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To cite this article: Jun Lu, Ahmed Zainelabdin, Saima Zaman, Gul Amin, Omer Nur, Magnus Willander & Lars Hultman (2013) Nanowires-assembled CuO Interpenetrated-leaf Architecture by () Twinning, Materials Research Letters, 1:1, 32-38, DOI: [10.1080/21663831.2012.749814](https://doi.org/10.1080/21663831.2012.749814)

To link to this article: <https://doi.org/10.1080/21663831.2012.749814>



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Published online: 07 Dec 2012.



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Nanowires-assembled CuO Interpenetrated-leaf Architecture by $(10\bar{1})$ Twinning

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(Received 13 September 2012; final form 8 November 2012)

High-resolution transmission electron microscopy characterization demonstrates that the petal-like complex three-dimensional (3D) CuO nanomaterial produced by self-assembly in low-temperature wet-chemical synthesis has a unique interpenetrated-leaf structure. The primary leaf consisting of semi-coherent CuO nanocrystallites was formed by bundling, coalescence, and hydrolysis of amorphous $\text{Cu}(\text{OH})_2$ nanowires. The petal-like CuO was constructed by growing the secondary leaf on the primary one with a twin relationship $(10\bar{1})[010]_p // (10\bar{1})[0\bar{1}0]_s$ between them and the twin axis is $[101]$. The co-axis $\langle 010 \rangle$ of leaves is the growth orientation. The 3D complex nanostructure is different from normal low-dimensional nanostructures, e.g. nanorods, nanorings, regarding the formation mechanism and inherent structure.

Keywords: Interpenetrated Architecture, CuO, HRTEM, Nanowire and Twin Structure

Assembly-based growth of nanocrystallites in solution at low temperature is an attractive materials synthesis method [1,2]. Examples of ordered nanostructures synthesized by spontaneous self-assembling of nanocrystallites are silver nano-prisms grown from silver nano particles [3], spontaneous aggregation of $\text{Fe}(\text{OH})_3$ grown into defective single-crystals [4], CdTe [5], and CuO [6,7]. The nanostructure growth depends on the material crystal structural properties. For example, the CuO monoclinic structure is anisotropic with respect to the surface energy. The (001) plane with the maximum atomic number density has the lowest surface energy and is consequently easy to form, whereas the (010) plane with the lowest surface atomic number and highest surface energy is the most unstable [8–10]. Because of this anisotropy, various CuO nanostructures were grown [10–12]. These usually assemble in the same orientation and form low-dimensional structures, but high-dimensional nanostructures with complex architecture are less explored. In the present work, we show a self-assembled petal-like three-dimensional (3D) CuO structure synthesized by a low-temperature wet-chemical method using copper nitride. A high-resolution

transmission electron microscopy (HRTEM) is used to reveal the formation mechanism of this unique structure.

Copper oxide particles were grown on a glass substrate by a wet-chemical method. In the typical procedure, 5 mM of $[\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}]$ was dissolved in deionized water under vigorous stirring. About 2 ml of NaOH solution was added to the precursor solution. The glass substrate was ultrasonically cleaned sequentially in isopropanol and acetone followed by distilled water, and dried using nitrogen blow. The precursor solution was then transferred to a laboratory furnace held at 90°C for 4–5 h to grow CuO nanostructures and for 15–60 min to obtain nucleus of β -shaped grains. A single-phase CuO film was deposited on the glass substrate. The morphology of the deposited material was observed by scanning electron microscopy (SEM) with a Zeiss LEO 1550 instrument. The transmission electron microscopy (TEM) analysis was carried out in an FEI Tecnai G2 field emission gun instrument operated at 200 kV with 1.9 Å point resolution. The microstructure was analyzed by selected area electron diffraction (SAED) and HRTEM, respectively. The TEM powder specimen was prepared by collecting the nano materials from the film grown on

