Supporting Information

Enhanced Performance of Electric Double Layer Micro-supercapacitor Based on Novel Carbon Encapsulated Cu Nanowire Network Structure as Electrode

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Suppressing CuO Growth in Synthesis of $Cu(OH)_2$ Nanowires

$Cu(OH)_2$ and CuO nanostructures can be formed on Cu substrates via a surface oxidation process in an alkaline solution in the following equations:[1]

$$Cu + 4NaOH + (NH_2)_4S_2O_8 \rightarrow Cu(OH)_2 + 2Na_2SO_4 + 2NH_3 + 2H_2O \quad (1)$$

$$2Cu + 8NaOH + 2(NH_2)_4S_2O_8 \rightarrow Cu(OH)_2 + CuO + 4Na_2SO_4 + 4NH_3 + 5H_2O \quad (2)$$

$$Cu + 4NaOH + (NH_2)_4S_2O_8 \rightarrow CuO + 2Na_2SO_4 + 2NH_3 + 3H_2O \quad (3)$$

It is also proposed that in addition to forming CuO directly from Cu, $Cu(OH)_2$ can also undergo reaction in an alkaline environment to form CuO according to the two-step reaction below[2]

$$Cu(OH)_2 + 2OH^- \rightarrow Cu(OH)_4^{2-} \quad (4)$$

$$Cu(OH)_4^{2-} \leftrightarrow CuO + 2OH^- + H_2O \quad (5)$$

Although $Cu(OH)_2$ is fairly stable in water with a solubility of 1.3×10^{-5} mol L^{-1}, it dissolves much quicker in the alkaline solution of a solubility of 6×10^{-2} mol L^{-1}, forming $Cu(OH)_4^{2-}$ ions[3-4] according to eqn. (4). A condensation process follows (eqn. (5)) and CuO particles are formed. Hence, in order to inhibit the formation of CuO particles, growth of $Cu(OH)_2$ nanowires (eqn (3)) has to be much faster than formation of CuO particles (eqn (4) and (5)). For this purpose, a 10 times less concentrated reaction solution was prepared to reduce the alkalinity while keeping the ratio of [APS]/[NaOH] the same[2]. As a result, almost no CuO nanoparticles were formed. CuO particles are clearly visible as illustrated in Fig. S1a and Fig. S1b when a one-step concentrated reactant solution was used.

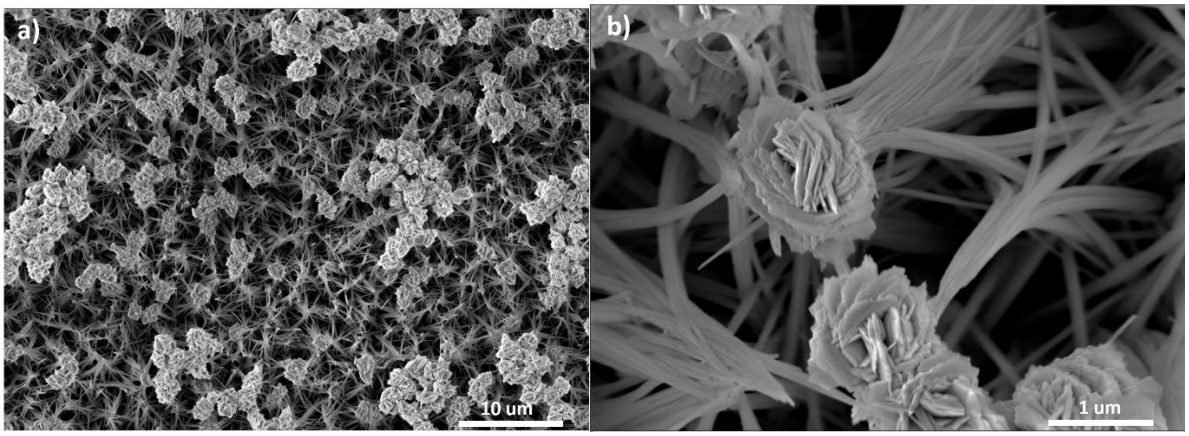

Figure S1. *(a) SEM images of $Cu(OH)_2$ nanowires with CuO nanoparticles and (b) and high magnification view of CuO nanoparticles.*

XPS analysis on Cu nanowire network

Figure S2 shows the Cu 2p XPS spectrum of the Cu nanowires. The peak at 932.5 eV can be attributed to Cu 2p3/2 of Cu phase while the smaller peak at 952.3 eV results from Cu 2p1/2 of Cu.[5]The absence of strong Cu2+ satellite peaks at ~943 eV region suggests the sample did not contain CuO phase.[5] In addition, Cu LMM spectrum is useful in distinguishing between Cu2O and Cu. As Cu is expected to have a binding energy between 567.7 – 567.9 eV, while Cu2O should have a peak at about 570 eV.[6] A peak at 568.1 eV in the LMM spectrum (Figure 3b) suggests that Cu2O is not present.

