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ZINC SULFIDE: MANGANESE DOPED QUANTUM RODS FOR DETECTION OF METAL IONS AND A BUSINESS MODEL FOR FUTURE SALES

by:

ANDREW TEBLUM B. S. University of Central Florida 2012

A thesis submitted in partial fulfillment of the requirements for the degree of Master's of Science in the Department of Interdisciplinary Studies in the College of Graduate Studies at the University of Central Florida Orlando, Florida

Spring Term 2014

Major Professor: Swadeshmukul Santra

ABSTRACT

Hexavalent chromium is an extremely carcinogenic chemical that has been widely produced in the United States. This has led to major waste contamination and pollution throughout the country. According to the Environmental Working Group Hexavalent chromium has been found in 89% of city tap water. Most people believe they are safe using regular home filter systems however that is not true. A more expensive ion exchange water treatment unit is required. Therefore to protect yourselves from this carcinogenic metal a reliable test is required. In this study we have developed a Zinc Sulfide Manganese doped Quantum Rod technology to detect for presence of chromate and other harmful transitional metals in drinking water. Quantum Rods were synthesized using a hydrothermal reaction method. They were fully characterized using UV-visible absorption spectroscopy, fluorescence emission spectroscopy, X-ray Photoelectric Spectroscopy (XPS) and High Resolution Transmission Electron Microscopy (HRTEM). Quantum Rod metal detection studies were done with 28 different ions in a 96-well fluorescent plate reader. Results show that highest sensitivity to 8 ions including the toxic ions of chromate and mercury allowing us to create a sensor to detect these items.

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CHAPTER 1: INTRODUCTION AND BACKGROUND

Fluorescent Semiconductor Nanostructures, in particular Quantum Dots and Quantum/NanoRods, have been extensively studied due to their unique optical and electrical properties. In the biomedical field Quantum Dots have been extensively used for imaging, labeling and sensing applications. [1, 2] They can be used as probes for in vitro and in vivo biological processes [3] and as multimodel/multifunctional drug delivery vehicles [4]. Quantum Dots and Rods may also be used for a wide variety of detection tools due to their fluorescent properties including Electrophoresis, chip detection and capillary electrophoresis (CE), Chromatography, Flow analysis, monitoring DNA hybridization, test enzymatic activity, pH detection, enzyme-linked immunosorbent assay (ELISA), polymerase chain reaction (PCR), fluorescence resonance-energy transfer (FRET), detection of small molecules such as DNA and proteins, analysis, fluorescence in-situ hybridization (FISH) and western blot analysis.[5-7]

Zinc Sulfide a particular material used for Quantum Dots and Quantum Rods is an extremely attractive material due to being a II-VI semiconductor compound [8-10] Depending on the configuration of the material it can either have be a Cubic structure with a band gap of ≈ 3.72 eV [11] or have a hexagonal structure with a band gap of ≈ 3.77 eV [12] These properties allow for it to be highly fluorescent which gives it other non-biomedical applications including electroluminescence, [13] displays, [14] sensors, [15] and light-emitting diodiodes. [16]

Methods in making Zinc Sulfide material into Zinc Sulfide Nano/Quantum Rods include Catalyst free colloidal chemistry strategy, [17-19] a termperature controlled catalytic growth by evaporation of ZnS nanopowders, [20] size- and shape-dependent growth of fluorescent ZnS nanorods and nanowires using Ag nanocrystals as seeds,[21] an oriented attachment mechanism [22]and a simple wet chemical method while under reflex condition[23].

Zinc Sulfide and Cadmium Sulfide Nanoparticles in particular quantum dots have a very low fluorescence intensity therefore to greatly increase the intensity of the material the dopant manganese is used. This also causes the wavelength to shift to around 590nm. [24-28]. With similar properties as the quantum dot material Alloy based Cd_{1-x}Zn_xS have been synthesized as well as adding the manganese dopant in a Core-Shell CdS-Mn/ZnS Nanorod [29, 30]

A prevalent pollutant Hexavalent chromium is an extremely carcinogenic chemical that has been widely produced in the United States. Approximately 300,000,000lb of chromates and dichromates were produced in 1985 for industries such as chrome plating and paints. [31] This has led to major waste contamination and pollution throughout the country. According to the Environmental Working Group Hexavalent chromium has been found in 89% of city tap water that has been detected. [32] For a long time the effects of breathing Chromium was well established however not until recently has it become known that toxic effects of having chromium in your drinking water. Currently the EPA has a MCLG for Chromium at 1 mg/L or 100ppb. [33]

Due to this issue of Chromate either sensors or filters are required to detect and remove it, however not all filtration systems, such as your common household Brita filter, are capable of removing hexavalent Chromium. A more expensive ion exchange water treatment unit is required. [34] Therefore sensors are cheaper test for your drinking water to determine if it is contaminated by hexavalent chromium.

Recently there has not been much detection of Chromate in articles especially using fluorescent sensors. Currently research how been focused on materials such as Cthiophenecalix(4)resorcinarene and crown ethers as selective ionophores for the quantification of chromate ions [35, 36]. There have however been many optical based semiconductor nanomaterial sensors just not for the detection of Chromate. Most of these optical Quantum Dot based sensors are used to detect copper, Silver or mercury ions. There are two types of fluorescent sensors, fluorescent quenching and fluorescent enhancement. Examples of fluorescent quenching copper detectors include CdSe-ZnS Quantum Dots, [37] L-Cysteine coated CdSe/CdS Quantum Dots, [38] ZnSe Quantum dots, [39] Nonstoichiometric CdS Nanoparticles, [40] Zn_xHg_{1-x}Se Quantum Dots, [41]L-Cysteine coated ZnS Quantum Dots, [42] and Graphene Quantum Dots, [43]. Mercury can be detected with fluorescent quenching using L-Cysteine coated CdS Quantum Dots, [44] N-Acetyl-L-Cysteine coated CdTe Quantum Dots, [45] and CdSe nanoclusters [46]. Another ion that can be detected is silver using CdS Quantum Dots [47]. Fluorescent enhancement materials that can detect Silver include functionalized CdS Quantum Dots [48] and to detect Mercury and silver mercaptoethanol coated PbS Quantum dots can be used [49].

