SYNTHESIS AND CHARACTERIZATION OF TANTALUM OXIDE-BASED NANOWIRE
HETEROSTRUCTURES FOR PHOTOCATALYSIS

by

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A THESIS

Submitted in partial fulfillment of the requirements
for the degree of Master of Science
in the Department of Metallurgical and Materials Engineering
in the Graduate School of
The University of Alabama

TUSCALOOSA, ALABAMA

2012
ABSTRACT

Semiconductor nanostructures under irradiation catalyze the mineralization of organic dyes in solution. To improve the efficiency of this process, many novel nano-heterostructures have been fabricated using a variety of synthetic methods, however, many of these methods require management of difficult to control parameters, days of aging, and dangerous or expensive precursors to synthesize nanomaterials that may lack uniformity, recoverability, or efficiency. In this thesis, 1D CuO-TaO$_x$-NiO$_y$ nano-heterostructures are fabricated using a combination of thermal oxidation and DC magnetron sputter deposition. CuO nanowires were synthesized by thermal oxidation, and TaO$_x$ and NiO$_y$ were deposited onto CuO nanowire template by sputter deposition of the metal followed by thermal annealing in air. A systematic study was done on the effect of sputter deposition parameters and annealing temperature for Ta. The completed heterostructure was evaluated by its performance in the degradation of various organic dyes. CuO-TaO$_x$-NiO$_y$ nanowires with thin (10 nm thick) layers in methylene blue (concentration = 20 mg/L) with a catalyst dose of 1.0 g/L were found to be the most efficient catalyst. Rationally engineered semiconductor nano-heterostructures can be applied in environmental remediation and reduce the amount of pollution from industrial waste effluent.
DEDICATION

This thesis is dedicated to my friends and family.
### LIST OF ABBREVIATIONS AND SYMBOLS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AOP</td>
<td>Advanced Oxidation Process</td>
</tr>
<tr>
<td>Ar</td>
<td>argon</td>
</tr>
<tr>
<td>$C_0$</td>
<td>Initial concentration</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon nanotube</td>
</tr>
<tr>
<td>$C_t$</td>
<td>Concentration at time $t$</td>
</tr>
<tr>
<td>Cu</td>
<td>Copper</td>
</tr>
<tr>
<td>CuO</td>
<td>Cupric oxide</td>
</tr>
<tr>
<td>$CuO_x$</td>
<td>Non-stoichiometric copper oxide</td>
</tr>
<tr>
<td>$Cu_2O$</td>
<td>Cuprous oxide</td>
</tr>
<tr>
<td>DC</td>
<td>Direct current</td>
</tr>
<tr>
<td>DRS</td>
<td>Diffuse Reflectance Spectroscopy</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy Dispersive X-ray Spectroscopy</td>
</tr>
<tr>
<td>$g-C_3N_4$</td>
<td>Graphitic carbon nitride</td>
</tr>
<tr>
<td>HAADF</td>
<td>High Angle Annular Dark Field</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>---------</td>
<td>------------------------------------------------</td>
</tr>
<tr>
<td>$m_{CuO}$</td>
<td>Mass of cupric oxide nanowires on copper substrate</td>
</tr>
<tr>
<td>$m_{CuO-Ta}$</td>
<td>Mass of cupric oxide nanowires and tantalum film</td>
</tr>
<tr>
<td>$m_{Ta}$</td>
<td>Mass of tantalum</td>
</tr>
<tr>
<td>$M_{Ta}$</td>
<td>Molar mass of tantalum</td>
</tr>
<tr>
<td>$m_{Ta_{2}O_{5}}$</td>
<td>Mass of tantalum pentoxide</td>
</tr>
<tr>
<td>$M_{Ta_{2}O_{5}}$</td>
<td>Molar mass of tantalum pentoxide</td>
</tr>
<tr>
<td>$n_{Ta}$</td>
<td>Moles of tantalum</td>
</tr>
<tr>
<td>$n_{Ta_{2}O_{5}}$</td>
<td>Moles of tantalum pentoxide</td>
</tr>
<tr>
<td>$N$ or $N_{2}$</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>$NH_{3}$</td>
<td>Ammonia</td>
</tr>
<tr>
<td>$Ni$</td>
<td>Nickel</td>
</tr>
<tr>
<td>$NiO$</td>
<td>Nickel oxide</td>
</tr>
<tr>
<td>$NiO_{y}$</td>
<td>Non-stoichiometric nickel oxide</td>
</tr>
<tr>
<td>$O$ or $O_{2}$</td>
<td>Oxygen</td>
</tr>
<tr>
<td>·$O_{2}^{-}$</td>
<td>Superoxide anion</td>
</tr>
<tr>
<td>·$OH$</td>
<td>Hydroxyl radical</td>
</tr>
<tr>
<td>$PVP$</td>
<td>Poly(vinyl pyrrolidone)</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>---------------------------------</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning Transmission Electron Microscopy</td>
</tr>
<tr>
<td>Ta</td>
<td>Tantalum</td>
</tr>
<tr>
<td>Ta&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;</td>
<td>Tantalum pentoxide</td>
</tr>
<tr>
<td>TaO&lt;sub&gt;x&lt;/sub&gt;</td>
<td>Tantalum oxide</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>VLS</td>
<td>Vapor-liquid-solid</td>
</tr>
<tr>
<td>VS</td>
<td>Vapor-solid</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
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</table>
ACKNOWLEDGMENTS

I would like to greatly thank my advisor, Dr. Nitin Chopra for his support and guidance. I would also like to thank my group members who helped me at every step of my master’s, with special thanks to Mr. Junchi Wu (Graduate Student) and Mr. Wenwu Shi (Graduate Student). Thanks to the Central Analytical Facility (CAF) staff including Mr. Rich Martens, Mr. Johnny Goodwin, and Mr. Robert Holler for providing training and lessons. I would also like to thank staff from MTE department and MINT center including Ms. Jan Creitz, Mr. Bob Fanning, Ms. Lyndall Wilson, Ms. Kim Walker, Ms. Casey Mcdow, Ms. Jamie Crawford, and Mr. John Hawkins. I would also like to thank Dr. Reddy and Dr. Turner for serving on my committee.

I would like to thank financial support from NSF LSAMP, CAF, University of Alabama’s Office of Sponsored Programs, Research Grant Committee Award, and NSF award (0925445) for my tuition, stipend, instrument time, supplies and infrastructure/resource.

Finally, I would like to thank my family and friends with all encouragement and support.
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CHAPTER 1

INTRODUCTION

Nanomaterials, defined as materials having at least one dimension measuring less than 100 nm, have attracted a significant amount of attention in the past few decades due to their novel size-dependent properties that differ from bulk materials. Nanomaterials can be broadly categorized into three classes based on confinement of charge carriers – 0D (nanoparticles), 1D (nanowires, nanorods, nanotubes), and 2D nanomaterials (thin films, nanosheets). The surge in interest in nanomaterials is due the potential for solving problems in energy generation and storage, microelectronic devices, environmental remediation, and gas sensing. Nanomaterials have several advantages over their bulk counterparts. First, nanomaterials have greater surface area than their bulk counterparts. Secondly, many properties of nanomaterials (electronic, chemical, optical, and thermal) are dependent upon the size and shape material and can be rationally engineered to produce the desired effects. Finally, nanomaterials allow atomic scale control of properties. However, many of the applications mentioned can be significantly improved by the combination of different materials in a single, rationally engineered structure.

Nano-heterostructures are a logical next step in the development of nanomaterial technologies. Nanomaterials can be combined at the nanoscale and can be individually constructed and tuned to enhance certain properties. The ability to heterostructure nanomaterials
can be exploited to improve the properties and to increase the functionality of materials in a controllable way. Nano-heterostructures can be categorized as nanoparticle-, nanotube-, nanowire-, and thin film-based.\textsuperscript{21} As an example of a nanoparticle-based heterostructure, Cu nanoparticles were selectively deposited on the \{111\} facets of micrometer-scale, 26-facet (8 \{111\}, 6 \{100\}, and 12 \{110\} facets) polyhedral Cu$_2$O particles (shown in Figure 1.1).\textsuperscript{22} The pristine particles with no Cu nanoparticles were compared to the Cu-Cu$_2$O heterostructures in the photocatalytic degradation of methyl orange dye under UV irradiation.\textsuperscript{22} The amount of degradation was measured by UV-vis spectroscopy.\textsuperscript{22} After 90 min, the methyl orange was degraded by only 20\% when pristine Cu$_2$O particles were used.\textsuperscript{22} After the same amount of time, the dye was degraded by 80\% when the Cu-Cu$_2$O particles were used.\textsuperscript{22} The adsorption of methyl orange after 30 min increased from 1.6\% to 13.4\% by the addition of Cu particles on the \{111\} facets.\textsuperscript{22} The superior performance of these heterostructures was attributed to their increased adsorptive abilities and the Schottky junction formed at the Cu-Cu$_2$O interface.\textsuperscript{22} Noble metal nanoparticles are often added to semiconductor nanostructures to improve the photocatalytic properties for this reason, but they are much more expensive.\textsuperscript{22} By heterostructuring with cheaper Cu nanoparticles, superior performance was achieved at reduced cost.\textsuperscript{22} The heterojunction lowers the rate of charge carrier recombination because holes and electrons separate at the junction.\textsuperscript{22-25} An example of nanotube-based heterostructures would be single- and multi-walled carbon nanotubes in composites or decorated with nanoparticles.\textsuperscript{26-35} For instance, carbon nanotubes (CNTs) decorated with Pd nanoparticles can be placed on flexible polymer substrates to function as hydrogen sensors.\textsuperscript{35} CNT-Pd heterostructure is intended to replace older, rigid materials typically used for sensing H$_2$.\textsuperscript{35} An example of a nanowire-based heterostructure is a core-brush photocatalyst with a single crystal ZnO core and
a polycrystalline TiO$_2$ shell. The photocatalytic activity was evaluated by observing the photodegradation of Bromo-Pyrogalol Red under UV irradiation at 245 nm and visible-light irradiation at 450 nm. The improved photocatalytic properties are due to increased charge transfer rate, increased charge carrier lifetime, and lower band gap as a result of the interface between the two semiconductors and the band gaps of the individual components. Finally, an example of a thin film-based heterostructure is thin film with epitaxial layers. High efficiency multi-junction GaAs-based solar cells have been reported. Nano-heterostructures are also being developed to improve thermoelectric properties, Li-ion battery performance, and more advanced composite devices.

