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Scalable Synthesis of Alumina Nanowires by Wet Chemical Method

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SCALABLE SYNTHESIS OF ALUMINA NANOWIRES BY WET CHEMICAL METHOD

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Abstract

Scalable Synthesis of Alumina Nanowires by Wet Chemical Method

Luis N. Moreno

To satisfy an increasing demand for large-scale processes for producing alumina nanomaterials, a wet chemical method was evaluated. A potassium salt precursor was combined with aluminum to produce alumina – based nanowires. Compared with current methods such as thermal oxidation, sol-gel, and laser ablation, this method is highly scalable due to relatively low energy requirements and the ability to carry out the primary reaction under ambient conditions. The nanowire samples were evaluated using SEM, XRD, BET, and TEM to confirm morphology, phases present, and surface area. A porous nanowire structure was confirmed which has a BET surface area of 324.6 m^2/g. The alumina consisted primarily of the γ phase with some α phase present as well. Proof – of – concept water treatment testing was conducted using the prepared nanowires to evaluate the potential for use as a heavy metal adsorbent in industrial wastewater streams. The nanowires were able to remove 88% of hexavalent chromium and 84% of hexavalent selenium from mock solutions in 24 hours under acidic conditions. The used nanowire sorbent material was recovered and annealed, forming a solid chromium – alumina solution. This demonstrates potential for follow – on applications in catalysis and could provide additional cost benefit to industry.

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Introduction

Alumina – based nanomaterials have a wide range of applications across multiple fields. This is due to highly desirable properties including high surface area, non-toxicity, mechanical strength, and thermal stability to name a few [1]. Due to the multitude of potential uses, scalable and economic methods for preparing alumina nanomaterials are being investigated [2]. The challenge which current preparation methods have struggled to meet is to achieve desired properties in a scalable and economic manner with relatively low energy requirements.

In this work, for the first time, γ – alumina nanowires were successfully prepared using a wet chemical technique which is highly scalable and low cost. The highlight of this method is the ease of which it allows for large – scale synthesis of highly porous alumina – based nanowires. Using a laboratory setup, kilograms of material can be produced in a single batch. The process steps can also be tuned depending on the desired properties and end use of the material. Additionally, the aluminum hydroxide forming step can be carried out at room temperature and pressure. This offers a significant advantage over the traditional Bayer-process which involves heating Bauxite in a pressurized environment [3]. The simple, scalable, and low-cost method described in this work produced quality alumina nanowires which have a multitude of potential applications. Two potential applications of the prepared alumina nanowires discussed in the following sections are water treatment and catalysis. From an industrial perspective, alumina is highly sought – after for these applications.

To maintain compliance with regulatory bodies such as the Environmental Protection Agency, industries are exploring costly methods for removing heavy metals from wastewater streams. These methods include reverse osmosis, thermal evaporation, and biological treatment which can range from $1,500 - $13,333/GPM [4]. One reason the task of removing heavy metals is a topic of regulatory requirement is the health ramifications of releasing certain these materials into the environment. Arsenic, cadmium, boron, chromium, mercury, selenium, and copper are all examples of toxic heavy metals which are present in industrial wastewater streams. These elements are known to cause cancer, heart disease, kidney damage, and neurological issues if ingested [5]. The risk of toxic waste products traveling to surface water sources and eventually contaminating drinking water sources is present. Requiring industries to reduce the level of toxic contaminants in waste streams is one way the risk is being managed.

Alumina has been established as an effective adsorbent to treat wastewater streams and remove heavy metals [6]. One property which allows alumina to be highly effective for this application is its porosity. Alumina is typically prepared from aluminum hydroxide which undergoes dihydroxylation. When the hydroxide groups are removed from the lattice of the structure, pores result. This is especially true for the ordered γ – phase. Additionally, alumina can be purchased at very low cost. In 2019, the price of alumina was $333.94 per metric ton [6]. The low cost and high porosity of alumina makes it a highly sought-after material for industrial wastewater treatment by adsorption.

In this work, proof of concept testing was conducted to establish the prepared alumina nanowire's ability to remove heavy metals by adsorption. The focus of the testing was removal of selenium and chromium. The selenium present in industrial wastewater is typically present in the hexavalent or trivalent states with the hexavalent state being more difficult to remove. Similarly, chromium is typically present in the hexavalent or trivalent states with the hexavalent state being more difficult to remove. For this study, the hexavalent states of both metals were used. Wastewater streams which contain selenium include those from agriculture runoff, electric power plants, mining, and oil refining [7]. Chromium can be found in waste streams from power plants, steel production plants, paint manufacturing, paper processing, as well as mining [8].

