Electronic Supplementary Information

Pd-Cu_2O nanocomposite as an effective synergistic catalyst for selective semi-hydrogenation of terminal alkynes only

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Experimental Section

Materials: Triethylene glycol (99 %) was provided by Sigma-Aldrich.Copper(II) acetylacetonate (99 %), 1,3,5-trimethylbenzene (98 %), 1-chloro-4-ethylnylbenzene (98 %), 1-ethynyl-4-flurobenzene (99 %), 4-ethynyltoluene (98 %), phenylacetylene (98 %), 4-acetylphenylacetylene (98 %) and 1-octyne (99 %)were provided by J&K scientific Co., Ltd. Acetonitrile, ethanol, THF, dioxane, toluene, n-hexane, acetone and DMF (A. R. grade) was produced by Beijing Chemical Reagent Company. MWCNTs (d = 60~100 nm, L = 5~15 um) was purchased from ShenzhenNanotech Port Ltd Co, China. Palladium 5% on calcium carbonate (poisoned with Lead) was produced by TCI (Shanghai) Development Co., Ltd. The Pd/C (5 % wt, dry), Pd/C (10 % wt, dry), 2-(trifluoromethyl)phenylacetylene(97 %), Iron(III) 2,4-pentanedionate (99 %), 4-methoxyphenylacetylene (99 %), 1-phenyl-1-pentyne (98 %), nitrobenzene (99 %), 4-tert-butylphenylacetylene (90+ %), 4-octyne (99 %), 1-phenyl-1-pentyne (98 %), diphenylacetylene (99 %) and styrene (99 %) were obtained from Alfa Aesar. CO_2 (>99.95%) and H_2 (99.99%) were provided by Beijing Analytical Instrument Factory.

Synthesis of MWCNTs-Fe_3O_4-Cu (M-1): In a typical procedure, 146 mg $Fe(acac)_3$, 54 mg $Cu(acac)_2$ and 50 mg MWCNTs were added to 30 mL triethylene glycol (TREG) which was loaded in a 50 mL flask and then the mixture was ultrasonicated for 10 min. The resulting composites was rapidly heated to 190 ^oC, maintained there for 30 min under argon protection, then rapidly heated to 278 ^oC, and held there for an additional 30 min. After cooling to room temperature, the obtained mixture was centrifugated and washed with ethyl acetate for 5 times and dried in vacuum at room temperature for 5 h.

Synthesis of MWCNTs-Fe_3O_4-Cu_2O-Pd (M-2): For a typical synthesis of MWCNTs-Fe_3O_4-Cu_2O-Pd, 40 mg **M-1** was added to 20 mL H_2O and ultrasonicated for 1 min, then 150 μL $Na_2Pd_2Cl_4$ solution (0.0564 mol/ L) was added into the above-mentioned solution. After kept stirring for 4 h at room temperature, the precipitates were separated by centrifugation and washed with water for two times and ethanol for two times and dried at room temperature in vacuum for 5 h. MWCNTs-Fe_3O_4-Pd (**M-3**) was synthesized with $H_2Pd_2Cl_4$(8 mL 1.13 mmol/L H_2PdCl_4 was used) instead of $Na_2Pd_2Cl_4$ solution.

Typical reaction procedure for the hydrogenation reaction: M-2 (15.0 mg), alkyne (0.91 mmol) and 1,3,5-trimethylbenzene (126 μL, 0.91 mmol) were added into 2 mL acetonitrile. The air in the reactor was replaced by H_2 for three times. Then, the mixture was stirred in a 30 ^oC water bath for desired time. The product was analyzed by a gas chromatograph (Shimadzu GC-2010) equipped with a flame ionization detector (FID) and a Rtx-5 capillary column (0.25 mm in diameter, 30 m in length). The identity was ascertained by GC-MS (Shimadzu GCMS-QP2010S).

General procedure for recycling test: After the first cycle of the reaction, the catalyst was recovered by centrifugation (also the magnet will do), rinsed with acetonitrile for three times. Then, the next run was started with the same substrate loadings. The yield and selectivity was determined by GC analysis using internal standard method.

