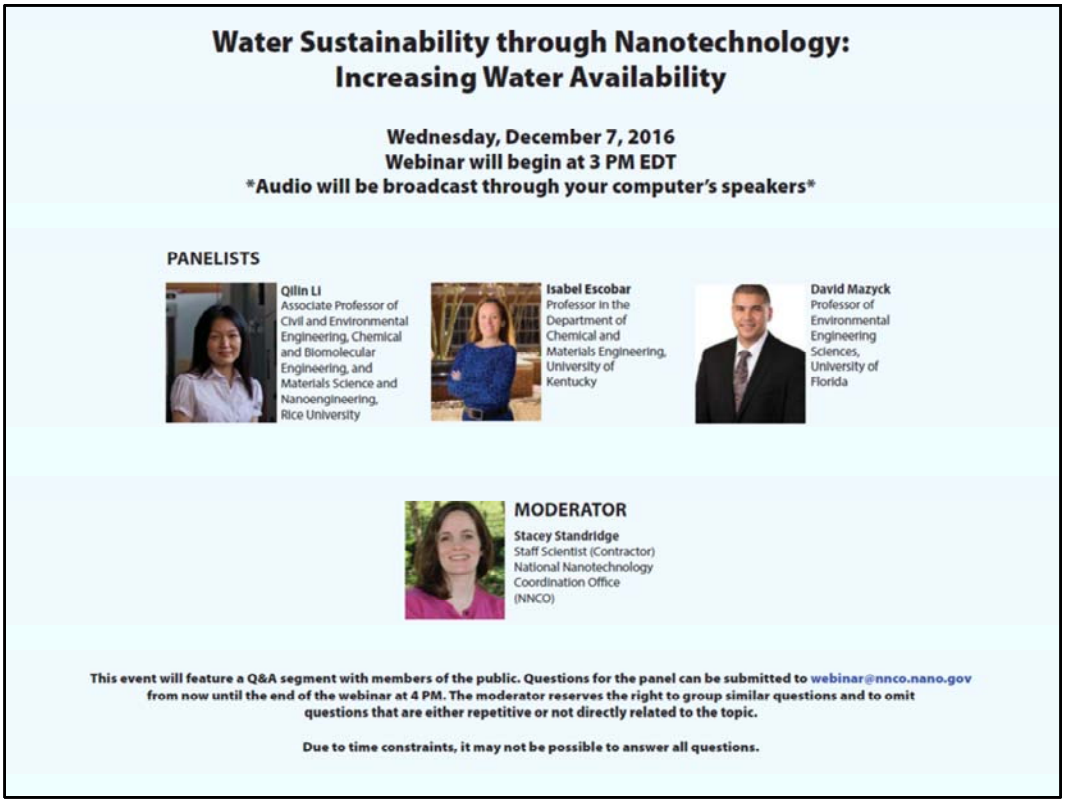


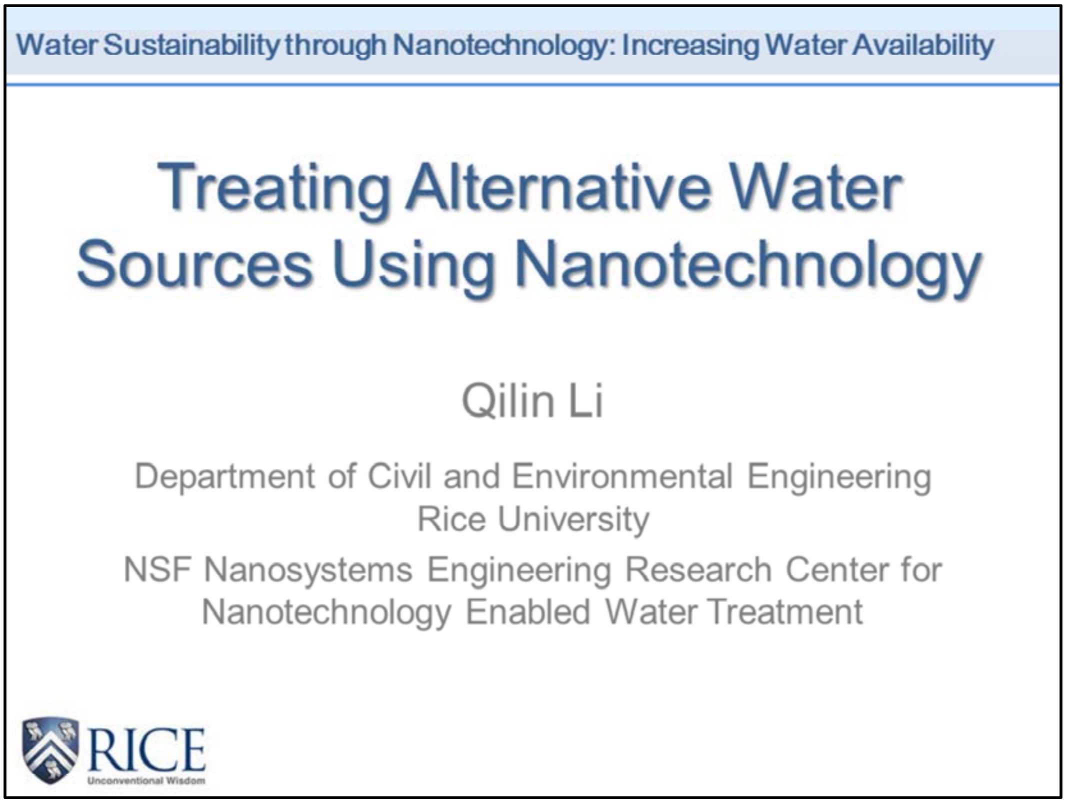
>> Stacey Standridge: Good afternoon and welcome to today's Water Sustainability through Nanotechnology webinar. My name is Stacey Standridge. I am a Staff Scientist at the National Nanotechnology Coordination Office, and I will be your moderator today.

Today's webinar is hosted by the National Nanotechnology Initiative's Signature Initiative, *Water Sustainability through Nanotechnology*, and this event is the second in a series exploring the intersections of water and nanotechnology. An archive of the first webinar is available at www.nano.gov/publicwebinars, along with information on other upcoming webinars. The next webinar in this series is entitled *Enabling Next-Generation Water Monitoring Systems*, and it will take place on January 18th at 3 pm Eastern.

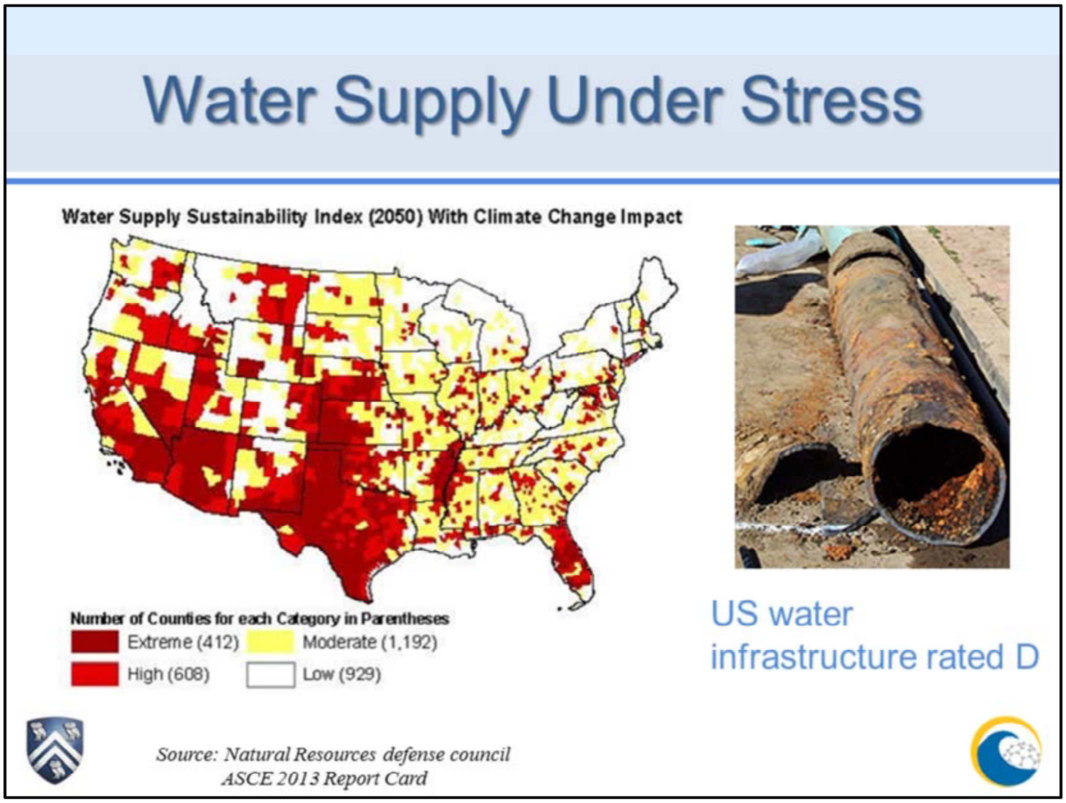
Today's event will explore the topic of increasing water availability, and we have a great panel of speakers. I invite you to read their full bios on the webinar webpage, but by way of brief introduction,

- Qilin Li will give a broad technical overview and talk a little bit about alternatives to reverse osmosis. Dr. Li is a professor of Civil and Environmental Engineering, Chemical and Biomolecular Engineering, and Materials Science and Nanoengineering at Rice University in Houston, where there is a 2% chance of precipitation today.
- Isabel Escobar will discuss membranes, and she is a professor in the Department of Chemical and Materials Engineering at the University of Kentucky in Lexington, which is currently experiencing a severe drought.
- David Mazyck will address catalysis, and he is a professor of Environmental Engineering Sciences at the University of Florida in Gainesville, where they get a monthly average of 2.5 inches of rain this time of year.

Without further ado, I will hand the floor over to Qilin.

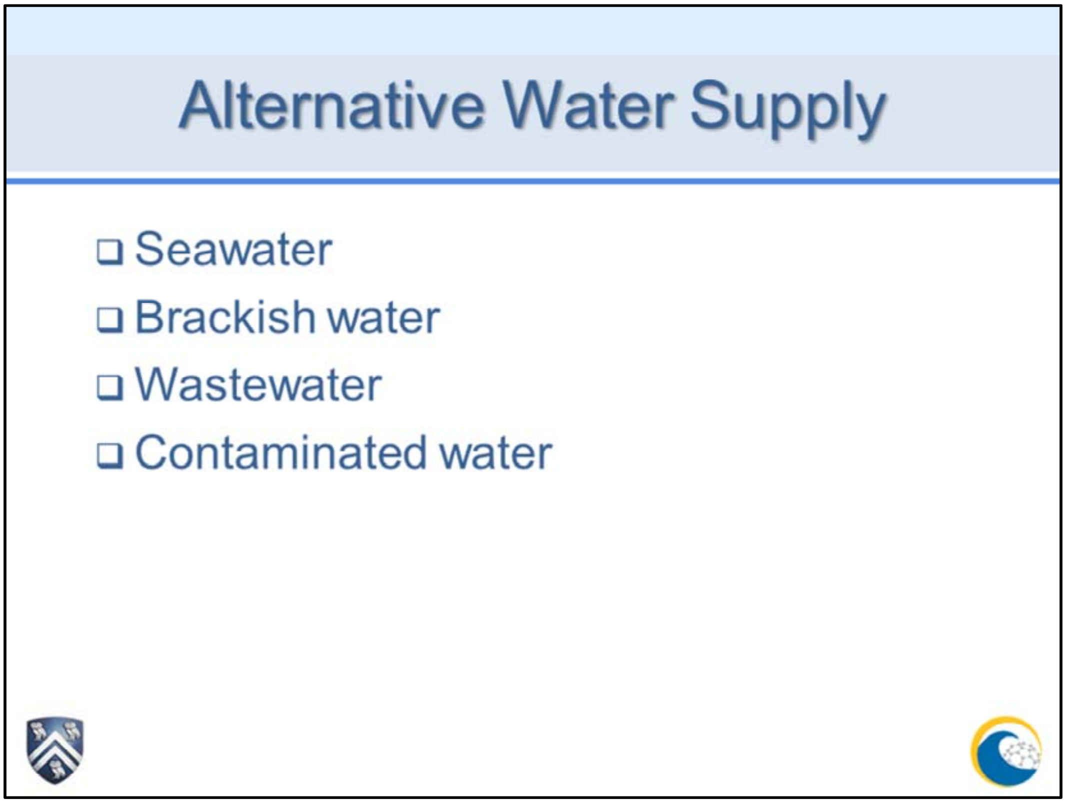


>> Qilin Li: Thank you, Stacey. So I want to tell you a little bit about my view of methods available to treat alternative water sources based on nanotechnology.

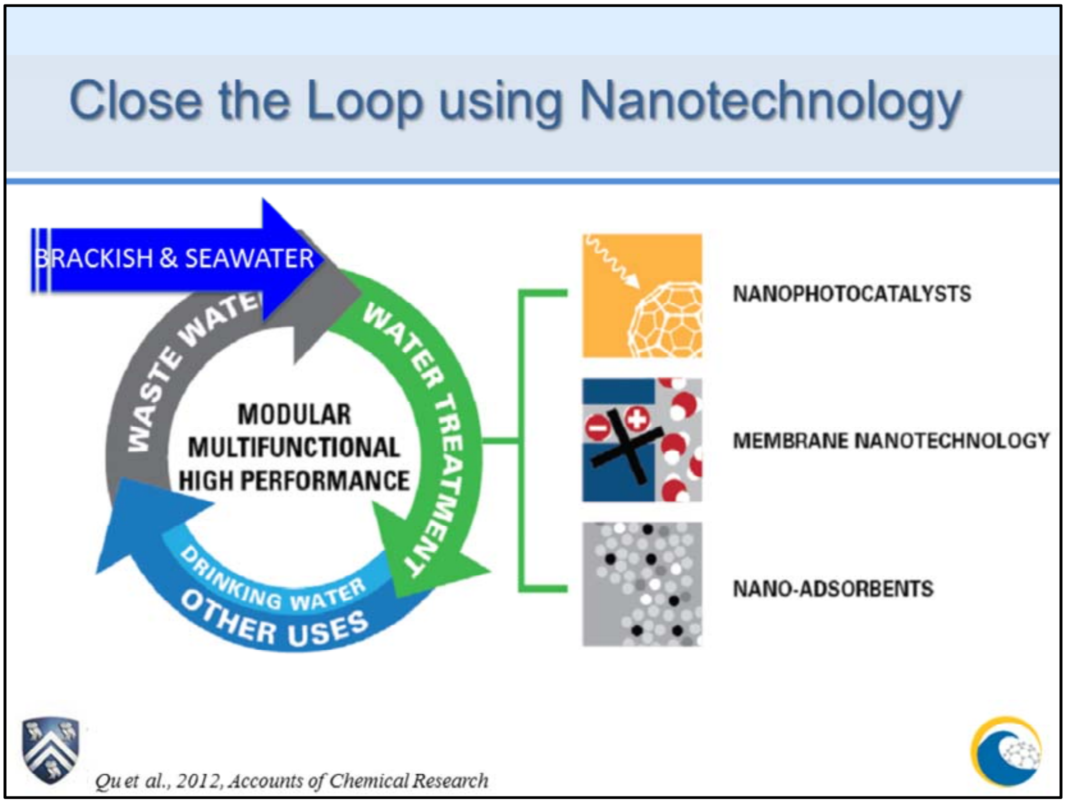


>> Qilin Li: I wanted to start by looking at the global water crisis. We all know that the world's water resources are stressed by rapid population growth, industrial contamination, and climate change. Even for the United States, a country that is considerably rich in water, the predicted level of water stress due to climate change is quite alarming. This map here shows the result of a survey of people's expected water stress in the continental United States. The study found that more than 1,100 counties, more than one third of all the counties looked at, are expected to face higher risks of water shortage by mid-century as a result of global warming, and more than 400 of these counties will face extremely high risk of water shortage.

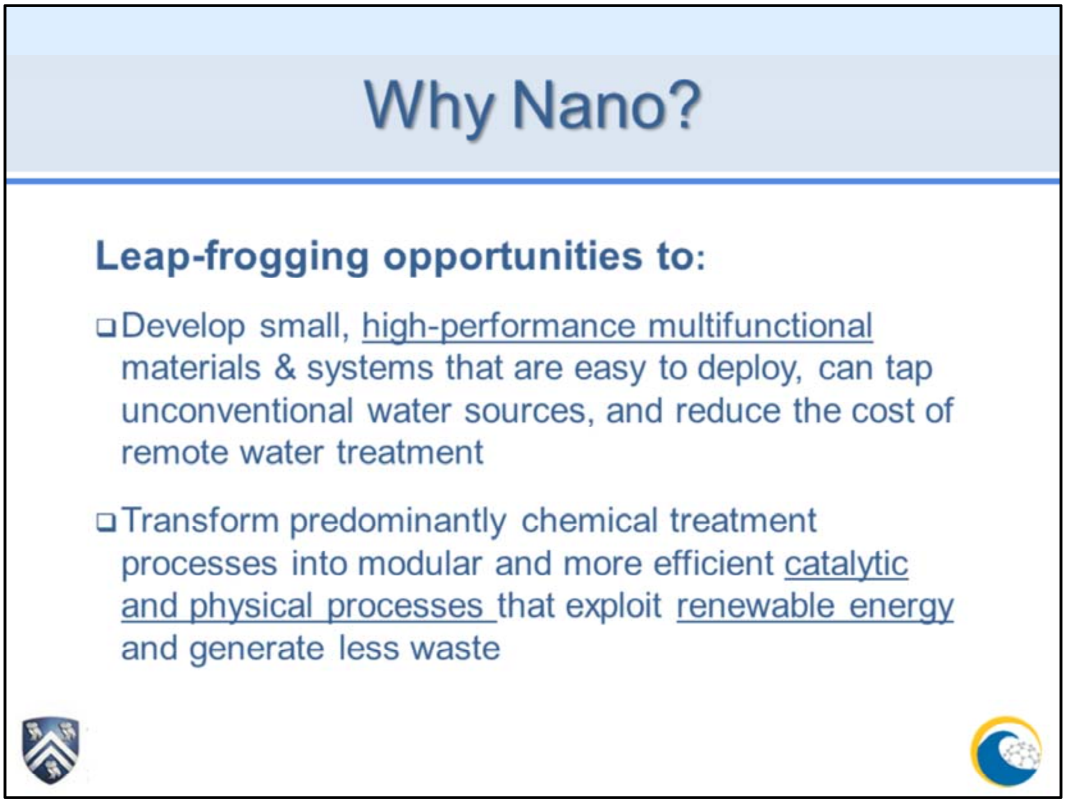
In addition to that, we are also facing the tremendous challenge of an aging infrastructure. The American Society of Civil Engineers rated the Nation's water infrastructure with a rating of D. That's obviously a poor rating. This is a major threat to public health, as well as a huge barrier for water and energy efficiency. All of these challenges, however, provide us also an opportunity to rethink our conventional approach to water supply, which has heavily relied upon pristine fresh water sources that are becoming increasingly stressed.