CHAPTER 2: MATERIALS AND METHODS

2.1 Materials

All reagents were purchased at reaction grade purity from commercial vendors and used without addition purification: Ethylene-Diamine (Acros), Thiourea (Fisher), Copper Acetate (sigma Aldrich), Silver Trifluoromethane (Acros), Zinc Acetate dehydrate (Aldrich), Aluminum Oxide (Sigma Aldrich), Potassium Chromate, Arsenic Pentoxide, Cadmium Acetate (Acros), Iron (II) Chloride (Fluka). Iron (III) Chloride (Fluka), Manganese Acetate (Acros), Selenium (Acros), Sodium Sulfide (Aldrich), Magnesium Sulfate (Acros), Calcium Chloride (Fisher), Sodium Chloride (Fisher), Cerium (II) Acetate (Aldrich), Potassium Phosphate (Fisher), Potassium Iodide, Lead Chloride (Fisher), Mercury (II) Chloride (Alfa Aeser), Ammonium Fluoride (Sigma-Aldrich), Vanadium Oxide (Sigma-Aldrich), Germanium (IV) Isopropoade (Alfa Aeser), Cobalt (II) Chloride, Nickel (II) Acetate (Alfa Aeser), Molybdenum Powder (Alfa Aeser), Bismuth Chloride (Alfa Aeser), Indium (III) Nitrate, Chromium Chloride (Fisher) and Deionized water (DI) was obtained from Nanopure (barnstead Model #D11911).

2.2 Instrumentation

Quantum Rod Fluorescence was viewed using a handheld UV excitation Source. (Mineralight, multiband UV 254/365nm Lamp, Model UVGI-58). All Fluorescence Emission was collecting using the Tecan infinite M200 Pro Fluorescent 96-well Plate reader. UV-VIS readings were done using Agilent 8453 UV-Visible Spectrophotometer. Quantum Rods size, shape, crystallinity and elemental analysis were characterized using a FEI Technai F30 TEM. X-ray photoelectric spectroscopy was done using a Physical Electronics 5400 ESCA (XPS) spectrometer.

2.3 Methods

2.3.1 Synthesis of ZnS:Mn Quantum Rods

The ZnS:Mn Quantum rods procedure is as follows: Prepare in a Teflon lined steal cylinder

220mg of Zinc Acetate dehydrate, 190mg of Thiourea and 6.1mg of Manganese acetate. Add

15ml of DI water and 15ml of EthyleneDiamine. Seal the steal cylinder and place in oven at

180°C for 3 hours. Let cool then wash samples 3 times in DI water.

2.3.2 Characterization of ZnS:Mn Quantum Rods 2.3.2.1 UV-Visible Absorption Spectroscopy

UV-Visible spectroscopy of the ZnS:Mn Qrods were taken using a 3mL quartz cuvette. The sample was first blanked with Deionized water. Absorbance of the sample in DI water was measured between 200-350nm with a peak absorbance 0.2.

2.3.2.2 Fluorescence Spectroscopy

Each well was loaded with 100uL of Qrods in DI water. The Z-position and the Gain were calculated using well A1. Run Fluorescent scan at 350nm Excitation with emission between 525 and 650nm for each well, making sure no well went over the maximum 80,000 photon count and that all wells were within similar photon counts on the same plate. Run Fluorescent scan at 350nm Excitation with emission between 525 and 650nm.

2.3.2.3 High Resolution Transmission Electron Microscopy

Three TEM Carbon coated copper grids -400 mesh (Electron Microscopy Sciences) were prepared. Grid A was prepared with 1 drop of ZnS:Mn Qrods Solution. Grid B was prepared with 1 drop of ZnS:Mn-Hg Qrods Solution and grid C was prepared with 1 drop of ZnS:Mn-Cr Qrods Solution. Grids were carried to UCF-AMPAC-MCF for HRTEM imaging. All measurements were done at UCF-AMPAC-MCF including crystal size, lattice spacing and elemental analysis.

2.3.2.4 X-Ray Photoelectron Spectroscopy

Three Samples were prepared for XPS. Sample A was ZnS:Mn Qrods Solution. Sample B and C were modified of sample A with addition of Hg Ions for Sample B and Cr Ions for sample C. Samples were stirred overnight. Then frozen and lyophilized into a dry powder.

2.3.2.5 Stern-Volmer Relationship

Graphing the Stern-Volmer equation uses the baseline QRod fluorescent reading divided by the reading for the Ion added fluorescent reading. These number acts as the Y value. For the X value use the concentration of the ion added for the fluorescent reading. Calculate the slope using the formula $F_0/F=1+K[Q]$. [50]

2.3.3 Detection of Metal Ions using Quantum Rod Fluorescence

Each well was loaded with 100uL of Qrods in DI water. The Z-position and the Gain were calculated using well A1. A baseline of the fluorescence of each well was taken, making sure no well went over the maximum 80,000 photon count and that all wells were within similar photon counts on the same plate.

