Electronic Supplementary Material (ESI) for Chemical Communications

Reduction of alkenes catalyzed by copper nanoparticles supported on diamond nanoparticles

Amarajothi Dhakshinamoorthy, Sergio Navalon, David Sempere, Mercedes Alvaro and Hermenegildo Garcia*

Instituto Univ.de Tecnología Química CSIC- UPV and Departamento de Química, Univ. Politécnica de Valencia, Av. De los Naranjos s/n, 46022 Valencia, Spain. Fax: (+) 34 9638 7807; E-mail: hgarcia@qim.upv.es

Experimental

Materials: Hydrogen peroxide solution in water (30%, v/v), nitric acid (65 %), hydrochloric acid (37%, ACS reagent), sulphuric acid (98 %), $HAuCl_4.3H_2O$, $Cu(NO_3)_2.2H_2O$, palladium nitrate, NaOH (ACS reagent), aqueous ammonia, hydrazine hydrate, ethanol, various substrates and diamond nanopowder (ref: 636444, 95 %), activated carbon (7440-44-0), graphite (7782-42-5) were commercial samples from Sigma–Aldrich. Milli-Q water was used in all the experiments. The other reagents used were of analytical or HPLC grade. Starting materials were obtained commercially from Aldrich and used without any further purification unless otherwise noted.

Catalyst preparation: Fenton treatment of commercial diamond NPs was carried out by suspending raw diamond nanopowder (0.5 g) in 150 mL H_2O_2 (30 %, v/v) in a 500 mL open flask. The pH was adjusted at 3 using HNO_3 (0.1 M) and maintained at this value during all the process. This slurry was sonicated in an ice-refrigerated ultrasound bath and held at 1–5 ºC for 20 min. Then, a freshly prepared aqueous solution of $Fe(SO_4)\cdot7H_2O$ (mg/ml) at pH 3 was slowly dropped for 1 h while observing intense gases evolution. (caution: the Fenton reaction is a highly exothermic reaction and occurs with evolution of heat and gases. The process must be carried out cautiously in a well-ventilated fume hood whilst wearing goggles and appropriate personal safety items). After 1 h, additional amounts of H_2O_2 (50 mL) and $Fe(SO_4)\cdot7H_2O$ were added until complete H_2O_2 decomposition as evidenced by titration with titanyl oxalate.

After the Fenton treatment, the suspension was diluted with distilled water and allowed to reach room temperature. Then, several washings were made using an aqueous solution of sulphuric acid (0.1 M) until the absence of iron detected by colorimetric method using KSCN. The excess of acid was removed by performing five consecutive centrifugation–re-dispersion (14,000 rpm) cycles with Milli-Q water. Diamond NPs sediment at the bottom of the centrifuge tube under these conditions and can be easily recovered and re-suspended. The pH value of the supernatant at the fifth centrifugation–re-dispersion cycle was neutral. Finally, the Fenton-treated diamond NPs were submitted to overnight freeze-drying to give dry, purified diamond NPs (D).

Additionally, D was submitted to a subsequent annealing treatment under continuous H_2 flow. In particular, D powder was placed in a quart reactor under H_2 flow (100 ml/min) and heated using a ramp of 8 ºC/min until the temperature reached 500 ºC and maintained for 6 h. Then, the sample was cooled at room temperature and the support labelled as DH. This reduction treatment decrease the number of surface defects by increasing the population of –OH groups.[13]

Preparation of Cu/D, Cu/DH and Au/DH catalysts was accomplished using the polyol method.[14, 15] Briefly, 200 mg of the diamond support (D or DH) were suspended in 80 mL of ethylene glycol and sonicated for 30 min. Then, the corresponding amount of gold or copper salts dissolved in water was added to the diamond suspension to achieve 0.5 wt. % loading. Under vigorous stirring the suspension was heated up to 85 ºC and allowed to react for 4 h. After cooling the reaction at room temperature the powder suspended was recovered by centrifugation at 14,000 rpm. Then the supernatant was removed and the catalyst dispersed in ethanol and washed by performing three consecutive centrifugation-re-dispersion cycles with acetone and subsequently other three using water. Finally, the catalysts (Cu/D, Cu/DH and Au/DH) were freeze-dried. Similar procedures were followed for the preparation of Cu NPs deposited on AC (Cu/AcH) on G (Cu/GH) and on MWCNT (Cu/MWCNTH).

Catalyst characterization: Using inductively coupled plasma atomic emission spectroscopy (ICP-AES) chemical analysis the metal loading (0.5 wt. %) deposited on the functionalized diamond NPs was confirmed. FT-IR spectra of the different samples were recorded on a Nicolet 710 FTIR spectrophotometer by using KBr disks of the samples prepared by compression at 10 Ton for 2 min. Diffuse reflectance optical spectra were recorded with a CARY 5G UV-Vis-NIR spectrophotometer adapted with an integrating sphere. X-ray diffractograms (XRD) were recorded by using a Philips X-Pert diffractometer equipped with a graphite monochromator, operating at 40 kV and 45 mA and employing Ni filtered CuKα radiation (λ=0.1542 nm). Transmission electron microscopy (TEM) and high resolution TEM (HRTEM) of the different samples were obtained using a TECNAI G2 F20 (FEI) instrument operating at 200 kV. The particle size distribution was estimated by counting over 300 particles. The percentage conversion, purity and relative yields of the final products were determined by using a Hewlett Packard 5890 series II gas chromatograph with an FID detector and high purity helium as the carrier gas. The products were identified by GC–MS by using a Hewlett Packard 6890 series spectrometer and by comparison with authentic commercial samples.

Typical reaction procedure: A 50 mL round-bottomed flask was charged with catalyst (20 mg) in ethanol (4 mL) and substrate (1 mmol), and hydrazine (2 mmol). This reaction mixture was stirred for the required time at 60 ^{o}C. The reaction was monitored periodically by analyzing the sample with GC until the completion of reaction. The mass balances of the recovered reaction mixture accounted for more than 97 % of the initial substrate, as confirmed by GC using nitrobenzene as the external standard. The yields of the product were determined by using nitrobenzene as the external standard considering the response factors unity.

Reuse experiment

After the catalytic reaction the catalyst was recovered by centrifugation. Then, the catalyst was washed in ethanol, acetone and water three times each solvent, and dried under air and room temperature. The recovered catalyst was used for the next run with fresh styrene.

Effect of pretreatments

In the present study, we have used Fenton-treated diamond NPs (D) submitted to annealing with hydrogen (DH). The surface of D contains some carboxylate and carbonyl groups that tend to give larger metal particles by favouring the growth of the initial metal clusters. Hydrogen treatment at appropriate temperatures of D reduces the population of these oxygen functionalities increasing the density of surface hydroxyl groups that play a positive role in the initial steps of the metal deposition on the surface. For this reason in the present case, we have compared the catalytic activity of two copper containing materials using D or DH as supports. TEM images of Cu/D and Cu/DH show that even though the loading of Cu on these two solids is the same and the preparation procedure was identical, the average particle size of Cu NPs on Cu/DH (3.7 nm) is smaller than for Cu/D (6.7 nm). These differences in particle size should be responsible for differences in the catalytic activity of the materials since as a general rule smaller metal NPs exhibit higher activity provided that they are stable under the reaction conditions.

