CHAPTER 4

CuO nanorods assembly and their toluene $\pi$ electron interaction and breath figure assisted whisker transformation

The low temperature synthesis and characterization of CuO nanorods, their self assembly at water-toluene interface and transformation into whiskers and 3D structures is studied in detail in this chapter. Rietveld structural refinement of X-ray diffraction and X-ray photoemission spectroscopy (XPS) analysis on powder samples show that the rods are composed of CuO and Cu(OH)$_2$ phases. Reversal in the XRD intensities of the Bragg reflection peaks $\bar{1}11$ and 111 of bulk CuO was observed and attributed to the anisotropy in the growth of rods as seen by transmission electron microscopy. The Cu 2p XPS spectrum confirms the Cu$^{+2}$ oxidation state of the rods as depicted by a satellite due to multielectron excitations that interact with valence electrons within the rods resulting in a bandgap of 3.2 eV as revealed by ultra-violet photoemission spectroscopy. Real time observations by atmospheric scanning electron microscope (ASEM) revealed fluctuations and chain-like assemblies of rods in colloidal solutions thereby opening up a way of studying the dynamics of nanoparticles at liquid-liquid interface. Moreover, the rods were found to transform into whiskers and 3D structures upon spin-casting on silicon substrates. ASEM and atomic force microscopy results provide compelling evidence that, this transformation is driven by the rods-toluene $\pi$ electron interaction and to less extent by breath
figure dynamics rather than solution-liquid-solid mechanism previously believed to account for the whiskers formation.

4.1 Introduction

There are several reports in the scientific literature about the growth of CuO nanorods and whiskers [1-4]. From the point of view of soft chemistry synthesis the growth mechanism of the nanorods is associated with anisotropic growth of Cu(OH)$_2$ nanocrystals [5,6]. Initially a compound with a structure where the Cu$^{+2}$ ion is coordinated by six water molecules, four in the 2D plane and two located perpendicular to the plane is formed. In addition, Hydrogen bonds are formed if NaOH is added during sample preparation. This leads to the formation of Cu(OH)$_6^{4-}$ units and causes the abundance of OH$^-$ groups. The dehydration of OH$^-$ groups located at the axis of Cu(OH)$_6^{4-}$ results in the directed axial growth of CuO nanorods [6,7]. This process is associated with a contraction of the O-Cu-O bridges and the formation of CuO$_4$ groups. On the other hand, methods such as templated synthesis [8,9], thermal oxidation [10,11], solid-state reaction [12], copper substrate by a solution-immersion step [13] and liquid-liquid interface [14,15] have all been used to produce CuO whiskers. The latter method was used by Saravanan et al. [16,17] to make CuO nanowhiskers from a water-toluene interface. These authors excluded all mechanisms such as vapour-liquid-solid (VLS) [18,19], vapour-solid (VS) [20,21] and solution-liquid-solid (SLS) [22,23] to account for the whiskers formation. The VLS and VS mechanisms were excluded, as they only account for the growth of whiskers or nanowires in the gas phase. In addition, the SLS mechanism which suggests that a liquefied metallic particle acting as a catalyst for the growth of 1D nanostructures was found not suitable for the whiskers formation as no evidence for the droplet-like structure growing front of the whiskers was
found. Therefore the aforementioned mechanisms alone were not able to explain the formation of the CuO whiskers.

Recently ring-like assemblies of gold spherical and rod nanoparticles have been reported and attributed to the effect of breath figures [24]. These breath figures are droplets due to the condensation of water and sometimes used as templates to form metallic rings on the circumference of droplets once the water evaporation is completed. With this in mind, together with inability of SLS mechanism to explain the formation of whiskers, our research interest was to explore the dynamics of nanorod formation at water-toluene interface and to investigate if the breath figures can lead to the formation of CuO whiskers or not.