Characterizations: X-ray diffraction (XRD) patterns were performed on a Rigaku D/max-2500 diffractometer with Cu K*α* radiation (λ= 1.5418 Å) at 40 kV and 200 mA. The morphology and microstructures of the samples were characterized by scanning electron microscopy (HITACHI S-4800 SEM), transmission electronmicroscopy (TEM, JEOL-1011) and high-resolution transmission electron microscopy (HRTEM) (FEI Tecnai G2 F20U-TWIN). Element mapping was obtained on HRTEM equipped with Oxford detection. XPS measurement was performed on the VG Scientific ESCALab220i-XL spectrometer using Al Kα radiation. The loading content of Pd was determined by ICP-AES (Shimadzu ICPE-9000).

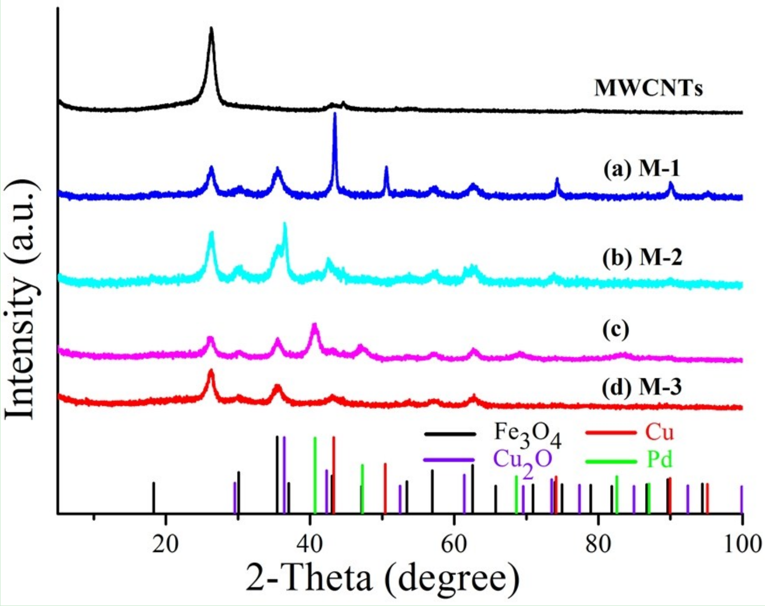


Fig. S1 XRD patterns of the MWCNTs, MWCNTs-Fe_3O_4-Cu (**a**, **M-1**), MWCNTs-Fe_3O_4-Cu_2O-Pd (**b, M-2**), MWCNTs-Fe_3O_4-Pd (**c**, absolutely galvanic replacement) and MWCNTs-Fe_3O_4-Pd (**d, M-3**).

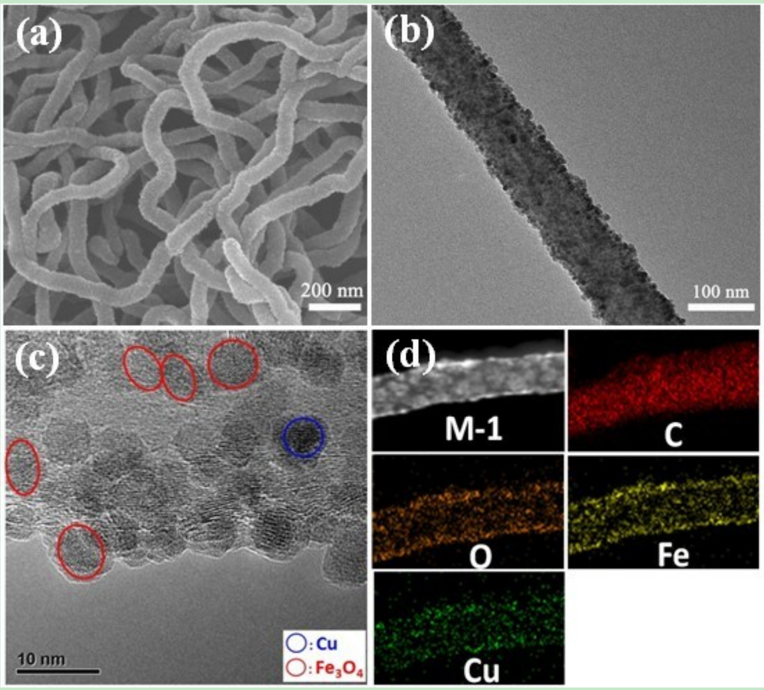


Fig. S2 (a) FESEM, (b) TEM, (c) HRTEM images and (d) element mapping images of MWCNTs-Fe_3O_4-Cu **(M-1)**.

