

# Adsorption of Arsenic in Water by Cupric Oxide Nanowires

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## Introduction

Arsenic is a naturally occurring trace element that contaminates ground water worldwide [1]. The contamination particularly affects various countries, such as the United States, India and Bangladesh, where water supplies naturally contain arsenic concentrations above the safe limit for drinking water, 10  $\mu\text{g/L}$ , set by both the World Health Organization (WHO) and the United States Environmental Protection Agency (EPA) [2,3,4,5]. Arsenic concentrations above the safe limit can cause acute or chronic health issues including gangrene, intestinal problems and many types of cancer. Therefore, the removal of arsenic from drinking water is important for public health and safety.

Previous research indicates that cupric oxide nanowires have potential for being a successful arsenic adsorbent. In particular, cupric oxide nanoparticles have been demonstrated to be capable of adsorbing arsenic from ground water samples [7]. In those studies, the nanoparticles were synthesized under reflux in a multi-step process, which is complex and the post-treatments are expensive. On the other hand, the synthesis of the cupric oxide nanowires have been reported in Chien research group through a one-step direct oxidation in a tube furnace under controlled atmosphere [8]. This growth process is a single step synthesis and produces nanowires with features that can be controlled by oxidation time and temperature, making this method a potential approach for the application of the arsenic from water samples.

This study tested whether Cupric oxide nanowires could be (1) grown in open air environment and (2) if they have the ability of adsorbing arsenic from contaminated groundwater. Our results show that, first, the growth of cupric oxide nanowires in open air is feasible. By removing the requirement of controlled atmosphere for the nanowire growth, the synthesis process becomes much economical viable – a household cooking range will be sufficient to synthesize cupric oxide nanowires. Secondly, the removal of arsenic from arsenic-added distilled water with the cupric oxide samples has been demonstrated. However, further improvement is needed since the residual arsenic is still above the safe limit (10  $\mu\text{g/L}$ ) in these trials. Potential methods of improvements will be discussed here as well.

## Methods

### Materials

99.9 % pure copper foil was used as the growth substrate. For washing and sonicating, laboratory grade acetone and isopropanol were used. Bottled distilled water (DI water) was used for the solvent of the arsenic solutions. Powdered arsenic (III) and arsenic (V) were used separately to provide arsenic in the oxidation states of (III) and (V) in solution.

### Equipment

An Elmasonic P30H sonicator was used to wash the samples. A Cole-Parmer hotplate was used to oxidize the samples. Characterization of the copper foils after oxidation was performed with a FEI Quanta FEG 450 Scanning Electron Microscope with a beam energy of 20 kV, a Raman Spectrometer with a 532 nm wavelength diode-pumped laser, and a Rigaku Smart Lab X-Ray Diffractometer with a Cu- $k_{\alpha}$  source at 40 kV and 40 mA. Arsenic Solutions were characterized with an Inductive Coupled Plasma Mass Spectrometer (ICP-MS).

### CuO preparation

Cupric oxide nanowires were grown following a modified open-air recipe based on the controlled-environment recipe developed by Hillman et al. [8]. The copper foils were cut into 3 cm  $\times$  7 cm strips and sonicated for 5 minutes in acetone, and 5 minutes in isopropanol. The copper foils were then allowed to dry before placed on the hotplate. The samples were oxidized by direct heating on the hot plate at 300 °C for 3 hours after temperature ramping.

### Arsenic solution preparation

Arsenic solutions were prepared by serial dilution to approximately ~75  $\mu\text{g/L}$ . The powdered arsenic was weighed out by mass and added to a 1 L bottle to dissolve into solution. The solutions were hand agitated prior to use to ensure homogenous solutions were withdrawn for analysis. The arsenic solutions were introduced to cupric oxide nanowires for 3 hours, in batch trials. Ten sheets of cupric oxide nanowires (grown on copper foils) were placed in 5 mL of arsenic solution and let stand, without agitation. After the trials, the solutions were passed through a 0.45-micron filter to remove large particles prior to ICP-MS analysis.