Transition metal oxide nanostructures offer a huge number of morphological features, structural motifs, and a large variety of electrical and magnetic properties. This class of nanomaterials has potential applications in nanomedicine, catalysis, sensing, solid oxide fuel cells, and information storage. The catalytic properties of TiO$_2$ were first reported in 1921. Studies on catalysis involving oxide materials go back to the 1960s. During this decade, experiments were performed to examine the mechanism of gas/solid reactions on the surface of dark and illuminated ZnO with O$_2$ and CO. A few years later during the same decade, the oxidation of propylene, isobutene, and benzene over a thin film of PbO was studied. The same reaction was also tested under near-UV and visible light, but, while PbO did catalyze the reaction of the three organic compounds, irradiation had no effect on the reaction. In 1972 a major breakthrough occurred when a TiO$_2$ semiconductor electrode was used to catalyze the splitting of water in a photoelectrochemical cell. Since then many studies have been done on a myriad of oxides for photocatalytic water splitting and other energy generating applications and environmental remediation.
1.1 Synthesis and Characterization of metal oxide nanostructures

Metal oxide nanostructures are ceramic materials, but the commonly used, industrial solid-state methods for producing ceramics are often unsuitable for producing nanomaterials and taking full advantage of their properties.\textsuperscript{40} Full exploitation of the properties arising from small size, large surface area, morphology, and heterostructuring requires the use of specialized fabrication methods.\textsuperscript{40} These methods include hydrothermal and solvothermal synthesis,\textsuperscript{9,24,40,46} sol-gel processes,\textsuperscript{47,48} electrospinning,\textsuperscript{23,49} thermal annealing,\textsuperscript{50–54} CVD and PVD.\textsuperscript{40,55,56–63}

1.1.1 Synthesis of metal oxide nanostructures

1.1.1.1 Synthesis of metal oxide nanostructures by hydrothermal and solvothermal methods

The most used of these techniques are hydrothermal and solvothermal synthesis.\textsuperscript{40} In these processes, an aqueous or organic solution is prepared with a precursor of the required material. The solution is then heated in an autoclave. In some hydrothermal processes, the solution has two temperature zones. In the high temperature zone, the precursor is soluble. The dissolved material then moves by convection to the low temperature zone. The low temperature zone becomes supersaturated and crystallization begins. Supersaturation can also be achieved by gradually cooling or quenching of the solution. Solvothermal synthesis is similar to the hydrothermal method except that the precursor solution may not be aqueous. They are simple, relatively low-temperature techniques that allow control of various reaction parameters and can be made into a scalable, continuous process.\textsuperscript{40,64–66} Using these methods, metastable phases and certain morphologies that would be difficult to make using other methods can be fabricated.\textsuperscript{40} One of the disadvantages of this technique, however, is the inability to synthesize nanomaterials with vertical alignment. Another disadvantage concerns the tendency of nanoparticles to
aggregate which necessitates the use of stabilizing agents that can reduce the performance of the material.\textsuperscript{67,68} Contamination with impurities from the solution is another issue.\textsuperscript{69,70} Also, synthesizing tertiary or quaternary oxides good control over the morphology and composition is very difficult using hydrothermal and solvothermal methods.\textsuperscript{40,71–76} Shape control can be achieved through organic or inorganic additives or by choice of solvent.\textsuperscript{40,69,77} Hydrothermal and solvothermal methods often use surfactants, capping reagents, or certain solvents to suppress the growth of certain facets.\textsuperscript{78,79} Ceria nanoparticles were synthesized using hydrothermal synthesis using Na\textsubscript{3}PO\textsubscript{4} to avoid the problem of contamination and achieve shape control through reaction time.\textsuperscript{69} The results are shown in Figure 1.2.

Figure 1.1 SEM images of ceria nanoparticles and nanorods by hydrothermal synthesis at 170°C for (a) 12, (b) 24, (c) 48, and (d) 144 h (Reprinted with permission from Yan, L.; Yu, R.; Chen, J.; Xing, X. Template-Free Hydrothermal Synthesis of CeO\textsubscript{2} Nano-octahedrons and Nanorods:}

The nanostructures were grown from an aqueous solution of Ce(NO$_3$)$_3$·6H$_2$O and Na$_3$PO$_4$·6H$_2$O in a Teflon-lined autoclave at 170°C. However, using this method, the morphology of the ceria nanostructures is limited to nanorods, nanoparticles, and the intermediate structures.

1.1.1.2 Synthesis of metal oxide nanostructures by sol-gel processes

The sol-gel process is another solution-based synthesis method that is widely used in the synthesis of glass and ceramic materials. In the most general sense, this method involves the formation of a gel from a colloidal solution of precursors that will form the final compound. The sol can be a solution of colloidal powders, alkoxide precursors, or nitrate precursors. A colloidal powder sol undergoes gelation. The alkoxide or nitrate precursors undergo hydrolysis and polycondensation reactions. The resulting gels are then aged and dried in hypercritical conditions to produce aerogels or dried in atmospheric conditions to produce xerogels. Shape control in a sol-gel process can be achieved via templating methods or choice of solvent. Sol-gel methods have many advantages. First, this is a solution-based method that involves liquid mixtures. This allows rapid and thorough mixing of the precursors which leads to homogenous gels. Because of this homogeneity, the chemical reaction requires a much lower temperature to activate which reduces contamination from undesired reactions with the containers and atmosphere. Thin films can be readily synthesized by dip coating in the solution. Moreover, the sol-gel method can be used to synthesize materials with very high surface areas. The drawbacks of the process include large volume reduction upon the formation and drying of gels, remaining pores after the removal of residual compounds, expensive raw
materials, and long reaction time which is on the order of several hours or days. As an example, TiO$_2$/SiO$_2$ was synthesized with the sol-gel method for photocatalytic degradation of Rhodamine 6G. Rhodamine 6G will adsorb onto SiO$_2$ and not TiO$_2$, but SiO$_2$ will not degrade Rhodamine 6G when irradiated with UV without a photocatalyst present. The sol-gel synthesized heterostructure takes advantage of the adsorptive properties of SiO$_2$ and the photocatalytic properties of TiO$_2$ to make a photocatalyst that exhibits a higher rate constant and specific surface area than Degussa P-25 TiO$_2$. However, the gelling process took 1 week followed by heating at 12 h. The processing time is a significant drawback to the sol-gel process.

1.1.1.3 Synthesis of metal oxide nanostructures by electrospinning

The electrospinning process is a method for making extremely long nanofibers with uniform diameters. In the electrospinning process, a jet of a polymer melt or solution in a syringe is drawn from the tip by an electric field applied between the syringe and a collector. The electric field voltage is on the order of kV, and at the tip of the syringe is formed a Taylor cone, a cone-shaped fluid structure. At the critical voltage the force of the electric field is strong enough to overcome the surface tension of the solution and the fluid begins to flow from the tip of the Taylor cone; however, the voltage must still be high enough to produce a smooth flow as opposed to the unstable, droplet flow.
Figure 1.2 A basic electrospinning apparatus. The Taylor shown at the top right forms at the tip of the syringe. SEM image of nonwoven mat of poly(vinyl pyrrolidone) (PVP) nanofibers. (Reprinted with permission from Li, D.; Xia, Y. Electrospinning of Nanofibers: Reinventing the Wheel? Adv. Mater. 2004, 16, 1151-170. Copyright 2004 John Wiley and Sons.)

For ceramics, typical sol-gel precursors have been found to be usable for electrospinning if the viscoelasticity of the gel is properly controlled. Poly(vinyl pyrrolidone) or another polymer is often added with the appropriate solvents to the sol-gel. This technique has been used to synthesize several different oxide nanofibers for applications in photocatalysis, antimicrobials, and gas sensing. The electrospinning method has also been the platform for creating new polymer/ceramic composites, hierarchical, nanostructures. A duel-spinneret method was used to fabricate a TiO$_2$/SnO$_2$ photocatalyst with both oxides’ surfaces fully exposed.

By using this method, the surface area was increased, charge carrier recombination was decreased, and holes and electrons were able participate in the reaction.\textsuperscript{23} This system was evaluated by use in the photodegradation of Rhodamine B under UV irradiation and showed improved photocatalytic properties when compared to a TiO\textsubscript{2} nanofiber catalyst.\textsuperscript{23}

Electrospinning has several drawbacks. One issue with the use of electrospinning is the formation of beads in the electrospun fiber.\textsuperscript{95} Proper control over the rheological properties of the precursor solution are a major concern.\textsuperscript{95} Furthermore, electrospun metal oxides are often synthesized from sol-gel precursors which can take several days to achieve the proper viscosity for electrospinning.\textsuperscript{23,95} The dependence of viscosity on aging time affects the ability to spin fibers with controllable diameters.\textsuperscript{95}
1.1.1.4 Synthesis of metal oxide nanostructures by thermal annealing

Thermal annealing is the simple process of heating the material in the appropriate atmosphere. Most metals form an oxide layer simply sitting in air at room temperature. Still, to produce an oxide film with the required parameters heating the material to a certain temperature for a certain time may be necessary. Thermal annealing can be used as a post-processing technique to alter the properties of an already prepared material, be used to oxidize a material, and grow nanowires and thin films. CuO, ZnO, W\textsubscript{18}O\textsubscript{49} nanowires have all been grown using this technique. In the case of W\textsubscript{18}O\textsubscript{49}, a tungsten carbide substrate is first heated in a nitrogen atmosphere. This causes the formation of W\textsubscript{2}C nanowire nuclei to form. Then, the substrate is heated in pure oxygen to produce W\textsubscript{18}O\textsubscript{49} nanowires. In the case of CuO and ZnO, the heating is done in oxygen or in air. ZnO may form several nano-architectures at different conditions. Other metals simply produce thin films when oxidized in air. Thermal annealing, however can introduce defects and stresses due to phase changes or the formation of new compounds. For this reason, thermal annealing is often avoided for certain applications. For the synthesis of certain nanomaterials, such as nanowires and hollow nanoparticles, this is a simple, effective method for producing high quality nanostructures.

