

Supporting Information

In-situ Nano Au Triggered via Metal Boron Organic Polymers: Efficient Electrochemistry N₂ Fixation to NH₃ under Ambient Conditions

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M-BOPs crystal culture details and crystal structure parsing methods

M-BOPs crystal culture details

10 mg M-BOPs were re-dispersed in a mixture of 15 mL N, N-dimethylformamide and H₂O (V/V=1:1), and then transferred to a 25 mL hydrothermal reactor containing Teflon liner. The reactor temperature was raised to 140 °C in 10 min and maintained for 24 h. Then, the temperature was lowered to room temperature at a temperature decreasing rate of 0.1 °C/min, and a magenta crystal was obtained and used for the test of the single crystal structure.

Crystal structure parsing methods

Crystal data of M-BOPs were collected at 123.0(1) K on an Agilent Super-Nova diffractometer using mirror-monochromatized Cu-K α ($\lambda = 1.54184 \text{ \AA}$) radiation. The crystals were mounted on a Hampton cryoloop with light oil to prevent water loss. The SHELX package (Bruker) is used to solve and improve the structure. Apply the SADABS program to empirical absorption correction. The structure is solved by a direct method, and the anisotropic thermal parameters of all the heavy atoms contained in the model are refined by the full matrix least squares method ($\sum w(|F_o| - |F_c|)^2$). A hydrogen atom of an organic group is introduced at a geometrically calculated position. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif (code: 1899654).

Possible pollution control

1. The entire electrolyzer (without CP and catalyst) was tested at an open circuit potential for 2 h to determine if ammonia was introduced during the production of the device, and the device without ammonia contamination was washed with ultrapure water at least five times before each use.
2. In order to prevent contamination from commercial hydrochloric acid, the raw materials used to prepare 0.1M HCl electrolyte:

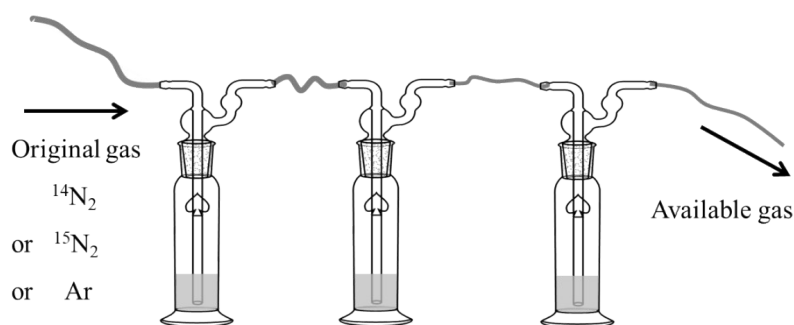
Ultrapure water: Milli-Q ultrapure water ($18 \text{ M}\Omega\cdot\text{cm}^{-1}$)

0.1M HCl was prepared by the following method:



Make sure that the 0.1M HCl prepared was not sufficient to change the color of the indophenol blue developer relative to the blank before use it.

3. The ultrapure Ar, $^{14}\text{N}_2$ and $^{15}\text{N}_2$ used in the experiment were previously passed through multiple acid trap ($0.05 \text{ M H}_2\text{SO}_4$) wash. The number of $0.05 \text{ M H}_2\text{SO}_4$ lotion devices set was based on the fact that the ammonia in wash solution in the last device was not detected by indophenol blue colorimetry (or almost no change in color of indophenol blue relative to the blank).



4. Carbon paper (CP) was soaked for several times with a large amount of 0.1m HCl until the presence of ammonia could not be detected in the last soaking solution by indophol blue colouring, and then it was electrolyzed for 2h at the open circuit voltage (Ar filling) until no ammonia could be detected in the electrolyte, which was used for catalyst load after continuous vacuum drying.
5. The catalyst was washed with a large amount of 0.1m HCl for several times in

advance, until the presence of ammonia could not be detected in the washing liquid, so as to prevent the interference of raw materials not completely removed in the preparation process.

6. The nafion proton exchange membrane treated with H_2O_2 , H_2SO_4 , and ultrapure water was washed with a large amount of ultrapure water and electrolyzed at an open circuit voltage for 2 h (under Ar flow). The above two processes were alternated until it was difficult to detect ammonia.

