2022 Project Abstract
For the Period Ending June 30, 2022

PROJECT TITLE: Develop Small and Inexpensive Purification System for Community Drinking Water
PROJECT MANAGER: Tianhong Cui
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FUNDING SOURCE: Environment and Natural Resources Trust Fund
LEGAL CITATION: M.L. 2018, Chp. 214, Art. 4, Sec. 02, Subd. 04e

APPROPRIATION AMOUNT: $425,000
AMOUNT SPENT: $425,000
AMOUNT REMAINING: $0

Sound bite of Project Outcomes and Results
This project designed a small water purification system for drinking water that can simultaneously remove the organic pollutants and heavy metal ions in the water. The system can be connected either to domestic drinking water taps or to water in lakes and rivers.

Overall Project Outcome and Results
This project is dedicated to providing clean drinking water to the Minnesota community by designing and manufacturing a small water purification system and providing a possible solution for the water treatment of large water plants. A compact size prototype was first designed to verify the mechanism. Photocatalysis technology was used to remove the organic pollutants, and titanium dioxide was selected as the photocatalyst. Electrochemical reduction was applied to remove heavy metal ions in the water. Finally, the team innovatively combined photocatalysis and electrochemistry to develop a photoelectrocatalytic solution that can simultaneously remove organic matter and heavy metal ions from water. The result shows that the compact system can remove 91.6% percent of the 10-micrometer methylene blue when the mass flow rate is 14.4 milliliters per hour (mL/h), and around 97.5% of 200 parts per million of copper(II) cations (Cu2+) can be removed at the same time. After the theory of photoelectrocatalysis was verified, standard-sized systems were designed and fabricated comprising an ultraviolet lamp, a chamber with active carbon, and a microfluidic system with immobilized photocatalyst. The standard-size system can remove nearly 100% of the 10-micrometer methylene blue and 96% of the Cu2+ in the water with a flow rate of 50 mL/h. The team conducted the field test with the drinking water from Commonwealth Terrace Cooperative, a community for University of Minnesota students and their families, and the water from Mississippi River. The testing results demonstrate the capability of using the designed system to remove organic pollutants and heavy metal ions in the water.

Project Results Use and Dissemination
On-site demonstration and tests as described in the activities at a student housing community and Mississippi river from May through June 2022. Communications with interested entrepreneurs have been ongoing with interested parties including local companies and individuals.

The following papers published in archived journals and prestigious conferences:
1. Zhou, P., & Cui, T. (2020). Enhanced photocatalytic efficiency by layer-by-layer self-assembly of graphene and titanium dioxide on shrink thermoplastic film. Microsystem Technologies, 26(12), 3793-3798.
2. Zhou, P., Zhang, T., Simon, T. W., & Cui, T. (2021). Simulation and Experiments on a Valveless Micropump With Fluidic Diodes Based on Topology Optimization. Journal of Microelectromechanical Systems, 31(2), 292-297.

3. Zhang, T., Zhou, P., Simon, T., & Cui, T. (2022). Vibrating an air bubble to enhance mass transfer for an ultra-sensitive electrochemical sensor. Sensors and Actuators B: Chemical, 354, 131218.

Professor Tianhong Cui presented five invited public seminars and talks on water sensors:
Invited Talk, University of Bath, July 4, 2022
Invited Talk, University of Cambridge, July 11, 2022
Invited Talk, EcoLab, May 4, 2022
Invited Talk, French-American Innovation Days, Water Management in Cities, April 8, 2021 (on-line)
Invited Talk, University of Texas at San Antonio, September 13, 2019

Environment and Natural Resources Trust Fund (ENRTF)
M.L. 2018 FINAL REPORT

Date of Report: August 15, 2022

Date of Work Plan Approval: 06/05/2018

Project Completion Date: June 30, 2022

PROJECT TITLE: Develop Small and Inexpensive Purification System for Community Drinking Water

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Location: Minneapolis, MN

Total Project Budget: $425,000

Amount Spent: $425,000

Balance: $0

Legal Citation: M.L. 2018, Chp. 214, Art. 4, Sec. 02, Subd. 04e as extended by M.L. 2021, First Special Session, Chp. 6, Art. 6, Sec. 2, Subd. 18

Appropriation Language: $425,000 the second year is from the trust fund to the Board of Regents of the University of Minnesota to develop a small and inexpensive purification-technology system for community drinking-water facilities to remove toxic contaminants, make water safe to drink, and improve drinking-water quality. This appropriation is subject to Minnesota Statutes, section 116P.10. This appropriation is available until June 30, 2021, by which time the project must be completed and final products delivered.

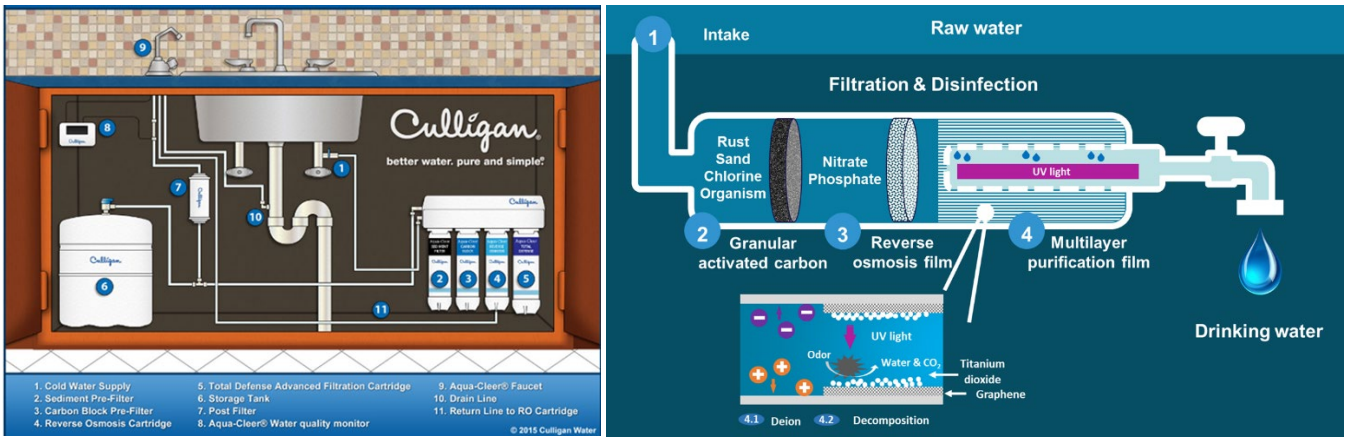
M.L. 2021, First Special Session, Chp. 6, Art. 6, Sec. 2, Subd. 18 ENVIRONMENT AND NATURAL RESOURCES TRUST FUND; EXTENSIONS. [to June 30, 2022]

I. PROJECT TITLE: Develop Small and Inexpensive Purification System for Community Drinking Water

II. PROJECT STATEMENT:

The objective of this project is to develop a small cheap purification system for cleaner community drinking water, as show in Figure 1. Current drinking water purification systems for community water are usually large, expensive, and difficult to operate. The proposed community water purification system is very small and low-cost, but more efficient to remove organic and inorganic contaminants. The water purification system is composed of porous activated carbon, reverse osmosis film, columnar UV light source, and a roll of multilayer purification film. The multilayer purification film is made of an electrically conductive film, by self-assembly of graphene and titanium oxide nanoparticles on the surface of plastic. When water purification is in progress, a small biased potential is applied to the conductive film, and the UV light is turned on. Water flowing into the system will be pre-treated by the activated porous carbon and reserve osmosis film, and some microbes, organic matters, small particles, nitrate and phosphate are removed. Next, the pre-treated water enters the multilayer purification film, where microbes can be further deactivated by the UV light and the porous structures. Water soluble ions, such as lead, cadmium, etc. can be reduced electrochemically or absorbed by the electric field. Titanium oxide, as a photosensitive material, will have photochemical behavior under UV illumination, to detoxify some organic matters. Through the above process, much cleaner drinking water can be obtained very efficiently. This project is intended to develop small, cheap, but efficient purification system for cleaner community drinking water.

In the next phase of the research, we will closely work with state agencies, water pollutant researchers, and industry to develop an implementation plan for pollutants reduction of drinking water in heavy industrial or agricultural regions in Minnesota.



Current Technology **New Technology Proposed**

Figure 1. A comparison of drinking water purification system between the current and proposed technologies.

III. OVERALL PROJECT STATUS UPDATES:

First Update December 31, 2018:

The University of Minnesota team started this project on July 1, 2018. Professors Cui recruited one full-time research assistant conducting the work. Significant progress has been made. In this report are summaries of progress including the following sections: (1) Titanium dioxide with anatase crystal form was synthesized by sol-gel method and been used for photocatalytic water treatment. (2) Dispersion of titanium dioxide in water was also studied, and a feasible dispersion scheme was proposed. (3) The self-assembly method was used to immobilize titanium dioxide on glass substrate. (4) The structure and performance of the immobilized titanium dioxide thin film was tested by both atomic force microscope (AFM) and photodegradation of methylene blue. In summary, the initial 6-month work was successful.

