# All-Dielectric Metasurface for Sensing Microcystin-LR

Subjects: Engineering, Electrical & Electronic Contributor: Qiang Li

Microcystin is a kind of biotoxin widely found in freshwater bodies across the world. It is one of the indicators of water eutrophication which makes water consumption harmful to human beings. Microcystin can inhibit the production of protein phosphatase in cells and exposure to microcystin can severely damage organs, including liver, intestines, lungs, and kidneys. There are many variants of microcystin, such as MC-LR, MC-RR, and MC-YR (L, R, and Y stand for leucine, arginine, and tyrosine, respectively). Among them, MC-LR is the most common and the most toxic variant.

Keywords: all-dielectric metasurface ; quasi bound states in the continuum ; microcystin-LR ; specific recognition ; high sensitivity

## 1. Overview

Sensing Microcystin-LR (MC-LR) is an important issue for environmental monitoring, as the MC-LR is a common toxic pollutant found in freshwater bodies. The demand for sensitive detection method of MC-LR at low concentrations can be addressed by metasurface-based sensors, which are feasible and highly efficient. Here, we demonstrate an all-dielectric metasurface for sensing MC-LR. Its working principle is based on quasi-bound states in the continuum mode (QBIC), and it manifests a high-quality factor and high sensitivity. The dielectric metasurface can detect a small change in the refractive index of the surrounding environment with a quality factor of ~170 and a sensitivity of ~788 nm/RIU. MC-LR can be specifically identified in mixed water with a concentration limit of as low as 0.002 µg/L by a specific recognition technique for combined antigen and antibody. Furthermore, the demonstrated detection of MC-LR can be extended to the identification and monitoring of other analytes, such as viruses, and the designed dielectric metasurface can serve as a monitor platform with high sensitivity and high specific recognition capability.

# 2. Microcystin

Microcystin is a kind of biotoxin widely found in freshwater bodies across the world [1][2][3][4]. It is one of the indicators of water eutrophication which makes water consumption harmful to human beings [5][6][7][8]. Microcystin can inhibit the production of protein phosphatase in cells and exposure to microcystin can severely damage organs, including liver, intestines, lungs, and kidneys [5][6][7][8][9][10][11][12]. There are many variants of microcystin, such as MC-LR, MC-RR, and MC-YR (L, R, and Y stand for leucine, arginine, and tyrosine, respectively). Among them, MC-LR is the most common and the most toxic variant [5][6][13]. According to the World Health Organization recommendations, the MC-LR content in drinking water shall not exceed 1 µg/L [14]. In order to effectively manage microcystin and reduce its health risks, there is an urgent need for a sensitive and reliable method to detect microcystin, especially MC-LR.

Traditionally, the detection of MC-LR relies on an enzyme-based biochemical or chemical chromatography method, and it involves a trade-off between sensitivity and response speed [15][16][17][18][19]. In this regard, metasurface-based sensors can provide a feasible solution with their high sensitivity, real-time analysis, and label-free process [20][21][22]. The metasurface is ultrathin metamaterials consisting of planar microstructures (e.g., meta-atoms) with pre-determined electromagnetic responses arranged in specific sequences, and it enables strong interactions with the electric and/or magnetic components of the incident electromagnetic fields [21][22][23][24][25][26][27]. Due to strong enhancement of the electric field, metasurface based on surface plasmon resonances (SPR metasurface) using metal can detect the presence of MC-LR even at very low concentrations. Hu et al. introduced an indirect SPR immune sensor by covalently linking the coupling of bovine serum albumin and microcystin to the carboxymethyl dextran on the gold surface of a sensor chip [20]. Sonia Herranz et al. systematically evaluated the performance of an SPR biosensor with a sensitivity of 0.2 µg/L [21]. The quality factor is also used to evaluate the performance of metasurface-based sensors [21][24][25]. The quality factor is defined as the underdamped condition of resonance [24][25]. Although the SPR metasurface provides a highly sensitive detection strategy for MC-LR, the quality factor is limited by the intrinsic loss of metal, and the thermal effect of metal inevitably damages the living tissues in case of an in vivo sensing [26][27][28][29].

