Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.
This journal is © the Partner Organisations 2018

Supplementary Information

Facile one-pot synthesis of MOF supported gold pseudo-single-atom catalysts for hydrogenation reaction

ZuminWang, [a] LinGu, [b] Li Song, [c] Hao Wang [d] and Ranbo Yu *[ad]

a. Department of Physical Chemistry, School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, PR China.
b. Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China.
c. National Synchrotron Radiation Laboratory, CAS Center for Excellence in Nanoscience, University of Science and Technology of China, Hefei, Anhui 230029, PR China.
d. Centre for Future Materials, University of Southern Queensland, Queensland, Australia.

*Corresponding writer. E-mail: ranboyu@ustb.edu.cn; Fax: +86-10-62332525; Tel: +86-10-62332525.

Materials Preparation

Chemicals

All chemicals were used as received of analytical grade without further purification. Cobalt chloride ($CoCl_2·6H_2O$), nickel chloride ($NiCl_2·6H_2O$)and cupric chloride ($CuCl_2·2H_2O$) were from Sinopharm Chemical Reagent Co.Ltd. 1-Dodecanethioland polyvinyl pyrrolidone (PVP) with Mw = 55000were purchased from Sigma-Aldrich. Other chemicals information was provided in the main manuscript.

Methods

Synthesis of other hydroxides

Copper hydroxide ($Cu(OH)_2$), cobalt hydroxide ($Co(OH)_2$), nickel hydroxide ($Ni(OH)_2$) suspension were prepared using the same procedure described above except that $CuCl_2·2H_2O$, $CoCl_2·6H2O$, $NiCl_2·6H_2O$ was used instead of $FeCl_2·4H_2O$.

Deposition- precipitation of Au precursors

The synthesis was the same in the main manuscript.

Synthesis of other Au/MOFs

The synthesis was the same for Au/FeBTC by mixing Au containing hydroxide solution and linker solution.

Synthesis of Pure MOFs

The synthesis was the same as the aforementioned process, except there was no $HAuCl_4$ added.

Synthesis of Au/Al_2O_3 and Au/P25

A suspension of Al_2O_3/P25 in deionized water was formed, after homogenization by ultrasonication for 30 min, to achieve a reaction mixture. Then the procedures of Deposition- Precipitation of Au precursors were almost the same from above. After the mixing Al_2O_3/P25 suspension and treated gold precursor and readjusting the pH value of the mixture, the product was aged under stirring for 18h and then purified by filtration, washed with ethanol, then water and dried at 65 °C.

Synthesis of other Au NPs supported MOFs

The synthesis were almost the same expect that during the deposition- precipitation process there is no adjusting pH value of chloroauric acid solution.

Synthesis of catalysts with method 1

Method 1 refers to a pre-synthesized method, which involves synthesis of NPs individually first and subsequent mix metals with organic ligands to construct the MOF around them. So the synthesis can be dived into two steps:

First the NPs were prepared with PVP as ligands for protection and stabilization. Typically, a solution of PVP (0.5 g) in water (20 ml) was added dropwise to an aqueous solution of $HAuCl_4$ (0.026 mM, 150 ml) with rapid stirring in a round bottom flask (250 ml) under ice bath. Quickly, newly prepared $NaBH_4$ solution (100 mM, 10mL) was poured into the flask to trigger the reduction reaction. The mixture was refluxed with stirring for another 20 minutes. Then the mixture was further stirred at room temperature for 24 hours. The PVP-stabilized Au NPs were collected by centrifugation at 14,000 rpm for 30 minutes, washed by methanol for three times.

Then the as-prepare NPs were placed in the solution of $FeCl_2$.The following procedures are the same as the synthesis of pure MOF.

