Electronic Supplementary Information for

Ag-NPs embedded in two novel Zn_3/Zn_5-cluster-based metal- organic frameworks for catalytic reduction of 2/3/4-nitrophenol

Xue-Qian Wu,[a] Dan-Dan Huang,[a] Zhi-Hang Zhou,[a] Wen-Wen Dong,[a] Ya-Pan Wu,[a] Jun Zhao,[a] Dong-Sheng Li,[a]* Qi-Chun Zhang[b]* and Xianhui Bu[c]

[a] *College of Materials and Chemical Engineering, Hubei Provincial Collaborative Innovation Center for New Energy Microgrid, Key Laboratory of Inorganic Nonmetallic Crystalline and Energy Conversion Materials, China Three Gorges University, Yichang, 443002, PR China*

[b] *School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore*

[c] *Department of Chemistry and Biochemistry, California State University, Long Beach, 1250 Bellflower Boulevard, Long Beach, CA 90840, USA*

* Corresponding author: College of Materials and Chemical Engineering, China Three Gorges University, Yichang, P. R. China. Tel./Fax: +86-717- 6397506 E-mail address: lidongsheng1@126.com (D.-S. Li) ;

* Corresponding author: School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore;E-mail address: qczhang@ntu.edu.sgc (Q.-C. Zhang)

Table S1 Selected bond lengths (Å) and bond angles (°) for CTGU-3 and CTGU-4

CTGU-3			
Zn(1)-O(11)	2.064(2)	O(11)-Zn(1)-O(1)#1	88.99(11)
Zn(1)-O(1)	2.065(3)	O(11)-Zn(1)-O(10)	96.32(10)
Zn(1)-O(10)	2.163(3)	O(1)#1-Zn(1)-O(10)	90.40(11)
Zn(2)-O(7)#2	1.922(3)	O(7)#2-Zn(2)-O(2)	116.84(13)
Zn(2)-O(2)	1.951(3)	O(7)#2-Zn(2)-O(11)	109.40(11)
Zn(2)-O(11)	1.969(2)	O(2)-Zn(2)-O(11)	116.49(11)
Zn(2)-O(6)#3	1.988(3)	O(7)#2-Zn(2)-O(6)#3	104.90(13)
Zn(3)-O(3)#4	1.927(3)	O(2)-Zn(2)-O(6)#3	99.60(13)
Zn(3)-O(9)	1.946(3)	O(11)-Zn(2)-O(6)#3	108.10(11)
Zn(3)-O(5)#3	1.964(3)	O(3)#4-Zn(3)-O(9)	124.06(14)
Zn(3)-O(11)	1.970(2)	O(3)#4-Zn(3)-O(5)#3	109.49(15)
O(9)-Zn(3)-O(5)#3	101.78(13)	O(3)#4-Zn(3)-O(11)	104.22(13)
O(9)-Zn(3)-O(11)	110.06(11)	O(5)#3-Zn(3)-O(11)	106.14(12)
Zn(3)-O(11)-Zn(2)	113.54(12)	Zn(3)-O(11)-Zn(1)	112.66(11)
Zn(2)-O(11)-Zn(1)	107.40(11)		

CTGU-4			
Zn(1)-O(7)	2.072(4)	O(7)#1-Zn(1)-O(1)#1	89.05(15)
Zn(1)-O(1)	2.088(3)	O(7)#1-Zn(1)-O(8)	88.05(15)
Zn(1)-O(8)	2.113(5)	O(1)#1-Zn(1)-O(8)	87.30(15)
Zn(1)-O(6)	2.178(4)	O(7)#1-Zn(1)-O(6)	90.04(12)
Zn(2)-O(4)#2	1.903(3)	O(1)#1-Zn(1)-O(6)	94.62(11)
Zn(2)-O(2)	1.929(3)	O(8)-Zn(1)-O(6)	177.3(2)
Zn(2)-O(6)	1.966(2)	O(4)#2-Zn(2)-O(2)	111.79(17)
Zn(2)-O(5)#3	1.970(3)	O(4)#2-Zn(2)-O(6)	122.02(18)
O(2)-Zn(2)-O(6)	109.86(15)	O(4)#2-Zn(2)-O(5)#3	98.38(15)

O(2)-Zn(2)-O(5)#3	103.19(15)	O(6)-Zn(2)-O(5)#3	109.34(12)
Zn(2)-O(6)-Zn(1)	112.15(12)	Zn(2)-O(6)-Zn(2)#1	107.93(19)

Symmetry codes: #1: -x + 2, -y + 1, -z + 1; #2: x, y + 1, z; #3: -x + 1, -y + 1, -z + 1; #4: x, y, z + 1 for **1;** #1: -x, y, z; #2: - x + 1/2, -y + 2, z + 1/2; #3: x, y + 1, z for **2**.

