

Electronic Supplementary Information

Synthesis of graphene-wrapped CuO hybrid materials by CO₂ mineralization

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Experimental Details

Materials: Calcium chloride (anhydrous, granular, 93.0%), hydrazine solution (35 wt% in water), ammonium hydroxide solution (5.0 N), and copper (II) chloride (97%) were purchased from Sigma-Aldrich (St. Louis, USA). Sodium hydroxide was obtained from Junsei Chemical (Tokyo, Japan). All chemical reagents were used without further purification. GO was prepared from graphite powder (particle size 3 -5 μm) (Samjung C&G, Korea) according to a modified Hummers method (*J. Am. Chem. Soc.* 1958, **80**, 1339).

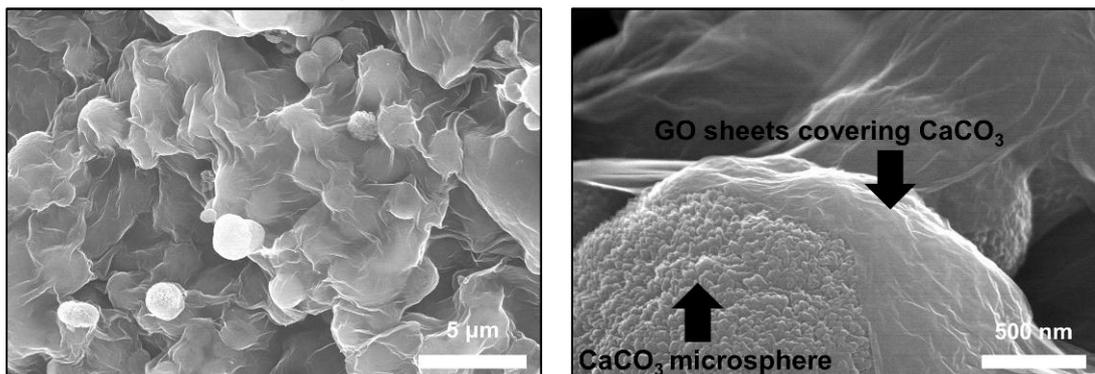
Synthesis of GO/CaCO₃, graphene/CaCO₃, graphene/Cu₂Cl(OH)₃, graphene/CuO: GO/CaCO₃ was prepared by sparging CO₂ gas at a flow rate of 3 L/min in an aqueous solution (80 mL) containing CaCl₂ (0.1 M), NH₄OH (0.25 N), and GO (1.25 mg/ml) for 90 min. The mixture was filtered through an anodic aluminum oxide (AAO) membrane (0.1 μm pore size) (Whatman, U.K.). The remnant (i.e., GO/CaCO₃) was washed several times with deionized water to remove residual ions. To synthesize graphene/CaCO₃, GO/CaCO₃ was dispersed in deionized water (100 mL) with 50 μL of hydrazine (35 wt% in water) and 3.75 mL of NH₄OH (5.0 N). It was kept at 95 °C for 90 min for the chemical reduction of GO to graphene. We obtained graphene/Cu₂Cl(OH)₃ by immersing the slurry in CuCl₂ solution (0.1 M, 200 mL, pH < 3) for 2 hrs, which was dispersed and stirred in NaOH solution (1 M) for 1 hr for an anion exchange reaction that converts graphene/Cu₂Cl(OH)₃ to graphene/Cu(OH)₂. The final product, graphene/CuO, was obtained from graphene/Cu(OH)₂ through a hydrothermal reaction for 24 hrs at 100 °C. After each step, the resulting product was filtered with an AAO membrane or nylon membrane (0.2 μm pore size) (Whatman, U.K.) and

washed several times with deionized water.