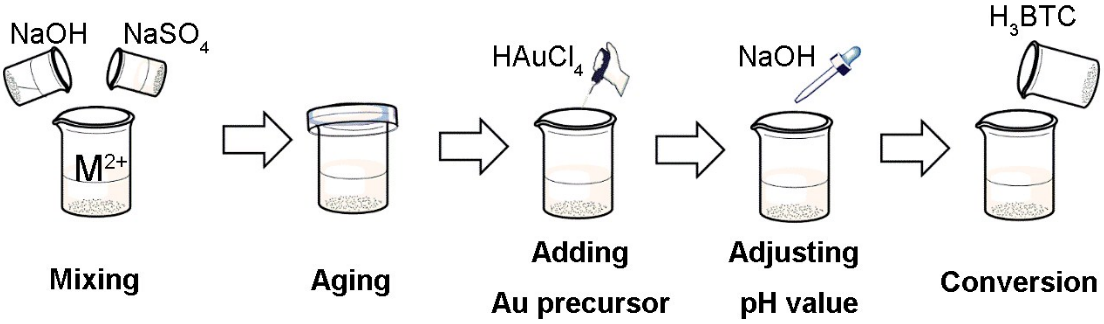
Synthesis of catalysts with method 2

Method 2 was the same as method 1, which the pre-synthesized Au NPs were stabilized by 1-Dodecanethiol.Ethanolic solution of 1-dodecanethiol (20 mM, 50 mL) was added to the solution of $HAuCl_4$ (0.026 mM, 100 mL) for surface capping. Then, newly prepared $NaBH_4$ solution (100 mM, 10mL) was added. And the mixture was stirred for 6 hours at room-temperature. The thioalcohol -stabilized Au NPs were collected by centrifugation at 14,000 rpm for 30 minutes, washed by ethanol and acetone repeatedly for three times. Then the as-prepare NPs were placed in the solution of $FeCl_2$.The following procedures are the same as the synthesis of pure MOF.

Synthesis of catalysts with method 3

Method 3 refers to a widely used pre-synthesized approach which use pre-synthesized MOFs as scaffold providing a confined space and heterogeneous sites for nucleation of the introduced the metal precursors. First pure MOFs were synthesized by aforementioned method. They were dispersed in water again. Then a solution of

$HAuCl_4$, which was brought to pH 10 by the addition of 0.2M NaOH, was added .Followed by the reduction by newly prepared $NaBH_4$ solution.



Scheme S1. Schematic illustration of the fabrication process of Au/MOF catalyst through pure beaker and solution chemistry by an in-situ reduction and conversion strategy

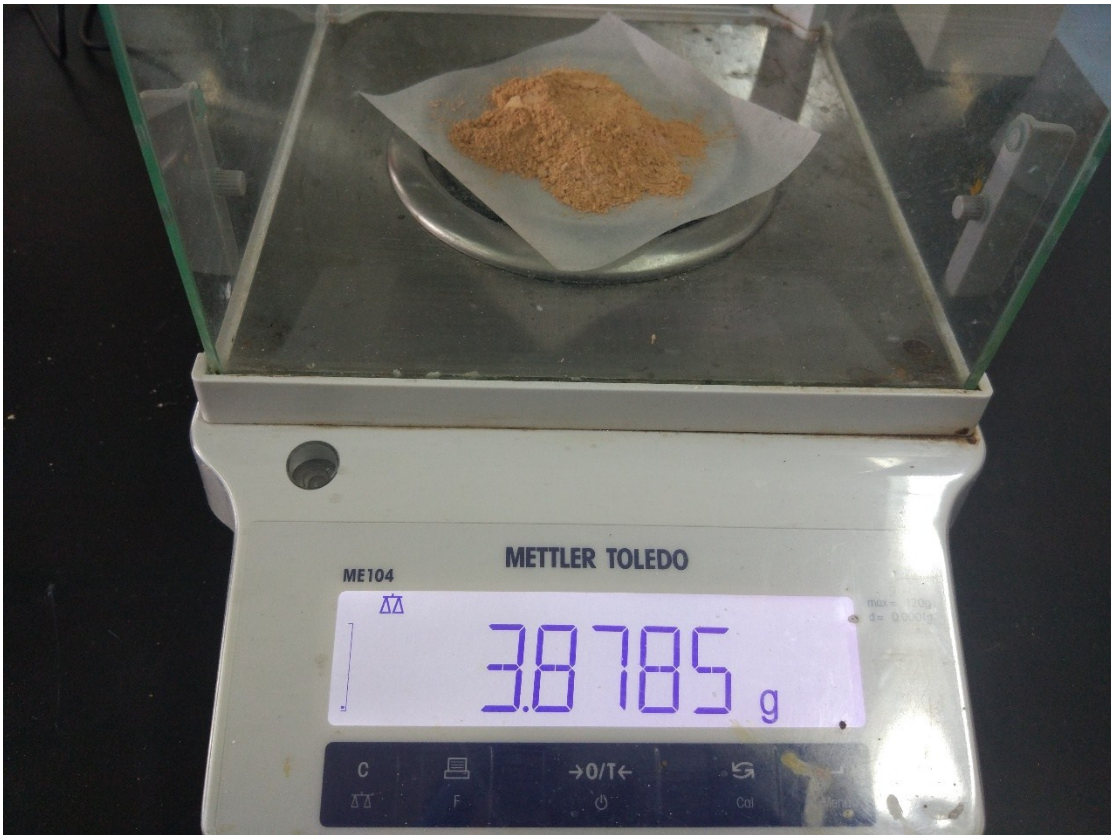


Figure S1. Digital photographs of products at gram level obtained from single synthetic batch

