

<Supporting Information>

**Facile synthesis of metal/metal oxide nanoparticles inside nanoporous carbon matrix  
(M/MO@C) through morphology-preserved transformation of metal-organic  
framework**

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## Reagents

All the reagents and solvents were commercially available and used as received.  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  (> 98%) and paraformaldehyde (95%) were obtained from Aldrich. 1,3,5-benzenetricarboxylic acid ( $\text{H}_3\text{btc}$ , > 98%), phenol (> 98%) were purchased from TCI. Acetonitrile (MeCN, 99.5%) and tetrahydrofuran (THF, 99.5%) were supplied by JUNSEI. N,N-dimethylformamide (DMF, 99.5%) was purchased from DAEJUNG.

## Characterization

Transmission electron microscopy (TEM) images and Energy dispersive X-ray (EDS) were obtained with JEOL JEM-2100F microscope. Samples were crushed and supported on a holey carbon-coated copper grid (Ted Pella, Inc.) for the TEM investigation. EDX analysis and elemental mapping were performed using the energy-dispersive X-ray spectroscopy attached to the OXFORD INCA. Scanning electron microscopy (SEM) images were obtained with a HITACHI S-4800 microscope with an accelerating voltage of 15.0 kV and an applied current of 10 mA, and HITACHI SU8010 microscope with an accelerating voltage of 5.0 kV an applied current of 10 mA. For SEM imaging, MOF and polymer samples were coated with Pt or Os while carbon samples were imaged without coating. The thermo-gravimetric analysis (TGA) was performed using an SDT Q600 (TA Instruments Inc.) to 800 °C with a heating rate of 10 °C/min in air. X-ray diffraction (XRD) data were recorded on a Rigaku, D/MAX-2500/PC equipped with  $\text{Cu K}_\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) at 40 kV and 100 mA. The crystallite size of Cu, CuO and  $\text{Cu}_2\text{O}$  nanoparticles was calculated by applying the Scherrer equation to the (111), (-111) and (111) reflection ( $2\theta = 43.2^\circ$ ,  $35.4^\circ$  and  $36.2^\circ$ ) of their XRD patterns with accompanying a shape factor ( $K = 0.9$ ), respectively. The nitrogen sorption isotherms were measured at 77K using liquid nitrogen on a Belsorp Mini-II. HKUST-1 and polymer samples were degassed at 80 °C under a dynamic vacuum ( $p < 10^{-5}$  mbar) for 12 h and metal/metal oxide@carbon samples were degassed at 150 °C under a dynamic vacuum ( $p < 10^{-5}$  mbar) for overnight. The equilibrium criteria were set consistent throughout all the measurements (change in adsorption amounts less than  $0.1 \text{ cm}^3/\text{g}$  within 180 sec). The Brunauer–Emmett–Teller (BET) method was applied to estimate specific surface areas and total pore volumes were obtained at  $P/P_0 (= 0.99)$ . Pore size distributions were obtained from the corresponding isotherms using the Barrett-Joyner-Halenda (BJH) method. Micropore volumes were calculated from the corresponding isotherms using the  $t$ -plot method.

## Synthesis of HKUST-1 [ $\text{Cu}_3(\text{btc}_2)$ ]

HKUST-1 was prepared according to the reported method.<sup>[1]</sup>  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  (500.0 mg, 2.15 mmol) was dissolved in DMF (15 ml) and btc (301.2 mg, 1.43 mmol) was added. After stirring for 30 min, the solution was kept in a glass vial at 80 °C for 6 h, and then cooled to room temperature. Octahedral blue crystals were collected. After washing with DMF and solvent-exchange with MeCN for 1 d, the product was heated to 80 °C under a static vacuum ( $p < 10^{-5}$  mbar) for 12 h. Then, the activated HKUST-1 was used for vapor phase polymerization.

