Epitaxial Growth of Hyper-branched Cu/Cu₂O/CuO Core-Shell Nanowire Heterostructures for Lithium-Ion Battery

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ABSTRACT

A scrupulous design of nano-architectures and smart hybridization of expected active materials can lead to more advanced properties. Here we engineered a novel hierarchical branching Cu/Cu₂O/CuO hetero-nanostructure by combining a facile hydrothermal method and subsequent control oxidation process. The fine structures and epitaxial relationship between the branches and backbone are investigated by high-resolution transmission electron microscopy. Moreover, the evolution of the branches growth has also been revealed gradually during the oxidation of Cu nanowire surface. The experimental results suggest that the surface oxidation needs to be performed via a two-step exposure process with various humilities in order to achieve optimized formation of core-shell structural branching architecture. Finally, a proof-of-concept of the function of such a hierarchical framework as anode design alternatives in lithium-ion batteries is demonstrated. The branching core-shell heterostructure improve battery performance by means of (i) epitaxial grown branches provide high surface area for enhanced electrolyte accessibility and high resistance to volume change induced by Li⁺ intercalation/extraction as well, (ii) core-shell structure with well-defined heterojunction increases contact area which facilitates effective charge transport during lithiation and (iii) copper core acts as current collectors as well as structural reinforcements.

1 Introduction

Branched nanowires (NWs) have recently been of

great scientific and technological interests in energy conversion and storage due to their unique properties from the interesting combination of the primary one dimensional (1D) structure and

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secondary attaching structures [1]. Moreover, well-controlled variations in the composition of NW backbone and branches could further generate a huge amount of homogenous/heterogeneous junctions to gain the novel functions and promoted performance which cannot be realized from each of the components separately [2-5]. For high performance Li ion batteries (LIBs), such 1D heterostructured nanomaterials with hierarchical architecture play the more and more important role in particular, because of: (1) 1D NW backbone provide short path lengths for electronic and Li^+ transport to facilitate higher charge/discharge rates [6]; (2) The increased surface area of three-dimensional (3D) branched NW structures offers adequate surface for the active materials, which allows easy access of Li^+ [7]; (3) The volume change induced by charging-discharging processes could be minimized and sustained when the branched structure serves as an elastic buffer [8]. To date, much ongoing efforts have been intensively devoted to the rational synthesis of branched heterostructure NWs from post-growth strategy involving vapor-phase deposition [9-11], sol-flame techniques [12], and electro-deposition [13] *etc.* Apart from expensive apparatus for high vacuum and heating temperature, the previously reported approaches generally increase complexity in synthetic procedures, limit large-scale production and also lack flexibility in structural control on the products. Therefore, the economic, mild, and controllable alternative to decorate an integrated smart architecture with enhanced conductivity and stability for guaranteeing fast charge/discharge and subdued agglomeration required in superb LIBs still remains a significant challenge. Meanwhile, further illustration on the growth of the 1D branched structures and the influence of the different crystal components is also desirable to understand the relations between materials structures and resulted performance.

In this research article, we successfully prepared 3D high-density hierarchical branching $\text{Cu/Cu}_2\text{O/CuO}$ NWs with gram-scale by combining a facile hydrothermal process and subsequent

oxidation treatment under mild conditions. The heterostructure obtained here includes 1D highly conductive Cu NWs core as the structural support as well as built-in current collector to promote effective charge transport. The secondary two-dimensional (2D) nanosheets (NSs) grow epitaxially on the NW backbone as the medium to react with Li^+ . The interior multi-shelled heterostructure with minimized lattice fringe distortion ensures smooth interfacial electronic transmission between external branched NSs and NW core. Benefiting from these unique features, the function of obtained nanostructure as LIBs anode exhibits decent performance in term of capacity and cycling.

2 Experimental Section

Sample Synthesis: All chemicals were of reagent grade quality and were used as received from a commercial source (Sigma-Aldrich). In a typical synthesis, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.44 g) and NaOH (85.65 g) were dissolved in deionized water (250 mL). Afterwards the resulting solution was transferred to 400 mL conical flask and heated to 80 °C in an oil-bath. Then 2.14 mL ethylenediamine (EDA) and 0.18 mL hydrazine (N_2H_4) were quickly injected into the mixture. After 1 hr reaction, the color of the solution changed from dark blue to reddish, indicating the formation of the Cu NWs. The obtained Cu NWs were purified by three rounds of centrifugation/re-dispersion in ethanol and deionized water respectively prior to oxidation process. Subsequently, the $\text{Cu/Cu}_2\text{O/CuO}$ hierarchical structures were prepared by successive 55 min dry air (<5 % humidity) exposure and 545 min wet air exposure (70-80 % humidity) in a compact tube furnace (Nabertherm GmbH) equipped with manual gas supply system. In order to precisely control the heating time, gradual heating and cooling were avoided. When the temperature inside the chamber got stabilized at 60 °C the samples were introduced and then immediately taken out after achieving the required duration time.

