Room-Temperature Chemoselective Reduction of

3-Nitrostyrene to 3-Vinylaniline by Ammonia Borane

over Cu Nanoparticles

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Chemicals and Materials.

All reagents were used as received. Borane tert-butylamine complex (BBA, 97%), ammonia borane (AB) (NH_3BH_3, 90%), nitroarenes, copper (I) acetate (CuOAc, 97%), trioctylamine (TOA, 98%), tetradecylphosphonic acid (TDPA, 97%), oleylamine (OAm, > 70%), oleic acid (OAc, 90%), 1-octadecene (ODE, 90%), and Nafion solution (5% in a mixture of lower aliphatic alcohols and water) were from Sigma-Aldrich. Copper (II) acetylacetonate ($Cu(acac)_2$, 97 %), palladium(II) acetylacetonate ($Pd(acac)_2$, 99%), nickel(II) acetylacetonate ($Ni(acac)_2$, 95 %) and tungsten(IV) chloride (WCl_4, 97%) was purchased from Strem Chemicals. Hexane (98.5%) and ethanol (99%) were from Fisher Scientific. These chemicals were used without further purification. The deionized water was obtained from a Millipore Autopure System.

Experimental Section

Synthesis of Cu nanoparticles (NPs): The Cu NPs were synthesized according to the method reported[1].

In a typical synthesis, in a four-neck flask, a mixture of 1 mmol copper(I) acetate, 0.5 mmol tetradecylphosphonic acid (TDPA) and 5 mL trioctylamine (TOA) was stirred and degassed at 403 K under an Ar atmosphere for 0.5 h. Then solution was heated to 453 K and maintained at this temperature for 0.5 h. The solution was then heated to 523 K in 5 min and held at this temperature for 10 min to obtain 7 nm Cu NPs. The Cu NPs were separated by adding 100 mL ethanol and centrifuging at 8500 rpm for 8 min. The product was purified by dispersing in hexane and flocculating with ethanol, and precipitated by centrifugation (8500 rpm, 8 min). The purification process was repeated once, and the final Cu NPs product was re-dispersed into hexane for further

use.

Synthesis of WO$_{2.72}$ nanorodes (NRs): The WO$_{2.72}$ NRs were prepared according to the reference[2]. In a typical synthesis, 0.25 mmol WCl$_4$, 5 mL ODE, 3 mL OAm were first mixed in a 20 mL vial through sonication to form a dark brown solution, and transferred into a 100 mL four-neck round bottom flask. 10 mL ODE and 6 mL OAc were then added into the flask. The mixture solution was first heated to 393 K in a gentle Ar flow and magnetic stirring for 0.5 h to remove air and moisture from the reaction system. The clear dark green solution was heated to 563 K in 0.5 h (when the reaction temperature reached 473 K, the Ar gas was switched to form an Ar blanket over the reaction system and the solution started to turn to blue). The reaction solution was kept at 563 K for 10 h before it was cooled to room temperature. The product was separated from the solution by adding 80 mL ethanol and centrifuging at 9500 rpm for 8 min. Then 20 mL hexane was added to re-disperse the synthesized NRs and centrifugation (6000 rpm, 4 min) was applied to precipitate any undispersed. The product in the dispersion was then precipitated by adding 35 mL ethanol followed by centrifugation. The NRs were purified again with 15 mL hexane and 35 mL ethanol, and after separation by centrifugation, was dispersed in hexane for further use.

Synthesis of Cu/WO$_{2.72}$: 0.5 mmol Cu NPs, 1.0 mmol WO$_{2.72}$ NRs, 16 mL OAm and 4 mL OAc were mixed into a 100 mL four-neck round bottom flask. Under a gentle argon flow, the mixture solution was quickly heated to 553 K and kept at 553 K for 0.5 h under magnetic stirring before it was cooled to room temperature. The product was washed by adding 100 mL ethanol and centrifuging at 8500 rpm for 8 min. The product was purified again with 20 mL hexane and 80 mL ethanol, and after separation by centrifugation, was dispersed in hexane for further use.