1.1.1.5 Synthesis of metal oxide nanostructures by CVD and PVD

Chemical vapor deposition (CVD) and physical vapor deposition (PVD) techniques are widely used techniques in the deposition of a large variety of compounds in an array of morphologies. These methods are used in microelectronics, optics, and photocatalysis to deposit metal oxides. For metal oxides, the CVD process is
usually done with a metallorganic precursor. Depending on the application, CVD has several major advantages. Films deposited by CVD are dense, pure, and uniform and have good reproducibility and adhesion to the substrates along with high deposition rates. Also, CVD can produce uniform films with good conformal coverage on substrates with complex morphologies. By controlling the process parameters, the crystal structure, morphology, and orientation of the films can be controlled. The deposition rate can be easily adjusted and is usually low for producing epitaxial films and high for producing protective coatings. A wide range of usable precursors can be used therefore granting access to a wide range of products. Moreover, films can be deposited at relatively low deposition temperatures achieved through vapor phase reactions and subsequent nucleation and growth on the substrate, which is especially important for depositing refractory materials. The disadvantages of CVD are the hazards posed by the use of dangerous precursor gases (e.g. SiH₄) and the difficulty in depositing multicomponent materials with well-controlled stoichiometry.

PVD is a term that covers a number of techniques such as sputter deposition, cathodic arc deposition, molecular beam epitaxy, electron-beam evaporation, and thermal evaporation, however, the techniques all involve a solid or liquid material that is evaporated to the gas phase and condenses on the substrate. CVD is often used for protective coatings, but many ceramic coatings still require a high deposition temperature. For applications where such a coating is needed and the substrate cannot be heated above a certain temperature, a PVD method may be the preferred alternative. Because PVD methods use purely physical methods to get the material to the gas phase, ceramic materials are often synthesized by a reactive deposition process. RF sputtering of ceramics can be done directly from a target of the material, but the target may be expensive to fabricate and the deposition rate is not as high as DC
sputtered materials. Even with reactive DC magnetron sputtering of materials, the fabrication of dense films without defects is difficult.\textsuperscript{108} Also, arcs can occur at the target affect the structure, properties, and composition of the coating, pulsed reactive deposition, variant of sputter deposition, can overcome these shortcomings.\textsuperscript{108}

One disadvantage of PVD processes is line-of-sight deposition. Materials with complex geometries require the use of multiple deposition sources, rotating substrate holders, or movable gun.\textsuperscript{61,108} Line-of-sight deposition also means that the angle of deposition leads to a columnar structure.\textsuperscript{61} Other drawbacks are the targets often time-consuming and difficult manufacture, the difficulty in large-area deposition, except for laser ablation, the difficulty in controlling film stoichiometry, and the high cost because of sophisticated reactor and vacuum systems.\textsuperscript{61} One of the major advantages of PVD techniques is the ability to fabricate vertically aligned nanomaterials on a substrate. Also, PVD processes are environmentally friendly alternatives to other coating methods because they require no toxic chemical precursors.\textsuperscript{61,119} Furthermore, because of the high vacuum and lack of precursors and solvents used in wet chemical methods, very pure films can be synthesized with no contamination.

1.1.2 Characterization of metal oxide nanostructures

XRD, SEM, TEM, EDX, Raman spectroscopy and XPS are well-known techniques, but for more specialized applications such as photocatalysis, characterization techniques that offer insight into the properties relevant to the process are required.\textsuperscript{23,120} For photocatalytic applications, the material, its crystallinity (single-, poly-, amorphous), its morphology, surface energy, band gap energy, band edge locations, recombination rates, and the presence of defects that can act as recombination centers or traps for charge carriers all affect the efficiency of the
catalyst. The material and its crystallinity can be determined by XRD. The material’s morphology and some defects (grain boundaries, stacking faults, etc.) can be studied with SEM and TEM. Band edge locations can be determined with XPS. Photoluminescence spectroscopy can be used to determine how much recombination is occurring in the material. For photocatalysis, a high recombination rate diminishes the effectiveness of the process. The charge carriers must migrate to the surface to react before recombining. A low recombination rate manifests as a weak photoluminescence response. The surface photovoltage spectroscopy (SPS) method is also an important tool for characterizing photocatalysts. A strong SPS signal corresponds to higher charge separation rate.

1.2 Metal oxide nano-heterostructures in photocatalysis

Transition metal oxides that show d⁰ or d¹⁰ electronic configuration are widely used for photocatalytic applications in water-splitting and environmental remediation. Oxides are versatile materials that can be crafted with an array of technologies with a myriad of morphologies. Using these techniques, it has been shown that the photocatalytic properties can be significantly improved by improving the relevant materials properties.

1.2.1 Why photocatalysis?

The photocatalytic properties of TiO₂ were observed in 1921. Studies on ZnO, O₂, and CO under UV irradiation were performed in the 60s. Photodegradation of propylene, isobutene, and benzene was explored over PbO in the same decade. In 1972, a significant milestone in the application of transition metal oxides to energy generation was reached when
TiO$_2$ was used for photolysis of H$_2$O. Advances in photocatalysis could lead to efficient, green energy generation and environmental remediation using solar energy.

Fossil fuels are a limited resource that is concentrated in a few parts of the world. The continued use of fossil fuels introduces harmful pollutants into the atmosphere every day. New sources of energy must be found to prevent this. Hydrogen may be able to replace fossil fuels if it can be generated efficiently and cleanly.$^{130,131}$ Photocatalytic water-splitting involves the use of a semiconducting material under irradiation to generate H$_2$ and O$_2$ gas.$^4,5,132,133$ Through proper materials selection, synthesis, processing, and heterostructuring, nanomaterials could be rationally engineered to meet the challenge of producing clean energy and mitigate or prevent environmental pollution from liquid and gaseous industrial waste.$^{130,131}$

A significant portion of the wastewater coming from industrial processes is contaminated with organic dyes. Of the total amount dyes produced, 1-20% of total global production of these dyes is lost and released into the environment.$^{134}$ These dyes are highly visible in low concentrations, resistant to fading in light, water, and many chemicals, and are difficult to decolorize.$^{135}$ Not only that, but there are over 100,000 dyes having a large structural variety (acidic, basic, disperse, azo, diazo, anthroquinone bases, and metal complex dyes).$^{135}$ Moreover, aerobic treatments and conventional biological treatments are ineffective.$^{134,135}$ Adsorption and coagulation methods cause secondary pollution and anaerobic processes azo dyes reduce to dangerous aromatic amines.$^{134}$ Also, most of the dyes themselves are toxic with basic and diazo direct dyes being the most toxic.$^{135}$ In response to this problem, AOPs have been developed.$^{134}$ One subset of these processes involves using a semiconductor submerged in the wastewater under irradiation to generate radical species such as hydroxyl radicals (•OH) from water.$^{10}$
These radicals are highly reactive and this obviates the need to find a way to degrade these dyes using more complex chemistry.

1.2.2 Relevant materials properties and their effects on photocatalytic efficiency

The band gap energy and band edge locations determine the absorption of photons, excitation and migration of charge carriers, and the redox capability of those photoexcited electrons and holes. The direct or indirect nature of the band gap energy is also important. Direct, narrow band gap semiconductors tend to show high absorbance, but indirect band gap semiconductors are thought to be better for charge separation. Dopants are employed to change the band gap energy. 3d transition metals, cations with d^{10}/d^{10}s^{2}, and nonmetals are used as dopants to raise the valence band level. Narrowing the band gap, however, also reduces the redox potentials and tends to decrease carrier lifetime. Substitution of alkali or alkaline earth metals, p-block cations with d^{10} configuration, and d-block cations with d^{0} configuration changes the conduction band minimum. The conduction band level determines the rate of generation of H_{2} and O_{2}^{-}, so tuning of the conduction band minimum is extremely important. Because of quantum size effects, the band gap energy of semiconductor nanoparticles can also be tuned by varying the size.

The chemistry between at the semiconductor-solution interface is also very important. Higher surface energy generally leads to higher catalytic activity; moreover, the surface energy determines the selectivity, the overpotential the redox reactions, and the susceptibility of to photocorrosion. The surface roughness, state of hydration, hydroxylation, crystallinity, and charge on the surface all influence photocatalytic activity. One goal in the fabrication of semiconductors for photocatalysis is the synthesis of nanostructures with a high percentage of
high energy facets. To illustrate, hydrothermal synthesis with tetrabutyl titanate and 47% hydrofluoric acid as a solvent was used to synthesize TiO$_2$ nanosheets (shown in Fig. 6) with up to 89% (001) exposed facets.