For Ion testing 5uL of different ions and concentrations were added to each well for a final volume of 105uL to determine ion effects on the Qrods. Run Fluorescent scan at 350nm Excitation with emission between 525 and 650nm.

CHAPTER 3: RESULTS AND DISCUSSION

Based on the results of the fluorescence tests we can use the Quantum Rods printed onto filter paper as a handheld chromate test strip. The test strip works by using the fluorescence quenching of the Quantum Rods when in contact with chromate ions as a sensor. The fluorescence quenching with chromate works based on the static quenching where the chromate is forming a Zinc-Chromate bond on the quantum rod shutting off the fluorescence caused by the Mn^{2+} band gap.

3.1 Absorption and Fluorescence characterization

ZnS:Mn Quantum Rods have a white color under visible light (**Figure 1**), however under a handheld 365nm UV light sources and other similar UV excitation sources a fluorescent emission is seen with a yellow-orange color and a maximum intensity at 590nm. (**Figure 2**) This fluorescence is caused by the $Mn^{2+4}T_1-^6A_1$ energy band gap.

UV-Visible absorption shows a high amount of scattering due to the lack of solubility of the material. This is shown by the upwards shift of the entire reading from the baseline. The spectra visible from the material is that of a Semi-Conductor material. (**Figure 3**) Normalized fluorescence reading shows a maximum peak fluorescence at 590nm. (**Figure 4**) With the addition of metal ions static quenching occurs due to binding of the contaminating ion to the surface of the Qrods as seen below in sections 3.2 and 3.3. All fluorescent data was done in triplicate with comparisons of different concentrations of ions.

3.2 X-Ray Photoelectron Spectroscopy

Using X-Ray Photoelectron Spectroscopy (XPS), a survey spectra was collected for four samples to confirm elemental mapping. The first sample was ZnS:Mn Quantum Rods which showed the presence of Zn, Mn and S. (Figure 5) The second sample was the Quantum Rods with the addition of Chromate. This sample showed the presence of Zn, Mn, S and Cr. (Figure 6) The third sample was the Quantum rods with the addition of Mercury. This sample did not show any presence of Hg or Mn however Zn and S were still visible. (Figure 7) The last sample for XPS was the Quantum Rods with the addition of chromium. This did not show the presence of Cr however Zn, Mn and S were all visible. (Figure 8)

3.3 High Resolution Transmission Electron Microscopy

High resolution transmission electron microscopy obtains three types of data: Selected area electron diffraction (SAED), energy dispersive X-Ray spectroscopy (EDX) and high resolution images. Data for three samples were acquired for each method: ZnS:Mn Quantum Rods, ZnS:Mn Quantum Rods with chromate and ZnS:Mn Quantum Rods with mercury. For EDX the presence Zn, Mn and S was confirmed in the plain ZnS:Mn Quantum Rods. (Figure 9) For the ZnS:Mn Quantum Rods with Chromate chromium ions were observed, (Figure 10) however for the ZnS:Mn Quantum Rods with mercury no mercury was observed. (Figure 11) For all samples Copper and carbon were present due to the carbon film and TEM grid.

To visualize the Quantum Rods high and low resolution transmission electron microscopy images were acquired. Due to the minor changes from the ion addition it is impossible to visualize a difference between the samples. For the low resolution images we see clusters of Quantum Rods. ZnS:Mn Quantum Rods (**Figures 12-14**), ZnS:Mn Quantum Rods with Chromate (**Figure 15-17**) and ZnS:Mn Quantum Rods with mercury (**Figure 18-20**). The high

resolution images we can clearly make out the lattice planes of the rods. ZnS:Mn Quantum Rods (**Figures 21-23**), ZnS:Mn Quantum Rods with Chromate (**Figures 24-26**) and ZnS:Mn Quantum Rods with mercury (**Figures 27-29**). From the low resolution images you can see that the material looks clearly like nanorod shaped however with the high resolution images they can be considered rod like nanoplates instead of the normal shaped nanorods.

The ZnS:Mn Quantum Rods are proved to be crystalline particles due to results from the SAED. You can clearly see nice bright distinct rings for each of the three samples. ZnS:Mn Quantum Rods (**Figures 30-31**), ZnS:Mn Quantum Rods with Chromate (**Figure 32-33**) and ZnS:Mn Quantum Rods with mercury (**Figure 34-35**). For each sample the ring spacing were almost identical and most likely were different due to human error measuring the distances. Six rings were clearly detected for each sample of Quantum Rods. The Six rings spacing are listed in the Table. (**Table 1**). This data corresponds to Zinc Sulfide spacing references. [31]

3.4 Detection of Metal Ions using Quantum Rod Fluorescence

Twenty Eight different ions were tested for using the Quantum Rod fluorescent quenching tests in the plate reader. (**Figure 36**) These ions were Copper, Silver, Zinc, Aluminum, Chromate, Arsenic, Cadmium, Iron II, Iron III, Manganese, Selenium, Sodium Sulfide, Magnesium, Calcium, Sodium Chlroide, Cerium, Potassium Phosphate, Potassium Iodide, Lead, Mercury, Ammonium Fluoride, Vanadium, Germanium, Cobalt, Nickel, Molybdenum, Bismuth and Indium. Studies were done using 500uM solutions of each ion added to a well of Quantum Rods.