Synthesis of Cu/C and Cu/SiO$_2$ NPs catalysts: The Cu/C and Cu/SiO$_2$ NPs were prepared according to the reference[3].
The 10 mg of Ketjen carbon were suspended in 20 mL of hexane and sonicated for 1 h. Next, 10 mg of Cu NPs in hexane was added dropwise into the carbon support mixture under sonication. Then the resulted mixture was sonicated for 1 h to ensure Cu NPs adsorption onto the carbon support. The Cu/C NPs were separated by centrifugation and washed with ethanol. This washing procedure was repeated three times. The Cu/C NPs were recovered and dried under vacuum. Cu/SiO$_2$ NPs catalysts were prepared by the same method.

Synthesis of CuNi NPs: The CuNi NPs were prepared according to the reference[4].
In a typical synthesis, 0.26 mmol of Cu(acac)$_2$, 0.26 mmol of Ni(acac)$_2$ were mixed with 7.5 mL of OAm, and 0.16 mL of OA under magnetic stirring in N$_2$ environment. The formed solution was heated to 383 K and kept at this temperature for 0.5 h to remove moisture and oxygen from the reaction system. The reaction solution was further heated to 473 K (ramp rate of 20 K/min) and 160 mg of BBA dissolved in 1 mL of OAm was quickly injected into the solution. A visible color change from green to dark-brown was observed. The reaction was allowed to proceed for 40 min and cooled to room temperature. 100 mL ethanol was added, and the NP product was separated by centrifugation at 9000 rpm for 10 min. The NPs were washed twice with hexane/ethanol (v/v= 1:15) and then stored in hexane for further use.

Synthesis of CuPd NPs: The CuPd NPs were prepared according to the reference[5].

In a typical synthesis, 0.25 mmol $Cu(acac)_2$, 15 mL OAm, and 0.32 mL OAc were first mixed by magnetic stirring in a 50 mL four-neck flask and degassed under a gentle flow of argon at 343 K for 0.5 h to form a clear solution. Then 0.25 mmol Pd NPs dispersed in 2 mL hexane was dropped into the solution. The solution was heated to 533 K at 2 K/min and kept at 533 K for 1 h before it was cooled to room temperature. The CuPd NPs were separated by adding 100 mL ethanol and centrifuging at 9500 rpm for 8 min. The product was purified by dispersing in hexane and flocculating with ethanol, and precipitated by centrifugation (9500 rpm, 8 min). The purification process was repeated once, and the final NP ($Cu_{49}Pd_{51}$) product was redispersed into hexane for further use.

Ethanolysis of AB: A two-necked reaction flask (25 mL) containing a Teflon-coated stir bar was placed on a magnetic stirrer and thermostated to 298 K by using a constant temperature bath. A gas burette filled with water was connected to one neck of the flask (the other neck was sealed) to measure the volume of hydrogen gas evolved from the reaction. 8.0 mL of ethanol suspension of the catalyst was transferred into the reaction flask, and 2.0 mL of 100.0 mg (3 mmol) of AB ethanol solution was added into the stirred (800rpm) solution. The volume of hydrogen gas evolved was measured by recording the volume of water displaced. The reaction was considered to cease when hydrogen gas generation was no longer observed.

Chemoselective hydrogenation reaction: Before the test, a two-neck round bottom flask (25 mL) containing a Teflon-coated stir bar was placed on a magnetic stirrer and thermostated to 298 K. Then 3 mmol AB and 1 mmol nitroarenes were dissolved into 2 mL ethanol, respectively. The solution of nitroarenes compounds ethanol was added into the flask. Once the neck was connected to a balloon, and the other neck was sealed by rubber stopper. Afterwards, Cu-based catalysts were dispersed by sonication in ethanol (6 mL) and then transferred into the reaction flask. Next, the mixed solution was stirred with magnetic stirring for 15 min in the reaction flask. Finally, when the desired amount of AB was rapidly injected drop by drop into the flask using a syringe from the rubber stopper neck at a stirring rate of 800 rpm. After the experiment was over, the catalyst was separated from the suspension by centrifugation, and the yield of the product were determined by GC-MS with dodecane as the internal standard. The sample solution (0.2 μL) was directly injected into the GC-MS for quantitative analysis.