Dielectric metasurface with high-refractive index and low intrinsic loss has the potential to overcome these limitations <sup>[30]</sup> <sup>[31]</sup><sup>[32]</sup><sup>[33]</sup><sup>[34]</sup><sup>[35]</sup><sup>[36]</sup><sup>[37]</sup><sup>[38]</sup><sup>[39]</sup><sup>[40]</sup><sup>[41]</sup><sup>[42]</sup><sup>[43]</sup><sup>[44]</sup><sup>[45]</sup><sup>[46]</sup><sup>[47]</sup>. Compared with an SPR metasurface, a dielectric metasurface has three distinct advantages. Firstly, a dielectric metasurface can achieve a higher quality factor compared to an SPR metasurface due to its low intrinsic loss <sup>[31]</sup><sup>[32]</sup><sup>[33]</sup><sup>[34]</sup>. Secondly, dielectric such as silicon is harmless to biomolecules without the thermal effect, and thereby, the dielectric metasurface can work for in vivo sensing <sup>[35]</sup><sup>[36]</sup>. Finally, the dielectric metasurface supports not only electric resonance mode but also magnetic resonance mode and higher-order multipole modes <sup>[37]</sup><sup>[38]</sup><sup>[39]</sup><sup>[40]</sup><sup>[41]</sup><sup>[42]</sup><sup>[43]</sup><sup>[44]</sup><sup>[45]</sup><sup>[46]</sup><sup>[47]</sup>. Therefore, dielectric metasurfaces are expected to provide new directions and technologies for label-free detection of MC-LR owing to its high-quality factor and high sensitivity.

In this article, we demonstrate an all-dielectric metasurface based on periodic arrays of elliptical silicon disc pairs for sensing MC-LR with high-quality factor and high sensitivity. These elliptical silicon disc pairs support quasi-bound states in the continuum mode (QBIC), which, in turn, supports resonance with narrow linewidth and strong electric field enhancement in the near-field region of QBIC. Based on this technique, small changes in the refractive index of enhancement region can be detected by the dielectric metasurface with a quality factor of ~170 and a sensitivity of ~788 nm/RIU (refractive index unit). In addition, combined with the antigen-antibody binding technique, the dielectric metasurface realizes the specific recognition of MC-LR even at low concentrations. The limiting concentration for sensing MC-LR in the experiment turns out to be as low as 0.002 µg/L.

## 3. Conclusions

This entry demonstrates an all-dielectric metasurface for sensing MC-LR experimentally with high-quality factor and high sensitivity. First, the all-dielectric device provides a harmless, feasible, and stable detection platform for precise biological monitoring. As the dielectric has no thermal effect, the dielectric metasurface does not damage living tissues for in vivo sensing. Second, the high sensitivity enables it to promptly warn about the presence of MC-LR pollution in freshwater bodies to prevent catastrophic harm to human and animal lives. Third, the dielectric metasurface can also be combined with microfluidics to realize real-time dynamic monitoring of biologically active molecules. Finally, the dielectric metasurface can be fabricated on flexible material and used in smart wearable devices to achieve real-time health monitoring. Essentially, the dielectric metasurface provides a highly sensitive sensing platform for MC-LR and can be extended to other target analytes, such as viruses.