Second Update June 30, 2019:

The University of Minnesota team made great progress from January 1, 2019 to June 30, 2019. Professors Cui, his full-time research assistant, and his part-time researcher have been conducting the research for this project. We investigated layer-by-layer self-assembly of titanium dioxide nanoparticles successfully. We studies different approaches to improve photocatalytic efficiency of titanium dioxide, including optimizing the number of deposition layers, synthesizing graphene-based titanium dioxide composite material, and using PMMA substrate with large surface area for water purification. We lined up resources and labs for the testing needs. In summary, the second 6-month work was productive and successful.

Third Update December 31, 2019:

The University of Minnesota team made great progress from July 1, 2019 to December 31, 2019. Professors Cui, his full-time research assistant, and his part-time researcher have been conducting the research for this project. We successfully synthesized graphene-based titanium dioxide composite material, and immobilized it on glass and polymer substrates using layer-by-layer self-assembly. We studied photocatalytic efficiency of the composite material, and compared with pure TiO_2. We also studied the effect of substrate materials, and the result indicates that immobilized composite material on shrink thermoplastic film has doubled photocatalytic efficiency than TiO_2 on a glass substrate. We also tested long-term stability of the immobilized composite material, and we observed no decrease of photocatalytic efficiency. In summary, the third 6-month work was productive and successful.

Fourth Update June 30, 2020:

The University of Minnesota team made steady progress from January 1, 2020 to June 30, 2020. Professors Cui, his full-time research assistant, and his part-time researcher have been conducting the research for this project. We successfully designed and fabricated microfluidic devices as a carrier of catalysis to further improve the mass transfer efficiency in the photocatalytic process and better achieve systematization. We used rGO/TiO_2 composite material as the photocatalyst, and the valveless micropump as an actuator of the system. We studied the performance of valveless micropump, and then evaluated water purification efficiency by photodegrading of methylene blue (MB). The result

shows that the system can remove 75% of the organics in water under the flow rate of 11 mL/h, and fully removal of the organics can be achieved under a lower flow rate. We will conduct detailed assessment in the next stage. In summary, the third 6-month work was progressive, even though the lab has been closed from March through June 2020 due to pandemic.

Fifth Update December 31, 2020:

The University of Minnesota team made steady progress from July 1, 2020 to December 31, 2020. Professors Cui, his full-time research assistant, and his part-time researcher have been conducting the research for this project. The full-size prototype was designed and fabricated in this stage. The core component of the water purification system is a microchannel array with photocatalyst coated. In addition, activated carbon was used to adsorb suspended solids and some organic pollutants in water. The performance of individual microchannel and a full-size prototype was evaluated by photodegrading of methylene blue (MB). The result shows that each microchannel can remove more than 90% of the organics in water under the flow rate of 14.4 mL/h, and full removal of the organics can be achieved under a lower flow rate of 3.6 mL/h. The full-scale model contains ten of the aforementioned microfluidic devices. Therefore, ten times the flow rate can be achieved without changing the degradation ratio. Due to pandemic, there is some delay in the research progress.

Project extended to June 30, 2022 by LCCMR 7/1/21 as a result of M.L. 2021, First Special Session, Chp. 6, Art. 6, Sec. 2, Subd. 18, legislative extension criteria being met.

Sixth Update June 30, 2021:

The University of Minnesota team made steady progress from January 1, 2021 to June 30, 202. Professors Cui, his part-time research assistant, and his part-time researcher have been conducting the research for this project. The main work of this stage is to add the function of removing heavy metal ions on the basis of the original system. The electrochemical reduction was first applied to remove heavy metal ions in the water, and the heavy metal ions removal was first considered as an individual module for the system. Cu2+ was considered as an example of heavy metal ions. The designed module can achieve 97.5% removal of 20 ppm Cu2+ ions in the water with a throughput of 2.5 ml/h. The Cu2+ concentration after purification was lower than the EPA standard for drinking water. Then the heavy metal reduction module was integrated with the photocatalyst organics removal module to simultaneously remove organic pollutants and heavy metal ions. The result shows the consistent performance of heavy metal reduction, and 25% enhanced organic removal efficiency. Due to pandemic, there is some delay in the research progress.

Seventh Update December 31, 2021:

The University of Minnesota team made steady progress from July 1, 2021 to December 31, 2021. Professors Cui, his part-time research assistant, and his part-time researcher have been conducting the research for this project. The main work of this stage is to further enhance the water purification efficiency by integrating the photocatalytic organics removal and heavy metal ions reduction into microfluidic devices. The influence of the microfluidic device was obtained by photocatalytic degradation of methylene blue in micro-channels with different thicknesses. The results show that the thinner the microfluidic channel has the higher the photocatalytic efficiency. Among them, a micro-channel with a thickness of 80 μm can degrade around 90% of methylene blue in one cycle, while the

photocatalyst in a 200 µm micro-channel can only degrade 60.4% of methylene blue with the same mass flow rate. Then the mass transfer efficiency was further improved by introducing air bubbles and vibration in the microchannel. Experiments have proved that with the help of the vibrating bubble, more than 97% of methylene blue can be degraded in one cycle. Due to pandemic, there is some delay in the research progress.

Overall Project Outcomes and Results as of June 30, 2022

This project is developed to provide clean drinking water to the Minnesota community by designing and manufacturing a small water purification system, a possible solution for the water treatment of large water plants. The University of Minnesota team completed the project successfully by June 30, 2022. Professors Cui, worked with one full-time research assistant, and one post-doc conducting the research. The team finished the proposed research in the proposed activities. A compact size prototype was first designed to verify the working mechanism. The photocatalysis technology was used to remove the organic pollutants, and the titanium dioxide was selected as the photocatalyst. Then the electrochemical reduction was applied to remove the heavy metal ions in the water. Finally, the team combined photocatalysis and electrochemistry to develop a photoelectrocatalytic solution that can simultaneously remove organic matters and heavy metal ions from drinking water. The result shows that the compact system can remove 91.6% percent of the 10 µM methylene blue when the mass flow rate is 14.4 mL/h, and the around 97.5% of 200 ppm Cu2+ can be removed at the same time. After the theory of photoelectrocatalysis was verified, standard-sized systems were designed and fabricated. The system consists of a UV lamp, a chamber with active carbon, and a microfluidic system with immobilized photocatalyst. The standard-sized system can remove nearly 100% of the 10 µM methylene blue and 96% of the Cu2+ in the water with a flow rate of 50 mL/h. The team conducted the field test with the drinking water from Commonwealth Terrace Cooperative, a community for University of Minnesota students and their families, and the water from Mississippi River. The testing results demonstrate the capability of using designed system to remove organic pollutants and heavy metal ions in the water.

Amendment Request as of 10/31/22

We are requesting funds be shifted from the travel and scientific services budget line to personnel.

- Travel budget would be reduced by $8,250 to a revised budget of $0
- Scientific services budget would be reduced by $63,764.62 to a revised budget of $26,235.38
- Personnel budget would increase by $44,599.49 to a revised budget of $348,730.49
- Equipment and supplies budget would increase by $415.13 to a revised budget of $50,034.13

These changes are being requested because more staff time was needed to accomplish Activity 2.

Amendment approved by LCCMR 12/16/22

IV. PROJECT ACTIVITIES AND OUTCOMES:

ACTIVITY 1: Development of small cheap community water purification systems

Description: The objective of this activity is to develop water purification systems using plastic, graphene and titanium oxide nanoparticles. The system is very small, cheap, and reliable to remove organic and inorganic contaminants in Minnesota community waters. The system will reduce the

water contaminants to meet the EPA and Minnesota standards, while the cost is one tenth and the room is one fifth of the traditional systems at most.

We propose a new drinking water purification system to be an alternative to conventional ones. We will develop new technologies enabling easy installation of smaller drinking water purification systems with very low cost and high efficiency. When water purification is in progress, a small biased potential is applied to the conductive plastic film, and the UV light is turned on. Water flowing into the system will be firstly pre-treated by the activated porous carbon and the reserve osmosis film, and some microbes, organic matters, small particles, nitrate and phosphate are removed. We will use a reverse osmosis film to remove nitrate and phosphate. Next, the pretreated water enters the multilayer purification film, where microbes can be further deactivated by the UV light and the porous structures. Water soluble ions, such as lead, cadmium, or nitrates, can be reduced electrochemically or absorbed by the electric field. Titanium oxide, as a photosensitive material, will have photochemical behavior under UV illumination, to detoxify some organic matters. Due to the outstanding material properties of graphene/ Titanium oxide and the advanced micromanufacturing techniques available at the University of Minnesota, we propose to make drinking water systems, which are small, cheap, and highly efficient. To meet the goal of the MPCA, this project will make significant impacts on drinking water purification in Minnesota waters.

Specific tasks will be:

1. Materials and hardwares development

Materials and hardwares are developed and demonstrated, which is expected to:
(1) Layer-by-layer self-assembled graphene/titanium dioxide nanocomposites.
(2) Hardwares for water purification systems.
(3) Initial testing results of water purification to remove organic and inorganic particles.