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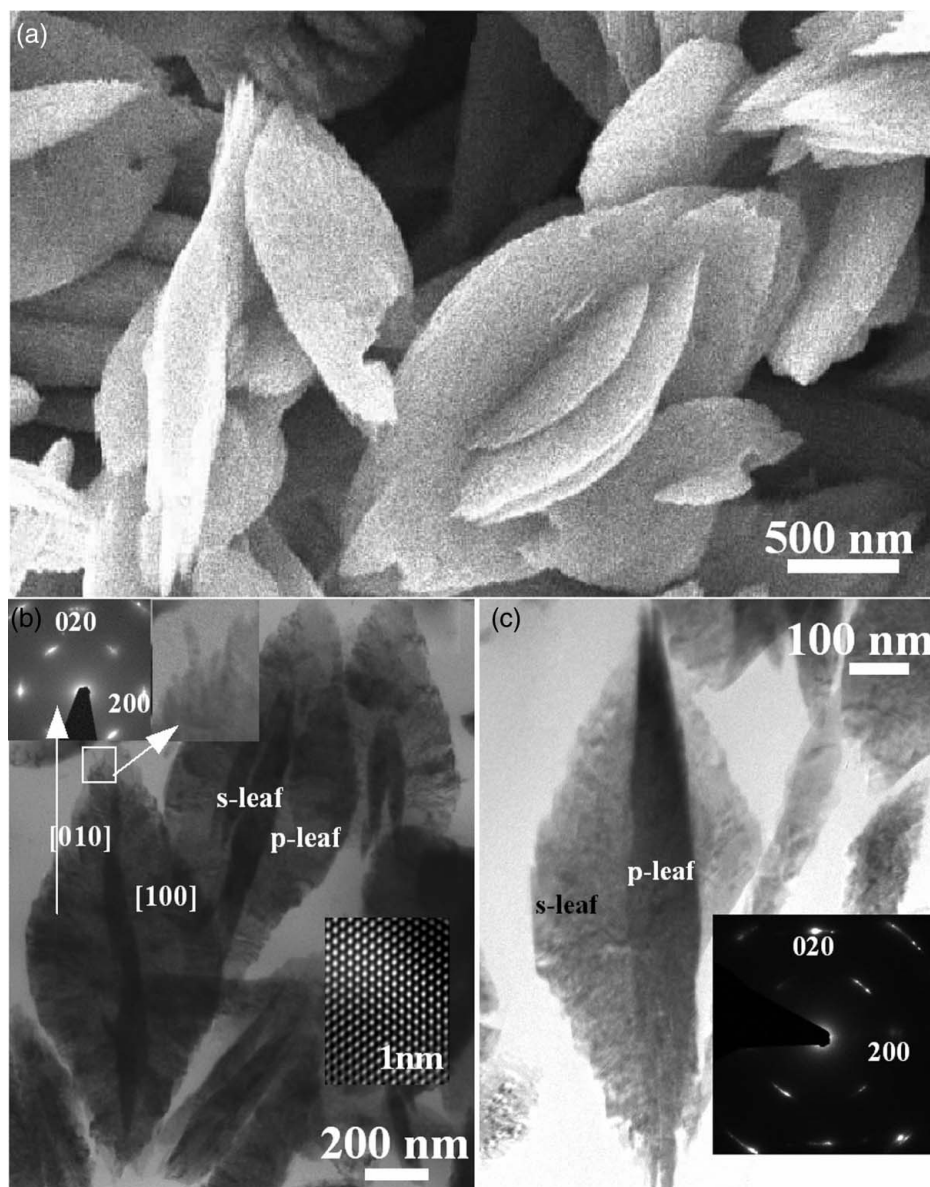


Figure 1. (a) SEM image of the interpenetrated leaves structure copper oxide grains; (b and c) bright-field TEM images with corresponding SAED patterns and HRTEM inset projected along the $[010]$ of s-leaf and p-leaf.

the substrate or directly from the solutions by using Au grids with a holey carbon film. For characterization of the crystal relationship between primary and secondary leaves, a cross-sectional TEM specimen was made by slicing β -shaped CuO grains across the $[010]$ axis. The CuO grains were clumped by two pieces of Si wafers. The sandwich-like sample was cut, polished, and finally ion milled to make it electron transparent.