Figure 1.4 (A) Typical XRD pattern and (B) TiO$_2$ nanosheets synthesized at 180°C using 5 mL of tetrabutyl titanate and 0.6 mL of hydrofluoric acid. (C) Individual nanosheet with SAED pattern (inset). (D) High-resolution of vertical nanosheets. (Reprinted with permission from Han, X.; Kuang, Q.; Jin, M.; Xie, Z.; Zheng, L. Synthesis of Titania Nanosheets with a High Percentage of Exposed (001) Facets and Related Photocatalytic Properties. *J. Am. Chem. Soc.* 2009, *131*, 3152-153. Copyright 2009 American Chemical Society.)
Methyl orange was used to evaluate the photocatalytic activity of these nanostructures with Degussa P25 TiO₂ used for comparison. Improved photocatalytic activity was observed when compared to P25 TiO₂ after cleaning adsorbed fluorine and inorganics off with an alkaline solution of NaOH.

Another major issue in photocatalysis is the recombination of charge carriers. The introduction of dopants that change the band gap energy decreases carrier lifetime because these dopants act as traps for charge carriers. Heterostructuring the nanowires can help to overcome this problem. The difference in the conduction and valence band between the semiconductors facilitates charge separation at the interface. Electrons in the conduction band want to go from the more negative band to the more positive band. Holes in the valence band want to go from the more positive valence band to the more. Type II heterojunctions facilitate charge separation because the holes and electrons want to be on opposite sides of the junction. This makes heterostructuring of nanomaterials is superior to mixing different oxides.

1.3 Motivations, challenges, and goals

1.3.1 Motivations and challenges

Many challenges must be overcome to achieve an efficient photocatalyst. The first is the fabrication of nano-heterostructures for photocatalysis. Since, a major purpose of developing photocatalytic methods is to develop clean energy sources to replace fossil fuels and clean up industrial waste, the fabrication methods should be environmentally friendly, be cost-effective and efficient, and allow large-scale synthesis of the materials. Solvothermal methods have been developed that allow continuous synthesis of nanomaterials, but these methods often require the
use of expensive and possibly toxic precursors. CVD is also widely used in industry, but suffers from similar problems. PVD is environmentally friendly, but the efficient deposition of oxide materials often necessitates the use of reactive methods which can be more difficult and tedious to control. Thermal annealing is low-cost, but this method alone does not allow the user to take full advantage of the morphological control offered by other methods. Also, it can introduce stresses and defects into the material. Sol-gel method requires long reaction times and expensive precursors. Since, metal oxides deposited by electrospinning use sol-gel precursors, it suffers from the same drawbacks as the sol-gel process. Also, the aging process for the sol makes the fabrication of uniform fibers more difficult.

The second challenge is recovery and recyclability of the photocatalyst. Nanoparticles are often used in the degradation of organic materials in wastewater effluent from industrial processes, but even if the material proves to be an effective catalyst, it must be recovered from the solution. Sedimentation is often used to recover the catalyst, but smaller nanoparticles often can remain in the solution that may be toxic to human beings and wildlife.\textsuperscript{143,144} Heterostructured core-shell Fe\textsubscript{3}O\textsubscript{4}/WO\textsubscript{3} heterostructures have been developed to help resolve this problem.\textsuperscript{96} The Fe\textsubscript{3}O\textsubscript{4} cores allow the catalyst to be recovered with a magnetic field,\textsuperscript{96} however, using only that method would limit materials selection so that each heterostructured catalyst would have to have at least one component recoverable in a magnetic field. Electrospinning produces 1D nanofibers of extremely long length, giving the catalyst a favorable morphology for recovery. PVD methods can produce nanostructures on substrates that are easily of recoverable. Even so, photocatalyst performance degrades over time; consequently, an effective photocatalyst is one that must also be reusable.
The third challenge is increasing the efficiency of the photocatalyst. There are many trade-offs to be considered in the rational engineering of an effective photocatalyst. Direct band gap semiconductors tend to show high absorption. If the band gap is also narrow, then the material will be able to absorb a large fraction of incident photons from the sun. Indirect band gaps, however, tend to have lower recombination rates, but they do not show the immediate onset of absorption shown by direct band gap semiconductors.\textsuperscript{121} A wide band gap photocatalyst may be doped to narrow the band gap, but this may introduce defects that act as recombination centers into the material. Heterostructuring of the material can increase carrier lifetime by promoting charge carrier separation at the interface without the drawbacks of doping. Also, intelligent heterostructuring oxides together may obviate the need to use more expensive materials such as noble nanoparticles in the system, thereby reducing the cost. Earth-abundant transition metals could be used. Intelligent choices in the catalyst and co-catalyst(s) can help produce a more efficient system.

1.3.2 Goals

CuO nanowires ($E_g = 1.70$ eV) were synthesized and used as templates for making heterostructures with Ta$_2$O$_5$ ($E_g = 4.00$ eV) and NiO ($E_g = 3.50$ eV) using facile, dry synthesis methods for the photodegradation of organic dyes in solution.\textsuperscript{145} In order to achieve this goal, the structure was fabricated using a combination of thermal annealing and DC magnetron sputter deposition. 1) CuO nanowires were synthesized by thermal annealing in air. 2) Ta was sputtered onto the CuO nanowires to make a CuO-Ta heterostructure. 3) This structure was annealed in air to produce a CuO-TaO$_x$ heterostructure. 4) In an attempt to dope this structure with N, the CuO-TaO$_x$ heterostructure was annealed with N$_2$, NH$_3$, and urea by ammonolysis. Instead a thin shell
of g-C₃N₄ was produced on the surface. 5) Ni was sputtered onto the CuO-TaOₓ heterostructure and annealed in air to produce CuO-TaOₓ-NiOᵧ heterostructure. The process was also reversed so that Ni was sputtered and annealed first and Ta second to produce a CuO-NiOᵧ-TaOₓ heterostructure. 6) The CuO-TaOₓ-NiOᵧ and CuO-NiOᵧ-TaOₓ heterostructures were used for photocatalysis experiments with several dyes and the parameters of photocatalysis were systematically studied.

Figure 1.5 Schematic detailing the goals of this thesis
2.1 Synthesis of CuO nanowires

CuO nanowires were synthesized by annealing acid-etched Cu foil in air at 410°C for 6 h. The Cu foil’s surface was etched by placing small rectangular samples of Cu foil (Alfa Aesar, Ward Hill, MA) into a 33% (v/v) solution of nitric acid (Fisher Scientific, Fair Lawn, NJ) and DI water for approximately 15 sec. The samples were removed, rinsed with DI water, and dried with a stream of air. The etched samples were then annealed in a CMF 1100 box furnace picture in Figure 2.1. The result was CuO nanowires on a Cu₂O film on the Cu substrate. This was confirmed by XRD and scanning electron microscopy SEM.
2.2 Systematic studies on the sputter deposition of Ta

A systematic study of Ta sputtering on the CuO nanowires was performed. The sputtering system (ATC Orion Sputtering System with DC and RF power sources, AJA International, N. Scituate, MA) was run in DC mode with Ar gas providing the plasma. The Ta target (2 in. diameter × .250 in. thick, 99.95% purity) was used for all experiments. A calibration curve was created using the quartz thickness monitor on the sputtering system. The effect of sputtering duration, pressure, and power were considered. Table 2.1 lists all of the different sputtering conditions used. The sample sputtered for 15 min at 2 mTorr pressure and 100 W was used as the base sample for comparison.
Table 2.1 Systematic study on the effect of sputtering conditions on the deposited Ta film

<table>
<thead>
<tr>
<th>Power (W)</th>
<th>Duration (min)</th>
<th>Pressure (mTorr)</th>
<th>Argon flow rate (scm³/min)</th>
<th>Sputtering Rate on a flat substrate (Å/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>1</td>
<td>2</td>
<td>25</td>
<td>45</td>
</tr>
<tr>
<td>100</td>
<td>5</td>
<td>2</td>
<td>25</td>
<td>45</td>
</tr>
<tr>
<td>100</td>
<td>10</td>
<td>2</td>
<td>25</td>
<td>45</td>
</tr>
<tr>
<td><strong>100</strong></td>
<td><strong>15</strong></td>
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<td><strong>25</strong></td>
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</tr>
<tr>
<td>100</td>
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<td>2</td>
<td>25</td>
<td>45</td>
</tr>
<tr>
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<td>25</td>
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</tr>
<tr>
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<td>60</td>
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<td>25</td>
<td>45</td>
</tr>
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<td>100</td>
<td>75</td>
<td>2</td>
<td>25</td>
<td>45</td>
</tr>
<tr>
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</tr>
<tr>
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<td>15</td>
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<td>25</td>
<td>65</td>
</tr>
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<td>2</td>
<td>25</td>
<td>86</td>
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<td><strong>2</strong></td>
<td><strong>25</strong></td>
<td><strong>45</strong></td>
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<td>42</td>
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<tr>
<td>100</td>
<td>15</td>
<td>20</td>
<td>25</td>
<td>38</td>
</tr>
</tbody>
</table>

All of the samples were then examined using XRD, SEM, TEM, Raman spectroscopy, and UV-vis spectroscopy. XPS was performed on the 75 min sputtered sample.

