NATIOMEM Report Summary

Project ID: 245513
Funded under: FP7-NMP
Country: Denmark

Final Report Summary - NATIOMEM (Nano-structured TiON Photo-Catalytic Membranes for Water Treatment)

Executive Summary:

The main objective of the NATIOMEM project was to develop a novel photocatalytically active membrane for drinking and waste water treatment. The membrane consists of a porous substrate with a photocatalytic coating on the surface. The coating is made of nitrogen-doped titanium dioxide (TiON), which can induce photocatalysis by irradiation in the visible range of the solar spectrum. The coated membrane should be integrated into a point-of-use treatment system for rural application in areas where electricity is not available, and for decentralized treatment of waste water for non-potable recycling.

The NATIOMEM consortium applied several coating techniques such as sol-gel, sputter deposition, atmospheric pressure plasma jet and filtered vacuum arc deposition. Several of these techniques have produced TiON coatings with good photocatalytic activity under solar irradiation. The coatings were characterized with various techniques for optimisation of the coating processes.

The TiON coatings were transferred to microfiltration membrane substrates, including ceramic and metal membranes. The photocatalytic activity of the coated membranes was quantified in the laboratory, using a custom-made flow cell equipped with a solar simulator. The best results were achieved with a sol-gel coating on an aluminium oxide (Al2O3) membrane. Compared to undoped titanium dioxide (TiO2), the TiON-coated membranes had significantly higher photocatalytic activity when illuminated with the full solar spectrum, lower dependence on wavelength in the UV region, and some activity in the visible range of the spectrum. Also, a high inactivation of model viruses could be achieved.

Based on the results from laboratory testing, three pilot plants with photocatalytic membranes were designed and set up in South Africa and Jordan. The degradation of a model compound in pilot scale was about an order of magnitude lower than in the laboratory. Also disinfection was less efficient, and produced conclusive results only when the water was passed over the coated membrane several times. The low efficiency was explained by interference from constituents in pre-treated, natural feed water, and by the hydraulic conditions. The low pressure, low flux, low fouling strategy was not successful. To function optimally, the photocatalytic membrane needs to be preceded by efficient pre-filtration - a bio-sand filter being a simple and low-cost option. Recirculation of the water for operation and cleaning can be achieved by a small pump, powered by electricity from the grid, or from a solar panel. Although, this would make the unit and its operation more complex as well as increase the cost, the desired simple, low-cost treatment technology is not out of reach.

The findings from the lab and pilot tests were translated into updated recommendations for the design and the technical application of the coated membranes. The TiON-coated membrane has good potential for commercialisation. The involved coating and engineering partners have initiated a product development phase.
Good progress was made within NATIOMEM on TiON doping and material science. In addition to the sol-gel coatings applied to the membranes, some novel coatings were developed, including TiON formation by oxidation of titanium nitride (TiN), and TiO2/TiN bi-layer thin films. These have potential for other applications, such as hydrogen production and low cost solar cells. Details on these coatings were made available to the research community by publication in high-ranking scientific journals.

Project Context and Objectives:

Project context:

According to the World Health Organization, there is a substantial global shortfall in availability of potable water - primarily arising from population growth, over-exploitation and industrial contamination and pollution. Implications for the population’s poverty and health, the planet’s sustainability, disease propagation and conflict are significant. Although progress has been made in the application of conventional treatment processes, there is a continuous need for the development of treatment technologies that produce high quality water and do not cause detrimental effects to human beings or the environment. Novel treatment methods based on nanotechnology have promising potential to provide drinking water from water sources such as contaminated surface water and wastewater, by removing harmful substances in a cost-effective and sustainable manner. This was the main idea leading towards the NATIOMEM project.

NATIOMEM addressed the key topic in the FP7-NMP-2009-SMALL-3 call text: “Development of functionalised membranes with catalytic activities for mineralisation or retention of micro-pollutants”. State-of-the-art photocatalytic coatings are mainly based on titanium dioxide (TiO2) in anatase crystalline form, irradiated by UV light. NATIOMEM developed nitrogen-doped TiO2 coatings (TiON) with photocatalytic activity also from visible light, thus significantly progressing beyond the state-of-the-art. The project contributed to the expected impact mandated in the call text, through the deliverables mentioned in the project description: photocatalytic membrane prototypes demonstrated with a pilot plant, fabrication methods and performance data for documenting the new technology.

NATIOMEM supported the declared policies of the EU regarding water, such as the EU Water Initiative (EUWI), where the overall goal is to halve by 2015 the proportion of people who are unable to reach or afford safe drinking water and the proportion of people who do not have access to adequate sanitation. Also EU’s Water Framework Directive, which focuses on water pollution control and water protection, was supported by addressing the reuse of waste water. EU’s chemical legislation (REACH) aiming at reducing chemical use, is supported in NATIOMEM with the aim of developing a chemical-free water treatment system. The project was furthermore in line with the strategic research agenda of Water Supply and Sanitation Technology Platform (WSSTP), where priority subjects include efficiency through modular approaches, energy-efficiency and use of solar energy.

The NATIOMEM consortium was composed of internationally leading research and technology institutes combined with industrial partners that have a proven track record of scientific and technological innovation. Two partners were from the Middle East, and another from Africa. The consortium included Jordanian and Israeli partners in a joint effort to develop the technology, to solve the overwhelming water scarcity problem in the region.

Overall project objectives:

The main objective of the NATIOMEM project was to develop a novel photocatalytically active membrane for drinking and waste water treatment. The membrane consists of a porous substrate with a photocatalytic coating on the surface. The coating is made of nitrogen-doped titanium dioxide (TiON), which can induce photocatalysis by irradiation in the visible range of the solar spectrum.
The coated membrane should be integrated into a point-of-use treatment system for rural application in areas where electricity is not available, and for decentralized treatment of waste water for non-potable recycling.

Prototypes of the novel photocatalytic treatment should be constructed, tested and demonstrated. The combined filtration and oxidation process should trap and inactivate microorganisms, as well as mineralize chemical micropollutants. It was envisaged to develop the point-of-use treatment system into a technically and economically viable treatment option for:

- Production of safe drinking water from contaminated ground water and surface water after simple pre-treatment, in rural areas with limited infrastructure (e.g. no electric power grid).
- Disinfection of microbial unsafe piped drinking water.
- Treatment of grey wastewater after pre-treatment, for non-potable reuse.

In South Africa, the targeted application was local production of safe drinking water for people living in rural communities. The available raw water sources are rain, ground and surface water. Due to the lack of electric power and infrastructure, the photocatalytic membrane unit should be inexpensive and easy to use, and only require minimum maintenance. The treatment solution would provide the water supplier Umgeni Water with a treatment system suitable for remote villages within their region. When fully optimised and commercialised, the low-tech treatment unit should bring safe drinking water to villages also in other disadvantaged regions.

