

# Solar-driven photocatalytic decomposition of microcystin-LR: from laboratory development to on-site demonstration

Hesam Zamankhan Malayeri, Mallikarjuna Nadagouda and Hyeok Choi

## ABSTRACT

Harmful algal blooms (HABs) found in various water bodies worldwide have been a huge concern due to their adverse impacts on human health and ecosystems. In particular, HABs associated with cyanobacteria have been of great interest because of their potential to generate and release biological toxins, especially, lethal microcystins (MCs). The overall goal of this study was to develop a new sustainable approach to decompose MCs, preferably on-site and in real-time with minimal effort, fewer chemicals, and low energy inputs. To achieve the goal, a high efficiency nitrogen-doped TiO<sub>2</sub> photocatalytic film immobilized onto a glass substrate was fabricated via integrated sol-gel synthesis employing nitrogen-containing surfactants as pore-templating agent and nitrogen-dopant. The film exhibited visible light-activated, nanoporous, and transparent properties. Effects of surfactant type, calcination temperature, coating layers, and reaction pH on the photocatalytic decomposition of microcystin-LR (MC-LR) were investigated under visible light. Eventually, the TiO<sub>2</sub> film was able to successfully decompose MC-LR on-site in a lake under solar radiation in real-time. This study implies the high potential of the TiO<sub>2</sub> film for on-site and real-time decomposition of many organic contaminants in water by using sustainable solar energy.

**Key words** | biological toxins, harmful algal blooms, microcystins, on-site treatment, solar radiation, TiO<sub>2</sub> photocatalysis

**Hesam Zamankhan Malayeri**  
**Hyeok Choi** (corresponding author)  
Department of Civil Engineering,  
The University of Texas at Arlington,  
Arlington,  
TX 76019-0308,  
USA  
E-mail: [hchoi@uta.edu](mailto:hchoi@uta.edu)

**Mallikarjuna Nadagouda**  
Department of Mechanical and Materials  
Engineering,  
Wright State University,  
Dayton,  
OH 45324,  
USA

## INTRODUCTION

Contamination of water resources with natural and anthropogenic chemicals has been a huge concern worldwide. Particularly, the increasing occurrence of harmful algal blooms (HABs) alarms water and health authorities and the general public (Nfodzo *et al.* 2013). Specifically, HABs associated with cyanobacteria (so-called cyano-HABs) produce and release lethal biological toxins such as microcystins (MCs) (Bownik 2016). MCs are a group of natural toxins that act as hepatotoxins and promote formation of tumors (Antonioni *et al.* 2005). Animal poisoning and fish killing have been reported in conjunction with MCs, resulting in significant economic losses (Svircev *et al.* 2015; Bownik 2016). Among more than 100 MC congeners, microcystin-LR (MC-LR) is the most notorious due to its high toxicity and prevalence and thus the United States

Environmental Protection Agency has placed the toxin on the drinking water health advisories (USEPA 2015).

Particulate algae can be easily removed by conventional water treatment processes but cyanobacterial toxins dissolved in water are usually recalcitrant and hard to remove (Lawton & Robertson 1999). Many technologies, including activated carbon adsorption, coagulation/sedimentation, membrane separation, and chemical oxidation, have been tested for treatment of MC-LR (Campinas & Rosa 2010; Li *et al.* 2014; Roegner *et al.* 2014; Jasim & Saththasivam 2017). However, these ex-situ treatment approaches benefit only those who directly use treated water. They do not provide a systematic tool to protect the ecosystem in HAB sites. As a result, the overall goal of this study is to develop an on-site (or *in-situ*) treatment

approach for removal of cyanobacterial toxins. Considering many limitations occurring during on-site applications, such a treatment approach should be characterized, if possible, with minimal effort, fewer chemicals, and low energy inputs. Once developed, the approach is also important with respect to source water management.

In order to achieve the goal and to fulfill the requirements, this study proposes to use a high efficiency nitrogen-doped TiO<sub>2</sub> photocatalytic film immobilized onto a glass substrate. TiO<sub>2</sub> photocatalysis is one of the most effective water treatment processes (Choi *et al.* 2010; Lazar *et al.* 2012; Pelaez *et al.* 2012). Strong hydroxyl radicals generated from TiO<sub>2</sub> non-selectively and readily attack and decompose organic contaminants in water including MCs. The catalytic process does not either require addition of other chemicals or consume TiO<sub>2</sub> materials. However, the only requirement is to irradiate the TiO<sub>2</sub> surface with UV with high photon energy above the band gap of TiO<sub>2</sub>. This greatly inhibits the utilization of solar radiation as a sustainable energy source for the TiO<sub>2</sub> activation because only 4–5% of the incoming solar energy onto the earth's surface is in the UV range. Consequently, activation of TiO<sub>2</sub> under visible light can facilitate the development of promising processes for on-site remediation of contaminated water under solar radiation without introduction of complicated facilities for generating and introducing UV. Dye-sensitized or metal ion-doped TiO<sub>2</sub> has shown promising results for the activation of TiO<sub>2</sub> under visible light, as summarized by Pelaez *et al.* (2012). More recently, doping of TiO<sub>2</sub> with anions such as nitrogen is also the most common method to narrow the band gap of TiO<sub>2</sub> (Yang *et al.* 2010; Pelaez *et al.* 2012, 2016; Petala *et al.* 2015; Ansari *et al.* 2016).