2.3 Annealing study on Ta films

The 75 min sputtered film was selected for further processing. Several samples of the film were annealed in air at atmospheric pressure at different temperatures for 2 h in the box furnace. Table 2.2 shows the different temperatures chosen for annealing. The resulting films were characterized using XRD, SEM, TEM, Raman spectroscopy, and UV-vis spectroscopy in diffuse reflectance mode (DRS). TaOₓ XRD peaks only began to appear at 600°C.
Table 2.2 Study on the effect of annealing temperature on Ta film sputtered for 75 min.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>2</td>
</tr>
<tr>
<td>400</td>
<td>2</td>
</tr>
<tr>
<td>600</td>
<td>2</td>
</tr>
<tr>
<td>700</td>
<td>2</td>
</tr>
<tr>
<td>800</td>
<td>2</td>
</tr>
</tbody>
</table>

2.4 Annealing studies with urea, nitrogen, and ammonium hydroxide

The 75 min sputtered film that was annealed at 700°C for 2 h was selected for attempts at nitridation. First, an excess of NH₄OH solution (10-35% ammonia, Mallinckrodt Chemicals, Phillipsburg, NJ) was poured into an Erlenmeyer flask. Then, the flask was sealed at the top with vacuum grease and aluminum foil except for a tube that connected to the back of the box furnace. Finally, the flask was placed on a hot plate and turned up to 50°C, and the TaOₓ sample was annealed in the furnace at 700°C for 2 h. The experimental setup is shown in Figure 2.2.
The same setup was used again for other experiments where nitrogen gas was fed through another tube along with ammonia.
Table 2.3 Annealing experiments done with ammonia and nitrogen in the box furnace

<table>
<thead>
<tr>
<th>w/ NH₃</th>
<th>Hot plate temperature (°C)</th>
<th>w/ N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>+</td>
<td>50</td>
<td>Not used</td>
</tr>
<tr>
<td>+</td>
<td>50</td>
<td>+</td>
</tr>
<tr>
<td>+</td>
<td>100</td>
<td>+</td>
</tr>
</tbody>
</table>

Urea pellets were crushed and sprinkled onto the film in certain mass ratios with a calculated amount of Ta₂O₅. To find the mass of the tantalum oxide, a CuO substrate was prepared using the same method described earlier and weighed. Then, the substrate was sputtered with Ta for 75 min and weighed again. After annealing in air for 2 h at 700°C the film was weighed a last time. The weight of the substrate was subtracted from the weight after sputtering with Ta for 75 min. For the purposes of calculating the urea:Ta₂O₅ mass ratio, the Ta was assumed to have completely oxidized to Ta₂O₅. The following equations and reaction were used in calculating the mass of oxide present:

\[ m_{CuO-Ta} - m_{CuO} = m_{Ta} \quad (2.1) \]

\[ \frac{m_{Ta}}{M_{Ta}} = n_{Ta} \quad (2.2) \]

\[ n_{Ta} \times \frac{2}{4} = n_{Ta_2O_5} \quad (2.3) \]

\[ n_{Ta_2O_5} \times M_{Ta_2O_5} = m_{Ta_2O_5} \quad (2.4) \]

\[ 4Ta + 5O_2 \rightarrow 2Ta_2O_5 \quad (2.5) \]
Where \( m_{\text{CuO}} \) is the mass of CuO nanowires on the Cu substrate, \( m_{\text{CuO-Ta}} \) is the mass after sputtering with Ta, \( m_{\text{Ta}} \) is the mass of Ta, \( M_{\text{Ta}} \) is the molar mass of Ta, \( m_{\text{Ta2O5}} \) is the mass of Ta\(_2\)O\(_5\), \( M_{\text{Ta2O5}} \) is the molar mass of Ta\(_2\)O\(_5\), \( n_{\text{Ta}} \) is the number of moles of Ta, and \( n_{\text{Ta2O5}} \) is the number of moles of Ta\(_2\)O\(_5\).

This method was used because unreacted Cu would also react to produce Cu\(_2\)O and some Cu\(_2\)O would be further oxidized to CuO. Simply subtracting the substrate weight of the original CuO substrate from the weight after annealing the Ta film would not be sufficient to calculate the mass of tantalum oxide produced. The urea was then weighed, crushed with a mortar and pestle, and spread onto the film. Table 4 shows the urea:Ta\(_2\)O\(_5\) ratios used from the results of the gravimetric analyses. All samples had urea put onto the film and were annealed at 600°C for 1 h except for sample 8, which was annealed at 800°C, and sample 9, which was annealed by putting the urea in a crucible and inverting the film on top of it.
Table 2.4 Gravimetric analysis and urea to weight ratio for all films annealed with urea present in the box furnace

<table>
<thead>
<tr>
<th>Sample #</th>
<th>CuO Weight (mg)</th>
<th>Weight after Ta sputter for 75 min (mg)</th>
<th>Weight after 700°C heating in air for 2 h (mg)</th>
<th>Weight of Urea used (mg)</th>
<th>Ratio of urea to Ta₂O₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4465.8</td>
<td>4474.2</td>
<td>4541.3</td>
<td>125</td>
<td>12.1:1</td>
</tr>
<tr>
<td>3</td>
<td>3410.2</td>
<td>3414.5</td>
<td>3449.3</td>
<td>108.8</td>
<td>20.5:1</td>
</tr>
<tr>
<td>4</td>
<td>2969.5</td>
<td>2969.7</td>
<td>3038.3</td>
<td>228</td>
<td>950:1</td>
</tr>
<tr>
<td>6</td>
<td>4196.4</td>
<td>4196.9</td>
<td>4214</td>
<td>31.4</td>
<td>51.4:1</td>
</tr>
<tr>
<td>7</td>
<td>4492.1</td>
<td>4499.2</td>
<td>4533.8</td>
<td>341</td>
<td>39.3:1</td>
</tr>
<tr>
<td>8</td>
<td>4204.1</td>
<td>4212.8</td>
<td>4332.9</td>
<td>990.9</td>
<td>93.3:1</td>
</tr>
<tr>
<td>9</td>
<td>4698.7</td>
<td>4705.5</td>
<td>4696.8</td>
<td>40.95</td>
<td>4.9:1</td>
</tr>
</tbody>
</table>

2.5 Addition of NiO layer

For the preparation of the photocatalyst samples, a Ta film was sputtered and annealed in air at 700°C for 2 h. A calibration curve was prepared for the Ni target (2 in. diameter × 3 mm thick, 99.99% purity). Ni was sputtered onto the already-prepared TaOₓ film and annealed at 500°C for 2 h. Table 3 shows the sputtering conditions for the preparation of each potential CuO-TaOₓ-NiOᵧ catalyst.
Table 2.5 Sputtering conditions for Ta and Ni films

<table>
<thead>
<tr>
<th>Element</th>
<th>Power (W)</th>
<th>Duration (min)</th>
<th>Pressure (mTorr)</th>
<th>Argon flow rate (scm³/min)</th>
<th>Sputtering Rate on a flat substrate (Å/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta (thick)</td>
<td>100</td>
<td>30</td>
<td>2</td>
<td>25</td>
<td>45</td>
</tr>
<tr>
<td>Ni (thick)</td>
<td>100</td>
<td>25</td>
<td>4</td>
<td>25</td>
<td>37</td>
</tr>
<tr>
<td>Ta (thin)</td>
<td>100</td>
<td>2.23</td>
<td>2</td>
<td>25</td>
<td>45</td>
</tr>
<tr>
<td>Ni (thin)</td>
<td>100</td>
<td>2.67</td>
<td>4</td>
<td>25</td>
<td>37</td>
</tr>
</tbody>
</table>

The first catalyst prepared was CuO nanowires sputtered with Ta for 30 min, annealed at 700°C for 2 h, sputtered with Ni for 25 min, and annealed at 500°C for 2 h. Then a catalyst with thinner layers (roughly 10 nm each on a flat substrate) was prepared in a similar way. The annealing temperature and duration remained the same. Thick and thin layer photocatalysts were also prepared with the Ni layer sputtered and annealed first.

To prepare the nanotubes, hydrochloric acid (HCl) and ammonium hydroxide (NH₄OH) were used to etch CuO nanowires leaving only the TaOₓ and NiOᵧ layers. First, to get the TaOₓ nanotubes (30 min Ta sputter, 700°C anneal in air), they were placed in a centrifuge tube with HCl agitated for 5 min. The tube was then centrifuged. The supernatant was removed, DI water was added, the contents were agitated, and the tube was centrifuged again. This was repeated at least 5 times to ensure the complete removal of the acid. For the samples with NiOᵧ, NH₄OH was used as an etchant and the same procedure was followed.

2.6 Photocatalysis with the core-shell oxide nanowires and nanotubes

Methyl orange was used to evaluate the photocatalytic ability of the different nanowires and nanotubes. The catalyst loading for each experiment was kept at 1 gram of catalyst per liter.
of solution, and the initial concentration of the dye was kept at approximately 10 mg solvent per liter of solution. About 5 to 7 grams of a catalyst was weighed and placed in a quartz tube with a magnetic stirrer. The tubes were then covered with Parafilm. UV-vis spectroscopy was used to evaluate the degradation. The tubes were stirred in the dark for 30 min, and the concentration was tested to ensure that the mixture was at equilibrium and to evaluate the adsorptive ability of the catalyst. Each catalyst was then evaluated under different light sources and in the dark for 5 h. An aliquot of solution was taken and tested each hour using UV-vis spectroscopy to evaluate the degradation rate. All catalysts were tested in the dark, under white light, and under UV (254 nm). Table 6 shows all of the experiments performed. CuO-NiO$_y$-TaO$_x$ nanowires with thick layers under UV were found to be the most efficient combination.

The next step was to find the best dye for degradation experiments. CuO-NiO$_y$-TaO$_x$ nanowires were used for all dyes. The dye without catalyst was placed in one quartz tube and dye with the catalyst was placed in another with a magnetic stirrer. The catalyst loading is the same (1 g catalyst:1 L solution) and the volume of dye solution in each tube is the same. The dyes tested were methyl orange, methylene blue, rhodamine B, rhodamine 6G, congo red, and phenol with hydrogen peroxide. Because it showed the greatest increase in degradation when the catalyst was added, methylene blue was determined to be the best dye. To optimize the material used, CuO-TaO$_x$-NiO$_y$ and CuO-NiO$_y$-TaO$_x$ were both made with thin layers and the photocatalysis experiments were repeated in the same way was before. CuO-TaO$_x$-NiO$_y$ nanowires with thin layers were found to be the best material.