Based on quenching studies certain transition metals showed the most detection based on their quenching capabilities. These 9 ions were Copper, Silver, Chromate, Iron II, Iron III, Mercury, Vanadium, Lead and Cobalt. Further studies of these metals were done at 5uM, 50uM and 500uM. (Figure 37) This data showed highest quenching of Copper, Chromate, Mercury and Vanadium. Out of these four ions the two most toxic were Chromate and Mercury therefore 10 point concentration (Figure 38) and 9 point concentration (Figure 39) were done for these materials. These graphs were used to determine the Stern-Volmer relationship below. Using these studies the Chromate sensor product was created as seen in the business plan section of this thesis.

3.5 Stern-Volmer Relationship

The Stern-Volmer equation equation helps determine the efficiency of quenching of the fluorescent material being testing as well as to determine if the material is having a static or dynamic interaction with the quencher and fluorophore. Quantum Rod testing for Chromate and Mercury were taken at 10 and 9 points respectively. For Chromate the Stern-Volmer costant was calculated to be k=0.044 uL/Mol (R(linear regression coefficient): 0.9968). (Figure 40) For Mercury the Stern-Volmer costant was calculated to be k=0.0081 uL/Mol (R(linear regression coefficient): 0.9738). (Figure 41) Both systems were determined to be static quenching due to their ability to stay quenched after excess ions were washed out of Quantum Rod.



Figure 1- Digital Photograph of Quantum Rods under Room light



Figure 2- Digital Photograph of Quantum Rods under UV excitation source



Figure 3- UV-Visible spectrum of Quantum Rods



Figure 4- Normalized fluorescence spectra of Quantum Rods suspended in DI water. Excitation

wavelength: 350nm



Figure 5- X-ray photoelectron spectroscopy (XPS) survey spectrum of ZnS:Mn Quantum Rods showing the characteristic peak of constituent elements.





Chromate showing the characteristic peak of constituent elements



Binding Energy (eV) Figure 7- X-ray photoelectron spectroscopy (XPS) survey spectra of ZnS:Mn Quantum Rods after

treatment with Mercury showing the characteristic peak of constituent elements



Figure 8- X-ray photoelectron spectroscopy (XPS) survey spectra of ZnS:Mn Quantum Rods after treatment with Chromium showing the characteristic peak of constituent elements



Figure 9- HRTEM Energy-dispersive X-ray spectrum (EDX) of ZnS:Mn Quantum Rods showing

elemental composition



Figure 10- Energy-dispersive X-ray spectrum (EDX) of ZnS:Mn Quantum Rods after treatment with

chromate



Figure 11- Energy-dispersive X-ray spectrum (EDX) of ZnS:Mn Quantum Rods after treatment with

mercury



Figure 12- HRTEM ZnS:Mn Low magnification 1



Figure 13- HRTEM ZnS:Mn Low magnification 2



Figure 14- HRTEM ZnS:Mn Low magnification 3



Figure 15- HRTEM ZnS:Mn after treatment with Chromate Low magnification 1



Figure 16- HRTEM ZnS:Mn after treatment with Chromate Low magnification 2


Figure 17- HRTEM ZnS:Mn after treatment with Chromate Low magnification 3



Figure 18- HRTEM ZnS:Mn after treatment with mercury Low magnification 1



Figure 19- HRTEM ZnS:Mn after treatment with mercury Low magnification 2



Figure 20- HRTEM ZnS:Mn after treatment with mercury Low magnification 3



Figure 21- HRTEM ZnS:Mn high magnification 1



Figure 22- HRTEM ZnS:Mn high magnification 2



Figure 23- HRTEM ZnS:Mn high magnification 3



Figure 24- HRTEM ZnS:Mn after treatment with Chromate high magnification 1



Figure 25- HRTEM ZnS:Mn after treatment with Chromate high magnification 2



Figure 26- HRTEM ZnS:Mn after treatment with Chromate high magnification 3



Figure 27- HRTEM ZnS:Mn after treatment with mercury high magnification 1



Figure 28- HRTEM ZnS:Mn after treatment with mercury high magnification 2



Figure 29- HRTEM ZnS:Mn after treatment with mercury high magnification 3



Figure 30- HRTEM-SAED of ZnS:Mn Quantum Rods 1



Figure 31- HRTEM-SAED of ZnS:Mn Quantum Rods 1 (with Circles)



Figure 32- HRTEM-SAED of ZnS:Mn Quantum Rods with Chromate 2



Figure 33- HRTEM-SAED of ZnS:Mn Quantum Rods with Chromate 2 (with Circles)



Figure 34- HRTEM-SAED of ZnS:Mn Quantum Rods with mercury 3



Figure 35- HRTEM-SAED of ZnS:Mn Quantum Rods with mercury 3 (with Circles)

Ring	ZnS:Mn (nm)	Chromate (nm)	Mercury (nm)
1	0.325	0.306	31.4
2	0.228	0.225	22.2
3	0.192	0.191	18.72
4	0.176	0.175	17.04
5	0.161	0.163	15.87
6	0.129	0.13	12.55

Table 1- ZnS:Mn Quantum Rods lattice spacing estimated from HRTEM-SAED patterns



Figure 36- A histogram showing change in relative fluorescence intensity of ZnS:Mn QRods

after treatment with 500uM concentration of 28 different metal ions



Figure 37- A histogram showing change in relative fluorescence intensity of ZnS:Mn QRods

after treatment with 500/50/5uM concentration of the 9 most sensitive metal ions



Figure 38- ZnS:Mn Quantum Rod fluorescence after treatment with Chromate



Figure 39- ZnS:Mn Quantum Rod fluorescence after treatment with mercury



Figure 40- Stern-Volmer plot showing the change of F_0/F (relative fluorescence intensity of







