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Copper oxide nanorods assembly and their whisker transformation at liquid–liquid interface and on solid surfaces

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ABSTRACT

We report on real time fluctuations and chain-like assemblies of copper oxide (CuO) nanorods at the liquid–liquid interface. The rods were found to transform into whiskers and 3D structures upon spin-casting on silicon substrates. The results of atmospheric scanning electron microscope (ASEM) and atomic force microscopy (AFM) provide compelling evidence that both the transformation and the assembly are driven by interaction between the π electrons of toluene and CuO nanorods, and to a smaller extent by breath figure dynamics rather than the solution-liquid–solid mechanism that was previously believed to account for whisker formation. These results open up a way for studying and understanding the dynamics of nanoparticles at liquid–liquid interfaces.

1. Introduction

There are several reports in the scientific literature about the growth of CuO whiskers [1–4]. Methods such as template synthesis [5,6], thermal oxidation [7,8], solid-state reaction [9], copper substrate by a solution-immersion step [10] and liquid–liquid interfaces [11,12] have been used to produce CuO whiskers. The latter method was used by Saravanan et al. [13,14] to make CuO nanowhiskers from a water–toluene interface. These authors excluded other possible growth mechanisms such as vapour–liquid–solid (VLS) [15,16], vapour-solid (VS) [17,18] and solution-liquid–solid (SLS) [19,20] to account for the whisker 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 acts as a catalyst for the growth of 1D nanostructures was found unsuitable for the whisker formation as no evidence for droplet-like structure growing front of the whiskers. Consequently, the aforementioned mechanisms alone cannot explain why the CuO whiskers are formed.

Recently, the formation of ring-like assemblies of gold spherical and rod nanoparticles has been reported and was attributed to the effect of breath figures [21]. 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. This, together with inability of SLS mechanism to explain the formation of whiskers has motivated us to explore the dynamics of nanorod formation at water–toluene interface and to investigate whether the breath figures can lead to the formation of CuO whiskers or not.

In this work, we investigate the CuO nanorods' assembly at water–toluene and water–toluene–solid interfaces. Based on real time observations and different experimental evidences, we propose two mechanisms where CuO nanorods transform to whiskers. These proposed mechanisms explain the dynamics of whisker growth previously reported in the literature [13,14]. The first mechanism is based on direct interaction between the rods and toluene π-electrons and the second one is the breath figure dynamics formed at the water–toluene–solid interface. Indeed the importance of the second mechanism goes beyond breath figures

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in ring formation for the metallic nanoparticles to other structural forms including whiskers.

2. Experimental

Samples with nanorod morphology were prepared using a simple soft chemistry procedure [22]. Copper (II) nitrate ($Cu(NO_3)_2$) and sodium hydroxide (NaOH) were used as the starting materials without further purification. In details, 300 mL of 0.02 M $Cu(NO_3)_2$ solution was prepared in deionized water 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 min. Subsequently, the resulting products were centrifuged, washed with water and ethanol and dried in air for 24 h at room temperature.

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 an atmospheric scanning electron microscope (ASEM) [23–25] consisting 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 Fig. 1a. The CuO particles 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 Fig. 1b with 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 in water from the SiN surface (see Fig. 1c).

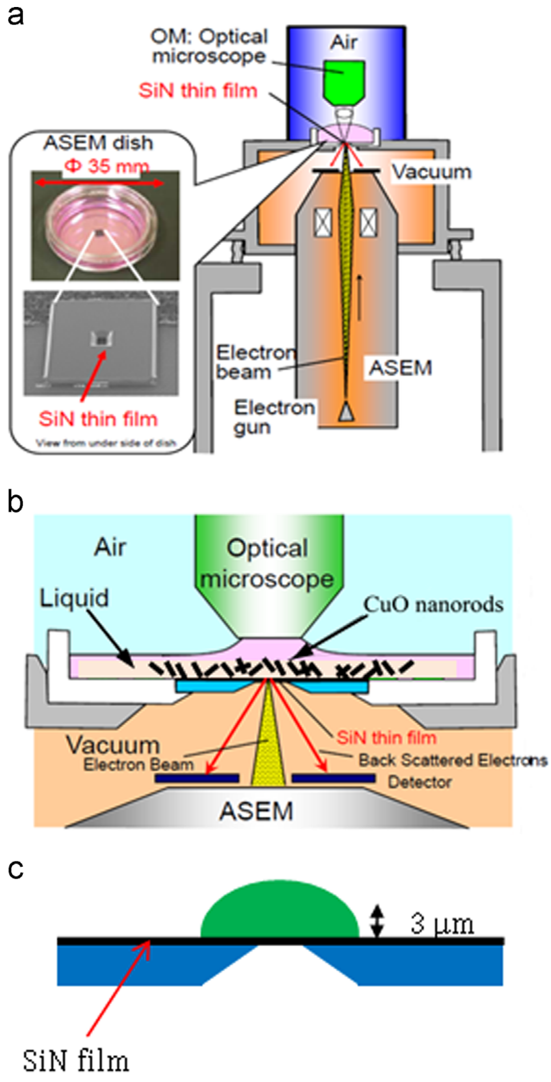

Fig. 1. (a) Schematic cross-sectional view of ASEM showing the optical microscope, SiN film and inverted SEM. (b) SiN film and electron backscattered from CuO detection geometry. (c) CuO sample and SiN film showing the sampling height of ~3 μm in water when 30 keV electron beam energy is used to probe the sample.

This sampling height was enough to detect the backscattered electrons from CuO nanorods at atmospheric pressure.

Spin casted samples were prepared with 0.3% concentration of the powder CuO nanorods by dispersing in toluene. The solutions were ultra-sonicated for 15 min. Si (100) substrates were cleaned in ethanol and distilled water and then flashed with cleaned 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 s. The characterization of the CuO thin films was performed using a Nanoscope V multimode atomic force microscope (AFM) in tapping mode and a field emission scanning electron microscope (FESEM). 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.

3. Results and discussion

3.1. Interfacial colloidal dynamics and assembly of CuO rods

3.1.1. Water–air, toluene–air interface

Fig. 2a and 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 Fig. 2b and 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 Fig. 2b are located at water-air interface as the 6 μL volume of water added is expected to produce sampling column height (i.e. the height in the middle of the sample holder cylinder away from the water concave meniscus) within the 3 μm height detection limit of ASEM instrument. However, those small cultures (e.g. those enclosed by a dashed rectangle in Fig. 2b) are found to float just below the interface as a result of their weight exceeding the bouncy force due to water and interfacial tension acting on them. It should be noted that adding large amount of water or toluene (i.e. larger than 6 μL) will result 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 water–air interface or the toluene–air interfaces are located (see Fig. 4h). This point is revealed from the data shown Fig. 2d obtained by addition of 20 μL of toluene on powder sample shown in Fig. 2c.

3.1.2. Water–toluene interface

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 420 s until they reach the equilibrium. In fact the maximum fluctuation amplitude reached above their equilibrium position is the water–toluene interface. Experimental realization of this dynamic phenomenon is depicted in Fig. 3a–g. Initially as seen in Fig. 3a, individual rods