The final step was to optimize the photocatalysis parameters. First, the initial concentration of the dye solution was changed, and the experiments were performed exactly as
all previous experiments under UV irradiation. The experiments performed are shown in Table 6. Then, when the best initial concentration had been determined (20 mg/L), the catalyst loading was changed. The catalyst loading experiments are shown in Table 7.

Table 2.6 Effect of initial concentration on experiments

<table>
<thead>
<tr>
<th>Initial Concentration mg/L</th>
<th>M</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1.56E-05</td>
</tr>
<tr>
<td>10</td>
<td>3.13E-05</td>
</tr>
<tr>
<td>15</td>
<td>4.69E-05</td>
</tr>
<tr>
<td>20</td>
<td>6.25E-05</td>
</tr>
<tr>
<td>25</td>
<td>7.82E-05</td>
</tr>
<tr>
<td>50</td>
<td>1.56E-04</td>
</tr>
</tbody>
</table>

Table 2.7 Effect of initial concentration on experiments

<table>
<thead>
<tr>
<th>Catalyst Loading g cat/L solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
</tr>
<tr>
<td>0.6</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>1.3</td>
</tr>
<tr>
<td>1.6</td>
</tr>
</tbody>
</table>
2.7 Characterization

2.7.1 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy uses an electron beam focused with magnetic lenses to image very small objects. Qualitative and quantitative analysis can be performed on a sample using an EDX detector. The electron beam bombards the surface and causes the ejection of secondary electrons (SE), backscattered electrons, characteristic X-rays (used in EDX analysis) and Auger electrons. Figure 2.3 illustrates the process. SEM images were generated by recording intensities of electrons at different locations. SEM images were collected using a JEOL 7000, and EDX spectra were collected using an Oxford detector. No special preparation was needed to observe the sample, but artifacts do appear in some of the images of the oxides because of their semiconducting nature.
Figure 2.3 (A) Schematic detailing the basic operation of SEM, (B) JEOL 7000 Scanning Electron Microscope
2.7.2 Transmission Electron Microscopy (TEM)

Transmission Electron Microscopy was utilized in this thesis for high magnification, high resolution morphology characterization. Unlike SEM, the voltage is high enough to penetrate the sample and examine it at the near-atomic level. TEM samples were prepared by grinding a piece of the film from a sample in an agate mortar and pestle with acetone. This was then dropped by pipet on a lacey carbon copper grid. Each sample was dried in vacuum for several hours before use. All TEM images were collected at 200 kV accelerating voltage. EDX line profiling spectra were collected in TEM. Figure 2.4 shows the Tecnai F-20 TEM used for all TEM imaging.
Figure 2.4 Tecnai F-20 Transmission Electron Microscopy
2.7.3 X-ray Diffraction (XRD)

X-ray diffraction was used to identify the phases present after all processing steps. An XRD peak only appears when a crystalline sample is irradiated with X-rays at an angle meeting the Bragg condition for that lattice. Figure 2.5 illustrates the appropriate conditions as well as Bragg’s law stated mathematically. All XRD patterns were collected with a Philips APD 3720 X-ray Diffractometer pictured in Figure 2.5.

2.7.4 X-ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy was used to determine the chemical states. Figure 2.6 shows a rudimentary schematic of XPS and the Kratos Axis 165 which was used to gather all XPS spectra. When a sample is irradiated with X-rays, electrons from the sample will be emitted with a certain kinetic energy equal the energy of the incident photon less the binding energy and work function of the detector.

\[ h\nu = E_{\text{binding}} + E_{\text{kinetic}} + \phi \]  \hspace{1cm} (2.2)

where \( h\nu \) is the energy of incident X-rays, \( E_{\text{binding}} \) is the binding energy, and \( \phi \) is the work function of detector.
Figure 2.5 (A) schematic showing Bragg’s law; (B) Digital image of X-ray Diffractometer
Figure 2.6 Schematic of X-ray photoelectron spectroscopy (Reprinted with Permission from Wikipedia); (B) digital picture of Kratos Axis 165.
2.7.5 Raman Spectroscopic characterization

Raman spectroscopy is used to study low-frequency vibrational and rotational modes in molecules or crystals. A light of known wavelength is shone on the sample. Most of the light will be scattered elastically. This is called Rayleigh scattering. A small fraction of light will be scattered inelastically (Raman scattering). This happens when a molecule is excited from its ground state to some virtual state and returns to a different state of vibration or rotation. When the molecule returns to a lower energy state than the original energy, this is called Stokes scattering. When the opposite occurs and the molecule returns to a higher state of energy, this is called Anti-Stokes scattering. Raman spectroscopes measure this shift. The possible scattering effects are shown in a diagram in Figure 2.7.

Figure 2.7B shows the Bruker Senterra system used for Raman spectra collection. A 785 nm excitation wavelength was used. Images of samples were collected at 50X or 100X magnification using a CCD camera. Laser power was kept at 10 or 25 mW. Integration time was 20 sec, 2 co-additions were used for all samples.
Figure 2.7 (A) Schematic of Raman scattering, (B) Bruker Senterra Raman system
2.7.6 UV-vis spectroscopy

UV-vis spectroscopy measures the amount of light a solution has absorbed to measure its concentration. It only works with substances that are active in the UV and visible regions. UV-vis was used to measure the degradation of the dye by measuring the absorption of an aliquot of dye every hour. This concept is based on Beer’s law. Absorbance is directly proportional to concentration until too high a concentration is reached.

\[ A = \varepsilon bc \quad (2.2) \]

Where \( A \) is absorbance (no units), \( \varepsilon \) is the molar absorptivity with units of \( \text{L mol}^{-1} \text{ cm}^{-1} \), \( b \) is the path length of the sample, which is the path length of the cuvette in which the sample is contained, \( c \) is the concentration of the compound in solution, expressed in \( \text{mol L}^{-1} \).

Ocean optics USB-4000 spectrometer equipped with DH-2000 UV-vis-NIR light source was used to collect UV-vis spectra (Figure 2.9). All collections were conducted inside quartz cuvette.
Figure 2.8 Digital pictures of UV-vis spectrometer
CHAPTER 3

RESULTS AND DISCUSSION

3.1 Synthesis of CuO nanowires and systematic study of Ta sputtering

Ever since the ability of titanium dioxide to split water in a photoelectrochemical cell was demonstrated, metal oxides have gained a huge amount of attention for their optical, electronic, sensing, and photocatalytic applications.14,15,28,46,55,57–60,94,146 Core shell nanowires can be synthesized through a variety of methods discussed previously including solvothermal, sol-gel, electrospinning, thermal annealing, CVD, and PVD processes.

Thermal annealing and PVD are combined to synthesize these nanowires. These techniques are simple, environmentally friendly, and completely dry methods that avoid the problems of contamination and aggregation dealt with in other methods. CuO nanowires were first synthesized using a simple, catalyst-free thermal annealing method.50,54,99 The nanowires were grown at 410°C in air for 6 h. The as-prepared nanowires were generally straight and tapered in shape as shown in Error! Reference source not found.A. Error! Reference source not found.B, C, and D show the diameter distribution, EDX spectra, and XRD pattern for these nanowires. Figure 3.1E shows that the preferred plane for CuO growth is (-111), and the direction of growth is [011]. Oxide formation in Cu at 410°C occurs via a short-circuit diffusion mechanism where the rate is controlled by the diffusion of atoms and ions through dislocations and grain boundaries in the oxide.147,148 The growth of CuO nanowires cannot be explained
through the VLS or VS mechanism. In the VLS mechanism, a metal droplet acts as a catalyst for nanowire growth.\textsuperscript{50} The diameter of the nanowire is determined by the diameter of the droplet.\textsuperscript{50} Moreover, the droplet can be found at the tip or base of the newly formed nanowire.\textsuperscript{50} CuO nanowires observed here and in the literature, however, have a tapered shape such that the diameter at the base of the nanowire is greater than the diameter at the tip.\textsuperscript{50,99,147,148} Also, no metal droplets could be observed on the tips or base of the nanowires. In the VS mechanism, the precursors evaporate in a high temperature zone and condense in a low temperature zone.\textsuperscript{50} The melting temperature of Cu, CuO, and Cu\textsubscript{2}O are all above 1000°C, which is much higher than the temperature of oxidation (410°C).\textsuperscript{50} The homologous temperatures for Cu, CuO, and Cu\textsubscript{2}O are 0.38, 0.28, and 0.33 respectively.\textsuperscript{147} The VLS and VS models cannot be used to explain the growth of CuO nanowires. Several mechanisms have been proposed in the literature. CuO nanowires may grow through a stress-relaxation mechanism, screw dislocations forming on the face of the crystal, or through Cu ion diffusion through dislocations.\textsuperscript{50,99,147,148}
Figure 3.1 (A) SEM image of CuO nanowires, (B) diameter distribution of nanowires (41.94 ± 13.66 nm), (C) EDX composition profile of nanowires, (D) XRD spectrum of CuO nanowires, and (E) TEM image of CuO nanowires.
3.1.1 Effect of sputtering duration