Cyclic voltammograms (CV) measurements: 20 mg of KetjenBlack EC-300-J carbon (C) was mixed with 20 mL of hexane, which was then sonicated for 0.5 h to form a uniform suspension. Then each of $Cu/WO_{2.72}$ and Cu NPs in hexane was added into the suspension dropwise under sonication. After 1 h sonication, the C-supported powder was separated by centrifugation (8000 rpm, 8 min), washed with ethanol (three times), and dried at room temperature. Catalyst ink for electrochemical study was prepared by mixing the C-supported catalysts with 800 μL of ultrapure water, 200 μL of 2-propanol, and 10 μL of Nafion solution (5 wt %) for 1 h. 20 μL of catalyst ink was then deposited onto the glassy carbon rotating disk electrode (5 mm in diameter) for electrochemical measurements. An Autolab 302 potentiostat (Eco Chemie B.V., Holland) together with Pt wire as a pseudo-reference electrode and graphite bar as a counter electrode were used to obtain cyclic voltammetry (CV). CV measurement was scanning at room temperature between -1.0 V and 0.5 V at 100 mV/s

in N_2-saturated CH_2Cl_2 solution (0.1 M Et_4NBF_4).

Characterizations

Transmission electron microscopy (TEM) images were from a Philips CM20 operating at 200 kV. High-resolution TEM (HR-TEM) images were recorded with a JEOL 2100F transmission electron microscopy operated at an acceleration voltage of 200 keV. X-ray photoelectron spectroscopy (XPS) was performed on an ESCA 210 and MICROLAB 310D spectrometer