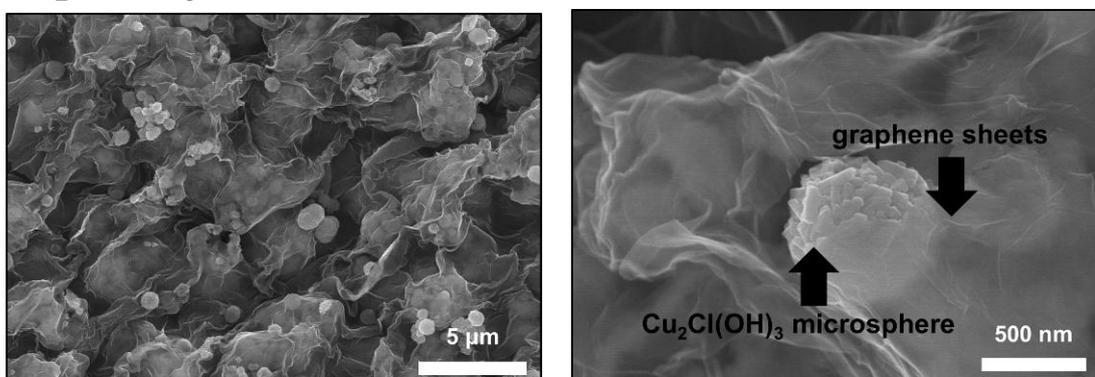
Characterization: Morphological changes of hybrid materials were observed by using an S-4800 field-emission scanning electron microscopy (Hitachi Co., Japan) at an acceleration voltage of 10 kV and a Tecani F20 field-emission transmission electron microscope (FEI Co., USA) operating at 200 kV. X-ray diffraction patterns were obtained by using a D/MAX-RB conventional X-ray diffractometer (Rigaku Co., Japan) with a scan rate of 3 °/min, a Cu K α radiation wavelength of 1.5418 Å, and a scan range of 20 °- 60 °. XPS analysis was conducted using Sigma Probe (Thermo VG Scientific, UK) in the range of 0 – 1300 eV. Raman spectra were obtained by using a high-resolution dispersive Raman microscope (Horiba Jobin Yvon, France). Thermal gravimetric analysis was performed using TG-209-F3 (NETZSCH, Germany) from room temperature to 800 °C with the heating rate at 10 °C/min under air flow. **The cyclic voltammetry (CV) test was conducted at a scan rate of 0.1 mV s⁻¹ using WBSC 3000 battery cycler (Won-A Tech, Seoul, Korea) at room temperature. The BET specific surface area was measured using TriStar II 3020 surface area analyzer (Micromeritics, USA).**

Li-ion battery performance: Li-ion battery performance was tested with a CR2016-type coin cell using WBSC 3000 battery cycler (Won-A Tech, Korea) at a voltage range from 0.01 to 3.0 V and current density from 100 to 1000 mA g⁻¹. The test electrode was prepared by casting a slurry of 70 wt% of active materials (graphene/CuO or nano-CuO), 20 wt% of carbon black (called Super P), and 10 wt% of polyvinylidene fluoride binder dissolved in N-methylpyrrolidone onto aluminum foil. The coin cell was assembled in an argon-filled glove box, which included an Li metal counter electrode, an electrolyte (1 M LiPF₆ in 1:1 v/v mixture of ethylene carbonate and dimethyl carbonate), a separator, and a test electrode for a working electrode.