#### References

- 1. van Apeldoorn, M.E.; van Egmond, H.P.; Speijers, G.J.A.; Bakker, G.J.I. Toxins of cyanobacteria. Mol. Nutr. Food Res. 2007, 51, 7–60.
- 2. Humbert, J.F. Toxins of cyanobacteria. In Handbook of Toxicology of Chemical Warfare Agents; Elsevier Inc.: Amsterdam, The Netherlands, 2009; pp. 371–379.
- Mantzouki, E.; Lürling, M.; Fastner, J.; de Senerpont Domis, L.; Wilk-Woźniak, E.; Koreivienė, J.; Seelen, L.; Teurlincx, S.; Verstijnen, Y.; Krztoń, W.; et al. Temperature effects explain continental scale distribution of cyanobacterial toxins. Toxins 2018, 10, 156.
- Zhang, C.; Massey, I.Y.; Liu, Y.; Huang, F.; Gao, R.; Ding, M.; Xiang, L.; He, C.; Wei, J.; Li, Y.; et al. Identification and characterization of a novel indigenous algicidal bacterium Chryseobacterium species against Microcystis aeruginosa. J. Toxicol. Environ. Health Part A 2019, 82, 845–853.
- 5. Massey, I.Y.; Yang, F.; Ding, Z.; Yang, S.; Guo, J.; Tezi, C.; Al-Osman, M.; Kamegni, R.B.; Zeng, W. Exposure routes and health effects of microcystins on animals and humans: A mini-review. Toxicon 2018, 151, 156–162.
- Alosman, M.; Cao, L.; Massey, I.Y.; Yang, F. The lethal effects and determinants of microcystin-LR on heart: A mini review. Toxin Rev. 2020, 1–10.
- An, J.S.; Carmichael, W.W. Use of a colorimetric protein phosphatase inhibition assay and enzyme linked immunosorbent assay for the study of microcystins and nodularins. Toxicon 1994, 32, 1495–1507.
- Zhang, S.; Liu, C.; Li, Y.; Imam, M.U.; Huang, H.; Liu, H.; Xin, Y.; Zhang, H. Novel role of ER stress and autophagy in microcystin-LR induced apoptosis in chinese hamster ovary cells. Front. Physiol. 2016, 7, 527.
- 9. McLellan, N.L.; Manderville, R.A. Toxic mechanisms of microcystins in mammals. Toxicol. Res. 2017, 6, 391–405.
- 10. Yang, S.; Chen, L.; Wen, C.; Zhang, X.; Feng, X.; Yang, F. MicroRNA expression profiling involved in MC-LR-induced hepatotoxicity using high-throughput sequencing analysis. J. Toxicol. Environ. Health Part A 2018, 81, 89–97.