$^{15}\text{N}_2$ Isotope Labeling Experiments

An isotopic labeling experiment used $^{15}\text{N}_2$ (98 atom% ^{15}N purchased from Sigma-Aldrich Chemical Reagent Co.) as the feed gas was conducted to elucidate the activity origin of ammonia under Au/M-BOPs. The electrolyte volume was 75 ml and $^{15}\text{N}_2$ gas was purified by acid trap (0.05 M H_2SO_4) before entering the electrochemical chamber (the flow rate of $^{15}\text{N}_2$ was 5 sccm). After ^{15}NRR for 2h at -0.2 V vs. RHE in 0.10 M HCl solution, the obtained $^{15}\text{NH}_4^+$ electrolyte was determined by ^1H nuclear magnetic resonance (NMR, 400 MHz). To prepare the NMR sample, 75mL of electrolyte after NRR was concentrated to near dryness. Then 1.0 mL of deuterated DMSO was added for NMR test and the NMR measurement was carried out with 1024 scans (1 h).

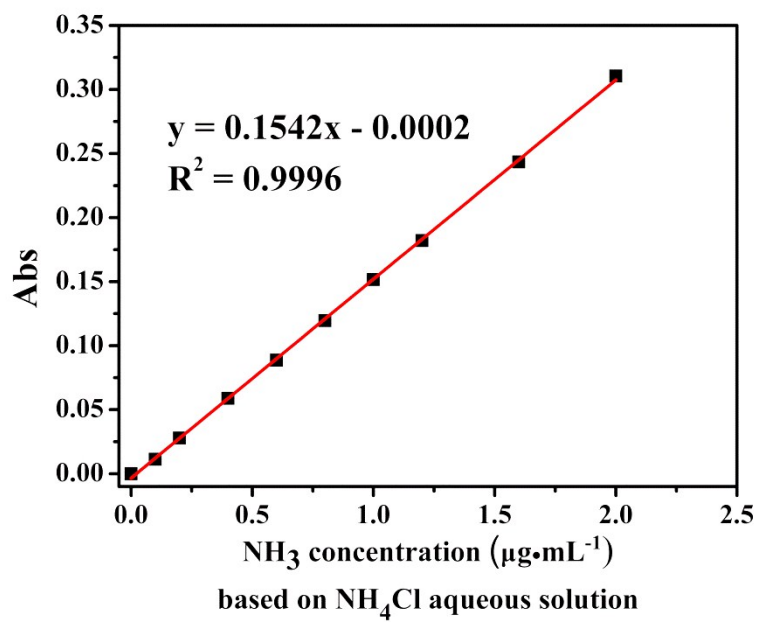


Fig. S1 Standard curve of NH₄Cl based on indophenol blue colorimetry.

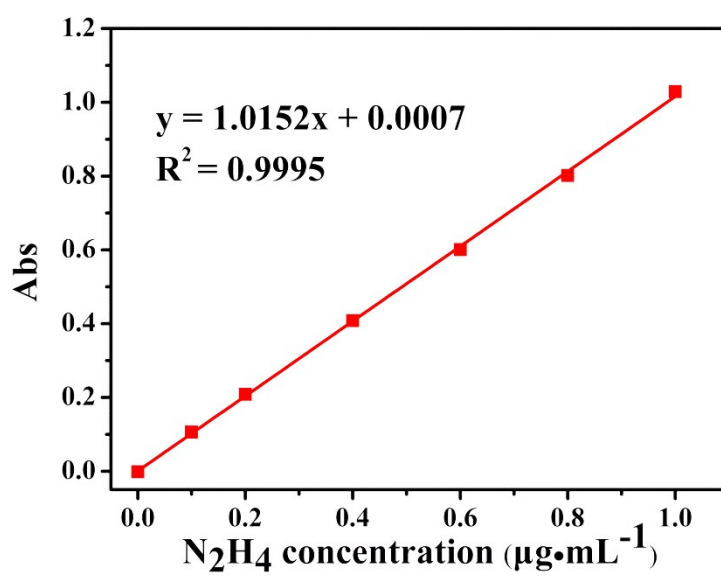


Fig.S2 N₂H₄ standard curve based on Watt-Chrisp method.