Table S1. Textural properties of various supports used in the present study.

Support	S_{BET} (m^2/g)[a]	size
D NPs	200-450	< 10 nm[b]
AC[c]	1300	100 mesh size
G[c]	47	200-500 nm[b]
MWCNT	200-350	10-20 nm diameter[b] and 10-500 nm length

[a] Data taken from Sigma Aldrich.

[b] Determined by TEM.

[c] Commercial sample from Sigma Aldrich.

Table S2. Cu NPs size in various catalysts determined by statistical analysis of the corresponding TEM images.

Catalysts	Average particle size (nm)
Cu/D[b]	12.3
Cu/G[b]	7.0
Cu/AC[b]	6.7
Cu/MWCNT[a]	7.1
Cu/D	6.7
Cu/G	8.1
Cu/AC	8.4
Cu/MWCNT	8.3
Cu/DH	3.7
Cu/GH	7.8
Cu/ACH	7.9
Cu/MWCNTH	7.3
Au/DH	5.3
Pd/DH	3.7

[a] Support without any treatment. Cu NPs were deposited on commercial samples as received.

Table S3. Hydrogenation of styrene to ethylbenzene using hydrazine as reducing agent promoted by various catalysts.[a]

Run	catalyst	time (h)	conversion (%)[b]	selectivity (%)[b]
1	Cu/D[c]	1	24	>99
2		2	28	>99
3		3	31	>99
4	Cu/D	1	40	>99
5		2	56	>99
6		3	64	>99
7	Cu/DH	1	58	100
8		2	88	100
9		3	100	100
10	Cu/AC[c]	1	19	98
11		2	28	98
12		3	42	99
13	Cu/AC	1	15	99
14		2	22	99
15		3	28	99
16	Cu/ACH	1	20	99
17		2	29	99
18		3	35	99
19	Cu/G[c]	1	26	99
20		2	38	99
21		3	51	99
22	Cu/G	1	19	98
23		2	25	99
24		3	30	99
25	Cu/GH	1	20	99
26		2	28	99
27		3	32	99
28	Cu/MWCNT[c]	1	28	98
29		2	43	99

30		3	48	99
31	Cu/MWCNT	1	21	99
32		2	32	99
33		3	40	99
34	Cu/MWCNTH	1	28	99
35		2	36	99
36		3	47	99

[a] Reaction conditions: styrene (1 mmol), catalyst (20 mg), $N_2H_4.H_2O$ (0.1 mL), aq. NH_3 (0.025 mL), ethanol (4 mL), 60 °C.

[b] Determined by GC.

[c] Without any treatment.

TEM images:

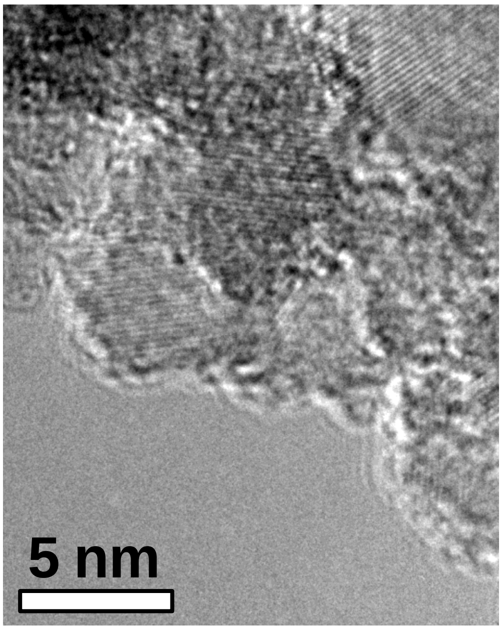

Figure S 1. HRTEM image of D NPs support

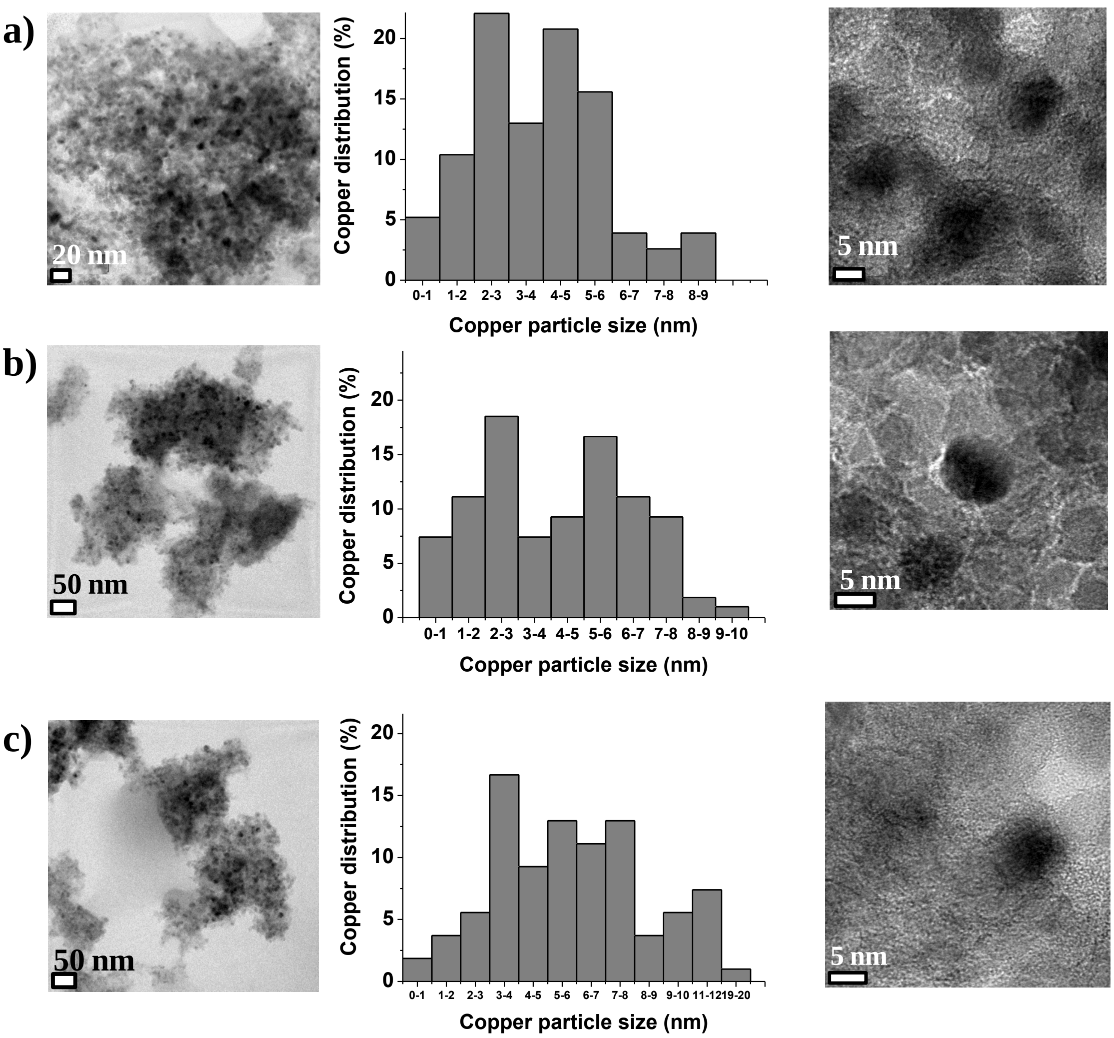

Figure S2. Representative TEM images and Cu particle size distribution of Cu/DH (fresh), Cu/DH (after 3rd reuse) and Cu/DH after productivity test.