Following sputtering for 1 min, the nanowires are covered with a thin, largely amorphous layer of tantalum. Crystallinity in the 1 min Ta film becomes apparent when observing the TEM images of the film. β-Ta grains were observed with (400) texture. The nanowires still have a tapered shape, but this diminishes with further sputtering. The nanowires also become curlier with more sputtering time. After 5 min, the nanowires appear to have flatter, more cylindrical tips. Also, the increasing curliness is very apparent after 5 min. At 5 min of sputtering, crystalline Ta nanoparticles are formed and are shown in Figure 3.4C and D. The Ta begins to nucleate and form crystalline nanoparticles. After 10 min of sputtering, the branched structure has formed and this structure persists for the samples sputtered for longer durations. From 30 min onward, some nanowires appear to be buried, and some appear broken and flattened on the surface. Also, the nanowires are still curlier, but the tips are more vertically aligned. In Figure 3.3, the average diameters and standard deviations of the nanowires are shown. The average diameter increases linearly with time. Crystallinity only becomes apparent in XRD after sputtering for at least 30 min. At 30 min, three tantalum peaks appear—(002), (202), and (513). The films have (002) texture with the (513) peak being the second strongest in intensity until 75 min is reached. The growth of (002) “fiber-texture” at low sputtering pressure is also reported elsewhere.\textsuperscript{110}

The growth of the film initially resembles the Stranski-Krastanov (SK) structure up to 5 minutes of sputtering.\textsuperscript{149} In the SK growth mode, the substrate is covered with completely with a film, and clusters form on top of the film.\textsuperscript{149} The clusters are (202) β-Ta nanoparticles shown in Figure 3.4C and D. The clusters, however, do not adhere well to the underlying film and are not
found on the nanowires’ surfaces. After 10 minutes of sputtering, a columnar structure forms the nanowires. This process begins when the nanoparticles reach a critical size.\textsuperscript{149} In this case, diffusion on the surface is very limited. This results in the formation of the columnar structure instead of a polycrystalline which would form if the incoming atoms were able to diffuse laterally.\textsuperscript{149}
Figure 3.2 SEM and TEM images of core-shell nanowires with different sputtering duration. (A) and (B) 1 min, (C) and (D) 5 min, (E) and (F) 10 min, (G) and (H) 15 min, (I) and (J) 30 min, (K) and (L) 45 min, (M) and (N) 60 min, (O) and (P) 75 min
Figure 3.3 (A) Diameter of nanowires plotted against time (1D, 1A–8A) [Diameter (nm) = 42.454 + 2.148t (min), $R^2 = 0.9885$], (B) XRD spectra of CuO nanowires and nanowires with Ta film sputtered for different durations, and (C) table identifying the $\beta$-Ta peaks in the samples.
Figure 3.4 Morphological evolution of Ta film over time. (A) and (B) 1 min, (C) and (D) 5 min, and (E) 10 min
3.1.2  Effect of sputtering pressure

The effect of sputtering pressure was also tested. Figure 3.5 shows the SEM and TEM images for these nanowires. The XRD data and average diameters of the nanowires are in Figure 3.6. The “fir tree” grain structure also appears on these nanowires, but increasing pressure seems to suppress crystallinity. The average diameter of the core-shell nanowires increases with pressure over the interval observed, but it does so irregularly. The higher pressure films show no crystallinity in tantalum except for a slight peak at 3 mTorr (0.4 Pa). Crystallinity in sputtered Ta films has been reported at higher pressures, but the grains were randomly-oriented.\textsuperscript{110} Even at lower pressures, however, the films reported here show little or no crystallinity. Crystallinity may be present in the films, but it is not enough to be detected by XRD.
Figure 3.5 SEM and TEM images of samples prepared at different sputtering pressure. (A) and (B) 3 mTorr, (C) and (D) 5 mTorr, (E) and (F) 8 mTorr, (G) and (H) 12 mTorr, (I) and (J) 20 mTorr.
Figure 3.6 XRD patterns (A) and diameter distribution (B) of samples prepared at different sputtering pressure.
3.1.3 Effect of sputtering power

The sputtering rate is linearly dependent on power (Diameter (nm) = 1.7386 + 0.1618 × P(Watts)). Figure 3.7 shows the microstructural evolution of the nanowires and their average diameters. At higher power (150 and 200 W), nanowires are curlier and some are broken and buried by the film. The 50 W nanowires shown in Figure 3.7B appear to have the nascent fir tree structure, but no crystallinity was observed in the film. Also, no Ta nanoparticles were observed. XRD spectra for these samples are in Figure 3.8. At 100 W, the (002) texture predominates. At 150 W, the (002) and (202) peak are both present, but it is difficult to tell how the crystallinity will evolve over time without a similar study varying the time being performed at this power. At 200 W, the (202) peak predominates and is the only Ta peak present. This means that the films texture also varies with power.
Figure 3.7 SEM and TEM images of core-shell nanowires sputtered at different sputtering power. (A) and (B) 50 W, (C) and (D) 150 W, (E) and (F) 200 W. (G) Diameter of nanowires and thickness of shell against sputtering power.
Figure 3.8 XRD patterns of samples prepared at different sputtering powers.
3.2 Annealing study on tantalum films

After the sputter deposition systematic study was completed, an annealing study was performed on the Ta films. The film sputtered for 75 min at 2 mTorr and 100 W was chosen for further study. Several of these samples were prepared and annealed in air in a box furnace at different temperatures. The SEM and TEM images are shown in Figure 3.9. Figure 3.10 shows the XRD spectra. At 200°C, tantalum peaks are present with the strongest reflection coming from (002). These peaks disappear after annealing at 400°C, and at 600°C and higher temperatures, several oxide peaks appear. The formation of new phases may explain the sudden drop in diameter at 700°C. The increase in diameter from the 75 min sputtered sample to the sample annealed at 200°C may be due to the formation of more crystalline tantalum and the diffusion of copper and oxygen into the film, which is apparent from the line profile of the nanowire annealed at 200°C shown in Figure 3.11. At 600°C oxides begin to form, but at 700°C, several different oxide peaks appear. Most oxide phases have a lower density than β-tantalum (16.3 g/cm³) which helps explain the volume increase. After annealing at 200°C, the film’s surface has not changed considerably, but at 400°C, the regular, branched appearance gives way to a lumpier film. At 800°C, there appears to be some faceting on the surface of the nanowires. Oxide forms at 600°C and at higher temperatures. When Ta oxidizes, suboxides are formed first which gradually change to Ta₂O₅, which is reflected in Figure 3.10A. Also, Ta does not react to form tantalum oxides until the entire matrix is saturated with O₂. The O/Ta ratio shown in Figure 3.10C increases rapidly until the annealing temperature reaches 600°C. As the temperature increases, the concentration of O₂ reaches the saturation point more quickly. The formation of TaOₓ changes the nature of O₂ diffusion. Initially, O₂ diffuses through Ta metal. Then, when oxidation begins, the O₂ must diffuse through a mixture of Ta metal and TaOₓ.
Also, the grain fir tree structure starts to disappear at higher annealing temperatures. The grains coalesce and the film gets smoother with time. In Figure 3.12, Raman spectra were collected for the various oxides. These show no shifting in the CuO peaks. This indicates that there is little to no strain at the interface. The reflectance spectra in Figure 3.13A show that the oxide films (600°C, 700°C, and 800°C) have flat and low reflectance profiles throughout the UV and visible regions. The band gaps were derived from the Tauc plots made based on Kubelka-Munk theory.\textsuperscript{150}

Figure 3.9 Oxidation of core-shell nanowires at different temperature. (A) and (B) 200 °C, (C) and (D) 400 °C, (E) and (F) 600 °C, (G) and (H) 700 °C, (I) and (J) 800 °C
Figure 3.10 XRD patterns (A), diameter distribution (B), and O/Ta ratio from EDX of nanowires annealed at different temperatures
Figure 3.11 (A) HAADF image, (B) line profiling of sample annealed at 200 °C.
Figure 3.12 Raman spectra comparison of samples with different annealing temperatures. (A) Raman spectra of CuO nanowires with and without Ta coating. (B) Raman spectra of coated sample annealed at different temperature.
Figure 3.13 UV-vis DRS of Ta films sputtered for 75 min annealed at different temperatures for 2 h: A) Raw reflectance spectra and the Tauc plots and band gaps for B) 200°C, C) 400°C, D) 600°C, E) 700°C, and F) 800°C
3.3 Annealing study on tantalum oxide films with N$_2$, NH$_3$ and urea

Two of the films subjected to annealing with urea produced interesting results in XRD. Sample 1 and Sample 3 both showed evidence of a graphitic carbon nitride (g-C$_3$N$_4$) peak. Figure 3.14 shows the TEM images of the films left deposited on both of the samples. The film is partially amorphous, but has some crystallinity which can be seen in Figure 3.14B. The Raman spectra were collected for these two samples and an initial CuO-TaO$_x$-NiO$_y$ core-shell nanowire sample. No peaks were observed however for g-C$_3$N$_4$. The Raman spectra in Figure 3.15 show very little shift in the CuO peaks.
Figure 3.14 TEM photos of (A,B) sample 1 and (C,D) sample 3
Figure 3.15 Raman for CuO sample, TaOx sample, NiO sample in two different spots, and the two urea samples examined. Peaks marked by dotted line show that there is very little shift after sputtering and annealing process.
Figure 3.16 XRD of urea-annealed samples 1 and 3 compared with CuO nanowires
3.4 Addition of NiO<sub>y</sub> layer and photocatalytic studies

The nanowires sputtered with Ta for 30 min and annealed in air at 700°C for 2 h are shown in Figure 3.17. The fir tree structure on these nanowires has disappeared. The film is smooth and polycrystalline, and several oxide phases are present. Figure 3.19 shows selected TEM images from the thin layer CuO-TaO<sub>x</sub>-NiO<sub>y</sub> nanowires. Figure 3.21 and Figure 3.22 show the XRD patterns for the thick and thin photocatalysts with the Ta layer fabricated first. The crystallinity of the TaO<sub>x</sub> is apparent from the XRD pattern. No NiO<sub>y</sub> peaks were detected in any of the samples. Crystallinity was observed in XRD only in the thick films and the thin CuO-TaO<sub>x</sub>-NiO<sub>y</sub> heterostructure. Figure 3.24 and Figure 3.25 show the XPS data for the thick CuO-TaO<sub>x</sub> heterostructure and the thick CuO-TaO<sub>x</sub>-NiO<sub>y</sub> heterostructure. Figure 3.27B confirms the existence of NiO on the nanowires, but it may not be crystalline.