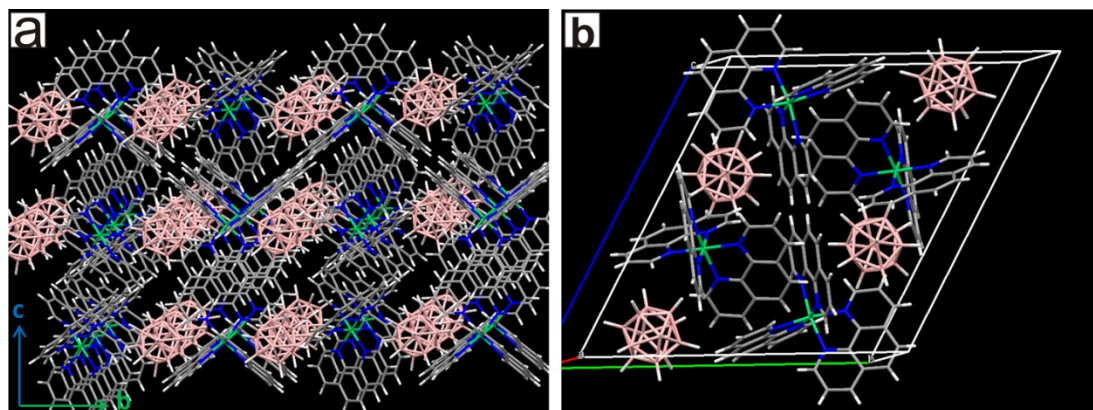


Fig.S3 Crystal structure of precursor M-BOPs. (a) a-axis field of view and (b) cell view.

Table S1. Crystal data and structure refinement for M-BOPs.

Identification code	2
Empirical formula	C ₈₁ H ₉₅ B ₂₄ N ₁₅ Ni ₂ O ₄
Formula weight	1719.57
Temperature/K	150.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	13.8650(4)
b/Å	18.8050(5)
c/Å	19.2331(5)
α/°	61.953(3)
β/°	87.914(2)
γ/°	84.292(2)
Volume/Å ³	4403.5(2)
Z	2
ρ _{calc} /g/cm ³	1.297
μ/mm ⁻¹	0.984
F(000)	1788.0
Crystal size/mm ³	0.18 × 0.16 × 0.14
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	7.956 to 131.996
Index ranges	-15 ≤ h ≤ 16, -22 ≤ k ≤ 22, -22 ≤ l ≤ 22
Reflections collected	24908
Independent reflections	15228 [R _{int} = 0.0419, R _{sigma} = 0.0551]
Data/restraints/parameters	15228/118/1192
Goodness-of-fit on F ²	1.033
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0549, wR ₂ = 0.1509
Final R indexes [all data]	R ₁ = 0.0638, wR ₂ = 0.1613
Largest diff. peak/hole / e Å ⁻³	0.72/-0.93

Identification code	Analysis target name	Intensity (corrected)	Concentration (corrected)	Calibration unit	Standard deviation	Relative standard deviation (concentration)
Calibration blank 1	Au 267.595	297.4125453	[0.00]	mg/L	0	0
Calibration standard sample 1	Au 267.595	2348.918512	[0.10]	mg/L	1.32E-09	1.32E-06
Calibration standard sample 2	Au 267.595	4832.382822	[0.20]	mg/L	2.63E-09	1.32E-06
Calibration standard sample 3	Au 267.595	9830.452548	[0.40]	mg/L	5.27E-09	1.32E-06
Calibration standard sample 4	Au 267.595	24921.80209	[1.0]	mg/L	0	0
Calibration standard sample 5	Au 267.595	103075.8024	[4.0]	mg/L	0	0
Calibration standard sample 6	Au 267.595	251587.3171	[10]	mg/L	0	0
Au (sample)	Au 267.595	152304.2649	[6.034]	mg/L	0.064433715	1.067843376
Repeat measurement number 1	Intensity (net value)1	Intensity(corrected)1	Concentration(corrected)1	Preparation method of ICP-OES test sample:		
1	374.8781287	374.8781287		5.0 mg Au/M-BOPs were dissolved in 10 mL aqua regia, then 1 mL of the supernatant was removed and diluted to 10 mL with ultrapure water for ICP-OES determination.		
1	2654.05529	2356.642745		ICP-OES determination concentration: 6.034 mg / L		
1	5186.36917	4888.956625		Results: The mass percentage of Au in Au/M-BOPs is: 12.068 w%		
1	10137.88127	9840.468726				
1	24965.66373	24668.25119				
1	104209.2867	103911.8742				
1	252052.1746	251754.7621				
1	154312.2137	154014.8011	6.101804155			
Repeat measurement number 2	Intensity (net value)2	Intensity(corrected)2	Concentration(corrected)2			
2	264.6234291	264.6234291				
2	2612.128069	2314.715524				
2	5142.0889	4844.676355				
2	10082.96721	9785.554668				
2	25395.47477	25098.06223				
2	102131.245	101833.8325				
2	250745.7449	250448.3323				
2	151076.9617	150779.5492	5.973569714			
Repeat measurement number 3	Intensity (net value)3	Intensity(corrected)3	Concentration(corrected)3			
3	252.7360779	252.7360779				
3	2672.809811	2375.397266				
3	5060.928032	4763.515487				
3	10162.7468	9865.334251				
3	25296.50539	24999.09285				
3	103779.1131	103481.7006				
3	252856.2693	252558.8568				
3	152415.857	152118.4445	6.026638993			

