SUPPORTING INFORMATION

Monodisperse CuB_{23} nanoparticles grown on graphene as highly efficient catalysts for unactivated alkyl halides Heck-couplings and levulinic acid hydrogenation

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Summary: 27 Pages; 2 Tables; 26 Figures

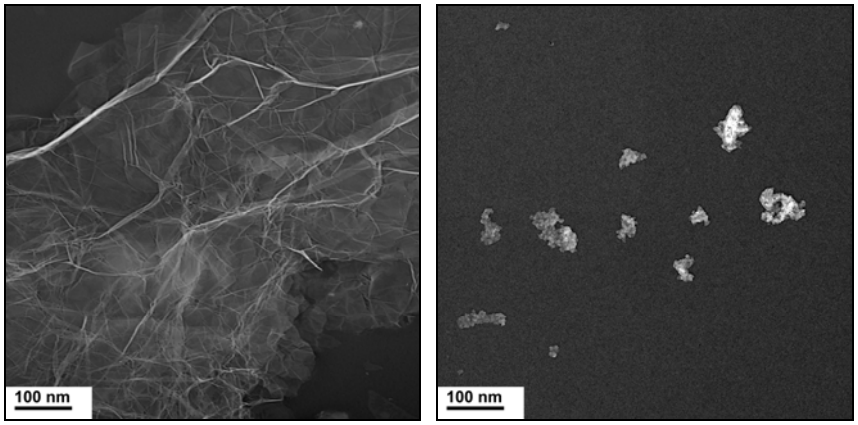
Table S1 Physico-chemical properties of the samples

Samples	Cu-loading/wt.%	Compositions/at.%	S_{BET}/m^2g^{-1}	Average particle sizes/nm	S_{Cu}/m^2g^{-1}
CuB_{23}	-	$CuB_{22.99}$	28.2	30	15.9
Graphene	-	-	229.5	-	-
3.54 wt.% CuB_{23}/graphene	0.73 wt.%	$CuB_{23.00}$	156.7	2.3	46.2
6.67 wt.% CuB_{23}/graphene	1.36 wt.%	$CuB_{22.98}$	133.2	3.4	60.1
9.93 wt.% CuB_{23}/graphene	2.02 wt.%	$CuB_{23.01}$	125.4	4.8	67.9
13.62 wt.% CuB_{23}/graphene	2.77 wt.%	$CuB_{23.00}$	104.5	6.7	59.4
20.58 wt.% CuB_{23}/graphene	4.13 wt.%	$CuB_{23.01}$	86.2	9.9	48.6
9.93 wt.% CuB_{23}/C	2.02 wt.%	$CuB_{23.01}$	140.9	5.0	50.2
2.02 wt.% Cu/graphene	2.02 wt.%	-	160.4	5.1	45.4
2.02 wt.% Cu/C	2.02 wt.%	-	172.5	5.2	40.9

Table S2 Hydrogenation of LA to GAL over 9.93 wt.% CuB_{23}/graphene with different solvents. [a]

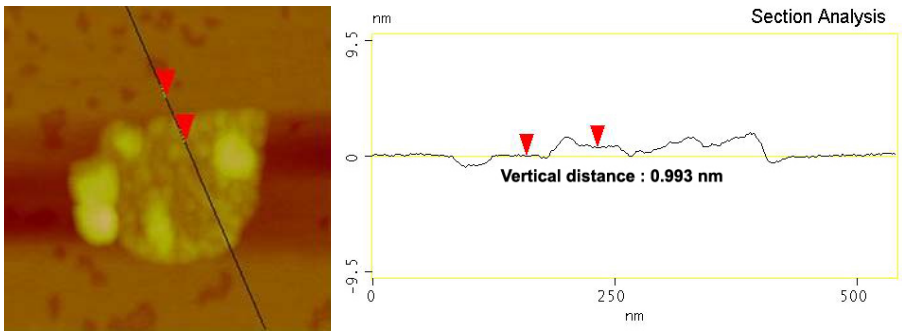
Solvents	Conversion / %	Yield / %
No solvent	82	76
n-dodecane	100	99
Toluene	56	47
CH_3OH	64	55
H_2O	12	5
1,4-Dioxane	23	16

[a] Reaction conditions: Catalyst containing 2.54 mg Cu, 20 mmol LA, 50mL of n-dodecane, PH_2 = 4.2 MPa H_2, T = 413 K, Reaction time = 4 h, stirring rate = 1100 rpm.



a b

Fig.S1 STEM images of (a) Graphene and (b) CuB_{23}.



a b

Fig.S2 (a) AFM image and (b) the cross section analysis of graphene prepared in our work

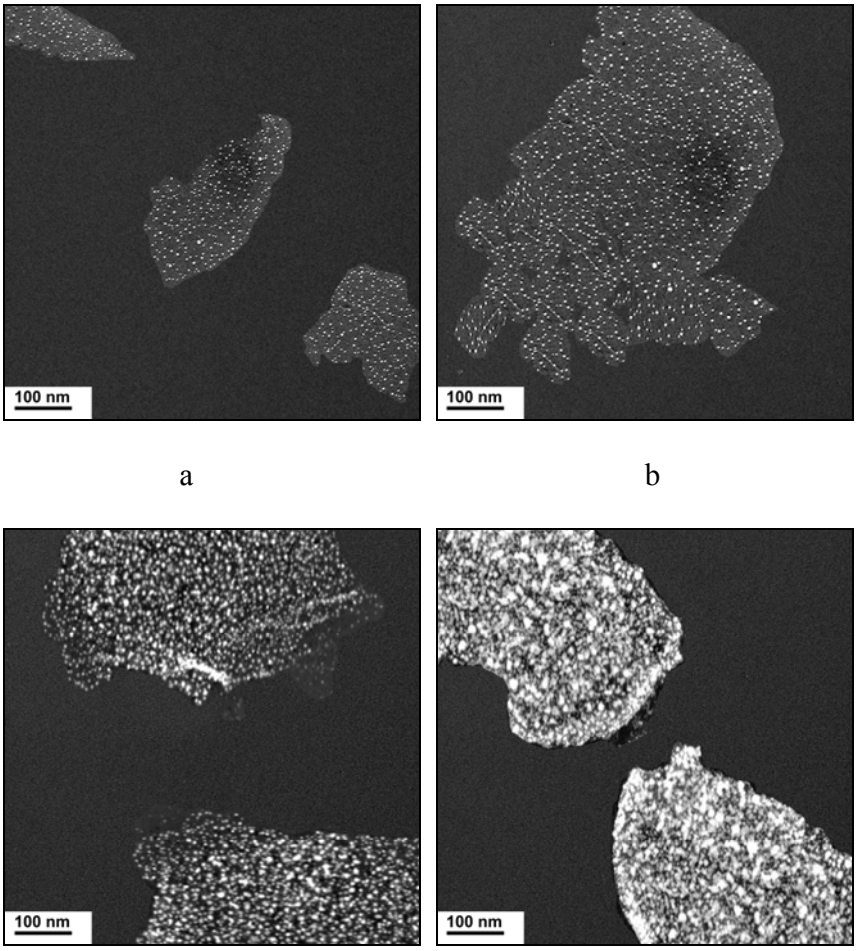


Fig.S3 STEM images of (a) 3.54 wt.% CuB_{23}/graphene, (b) 6.67 wt.% CuB_{23}/graphene, (c) 13.62 wt.% CuB_{23}/graphene and (d) 20.58 wt.% CuB_{23}/graphene.