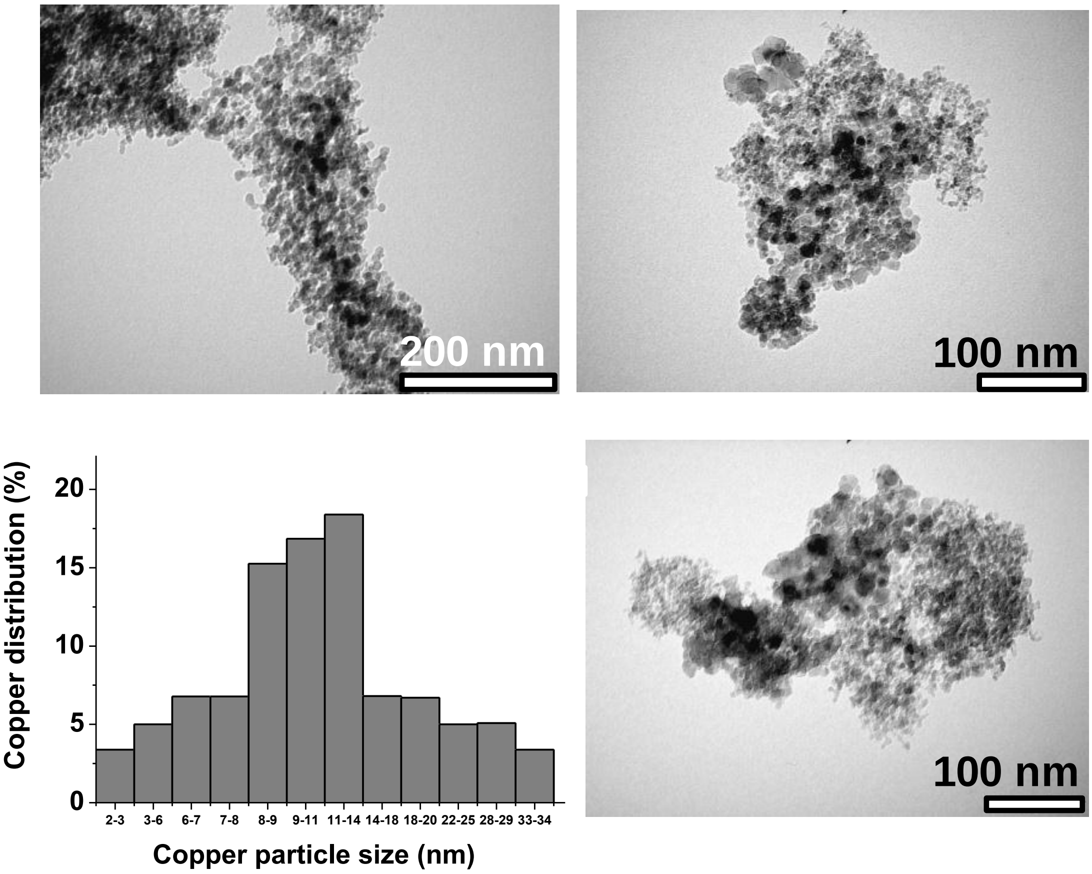

Figure S3. TEM images and particle size distributions of Cu/D without any treatment. Average particle size = 12.3 nm.

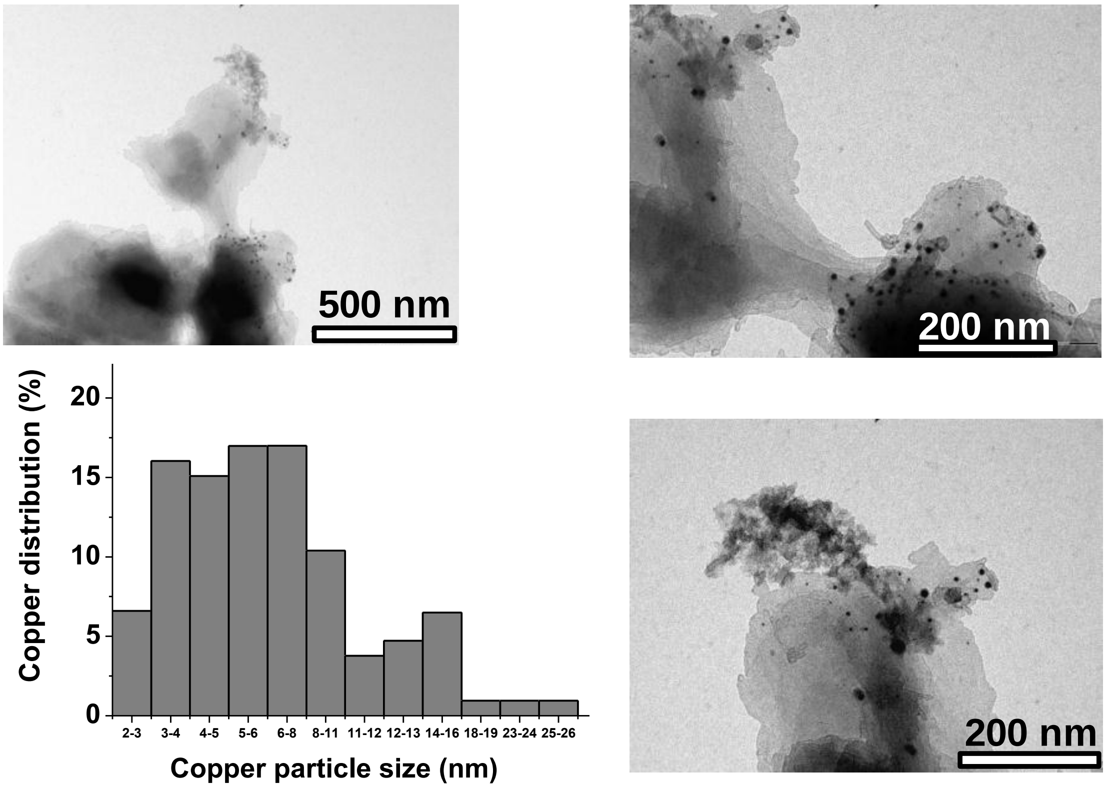

Figure S4. TEM images and particle size distributions of Cu/AC without any treatment. Average particle size = 6.7 nm.

