DOI: 10.1002/anie.200906562

Nanostructures

Understanding Ionic Vacancy Diffusion Growth of Cuprous Sulfide Nanowires**

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Cu_2S, with an indirect bandgap of approximately 1.2 eV, is an appealing photovoltaic material. Studies have predicted a practical power conversion efficiency of 17.8% on Cu_2S- and ZnO-based solar cells,[1] and efficiencies of up to 9.15% have been experimentally demonstrated on devices formed from Cu_2S and CdS thin films.[2] However, because copper is unusually mobile within the close-packed sulfur sublattice, the crystal structures of Cu_2S are poorly defined.[3–5] Furthermore, mobile copper can easily diffuse across the p/n junction formed by, for example, Cu_2S and CdS, causing rapid performance degradation, which led to the eventual abandonment of research on Cu_2S as a photovoltaic material.[6]

Recently, with the development of various Cu_2S nanostructure syntheses, a renewed interest in this material for solar energy conversion has been observed.[7–11] Among the reported morphologies, nanowires (NWs) are of particular interest because the anisotropic nature of NWs promises an optimal combination of light absorption and charge separation.[12–17] To this end, the synthesis of Cu_2S NWs on a copper substrate, developed by Yang et al., has attracted considerable attention.[10,18] An oxide-assisted nucleation and growth model has been proposed and widely used to account for the unique growth of Cu_2S. Although Yang et al. did allude to the alternative mechanism that would involve ionic vacancy diffusion,[18,19] a detailed understanding has been missing. More importantly, an oxide-assisted nucleation process still remains indispensable in the proposed mechanism.

Herein, we present the first study of the ionic vacancy diffusion mechanism that governs NW synthesis. Despite the fact that O_2 acts as a necessary reactant, no copper oxide was observed in the product, which suggests that O_2 plays a different role from what has been reported. By focusing on how ionic vacancies are annihilated in the supporting substrate that also serves as the copper supply source, we uncover the ionic diffusion nature of the Cu_2S growth. This understanding has allowed us to create uniform and aligned Cu_2S NWs on transparent conductive substrates that can be utilized directly to construct solar cells. Our results highlight the importance of controlling ionic behavior in the synthesis. Because the success of Cu_2S-based solar cells relies on the ability to understand and control copper diffusion in Cu_2S, this work will also shed light on how to achieve high practical energy conversion efficiencies using Cu_2S.

The critical role of H_2O has not been previously recognized. Furthermore, although we sought to vary the gaseous precursor parameters, such as flow rate ratios, our study focuses on how these variations influence the ionic vacancy generation, diffusion, and annihilation. This approach is in stark contrast to the existing methods in which attention was concentrated on how various parameters influence the gas-phase feeding whilst the role of copper supply remained unexplored.

Typical scanning electron micrographs (SEM) of the as-grown Cu_2S NWs are shown in Figure 1 a. Uniform Cu_2S NWs with $d \approx 100$ nm and $l \approx 500$ nm were produced by a 3 h

