

Supplementary Information

Printed Cu Source/Drain Electrode Capped by CuO Hole Injection Layer for Organic Thin Film Transistors

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Experimental Details

Synthesis of Cu/CuO core-shell Nanoparticles. Cu nanoparticles were synthesized via chemical reduction of Cu ions in toluene ($C_6H_5CH_3$, Aldrich, anhydrous 99.8%) under inert atmosphere. To prevent the interparticular agglomeration and surface oxidation, oleic acid ($C_{18}H_{34}O_2$, Aldrich, 99%) was incorporated as a surface capping molecule and hydrazine (NH_2NH_2 , Junsei, 98%) was used as a reducing agent. 16.6 g of Cu acetate ($Cu(CO_2CH_3)_2$, Aldrich, 98%), 10 g of oleic acid, and 16.6 g of hydrazine were added into a three-neck round-bottomed flask containing 100 mL of toluene. The flask was fitted with a reflux condenser and mechanical stirrer. The solution was purged with nitrogen for at least 30 min and then heated to 100 °C. Reaction was continued for 120 min and then cooled to room temperature. Then, the synthesized Cu nanoparticles were separated by centrifugation and washed with ethanol. The resulting Cu nanoparticles were well-dispersed in toluene, but not in aqueous medium. To endow the water-compatibility, we modified the surface of synthesized Cu nanoparticles by dipping Cu nanoparticles in methanol-based solution in which 6 wt% of carboxyl-terminated anionic polyelectrolyte, 16 wt% of mixture of polyoxyethylene oleylamine ether (Wako, $M_w = 1,000$) and oxalic acid ($C_2H_2O_4$, Aldrich, 99%) are dissolved. After reaction for 30 min under nitrogen atmosphere, the surface-

modified Cu nanoparticles were separated by centrifugation and washed with methanol, and resulting Cu nanoparticles were easily well-dispersed in DI-water.

Preparation of Aqueous Cu/CuO Nanoparticle Ink. For preparation of the Cu conductive ink, the obtained Cu nanoparticles were dispersed in DI-water, and 2-methoxyethanol ($C_3H_8O_2$, Aldrich, 99%) and glycerol ($C_3H_5(OH)_3$, Aldrich, >99.5%) were added to reduce the surface tension and evaporation rate of the aqueous ink, respectively. Ethylene glycol ($C_2H_6O_2$, Aldrich, 99%) was additionally incorporated for obtaining the printed pattern with a uniform surface morphology. The solvent composition was DI-water : 2-methoxyethanol : glycerol : ethylene glycol = 50 : 20 : 5 : 25 vol%. The solid loading was 40 wt% and the prepared ink was subjected to ball milling for 1 hr prior to ink-jet printing.

TFT Fabrication and Measurement. A bottom-contact electrode architecture was used for testing the OTFT with printed Cu/CuO bilayer S/D electrode. Cu/CuO nanoparticle conductive ink was printed on a heavily-doped silicon wafer with 300 nm-thick SiO_2 as a gate insulator ($C_i=11$ nF/cm²). The substrate temperature was maintained at 25 °C. The printer set up is composed of a drop-on-demand piezoelectric ink-jet nozzle manufactured by Microfab Technologies, Inc. (Plano, TX) and the nozzle with the orifice diameter of 30 μ m was used. The channel length (L) and width (W) were 96 μ m and 886 μ m, respectively. The ink-jet printed electrode pattern was annealed for 30 min at various temperatures from RT to 400 °C under vacuum of 6×10^{-5} torr. Pentacene layer with the thickness of 60 nm was deposited on the substrate heated at 90 °C and the deposition rate was 1 $\text{Å}/s$. For comparison, the OTFT with vacuum deposited Au electrode was fabricated with a top-contact electrode architecture. Pentacene was deposited on a heavily-doped silicon wafer with 300 nm-thick SiO_2 as a gate insulator and then Au S/D electrodes with the thickness of 50 nm were deposited by thermal evaporation (pressure $\sim 10^{-6}$ torr) through shadow masks, affording channel dimensions of 100 μ m (L) x 1000 μ m (W). Another transistor with Au electrode was