## Synthesis of PF@HKUST-1

PF@HKUST-1 composites were synthesized via vapor phase polymerization of phenol-paraformaldehyde into HKUST-1 crystals which were already heated to 80 °C under a static vacuum ( $p < 10^{-5}$  mbar) for 12 h. The activated crystals of HKUST-1 have open metal sites (200 mg) employed as polymerization catalysts, and were sealed in a reaction vessel with phenol (360 mg) and paraformaldehyde (260 mg) under a static vacuum ( $p < 10^{-5}$  mbar) for 2 h at room temperature and heated at 100 °C for 24 h, designated as a PF@MOF\_100%. In addition, the reduced amounts of precursors (phenol and paraformaldehyde) such as 50, 30, 10% were used to prepare the samples of PF@MOF\_50, 30, 10%, respectively. In order to remove less polymerized phenol-paraformaldehyde during polymerization process on the surface of the composites, PF@HKUST-1 composites were washed several times with THF and dried at 80 °C for 12 h under a static vacuum ( $p < 10^{-5}$  mbar) prior to the thermolysis process.

## Synthesis of Cu@C composites

As-synthesized PF@HKUST-1 composites (100 mg, PF@MOF\_100%) were taken in a crucible and

then placed in a tube furnace and heated to 800 °C under N<sub>2</sub> (99.999%) with a heating rate of 26, 13 or 4.3 °C /min. After reaching the target temperature, the material was maintained for 1, 3, 6, 12 h and then naturally allowed to cool down to room temperature. The final black powder was further analyzed. For porosity control of carbon framework, the PF@MOF\_50, 30, 10% composites underwent the same thermolysis condition (800 °C under N<sub>2</sub> (99.999%) with a heating 4.3 °C /min.)

#### **Synthesis of Cu<sub>2</sub>O@C composites**

As synthesized Cu@C composites were heated to 200 °C for 1 h under the mixture (N<sub>2</sub>:O<sub>2</sub> = 10:1 in volume ratio) atmosphere. The materials were maintained at 200 °C for 30, 75, 90 min, respectively. After cooling to room temperature, black powder was obtained.

#### **Synthesis of CuO@C composites**

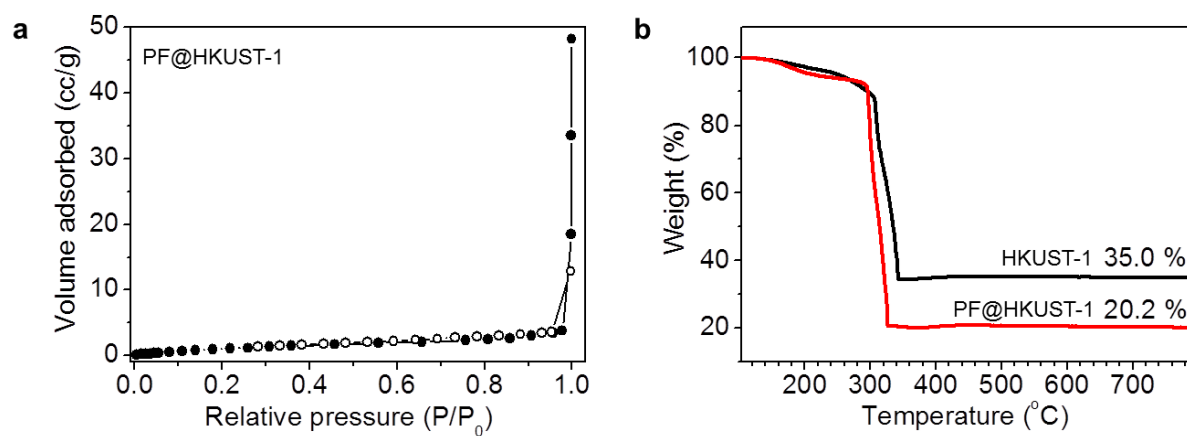
As synthesized Cu@C composites were heated to 200 °C for 1 h under O<sub>2</sub> atmosphere. After reaching the target temperature (200 °C), the materials were maintained for 3 h and 9 h, and then cooled to room temperature. The CuO@C composites was obtained.