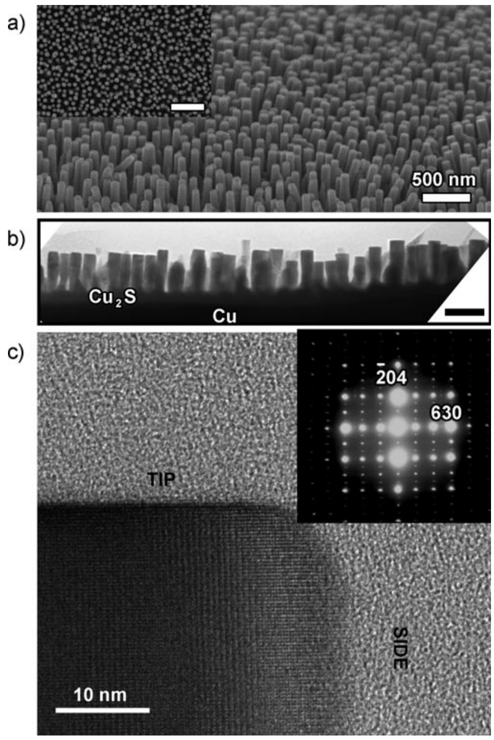

Figure 1. Electron micrographs of as-produced Cu_2S NWs. a) The uniformity of the products is seen in the perspective view (main frame) and top view (inset; scale bar: 1 μm). b) A cross-section TEM image reveals the existence of a Cu_2S buffer layer. Scale bar: 500 nm. c) High-resolution TEM image showing the atomically smooth tip and side of a Cu_2S NW. Inset: electron diffraction pattern verifying that the product is low-chalcocite Cu_2S.

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[**] This work is supported by Boston College. We thank Y. Lin, G. McMahon, and S. Shepard for technical assistance.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200906562.

growth. Cross-sectional transmission electron microscopy (TEM) examinations revealed that the NW tips and sides are free of impurities and are atomically flat (Figure 1 b,c), thus ruling out the possibility of seeded growth.[10] The NW array is separated from the copper substrate by an underlying Cu_2S layer of 250 nm, the importance of which in understanding the detailed growth mechanism will be discussed below. Both electron diffraction (ED, Figure 1 c inset) and X-ray diffraction (Supporting Information, Figure S1) patterns confirmed that the as-grown Cu_2S is of the low chalcocite structure. Optical characterizations showed that the product has an indirect bandgap of 1.20 eV (Supporting Information, Figure S2), which is in good agreement with the literature.[8,20]

The key uniqueness of this growth result is found in how sulfur and copper are fed. Existing reports of NW growth can be generally described by either a base-feeding or a tip-feeding mechanism. When fed from the base, the new addition of species "pushes" up the NWs and leads to axial elongation.[21] Conversely, the elongation of NWs is a natural consequence of tip addition, as in a vapor–liquid–solid or solution-liquid-solid growth.[22,23] The present synthesis, however, requires the addition of one component (sulfur) from the tip and the other component (copper) from the base. A surface diffusion model was proposed by Yang et al. to explain this phenomenon.[10,24] Our observation of the existence of the Cu_2S buffer layer between copper and Cu_2S NWs rules out the possibility of surface diffusion, and instead supports an internal diffusion model that we next identify as ionic vacancy diffusion.

Figure 2 illustrates the proposed growth mechanism. H_2S and O_2 react to produce H_2O and S^{2-}. S^{2-} forms a close-packed sublattice, the polyhedral sites of which are to be occupied by Cu^+. In the absence of Cu^+, ionic vacancies (V_{Cu}') form, which subsequently diffuse in Cu_2S to reach the copper substrate, where they are annihilated by defects in the copper. Initially this process yields a layer of Cu_2S that is continuous.[25] As the reaction continues, the volumetric expansion, and also the annihilation of V_{Cu}' by the defects in the Cu_2S film, leads to cracks in the Cu_2S film, creating NWs (Supporting Information, Figure S6). Although the vacancy diffusion has been utilized to explain metal scale growth,[26] and it has been alluded to contribute to the Cu_2S NW growth,[18] a detailed study to unambiguously validate this mechanism in governing NW growth has been absent.

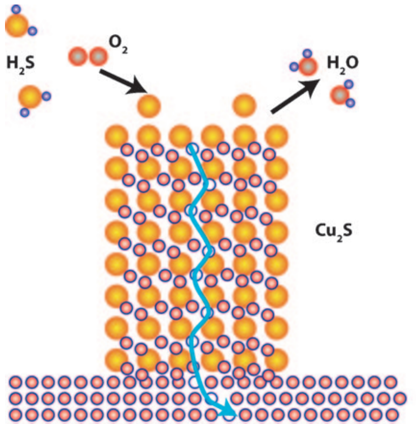

Figure 2. The ionic vacancy diffusion growth model. The cartoon does not represent the actual atomic arrangements of Cu_2S. A diffusion channel is indicated by the blue arrow.