Fig.S4 ICP-OES test results for Au/M-BOPs.

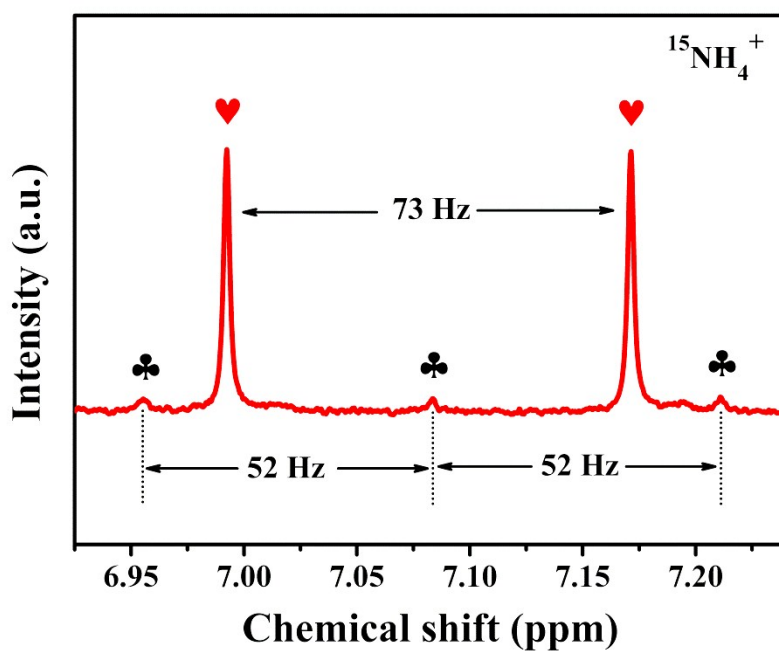


Fig. S5 Isotopic label result of $^{15}\text{NH}_4^+$ obtained from the NRR reaction (at -0.2 V vs RHE) using $^{15}\text{N}_2$ as the nitrogen source. (♥ is the signal of H in $^{15}\text{NH}_4^+$; ♣, this extremely low value can be regarded as caused by $^{14}\text{NH}_4^+$, $^{14}\text{N}_2$ is difficult to completely remove from the electrolyte).

