Supplementary Information for

Potassium Ions Promote Electrochemical Nitrogen Reduction on Nano-Au Catalysts Triggered by Bifunctional Boron Supramolecular Assembly

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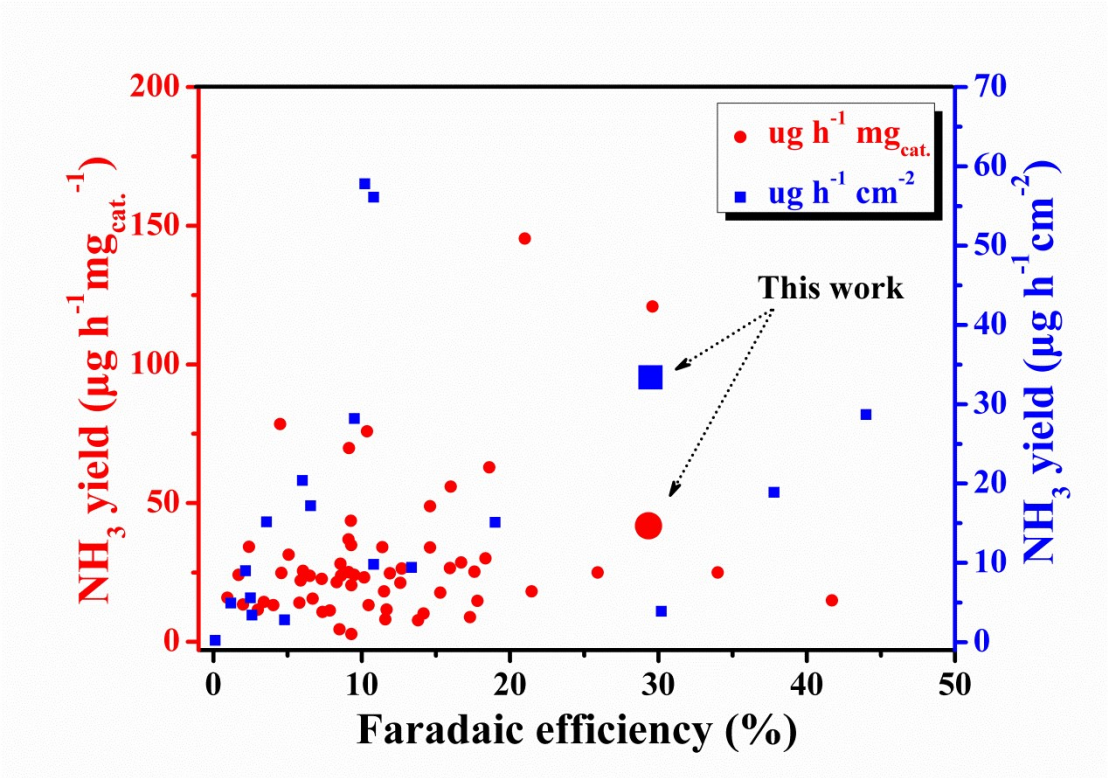

Figure S1. ENRR Performance Status of Reported Catalysts

Table S1. Literature on electrochemical nitrogen reduction.