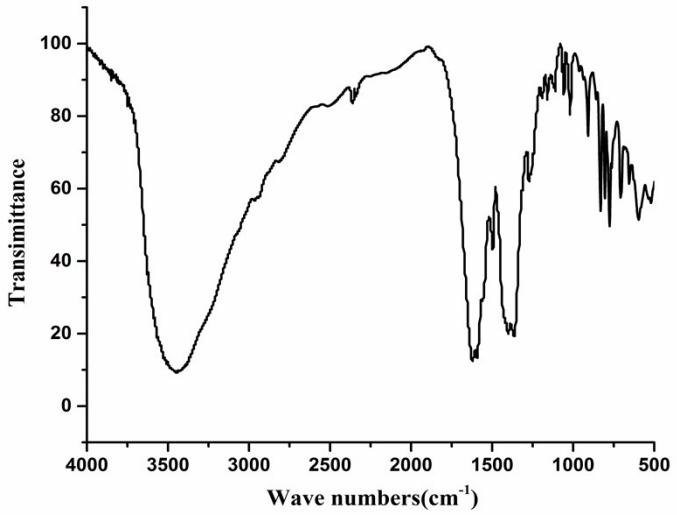

Fig. S1 Infrared spectra of CTGU-3

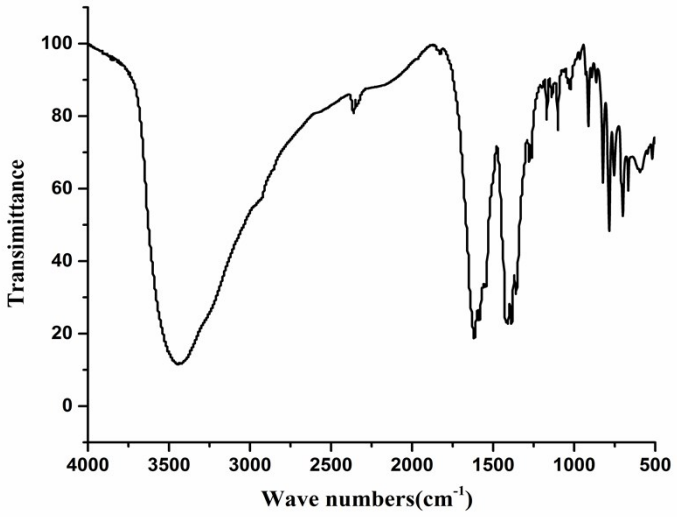

Fig. S2 Infrared spectra of CTGU-4

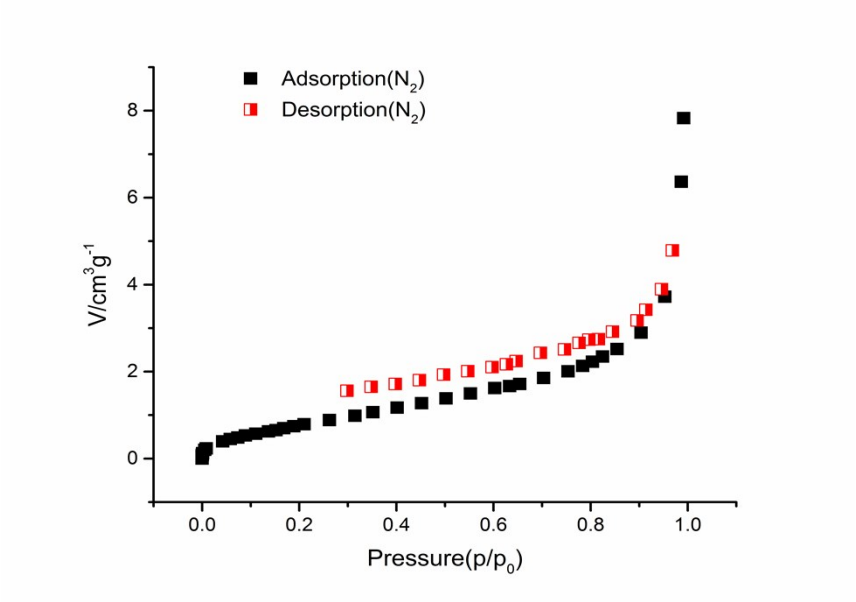

Fig. S3 N_2 sorption isotherms for CTGU-4 at 77 K.