In Jordan, the government has issued an official strategy to reuse grey wastewater for non-potable purposes. The NATIOMEM consortium decided to develop a photocatalytic unit to treat domestic grey water. The design aims at a roof-top solution for urban areas. NATIOMEM’s Jordanian end user partner Kawar Energy should promote the technology from their base in Amman. Decentralised reuse of treated grey water for toilet flushing and irrigation would reduce fresh water consumption and alleviate the drastic water scarcity in the region.

Specific scientific and technological objectives:

The specific objectives of the NATIOMEM project were:

1. Developing efficient processes for depositing good quality nanostructured photocatalytic TiON films and electro-spinning TiON fibres.
2. Determining the optimum membrane/coating combination in terms of cost effectiveness and lifetime.
3. Understanding the photocatalytic processes induced by the coated membranes in contaminated water.
4. Determining and understanding the relationship between the photocatalyst preparation technique, deposition or electro-spinning parameters, composition, nanostructure, and performance of the TiON coated-based photocatalytic membranes.
5. Developing an optimal process for regenerating the photocatalytic membranes.
6. Developing a pilot water treatment plant based upon the optimised photocatalytic membranes

As can be seen, a mix of scientific (3,4) and technological (1,2,5,6,7) objectives are defined. There were main 4 project results (main deliverables):

a) A prototype of a small-scale pilot water treatment plant. (Objective 6)
b) A novel and efficient nanostructured photocatalytic membrane material. (Objectives 1,2,3,4,5,6)
c) Documentation (reports) of photocatalyst preparation techniques, characterisation results and the process-structure-property relationships of TiON nanostructured coatings. (Objectives 1,2,3)
d) Documented performance data of efficacy towards different water contaminants as well as HSE (health, safety, and environment) effects. (Objectives 4,5,6,7)
The project should develop and test nanostructured photocatalytic membranes for water treatment, incorporate them into a pilot plant, and thus prove the concept of using these membranes for water treatment, and encourage follow-up projects (beyond the scope of NATIOMEM) to further develop these membranes and systems incorporating them, and deploying them on a wide scale. The relation to the topics in the NMP call is depicted below. Functional membranes, catalytic activities, and mineralisation and retention of micropollutants were directly addressed by the project objectives. Chemical-free sanitation is the overall objective, as the nanostructured photocatalytic membranes should work without adding chemicals. New membrane production methods were addressed in the work with electro-spun membranes as well as coating membranes with a photocatalyst, both producing membranes with added photocatalytic function. Membrane in bioreactor was one of several possible foreseen applications, although focus in this project was on simpler membrane systems. Costs and User-friendliness were key elements in the work.

Figure: From NMP call topics to NATIOMEM objectives and NATIOMEM deliverables

Project Results:

Preparation of photocatalytic membranes

Within NATIOMEM, photocatalytic coatings were prepared at the University of L’Aquila (UNIAQ, Italy), University Pierre & Marie Curie (UPMC, Paris, France), and the Electrical Discharge and Plasma Laboratory at Tel Aviv University (TAU, Israel).

A broad range of coating techniques was used to deposit photocatalytic TiON coatings, and the morphological, crystalline, optical, structural, composition, and photoactive properties were investigated. Each of the techniques was able to produce coatings that absorb sunlight better than undoped anatase TiO2.

A radio-frequency (RF) magnetron sputtering system was used at UPMC to deposit films of TiO2, TiN, and TiON using three different strategies: simultaneous introduction of nitrogen and oxygen as reactive gases at the same time during depositions (dual gas sputtering), thermal oxidation of TiN films, and elaboration of novel TiO2/TiN bi-layer film stacks. Each of the three fabrication methods has shown the ability to improve optical absorption and photocatalysis under visible light. Nitrogen was incorporated in two main sites in the structure of TiO2 (interstitial and substitutional sites), depending on the deposition method and parameters (pressure, RF power, nitrogen concentration).

A filtered vacuum arc deposition (FVAD) method was used to deposit TiON films by TAU. By changing the composition of the gas in the plasma (oxygen and nitrogen), it was possible to obtain thin films having different stoichiometries from TiN to TiO2.

At UNIAQ, thin films of nitrogen-doped TiO2 were deposited by sol-gel dip-coating, spiral-bar and drop-coating methods. The precursors containing titanium (Ti) and nitrogen (N) were introduced in the solution. Then the deposited films were annealed in air for drying and for allowing the formation of crystallised thin film. The sol-gel N-doped TiO2 films deposited by drop-coating on aluminium oxide (Al2O3) membranes have shown the best photocatalytic activity under visible light and were chosen for the realization of the pilot-plants.

Recently, at UPMC, an atmospheric pressure plasma jet (APPJ) system has been modified and used for the deposition of highly porous thin films of titanium at high deposition rate. The titanium precursor (TTIP) was introduced in the form of spray rather than vapour in nitrogen and air plasma.

The thin films were optimized for performance, with a deeper understanding gained on the fundamental properties of the materials. Post-deposition annealing was found to be essential for obtaining best photocatalytic activity.
Sputter Deposition:

Three different ways to dope nitrogen into TiO2 by means of RF reactive sputtering were compared, and the structural, optical, and photo-active performance of these materials were explored. First, multi-layered thin films of TiO2 and TiN were prepared by sputtering a titanium target and alternating oxygen and nitrogen reactive gases in the deposition chamber. The total thickness of each multi stack was kept constant while the overall composition of the films (TiN to TiO2 ratio) was varied between 5% and 30% and the number of TiN/TiO2 bi-layers was increased from 9 to 45. Secondly, TiON coatings were achieved by introducing oxygen and nitrogen reactive gases simultaneously during the depositions (dual gas). The ratio of oxygen to nitrogen and the total pressure were systematically changed, to control the concentration of nitrogen sites incorporated into the films. The total concentration of nitrogen was between 0% and 6% in the doped TiO2. Finally, different morphologies of TiN thin films were prepared, and then oxidized at various temperatures and time intervals.

X-ray photoelectron spectroscopy (XPS) showed that nitrogen was doped into all of the TiO2 films in substitutional and/or interstitial sites, depending on the deposition conditions and the post-deposition annealing. The variance in the concentration and position of the nitrogen doping had a significant effect on the optical, structural and photoactive properties of the three types of TiON films. The parameters of sputtering deposition were optimized using both plasma diagnostics and Design of Experiments. Each doping methods has shown the ability to improve optical absorption and photocatalysis under visible light. Nitrogen was incorporated into TiO2 using the three distinctly different methods, all of which enhance visible light absorption, photocatalysis, and photocurrent generation. The comparison of these methods indicated substantial differences in structural and electronic properties, and has revealed several of the key aspects that are essential for visible light photocatalysis.

Figure 1 On the left, a photo of the RF sputtering deposition system, and on the right, the schematics for the mechanism of deposition, as well as the plasma diagnostics set-up.