We begin with characterization of CuO nanorods and investigation of their assembly in water, toluene, at water-toluene and at water-toluene-solid interfaces. Based on real time observations and different experimental evidences we propose two mechanisms where CuO rods transform to whiskers. The first mechanism is based on direct interaction between the rods and toluene $\pi$ electrons and the second is breath figure dynamics formed at the water-toluene-solid interface. The proposed mechanisms explain the CuO whisker formation similar to those reported by Saravanan et al. [16, 17] and many whisker growth works reported in the literature. Furthermore, the second mechanism goes beyond the importance of the breath figures in the ring formation for the metallic nanoparticles to other structures such as whiskers.

4.2 Experimental

Samples with nanorod morphology were prepared using a simple soft chemistry procedure [25]. Pure Cu(NO$_3$)$_2$ and NaOH were used as the starting materials without further purification. In a typical procedure, 300 mL
of 0.02 M Cu(NO$_3$)$_2$ solution was prepared by dissolving Cu(NO$_3$)$_2$ in deionized water, the solution was then added into a round bottom flask at 2 °C. 0.5 g of NaOH was added into this solution to form nanocrystalline CuO. The precipitate was then heated at 100 °C for 10 minutes. At the end, the resulting products were centrifuged, washed with water and ethanol and dried in air for 24 hours at room temperature.

X-ray powder diffraction (XRD) patterns were obtained using a standard Phillips Diffractometer (Philips PW1710) employing Cu-k$_\alpha$ ($\lambda$=1.5406 Å) radiation. The program “WinMProf” was used to perform simple XRD Rietveld refinements [26].

The size and morphology of the samples were investigated by high-resolution field emission (HR-FETEM) microscope operated at 200 kV (JEM-2100F). The surface composition and electronic structure analysis of the CuO powder samples were carried out by X-ray Photoelectron Spectroscopy (XPS) and Ultra-violet Photoemission Spectroscopy (UPS) techniques respectively. For the XPS measurements, a monochromated Al K$_\alpha$ radiation ($h\nu$ = 1486.6 eV) obtained from radiation source of 15 kV and emission beam current of 20 mA was used. The base pressure at which the scans were done was $10^{-10}$ mbar. In order to avoid charging effect during the scans, an electron gun flooding was used for charge compensation. Carbon binding energy at 284.6 eV was used to calibrate the XPS spectra. He I source with probe energy of 21.2 eV was employed for the density of state measurements by UPS.

Agglomeration of CuO nanorods and their real time dynamics and self-assembly in water, toluene and at water-toluene and water-toluene-solid interfaces were monitored by Atmospheric Scanning Electron Microscope (ASEM) [27,28].
The ASEM consisted of an optical microscope, inverted electron gun and 100 nm SiN film fixed on ASEM dish to separate the vacuum from the sample as shown in Figure 4.1(a). The CuO samples either in powder form or as colloidal solutions were positioned on the atmospheric side of the SiN film for the analysis as schematically illustrated in Figure 4.1(b). The gun focusing an electron beam on the sample through the SiN film and the backscattered electrons being detected by a detector located in the vacuum side of the microscope. The ASEM was operated at 30 kV beam energy which provided a sampling height of about 3 µm from the SiN surface [Figure 4.1(c)].