1

One consideration for adsorption treatment methods is the storage of used sorbent material. Once the contaminant – containing material is recovered, it is typically disposed of in a landfill or other solid waste storage facility. This can pose issues if storage space is limited and can also present a leaching hazard if the adsorbed contaminant escapes to its surrounding environment over time or when subjected to acidic rainfall.

The alumina nanowires prepared in this study can be used to overcome this challenge. Their nanomorphology leads to potential for follow-on applications after use as a heavy metal sorbent. Alumina nanowires, as opposed to traditional alumina, offer advantages, including low ion dissociation energy, which have been demonstrated in catalysis, battery, and corrosion research [9,10,11]. Additionally, γ – alumina nanomaterials used as a catalyst support have been shown to have relatively low precipitation of coke across the surface [12,13]. In this study, an annealing step is used to form a chromium – alumina solid solution from the prepared alumina nanowires and adsorbed chromium. This solid solution is far less likely to leach the contaminant and has potential for follow-on uses for heterogeneous catalysis applications.

Materials and Methods

2.1 Synthesis recipe (Wet Chemical)

In a 5 L beaker deionized water was added and placed on a hotplate. The hotplate was set to 250C with magnetic stirring to allow the water to heat. While heating, potassium salt and aluminum were measured in separate containers in the proper ratio. After water was heated for approximately 10 minutes, the potassium salt was slowly added to the water and allowed to dissolve completely. Aluminum powder was then added slowly over a period of approximately 15 minutes. The solution was allowed to stir with heating for 6 to 7 hours. A thermocouple was used to measure the temperature of the solution every 30 minutes to ensure ideal range was maintained. The ideal temperature range for this preparation is 80C to 100C. After stirring with heat for 6 to 7 hours, the solution turned white in color and was allowed to dry. The resulting alumina was washed using deionized water before undergoing calcination at 600C. Figure 1, below, graphically describes the alumina nanowire preparation process.
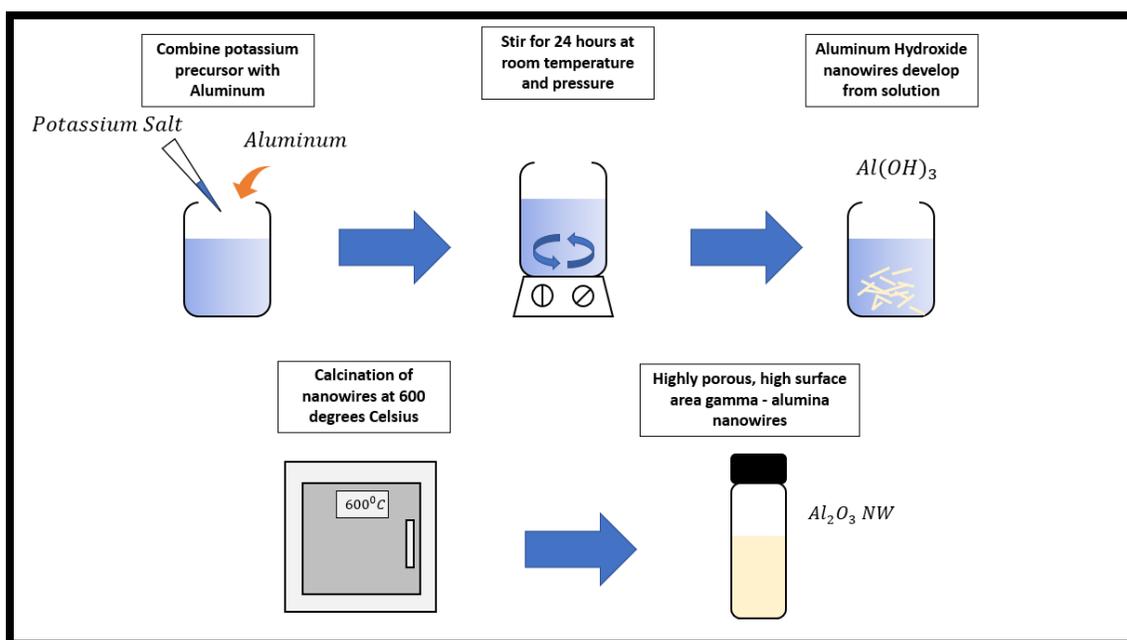

Figure 1: Schematic of Wet Chemical method for alumina nanowire preparation

Stirring of the potassium salt – aluminum solution can be carried out at room temperature but will require more time to react, approximately 24 hours. The resulting highly porous, ultra-thin alumina nanowires were analyzed using the characterization techniques described in the following section.