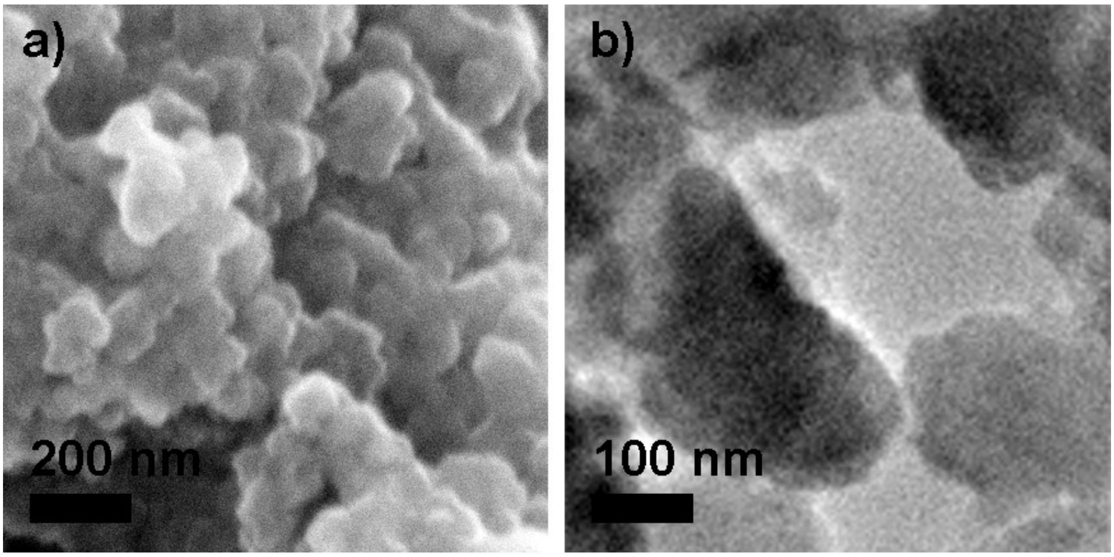


Figure S2. SEM and TEM images of as-prepared PSAC Au/FeBTC

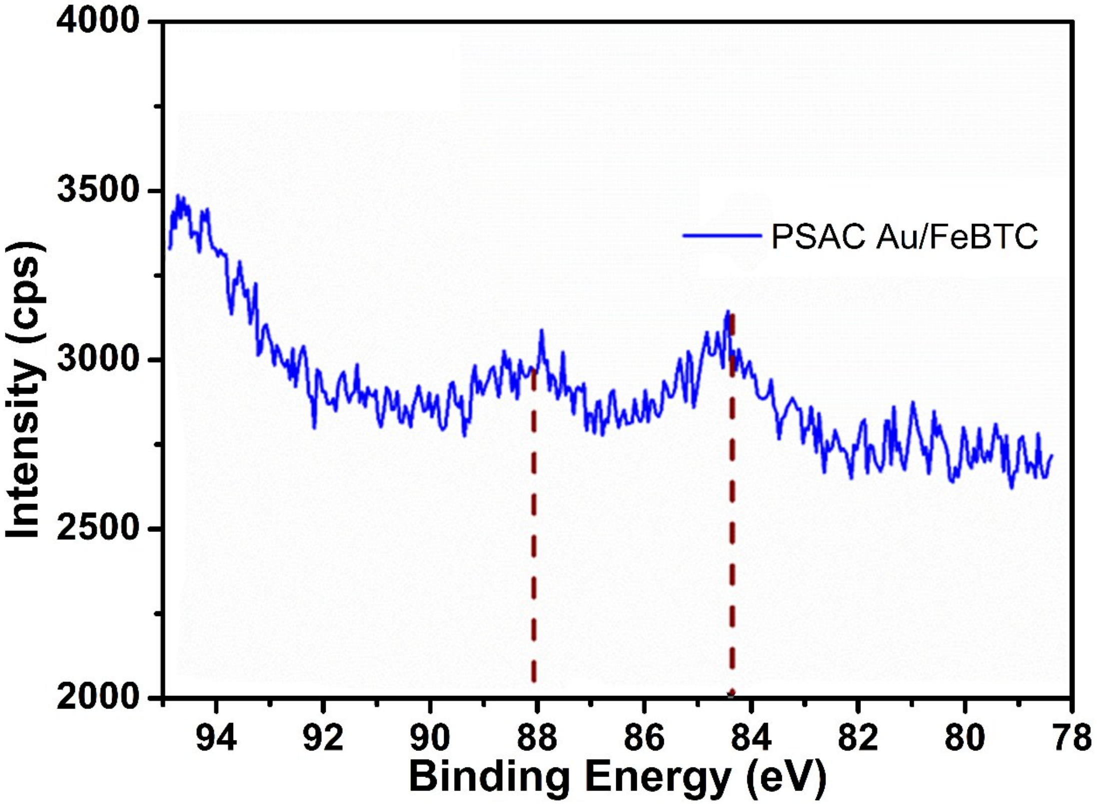


Figure S3. X-ray photoelectron spectroscopy analysis of the Au 4f of PSACs Au/FeBTC

