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Nanoplasmonic ecosystem sensors

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ABSTRACT

Rapid advances in design, materials, and fabrication technologies over the past decade have allowed scientists to construct novel sensors to map and investigate the marine environment in new ways. This paper investigates the potential of nanoplasmonic sensors to further improve our understanding of marine ecosystems by providing information on pressing physical, chemical, and biological ocean parameters.

Keywords: Nanoplasmonics, ecosystem sensor, localised surface plasmon resonance, oceanography, sensors

1. INTRODUCTION

Acquiring information and data from the marine environment can be a laborious process which requires expensive equipment or requires time consuming expert analysis of samples taken in the field. On top of this, scientists are being scrutinised regarding their carbon usage in cases where large research vessels, which consume large quantities of fuel and electricity, are required to make measurements. Alternatively, remote methods for measuring ocean colour, salinity, and temperature, such as satellite imaging, have distinct limitations. Currently, satellite-gathered sea surface salinity and temperature readings are estimated via thermal imaging measurements with a spatial resolution of a few tens of kilometers. To fully understand the influence environmental drivers are having on marine habitats and wildlife there is a need to advance past the limits of current observation systems.^{1,2} Nanoplasmonic sensing has the potential to resolve multiple issues surrounding current marine environmental monitoring. Not only can nanoscale sensors make laboratory grade measurements with only milliliters of ocean water, they have low power usage, require little maintenance, and do not impose any physical disturbance to the surrounding marine environment.

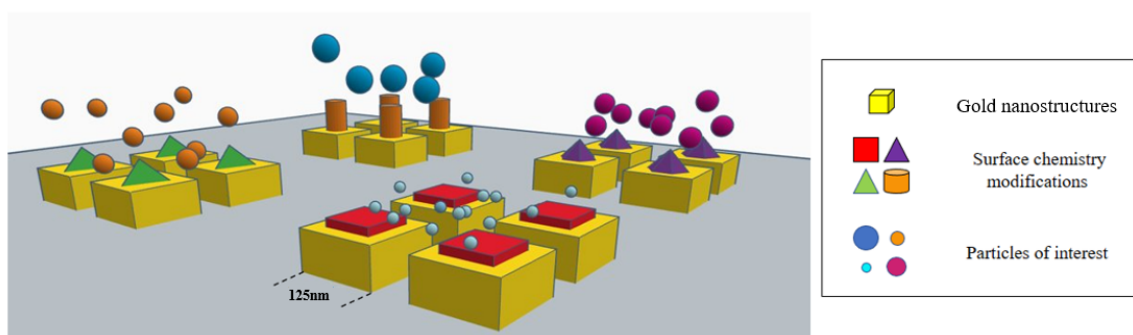


Figure 1. A schematic of a typical nanoplasmonic sensor array, modified with surface-bound capture molecules which are specific to particular analytes of interest. The gold nanostructures have dimensions 125 nm x 125 nm x 50 nm. Attached to the gold nanostructures are surface chemical modifications designed to engage specific molecules at each surface. These molecules are found naturally in the marine environment and range from salts and nutrients to heavy metal ions and pollutants.

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Major industrial advances in remotely operated vehicles have started a movement to replace large offshore vessels as a more environmentally conscious method to assess and repair sub-sea infrastructure.^{3,4} Marine scientists are exploring the possibility of re-purposing this technology for environmental monitoring. With these small vessels comes the need for smaller, portable, robust, low-cost sensors with the capacity to make a variety of accurate measurements across the marine environment. There is now a need for more accessible, multi-purpose sensing capabilities.^{5,6} In this paper, we demonstrate a nanoplasmonic sensor array as a proof-of-concept device for marine sensing; a device we seek to develop further to allow oceanographers to make laboratory grade observations in-situ.

2. NANOPLASMONIC SENSING

Metallic structures have unique properties when manufactured on the nanoscale. Certain wavelengths of light incident on these nanostructures induce a resonant oscillation of charge in the form of the metal's free electrons. This effect is called localised surface plasmon resonance (LSPR). The frequency of this resonance condition is influenced by the size, composition, and morphology of the nanostructure, and, crucial for their use as sensors, the refractive index of the surrounding medium.⁷ This results in easily measurable shifts in the colour of the light scattered from the structures when the molecular composition of their surroundings change. The versatility of this technique has led to the use of LSPR sensors in a broad range applications spanning the agricultural, environmental, and medical sectors.⁸⁻¹¹

3. EXPERIMENTAL SECTION

3.1 Nanostructure Fabrication

A borosilicate glass wafer was spin-coated with a poly(methyl methacrylate) (PMMA) bi-layer (thickness 180 nm). On to the resist 20 nm of aluminium was evaporated (Plassys MEB550S) as a charge conduction layer. Electron beam lithography (Raith EBPG5200 HS) was used to pattern the PMMA with 125 nm squares. After exposure, the aluminium layer was removed using Microposit CD26 developer and the PMMA was developed using an IPA:MIBK (1:2.5) mixture at 20°C for 60 seconds. A 2 nm/50 nm layer of Ti/Au was then evaporated onto the developed sample (Plassys MEB550S). Finally, lift off was performed in a 50°C acetone bath for 1 hour. The final structures can be seen in Figure 2.