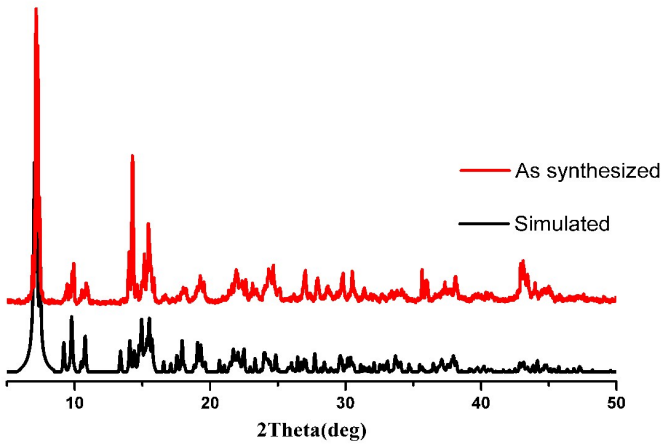

Fig. S4 The PXRD patterns of CTGU-3 sample

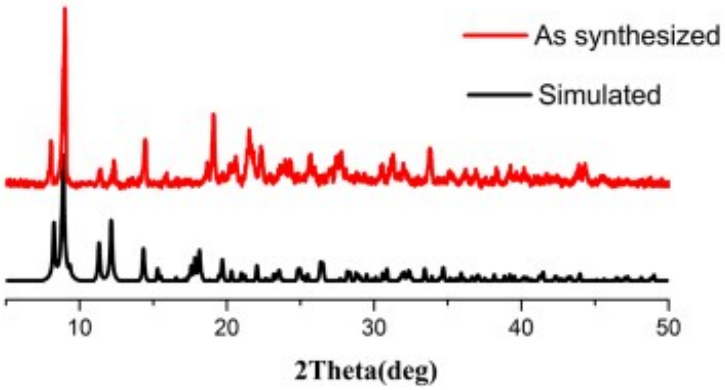

Fig. S5 The PXRD patterns of CTGU-4 sample

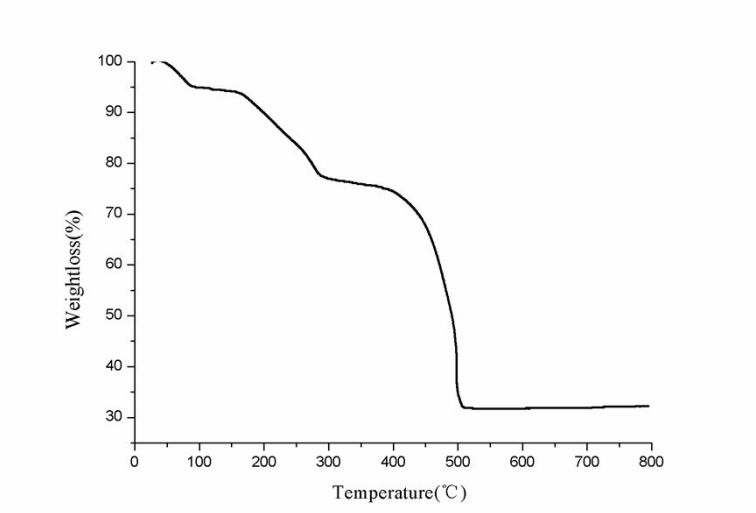

Fig. S6 Thermogravimetric analysis of CTGU-3 sample

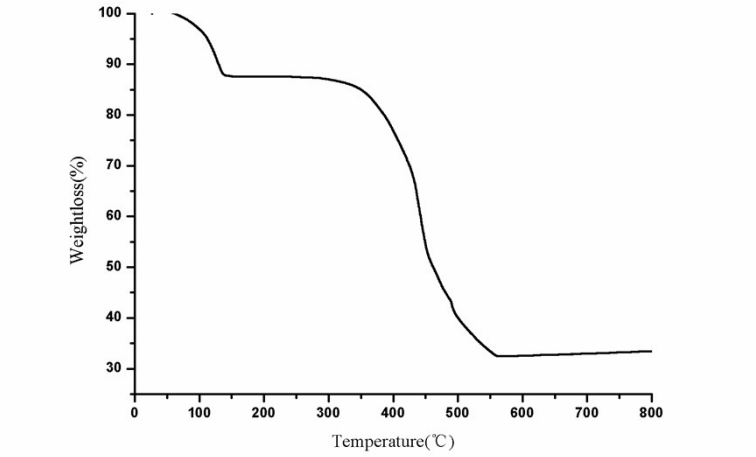

Fig. S7 Thermogravimetric analysis of CTGU-4 sample

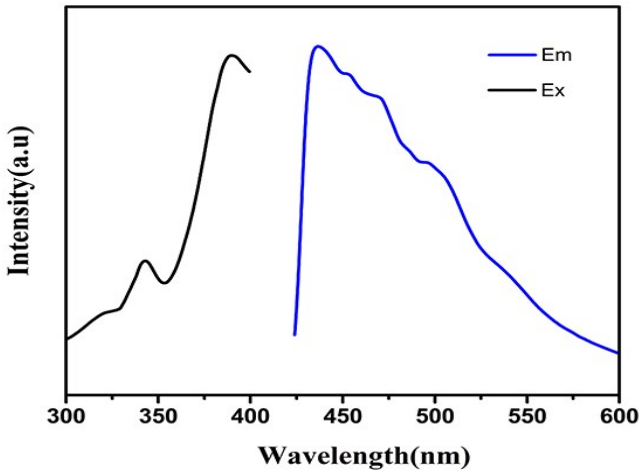

Fig S8 Solid-state photoluminescent spectra of free ligand H_5L1