Meanwhile, for on-site applications of TiO<sub>2</sub> photocatalysis, TiO<sub>2</sub> should be immobilized firmly onto a substrate such as glass. Both TiO<sub>2</sub> film and substrate should also be transparent to improve light penetration and utilization in particular when TiO<sub>2</sub> films are installed and stacked on-site in parallel (Choi *et al.* 2006). To exhibit high reactivity and thus to decompose MCs in real-time under solar radiation, the structural properties of TiO<sub>2</sub> films should also be controlled. In particular, a porous structure is beneficial to light absorbance of TiO<sub>2</sub> and accessibility of reactants to TiO<sub>2</sub> (Zakersalehi *et al.* 2013). Surfactants and block copolymers as pore templates have been widely used to control the

porous structure during sol-gel synthesis of TiO<sub>2</sub> (Bosc *et al.* 2004). Use of nitrogen-containing surfactants is interesting. They can play dual roles as a pore template to make porous TiO<sub>2</sub> and as a nitrogen source to dope the porous TiO<sub>2</sub> with nitrogen (Choi *et al.* 2007).

In this study, such a high efficiency nitrogen-doped mesoporous transparent TiO<sub>2</sub> photocatalytic thin film (N-TiO<sub>2</sub>) immobilized onto a glass substrate was fabricated via an integrated materials synthesis process, employing surfactant template-based sol-gel, dip coating, and calcination. Effects of surfactant type, calcination temperature, multiple coating layers, and reaction pH on the photocatalytic decomposition of MC-LR under visible light were investigated. Most importantly, we demonstrated the TiO<sub>2</sub> works under solar radiation for on-site decomposition of MC-LR in real-time.

## MATERIALS AND METHODS

### Fabrication of N-TiO<sub>2</sub> film

Three nonionic long chain nitrogen-containing surfactants, diethanolamine (DEA), benzyltrimethylammonium chloride (BTAC), and dodecylamin (DDAD) purchased from Aldrich, were used as a pore-directing agent and a nitrogen-doping source. Briefly, each surfactant was dissolved in isopropanol (i-PrOH, Fisher) and then acetic acid (Fisher) was added to the solution for the esterification reaction with i-PrOH, as demonstrated elsewhere (Choi *et al.* 2006). Titanium tetraisopropoxide (TTIP, Aldrich) was added under vigorous stirring. The molar ratio of surfactant/i-PrOH/acetic acid/TTIP was 1:45:6:1. Transparent TiO<sub>2</sub> sol was prepared.

A borosilicate glass with an effective surface area of 10 cm<sup>2</sup> (20 cm<sup>2</sup> for both sides) was dip-coated with the TiO<sub>2</sub> sol by using PTL-MM01 dip-coater (MTI Corporation) at a coating rate of 15 cm/min. After coating, the TiO<sub>2</sub> film was dried at room temperature for 1 hr and calcined in a programmable furnace (Paragon HT-22-D, Thermcraft). Temperature was increased at a ramp rate of 60 °C/hr to 100 °C and maintained for 1 hr, then further increased to different target temperatures at 350, 400, 450, and 500 °C for 2 hr, and then cooled down naturally, forming N-TiO<sub>2</sub>. To increase the number of coating layers up to seven, the dip-coating and calcination process was repeated. Control

TiO<sub>2</sub> prepared without the surfactants was also prepared only at 500 °C which generally results in high crystallinity and thus high reactivity (Aphairaj *et al.* 2011).

### Reactivity evaluation of N-TiO<sub>2</sub> film

To check quickly whether N-TiO<sub>2</sub> film can be activated under visible light, decomposition of methylene blue (MB) was initially tested because its decomposition can be easily quantified and even visually sensed. Two 15 W fluorescent lamps (Philips) were used at an intensity of 3.52 mW/cm<sup>2</sup> measured by a photonics power meter (Ophir version 15.01). The lamps were mounted with a UV block filter (UV420, Bower) to cut off the spectral range below 420 nm. The concentration of MB was 5 mg/L and the volume of the solution was 10 ml, where one TiO<sub>2</sub> film was submerged. The solution was mixed by using a shaker. Temperature was maintained at around 25 °C and initial pH at 6.5 was not adjusted. The solution was initially kept in dark conditions for 1 hr and then irradiated with visible light for 4 hr, as this was proven by preliminary tests as an appropriate reaction time to best distinguish the reaction kinetics over experimental conditions.