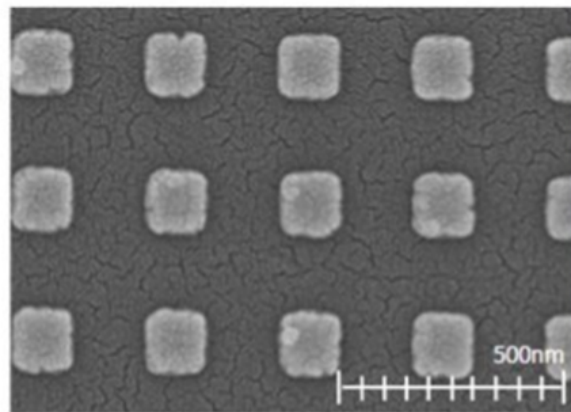


Figure 2. A scanning electron microscopy (SEM) image of a typical device, showing 125 nm gold squares patterned onto a borosilicate glass substrate with a period of 350nm.

3.2 Chemical surface modifications

Non-functionalised gold nanostructures were used to measure ocean salinity. To measure ocean acidity we modified the gold nanostructures with a pH-responsive polyaniline (PANI) polymer.¹² PANI is formed by the

oxidative polymerisation of aniline which was then attached to the gold nanostructures with the aid of a surfactant to decrease surface tension. The sensor was exposed to the chemical modifications for 4hrs and any excess was removed by IPA and acetone cleaning. The chain lengths of PANI polymer grown on the nanostructures were confirmed using an atomic force microscope (AFM) to be approximately 50 nm after a 4 hr functionalisation.

3.3 Sample Preparation

The artificial seawater samples used in this research were varied in concentration and pH in accordance with ASTM international standards.¹³ Exact quantities of different salts were added to solutions of de-ionised water to replicate the organic matter found in real seawater. The salts used were NaCl, MgCl, Na₂SO₄, CaCl and KCl. All sample volumes used in experimentation were 3 ml. Samples which varied in pH were controlled with differing concentrations of NaOH.

3.4 Optical Measurements

Tracking the resonance wavelength of our nanostructures requires only that we illuminate them with white light, and collect the light which is transmitted through the sensor. To do this we use a simple bench top microscope and spectrometer. The light source was a fibre-coupled 10dB broadband LED. This light is passed through an aspheric condenser lens (f=32mm, NA=0.76) and onto the sensor. The collection objective lens was a 10X, 0.25 NA, 10.6 mm WD Olympus Plan Achromat. The collected light was then fed into a StellarNet Blue Wave spectrometer using an optical fibre. The spectrometer uses a detector integration time of 350 ms and records the average intensity of 3 measurements over a wavelength range between 400nm to 900nm. To eliminate any background light interference, a dark and light reference measurement was taken before each reading. Spectra were smoothed using a Lorentzian fit.

4. RESULTS AND DISCUSSION

4.1 Ocean Salinity

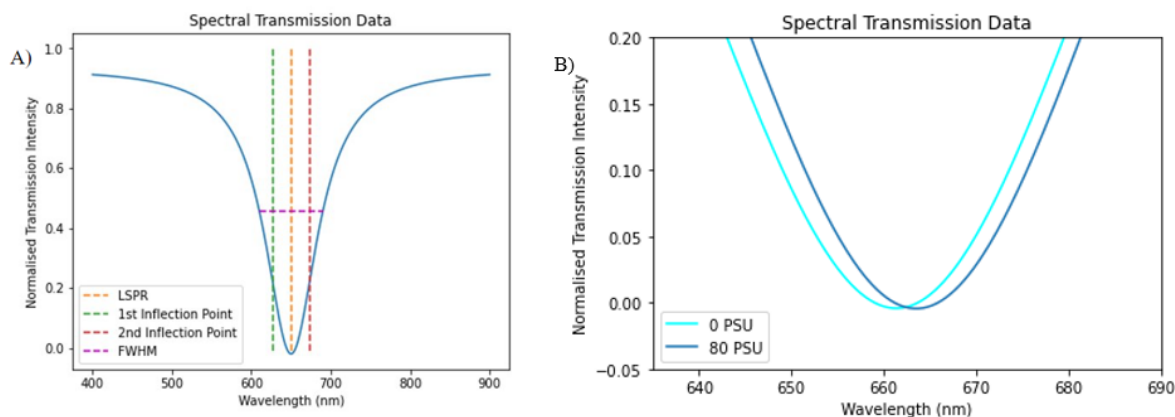


Figure 3. A) Transmission data demonstrating some of the spectral characteristics that are extracted for further analysis. LSPR is the minimum wavelength value of the curve; the 1st and 2nd inflection points are the points on the curve where the differential of the curve is equal to zero; and the FWHM is the width of the curve at half of the maximum intensity. B) A comparison of the transmission response from seawater solutions with salinity 0 PSU and 80 PSU.