Characterization: The samples were characterized by X-ray diffraction (XRD, PAN alytical D/max-III A with Cu K α radiation, $\lambda=1.5406$ Å), scanning electron microscopy (FEI.Co Sirion 200) equipped with energy dispersive X-ray spectroscopy (EDS), and high resolution transmission electron microscopy (HRTEM, JEOL/200-kV). XPS and X-ray induced Cu LMM Auger spectra were used to assess the chemical state and surface composition of the samples. An XPS analysis was carried out in a JPS-9010MC (Japan) with monochromatic X-ray generated from Al K α (200 W). The pressure in the analysis chamber was approximately 5×10^{-10} Torr, and the pass energy constant was 20 eV for the high resolution scans. Electrochemical characterizations were carried out using standard two-electrode coin-cell configuration (CR 2032). The composite electrodes were prepared by mixing active material (Cu/Cu₂O/CuO-NS-NWs

or Cu/Cu₂O/CuO-NWs), acetylene black, and binder (PVDF) with a weight ratio of 8:1:1 (the areal mass loading of the active materials is better in the range of 1.1-1.5 mg/mm²). The above prepared nanowire mesh films were pressed on a copper foil (disk electrode with diameter of 14 mm) current collector and dried at 100 °C for 12 hrs before conducting cell assembly in an Ar filled glove box (MIKROUNA super, H₂O<0.1 ppm, O₂<0.1 ppm). The electrodes were separated by a Celgard polypropylene membrane. A mixture of 1 M LiPF₆ in ethylene carbonate, dimethyl carbonate and diethyl carbonate (EC/DMC/DEC, 1:1:1 v/v/v) was used as the electrolyte solution. Cyclic voltammetric (CV) measurements of the electrodes were carried out on a PARSTAT4000 (AMETEK, Inc.) electrochemical potentiostats at a scan rate of 2 mVs⁻¹ between 0.02~3 V. Galvanostatic cycling performances were recorded

Figure 1. a) Schematic illustration of triplex Cu/Cu₂O/CuO NS-NW evolution and corresponding SEM images for morphology evolution. Scale bars, 100 nm. b) XPS Cu 2p and c) O 1s spectra of the sample series obtained at different stages.

at constant current mode between 0.005 and 3 V vs. Li at the given current density using a LAND battery testing system.

3 Results and Discussion

3.1 Epitaxial Growth and Illustration of Cu/Cu₂O/CuO NS-NWs.

Figure 1a illustrates the process of hyper-branched NW architectures developed in this work, which will be abbreviated as Cu/Cu₂O/CuO NS-NW. Cu NWs were first produced by the hydrothermal method in alkaline aqueous solution then purified in deionized water and ethanol to remove surface coating. The NWs were subsequently exposed to dry air (60 °C, <10 % humidity) and wet air (60 °C, 75-80% humidity) respectively with certain durations. NSs grew in the NW matrix and their densities increased gradually during this ageing process. A morphological evolution during the post-processing was collected as a function of the exposure time, as shown in corresponding SEM images. It can be seen that after the initial 55 min oxidation in dry air, there were no visible branches formed on the surface of bare Cu NWs. However, after another 155 min growth in wet air at the same temperature, small burrs with the thickness of 10 nm nucleated on the surfaces of the NWs were observed, indicating the tendency of anisotropic growth. When the reaction time was prolonged to 5 h, the earlier formed nano-burrs elongated, establishing the rudiments of NSs. By further increasing the reaction time to more than 7 h, the NWs are decorated with a high coverage density of NSs fanning radially outward from the NW axes. X-ray photoelectron spectroscopy (XPS) also revealed the phase transmutation of NW surface composition. Detailed scans of the Cu 2p range are illustrated in Figure 1b. For NW samples obtained after dry air exposure treatment, only CuI (2p_{1/2}) and CuI (2p_{3/2}) peaks are observed at 952.5 and 932.3 eV, respectively. For the NWs treated via continuing moist oxidation, with the reaction time increasing, the Cu 2p_{1/2} and Cu 2p_{3/2} peaks moved towards 953.8 and 933.8 eV respectively. Moreover, their satellites centering at 942.4 eV and 961.3 eV which has been usually

encountered within CuO are also present in final samples, in accordance with the electronic state of Cu²⁺ [14]. This observation has been further confirmed by O 1s spectra (Figure 1c), where O 1s signal was shifted gradually from 528.9 eV to 530.3 eV during the process of construction ripening, as expected, indicating the cleanliness of the CuO surface.