prepared using the heavily-doped silicon wafer with 300 nm-thick SiO₂ annealed at 300 °C under vacuum of 6x10⁻⁵ torr. The gate dielectric was annealed prior to pentacene deposition and Au evaporation. All measurements for devices were performed in ambient and at room temperature. The carrier mobilities was calculated in saturation using the equation:

$$\mu_{\text{sat}} = (2I_{\text{D}}L)/[WC_i(V_{\text{G}} - V_{\text{T}})^2]$$

where L and W are the device channel length and width, respectively, C_i is the capacitance of the oxide insulator and V_{th} is the threshold voltage. The threshold voltage can be estimated as the x intercept of the linear section of the plot of V_G versus $(I_D)^{1/2}$.

Characterization. The size and shape of the synthesized Cu/CuO core-shell nanoparticles, and the microstructure of the Cu/CuO bilayer electrode were observed by scanning electron microscopy (SEM, JSM-6700, JEOL) and transmission electron microscopy (TEM, JEM-4010, JEOL). The crystal structure of Cu/CuO core-shell nanoparticles was analyzed using an x-ray diffractometer (XRD, D/MAX-2200V, Rigaku) and chemical structural analysis of Cu/CuO core-shell nanoparticles and printed Cu/CuO bilayer electrode were performed with x-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo Fisher Scientific). The contact angle was measured with a dynamic contact angle system (SEO 300, SEO) and the thermal behavior of Cu/CuO core-shell nanoparticles was monitored using thermal gravimetric analysis (SDT2960, TA Instruments). The morphology and resistivity of the printed Cu/CuO bilayer electrodes were analyzed using a laser scanning confocal microscopy (LEXT OLS3000, Olympus) and four point probe station equipped with a semiconductor characterization system (Keithley 4200, Keithley), respectively.

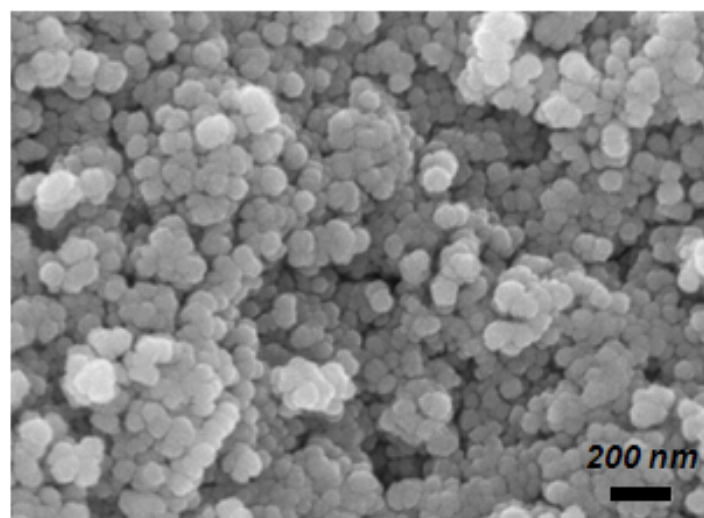


Figure S1. SEM image of the synthesized Cu/CuO core-shell nanoparticles.