To determine the sensitivity to salinity, an un-modified sensor was tested using a series of artificial seawater samples. Samples were varied across a large range of salinity (0 PSU to 80 PSU, which is equivalent to $\Delta 0.0144$ RIU) with their concentration verified using a refractometer. The same sensor was used throughout the experiment. Between each reading, the sensor was cleaned using DI water and ethanol, before being dried with nitrogen.

Figure 3 A) shows a typical transmission response. The key spectral characteristics of the transmission curve are the full-width half maximum, and the LSPR wavelength, and the 2 inflection points of the curve's differential. Tracking these inflection points has been shown to improve the sensitivity of nanoplasmonic sensors (when compared to merely tracking the peak resonance wavelength).^{14,15}

By taking an abundance of transmission measurements across a large range of ocean salinity, we can establish a salinity measurement scale based upon the LSPR wavelength. Figure 3 B) illustrates that the LSPR red-shifts from 661.25nm to 663.5nm as we increase the salinity of the samples. The sensitivity of 147 nm/RIU is calculated from regression analysis of the LSPR data over the measured range of salinity. With the current experimental setup, spectrometer resolution (0.25 nm) and device sensitivity, we can differentiate salinity in steps of 9 PSU ($\Delta 1.6 \times 10^{-3}$ RIU).

If a sensor of this type were to be used in the field, a more sensitive response would likely be required. Ocean salinity typically falls within a range of 32 PSU to 37 PSU, which in terms of RIU equates to a difference of $\Delta 9 \times 10^{-4}$ RIU. Measuring salinity to 1 PSU over the oceanic range using a plasmonic sensor would require a sensitivity around 1400 nm/RIU.

4.2 Ocean Acidity

A similar experimental procedure was applied to measure ocean acidity. Here, we investigated if different ions could be detected using a single sensor. Initially, a sensor modified with PANI polymer was submerged in varying solutions of pH controlled by solutions of NaOH. The LSPR wavelength response of the sensor was investigated from pH 8 to pH 14, which refers to NaOH solutions varying in concentration from $1 \mu\text{M}$ to 1M. The results show a red-shift in LSPR wavelength as pH increases.

To test the selective nature of the sensors response to different ions, a second sensor modified with PANI polymer was submerged in several ionic solutions including NaOH, NaCl, NaNO₃, NaCO₃ and Na₂SO₄ (1M concentration of all solutions). These ions are selected to represent different organic materials typically found in seawater. The results show a unique resonance response across the 5 ionic solutions measured in this experiment.

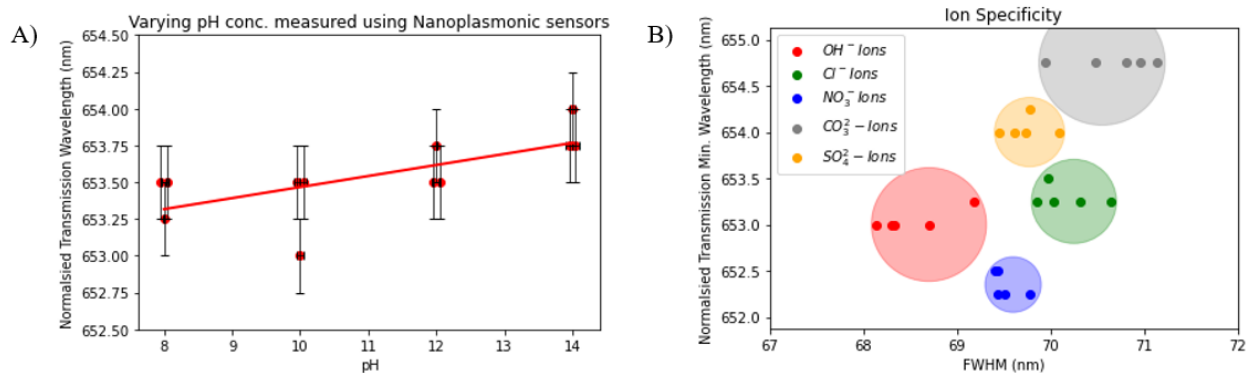


Figure 4. A) LSPR peak values for a range of solutions with different pH values. B) Interaction specificity of a PANI functionalised surface with hydroxide, chloride, nitrate, carbonate and sulphate ions. This figure compares the LSPR wavelength and FWHM of each transmission spectral curve.