After the test with MB, decomposition of MC-LR (Cayman Chemicals) was targeted under the same conditions except for the initial concentration of MC-LR at 1 mg/L. The effects of various parameters on the decomposition of MC-LR, including calcination temperature, multiple coating layers, and reaction pH, were investigated. Standard conditions (calcination temperature of 500 °C, coating layers of 3, and natural pH of 6.5) were fixed while one parameter was varied. Reaction pH towards acidic conditions was adjusted in sodium phosphate buffer (Fluka) by using H<sub>2</sub>SO<sub>4</sub> (Fluka).

### On-site decomposition of MC-LR

To evaluate the field application potential of the TiO<sub>2</sub> film, an on-site test was briefly conducted in Lake Arlington (Arlington, TX), in which HABS have often occurred. The MC-LR concentration was periodically monitored from July to October in 2016. However, the level of MC-LR during this period was too low to implement a field test and thus some lake water was removed, placed into a

confined area, and spiked with MC-LR to a target of 0.1 mg/L. The volume of the reaction solution was 10 ml. After installing one TiO<sub>2</sub> film, the whole system was directly exposed to solar radiation for 4 hr without a UV filter, as intended. Solar intensity at the top of the reactor was measured with a photonics power meter (Ophir version 15.01).

### TiO<sub>2</sub> characterization and chemical analysis

A Tristar II 3020 (Micromeritics) porosimetry analyzer was used to determine the structural properties of TiO<sub>2</sub> including surface area, pore volume, and pore size and distribution. The zeta potential of the TiO<sub>2</sub> surface at different pH values was measured using a Zeta potential analyzer (SZ-100, Horiba, Japan) and thus the point of zero charge (PZC) of TiO<sub>2</sub> was determined. A Kristalloflex D500 diffractometer (Siemens) was employed to examine the crystal phase of TiO<sub>2</sub>. Nitrogen content in TiO<sub>2</sub> was measured with an X-ray photoelectron spectroscope (Kratos Analytical). Concentration of MB was measured using a UV-Vis spectrophotometer (UV-2550, Shimadzu). MC-LR was monitored with a reversed-phase high performance liquid chromatograph (1200 series, Agilent) and UV detector at 238 nm. Concentration of natural organic matter (NOM) in Lake Arlington was measured by using a total organic carbon (TOC) analyzer (Shimadzu TOC-Vcsn).

## RESULTS AND DISCUSSION

### Physicochemical properties of N-TiO<sub>2</sub> and control TiO<sub>2</sub>

The physicochemical properties of N-TiO<sub>2</sub> made with DEA, which showed the best reactivity under visible light later, are summarized in Table 1. A series of N-TiO<sub>2</sub> films were synthesized at different calcination temperatures. The synthesis temperature is known to greatly influence the properties of TiO<sub>2</sub>, in particular, the crystal phase, structural properties and nitrogen content, and thus its overall reactivity (Sathish *et al.* 2005). The surface area decreased from 151 to 61.1 m<sup>2</sup>/g and porosity also decreased from 41% to 22% when the calcination temperature increased from 350 to 500 °C. Calcination is required to remove surfactant templates

**Table 1** | Physicochemical properties of N-TiO<sub>2</sub> films prepared with DEA at different calcination temperatures

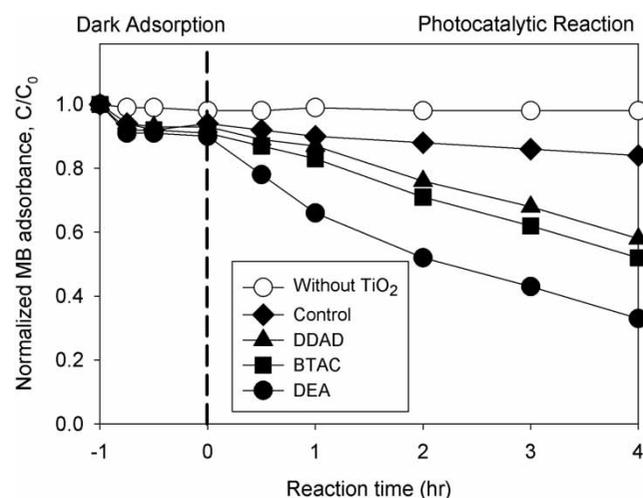
TiO <sub>2</sub> films	Calcination temperature (°C)	Surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Pore size (nm)	Porosity (%)	Crystal phase	Nitrogen content (%)	PZC
N-TiO <sub>2</sub>	350	151	0.181	3.7	41	Anatase	6.3	6.2
N-TiO <sub>2</sub>	400	136	0.142	4.5	35	Anatase	5.2	6.4
N-TiO <sub>2</sub>	450	88.8	0.109	4.8	30	Anatase	3.8	6.5
N-TiO <sub>2</sub>	500	61.1	0.074	4.7	22	Anatase	3.1	6.7
Control TiO <sub>2</sub>	500	50.1	0.012	5.7	4.0	Anatase	0.5	5.4

for creating a porous structure while prolonged calcination at high temperatures also collapses the formed porous structure (Choi *et al.* 2006). All N-TiO<sub>2</sub> films were found to have an anatase crystal phase and to be optically transparent.