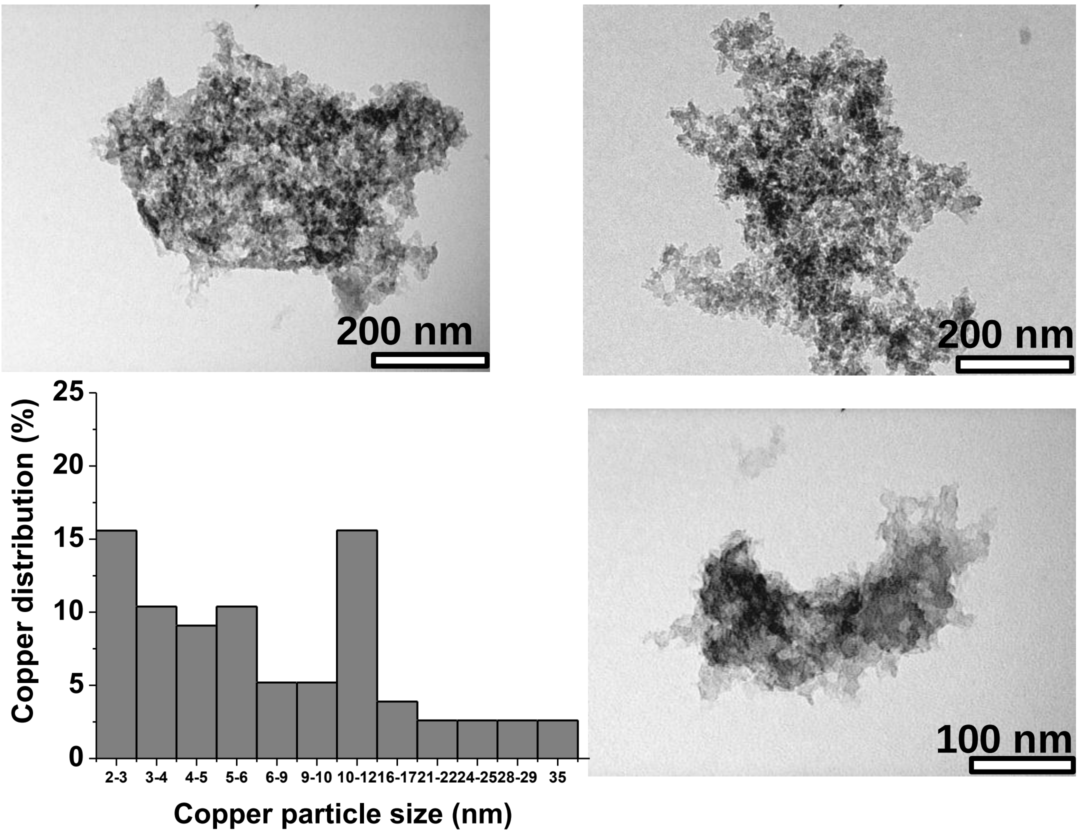

Figure S5. TEM images and particle size distributions of Cu/AC. Average particle size = 8.4 nm.

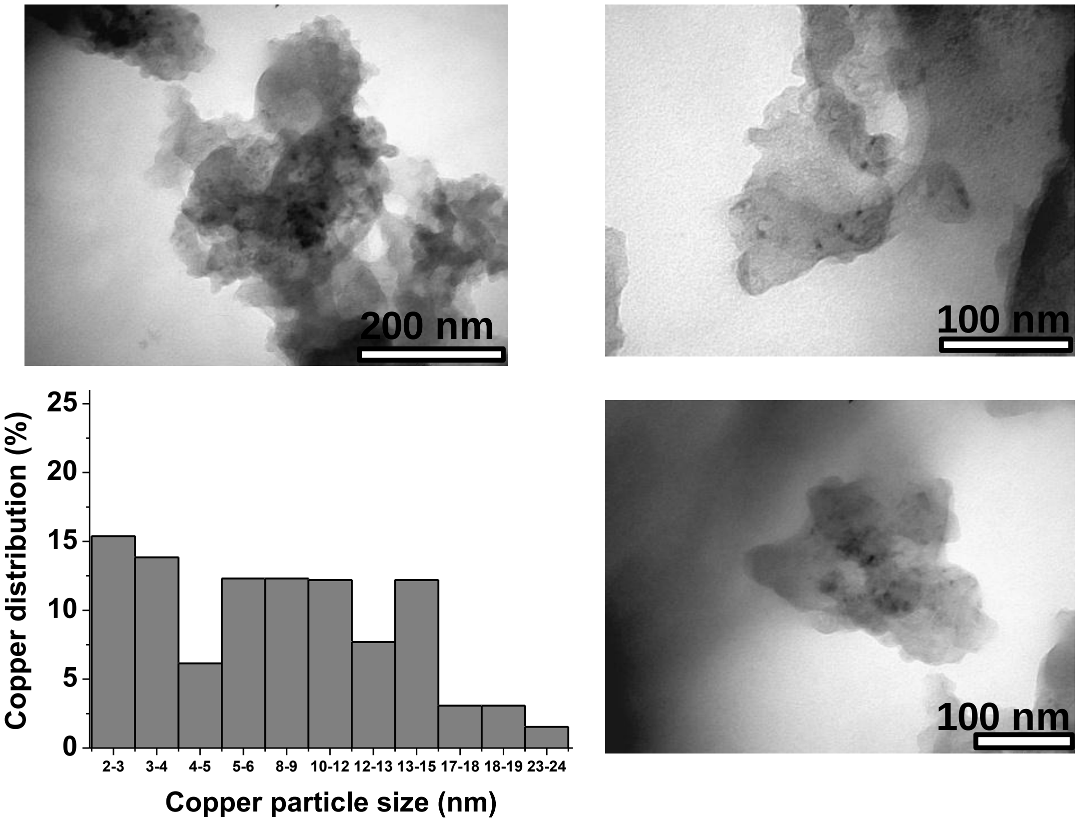

Figure S6. TEM images and particle size distributions of Cu/ACH. Average particle size = 7.9 nm.