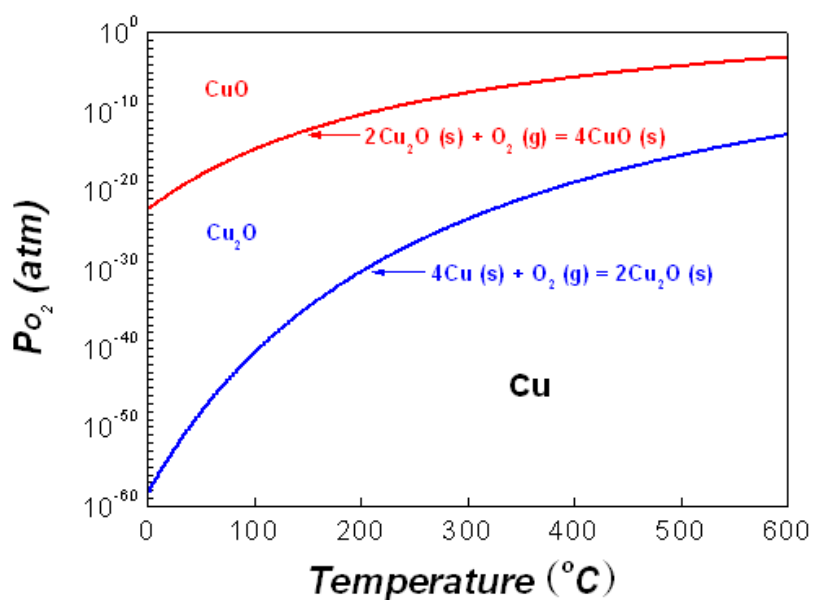


Figure S2. Thermodynamic phase transition behavior from Cu to Cu₂O or CuO as a function of oxygen partial pressure and temperature. The detail on thermodynamics-based calculation is fully described in previous study.⁹

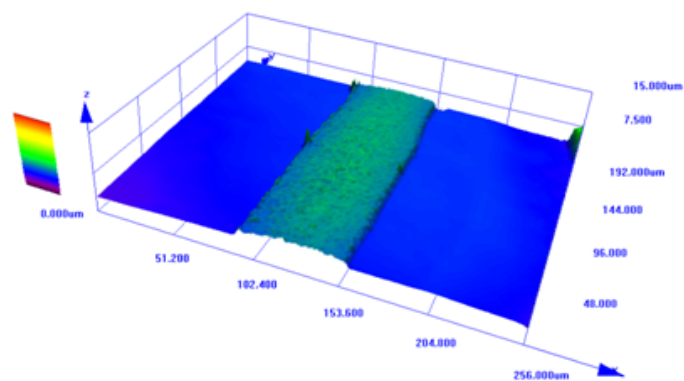


Figure S3. Confocal microscope image of printed Cu/CuO bilayer S/D electrode.

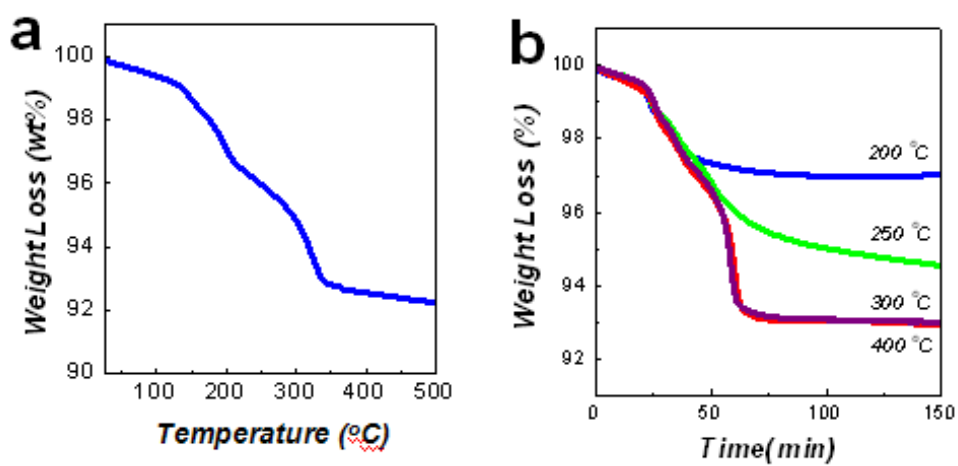


Figure S4. Thermal gravimetric analysis curves of Cu nanoparticles extracted from aqueous Cu ink.