Entry	Published date	Title	NH_3 yield		FE (%)	Journal	Ref.
			$\mu g\ h^{-1}\ mg_{cat.}^{-1}$	$\mu g\ h^{-1}\ cm^{-2}$			
This work	-	**Potassium Ions Promote Electrochemical Nitrogen Reduction on Nano-Au Catalysts Triggered by Bifunctional Boron Supramolecular Assembly**	**41.69**	**33.36**	**29.53**	-	**This work**
1	2018	A Spectroscopic Study on the Nitrogen Electrochemical Reduction Reaction on Gold and Platinum Surfaces		0.2346	0.12	*J. Am. Chem. Soc.*	1
2	2018	Ammonia Synthesis from Electrocatalytic N_2 Reduction under Ambient Conditions by Fe_2O_3 Nanorods	15.9		0.94	*ChemCatChem*	2
3	2018	Electrochemical Ammonia Synthesis via Nitrogen Reduction Reaction on a MoS_2 Catalyst: Theoretical and Experimental Studies		4.94	1.17	*Adv. Mater.*	3
4	2019	Glycerol oxidation assisted electrocatalytic nitrogen reduction: ammonia and glyceraldehyde co-production on bimetallic RhCu ultrathin nanoflakes nanoaggregates	95.06		1.5	*J. Mater. Chem. A*	4
5	2019	Hierarchical nanoporous Pd1Ag1 alloy enables efficient electrocatalytic nitrogen reduction under ambient conditions	24.1		1.7	*Chem. Commun.*	5
6	2019	Electrochemical Ammonia Synthesis from N_2 and H_2O Catalyzed by Doped $LaFeO_3$ Perovskite under Mild Conditions	13.46		1.99	*Ind. Eng. Chem. Res.*	6
7	2018	Ambient NH_3 synthesisvia electrochemical reduction of N_2 over cubic sub-micron SnO_2 particles		9	2.17	*Chem. Commun.*	7
8	2019	Direct fabrication of bi-metallic PdRu nanorod assemblies for electrochemical ammonia synthesis	34.2		2.4	*Nanoscale*	8
9	2018	Enabling Effective Electrocatalytic N_2 Conversion to NH_3 by the TiO_2 Nanosheets Array under Ambient Conditions		5.6	2.5	*ACS Appl. Mater. Interfaces*	9
10	2018	Ambient N_2 fixation to NH_3 electrocatalyzed by a spinel Fe_3O_4 nanorod		3.43	2.6	*Nanoscale*	10
11	2018	Mn_3O_4 Nanocube: An Efficient Electrocatalyst Toward Artificial N_2 Fixation to NH_3	11.6		3	*Small*	11
12	2018	Boron-Doped TiO_2 for Efficient Electrocatalytic N_2 Fixation to NH_3 at Ambient Conditions	14.4		3.4	*ACS Sustainable Chem. Eng.*	12
13	2018	Highly efficient electrochemical ammonia synthesisvia nitrogen reduction reactions on a VN nanowire array under ambient conditions		15.17	3.58	*Chem. Commun.*	13
14	2019	Boron Nanosheet: An Elemental Two-Dimensional (2D) Material for Ambient Electrocatalytic N_2-to-NH_3 Fixation in Neutral Media	13.22		4.04	*ACS Catal.*	8
15	2018	Electrochemical N_2 fixation to NH_3 under ambient conditions: Mo_2N nanorod as a highly efficient and selective catalyst	78.5		4.5	*Chem. Commun.*	14
16	2019	MoS_2 nanosheet-reduced graphene oxide hybrid: an efficient electrocatalyst for electrocatalytic N_2 reduction to NH_3 at ambient conditions	24.82		4.58	*J. Mater. Chem. A*	15
17	2018	Ag nanosheets for efficient electrocatalytic N_2 fixation to NH_3 under ambient conditions		2.83	4.8	*Chem. Commun.*	16
18	2018	Ammonia Synthesis Under Ambient Conditions: Selective Electroreduction of Dinitrogen to Ammonia on Black Phosphorus Nanosheets	31.37		5.07	*Angew. Chem., Int. Ed.*	17
19	2019	Electrospun TiC/C nanofiber for ambient electrocatalytic N_2 reduction	14.1		5.8	*J. Mater. Chem. A*	18
20	2019	An Fe_2O_3 nanoparticle-reduced graphene oxide composite for ambient electrocatalytic N_2 reduction to NH_3	22.13		5.89	*Inorg. Chem. Front.*	19
21	2018	Mechanistic Insights into Electrochemical Nitrogen Reduction Reaction on Vanadium Nitride Nanoparticles		20.38	6	*J. Am. Chem. Soc.*	20

