Supporting information

High-dispersion Ultrafine Shell-like Nano-Pt with Efficient Hydrogen Evolution Evolved via Metal Boron Organic Polymers

Xue Zhao,[a] Ziqiong Yang,[a] Wenjing Wang,[b] Yuxin Li,[d] Xiaohai Zhou*[a,e] and Haibo Zhang*[a,c]

a College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, P. R. China. *E-mail:* haibozhang1980@gmail.com; zxh7954@whu.edu.cn

b The State Key Laboratory of Refractories and Metallurgy, School of Chemistry and Chemical Engineering, Wuhan University of Science and Technology, Wuhan 430081, P. R. China

c National Demonstration Center for Experimental Chemistry, Wuhan University, Wuhan 430072, P. R. China

d Key Laboratory of Function Inorganic Material Chemistry (MOE), School of Chemistry and Material Science, Heilongjiang University, Harbin 150080, P. R. China

e Engineering Research Center of Organosilicon Compounds & Materials, Ministry of Education, Wuhan 430072, P. R. China

*Corresponding Author

Prof. Dr. **Haibo Zhang**, *E-mail*: haibozhang1980@gmail.com,

Prof. Dr. **Xiaohai Zhou**, *E-mail*: zxh7954@whu.edu.cn

Dodecahydro-*closo*-dodecaborate dianion (*closo*-$[B_{12}H_{12}]^{2-}$) has the properties of a reducing agent

The principle of reduction of *closo*-$[B_{12}H_{12}]^{2-}$ is similar to that of $NaBH_4$. Due to the strong polarization of B, each hydrogen atom carries 0.00823*e* in *closo*-$[B_{12}H_{12}]^{2-}$ (while the core cage structure composed of B is enriched with a large amount of negative charge).[1,2] However, compared to H^{-1} in $NaBH_4$, *closo*-$[B_{12}H_{12}]^{2-}$ is relatively less reductive and can only reduce some precious metal ions to the corresponding zero-valent state in a mild manner (such as Au^{3+}, Pd^{2+}, Pt^{4+} and Ag^{+}).[3-7]