2. Development of drinking water purification systems

Drinking water purification systems are developed and demonstrated, which is expected to:
(1) Purification efficiency of small drinking water purification systems will be tested.
(2) Improved systems with optimized design, fabrication, and testing.
(3) Drinking water systems testing in Minnesota.
(4) Comprehensive assessment of the techniques.

Summary Budget Information for Activity 1:

ENRTF Budget:	**$ 275,569**
Amount Spent:	**$ 275,569**
Balance:	**$ 0**

Outcomes	Completion Date
1. Layer-by-layer self-assembly of graphene/titanium dioxide nanocomposites; hardware will be developed for water purification systems; Initial testing results of water purification to remove organic and inorganic particles	*6/30/2019*
2. Purification efficiency on small systems will be tested in comparison with conventional results in lab; Improved systems with optimized design, fabrication, and testing; Systems testing of water in Minnesota	*6/30/2020*

3. Comprehensive assessment of the techniques will be completed	*6/30/2020*

First Update December 31, 2018:

There are various methods for TiO_2 synthesis including sol-gel, liquid phase deposition, atomic layer deposition and self-assembly. The sol-gel is preferred because it can synthesize TiO_2 powder with simple equipment and process. The high chemical homogeneity in multi-component systems and doped systems makes it can be further used for the doping and surface modification process.

The synthesis process consists of two reactions: hydrolysis and condensation. The titanium isopropoxide is used as the precursor. The hydrolysis procedure of titanium isopropoxide produce titanium hydroxide, and the further condensation of titanium hydroxide produce titanium dioxide. The key point for this method is the hydrolysis speed. The high hydrolysis speed cause the agglomeration and coagulation, and large size TiO_2 particles can be expected. Too slow hydrolysis reaction extends the time for condensation from hours to days. The acetic acid is used as the chelating agent in the process as it can form the chelation with precursor and reduce the hydrolysis speed.

A series of experiments with different molar ratio of precursor to acetic acid were conducted to optimized the reaction speed and generate the best reactant ratio. The experiment results shows that the perfectly transparent sol can be generated when the molar ratio of precursor to acetic acid is 1:4, and it took 5 hours to transfer from sol to gel. The gel was dried in atmosphere pressure and 80°C for 24 hours and in vacuum for 1 hour. After that, the crystal was grind into powder and heated in furnace at 500°C for 2 hours. The multi-stage heating is required to evaporate the organic reactants and prevent the carbonization of organic components.

As the pre-processing for self-assembly, the dispersion of TiO_2 powders in water was also studied. The effect of pH was tested, and the particle size were also measured in different conditions. Based on the DLVO theory, when the pH is lower than isoelectric point pH, which is around 5 for the synthesized TiO_2 nanoparticles, the surface of the particle is positive charged, and the zeta potential is also positive. When the pH is higher than isoelectric point pH, the negative charged surface and zeta potential can be expected. However, the too low or too high pH value also means the high concentration of ionic, and the increasing ionic strength leads to the compression of the electrical double layer, and hence reduce zeta potential and increasing the aggregation of nanoparticles.

We obtained experiment results for particle size measurement under different pH value. The polyethylene glycol (PEG) with 400 molecular weight is used as the dispersant to cause steric repulsion between particles and help prevent the agglomeration. The ultrasonic treatment was also applied to reduce the particle size. The result shows that the smallest particle size can be expected when pH value is around 3 in acidic condition and 12 in alkaline condition. Thus, the 1 wt% TiO_2 water dispersion was prepared with both pH of 3 and 12.

Layer-by-layer self-assembly was used to immobilize TiO_2 nanoparticles on glass substrate. The 18mm × 18mm cover glass was used as the substrate. The glass was first treated by piranha solution for surface cleaning and hydroxylation. The surface of the pretreated glass was negative charged. Then the glass was immersed into the PDDA solution, which is positive charged, to generate the first layer thin film of PDDA, and the surface of the glass was now positive charged. For the TiO_2 water dispersion with pH=12, and the surface of the TiO_2 nanoparticles is negative changed, so the glass can be immersed into the solution directly to form a layer of TiO_2 thin film. The glass can be immersed in the PDDA and TiO_2 solution alternatively to generate multi-layer thin films. When the TiO_2 water dispersion with pH=3 was used, the surface of nanoparticles is positive charged, so that the PSS solution, which is negative changed, need to be used as the intermediate. The alternative deposition of PSS and acidic TiO_2 solution can also build multi-layer thin films.

The structure and features of the immobilized $\mathrm{TiO_2}$ thin film was characterized by AFM. It can be found that the surface area is increased by 7% compared to the original glass surface, and the higher surface area means the more location for photodegradation reaction and higher photocatalytic efficiency.

The photocatalytic efficiency was also been tested by photodegradation of organic compounds. The methylene blue was used for such experiment as photodegradation procedure of methylene blue can be tracked by the color change. It was found that 3 ml 100nmol/L methylene blue can be degraded by the immobilized $\mathrm{TiO_2}$ thin film on a 18mm $\times$ 18mm cover glass in 10 hours.

Second Update June 30, 2019

The previous work has been successfully prepared titanium dioxide (TiO_2) water dispersion, and the layer-by-layer self-assembly method was used to immobilize TiO_2 nanoparticles. The performance of the immobilized PSS/ TiO_2 composite material was tested by photodegradation of methylene blue, and the relatively low photocatalytic efficiency can be observed. Therefore, work in this stage focused on improving the photocatalytic efficiency of TiO_2.

The efficiency of photocatalysts is largely affected by the speed of generation and recombination of photoexcited holes and electrons. Compared to pure anatase or rutile, TiO2 consists of a mixture of these two crystal structures, showing higher photoreactivity because of the synergetic effect. Due to the difference of energy level of anatase and rutile, the photoexcited electrons can migrate to the conduction band of anatase, and the holes remain in the rutile. Therefore, the recombination is suppressed and the photoreactivity is increased. Thus, the commercial product Degussa P25, which consist of a mixture of anatase and rutile in a ratio of 79:21, is used as the photocatalysts for the following experiment.

Another effective way to increase photocatalytic efficiency is the graphene-based titanium dioxide. Graphene is an atomic sheet of sp2-bonded carbon atoms arranged into a honeycomb structure. The graphene/ TiO_2 composite material for water treatment has been studied in the last decades. It is believed that graphene can help increasing the photocatalytic efficiency in three ways: better adsorption of organics from water into the surface of TiO_2 due to the nature of carbon material, lower rate of electrons and holes recombination as it can transport the electrons, and achieve visible light photocatalytic possibly because of the low band gap of graphene/ TiO_2 composite material. The existing graphene based TiO_2 preparation methods are mainly chemical methods, requiring complex reaction processes as well as various chemicals and equipment. As the surface of graphene-based materials are negatively charged, the layer-by-layer self-assembly method can be applied to fabricate graphene-based TiO_2.

The immobilized $\mathrm{TiO_2}$ thin film was prepared using layer-by-layer self-assembly method. The surface hydroxylation treated cover glass is used as the substrate, and then the $\mathrm{TiO_2}$ thin film was deposited with a sequence of $[\mathrm{PDDA} + \mathrm{PSS} + \mathrm{PDDA}] + [\mathrm{PSS} + \mathrm{TiO_2}]_x$. The substrate was immersed into each solution for 10 min and rinse with DI water, then it was immersed into the next solution. The number of PSS/ $\mathrm{TiO_2}$ bilayers can be changed by alternative deposition of PSS and $\mathrm{TiO_2}$ on the substrate.

The effect of the number of PSS/ $\mathrm{TiO_2}$ bilayers was first studied. Different numbers of PSS/ $\mathrm{TiO_2}$ bilayers was deposited in glasses. The photocatalytic efficiency was evaluated by photodegradation of 100 μM methylene blue solution. The glass sample was placed in the glass tube filling with 6 mL methylene blue solution. The tube was first placed in dark for 1 h to reach a state of adsorption-desorption balance. Then the tube was radiated by a 15W 365nm UV lamp (XX-15L, Analytik Jena US LLC) for 5 h. 100μL solution was taken out every hour and the concentration of methylene blue was

measured by UV/VIS spectrometer. It can be inferred from the figure that the amount of methylene blue absorbed on the surface of TiO_2 in dark increases as the number of layers increases. The reason is that the amount of TiO_2 immobilized on the substrate is more when the number of layers is bigger, and the surface area of TiO_2 is also higher. Different from the continuous increasing of absorption, the photodegradation speed has a peak value when the number of bilayers is 5. This is because of the transparency change of the glass. With the increasing of PSS/ TiO_2 bilayers, the transparent of the glass decrease. When the number of bilayers is larger than 5 the glass is almost opaque, so the titanium dioxide on the back side of the glass is not exposed to ultraviolet light. Thus, the number of PSS/ TiO_2 bilayers has higher photodegradation efficiency and this value will be used as the reference to compare with the following experiments.