Nitrogen content decreased from 6.3 to 3.1% over the temperature increase from 350 to 500 °C because nitrogen is subject to thermal decomposition during the calcination process. The PZC of N-TiO<sub>2</sub> was around 6.2–6.7. When comparing N-TiO<sub>2</sub> (made with DEA) and control TiO<sub>2</sub> prepared at 500 °C, N-TiO<sub>2</sub> had a slightly higher surface area (61.1 m<sup>2</sup>/g) than control TiO<sub>2</sub> (50.1 m<sup>2</sup>/g) and superior porosity (22%) to control TiO<sub>2</sub> (4.0%). In addition, N-TiO<sub>2</sub> contained 3.1% nitrogen while control TiO<sub>2</sub> showed negligible nitrogen (0.5%, most probably from the impurities of the ingredients used as well as from gaseous nitrogen in the air). The properties proved the dual role of DEA as a nitrogen-doping source and a pore-directing agent.

### Photocatalytic decomposition of MB under visible light

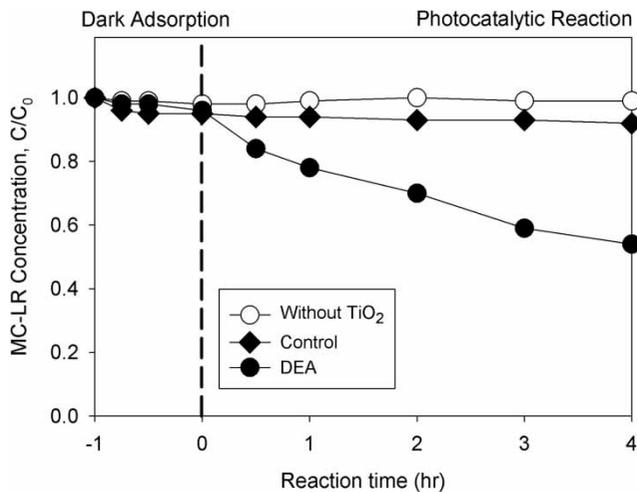
To check quickly whether TiO<sub>2</sub> films prepared with different surfactants are reactive under visible light, decomposition of MB was investigated, as shown in Figure 1. Although MB absorbs visible light mainly at 609 nm and 668 nm, there was no photolysis most probably due to the low light intensity at 3.52 mW/cm<sup>2</sup> (Vaiano *et al.* 2015). Around 4–8% of MB was adsorbed onto N-TiO<sub>2</sub> and control TiO<sub>2</sub> under dark conditions. Control TiO<sub>2</sub> showed negligible reactivity under visible light above 420 nm while all N-TiO<sub>2</sub> films demonstrated significant decomposition of MB. The result implies that the surfactants worked effectively as a nitrogen-doping source for visible light activation of TiO<sub>2</sub>. In particular, N-TiO<sub>2</sub> made with DEA showed the fastest MB decomposition kinetics, i.e., 67% decomposition after 4 hr.



**Figure 1** | Photocatalytic decomposition of MB under visible light (>420 nm) by TiO<sub>2</sub> thin films prepared with different surfactants (N-TiO<sub>2</sub>) (MB concentration: 5.0 mg/L, calcination temperature: 500 °C, number of coatings: 3, and pH: natural at around 6.5). Control TiO<sub>2</sub> was also prepared without surfactants.

### Photocatalytic decomposition of MC-LR under visible light

The N-TiO<sub>2</sub> film made with DEA was further tested with MC-LR, as shown in Figure 2. There was no photolysis of MC-LR since MC-LR does not absorb visible light (Graham *et al.* 2010). Adsorption of MC-LR to TiO<sub>2</sub> films was negligible in this specific case mainly due to *almost neutral* charge of TiO<sub>2</sub> surface at natural pH of around 6.5 (PZC is 6.7 for N-TiO<sub>2</sub> prepared at 500 °C), and partly a small amount of TiO<sub>2</sub> catalyst used in this test. Under visible light, control TiO<sub>2</sub> showed negligible reactivity with MC-LR while N-TiO<sub>2</sub> exhibited significant reactivity, i.e., 47% decomposition of MC-LR after 4 hr. The result confirms that DEA worked effectively as a nitrogen-doping source. Considering that different concentrations for

