Supporting Information

Experimental

Synthesis and characterization

All chemicals used in this work were analytical reagent grade and commercially available, and used without further purification. $[Cu_3(btc)_2]_n$ polyhedron have been fabricated by the microwave irradiation previously. In our case, we obtained the $[Cu_3(btc)_2]_n$ polyhedron by a solvothermal method. In a typical synthesis, 41 mg $Cu(NO_3)_2 \cdot 3H_2O$, 1.902 g lauric acid and 20 mg Benzene-1,3,5-tricarboxylic acid were dissolved in 10 mL of butanol. After being stirred vigorously for 10 min, the mixture was put into a 50 ml Teflon-lined stainless steel autoclave. The autoclave was treated at 140 °C and maintained for 3 h before cooled in air. The precipitates were isolated by centrifugation, washed with distilled water and absolute ethanol for several times to remove the possible residues, vacuum-dried, and kept for further characterization. The CuO/Cu_2O hollow polyhedrons were obtained by thermal decomposition of $[Cu_3(btc)_2]_n$ in air at 350℃ after 1 h.

The obtained products were characterized on an X-Ray powder diffractometer with Cu Kα radiation (λ = 1.5406 Å) (Shimadzu Corporation, Japan). The morphology was examined with a JSM-6700F scanning electron microscope (SEM). The transmission electron microscope (TEM) image was obtained from a TEM (Hitachi model H-800) at an accelerating voltage of 200 kV, and high-resolution transmission electron microscope (HRTEM, JEOL-2011) was operated at an acceleration voltage of 200 kV. Thermogravimetric analysis (TGA) was carried out using a Shimadzu-50 thermoanalyser under air flow at 10 ℃ min^{-1} in the temperature range 30-800 ℃. Specific surface areas were computed from the results of N_2 physisorption at 77 K (Micromeritics ASAP 2020) by using the BET (Brunauer–Emmet–Teller) and BJH (Barrett–Joyner–Halenda). The FT-IR spectrum was obtained using a Magna-IR 750 spectrometer in the range of 500-4000 cm^{-1} with a resolution of 4 cm^{-1}. After 250^{th} cycle, the impedance spectrum of the cell was measured on an electrochemical workstation (CHI 604 B) in the frequency range of 0.001-100 kHz.

Battery fabrication and measurement

The electrochemical behavior of the CuO/Cu_2O hollow polyhedrons was examined using CR2032 coin type cells vs. Li with 1M $LiPF_6$ in ethylene carbonate and diethyl carbonate (EC:DEC = 1:1, v/v) as the electrolyte. The working electrode was fabricated by compressing a mixture of the active materials, conductive material (acetylene black, ATB), and binder (polyvinylidene fluoride (PVDF)) in a weight ratio of CuO/Cu_2O hollow polyhedrons /carbon/PVDF= 50:30:20 onto a copper foil current collector. The cells were assembled in an argon-filled glove box (MBraun Labmaster 130). The electrode capacity was measured by a galvanostatic discharge-charge method at a current density of 100 mA g^{-1}.

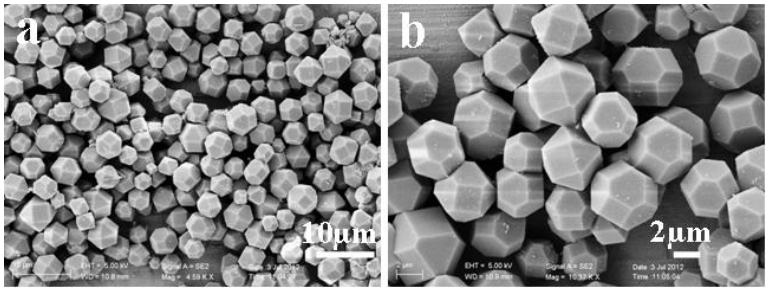

Figure S1 SEM images of $[Cu_3(btc)_2]_n$ at different magnifications.

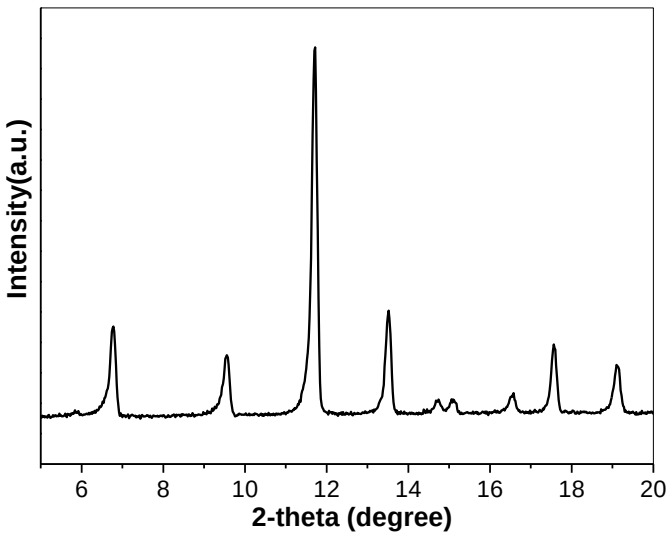

Figure S2 XRD pattern of $[Cu_3(btc)_2]_n$ polyhedrons.