To the best of our knowledge, thin film stacks of TiO2/TiN bi-layers were fabricated for the first time and characterized to determine their crystalline, optical, and photoactive properties. The crystalline properties were found to be dependent on the annealing temperature and the thickness of each TiO2 layer. In particular, the phase transition temperature from anatase to rutile can be easily controlled by changing the thickness and number of the TiO2 and TiN layers, which can be suitable for many low and high temperature applications. The optical properties also show a great variance in the absorption and band gap of the materials. Specifically, all the bi-layer samples show a shift to visible light absorption as compared to pure TiO2, with the largest shift seen in the 9 and 18 bi-layer samples. The photoelectrochemical results gave very interesting results, showing that the number of layers and thickness of the layers play an important role in the charge generation and transport properties of each film, as well as the emergence of visible light photoactivity, which is not seen in TiO2 alone. The results are very promising for many optoelectronic applications, and also leave ample room in the future for further improvement.

Figure 2 Photograph of the as-deposited films on glass showing the range of colours produced for the different samples with (a) pure TiO2, (b) 9 bi-layers, (c) 18 bi-layers, (d) 27 bi-layers, (e) 36 bi-layers and (f) 45 bi-layers.

TiN/TiO2 bilayers showed promising photoelectrochemical and photocatalytic properties. The best photocatalytic activity (PCA) was obtained for the 9 bilayers on glass slides. The deposition conditions of the bilayers were optimized for thin films deposited on glass substrates, as shown in Figure 3.

Figure 3 Optimisation of TiO2/TiN bilayers deposited by RF sputtering, according to PCA

For dual gas sputtering, there was delicate balance between the concentration and the nature of nitrogen doping in TiO2 that can lead either to improved or deteriorated photoactivity. We have shown that there were optimal deposition conditions to maximize the photocatalytic efficiency of N-doped TiO2 and other conditions to optimize the photo-electrochemical activities. It was found also that the porosity, surface area, crystalline properties, crystal size and the nitrogen doping sites played an
important role in the improvement of the photoactivity.

Similarly, various N-doped TiO2 nanostructures were fabricated by oxidizing TiN thin films having different morphologies. The performance of these films depended on the initial TiN porosity (deposition pressure), the oxidation temperature and the oxidation time.

In general, nitrogen in interstitial doping sites was more efficient for photocatalytic applications than substitutional ones. This was attributed to the enhanced charge separation in the case of interstitial doping sites. However, the synergic effect of substitutional and interstitial nitrogen sites in dense films were more efficient for photoelectrochemical applications, due to good light absorption, good charge transfer in the substitutional doping, and good charge separation in the interstitial nitrogen doping.

Filtered vacuum arc deposition

Reactive Filtered Vacuum Arc Deposition (FVAD) in an oxygen, nitrogen or mixed oxygen-nitrogen environment was used to produce TiO2, TiN and TiON thin films. During TiON deposition, nitrogen and oxygen gases were introduced at the same time under various conditions including; different nitrogen/oxygen ratios and substrate temperatures up to 500°C. The films were annealed after deposition to improve their photocatalytic activity.

Nitrogen was successfully incorporated into TiO2 under different deposition conditions, which enhanced visible light absorption and photocatalysis. All the films were well adhered and reproducible. Several TiO2 and TiON films were also deposited on membranes and delivered for further photocatalytic testing. However, the FVAD films worked best on smooth surfaces. Further tests were carried out to improve photocatalytic activity in visible light, such as combined FVAD and radio-frequency (RF) techniques.

Dielectric Barrier Discharge

Attempts were made to deposit thin films of TiO2 and N-doped TiO2 by Dielectric Barrier Discharge (DBD). The fundamental processes involved with this technique were the plasma generation, and the injection of titanium-containing precursor, in our case TTIP. Using TTIP is very difficult as it is incredibly hygroscopic, and thus it reacts with the humidity in the air very easily. To alleviate this problem, a custom-built precursor injection system was designed and fabricated. After several months of constructing and testing the apparatus, the problem however persisted, and we were not able to create TiO2 films or powders with this system. However, we have discovered an alternative use for this DBD system. We found that if TiO2 powders were placed into the DBD plasma discharge region in nitrogen, they changed from white to yellow, indicating the introduction of nitrogen.

Atmospheric pressure plasma jet

Using the APPJ technique, air and nitrogen were used as plasma gases and were directly introduced through the torch at a constant flow rate of 40 slm (standard litre per minute). The TTIP precursor was introduced in the torch by means of an air stream of a flow rate of 5 slm. The torch can be moved in the x- and y- directions, to deposit films over large surfaces, with a typical velocity of 10 to 70 m/min. The number of passes and the substrate to nozzle distance were kept constant at 1 and 10 mm, respectively. The TTIP precursor was directly sprayed in the plasma near the output of the torch using dry air as a holding
A pre-treatment with air plasma at jet velocity of 10 m/min and a frequency of 25 kHz was also carried out to activate the substrate. The substrate holder was maintained at 300°C and no bias was applied. The controlled deposition parameters were the plasma gas (air, nitrogen...), the frequency, the speed of the jet and the power.

Figure 6 (a) Picture of the APPJ system, with components labelled accordingly. (b) Zoom in of the plasma jet with precursor injection (vapour) and (c) the new injection system (spray).

The coatings deposited by the APPJ technique were more porous than the sputtered coatings (Figure 7). Although the thickness of these films was relatively high (about 500 to 3000 nm), the pores of the Al2O3 membranes were not clogged, which was confirmed by the measurements of permeability. Titania thin films deposited by APPJ have both nano and micro porosities with an average pore size of 30 nm and 1000 nm, respectively. In comparison, the maximum pore size was 30 nm in the case of TiON thin films deposited by sputtering.

Figure 7 SEM-FEG images of the surface of TiON thin films deposited by (a) sputtering at low pressure and (b) APPJ at atmospheric pressure.

Sol-Gel deposition

UNIAQ deposited N-doped TiO2 thin films using the sol-gel process and three different deposition methods: dip-coating, spiral-bar and drop-coating. For the preparation of the solution we have used precursors containing titanium and nitrogen. These compounds were dissolved in solvent, and the solution was vigorously stirred.

In the spiral-bar method the solution was deposited on the substrate using a pipette. Then a stainless steel cylindrical bar wound with a stainless steel wire (4-10 µm thick) moved on the substrate on which the liquid solution has been deposited, forming a thin film. After the deposition, the substrate was annealed in for 1 hour for the evaporation of the solvent and the formation of the N-doped TiO2 nanocrystals.

In the drop-coating method, the solution was simply deposited on the substrate using a pipette. This method was useful on rough surfaces such as membranes, where the spiral-bar did not work very well.

These coatings were deposited on various smooth substrates (glass, silicon, quartz, alumina) and porous membranes (alumina oxide, stainless steel, silicon carbide). After the deposition, the chemical composition, the structural morphological and optical properties of the samples were analysed, and the photocatalytic activity was measured.