22	2018	**Ambient Electrochemical Synthesis of Ammonia from Nitrogen and Water Catalyzed by Flower-Like Gold Microstructures**	25.57		6.05	***ChemSusChem***	**21**
23	2019	**Amorphous Sn/Crystalline SnS_2 Nanosheets via In Situ Electrochemical Reduction Methodology for Highly Efficient Ambient N_2 Fixation**	23.8		6.5	***Small***	**22**
24	2019	**Boosting selective nitrogen reduction to ammonia on electron-deficient copper nanoparticles**		17.2	6.56	***Nat. Commun.***	**22**
25	2018	**Chromium Oxynitride Electrocatalysts for Electrochemical Synthesis of Ammonia Under Ambient Conditions**	15.56		6.7	***Small Methods***	**23**
26	2019	**Nitrogen-Doped NiO Nanosheet Array for Boosted Electrocatalytic N_2 reduction**	22.7		7.3	***ChemCatChem***	**24**
27	2018	**Hierarchical Cobalt Phosphide Hollow Nanocages toward Electrocatalytic Ammonia Synthesis under Ambient Pressure and Room Temperature**	10.78		7.36	***Small Methods***	**25**
28	2018	**Molybdenum Carbide Nanodots Enable Efficient Electrocatalytic Nitrogen Fixation under Ambient Conditions**	11.3		7.85	***Adv. Mater.***	**26**
29	2019	**Efficient Electrocatalytic N_2 Reduction on CoO Quantum Dots**	21.5		8.3	***J. Mater. Chem. A***	**27**
30	2018	**Ambient ammonia synthesis via palladium-catalyzed electrohydrogenation of dinitrogen at low overpotential**	4.5		8.5	***Nat. Commun.***	**28**
31	2018	**Cr_2O_3 nanofiber: a high-performance electrocatalyst toward artificial N_2 fixation to NH_3 under ambient conditions**	28.13		8.56	***Chem. Commun.***	**29**
32	2019	**Cr_3C_2 Nanoparticle-Embedded Carbon Nanofiber for Artificial Synthesis of NH_3 through N_2 Fixation under Ambient Conditions**	23.9		8.6	***ACS Appl. Mater. Interfaces***	**30**
33	2019	**Biomass-derived oxygen-doped hollow carbon microtubes for electrocatalytic N_2-to-NH_3 fixation at ambient conditions**	25.12		9.1	***Chem. Commun.***	**31**
34	2019	**Fluorine-free Ti_3C_2Tx (T ¼ O, OH) nanosheets (50 – 100 nm) for nitrogen fixation under ambient conditions**	36.9		9.1	***J. Mater. Chem. A***	**32**
35	2019	**Sulfur vacancy-rich N-doped MoS_2 nanoflowers for highly boosting electrocatalytic N_2 fixation to NH_3 under ambient conditions**	69.82		9.14	***Chem. Commun.***	**32**
36	2018	**Ambient N_2 fixation to NH_3 at ambient conditions: Using Nb_2O_5 nanofiber as a high-performance electrocatalyst**	43.6		9.26	***Nano Energy***	**33**
37	2019	**Rational Design of Fe–N/C Hybrid for Enhanced Nitrogen Reduction Electrocatalysis under Ambient Conditions in Aqueous Solution**	34.83		9.28	***ACS Catal.***	**34**
38	2018	**Ti_3C_2Tx(T 1/4 F, OH) MXene nanosheets: conductive 2D catalysts for ambient electrohydrogenation of N_2 to NH_3**	20.4		9.3	***J. Mater. Chem. A***	**35**
39	2018	**Anchoring PdCu Amorphous Nanocluster on Graphene for Electrochemical Reduction of N_2 to NH_3 under Ambient Conditions in Aqueous Solution**	2.8		9.3	***Adv. Energy Mater.***	**36**
40	2019	**Improving the electrocatalytic N_2 reduction activity of Pd nanoparticles through surface modification**	24.12		9.49	***J. Mater. Chem. A***	**37**
41	2019	**Ambient Electrosynthesis of Ammonia on a Core–Shell-Structured Au@CeO_2 Catalyst Contribution of Oxygen Vacancies in CeO_2**		28.2	9.5	***Chem. - Eur. J.***	**38**
42	2018	**An Amorphous Noble-Metal-Free Electrocatalyst that Enables Nitrogen Fixation under Ambient Conditions**	23.21		10.16	***Angew. Chem., Int. Ed.***	**39**
43	2018	**Metal-organic framework-derived nitrogen-doped highly disordered carbon for electrochemical ammonia synthesis using N_2 and H_2O in alkaline electrolytes**		57.8	10.2	***Nano Energy***	**40**
44	2019	**In situ nano Au triggered by a metal boron organic polymer: efficient electrochemical N_2 fixation to NH_3 under ambient conditions**	75.89		10.35	***J. Mater. Chem. A***	**41**
45	2019	**2D Mosaic Bismuth Nanosheets for Highly Selective Ambient Electrocatalytic Nitrogen Reduction**	13.23		10.46	***ACS Catal.***	**42**
46	2018	**Boron-Doped Graphene for Electrocatalytic N_2 Reduction**		9.8	10.8	***Joule***	**43**