Figure 1(a) is an SEM image showing the morphology of a typical as-deposited copper oxide sample. The CuO grains have an interpenetrated-leave-like structure of a similar size. Each grain consists of an ellipsoidal primary leaf that can be up to $\sim 2,000$ nm long, 1,000 nm wide, and 100 nm in thickness co-growing with one or

a few secondary leaves of a smaller size. Such inter-grown leaves are also called β -shaped structures [13,14]. The symmetrical growth of the interpenetrated leaves indicates that there is a crystallographic relationship within the leaf couples. Thus, a crystal structure analysis was performed by using HRTEM together with SAED. Figure 1(b,c) shows TEM images of petal-like CuO grains, viewed flat-on the primary and secondary leaves. The narrow stripes along the axis of primary leaf are secondary leaves in Figure 1(b). The corresponding HRTEM image and SAED pattern from the primary leaf demonstrate that the leaves are single crystal-like. The contribution from the secondary leaves to the diffraction pattern can be ignored because they are too thick and

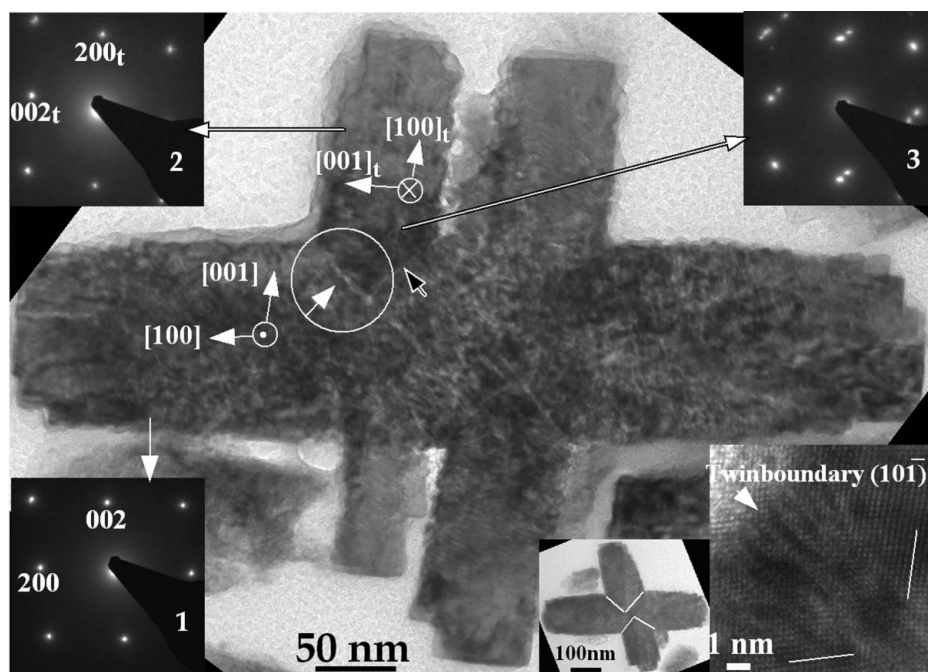


Figure 2. A cross-sectional TEM image of interpenetrated leaves in the $[010]$ direction with SAED pattern insets from (1) p-leaf, (2) s-leaves, and (3) both p-leaves and s-leaves. The twin boundary is marked by white arrows in the ring and shown by the HRTEM image at the right-bottom corner.