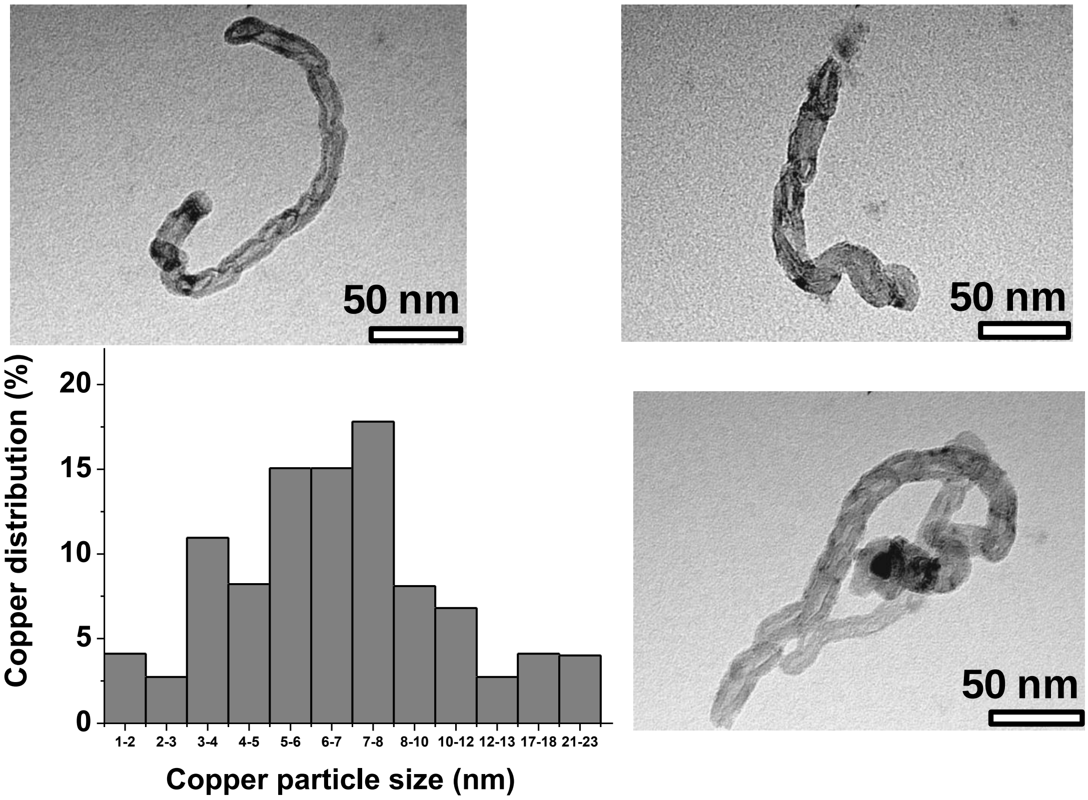

Figure S7. TEM images and particle size distributions of Cu/MWCNT without any treatment. Average particle size = 7.1 nm.

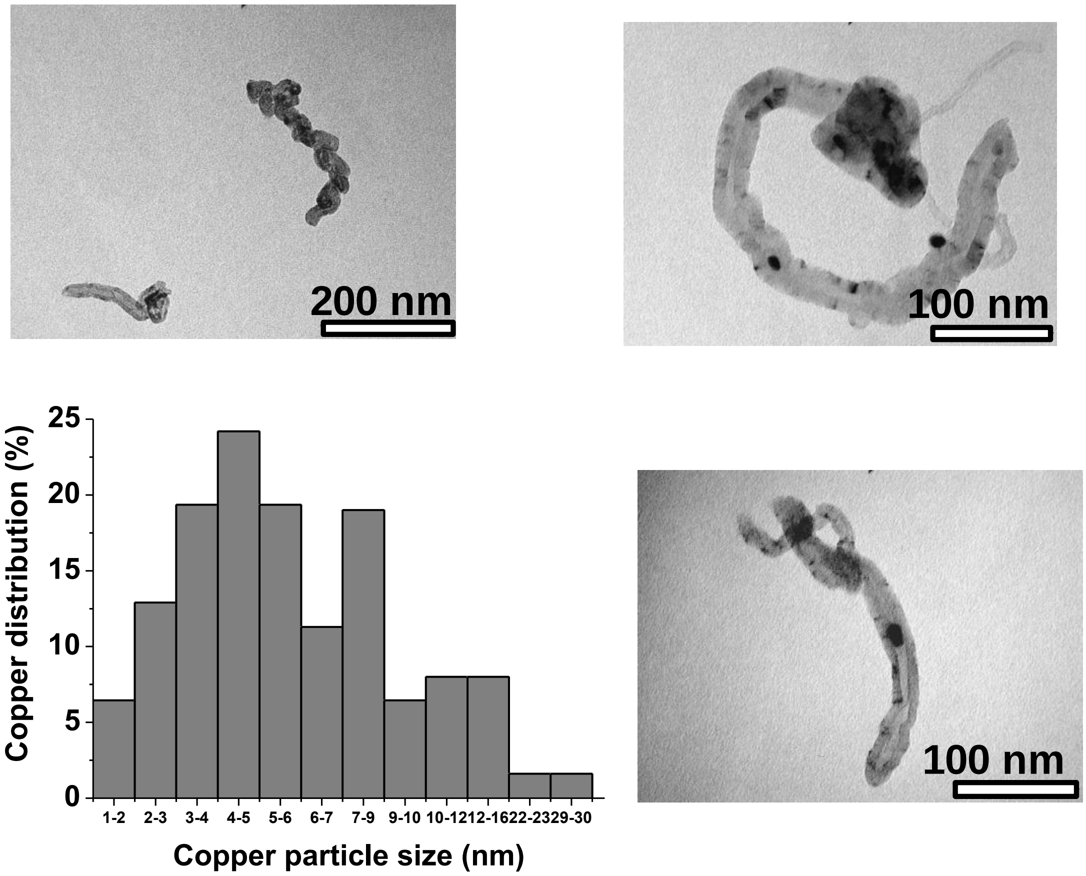

Figure S8. TEM images and particle size distributions of Cu/MWCNT. Average particle size = 8.3 nm.

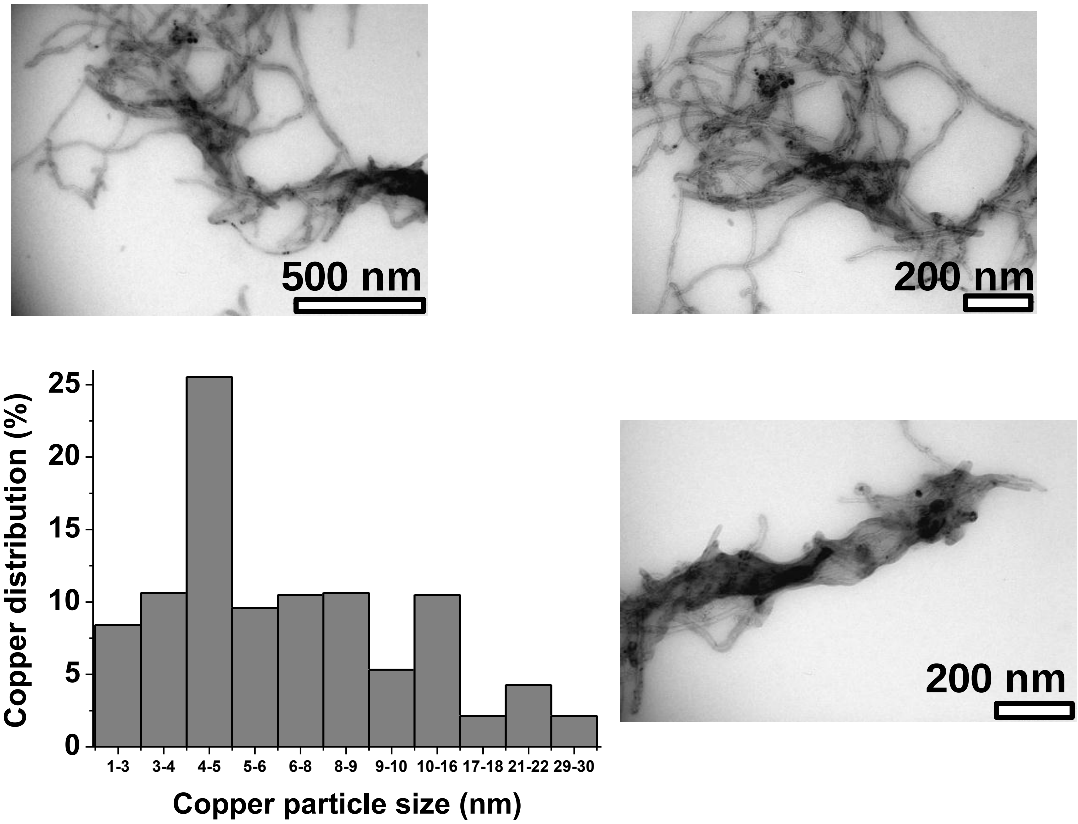

Figure S9. TEM images and particle size distributions of Cu/MWCNTH. Average particle size = 7.3 nm.