(A) GO-wrapped CaCO_3 Microspheres



(B) $\text{Cu}_2\text{Cl}(\text{OH})_3$ Integrated with Graphene



(C) Graphene/ CuO Hybrid Material

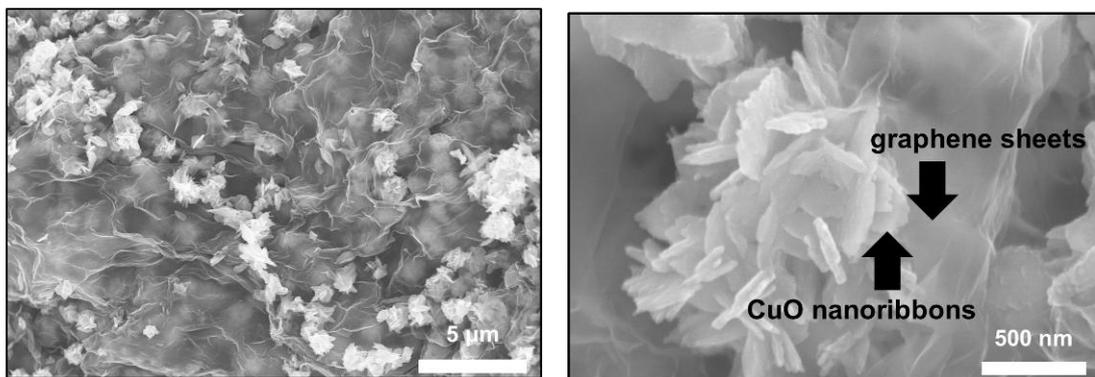


FIGURE S1. Additional SEM images of (A) GO/ CaCO_3 , (B) graphene/ $\text{Cu}_2\text{Cl}(\text{OH})_3$, and (C) graphene/ CuO hybrid materials shown in different scales.