The photocatalytic efficiency of graphene-based TiO_2 composite material was also tested. As the amount of negative charged functional group on graphene is relatively small, it can only attract small amount of TiO_2 nanoparticles. In order to get a composite material with more TiO_2 nanoparticles, graphene oxide (GO) was used as there are more functional groups on graphene oxide. The GO/ TiO_2 composite material is fabricated by layer-by-layer self-assembly method in a sequence of $[PDDA + PSS + PDDA] + [PSS + TiO_2]_x + [GO + TiO_2]_y$. The total number of TiO_2 layers is 5, based on previous experiment, and the number of GO layers was changed from 0 to 5. When the number is 0 which means there is no GO/ TiO_2 but all PSS/ TiO_2 bilayers. It is as same as the reference condition. It can be found that the absorption in dark is less when there is GO/ TiO_2 bilayer exist. It is because that even though GO has more functional group than graphene, but it is still not comparable with the PSS, so the amount of TiO_2 nanoparticles is less in GO/ TiO_2 bilayers. However, the photodegradation speed of GO/ TiO_2 composite material is faster than pure PSS/ TiO_2 composite material although the amount of TiO_2 is less in GO/ TiO_2 composite material. The highest photodegradation efficiency occur when the number of GO/ TiO_2 bilayers is 3, and the efficiency is 56% higher than the reference group. The hypothesis of this phenomenon is that there is a tradeoff between the amount of GO and TiO_2, and it reaches a balance when there is 2 layers of PSS/ TiO_2 and 3 layers of GO/ TiO_2. More experiments will be designed to further explore this phenomenon and verify the hypothesis.

As a substitute for glass, PMMA film with large surface area was fabricated. The UV transparent PMMA film (0F058, Evonik Cyro LLC) can pass over 90% of ultraviolet light, which makes it possible to be used as substrate for photocatalytic water treatment. The hot embossing technique is used to increase the surface area of the material. The V shape Anodic Aluminum Oxide (AAO) is used as the mold. The diameter of the hole is 450 nm, and the depth is 1500 nm. The average height of the bulges is 678 nm, and the surface area is 3.14 times higher than flat surface. Next, the PMMA film will be used as the substrate of GO/ TiO_2 composite material, and the higher photocatalytic efficiency can be expected.

The PSS/TiO_2 and GO/ TiO_2 composite material was successfully fabricated by layer-by-layer self-assembly method. The number of bilayers was optimized by evaluating the photodegradation efficiency. The result shows that 5 bilayers lead to the best photodegradation performance. The performance of graphene based TiO_2 is also tested, and up to 56% enhancement of the photodegradation efficiency can be obtained by using GO/ TiO_2 composite material. The substrate of the TiO_2 will be changed from glass to PMMA film in the following experiments. The hot embossing of the PMMA film with AAO mold introduce nano-structures on the surface and therefore helps increasing the surface area 3.14 times higher.

Third Update December 31, 2019:

The previous work has been successfully immobilized TiO_2 and graphene oxide/TiO_2 (GO/TiO_2) composite material on glass substrate. Up to 56% enhancement of the photocatalytic efficiency was observed by using graphene-based material. The work in this stage wants to further enhance the efficiency by using different substrate material.

The glass was widely been used as the substrate for photocatalysis as it is ultraviolent transparent and cheap. However, glass substrate also brings some problems such as fragility and low specific surface area, and the photocatalytic efficiency is highly related to the amount of photocatalyst deposited in a physical area. Therefore, different substrate materials were used to increase the relative surface area of the photocatalyst and hence increase the photocatalytic efficiency. For example, the TiO_2 was deposited on glass spheres with a diameter of 5mm, and then put in a lab scale compound parabolic collector to photodegrade MB. Wang et al. successfully fabricated carbon nanotubes and TiO_2 composite films on cotton fabrics to achieve high photocatalytic efficiency. However, their irregular shapes and material properties make them hard to use when fabricating microfluidic systems or flexible structures.

In recent years, polymer-based devices have been considered to have great application potential due to some special properties of polymers such as low-cost, enhanced device performance, flexibility of the materials, and ease of fabrication. Thus, the polymer materials were considered as the substrate material. In order to increase the specific surface area, the surface modification of PMMA film and application of shrink thermoplastic film were two of the promising choices.

In previous work, the specific surface area of surface modification of PMMA film was increased by 3.14 times after hot embossing with Anodic Aluminum Oxide mold. On the other hand, shrink thermoplastic film can shrink more than 80% of its original size after heating, more than 5 times higher specific surface area can be expected. It has been successfully used in microsensors to enhance sensitivity and reduce the limit of detection, but it has never been used in photocatalytic water treatment.

The TiO_2 and GO/TiO_2 composite material was immobilized on glass and shrink thermoplastic material using layer-by-layer self-assembly method in a sequence of $[PDDA + PSS + PDDA] + [PSS/GO + TiO_2]_x$. Samples with different numbers of bilayers were prepared to optimize the performance. The size of film after shrinking was 18 cm by 18 cm which was the same as the cover glass. The coated shrink thermoplastic films were heated in the oven under 150 °C. Then the Ultraviolet light illumination was applied to reduce GO into rGO.

The structural and morphological properties of different photocatalysts on different substrates were investigated using scanning electron microscope (SEM) and atomic force microscope (AFM). It can be found that the PSS/TiO_2 bilayers on glass substrate were relatively flat, and the porous structure between photocatalysts was in nanoscale. The high-resolution images clearly show the TiO_2 nanoparticles. The size of TiO_2 nanoparticles were around 20-25 nm which matches with the particle size of P25. They also show that the surface of PSS/TiO_2 film on shrink thermoplastic film is rougher than rGO/TiO_2 film on shrink thermoplastic film, and it is because there is more TiO_2 immobilized on PSS than rGO as the negatively charged functional groups on rGO is much less than PSS.

The photocatalytic efficiency was evaluated by photodegradation of MB solutions. 10 mL MB with a concentration of 100 μM was used for photodegradation tests. Different numbers of PSS/TiO_2 bilayers on shrink polymer were first tested and compared. As shown in Figure 3a, concentration of MB kept decreasing with increasing illumination time. The concentration changes of MB slowed when its concentration was lower, which means that the kinetics of MB photodegradation can be described by the first order kinetics equation

$$\ln \ln (C/C_0) = -kt$$

where C and C_0 are the contaminant concentrations at the beginning and during light illumination, respectively, k is the reaction rate constant, and t is time. The photocatalytic efficiency can be represented by reaction rate constant k.

The same tests were also done with different numbers of PSS/TiO_2 bilayers on glass substrate and rGO/TiO_2 bilayers on shrink polymer substrate. It shows that the PSS/TiO_2 bilayers on glass substrate always have the lowest photocatalytic efficiency, and the highest photocatalytic efficiency observed was $k = 0.0106/\mathrm{min}$. The highest photocatalytic efficiency was obtained in shrink polymer with 6 rGO/TiO_2 bilayers. The highest reaction rate constant was $k = 0.0222/\mathrm{min}$, 2.1 times higher than PSS/TiO_2 bilayers on glass substrate and 1.28 times higher than PSS/TiO_2 bilayers on the shrink polymer substrate.

The cycling tests were also performed to show the long-term stability of LBL self-assembled rGO/TiO_2 bilayers on shrink polymer. A sample with 4 rGO/TiO_2 bilayers on shrink polymer was used for this test. 10 mL MB solution with 10 µM concentration was fully degraded within 1 h. It can be inferred from the figure that no decrease of photocatalytic efficiency was observed, which means that the bonding between photocatalyst and substrate is firm and the performance of photocatalyst is stable.

This study shows that the TiO_2 and rGO/TiO_2 can be firmly immobilized on glass and shrink thermoplastic film using LBL self-assembly method. The combined effect of folds structure induced by shrinking and the introduction of graphene material enhances the photocatalytic efficiency to 2.1 times higher than pure TiO_2 immobilized on glass substrate. Overall, more than 70% of 100 µM MB was removed in 1-hour using rGO/TiO_2 bilayers immobilized on shrink thermoplastic film, and the 10 µM MB can be fully removed within 1 hour. Next, the LBL self-assembly method will be performed in microfluidic device fabricated with polymer material. The photocatalytic efficiency will be further enhanced, and the model of proposed water purification system will be build based on microfluidic device.

Fourth Update June 30, 2020:

The MEMS technology was used to fabricate the microfluidic device that can be used for photocatalytic water purification. The microfluid device consists of two parts, a glass slide with photocatalyst and a polymer film with a microchannel structure. The glass slide was first covered by photoresist, and the photolithography was used to expose the window for photocatalyst. Then the rGO/TiO_2 composite material was coated on a glass slide using LBL self-assembly method, and the lift-off of photoresist helped to remove the photocatalyst outside the reaction chamber. The microchannel was first fabricated on a silicon wafer with SU8 photoresist by photolithography. Then a PDMS mold was fabricated based on the silicon mold. UV curing glue was applied between the PDMS mold and the organic film to build the micro-channel. The PDMS mold was removed before the UV curing glue was fully cured, and then the polymer film with microchannel and the glass slide with photocatalyst were attached. The microfluidic device for photocatalytic water purification can be obtained by fully curing the UV curing glue. A piezoelectric ceramic disk (lead zirconate titanate, PZT) was attached to the polymer film as an actuator.