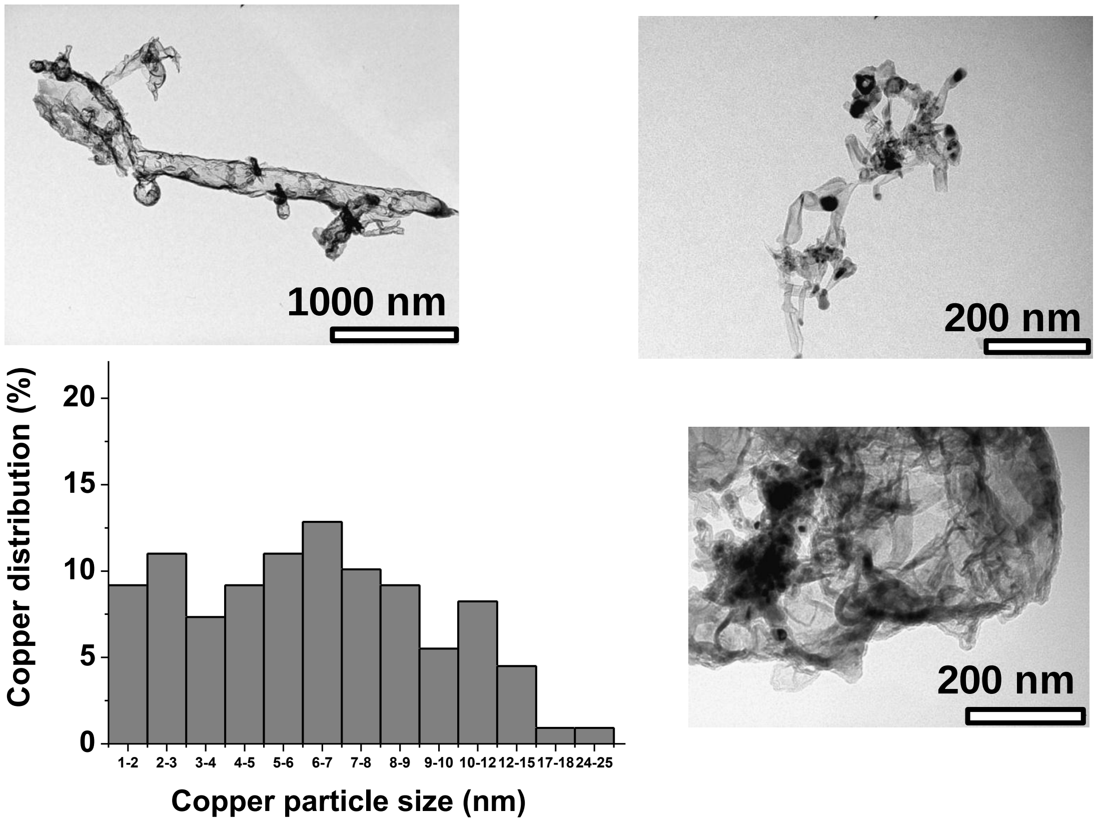

Figure S10. TEM images and particle size distributions of Cu/G without any treatment. Average particle size = 7.0 nm.

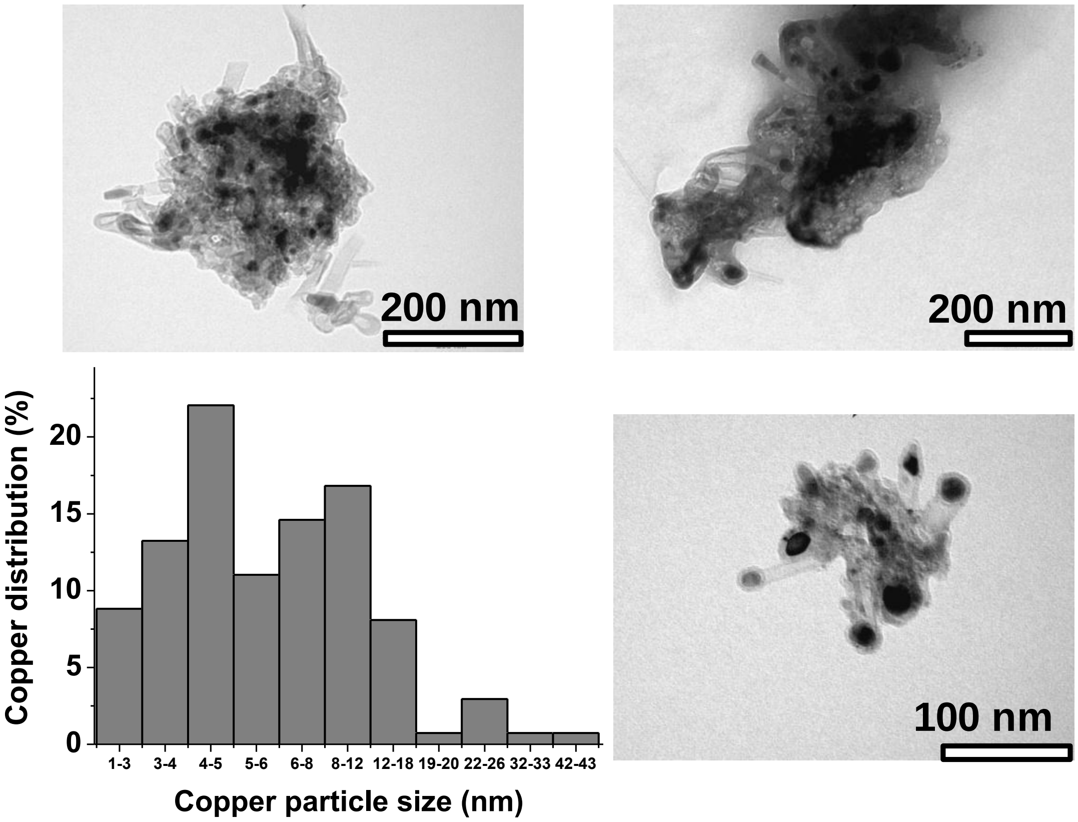

Figure S11. TEM images and particle size distributions of Cu/G. Average particle size = 8.1 nm.

