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

<table>
<thead>
<tr>
<th>Samples</th>
<th>Cu-loading/wt.%</th>
<th>Compositions/at.%</th>
<th>S_{BET}/m^{2}g^{-1}</th>
<th>Average particle sizes/nm</th>
<th>S_{Cu}/m^{2}g^{-1}</th>
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<tbody>
<tr>
<td>CuB_{23}</td>
<td>-</td>
<td>CuB_{22.99}</td>
<td>28.2</td>
<td>30</td>
<td>15.9</td>
</tr>
<tr>
<td>Graphene</td>
<td>-</td>
<td>-</td>
<td>229.5</td>
<td>-</td>
<td>-</td>
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<tr>
<td>3.54 wt.% CuB_{23}/graphene</td>
<td>0.73 wt.%</td>
<td>CuB_{23.00}</td>
<td>156.7</td>
<td>2.3</td>
<td>46.2</td>
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<tr>
<td>6.67 wt.% CuB_{23}/graphene</td>
<td>1.36 wt.%</td>
<td>CuB_{22.98}</td>
<td>133.2</td>
<td>3.4</td>
<td>60.1</td>
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<tr>
<td>9.93 wt.% CuB_{23}/graphene</td>
<td>2.02 wt.%</td>
<td>CuB_{23.01}</td>
<td>125.4</td>
<td>4.8</td>
<td>67.9</td>
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<td>13.62 wt.% CuB_{23}/graphene</td>
<td>2.77 wt.%</td>
<td>CuB_{23.00}</td>
<td>104.5</td>
<td>6.7</td>
<td>59.4</td>
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<tr>
<td>20.58 wt.% CuB_{23}/graphene</td>
<td>4.13 wt.%</td>
<td>CuB_{23.01}</td>
<td>86.2</td>
<td>9.9</td>
<td>48.6</td>
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<td>9.93 wt.% CuB_{23}/C</td>
<td>2.02 wt.%</td>
<td>CuB_{23.01}</td>
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<td>5.0</td>
<td>50.2</td>
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<td>-</td>
<td>160.4</td>
<td>5.1</td>
<td>45.4</td>
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<tr>
<td>2.02 wt.% Cu/C</td>
<td>2.02 wt.%</td>
<td>-</td>
<td>172.5</td>
<td>5.2</td>
<td>40.9</td>
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**Table S2** Hydrogenation of LA to GAL over 9.93 wt.% CuB$_{23}$/graphene with different solvents.$^a$

<table>
<thead>
<tr>
<th>Solvents</th>
<th>Conversion / %</th>
<th>Yield / %</th>
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<tr>
<td>No solvent</td>
<td>82</td>
<td>76</td>
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<tr>
<td>n-dodecane</td>
<td>100</td>
<td>99</td>
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<tr>
<td>Toluene</td>
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<tr>
<td>CH$_3$OH</td>
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<td>H$_2$O</td>
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<td>5</td>
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<tr>
<td>1,4-Dioxane</td>
<td>23</td>
<td>16</td>
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</table>

$^a$ 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.
**Fig.S1** STEM images of (a) Graphene and (b) CuB$_{23}$.

**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.
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\textsubscript{23}/graphene, (b) 6.67 wt.% CuB\textsubscript{23}/graphene, (c) 9.93 wt.% CuB\textsubscript{23}/graphene, (d) 13.62 wt.% CuB\textsubscript{23}/graphene, (e) 20.58 wt.% CuB\textsubscript{23}/graphene and (f) CuB\textsubscript{23}.

Fig. S11 The typical Cu\textsubscript{2p\textsubscript{3/2}} XPS spectra of 2.02 wt.% Cu/graphene, 2.02 wt.% Cu/C and 9.93 wt.% CuB\textsubscript{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\textsubscript{23}/graphene. Cu/Graphene and Cu/C prepared by reduction with N\textsubscript{2}H\textsubscript{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) NH₃ (gas), (c) NH₃·H₂O (5 wt%), (d) Cu(NO₃)₂ solution (5.5 mM) and (e) Cu(NH₃)₄²⁺ (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$_2$CO$_3$ (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_{2}CO_{3} (7.5 mmol), DMF (10 mL), T = 353 K, stirring rate = 800 rpm.
**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, cyclohexyl iodide (5.0 mmol), styrene (6.0 mmol), Na_{2}CO_{3} (7.5 mmol), DMF (10 mL), T = 353 K, stirring rate = 800 rpm.
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$_2$CO$_3$ (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.% CuB23/graphene after 5 cycles. Reaction conditions: a catalyst containing 6.35 mg Cu, cyclohexyliodide (5.0 mmol), styrene (6.0 mmol), Na2CO3 (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\textsubscript{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\textsubscript{2} = 4.2 MPa H\textsubscript{2}, T = 413 K, Reaction time = 4 h, stirring rate = 1100 rpm.