The 10 µM MB solution was pumped through the microchannel to evaluate the photocatalytic efficiency. The mass flow rate was controlled by the voltage applied on PZT disk. It is clear that the mass flow rate increases as the voltage applied to the PZT increases because of the larger displacement of the PZT disk. The maximum mass flow rate of 11 mL/h can be achieved when the voltage applied on PZT disk is 60 V. This is because the residence time of the solution in the reaction chamber is inversely proportional to the flow rate. Therefore, a faster flow rate leads to shorter reaction time and higher

output concentration. As a result, around 75% of the MB can be removed when the highest mass flow rate was used, and more than 95% of the MB can be removed when the mass flow rate was 2 mL/h.

The nozzle-diffuser type valveless micropump was used for the above experiments, while the fluidic diode was believed that can be used to replace the nozzle-diffuser to achieve higher energy efficiency. The two-dimensional fluidic diode was first obtained using topology optimization based on the Density Model with Darcy interpolation. The ratio of energy dissipation between backward and forward flows was set as the objective function for topology optimization. Different sizes of the computational domains were used to obtain fluidic diodes of different geometries. It can be seen that the backward flow is divided into several tributaries which then interact with one another at their confluence, which leads to more resistance in the backward flow than in the forward flow.

The simulation of valveless micropumps was conducted by CFD. The mass flow rate through the micropump with the fluidic diode in the inlet and outlet surfaces. The net mass flow rate was calculated as 35.1 μg/cycle. The same calculation was conducted for the nozzle-diffuser micropump with a similar structure and the mass flow rate was 29.4 μg/cycle. Finally, the pressure of the actuation chamber was calculated. The pressure in the fluidic diode micropump is significantly smaller than for the nozzle-diffuser micropump. The performance of each micropump was evaluated using the net mass flow rate provided by a mechanical power, calculated as the average value of the integral of the product of force and speed over each point on the piezoelectric actuator total area over one cycle. The results show that the optimized fluidic diode micropump gives 27 times the pumping efficiency of the nozzle-diffuser micropump.

We verified the feasibility of graphene-based titanium dioxide as a photocatalyst for water treatment. We also verified the design of the reaction system based on microfluidic devices. The test result shows the correlation between the mass flow rate and the outlet pollutant concentration. We used rGO/TiO2 composite material as the photocatalyst, and the valveless micropump as an actuator of the system. We studied the performance of valveless micropump, and then evaluated water purification efficiency by photodegrading of methylene blue (MB). The result shows that the system can remove 75% of the organics in water under the flow rate of 11 mL/h, and fully removal of the organics can be achieved under a lower flow rate. We will conduct detailed assessment in the next stage.

Fifth Update December 31, 2020:

Purification efficiency on a small system was tested. Improved systems with optimized design, fabrication, and testing was also conducted. 10 μM methylene blue (MB) solution was flowed through the microchannel to evaluate the photocatalytic efficiency. The height difference between the inlet and outlet reservoir was adjusted for different mass flow rates. The concentration of the MB solution was measured by a spectrophotometer. It can be found that the removal ratio of the MB was inversely proportional to the mass flow rate. 91.6% percent of the MB was degraded when the mass flow rate is 14.4 mL/h. The MB degradation ratio increases with the increase of residence time. This is because a longer residence time means more chemical reaction time, making the degradation more thorough. At the same time, it can also be found that with the increase of residence time, the increase of MB degradation ratio becomes slow. This is because when the concentration of the reactant is too low, the mass transfer becomes a restrictive factor of the chemical reaction rate. At this time, more reaction time is required to degrade the same amount of organic matter. Although micro-channels have high mass transfer characteristics, for photocatalytic reactions with low concentrations, more effective mixing based on micro-channels, including passive mixing and active mixing, will be verified in subsequent improvements.

Sixth Update June 30, 2021:

Previous work has designed a full-size prototype of the photocatalytic water purification system. Organic pollutants in water can be effectively removed by photocatalytic technology, while the heavy metal removal mainly depended on the adsorption of activated carbon. Taking into account the increasingly serious heavy metal pollution and relatively inefficient activated carbon adsorption, the electrochemical reduction was integrated into the new system because of its higher heavy metal ions removal efficiency. In order to effectively remove heavy metal ions in the water body, in addition to the activated carbon adsorption in the pretreatment, we have introduced electrochemical reduction, a more efficient heavy metal ion removal technology. The traditional three electrodes system was applied, and a negative potential, which is lower than the redox potential of heavy metal ions, was applied on the working electrode. The heavy metal ions will be reduced to heavy metal elements when flowing through the working electrode, and the reduced heavy metal elements will be immobilized on the working electrode.

The microfluidic system was also integrated with electrochemical heavy metal removal because of its higher mass transfer rate. By replacing the counter electrode in electrochemical reduction with a photocatalyst, it is possible to simultaneously remove organic pollutants and heavy metal ions. The electrons generated by photocatalysis are transmitted to the working electrode to reduce heavy metal ions, which further promotes the separation of electrons and holes in the photocatalyst and improves the efficiency of photocatalysis.

The device was fabricated with PMMA to achieve low-cost fabrication. The copper foil was used as a working electrode because of its good adhesion with reduced heavy metal elements. The carbon paste was used as a counter electrode in the early stage of the experiment, and then it was replaced by rGO/〖TiO〗_2 composite material to achieve simultaneous removal of organic pollutants and heavy metal ions. The commercial Ag/AgCl electrode was used as a reference electrode.

Instead of using the planar reaction chamber as the previous work, a long microchannel was designed to achieve longer resident time and higher mass transfer rate. The total length of the microchannel is 60cm, which leads to around 60s residence time when the mass flow rate is 14.4 mL/h. The width of the microchannel is 1mm, and the height is 200 μm.

The Cu2+ ion was used as an example of heavy metal ions. Solution with 200 ppm Cu2+ was flowed through the microchannel to evaluate the performance of the heavy metal removal module. -0.8 V bias potential was applied on the working electrode to reduce the Cu2+ ions. The concentration of Cu2+ at the outlet was measured by a spectrophotometer with help of sodium diethyldithiocarbamate as it can form a yellow complex with Cu2+.It shows a significant enhancement of the Cu2+ removal after a long time operation. It was because the surface area of the working electrode was increased after immobilization of reduced Cu2+, and the number of active sites for reduction was also increased. It can be found that the concentration of Cu2+ at the outlet is lower than Environmental Protection Agency (EPA) standard after 3 hours of operation, and around 97.5% of Cu2+ was removed. Since the heavy metal adsorption on the working electrode is permanent and continuous, when the device is used next time, its removal efficiency will be further improved on the basis of 3-hour operation.

Then the counter electrode was replaced by rGO/TiO2 composite material. The testing was performed in bulk solution, and Methylene Blue (MB) was still used as an example of organic pollutants. The result shows the photocatalytic efficiency was enhanced by 25% when combine with the heavy metal removal module to form the photoelectrocatalysis. It is because the reduction reaction occurred at the working electrode and the electrons were transferred from the counter

electrode to the working electrode. Therefore, the photoexcited electrons were separated with holes and transferred to the working electrode. The prevented electron-hole recombination and longer lifetime of holes promote the oxidation of organics in counter electrode.

Seventh Update December 31, 2021:

N/A

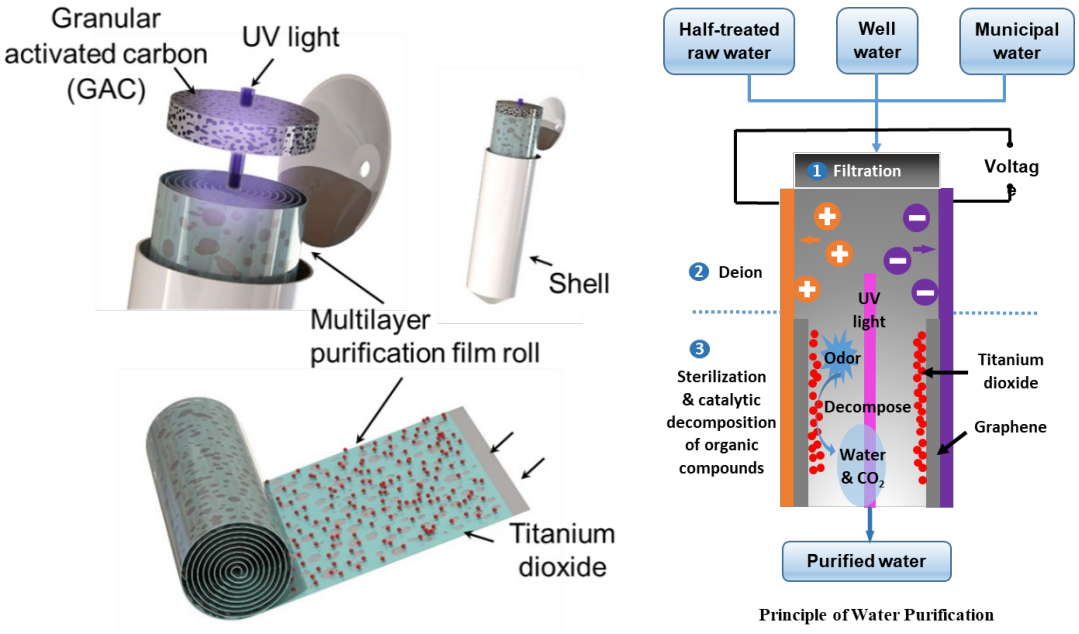
Final Update June 30, 2022

The team developed a water purification system for the drinking water treatment. The system combined titanium dioxide based photocatalysis and electrochemical heavy metal ions reduction. The team successfully got initial testing results using glass-based compact microfluidic devices in lab. Methods including optimization of microchannel design and air bubble vibration were conducted to enhance the mass transfer as well as water purification efficiency. The methylene blue and Cu2+ were chosen as the example of organic pollutants and heavy metal ions. As a result, the compact system can remove 91.6% percent of the 10 µM methylene blue when the mass flow rate is 14.4 mL/h, and the about 97.5% of 200 ppm Cu2+ can be removed at the same time.