47	2019	**Self-organized growth of flower-like SnS_2 and forest-like ZnS nanoarrays on nickel foam for synergistic superiority in electrochemical ammonia synthesis**		56.12	10.8	***J. Mater. Chem. A***	**44**
48	2019	**An MnO_2–Ti_3C_2Tx MXene nanohybrid: an efficient and durable electrocatalyst toward artificial N_2 fixation to NH_3 under ambient conditions**	34.12		11.39	***J. Mater. Chem. A***	**45**
49	2019	**Construction of PdO–Pd Interface Assisted by Laser Irradiation for Enhanced Electrocatalytic N_2 Reduction Reaction**	18.2		11.5	***J. Mater. Chem. A***	**46**
50	2018	**Defect Engineering Metal-Free Polymeric Carbon Nitride Electrocatalyst for Effective Nitrogen Fixation under Ambient Conditions**	8.09		11.59	***Angew. Chem., Int. Ed.***	**47**
51	2019	**Nitrogen Vacancies on 2D Layered W_2N_3: A Stable and Efficient Active Site for Nitrogen Reduction Reaction**	11.66		11.67	***Adv. Mater.***	**48**
52	2019	**Boosting electrocatalytic nitrogen fixationvia energy-efficient anodic oxidation of sodium gluconate**	24.7		11.9	***Chem. Commun.***	**49**
53	2019	**Electrocatalytic N_2-to-NH_3 conversion using oxygen-doped graphene: experimental and theoretical studies**	21.3		12.6	***Chem. Commun.***	**50**
54	2019	**Ambient electrohydrogenation of N_2 for NH_3 synthesis on non-metal boron phosphide nanoparticles: the critical role of P in boosting the catalytic activity**	26.42		12.7	***J. Mater. Chem. A***	**34**
55	2019	**Electrochemical Fabrication of Porous Au Film on Ni Foam for Nitrogen Reduction to Ammonia**		9.42	13.36	***Small***	**51**
56	2019	**B-N Pairs Enriched Defective Carbon Nanosheets for Ammonia Synthesis with High Efficiency**	7.75		13.79	***Small***	**52**
57	2019	**Identification of FeN_4 as an Efficient Active Site for Electrochemical N_2 Reduction**	10.25		14.17	***ACS Catal.***	**53**
58	2018	**Atomically dispersed Mo catalysts for high-efficiency ambient N_2 fixation**	34		14.6	***Angew. Chem., Int. Ed.***	**54**
59	2019	**Stable Confinement of Black Phosphorus Quantum Dots on Black Tin Oxide Nanotubes-A Robust, Double-Active Electrocatalyst toward Efficient Nitrogen Fixation**	48.87		14.6	***Angew. Chem., Int. Ed.***	**55**
60	2019	**Greatly Enhanced Electrocatalytic N_2 Reduction on TiO_2 via V Doping**	17.73		15.3	***Small Methods***	**56**
61	2018	**High-performance artificial nitrogen fixation at ambient conditions using a metal-free electrocatalyst**	26.57		15.95	***Nat. Commun.***	**57**
62	2019	**Ambient electrocatalytic N_2 reduction to NH_3 by metal fluorides**	55.9		16	***J. Mater. Chem. A***	**58**
63	2019	**B_4C nanosheets decorated within situ-derived boron-doped graphene quantum dots for high-efficiency ambient N_2 fixation**	28.6		16.7	***J. Mater. Chem. A***	**59**
64	2019	**Doping strain induced bi-Ti^{3+} pairs for efficient N_2 activation and electrocatalytic fixation**	8.9		17.3	***Nat. Commun.***	**60**
65	2019	**Facile, Cost-Effective Plasma Synthesis of Self-Supportive FeS_x on Fe Foam for Efficient Electrochemical Reduction of N_2 under Ambient Conditions**	25.28		17.6	***J. Mater. Chem. A***	**61**
66	2019	**Enhanced Electrocatalytic N_2 Reduction via Partial Anion Substitution in Titanium Oxide–Carbon Composites**	14.8		17.8	***Angew. Chem., Int. Ed.***	**62**
67	2019	**Synergistic Electrocatalytic Nitrogen Reduction Enabled by Confinement of Nanosized Au Particles onto Two-Dimensional Ti_3C_2 Substrate**	30.06		18.34	***ACS Appl. Mater. Interfaces***	**63**
68	2019	**Nitrogen coordinated single Fe sites for efficient electrocatalytic N_2 fixation in neutral media**	62.9		18.6	***Nano Energy***	**64**
69	2019	**Electron localization of gold in control of nitrogen-to-ammonia fixation**		15.1	19	***Angew. Chem., Int. Ed.***	**65**
70	2019	**Highly Efficient and Selective Generation of Ammonia and Hydrogen on a Graphdiyne-based Catalyst**	145.4		21	***J. Am. Chem. Soc.***	**66**
71	2019	**Tunable synthesis of multiply-twinned intermetallic Pd_3Pb nanowire networks toward efficient N_2 to NH_3 conversion**	18.2		21.46	***J. Mater. Chem. A***	**67**

72	2019	**Interfacial engineering of cobalt sulfide/graphene hybrids for highly efficient ammonia electrosynthesis**	25		25.9	***Proc. Natl. Acad. Sci. USA***	**68**
73	2018	**Achieving a Record-High Yield Rate of 120.9 μgNH_3 $mg_{cat.}^{-1}$ h^{-1} for N_2 Electrochemical Reduction over Ru Single-Atom Catalysts**	120.9		29.6	***Adv. Mater.***	**69**
74	2018	**Enhancing the rate of electrochemical nitrogen reduction reaction for ammonia synthesis under ambient conditions using hollow gold nanocages**		3.9	30.2	***Nano Energy***	**70**
75	2019	**Antimony-Based Composites Loading on Phosphorus-Doped Carbon for Boosting Faradaic Efficiency of the Electrochemical Nitrogen Reduction Reaction**	25		34	***Angew. Chem., Int. Ed.***	**71**
76	2019	**Photoelectrochemical Synthesis of Ammonia on the Aerophilic-Hydrophilic Heterostructure with 37.8% Efficiency**		18.9	37.8	**Chem**	**72**
77	2019	**Atomically dispersed metal dimer species with selective catalytic activity for nitrogen electrochemical reduction**	14.95		41.7	***J. Mater. Chem. A***	**73**
78	2019	**Nanoporous Gold Embedded ZIF Composite for Enhanced Electrochemical Nitrogen Fixation trochemical Nitrogen Fixation**		28.7	44	***Angew. Chem., Int. Ed.***	**74**