#### **Reference**

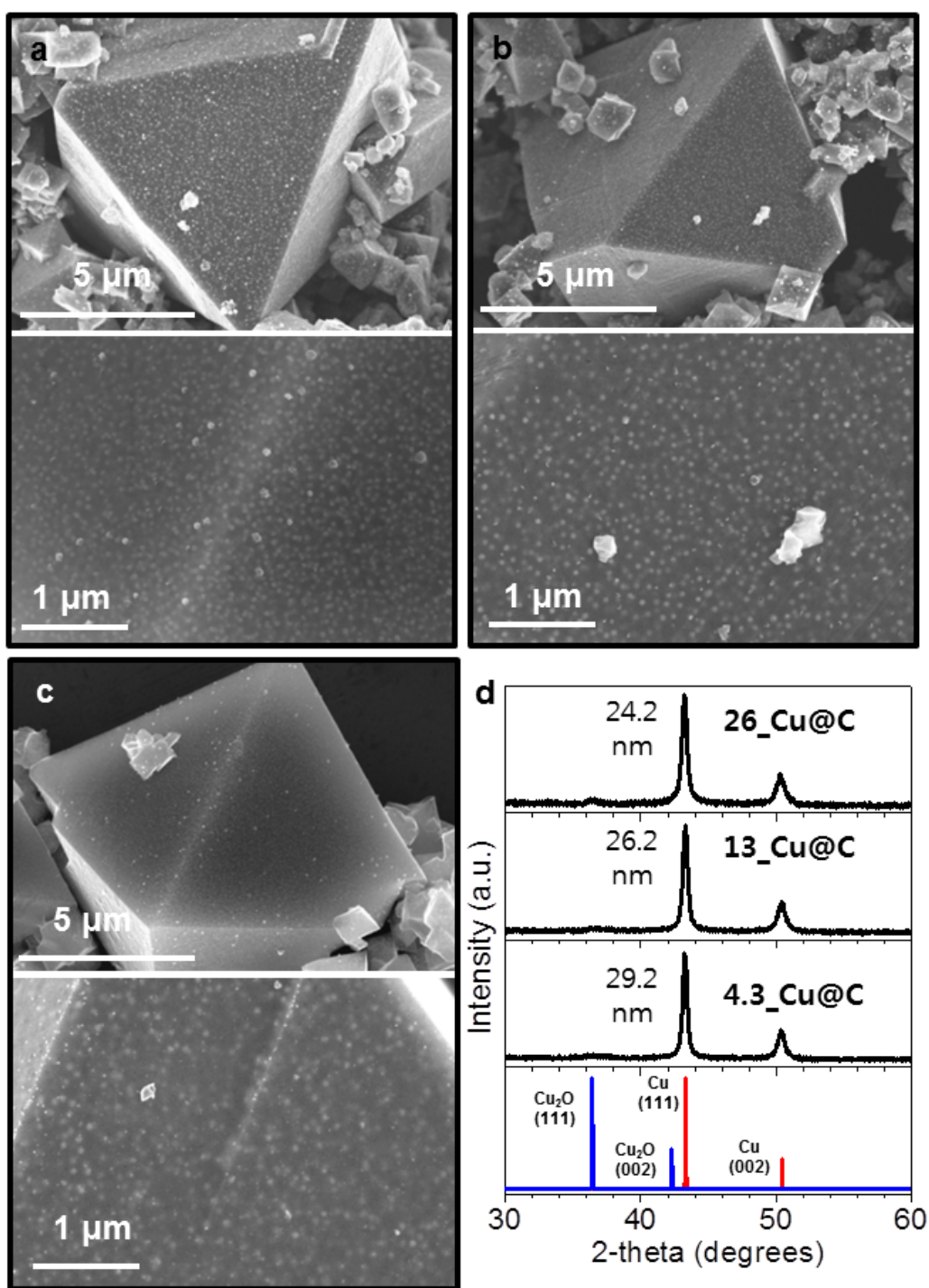
[S1] S. S. Y. Chui, S. M. F. Lo, J. P. H. Charmant, A. G. Orpen, I. D. Williams, *Science* **1999**, 283, 1148-1150.