Fig.S21 Reaction profiles of LA (■) hydrogenation to GAL (●) over CuB\textsubscript{23}. Reaction conditions: Catalyst containing 2.54 mg Cu, 20 mmol LA, 50mL of n-dodecane, PH\textsubscript{2} = 4.2MPa H\textsubscript{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.
Fig. S24 (a) Low magnification STEM image and (b) SAED pattern 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.
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.
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

\((E)-(2\text{-cyclohexylvinyl})\text{ benzene}\):\(^{[1]}\)

Yellow oil. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\ 7.40-7.23\ (m, \ 5H), 6.39\ (d, \ J = 12.0\ Hz, \ 1H), 5.55-5.46\ (m, \ 1H), 2.59-2.44\ (m, \ 1H), 1.40-1.14\ (m, \ 10H)\); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\ 137.4, 128.6, 127.4, 126.9, 126.1, 41.3, 33.1, 29.8, 26.3, 26.2\). HRMS calculated for \([C_{14}H_{18}]^+\): 186.30, found: 186.28.

2. Entry 6

\((E)-1-(2\text{-cyclohexylvinyl})-4\text{-methoxybenzene}\):\(^{[2]}\)

Colorless oil. \(^1\)H NMR (200 MHz, CDCl\(_3\)): \(\delta\ 7.27\ (dt, \ J = 8.4, 2.2\ Hz, \ 2H), 6.82\ (dt, \ J = 8.4, 2.2\ Hz, \ 2H), 6.37\ (d, \ J = 16.0\ Hz, \ 1H), 6.02\ (dd, \ J = 16.0, 6.8\ Hz, \ 1H), 3.78\ (s, \ 3H), 2.13-2.04\ (m, \ 1H), 1.80-1.60\ (m, \ 5H), 1.43-1.20\ (m, \ 5H)\); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\ 158.7, 134.8, 131.0, 127.0, 126.6, 113.9, 55.2, 41.0, 33.0, 26.1, 26.0\); HRMS calculated for \([C_{15}H_{20}O+H]^+\): 217.15, found: 217.18.

3. Entry 7

\((E)-1-(2\text{-cyclohexylvinyl})-4\text{-methylbenzene}\):\(^{[3]}\)

Pale orange oil. \(^1\)H NMR (200 MHz, CDCl\(_3\)): \(\delta\ 7.24\ (d, \ J = 8.1\ Hz, \ 2H), 7.09\ (d, \ J = 8.1\ Hz, \ 2H), 6.31\ (d, \ J = 15.9\ Hz, \ 1H), 6.12\ (dd, \ J = 15.9\ Hz, 6.9Hz, \ 1H), 2.32\ (s, \ 3H), 2.00-2.16\ (m, \ 1H), 1.09-1.84\ (m, \ 10H)\); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\ 136.5, 136.0,
4. Entry 8

(E)-1-(2-cyclohexylvinyl)-4-(trifluoromethyl)-benzene: \(^{[4]}\)

White crystals. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 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\(_3\)): \(\delta\) 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\(_3\)): \(\delta\) 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\(_3\)): \(\delta\) 139.3, 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\(_3\)): \(\delta\) 7.24 - 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$_3$): $\delta$ 164.4, 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: Colorless oil. $^1$H NMR (200 MHz, CDCl$_3$): $\delta$ 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$_3$): $\delta$ 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: Colorless oil. $^1$H NMR (200 MHz, CDCl$_3$): $\delta$ 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$_3$): $\delta$ 138.2, 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: Colorless oil. $^1$H NMR (200 MHz, CDCl$_3$): $\delta$ 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$_3$): $\delta$ 138.2, 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.
Colorless oil. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.45-7.34 (m, 4H), 7.30-7.24 (m, 1H), 6.40 (d, $J = 16.0$ Hz, 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$_3$): $\delta$ 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:

Pale yellow oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 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$_3$): $\delta$ 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