>> Qilin Li: If we look at what other water sources are available, the large gap between our water demand and supply could potentially be met by utilizing alternative water supplies, and these include sea water, brackish water, waste water, contaminated water, surface water, and ground water.

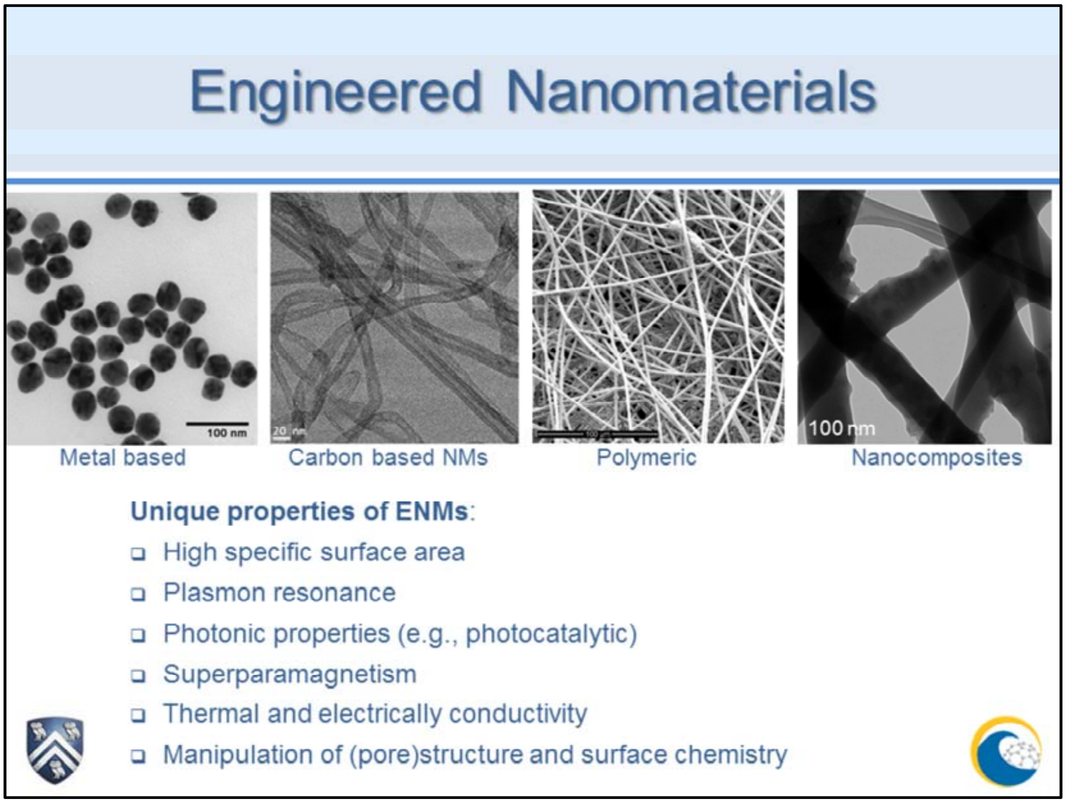


>> Qilin Li: Treating these alternative water sources will obviously be much more challenging than treating our conventional fresh water sources. That forces us to take a different look at what we had been doing for water and waste water treatment and consider some new approaches. Many of us realized that nanotechnology presents a great opportunity to potentially change our existing water treatment paradigm. My vision, which I presented in a paper we published in *Accounts of Chemical Research*, is that we can enable the utilization of unconventional water sources at low cost and high energy efficiency using nanotechnology. We hope that this can be done by using more efficient catalysts, better fouling-resistant membranes, and higher capacity adsorbents, and these can all be potentially achieved using nanotechnology.

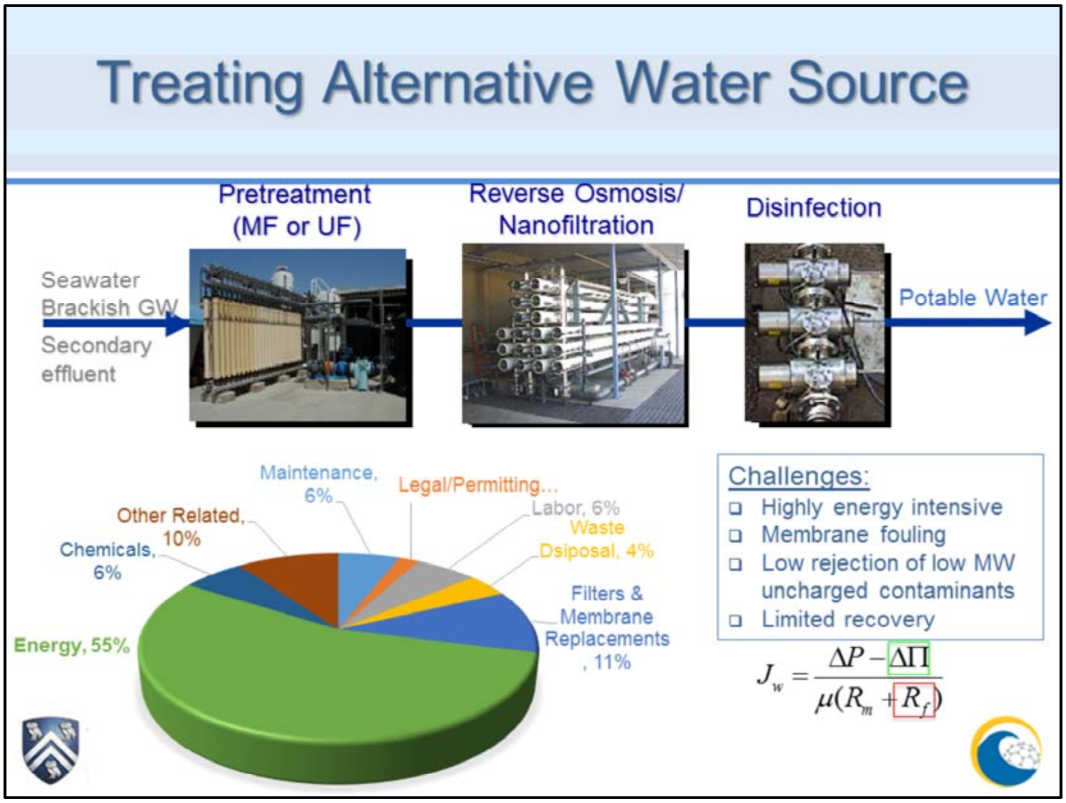


>> Qilin Li: So the best advantages of nanotechnology, I believe, lie in two factors. First is that the unique properties of nanomaterials allow us to develop small-sized, high-performance, and multifunctional materials and systems. So this gives us the opportunity to basically miniaturize our traditionally very large water and waste water systems at two different levels: we can reduce the size at the materials level so we can make multifunctional particles using different types of very small nanoparticles; and you can put different types of nanoparticles in one system or reactor to achieve multifunctionality at the reactor level. So these features allow us to combine multiple treatment goals in one single reactor and also significantly reduce the size of the system. Making these systems modular and much more flexible allows for reconfiguration based on the quality of the source water and the needed treated water quality.

Another factor is that we can use nanotechnology to help us transform from predominantly chemical reaction-based processes, such as coagulation and flocculation, to processes that are catalytic and physical process-based removal mechanisms. And also some of the properties of the nanomaterials, which I will discuss later today, help us to exploit renewable energy instead of the traditional electric power source as the driving force for treatment, and generate less waste because we're not using chemical reaction-based treatment processes.

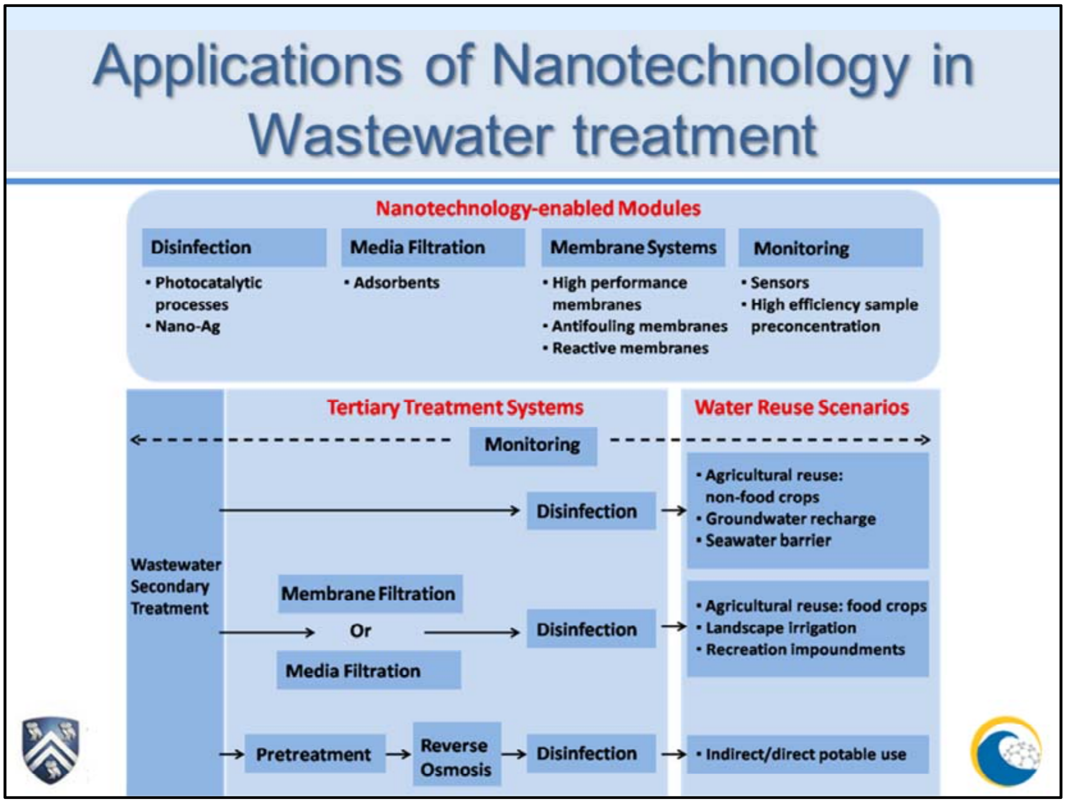


>> Qilin Li: The center of nanotechnology is obviously nanomaterials, and people have exploited multiple types of nanomaterials in water and waste water treatment. We typically categorize the nanomaterials based on the nature of the ingredients or the components that are used to make the nanomaterial, and they are metal-based, carbon-based, polymeric nanomaterials, and nanocomposite materials that include more than one component and at least one of them is nanoscale in size.

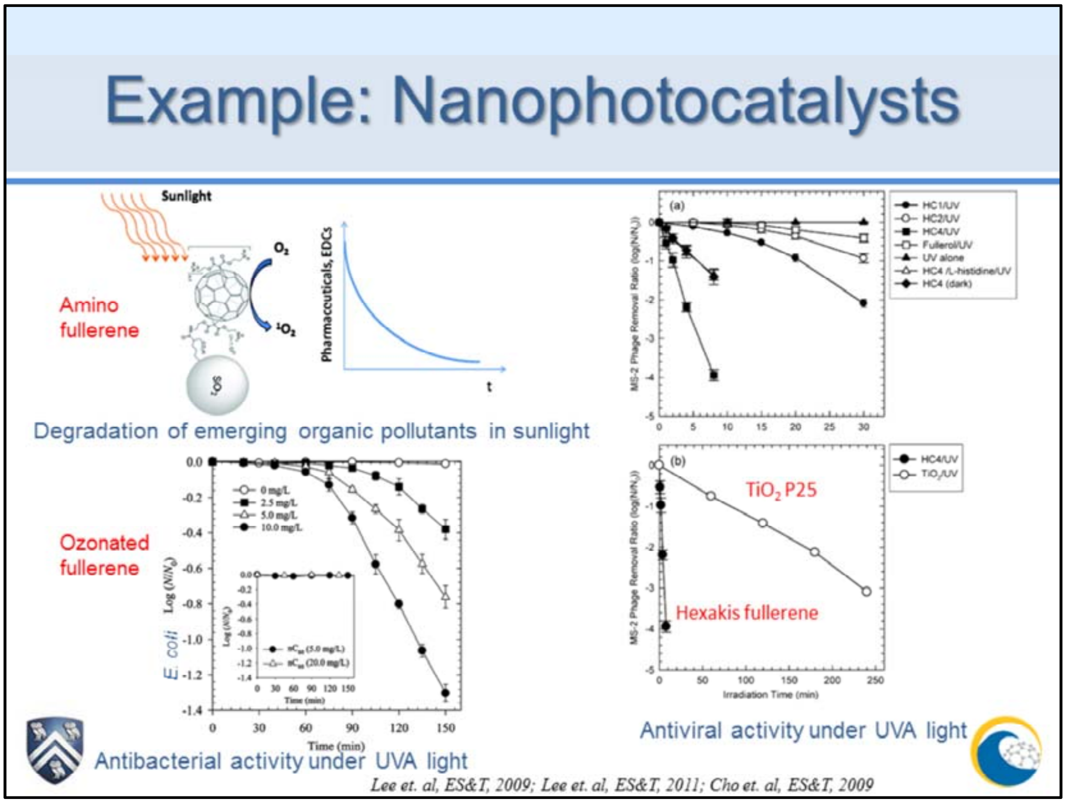


>> Qilin Li: If we look at what roles these nanomaterials or nanotechnologies can play in the treatment of these alternative water sources, we think about desalination of sea water and brackish ground water, and we think about waste water reuse. If we first look at desalination, the typical treatment would include a pretreatment using either microfiltration or ultrafiltration, followed by reverse osmosis (RO) if it is sea water desalination. Or you can potentially use nanofiltration if it's low-salinity brackish water. And that desalinated water is then disinfected before it is distributed for potable uses.

And in this treatment process chain, you can see that if you break down the cost of desalination or waste water reuse, more than half of the cost is for energy use and primarily for the energy that is used to drive reverse osmosis or the nanofiltration process. And if you look at the energy used for the reverse osmosis or nanofiltration process, which is mostly to provide the high pressure that pushes water through the membranes, this equation at the lower right corner here shows the water flux as a function of its driving force, which is the difference between applied pressure and osmotic process across membrane. And it's also determined by the resistance of the membrane materials themselves, that's the R_m, and the resistance caused by fouling of the membrane materials. So here we're really limited by the osmotic pressure, if we're talking about seawater desalination. So there has been a lot of analysis in recent publications showing that further development in high-permeability reverse osmosis materials may not be as helpful as developing fouling-resistant membranes because for seawater desalination, the Δπ—the osmotic pressure difference at the outlet of the membrane module—pretty much determines what that ΔP needs to be. So here when we look at seawater desalination, we need to think about more fouling-resistant reverse osmosis membranes. When we look at wastewater treatment, we know there are other challenges involved in addition to high energy intensity, and that is that our own current membranes don't reject low molecular weight uncharged contaminants very well. In many cases our own membranes actually overtreat the salt but do not provide adequate removal of low molecular weight organic contaminants. So selectivity is something that we can work on as well.

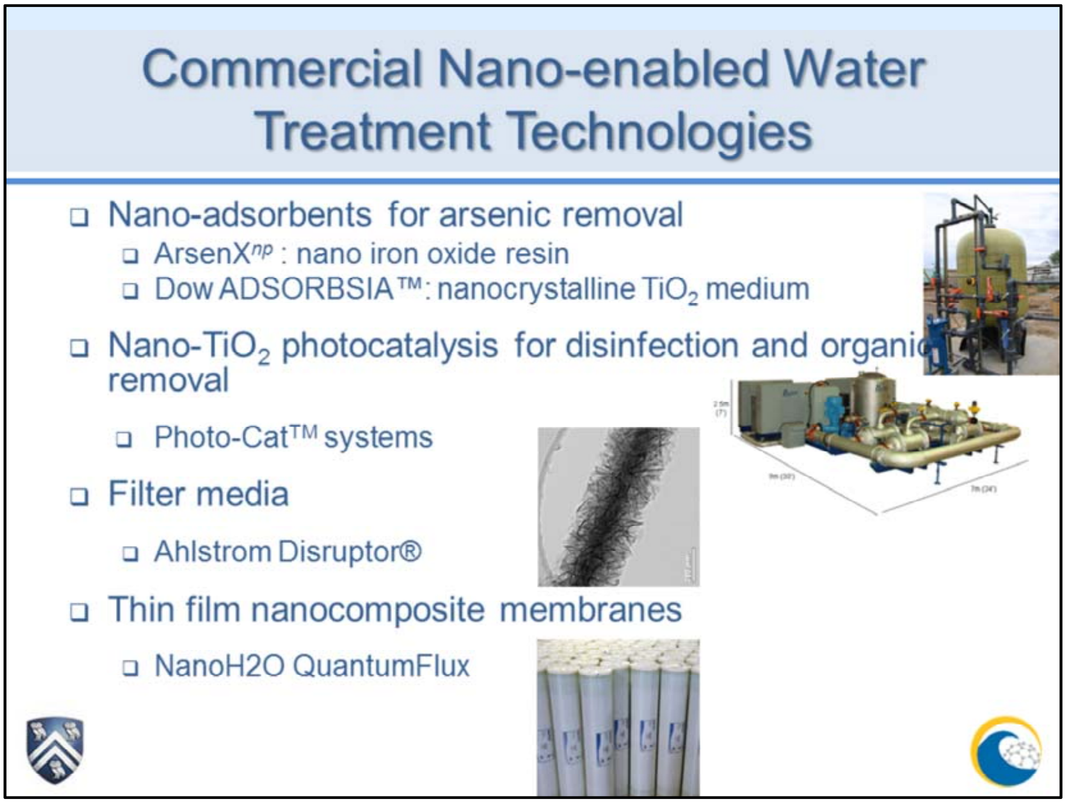


>> Qilin Li: When we look at wastewater reuse processes, depending on the reuse purpose, different processes are needed. So let's say if you are reusing the waste water for agriculture purposes, for irrigation, a lot of times the secondary effluent can simply be disinfected then applied to irrigation. But if we wanted to consider the reclaimed waste water for potable applications, either indirect or direct, then we have to go through a process that's very similar to what we saw in seawater desalination, and that's some level of pretreatment followed by the gold standard today—that's again reverse osmosis—and followed by disinfection. Nanotechnology can play an important role in every one of these processes. So for disinfection, for example, we're going to hear the last presentation on photocatalysis, so nanophotocatalysts can be used to do disinfection. For filtration or adsorption, nanomaterials have superior adsorption properties compared to convention adsorbents. Professor Escobar will talk in detail about membranes that are based on nanotechnology, so I will not go into detail here. And, of course, a very important aspect of waste water reuse, especially potable reuse, is the monitoring of the water quality, making sure that reclaimed water is safe for its proper end use. So there are nanosensors and high-efficiency sample preconcentration kits that are used as real-time detection of pathogens and other contaminants and are becoming extremely important.