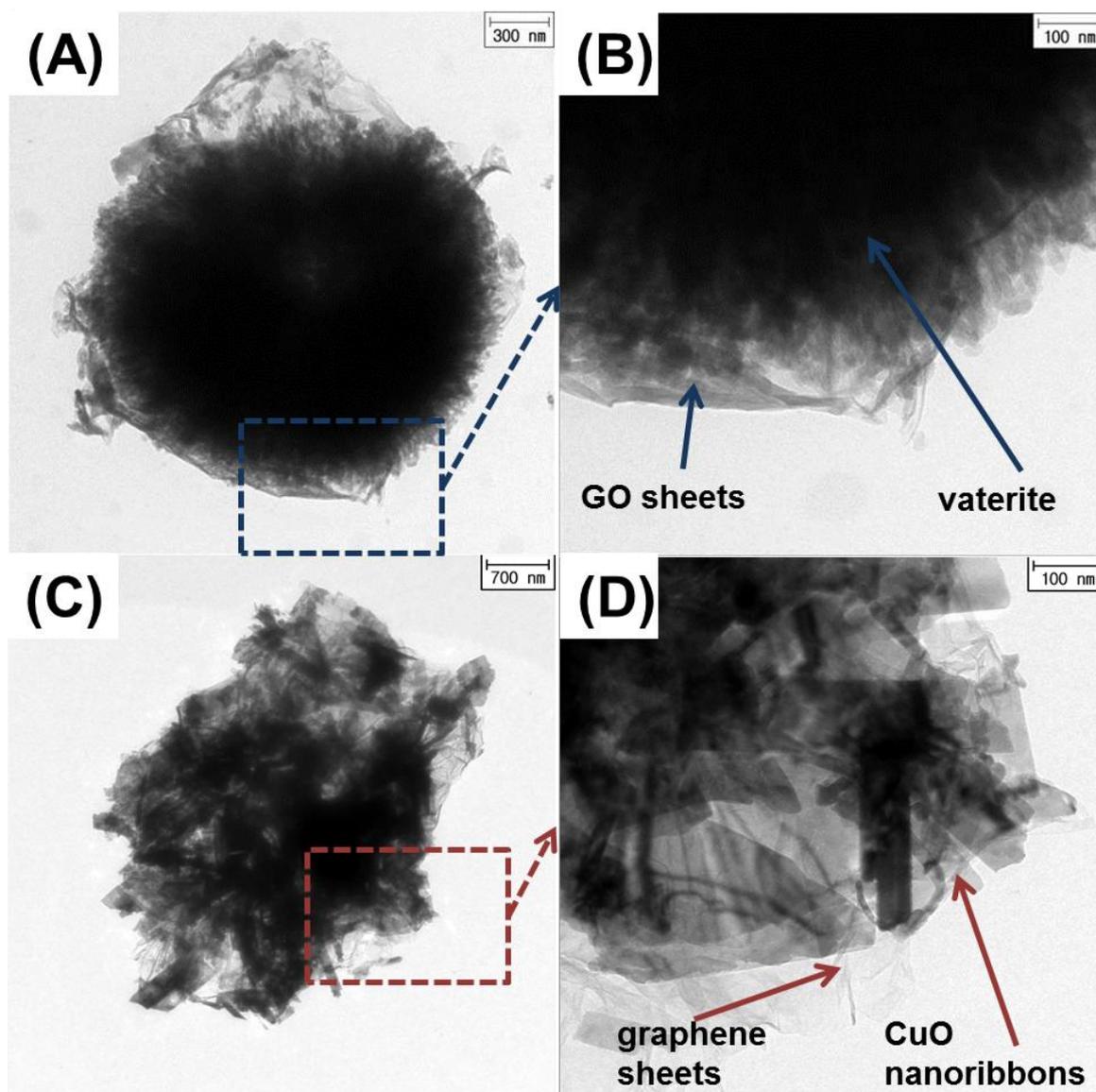


FIGURE S2. (A, B) TEM images of GO/CaCO₃ showing individual vaterite microsphere covered by flexible GO sheets. (C, D) TEM images of graphene/CuO showing CuO nanoribbons interconnected and aggregated into a graphene-wrapped microsphere.

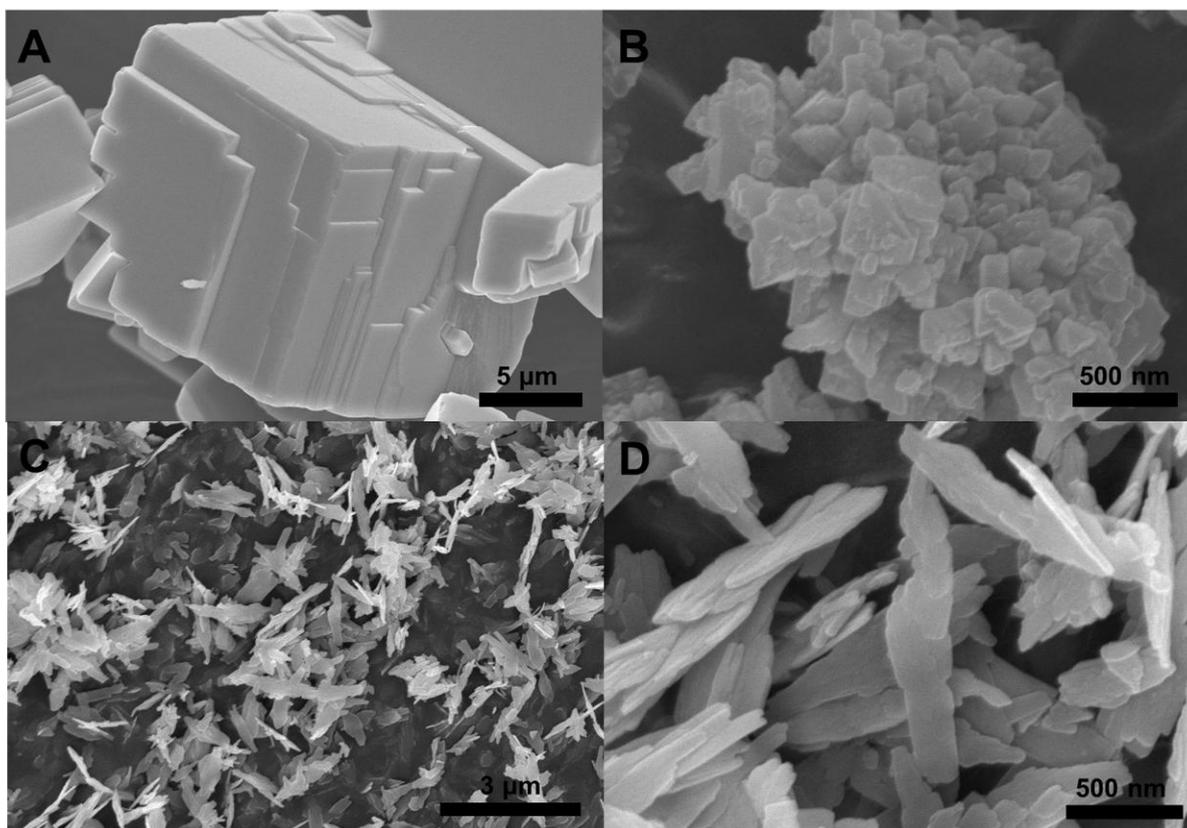


FIGURE S3. (A) SEM image of rhombohedral calcite phase of CaCO_3 synthesized in the absence of graphene oxide. (B) SEM image of $\text{Cu}_2\text{Cl}(\text{OH})_3$ synthesized from the calcite CaCO_3 in an CuCl_2 solution. (C,D) SEM images of CuO synthesized from the $\text{Cu}_2\text{Cl}(\text{OH})_3$, which exhibits plate-like structures.

