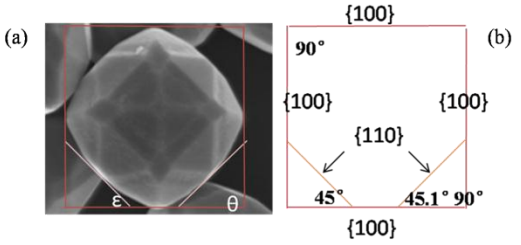
Supporting Information

Experiments section

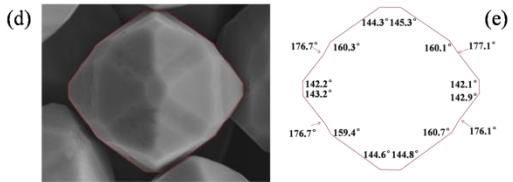
In a typical synthesis, 100 mL of 0.01 M cupric sulfate ($CuSO_4 \cdot 5H_2O$) aqueous solution was stirred at 60 °C for 10 min. Afterwards, sodium hydroxide (NaOH) solution (25 mL) with different concentrations was added dropwise to form a black suspension. After stirred for 5 min, 25 mL of 0.1M ascorbic acid solution was added to the suspension and stirred for another 1h at 60 °C. Finally, the brick-red product was washed thoroughly with deionized water by centrifugation and dried under vacuum for 6h.

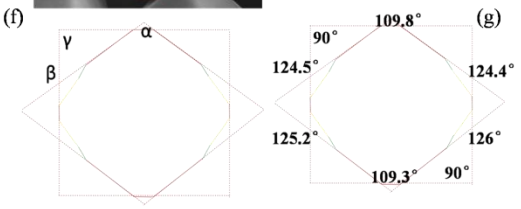
The morphologies and the structures of the samples were characterized by scanning electron microscopy (SEM, S4800). X-ray powder diffraction (XRD, Rigaku D/max-2500 diffractometer with Cu Kα radiation, λ=0.1542nm, 40 kV, 100 mA).



(c)

Angle \ {hlk}	{110} vs. {100}	{100} vs. {100}
Theoretical angle	45°	90°
Measured angle	45.1°	90°





(h)

Angle \ {hlk}	{110} vs. {111}	{111} vs. {211}	{211} vs. {744}	{744} vs. {100}	{111} vs. {100}	{111} vs. {111}	{110} vs. {100}
Theoretical angle	144.7°	160.5°	176.3°	141.1°	125.3°	109.5°	90°
Measured angle	144.8°	160.1°	176.7°	142.6°	125.0°	109.6°	90°

Fig. S1. (a) The SEM image of 74-facets Cu_2O crystal viewed along the <100> direction, ∠θ and ∠ε show the dihedral angel of {100} vs. {100} and {100} vs. {110} and corresponding measured values are shown in (b). (c and h) theoretical and measured values of dihedral angle of 74-facet Cu_2O crystal bounded by different facets. (d) The SEM image of 74-facets Cu_2O crystal viewed along the <110> direction, (e) the solid represent the projected contour of the 74-facet Cu_2O polyhedron from <110> direction, and the measured values of dihedral angle shown as black, (f) dotted ling represent the extension along the <111>, <110> and <100> direction; ∠α, ∠β and ∠γ represent the dihedral angel of {111} vs. {111}, {100} vs. {111} and {100} vs. {110}, and corresponding measured values are shown in (g).

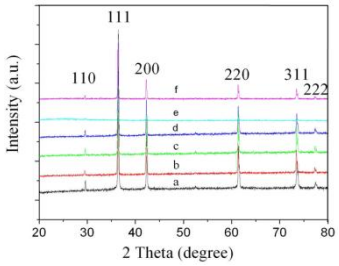


Fig. S2. XRD patterns of the prepared different morphology Cu_2O crystals. (a) cubes; (b) 18-facet Cu_2O polyhedrons; (c) 26-facet Cu_2O polyhedrons; (d)50-facet Cu_2O polyhedrons with {522} high index facets; (e)50-facet Cu_2O polyhedrons with {211} high index facets; (f)72-facet Cu_2O polyhedrons.

