# Supporting Information for:

# Polyhedral $Cu_2O$ Particles: Shape Evolution and Catalytic Activity on Cross-coupling Reaction of Iodobenzene and Phenol

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**Experiment Section:**

**Table S1:** Detailed experimental conditions for scale-up preparing cube, octahedron, 18-facet polyhedron and sR, small 50-facet $Cu_2O$ polyhedron.

| $Cu_2O$ particles | Concentration of NaOH (mol/L) | Volume of ethanol added (ml) | Reaction duration time (min) |
|---|---|---|---|
| Cube | 0.05 | 0 | 40-60 |
| 18-facet polyhedron | 0.75 | 0 | 10-15 |
| sR | 0.85 | 0 | 10-15 |
| Small 50-facet polyhedron | 1.5 | 0 | 10-15 |
| Octahedron | 1 | 20 | 10-15 |

*Generally, 0.6 g $Cu(CH_3COO)_2{\cdot}H_2O$ (~ 3 mmol) and 60 ml solvent (either pure water or a mixture consisted of 20 ml ethanol and 40 ml pure water) were added to a 250 ml flask also kept in a thermostat water bath at 60 ℃. The volume of added NaOH aqueous solution with different concentrations shown in this table is 10 ml. The added volume of 0.25 mol/L Vc (~0.44 g) aqueous solution was 10 ml. The reactions were undertaken for the time durations shown in above table.

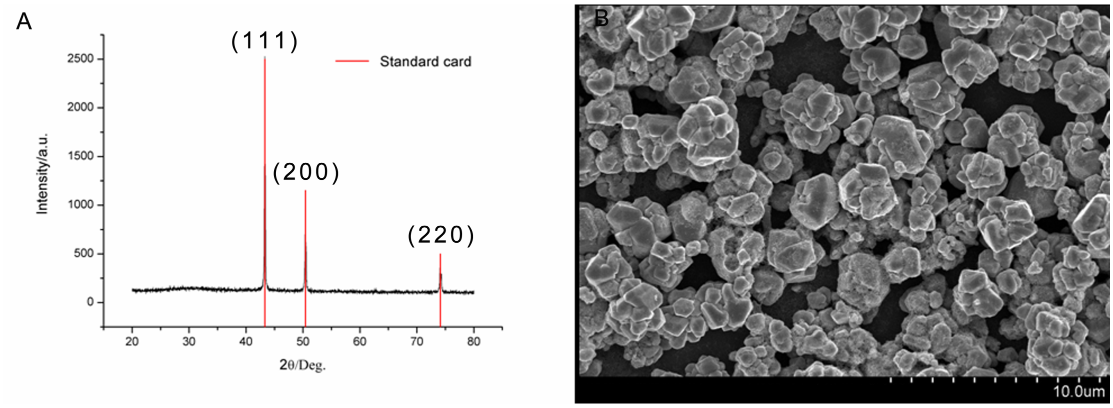


**Figure S1.** XRD (A) and SEM (B) image of Cu obtained when the concentration of NaOH is 0 M.

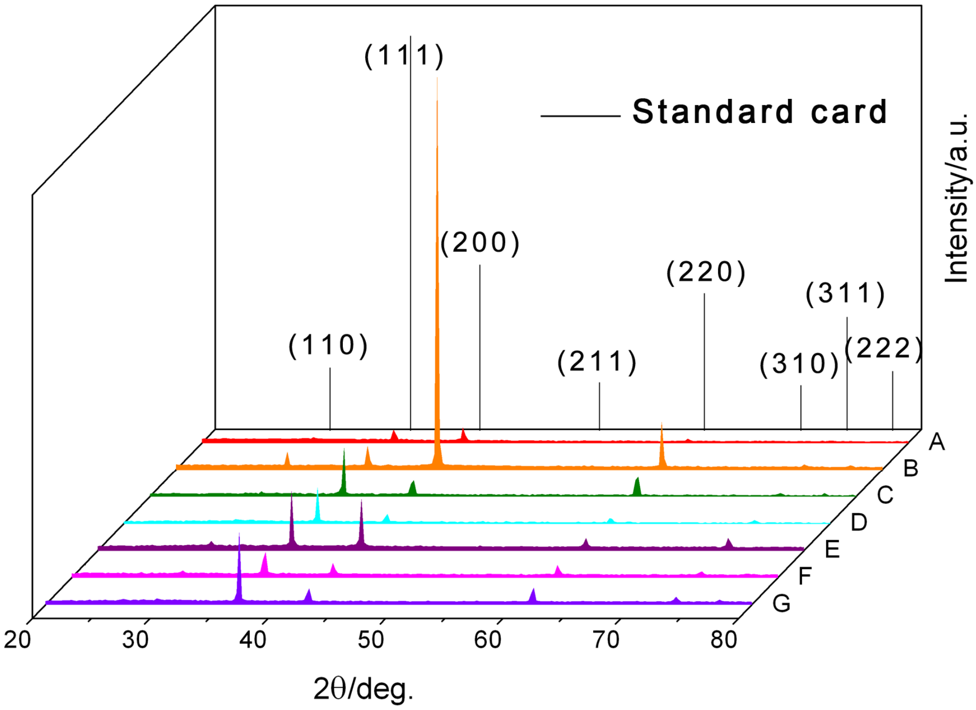


**Figure S2.** XRD patterns of the as-prepared $Cu_2O$ particles and the standard card of cuprous oxide cubic phase. (A) cubes, (B) 18-facet polyhedra, (C) beveled cubes, (D) sR, (E) 50-facet polyhedra, (F) bevelled octahedra, (G) truncated octahedra.

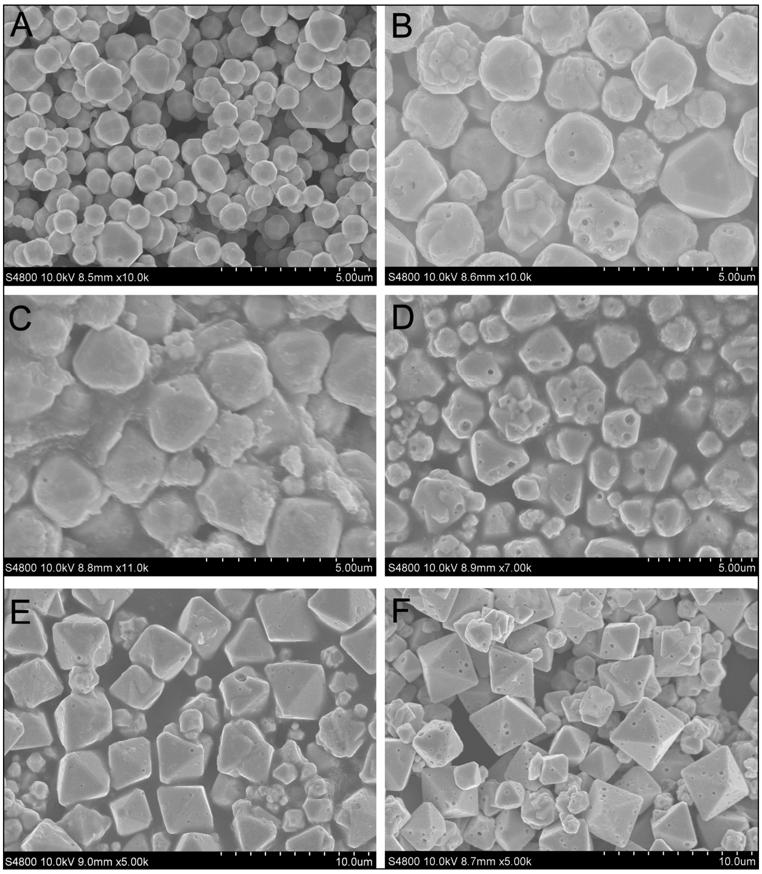


**Figure S3.** FESEM images of $Cu_2O$ particles obtained with the volume of ethanol in the rang of 1.4 to 3.4 ml. (A) 1.4 ml, (B) 2.0 ml, (C) 2.5 ml, (D) 2.8 ml, (E) 3.0 ml, (F) 3.4 ml.