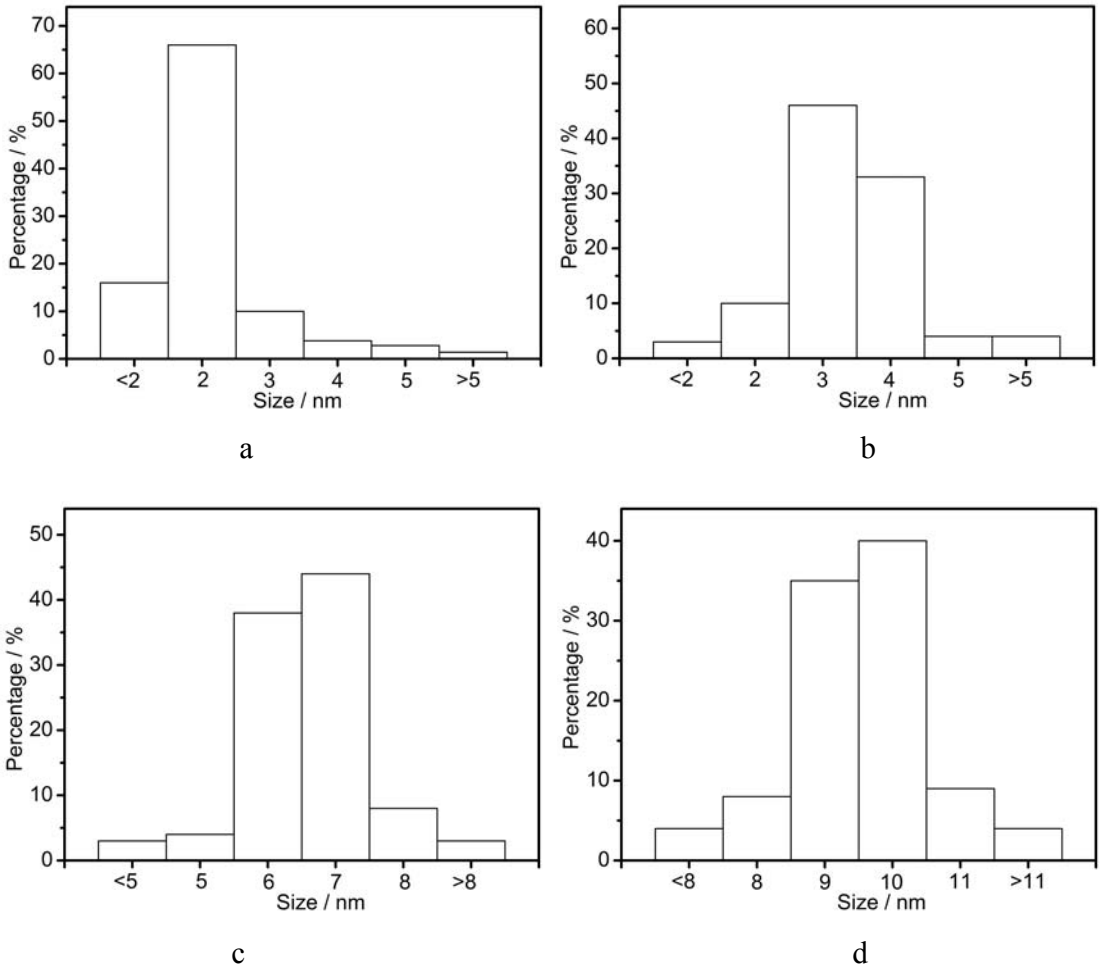


Fig.S4 Particle size distribution histograms of (a) 3.54 wt.% CuB_{23}/graphene, (b) 6.67 wt.% CuB_{23}/graphene, (c) 13.62 wt.% CuB_{23}/graphene and (d) 20.58 wt.% CuB_{23}/graphene.

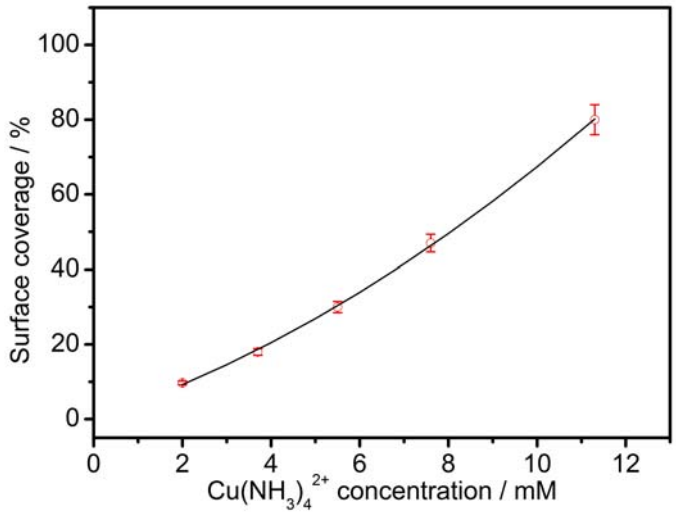
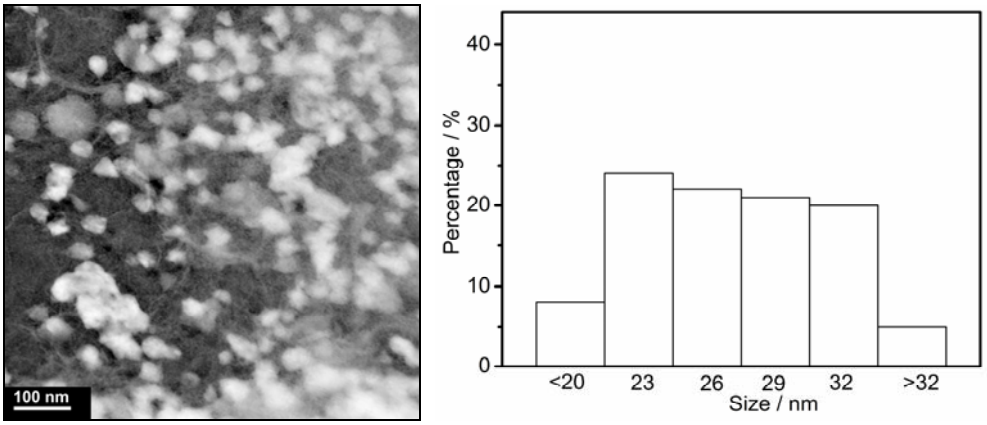
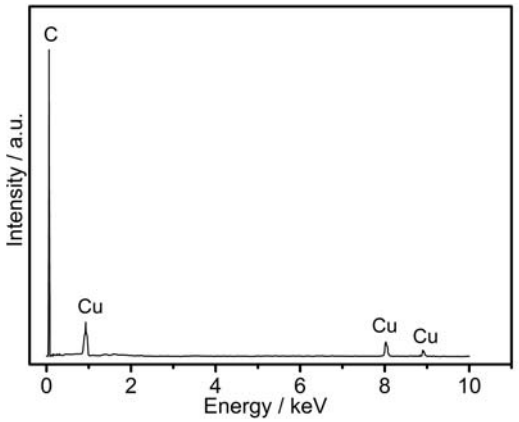


Fig.S5 Dependence of the total coverage percentage of CuB_{23} NPs on graphene with respect to the $Cu(NH_3)_4^{2+}$ concentrations. The total coverage percentage was measured from 6 images of different CuB_{23}/graphene composites on each individual sample using Image Pro Plus.



a b



c

Fig.S6 (a)STEM images; (b) the corresponding size distribution and (c) EDAX of Cu/graphene composites prepared from $Cu(NO_3)_2$.