Figure 4.1: (a) Schematic cross-sectional view of ASEM which consists of an optical microscope, SiN film and inverted SEM, (b) SiN film and electron backscattered from CuO detection geometry, (c) CuO sample and SiN film showing the sampling height of ~ 3 µm when 30 keV electron beam energy is used to probe the sample.
This sampling height was enough to detect the backscattered electrons from CuO nanorods at atmospheric pressure with resolution of 8 nm. Spin casted samples were prepared with 0.3% concentration of the powder nanorods by dissolving them into toluene solvent. The solutions were ultra-sonicated for 15 minutes. Si(100) substrates were cleaned in ethanol and distilled water and then flashed with air. This cleaning process was purposely adapted to ensure the existence of a wetting water thin film on Si(100) substrates which forms water droplets (i.e. breath figures) just before the deposition of the CuO rods. The ultra-sonicated nanorod solution was then deposited drop wise on the substrates and spin-casted at 8000 rpm for 30 seconds. The characterization of the thin films formed was performed in tapping mode using a Nanoscope V Multimode AFM Veeco Instrument and Field Emission Scanning Electron Microscope (SEM). To prevent the soft liquid film from damage, the tip scan rate was set at 0.1 Hz at a minimum tapping tip amplitude. Ultra-high resolution tungsten tips (Micro Masch) with tip radius < 1 nm and backside coated with aluminum were used in all AFM experiments at imaging resolution of 512 pixels. All tips had a force constant of 75 N/m and a resonance frequency of 400 kHz.

4.3 Results and Discussion
4.3.1. Nanorods characterization

Figure 4.2(a) shows the experimental data and corresponding Reitveld-derived theoretical fit of the XRD profile of the nanorods prepared at 2 °C. The parameters resulting from the Rietveld structural refinement are summarized in Table 4.1. The XRD data was not amenable to a structural model corresponding to a CuO phase alone. The presence of Cu(OH)$_2$ phase, as is supported by two XRD peaks indicated by arrows in Figure 4.2(a) at diffraction angles below 24° was investigated. Indeed a satisfactory refinement
was only attained when a second Cu(OH)$_2$ phase, amounting to ~ 9% of the whole profile, was introduced.

Table 4.1: The XRD refinement parameters of the CuO samples prepared at 2 $^\circ$C.

<table>
<thead>
<tr>
<th>Sample and R factors</th>
<th>phase</th>
<th>ion</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>wt%</th>
<th>Lattice parameters (Å)</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO</td>
<td>CuO</td>
<td>Cu$^{2+}$</td>
<td>0.25</td>
<td>0.25</td>
<td>0.0</td>
<td>91.1</td>
<td>a = 4.6893</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O$^2$</td>
<td>0.0</td>
<td>0.91</td>
<td>0.75</td>
<td></td>
<td>b = 3.4270</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>c = 5.1319</td>
<td></td>
</tr>
<tr>
<td>Cu(OH)$_2$</td>
<td>Cu$^{2+}$</td>
<td>0.5</td>
<td>0.68</td>
<td>0.25</td>
<td></td>
<td>8.9</td>
<td>a = 2.948</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>O$^2$(1)</td>
<td>0.0</td>
<td>0.55</td>
<td>0.25</td>
<td></td>
<td></td>
<td>b = 10.566</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O$^2$(2)</td>
<td>0.0</td>
<td>0.81</td>
<td>0.20</td>
<td></td>
<td></td>
<td>c = 5.268</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O$^2$</td>
<td>0.0</td>
<td>0.91</td>
<td>0.75</td>
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</tr>
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</table>

It is interesting to note the way in which the intensities of the Bragg reflection peaks $\bar{1}11$ and $111$ at $2\theta \sim 35.7^\circ$ and $38.7^\circ$ have reversed relative to those expected from a single crystal of CuO [29,30]. To appreciate the origin of this peak-intensity reversal, we need to note that as our original reagents are highly pure and that our Reitveld refinement has shown no cationic/anionic vacancies to exist in the refined structure, we ruled out the preferential presence of point defects to be the reasons for the observed XRD peaks’ reversal. Additionally we recall that in order for a polycrystalline powder XRD pattern to yield similar information about the atomic arrangement as given by a single crystalline pattern, as depicted by the relative peak intensities in the diffraction patterns, certain conditions must be satisfied. Namely (i) there must be a sufficient powder sample, (ii) the crystallites must be of sufficient size and (iii) the crystallite orientation in the sample must be random. The ample amount of the sample used for the XRD measurements together with a sufficient crystallite size show conditions (i) and (ii) above to be satisfied. This leaves the crystallite orientation to be
the possible reason for the observed peak intensity reversal. As we are dealing with CuO powder samples, as opposed to an extended bulk CuO, this peak reversal is suggestive of morphological features wherein the CuO particles’ growth is pronounced in a particular direction relative to the others (e.g. rod-shaped). This leads to a significant increase in the number of reflecting planes normal to that direction thus enhancing the intensity of their constructively interfering scattered photons relative to the other planes.