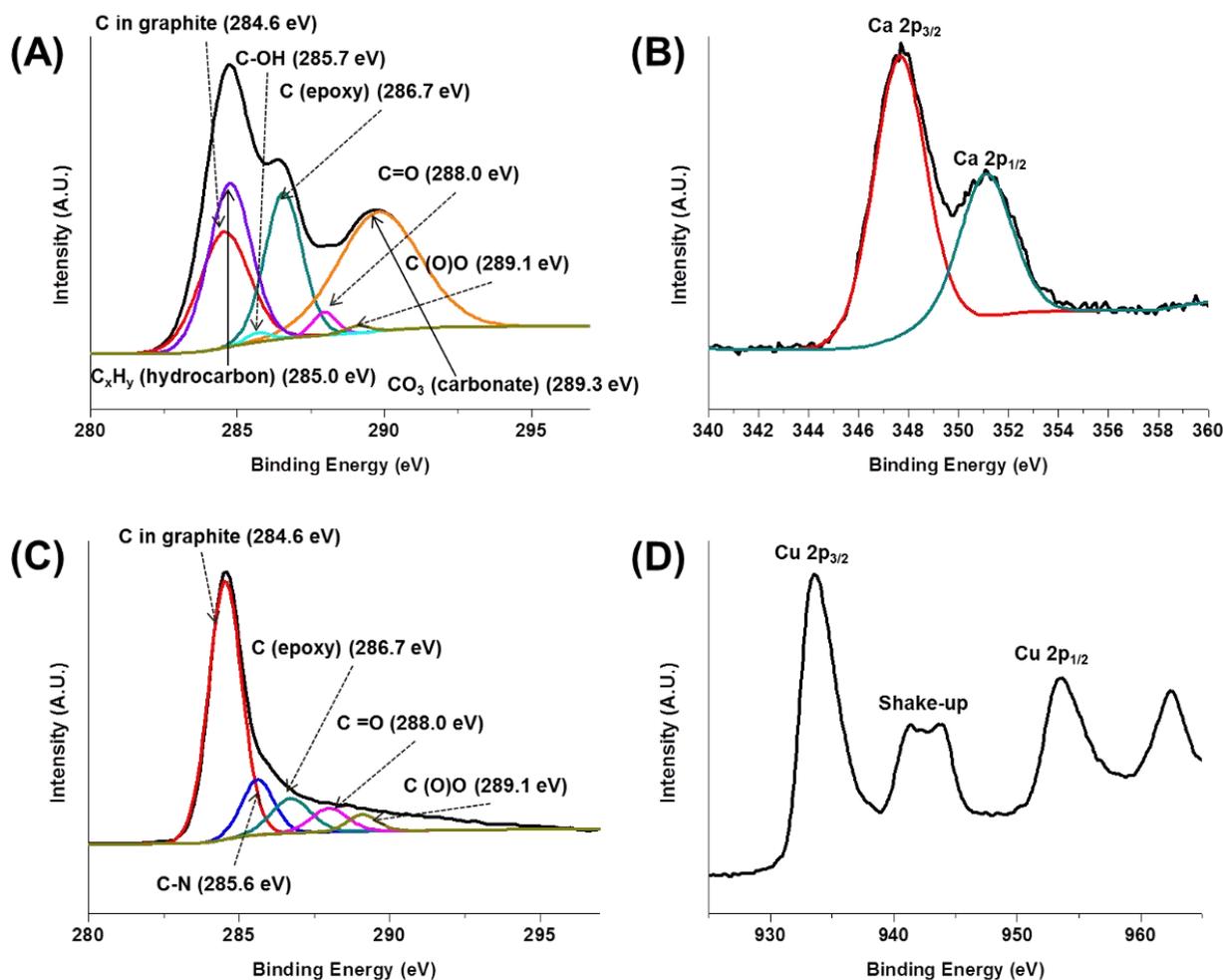


FIGURE S4. XPS spectra of GO/CaCO₃ and graphene/CuO in magnified scales. (A) C 1s spectrum of GO/CaCO₃ showing multiple, functionalized C groups. (B) Ca 2p spectrum of GO/CaCO₃ exhibiting typical peaks that correspond to Ca²⁺ ions. (C) C 1s spectrum of graphene/CuO. A significant change in the ratio of peak intensities for C in graphite to other C groups was observed in graphene/CuO when compared to GO/CaCO₃ due to the chemical reduction of GO to graphene. (D) Cu 2p spectrum of graphene/CuO confirming the existence of Cu²⁺ ions in graphene/CuO.