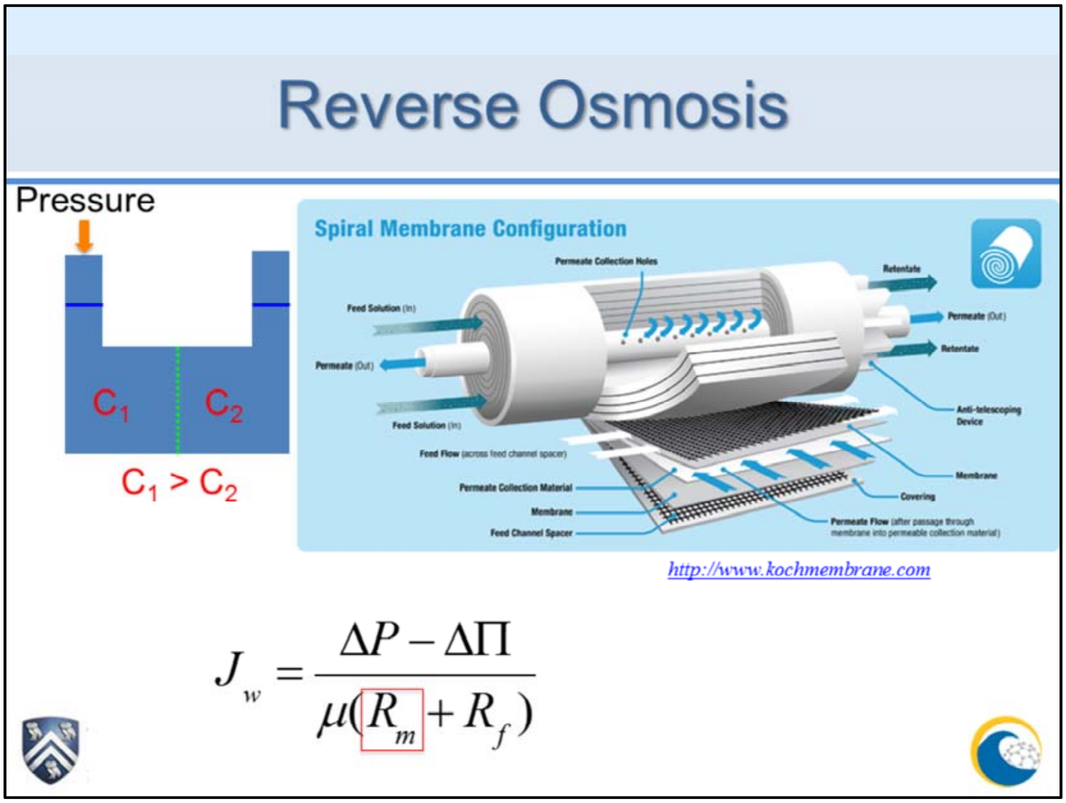


>> Qilin Li: Here I'm showing some examples of nanophotocatalysts that have been developed out of research teams here at Rice University. These are carbon-based photocatalysts. We've tested them for removal of those pathogens, as well as emerging organic contaminants. So these are functionalized fullerenes. The first example I'm showing here is amino fullerene, and these were tested for removal of emerging contaminants. As you can see here, if you functionalize fullerenes using carbon chains of different lengths with amino groups, we get different removal efficiency, but all of them are much better than the traditional photocatalyst, which is TiO_2 P25.

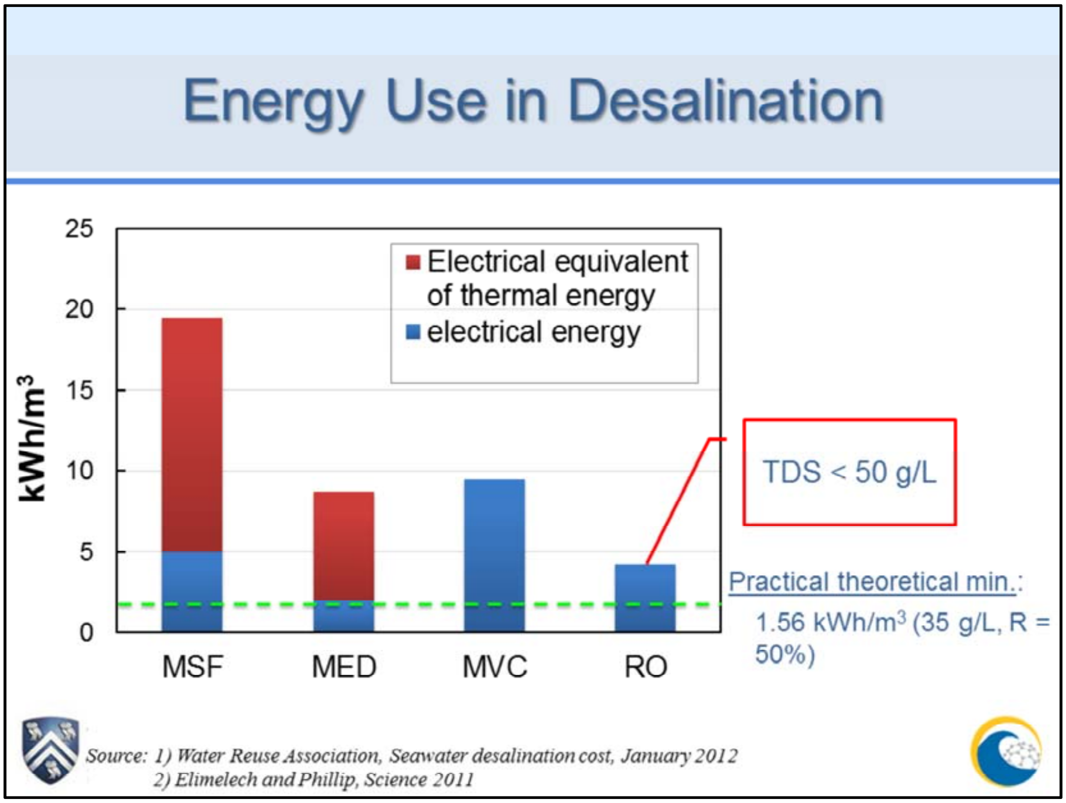
And we also looked at inactivation of pathogens. The example I'm showing you here is E. coli inactivation using ozonated fullerene. This is very similar to the amino fullerene. These are basically oxidized fullerene molecules that can be activated by UVA light and generate reactive oxygen species to inactivate E. coli cells.



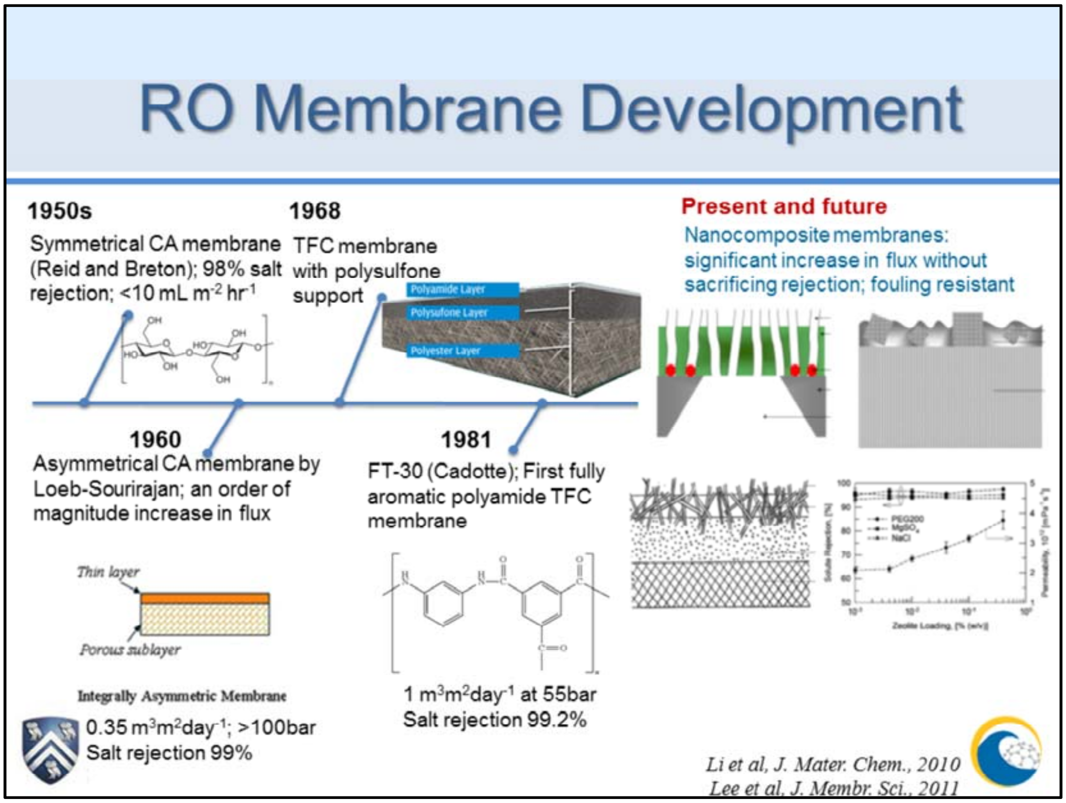
>> Qilin Li: So far there have been a small number of commercial nanotechnology-enabled water treatment systems out there. A large number of them are adsorbents. Nanoadsorbants have superior specific surface area and they have specifically been developed for arsenic removal. Here I'm giving you two examples of commercial nanoadsorbents that have demonstrated superior arsenic removal efficiency. And we've also seen nano-sized titanium dioxide-based photocatalysis systems. The Photo-Cat system basically utilizes a titanium dioxide nanoparticle slurry in a photoreactor followed by a ceramic membrane system to retain the nanoparticles and recirculate and reuse the nanoparticles. We also see the nanomaterials used as filter media. The Ahlstrom Disruptor uses a nanostructured aluminum oxide and utilizes positive charges on this material surface to trap negatively charged particles, bacteria, and viruses from water. An example of nanotechnology-based membrane materials is the nano-H2O QuantumFlux.



>> Qilin Li: I was asked to talk about alternative technologies to reverse osmosis. Reverse osmosis is a process that basically applies hydraulic pressure to overcome the osmotic pressure so that clean water goes from the high salt concentration side to the low salt concentration side. Commercial reverse osmosis modules usually use a spiral wand configuration that allows us to pack a significant amount of membrane area in a membrane module. Again, I'm showing you the same equation here to demonstrate what are some of the factors that affect the water flux through our own membrane. In the early development stages of reverse osmosis technology a lot of effort was put into improving membrane permeability. So that's to reduce this R_m term in this equation.



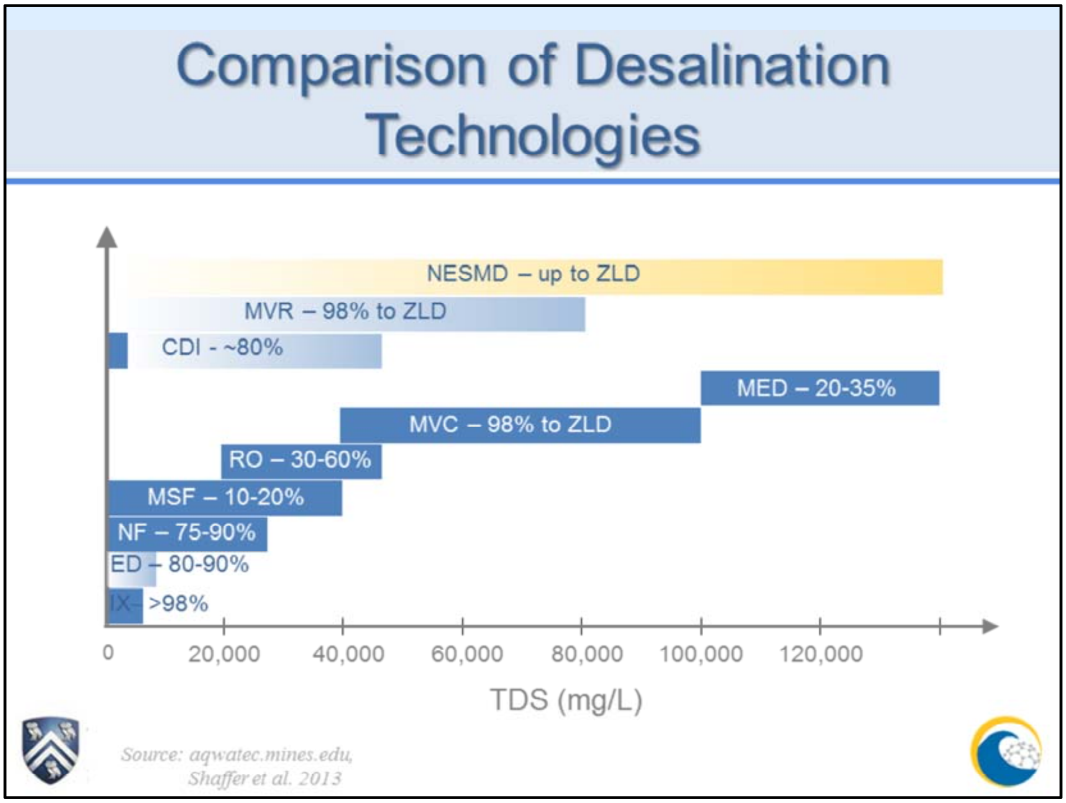
>> Qilin Li: So if we look at the energy consumption of the different desalination technologies today, because of the significant improvement of the RO membrane permeability we have achieved so far, reverse osmosis today is by far the most energy-efficient desalination technology among all available desal technologies out there. And it's getting very close already to the practical theoretical minimal energy consumption, which is 1.6 kilowatt hour per cubic meter of water treated. Still, the limitation is that RO is not able to treat water that has total dissolved solids of more than 50,000 milligram per liter.



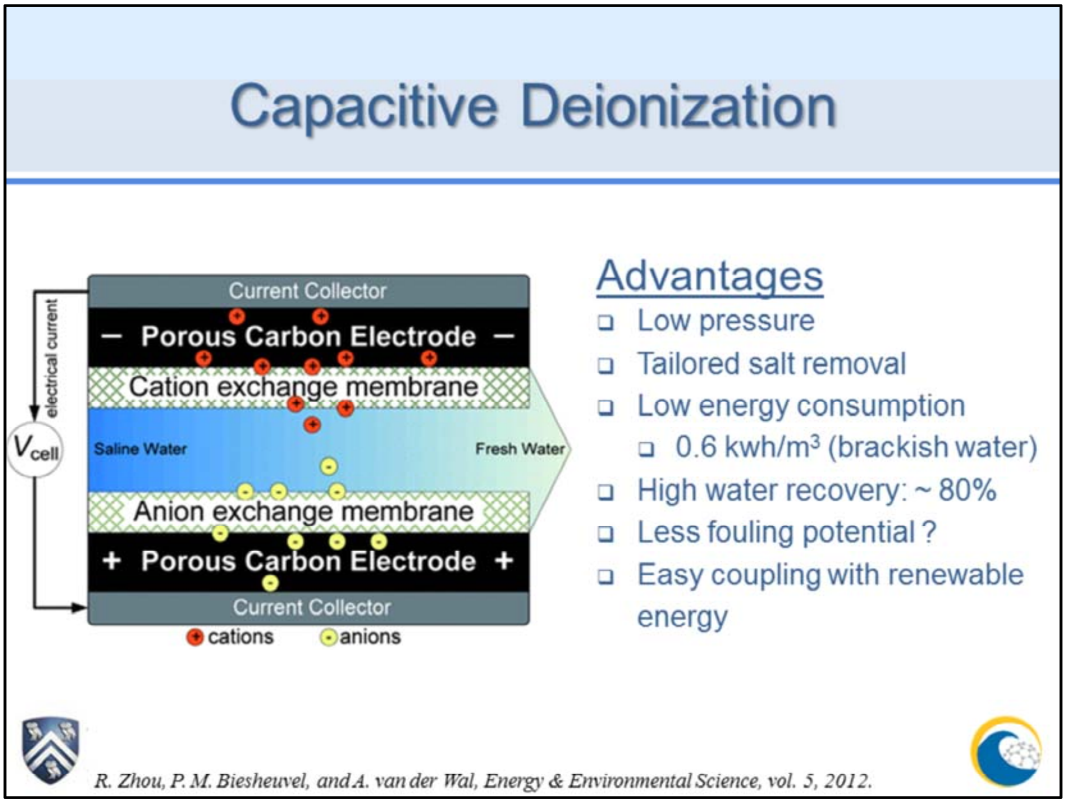
>> Qilin Li: So if you look at what people have done to improve the permeability of reverse osmosis membranes, this slide shows the brief history of RO membrane development. You can see that for several decades, starting from the 1950s up to the 1990s, the focus was on improving the permeability of the membrane. The membrane permeability or the flux increased about 2 orders of magnitude from the invention of the RO to the modern-day reverse osmosis membranes.