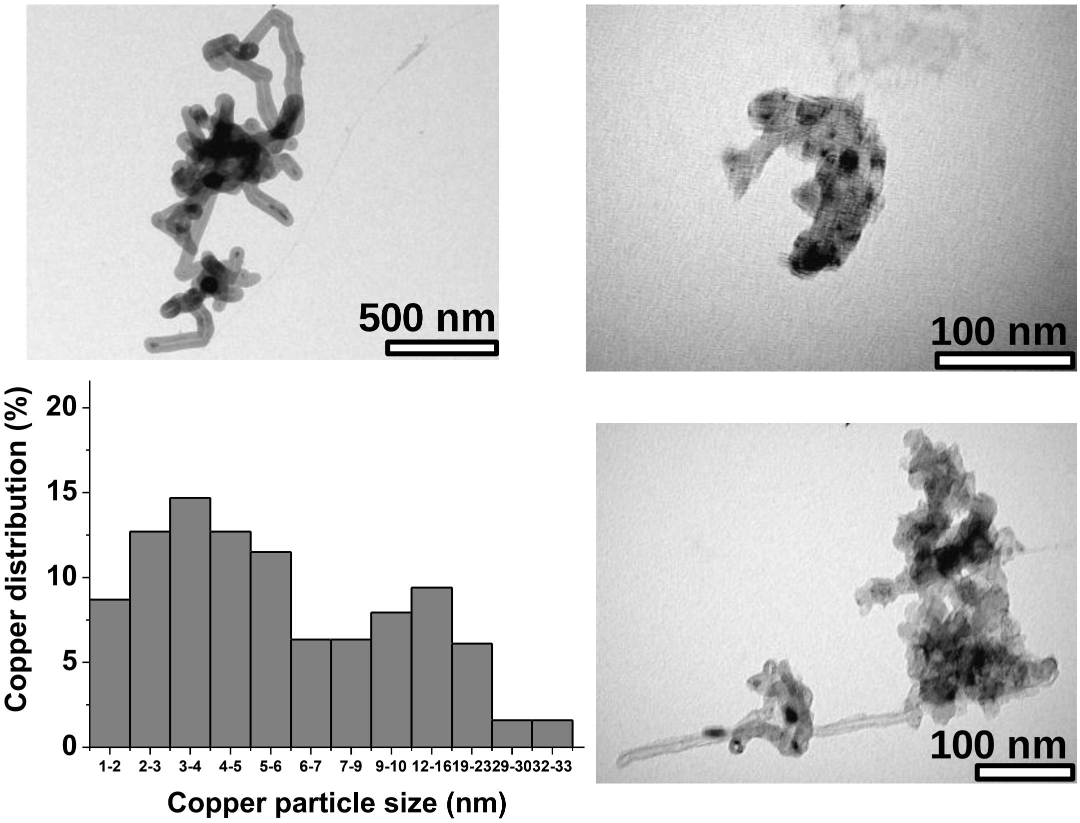

Figure S12. TEM images and particle size distributions of Cu/GH. Average particle size = 7.8 nm.

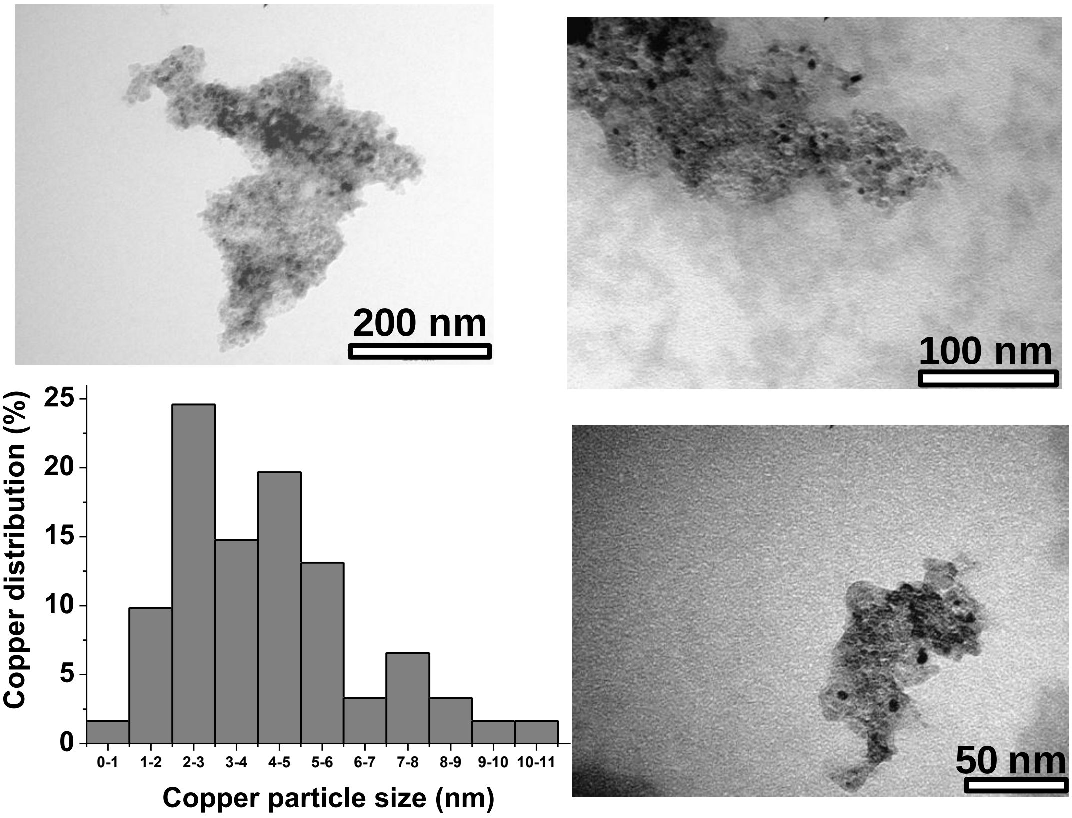

Figure S 13. TEM images and particle size distributions of Pd/DH. Average particle size = 3.7 nm.

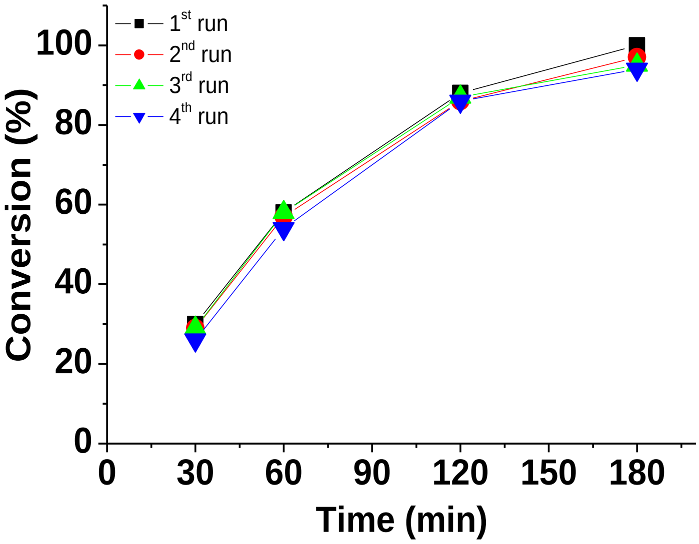

Figure S 14. Kinetic profile for the hydrogenation of styrene to ethylbenzene using Cu/DH as catalyst for the first, second, third and fourth run.