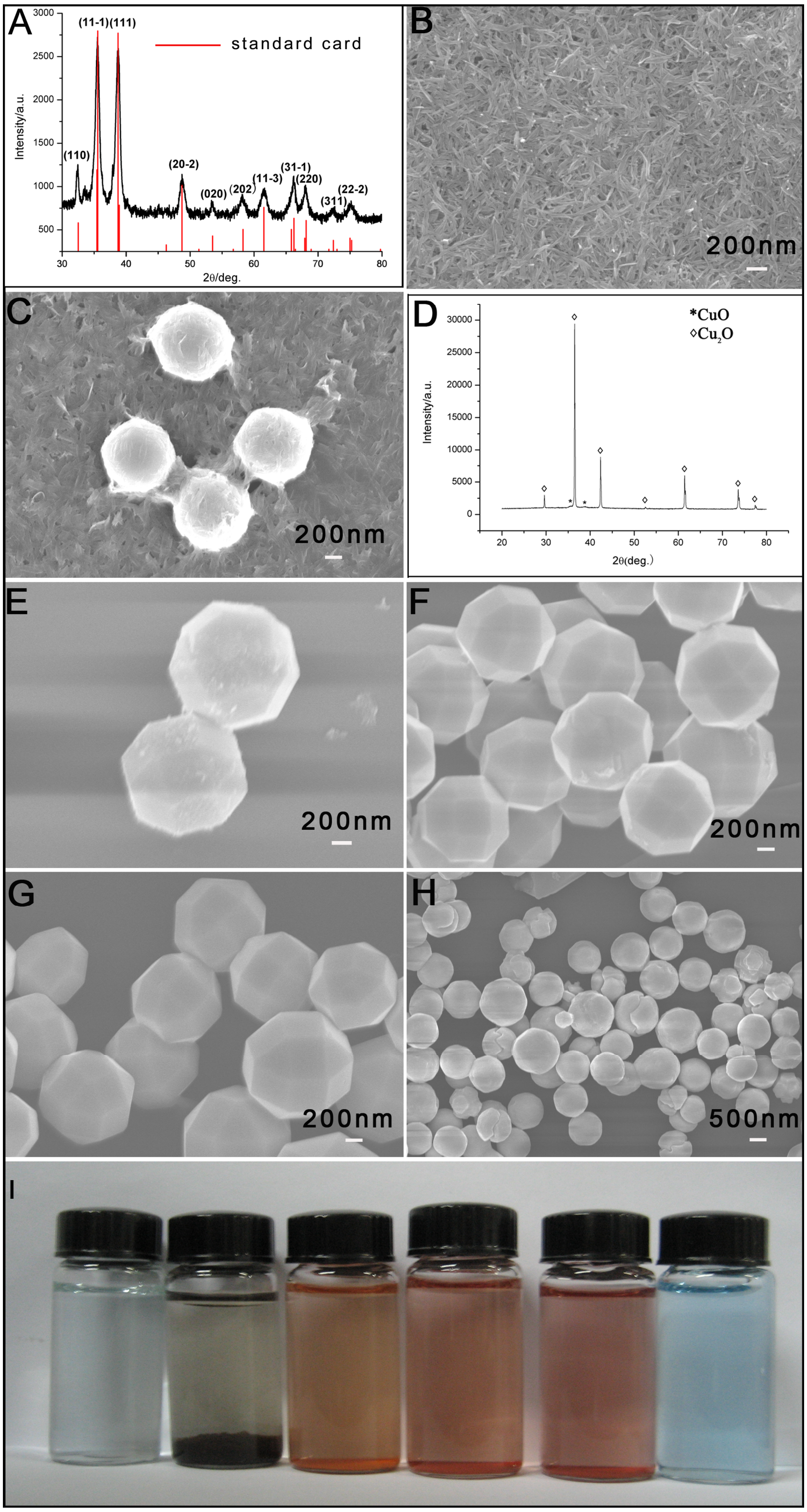


**Figure S4.** XRD patterns (A, D) of sample obtained at 0 min and 1 min respectively; FESEM images (B, C, E-F) and photographs (G) of intermediates at different interval during the growth process of sR: (B) 0 min, (C) 1 min, (E) 5 min, (F) 15 min, (G) 30 min, (H) 60 min, (I) the times from left to right is 0 min, 0 min, 1 min, 15 min, 30 min, 2.5 h..

**Table S2:** Area percentage of each exposed facet on different polyhedra.

| $C_{NaOH}$ ($mol \cdot L^{-1}$) | Polyhedron | Area percentage of each exposed facet (%) | | | |
|---|---|---|---|---|---|
| | | (100) | (110) | (111) | (311) |
| 0.05 | Cube | 100 | 0 | 0 | 0 |
| 0.6 | 18-facet[1] | 16.14 | 83.86 | 0 | 0 |
| 0.8 | Beveled Cube | 66.5 | 31.35 | 2.15 | 0 |
| 1.0 | SR | 27.95 | 55.91 | 16.14 | 0 |
| 1.5 | 50-facet | 14.67 | 39.14 | 11.30 | 34.89 |
| 1.8 | Beveled Octahedron | 12.75 | 54.11 | 33.14 | 0 |
| 2.0 | Truncated Octahedron[2] | 2.76 | 0 | 97.24 | 0 |