Quantum Rods) with respect to the increase of mercury Ion Concentration

CHAPTER 4: CONCLUSION

In the present work ZnS:Mn Quantum Rods were synthesized and characterized. UV-visible spectroscopy and fluorescence spectroscopy were completed for the material showing bright yellow-orange emission at 590nm. Transmission electron miscopy images were taken confirming the Rod like structure of the material. EDX and XPS were taken confirming the material makeup of the Quantum Rods of that of Zn, S and Mn. Also samples with Hg and Cr were confirmed. SAED was done to show the crystallinity of the rods. Testing of 28 different ions were done showing 8 with high levels of fluorescent quenching. Out of these 8 ions Mercury and Chromate were shown to have extremely high quenching abilities as well as having known toxic effects to humans and the environment therefore more in-depth studies including Stern-Volmer relationships were completed for these materials to create a fluorescent chemical test strip to test for Ion water contamination of chromate and mercury. Further studies are recommended after surface modification of the Quantum Rods to see if small molecules such as N-Acetyl-L-Cysteine or Lipoic Acid have any effect on fluorescent intensity with ion or other chemical addition.

4.1 Future Work

Future work for fluorescent testing of the Quantum Rods would be to test the Quantum Rods against other sources of water. This can include testing it against other direct water sources such as lake or ocean water or it can be drinks such as soda, juices or other drinks. They will need to be tested both filtered and unfiltered with controls that could be found in these sources such as dirt. Another future work would be to test the Quantum Rods against varying

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pH's to see the effect of pH on the Rods as well as the possibility of it being used as a pH test. On top of testing other water sources and chemicals, modifying the Quantum Rods with small molecules such as DHLA or NAC can be done to effect the sensitivity of the Quantum Rods against chromate and other ions or organics molecules.

BUSINESS PLAN

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Executive Summary

The prevalent pollutant Hexavalent chromium is an extremely carcinogenic chemical that has been widely produced in the United States. We have created a Quantum Rod technology detection system using On-Off fluorescence to determine the contamination levels of chromium-6 in water sources.

QMD operates within the "Analytical Laboratory Instrument Manufacturing" industry that in 2012 had a reported industry revenue of \$14.6 billion. There are many competitors in this market and even though our product is only a single product in this massive industry with these direct competitors it is still valuable in its cheap production while using advanced scientific testing methods.

Our target markets will be either individual users of all ages who are health conscious and/or are living with the fear of a possible Chromate contamination. Specifically, people utilizing a water reservoir or well built on their property. The other market would be large manufacturing companies who have liquid waste that use chromium-6 in their manufacturing process to ensure and their treatment processes are adequately removing all chromium-6 waste.

Our product will be sold in individually for \$50 for the unit and a set of 10 test strips, \$30 for addition sets of 10 test strips. The bulk price will be \$350 for the unit and a set of 150 test strips and \$300 for addition sets of 150 test strips. The product will be distributed to customers both online and through retailers. On top of these sales, a sales team and field reps will be used to

generate leads on large orders. Promotional activities will include both advertising media and sales promotions.

The operation strategy will include both in-house and outsourced activities. While the testing strips will produced in-house, we will use vendors for necessary supplies and packing materials and the UV-Light unit will be outsourced.

Our management team will be broken up into three departments under the president, Sales Team, Product Production + Research and Development Team and the Operations Team.

Future work to improve upon our test strip product will be done to increase the sensitivity of our test as well as create tests for other toxic ions or chemicals using surface modifications of our Quantum Rod fluorescent technology. Based on the strategies in this plan it is anticipated the Quantum Metal Detector is likely to achieve goal from financial summary

1. COMPANY OVERVIEW

The company overview is a brief description of this business startup. This section is broken down into three subsections the mission statement, business description and product information.

1.1 Mission Statement

Quantum Metal Detection's mission is to provide a cutting edge, user friendly platform to detect the presence of certain transition metal with highest specificity to Chromate in water samples using Fluorescent Quantum Rod Technology.

1.2 Business Description

Quantum Metal Detection (QMD) is a start-up company in Orlando Florida currently registered as a small limited liability company that provides analytical tools to detect toxins in water.

QMD is a small laboratory firm that produces a product for any customer that would benefit from quickly, easily and cheaply testing if their water is contaminated with high levels of chromate or extreme levels of certain other transition metals.

QMD is an innovator in synthesizing Quantum Rods that are non-toxic and extremely fluorescent allowing low-cost, quality, volume production to profitably exploit their targeted test strip market niche.

1.3 Product Information

Quantum Metal Detection produces a Quantum Rod technology Fluorescent Chromate Ion Detector.

The product will be a battery powered UV-light system unit, around the size of the average smart phone. Inserted into these units will be the replaceable patented Fluorescent test strips used to test the chromate levels of your water source. The initial purchase will include X testing strips, the UV-light system unit and an instructional pamphlet explaining use and how to identify positive and negative results. Due to the one time use test strips future purchases of more test strips will cause sales to continue as long as there is a threat of chromate contamination in water sources.

Prior to disclosing the product a patent will be required to protect the intellectual property of the company. On top of the patent future research will be done to improve upon and possibly expand the use of the material.

The UV-light system units manufacturing will be contracted for the cheapest price while the chemical test strips will be made in our in house laboratory. They will then be sold either directly to end users online or to large distributors or other companies.

2. INDUSTRY ANALYSIS

The industry analysis section will provide an explanation of the current situation for the "Analytical Laboratory Instrument Manufacturing" industry. This background will provide information critical to understanding current market conditions for potential investors as well as understanding the dynamics, problems, and opportunities driving the industry.