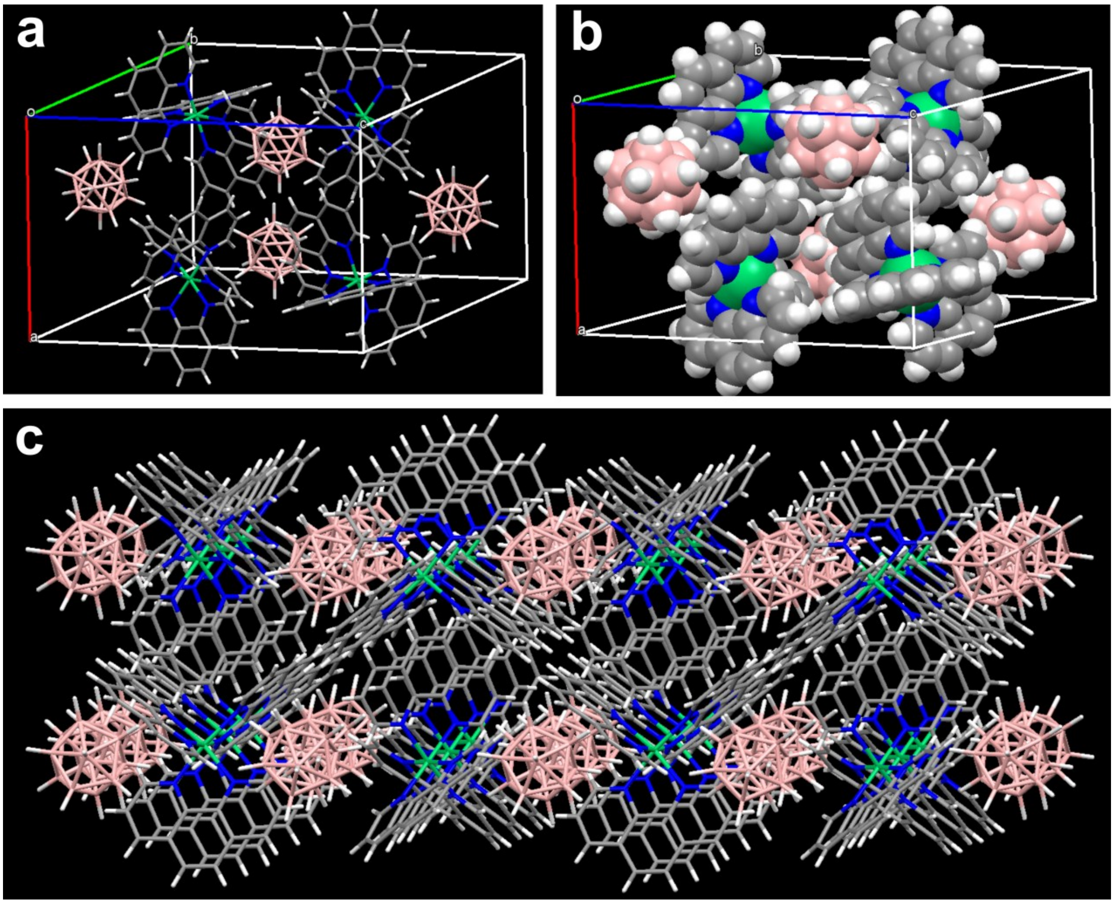

Figure S1. Crystal structure of M-BOPs (solvent molecules have been hidden for clarity). **a**-**b**) Unit cell views and **c**) wide view of M-BOPs crystal

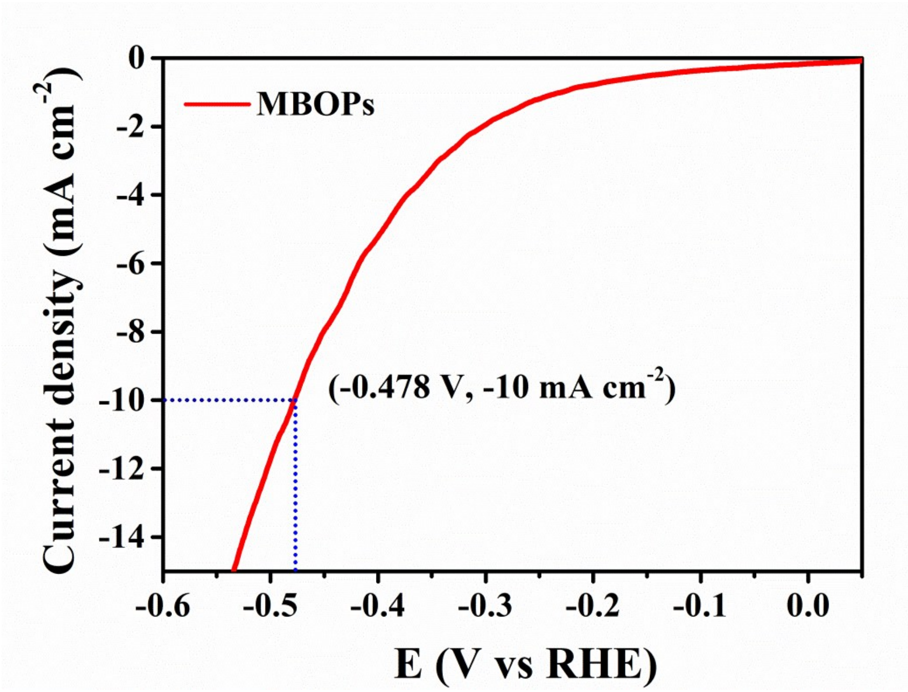

Figure S2. LSV curve obtained with MBOPs as catalyst

Table S1. Overpotentials of Pt/MBOPs with other recently reported Pt-based E-HER catalysts in 1M KOH.