using an Mg KR source. X-ray diffraction (XRD) patterns were collected on a Bruker AXS D8-Advanced diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å). The inductively coupled atomic emission spectroscopy (ICP-AES) analyses were performed on a JY2000 Ultrace ICP atomic emission spectrometer equipped with a JY AS 421 autosampler and 2400 g/mm holographic grating. The analyses of products after chemoselective hydrogenation reaction were carried out by GC-MS using an Agilent 6890 GC coupled to a 5973 Mass spectrometer detector with a DB-5 (Agilent) fused silica capillary column (L × I.D. 30 m × 0.25 mm, df 0.25 µm) and helium as carrier gas. The gas chromatograph was temperature programmed from 338 K (3 min initial time) to 573 K at 6 K/min (isothermal for 20 min final time). The mass spectrometer was operated in the electron impact mode at 70 eV ionization energy. Mass spectrometric data were acquired and processed using the GC-MS data system (Agilent Chemstation), and compounds were identified by gas chromatographic retention index and mass spectrum comparison with authentic standards, literature and library data.
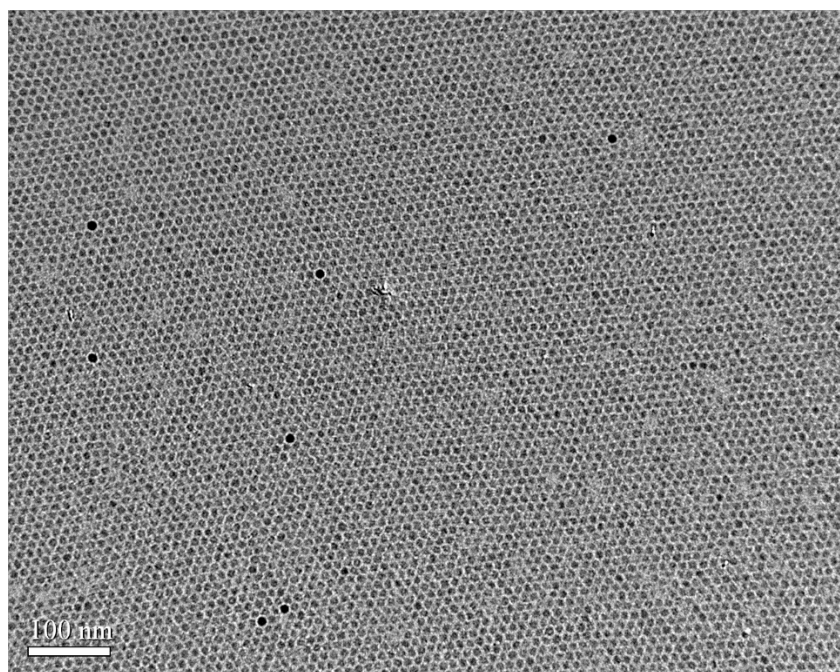
Figure S1. TEM image of self-assembly of Cu NPs.
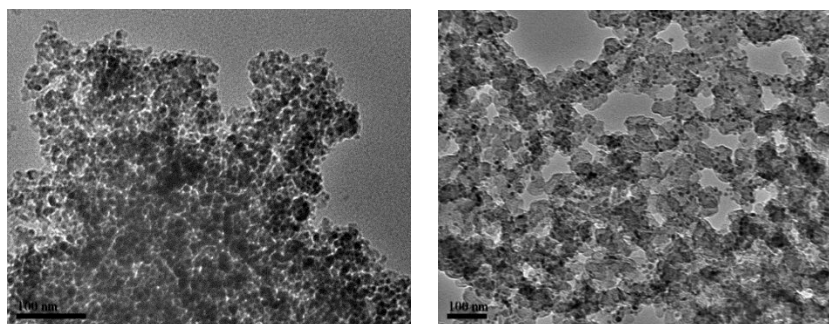
Figure S2. TEM images of (**A**) Cu/SiO$_2$ and (**B**) Cu/C.
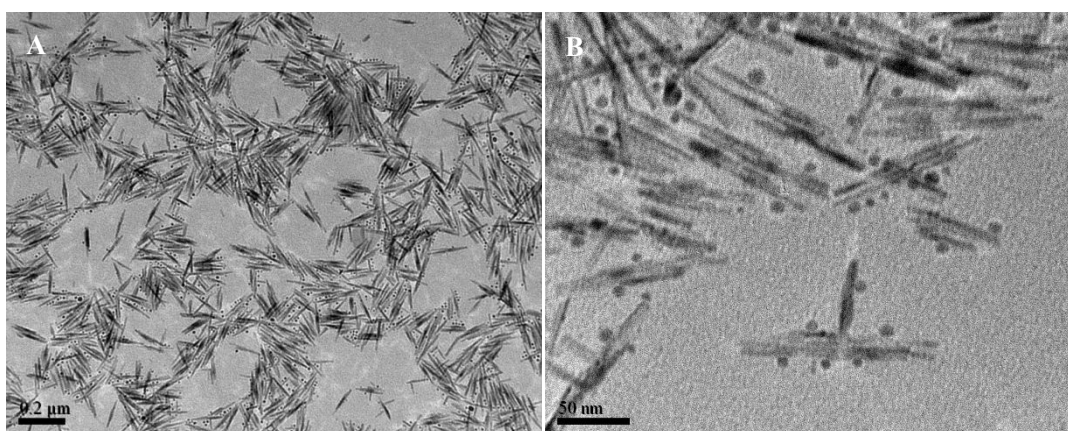
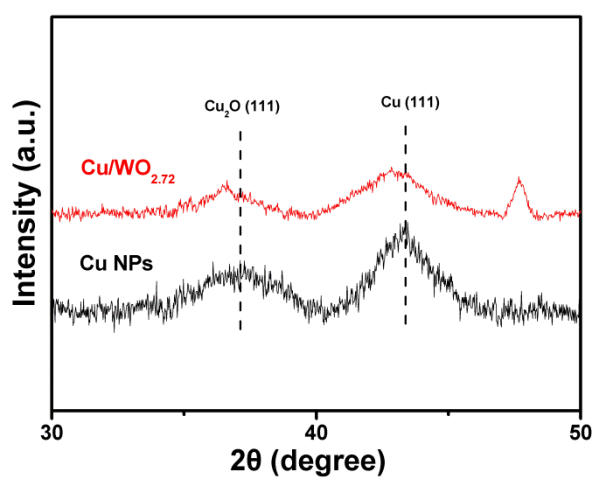Figure S3. TEM images of the Cu/WO$_{2.72}$ catalyst.