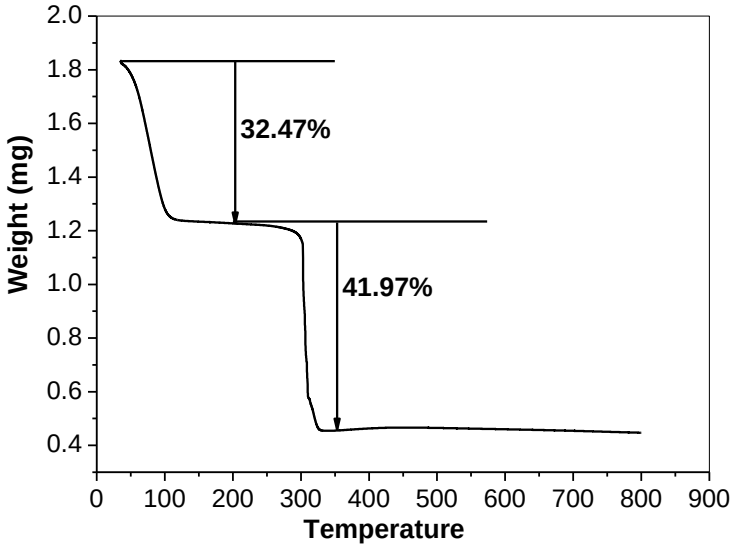

Figure S3 TG curve of $[Cu_3(btc)_2]_n$ polyhedrons in air.

[anniemin-1.raw] 1 — Peak Search Report

SCAN: 20.0/80.0/0.02/.15(sec), Cu(40kV,200mA), I(max)=1270, 05/24/12 00:00

PEAK: 29-pts/Parabolic Filter, Threshold=3.0, Cutoff=0.1%, BG=3/1.0, Peak-Top=Summit

NOTE: Intensity = Counts, 2T(0)=0.0(°), Wavelength to Compute d-Spacing = 1.54056A(Cu/K-alpha1)

#	2-Theta	d(A)	BG	Height	I%	Area	I%	FWHM
1	32.200	2.7776	449	76	11.5	3092	15.3	0.692
2	32.519	2.7511	451	93	14.1	3005	14.9	0.549
3	35.540	2.5239	610	660	100.0	14803	73.4	0.381
4	36.461	2.4622	615	620	93.9	9855	48.9	0.270
5	38.740	2.3225	493	590	89.4	20155	100.0	0.581
6	42.339	2.1330	432	174	26.4	3667	18.2	0.358
7	48.976	1.8583	403	131	19.8	4405	21.9	0.572
8	49.290	1.8472	419	71	10.8	2581	12.8	0.618
9	58.281	1.5818	380	75	11.4	1311	6.5	0.297
10	61.460	1.5074	372	172	26.1	5520	27.4	0.546
11	68.093	1.3758	368	68	10.3	1910	9.5	0.477
12	73.652	1.2851	358	70	10.6	1167	5.8	0.283
13	75.113	1.2637	343	73	11.1	1275	6.3	0.297

Figure S4 XRD date of CuO/Cu_2O composite.

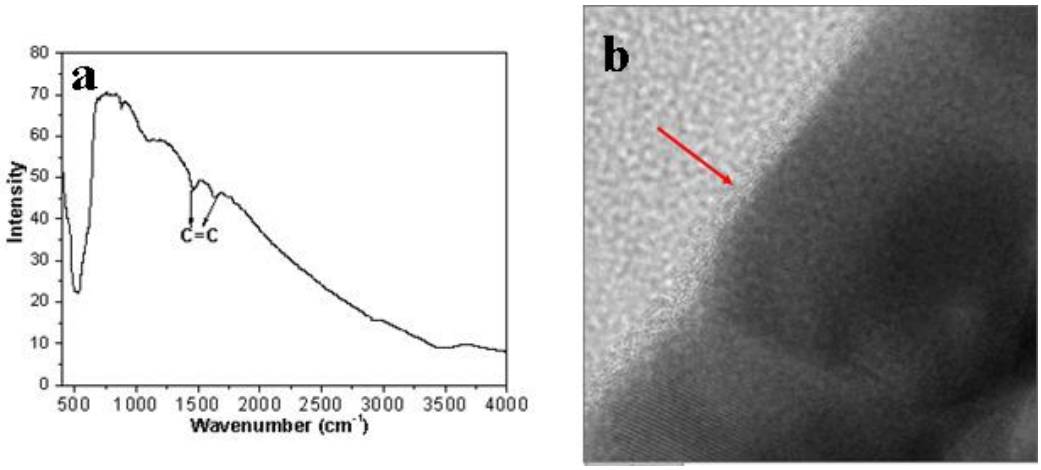

Figure S5 The infrared spectrum (IR) and TEM of CuO/Cu_2O composite.