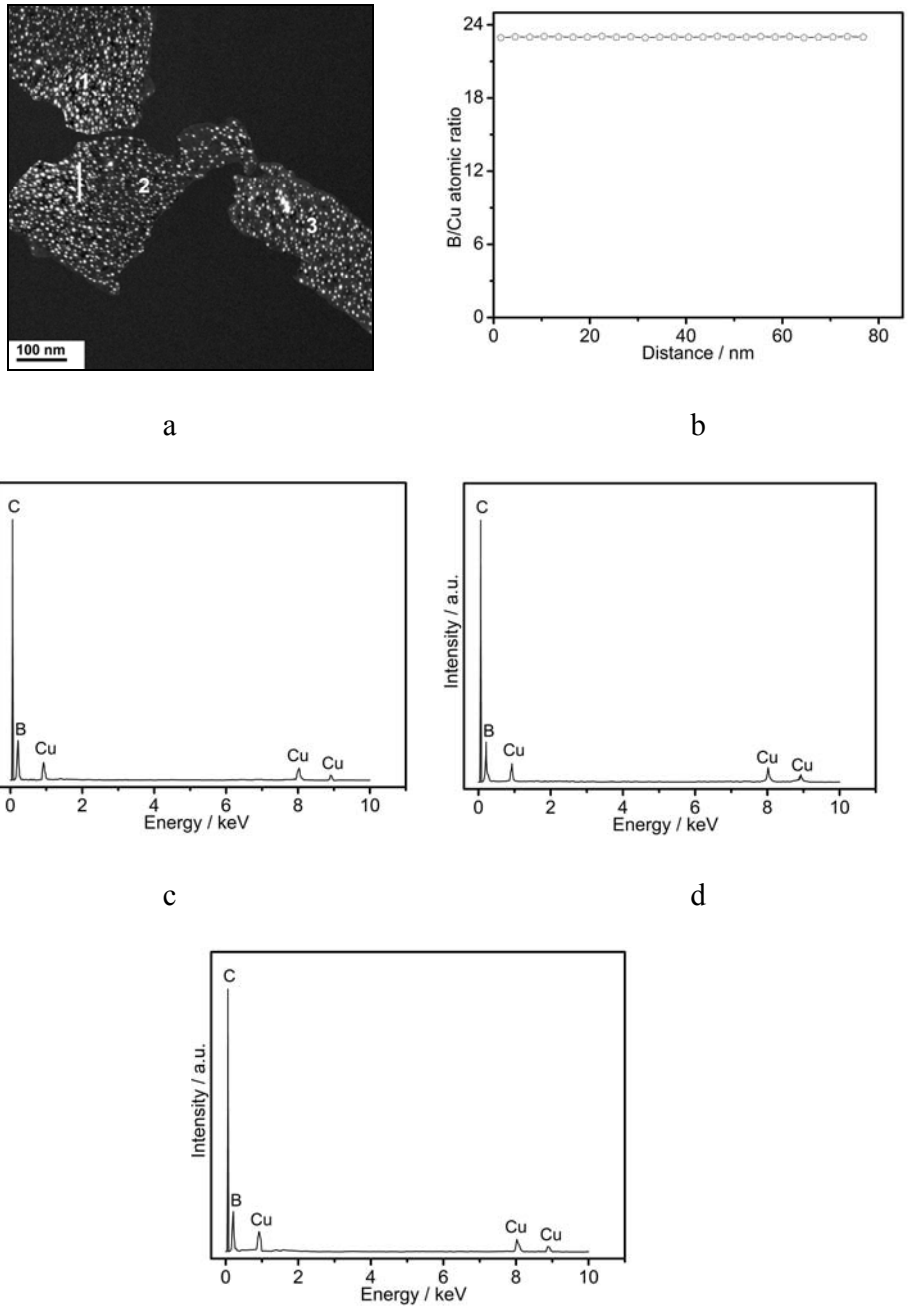


Fig.S7 (a) The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM); (b) B/Cu atomic ratio recorded along the white cross-sectional compositional line shown in (a); (c)-(e)the Energy-dispersive X-ray spectroscopy (EDAX) at points 1-3 in (a) of the as-prepared 9.93 wt.% CuB_{23}/graphene.

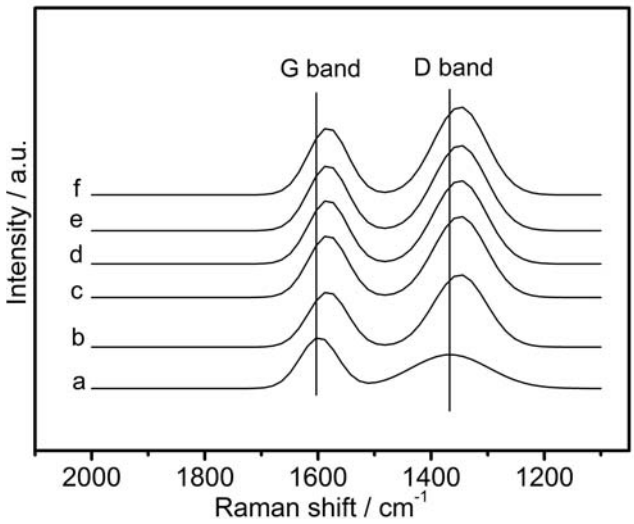


Fig.S8 Raman spectra of (a) Graphene oxide, (b) 3.54 wt.% CuB_{23}/graphene, (c) 6.67 wt.% CuB_{23}/graphene, (d) 9.93 wt.% CuB_{23}/graphene, (e) 13.62 wt.% CuB_{23}/graphene and (f) 20.58 wt.% CuB_{23}/graphene.

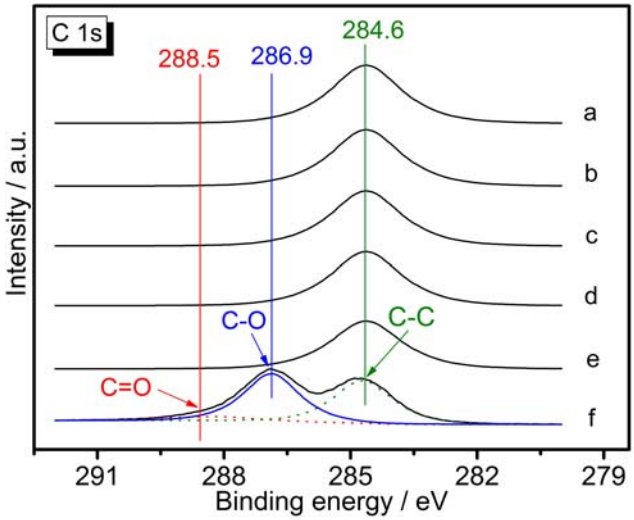


Fig.S9 C 1s XPS spectra of (a) 3.54wt.% CuB_{23}/graphene, (b) 6.67 wt.% CuB_{23}/graphene, (c) 9.93 wt.% CuB_{23}/graphene, (d) 13.62 wt.% CuB_{23}/graphene , (e) 20.58wt.% CuB_{23}/graphene and (f) GO.

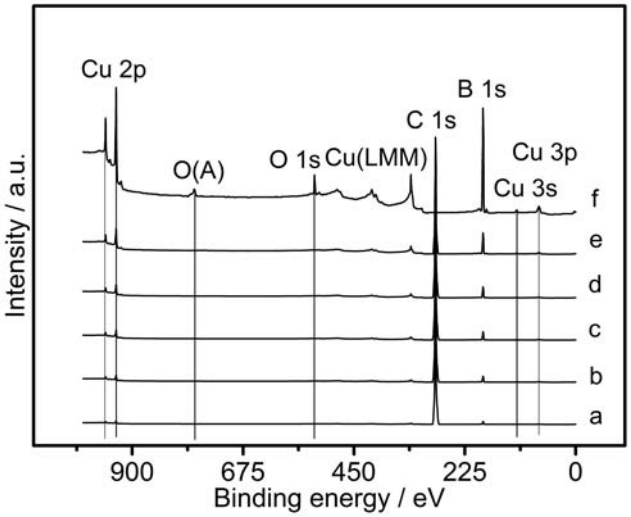


Fig.S10 Overall XPS spectra of spectra of (a) 3.54 wt.% CuB_{23}/graphene, (b) 6.67 wt.% CuB_{23}/graphene, (c) 9.93 wt.% CuB_{23}/graphene, (d) 13.62 wt.% CuB_{23}/graphene, (e) 20.58 wt.% CuB_{23}/graphene and (f) CuB_{23}.