**Table S1.** Summary of N<sub>2</sub> sorption analysis

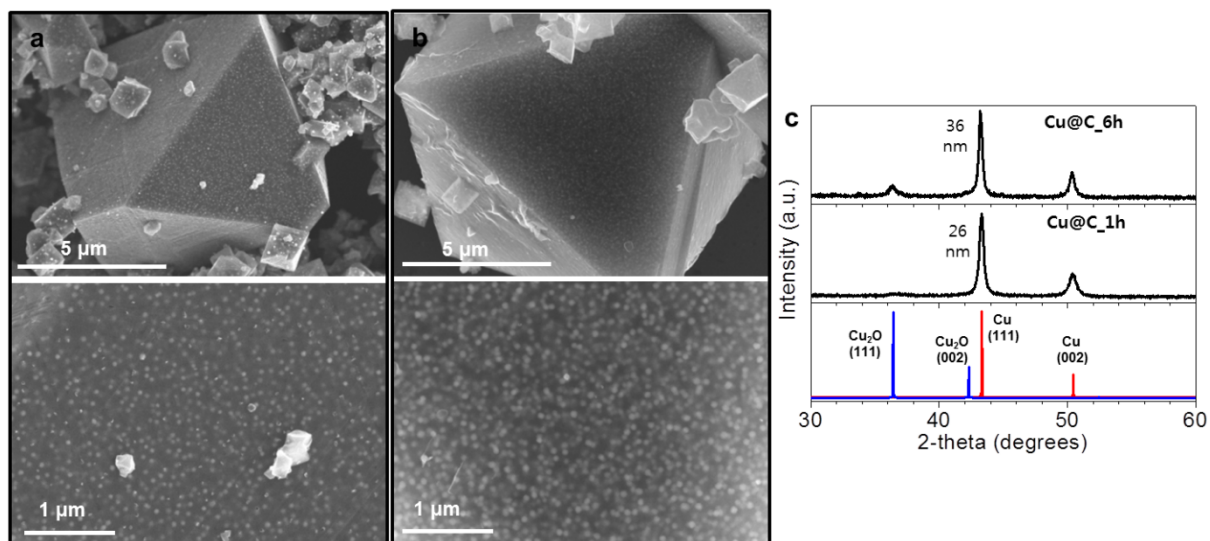
<b>sample</b>	<b>S<sub>BET</sub> (m<sup>2</sup>g<sup>-1</sup>)</b>	<b>V<sub>tot</sub> (cm<sup>3</sup>g<sup>-1</sup>)</b>	<b>V<sub>micro</sub> (cm<sup>3</sup>g<sup>-1</sup>)</b>
Cu@C_100%	584.02	0.26	0.24
Cu@C_50%	557.14	0.26	0.23
Cu@C_30%	534.95	0.34	0.19
Cu@C_10%	422.74	0.35	0.12



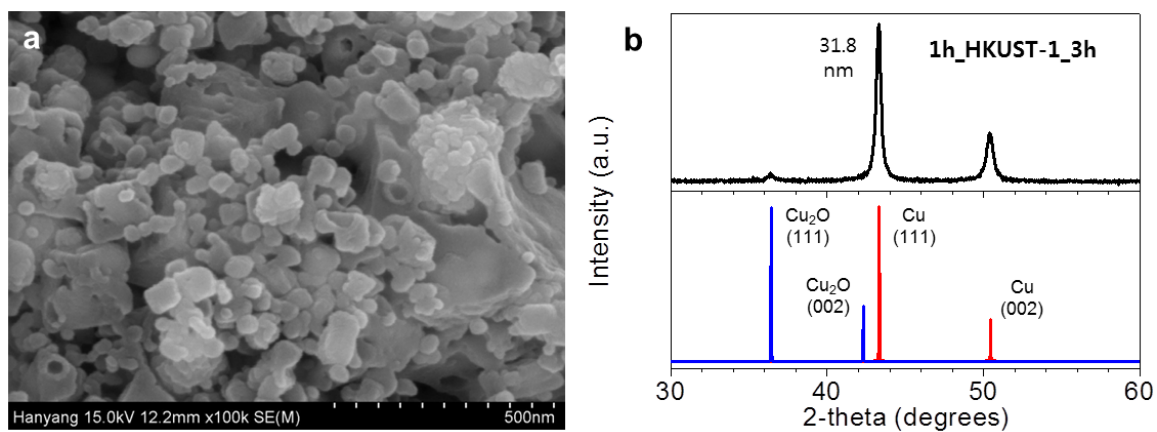
**Figure S1.** Nitrogen sorption isotherm (a) and TGA data (b) of the PF@HKUST-1 composite.



**Figure S2.** SEM images (low and high magnifications) for the Cu@C composites with different ramping rates to 800 °C with 26 (a), 13 (b) or 4.3 (c) °C/min, respectively. All samples were stayed at 800 °C for 1h. XRD data (d) for the Cu@C composites with different ramping rates (i.e., 26\_Cu@C, 13\_Cu@C and 4.3\_Cu@C). The particle sizes in the XRD (d) were measured by the Scherrer equation.