## Results and Discussion

SEM imaging of the oxidized samples is shown in figure 1. The samples have nanowire structures formed throughout the surface, and have similar features compared to the previous controlled-environment grown samples [8].

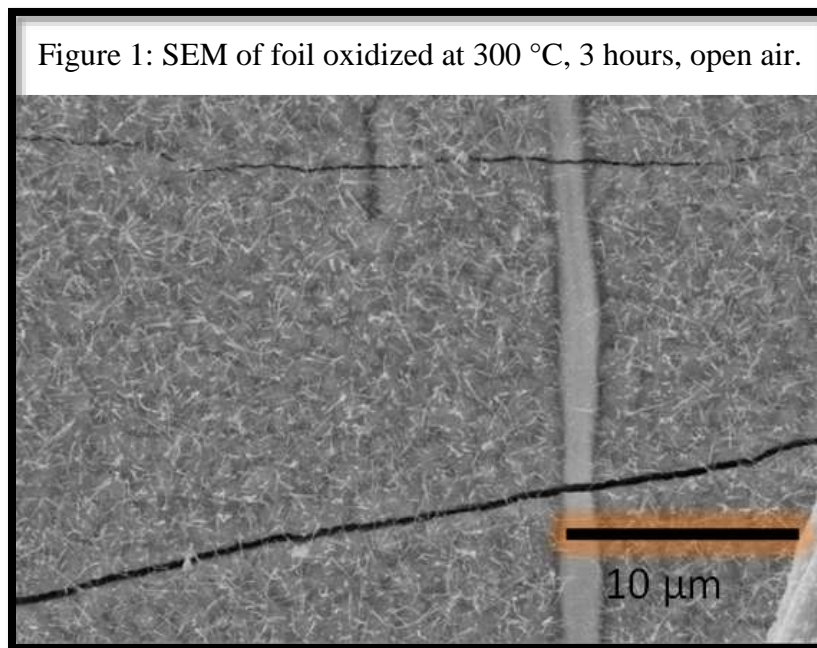


Figure 1: SEM data demonstrates nanowire growth.

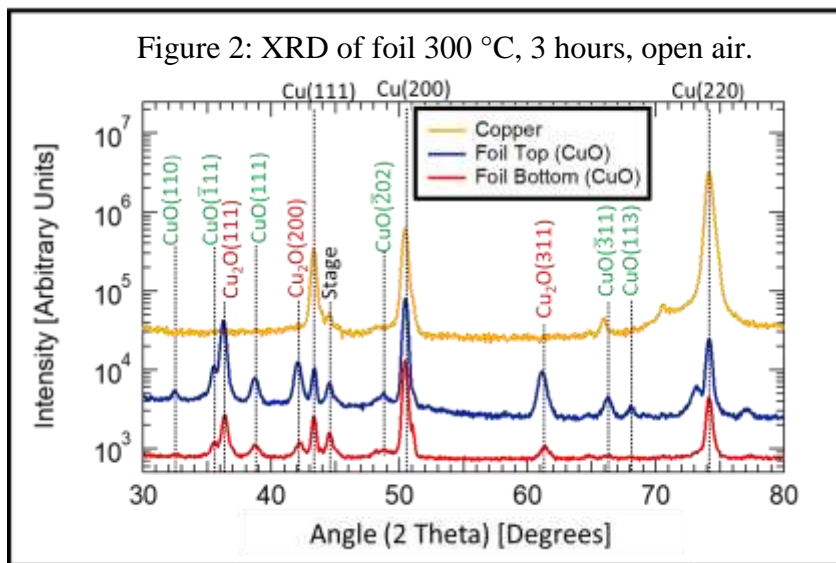


Figure 2: XRD data indicates that the grown nanowires have similar properties as those grown previously [8].