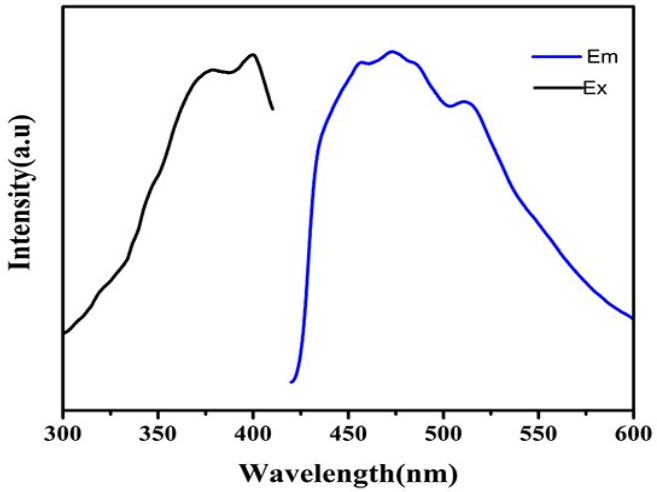

Fig S9 Solid-state photoluminescent spectra of free ligand H_5L2

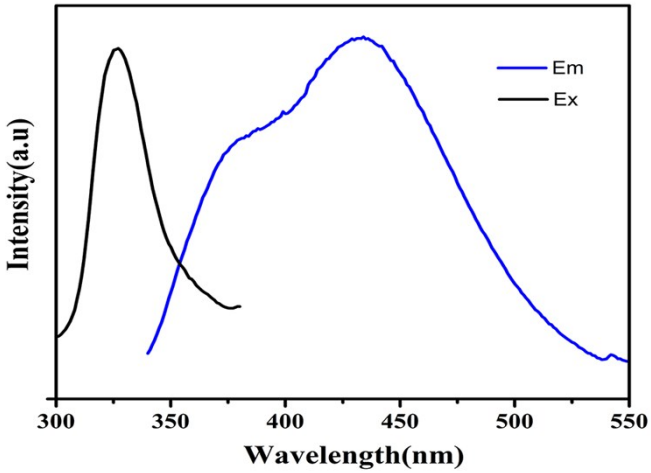

Fig S10 Solid-state photoluminescent spectra of CTGU-3

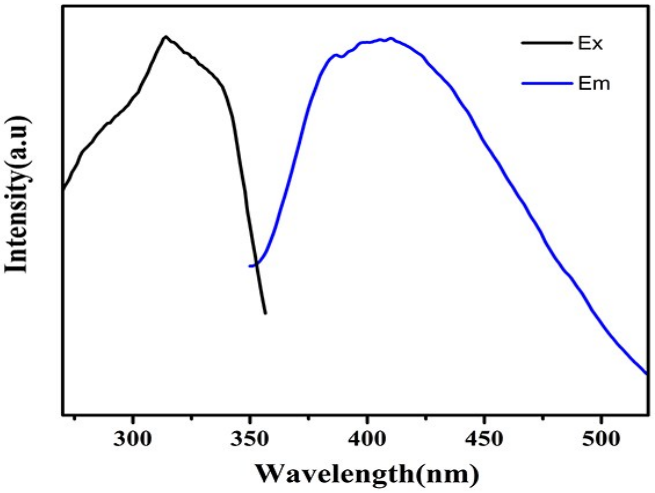

Fig S11 Solid-state photoluminescent spectra of CTGU-4

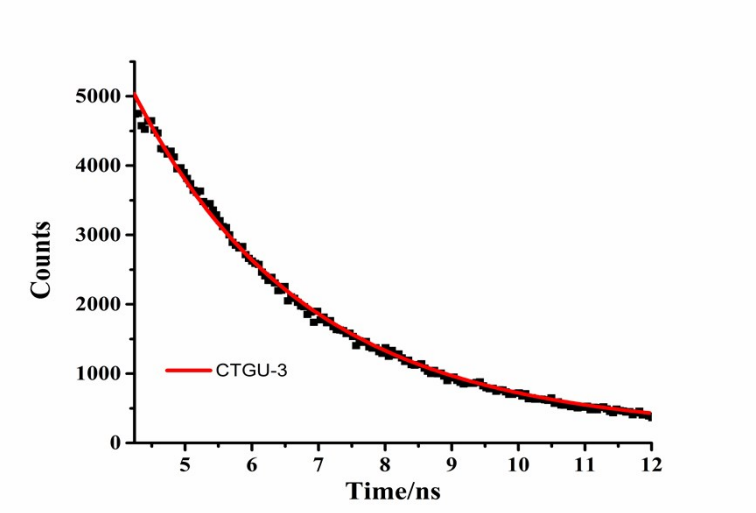

Fig S12 Emission lifetime of CTGU-3

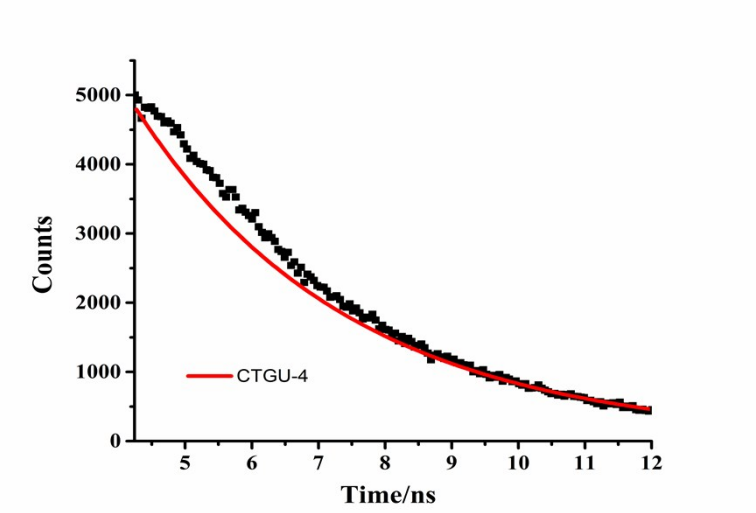

Fig S13 Emission lifetime of CTGU-4

Table S2 Summary of rate constants of other similar 4-nitrophenol reduction reactions catalyzed by previously reported catalysts

Name of Catalyst	reaction rate constants per unit mass (s^{-1} g^{-1})	Reference
Pd@Y-DDQ	3.40	*Sci. Rep*., 2016, **6**, 29728.
CuO-Ag	6.40	*J. Phys. Chem. C*., 2016, **120**, 21580.
Au/ZSBA-PL	2.36	*Nano Res*., 2016, **9**, 3099.
Fe3O4@SiO2@C@Ni	4.50	*Nanoscale*, 2016, **8**, 15978.