Now more recently, the development has been to incorporate nanomaterials into RO membranes' thin layer structure to further improve that membrane permeability or to impart fouling resistance on the membrane surface. Again, as I explained previously, several analyses have shown that further improvement in membrane permeability has limited impact on the overall energy efficiency of reverse osmosis for both sea water desalination as well as brackish ground water. Fouling-resistant membranes are perhaps a more important research need in the future.

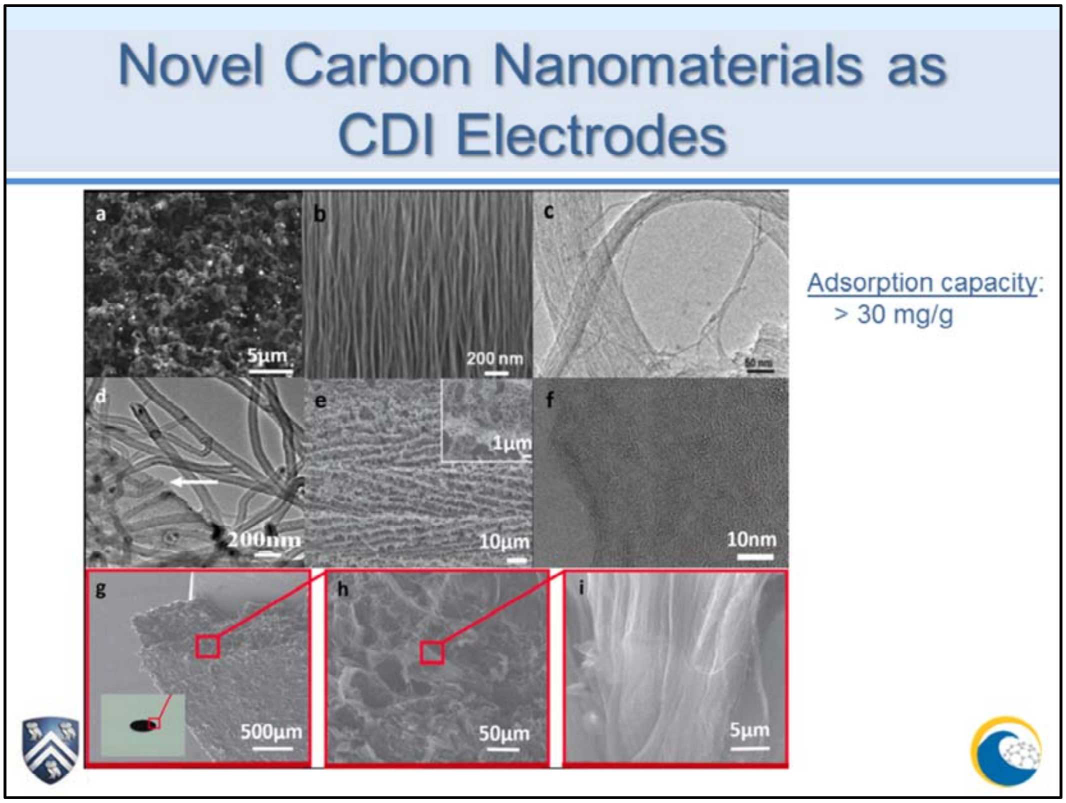
>> Qilin Li: When we think about alternatives to reverse osmosis, we need to think about what do we need, what are we looking for in the desalination technology? Obviously, we want to have adequate salt rejection based on the feed water salinity and the treated water quality we want. As I was explaining before, for some waste water reuse applications, RO sometimes is overkill for salt removal, but does not provide adequate low molecular weight organic contaminant removal. We also want in a desalination technology high water recovery. We're trying to get fresh water from these alternative water sources. And so the higher water recovery we get, the better. And obviously high energy efficiency is always a top priority. Simple maintenance and overall low cost. So these are the factors we consider when we try to develop alternative technologies and that could potentially replace RO.



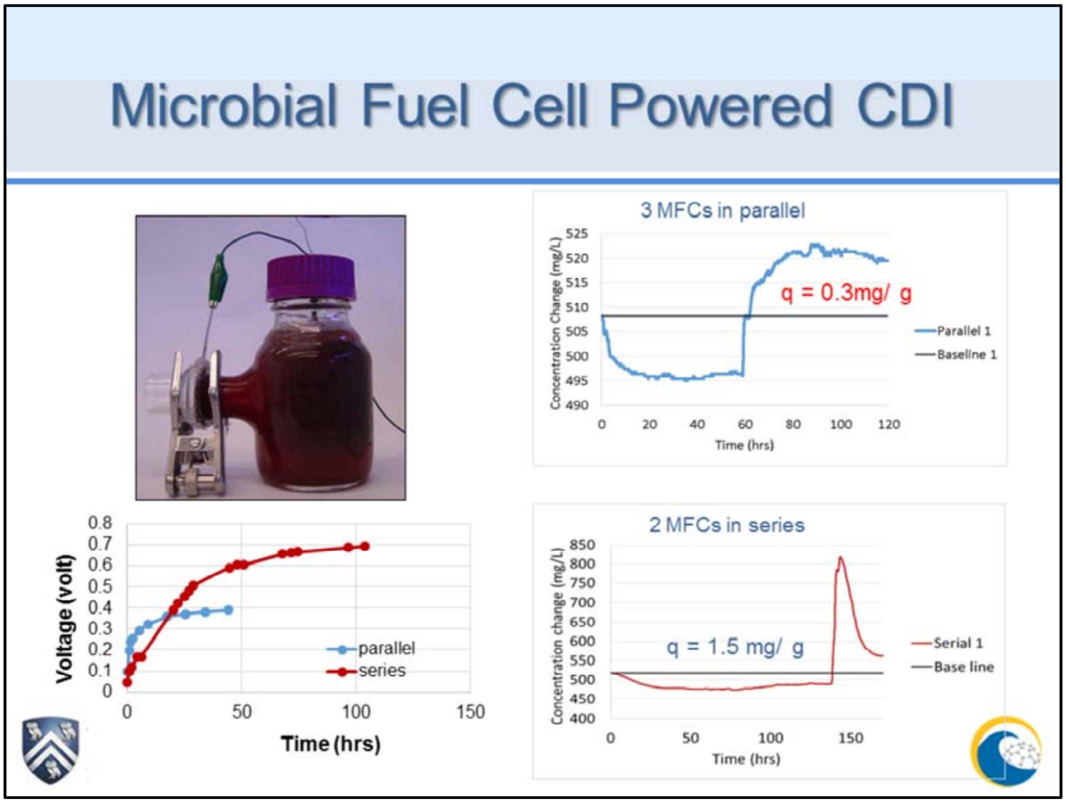
>> Qilin Li: Now if we compare some of the existing and emerging desalination technologies for their applicable salinity level, as well as water recovery, we can see every desalination technology has its own pros and cons. For example, reverse osmosis can be applied to a TDS (total dissolved solids) strength up to 50,000 ppm. At this high salinity level, the recovery of water is fairly low, somewhere between 30% and 60%. But if you look at some of the other desalination technologies that can handle much higher salinity levels, such as multiple-effect distillation, the water recovery is even worse. And there are some technologies, a few of them, that cover a relatively wide range of total dissolved solids and offer good water recovery. In particular, I wanted to talk about two of them today. One is membrane distillation shown in this orange bar on top. NESMD stands for Nanophotonics-Enhanced Solar Membrane Distillation. It's a technology that we've been working on here at Rice University. Another technology is capacitive deionization, which has been shown to be competitive at the low salinity level. But people are working very hard to extend applicability to higher TDS levels, and this technology offers a fairly good water recovery as well.



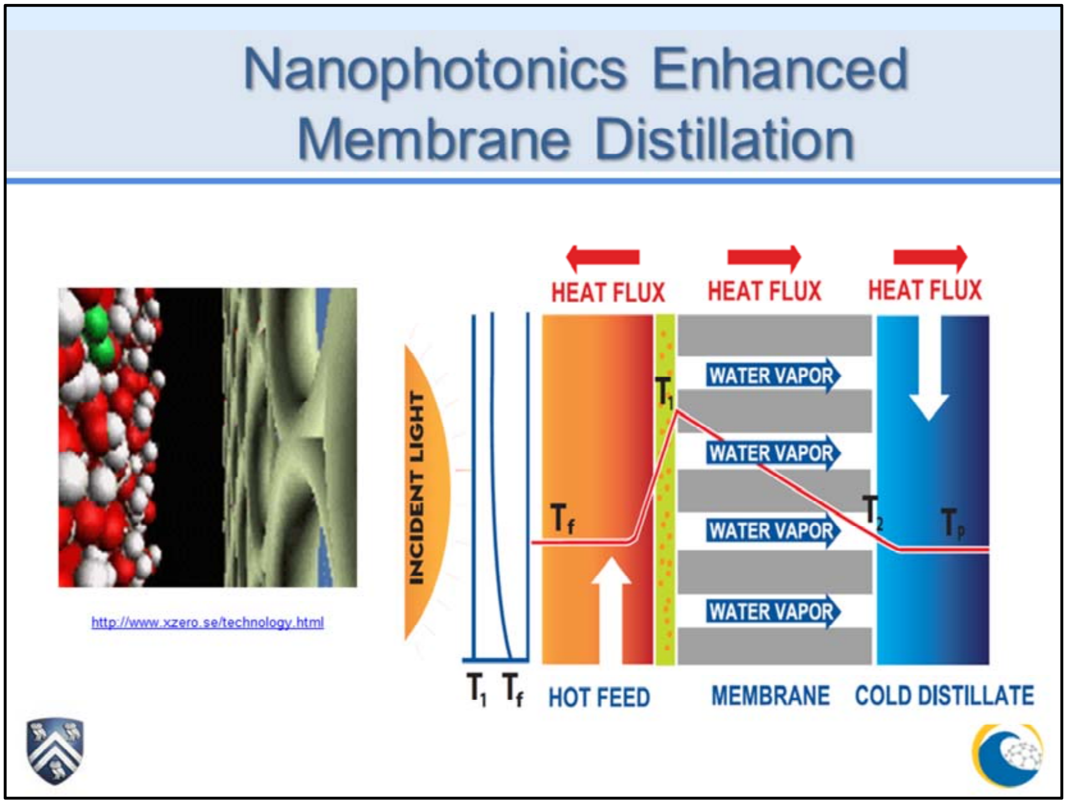
>> Qilin Li: Then to talk about capacitive deionization (CDI) first. Capacitive deionization is an electrosorption process. Basically, you charge two electrodes, and this forms a capacitor. When you pass the salt water through the channel between the two electrodes, the cations are adsorbed on to the negatively charged electrode surface, and the anions are adsorbed on to the positively charged surface. That generates a stream of fresh water. Once adsorption is complete, you can then discharge the electrodes, and the release of these ions forms a stream of brine. This technology has been shown to be highly competitive in terms of energy efficiency at the low salinity level; for brackish water, the energy consumption is around 0.6 kilowatts per cubic meter with a water recovery of 80%. This is an emerging technology, so there are very few studies on the long-term performance of this technology. However, it is expected to be less prone to fouling than reverse osmosis because it's a low pressure process. Another advantage of this process, which is very attractive to me, is that the voltage required to charge the electrodes is very low. It's 1.2 volts. So you can potentially couple this technology with low-grade energy sources and make it much cheaper in terms of energy consumption.



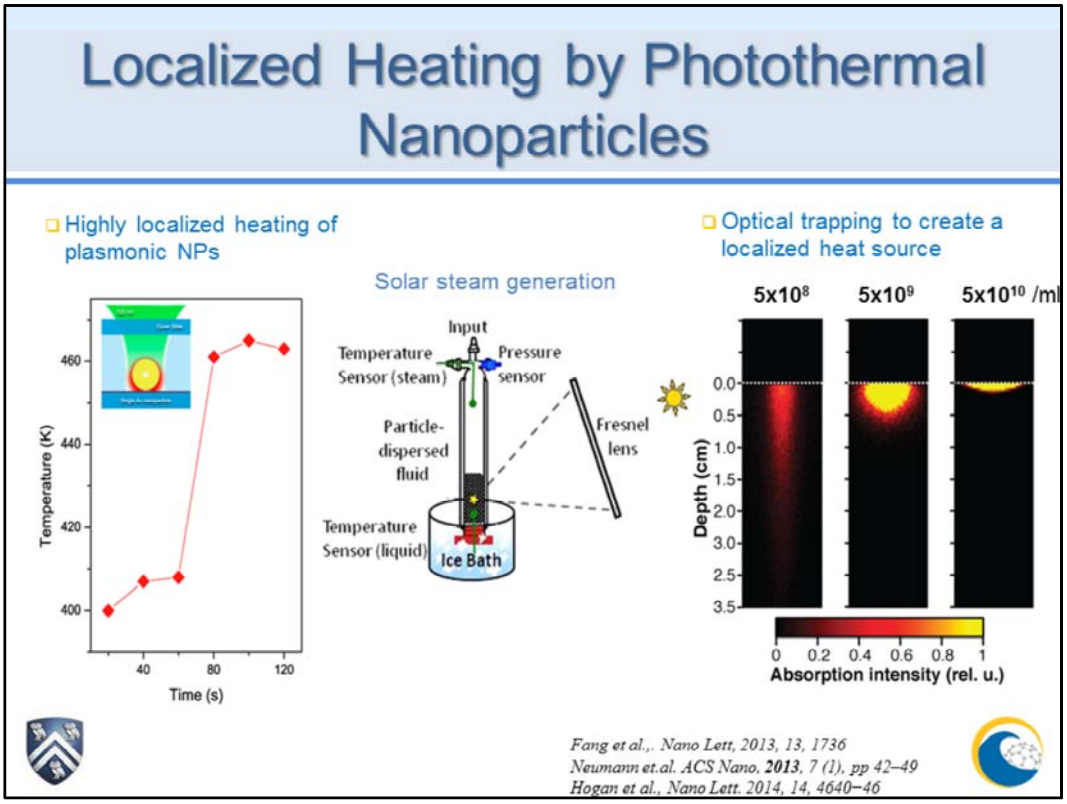
>> Qilin Li: The key to this technology is the electrodes. To achieve high salt adsorption efficiency, we want electrodes that are high in surface area and high in electrical conductivity. The team here at Rice University has been developing multiple carbon nanomaterial-based electrodes. I'm showing you some pictures of carbon nanotubes, graphene materials, and carbon nanotube foams with different morphologies and different pore structures that have been shown to have superior specific surface area and electrical conductivity and also much better salt absorption capacity. Some of the materials we've tested achieved more than 13 milligram per gram of salt absorption capacity. This is several times higher than existing commercial carbon-based electrode materials. More importantly, we could utilize the energy in wastewater to power these electrodes.



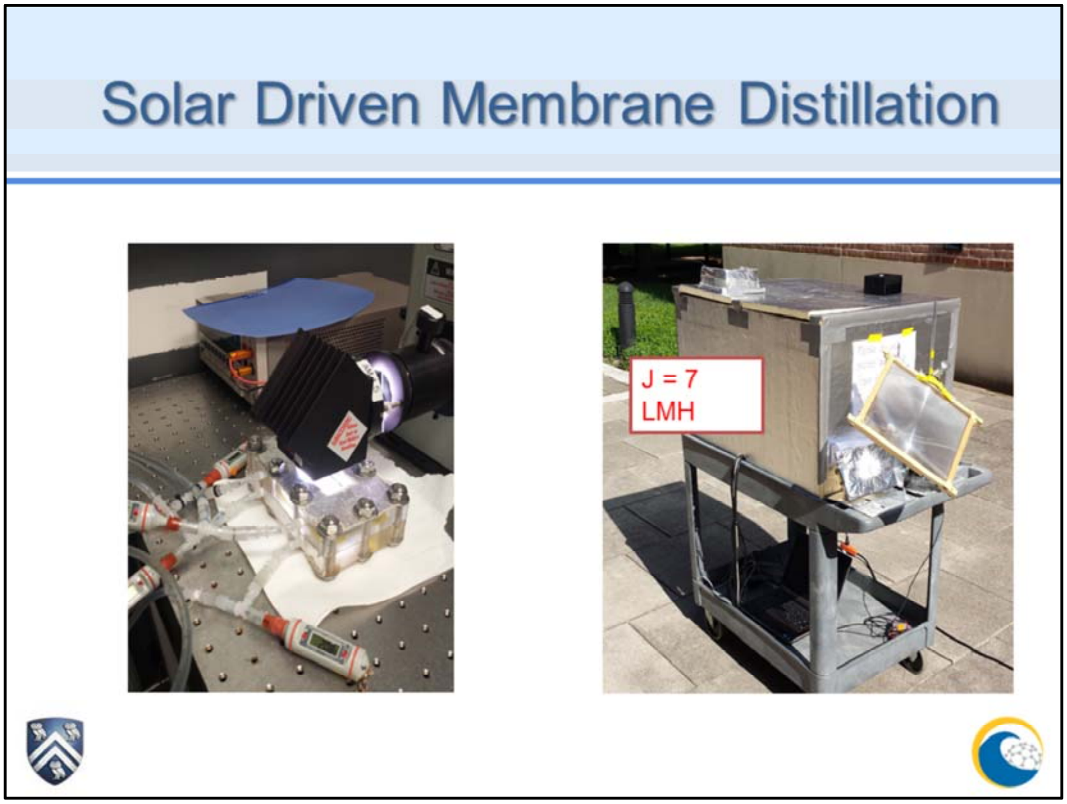
>> Qilin Li: So in one of the studies we did, we used high-salinity oil and gas-produced water as our energy source. This picture here shows you a small, bench-scale microbial fuel cell that is run with this high-salinity, produced water, up to 200 gram per liter of salinity. These microbial fuel cells basically utilize anaerobic bacteria to degrade organic compounds in the waste water and at the same time pass the electrons obtained to an external circuit. We use that external current to power our capacitive deionization electrodes. So here you can see when we couple this microbial fuel cell with our CDI device, we were able to show salt removal using the CDI device, even though the removal level is very low. The best removal capacity we got is 1.5 milligram per gram, but this at least starts at a demonstration of the feasibility of this technology. Here the only energy source we have is the carbon in this high-salinity waste water, and that was converted electricity in this microbial fuel cell.