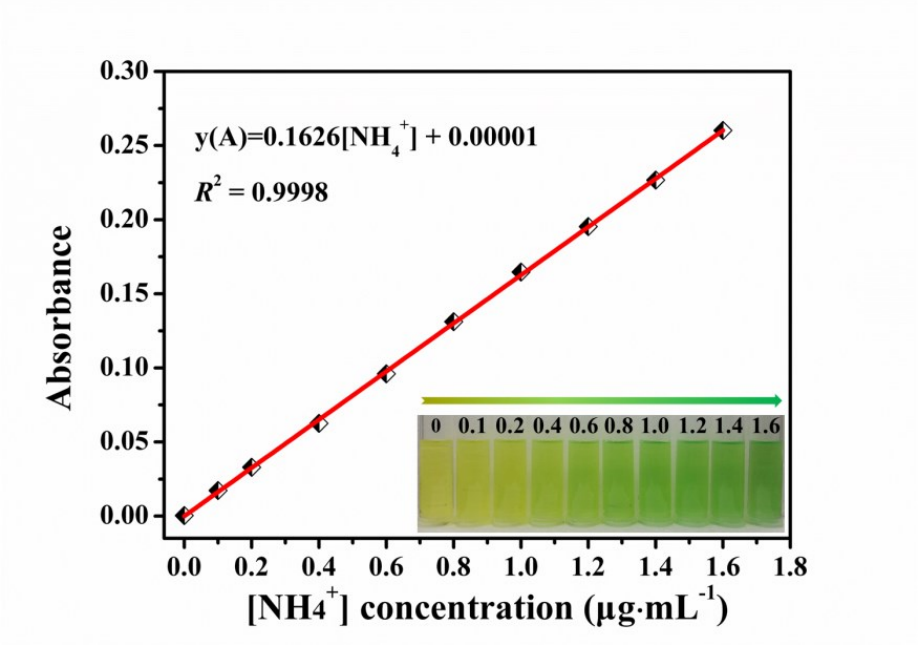

Figure S2. NH_4Cl standard curve by indophenol blue colorimetric method

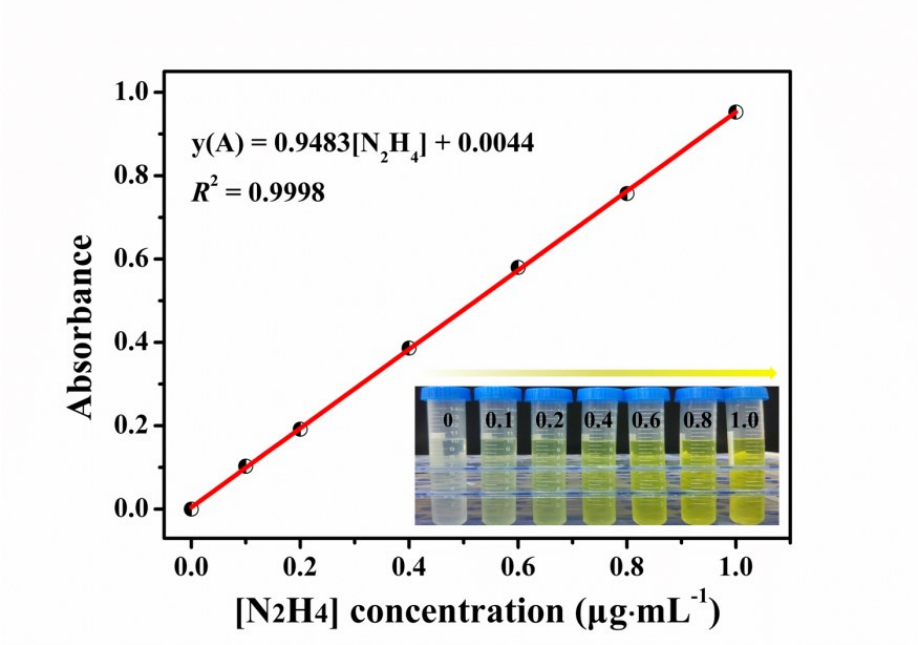