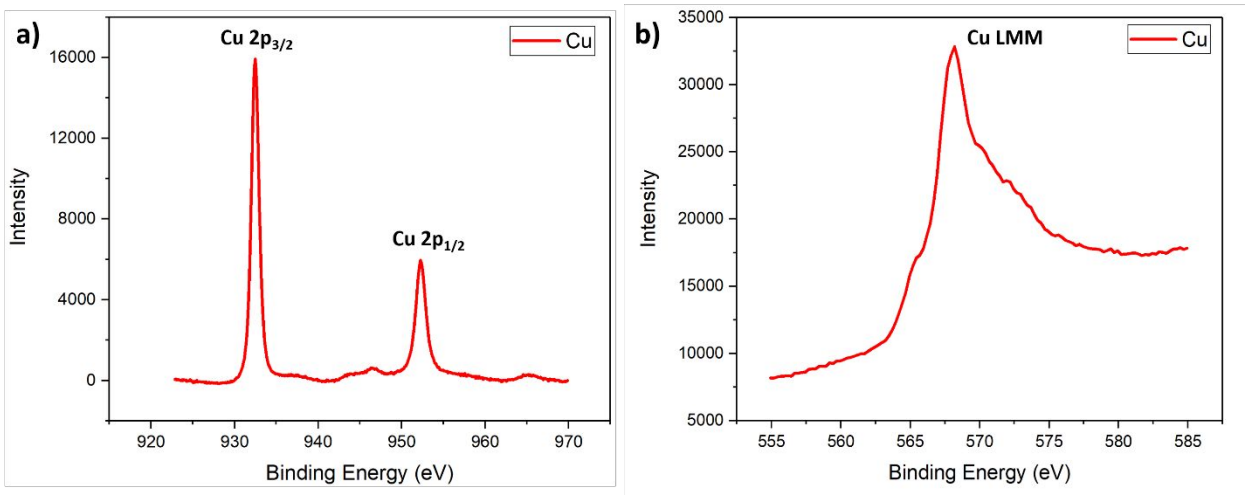

Figure S2. *(a) XPS spectra at Cu2p binding energy and (b) Cu LMM binding energy of Cu nanowires after thermal reduction of Cu(OH)2 at 300 oC in H2 environment for 1 hr.*

SEM-EDX of 300°C grown carbon

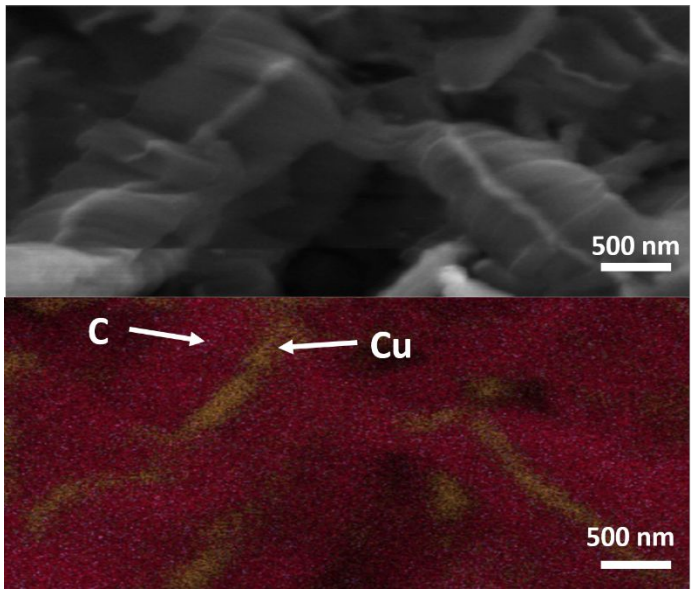

Figure S3*. SEM-EDX elemental mapping of Carbon grown at 300oC shows the growth of carbon to be perpendicular to a single Cu nanowire in opposite direction in a fin shaped structure.*

C/Cu Electrode EDX Mapping

SEM-EDX analysis was done on the carbon grown copper nanowire network electrode. EDX mapping was done on the selected area in the SEM image (Fig. S4a) to observe for the distribution of the grown carbon. From Fig. S4b, carbon can be clearly observed to be grown on Cu nanowire network. Fig 43c shows the Cu nanowire network.