Since the photocatalytic activity on the metallic membranes was always quite low, probably because of the effect of the substrate that decreases the lifetime of the electron-hole pairs or reduces their concentration, we have also tried to coat these membranes with a thin SiO2 film barrier, deposited by sol-gel. The results were however not satisfactory.

Finally, the drop-coating technique was applied to deposit the coating on large membranes (26 x 11 cm) for the pilot plants.

Development of non-woven membranes based on electrospun TiON fibres

This deposition method was discarded, because the samples showed a low photocatalytic activity, bad adhesion with the substrates and because of the brittleness of the nanofibers.

Characterisation of the chemical composition & nanostructure

For this project, one of the major technical advances was the use of a coated membrane to improve the water quality through
visible light induced photocatalysis. Hence, it is crucially important to understand the physical structure of the chosen aluminium oxide (Al2O3) membrane, together with the chemical composition, nitrogen doping and crystallographic structure of the N-doped TiO2 coating. It was also very important to understand how the N-doped TiO2 coating structure, composition and coverage affected the photocatalytic properties (ability to degrade pollutants and inactivate viruses). A number of different analytical techniques were used at the University of Surrey (UoS) to study morphology, structure, chemical and crystallographic composition of the membranes and deposited N-doped TiO2 coatings. The quantification of photocatalytic activity was carried out at the water laboratory of Tel Aviv University (TAU), and is further described in the next chapter.

Alumina Membranes:

Alumina membranes were chosen to filter the water, as the photocatalytic properties of the N-doped TiO2 coatings were not found to be good when using stainless steel or silicon carbide membranes. Two alumina membranes with different pore sizes were studied. Figure 8 (a) and (d) show X-ray diffraction (XRD) spectra, which provide information on the crystallographic structure of the 200 and 800 nm pore size membranes respectively. As the membranes are nominally alumina, it was expected that only alumina (Al2O3) peaks would occur in the spectrum, but the 200 nm membrane also showed the presence of small particles from other metal oxides (e.g. zirconia, ZrO2) in addition to alumina in the membrane. Scanning electron microscopy (SEM) is a technique which enables the surface of a material to be examined at high magnification. Figure 8 (a) shows the top surface of the 200 nm pore membrane. The small impurity metal oxide particles are attached to the surface of the larger alumina grains and it is clear that these small impurity particles will not have a significant adverse effect on the water flow through the membrane.

An SEM micrograph showing the 200 nm membrane in cross-section is given in Figure 8 (b) shows the presence of a 4-5 µm surface layer which is acting as the tight pore size filter in this membrane. Below this surface layer, the pore size is much larger (allowing the easy passage of water) through the membrane. The SEM image in Figure 8 (c) shows the surface of the 800 nm alumina membrane. There are no small impurity oxide grains present and the alumina grains can be seen to vary in size from sub-micron to a few microns in size.

Figure 8: (a) X-ray diffraction spectrum and (b) SEM (cross-section) micrograph of the 200 nm pore size alumina membrane; (c) SEM micrograph (surface) and (d) X-ray diffraction spectrum of the 800 nm pore size membrane.

N-doped TiO2 Coated Alumina Membranes

The photocatalytic results for the N-doped TiO2 coatings deposited by different methods showed the best performing coatings to be those deposited by sol-gel deposition. The investigated N-doped TiO2 films were deposited on the 200 nm pore size alumina membrane by sol-gel in two different ways: using a pipette drop method and using a spiral bar applicator. Analytical results from the sol-gel coating deposited coated membrane are shown in Figure 9. The SEM image of the coated membrane surface, given in Figure 9 (a), shows the presence of the small impurity oxide particulates on the larger alumina grains (as mentioned previously) and the coating is so thin that it cannot be discerned from the SEM image. However, surface sensitive analytical techniques, such as X-ray photoelectron spectroscopy (XPS), with an analysis depth of approximately 5 nm can show the presence of a thin surface coating. XPS analysis of the coated membrane surface gave a Ti concentration of 18.4 atomic % (indicative of the coating) and an Al concentration of 5.2 at.% (indicative of the alumina substrate) proving the presence of the N-doped TiO2 coating on the surface. From this data, the coating was estimated to cover 78% of the underlying alumina membrane. Atomic force microscopy (AFM) is another surface sensitive analytical technique which can be used to map surface topography and when AFM is used in the ‘phase contrast mode’ it can show the presence of different materials on a surface. Figure 9 (c) shows the AFM phase contrast image of the N-doped TiO2 coated 200 nm membrane surface. The bright and dark areas in this image respectively represent the N-doped TiO2 coating and alumina membrane present at the surface.

TiO2 can form different crystallographic phases, but previous scientific work has shown that the anatase phase is the most
active phase for photocatalysis. So, confirming that the sol-gel coating has this structure is important. The XRD spectrum in Figure 9 (d) shows that the sol-gel coating is forming with crystal structure of anatase (peaks labelled •). The width of the anatase peaks in the XRD spectrum can be used to determine the size of the individual crystalline alumina grains within the coating. The coating was found to have an average TiO2 grain size of 12 nm.

Figure 9: Analytical results for the sol-gel N-doped TiO2 coated 200 nm pore size membrane. (a) SEM image of the coated membrane surface; (b) XPS N 1s spectrum; (c) AFM phase contrast image; (d) XRD spectrum.

N doping of TiO2 results in a small change in the electronic structure of TiO2 which promotes the absorbance of visible light and the photocatalytic properties of TiO2 can then extend into the visible light range. The N doping of TiO2 in the sol-gel coating occurred with N being present at a concentration of &lt; 1 atomic %. Recording XPS spectra at high energy resolution enables the different bonding states for atoms in a solid material to be examined. The XPS N 1s peak in Figure 9 (b), has been peak fitted to reveal the presence of N at four different binding energies, representing four different bonding states. Using binding energy assignments from the literature, it was found that the different bonding sites correspond to: (i) N atoms substituting for O atoms in the TiO2 structure; (b) N atoms being located between the Ti and O atoms (interstitial) in the TiO2 structure and (iii) N present within a surface hydrocarbon contamination layer. Interestingly, for the sol-gel coating N is predominantly located at interstitial sites within the TiO2 structure. The photocatalytic performance for this sol-gel coated membrane was 62 % removal of carbamazepine pollutant molecules after 1 hour of exposure to the solar simulator.

Characterisation results from the spiral bar deposited N-doped TiO2 sol-gel coating on the 200 nm pore membrane showed many similarities with regard to structure, N content, N bonding and PCA compared to the pipette drop deposited coating (see Table 1).

Table 1 Comparison of the coating characteristics and photocatalytic activity for pipette drop and spiral bar sol-gel deposited coatings on the 200 nm pore size membrane.