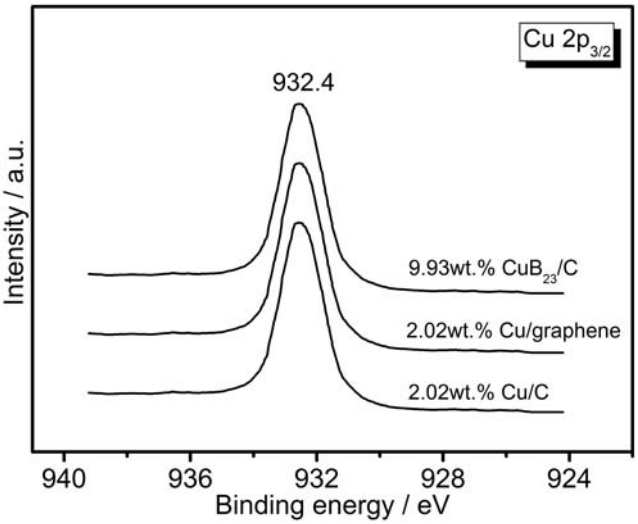


Fig.S11 The typical $Cu2p_{3/2}$ XPS spectra of 2.02 wt.% Cu/graphene, 2.02 wt.% Cu/C and 9.93 wt.% CuB_{23}/C. All of three samples have an average particle size of about 5 nm, which is similar to that of 9.93 wt.% CuB_{23}/graphene. Cu/Graphene and Cu/C prepared by reduction with N_2H_4.

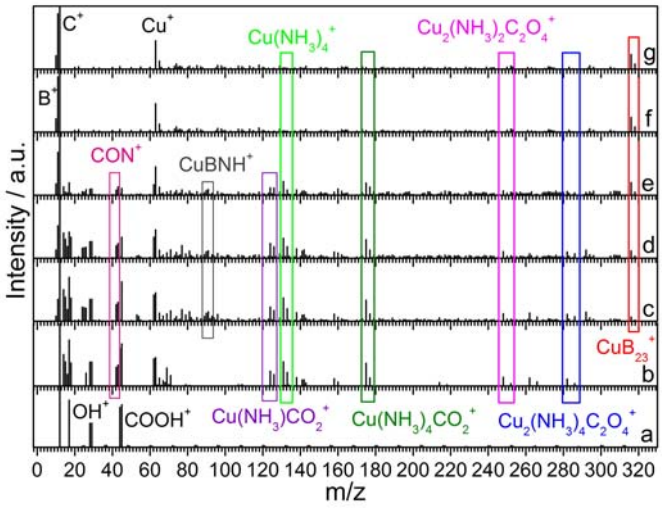


Fig.S12 ToF-SIMS spectra of (a) graphene oxide and the samples prepared during SPP: (b) 0 min; (c) 0.5 min; (d) 1 min; (e) 2 min; (f) 5 min and (g) 10 min.

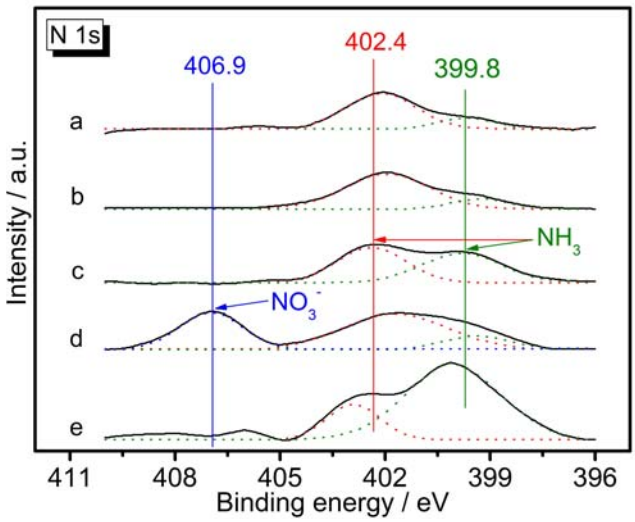


Fig.S13 N1s XPS spectra of GO after absorption in (a) air (gas), (b) NH_3 (gas), (c) $NH_3 . H_2O$ (5 wt%), (d) $Cu(NO_3)_2$ solution (5.5 mM) and (e) $Cu(NH_3)_4^{2+}$ (5.5 mM).

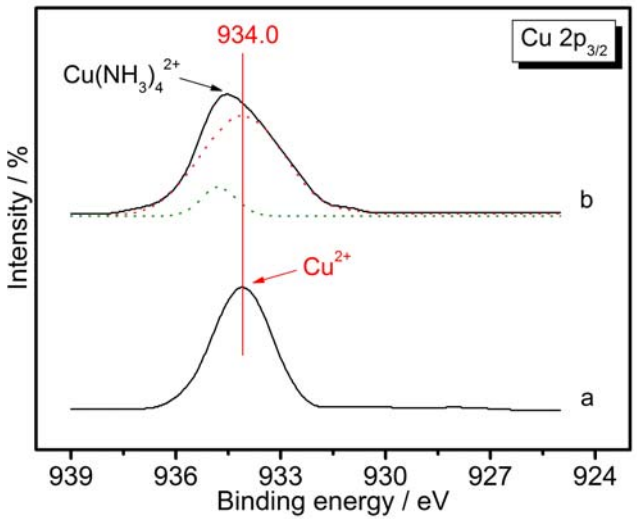


Fig.S14 Cu $2p_{3/2}$ XPS spectra of GO after absorption in (a) $Cu(NO_3)_2$ (5.5 mM) and (b) $Cu(NH_3)_4^{2+}$ (5.5 mM).

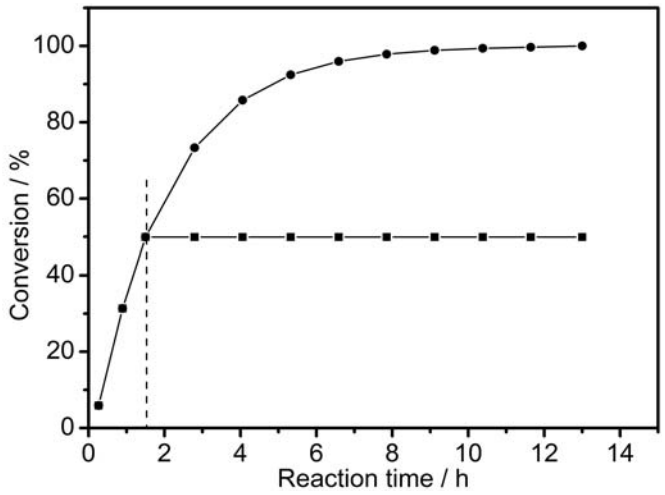


Fig.S15 Residual activity after filtration for Heck coupling reaction between cyclohexyliodide and styrene over 9.93 wt.% CuB_{23}/graphene after 1.5 h reaction (■) versus standard catalyst run (●). Reaction conditions: a catalyst containing 6.35 mg Cu, cyclohexyliodide (5.0 mmol), styrene (6.0 mmol), Na_2CO_3 (7.5 mmol), DMF (10 mL), T = 353 K, stirring rate =800 rpm.