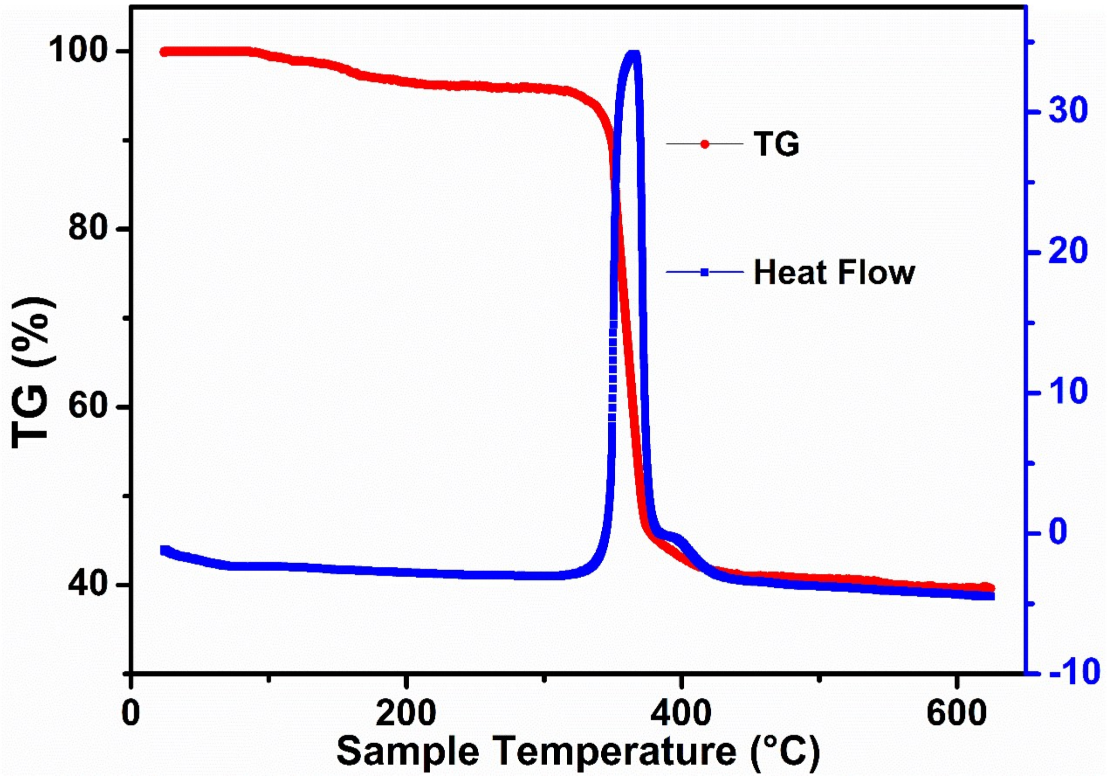


Figure S4 TG-DTA diagram of PSAC Au/FeBTC

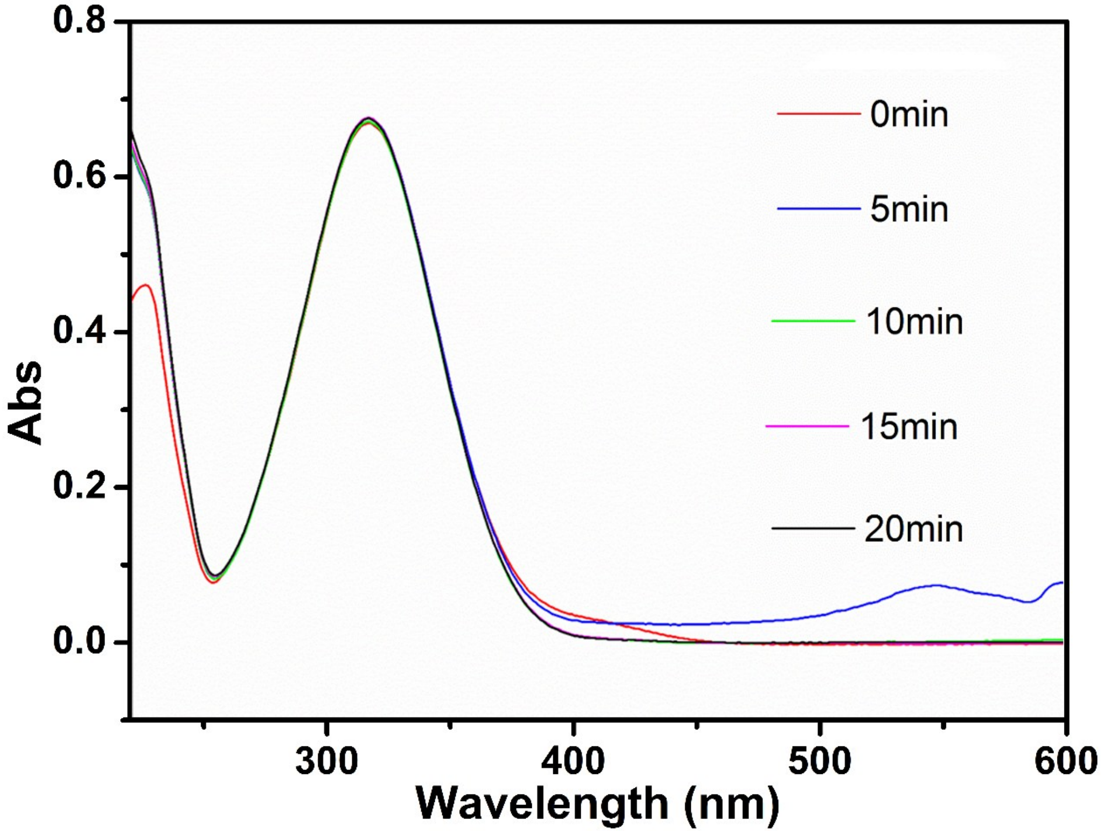


Figure S5. UV-vis spectrum for samples with