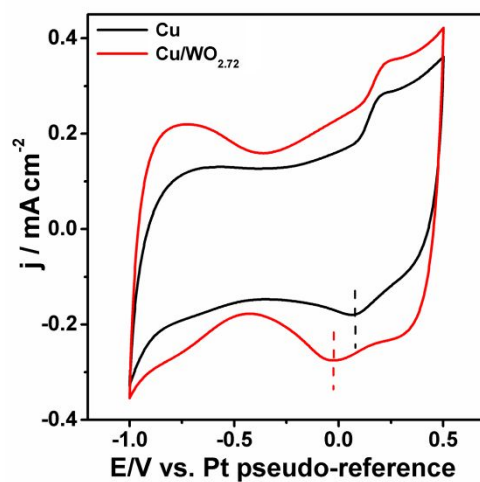Figure S4. XRD patterns of Cu NPs and Cu/WO$_{2.72}$.

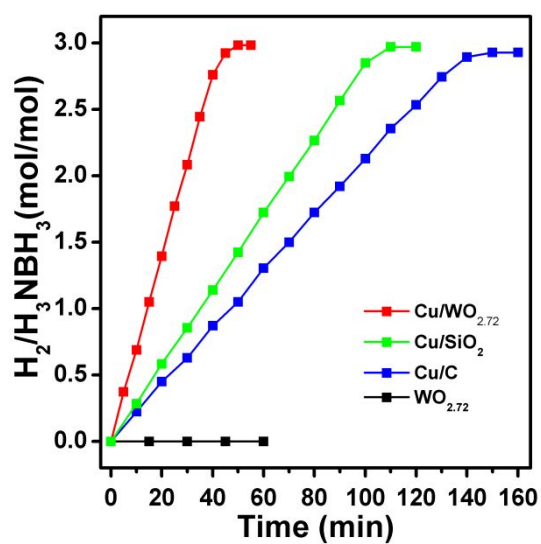Figure S5. Cyclic voltammograms of Cu/WO$_{2.72}$ (red line) and Cu (black line).

Figure S6. AB hydrogen evolution over Cu NPs with different supports, Cu-based catalysts (2 mole % Cu), AB (3 mmol), ethanol (10 ml), 298 K.
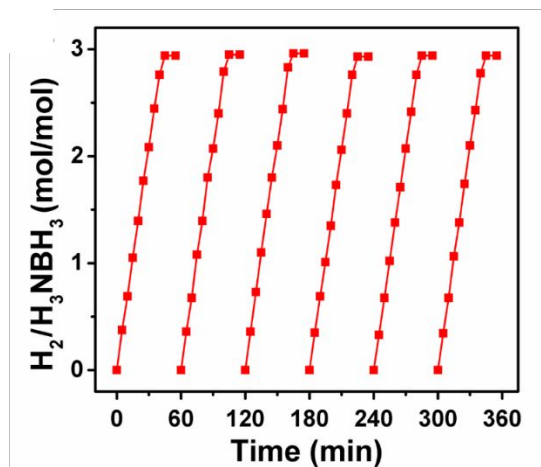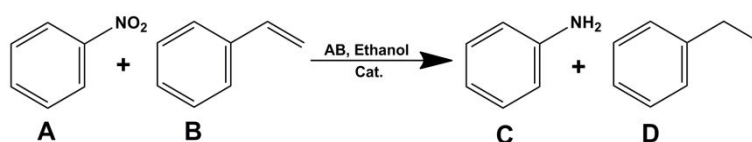
Figure S7. Recycling test for Cu/WO$_{2.72}$ catalyst in AB hydrogen evolution, Cu-based catalysts (2 mole % Cu), AB (3 mmol), ethanol (10 ml), 298 K.