However, the coating deposited by the spiral bar method was thicker than the pipette drop deposited coating and is clearly visible in SEM images of the coated membrane surface (Figure 10). It can be seen that the spiral bar deposited coating exhibits a ‘mud-cracked’ morphology, which may be expected also for the much thinner pipette drop deposited coating. It was decided to progress the project using the pipette drop deposited coating as the spiral bar method gives rise to partial blockage of the membrane pores (as seen from Figure 10), reducing water flow and probably leading to a less durable coating. Iron-rich marks on the coating were also observable on the coating surface from the iron bar, which may have a deleterious effect on the photocatalytic activity.

Figure 10: SEM images of the spiral bar deposited N-doped TiO2 coating showing a ‘mud-cracked’ morphology and partial membrane pore blockage

Laboratory testing of coated membranes for water treatment

The quantification of photocatalytic activity of various coated materials and under various conditions was carried out at the water laboratory of Tel Aviv University (TAU).

The coated membranes were investigated using a versatile flow cell, designed and built within the project (Figure 11). The filtration and irradiated area of the filtration cell was 43.6 mm x 21.6 mm, with a quartz cover placed above the membrane. The flow cell could be irradiated by a solar simulator with an intensity of 2 suns (Figure 12).

Figure 11: filtration cell – dead end filtration mode
Quantification of photocatalytic activity (PCA)

The photocatalytic activity (PCA) was quantified by the degradation of the model micropollutant molecule Carbamazepine (CBZ), and disinfection was quantified by inactivation of a model virus, MS2 bacteriophage.

Various substrates were examined as listed below. The photocatalytic activity (PCA) of N-doped TiO2 coatings was quantified, to identify the best combination of substrate and coating for the pilot plant application. Sol-gel coated Al2O3 membranes showed the highest potential, with significant advantage in performance over non-porous substrates (e.g. glass) and over membranes coated with undoped anatase-TiO2.

Membrane substrates Coating methods

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Coating method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stainless steel, 2 µm pore size</td>
<td>Sol-gel by UNIAQ</td>
</tr>
<tr>
<td>Silicon carbide (SiC), 3 µm</td>
<td>RF sputtering by UPMC</td>
</tr>
<tr>
<td>Aluminium oxide (Al2O3), 200 and</td>
<td>Filtered vacuum arc deposition (FVAD) by TAU</td>
</tr>
<tr>
<td>800 nm</td>
<td></td>
</tr>
</tbody>
</table>

The degradation was measured as decreasing CBZ concentration, and reported as removal percentage of CBZ. For comparing the PCA of coated membranes, an apparent CBZ degradation rate constant for the system is calculated, with the unit min⁻¹.

Removal (%)=(C₀-Cᵢ)/C₀ ×100

Apparent reaction rate constant k=ln(Cᵢ/C₀ )/t

C₀ - Initial pollutant concentration (mg/L)
Ci - Pollutant concentration after batch run i (mg/L)
t - Total experiment time (min)

Stainless steel (electrically conductive) and SiC (semiconductor) displayed poor photocatalytic activity for all deposition techniques. N-doped TiO2 coatings obtained by sputtering and FVAD technology showed poor PCA on the membrane substrates. N-doped TiO2 coatings on Al2O3 membranes with the sol-gel coatings by UNIAQ showed the highest photocatalytic activity. An initial CBZ concentration of 1 mg/l was decreased by 60-70% after 2 hours, as opposed to only negligible effect by irradiation only (Figure 13). The disinfection potential of the coated membranes was examined by MS2 virus inactivation as well. The coated membrane showed high inactivation (5 log10 or 99.999%) of MS2 in ultrapure water, as opposed to irradiation with a non-coated membrane.

With regard to reproducibility, the sol-gel coated membranes showed variability in the photocatalytic activity (PCA) performance (Figure 14). After a substantial effort was made to improve the reproducibility, the coated membranes consistently performed in the higher end of that range.

In addition to fouling at normal membrane operation conditions, photocatalytic membranes may face a reduction in activity due to active site saturation by organic and inorganic substances dissolved in water. In order to maintain the PCA of the coated surface, chemical cleaning will be required. The durability of the coated membranes against classical membrane cleaning agents was examined, such as hydrochloric acid and citric acid to remove inorganic foulants, and sodium hydroxide.
against organic fouling. The membranes were immersed and soaked in the cleaning solutions and rinsed by ultrapure water. The coated membranes withstood all the tested cleaning agents.

TiON vs. TiO2

N-doped TiO2 coated membranes were compared to membranes coated with un-doped anatase TiO2 produced by the same sol-gel method. When applying the full wavelength spectrum, the TiON resulted in a significantly higher removal rate (by 80%) compared to the un-doped TiO2. In addition, the TiO2 coated membranes showed an obvious dependence on wavelength; when the UVB part of the spectrum was removed (320 nm ≤ λ), the reaction rate decreased by 57% as opposed to full spectrum operation. This dependence was not observed for the N-doped TiO2 coated membranes. Finally when applying visible light, only the N-doped TiO2 coated membranes showed photocatalytic activity.

Figure 15 CBZ degradation by TiON and TiO2 coated membranes under full solar simulator spectrum (UVB+UVA+VIS), using a 320 long pass (LP) filter (UVA+VIS), and using a 400LP filter (visible spectrum only)

Influence of water quality parameters

The impact of water quality on the photocatalytic activity of the sol-gel coated Al2O3 membranes were examined, by the addition of commonly found ions and natural organic matter (NOM), and by experiments with natural surface water. The disinfection efficiency was also investigated by MS2 bacteriophage inactivation.

Investigating the effect of different ions on the photocatalytic reaction provided important information regarding the potential efficiency of the process when treating water with different characteristics. The results indicate that alkalinity and calcium can significantly inhibit the photocatalytic reaction at high concentrations (e.g. hard water, 120 mg/l CaCO3), while chloride, nitrate and sulphate did not affect the PCA. The effect of bicarbonate alkalinity on inactivation of microorganisms was also investigated. Even though bicarbonate at low concentration had no inhibiting effect on CBZ degradation, a decrease in MS2 inactivation was observed.

The tests with NOM resulted in inconclusive data regarding the beneficial or inhibiting impact on the photocatalytic process. The effect of NOM will probably depend on its origin and characteristics. The combined effect of water quality parameters was examined by using Lake Kineret water (Israel) as a natural water source. The results showed a significant reduction in CBZ degradation reaction rate. MS2 inactivation in Lake Kineret water revealed complex interactions of the virus with the coated membrane.

The degradation rate of CBZ increased with temperature, in spite of the decrease in dissolved oxygen (DO) concentration. It shows that adsorption/desorption equilibrium of CBZ and by products with active sites on the catalytic surface is a more significant limiting factor than DO concentration.