catalysts but without adding hydrogen source

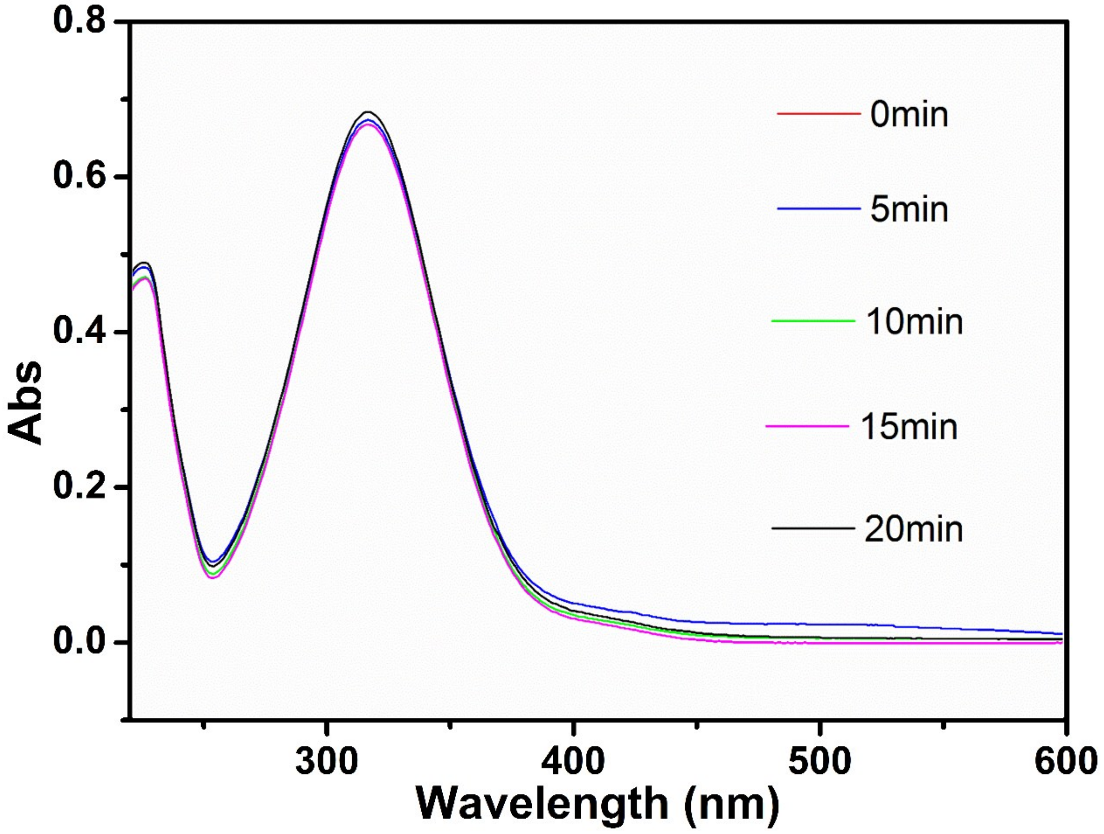


Figure S6. UV-vis spectrum for samples with hydrogen source but without adding catalysts