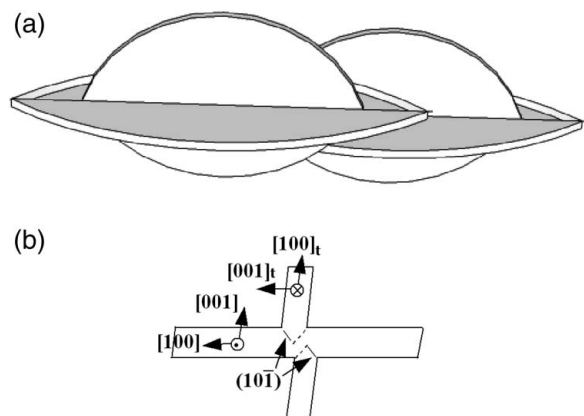


Figure 3. Structure model of the interpenetrated-leaf structure in (a) side and (b) cross-section view.

narrow in this projection. It is found that the primary leaf has a main axis in $[010]$, which is also the dominant growth direction of the leaf. The transverse direction of the leaf is $[100]$, perpendicular to the leaf axis. The surface of the leaf is (001) , the plane with the lowest surface energy. These observations present a crystal orientation dependence of growth rate order: $010 > 100 > 001$, which is consistent with previous results [8–10].

Similar to other low-temperature CuO nanostructures, the leaves here are assembled by nano-crystallites. The nano-crystallites are visible at the thinner region of leaves (see the inset at right-top in Figure 1(b)). The mean size of the nano-crystallites is ~ 50 nm long and

10–20 nm wide. The slightly elongated diffraction spots indicate the nature of multiple nano-crystallites with a limited orientation deviation. The non-uniform contrast of the leaf results also from a slight misalignment between the nano-crystallites. The orientation distribution is $\sim 10^\circ$, measured from the dispersion of the diffraction dots. All the nano-crystallites are thus assembled in similar crystal orientations with low-angle semi-coherent domain boundaries. This condition decreases the total energy and thus forms the quasi-single crystal leaf. The structural disorder is believed to form by the incomplete coalescence of the attaching nanocrystallites at the low synthesis temperature.

Occasionally, grains sit with the secondary leaf on the grid surface, as shown in Figure 1(c). In this case, the SAED pattern from the secondary leaf can be obtained and the corresponding orientation is measured. Similar to the primary leaf, the secondary leaf also has $[010]$ as the main growth direction and (001) as its surface. In other words, both primary and secondary leaves share $[010]$ as their main axis. In order to determine the angle and/or crystal relationship between the primary and secondary leaves, a characterization with the electron beam parallel to the axis of the petal-like CuO grains is necessary.

Figure 2 shows a cross-sectional TEM image of a typical twinned CuO grain along the $[010]$ zone axis with both p-leaf and s-leaves. The secondary leaves are parallel to each other, but at $\sim 95^\circ$ angle to the p-leaf. This angle is not the same as the angle β (99.47°) of the monoclinic structure of the CuO cell. The SAED