The elements present were quantified with the EDX as shown in the spectrum in Fig. S4. Observed elements were mostly Cu (77.7 weight%) and C (20.2 weight%) with only trace amount of O (1.6 weight%) and Si (0.6 weight%).

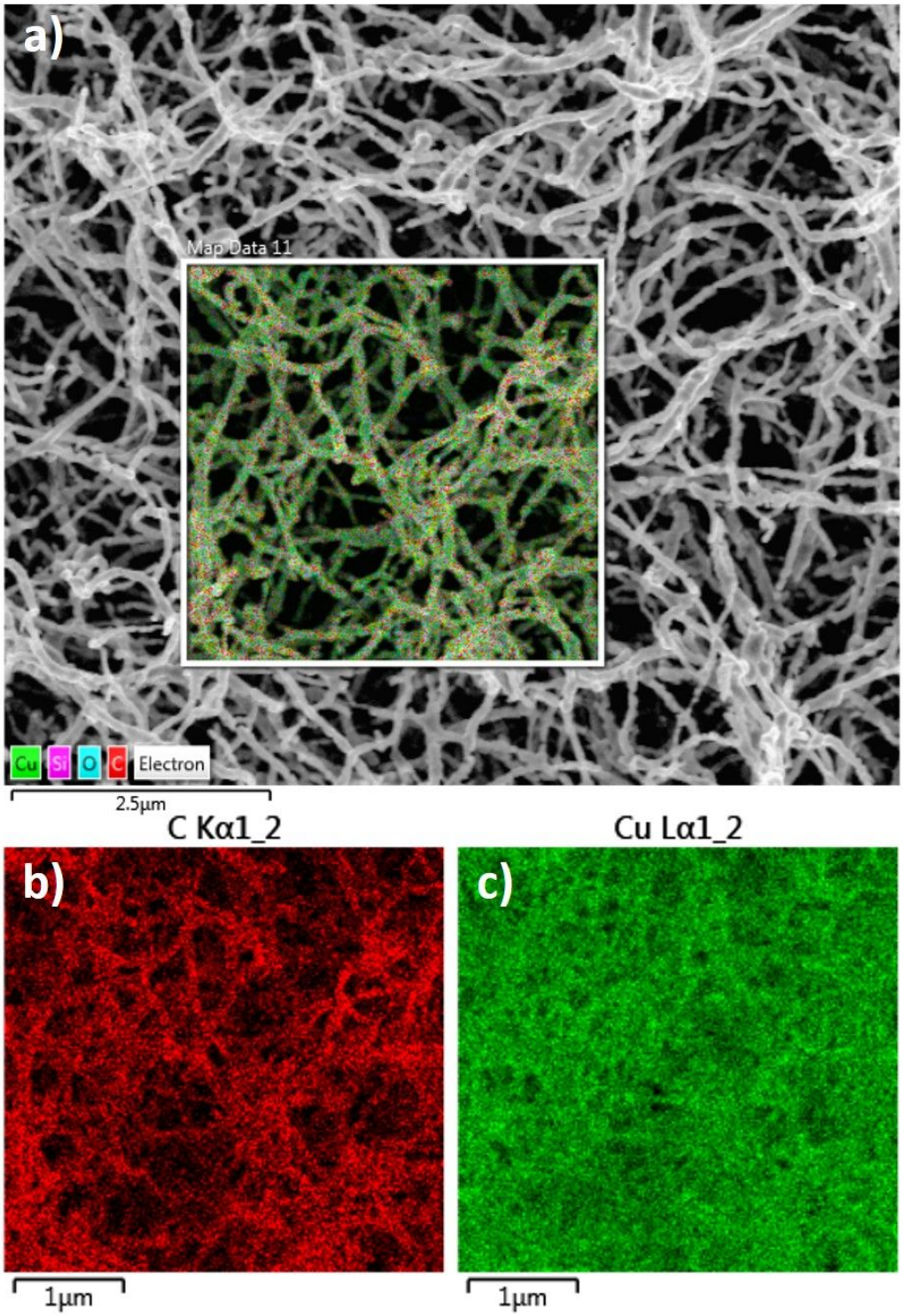

Figure S4. *(a) SEM and EDX mapping image overlay of carbon grown on Cu at 600 °C, (b) elemental distribution map of C, and (c) Cu.*