Catalyst	Electrolyte	η_{10} (mV)	Information Sources
Pt/MBOPs	1M KOH	22.8	***This work***
Pt/C	1M KOH	36.1	***This work***
Pt/OLC	1M KOH	38	*Nature Energy*, 2019, 4, 512-518
PtNi-O/C	1M KOH	39.8	*Journal of the American Chemical Society*, 2018, 140, 9046-9050
PtNWs/SL-$Ni(OH)_2$	1M KOH	70	*Nature Communications*, 2015, 6, 6430
NiOx/Pt_3Ni	1M KOH	40	*Angewandte Chemie International Edition*, 2016, 55, 12859
Pt_3Ni_2-NWs/SC	1M KOH	42	*Nature Communications*, 2017, 8, 14580
Mo_2C@NC@Pt	1M KOH	47	*ACS Applied Materials & Interfaces*, 2019,11, 4047-4056
Pt on WS_2	1M KOH	45	*Advanced Materials*, 2018, 30, 1704779
Pt/NiO@Ni/NF	1M KOH	34	*ACS Catalysis*, 2018, 18, 8866-8872
Pt/$Ni(HCO_3)_2$	1M KOH	44	*Angewandte Chemie International Edition*, 2019, 58, 5432-5437
CDs/Pt PANI	1M KOH	56	*Applied Catalysis B: Environmental*, 2019, 257, 117905
A-CoPt-NC	1M KOH	32	*Angewandte Chemie International Edition*, 2019, 58, 9404
C Pt@ZIF-67	1M KOH	32	*Journal of Materials Chemistry A*, 2018, 6, 1376-1381
Pd/Cu-Pt	1M KOH	22.8	*Angewandte Chemie International Edition*, 2017, 56, 16047
PtCoFe@CN	1M KOH	45	*ACS Applied Materials & Interfaces*, 2017, 9, 3596-3601

Table S2. TOF value of Pt/MBOPs with other recently reported Pt-based catalysts in hydrolysis hydrogen evolution of ammonia borane.

Catalyst	T (°C)	$TOF_{molH_2\ molPt^{-1}\ min^{-1}}$	Information Sources
Pt/MBOPs	25	1654.9	***This work***
BOPs@Pt	25	131	*ChemCatChem, 2019, 11, 2362-2369*
SiO_2@Pt@NGO	25	324.6	*Sustainable Energy Fuels, 2017, 1, 2128-2133*
Pt@MIL-101	RT	~414	*Journal of the American Chemical Society*, 2012, 134, 13926-13929
Pt/CNT	30	~414	*Journal of the American Chemical Society, 2014, 136, 16736-16739*
Pt-CNTs-O-HT	25	~580	*ACS Catalysis, 2016, 6, 6892-69059*
Pt-CNT	30	567	*Chemical Communication, 2014, 50, 2142-2144*
Pt/CeO_2	25	182	*Chemical Communication, 2012, 48, 10207-10209*
$Pt_{25}Pd_{75}$ NPs	25	69.76	*Nanoscale, 2020,12, 638-647*
PtAuNi	25	496	*Nano Energy 2016, 23, 145-152*
NiPt@MIL-101	50	25.25	*Inorganic Chemistry, 2017, 56, 19, 11938-11945*
PtNi@PVP	RT	511	*ACS Applied Materials & Interfaces, 2014, 6, 12429-12435*
Pt-Ni/NiO	30	1240.3	*ACS Applied Materials & Interfaces, 2017, 9, 3749-3756*
Pt_3Ni_7O-NGO	25	709.6	*Catalysis Science & Technology, 2017, 7, 5135-5142*
Pd-Co	35	118.25	*International Journal of Hydrogen Energy, 2017, 42, 27055-27065*
Pt-CoCu@SiO_2	30	272.8	*ACS Sustainable Chemical & Engineering, 2017, 5, 1675-1684*
PtCo@PG	30	461.17	*International Journal of Hydrogen Energy, 2017, 42, 26617-26625*
$Pt_1Co_1Ni_2$-BOFs	25	1490	*ACS Applied Materials & Interfaces, 2019, 11, 26, 23445-23453*