To find out the structure evolution and crystal growth, the as-obtained branched NW heterostructure, in particular, the crystal interface were further investigated in detail by using TEM and HRTEM. Figure 2a presents the overall morphology of the NW after 55 min arid oxidation. The inter-planar spacing 3.01 and 2.49 Å match well with those for (110) planes of fcc Cu and (110) planes of cubic Cu₂O, respectively. The resulting Cu₂O-Cu interface is relatively flat due to the coordinated deposition of the oxide. The moiré fringe contrast in this image can also be distinctly observed, which is formed as a result of interference between diffracted beams from an overlapping Cu₂O lattice and the underlying Cu background lattice. This scene implies the continuous exptaxial growth of the Cu₂O (110) plane from the Cu surface. As corroborating evidence, we found in fast Fourier transform (FFT) patterns that two sets of diffraction spots can be indexed with the strong reflections from the Cu substrate and Cu₂O overlayer with the epitaxial relations. Generally, the lattice constant of an oxide is significantly larger than that of the metal. The natural lattice misfit, between Cu and Cu₂O is 15.3 %, leading to large lattice strain. However, the crystallographically aligned oxide formation occurs only when lattice strain is small enough for energetically feasible hetero-epitaxial growth. In this case, the bi-layer would be in a local minimum energy state if the mth atom of the overgrowth coincides with the nth atom of the substrate surface layer [15-19]. For moiré fringes generated by two sets of planes across an interface with spacing d₁=d₂₂₀(Cu₂O) and d₂=d₂₂₀(Cu), the number of plane n of spacing d₂ between the moiré repeat is given by n=d₂/(d₁-d₂) [20]. As revealed in constructed inverse FFT image of Figure 2a, each repeat of the moiré fringes contains 6 Cu {220} planes

Figure 2. TEM/HRTEM observations of the epitaxial growth of NSs, and each panel involves low-resolution TEM image (scale bars: 50 nm), HRTEM image of as-grown nanostructure (scale bars: 5 nm), FFT patterns from white dashed rectangular areas and corresponding partial lattice-resolved constructed inverse FFT image: a) Cu@Cu₂O core-shell NW structure taken after 55 min exposure; b) The earlier formed thin branch elongated after 210 min exposure; c) NW backbone surrounded by Cu₂O/CuO NSs with radial orientation after 420 min exposure.

($d_2=1.275\text{\AA}$). This yields a Cu₂O {220} d-spacing of $d_1=1.487\text{\AA}$. Thus the number of {220} planes of Cu₂O in a moiré repeat is calculated as $m=nd_2/d_1$, which is

5. This means that every 5 {220} planes in the Cu₂O overlayer match 6 {220} planes of the Cu substrate, thereby experiencing a significantly reduced strain of

1.43 %. Accordingly, the overlayer will tolerate a strain which is significantly smaller than the natural misfit between Cu_2O and Cu. In order to clearly reveal the interface between Cu core and Cu_2O shell, the square region in constructed inverse FFT image was reconstructed along (110) plane orientation (Figure S1). As expected, it is apparent that the lattice fringes of Cu_2O nanocrystals linked smoothly with that of Cu NW core with no obvious defects, which affirms the Cu_2O nanocrystal epitaxially grew on the Cu core. Ultimately, volume mismatch between the oxide layer and the metal NW substrate can be efficiently suppressed to keep the structural stable and relative robust for subsequent hetero-epitaxial growth, thereby guaranteeing the formation of high quality tunnel junctions.

However, the above observed smooth surface of as-grown $\text{Cu@Cu}_2\text{O}$ coaxial NW indicates that the crystal growth at the radial direction of the NW (in the (110) plane) is kinetically hindered in dry air atmosphere. It has been known that the nucleation at the pristine surface of NWs may need to overcome a larger energy barrier, caused by a close-to perfect atomic arrangement that provides fewer nucleation sites. In early trials, we found that using the NWs exposed to dry air in the absent of moisture only produces core-shell NWs consisting of a crystalline core NW coated by oxides shell (i.e., $\text{Cu@Cu}_2\text{O@CuO}$ NWs, Figure S2). In contrast, using the monotonous moist air treatment gives rise to a growth of NSs along the radial direction of the NW, but exhibiting tubular structure owing to the Kirkendall effect (see supporting information, Figure S3). It seems that the mobility of copper atoms from NW during dry air treatment is much lower than that during wet air treatment and the presence of moisture could significantly modify the NW surface properties (e.g., defects, surface energy and strain energy) to overcome the kinetic hindrance for realizing the epitaxial growth of NSs at the radial direction of NWs. Hence we performed the synthesis of heterostructures using two-step process that was designed to introduce different degrees of humidity (all other conditions remain un-changed).