Figure 4.2: (a) XRD data and corresponding theoretically-fitted profile of the nanorods sample prepared at 2 °C, (b) TEM image showing CuO nanorods, the inset shows the CuO nanorods length size distribution.
Indeed the rod-shape of these CuO nanostructures can be clearly seen in the TEM micrograph in Figure 4.2(b) that suggests that the crystallite packing to be not random, resulting in preferred crystallite orientation. While this crystallite packing in the sample does not affect the atomic order within the crystal structure, it could nevertheless explain the observed peak intensity reversal. CuO is made up of sheets of CuO$_4$ square planar units [31], and, with the sample being composed of nanorods, it is highly likely that sample packing will lead to the sheets of CuO$_4$ units lying preferentially in one direction. This will lead to reflections from this plane appearing stronger than what might be expected from a truly random sample.

The presence of Cu(OH)$_2$ and Cu$^{+2}$ oxidation state of the CuO nanorods is revealed by the XPS results shown in Figure 4.3. The wide survey spectrum shows all expected elements (Cu and O) from the nanorods. Deconvolution of the high resolution Cu 2p$_{3/2}$ peak shown in the inset of Figure 4.3 reveals two components (labeled 1 and 2) at binding energies of 933.8 eV and 934.4 eV attributed to the core level emissions of CuO and Cu(OH)$_2$ respectively [32]. Indeed this is reflected in the O 1s peak which shows three components; A, B and C corresponding to the oxygen contents in CuO, Cu(OH)$_2$ and native oxide respectively [33].
Figure 4.3: XPS survey spectrum showing all elements expected from the CuO rods under investigation. Inset shows the Cu 2p$_{3/2}$ spectrum with two components 1 and 2 arising from CuO and Cu(OH)$_2$ phases respectively. Satellite in the Cu 2p$_{3/2}$ spectrum is a characteristic signature of Cu$^{+2}$ oxidation state of CuO compound and the binding energy difference between components 3 and 4 in this satellite provides information on the nature of the surface composition of the rods and possible interaction between multi-electron excitation and valence electrons within the rod structure. Also O 1s spectrum in the inset reveals components A, B and C associated with CuO and Cu(OH)$_2$ phases and native oxide on the surface of the rods.

The Cu 2p$_{3/2}$ peak analysis (areas under peaks 1 and peak 2) suggests that the nanorods are covered by the Cu(OH)$_2$ layer. This fact not only reinforces the finding of 9% of Cu(OH)$_2$ detected by XRD, but also suggests the hydrophilic nature of CuO nanorods. It is well known that the satellite seen in the Cu 2p spectrum acts as a signature of Cu$^{+2}$ oxidation state of CuO or Cu(OH)$_2$ phases—this satellite is always absent in the pure copper metal XPS spectrum [34]. McIntyre et al. [35] showed that, this satellite can be fitted by two components...
with binding energy separation (Δ) of 1.3 eV and 1.9 eV for pure CuO and pure Cu(OH)₂ compounds respectively. In our case as shown in the inset of Figure 4.3 this satellite in Cu 2p spectrum can be fitted by two components (labeled 3 and 4) to provide Δ = 3.2 eV, suggesting the formation of rods of CuO covered by Cu(OH)₂ (i.e. Δrod = ΔCuO(1.3 eV) + ΔCu(OH)₂(1.9 eV)). This information obtained from XPS satellites of metallic oxides and hydroxides can be used to identify the surface composition of different nanomaterials prepared by soft chemistry and to confirm if the produced nanomaterials are products of pure metallic oxides or combination with their corresponding metallic hydroxides phases. It has been suggested that, the origin of these additional XPS satellites are due to the multiple electron excitations [36] and to the coupling between unpaired electrons in the atom [37] which results in the interaction of these excitations with valence electrons [38]. Experimental realization of this interaction is obtained by probing the valence band structure of the rods by UPS at different tilt angles which confirmed the 3.2 eV bandgap of the rods as shown in Figure 4.4.