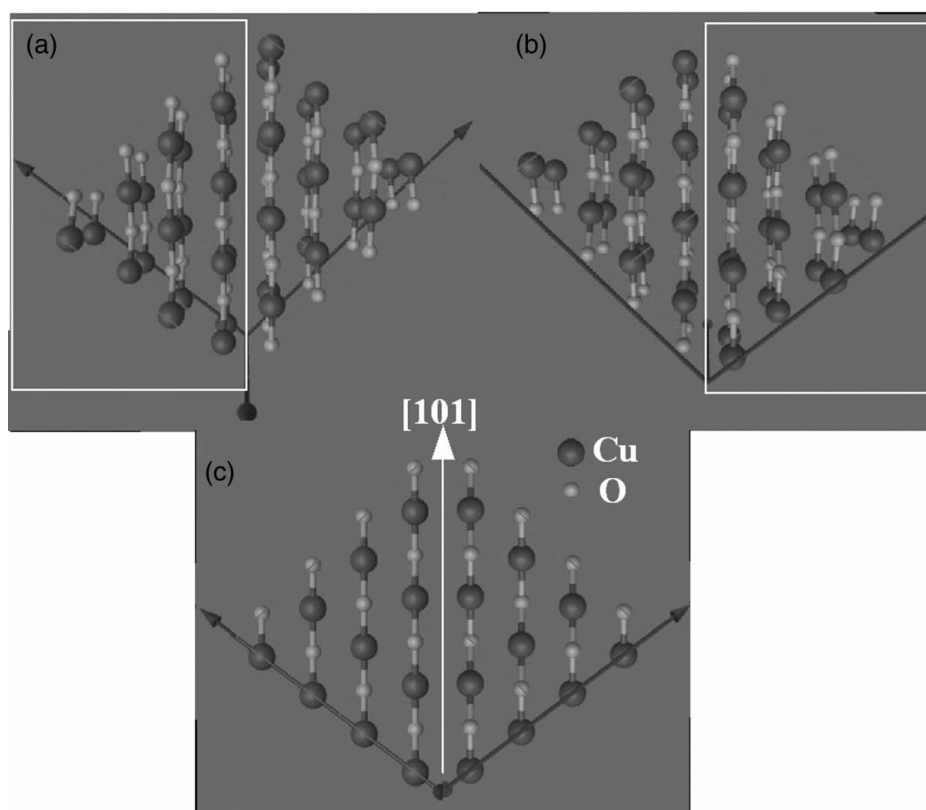


Figure 4. CuO crystal structure in (a) $[010]$ projection, (b) after 180 degree rotation around $[101]$, and (c) $(10\bar{1})$ twin constructed by the half part of the structures in (a) and (b) labeled with a white rectangle.

pattern (#1) from the primary leaf demonstrates again that the whole leaf has the same orientation. The zone axis of the SAED pattern is $[010]$, which is the main growth direction of the petal-like CuO grain. The horizontal growth direction and the leaf surface are $[100]$ and (001) as can be seen from Figure 2, and constitutes the transverse growth direction in Figure 1(b). Furthermore, electron diffraction confirms that all the secondary leaves have an identical crystal orientation. The SAED pattern (#2) from one of the secondary leaves is displayed at the top left corner of Figure 2. The zone axis of the secondary leaves was determined to be $[0\bar{1}0]$. Thus, the primary and secondary leaves have a common axis $\langle 010 \rangle$, but in the opposite directions. The SAED patterns #1 and #2 are similar and show a symmetry twin relationship, $(10\bar{1})[010]_{\text{p-leaf}} // (10\bar{1})[0\bar{1}0]_{\text{s-leaves}}$. The boundary between the primary and the secondary leaves is the twin boundary, which is marked by a white arrow in the circled region. The corresponding SAED pattern (#3) from the twin region is shown at the top right corner of Figure 2. Obviously, the SAED pattern #3 is the overlap of patterns #1 and #2, confirming the crystallographical determination.

The twin boundary in the interpenetrated-leaf CuO structure was also characterized by HRTEM, showing the lattice image of the primary and secondary leaves in their respective $[010]$ and $[0\bar{1}0]$ zone axes (see the inset at

the right-bottom corner). The subgrain boundary between them is the twin plane $(10\bar{1})$; however, with inclined steps as seen by the Moiré contrast in the figure. There is a two-fold rotation symmetry as the structure of the primary leaf coincides with that of the secondary leaf by just 180° rotation operation around $[101]$. Based on the results, we derive a structural model for the interpenetrated leaves structure of CuO. Figure 3(a) schematically shows a side view of two β -shaped CuO grains and Figure 3(b) depicts the twin relationship between the primary and secondary leaves. The angle between $(100)_{\text{p-leaf}}$ and $(100)_{\text{s-leaves}}$, calculated from the known CuO monoclinic structure of 95.1° , agrees with the angle measured in the TEM image of Figure 2. The atomic structure model of the twin is shown in Figure 4. The left part of CuO rotates 180° around $[101]$ to create the right part (twin) structure. The rotation axis $[101]$ is given in Figure 4(c).