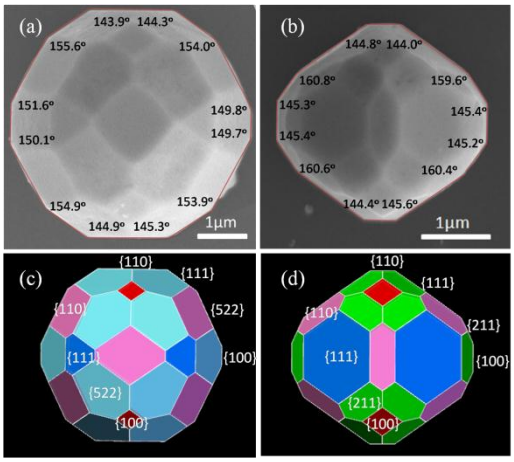


Fig. S3. The polyhedral Cu_2O crystals with different shapes and their corresponding simulated structures marked with the measured of dihedral angle. (a,c) 50-facet Cu_2O polyhedron with {522} facets ; (b,d) 50-facet Cu2O polyhedron with {211} facets.

The Miller indices of exposed facets of the obtained two type 50-facet Cu_2O polyhedrons can be identify by Steno's law as depicted in follows:

As displayed in (Figure S3a and b), dihedral angles between high-index facets and {100} facet of 150.1° (Figure S2a) and 145.4° (Figure S2b) are measured, respectively, which are in good agreement with the theoretical values of 150.5° and 144.5° between {522} vs. {100} and {211} vs. {100}. Moreover, the dihedral angles between high-index facets and {111} facet of 154.9° and 160.4° are also measured, respectively, which are in good agreement with the theoretical values of 154.8° and 160.5° between {522} vs. {111} and {211} vs. {111}. Therefore, it could be concluded that, exposed high-index facets in these two types of 50-facet Cu_2O polyhedron are {522} and {211}. In addition, the structural simulations of the two polyhedrons were also provided in Figure S2c and d, in which the high-index {522} and {211} facets are respectively marked in light blue and green.

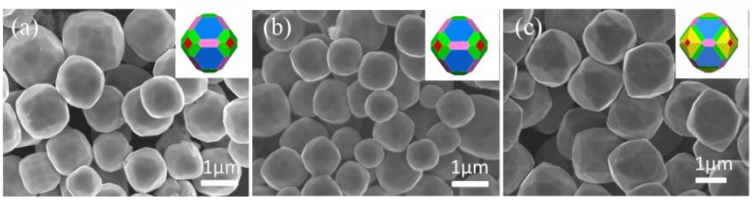


Fig. S4. SEM images and simulated structures of the products obtained using $CuCl_2$, $Cu(CH_3COO)_2$ and $Cu(NO_3)_2$ as copper ions sources when NaOH solution was set 9.5 M and otherwise the same reaction conditions. (a) $CuCl_2$; (b) $Cu(CH_3COO)_2$; and (c) $Cu(NO_3)_2$.

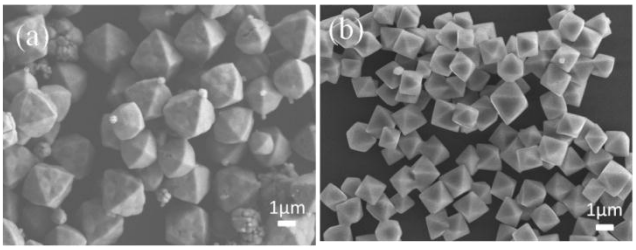


Fig. S5. SEM images of Cu_2O micro-crystals synthesized with different reducing agent when set NaOH solution at 9.5 M and otherwise the same reaction conditions. (a) D-(+)-glucose aqueous solution; (b) $N_2H_4 \bullet H_2O$ aqueous solution.