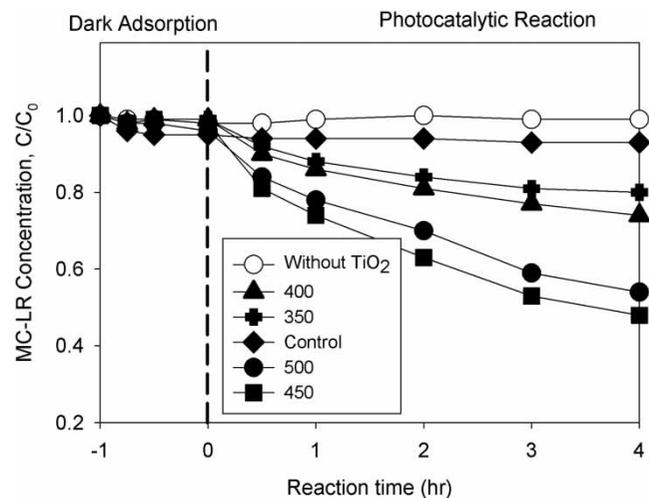


**Figure 2** | Photocatalytic decomposition of MC-LR under visible light (>420 nm) by  $\text{TiO}_2$  thin films prepared with DEA ( $\text{N-TiO}_2$ ) and without DEA (control  $\text{TiO}_2$ ) (MC-LR concentration: 1.0 mg/L, calcination temperature: 500 °C, number of coatings: 3, and pH: natural at around 6.5).

MC-LR (1 mg/L) and MB (5 mg/L) were used, decomposition of MC-LR was much slower than that of MB due to its cyclic structure that is known to provide more chemical stability (Kenefick *et al.* 1993; Sui *et al.* 2014).

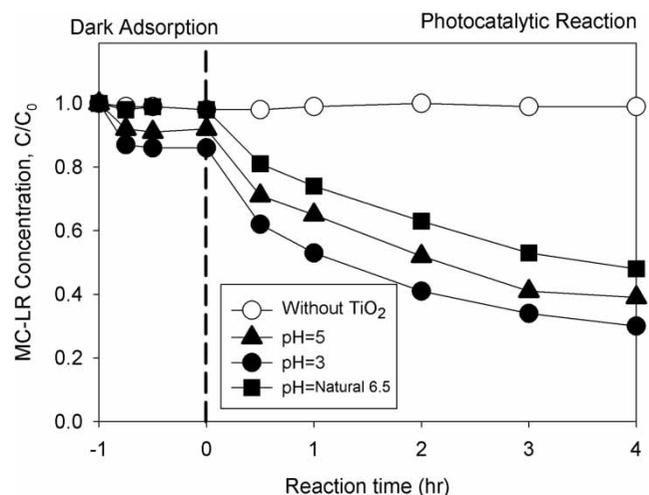
### Decomposition of MC-LR under various conditions

A series of  $\text{N-TiO}_2$  films prepared at different calcination temperatures were examined for the decomposition of MC-LR under visible light, as shown in Figure 3. All  $\text{N-TiO}_2$  films showed high reactivity. When the calcination temperature was increased from 350 to 400 and 450 °C, the reactivity significantly increased although the nitrogen content decreased and the porous structure collapsed. This can be explained by a trade-off effect between crystallization and nitrogen content over calcination temperature (Aphairaj *et al.* 2011). Initial amorphous  $\text{TiO}_2$  is transformed to the most active anatase phase at calcination temperatures above 300 °C and to a less active rutile phase at calcination temperatures above 550 °C (Yu & Wang 2010). It has been well reported that  $\text{TiO}_2$  prepared at around 450–550 °C shows the greatest reactivity due to the formation of the anatase phase with high crystallinity (Kang & Chen 2010; Lin *et al.* 2015; Vaiano *et al.* 2015). A further increase in calcination temperature to 500 °C resulted in a slight decrease in the reactivity most probably due to too low nitrogen content (Choi *et al.* 2007).



**Figure 3** | Photocatalytic decomposition of MC-LR under visible light (>420 nm) by  $\text{N-TiO}_2$  thin films prepared with DEA ( $\text{N-TiO}_2$ ) at different calcination temperatures (MC-LR concentration: 1.0 mg/L, number of coatings: 3, and pH: natural at around 6.5). Control  $\text{TiO}_2$  was also prepared without surfactants at 500 °C.