2.1 Current Situation

A prevalent pollutant Hexavalent chromium is an extremely carcinogenic chemical that has been widely produced in the United States. Approximately 300,000,000lb of chromates and dichromates were produced in 1985 for industries such as chrome plating and paints. [31] This has led to major waste contamination and pollution throughout the country. According to the Environmental Working Group Hexavalent chromium has been found in 89% of city tap water that has been detected. These cities that were discovered to have the highest levels of chromates are: Norman, Ok. Honolul, Hi. Riverside, Ca. Madison, WI. San Jose, Ca. Tallahasse, Fl. Omaha, NE. Albuquerque, NM. Pittsburgh, PA. and Bend, OR. For a long time the effects of breathing Chromium was well established however not until recently has it become known that toxic effects of having chromium in your drinking water. [32] Currently the EPA has a MCLG for Chromium at mg/L or 100ppb. [33]

With the change in education levels of the American public people have become increasingly health conscious and aware of environmental concerns. Therefore people have become more wary of toxins that can be in their water systems. With all these studies coming to light about the contamination of water systems people are more likely to do self-tests to make sure they have safe drinking water.

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2.2 Market Overview

QMD operates within the "Analytical Laboratory Instrument Manufacturing" industry (NAICS 334516), specifically within the "Specific ion measuring instruments, laboratory-type, manufacturing" subsector. [51] Alternatively, according to SIC coding, QMD is qualified as a company within the "water testing apparatus" industry (SIC 38260308). In a broad view, QMD is a part of the "Laboratory Apparatus And Analytical, Optical, Measuring, And Control Equipment" industry (SIC 382) which has 3,806 companies however the relevant market size is much more specific identifying only 37 companies that sell water testing apparatus's exclusively. [52]

2.3 SWOT Report

Strengths

- Simply ease of use with On-Off fluorescent testing
- Can be expanding upon in the future for more testing with material surface modification
- Patent with in house scientist who created the material

Weaknesses

• Requires full laboratory build out and full time scientist for material synthesis

Opportunities

• High amounts of chromium-6 in current environment with many public published studies

- Low economies of scale
- No government regulation
- Worldwide market

Threats

- Many other similar products on the market
- United States has lowered the use of Chromium-6 production due to toxicity.
- Industry growth stagnant
- Buyers purchase small volumes

2.4 Market Size

Our market under the NAICS industry 334516 consists mostly of manufacturers who build instruments and instrumentation systems for laboratory analysis of the chemical or physical composition or concentration of samples of solid, fluid, gaseous or composite material.

In 2012 reported industry revenue was \$14.6 billion, with export being \$8.7 billion in merchandise over 205 countries. Import was \$5.6 billion from 116 countries the total domestic demand for the industry in 2012 was \$11.5 billion with an estimated gross profit of 35.98%. [53]

Based on the Environmental Working Group's Hexavalent chromium report an estimated population living in the cities that were discovered to have the highest levels of chromates:

Norman, Ok. (115,562) Honolul, Hi. (374,701) Riverside, Ca. (313,673) Madison, WI. (240,323) San Jose, Ca. (982,765) Tallahasse, Fl. (186,971) Omaha, NE. (421,570) Albuquerque, NM. (555,417) Pittsburgh, PA. (306,211)and Bend, OR. (79,109), would be about a total of 3,576,302 possibly customers for the chromate test kit just in the top contaminated cities. [54]

3. CUSTOMER ANALYSIS

This section will identify potential target customers as long with their needs for the marketplace. Target market segmentation identifies multiple consumer groups which are described below.

3.1 Target Customers

QMD has determined that the adoption of their product needs to be driven by two identifiable markets.

- Individual Users: People of all ages who are health conscious and/or are living with the fear of a possible Chromate contamination. Specifically people utilizing a water reservoir or well built on their property. Additionally, people who have bodies of water on their land, for example a fresh water spring, pond, lake, etc. In both of these cases, water used is not monitored by a city utility company that regularly monitors contaminants. It could also be marketed toward customer who live close to a factory producing hazardous Chromium as waste to confirm water treatment (either utility or by the factory) is eliminating all traces of the toxic chemical. We will sell our product online and at local stores for the average user.
- <u>Waste Water Facilities and Factories</u>: Waste management, or manufacturing factories that have liquid waste that use chromium-6 in their manufacturing process to ensure that their treatment processes are adequately removing all chromium-6 waste. As quality assurance for water treatment or checks and balances for output on a regular basis that is quick and clear as to identifying trace amounts of Chromium. Additionally, it can be used

to test reservoirs or holding pools are containing contaminants by sampling surrounding areas and checking for a positive result.

3.2 Customer Needs

The Rise in, in home water filtration systems reflects costumer awareness and want of prevention of these toxins in water. However not all filtration systems, such as your common household Brita filter, are capable of removing hexavalent Chromium. A more expensive ion exchange water treatment unit is required. [34] Therefore before purchasing these expensive units cheap at home test kits can be used to access if your drinking water is contaminated by hexavalent chromium.

While many water Analytical Laboratory Instrument Manufactures create kits for testing water quality, there is no all-inclusive kit that includes chromium. Chromium testing still remains as a separate product, eliminating competitive concerns of all inclusive kits. This establishes a secondary business to business market with the potential to sell the Chromate testing kit to be included in larger kits from other companies.

Our product addresses the customers concern for their safety to set health standards for chromate levels and control.