After introducing moisture, the longitudinal

surface diffusion coefficient of O atoms will be reduced and the presence of the oxygen/water species on the surface mostly acting as obstacles for the metal migration along the NW axis. The separated Cu_2O nuclei on the surface will tend to minimize the surface energy via agglomeration of metal and oxygen/water species. These nuclei will preferentially expand perpendicularly to the surface leading to the formation of intermittent islands instead of a dense continuous layer. Notably, with time prolonging (210 min), the continued anisotropic growth of the oxide layer leads to its propagation into the exterior space, as seen from Figure 2b. The measured lattice spacing of 3.01 Å, 2.45 Å and 2.11 Å in this region corresponds to the (110), (111) and (002) inter-planar distances of cubic Cu_2O , respectively. Additionally, the (002) planes of Cu_2O NS stack parallel to the (002) ones of Cu NW core, implying that the branches epitaxially grow along the normal direction of (002) Cu_2O planes on the (002) basal planes of the Cu. For both Cu_2O and Cu with cubic structure ($a_0=b_0=c_0$) (see FFT patterns b1, b2), the Cu_2O (002) plane and Cu [002] direction are perpendicular. Thus the growth direction of the Cu_2O branch, determined to be [002], is perpendicular to the backbone [110] growth direction. This is in accordance with observed 90° angle between the NS and the NW. As the oxidation degree becoming more serious with longer exposure time (420 min), the NSs grew up in the NW matrix and their densities increased gradually (Figure 2c). The lattice-resolved HRTEM on NS branch area (region α) as indicated by red arrow clearly shows the different lattice spacing of 0.252 nm, 0.232 nm and 0.255 nm that correspond to the (11 $\bar{1}$), (111) and (002) planes of CuO , respectively. This is in accordance with the selected area FFT patterns (region c1 and c2), in which the diffraction spots can be indexed with the strong reflections from the monoclinic CuO crystals. Structural analysis of the crystallographic connection between the NS and NW (region β) shows lattice planes (i.e., (110) and (002) Cu_2O planes) still nicely extend from the isolated branch to the local thin crystalline shell of the backbone, which is again similar to the scene at the heterojunction between standalone Cu_2O burrs and Cu NW backbone in

Figure 2b and matches our expectation for the epitaxial growth of $\text{Cu}_2\text{O}/\text{CuO}$ NSs. FFT patterns obtained from this junction area (region c3, c4) also demonstrate duplex diffraction spots caused by superimposition between CuO outer layer and Cu_2O base, suggesting that the branch basal plane possess transitional state from CuO to Cu_2O . Furthermore, in HRTEM image of another joint area between branch and backbone (region γ), it can be distinctly found that the Cu_2O (002) planes of branch stack parallel to the Cu_2O (002) ones of junction and surface layer of NW without showing any obvious structural defects or interface. The observation of Cu_2O (110) planes extend from the adjacent and access directly into the branch further confirm the Cu_2O branch grows epitaxially from the crystallographic planes of the NW backbone that lie in the [002] zone axis. More evidence can be supported by FFT patterns. The two white dashed squares (region c5, c6) denote the two areas (branch and junction) we performed FFT, both resulting in identical patterns. Significantly, along the (110) plane oriented direction, the inverse FFT image (Figure S4) of selected junction area exhibits the negligible lattice mismatch because of its single component, allowing epitaxial growth throughout

the entire structure with minimal formation of structural defects. In region δ , the selected inverse FFT image from HRTEM negative shows that most of the lattice fringes are smooth and continuous across the $\text{Cu}/\text{Cu}_2\text{O}$ interface, and that no obvious distortion derived from lattice mismatch exist at the heterostructure boundary in the marked area. The FFT patterns of region c7 and c8 also indicate the growth direction of the Cu_2O stratum still remains intact, which is consistent with previous inspections in Figure 2a. This result reveals that the surface protection from re-oxidation could retain the smooth interface after oxidation under humid conditions. Therefore, the as-made structure obtained via two-step treatment is very promising for enabling excellent charge separation and consequent transition with minimal minority obstruction.