ACTIVITY 2: Development of standard size water purification systems and field testing

Description: A prototype standard size purification system to be assembled with the community water supply will be designed and constructed. We will develop prototype standard size purification system, as shown in Figure 2. The water purification system is composed of porous activated carbon, reverse osmosis film, columnar UV light source, and a roll of multilayer purification film.

Test sites will be set up to demonstrate the feasibility of the systems. Field testing will include picking up community sites and testing the efficiency of the systems in the field. Upon completion of the project, we will demonstrate the purification systems to the stakeholders, LCCMR committee members and officials.



Principle of Water Purification

Figure 2. New Design of Drinking Water Purification System.

Specific tasks will be:

Development of standard size water purification systems and field testing

Standard size water purification systems and field testing are done, which is expected to:

(1) Designed and developed drinking water purification systems in standard size.

(2) Test sites with residential community water sites.

(3) Field testing at field sites, and tested purification efficiency.

Summary Budget Information for Activity 2:

ENRTF Budget: $ 149,431
Amount Spent: $ 149,431
Balance: $ 0

Outcomes	Completion Date
1. Standard size systems will be designed and developed	*12/31/2020*
2. One or two test sites with residential community water sites will be set up	*3/31/2022*
3. Field testing will be performed with filed sites, and purification efficiency will be tested	*6/30/2022*

First Update December 31, 2018:

N/A

Second Update June 30, 2019:

N/A

Third Update December 31, 2019:

N/A

Fourth Update June 30, 2020:

N/A

Fifth Update December 31, 2020:

Full-size prototypes of the photocatalytic water purification system have been fabricated. The testing based on an individual microfluidic device and the integrated system has shown relatively high photodegradation efficiency, and the feasibility of the design has also been verified. The only thing that is missing is that the fabrication of microchannels on large-sized flexible substrates is still in progress. It is believed that the flexible polymer-based microfluidic device will be deployed in the improved system as soon as possible, and the mass flow rate of the system will be further increased.

We fabricated a full-size prototype with a microchannel array. The model was fabricated by PMMA, and the inlet and outlet reservoirs were set at the upper and lower ends of the system, respectively. The water will flow through the activated carbon and the microchannel array in sequence.

Ten microfluidic devices were distributed around the ultraviolet lamp. The height difference between inlet and outlet reservoirs was 10cm, which leads to a mass flow rate of around 150 mL/h for the system, and 90.6% percent of the MB can be removed after the purification.

Due to the pandemic, there is some delay of the research progress. We applied for a no-cost extension for one more year to finish the overall project.

Sixth Update June 30, 2021:

In this stage of work, the heavy metal reduction module was added to the water purification system. The integration of heavy metal reduction and photocatalytic organic removal shows the high efficiency of simultaneous heavy metals and organic pollutants removal. A comprehensive assessment of the system will be completed, and some modification and optimization will be performed based on the testing result. The field test was delayed because of the COVID-19 pandemic and will be performed in the next stage. We plan to conduct the field tests during the 1-year extension.

Seventh Update December 31, 2021:

In this stage of work, the mass transfer efficiency was focused on to further improve the photocatalytic efficiency. Micro-channels and bubble vibration are introduced at the same time so that the photocatalytic efficiency is greatly improved, and finally, 97.5% of the organic matter can be removed in one flow.

The design of the microchannel with detailed structure of pockets for air bubble trapping was completed for enhancement of mass transport. The width of the microchannel is 1 mm, and the total length is 660 mm. In order to enhance the adhesion between photocatalyst and substrate, the glass slides used in previous work were replaced by Fluorine-doped Tin Oxide (FTO) glass. As a conductive metal oxide, the application of FTO makes it possible to combine the microfluidic device and photoelectrocatalysis system. All the other fabrication process was almost as same as previous work.

The photocatalysis performance in the microchannel was first studied without vibration. Different mass flow rate and different thickness of microchannel were compared. 10μM methylene blue flowed through the microchannel with solar light illumination, and the solution at the outlet is collected. The concentration of outlet methylene blue was measured by UV-Vis spectrometer. The microchannel 200 μm thick was first tested with different mass flow rates. It can be inferred from the result that the lower mass flow rate led to more degradation of methylene blue. This is due to the longer residence time of the solution in the microchannel at low flow rates, which also means more time for photocatalytic degradation. It can also be noticed that only 10% more methylene blue was degraded when the residence time is doubled. It is because the mass transfer rate is lower when the fluid flow is slower, and the total transmission mass is also limited at low concentrations. Experiments in a microchannel with 80 μm thickness confirmed this theory. It can be found that around 90% of the pollutants can be removed when flowing through the microchannel, which is 50% more than the microchannel 200 μm thick at the same mass flow rate. This result further illustrates the limitation of the mass transfer rate on the photocatalytic process, and the mass transfer rate is not high enough to rely on micro-channels alone.

The air bubble vibration was applied to further enhance the mass transfer. The air bubble was formed in the pocket structure shown because of the surface tension when the solution flows through. The PZT disk is used as the actuator for vibration. Microbeads 2 μm in diameter were used for particle image velocimetry (PIV). Different frequency was applied on the PZT disk and the flow field is characterized by the movement of the microbeads. The strongest circulation occurs at 8 KHz, the

resonance frequency of air bubbles, and the highest mass transfer coefficient can be expected. It can be found that 97.5% of the methylene blue can be removed with air bubble vibration. Although only 8.3% more methylene blue was removed compared to the case without air bubble vibration, the enhancement is still significant as the chemical reaction rate will become slower and slower as the concentration decreases. The impact of vibration intensity is studied by changing the voltage applied to the PZT disk. Not surprisingly, higher vibration intensity brings faster mass transfer efficiency, which further accelerates the photodegradation rate.

The field test was delayed because of the COVID-19 pandemic and will be performed in the next stage. We plan to conduct the field tests during the 1-year extension.

Final Update June 30, 2022

This project aims to design small and cheap water purification system for simultaneous removal of organic pollutants and heavy metal ions in drinking water. The standard-sized prototype was fabricated based on cheap polymer materials. Photoelectrocatalysis is the basic mechanism for organic and inorganic pollutants removal, and titanium dioxide was selected as the photocatalyst. The lab testing has shown compete organics removal and 96% removal of the heavy metal ions, and the field test also proved the performance of the system.

The microchannel was fabricated with the roll-to-roll technique. The structure of the microfluidic channel was first fabricated on double-sided tape by laser cutting. Then the two polymer sheets covered both sides of the tape to form the sealed microchannels. All operations are carried out on a roller 10 cm in diameter to reduce the internal stress after bending. The photocatalyst was deposited on the channel surface with layer-by-layer self-assembly technique, and half of the microchannels was covered with a thin layer of copper foil to serve as the electrode for electrochemical deposition. The standard-sized prototype consists of a UV lamp, a chamber with active carbon, and a microfluidic device with immobilized photocatalyst and copper foil.

The system was first tested in the lab with methylene blue and Cu2+ solutions. The efficiency of photodegradation and electrochemical reduction was evaluated separately. The number of TiO_2 layers and mass flow rate were two of the main factors that affect photodegradation efficiency. Different numbers of TiO_2 layers ranging from 1 to 9 were deposited in the microchannels, and the mass flow rate ranging from 10 mL/h to 50 mL/h was applied for the experiment. 10 μM methylene blue was still used as an example of the organic pollutants. The concentration of methylene blue in the outlet solution was measured by spectrophotometer. The result shows that more layers of TiO_2 always lead to more removal of methylene blue. Complete removal of methylene blue at 50 mL/h occurs when 9 layers of TiO_2 were deposited. The lower mass flow rate means a longer residence time of solution in the microchannels, and thus results in a higher removal rate with different number of TiO_2 layers. The complete removal of methylene blue can also be achieved with 7 layers of methylene blue and a mass flow rate of 20 mL/h.