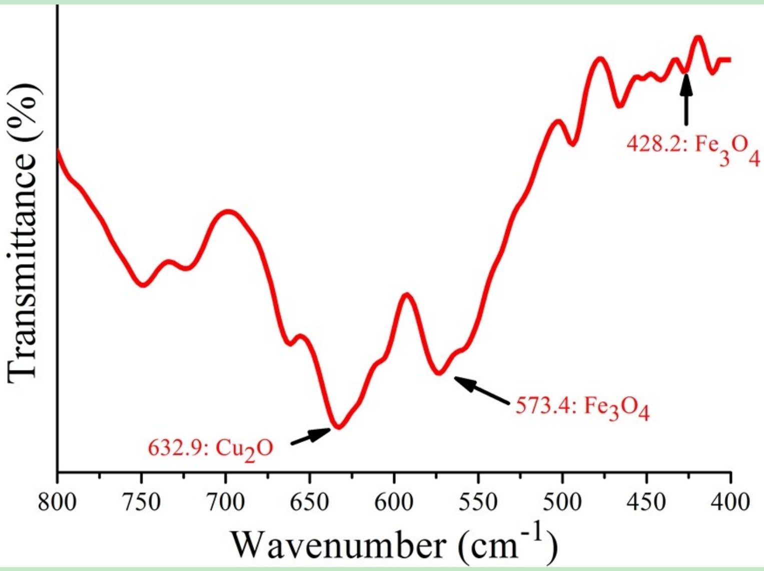


Fig. S3 FT-IR spectroscopy of the MWCNTs-Fe$_3$O$_4$-Cu$_2$O-Pd (**M-2**). The peak at 573 and 428 cm^{-1} are associated with the Fe-O stretching. The peak at 633 cm^{-1} can be attributed to the Cu$_2$O vibration.[1]

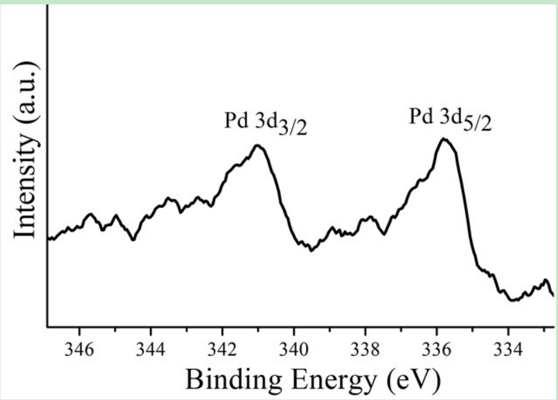


Fig. S4 Pd 3d XPS spectrum of MWCNTs-Fe$_3$O$_4$-Cu$_2$O-Pd (**M-2)**.

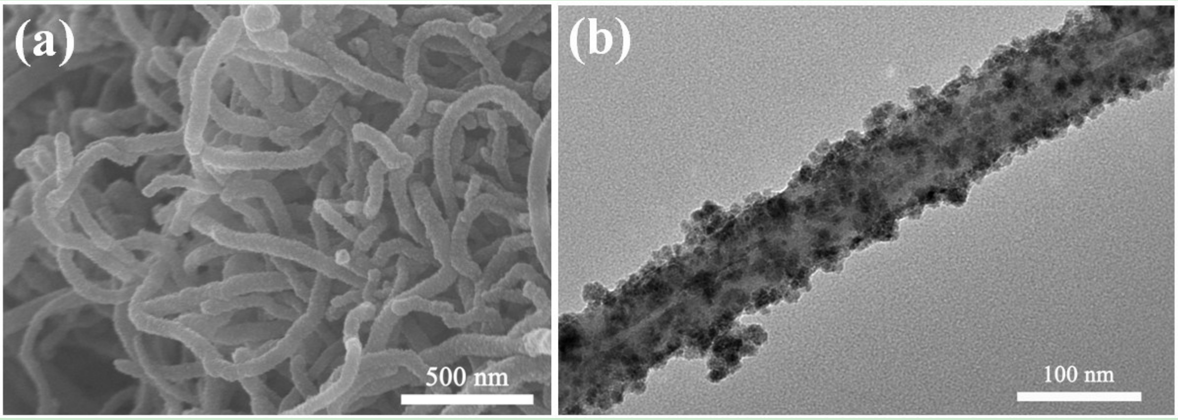


Fig. S5 (a) FESEM and (b) TEM images of the prepared MWCNTs-Fe_3O_4-Pd (**M-3**).