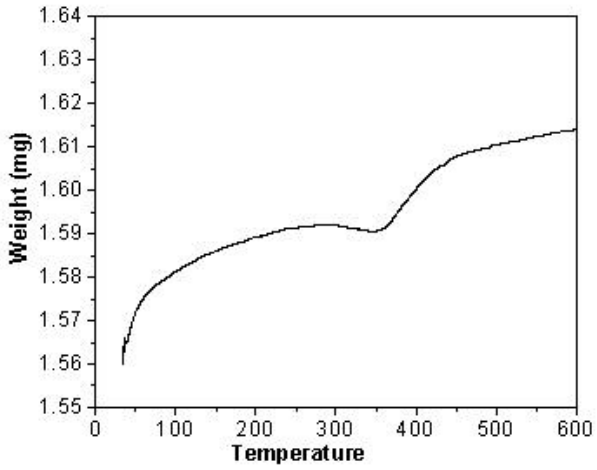

Figure S6 TG curve of CuO/Cu_2O composite in air.

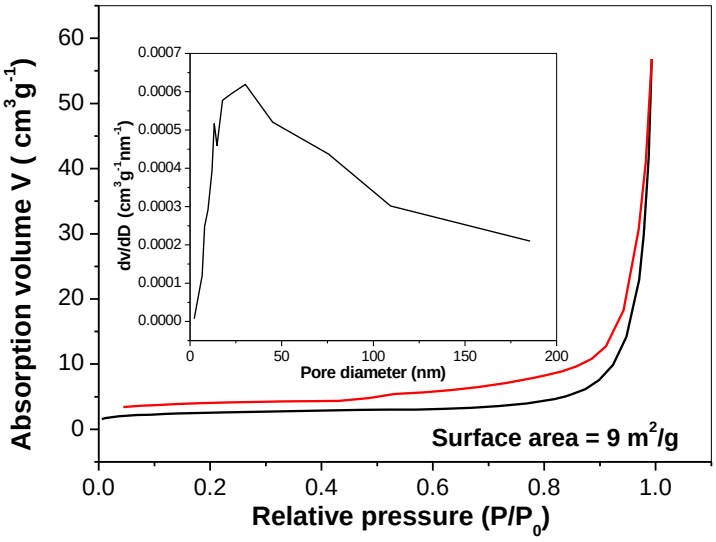

Figure S7 N_2 adsorption/desorption isotherm (77 K) curve of CuO/Cu_2O hollow

polyhedrons and porous volume distribution of the pore size (the inset).

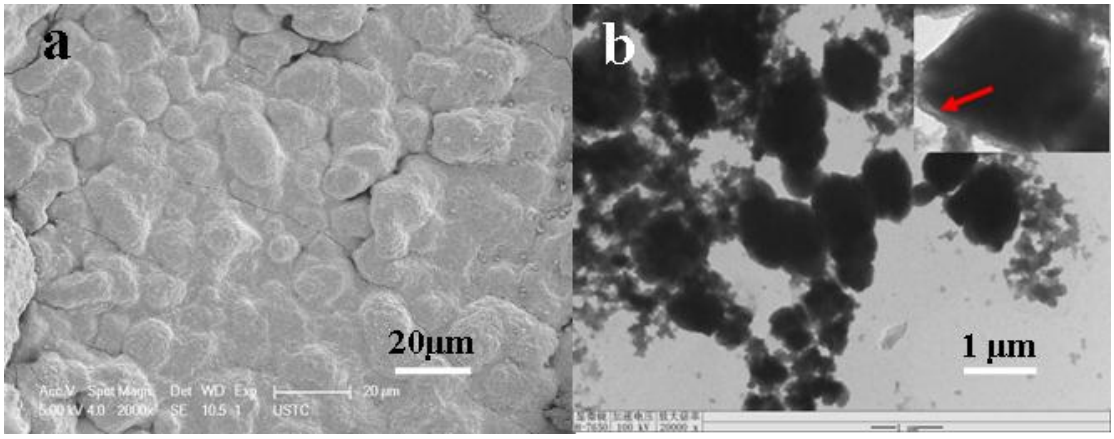

Figure S8 The SEM and TEM images of the electrode after 250 th cycles.