Table S1 AB-initiated hydrogenation of nitrobenzene and styrene mixture in the presence of the Cu NP catalyst.

Entry	Cat.	Yield / %		T / K	Time / h
		C	D		
1	Cu/WO$_{2.72}$	>99	0	298	1.5

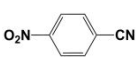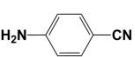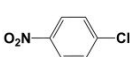|					
2	Cu/SiO₂	>99	0	298	2.5
3	Cu/C	>99	5	298	3
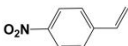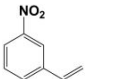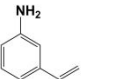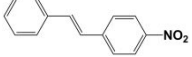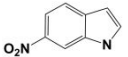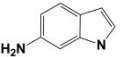
Reaction conditions: Cu: 6 mol %; solvent: ethanol (10 mL); Internal standard: dodecane; Substrates: styrene (0.5 mmol); nitrobenzene (0.5 mmol).
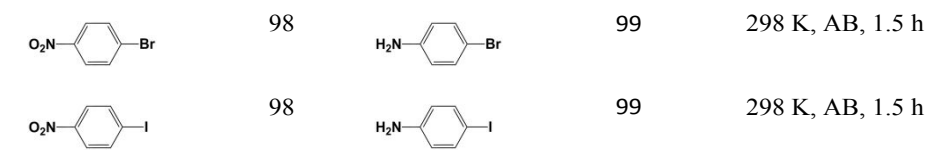
Table S2 Chemoselective hydrogenation of 3-nitrostyrene to 3-vinylaniline over various non-noble metal catalysts.

Catalyst	Reductant	T(K)	P(bar)	Time(h)	Yield(%)	Conversion(%)	Reference
Cu/WO₂.₇₂	AB	298	/	1.5	>99	>99	This work
Cu/SiO₂	AB	298	/	2.5	98	>99	This work
Cu/C	AB	298	/	3	95	>99	This work
Ni/TiO₂	H₂	673	40	3	82	99	6
Fe₂O₃-N/C	H₂	393	50	16	96	93	7
Co₃O₄-L1/C	H₂	383	50	6	91	97	8
CoO-Co₃O₄	H₂	383	30	12	98	98	9
Co₃O₄-NGr@C	FA	373	/	16	93	100	10
Co NPs	H₂	383	50	15	82	/	11
FeS₂	H₂	393	50	18	100	100	12
Co-Mo-S	H₂	423	11	8	88	95	13
CoS₂	H₂	383	30	7	98	>98	14

*AB = Ammonia borane, FA = Formic acid.

Table S3 Chemoselective hydrogenation of nitroarenes over Cu/WO₂.₇₂ catalyst.

Substrate	Yield(%)	Product	Selectivity(%)	Condition
	97		99	298 K, AB, 1.5 h
	99		99	298 K, AB, 1.5 h
	95		99	333 K, AB, 3 h
	80		99	333 K, AB, 3 h
	95		99	298 K, AB, 1.5 h
	97		99	298 K, AB, 1.5 h

Substrate	Conversion	Product	Yield	Conditions
O_2N—⬡—Br	98	H_2N—⬡—Br	99	298 K, AB, 1.5 h
O_2N—⬡—I	98	H_2N—⬡—I	99	298 K, AB, 1.5 h