Figure S3. N_2H_4 standard curve by Watt-Chrisp colorimetric method

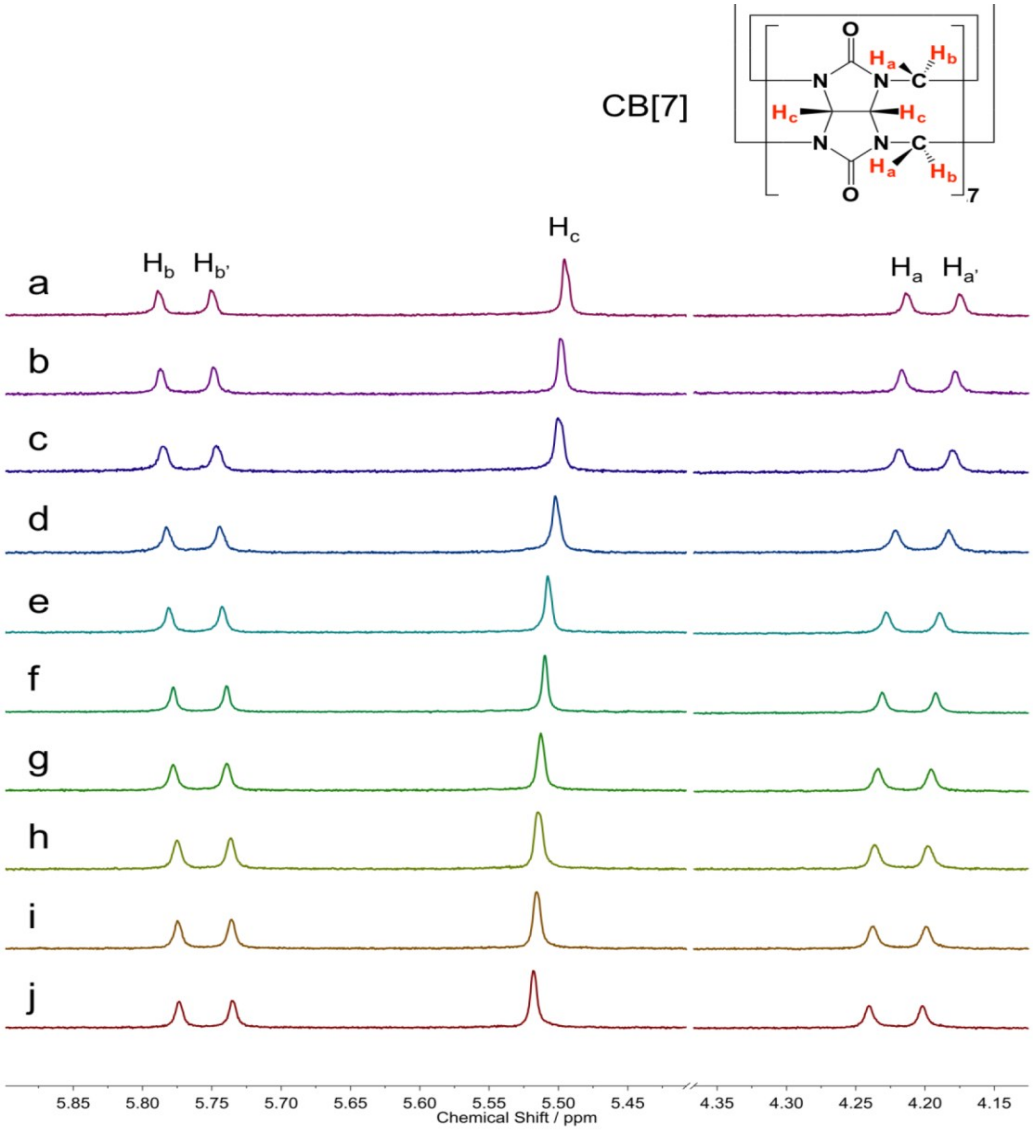

Figure S4. ^{1}H NMR Titration Experiment of *closo*-$[B_{12}H_{12}]^{2-}$ and CB[7]