Figure 4 A) shows the change in LSPR wavelength over an alkaline range of pH. Further investigation is needed to optimise the polymer chain length to maximise response to changing pH. Figure 4 B) demonstrates the selective spectral responsive of a PANI functionalised sensor with regard to 5 different ionic solutions. The ability to measure salinity and acidity is important to oceanographers as it is a measure of the balance of nutrients in the ocean. Having the ability to sense each component of seawater individually would give a far greater understanding of our complex marine ecosystems. This technology shows promising signs of recognising distinct interactions with the hopes of expanding this research to measure more organic matter with a useful limit of detection.

5. CONCLUSION

We have demonstrated a proof-of-concept device capable of measuring changes in salinity and acidity of artificial ocean water samples. The versatility and simplicity of the nanoplasmonic sensors shown here make them a useful addition to the suite of environmental monitoring technologies available to researchers. Further refinements aimed at measuring nutrients and other natural ocean elements are now being developed.

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REFERENCES

- [1] Foltz, G. R., Brandt, P., Richter, I., Rodríguez-Fonseca, B., Hernandez, F., Dengler, M., Rodrigues, R. R., Schmidt, J. O., Yu, L., Lefèvre, N., et al., “The tropical atlantic observing system,” *Frontiers in Marine Science* **6**, 206 (2019).
- [2] Davies, E. J., Basedow, S. L., and McKee, D., “The hidden influence of large particles on ocean colour,” *Scientific Reports* **11**(1), 1–9 (2021).
- [3] McLean, D. L., Parsons, M. J., Gates, A. R., Benfield, M. C., Bond, T., Booth, D. J., Bunce, M., Fowler, A. M., Harvey, E. S., Macreadie, P. I., et al., “Enhancing the scientific value of industry remotely operated vehicles (rovs) in our oceans,” *Frontiers in Marine Science* **7**, 220 (2020).
- [4] Macreadie, P. I., McLean, D. L., Thomson, P. G., Partridge, J. C., Jones, D. O., Gates, A. R., Benfield, M. C., Collin, S. P., Booth, D. J., Smith, L. L., et al., “Eyes in the sea: unlocking the mysteries of the ocean using industrial, remotely operated vehicles (rovs),” *Science of the Total Environment* **634**, 1077–1091 (2018).
- [5] Ho, C. K., Robinson, A., Miller, D. R., and Davis, M. J., “Overview of sensors and needs for environmental monitoring,” *Sensors* **5**(1), 4–37 (2005).
- [6] Butt, M. A., Voronkov, G. S., Grakhova, E. P., Kutluyarov, R. V., Kazanskiy, N. L., and Khonina, S. N., “Environmental monitoring: A comprehensive review on optical waveguide and fiber-based sensors,” *Biosensors* **12**(11), 1038 (2022).
- [7] Kelly, K. L., Coronado, E., Zhao, L. L., and Schatz, G. C., “The optical properties of metal nanoparticles: the influence of size, shape, and dielectric environment,” (2003).
- [8] Sepúlveda, B., Angelomé, P. C., Lechuga, L. M., and Liz-Marzán, L. M., “Lspr-based nanobiosensors,” *Nano today* **4**(3), 244–251 (2009).
- [9] Petryayeva, E. and Krull, U. J., “Localized surface plasmon resonance: Nanostructures, bioassays and biosensing—a review,” *Analytica chimica acta* **706**(1), 8–24 (2011).
- [10] Masson, J.-F., “Portable and field-deployed surface plasmon resonance and plasmonic sensors,” *Analyst* **145**(11), 3776–3800 (2020).
- [11] Jackman, J. A., Ferhan, A. R., and Cho, N.-J., “Nanoplasmonic sensors for biointerfacial science,” *Chemical Society Reviews* **46**(12), 3615–3660 (2017).
- [12] Gayathri, V., Jaisankar, S. N., and Samanta, D., “Temperature and ph responsive polymers: sensing applications,” *Journal of Macromolecular Science, Part A* **59**(2), 98–126 (2022).
- [13] Lake Products Company LLC, L., ““artificial seawater” astm d1141-98 composition,” (2019). <https://www.artificalseawater.com/products/-artificial-seawater-astm-d-1141-98>.
- [14] Jeon, H. B., Tsalu, P. V., and Ha, J. W., “Shape effect on the refractive index sensitivity at localized surface plasmon resonance inflection points of single gold nanocubes with vertices,” *Scientific reports* **9**(1), 1–8 (2019).
- [15] Chen, P., Tran, N. T., Wen, X., Xiong, Q., and Liedberg, B., “Inflection point of the localized surface plasmon resonance peak: a general method to improve the sensitivity,” *ACS sensors* **2**(2), 235–242 (2017).