![Figure 4.4: He I UPS spectra obtained at different sample tilt angles showing ~ 3.2 eV wide bandgap of the rods.](image-url)
4.3.2 Interfacial colloidal dynamics and assembly of CuO rods

Figures 4.5(a) and 4.5(c) show different amounts of CuO powder samples on SiN films as imaged by ASEM. Clearly, coalescence of CuO rods is dominant in both cases. However, as one would expect, partial disintegration and detachment of CuO rods from SiN film took place upon mixing with water and toluene as shown in Figure 4.5(b) and 4.5(d) respectively. The sign of detachment is judged from the reduction of the brightness of ASEM image and from the mobility of CuO rods after the solvent mixing. Individual CuO rods seen in Figure 4.5(b) are located at water-air interface as the 6 µL volume of water added is expected to produce sampling column height within the 3 µm height detection limit of ASEM instrument. However, those small cultures [e.g. those enclosed by a dashed rectangle in Figure 4.5(b)] are found to float just below the interface as a result of their weight exceeding the buoyancy force due to water and interfacial tension acting on them. On the contrary, addition of 20 µL of toluene results in the detection of only those CuO rods located within 3 µm, missing the majority of the rods expected to be at high level where the toluene-air interface is located.
Figure 4.5: ASEM images of CuO rods. (a) and (c) show two different regions after placing different quantities of CuO nanorods powder on the SiN film without any treatment. (b) CuO rods distribution after adding 6 µL of deionised water on sample shown in (a). (d) CuO rods distribution after adding 20 µL of toluene on sample (c).

Real time observations show that CuO rods gradually ascend to the water-toluene interface and those CuO rods that ascend first will be fluctuating below the interface for 7 minutes until they reach the equilibrium. In fact the maximum fluctuation amplitude reached above their equilibrium position is the water-toluene interface. Experimental realisation of this dynamic phenomenon is depicted in Figure 4.6. Initially as seen in Figure 4.6(a),
individual rods reach the water-air interface and clusters of rods (enclosed by a circle) position themselves below the interface, explaining the increase brightness of individual rods within a cluster compared to isolated rods. 60 seconds after the addition of 6 µL of toluene, water-toluene interface is created and new clusters emerge as indicted by an arrow in Figure 4.6(b). As the time elapses, the clusters start fluctuating and reach the water-toluene interface as shown in Figure 4.6(d). In this case the observed intensity of individual rods within a cluster is comparable to those of isolated rods at the interface. However, these clusters start descending back to their equilibrium position as seen from the switching behaviour (i.e. increase) of their intensity from Figures 4.6(e) to 4.6(g).

Figure 4.6: In situ video ASEM images of CuO in colloidal solutions. (a) Distribution of rods at water-air interface after adding 6 µL of deionised water on CuO powder directly placed on SiN film. (b) to (g) CuO dynamics at the time interval of 60 s after the addition of 6 µL of toluene on top of the water colloid shown in (a) to create water-toluene interface. After adding toluene the rods migrate and keep fluctuating as depicted in the brightness change of the structures enclosed by the circle in (b) to (g). Arrows show examples of areas consisting of more CuO rods after the creation of the water-toluene interface.
The order of mixing the rods with water or toluene plays an important role on the type of assembly observed. As observed in Figure 4.6, mixing the rods with water first then adding toluene afterwards causes fluctuations and formation of small clusters. On the other hand, addition of toluene followed by water induces gradual chain-like network assembly of CuO rods as seen from Figure 4.7(b) to 4.7(f) and illustrated in Figure 4.7(h).