2.2 Characterization Techniques

The following characterization instruments were used to analyze prepared nanowire samples and mock wastewater solutions:

Scanning Electron Microscopy (SEM): TESCAN VEGA3 SB-EasyProbe (TESCAN Analytics, Brno, Czech Republic)

Transmission Electron Microscopy (TEM): FEI Tecnai T20 (Chalmers, Gothenburg, Sweden)

Brunauer – Emmett – Teller (BET) Surface Area: Micromeritics TriStar 3000 porosimeter (Micromeritics Instrument Corporation, Norcross, GA)

X-ray Diffraction (XRD): AXS D8 Advance 2-Series X-ray Diffractometer (Bruker, Billerica, MA)

Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES): IRIS Intrepid II XSP Inductively Coupled Plasma Atomic Emission Spectrometer (Thermo Scientific, Waltham, MA)

2.3 Mock Solution Preparation

Mock solutions containing selenium and chromium at various concentrations were prepared. For the solution containing trivalent chromium at 3000 ppm, chromium acetate from Alfa Aesar was dissolved in twice deionized water. Potassium chromate and sodium selenate from Alfa Aesar were combined with twice deionized water to prepare the solution which contained both hexavalent chromium and selenium at a concentration of 15ppm with respect to the metal anion.

2.4 Batch Adsorption Experiments

For adsorption experiments, 10 mL of mock solution was placed in an HDPE bottle with a magnetic stir bar. The pH of the mock solution was measured and recorded as the initial pH level. The alumina nanowires were weighed and added to the 10 mL of mock solution. 50 mg of alumina nanowires were added to 10mL of mock solution corresponding to a sorbent load of 5g/L. The mixture was stirred using a magnetic stir bar and stir plate. After 10 minutes of stirring, the pH level was measured again, recorded, then placed back onto the stir plate. For samples which required pH adjustments, NaOH or HCl was used to increase or decrease the pH level. Total stirring time was 24 hours. All samples were prepared and stirred under room temperature and pressure. Upon completion of stirring, the pH was measured and recorded as the equilibrium pH level. The mixture was then transferred to a centrifuge tube and centrifuged using a Marathon 3200R centrifuge from Fischer Scientific for 60 minutes at 4000 rpm. The liquid portion was removed and filtered using a 0.45um syringe filter. The filtered liquid was analyzed for heavy metal content by ICP-AES. These results were compared with ICP-AES results for the original mock solution to determine the percentage of heavy metal reduction.

2.5 Annealing

Alumina nanowires used to remove trivalent chromium from a concentrated chromium acetate solution were subjected to an annealing step to form a solid alumina-chromium solution. After treatment with the trivalent chromium mock solution, the alumina nanowires were dried at 60C in a drying oven. The dried nanowires were then annealed using the chemical vapor deposition reactor shown below in Figure 2.
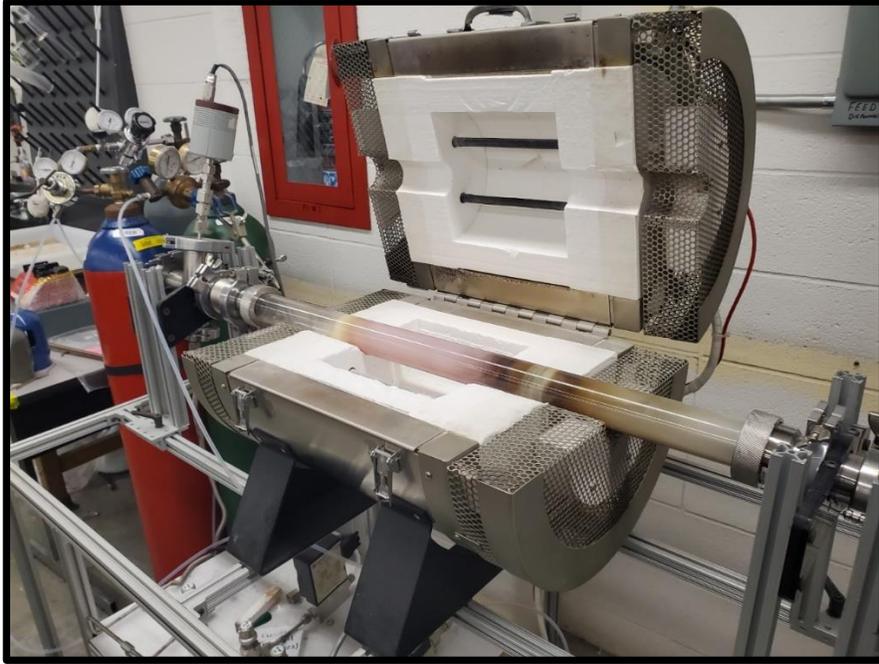