Reaction conditions: Catalyst ： Cu/WO$_{2.72}$ (Cu: 6 mol %); ethanol (10 mL); Internal standard: dodecane; Substrates (1 mmol).
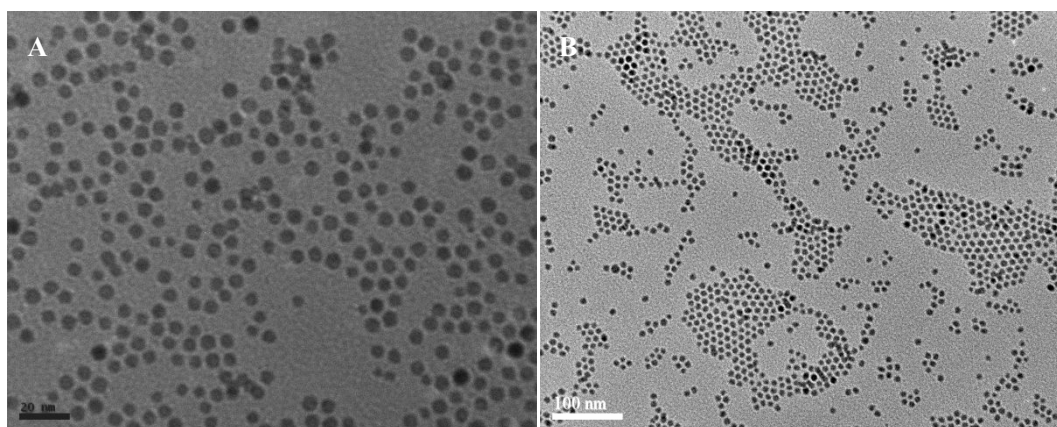

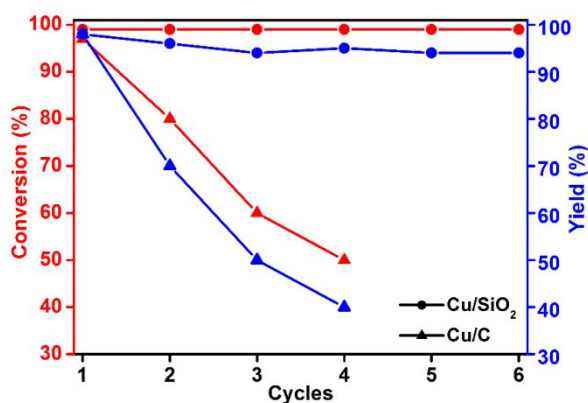Figure S8. TEM images of (**A**) CuNi NPs and (**B**) CuPd NPs.

Figure S9. Stability test for Cu/C and Cu/SiO$_2$ in the chemoselective hydrogenation reaction condition at 298 K.
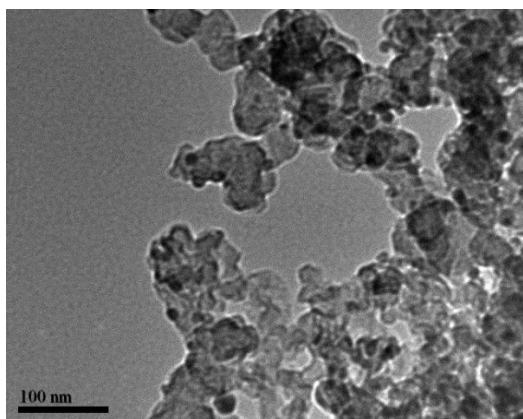
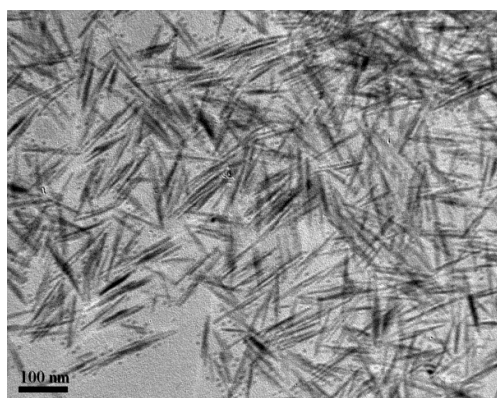Figure S10. TEM image of Cu/C NPs after the fourth catalytic reaction.

Figure S11. TEM image of the Cu/WO$_{2.72}$ catalyst after the sixth catalytic reaction.

Reference

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