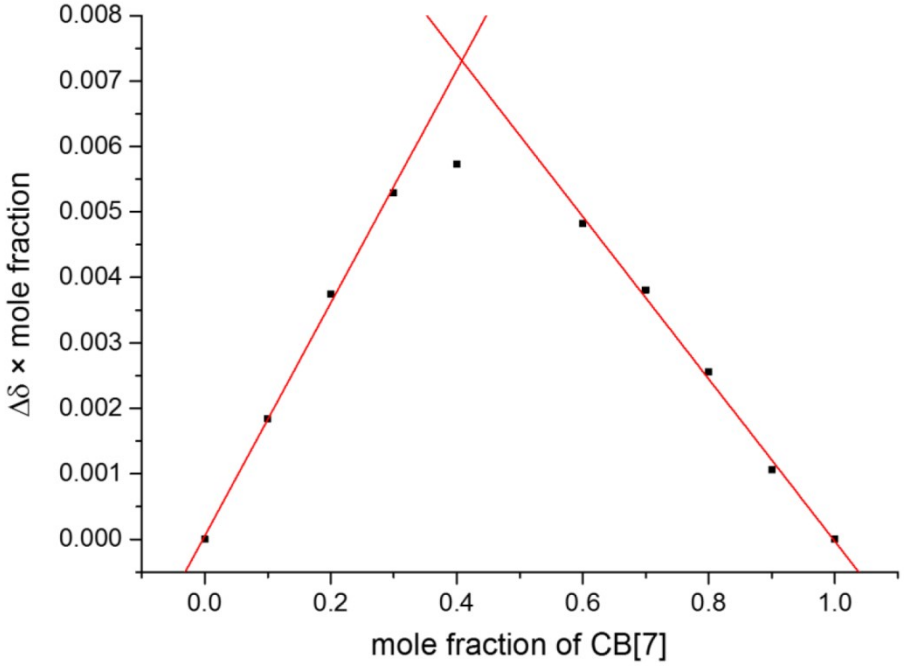

Figure S5. Corresponding Job's curves of ^{1}H NMR titration experiments

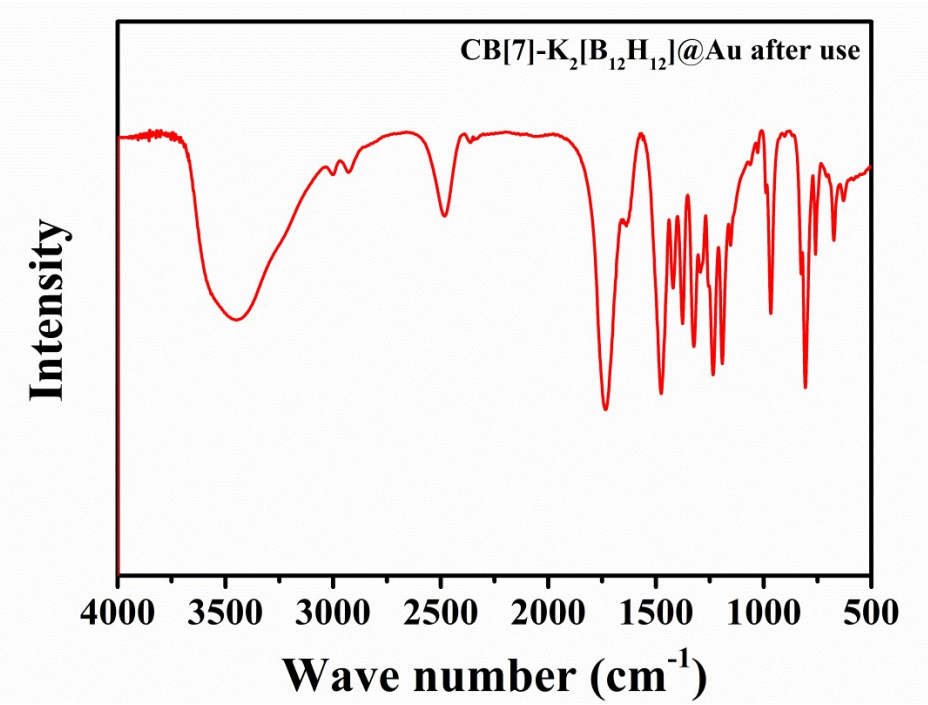

Figure S6. FT-IR spectrum of CB[7]-$K_2[B_{12}H_{12}]$@Au after reuse

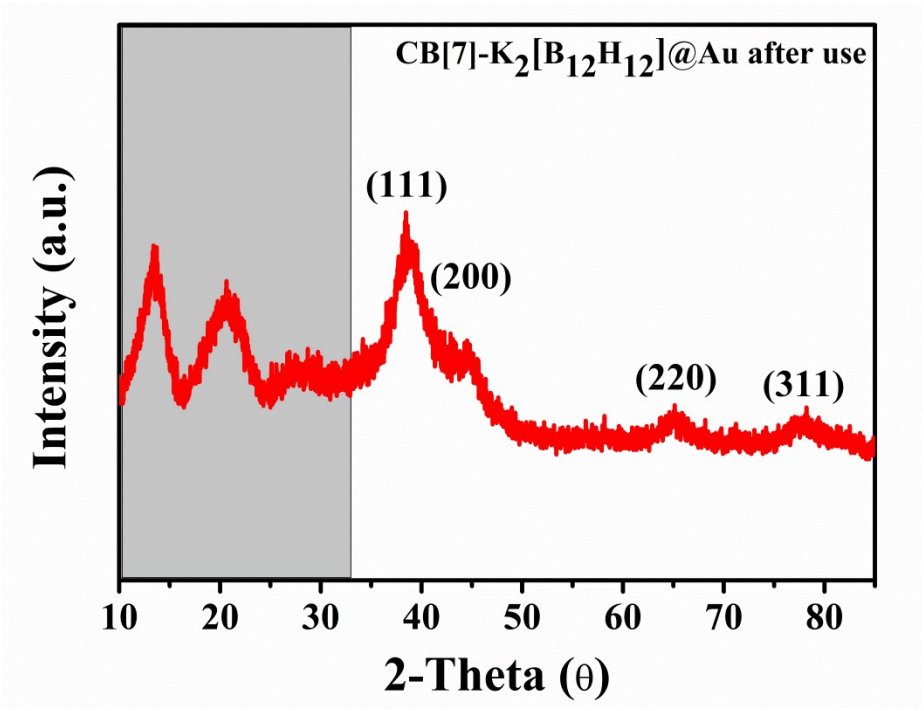