Figure 2: Annealing setup using vacuum furnace CVD reactor

Annealing was conducted for 3 hours at 600C under nitrogen flow of 50 g/L. After annealing, the chromium-doped alumina nanowires were allowed to cool at room temperature then analyzed using TEM.

Results and Discussion

3.1 Nanowire synthesis

The wet chemical synthesis method used in this work produced a fine, white, solid, alumina powder. SEM analysis was conducted to observe the morphology of the material. Figure 2 shows SEM images of the prepared alumina and clearly shows the nanowire morphology. The nanowires clump together forming closely – packed bundles which disperse when stirred or ground using a mortar and pestle.
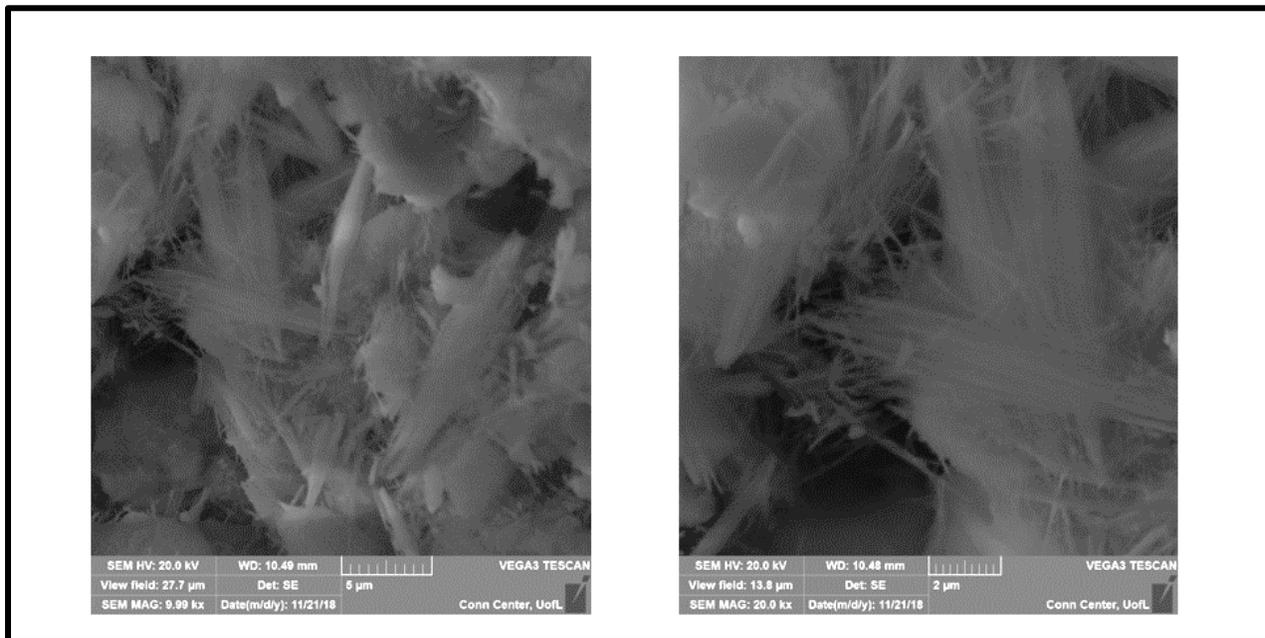

Figure 3: SEM imaging of high density, ultra-thin alumina nanowires

When added to mock solutions for batch adsorption experiments, the nanowires disperse uniformly throughout the solution causing it to appear white in color. Nanowires were easily separated from solution after adsorption by centrifugation. The solid nanowires were completely recovered and remained in the solid phase as expected.