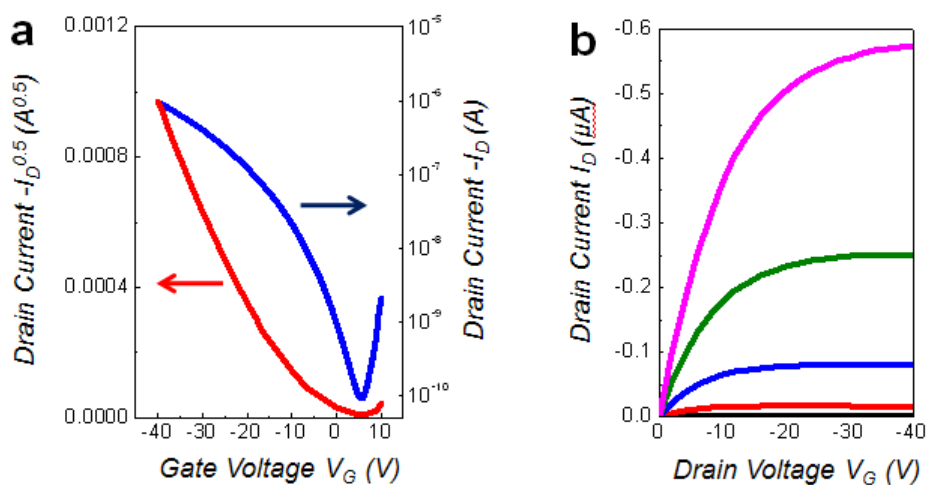


Figure S5. (a) Transfer ($V_D = -40$ V) and (b) output characteristic ($V_G = 0, -10, -20, -30,$ and -40 V) of pentacene TFT with the vacuum deposited Au S/D electrode and non-treated SiO_2 gate dielectric. The channel length and width were 100 μm and 1000 μm , respectively.

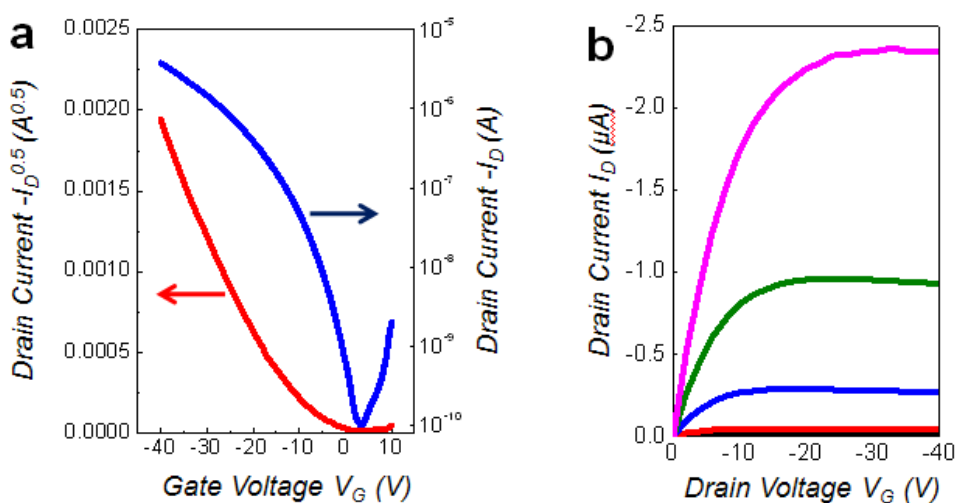


Figure S6. (a) Transfer ($V_D = -40$ V) and (b) output characteristic ($V_G = 0, -10, -20, -30,$ and -40 V) of pentacene TFT with the vacuum deposited Au S/D electrode and SiO_2 gate dielectric annealed at 300 °C under vacuum. The channel length and width were 100 μm and 1000 μm , respectively.