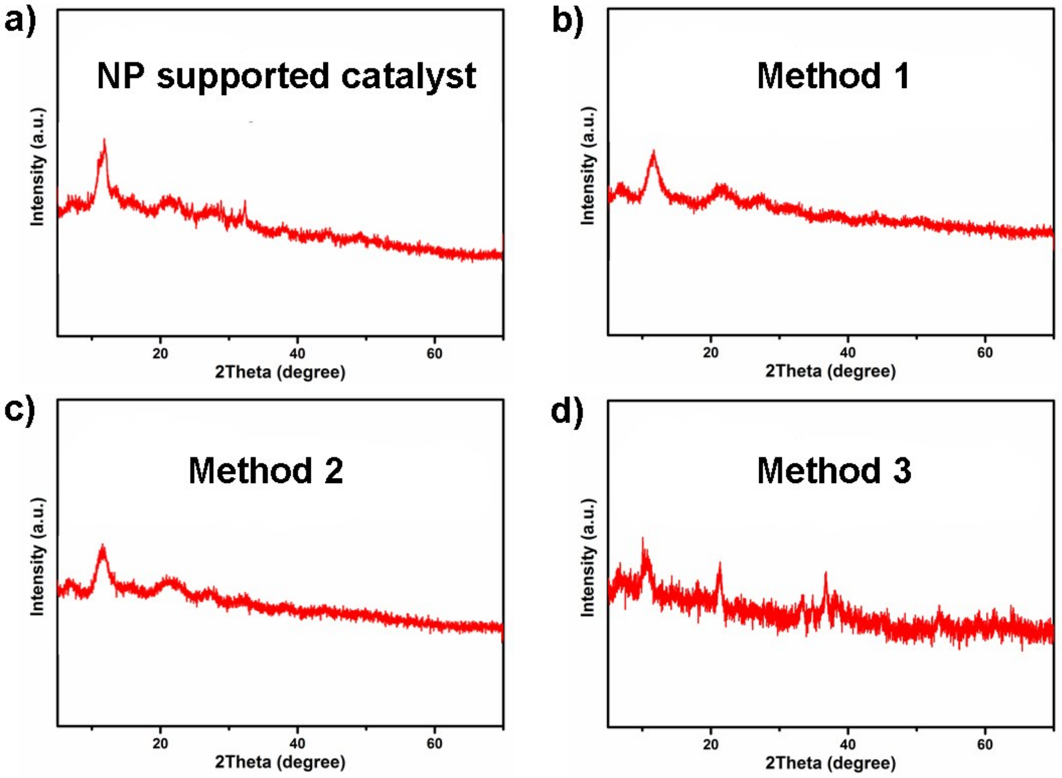


Figure S7 The morphology and crystallinity of the catalyst using different synthetic approach