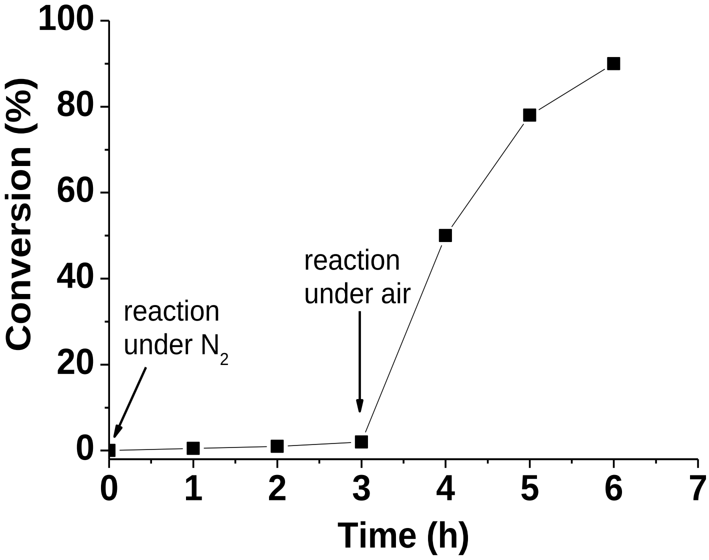

Figure S 15. Temporal profile for the reduction of styrene in the presence of nitrogen and air.

Productivity test

The turnover frequency and turnover number for this reaction under these conditions were 640 h^{-1} and 12800 cycles, respectively.

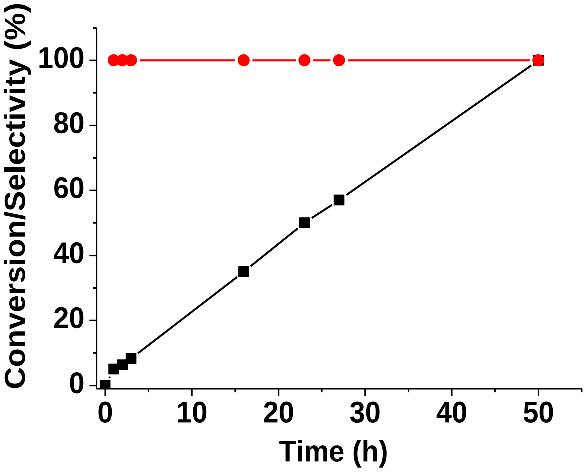

Figure S 16. Productivity test for the reduction of styrene to ethylbenzene at 20 mmol scale. The reaction conditions are given in Table 1. Reaction conditions: styrene (20 mmol), Cu/DH (20 mg), $N_2H_4.H_2O$ (2 mL), aq. NH_3 (0.5 mL), ethanol (20 mL), 60 ^oC.

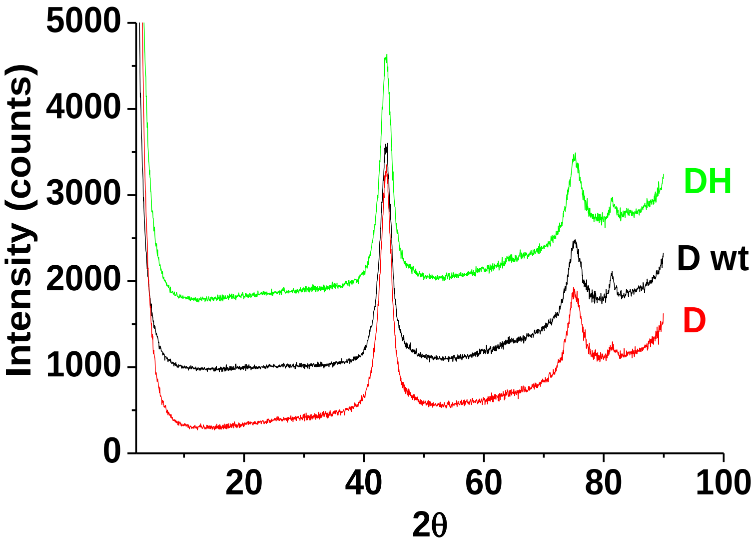

Figure S17. Powder XRD patterns of D NPs with and without treatments. Wt: represents without treatment.

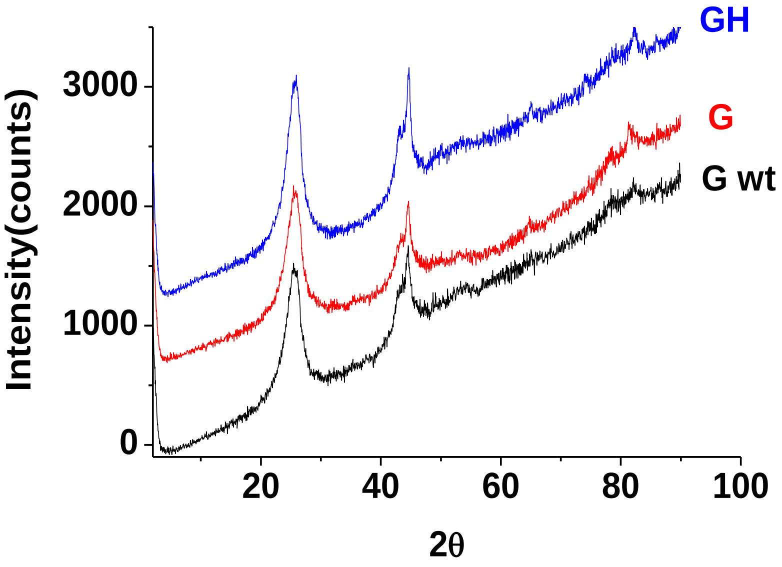

Figure S18. Powder XRD patterns of G with and without treatments. Wt: represents without treatment.

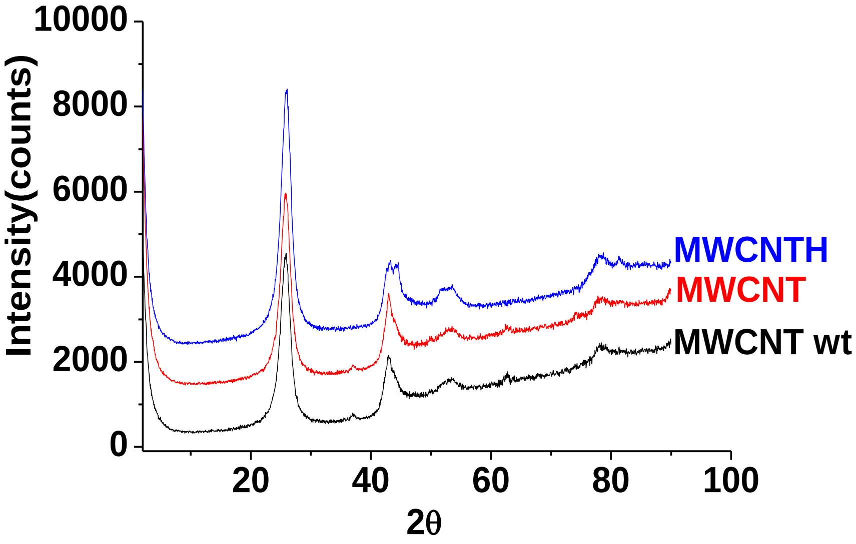

Figure S19. Powder XRD patterns of MWCNT with and without treatments. Wt: represents without treatment.