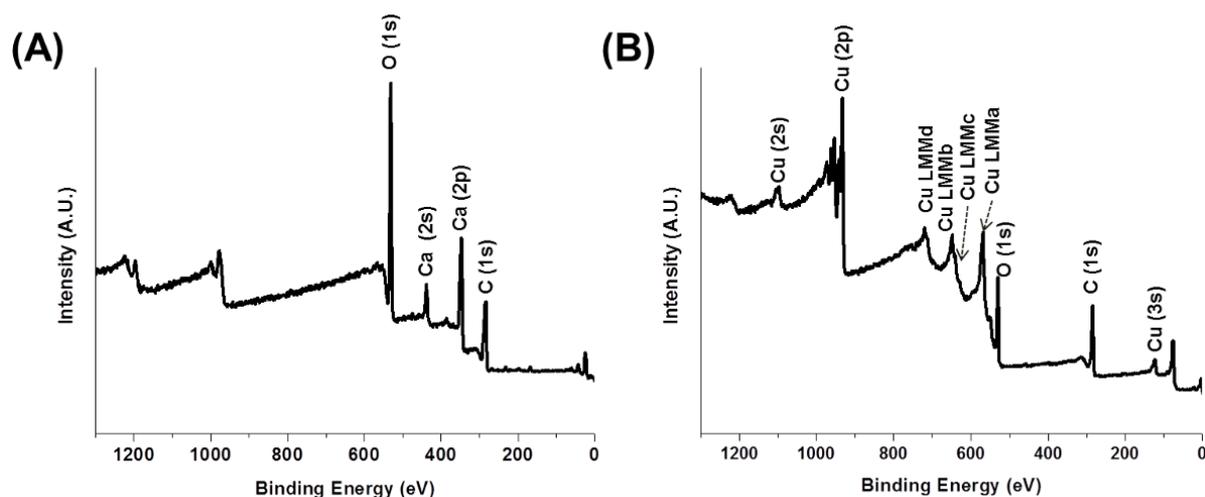


FIGURE S5. XPS spectra of GO/CaCO₃ and graphene/CuO in the wide range from 0 to 1300 eV. (A) The XPS scan of GO/CaCO₃ indicating three compositional elements (i.e., C, Ca, and O). (B) The XPS scan of graphene/CuO exhibiting multiple peaks corresponding to C, Cu, and O elements.