In addition to the observation of 90° angle between the branch and backbone, when extending duration time to 600 min, more and more NSs could also attached on the NW in an angle of $\text{ca. } 62^\circ \pm 2^\circ$, as displayed in Figure 3a. The lattice-resolved HRTEM images of the $\text{CuO}/\text{Cu}_2\text{O}$ interfacial area (as induced by white rectangular region) within NW backbone clearly suggest that the (110) CuO planes and

Figure 3. a) TEM image of Mature hyper-branched NS-NW heterostructures obtained after 600 min exposure, showing multiple branches grown on the backbones with 90° and $62^\circ \pm 2^\circ$ angles between the branches and the backbone, scale bar, 100 nm. b) HRTEM image of the square area, displaying $\text{Cu}_2\text{O}/\text{CuO}$ interface, scale bar, 5 nm, the right column insets are corresponding FFT patterns from selected regions and inverse TEM image of panel b. c) Schematics of the interface of the (110) CuO plane and the (110) Cu_2O plane and d) constructed inverse FFT image along the (110) plane direction, respectively.

(110)Cu₂O planes are not parallel but tilted at an angle of approximately 64°, which is equal to $\pm(10\bar{1})$ CuO planes (Figure 3b). As schematically illustrated in Figure 3c, parallel growth along the (110)Cu₂O planes would result in a lattice mismatch as large as 10 %. Instead, when the branches grow slantwise, the interfacial lattice mismatch can be dramatically reduced to 0.13 %. It implied the epitaxial growth on the single crystal Cu₂O 110 surface with an inclined angle (e.g., 64°) would be more favorable than the parallel growth which will generate less lattice distortion and strain force at the interface. Significantly, the inclined connection mode between Cu₂O and CuO lattices leads to a less-defective and abrupt interface, as revealed in right bottom inset of Figure 3d, which is beneficial to the transfer of the charge carriers within the NWs. Similar reasoning on the epitaxial relationship of the nano-heterostructures has also been reported in other work [9, 21, 22]. In addition to the observed oblique NS branches, the oxide also thickens via nucleation of new layers, dominated by the outward diffusion of metal ions through the oxide layer and the inward diffusion of oxygen [23, 24]. Consequently, it results in inward migration of the Cu₂O-Cu interface, while preserving unchanged smooth heterogeneous boundary throughout the entire NW (Figure S5). Thus, a structure with Cu/Cu₂O/CuO coaxial core-shell structured NW backbone embedded with high-density CuO or CuO/Cu₂O NSs was synthesized.

To verify the overall crystal structure and phase purity, powder X-ray diffraction (XRD) patterns of the final products were recorded, as seen in Figure 4. The peaks located at 43.3°, 50.4° and 74.1° (marked with ▲) correspond to (111), (200) and (220) diffraction of pre-grown cubic phase Cu NW backbone ($a=3.615\text{Å}$ JCPDS No. 85-1326). Diffraction peaks located at 29.5°, 36.4°, 42.3°, 52.5°, 61.4°, 65.6° and 73.5° (marked by ■) can be attributed to (110), (111), (200), (211), (220), (221) and (311) faces of cubic Cu₂O with lattice constant $a=4.267\text{Å}$ (JCPDS No. 78-2076). And the rest diffraction peaks (marked by ●) can be indexed as (110), (002), (111), (112), (202), (020), (202), (311) and (220) faces of monoclinic CuO

Figure 4. XRD pattern of as-prepared product.

with lattice constant $a=4.684\text{Å}$, $b=3.425\text{Å}$ and $c=5.129\text{Å}$, which are in good agreement with JCPDS No. 05-0661. The results indicate that oxidation of Cu NWs by two-step air exposure leads to the formation of CuO/Cu₂O/Cu composite architecture.