From a perspective that concerns how ionic vacancies are annihilated in copper, we describe the following experimental observations to support our hypothesis. 1) The growth is highly sensitive to the quality of the substrate. Cu_2S nanostructures with random morphologies were obtained on copper substrates with high density of defects. The high density of defects facilitates rapid V_{Cu}' annihilation, which is equivalent to fast copper feeding. As a result, fast nanostructure growth occurs and produces random morphologies. For example, we frequently observed Cu_2S NWs as long as 100 μm on defective copper substrates (Supporting Information, Figure S4). To further verify this hypothesis, we also fabricated micrometer-sized copper crystals by electrochemical deposition. On small (< 10 μm) copper crystals, uniform epitaxial growth was obtained (Figure 3 a). In contrast, a mixture of long and short NWs were grown on large crystals

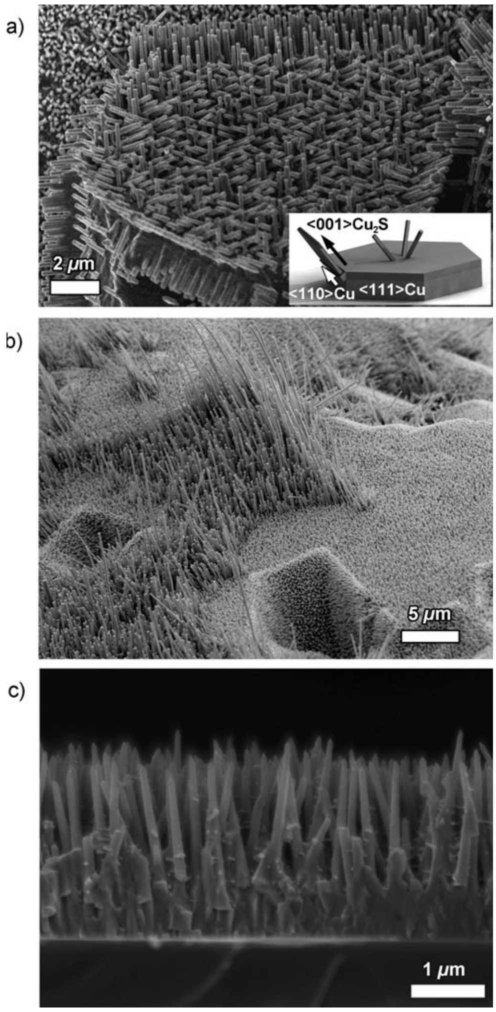

Figure 3. Various morphologies of Cu_2S NWs. a) Cu_2S grown on copper microcrystals. Inset: crystallography correlations. b) Binary growth, which occurs when a high density of defects are present in copper. c) Aligned Cu_2S NWs grown on an ITO substrate.

(Figure 3b), because more defects are present in these large crystals. Previous studies of the influence of the supporting substrate concerned how the crystallography changes the orientation of the as-grown NWs. To the best of our knowledge, this is the first report on how the nature of vacancy annihilation in the substrate determines the growth of NWs.

2) H_2O plays a critical role in the growth. Control experiments in which H_2O was absent failed to produce detectable Cu_2S during the first 8 h of reactions. Random and short NWs were observed only after 24 h. Note that H_2O is also the product of the reaction between O_2, H_2S, and Cu, which explains the eventual production of NWs in the absence of intentional H_2O supply. Humidity is known to facilitate electron transfer and ion formation in the growth of Cu_2S thin films.[25] The role of H_2O suggests that the growth depends on ionic behavior, and the dependence of the growth results on the relative humidity is quantitatively plotted in Figure 4a.