- Wharton, R.E.; Cunningham, B.R.; Schaefer, A.M.; Guldberg, S.M.; Hamelin, E.I.; Johnson, R.C. Measurement of microcystin and nodularin activity in human urine by immunocapture-protein phosphatase 2a assay. Toxins 2019, 11, 729.
- 12. Chen, L.; Yang, S.; Wen, C.; Zheng, S.; Yang, Y.; Feng, X.; Chen, J.; Luo, D.; Liu, R.; Yang, F. Regulation of microcystin-LR-induced DNA damage by miR-451a in HL7702 cells. Toxins 2019, 11, 164.
- Sanz Lobón, G.; Yepez, A.; Garcia, L.F.; Morais, R.L.; Vaz, B.G.; Carvalho, V.V.; De Oliveira, G.A.R.; Luque, R.; Gil, E.D.S. Efficient electrochemical remediation of microcystin-LR in tap water using designer TiO 2 @carbon electrodes. Sci. Rep. 2017, 7, 41326.
- 14. World Health Organization. Cyanobacterial toxins: Microcystin-LR in drinking-water. In Guidelines for Drinking-Water Quality, 2nd ed.; World Health Organization: Geneva, Switzerland, 1998; pp. 1–14.
- 15. Catanante, G.; Espin, L.; Marty, J.L. Sensitive biosensor based on recombinant PP1α for microcystin detection. Biosens. Bioelectron. 2015, 67, 700–707.
- Parker, C.H.; Stutts, W.L.; Degrasse, S.L. Development and Validation of a Liquid Chromatography-Tandem Mass Spectrometry Method for the Quantitation of Microcystins in Blue-Green Algal Dietary Supplements. J. Agric. Food Chem. 2015, 63.
- 17. Marsan, D.W.; Conrad, S.M.; Stutts, W.L.; Parker, C.H.; Deeds, J.R. Evaluation of microcystin contamination in bluegreen algal dietary supplements using a protein phosphatase inhibition-based test kit. Heliyon 2018, 4, e00573.
- Wharton, R.E.; Ojeda-Torres, G.; Cunningham, B.; Feyereisen, M.C.; Hill, K.L.; Abbott, N.L.; Seymour, C.; Hill, D.; Lang, J.; Hamelin, E.I.; et al. Quantification of Microcystin-LR in Human Urine by Immunocapture Liquid Chromatography Tandem Mass Spectrometry. Chem. Res. Toxicol. 2018, 31, 898–903.
- 19. Yuan, J.; Kim, H.J.; Filstrup, C.T.; Guo, B.; Imerman, P.; Ensley, S.; Yoon, K.J. Utility of a PCR-based method for rapid and specific detection of toxigenic Microcystis spp. in farm ponds. J. Vet. Diagn. Investig. 2020, 32, 369–381.
- 20. Hu, C.; Gan, N.; Chen, Y.; Bi, L.; Zhang, X.; Song, L. Detection of microcystins in environmental samples using surface plasmon resonance biosensor. Talanta 2009, 80, 407–410.
- Herranz, S.; Bocková, M.; Marazuela, M.D.; Homola, J.; Moreno-Bondi, M.C. An SPR biosensor for the detection of microcystins in drinking water. Anal. Bioanal. Chem. 2010, 398, 2625–2634.
- 22. Vinogradova, T.; Danaher, M.; Baxter, A.; Moloney, M.; Victory, D.; Haughey, S.A. Rapid surface plasmon resonance immunobiosensor assay for microcystin toxins in blue-green algae food supplements. Talanta 2011, 84, 638–643.
- 23. Sun, S.; He, Q.; Hao, J.; Xiao, S.; Zhou, L. Electromagnetic metasurfaces: Physics and applications. Adv. Opt. Photonics 2019, 11, 380.
- 24. Grupp, W. Optical performance monitoring in optical transport networks. In Optical Performance Monitoring; Elsevier Inc.: Amsterdam, The Netherlands, 2010; pp. 385–421.
- 25. Yang, Y.; Kravchenko, I.I.; Briggs, D.P.; Valentine, J. All-dielectric metasurface analogue of electromagnetically induced transparency. Nat. Commun. 2014, 5, 1–7.
- 26. Zijlstra, P.; Paulo, P.M.R.; Orrit, M. Optical detection of single non-absorbing molecules using the surface plasmon resonance of a gold nanorod. Nat. Nanotechnol. 2012, 7, 379–382.
- 27. Mahmoudi, M.; Lohse, S.E.; Murphy, C.J.; Fathizadeh, A.; Montazeri, A.; Suslick, K.S. Variation of protein corona composition of gold nanoparticles following plasmonic heating. Nano Lett. 2014, 14, 6–12.
- 28. Luo, H.; Li, Q.; Du, K.; Xu, Z.; Zhu, H.; Liu, D.; Cai, L.; Ghosh, P.; Qiu, M. An ultra-thin colored textile with simultaneous solar and passive heating abilities. Nano Energy 2019, 65, 103998.
- 29. Luo, H.; Zhu, Y.; Xu, Z.; Hong, Y.; Ghosh, P.; Kaur, S.; Wu, M.; Yang, C.; Qiu, M.; Li, Q. Outdoor Personal Thermal Management with Simultaneous Electricity Generation. Nano Lett. 2021, 21, 3879–3886.
- Bontempi, N.; Chong, K.E.; Orton, H.W.; Staude, I.; Choi, D.Y.; Alessandri, I.; Kivshar, Y.S.; Neshev, D.N. Highly sensitive biosensors based on all-dielectric nanoresonators. Nanoscale 2017, 9, 4972–4980.
- 31. Mie, G. Beiträge zur Optik trüber Medien, speziell kolloidaler Metallösungen. Ann. Phys. 1908, 330, 377–445.
- 32. Ginn, J.C.; Brener, I.; Peters, D.W.; Wendt, J.R.; Stevens, J.O.; Hines, P.F.; Basilio, L.I.; Warne, L.K.; Ihlefeld, J.; Clem, P.G.; et al. Realizing optical magnetism from dielectric metamaterials. Phys. Rev. Lett. 2012, 108, 097402.
- Caldarola, M.; Albella, P.; Cortés, E.; Rahmani, M.; Roschuk, T.; Grinblat, G.; Oulton, R.F.; Bragas, A.V.; Maier, S.A. Non-plasmonic nanoantennas for surface enhanced spectroscopies with ultra-low heat conversion. Nat. Commun. 2015, 6, 1–8.