Cu@eggshell	2.40	*Appl. Catal. B Environ*., 2016, **191**, 209.
Ag/CFN	0.14	*Appl. Catal. B Environ*., 2016, **188**, 245.
Au-Cu alloy	2.30	*Nat. Commun*., 2014, **5**, 4327.
Ni-P/NFM	6.01	*Appl. Catal. B Environ*., 2016, **196**, 223.
Au@S-CLLCS	2.30	*Langmuir,* 2016, **32**, 10895.
Au@L-CLLCS	1.35	*Langmuir,* 2016, **32**, 10895.
Au NPs	0.51	*ACS Nano,* 2016, **10**, 9470.
Au-Pd/clay	13.66	*Chem. Commun.,* 2014*,* **50**, 3014.
Cu@Ni/RGO	4.6	*Int. J. Hydrogen. Energ.,* 2016, **41**, 11608.
Pt@OMS	3.53	*Chem. Eur. J.* 2016, **22**, 9293.
Pt-in-ANTs	13.3	*Chem. Eur. J.* 2016, **22**, 8438.
Ni/C-400	6.3	*Catal. Commun.,* 2016, **79***,* 63.
Ag/POM-1	3.65	*Chem. Asian. J.,* 2016, **11**, 858.
Ag/POM-2	3.69	*Chem. Asian. J.,* 2016, **11**, 858.
Ag@CTGU-3	8.64	This Work
Ag@CTGU-4	3.03	This Work

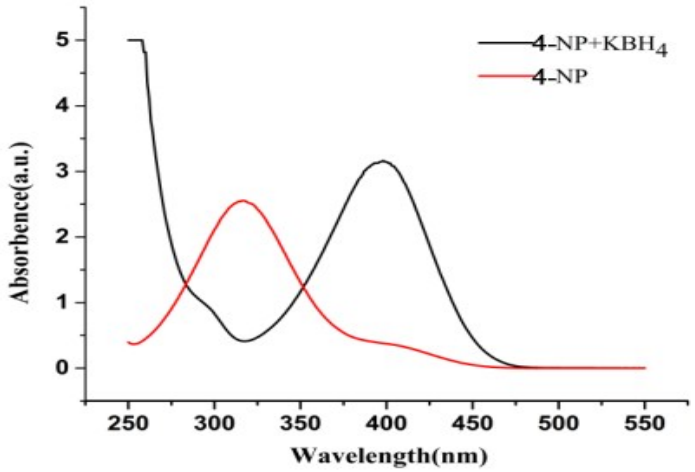

Fig S14 UV-Vis absorption spectra of the aqueous solution of 4-NP in the presence of KBH_4.

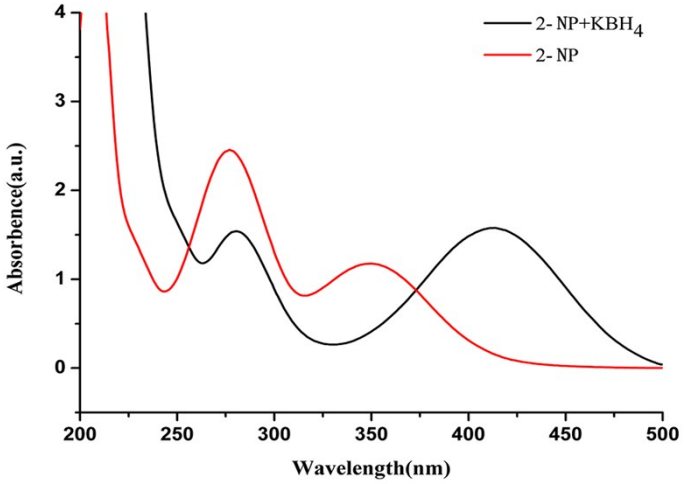

Fig S15 UV-Vis absorption spectra of the aqueous solution of 2-NP in the presence of KBH_4.

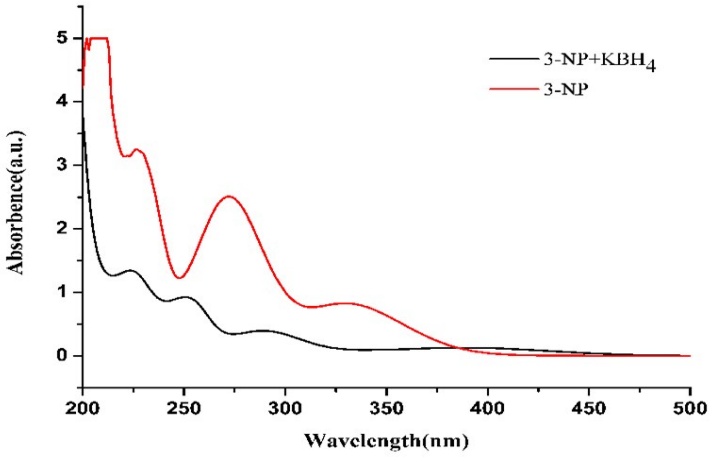

Fig S16 UV-Vis absorption spectra of the aqueous solution of 3-NP in the presence of KBH_4.