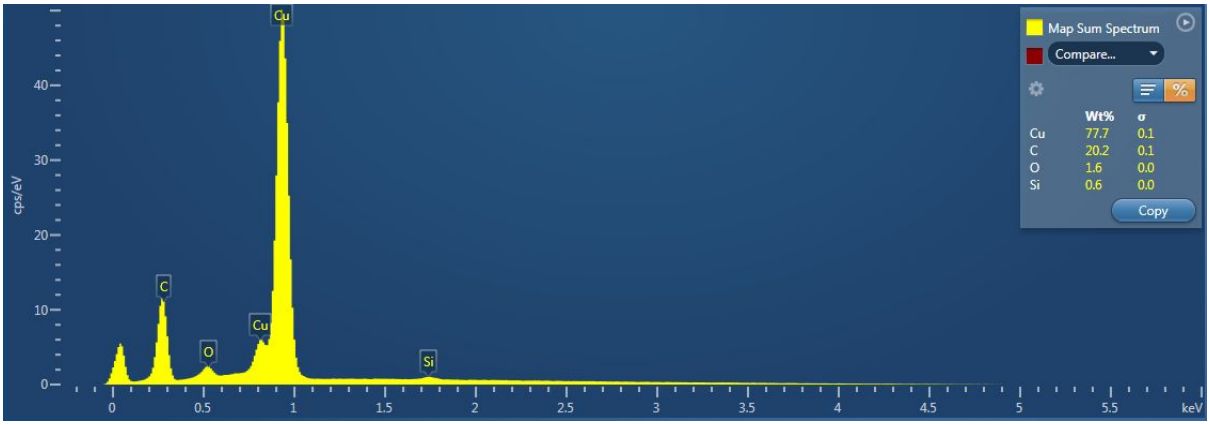

Figure S5. *EDX mapping spectrum of carbon grown on Cu at 600 °C shows 20 wt% C.*

GCD curve of 300°C sample

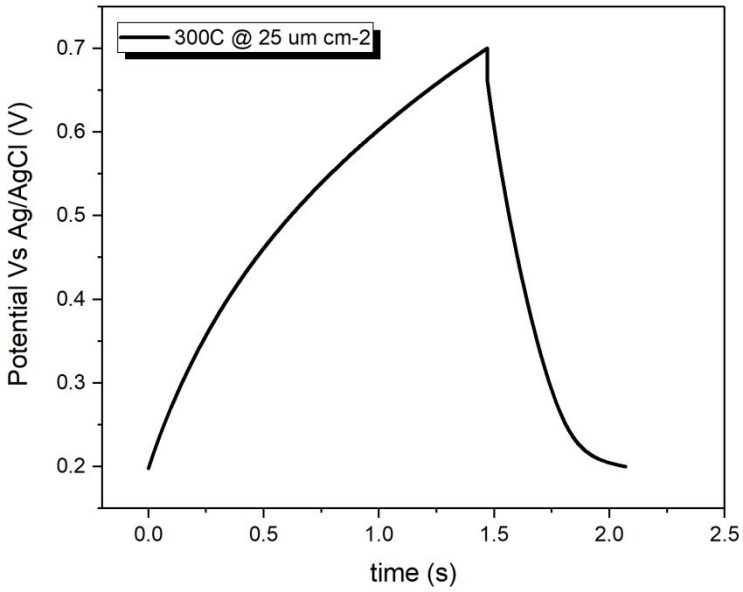

Figure S6. *GCD curve of 300°C sample with readjusted voltage window of 0.2 – 0.7 V.*

Figure S6 shows the GCD result of 300°C sample with readjusted voltage window that was attainable at 25 uA cm^{-2}. Despite the small current density, the maximum set voltage is reached in just 1.5s, while the discharging curve is highly unsymmetrical which discharges in about 0.5s.

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