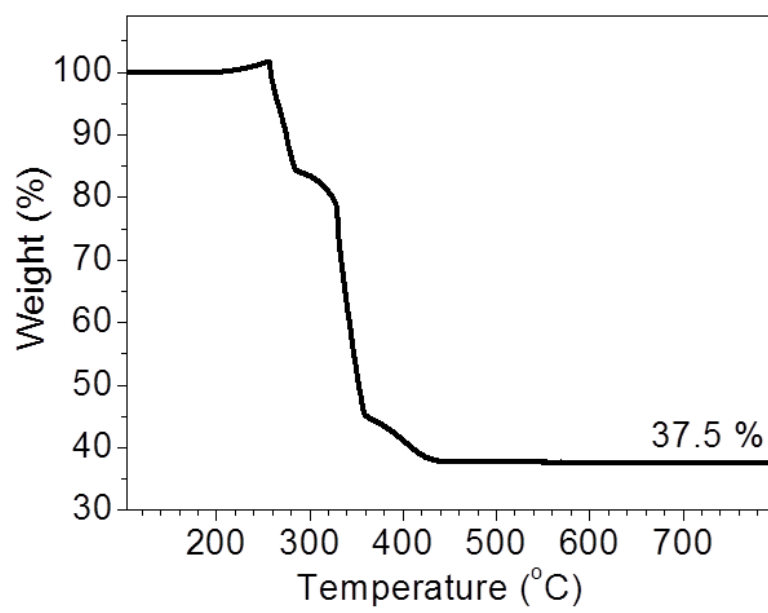


**Figure S3.** SEM images (low and high magnifications) for the Cu@C composites with different staying times at 800 °C with 1h (a) and 6 h(b). All samples were ramped up to 800 °C for 1h (13 °C/min). XRD data (c) for the Cu@C composites with different staying times at 800 °C (denoted as Cu@C\_1h, and 3h). The particle sizes in the XRD (d) were measured by the Scherrer equation.