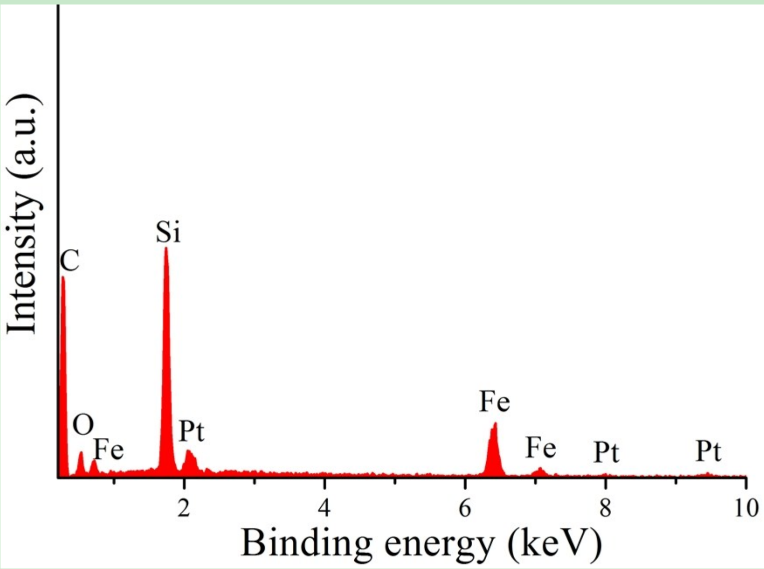
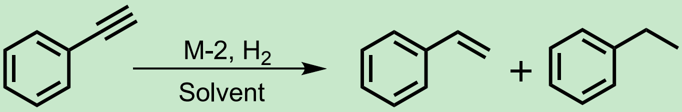


Fig. S6 EDX spectrum of the MWCNTs-Fe_3O_4-Pd (**M-3**). The signal of Pt in EDX image was originated from the sputtered platinum to enhancing electronic conductivity of the sample for SEM measurement in the experiment.

Table S1 Solvent optimization for the hydrogenation of phenylacetylene (**1a**).



1a **1b** **1c**

Entry	Solvent	Time/ h	Conversion[a]	Selectivity
1	EtOH	1.5	88%	97%
2	THF	1.5	97%	94%
3	Toluene	1.5	20%	98%
4	n-Hexane	1.5	80%	98%
5	Dioxane	1.5	24%	97%
6	Acetone	1.5	>99%	94%
7	THF+EtOH (V:V=1:1)	1.5	92%	96%
8	Acetonitrile	**1.5**	**>99%**	**98%**
9	DMF	1.5	96%	95%
10[b]	liquid CO_2	1.0	97%	97%
11[c]	$SCCO_2$	0.5	93%	94%

[a] reaction condition: catalyst (15.0 mg, 0.26 mol %), **1a** (100 μL, 0.91 mmol) in 2.0 mL solvent using the 1,3,5-Trimethylbenzene as the internal standard, 1 atm H_2, 30 °C. [b] H_2 (0.51 MPa), CO_2 (6.89 MPa) in a 50 mL steel autoclave at 30 °C. [c] H_2 (1.0 MPa), CO_2 (8.21 MPa) in a 50 mL steel autoclave at 35 °C.

Table S2 Recycle experiments of (runs 1-5) of **M-2** in the phenylacetylene hydrogenation.[a]

Entry	1st	2nd	3rd	4th	5th
Conversion	>99%	>99%	97%	94%	94%
Selectivity	98%	98%	98%	98%	98%

[a] reaction condition: catalyst (15.0 mg, Pd loading: 0.26 mol%), **1a** (100 μL, 0.91 mmol) in 2.0 mL acetonitrile using the 1,3,5-trimethylbenzene as the internal standard, 1 atm H_2, 30 °C for 1.5 h.