Figure 16: Temperature control experimental set up, including cooling/heating coil, thermocouple and dissolved oxygen (DO) meter

Membrane engineering and treatment system design

Physical characterization of membranes

As a result from the laboratory tests, a functional photocatalytic membrane was obtained by sol-gel coating of TiON on Al2O3 membranes. Membranes with two nominal pore sizes were tested: 800 nm and 200 nm.
The water permeability and retention of fluorescent particles by the uncoated and coated membranes were quantified. Furthermore, the membranes were physically characterised by capillary flow porometry, contact angle and zeta-potential.

The pure water permeability and selectivity tests were carried out at DHI with a duplicate of the flow cell used for the photocatalytic measurements at Tel Aviv University. The selectivity of the membranes was investigated with hydrophilic fluorescent particles with diameters of 0.2, 0.5 and 1.0 µm, added at a feed concentration of 2 x 10⁵ particles/ml. The flow cell was operated in cross-flow mode with a low pressure between 90-130 mbar. The results are summarized in Table 2.

Table 2: Summary of the physical properties of the photocatalytic membranes

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Coated 200 nm</th>
<th>Coated 800 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average pore size (µm)</td>
<td>0.27 ± 5%</td>
<td>Analysis not possible</td>
</tr>
<tr>
<td>Water permeability (LMH/bar)</td>
<td>2000 ± 35%</td>
<td>13000 ± 13%</td>
</tr>
<tr>
<td>Contact angle (glycerol)</td>
<td>30-33 ± 3%</td>
<td>Analysis not possible</td>
</tr>
<tr>
<td>Particle retention of 0.2 µm polystyrene particles</td>
<td>97% ± 3%</td>
<td>30-95%</td>
</tr>
<tr>
<td>Particle retention of 0.5 µm polystyrene particles</td>
<td>99.95% ± 0.05%</td>
<td>27-95%</td>
</tr>
<tr>
<td>Particle retention of 1.0 µm polystyrene particles</td>
<td>99.6% ± 0.6%</td>
<td>96.9% ± 4%</td>
</tr>
</tbody>
</table>

Water permeability measurements confirmed that the coated membranes are within the microfiltration area. The water permeability of the coated 200 nm membrane was found to be 2000 liter per square metre, hour and bar (LMH/bar), while it was 13,000 LMH/bar for the coated 800 nm membrane.

The median pore size of the coated 200 nm membrane, measured with porometry, was 0.27 µm. The pore size distribution indicated that especially the large pores were reduced in size when the substrate was coated.

The retention of bacteria-sized particles (0.5 µm and 1.0 µm) by the 200 nm membranes was in the range 2-4 log₁₀ (99-99.99%). The retention of particles by the coated 800 nm membrane was more variable, especially for the 0.2 µm and 0.5 µm particles.

Contact angle measurements with glycerol showed that the coated membranes are hydrophilic.

Design considerations:

The sol-gel TiON coated 800 nm membrane was used in lab and pilot plant experiments. The 800 nm membrane was chosen as coating substrate, mainly due to its higher water permeability. In terms of photocatalytic activity, the coated 200 and 800 nm membrane were comparable.

The design of the laboratory and pilot plant equipment applied reverse filtration direction, where only the filtered water (permeate) was exposed to the photocatalytic effect. The pilot unit included the photocatalytic membrane and an uncoated 200 nm membrane as a pre-filter to protect the coated membrane from fouling. The pre-filter and the photocatalytic membrane were built into the same housing (Figure 17).

Figure 17: Membrane set-up in the photocatalytic pilot unit.

If the photocatalytic membrane is going to be used with sunlight, parabolic reflectors may be used to intensify the incident light irradiation, as illustrated in Figure 18. The reverse filtration direction is also adapted in this case. The water flows from inside of the tube to the outer surface which is coated with TiON. This design would allow the use of commercially available tubular ceramic membranes and quartz tubes.
The suitability of UV-transparent acrylic was investigated as an alternative to quartz. The quartz had a transmittance above 90% for wavelengths above 260 nm, while the acrylic had a transmittance above 90% for wavelength above 300 nm. This meant that the acrylic allowed passage of UVA and most of the UVB irradiation, while UVC irradiation was blocked. The acrylic had the advantage of being less fragile compared to the quartz. In the lab tests, the PCA of the TiON-coating was unaffected by a long pass filter of 320 nm. Therefore, the acrylic material should be acceptable as a cover material for TiON coatings used with natural sunlight.

A literature review of disinfection by-products formed during photocatalysis and the influence of salinity on the PCA was prepared, to identify the components which should be investigated in lab and pilot scale. Except for bromate and bromoform, it appears that no problematic by-products are expected to be formed during photocatalysis of NOM. In case of chlorination after photocatalytic treatment, disinfection by-products like trihalomethanes (THM) and haloacetic acids (HAA) may be formed to a higher degree than before photocatalysis, due to incomplete mineralization and the presence of more reactive metabolites. Furthermore, toxic by-products may be formed due to incomplete mineralization of pesticides or pharmaceuticals.

Assessment of environmental, health and safety aspects and initial LCA life cycle assessment

A risk assessment was carried out at DHI to evaluate the risk to human health, when drinking water treated by a TiON coated membrane. Toxicological data for nano-TiON was unavailable. As the TiON developed in NATIOMEM predominantly consists of TiO2 (99%), the risks assessments were carried out for TiO2.

It was concluded that due to the low toxicity of nano-TiO2 described in the literature, and the low exposure expected, it can be considered safe for consumers to use the photocatalytic membrane for disinfection of drinking water, from a toxicological point of view. An initial worst-case scenario however revealed that a minor risk could not be ruled out if the TiO2 from the coated membrane was released rapidly in nano-size. The absence of high nano-TiO2 concentrations in the treated water needs to be verified before applying the technology for human consumption.

The environmental risk assessment was based on a literature review. The Predicted No Effect Concentration (PNEC) value derived for the aquatic environment was compared to the Predicted Environmental Concentrations (PEC). No environmental impact should be expected from the possible release of nano-TiON from the NATIOMEM treatment units to the environment.

In an initial life cycle assessment (LCA), the materials used to manufacture a hypothetical four-person family unit were investigated for their energy demand. The unit consists of a 60 x 75 cm solar collector with 0.21 m2 of coated membrane, and should produce 100 litres of drinking water per day, during 8 hours of sunlight, using gravity flow (Figure 19).

Figure 19: Illustration of the solar collector for a four-person family unit based on five flat sheet membranes. Membrane size 11x53 cm as available commercially.

It was found that the most energy-demanding part of the treatment unit would be the stainless steel frame, followed by the UV-transparent acrylic cover. The energy demand for the coated ceramic membranes was minor. The Cumulative Energy Demand (CED) was then compared to LCA data for piped tap water and for bottled water. Although some aspects of installing the unit and its operation were not part of the study, it can be concluded that local production of drinking water in remote areas without piped water supply will be more energy-efficient than transport of bottled drinking water.