The XRD spectra measured on both top and bottom oxidized foils are shown in figure 2, along with a spectrum taken on pure copper foil for comparison. The spectra taken on the top and bottom of the samples are similar, indicating that the crystallinity of each is similar. In addition, the peaks for copper, cuprous oxide, and cupric oxide are all present. This agrees with the reported data [8], indicates a similar growth process of the nanowires: thin  $\text{Cu}_2\text{O}$  layers formed prior to the  $\text{CuO}$  nanowires grown on top of that. Most importantly, this demonstrates that there are cupric oxide nanowires present on the samples.

The Raman spectra taken on top and bottom of the oxidized foils are shown in figure 3. Again, similar Raman spectra from the top and the bottom of the oxidized foils indicate that the  $\text{CuO}$  nanowires on both surfaces are similar in crystallinity. Particularly, the Raman signature only includes peaks produced by cupric oxide, indicating that the surface layer is made up of cupric oxide exclusively. This agrees with prior research, which proposed that the wires grown on a sublayer of cuprous oxide on top of the copper [8].

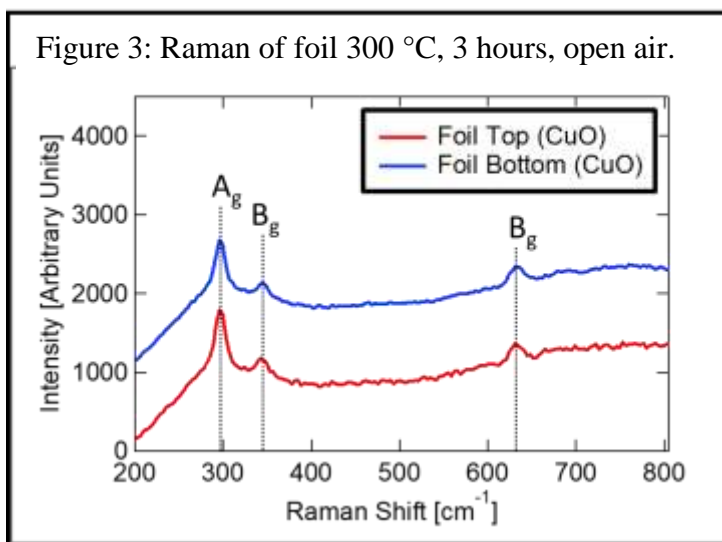


Figure 3: The Raman spectra indicates that the nanowires are made up of cupric oxide.

To recap, the above results clearly demonstrate that the oxidation process produced cupric oxide nanowire structures on cuprous oxide thin layers above the pure copper foils.

The ICP-MS concentration data collected from the samples is presented in figures 4 and 5. As shown in Fig. 4, the arsenic (V) concentrations dropped to 28.3 ppb (from 74.1 ppb) and to 30.6 ppb (from 74.1 ppb) while the arsenic (III) dropped to 28.4 ppb (from 90.9 ppb). This data demonstrates that the arsenic concentration dropped  $\sim 50 \mu\text{g/L}$  across the trials. Though the final

arsenic concentrations are still above the safe limit (indicated as red dashed line in Fig. 4), we believe this could be improved by adding more cupric oxide nanowires. While arsenic removal is the goal, copper concentration in water is desired to be remained low. In Fig. 5, as expected, the copper concentration increases due to the placement of copper compounds in the water. They are still below the suggested safe limit (indicated as the red dashed line in Fig. 5). It would be critical to test, in the next trials when the cupric oxide nanowires are increased, will this copper concentration goes beyond the safe limit.