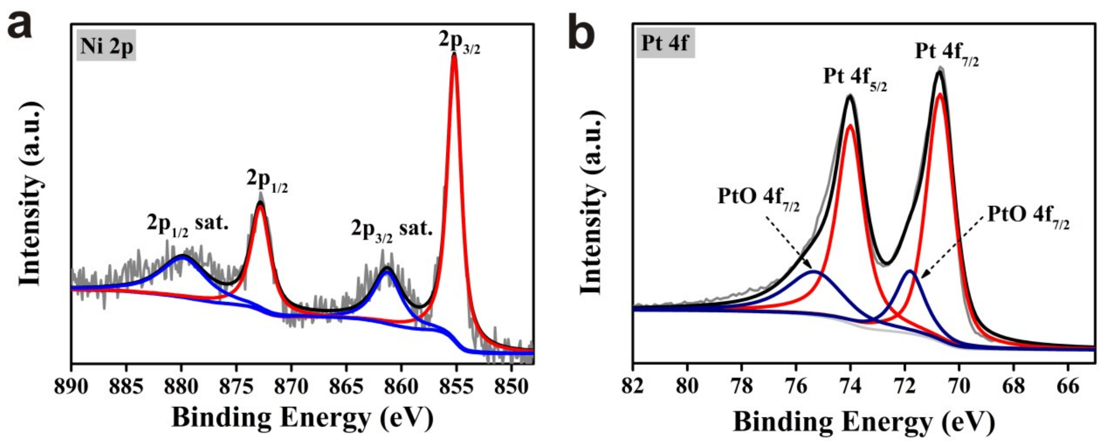

Figure S3. XPS spectrum of Pt/MBOPs after reused. **a**) Binding energy region of nickel and **b**) Binding energy region of platinum