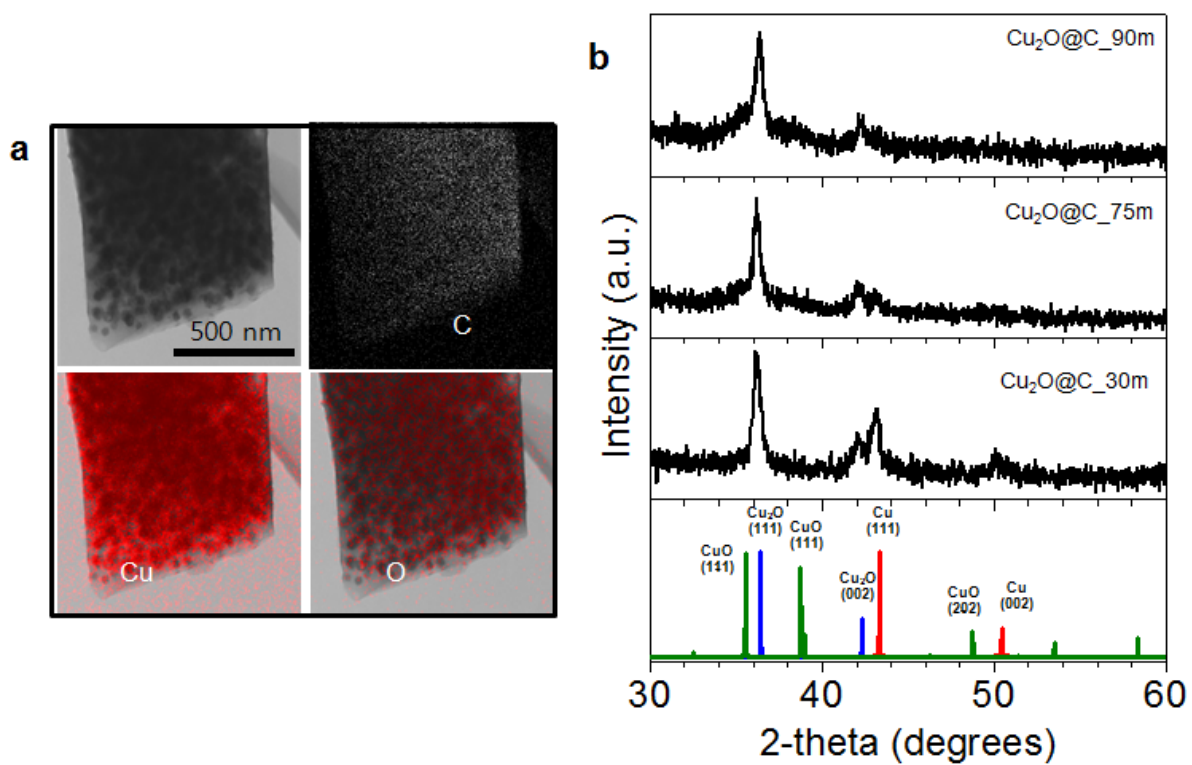


**Figure S4.** The collapsed image (SEM, a) for HKUST-1 after thermal conversion under nitrogen atmosphere to 800 ° C with ramping rate of 13 °C/min and 3 h staying at 800 ° C. XRD data (b) for the sample (a). The particle size in the XRD were measured by the Scherrer equation.

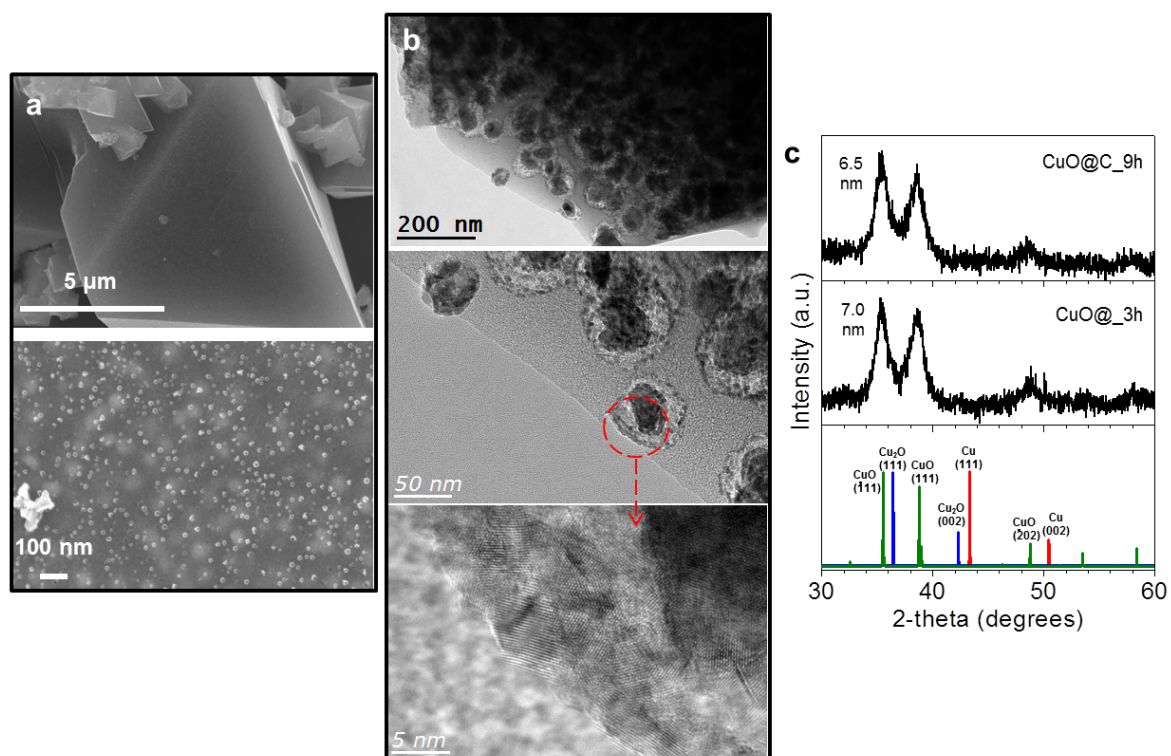




**Figure S5.** TGA data of Cu@C measured under air condition.



**Figure S6.** Elementary mapping using EDX analysis for  $\text{Cu}_2\text{O}@C_{75m}$  (a). XRD data (b) for a series of  $\text{Cu}_2\text{O}@C_{xm}$  ( $x=30, 75, 90$ ) composites.



**Figure S7.** SEM images of the CuO@C<sub>9h</sub> composite with low and high magnifications. TEM images (b) for of the CuO@C<sub>9h</sub> composite with different magnifications. And XRD data (c) for a series of CuO@C<sub>xh</sub> (x= 3, 9) composites.