The efficiency of heavy metal reduction was then studied by measuring the concentration of Cu2+ at the outlet. The deposition potential is the key factor for electrochemical deposition. It can be inferred from the result that lower deposition potential leads to a higher removal rate of Cu2+. It is because the lower deposition potential represents a larger potential difference and a higher chemical reaction constant. As a result, 96% of the Cu2+ can be removed from the water when the mass flow rate is 50 mL/h.

Finally, the performance of the standard-sized system was evaluated by the field test. The water samples from Commonwealth Terrace Cooperative, a community for University of Minnesota students and their families, and the Mississippi River were collected and used for testing. The

concentration of organic pollutants in the water samples before and after the purification was represented by the Chemical Oxygen Demand (COD), and the COD was measured with the colorimetric method. The performance of heavy metal reduction was evaluated by adding 1 ppm Cu2+ into the sample and measuring the removal rate of Cu2+ at the outlet. It can be found that the COD number was reduced to 67% and 82% for different samples, and the Cu2+ recovery rate was around 90% for both samples. Lower-than-expected organic removal may be due to the presence of refractory organics in the sample. Overall, the testing results demonstrate the capability of using the designed system to simultaneously remove organic pollutants and heavy metal ions in waters including drinking water and environmental water.

The field testing shows that the developed standard-sized system can simultaneously remove organics and heavy metal ions in the solution, and it's the first system that, to our knowledge, has this capability. The fabrication cost is mainly including the materials used and the PMDS mold for microchannel fabrication. Although the fabrication of the mold is relatively expensive, the mold can be used many times. Therefor the cost of a single system is around $20, which is much lower than existing water purification products. The low cost also makes it possible to scale up or pattern the system to overcome the problem of low throughput.

V. DISSEMINATION:

Description:

The findings will be disseminated through:

(1) On site demonstration as described in the activities
(2) Public seminars
(3) Progress update on www.me.umn.edu
(4) Presentations at national and international technical conferences
(5) Communications with interested entrepreneurs
(6) Peer reviewed papers
(7) Collaboration with MPCA

The technologies, if demonstrated successfully, may be implemented to community and home drinking water purification in the State of Minnesota and beyond. Any intellectual properties and related revenues as a result of the program will be shared between UMN and LCCMR.

First Update December 31, 2018:

N/A

Second Update June 30, 2019:

N/A

Third Update December 31, 2019:

N/A

Fourth Update June 30, 2020:

One peer reviewed journal paper was published in an archived journal in the following:
Zhou, P., & Cui, T. (2020). Enhanced photocatalytic efficiency by layer-by-layer self-assembly of graphene and titanium dioxide on shrink thermoplastic film. Microsystem Technologies.

Fifth Update December 31, 2020:

N/A

Sixth Update June 30, 2021:

Two research papers are under preparation for submission to academic journals.

Seventh Update December 31, 2021:

One peer reviewed journal paper was published in an archived journal in the following:
Zhou, P., Zhang, T., Simon, T. W., & Cui, T. (2021). Simulation and Experiments on a Valveless Micropump With Fluidic Diodes Based on Topology Optimization. Journal of Microelectromechanical Systems.

Final Update June 30, 2022
On-site demonstration and tests as described in the activities at a student housing community and Mississippi river from May through June 2022. Communications with interested entrepreneurs have been ongoing with interested parties including local companies and individuals.

The following papers published in archived journals and prestigious conferences:
1. Zhou, P., & Cui, T. (2020). Enhanced photocatalytic efficiency by layer-by-layer self-assembly of graphene and titanium dioxide on shrink thermoplastic film. Microsystem Technologies, 26(12), 3793-3798.
2. Zhou, P., Zhang, T., Simon, T. W., & Cui, T. (2021). Simulation and Experiments on a Valveless Micropump With Fluidic Diodes Based on Topology Optimization. Journal of Microelectromechanical Systems, 31(2), 292-297.
3. Zhang, T., Zhou, P., Simon, T., & Cui, T. (2022). Vibrating an air bubble to enhance mass transfer for an ultra-sensitive electrochemical sensor. Sensors and Actuators B: Chemical, 354, 131218.

Professor Tianhong Cui presented five invited public seminars and talks on water sensors:
Invited Talk, University of Bath, July 4, 2022
Invited Talk, University of Cambridge, July 11, 2022
Invited Talk, EcoLab, May 4, 2022
Invited Talk, French-American Innovation Days, Water Management in Cities, April 8, 2021 (on-line)
Invited Talk, University of Texas at San Antonio, September 13, 2019

VI. PROJECT BUDGET SUMMARY:

A. ENRTF Budget Overview: See attached budget spreadsheet

Explanation of Use of Classified Staff: N/A

Explanation of Capital Expenditures Greater Than $5,000: N/A

Number of Full-time Equivalents (FTE) Directly Funded with this ENRTF Appropriation: 1.11 FTE

Number of Full-time Equivalents (FTE) Estimated to Be Funded through Contracts with this ENRTF Appropriation: 0

B. Other Funds:

Source of Funds	$ Amount Proposed	$ Amount Spent	Use of Other Funds
State			
The university overhead unpaid	$205,087	$0	Develop a Small and Inexpensive Community Drinking Water Purification System
TOTAL OTHER FUNDS:	**$205,087**	**$0**	

VII. PROJECT STRATEGY:

A. Project Partners:

Tianhong Cui, Distinguished McKnight University Professor at the University of Minnesota, will serve as PI and project manager. Professor Cui is a leading expert on advanced manufacturing and micro devices. He will be responsible for overseeing the project, all reports, and deliverables. A research assistant and a post-doc will develop the systems, in-lab test sites with dirty water, and set-ups for field testing of the proposed purification systems for community drinking water.

B. Project Impact and Long-term Strategy:

Minnesota Pollution Control Agency (MPCA) works together with other agencies and advocacy groups in developing strategy to keep clean drinking water, reducing their impacts on human health and the environment. Water is one of the most valuable natural resources in the world. In everyday life, people use water in many ways, such as drinking, cooking, washing, etc. It is very important to ensure the supplied water is clean, especially the drinking water for daily life. Although tap water meeting federal and Minnesota state standards is usually safe to drink, people are still confronted with an increasing threat to contaminated water. It has been reported that over 200,000 violations to federal drinking water standards each year, among which more than 20% are due to poor water treatment facilities. Therefore, a small cheap but efficient community water purification system is very important to ensure a healthy drinking water supply, especially for those who are vulnerable to waterborne diseases. Commercially available community water treatment systems utilize various water cleaning technologies with several components, including activated carbon filter unit, ion exchange unit, reverse osmosis unit, and distillation unit. The purification system consists of a sediment pre-filter, a carbon block pre-filter, a reverse osmosis cartridge, and a total defense advanced filtration cartridge. Through the above units, contaminants, such as heavy metal ions, microbes, dissolved solids, organic pollutants can be removed from the water, so that clean drinking water can be obtained. The commercial systems provide the users with purified drinking water, but the price is relatively high, ranging from hundreds to thousands dollars. In addition, due to the large volume of the purification systems, it occupies much room. The proposed new purification system will provide a solution to current ineffective and expensive community water treatment systems, and thus ensure people's cleaner drinking water in Minnesota.

The knowledge learned throughout the project will provide a solid foundation for further research and development that would lead to eventual implementation of the new technique practically enabling broader treatment of Minnesota's water. This will provide a solution to current ineffective water treatment, ultimately help implement the MPCA's clean water strategy, and thus ensure people's safety in Minnesota.

In addition, we will plan to file patents on the proposed community drinking water purification system for commercialization in the future. We can also use the new technology for treatment of natural water, waste water, etc. As a result, the innovative technology can benefit the local residents and society by purifying the waters in Minnesota.

C. Funding History:

Funding Source and Use of Funds	Funding Timeframe	$ Amount
Mocon Inc., Graphene gas sensors	Nov. 2014 - July 2016	$173,199
Alexandria Extrusion Inc., Microstructures for Heat Transfer	Nov. 2011 - Dec. 2015	$165,516
DARPA, MEMS-Based Active Heat Sink Technology	Jan. 2009 - Sept. 2013	$2,579,025
MN Partnership, Nano-Sensors	Jan. 2010 – Dec. 2012	$637,500

VIII. FEE TITLE ACQUISITION/CONSERVATION EASEMENT/RESTORATION REQUIREMENTS:

IX. VISUAL COMPONENT or MAP(S):

X. RESEARCH ADDENDUM:

XI. REPORTING REQUIREMENTS:

- The project is for 4 years, will begin on 07/01/18, and end on 06/30/22.
- Periodic project status update reports will be submitted [06/30] and [12/31] of each year.
- A final report and associated products will be submitted between June 30 and August 15, 2022.