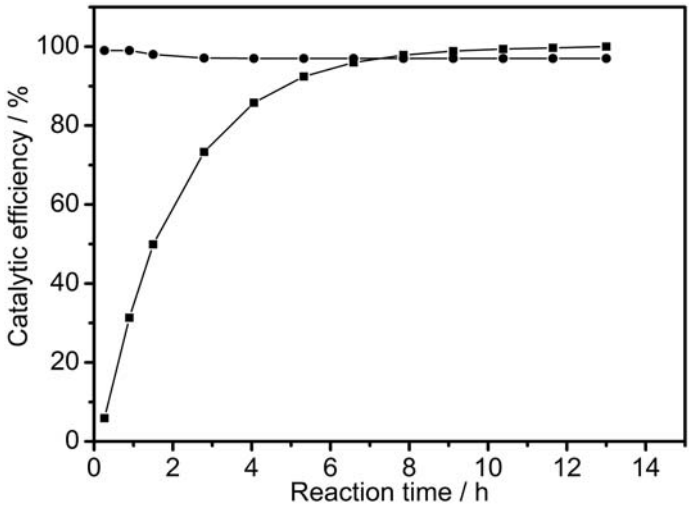
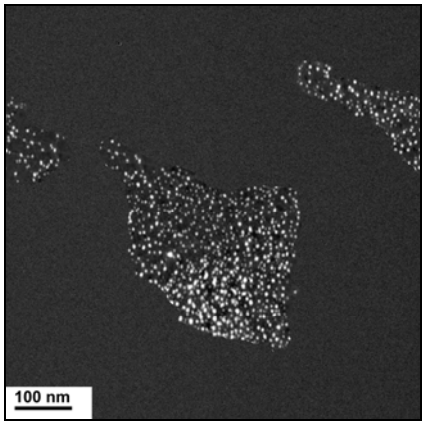
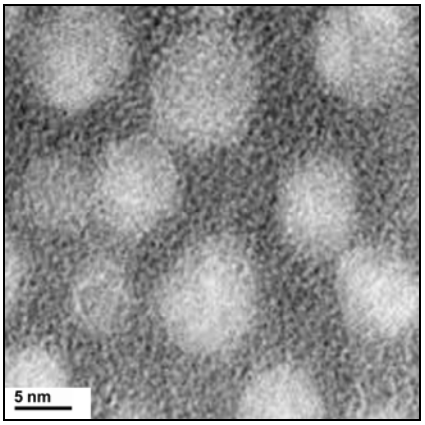


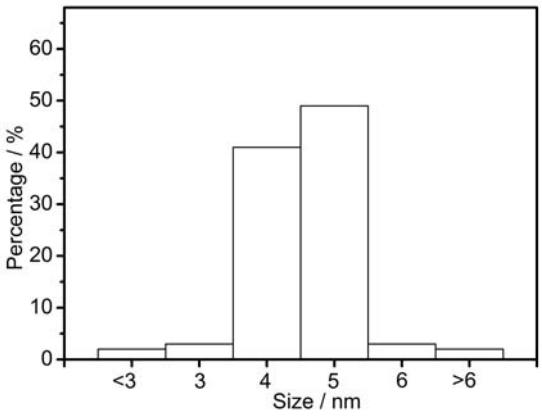
Fig.S16 Dependency of the cyclohexyliodide conversion (■) and the (E)-(2-cyclohexylvinyl)benzene selectivity (●) on reaction time over 9.93 wt.% CuB_{23}/graphene. Reaction conditions: a catalyst containing 6.35 mg Cu, cyclohexyliodide (5.0 mmol), alkenes (6.0 mmol), Na_2CO_3 (7.5 mmol), DMF (10 mL), T = 353 K, stirring rate = 800 rpm.



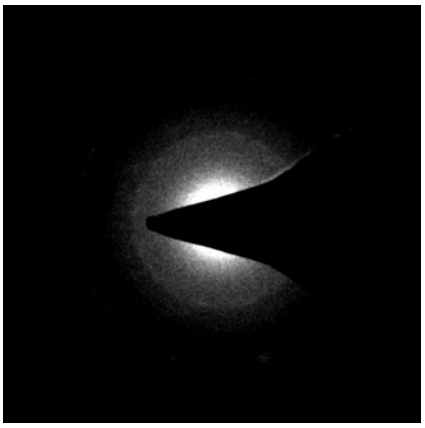
a



b

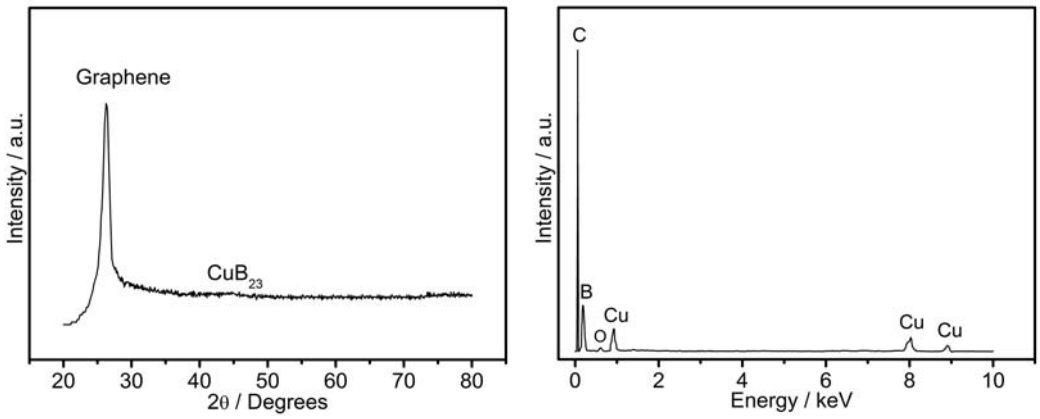


c



d

Fig.S17 (a) Low magnification STEM image；(b) High magnification STEM image; (c) Particle size distribution histograms; and (d) SAED pattern of the as-prepared 9.93 wt.% CuB_{23}/graphene after 5 cycles. Reaction conditions: a catalyst containing 6.35 mg Cu, cyclohexyliodide (5.0 mmol), styrene (6.0 mmol), Na_2CO_3 (7.5 mmol), DMF (10 mL), T = 353 K, stirring rate = 800 rpm.



a b

Fig.S18 (a) XRD pattern and (b) EDAX spectrum of 9.93 wt.% CuB_{23}/graphene after 5 cycles. Reaction conditions: a catalyst containing 6.35 mg Cu, cyclohexyliodide (5.0 mmol), styrene (6.0 mmol), Na_2CO_3 (7.5 mmol), DMF (10 mL), T = 353 K, stirring rate =800 rpm.