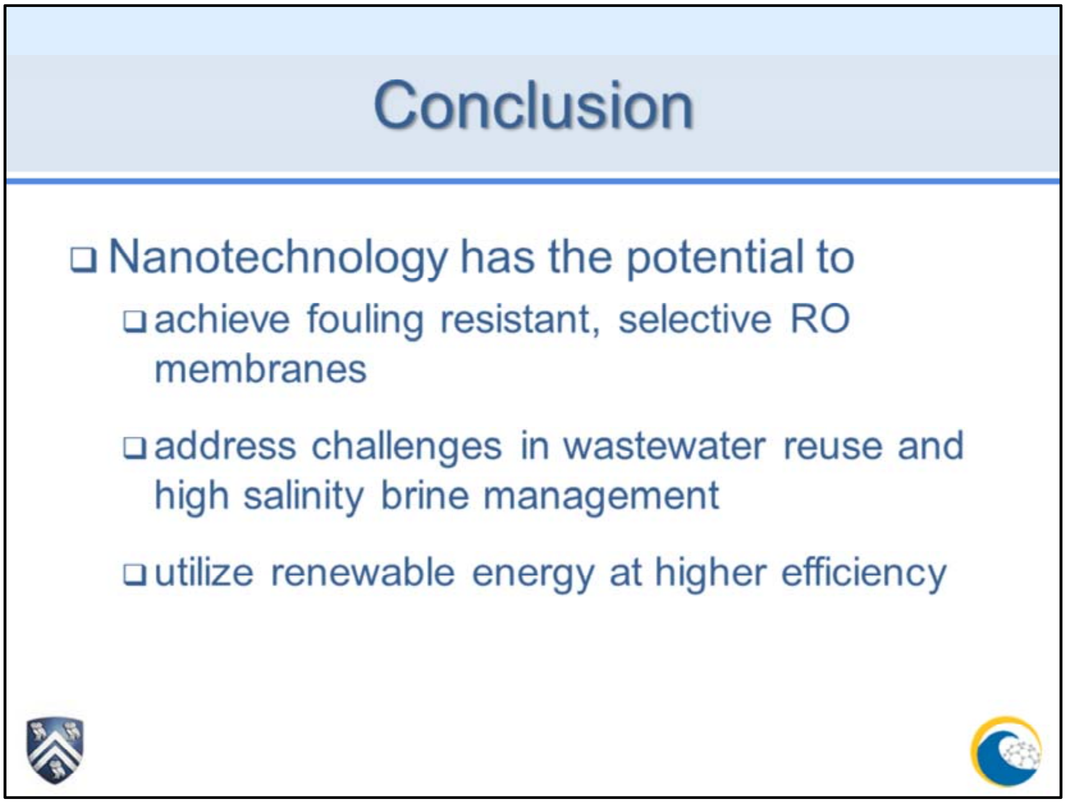
>> Qilin Li: Another example I wanted to give today is nanophotonics-enhanced membrane distillation as another potential desalination and water purification technology, as an alternative to RO. This technology is based on the membrane distillation principle. In membrane distillation, we use a hydrophobic membrane to basically separate the salty water from the clean water, and typically the feed water is heated to create a temperature difference across the membrane. That temperature difference creates a vapor pressure difference that drives vapor transport from the salty water side to the clean water side, the condensation of which generates pure water. In our technology instead of using electricity to heat up the feed water, we use sunlight to directly heat up the membrane right at the membrane surface. So here we apply a photothermal coating on a traditional PVDF (polyvinylidene difluoride) membrane surface. This photothermal coating was able to absorb sunlight highly efficiently and convert the energy in the photons to high-intensity heat right at the membrane surfaces. So in this case even if you have no temperature difference between the feed water and the permeate, the heating at the membrane surface will be able to generate a temperature gradient across the membrane, which drives the water vapor through the membrane.



>> Qilin Li: This photothermal coating was inspired by previous research in Professor Naomi Halas's lab, where they demonstrated a strong, localized heating effect of nanoparticles that have a good balance between light absorption and light scattering. Here we are looking at two different effects. One effect is highly localized heating on the nanoparticle surface. This is demonstrated here using a single gold nanoparticle when irradiated by a laser light at the resonant frequency of the gold nanoparticle. It was able to heat up very quickly to very high temperature and cause vaporization of the water surrounding its particle surface and generate a very high temperature zone around it. Of course for water treatment we don't use gold; it's way too expensive. We use a carbon-based nanoparticle, and we put the carbon-based nanoparticle in a water suspension and demonstrated that, using this suspension under natural sunlight, we were able to generate steam within 10 seconds while the rest of water remained below 10 degrees Celsius. So this effect is due to the highly localized photon absorption. Because of the balance between the multiscattering effect and light absorption, these nanoparticles effectively focus or concentrate all the photons within a very small spatial domain and therefore concentrate all the heat within a very, very small size and generate high temperature very locally and leave the rest of the solution cold. So that saves the energy to heat up the fraction or the volume of water that will not eventually become vapor.



>> Qilin Li: So we use these photothermal nanoparticles, and we created a polymer nanoparticle composite coating that is porous on the conventional MD (membrane distillation) membrane surface. And we've demonstrated photothermal activity in a laboratory set-up, as shown here on the left using a simulator. We also took our system outside and demonstrated that we were able to generate membrane flux of 7 liters per meter squared per hour under the natural sunlight with no applied temperature difference between the feed water and the permeate water. And this flux is similar to what people have measured in pilot-scale traditional membrane distillation systems at a temperature difference of 60 degrees Celsius.

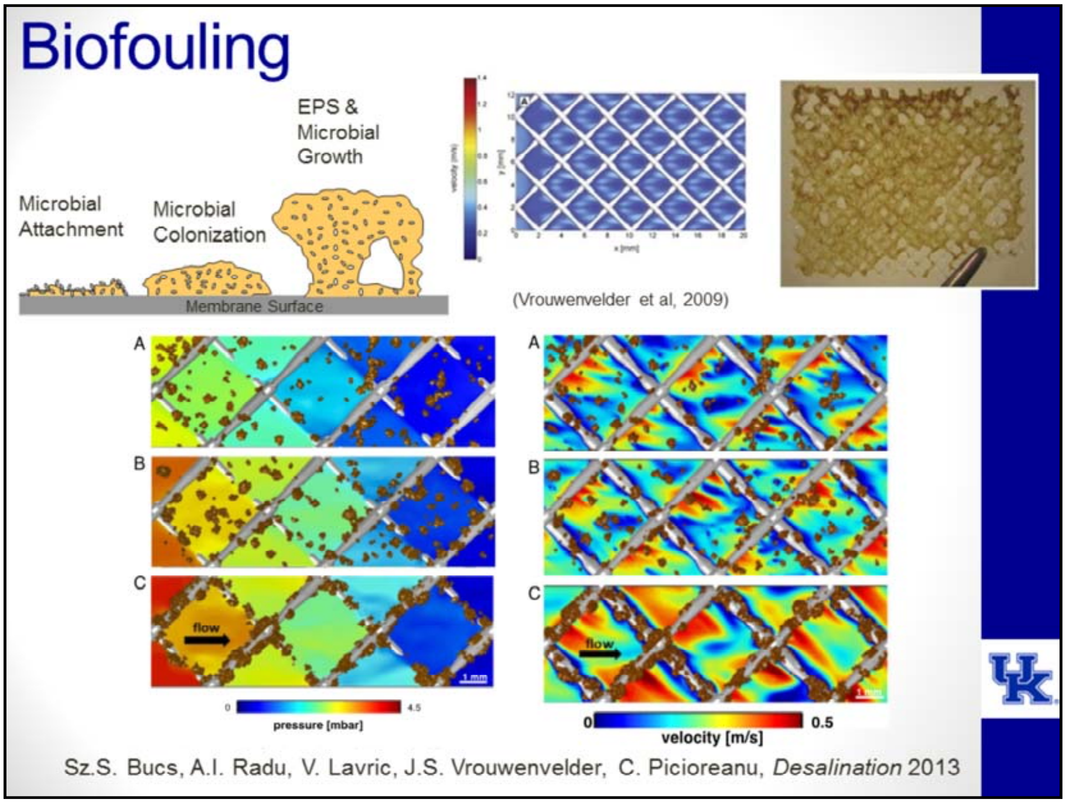


>> Qilin Li: With that, I hope I've shown you that nanotechnology has the potential to improve our way of treating alternative water sources in many different ways. We were able to achieve fouling-resistant, selective RO membranes, which you will see in our next presentation, and we were able to address challenges in waste water reuse in high-salinity brine management in terms of removing emerging contaminants or inactivating pathogens. We were able to utilize renewable energy or low-grade energy sources at higher efficiency than what we have been able to previously.

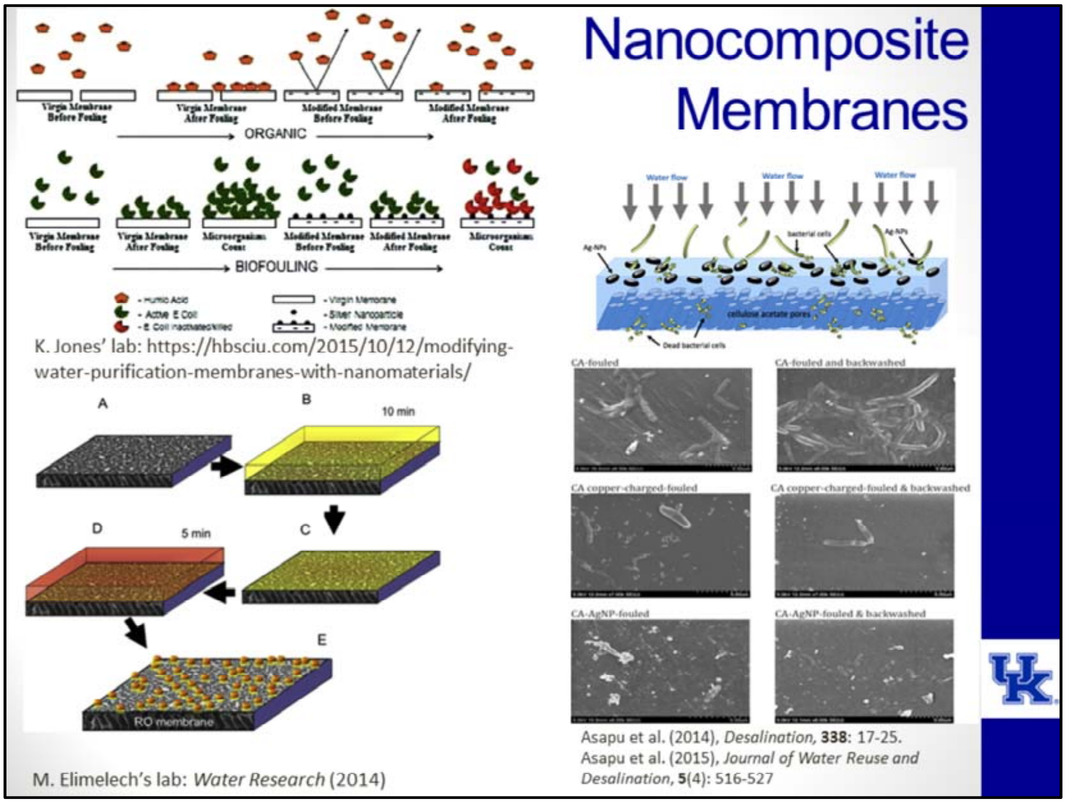
>> Qilin Li: With that I would like to thank you very much for your attention, and I think we'll take questions after other presentations.

>> Stacey Standridge: That's correct. Thank you, Qilin. That was a really great overview. For everybody who is listening on the line, feel free to submit questions as the webinar goes along. Next up is Isabel Escobar, and she's going to talk about membranes.

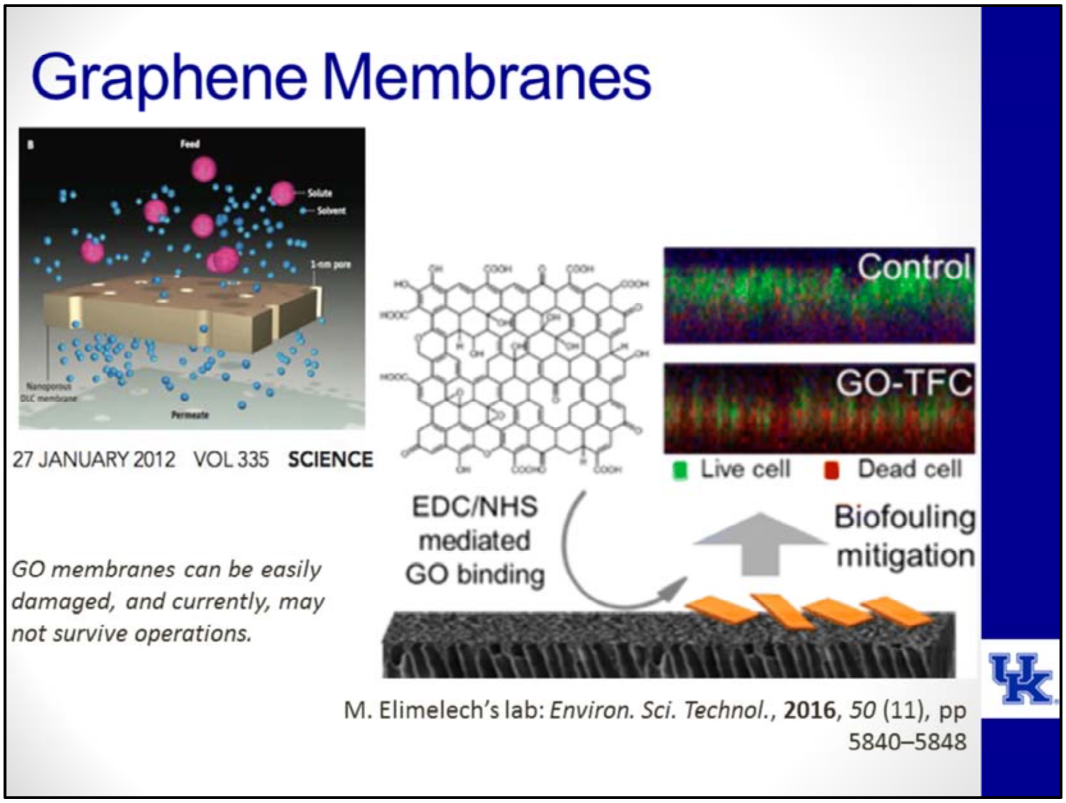
>> Isabel Escobar: I'll talk a little about filtration, membrane separations, and the future, where we're going. We'll talk a lot about nano, making membranes using nanotechnology, but I'll also talk about other advances. A lot of work has been happening lately with membranes. Qilin talked a lot about membrane fouling, and that is quite often one of the top problems with membranes. She focused a lot on reverse osmosis, but I'm going to talk about membranes in general because fouling really is a generalized membrane problem.



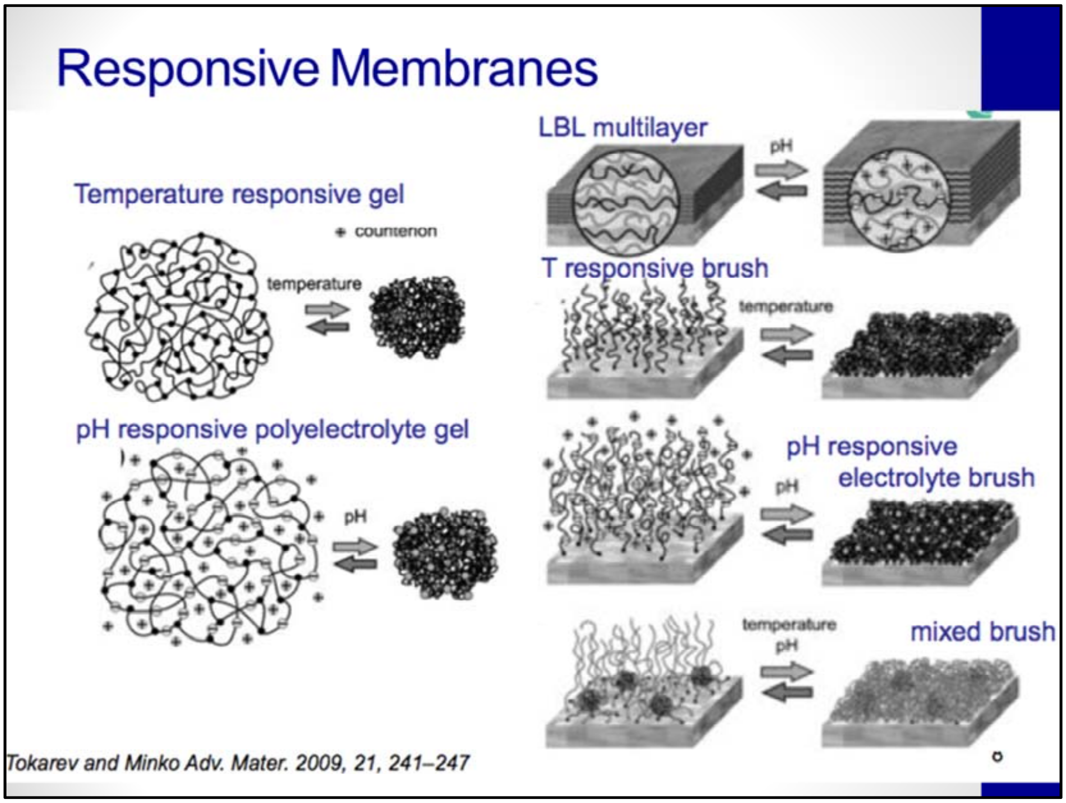
>> Isabel Escobar: Within the realm of fouling, biofouling has been often called by many researchers the cancer of membranes. And if you think about how microorganisms grow and how they form a biofilm, really it boils down to all you need is one. Once one microorganism attaches to the membrane, it starts releasing and forming some extracellular polymeric substances (EPS) that form a biofilm. That biofilm forms a safe bed for other microorganisms to grow on. That microorganism starts replicating and others can attach, and soon a very large biofilm, a very distinct and very complex biofilm forms with the anaerobic bacteria closer to the membrane surface, anoxic bacteria in the middle, and aerobic bacteria close to the water. Now you have release of nutrients among each other and across this biofilm. It becomes very difficult to clean. The preferred cleaning method that is used is a simple back washing or a back flushing. But that cannot really handle this very complex system that is attached to the membrane with these very strong polysaccharide biofilms. And if you look at the pictures that I have added here, they show the flow. The regions that are in the darker colors are the regions of higher flow, and then as the flow starts to decrease, microorganisms start to attach. They start attaching to that feed spacer that is put in the membrane envelopes to provide strength and to provide flow channels and to provide turbulence. And it starts releasing the EPS and forming this complex biofilm that is shown on the top right picture of a membrane biofilm.