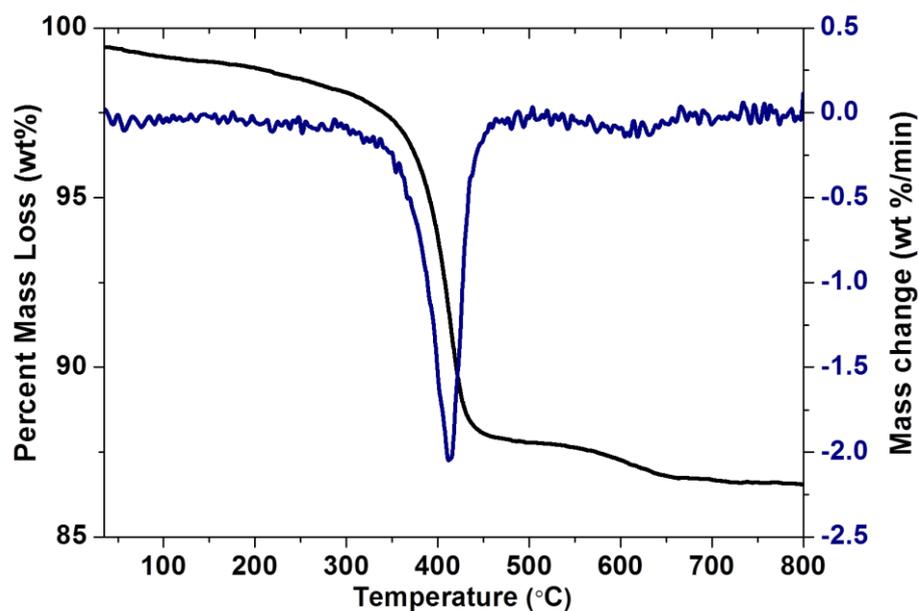


FIGURE S6. Thermal gravimetric analysis (TGA) plot demonstrating a loss of graphene in the graphene/CuO hybrid material (left column) and the mass change rate (right column) under air conditions. The weight loss occurs due to the combustion of carbon-carbon linkage in graphene sheets.

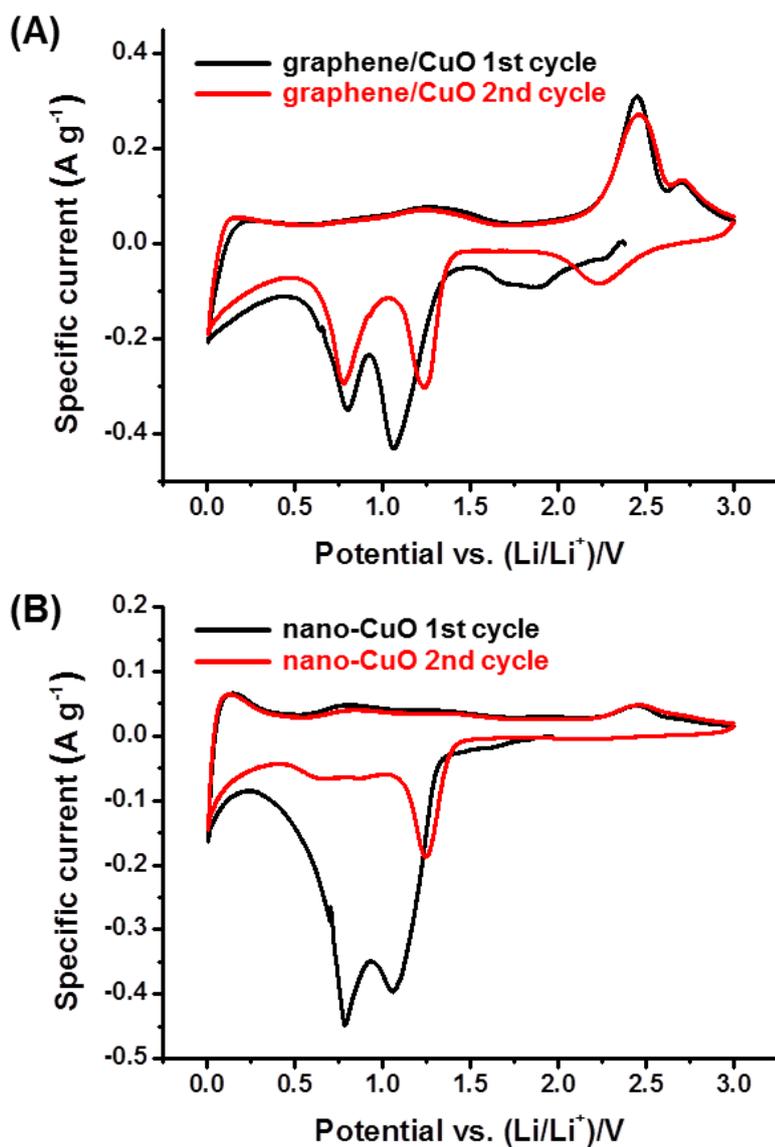


Figure S7. Cyclic voltammogram curves of (A) graphene/CuO and (B) nano-CuO at a scan rate of 0.1 mV s⁻¹.