Figure 5a shows a typical SEM perspective of the as-grown samples. It demonstrates that the products exhibit hierarchical structures with multiple secondary NSs grown on the major NW backbones (average diameter of 120 nm, length up to ~5 μm) in a random fashion. These on-wire NSs show a sliced cone structures. The thickness of the NSs varies in a con-fined range from several to tens of nanometers, while the length/width ratios of those NSs look similar which indicate a uniform formation during the crystal evolution. Inset of Figure 5a shows the scene viewed from the ridge of an individual NW, demonstrating rugged morphology with high-density NSs that are aligned on the surface of NW backbone. The TEM image in Figure 5b also reveals that the branches densely and uniformly cover the surface of the NW with a sharp tip and a wide bottom (ca. 20 nm wide) at the joint regions. In addition, a clear contrast variation at the nanostructure suggests that the plumpness of materials is varied from the core NW to the branched shell (Figure 5c). To investigate the elemental composition throughout the heterostructures, a detailed chemical analysis was carried out by using Energy Dispersive Spectroscopy (EDS). Figure 5d

Figure 5. a) Typical SEM image (scale bar: 1 μm), inset shows the close magnification of two overlapping branched NWs (NS-NWs), scale bar is 100 nm. b) TEM observation of prepared samples (scale bar: 1 μm) and c) a single NS-NW (scale bar: 100 nm), inset of panel c is corresponding SAED pattern. d) EDS point scanning data from the three regions of the NS-NW. Scale bar: 100 nm. Al signals generated from the Al substrate. e, f) the Cu, O elemental distribution across the axis of the heterostructures.

shows the quantitative chemical compositions performed by EDS point scanning via using e-beam on three different regions specified in STEM image (Figure 5e). In the region (1), Cu peaks are dominant while the O peak intensity is negligible. The Cu and O are present in the expected stoichiometric ratio (At% Cu > 90.3; At% O < 9.7). Similar energy spectra were consistently observed on every randomly selected spot along the axis of NW backbone. The EDS data from the region (2) reveals that a state of $\text{Cu}_x\text{O}_{1-x}$ ($x=0.68$) is obtained due to the inter-diffusion of Cu and O. In the branch region (3), stoichiometric composition of Cu and O was detected (At% Cu = 48.4;

At% O = 51.6). The chemical composition profile of Cu and O conducted as a function of distance, across the backbone along the length of the branch is depicted in Figure 5f. The O/Cu stoichiometric ratio firstly held steady at approximately 1:1 in the branch region involving the surface area of NW backbone (first 37 nm and last 40 nm regions), then gradually decreased to around 0.5:1 towards the inside (40–63 nm and 115–140 nm position) and 0.1:1 near the core region (ca. 40 nm thickness). This result confirms that such branched NWs are also be constructed by core-shell structure, with various certain levels of inter-diffusion of Cu and O.

Figure 6. a, b) Typical galvanostatic charge–discharge curves of Cu/Cu₂O/CuO NS-NW and Cu/Cu₂O/CuO NW cells at the current density of 100 mA g^{−1} between 0.005–3 V vs. Li, respectively. c) Cyclic voltammograms (CV) of Cu/Cu₂O/CuO NS-NW cell cycled between 0.02–3 V vs. Li at a scan rate of 2 mV s^{−1}. d) Cycling performances of Cu/Cu₂O/CuO NS-NW (black) and Cu/Cu₂O/CuO NW cells (red). Inset: Corresponding TEM images of triplex components NS-NW (black framed) and NW (red framed). e) Representative charge and discharge voltage profiles of Cu/Cu₂O/CuO NS-NW cell at various current densities. f) Capacity retention of Cu/Cu₂O/CuO NS-NW (black) and Cu/Cu₂O/CuO NW cells at various current rates.

3.2 Function as Lithium-Ion Battery Anode.

With the nanostructures successfully produced, our next goal was to identify its performing for the function as a LIBs anode material. As a reference we also include the triplex NWs without hierarchical branching structure (i.e., Cu/Cu₂O/CuO NWs) in some tests to prove superior of the as-suggest structures. Galvanostatic charge–discharge studies of

Cu/Cu₂O/CuO NS-NWs and Cu/Cu₂O/CuO NWs cells in ambient temperature conditions (25 °C) were conducted between 0.005 and 3 V vs. Li at the constant current density of 100 mA g^{−1} as presented in Figure 6a and b. It can be seen that both of their initial discharge capacities are over 900 mAh g^{−1}, which is higher than the theoretical capacity of CuO (674 mAh g^{−1}) and Cu₂O (375 mAh g^{−1}). This is mainly attributed to the formation of solid electrolyte