To observe the nanowire morphology on the nanometer scale, TEM analysis was conducted. Figure 3 shows TEM results in which high porosity can be observed in a single alumina nanowire that is less than 100nm wide.
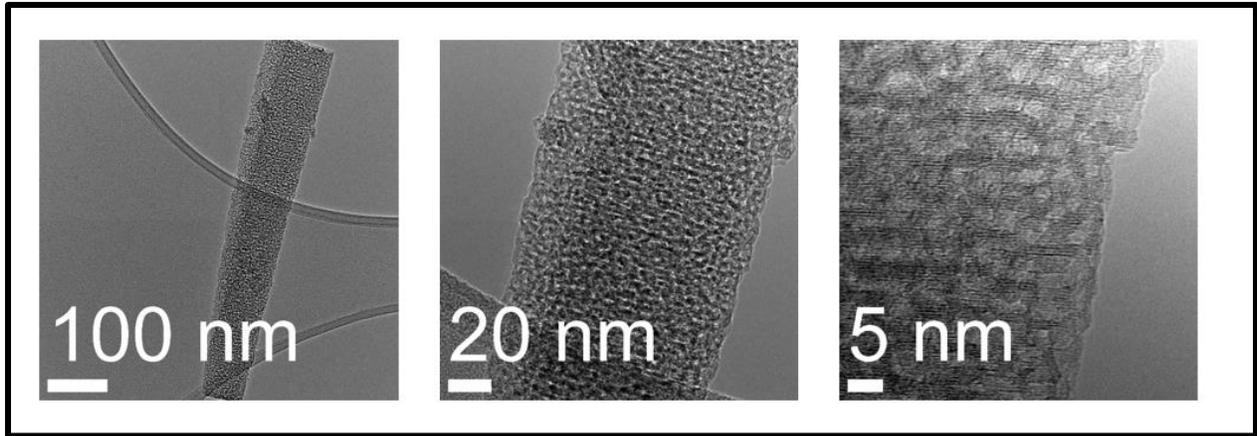
Figure 4: TEM of highly porous alumina nanowires

The BET surface area for the prepared nanowires was determined to be 324.6 m^2/g. This high surface area is a desirable property for adsorption materials. The performance of the prepared nanowires as a heavy metal sorbent will be discussed shortly.

EDX analysis was conducted in parallel with SEM to determine the composition of the nanowire preparation. Table 1 shows the weight percent and atomic percent of alumina and oxygen.

Table 1: Weight percent and atomic percent of nanowires by EDX

	Weight %	Atomic %	K-Ratio
O	54.66	67.03	0.2064
Al	45.34	32.97	0.2574
Total	100	100	

An XRD analysis of the prepared alumina nanowires was conducted to confirm the species and crystallographic structures present in the sample. The specimen was confirmed to contain γ – alumina. Figure 5, shown below, shows the resulting peaks.
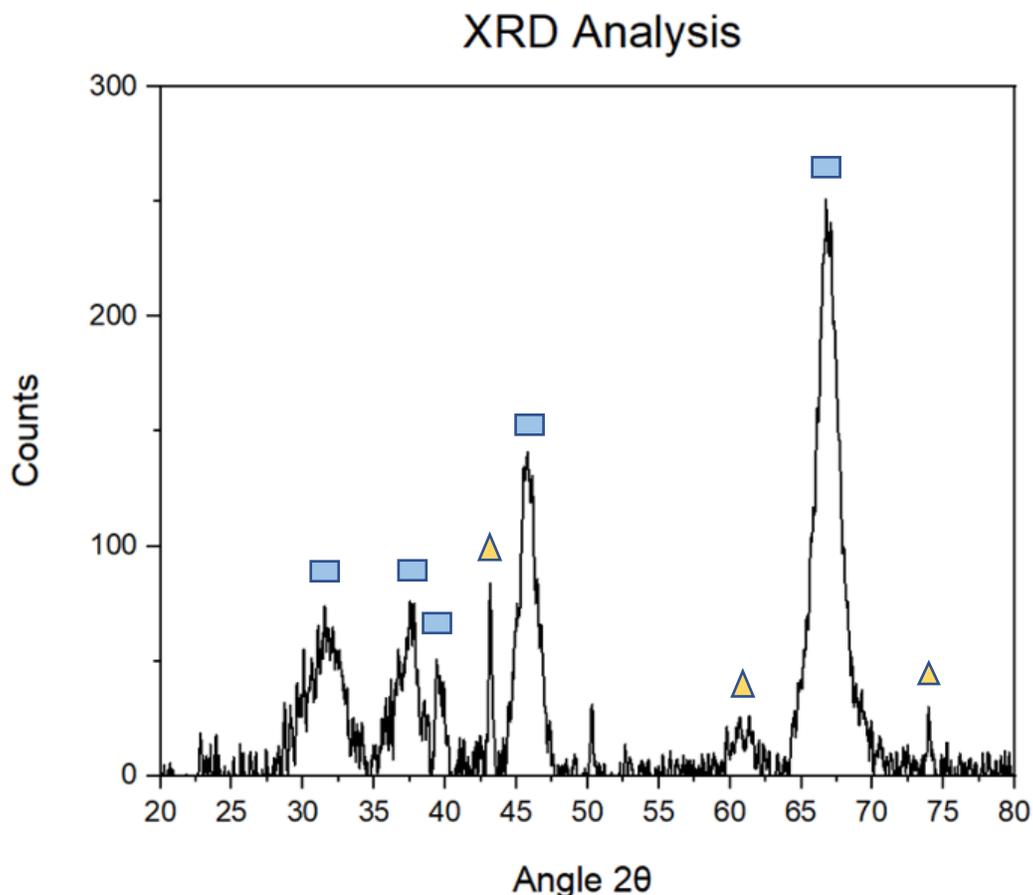
Figure 5: XRD Results for alumina nanowires. It shows that the material consists of $\gamma - Al_2O_3$ (peaks denoted by ☐) and α $- Al_2O_3$ (peaks denoted by △)