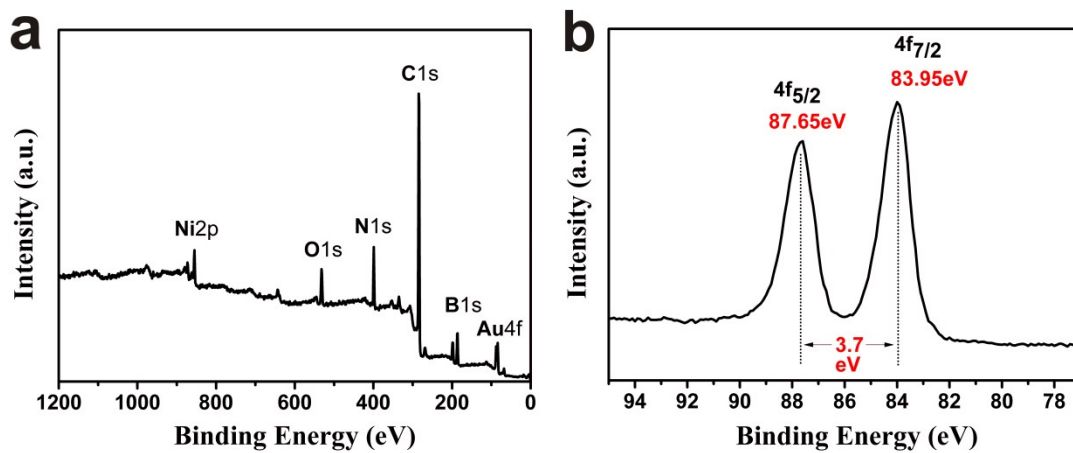


Fig.S6 XPS test result of Au/M-BOPs after electrochemical NRR test.

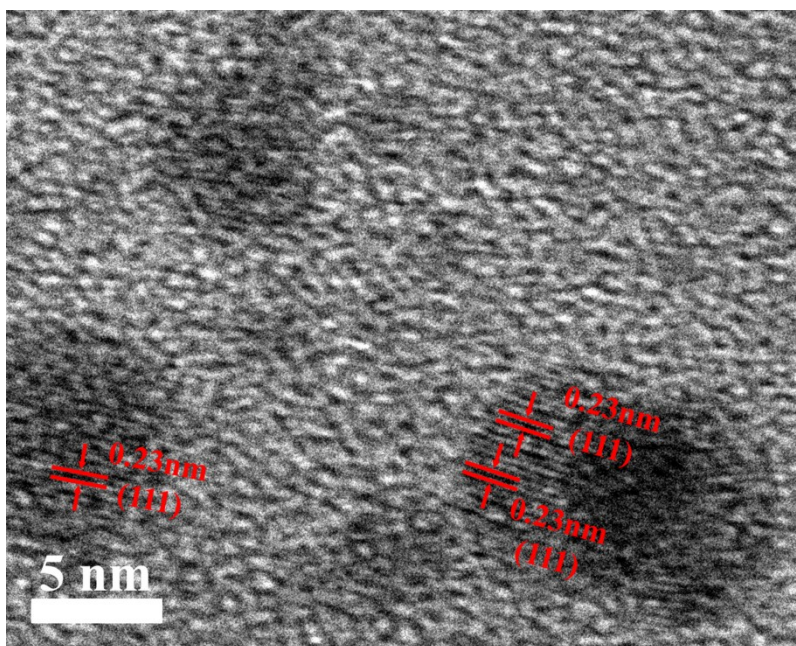


Fig.S7 HRTEM test result of Au/M-BOPs after electrochemical NRR test.

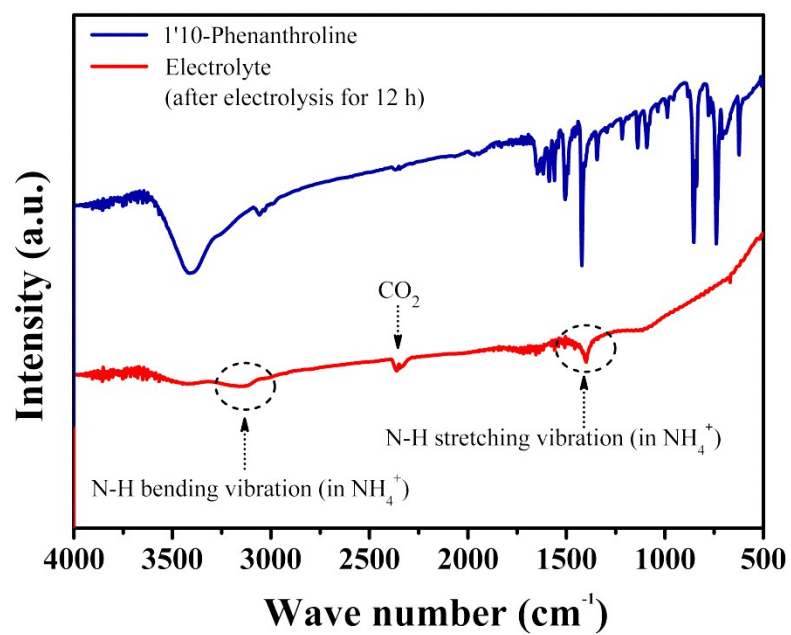


Fig.S8 The FT-IR spectrum of 1'10-phenanthroline and electrolyte (concentrate to dry)

Table S2. Comparison of electro-catalytic NRR performance of various catalysts (NH₃ yield: ug•h⁻¹•mgcat.⁻¹).