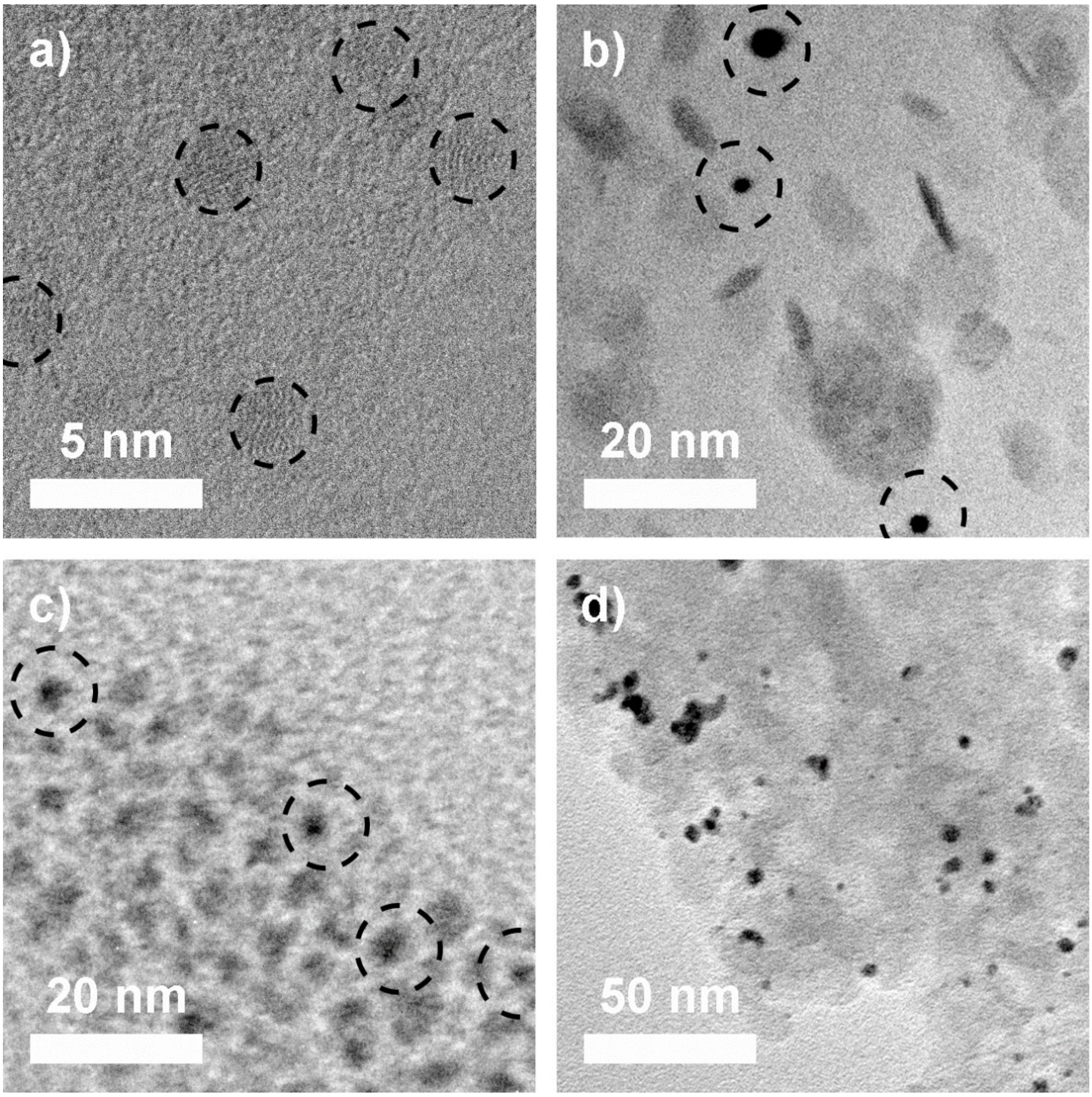
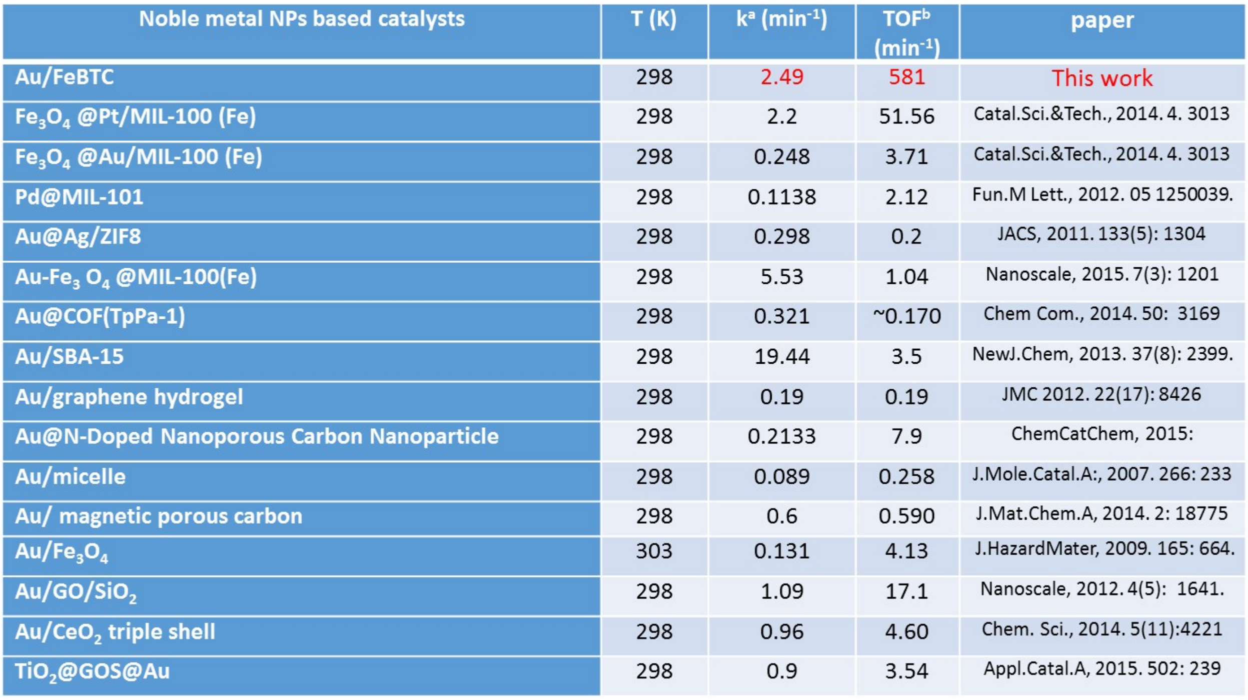


Figure S8 The morphologies of the catalyst using different synthetic approach

Table S1The comparison of hydrogenation of p-nitrophenol performance of different material



Noble metal NPs based catalysts	T (K)	k^a (min^{-1})	TOF^b (min^{-1})	paper
Au/FeBTC	298	2.49	581	This work
Fe_3O_4 @Pt/MIL-100 (Fe)	298	2.2	51.56	Catal.Sci.&Tech., 2014. 4. 3013
Fe_3O_4 @Au/MIL-100 (Fe)	298	0.248	3.71	Catal.Sci.&Tech., 2014. 4. 3013
Pd@MIL-101	298	0.1138	2.12	Fun.M Lett., 2012. 05 1250039.
Au@Ag/ZIF8	298	0.298	0.2	JACS, 2011. 133(5): 1304
Au-Fe_3O_4 @MIL-100(Fe)	298	5.53	1.04	Nanoscale, 2015. 7(3): 1201
Au@COF(TpPa-1)	298	0.321	~0.170	Chem Com., 2014. 50: 3169
Au/SBA-15	298	19.44	3.5	NewJ.Chem, 2013. 37(8): 2399.
Au/graphene hydrogel	298	0.19	0.19	JMC 2012. 22(17): 8426
Au@N-Doped Nanoporous Carbon Nanoparticle	298	0.2133	7.9	ChemCatChem, 2015:
Au/micelle	298	0.089	0.258	J.Mole.Catal.A:, 2007. 266: 233
Au/ magnetic porous carbon	298	0.6	0.590	J.Mat.Chem.A, 2014. 2: 18775
Au/Fe_3O_4	303	0.131	4.13	J.HazardMater, 2009. 165: 664.
Au/GO/SiO_2	298	1.09	17.1	Nanoscale, 2012. 4(5): 1641.
Au/CeO_2 triple shell	298	0.96	4.60	Chem. Sci., 2014. 5(11):4221
TiO_2@GOS@Au	298	0.9	3.54	Appl.Catal.A, 2015. 502: 239