The sample had peaks of $\gamma -$ alumina at angles 31.98˚, 37.62˚, 39.43˚, 45.88˚, and 66.91˚ with counts ranging from 88 to 252. The sample also had peaks of $\alpha -$ alumina at angles 43.12˚, 61.09˚, and 74.24˚ with counts ranging from 26 to 93. The $\gamma -$ alumina peaks correspond with PDF 00-029-0063 and the $\alpha -$ alumina peaks correspond with PDF 00-046-1212. The crystal structure of $\gamma -$ alumina consists of oxygen atoms packed in a cubic lattice with tetrahedral and octahedral sites being occupied by aluminum atoms [14]. This crystallographic structure is the most important catalyst support structure [15,16]. The crystal structure of $\alpha -$ alumina consists of oxygen atoms packed in a hexagonal lattice with aluminum atoms located in octahedral coordinates [17]. Due to the stoichiometry of alumina, vacancies exist throughout the crystal structure in both $\alpha -$ alumina and $\gamma -$ alumina phases.

The mechanism of growth which leads to the nanowire structure has yet to be clearly defined. One study defines a nanowire growth mechanism in which nuclei are formed followed by 1-D diffusion-driven growth and basal attachment [18]. If the alumina nanowire growth mechanism behaves similarly, the potassium precursor is dissolved in solution to form free moving potassium cations. The potassium cations form a liquid phase containing potassium and aluminum hydroxide. Supersaturation of the $K - Al(OH)_3$ liquid phase leads to formation of a nucleus from which nanowire growth occurs. The $K - Al(OH)_3$ is layered with active sites at the edges resulting in 1-D growth. Further TEM analysis should be conducted to confirm the crystallographic direction and mechanism of growth.