Pilot plant development & demonstration
The TiON coated photocatalytic membrane that produced promising results in the laboratory test was integrated into the pilot plant design by Skjølstrup & Granborg. Three pilot plants with photocatalytic membranes were operated at Umgeni Water’s test facility in Durban, South Africa and at Kawar Energy’s test site close in Amman, Jordan. The pilot plants were fed with pre-treated surface water (South Africa), with drinking water from an intermittent supply, and with grey water (both Jordan).

Based on a specific test protocol, the pilot plants were used to quantify the performance of the coated membrane treating natural water using sunlight, investigate fouling tendencies and develop suitable cleaning strategies.

Design and Construction of Pilot Plants

The pilot unit contained 16 individual housings, each with one photocatalytic membrane on top and one pre-filtration membrane in the bottom of the housing. The photocatalytic membranes were sol-gel TiON coated Al2O3 membranes with a nominal pore-size of 800 nm, while the pre-filtration membranes were 200 nm uncoated Al2O3 membranes. The cross-section of a membrane housing is illustrated in Figure 20. The feed water flows into the membrane housing from the bottom and passes the pre-filtration membrane. The pre-filtered water flows through the photocatalytic membrane, where the permeate is exposed to the photocatalytic surface.

Efficiency analysis on the pilot plant scale

A protocol was developed for the pilot tests with NATHOMEM's photocatalytic membrane units in Jordan and South Africa. The tested applications were:

- Natural water (ground water and surface water for portable use), South Africa
- Contaminated drinking water for potable use, Jordan
- Grey water for non-portable use, Jordan

Based on the objectives for the pilot tests, performance parameters were defined with which the treatment efficacy and operation of the treatment units could be quantified. The analytical programme also included parameters for the general characterisation of the feed and treated water qualities under the given operating conditions.

As the feed waters did not contain high enough concentrations of organic trace contaminants and microorganisms to quantify treatment efficacy, campaigns were carried out with controlled addition of contaminants. In these challenge tests, bacteria (E.Coli), virus surrogates (bacteriophages) and the drug carbamazepine were added to the feed. On a sunny day, samples were collected before and after treatment with the photocatalytic membrane, during light and dark conditions, and over an uncoated membrane. This allowed for the quantification of photolytic and photocatalytic inactivation, as well as retention by
filtration.

In Jordan, the 16 coated membranes in the grey and potable water pilots, respectively, were operated in parallel. In South Africa the 16 coated membranes were operated individually, to allow for rapid investigation of the research questions defined in the protocol. For some experiments, two or three membranes were operated in parallel or in series.

For the tests of photocatalytic activity (PCA), carbamazepine (CBZ), bacteriophages or E.Coli were added to ultrafiltered raw water. The single-pass degradation of CBZ in the pilot plant under full sunlight was only about 5% in average. With the small difference between spiked concentration \( c_0 \) and final concentration \( c \), analytical error influenced the data, and made it difficult to quantify the effect of test parameters on PCA. When the solution was passed through the membrane several times, more reliable PCA data was achieved. In NATIOMEM, natural sunlight was used to initiate the photocatalytic effect.

The pilot plant membranes were approximately one order of magnitude less effective in degrading CBZ than the flow-cell, treating ultrapure water in the lab, calculated as microgram CBZ degraded per square centimetre illuminated membrane area, per hour and per Watt of sunlight. This is in spite of the ten times lower water flux, and thus longer residence time of the water near the coated surface. When fed with natural water, also the efficiency in the lab declined by about 70%. The low pressure / low flow / low fouling strategy adopted for the pilot plants did not prove to be successful. No effect of the irradiation intensity on PCA could be seen.

The challenge tests with addition of somatic coliphages resulted in varying efficacy, but typically less than 1 to 2 log\(_{10}\) inactivation (90-99%) per single pass of a coated membrane in sunlight. Also virus inactivation was thereby significantly lower than in the lab.

Since the promising results from the laboratory tests could not be transferred to pilot scale, a straightforward analysis of cost-effectiveness was not possible. Instead, the poor degradation of carbamazepine and poor inactivation of virus in pilot-scale were analysed, and translated into recommendations for the design and technical application of the coated membranes.

Fouling analyses on the pilot plant scale

Tests with potable, pre-treated grey water and surface water as feed were carried out to monitor the fouling development.

In South Africa, important knowledge was obtained regarding the fouling potential of the ceramic membranes in a high raw water turbidity application. Results emanating from the fouling experiments indicated the following:

The 800 nm coated membranes require intermittent cleaning for long-term filtration sustainability.

Cleaning in place (CIP) of the membrane at low flux was not efficient. The membrane was restored to its original cleanliness when it was disassembled from the membrane support unit and cleaned by soaking in chemical solutions as per the revised cleaning procedure.

In Jordan, the pre-treatment membrane was affected by rapid fouling, even at the low flux applied, treating a supposedly low-fouling drinking water. The original design idea was that the 200 nm pre-treatment membrane should protect the photocatalytic membrane. Furthermore, the tighter pre-treatment membrane was expected to be relatively easy to clean, since larger particles cannot enter the pores, and should be retained on the surface. During the pilot plant tests, that hypothesis did not verify. Also in Jordan, CIP with chemicals at low flux was not suitable for restoring the permeability of the fouled membranes.

Even in relatively low-fouling waters, dead-end operation at low-flux with simple pre-treatment caused heavy fouling. Efficient pre-treatment will be needed to reduce sub-micron particles and colloids. Cleaning-in-place using a low flux was not effective.
Instead, the membranes needed to be removed from their frames, then soaked and cleaned mechanically. Fouled membranes were removed from the pilot plants and analysed for hydraulic conductivity and for surface contamination.

Demonstration activities:

The pilot unit in South Africa was selected for further tests and demonstration. Treated wastewater and natural surface water spiked with treated wastewater were used to quantify the removal of faecal indicator bacteria over the pilot plant. The reduction of E. Coli bacteria concentration over the coated 800 nm membrane was 2-3 log10 (99-99.9%), the same as over the uncoated 800 nm membrane. The reduction in bacteria concentration was presumably due to retention (filtration).

As expected, the pilot plants did not significantly affect the alkalinity, chemical oxygen demand (COD), hardness, total organic carbon (TOC) and total dissolved solids (TDS). Particularly, the photocatalytic treatment did not degrade natural organic matter (NOM). The membrane removed effectively particular matter causing turbidity. This probably contributes to the observed fouling.

The Trihalomethane Formation Potential (THMFP) increased after the photocatalytic treatment. This phenomenon is in agreement with our literature survey. An explanation is that the photocatalytic process breaks down large organic molecules to more reactive smaller molecules. The influence on the water quality as a result of a bio-sand filter pre-treatment unit was demonstrated. After some days of operation, the slow sand filter successfully decreased turbidity and suspended solids in the feed water to the pilot plant.