*1: Assuming all edges have unit length

2: Assuming the truncation degree of all vertices is 1/4

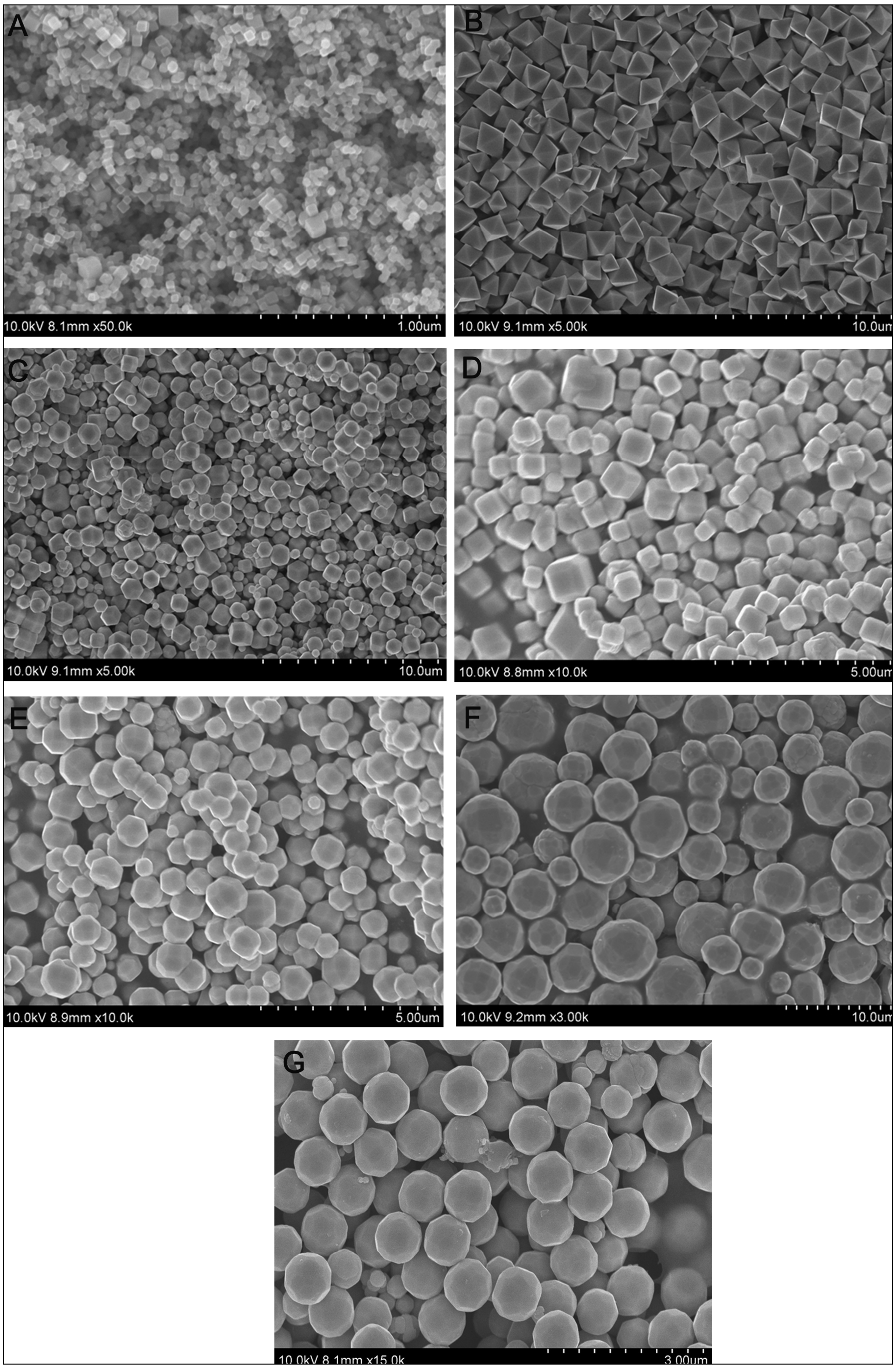


**Figure S5.** FESEM images of $Cu_2O$ products used as catalysts for the cross-coupling reaction of Iodobenzene and phenol. (A) cubes, (B) octahedra, (C) rhombic dodecahedra, (D) 18-facet polyhedra, (E) sR, (F) big 50-facet polyhedra, (G) small 50-facet polyhedra.