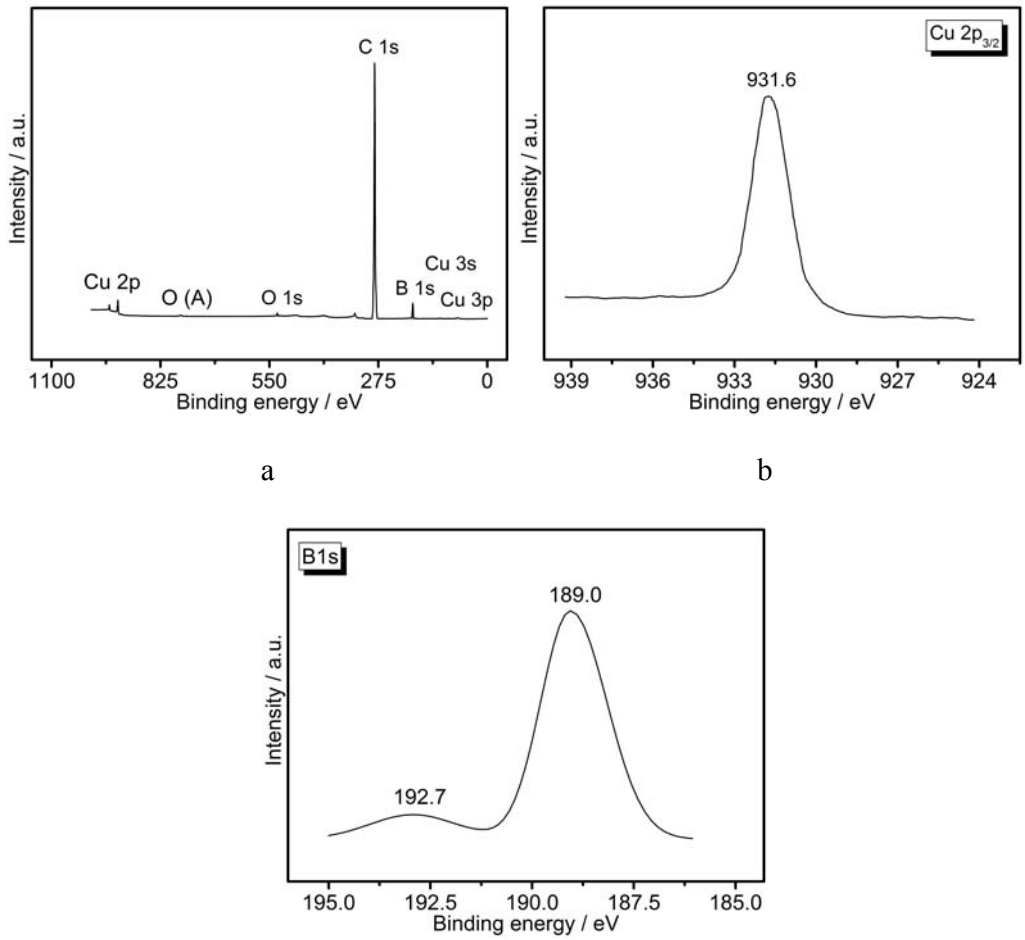


Fig.S19 (a) Overall XPS; (b) Cu2p3/2; (c) B1s and (d) O1s XPS spectra of 9.93 wt.% CuB_{23}/graphene after 5 cycles. Reaction conditions: a catalyst containing 6.35 mg Cu, cyclohexyliodide (5.0 mmol), styrene (6.0 mmol), Na_2CO_3 (7.5 mmol), DMF (10 mL), T = 353 K, stirring rate = 800 rpm.

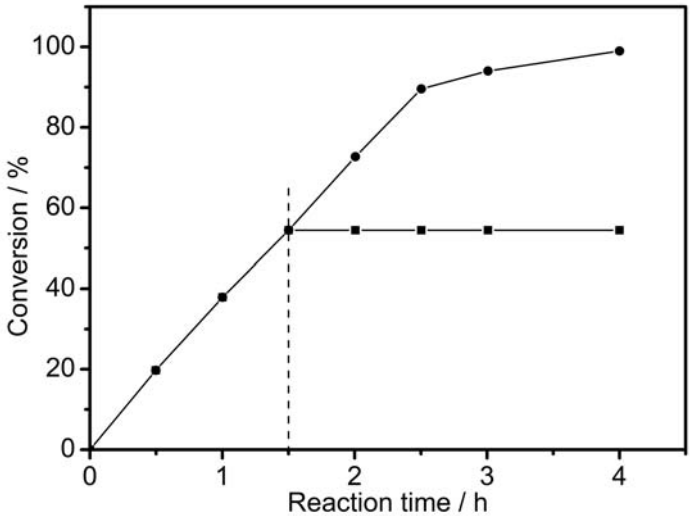


Fig.S20 Residual activity after filtration for LA hydrogenation over 9.93 wt.% CuB_{23}/graphene after 1.5 h reaction (■) versus standard catalyst run (●). Reaction conditions: Catalyst containing 2.54 mg Cu, 20 mmol LA, 50mL of n-dodecane, PH_2 = 4.2 MPa H_2, T = 413 K, Reaction time = 4 h, stirring rate = 1100 rpm.

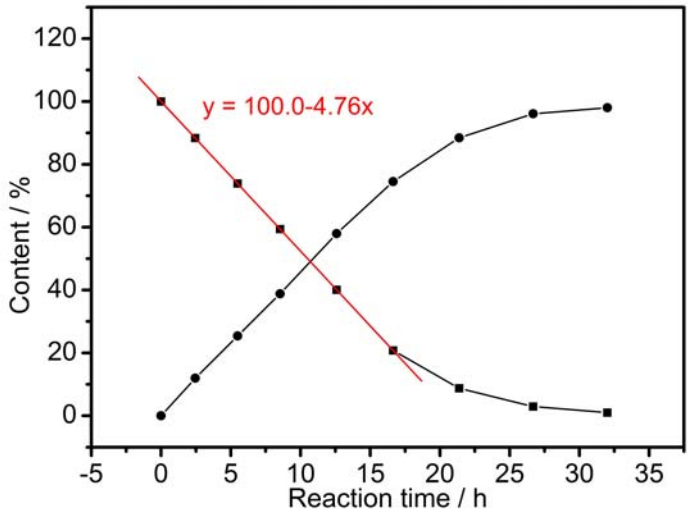


Fig.S21 Reaction profiles of LA (■) hydrogenation to GAL (●) over CuB_{23}. Reaction conditions: Catalyst containing 2.54 mg Cu, 20 mmol LA, 50mL of n-dodecane, PH_2 = 4.2MPa H_2, T = 413 K, stirring rate = 1100 rpm.

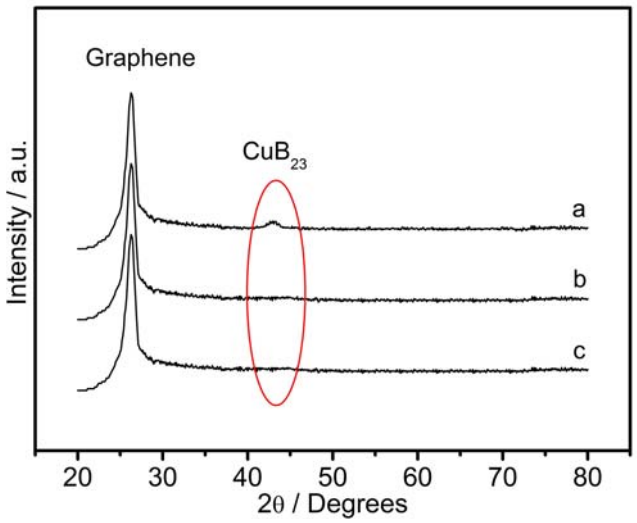


Fig.S22 XRD patterns of (a) 9.93wt.% CuB_{23}/graphene after heat-treated at 673 K under Argon; (b) fresh 9.93wt.% CuB_{23}/graphene; (c) 9.93wt.% CuB_{23}/graphene after 7 cycles. Reaction conditions: Catalyst containing 2.54 mg Cu, 20 mmol LA, 50mL of n-dodecane, PH_2 = 4.2MPa H_2, T = 413K, stirring rate = 1100 rpm.