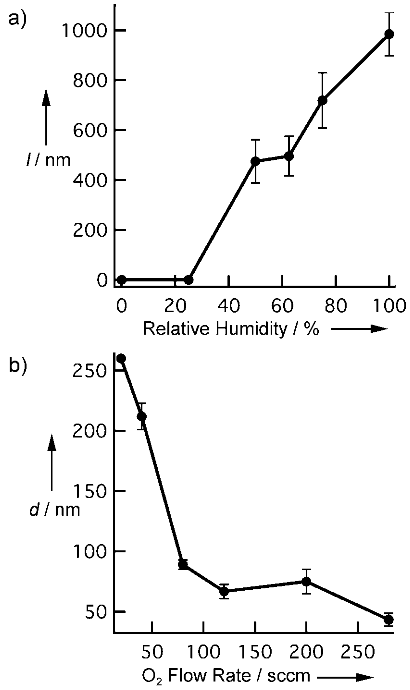

Figure 4. Influence of a) relative humidity and b) O_2 flow rate on the resulting morphologies of Cu_2S NWs (*l*: length; *d*: diameter). The growths, lasting 3 h, were performed on a copper substrate after electrochemical polishing.

Despite the similarities of our system with what has been reported,[24] the role of H_2O has not been identified before.

3) In principle, V_{Cu}' can be generated either on the tip or on the side walls of an existing Cu_2S nanowire. Nevertheless, V_{Cu}' diffuses significantly faster along the [001] direction of Cu_2S, leading to the anisotropic growth and producing the NW morphology. The increase of the precursor concentrations will promote V_{Cu}' generation, both on the tip and on the sidewalls. When the rate of V_{Cu}' generation exceeds the rate of its diffusion, the growth cannot be sustained. As a result, thinner and shorter nanowires will be produced. This prediction was validated by our observations (Figure 4b), in which higher O_2 flow rate results in a higher O_2 concentration in the reactor, and thus faster V_{Cu}' generation. Similarly, more H_2S is also predicted to produce smaller Cu_2S nanowires (Supporting Information, Figure S3).

Although O_2 was a critical reagent, oxide formation was not observed in our experiments. We propose that the key role of O_2 is to oxidize copper and to subsequently react with H_2S, which produces H_2O. Cu_xO is not a necessary product of this reaction. We acknowledge that the oxide has been proposed previously to assist the nucleation, which governs the NW growth.[10] However, we contend that the formation of NWs results from the vacancy in the thin film of Cu_2S, and no nucleation is involved in this process. Furthermore, Cu_2S nanostructures with varying degrees of complexity, ranging from double-comb to helical structures, that we obtained at room temperature (Supporting Information, Figure S5) stemmed from the fast annihilation of V_{Cu}' owing to the defective nature of the substrate. The effect of the fast annihilation is equivalent to fast feeding of Cu^+; that is, the growth of Cu_2S NWs is governed by the diffusion of Cu^+ vacancies in Cu_2S. Capabilities to balance the diffusion yield uniform NWs; failure to do so produces defective structures.

Cu^+ diffusion in Cu_2S is a known issue that has plagued research of Cu_2S as a photovoltaic material. Indeed, the main reason of the structural complexity of Cu_2S comes from the high mobility of copper in the sulfur sublattice,[5] which is also responsible for the high conductivity of Cu_2S.[27] A growth that is facilitated by the ionic vacancy diffusion should therefore be reasonable. Similar ion-diffusion driven growth has been observed in Ag NW growth.[28] An ionic exchange reaction has also been used to create other chalcogenide nanostructures.[29] The model studied herein sheds light on the recent reports of low temperature growths of oxide nanostructures as well.[30,31]

Understanding the ionic vacancy diffusion-governed growth leads to a significant implication: To minimize copper diffusion in Cu_2S nanostructures, the key will be to minimize the vacancy formation on the surface by minimizing excess sulfur surface sites. Minimizing the copper vacancy density leads to significantly reduced copper diffusion, which will enable the study of the true potential of using Cu_2S as a photovoltaic material.