The mixing order dependent behavior of CuO rods can be qualitatively understood based upon the following description. Initially addition of 20 µL of toluene on CuO powder directly placed on SiN film causes chain-like network assembly at toluene-air interface.

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**Figure 4.7:** ASEM images of CuO in colloidal solutions. (a) Distribution of rods at toluene-air interface after adding 20 µL of toluene on CuO powder directly placed on SiN film. This is illustrated in (g). (b) to (f) CuO dynamics and assembly at the time interval of 60 s after the addition of 20 µL of water on top of the toluene colloid shown in (a) to create water-toluene interface. As water and toluene exchange their position gradual migration to the interface and chain-like assembly of rods can be observed as seen in (b-f) and schematically illustrated in (h).
This assembly is not detected because the interface is far above the sampling height of the ASEM instrument. Therefore, only few rods can be seen as shown in Figure 4.7(a). The effect of adding water causes the chain-like assembly to move downwards within the sampling height of ASEM instrument, hence its gradual appearance as observed from Figure 4.7(b) to 4.7(f). This is facilitated by the movement of water downwards due to its higher density compared to toluene. This description does not yet explain the reason behind the formation of chain-like assembly when CuO rods are mixed with toluene first and why random clusters are formed when water is used instead. In order to understand this behavior it is imperative to recall the outcomes of the characterization of CuO nanorods. Cu$^{2+}$ oxidation state, CuO and Cu(OH)$_2$ phases of rods were confirmed by XPS and XRD techniques, where the latter phase suggests the moderate presence of OH$^-$ ions on the surface of the rods. On addition, toluene molecules displace the weakly bonded OH$^-$ ions and adsorb onto the positive charge in CuO rods. This adsorption is the result of electrostatic interaction between the positive charges on CuO rods and toluene $\pi$ electrons. Similar mechanism has been proposed to account for the chain-like formation of positively charged Au nanoparticles solvated by OH$^-$ ions in toluene [39]. Indeed, spin casting of toluene solution containing CuO rods on silicon substrate without any water treatment revealed the chain-like assembly formation as seen in the AFM image in Figure 4.8. It can be deduced that toluene molecules play three key roles of covering the CuO rods surfaces, acting as linkages between individual rods along their cylindrical axis to form whiskers and connecting the newly formed whiskers between them, forming a chain-like network. On the other hand, when CuO rods are initially mixed with water, adsorption of water molecules on the rods leads to an increase in their hydrophobicity,
forming clusters and reducing the probability of replacement of weakly bonded OH$^-$ ions by toluene, which facilitates direct interaction between the rods and the toluene $\pi$ electrons.

Figure 4.8: AFM phase image showing chain-like assembly formation after spin coating of rods mixed in toluene solution.

Figure 4.9 shows the time series ASEM images after dispersion of toluene based CuO rod colloid on SiN film followed by addition of a droplet of water (seen in dark contrast) to create a water-toluene-solid (i.e. SiN film) interface. CuO rods align themselves parallel or in perpendicular to the interface as shown in Figure 4.9(a). Within a period of 120 s as indicated by arrows in Figures 4.9(b) and 4.9(c) the contraction of the water droplet and the change in the interface curvature takes place, leading to either detachment or capture of the rods by the interface (e.g. those rods enclosed by circles). Importantly, rods captured by the interface act as seeds forming a link to nearby CuO rods present in the toluene side forming relatively short CuO whiskers.
Figure 4.9: ASEM real time at 60 s time interval observation of CuO rods motion in different media and at the triple water-toluene-SiN film interface. (a) A CuO colloidal water droplet of ~ 100 µm in diameter surrounded by CuO dispersed in toluene. Rods are seen to migrate from the water droplet and aligned themselves at the interface (shown by dashed line) either in parallel or perpendicular direction. (b) and (c) the contraction and the change of the interface curvature take place and cause the rods (enclosed by circles) to either detach or being captured by the interface. Those rods captured by the interface from the water side promote the formation of whiskers (enclosed by rectangles) pointing way from the water droplet as seen from the images shown in (e) and (d).
These whiskers are radially directed away from the interface towards the toluene side as revealed from the structures enclosed by rectangles shown in Figures 4.9(d) and 4.9(e).