**Figure S6-1.** GC trace of iodobenzene in THF.

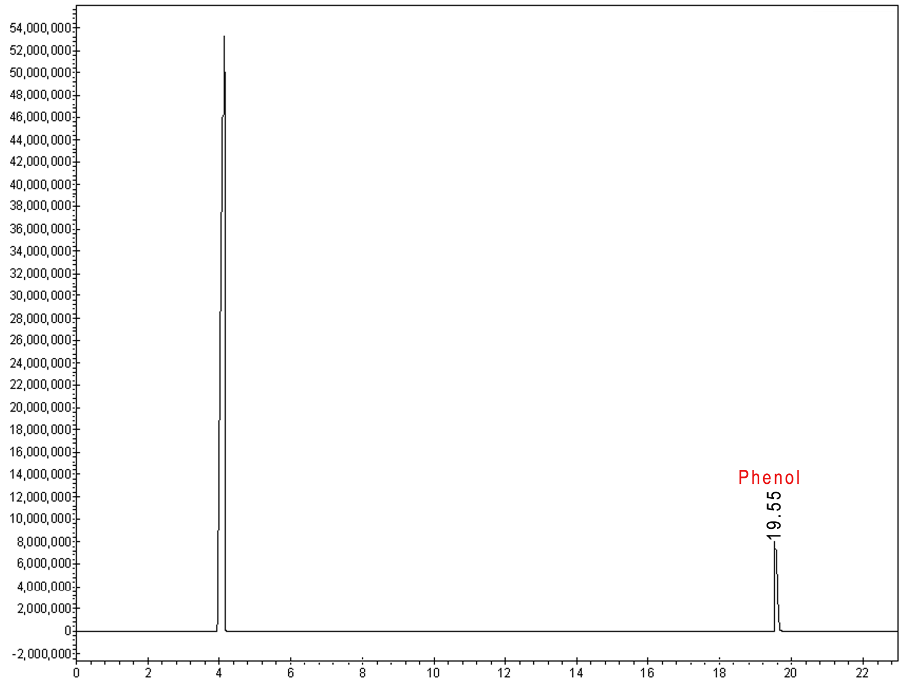


**Figure S6-2.** GC trace of phenol in THF.

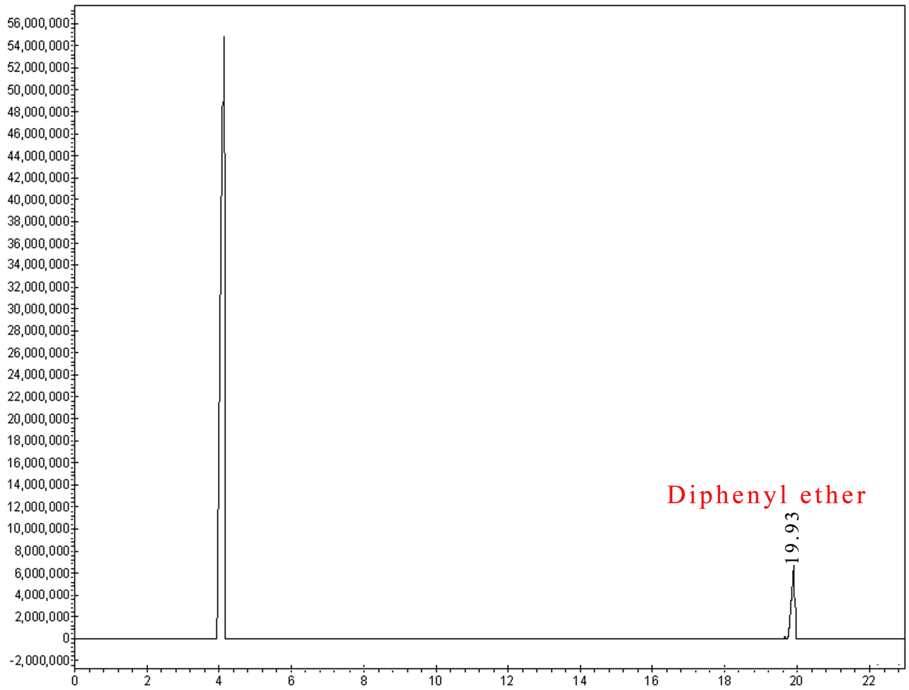


**Figure S6-3.** GC trace of diphenyl ether in THF.

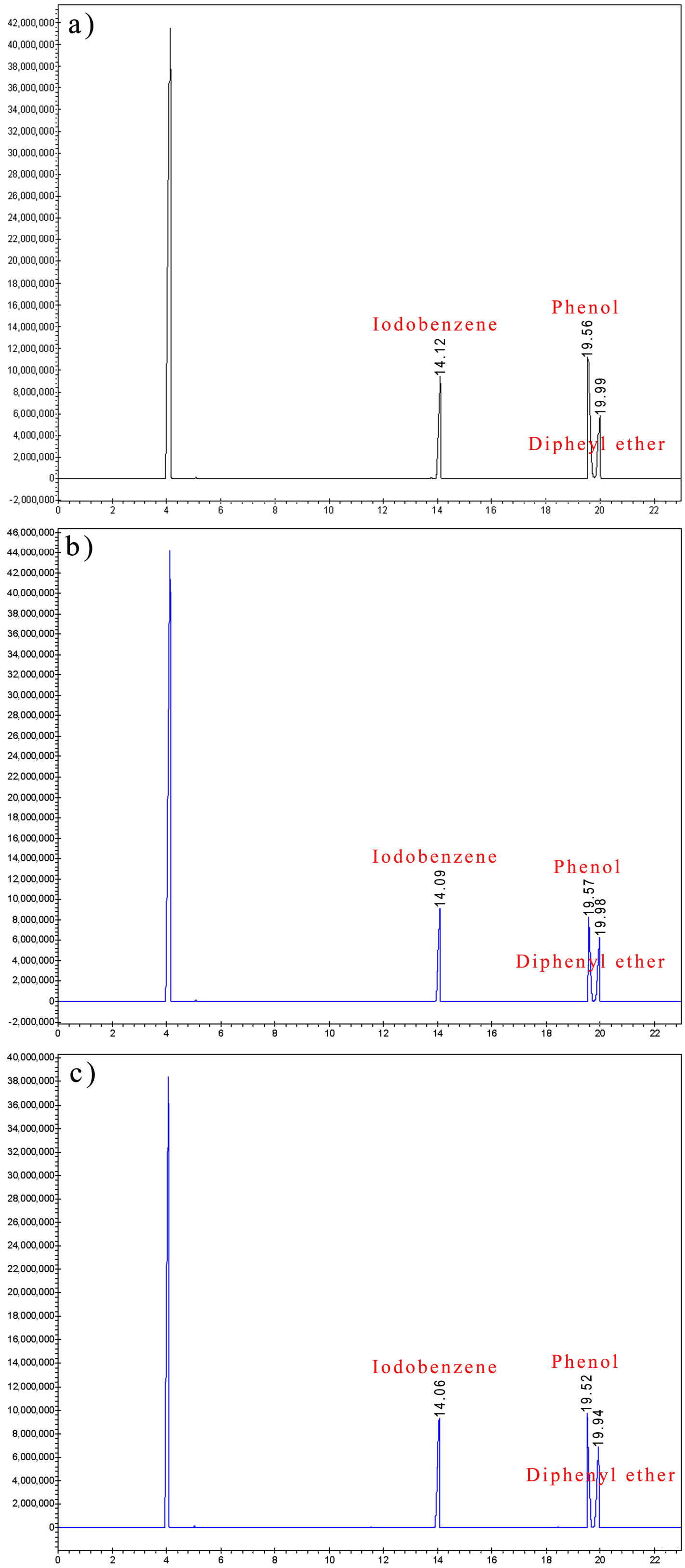


**Figure S6-4.** GC trace for the solution of reacting mixture collected at different reaction time when $Cu_2O$ big 50-facet polyhedra (SEM image in Figure S5F) were used as the catalyst for C-O coupling reaction at 150 ºC. Reaction times: a) 3 h; b) 6 h; c) 12 h. The yields of diphenyl ether for different time are shown in entry 12-14 in Table 1.

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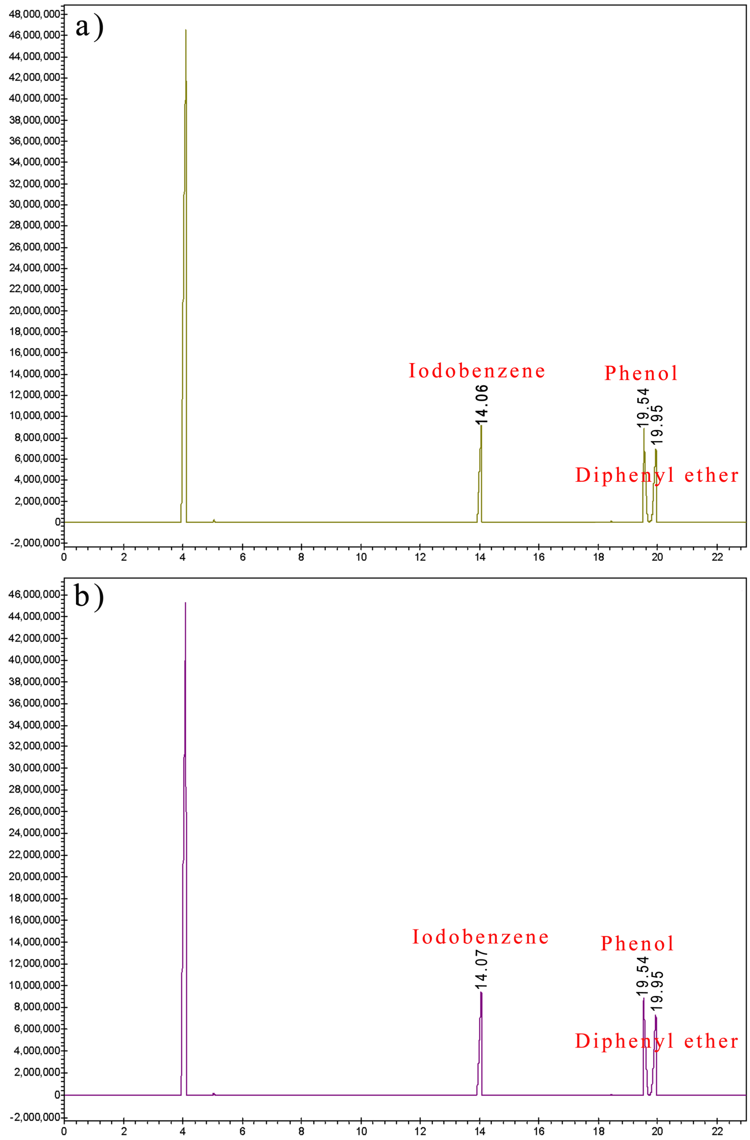


**Figure S6-5.** GC trace for the solution of reacting mixture collected at different reaction time when $Cu_2O$ cubes (SEM image in Figure S5A) were used as the catalyst for C-O coupling reaction at 150 ºC. Reaction times: a) 6 h; b) 12 h. The yields of diphenyl ether for different time are shown in entry 1-2 in Table 1.