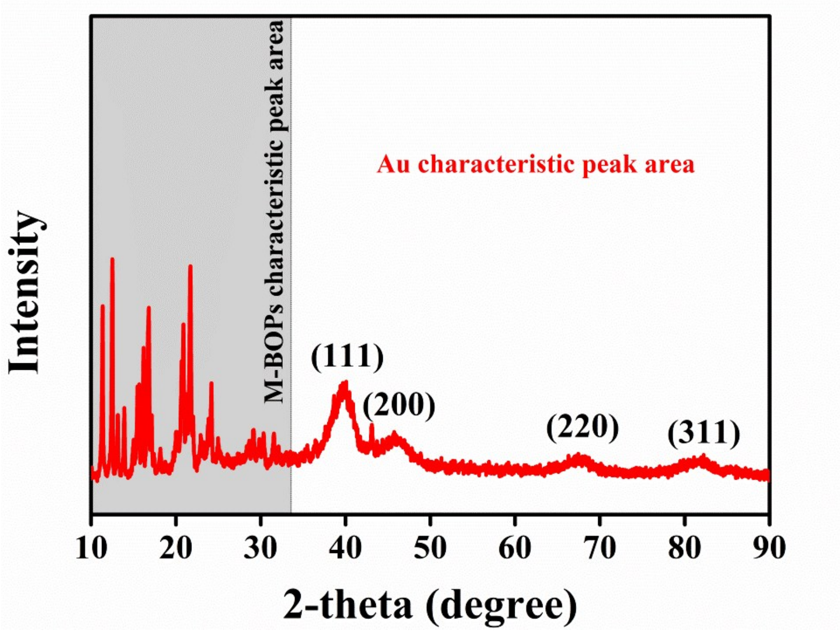

Figure S4. XRD spectrum of Pt/MBOPs after reused

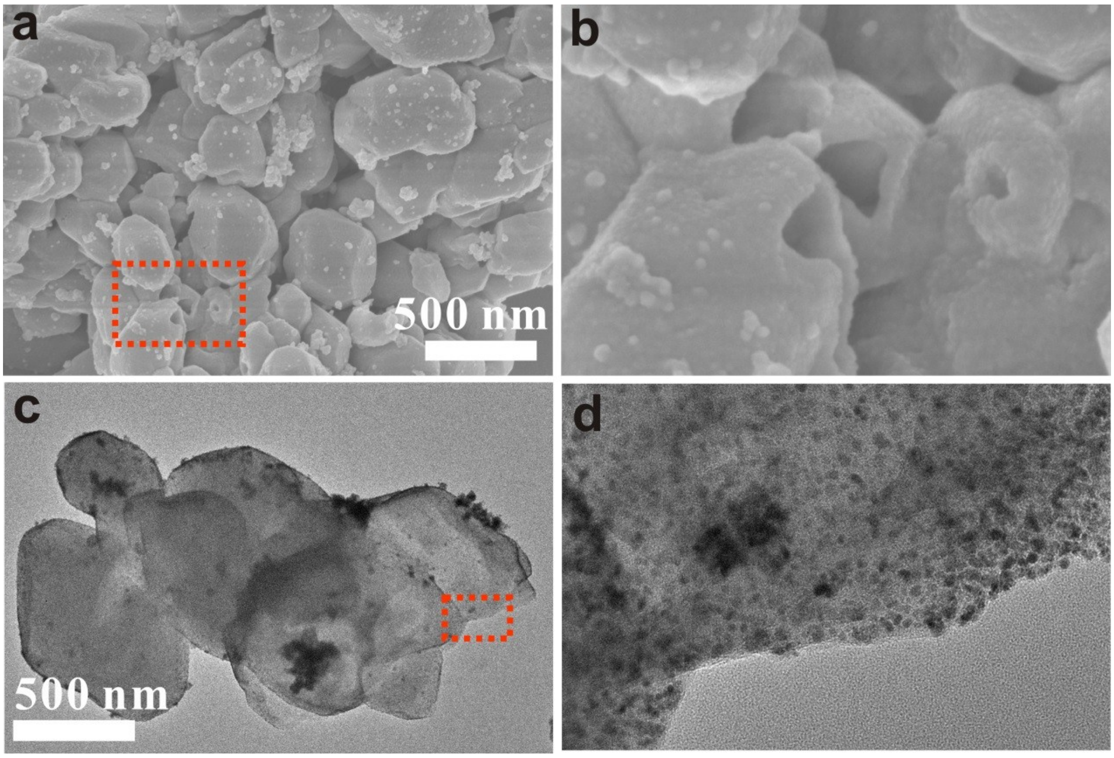

Figure S5. SEM images (a-b) and TEM images (c-d) of Pt/MBOPs after reused

References

1. B. R. S. Hansen, M. Paskevicius, M. Jørgensen, and T. R. Jensen, *Chemistry of Materials*, 2017, 29, 3423-3430.
2. N. Jiao, Y. Zhang, L. Liu, J. M. Shreeve and S. Zhang, *Journal of Materials Chemistry A*, 2017, 5, 13341–13346
3. B. Qi, L. Du, F. Yao, S. Xu, X. Deng, M. Zheng, S. He, H. Zhang and X. Zhou, *ACS Applied Materials & Interfaces*, 2019, 11, 23445-23453.
4. X. Zhao, Y. Fu, C. Yao, S. Xu, Y. Shen, Q. Ding, W. Liu, H. Zhang and X. Zhou, *ChemCatChem*, 2019, 11, 2362-2369.
5. X. Zhao, C. Yao, H. Chen, Y. Fu, C. Xiang, S. He, X. Zhou and H. Zhang, *Journal of Materials Chemistry A*, 2019, 7, 20945-20951.
6. B. Qi, C. Wu, L. Xu, W. Wang, J. Cao, J. Liu, S. Zhang, D. Gabel, H. Zhang and X. Zhou, *Chemical Communications*, 2017, 53, 11790-11793.
7. B. Qi, X. Li, L. Sun, B. Chen, H. Chen, C. Wu, H. Zhang and X. Zhou, *Nanoscale*, 2018, 10, 19846-19853.