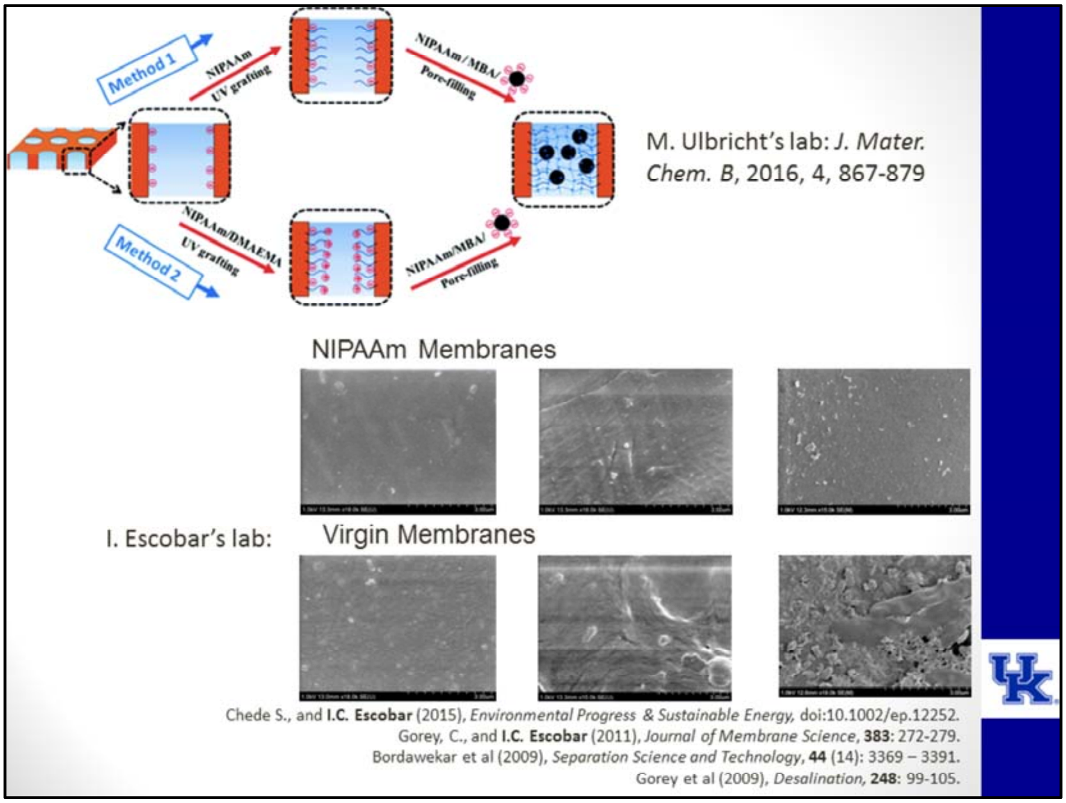
>> Isabel Escobar: So a lot of work has been done with nanocomposite membranes to handle this issue of biofilm. And I'm going to talk a little about what is done at Dr. Kim Jone's lab, Dr. Meny Elimelech's lab, and very briefly at my lab. What is done across the board with these, the one thing that we have in common is that we are adding nanoparticles in different methods following different surface functionalities in order to attempt to decrease the microbial growth. What we all do, we work mostly with metal nanoparticles—silver nanoparticles being some of the most important nanoparticles for the inactivation of bacteria on the surfaces. And if you see for the set of six scanning electron microscopy photos on the bottom right, regular virgin modified membranes even after a short period of time—and these pictures are after 5 and 7 hours, and the ones with 7 hours are also back washed—you see a large growth of bacteria on the surface. As you add the silver nanoparticles to the surface, you see much less growth on the surface. You see that there's a lot more control. But of greater importance, while there's still some bacteria on the surface, the key about these bacteria when nanocomposite membranes are used is that they're now not viable bacteria. They're not actively producing the EPS that is actually causing the most detrimental biofouling and allowing others to form the biofilm. So it's really just dead bacteria accumulating on the surface of the membrane.



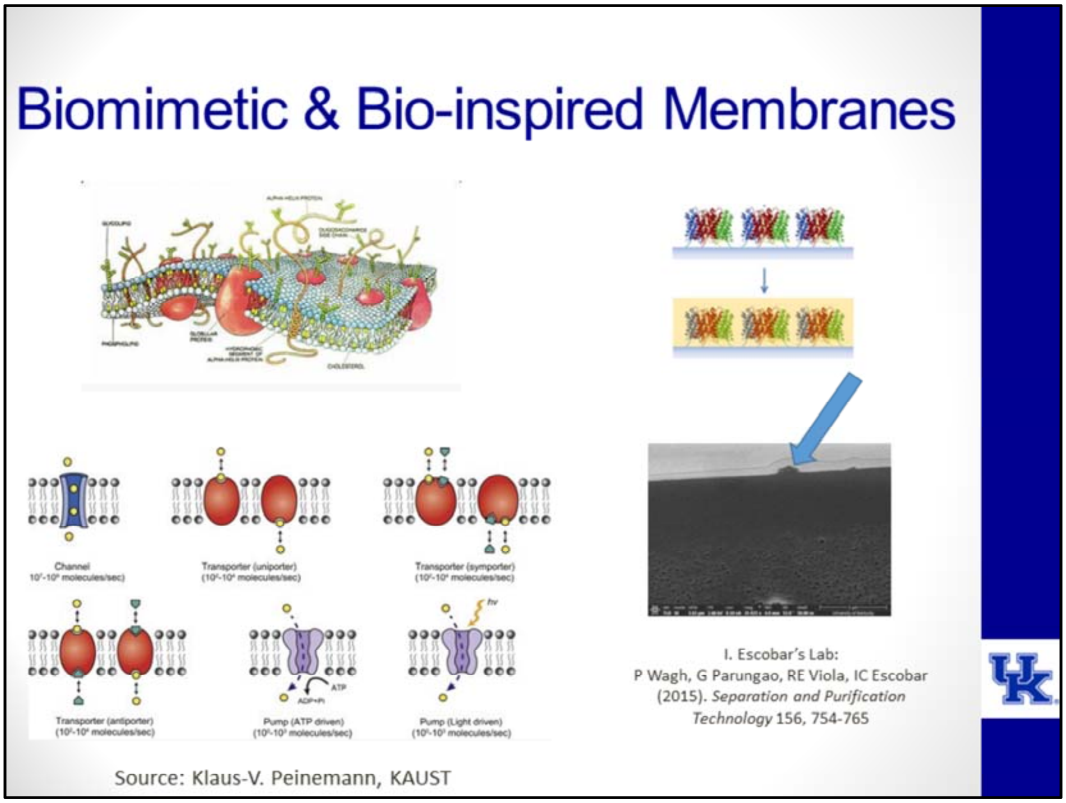
>> Isabel Escobar: I saw on the box at the side there was a question about graphene, and I'm going to touch on graphene membranes a little bit because it's also an upcoming nanocomposite membrane. Graphene has also been heavily used for biofouling control. There are a lot of questions of why biofouling is controlled by graphene. Some of the theories are that it could be potentially piercing the microorganisms, it could be providing some reactive oxidation on the surface, or could prevent attachment. And for the scaling up, which is really a significant question about graphene, there is some nice work that's currently being done at Monash University in Australia where they're looking at scaling up and at very targeted separations. A lot of these are still for gas separation membranes, but the world of water filtration is a potential. One of the key questions with graphene is also what the cost of the membranes would be. But if addressed, this could make very antimicrobial, antifouling membranes that would have very high filtration efficiencies.



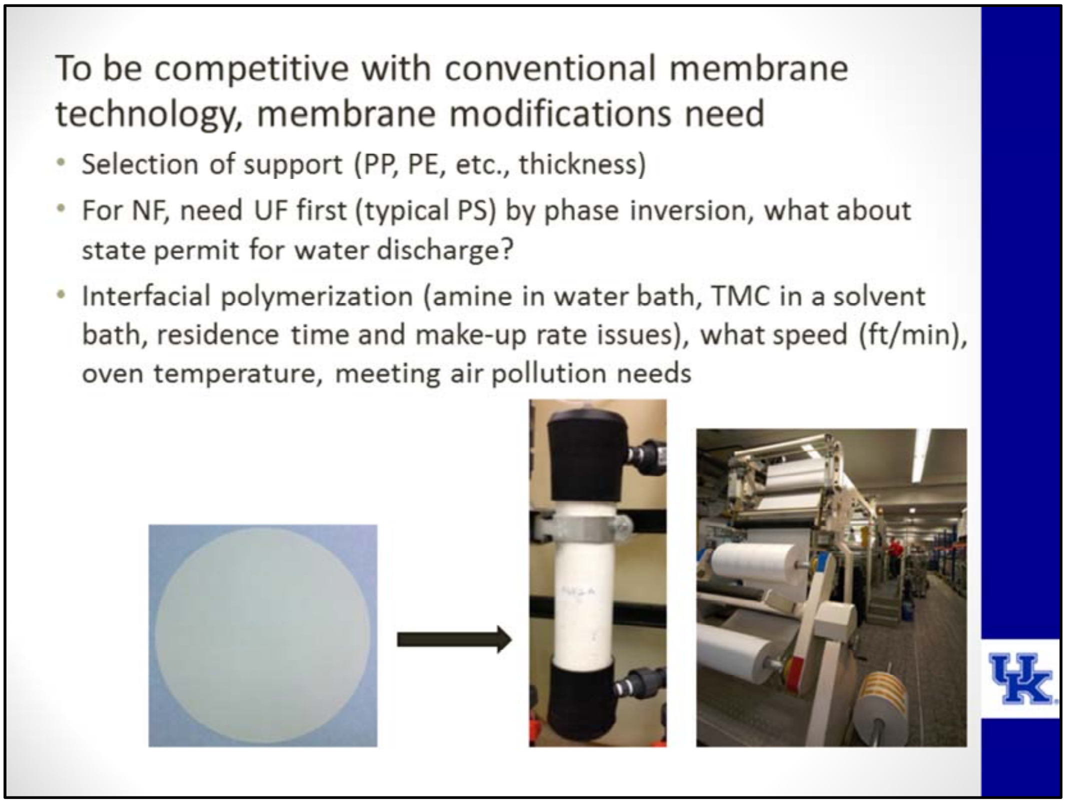
>> Isabel Escobar: Another current one that has been studied for quite a few years is responsive membranes. In the world of responsive membranes, it is making membranes using polymers that will respond, will change their activity, will change their conformation, and will change their properties in response to a stimulus. The stimulus can be anywhere from temperature, pH, light, but the more common ones are temperature and pH. With these membranes, in one case the polymer would be expanded, would be highly hydrophilic, and in another case once the trigger or once the stimulus is activated, it changes to much more hydrophobic and collapses on to itself. So this can be used for a self-cleaning type of material because it would be able to continuously be changed between hydrophobic-hydrophilic expanded-contracted systems or membranes.



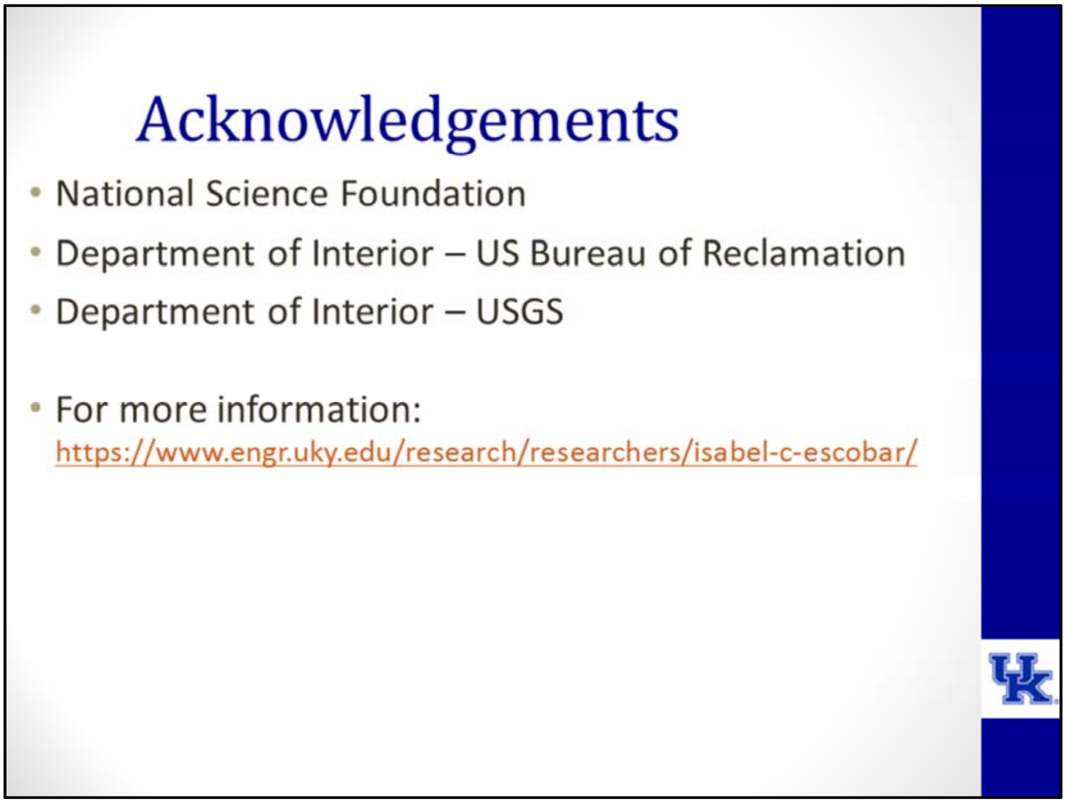
>> Isabel Escobar: Different groups are doing work on this. The group of Mathias Ulbricht has been doing a lot of work on this. They're putting in N-isopropyl acrylamide and crosslinking it into the membrane pores for very specific rejections and for cleaning the pores. When placed in pores, they will be able to trap some materials within the pores, and then by changing the activation, they would be able to release. So they would be able to obtain a very selective separation. Our group has also done work with this with N-isopropyl acrylamide, and we have added it directly to the membrane surface. If you see the set of six photos that I have added, the one on the bottom right shows a virgin membrane, and the one immediately above it shows the modified membrane, both after cleaning. It shows that just using the modified membrane with self-cleaning leads to a significantly cleaner membrane, and we can use superparamagnetic ferrous nanoparticles for the activation itself.



>> Isabel Escobar: One of the most upcoming methods of functionalizing and making membranes bio-inspired and biomimetic membranes. This is just trying to put aquaporins or other channel transport proteins on the surface. My group has done some work with aquaporin channels now as well. Some of the key issues with aquaporins are, again, the scaling up of the membranes and the aligning of the aquaporins directly on the surface of the membrane. But the key of the aquaporins is that they would allow nothing but the H_2O molecules to pass through the membrane to potentially lead to perfect rejections.

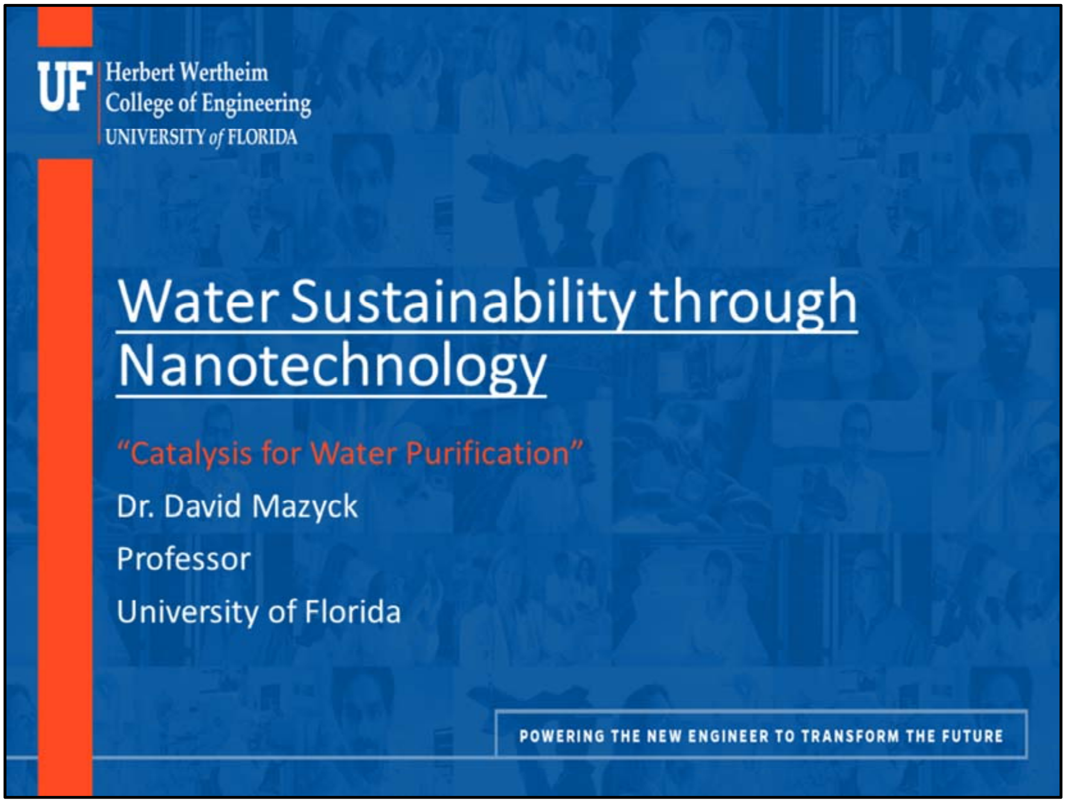


>> Isabel Escobar: However, of all of these—and I only gave a flavor of a very few upcoming forms of modifying membranes—is that to make these competitive, really the scaling up must be taken into account. The small round photo that I have on the bottom left shows about the scale where most of us have worked, that most of what this development type of work has been done in the past, and is currently being done. And what we need is to be able to up-scale these to the picture on the bottom right which shows a scaled-up process, a roll-to-roll type of making the membranes. So how are we going to make these? How are we going to prevent nanoparticles from agglomerating? How are we going to make the responsive membranes? How are we going to make the bio-inspired membranes and the graphene membranes becomes a much more important question.