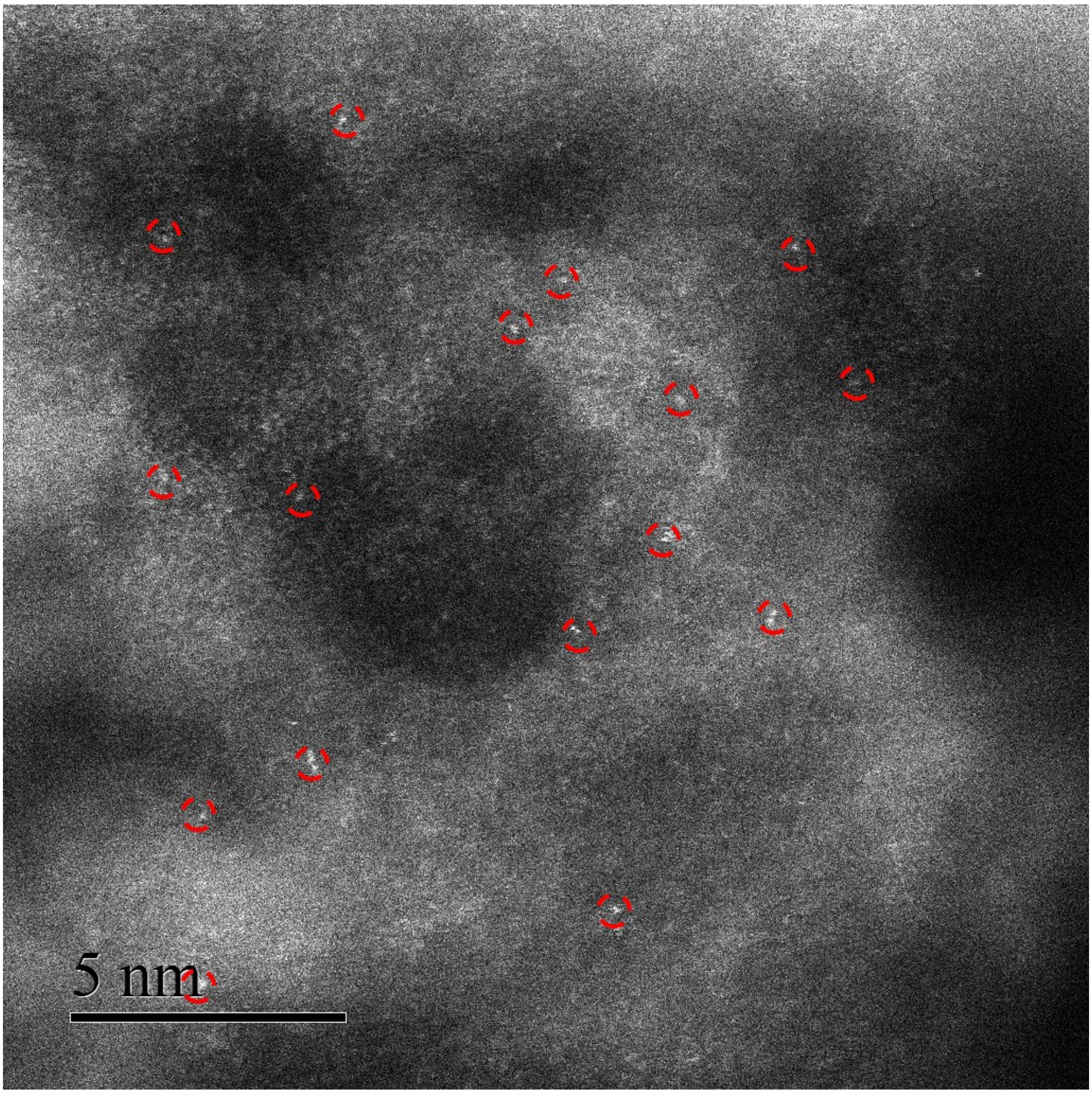


Figure S9 The morphology of the catalyst after the reaction from HAADF-STEM