In addition to whisker formation due to direct electrostatic interaction between rods and toluene, dynamics of the rods observed in Figure 4.9 suggests a possible role of triple interface established between the water droplets (i.e. breath figures) with toluene in whiskers formation. To demonstrate the potential of this interface, in Figure 4.10(a) and 4.10(b) we present evidence from AFM pictures imaged after assembly of CuO on breath figure decorated silicon substrates. It is important to note the non-uniformity of the solvent film thickness [Fig 4.10(a)] and different CuO assemblies in the AFM images (enclosed by rectangles from A to D) compared to that of rods found by TEM. The images show interaction between CuO rods with toluene (A), whisker formation (B) (i.e. needle-like structures), short whiskers attached to partially depleted breath figures (C) and CuO 3D structures (D).

Features enclosed by rectangles (A) and (B) confirm that individual rods within the whisker’s structure and whiskers are linked by toluene molecules respectively. These whiskers have larger diameter with needle ends and lengths up to several microns as shown in the inset of Figure 4.10(b). Based on AFM images, the calculated mean length of the whiskers is 4.04 μm and the population standard deviation σ = 0.17 μm. This corresponds to an increase by four orders of magnitude in length compared to the length of the precursor nanorods.
Figure 4.10: (a) AFM phase image showing the breakdown and bending of the whiskers (A), formation of whiskers (B), droplet-like structures (C), which act as seeds for the whiskers growth and for the 3D structures development (D) (b) AFM height image showing a close net of whiskers. Inset shows the length distribution of the whiskers.

4.3.3. Whiskers formation proposed model

Features (C) and (D) shown in Figure 4.10(a) are directly related to the presence of breath figures. Figure 4.11 shows a schematic of the proposed whisker formation process. Initially, breath figures are induced following the sample preparation method as shown in Figure 4.11(a). Once the rods are spin coated, they collide and accumulate themselves in the breath figures which act as...
reservoirs. In parallel the water-toluene-solid (i.e. Si substrate) interface is established as shown in dashed circles in Figure 4.11(b). As found from ASEM data if the breath figure contracted and the change in the interface curvature takes place, the rods are consumed to form whiskers. Rod density in the breath figure, size and their distribution on the boundary of the breath figure play crucial role on the type and the number of whiskers formed. A single whisker as illustrated in Figure 4.11(c) can be developed from a very small breath figure analogy of the drop-like structure in the SLS mechanism [40].

The process of depletion of the breath figure is based on mass transport within the figure and whisker's body.

Figure 4.11: Schematic diagrams showing proposed whisker formation model. (a) A breath figure on silicon substrate. (b) A breath figure with water-toluene-Si interface after spin casting rods in toluene solution. (c) A single whisker growth facilitated by a seed on the contract interface. (d) Multiple whisker formation which depends on the number of seeding rods at the interface. (e) The structure of the whisker which consists of CuO rods and a toluene shell. (f) 3D structures formation based on the layer by layer accumulation in the highly saturated breath figure.
As the rods at the interface are consumed for the growth of the whisker, new rods supplied from the inner parts of the breath figure compensate for particle shortage at the boundary. This explanation is consistent with observations made on hollow [41], net [42-45] and solid-structures [46] resulting from different depletion degree strengths of the breath figures. Partial or whole breath figure mass depletion can take place [structures enclosed by square C in Figure 4.11(a)]. The latter is always associated with development of whiskers without any traceable breath figure remains [47]. Residuals in the form of scattered solids can result from the shrinkage of breath figure contents or breakdown of the breath figure structures leading to their detachment from the whisker. These solid structures can then be filtered or easily washed away to produce pure whiskers [48]. Due to the change of solution curvature at the whisker-breath figure interface resulting from detachment, the shape of the whisker changes from wide base to narrow base. Multiple whisker formation from a single breath figure observed in this study and as reported previously [48-50] can be explained by our proposed model. This multiple whisker growth is similar to the multiprong growth of nanowires from the bottom of one catalyst cluster proposed by Kolasinski et al. [51]. In our case the whiskers and the breath figure act as the nanowires and the catalyst cluster respectively. The density of whiskers around a single breath figure depends on the number of seeding rods at the interface.