interphase (SEI) resulting from irreversible electrolyte decomposition [25–27]. Simultaneously, electrode exhibits three discharge plateaus of 2.25–1.85 V, 1.25–1.05 V and 0.80–0.01 V in the first discharge process, which corresponds to a multi-step reductive reaction from CuO to intermediate composite copper oxide phase ($\text{Cu}^{1-x}\text{Cu}^0\text{O}_{1-x/2}$, $0 \leq x \leq 0.4$), to Cu_2O and further decomposition into Cu and Li_2O , respectively [28, 29]. In the subsequent 50 cycles, the shapes of the discharge curves do not change significantly, indicating good capacity retention. However, the three discharge plateaus narrow down, compared with the first discharge curve. The differences can be ascribed to the activation of the battery, wherein the electrode has not been fully infiltrated by electrolyte yet during the initial discharge process [30]. The shape of charge curve also reveals no distinct variation after the 50th cycle, exhibiting a sloping potential range from 1.0 to 2.5 V, which is relevant to the decomposition of the SEI and the oxidation of Cu [31]. To better understand the conversion process during cycling, cyclic voltammetry (CV) measurements were then carried out with a potential range of 0.02–3V vs. Li at a scan rate of 2 mVs^{-1} . As shown in Figure 6c, the first scan curve differed significantly from subsequent three cycles. In the 1st cathodic scan, there are three peaks located at 2.16 V, 1.18 V and 0.65 V, respectively. The peak at 2.16 V vs. Li corresponds to the solid solution formation (Li_xCuO) [29, 32]. Another two sharp peaks around ~ 1.18 and ~ 0.65 V vs. Li are associated with the generation of Cu_2O , following further reduction into Cu^0 and amorphous Li_2O [29]. In the anodic scan, broader oxidation potential from 1.0 to 2.0 V is indexed to the oxidation of the SEI layer, while a strong oxidation peak near 2.4 V vs. Li can be ascribed to the formation of Cu_2O and oxidation of Cu_2O into CuO as well [33]. In the subsequent cycles, individual peak intensity and integral are decreased along with scan number, which suggests the initial capacity was lost in continuous way during the first few cycles. Furthermore, the cathodic peaks are observed to shift toward higher voltages likely 1.24 and 2.20 V vs. Li with a slow intensity decrease. Additionally, there is no substantial change can be found in the anodic

peak potentials. These results are all in good agreement with the discharge curves, effectively monitoring the minute electrochemical reactions associated with the Cu/ Cu_2O /CuO NS-NWs system. Figure 6d depicts the comparative cycling performance of the Cu/ Cu_2O /CuO-NS-NWs and Cu/ Cu_2O /CuO-NWs cell up to 50 cycles. It is apparent to notice that, the Cu/ Cu_2O /CuO-NS-NWs cell exhibited a stable cycling profile up to 8 cycles tested at constant current density of 100 mAg^{-1} . The cell delivered discharge capacity of 345 mAhg^{-1} after 50 cycles, which is almost triple the cell assembled with Cu/ Cu_2O /CuO-NWs (122 mAhg^{-1}). And its capacity fading is noted approximately 0.21 mAhg^{-1} per cycle with capacity retention of 71% after 50 cycles. This irreversible loss (29%) is much lower than that of Cu/ Cu_2O /CuO-NWs cell (65.5%). In addition, as-observed cycling profiles of NS-NWs in this work are also better than most of the literature values of CuO nanostructures either in native or composite form reported elsewhere, as described in table S1 (ESI). The improved cycling stability with high capacity preliminarily manifests the superiority of the branched NW anodes. Coulombic efficiency (CE) is another important consideration. The first cycle CE (76.9%) (85%) of Cu/ Cu_2O /CuO NS-NWs were not as high as expected since the initial SEI formation consumes some of the electrolyte. The CE can be improved (>95%) by prelithiation in future studies. As shown in Figure S5 (supporting information), high CE (>95%) of both electrodes were achieved in the following cycles due to the stable SEI formed.

To study the electrochemical performances of Cu/ Cu_2O /CuO NS-NWs at high current densities, a duplicate cell was assembled. Figure 6e shows the discharge and charge curves of electrode at various current densities from 100 mAg^{-1} to 10 Ag^{-1} . Along with the increase of current densities, the discharge potential decreased and the charge potential increased due to kinetic effects of the material. As shown in the plot of capacity versus cycle number at various current densities in Figure 7e, the 10th-cycle discharge capacity retention is gradually reduced to 66.2%, 50.1%, 40.1%, 31.3%, 17.8% and 11.4% at

Figure 7. Electrochemical impedance spectroscopy of Cu/Cu₂O/CuO NS-NWs and Cu/Cu₂O/CuO NWs anodes.