3.2 Proof of concept application testing

The prepared nanowires were effective at removing hexavalent chromium and hexavalent selenium from mock solutions. Figure 6 shows the removal percentage of both elements. Adsorption performance of the nanowires was highest under acidic conditions. When the pH of the system was lowered to 4.5, the nanowires were able to adsorb 88 percent of the chromium from the solution and 84 percent of the selenium.
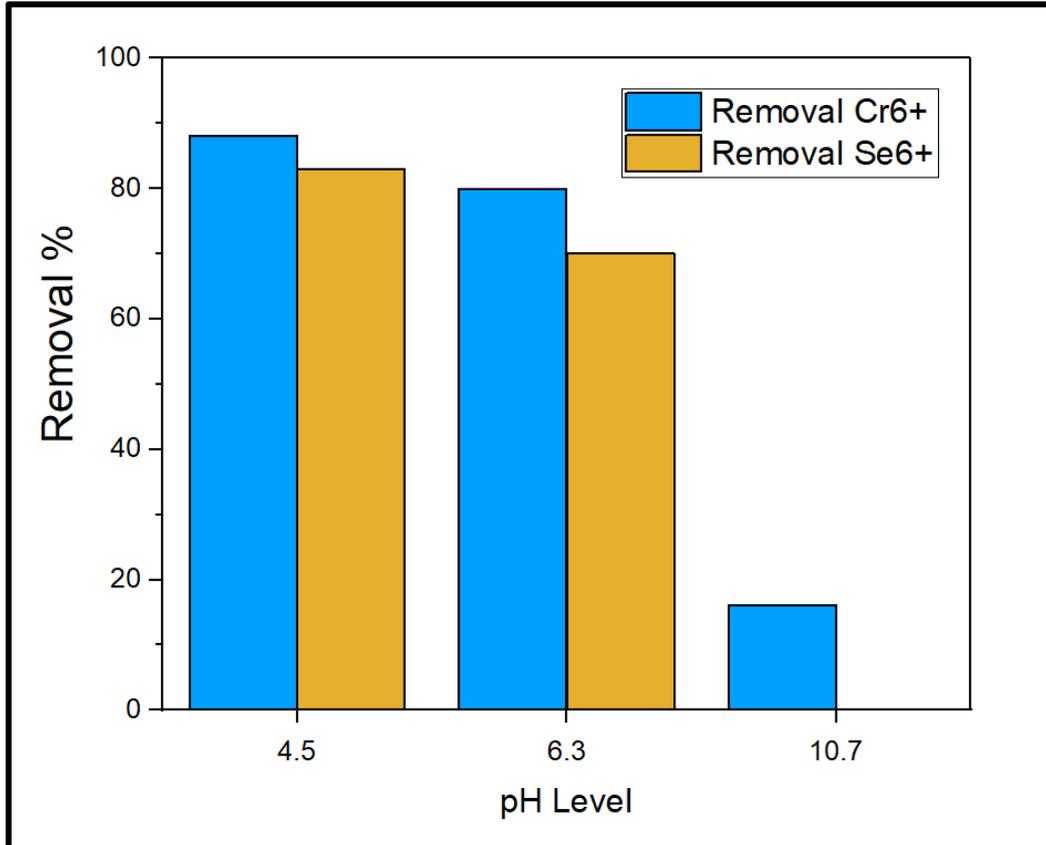

Figure 6: ICP results for metal removal percentage using alumina nanowires

Under a near neutral pH level, pH 6.3, the nanowires removed 80 percent of the hexavalent chromium and 72 percent of the hexavalent selenium. Under basic conditions, with a pH level of 10.7, the nanowires removed only 17 percent of the chromium from the solution and no selenium was removed from the solution.

The reason that adsorption performance is highest under acidic conditions and lowest under basic conditions involves the way that pH level effects the conditions on the surface of the nanowires. The surface of the nanowires become heavily protonated under acidic conditions [6]. Since the hexavalent chromium and selenium both exist in solution as the chromate ($CrO_4{}^{2-}$) and selenate ($SeO_4{}^{2-}$) anions, respectively. Since anions have a relatively high affinity for uptake onto a protonated surface, chromium and selenium removal is high under acidic conditions. On the other hand, basic conditions result in an abundance of hydroxide (OH^-) anions which greatly outnumber the heavy metal anions. The competition between hydroxide anions and metal anions for adsorption sites leads to much lower performance with respect to heavy metal adsorption.

3.3 Annealed nanowires with adsorbed chromium

While the alumina nanowires effectively removed hexavalent chromium under acidic conditions, trivalent chromium removal was carried out through a much different mechanism. Under basic conditions, at a pH of 11, the nanowires removed 100 percent of trivalent chromium from the concentrated chromium acetate solution. As the pH was raised using sodium hydroxide, chromium hydroxide was formed. The chromium hydroxide precipitated out of the solution and was captured by the surface of the alumina nanowires in less than 24 hours. ICP results indicated that the solution was completely free of chromium after the adsorption process was carried out.