Reaction pH is another important factor that can affect the photocatalytic decomposition of MC-LR under visible light. Significant decomposition of MC-LR was observed under natural pH of 6.5. When pH was adjusted to acidic conditions, MC-LR was decomposed much faster, as shown in Figure 4. Acidic pH was reported to be favorable for the photocatalytic degradation of MC-LR (Song *et al.* 2006). Under acidic pHs, the surface of MC-LR is negatively



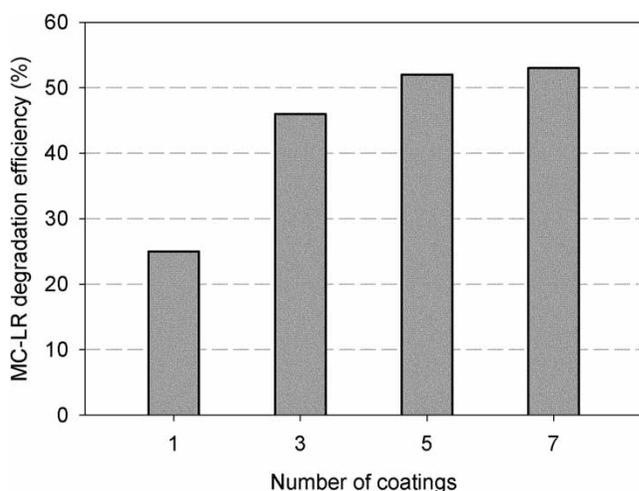
**Figure 4** | Photocatalytic decomposition of MC-LR under visible light (>420 nm) at different reaction pHs by  $\text{TiO}_2$  thin films prepared with DEA ( $\text{N-TiO}_2$ ) (MC-LR concentration: 1.0 mg/L, calcination temperature: 500 °C, and number of coatings: 3).

charged due to dissociation of its free carboxylic group while N-TiO<sub>2</sub> with PZC of 6.7 is positively charged, which leads to increased adsorption and decomposition of MC-LR onto N-TiO<sub>2</sub> due to electrical attraction.

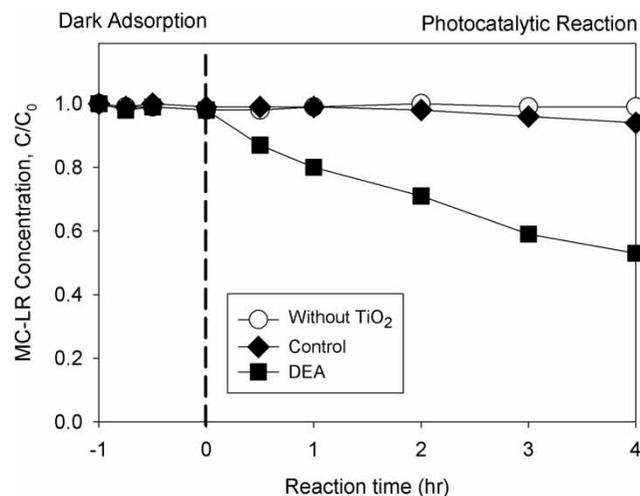
The effect of the number of coating layers was also examined, as shown in Figure 5. When the number of coating layers increased from 1 to 3, MC-LR decomposition almost doubled. Above 3, the number of coating layers did not affect the reactivity significantly. In general, multiple coatings bring more TiO<sub>2</sub> loading to the film, resulting in high reactivity. However, the disproportional increase in the reactivity could be explained by the porous structure of inner TiO<sub>2</sub> layers becoming more collapsed during the repeated calcination processes and thus less available for subsequent chemical reaction (Choi *et al.* 2006). In addition, a reaction rate-limiting factor might be the low intensity of the visible light used in this study (3.52 mW/cm<sup>2</sup>), rather than TiO<sub>2</sub> loading.

### On-site decomposition of MC-LR under solar radiation

The previous experiments were conducted under laboratory conditions employing MC-LR in pure water and artificial visible light. Subsequently, a field test was undertaken to evaluate whether the TiO<sub>2</sub> film can be activated under solar radiation and thus MC-LR in a real water matrix can



**Figure 5** | Photocatalytic decomposition of MC-LR under visible light (>420 nm) for 4 hr by TiO<sub>2</sub> films prepared with DEA (N-TiO<sub>2</sub>) with a different number of coating layers (MC-LR concentration: 1.0 mg/L, calcination temperature: 500 °C, and pH: natural at around 6.5).



**Figure 6** | On-site photocatalytic decomposition of MC-LR in Lake Arlington (Arlington, Texas) under solar radiation by TiO<sub>2</sub> thin film prepared with DEA (N-TiO<sub>2</sub>) (MC-LR concentration: 0.1 mg/L, light intensity: 1.55 mW/cm<sup>2</sup>, calcination temperature: 450 °C, pH = 3, and number of coatings: 5).

be decomposed, as shown in Figure 6. TOC in the lake water, representing NOM as a competing component for TiO<sub>2</sub>, was very high at 15.5 mg/L and solar intensity was at 1.55 mW/cm<sup>2</sup>. The concentration of MC-LR used in this study was 0.1 mg/L, which is much higher than 0.087 mg/L, the average of maximum detection of MCs in eight major lakes in the USA (USEPA 2015). MC-LR was not decomposed at all under solar radiation in the absence of TiO<sub>2</sub> and control TiO<sub>2</sub> was also unable to decompose MC-LR under solar radiation. Only N-TiO<sub>2</sub> showed significant reactivity under solar radiation to decompose MC-LR. Around 47% of MC-LR was decomposed after 4 hr exposure of N-TiO<sub>2</sub> to solar radiation. The result is significant, considering the low solar intensity, the high initial MC-LR concentration, and even the presence of NOM.