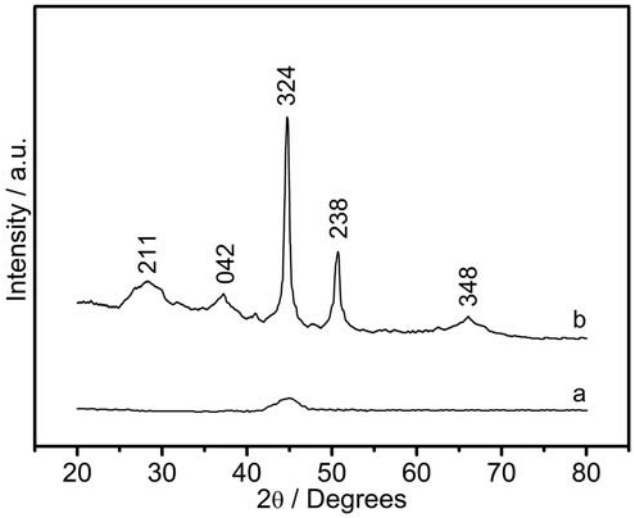
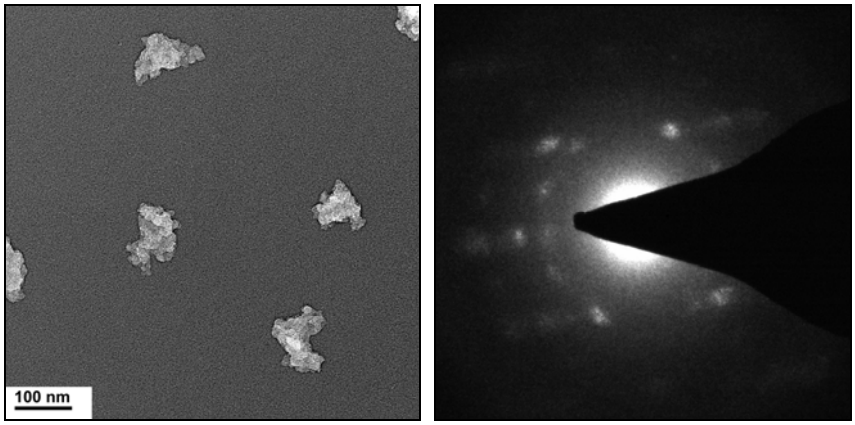
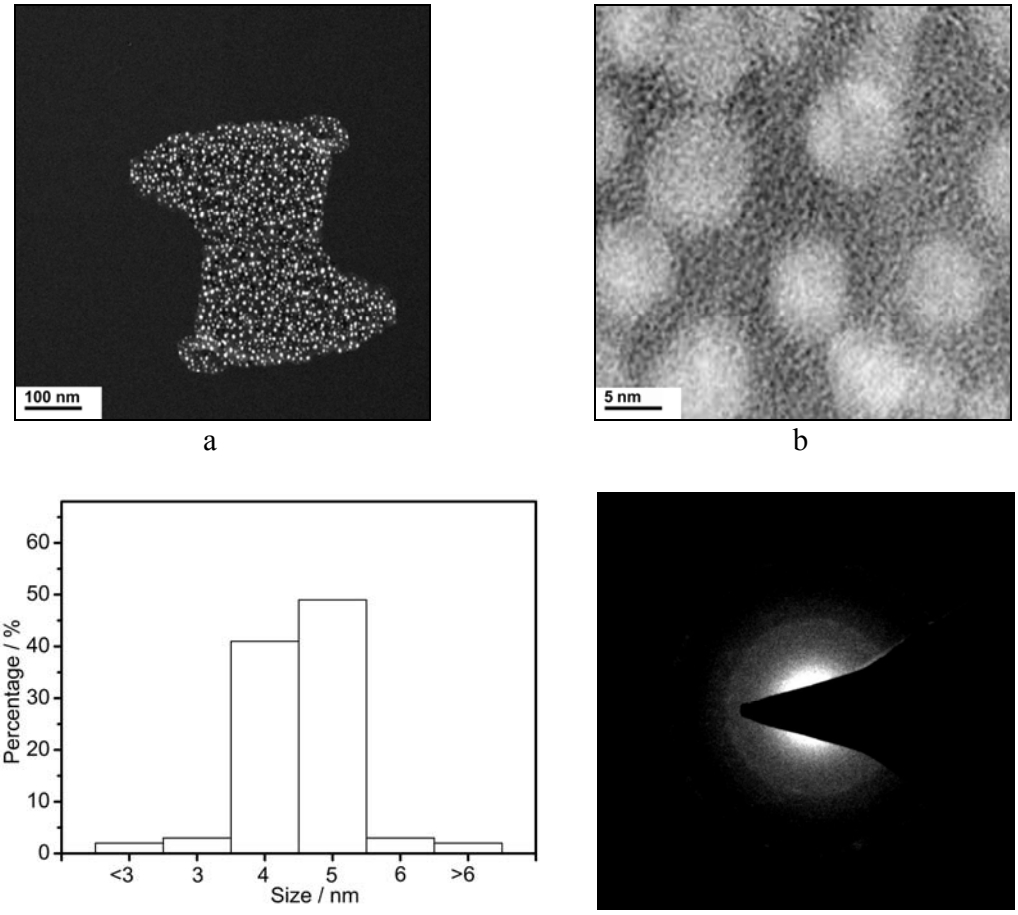


Fig.S23 XRD patterns of (a) fresh CuB_{23} and (b) CuB_{23} after 3 cycles during LA hydrogenation. Reaction conditions: Catalyst containing 2.54 mg Cu, 20 mmol LA, 50 mL of n-dodecane, PH_2 = 4.2 MPa H_2, T = 413 K, stirring rate = 1100 rpm.



a b

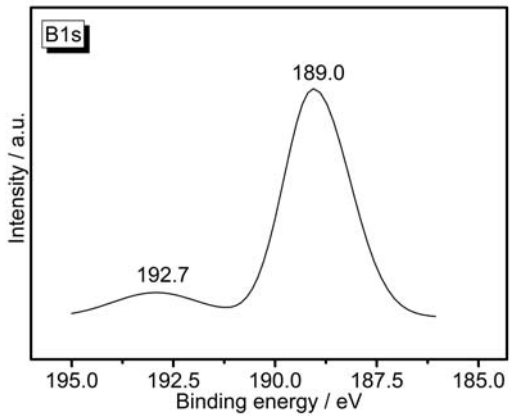
Fig.S24 (a) Low magnification STEM image and (b) SAED pattern of of CuB_{23} after 3 cycles. Reaction conditions: Catalyst containing 2.54 mg Cu, 20 mmol LA, 50mL of n-dodecane, PH_2 = 4.2MPa H_2, T = 413 K, stirring rate = 1100 rpm.



a b

c d

Fig.S25 (a) Low magnification STEM image；(b) High magnification STEM image; (c) Particle size distribution histograms; and (d) SAED pattern of the as-prepared 9.93 wt.% CuB_{23}/graphene after 7 cycles. Reaction conditions: Catalyst containing 2.54 mg Cu, 20 mmol LA, 50mL of n-dodecane, PH_2 = 4.2MPa H_2, T = 413 K, stirring rate = 1100 rpm.



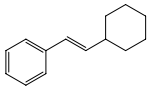
c

Fig.S26 B1s XPS spectra of the as-prepared 9.93 wt.% CuB_{23}/graphene after 7 cycles. Reaction conditions: Catalyst containing 2.54 mg Cu, 20 mmol LA, 50 mL of n-dodecane, PH_2 = 4.2 MPa H_2, T = 413 K, stirring rate = 1100 rpm.

Analytical data for Heck-coupling products

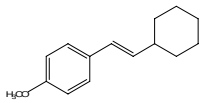
A. In Table 1 – entries 1-10:

1. Entries 1-5

(*E*)-(2-cyclohexylvinyl)benzene: [1] 

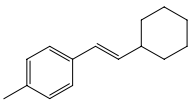
Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40-7.23 (m, 5H), 6.39 (d, J = 12.0 Hz, 1H), 5.55-5.46 (m, 1H), 2.59-2.44 (m, 1H), 1.40-1.14 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.4, 128.6, 127.4, 126.9, 126.1, 41.3, 33.1, 29.8, 26.3, 26.2. HRMS calculated for $[C_{14}H_{18}]^{+}$: 186.30, found: 186.28.