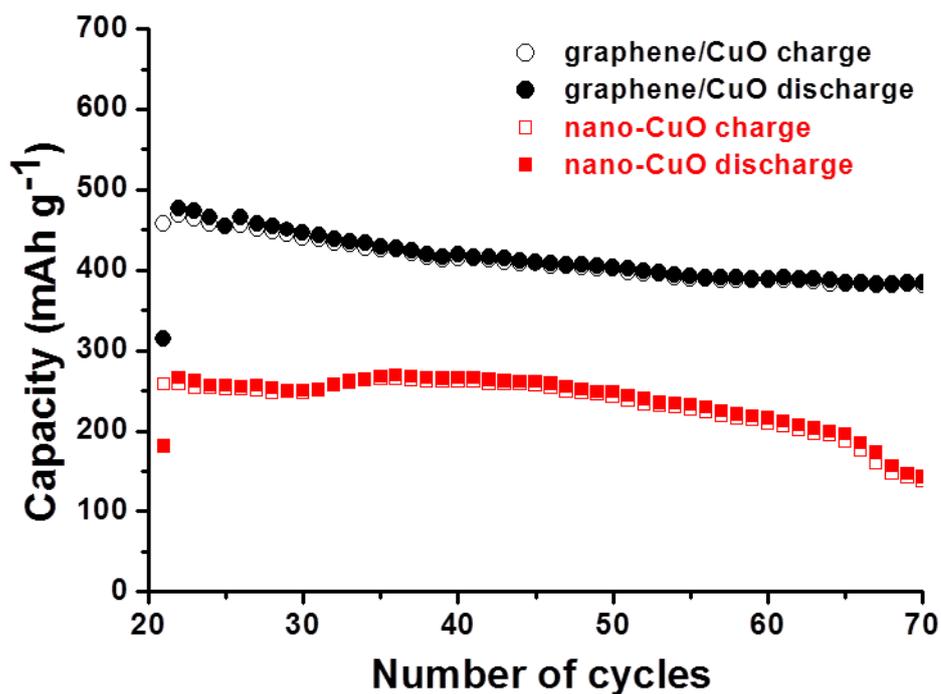


FIGURE S8. Capacity retention of graphene/CuO and nano-CuO for 50 cycles at 100 mA g⁻¹ followed after 20 cycles at different current densities from 100 to 1,000 mA g⁻¹.

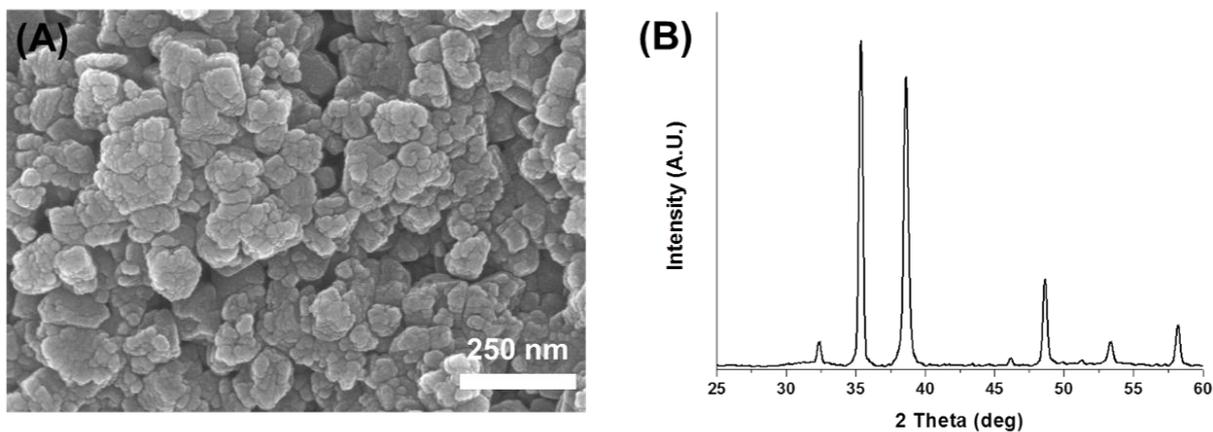


FIGURE S9. (A) SEM image and (B) XRD pattern of CuO nanoparticles (below 50 nm) purchased from Sigma-Aldrich (Cat. No. 544868). The XRD spectrum mirrored the pattern of CuO (JCPDS No. 65-2309).