as-prepared h-BN, NUS-8 (Zr) nanosheets and NUS-8/BNs hybrids.

Sample	Specific surface area (m ² g ⁻¹)	Total pore volume (cm ³ g ⁻¹)
h-BN	656	0.630
NUS-8	176	0.156
NUS-8/BN-1	783	0.665
NUS-8/BN-2	1019	0.727
NUS-8/BN-3	1232	0.901
NUS-8/BN-4	1194	0.758

References

1. P. W. Wu, S. Z. Yang, W. S. Zhu, H. P. Li, Y. H. Chao, H. Y. Zhu, H. M. Li and S. Dai, *Small*, 2017, **13**, 1701857.
2. H. Y. Yuan, G. L. Liu, Z. W. Qiao, N. X. Li, P. J. S. Buenconsejo, S. B. Xi, A. Karmakar, M. S. Li, H. Cai, S. J. Pennycook and D. Zhao, *Adv. Mater.*, 2021, **33**, 2101257.