- 34. Decker, M.; Staude, I.; Falkner, M.; Dominguez, J.; Neshev, D.N.; Brener, I.; Pertsch, T.; Kivshar, Y.S. High-Efficiency Dielectric Huygens' Surfaces. Adv. Opt. Mater. 2015, 3, 813–820.
- 35. Yavas, O.; Svedendahl, M.; Quidant, R. Unravelling the Role of Electric and Magnetic Dipoles in Biosensing with Si Nanoresonators. ACS Nano 2019, 13, 4582–4588.
- 36. Decker, M.; Staude, I. Resonant dielectric nanostructures: A low-loss platform for functional nanophotonics. J. Opt. 2016, 18, 103001.
- 37. Yang, Y.; Wang, W.; Boulesbaa, A.; Kravchenko, I.I.; Briggs, D.P.; Puretzky, A.; Geohegan, D.; Valentine, J. Nonlinear Fano-Resonant Dielectric Metasurfaces. Nano Lett. 2015, 15, 7388–7393.
- 38. Jahani, S.; Jacob, Z. All-dielectric metamaterials. Nat. Nanotechnol. 2016, 11, 23–36.
- 39. Proust, J.; Bedu, F.; Gallas, B.; Ozerov, I.; Bonod, N. All-Dielectric Colored Metasurfaces with Silicon Mie Resonators. ACS Nano 2016, 10, 7761–7767.
- 40. Kruk, S.; Kivshar, Y. Functional Meta-Optics and Nanophotonics Govern by Mie Resonances. ACS Photonics 2017, 4, 2638–2649.
- 41. Baranov, D.G.; Zuev, D.A.; Lepeshov, S.I.; Kotov, O.V.; Krasnok, A.E.; Evlyukhin, A.B.; Chichkov, B.N. All-dielectric nanophotonics: The quest for better materials and fabrication techniques. Optica 2017, 4, 814.
- 42. Yuan, S.; Qiu, X.; Cui, C.; Zhu, L.; Wang, Y.; Li, Y.; Song, J.; Huang, Q.; Xia, J. Strong Photoluminescence Enhancement in All-Dielectric Fano Metasurface with High Quality Factor. ACS Nano 2017, 11, 10704–10711.
- 43. Overvig, A.C.; Shrestha, S.; Malek, S.C.; Lu, M.; Stein, A.; Zheng, C.; Yu, N. Dielectric metasurfaces for complete and independent control of the optical amplitude and phase. Light Sci. Appl. 2019, 8, 92.
- 44. Leitis, A.; Heßler, A.; Wahl, S.; Wuttig, M.; Taubner, T.; Tittl, A.; Altug, H. All-Dielectric Programmable Huygens' Metasurfaces. Adv. Funct. Mater. 2020, 30, 1910259.
- 45. Ni, Y.; Chen, S.; Wang, Y.; Tan, Q.; Xiao, S.; Yang, Y. Metasurface for Structured Light Projection over 120° Field of View. Nano Lett. 2020, 20, 6719–6724.
- 46. Tian, J.; Li, Q.; Belov, P.A.; Sinha, R.K.; Qian, W.; Qiu, M. High- Q All-Dielectric Metasurface: Super and Suppressed Optical Absorption. ACS Photonics 2020, 7, 1436–1443.
- 47. Koshelev, K.; Kivshar, Y. Dielectric Resonant Metaphotonics. ACS Photonics 2021, 8, 102–112.

Retrieved from https://encyclopedia.pub/entry/history/show/26159