Lastly, we demonstrated that the growth result can be utilized to produce uniform and aligned NW arrays on transparent conductive substrates, such as ITO (indium tin oxide) glass. For this purpose, we deposited a layer of copper film on ITO glass by electron-beam evaporation and carried out the synthesis of Cu_2S NWs. The length of the resulting NWs is approximately 2.5 times that of the starting film. We envision that this structure can be readily used to construct photovoltaic devices, as has been done on other nanostructures of similar morphologies.[15,17,32]

In summary, we have discovered a unique growth model that produces uniform and aligned Cu_2S NWs at room temperature. Cu^+ vacancy diffusion in Cu_2S was found as the driving force of this growth. H_2O acts as an indispensable reagent to facilitate charge transfer and ionic vacancy formation. The NW formation is governed by the difference of Cu^+ vacancy diffusion in various crystal directions. We utilized the growth model to produce uniform NWs on transparent conductive substrate that can be potentially used to construct solar energy harvesting devices.

Experimental Section

Cu_2S nanowires were obtained by passing a steady flow of H_2S at 10 standard cubic centimeters per minute (sccm), O_2 at 80 sccm, and N_2 (saturated with H_2O) at 160 sccm over a polished copper substrate. For kinetics studies, the flow rate of one gas (H_2S or O_2) was varied with the other fixed. For relative humidity studies, varying fractions of the total N_2 flow were passed through a H_2O bubbler, whilst the remainder was kept dry.

Electrochemical polishing: A high-purity copper foil (Sigma Aldrich, 99.99%) was first cleaned in acetone, methanol, and isopropanol by ultrasonication to remove organic contaminations. The foil was then immersed in concentrated orthophosphoric acid (85 wt%, Alfa Aesar) together with a platinum wire as the counter electrode. 4.7 V dc was initially applied for 5 minutes; thereafter a lower voltage of 1.7 V dc was used, and the reaction continued for 10 minutes. The surface of the copper foil became mirror-smooth after this treatment.

Electrochemical plating: A seed layer of copper (80 nm) was thermally evaporated onto glass. The electrolyte for plating was 0.16 M $CuSO_4$ aqueous solution, and a copper electrode served as the anode. The plating process was conducted at room temperature with the current density between 1 and 10 $mA\,cm^{-2}$. The copper crystal sizes varied from circa 1 μm to circa 20 μm, the general trend being that larger current density produced larger copper grain sizes.

Film for Cu_2S growth: A copper film was deposited onto the indium tin oxide (ITO, Nanocs, 8–100 Ω/□, where Ω/□ denotes sheet resistance) substrate in an e-beam evaporator (Lesker). Different copper film thicknesses were tested: 100, 250, 500 and 1000 nm. The quality of the Cu_2S nanowire arrays was similar whereas the length varied with the thickness of the initial copper film.

Structural characterizations: The X-ray diffraction pattern was taken with a Bruker diffractometer using $Cu_{K\alpha}$ irradiation. Scanning electron microscopes (SEM; JOEL 6340F or 7001F) and a transmission electron microscope (TEM; JOEL 2010F) were used to study the morphology and crystal structure. The cross-sectional sample for TEM characterization was prepared with an argon-ion miller (Gatan, PIPS-691).

Optical characterizations: The bandgap of the as-produced Cu_2S nanowires was retrieved from the absorption spectrum obtained with a UV/Vis/near-IR spectrometer (Ocean Optics HR4000CG-UV-NIR, with Mikropack DH-2000-BAL UV-VIS-NIR light source). The nanowires were suspended in ethanol (Sigma–Aldrich, ≥99.5%, anhydrous). The spectrum was recorded in the wavelength range of 200–1100 nm.

Received: November 20, 2009

Keywords: copper sulfide · ionic diffusion · nanowires · photovoltaics

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