current densities of 200 mA g⁻¹, 500 mA g⁻¹, 1 Ag⁻¹, 2 Ag⁻¹, 5 Ag⁻¹, and 10 Ag⁻¹, respectively. Even after cycling at various current densities up to 10 Ag⁻¹, the 10th-cycle discharge capacity was able to return 332 mAh g⁻¹ (96.2% of initial reversible value) when the current density was reduced to 100 mA g⁻¹ again. Figure 6f also represents the cycling performance of Cu/Cu₂O/CuO-NWs structure as a comparison. The most important observation is the difference in the specific capacity, cycling stability, and rate capability in both cases. It is obvious that the Cu/Cu₂O/CuO NS-NWs structure is showing both higher specific capacity and cycling efficiency for all charge discharge current densities compared with Cu/Cu₂O/CuO NWs structure. Also, the cell performance was dropped to very low values for the Cu/Cu₂O/CuO NWs system when cycled at high current densities. However, the Cu/Cu₂O/CuO NS-NWs structure showed excellent capacity (65.3 mAh g⁻¹) and stability even when cycled at a very high current density of 10 Ag⁻¹. This outcome demonstrates the superior rate capability of branched Cu/Cu₂O/CuO NS-NWs, which is a very important finding that can be considered as enlightenment in anode material design for obtaining high power rate with long cycle lifetime. Most of the previous studies involving Cu_xO nanostructures have reported very fast decay in capacity (as shown in table S2, ESI) even at relative low cycling rates (<4 Ag⁻¹) which has been attributed to the structure collapse and exfoliation process happening in active component of cells [34, 35] This improved rate capability could first stem

from the presence of the robust Cu core support, and then the outside branches with their affiliated free spaces. Both two acts as physical buffering cushions against the intrinsic large volume change during alloying/dealloying, significantly suppressing the pulverization of architecture. In addition, the branches can also reduce the aggregation of NWs, which ensures a high utilization of electrode materials, and, thus, a high capacity density. In contrast, for the case without secondary branches, the Cu/Cu₂O/CuO NWs would be easily agglomerated and damaged after several cycles. That morphological degradation was accompanied by capacity decrease, further confirming that maintaining a highly conductive core in its intact form is the key to the high stability. The impedance spectrum of the both measured cells after the 10th cycle has also been tested, with amplitude of 5 mV vs. the open circuit potential at a frequency range of 0.01 Hz-100 kHz (Figure 7). Comparing to Cu/Cu₂O/CuO NWs anode, the anode made of Cu/Cu₂O/CuO NS-NWs exhibit smaller semicircles in the high and middle frequency regions, suggesting faster Li⁺ diffusion rates and smaller variation of diffusion paths. As the epitaxial growth analysis above, we suggest the formation of high-quality junctions between NW core and branches sheath with short carrier transport path (less than 100 nm) plays a positive role in reducing the contact resistance of CuO/Cu₂O/Cu and facilitating effective electron transfer from CuO to Cu. Equally important, the three dimensional structure of NS-NW also provided more active sites and easy accessibility for electrolyte, which led to the remarkable decrease in charge transfer resistance. Over all, these results confirm the success of our rational design of integrating the composite in a unique core-shell hierarchical branching structure, while also providing simple chemical synthesis for obtaining highly performing compounds as battery electrode materials.

4 Conclusions

In summary, we have presented a facile and high-efficiency strategy for the growth of hierarchical branching Cu@Cu₂O@CuO NWs. The uniqueness of

the structure is that, the Cu NW core is coated with Cu₂O interlayer and CuO shell including branched 2D NSs epitaxially growing on 1D NWs surface. The investigation on the structure evolution of the branched NWs indicated that the lattice mismatch at the interface played an important role in determining the growth of branches and resulted in the varied preferential growth directions. Evidently, the formation of Cu@Cu₂O@CuO NS-NWs remarkably enhanced Li⁺ storage capacity and stability, with a high reversibility at high current densities. The improvement could be ascribed to a synergetic effect between NW backbone and secondary on-wire branches as well as the less-defective homogenous/heterogeneous junctions which facilitates effective charge transfer. We believe the design ideas reported here may potentially be expanded to other high-capacity metal oxide anode material system for electrochemical energy storage.

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Electronic Supplementary Material: Supplementary material (additional SEM images, TEM/HRTEM images, and comparison of various Cu_xO based nanostructures rate capacity performances as anode for LIBs) is available in the online version of this article at http://dx.doi.org/10.1007/s12274-***-****- (automatically inserted by the publisher).

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Epitaxial growth of hyper-branched Cu/Cu₂O/CuO core-shell nanowire heterostructures for lithium-ion battery

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The epitaxial growth of Cu/Cu₂O/CuO branched nanowires was investigated and its function as anode materials in Li-ion battery demonstrates the superb performance.