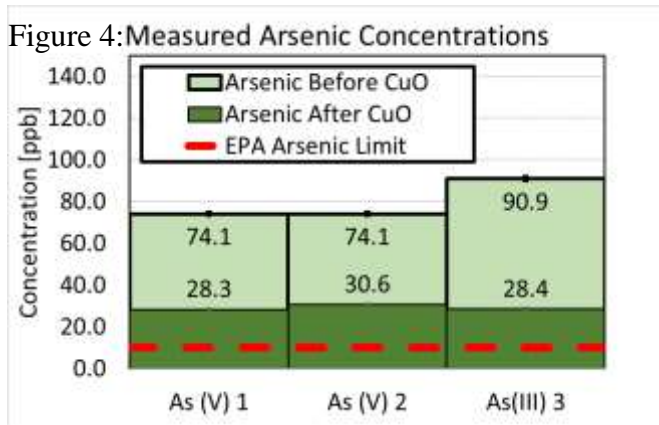


Figure 4: The before and after concentrations of arsenic indicate that the cupric oxide nanowires adsorbed arsenic from the solution.

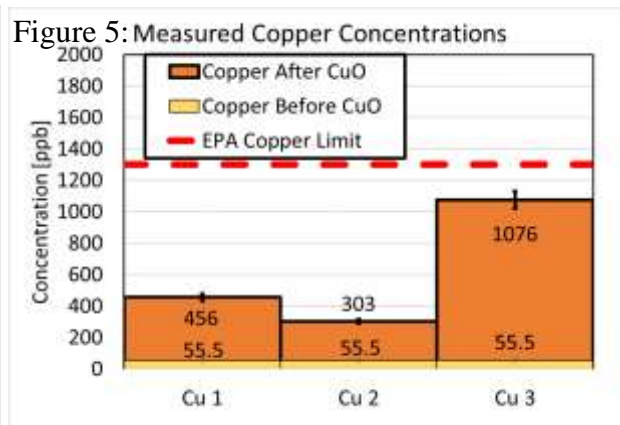


Figure 5: The before and after concentrations of copper indicate that the cupric oxide nanowires introduced copper contamination to the water.

## Conclusion

This project successfully demonstrates (1) the feasibility of synthesizing CuO nanowires in open air; and (2) the synthesized CuO nanowires have the ability of adsorbing arsenic in water samples. First, the cupric oxide nanowires were successfully grown by direct oxidation in open air. This further simplifies the growth process for cupric oxide and provides an inexpensive means to produce the adsorbent of arsenic in water. Additionally, the nanowires were then used to successfully adsorb arsenic from arsenic-added DI water solutions. The process did not drop the arsenic concentration below the EPA/WHO limit of 10  $\mu\text{g/L}$  but did provide significant adsorption. It is proposed that by adding more CuO nanowires into the solution, the arsenic concentration should be lower. Finally, the nanowires introduced copper to the water solution, but did not increase the concentration above the EPA or WHO limits.

Further research needs to be conducted into the nanowires and adsorption process. First, the cupric oxide nanowires need to be characterized further to provide insight into their

maximum adsorption concentration. First, BET Surface analysis could be used to provide information as to surface area to mass ratio. Second, XPS could provide information as to the bonding interaction of arsenic with the nanowires, as well as the oxidation state and concentration of the arsenic. Additionally, the adsorption performance of the nanowires needs to be improved to lower the arsenic concentration to below the EPA/WHO allowed limit. This would indicate that the nanowires can be used in an arsenic removal device. Finally, the nanowires need to be introduced into a flow-through device environment, and tested further in the presence of varying pH, competing anions and arsenic concentrations.

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## References

- [1] M. Amini, Environ. Sci. Technol. (2008), 42, 366-3675
- [2] D.K. Nordstrom, Science 296 (2002) 2143.
- [3] WHO, Arsenic in Drinking Water, 2011, WHO/SDE/WSH/03.04/75/Rev/1
- [4] WHO, Copper in Drinking-Water, 2004, WHO/SDE/WSH/03.04/88
- [5] US EPA, 2002, EPA 816-K-02-018. , US EPA, 2004, EPA 816-F-04-009.
- [6] J. C. Saha, Critical Reviews in Environmental Science and Technology, (1999), 29:3, 281-313
- [7] C. Martinson, Journal of Colloid and Interface Science, (2009), 336(2), 406-411
- [8] J. Hilman, Nano-Structures & Nano-Objects, (2017), 11, 124–128