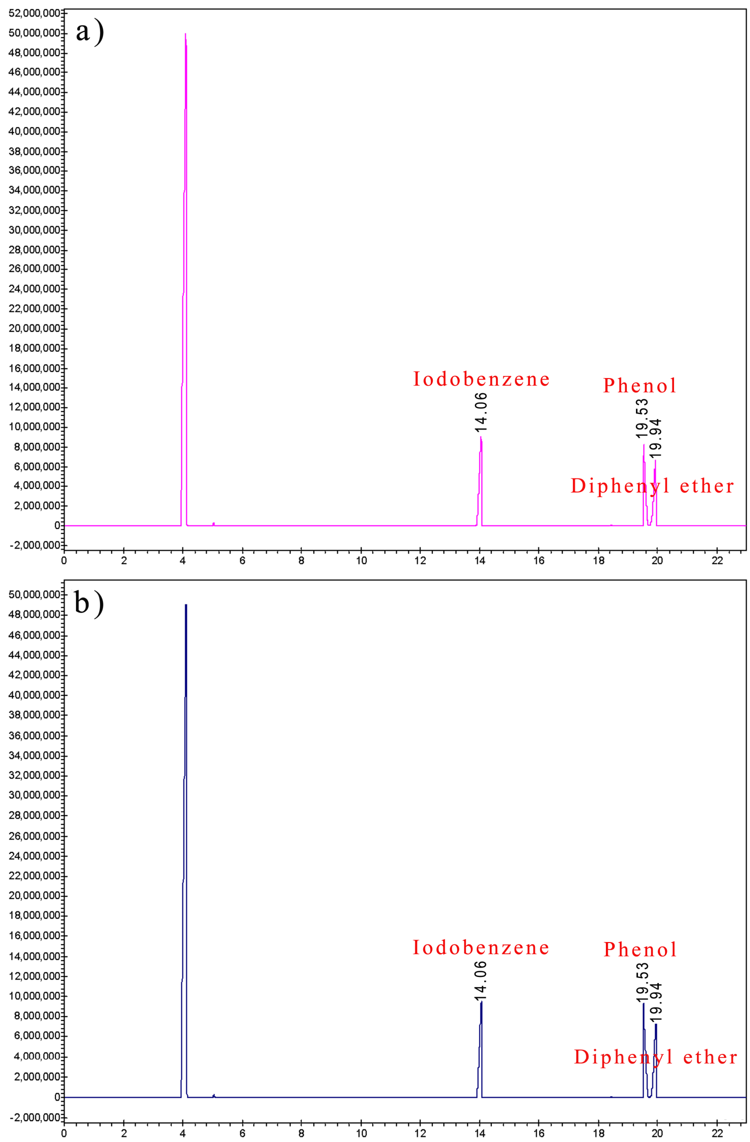


**Figure S6-6.** GC trace for the solution of reacting mixture collected at different reaction time when $Cu_2O$ octahedra (SEM image in Figure S5B) were used as the catalyst for C-O coupling reaction at 150 ºC. Reaction times: a) 6 h; b) 12 h. The yields of diphenyl ether for different time are shown in entry 3-4 in Table 1.

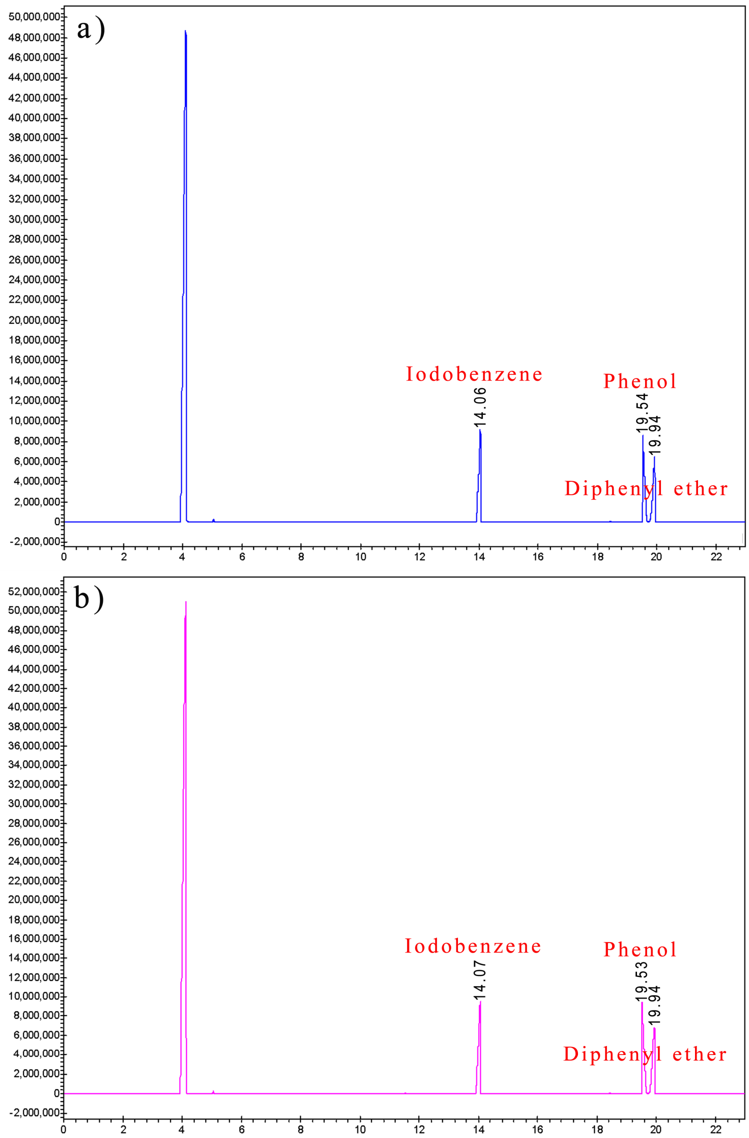


**Figure S6-7.** GC trace for the solution of reacting mixture collected at different reaction time when $Cu_2O$ rhombic dodecahedra (SEM image in Figure S5C) were used as the catalyst for C-O coupling reaction at 150 ºC. Reaction times: a) 6 h; b) 12 h. The yields of diphenyl ether for different time are shown in entry 5-6 in Table 1.