The NATIOMEM system was showcased to the members of a water research group from Durban University of Technology (DUT). The group has intensive experience in water technology development and transfer to rural communities; hence they were able to give technical, economic and social feedback about the NATIOMEM system.

Figure 23 NATIOMEM dissemination session at Umgeni Water’s test facilities, South Africa.

Conclusions regarding the application:

Finally, the findings from the pilot plant tests were interpreted, and applied to update the design recommendations for photocatalytic treatment units based on NATIOMEM’s TiON coated membranes.

The main purpose of NATIOMEM was to develop a high-tech photocatalytic membrane which could be used in a low-tech treatment system. The PCA efficiency for CBZ degradation and virus inactivation from lab tests could not be transferred to pilot scale. The low pressure / low flow / low fouling strategy adopted for the pilot plants proved to be inefficient.

The experience from the pilot plant tests show that the membrane system requires frequent cleaning when operated on natural water, and skilled personal to operate it. To function optimally, the photocatalytic membrane needs to be built into a treatment system with efficient pre-filtration. Therefore, an updated treatment system should include:

Efficient pre-filtration, using a bio-sand filter

Recirculation of the water, to achieve several passes of the coated membrane. The pump would be powered by electricity from the grid, or from a solar panel

Furthermore, the TiON coatings may be used for industrial applications, where anatase TiO2 is used today. The opportunities for commercialisation of the coated membrane are being investigated by the project partners.
Apart from water treatment, applications of the TiON coating within optoelectronics and renewable energy (water splitting) have been identified, as described in the journal publications.

Potential Impact:

Expected impact from the project

The expected research impacts described in the work programme for Theme 4 (NMP) of the 7th Framework programme were “1. Breakthroughs in the implementation of water reclamation and purification plants. Projects are expected to partly fill the gap between the 'technology push' and the 'market pull', thus contributing to 3. sustainable development, preservation of natural resources and the well-being of society.”

There was also an expected policy impact to improve the competitiveness of the European industry.

NATIOMEM was expected to develop a stand-alone, solar-driven treatment unit for contaminated drinking water and reuse of wastewater, based on a single-barrier against contaminants. The treatment unit should be user-friendly and independent of complex logistics, without the need for electrical power supply.

The project was furthermore expected to strengthen the co-operation between the EU, Middle East and Africa, and alleviate some of the water-related problems in Jordan and South Africa.

Contribution towards expected impacts:

A broad range of coating methods was applied in parallel to develop the photocatalytic nitrogen-doped titanium dioxide (TiON) coatings on membrane substrates. The coating laboratories at University Pierre & Marie Curie, University of L’Aquila and Tel Aviv University optimized the coatings for performance, and gained a deeper understanding of the fundamental properties of the materials.

In the course of the project, some novel coatings were developed. These include TiO2/TiN bi-layer thin films created by radio-frequency (RF) reactive magnetron sputtering, and TiON formation by oxidation of titanium nitride (TiN).

The coatings developed within NATIOMEM also have potential for other applications, such as hydrogen production and 3rd generation low cost solar cells. The bi-layer strategy developed during this project demonstrated effective separation between the photo-generated electron-hole pairs which enhanced photoactivity. This strategy can be applied to coat glass or quartz substrates, since very high photocurrents were obtained during water splitting measurements and further applications for hydrogen production could be developed.

Good progress was made within NATIOMEM on TiON doping and material science. Details on the coatings produced by the partners were made available to the research community by publication in high-ranking scientific journals. These results are expected to attract additional research funds and students to the area.

In the laboratory tests, NATIOMEM’s photocatalytic membranes have shown promising performance for disinfecting drinking water. In accordance with the work plan, a low pressure, low flux, low fouling strategy was chosen for the pilot plant tests on natural waters. This strategy proved to be ineffective, due to low photocatalytic activity measured as degradation of chemicals and as inactivation of viruses. Also, the cleaning of the membranes was impossible at low flow. This makes the concept unsuitable for the envisaged stand-alone, low-tech application. The treatment unit would require more effective pre-filtration and electric energy for recirculation of the water. This would make the unit and its operation more complex, less user-friendly, and also increase the cost.
The anticipated decentralised solar-powered water treatment plant may however still be in reach. The results from the pilot tests were used to update the design recommendations for the coated membrane and its application. The treatment units may be equipped with a pump for recirculation, powered by a solar panel in daytime. A simple, yet efficient pre-treatment such as bio-sand filtration will be required.

After integrating the findings from the lab and pilot tests into the design recommendations, the TiON-coated membrane has good potential for commercialisation. An efficient production may yield the high volume, low-cost product planned for in the project description. The coated membrane should become available at relatively low costs, about 100 EUR for a unit with 0.5 square metres of membrane area.

The involved coating and engineering partners have initiated a product development phase, which will be funded by private capital and a Eurostars application. The exploitation of NATIOMEM's results has therefore created a business opportunity for the partners that hold the IPR, but also for further SME partners needed for product development.

NATIOMEM has strengthened the links between university research and innovative SMEs. The project has particularly resulted in an intensified and deepened collaboration between partners in EU countries and Israel. There was also a fruitful cooperation with the end user partners Jordan and South Africa.

With the progress in material science and the planned commercialisation of the coated membrane, NATIOMEM has contributed to improved competitiveness of the European research and industry.

List of Websites:

Public project site:
www.natiomem.eu

Contact information:

Project coordinator: DHI, Agern Alle 5, DK-2970 Hørsholm, Denmark, www.dhigroup.com. Contact: Mr. Gerald Heinicke, Phone: +45 4516 9268, E-mail: ghe@dhigroup.com

University of L'Aquila, www.univaq.it. Contact: Mr. Luca Lozzi, luca.lozzi@aquila.infn.it

Tel Aviv University, http://english.tau.ac.il. Contact: Mrs. Hadas Mamane, hadasmg@post.tau.ac.il

University of Surrey, http://www2.surrey.ac.uk/, Contact: Mr. Mark Baker, m.Baker@surrey.ac.uk

University Pierre &amp; Marie Curie, www.enscp.fr, Contact: Mrs. Farzaneh Arefi-Khonsari, farzi-arefi@enscp.fr

Skjøelstrup and Groenborg ApS (Ultraaqua), www.ultraaqua.com, Contact: Mr. Ole Grønborg, gronborg@ultraaqua.com

Umgeni Water (South Africa), www.umgeni.co.za, Contact: Mr. Rachi. Rajagopaul, Rachi.Rajagopaul@umgeni.co.za

Kawar Energy (Jordan), www.kawar.com, Contact: Mr. Hanna Zaghloul, hanna.zaghloul@kawar.com

Related information

<table>
<thead>
<tr>
<th>Result In Brief</th>
<th>Water treatment membranes activated by the Sun</th>
</tr>
</thead>
<tbody>
<tr>
<td>Documents and Publications</td>
<td>final1-publishable-summary-2.pdf</td>
</tr>
</tbody>
</table>