It is observed that core-shell whisker structure formation is dominant for the mixture of rods and solution as illustrated in Figure 4.11(e). The core of the whisker is formed with a constant diameter, following the size of the rod on the boundary of the breath figure. This core structure formation mechanism is similar to that of VLS growth when volume of the metal catalyst is conserved [52]. The shell formation occurs on the side-wall of the core
structure of the whisker, probably due to the presence of toluene in the areas surrounding breath figure, which is consistent with the theory of whisker growth proposed by Sears [53]. In this theory the solute is transported to the whisker tip by the hydrodynamic flow driven by the surface tension gradient resulting from a gradient in the concentration of the adherent shell layer. We speculate that in this study the core consists of CuO rods linked by OH⁻ ions to the toluene layer which acts as shell.

4.3.4. CuO 3D structures

If the density of CuO rods in the breath figure and evaporation of the solvent are high, well known 3D flake-like CuO structures [54-56] are seen to develop, consisting of agglomerated rods. In this case the contraction of the breath figure can be stopped by figure contents and by allowing the flow of CuO rods in the vertical direction within the breath figure structure. Consequently, successive layers are deposited on top of each other as demonstrated in Figure 4.11(f). The outcome of this process is depicted in the AFM image shown in Figure 4.12(a). The 3D layer structure becomes obvious when the solvent evaporation rate is increased by annealing the breath figures at 300 °C as shown in Figure 4.12(b) and confirmed by SEM micrograph shown in Figure 4.12(c).
Figure 4.12: (a) AFM phase image showing the rods trapped in breath figures (b) AFM phase and (c) SEM images showing the flake-like CuO layers after annealing of the samples at 300 °C.

4.4 Conclusions

The observed CuO morphology in this work was significantly modulated by the 2 °C preparation temperature of the samples. Real time observations revealed the dynamics of these rods when mixed with water, toluene and when water–toluene or water–toluene-solid (i.e. SiN or Si) interfaces are
created. The rods were transformed into structures such as whiskers and 3D structures if spin casted on to silicon substrates from colloidal water/toluene solutions. This transformation was attributed to the direct interaction between toluene $\pi$ electrons with rods and to the contraction and change of curvature of the triple interface created by the presence of the breath figures. It should be noted that, there is possibility of creating whiskers from the toluene droplets directly, rather than having a breath figure surrounded by toluene environment. However, further investigations will be needed in this regard. The observed individual clusters and chain-like structures suggest not only their structural difference, but also their layer like evolution as a function of depth from the interface. This is in agreement with X-ray reflectivity and diffuse scattering of Au nanoparticles measurements reported at water-toluene interface [57]. Consequently, this process offers selective flexibility in the selection of any layer from a collection of layers needed for potential applications (i.e. if layers are well separated from the interface any one of them can be selected and transferred onto a substrate without affecting other layers). Although we looked specifically at CuO rods assembly and transformation, our results can also provide insights into the dynamics for other metallic oxide nanoparticles at different interfaces. Furthermore, controlling the network formation such as the one reported in this work will open up the possibility of device applications when this network is transferred from the interfaces to suitable substrates.
References


CuO nanorods assembly and their toluene π electron interaction…