Figure S7. PXRD result of CB[7]-$K_2[B_{12}H_{12}]$@Au after reuse

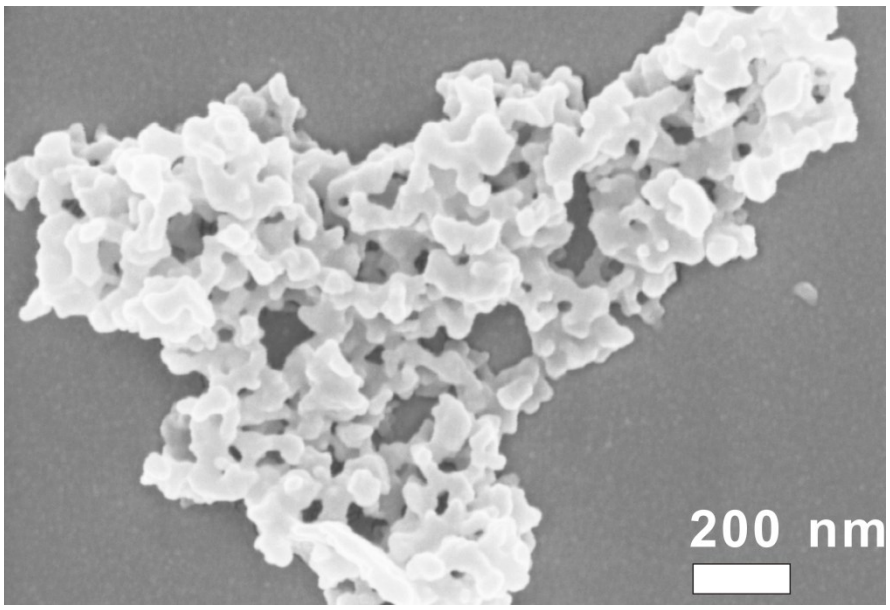

Figure S8. SEM image of CB[7]-$K_2[B_{12}H_{12}]$@Au after reuse

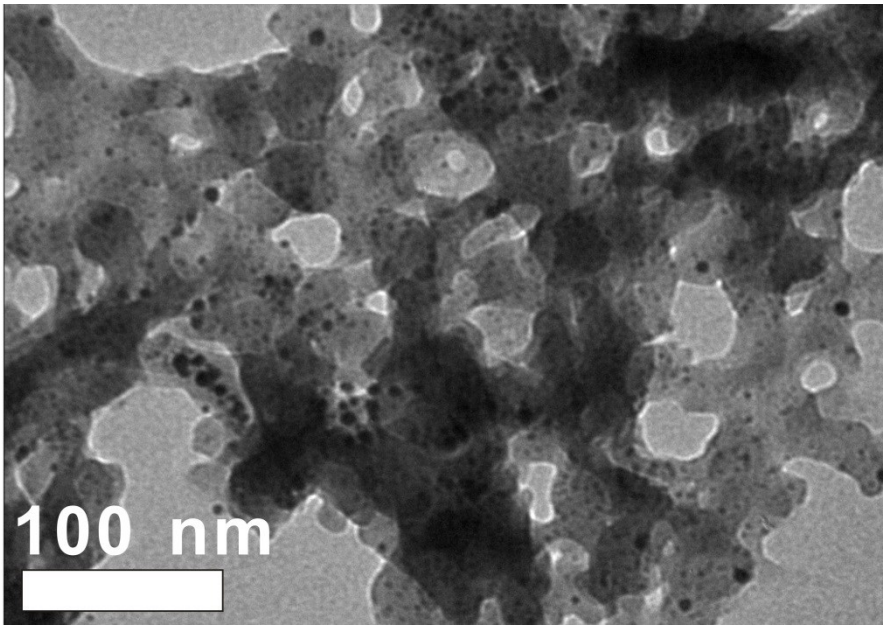

Figure S9. TEM image of CB[7]-$K_2[B_{12}H_{12}]$@Au after reuse

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