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4. COMPETITIVE ANALYSIS

The competitive analysis will identify existing companies that have an established position in the industry and have already developed distribution channels, promotional materials, and a customer base. These companies must be addressed to compare direct and indirect competitors vs. our market competitive advantage to take portion of the market share.

4.1 Direct Competitors

According to the NAICS companies that qualify under the "Analytical Laboratory Instrument Manufacturing" industry (NAICS 334516) include major companies such as Affymetrix, Inc., Agilent, Beckman Coulter, Inc., Bio-Rad Laboratories, Inc., Bruker BioSciences Corporation, Coherent, Inc., FEI Company, Hologic, Inc., IDEXX Laboratories, Inc., Integra LifeSciences Holdings Corporation, Life Technologies Corporation, Mettler-Toledo International Inc., Millipore Corporation, PerkinElmer, Inc., Siemens AG, Thermo Fisher Scientific, Thermo Fisher Scientific, Inc., Thoratec Corporation, Veeco Instruments, Inc., Waters Corporation.

Other companies that are not one of these major companies that sell chromate sensors include Quantofix, 3M, Water Works, CTL Scientific Supply Corp. and Hach.

4.2 Indirect Competitors

In order to evaluate a potential decline in the industry an evaluation of outside technologies that could eradicate the necessity for our product. Indirect competitors in this market can be very broad anywhere from ion exchange water treatment unit for entire house, to water management companies who come out and tests water specifically for chromate.

4.3 Competitive Advantage

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QMD testing using a fluorescent ON-OFF model compared to a color changing dye. The test can also pick up high levels of other toxins such as copper, mercury, Iron, and Silver with either color change or On-OFF fluorescent capability. Easy to use that the average user can read and figure out. The test strip is also an instant test that requires no time for results. Applications can include the identification of which samples contain Chromium-6 and whether these samples need to be sent to the lab for further evaluation.

5. MARKETING PLAN

Managers use the marketing mix to influence customer behavior based on a set of variables. These variables include product price, distribution (place) and promotion.

5.1 Product

QMD's product will be a Chromium-6 Sensor. The sensor will be made from our patented Quantum Rod technology. It will be packaged with one unit and will contain 10 test strips in the package. Included in the package will be the instructional packet on how to use the unit as well as determine a positive test from a negative test. On top of the instructional packet QMD will offer customer support for users during weekday hours.

Once this product reaches the maturity of the product cycle the product line will be extended to include advancements to testing strips.

The product consists of two parts. The first part is the Quantum Rod test strip as seen in figure #. The 2nd part of the product is the UV-Light unit which is seen in Figure #.



Figure 42: Quantum Rod Test Strip



Figure 43:Schematic diagram of a test device



Figure 44: detailed specifications of a test device

5.2 Price

QMD's pricing model is based on equivalent marketplace pricing of competitor products. We strongly believe that our product is superior to any in the marketplace and that we can comfortably, without any resistance, maintain our pricing structure without effecting the volume of buyers. However, if the demand increases or decreases we will vary our price to suit the market. Consequently, we will be a high profit margin.

> Individual price is: \$50 for the unit and a set of 10 test strips \$30 for addition sets of 10 test strips Bulk Price: \$350 for the unit and a set of 150 test strips \$300 for addition sets of 150 test strips

5.3 Distribution

Distribution channels provide varying functions depending on the distribution levels used. At a retail level channel selection must consider the number of retailers, the geographic location of retailers, the education level of sales staff and cost. Distribution to retailers for sale of our product will include such major retailers as Lowes, Home Depot, and Target. Physical distribution will involve moving the goods to the customers for cost saving and availability. A secondary form of distribution will be direct to customer end-users through online sales by creating an online presence through our own website or secondary websites such and Amazon.com. Another option for distribution can include sales to plumbers and other craftsmen who conduct water tests. This can also be a beneficial partnership since they can advertise their superiority over their competition by including our test that others don't conduct. After acquiring a domain name web design will assist in creating an online presence linked with networking cites such as Link-in, Twitter and Facebook. A sales force will be hired to target certain customers either geographically specifically areas based on studies showing high levels of Chromate or by type of business and to large scientific retailers such Fisher scientific.

The first priority for distribution will be created a company website to initiate sales.

5.4 Promotion

Promotional materials will include advertising media and sales promotions. Sales promotions can include couponing, dealer discounts and a partnership for bundling with other companies' products. Advertising media used for our product will include direct mailers to end-users in most contaminated water zones, online web advertisements and product shelf placement near water filtration systems in stores with explanations on the dangers of chromate contamination and how their water filter may not be doing enough. Point of purchase promotional materials will also be used on store shelves to inform customers about the need of our product. Sales promotions would include a sales force to sale from business to business and home improvement trade shows. A major benefit of utilizing trade shows for promotion of products is the ability to demonstrate usage of our product to potential customers.

6. OPERATIONS

The following section will identify how value will be created for QMD's customers business processes. Pertinent operations include manufacturing, logistics, transportation, consultation, etc. The average company incurs 80% of their total expenses from operations.

6.1 Operations Strategy

The operation strategy for QMD will include both in house and resourced activities. The production process consists of two parts. Acquisition of materials used in the production of the test strip will be purchased from Fisher Scientific. Outsourced supplies will primarily be packing materials including logos and information on the outside of packaging from a supplier and UV-Light Units contracted from the low-priced vendor. Creation of informational packets will be in-house. All chemical processes utilized in the testing strip as well as purchase of materials to make them will occur in-house from our hired scientist as well as the packing of products.