The chromium – adsorbed nanowires prepared from the chromium acetate solution were annealed then analyzed by TEM to determine whether the chromium was dispersed uniformly throughout the structure of the nanowire. Figure 7, below, shows a TEM image of the chromium – doped nanowire.
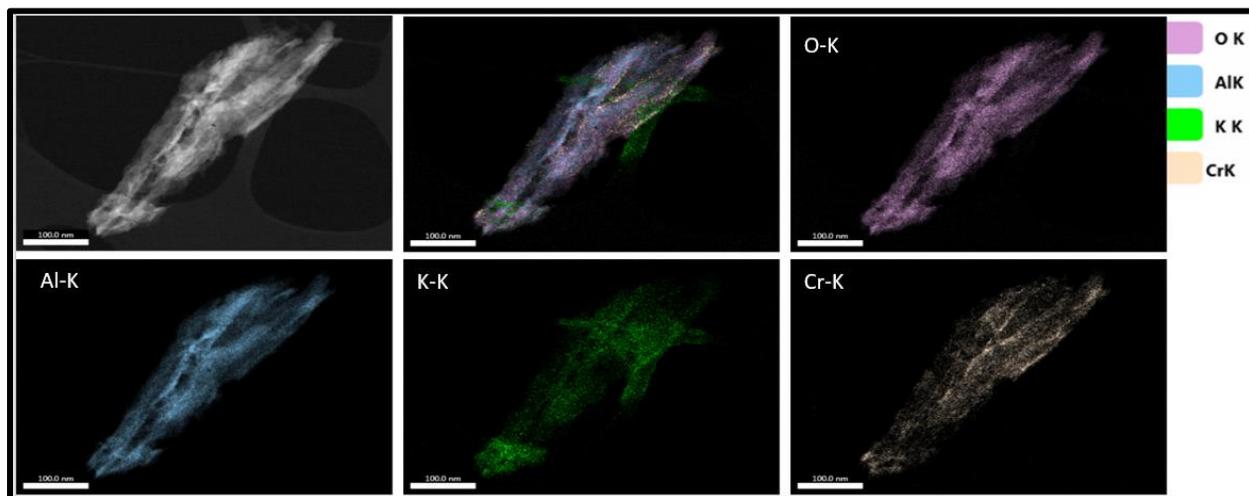

Figure 7: TEM imaging of Cr – doped nanowires

The TEM results show that the annealed nanowires contain chromium in a uniform distribution throughout the structure. This indicates that the chromium captured onto the surface of the alumina was integrated into the crystal lattice forming a solid solution.

The solid solution formed from annealing the chromium treated nanowires could potentially be used as a nano catalyst material. Similar chromium – alumina systems have been shown to be effective catalysts for propane and isobutane dehydrogenation processes [19,20]. Additional testing must be conducted to determine the catalytic activity of this chromium – alumina nanowire preparation. Catalytic functionality would provide a value-added aspect in that the alumina nanowires could be used for a primary function such as adsorption then could be recovered and sold for a secondary function such as catalysis. For the water treatment application, adsorption is already much more cost effective than many of the treatment processes previously mentioned. If the adsorption material were sold in the catalysis market, even more cost could be recovered.

Conclusion

A novel, scalable synthesis method for alumina – based nanowires has been demonstrated. Ultra – thin nanowires with high porosity were produced using a wet chemical method involving aluminum and a potassium salt precursor. Nanowire morphology was confirmed by SEM and TEM. High surface area was confirmed by BET. The lab – scale setup consisting of glass beakers and hotplates is suitable for production of kilograms of material per batch. The ordered γ – alumina crystal structure is dominant as

confirmed by XRD. This low-cost material has several potential applications including industrial wastewater treatment and catalysis.

The industrial wastewater treatment performance of the prepared alumina – based nanowires was demonstrated using selenium and chromium. Under acidic conditions, the nanowires were used as a sorbent to remove 88 percent of chromium and 84 percent of selenium from mock wastewater solutions. Further wastewater treatment DOEs should be conducted to determine the most effective adsorption conditions for this material to include sorbent loading, stirring time, stirring speed, and pH level. The proof-of-concept testing conducted in this study confirms that the prepared nanowires are suitable for use in water treatment applications.

The potential for the prepared nanowires to be used as a catalyst support after being used for wastewater treatment was established. The nanowires were annealed after heavy metal adsorption to secure the heavy metal within the lattice. TEM analysis confirmed the distribution of chromium throughout the nanostructure. This demonstrated the ability to form a solid solution from the alumina nanowire sorbent. As γ – alumina is a well-known catalyst support, further testing should be conducted to establish the catalytic activity of various solid solutions prepared through heavy metal adsorption. This potential follow-on application could provide a value-added resale opportunity for what would otherwise be considered a solid waste product generated through an industrial wastewater treatment process.

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