2. Entry 6

(E)-1-(2-cyclohexylvinyl)-4-methoxybenzene: [2] 

Colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.27 (dt, J = 8.4, 2.2 Hz, 2H), 6.82 (dt, J= 8.4, 2.2 Hz, 2H), 6.37 (d, *J* =16.0 Hz, 1H), 6.02 (dd, J = 16.0, 6.8 Hz, 1H), 3.78 (s, 3H), 2.13-2.04 (m, 1H), 1.80-1.60 (m, 5H), 1.43-1.20 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.7, 134.8, 131.0, 127.0, 126.6, 113.9, 55.2, 41.0, 33.0, 26.1, 26.0; HRMS calculated for $[C_{15}H_{20}O+H]^{+}$: 217.15, found: 217.18.

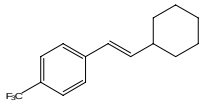
3. Entry 7

(E)-1-(2-cyclohexylvinyl)-4-methylbenzene: [3] 

Pale orange oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.24 (d, *J* = 8.1 Hz, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 6.31 (d, *J* = 15.9 Hz, 1H), 6.12 (dd, *J* = 15.9 Hz, 6.9Hz, 1H), 2.32 (s, 3H), 2.00–2.16 (m, 1H), 1.09–1.84 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.5, 136.0,

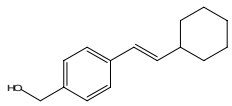
135.4, 129.2, 127.1, 125.9, 41.1, 33.0, 26.1, 25.0, 21.0. HRMS calculated for $[C_{15}H_{20}]^+$: 216.15, found: 216.12.

4. Entry 8

(E)-1-(2-cyclohexylvinyl)-4-(trifluoromethyl)-benzene: [4] 

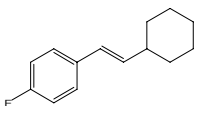
White crystals. ^{1}H NMR (400 MHz , $CDCl_3$): δ 7.61 (d, J = 8.3 Hz, 0.12 H), 7.56 (d, *J* = 8.1 Hz, 2 H), 7.45(d, J = 8.1 Hz, 2 H), 7.37 (d, J = 8.1 Hz, 0.12 H), 6.40 (d, J = 16.0 Hz, 1 H), 6.30 (dd, J = 6.6,16.0 Hz, 1 H), 5.62 (t, J = 11.0 Hz, 0.06 H), 2.61 - 2.49 (m, 0.06 H), 2.25 - 2.11 (m, 1 H), 1.91 -1.67 (m, 5 H), 1.44 - 1.15 (m, 5 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.57, 139.61, 128.6, 126.12, 126.05, 125.4, 124.3, 41.2, 32.8, 26.1, 26.0; LRMS calculated for $[C_{15}H_{17}F_3]^+$: 254.13, found: 254.20.

5. Entry 9

(E)-(4-(2-cyclohexylvinyl)phenyl)methanol: [3] 

colorless oil. ^{1}H NMR (400 MHz , $CDCl_3$): 7.36 (d, *J* = 7.8 Hz, 2 H), 7.30 (d, *J* = 8.4 Hz, 2 H), 6.36 (d, *J* = 16.2 Hz, 1 H), 6.20 (dd, *J* = 10.4 Hz, *J* = 7.2 Hz, 1 H), 4.68 (s, 2 H), 2.15 (m, 1 H), 2.14 (m, 1 H), 1.79 (m, 4 H), 1.70 (m, 1 H), 1.37 – 1.30 (m, 2 H), 1.25 – 1.16 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ139.3, 137.6, 137.0, 127.2, 126.8, 126.1, 65.2, 41.1, 32.9, 26.1, 26.0; LRMS (ESI) calculated for $[C_{15}H_{20}ONa]^+$: 239.14, found 239.16.

6. Entry 10

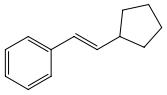
1-(2-cyclohexylvinyl)-4-fluorobenzene: [5] 

Colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ7.24 - 7.32 (m, 2H), 6.90 - 7.05 (m, 2H),

6.30 (d, J=16 Hz, 1H), 6.07 (dd, J=16, 6.8 Hz, 1H), 2.07 - 2.19 (m, 1 H), 1.60 - 1.90 (m, 5H),1.06 - 1.43 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ164.4, 159.5, 136.7, 136.6, 134.3, 134.2, 127.5, 127.3, 126.2, 115.5, 115.1, 41.0, 32.9, 26.1, 26.0; HRMS calculated for $[C_{14}H_{17}F]^+$: 204.13; found: 204.13.

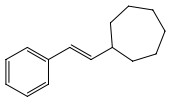
B. In Table 2 – entries 1-4:

1. Entry 1

(2-cyclopentylvinyl)benzene: [5] 

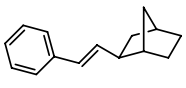
Colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.13 - 7.37 (m, 5H), 6.37 (d, J=16 Hz, 1H), 6.20 (dd, J=16, 7.6 Hz, 1H), 2.50 - 2.69 (m, 1 H), 1.30 - 1.93 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.0, 135.8, 128.5, 127.9, 126.8, 126.0, 43.8, 33.2, 25.2; HRMS calculated for $C_{13}H_{16}$: 172.27; found: 172.32.

2. Entry 2

(E)-(2-cycloheptylvinyl)benzene: [5] 

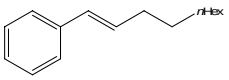
Colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.12 - 7.40 (m, 5H), 6.32 (d, J=15.8 Hz, 1H), 6.19 (dd, J= 6.6,15.8 Hz, 1H), 2.21 ± 2.37 (m, 1 H), 1.33-1.88 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$): δ138.2, 137.7, 128.5, 126.7, 126.3, 126.0, 43.2, 34.7, 28.3, 26.2; HRMS calculated for $C_{15}H_{20}$: 200.32; found: 200.35.

3. Entry 3

(exo)-2-(styryl)bicycle[2.2.1]heptane: [6] 

Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45-7.34 (m, 4H), 7.30-7.24 (m, 1H), 6.40 (d, *J* = 16.0Hz, 1H), 6.22 (dd, *J* = 8.0, 16.0Hz, 1H), 2.40-2.33 (m, 2H), 2.25-2.22 (m,1H), 1.70-1.24 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.9, 136.3, 128.4, 127.2, 126.6, 125.9, 45.4, 42.7, 37.9, 36.6, 35.8, 29.7, 29.0; HRMS calculated for $C_{15}H_{18}$: 198.31, found: 198.24.

4. Entry 4

(E)-dec-1-en-1-ylbenzene: [7] 

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.39 (m, 2H), 7.27-7.34 (m, 2H), 7.18-7.24 (m, 1H), 6.40 (d, *J* = 15.8 Hz, 1H), 6.25 (dt, *J* = 7.2, 15.8 Hz, 1H), 2.23 (qd, *J* = 1.6, 6.8Hz, 2H), 1.44-1.53 (m, 2H), 1.25-1.42 (m, 10H), 0.91 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.0, 131.3, 129.7, 128.5, 126.7, 125.9, 33.1, 31.9, 29.5, 29.4, 29.3, 29.2, 22.7, 14.1; HRMS calculated for $C_{16}H_{24}$: 216.37, found 216.29.

Reference

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[3] K. S. Bloome, R. L. McMahen and E. J. Alexanian, *J. Am. Chem. Soc.* 2011, **133**, 20146.

[4] C. M. McMahon and E. J. Alexanian, *Angew. Chem. Int. Ed.*, 2014, **53**, 5974.

[5] Y.-J. Jang, Y.-K. Shih, J.-Y. Liu, W.-Y. Kuo and C.-F. Yao, *Chem. Eur. J.*, 2003, **9**, 2123.

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[7] P. Andrews, C. M. Latham, M. Magre, D. Willcox and S. Woodward, *Chem. Commun.*, 2013, **49**, 1488.