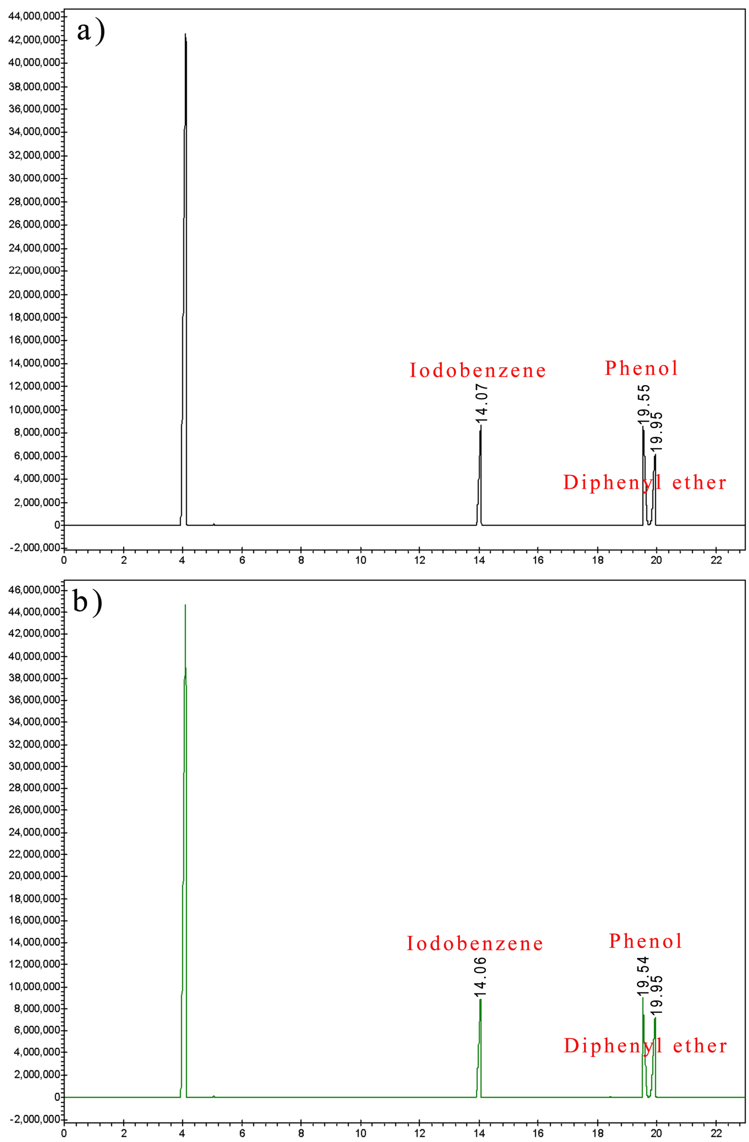


**Figure S6-8.** GC trace for the solution of reacting mixture collected at different reaction time when $Cu_2O$ 18-facet polyhedron (SEM image in Figure S5D) were used as the catalyst for C-O coupling reaction at 150 ºC. Reaction times: a) 6 h; b) 12 h. The yields of diphenyl ether for different time are shown in entry 8-9 in Table 1.

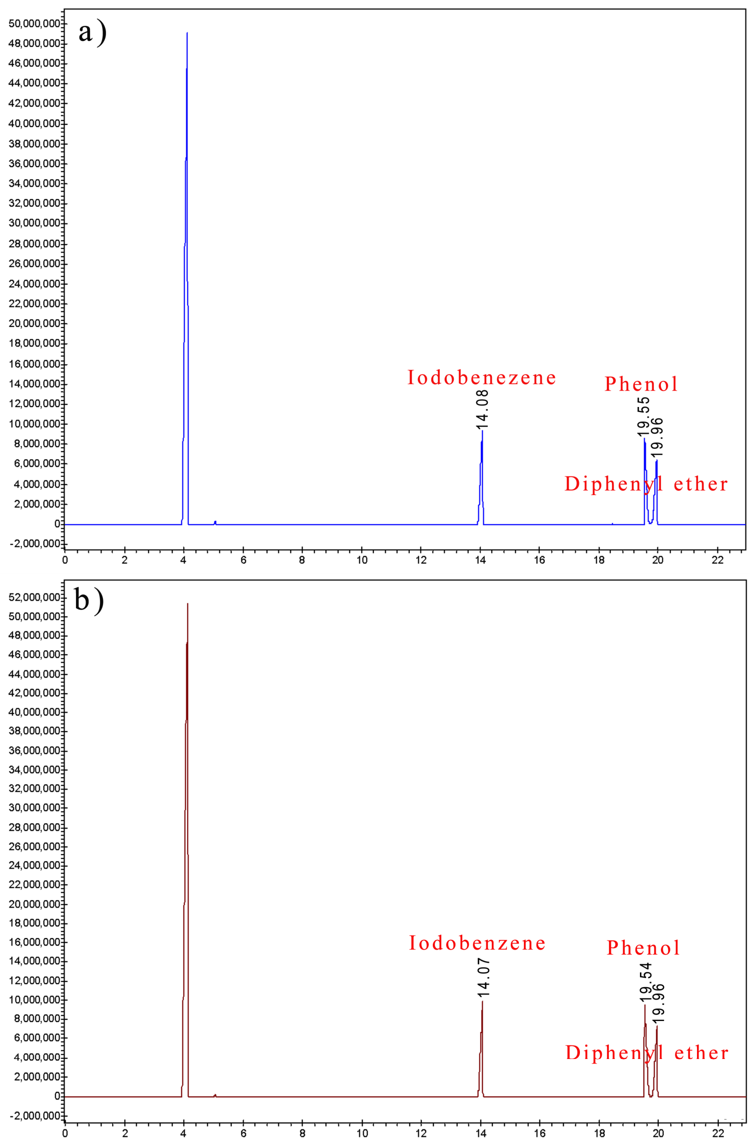


**Figure S6-9.** GC trace for the solution of reacting mixture collected at different reaction time when $Cu_2O$ sR (SEM image in Figure S5E) were used as the catalyst for C-O coupling reaction at 150 ºC. Reaction times: a) 6 h; b) 12 h. The yields of diphenyl ether for different time are shown in entry 10-11 in Table 1.