Catalyst	Electrolyte	NH ₃ yield (ug•h ⁻¹ •mgcat. ⁻¹)	FE (%)	Year	Ref.
Mo ₂ N nanorod		78.50	4.5	2018	1
Au/ M-BOPs	0.1 M HCl	75.89	10.35	2019	This work
Nb ₂ O ₅		43.60	9.26	2018	2
Fe-N/C		34.83	9.28	2019	3
SA-Mo/NPC	0.1 M KOH	34.0	14.6	2018	4
FL-BP NSs	0.01 M HCl	31.37	5.07	2018	5
Cr ₂ O ₃ nanofiber	0.1 M HCl	28.13	8.56	2018	6
B ₄ C	0.1 M HCl	26.57	15.95	2018	7
Au flowers	0.1 M HCl	25.57	6.05	2018	8
O-KFCNTs	0.1 M HCl	25.12	9.1	2019	9
MoS ₂ -rGO	0.1 M LiClO ₄	24.82	4.58	2019	10
BVC-A		23.21	10.16	2018	11
Co QD/RGO	0.1 M Na ₂ SO ₄	21.5	8.3	2019	12
Au/TiO ₂	0.1 M HCl	21.4	8.11	2017	13
Ti ₃ C ₂ Tx	0.1 M HCl	20.4	9.3	2018	14
Fe ₂ O ₃	0.1 M Na ₂ SO ₄	15.9	0.94	2018	15
CrO _{0.66} N _{0.56}		15.6	6.7	2018	16
B-TiO ₂	0.1 M Na ₂ SO ₄	14.4	3.4	2018	17
Bi NS	0.1 M Na ₂ SO ₄	13.23	10.46	2019	18
Mn ₃ O ₄	0.1 M Na ₂ SO ₄	11.6	3.0	2018	19
Mo ₂ C/C	0.5 M Li ₂ SO ₄	11.3	7.85	2018	20
α-Au/CeO _x -RGO		8.3	10.10	2017	21
PCN-VN ₄		8.09	11.59	2018	22
BCN		7.75	13.79	2019	23
Pd _{0.2} Cu _{0.8} /rGO	0.1 M KOH	2.8	9.3	2018	24
THH Au NRs.		1.648	4.0	2017	25
γ-Fe ₂ O ₃	0.5 M KOH	0.212	1.9	2017	26

Table S3. Comparison of electro-catalytic NRR performance of various catalysts (NH₃ yield: $\mu\text{g}\cdot\text{h}^{-1}\cdot\text{cm}^{-2}$).

Catalyst	Electrolyte	NH ₃ yield ($\mu\text{g}\cdot\text{h}^{-1}\cdot\text{cm}^{-2}$)	FE (%)	Year	Ref.
C-ZIF-1100-1h	0.1 M NaOH	57.8	10.2	2018	27
Au/ M-BOPs	0.1 M HCl	45.54	10.35	2019	This work
Au-PTFE/TS	0.05 M H ₂ SO ₄	18.9	37.8	2019	28
VN/CC	0.1 M HCl	15.17	3.58	2018	29
BC ₃	0.05 M H ₂ SO ₄	9.8	10.8	2018	30
SnO ₂ /CC	0.1 M Na ₂ SO ₄	9.0	2.17	2018	31
TiO ₂ /Ti	0.1 M Na ₂ SO ₄	5.6	2.5	2018	32
MoS ₂ /CC	0.1 M HCl	4.94	1.17	2018	33
AuHNCs	0.5 M LiClO ₄	3.9	30.2	2018	34
Fe ₃ O ₄ /Ti	0.1 M Na ₂ SO ₄	3.43	2.6	2018	35
Ag/CPE	0.1 M HCl	2.83	4.8	2018	36
PEBCD/C	0.5 M Li ₂ SO ₄ and 0.5 M H ₂ SO ₄	2.01	1.71	2017	37
Mo-D-R-5h	0.01 M H ₂ SO ₄	1.89	0.72	2017	38

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