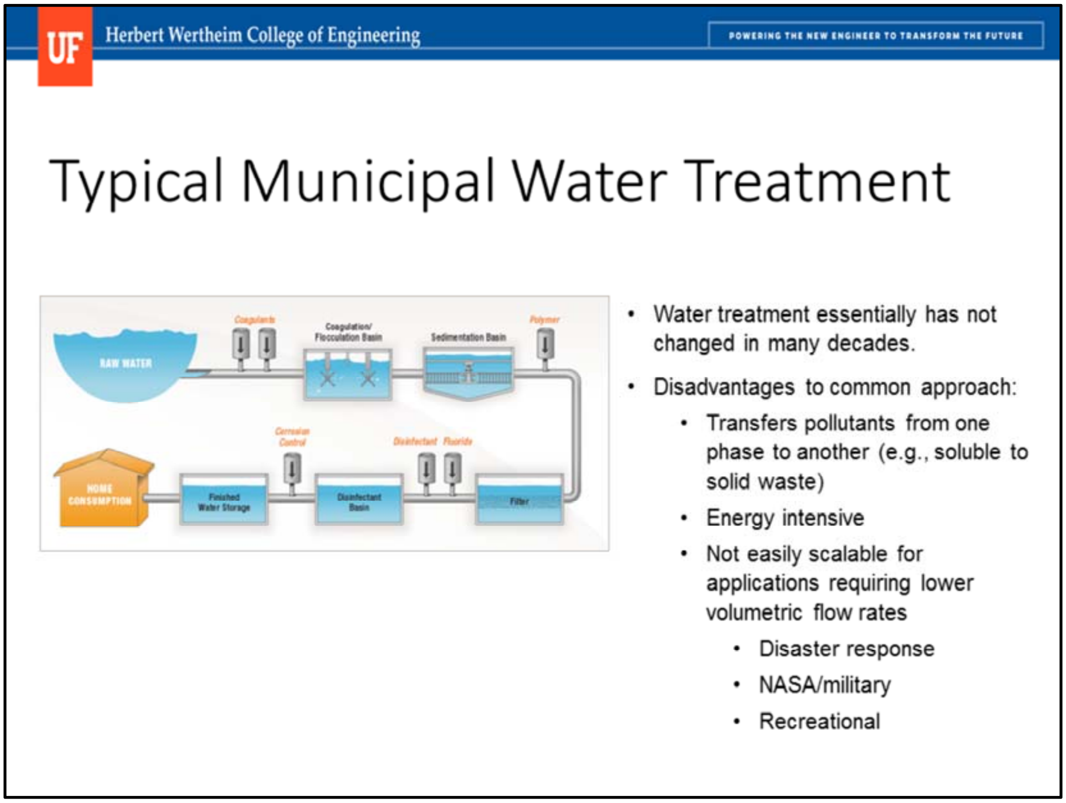


>> Isabel Escobar: So that's the last message that I want to leave you with, and my acknowledgement to my funding agencies.

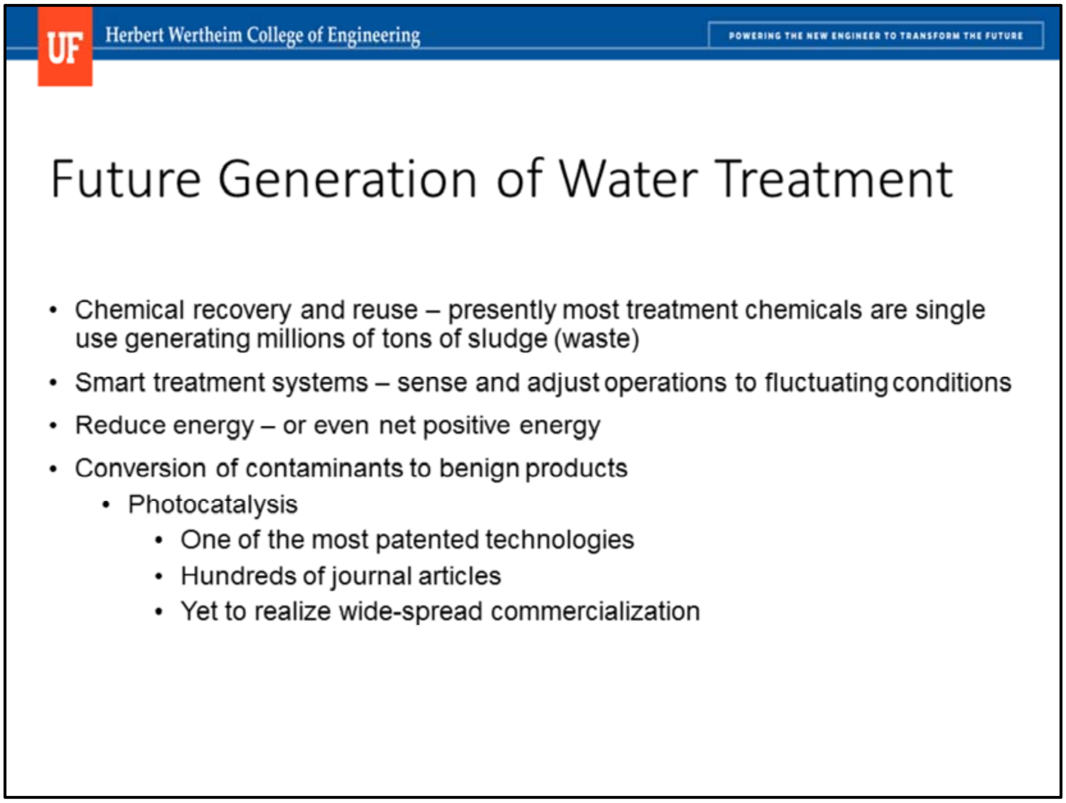
>> Stacey Standridge: Great, thank you. Isabel. I found your last point about the problems of scale-up to be particularly interesting and something we talk about a lot in our office. Thank you for that great overview. And our last speaker for today is David Mazyck from University of Florida. And he'll talk about photocatalysis.



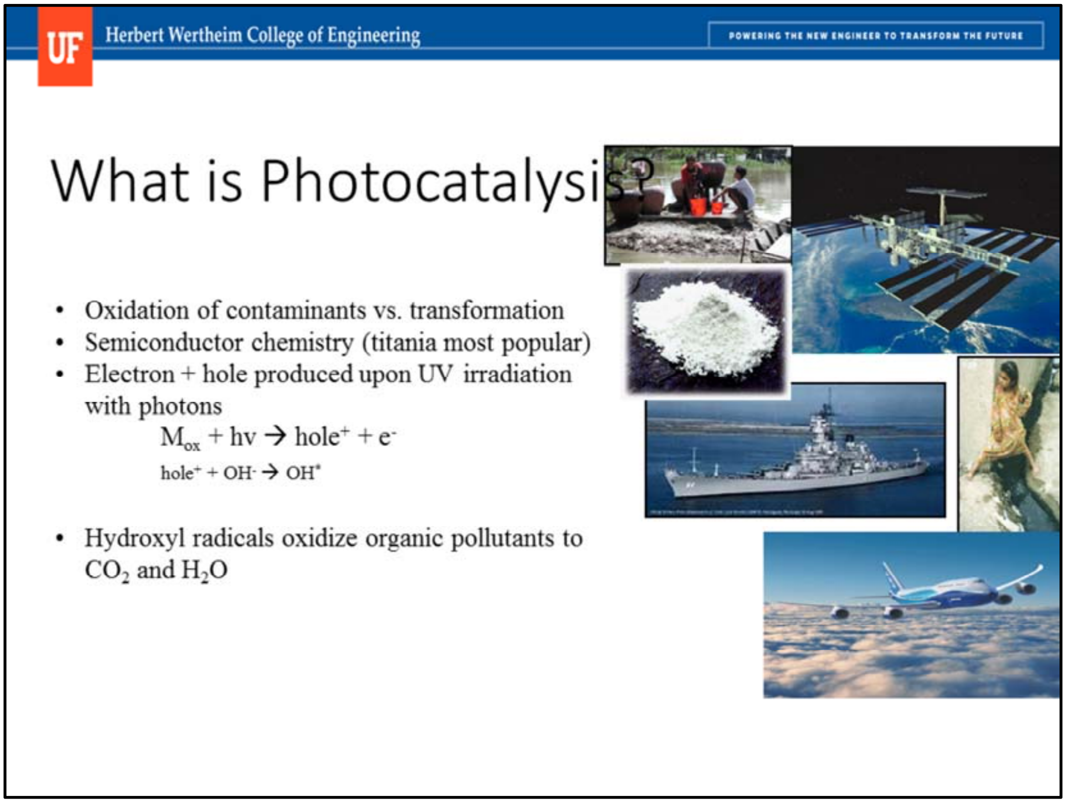
>> David Mazyck: Good afternoon. Thank you very much for the opportunity to share just some general concepts about photocatalysis and some of the work that we've been doing, and others around the world, in trying to advance this technology, particularly for water purification.



>> David Mazyck: Interestingly enough, all the talks today have been really about getting away from traditional municipal water treatment, which I'm sure all of us are very familiar with. But very briefly here in this particular cartoon, we add a lot of chemicals to lakes and river water and other types of surface waters to cause reactions to remove these impurities. In that process we're basically converting our water contamination into, for example, solid waste. Downstream from these clarifiers where this sludge collects, there may also be, for example, sand filtration. Dual media filtration where we have activated carbon is a popular treatment technology. And there again it's excellent for removing trace contaminants and contaminants that we're all very much concerned about in our drinking water, but here again we're converting these water phase issues into solid waste. So therefore can we be thinking beyond that and actually destroying these contaminants versus just transferring them from one phase to another. So for all intents and purposes, water treatment hasn't changed all that much. And as I've pointed out here, the disadvantages are the transformation, a very energy-intensive process. And although water treatment at a large scale for large cities, for example, works very efficiently, does it also work as well, for example, for disaster response, NASA, military applications, as well as recreational applications? And so can we come up with technologies that work better in those particular environments?



>> David Mazyck: Generally my thought about the future generation of water treatment, beyond just photocatalysis, is chemical recovery and reuse. Right now the chemicals that we use, coagulants, are single use. It generates millions of tons of sludge, which is wasted. I think smart treatment systems that adjust other operations to fluctuating conditions would also be areas for improvement. Perhaps that type of thought process in Flint, Michigan would work very well. Certainly reductions in energy, and the one I wanted to spend the most time on today was the conversion of contaminants ideally to benign products. That's certainly the intent of photocatalysis. Interestingly enough, if you look at the patent literature, it's one of the most widely patented technologies, and particularly in the '60s, '70s, '80s, and 1990s there's this widespread patenting of this particular technology, photocatalysis. There are hundreds and probably more like thousands of journal articles. Yet, it has not realized widespread commercialization, and there are reasons why. We'll talk about some of those this afternoon.



>> David Mazyck: So very briefly, if you're not familiar with photocatalysis, the concept here is really about the oxidation of contaminants versus transformation. It is premised on a semiconductor chemistry and titania or titanium dioxide. Degussa's P25 would be the most popular photocatalyst that is used. You'll see a lot of literature that looks at doping the TIO_2 to make it more efficient or various modifications, but basically the premise is that when irradiated with ultraviolet light—254 nanometers is that which is most commonly used—you create this electron-hole pair. The hole can then react with hydroxyl ions that are in solution, creating these very powerful hydroxyl radicals. These hydroxyl radicals then oxidize these organic pollutants, and the whole idea is to, for example, take benzene and be able to oxidize it completely to carbon dioxide and water. Some of the areas that we've applied photocatalysis are in these pictures. We've done about 10 years of research for NASA for International Space Station applications. We flew a photocatalytic system aboard a Boeing aircraft for air purification. We've also done work in the areas of disaster response in the military. So it's very widespread, particularly can work very well for these applications, but we still have many areas that we need to improve.

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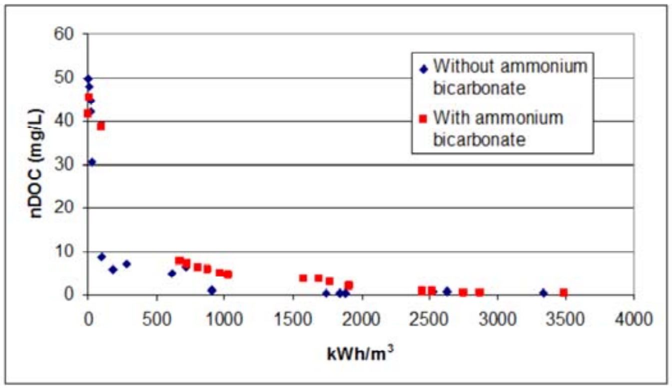
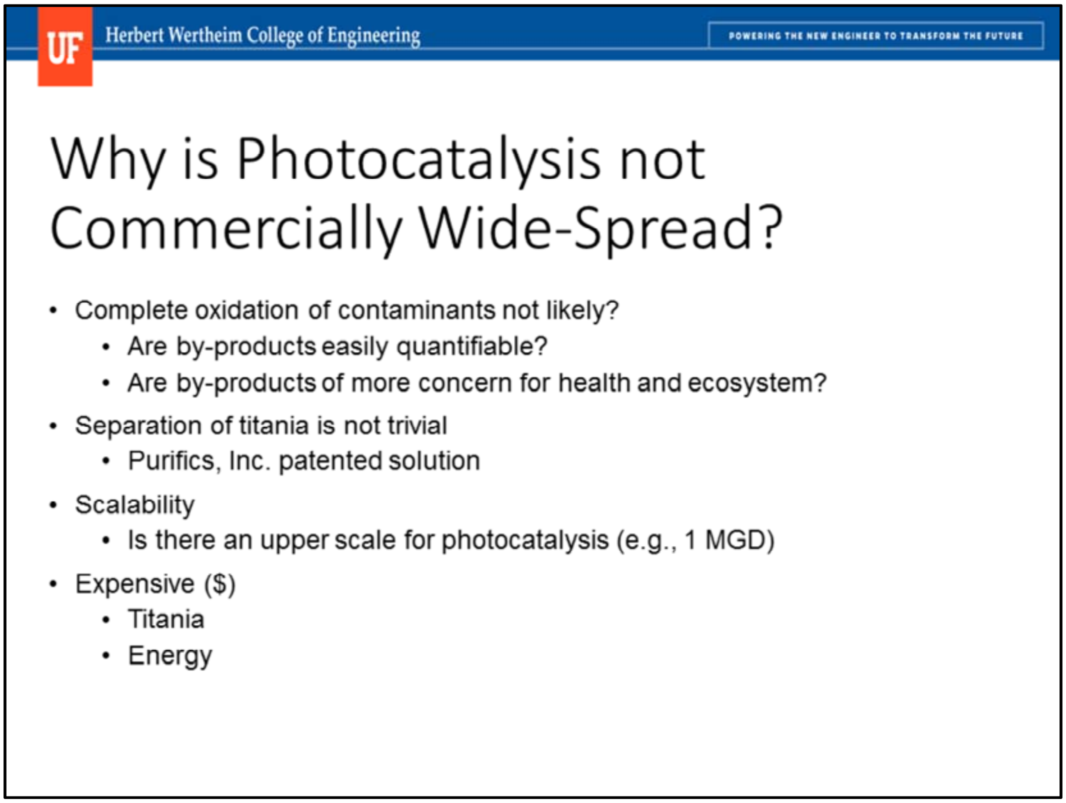
Example of Photocatalysis for Grey Water

Constituent	Amount Per Liter	
Ammonium bicarbonate	2726	mg
Sodium chloride	850	mg
Potassium bicarbonate	378	mg
Hippuric acid	174	mg
Potassium dihydrogen phosphate	173	mg
Potassium bisulfate	111	mg
Citric acid	92	mg
Glucuronic acid	60	mg
Johnson's Baby Shampoo	1.2	g
Ammonium hydroxide (14.8 N)	1	mL
Vegetable oil	667	µL
Water (Tap)	868.4	mL

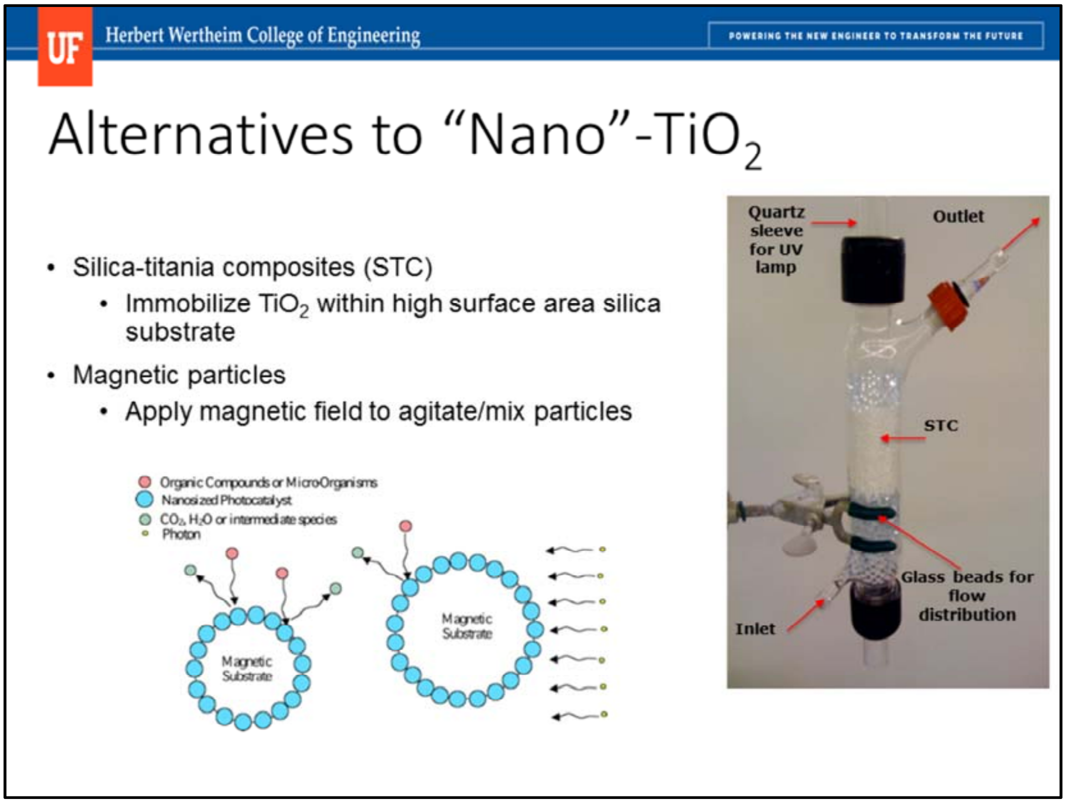


>> David Mazyck: I wanted to give you just one data set, which I feel is very challenging yet an excellent example of what photocatalysis is capable of, and this one here is for gray water. The formula, which is presented on the left-hand side, is that published by NASA and gives you this very concentrated solution of dissolved organic carbon (DOC). So the DOC here is around 50 milligrams per liter. If we think about DOC in many lakes and rivers and other surface waters, it would be—more often than not—an order of magnitude lower, typically for example 1-5 milligrams per liter.