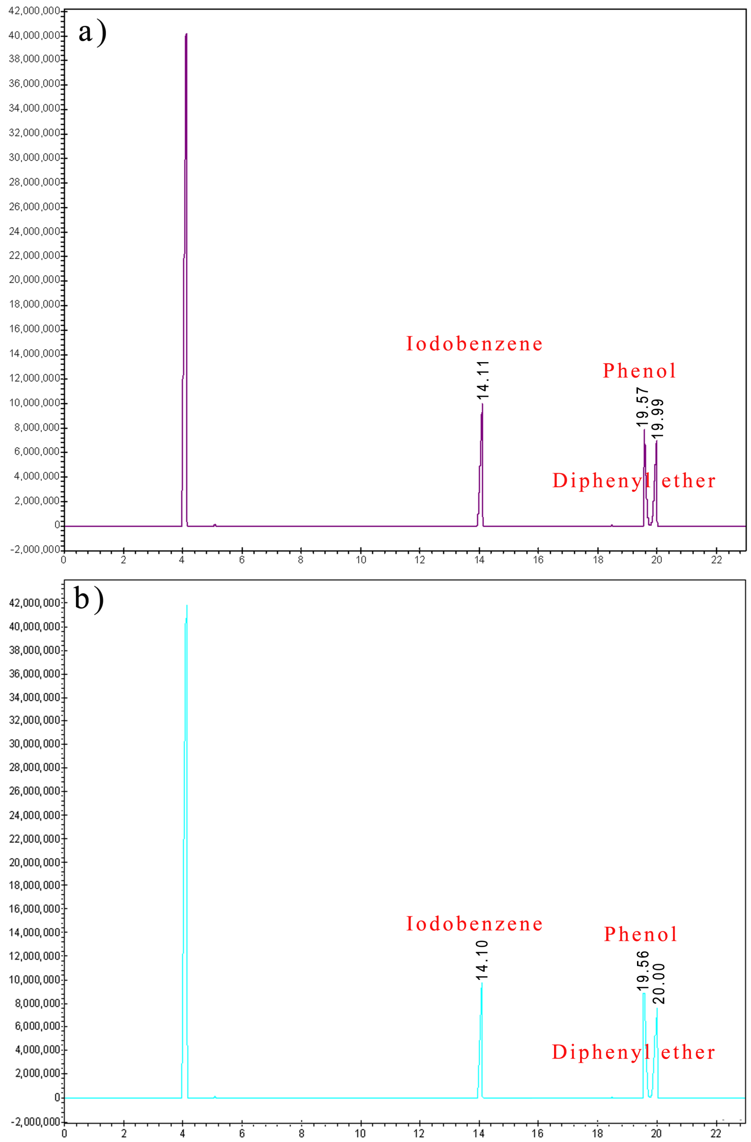


**Figure S6-10.** GC trace for the solution of reacting mixture collected at different reaction time when $Cu_2O$ small 50-facet polyhedron (SEM image in Figure S5G) were used as the catalyst for C-O coupling reaction at 150 ºC. Reaction times: a) 6 h; b) 12 h. The yields of diphenyl ether for different time are shown in entry16-17 in Table 1.

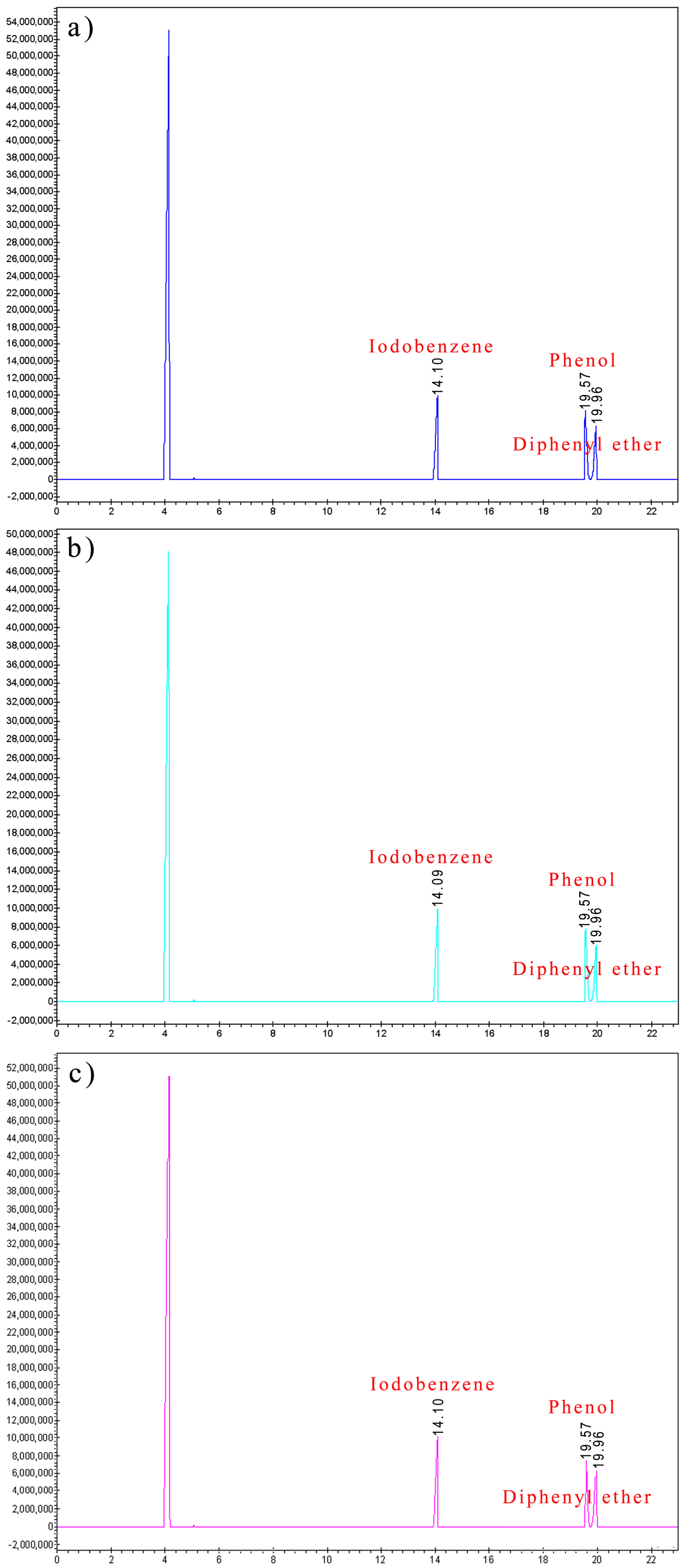


**Figure S6-11.** GC trace for the solution of reacting mixture collected at 12 h when different $Cu_2O$ particles (SEM images in Figure S5C, 5F and 5G) were used as the catalyst for C-O coupling reaction at 120 ºC. a) rhombic dodecahedra; b) big 50-facet polyhedra; c) small 50-facet polyhedra. The yields of diphenyl ether for different time are shown in entry 7, 15 and 18 in Table 1.