For the degradation experiments, all of the samples were stirred in the dark for 30 min. The graphs begin at zero, which is the time when each sample was placed under illumination. The drop in concentration observed is due to the adsorption of the dye onto the catalyst. Without the adsorption of the dye on the catalyst, photodegradation cannot occur. Figure 3.30 shows the degradation of methyl orange under UV with several catalysts. The best performing catalyst was selected thusly. Each experiment was performed with one sample with catalyst and one without catalyst samples run concurrently. The best conditions were selected based on the two samples with the largest difference in final concentration. The best performing catalyst was the thick CuO-NiO<sub>y</sub>-TaO<sub>x</sub> catalyst which degraded the material by 59.6%. This was used for finding the best dye (Figure 3.29) which was found to be methylene blue. Methylene blue did not degrade more than all of the other materials, but it showed the greatest difference in degradation between
the sample with catalyst and without catalyst. Phenol with H₂O₂ as a sacrificial reagent and congo red both degraded rapidly with or without catalyst; therefore, they were not useful for comparison. Rhodamine 6G and rhodamine B showed no difference in degradation with or without catalyst. This implies that the catalyst has no discernible effect on the process. Methyl orange had showed results similar to methylene blue, but the catalyst made the greatest difference in methylene blue. Afterwards, the thin layer heterostructures were synthesized and compared to the thick layer heterostructures. Figure 3.30 shows that thin layer CuO-TaOₓ-NiOᵧ was the best performing candidate, and it was used to test the effect of initial concentration and catalyst loading on the degradation rate. The results are in Figure 3.31 and Figure 3.32. The best initial concentration for photocatalysis was found to be 20 mg/L and the best catalyst loading was found to be 1.0 g/L. The best candidates were again chosen based on the difference in percent degraded between the sample with catalyst and without catalyst. Because the dye solution absorbs some of the incident light, if the concentration of the solution is too high, most of the incident light will be absorbed by the solution and the photocatalyst will not be activated. In the case of catalyst concentration, if too much catalyst is in the solution, a shadowing effect can occur and prevent all of the catalyst from being activated.

Rate constants for the different catalyst loads are shown in
Figure 3.34. They were calculated by assuming first-order kinetics. For comparison, a report on the degradation of methylene blue using Degussa P25 TiO$_2$ under UV irradiation was used.\textsuperscript{151} The TiO$_2$ catalyst decolorized a 10 mg/L solution ($3.12 \times 10^{-5}$ M) by approximately 96\% with 1.2 g/L catalyst concentration after 5 h.\textsuperscript{151} The thin layer CuO-TaO$_x$-NiO$_y$ catalyst decolorized the methylene blue by 75.3\% with 1.0 g/L catalyst concentration (Figure 3.28). However, the heterostructure shows superior performance when compared to CuO nanowires in the degradation of methyl orange (Figure 3.28). The difference in rate constants may be due to the nature of the catalyst. After fabrication of the catalyst, the film is scraped off and weighed. This may not contain an even proportion of nanowires that have the complete three-layer oxide
structure because new nanowires grow during each round of thermal annealing. There may be nanowires coated only with NiO or with no coating at all due to the fabrication method.
Figure 3.17 (A) and (B) SEM images of CuO-TaO$_x$ (30 min sputter) nanowires, (C) diameter distribution of CuO-30 min TaO$_x$ nanowires.
Figure 3.18 (A) SEM images of CuO-TaO$_x$ (30 min sputter)-NiO$_y$ (25 min sputter) nanowires, (B) diameter distribution of nanowires, (C) EDX composition of nanowires.
Figure 3.19 (A), (B), and (C) TEM images of CuO-TaO$_x$-NiO$_y$ (10 nm layers)
Figure 3.20 XRD pattern for CuO-TaO$_x$-NiO$_y$ system with 30 min sputtered layer of Ta annealed at 700°C and 25 min sputtered layer of Ni annealed at 500°C

Figure 3.21 XRD pattern for CuO-TaO$_x$-NiO$_y$ system with 10 nm sputtered layers
Figure 3.22 XRD pattern for CuO-NiO$_x$-TaO$_x$ system with 25 min sputtered layer of Ni annealed at 500°C and 30 min sputtered layer of Ta annealed at 700°C.

Figure 3.23 XRD pattern for CuO-NiO$_x$-TaO$_x$ system with 25 min sputtered layer of Ni annealed at 500°C and 30 min sputtered layer of Ta annealed at 700°C.
Figure 3.24 XPS spectra for 30 min sputtered Ta film annealed at 700°C for 2 h in air A) Ta 4f, B) Cu 2p, C) O 1s, D) C 1s
Figure 3.25 XPS spectra for 30 min sputtered Ta film annealed in air at 700°C, sputtered with Ni for 25 min, and finally annealed again at 500°C A) Ta 4f, B) Ni 2p, C) O 1s, D) C 1s
Figure 3.26 Tauc plots and band gap energies for (A) CuO nanowires, (B) CuO-30 min TaO$_x$ nanowires, (C) CuO-30 min TaO$_x$-25 min NiO$_y$ nanowires, (D) CuO-25 min NiO$_y$, (E) CuO-25 min NiO$_y$-30 min TaO$_x$. 
Figure 3.27 Tauc plots and band gap energies for (A) CuO-TaO$_x$ (10 nm sputter) nanowires, (B) CuO-TaO$_x$-NiO$_y$ (10 nm sputter) nanowires, (C) CuO-NiO$_y$ (10 nm sputter) nanowires, (D) CuO-NiO$_y$-TaO$_x$ (10 nm sputter) nanowires
Figure 3.28 Degradation of methyl orange under UV irradiation with several different catalysts

Figure 3.29 Degradation of several different dyes using the CuO-NiO$_y$(25 min sputter)-TaO$_x$ (30 min sputter) nanowires
Figure 3.30 Degradation of methylene blue with CuO-TaO$_x$-NiO$_y$ (10 nm layers) and CuO-NiO$_y$-TaO$_x$ (10 nm layers) nanowires
Figure 3.31 Degradation of methylene blue with different initial concentrations using the CuO-TaO$_x$-NiOy (10 nm layers) photocatalyst
Figure 3.32 Degradation of methylene blue with different catalyst loading using the CuO-TaO$_x$-NiO$_y$ (10 nm layers) photocatalyst
Figure 3.33 First-order reaction kinetics fitting for samples with varied catalyst loading of CuO-TaOₓ-NiOᵧ (10 nm layers) photocatalyst
Figure 3.34 First-order reaction rate constants fitting for samples with varied catalyst loading of CuO-TaO$_x$-NiO$_y$ (10 nm layers) photocatalyst

Rate Constant [h$^{-1}$]

0.132 h$^{-1}$

0.114 h$^{-1}$

0.054 h$^{-1}$

Catalyst loading (g catalyst/L solution)
CHAPTER 4

CONCLUSIONS AND FUTURE WORK

CuO-TaO_x-NiO_y nano-heterostructures were synthesized using a dry, step-by-step thermal annealing in air and DC magnetron sputter deposition. A systematic study on the effect of sputtering parameters on the morphology of the CuO-Ta nanowires and the crystallinity of the Ta film was performed. The thickness of the film was found to be linearly dependent on sputtering power and duration. Also, changing the sputtering power changes the texture of the film. Sputtering at 100 or 150 W produces β-Ta films with (002) texture. Sputtering at 200 W produces β-Ta films with (202) texture. Increasing the sputtering pressure diminishes the crystallinity of the film. An annealing study was then performed on the Ta film. The Ta film began to change to TaO_x at 600°C. The film has numerous suboxides of Ta. The O/Ta ratio revealed that as the temperature increased, the film quickly became saturated with more O_2 before reacting to form a film with numerous suboxides in addition to Ta_2O_5. No N-doping was observed after the nitridation experiments, but two of the samples developed a film of what appears to be g-C_3N_4. NiO is present in the final catalyst heterostructures, but it does not appear to be crystalline. The thick layer CuO-NiO_y-TaO_x catalyst outperformed both CuO nanowires and CuO-TaO_x nanowires in the degradation of methyl orange. The thin layer CuO-TaO_x-NiO_y catalyst outperformed the thick layer catalyst in the degradation of methylene blue but not Degussa P25 TiO_2. The best conditions for photocatalysis with the CuO-TaO_x-NiO_y
photocatalyst were 20 mg/L initial concentration of methylene blue and 1.0 g/L catalyst concentration.

In the future, photocatalytic water splitting will be explored with the goal of constructing a micro-reactor for the splitting of water. Such reactors have been demonstrated for the degradation of organic dyes and for water splitting. The advantage of the thermal annealing and PVD approach is the ability to easily fabricate vertically aligned nanostructures on a substrate. This allows for the fabrication of a suitable morphology for a simple photocatalytic flow reactor. After an active photocatalyst for water splitting under irradiation has been developed, a simple flow reactor can be developed for a continuous water photolysis process with a catalyst that splits water directly irradiation. With further study, this catalyst can be made to split water under visible light and photolysis under irradiation from direct sunlight can be explored.
REFERENCES


Figure A.0.1 XPS spectra for 75 min sputtered Ta film (A) Ta 4f, (B) O 1s, (C) C 1s, (D) Cu 2p
Table A.1 XPS peak assignment for 75 min Ta film, 30 min TaOx film and 30 min TaOx-25 min NiO film

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<th>Region</th>
<th>Peak Assignment</th>
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Figure A.0.2 Selection of photocatalyst and light for degradation