Depending on the twin direction, different types of twin structures can be formed in the CuO monoclinic structure. Kryukova et al. [15] found two twin types in CuO powder: (100) and (001) twin, of which the twin plane is (100) and (001) , respectively. In CuO nanowires (NWs), (111) twin structure along the axis of the wire is often observed [4,16]. In the above twin structures, transverse growths of the twins are coplanar thus resulting in low-dimensional structures. In contrast, the $(10\bar{1})$ twin of our petal-like CuO presents a unique characteristic:

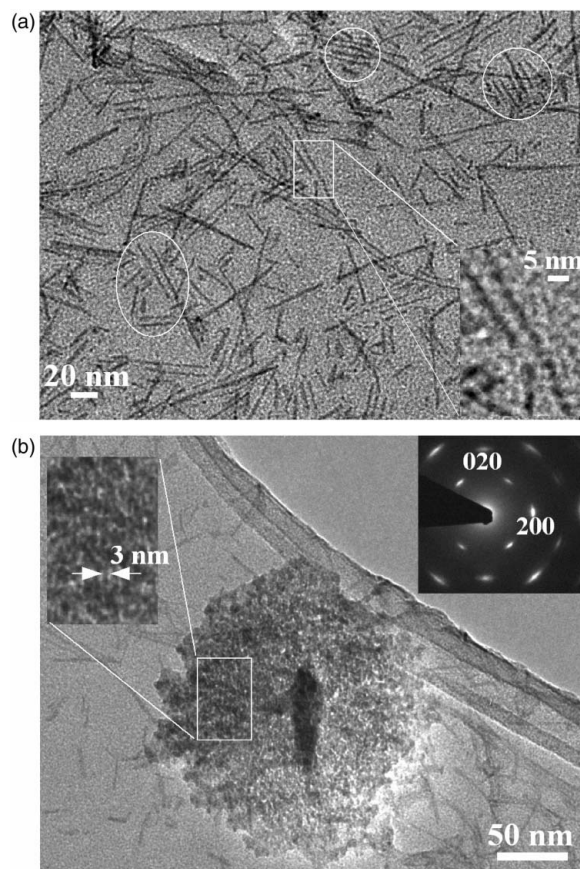


Figure 5. (a) NWs formation at 90°C for 15 min, some parallel NWs are marked by white circles and one part marked by a white rectangle is enlarged as the inset, and (b) β -shape CuO leaf, the inset on the left corner exhibits NW-like internal feature, the inset on the right corner is the corresponding SAED pattern.

the transverse growths on both sides of the twin are not in the same plane. Thus, the formation of a 3D structure becomes possible.

To reveal the formation mechanism of the β -shaped CuO structure, the suspensions heated at 90°C for 15, 35, and 60 min in a furnace were characterized by TEM. Figure 5(a) shows NWs with diameter of 2–5 nm and several hundred nanometres in length formed in the beginning of the reaction (15 min). The NWs are amorphous with a Cu/O ratio of ~ 0.5 , which is close to that of $\text{Cu}(\text{OH})_2$. The NWs typically decompose into CuO nano particles under an electron beam exposure. The NWs prefer to assemble in bundles parallel to each other. After 35 min heating, the solution becomes slightly brown and some nano leaf-like CuO grains and a few β -shaped CuO are formed as shown in the inset of Figure 5(b). An interesting feature is that there is a NW-like structure within the leaves (see the inset on the left corner in Figure 5(b)). The diameter (~ 3 nm) is the same as the diameter of NWs shown in Figure 4(a), which implies that the leaf-like CuO has resulted due to the assembling of NWs. After the assembly, the NWs crystallize into CuO nanograins which arrange in almost the same orientation and form

the single crystal CuO nano leaves. It was also found that the single leaf was dominant at the beginning, but finally all of them become β -shaped grains. Thus, we conclude that the secondary leaf nucleated on the surface of the first leaf.

The key feature for the formation of the twin structure is the $(10\bar{1})$ facet on the first leaf surface, from which the sub-grain CuO grows with the $10\bar{1}$ twin relationship to create secondary leaves. The structure model for the formation of the β -shaped CuO is given in Figure 6. The secondary leaves usually nucleate and grow from both sides of the first leaf, such that there are $(10\bar{1})$ facets on both sides of the first leaf.