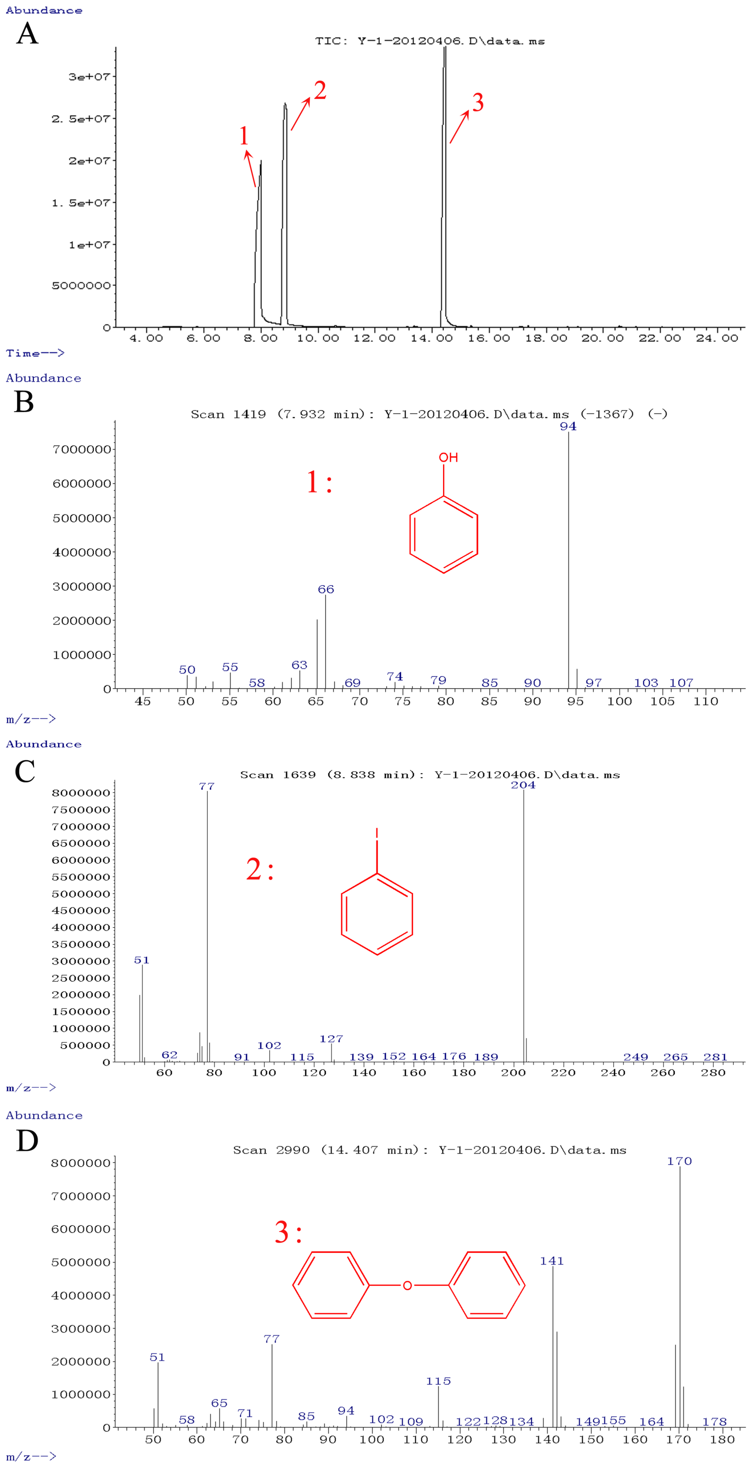


**Figure S6-12.** Typical GC-MS spectra of the reacting mixture. Peak 1, peak 2 and peak 3 in GC (Figure S3-12A) can be attributed to phenol, iodobenzene, diphenyl ether, respectively, according to the associated MS spectra (Figure S3-12B, C, D). It is clearly seen from GC-MS spectra that there are only the cross-coupled product (diphenyl ether) and unreacted starting materials without by-products in the reacting mixture, indicating that the products are diphenyl ether rather than any other by-products.

## Calculations.

GC yield per surface area of cross coupling reaction on different $Cu_2O$ polyhedra ( define as $Y_s$): Defining the GC yield of each reaction as Y, the total surface area of each kind of $Cu_2O$ polyhedra as S, the surface area of single $Cu_2O$ polyhedron as *s*, the volume of single $Cu_2O$ polyhedron as *v*, the mass of catalyst used as *m*, the number of $Cu_2O$ polyhedron in *m* as *N*. *m*=20 *mg*, $\rho$=6.0 g/cm$^3$.

$$Y_s = \frac{Y}{S} = \frac{Y}{N*s} = \frac{Y}{\frac{m/\rho}{v}*s} = \frac{Y*\rho*v}{m*s}$$

Cube: $s=1.188\times10^4\ nm^2$, $v=8.806\times10^4\ nm^3$, Y=25.86%

$$Y_s = \frac{25.86\%\times6.0g/cm^3\times8.806\times10^4 nm^3}{20mg\times1.188\times10^4 nm^2}$$

$$= \frac{25.86\%\times6.0g/cm^3\times8.806\times10^{-17} cm^3}{20\times10^{-3} g\times1.188\times10^{-10} cm^2}$$

$$= 57.51\times10^{-4}\%/cm^2$$

$$= 57.51\%/m^2$$

Octahedron: $s=5.072\ \mu m^2$, $v=0.835\ \mu m^3$, Y=25.27%

$$Y_s = \frac{25.27\%\times6.0g/cm^3\times0.835\mu m^3}{20mg\times5.072\mu m^2}$$

$$= \frac{25.27\%\times6.0g/cm^3\times0.835\times10^{-12} cm^3}{20\times10^{-3} g\times5.072\times10^{-8} cm^2}$$

$$= 1.248\times10^{-1}\%/cm^2$$

$$= 1248\%/m^2$$

Rhombic dodecahedron: $s=3.299\ \mu m^2$, $v=0.485\ \mu m^3$, Y=26.59%

$$Y_s = \frac{26.59\%\times6.0g/cm^3\times0.485\mu m^3}{20mg\times3.299\mu m^2}$$

$$= \frac{26.59\%\times6.0g/cm^3\times0.485\times10^{-12} cm^3}{20\times10^{-3} g\times3.299\times10^{-8} cm^2}$$

$$= 1.173\times10^{-1}\%/cm^2$$

$$= 1173\%/m^2$$

18-facet polyhedron: $s=1.652\times10^6\ nm^2$, $v=1.750\times10^8\ nm^3$, Y=26.21%

$$Y_s = \frac{26.21\%\times6.0g/cm^3\times1.750\times10^8 nm^3}{20mg\times1.652\times10^6 nm^2}$$

$$= \frac{26.21\%\times6.0g/cm^3\times1.750\times10^{-13} cm^3}{20\times10^{-3} g\times1.652\times10^{-8} cm^2}$$

$$= 8.329\times10^{-2}\%/cm^2$$

$$= 832.9\%/m^2$$

sR: $s=1.967\times10^6\ nm^2$, $v=2.417\times10^8\ nm^3$, Y=26.59%

$$\mathrm{Y}_s = \frac{26.59\% \times 6.0g/cm^3 \times 2.417 \times 10^8 nm^3}{20mg \times 1.967 \times 10^6 nm^2}$$

$$= \frac{26.59\% \times 6.0g/cm^3 \times 2.417 \times 10^{-13} cm^3}{20 \times 10^{-3} g \times 1.967 \times 10^{-8} cm^2}$$

$$= 9.802 \times 10^{-2} \% / cm^2$$

$$= 980.2\% / m^2$$

Big 50-facet polyhedron: $s$=51.160 $\mu m^2$, $v$=35.130 $\mu m^3$, Y=26.84%

$$\mathrm{Y}_s = \frac{26.84\% \times 6.0g/cm^3 \times 35.130 \mu m^3}{20mg \times 51.160 \mu m^2}$$

$$= \frac{26.59\% \times 6.0g/cm^3 \times 35.130 \times 10^{-12} cm^3}{20 \times 10^{-3} g \times 51.160 \times 10^{-8} cm^2}$$

$$= 5.529 \times 10^{-1} \% / cm^2$$

$$= 5529\% / m^2$$

Small 50-facet polyhedron: $s$=2.63 $\mu m^2$, $v$=0.41 $\mu m^3$, Y=28.79%

$$\mathrm{Y}_s = \frac{28.79\% \times 6.0g/cm^3 \times 4.1 \mu m^3}{20mg \times 2.63 \mu m^2}$$

$$= \frac{28.79\% \times 6.0g/cm^3 \times 4.1 \times 10^{-13} cm^3}{20 \times 10^{-3} g \times 2.63 \times 10^{-8} cm^2}$$

$$= 1.346 \times 10^{-1} \% / cm^2$$

$$= 1346\% / m^2$$