Appendix: Visual Component

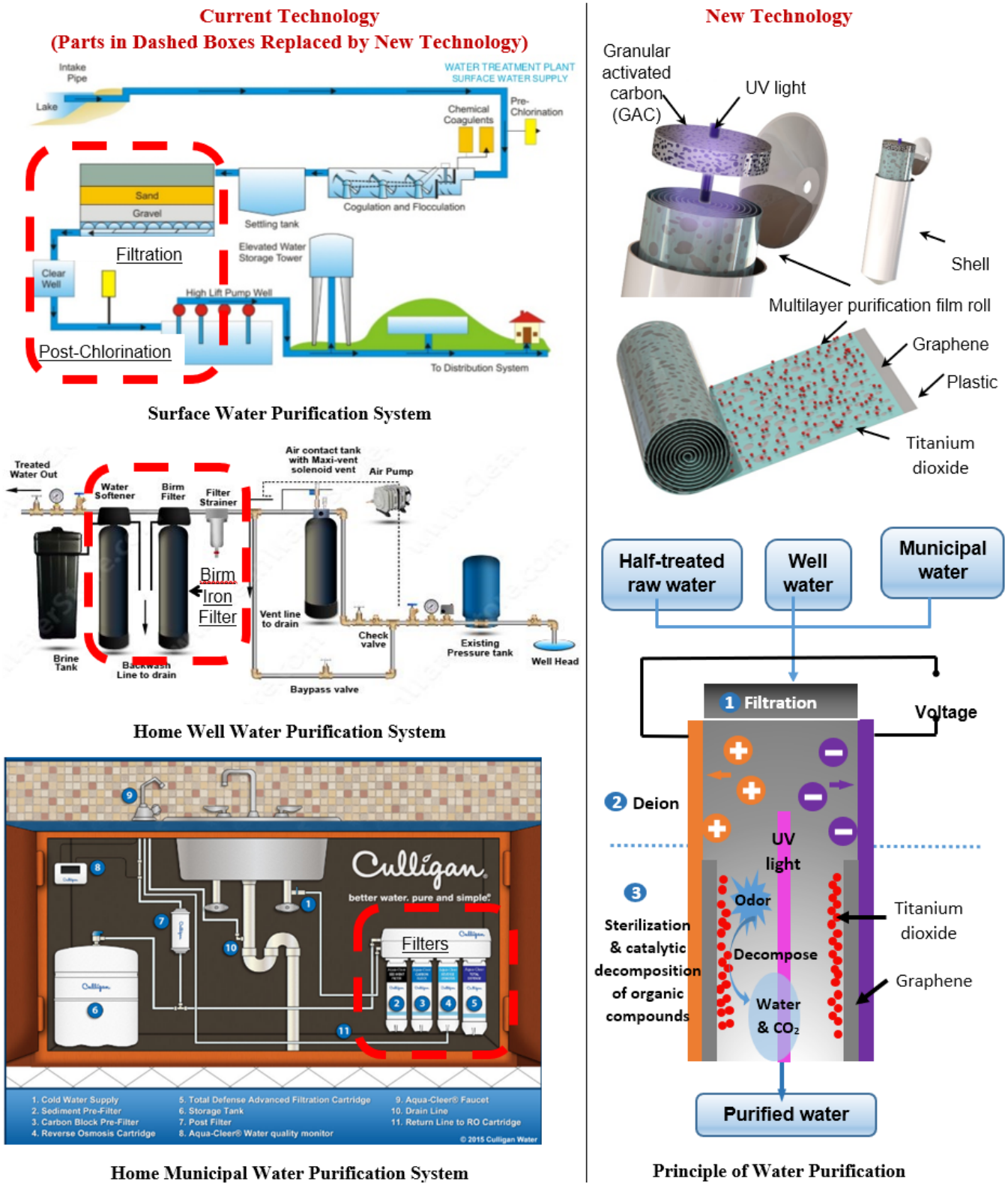


Figure 1: Design of the proposed water purification and comparison with existing technologies.

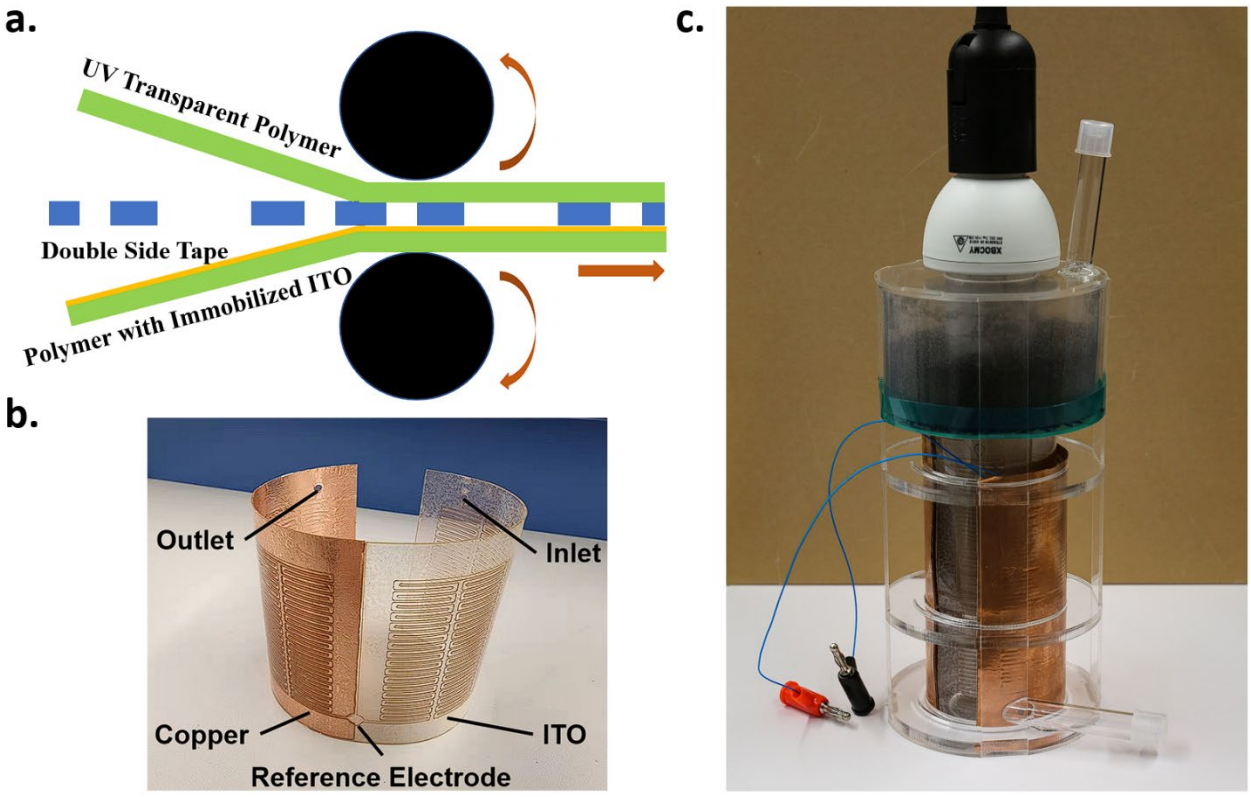


Figure 2: (a) Scheme of the polymer based microchannel fabrication (b) picture of fabricated microfluidic device based on polymer material (c) picture of standard size prototype for water purification.

Attachment A:
Environment and Natural Resources Trust Fund
M.L. 2018 Budget Spreadsheet - FINAL

Project Title: Develop Small and Inexpensive Purification System for Community Drinking Water
Legal Citation: ML 2018 ch214 Art4 Sec 2 Sub04e E8181PS
Project Manager: Dr. Tianhong Cui
Organization: University of Minnesota
College/Dept/Div: College of Science and Engineering, Dept of Mechanical Engineering
M.L. 2018 ENRTF Appropriation: $425,000
Project Length and Completion Date: 4 years/ June 30, 2022
Date of Report: Actuals 8/9/22

ENVIRONMENT AND NATURAL RESOURCES TRUST FUND BUDGET	Amended Budget	Amount Spent	Balance
BUDGET ITEM			
Personnel (Wages and Benefits) - overall	$348,730	$348,730	$0
Dr. Tianhong Cui, PI, 1 month summer salary (11% FTE) & 33.5% fringe for 3 years (Total estimated amount $69,512)			
Post-Doc or visiting scholar, 6 months (50% FTE) plus 21.4% fringe for 3 years Total estimated amount $90,056)			
Graduate Research Assistant, 50% FTE (fall & spring semesters include 16.9% fringe plus $18.94/hour tuition, summer 15% fringe only) for 3 years (Total estimated amount $144,563)			
Professional/Technical/Service Contracts			
Equipment/Tools/Supplies			
Lab Materials & Supplies: fabrication materials & supplies including polymer substrates ($10,000), nanomaterials and chemicals ($15,000), roll-to-roll manufacturing set-up items ($14,619), bottles, gloves, other electronics for testing, etc. ($10000)(Total estimated amount $49,619)	*$50,034*	*$50,034*	$0
Travel expenses in Minnesota			
Travel- Cui Domestic travels: Mileage, lodging, and meals for travel to and between the drinking water testing sites and the university based on the university compensation policy	*$0*	*$0*	$0
Other			
Scientific Services: User fees at Minnesota Nano Center and Characterization Facility at the University of Minnesota. The cost is estimated at about $1,000 per month for the Post-Doc, and $750 per month for the research assistant for 3 years. Actual charges based on equipment rate and time used will be charged. (See note below)	*$26,235*	*$26,235*	$0
COLUMN TOTAL	$425,000	$425,000	$0