In summary, β -shaped CuO grains with unique interpenetrated-leaf architecture of the defined grain size have been made from the copper salt solution at low temperature. The interpenetrated leaves are formed by self-assembled NWs. The complicated morphology originates from a twin structure with the crystallographic relationship $(10\bar{1})[010]_{\text{p-leaf}} // (10\bar{1})[0\bar{1}0]_{\text{s-leaves}}$. The axis of the petal-like CuO grain $\langle 010 \rangle$ is the main growth direction. This structure is different from other reported low-dimensional nano materials in that the transverse

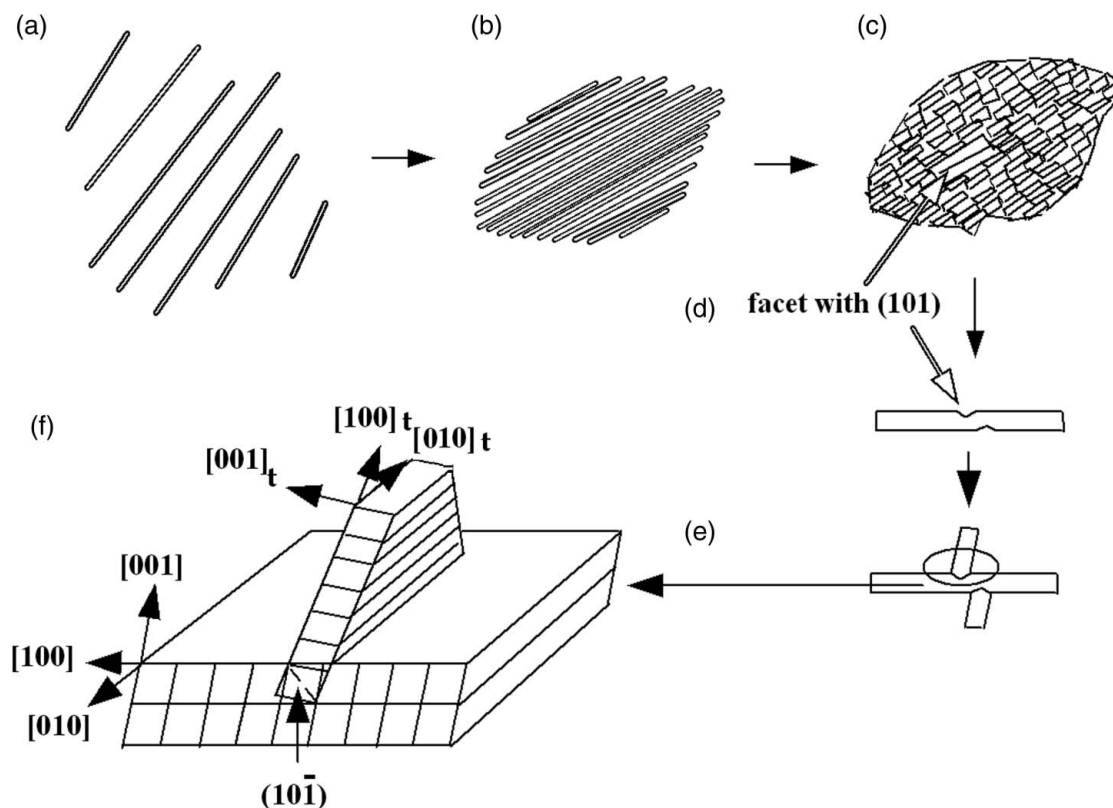


Figure 6. Schematic diagram showing the formation mechanism of β -shape, with assembling steps: (a) amorphous $\text{Cu}(\text{OH})_2$ NWs; (b) bundling of the NWs; (c) leaf-like CuO NWs crystallized from the bundling $\text{Cu}(\text{OH})_2$ NWs, and (d–f) nucleation of the secondary leaves, which in turn grow by aggregation (cf. (b)).

growth orientations on both sides of the twin are not coplanar. The $(10\bar{1})$ facet on the initial CuO leaves plans an important role for the formation of the interpenetrated leaves structure.

Acknowledgements The VR Linnaeus Environment LiLi-NFM, the Knut and Alice Wallenberg Foundation, and the Swedish Government Strategy Research Area Grant in Materials Science (SFO-MatLiU) on Advanced Functional Materials are acknowledged.

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