Services associated with the product include monitoring the sales force and online order fulfillment. This will require additional staffing along with training for employees to ensure efficiency. While online order fulfillment will be regulated in-house the created of the website itself and maintenance activities can be outsourced to a web development company. Administrative responsibilities will require one employee at minimum responsible for tasks such as HR, accounting, finance, etc. Customer service will be monitored by all employees throughout all processes and a customer relations manager will be hired as needed.

6.2 Future Goals

Future goals for our company would be to broaden and diversify the market potential for our product test strips. This expansion strategy will be pursued by modifying test strips to detect

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other types of toxic metal by using surface modification to our patented Quantum Rod technology. These product design changes will be timed once sufficient customer base is established to access financial investment to implement production and marketing of the expanded product line.

6.3 Future Work

Future work for fluorescent testing of the Quantum Rods test strip would be to test the Quantum Rods against other sources of water and drinking water to expand upon the uses of the test strip. This can include testing it against other direct water sources such as lake or ocean water or it can be drinks such as soda, juices or other drinks. They will need to be tested both filtered and unfiltered with controls that could be found in these sources such as dirt. Another future work would be to test the Quantum Rods against varying pH's to see the effect of pH on the Rods as well as the possibility of it being used as a pH test. On top of testing other water sources and chemicals, modifying the Quantum Rods with small molecules such as DHLA or NAC can be done to affect the sensitivity of the Quantum Rods against chromate and other ions or organics molecules.

Lastly head to head comparison need to be done to compare the Quantum Rods to other chromate test strips currently on the market to see which works more efficiently.

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7. MANAGEMENT

The following section will identify how our company is structured in terms of management.

7.1 Company Organization

QMD will be broken up into three divisions. The first department will be the sales team responsible for the Sales of our product through direct online sales to the end user or sales to distributors. The second department will be Product Production + Research and Development team. This team will be responsible for designing and producing the test strip for sale as well as improving the test strip and creating new products. The finally department will be the operations team who are responsible for administrative responsibilities such as HR, accounting, finance, etc.

7.2 Management Team

Biographies of the Management Team

Andrew Teblum

Andrew Teblum graduated from the University of Central Florida in 2012 with a degree in Micro and Molecular Biology. He is currently working on a Master's of Science in Nanotechnology and Business while developing the QMD sensor. He has 6 years of research experience from the UCF NanoScience Technology Center, one year of accounting experience and years of market research experience.

7.3 Management Structure and Style



Figure 45: Managements Chart

8. FINANCIALS

The financial section outlines the funds needed to start-up the company as well as estimated company growth.

8.1 Capital Requirements and offer

The capital needed for the company to start-up, build out a lab and pay salary for the first year will be \$300,000. For this required capitol the founders investment will be \$100,000 and for 20% of the company a VC can invest \$200,000.

8.2 Operating Forecast

For the first twelve months the estimated expenses will be almost \$300,000 and a sales profit of almost \$200,000 leaving a net loss of \$100,000 for the year.

8.3 Profit before Interest and Taxes

Table 2: Profit Before Interest & Taxes

(excluding investment capital)	Year 1	Year 2	Year 3	Year 4	Year 5
Profit Before Interest & Taxes	\$(98,000.00)	\$108,800.00	\$173,000.00	\$226,500.00	\$347,000.00



Figure 46: Profit Before Interest & Taxes

D	X 7 1	X 2	X 2	X7 A	V 5		
Revenues	Year I	Y ear 2	Y ear 3	Y ear 4	Y ear 5		
SALES	\$250,000.00	\$500,000.00	\$750,000.00	\$1,000,000.00	\$1,500,000.00		
Direct Cost of Sales	\$62,500.00	\$125,000.00	\$187,500.00	\$250,000.00	\$ 375,000.00		
Gross Margin	\$187,500.00	\$375,000.00	\$562,500.00	\$750,000.00	\$1,125,000.00		

8.4 Revenues Table 3: Revenues



Figure 47: Revenues

Table 4. Expenses								
Expenses	Year 1	Year 2	Year 3	Year 4	Year 5			
Laboratory Build out	\$100,000.00	\$ -	\$ -	\$ -	\$ -			
Payroll/Payroll related expenses	\$100,000.00	\$150,000.00	\$200,000.00	\$300,000.00	\$500,000.00			
Marketing & Advertising	\$ 25,000.00	\$ 50,000.00	\$ 75,000.00	\$100,000.00	\$150,000.00			
Rent	\$ 36,000.00	\$ 36,000.00	\$ 72,000.00	\$ 72,000.00	\$ 72,000.00			
Utilities	\$ 1,000.00	\$ 1,200.00	\$ 1,500.00	\$ 1,500.00	\$ 1,500.00			
Travel and Entertainment	\$ 5,000.00	\$ 5,000.00	\$ 10,000.00	\$ 15,000.00	\$ 15,000.00			
Legal & Accounting	\$ 5,000.00	\$ 5,000.00	\$ 7,500.00	\$ 7,500.00	\$ 12,000.00			
Equipment Lease(computer/copier/other)	\$ 6,000.00	\$ 8,000.00	\$ 8,000.00	\$ 12,000.00	\$ 12,000.00			
Insurance	\$ 3,500.00	\$ 3,500.00	\$ 3,500.00	\$ 3,500.00	\$ 3,500.00			
Office Expenses	\$ 4,000.00	\$ 7,500.00	\$ 12,000.00	\$ 12,000.00	\$ 12,000.00			
Total Operating Expenses	\$285,500.00	\$266,200.00	\$389,500.00	\$523,500.00	\$778,000.00			

8.5 Expenses Table 4: Expenses

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