### CONCLUSIONS

The overall goal of this study was to develop a new sustainable approach to decompose biological toxins, if feasible, on-site and in real-time with minimal effort, fewer chemicals, and low energy inputs. A high efficiency N-TiO<sub>2</sub> photocatalytic film immobilized onto a glass substrate was fabricated via integrated materials synthesis processing. The N-TiO<sub>2</sub> film was characterized with a highly porous,

anatase crystal, transparent, and nitrogen-doped nature. All the results proved the dual role of DEA surfactant as a nitrogen-doping source and a pore-directing agent. N-TiO<sub>2</sub> prepared with DEA at 450–500 °C exhibited fast decomposition of MC-LR under visible light due to its compromised properties with respect to surface area, crystal phase, and nitrogen content. N-TiO<sub>2</sub> film was able to successfully decompose MC-LR in a lake containing high NOM under solar radiation. This study implies the high potential of the N-TiO<sub>2</sub> film for on-site and real-time decomposition of organic contaminants in water by using sustainable solar energy.

## ACKNOWLEDGEMENTS

This research was supported by the Texas Higher Education Coordinating Board through the Norman Hackerman Advanced Research Program Fund (THECB13311).

## REFERENCES

- Ansari, S. A., Khan, M. M., Ansari, M. O. & Cho, M. H. 2016 Nitrogen-doped titanium dioxide (N-doped TiO<sub>2</sub>) for visible light photocatalysis. *New J. Chem.* **40**, 3000–3009.
- Antoniou, M., De La Cruz, A. A. & Dionysiou, D. D. 2005 Cyanotoxins: new generation of water contaminants. *J. Environ. Eng.* **131**, 1239–1243.
- Aphairaj, D., Wirunmongkol, T., Pavasupree, S. & Limsuwan, P. 2011 Effect of calcination temperatures on structures of TiO<sub>2</sub> powders prepared by hydrothermal method using Thai leucosene mineral. *Energy Procedia* **9**, 539–544.
- Bosc, F., Ayrat, A., Albouy, P. A. & Guizard, C. 2004 Mesosstructure of anatase thin films prepared by mesophase templating. *Chem. Mater.* **16**, 2208–2214.
- Bownik, A. 2016 Harmful algae: effects of cyanobacterial cyclic peptides on aquatic invertebrates - a short review. *Toxicol* **124**, 26–35.
- Campinas, M. & Rosa, M. J. 2010 Removal of microcystins by PAC/UF. *Sep. Purif. Technol.* **71**, 114–120.
- Choi, H., Stathatos, E. & Dionysiou, D. D. 2006 Synthesis of nanocrystalline photocatalytic TiO<sub>2</sub> thin films and particles using sol-gel method modified with nonionic surfactants. *Thin Solid Films* **510**, 107–114.
- Choi, H., Antoniou, M. G., Pelaez, M., de la Cruz, A. A., Shoemaker, J. A. & Dionysiou, D. D. 2007 Mesoporous nitrogen-doped TiO<sub>2</sub> for the photocatalytic destruction of the cyanobacterial toxin microcystin-LR under visible light irradiation. *Environ. Sci. Technol.* **41**, 7530–7535.
- Choi, H., Al-Abed, S. R., Dionysiou, D. D., Stathatos, E. & Lianos, P. 2010 TiO<sub>2</sub>-based advanced oxidation nanotechnologies for water purification and reuse. In: *Sustainability Science and Engineering, Volume 2: Sustainable Water for the Future* (I. Escobar & A. Schafer, eds). Elsevier Science, The Netherlands, pp. 229–254.
- Graham, D., Kisch, H., Lawton, L. A. & Robertson, P. K. J. 2010 The degradation of microcystin-LR using doped visible light absorbing photocatalysts. *Chemosphere* **78**, 1182–1185.
- Jasim, S. Y. & Saththasivam, J. 2017 Advanced oxidation processes to remove cyanotoxins in water. *Desalination* **406**, 83–87.
- Kang, X. & Chen, S. 2010 Photocatalytic reduction of methylene blue by TiO<sub>2</sub> nanotube arrays: effect of TiO<sub>2</sub> crystalline phase. *J. Mater. Sci.* **45**, 2696–2702.
- Kenefick, S. L., Hrudey, S. E., Peterson, H. G. & Prepas, E. E. 1993 Toxin release from microcystins aeruginosa after chemical treatment. *Wat. Sci. Technol.* **27**, 433–440.
- Lawton, L. A. & Robertson, P. K. J. 1999 Physicochemical treatment methods for the removal of microcystins (cyanobacterial hepatoxins) from potable water. *Chem. Soc. Rev.* **28**, 217–224.
- Lazar, M. A., Varghese, S. & Nair, S. S. 2012 Photocatalytic water treatment by titanium dioxide: recent updates. *Catalysts* **2**, 572–560.
- Li, X. Y., Zhang, W. H., Xie, Y. H., Zhang, B. J. & Ding, Q. Q. 2014 Microcystins removal by coagulation and chlorination under laboratory conditions. *Environ. Eng. Manag. J.* **13**, 915–922.
- Lin, J., Liu, X., Zhu, S., Liu, Y. & Chen, X. 2015 Anatase TiO<sub>2</sub> nanotube powder film with high crystallinity for enhanced photocatalytic performance. *Nanoscale Res. Lett.* **10**, 110–115.
- Nfodzo, P., Dionysiou, D. D. & Choi, H. 2013 Water supply and treatment. In: *Encyclopedia of Environmetrics Second Edition* (A. El-Shaarawi & W. Piegorisch, eds). John Wiley & Sons, Chichester, UK, pp. 1712–1726.
- Pelaez, M., Nolan, N. T., Pillai, S. C., Seery, M. K., Falaras, P., Kontos, A. G., Dunlop, P. S. M., Hamilton, J. W. J., Byrne, J. A., O'Shea, K., Entezari, M. H. & Dionysiou, D. D. 2012 A review on the visible light active titanium dioxide photocatalysts for environmental applications. *Appl. Catal. B: Environ.* **125**, 331–349.
- Pelaez, M., Falaras, P., Likodimos, V., O'Shea, K., de la Cruz, A. A., Dunlop, P. S. M., Byrne, J. A. & Dionysiou, D. D. 2016 Use of selected scavengers for the determination of NF-TiO<sub>2</sub> reactive oxygen species during the degradation of microcystin-LR under visible light irradiation. *J. Molec. Catal. A: Chem.* **425**, 183–189.
- Petala, A., Frontistis, Z., Antonopoulou, M., Konstantinou, I., Kondarides, D. I. & Mantzavinos, D. 2015 Kinetics of ethyl paraben degradation by simulated solar radiation in the presence of N-doped TiO<sub>2</sub> catalysts. *Water Res.* **81**, 157–166.
- Roegner, A. F., Brena, B., Gonzalez-Sapienza, G. & Puschner, B. 2014 Microcystins in potable surface waters: toxic effects and removal strategies. *J. Appl. Toxicol.* **34**, 441–457.