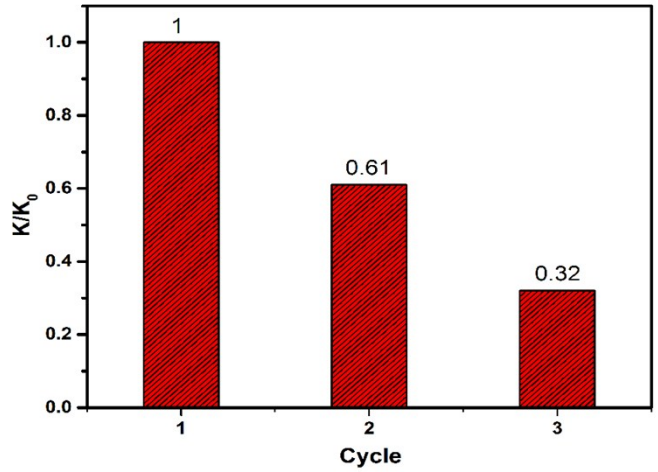

Fig S17 Cyclic test of Ag@CTGU-3 under the same experimental condition.

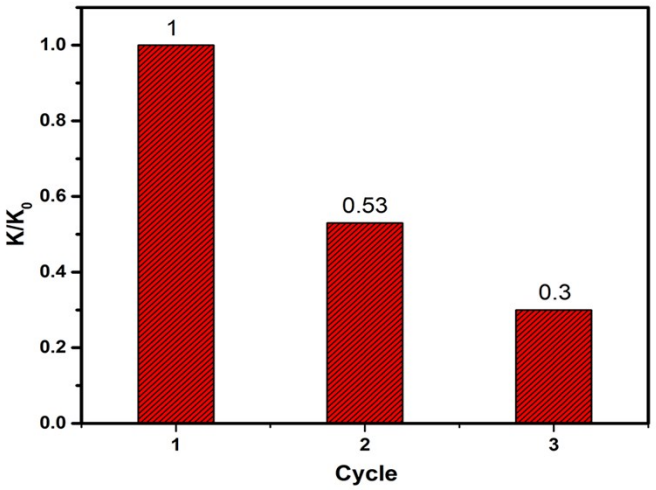

Fig S18 Cyclic test of Ag@CTGU-4 under the same experimental condition.