One of the nemeses to photocatalysis is going to be anions. So here for NASA, the idea was to demonstrate how we could essentially mineralize these organics, both in the presence of ammonium bicarbonate and without ammonium bicarbonate. You can see here, as the curves demonstrate, this is fairly effective in both cases. It does demonstrate that over a period of time. Typically in photocatalysis, we'll often look at this in units of watts of energy per cubic meter or volume of water. So it's a very applicable technology. In this particular case, it probably makes sense to have, for example, a carbon filter on the back end to capture any contaminants that were not completely mineralized. But one would argue that if photocatalysis can work for such a challenging environment such as this water, then perhaps we should be looking at it more so for other applications such as drinking water treatment.

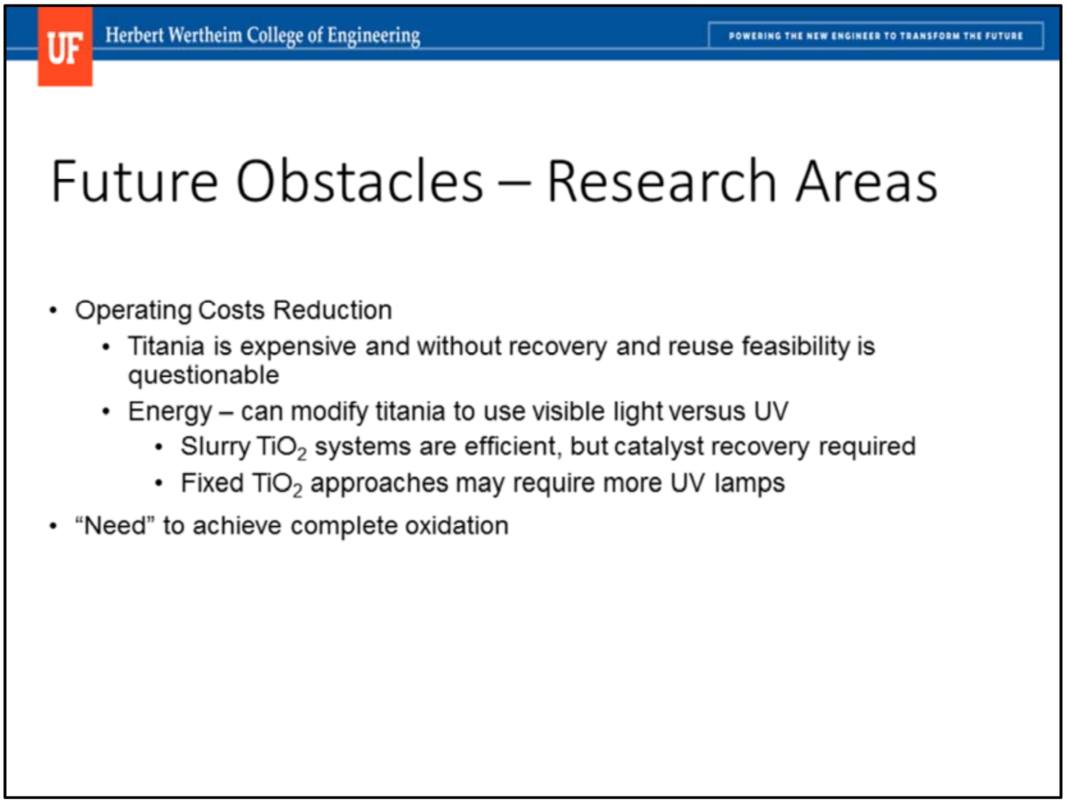


>> David Mazyck: And so why is photocatalysis not commercially widespread? And I think the reasons here are that complete oxidation is not always likely. There are many interferences in photocatalysis when these electron-holes are produced. The first thing that wants to happen is recombination. So often we'll look at metal doping with platinum or palladium to prevent this electron-hole recombination. Are these byproducts easily quantifiable? That's a concern. And are these byproducts of more concern for our health or ecosystem? All of these questions are raised when we think about photocatalysis. TiO_2 essentially is a nanoparticle, so its separation is not necessarily trivial. Qilin talked earlier about a Photo-Cat system, which is produced by Purific. They do have these operating I believe to an upper scale of about 1 million gallons per day, particularly for industrial water treatment. So there are examples where this is working well, but I think other separation technologies certainly need to be applied as well. And we're all very fortunate here in the U.S. that we don't think much about how much our water costs. It's very inexpensive. And so if we look at photocatalysis, the titania, and the energy requirements, are we willing to pay more for this technology that perhaps has a lot of advantages compared to what we're presently doing?



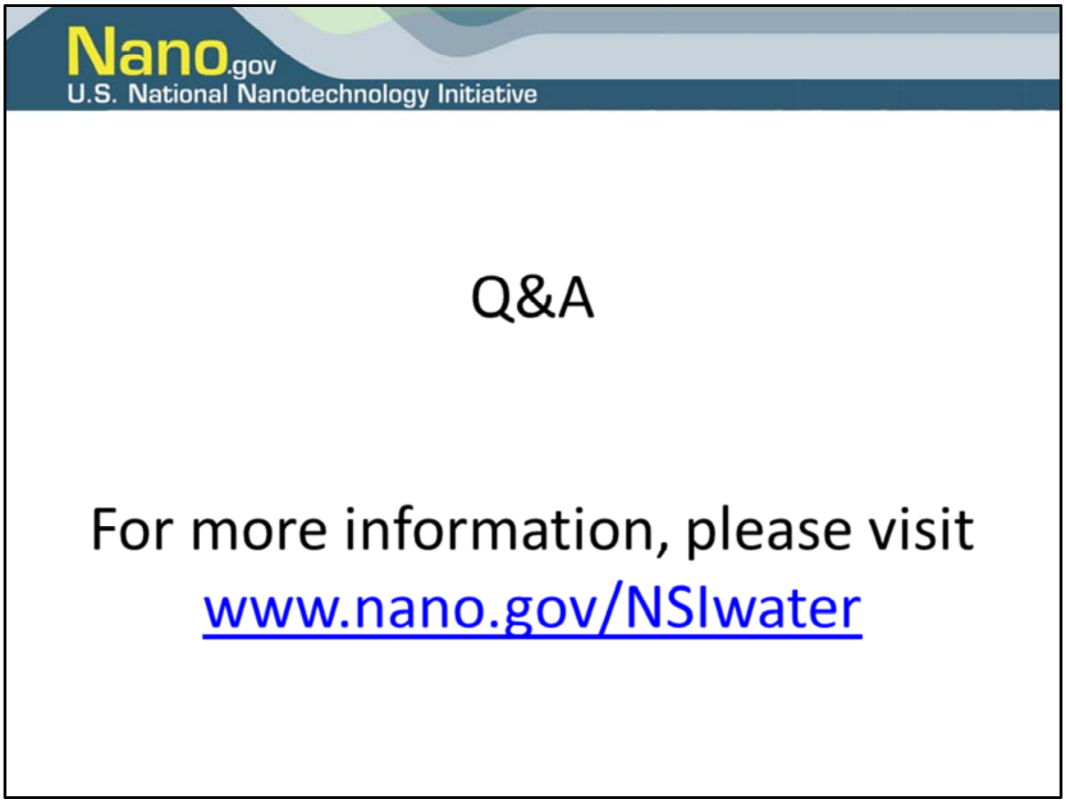
>> David Mazyck: So what has been done around the U.S. to overcome some of these issues? I put nano in quotation marks because TiO_2 is still very much involved here, but it is about immobilizing it to get away from the separation and try to get to some fixed structures. One of the technologies that we developed for NASA was looking at silica-titania composites. The silica is the backbone of the material as a very tunable surface area, anywhere from about 100 to 500 meters squared per gram, and then we impregnate it with the TiO_2 and then irradiate it. The pellet material, which is often the common form shown there on the right, is somewhat transparent to ultraviolet light. Although, the UV does not penetrate too far. Therefore, we're increasing the number of UV lamps. However, perhaps we're decreasing the overall reactor size because we're able to also rely on this very high-surface-area silica substrate.

Another technology that we developed is magnetic nanoparticles. This is again for NASA because we don't have gravity that we can use for separation, so the concept was that we would use a magnetic field to agitate these particles. So we took a magnetic material, we coated it with a silica precursor, and then we doped that with titania. We irradiate it with photons, and then we create a different magnetic field to create mixing. Both of these technologies have proven very well at the bench scale, and the silica titania has done well at the pilot scale as well. Yet, neither of these would be ready, for example, to treat up to about 1 million gallons per day.

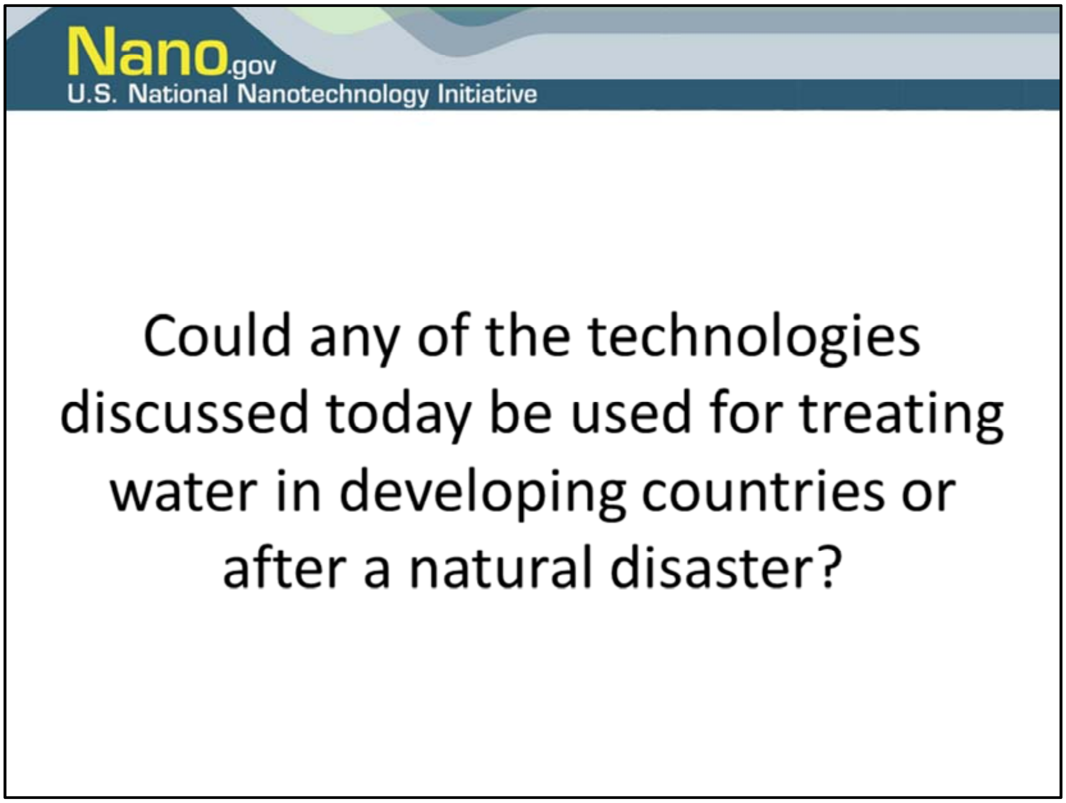


>> David Mazyck: So to wrap up, the photocatalysis work, where are those around the world looking to improve this technology? I think it's looking at ways of reducing costs, and if you cannot recover and reuse the titania, then the feasibility becomes highly questionable. Therefore, that's why I think fixed substrates, coating TiO_2 honeycomb backbones or on carbonaceous materials or impregnating the various matrices, becomes popular. How can we improve the energy requirements? So there would be work being done whereby the TiO_2 is modified either with inorganics or dyes or other methods so that instead of using UV light, we can rely on visible light. And that has a lot of promise. Slurry TiO_2 systems are efficient, but again catalyst recovery is required. The fixed TiO_2 approaches may require more UV lamps, but if in either case we can rely on visible light versus UV, that can overcome the energy and perhaps some of the cost requirements. And then finally we need, at least for potable water applications, to be able to achieve complete oxidation, or certainly be sure that the byproducts are going to be consistent and not be detrimental to our health. And I think that's really the biggest obstacle that we have yet to face. But I think in all the areas that we've talked about today, we're certainly making progress in these areas and we'll continue to do so.

>> Stacey Standridge: Great. Thank you so much, David.



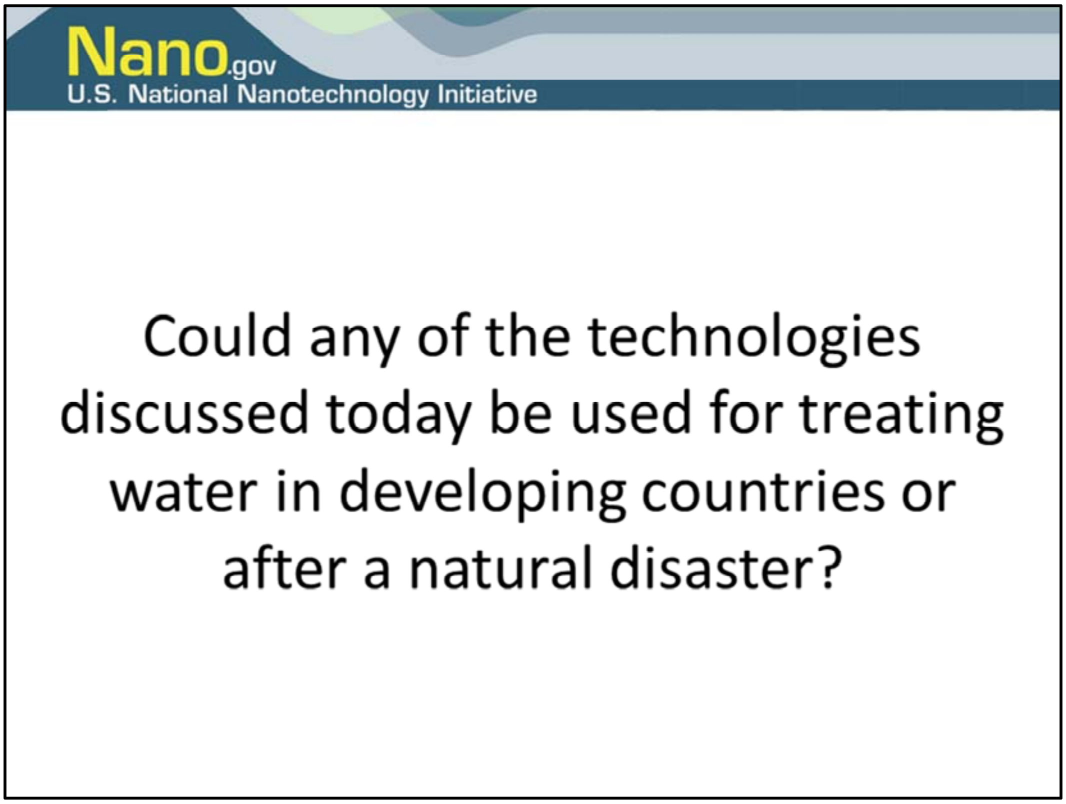
>> Stacey Standridge: We're now at the point of our webinar where we invite our listeners to ask questions. You can submit your question in the Adobe Connect webinar interface in the “Submit Your Questions Here” box.



>> Stacey Standridge: And David, you actually mentioned in passing that photocatalysis can be used for treating water after a disaster. And I thought I would throw that question to both Qilin and Isabel and see if any of the technologies that you talked about could be used for treating water in developing countries or after a natural disaster.

>> Isabel Escobar: This is Isabel. When I lived in Toledo, Ohio—I was at the university of Toledo for 15 years—there was an issue in 2014 that there was a harmful algal bloom that led to the presence of algal toxins in the water. What the Army National Guard brought to treat the water was membranes. They brought reverse osmosis membranes. But I think David hit on a very good thing, an important point: in the United States we have the funds to use these for disaster relief, in other countries maybe not so much. I know that in some more remote parts of Australia they use solar-powered membranes, but more at the microfiltration level, for the removal of microorganisms especially, to handle water treatment.

>> Stacey Standridge: Thank you.



>> Stacey Standridge: Qilin, do you have anything to add to that?

>> Qilin Li: Yes. I think those are two different applications for disaster relief. One is the recovery of the water quality in the water body. In that case something like a titanium dioxide—if it can be made floating on the water surface, and with sunlight activating the photocatalyst—would be a very attractive option. I know that in some developing countries such as China they are using approaches similar to this to clean up their inner city surface water bodies. For drinking water supply, I think small mobile water purification systems that, depending on what the feed water contaminants are, it could be an ultrafiltration system, it could be a reverse osmosis system. Those would be very good options when the resources are there. For low-resource locations, that's really the biggest challenge today. That's why we're trying to develop the example I gave in my presentation, the nanophotonics-enhanced solar membrane distillation technology. We're hoping that will be a low-cost system that can treat any source water with sunlight. The limitation there is, however, whenever you use sunlight and without electricity, the production rate of water would be fairly limited. So that would be able to provide water to a small population. If you're talking about a larger population, you'll have to rely on something like RO.

>> Stacey Standridge: Great, thank you. We've now reached the end of our hour. And I would first like to thank all of our panelists for taking their time to participate and their great presentations. I would like to thank the audience for listening today and for posing such great questions. We'll post the transcript and the presentation slide for this webinar at www.nano.gov/publicwebinars in the coming weeks, along with information on the upcoming webinar, *Enabling Next-Generation Water Monitoring Systems,* that is scheduled for January 18th. With that, again, my thanks to our panelists, and that concludes our webinar for today.