- Sathish, M., Viswanathan, B., Viswanath, R. P. & Chinnakonda, S. G. 2005 Synthesis, characterization, electronic structure, and photocatalytic activity of nitrogen-doped TiO<sub>2</sub> nanocatalyst. *Chem. Mater.* **17**, 6349–6353.
- Song, W., de la Cruz, A. A., Rein, K. & O'Shea, K. E. 2006 Ultrasonically induced degradation of microcystin-LR and -RR: identification of products, effect of pH, formation and destruction of peroxides. *Environ. Sci. Technol.* **40**, 3941–3946.
- Sui, X., Wang, X., Huang, H., Peng, G., Wang, S. & Fan, Z. 2014 A novel photocatalytic material for removing microcystin-LR under visible light irradiation: degradation characteristics and mechanisms. *PLOS ONE* **9**, e95798.
- Svircev, Z., Lujic, J., Marinovic, Z., Drobac, D., Tokodi, N., Stojiljkovic, B. & Meriluoto, J. 2015 Toxicopathology induced by microcystins and nodularin: a histopathological review. *J. Environ. Sci. Health: C-Environ. Carcinog. Ecotox. Rev.* **33**, 125–167.
- US EPA (Environmental Protection Agency) 2015 *Drinking Water Health Advisory for the Cyanobacterial Microcystin Toxins, EPA 820R15100; Water*. USEPA, Washington, DC.
- Vaiano, V., Sacco, O., Sannino, D. & Ciambelli, P. 2015 Nanostructured N-doped TiO<sub>2</sub> coated on glass spheres for the photocatalytic removal of organic dyes under UV or visible light irradiation. *Appl. Catal. B: Environ.* **170**, 153–161.
- Yang, G., Jiang, Z., Shi, H., Xiao, T. & Yan, Z. 2010 Preparation of highly visible-light active N-doped TiO<sub>2</sub> photocatalyst. *J. Mater. Chem.* **20**, 5301–5309.
- Yu, J. & Wang, B. 2010 Effect of calcination temperature on morphology and photoelectrochemical properties of anodized titanium dioxide nanotube arrays. *Appl. Catal. B: Environ.* **94**, 295–302.
- Zakersalehi, A., Nadagouda, M. & Choi, H. 2013 Suppressing NOM access to controlled porous TiO<sub>2</sub> particles enhances the decomposition of target water contaminants. *Catal. Comm.* **41**, 79–82.

First received 16 December 2016; accepted in revised form 13 March 2017. Available online 9 May 2017