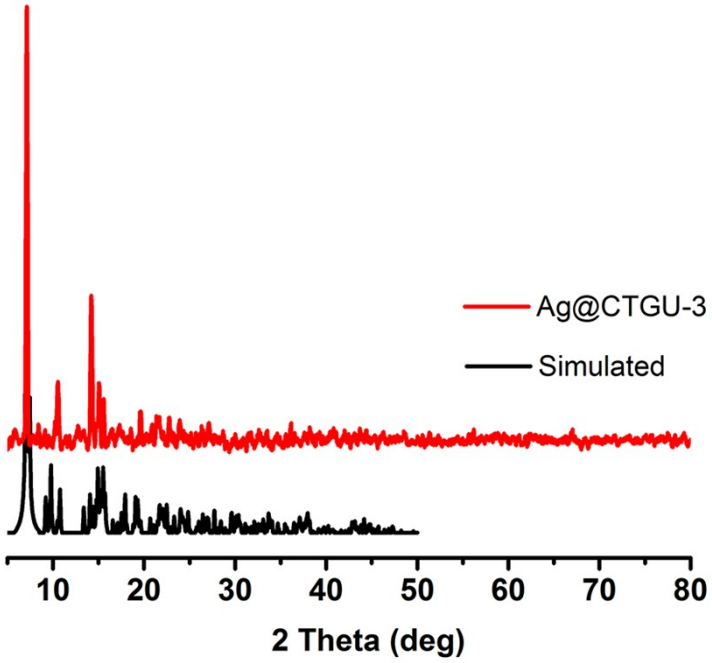

Fig S19 The PXRD patterns of Ag@CTGU-3 sample

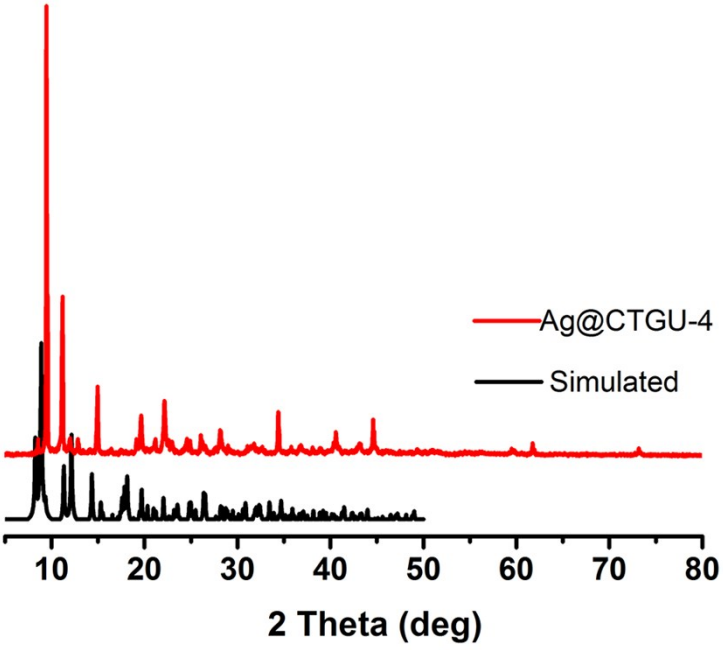

Fig S20 The PXRD patterns of Ag@CTGU-4 sample

Table S3 Summary of rate constants of other similar 2-nitrophenol reduction reactions catalyzed by previously reported catalysts

Name of Catalyst	reaction rate constants per unit mass (s^{-1} g^{-1})	Reference
Fe_3O_4/SiO_2@Ag	5.5	*Appl. Catal. A: Gen.,* 2012, **413**, 170.
Cu/CS-CMM	6	*Appl. Surf. Sci.*, 2016, **387**, 1154.
Ag@AuNPs	0.23 (s^{-1})	*Sci. Bull*, 2016, **61**, 1525.
Ag/AuNPs	0.55 (s^{-1})	*Sci. Bull*, 2016, **61**, 1525.
AuNPs	53	*Biotechnol. Lett*., 2016, **381**, 1503.
amid-p(MAc-co-AN)-Cu	1.9	*New J. Chem*., 2016, **40**, 1485.
amid-p(MAc-co-AN)-Co	0.92	*New J. Chem*., 2016, **40**, 1485.
Ni/p(SBMA)	6.9	*Coll. Surf. A,*., 2015, **486**, 223.
amid-p(AAm)-Cu	0.51	*Water Air Soil Poll*., 2015, **226**, 122.
p(APTMACl)-Cu	1.0	*Chem. Eng. J.*, 2015, **265**, 201.
p(APTMACl)-Co	0.8	*Chem. Eng. J.*, 2015, **265**, 201.
Au@CTGU-3	3.33	This work
Au@CTGU-4	0.85	This work .

Table S4 Summary of rate constants of other similar 3-nitrophenol reduction reactions catalyzed by previously reported catalysts

Name of Catalyst	reaction rate constants per unit mass (s^{-1} g^{-1})	Reference

Ag@AuNPs	0.69 (s^{-1})	*Sci. Bull*, 2016, **61**, 1525.
Ag/AuNPs	0.87 (s^{-1})	*Sci. Bull*, 2016, **61**, 1525.
AuNPs	73	*Biotechnol. Lett*., 2016, **381**, 1503.
Colloidal AuNPs	7.33	*Appl Nanosci*., 2016, **6**, 521.
Colloidal Pt-NPs	3.2 (s^{-1})	*J. Ind. Eng. Chem.*, 2015, **22**, 185.
Au-Ag bimetallic nanoparticles	1.1 (s^{-1})	*Spectrochim. Acta.,* 2015, **137**, 185.
Cu_2O@RGO	3.29 (s^{-1})	*RSC Adv*., 2015, **5**, 71259.
CuFe2O4	4.05 (s^{-1})	*Int. J. Hydrogen Ener*., 2014, **39**, 4895.
NiFe2O4	0.43 (s^{-1})	*Int. J. Hydrogen Ener*., 2014, **39**, 4895.
Ag@CTGU-3	4.5	This work
Ag@CTGU-4	1.58	This work