

Carbonate optical nanosensors: New mechanisms and their advantages

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In Situ concentration profile mapping of carbonate (CO_3^{2-}), bicarbonate (HCO_3^-) and dissolved carbon dioxide (CO_2) in natural waters (rivers, lakes etc.) as a function of depth is highly relevant for environmental analysis and might serve as a source of insight into the evolution mechanisms of such complex ecosystems. Numerous solutions for both potentiometric and optical sensing of carbonate and carbon dioxide in aqueous and gaseous samples have been proposed over the years,¹ yet such practical tools for spatially resolved analysis as emulsion-based nanooptodes have generally been overlooked.

We are here describing carbonate-selective nanosensors based on either a chromoionophore or a solvatochromic dye as an optical reporter. The sensing appears to predominantly take place on the surface of the nanoparticle and is subject to an influence from lipophilic cations present in the sample transferring into the sensor phase. This is successfully used to enhance sensor performance by adding a second dye into the sample with the subsequent use of a ratiometric readout (Fig. 1). We note that sample alteration is unfavorable for routine *in situ* applications of carbonate-selective nanoparticles. A thorough mechanistic study is carried out, the dual solvatochromic dye approach is expanded and the nature of the interactions between the dyes is investigated.

Solvatochromic Carbonate Sensors

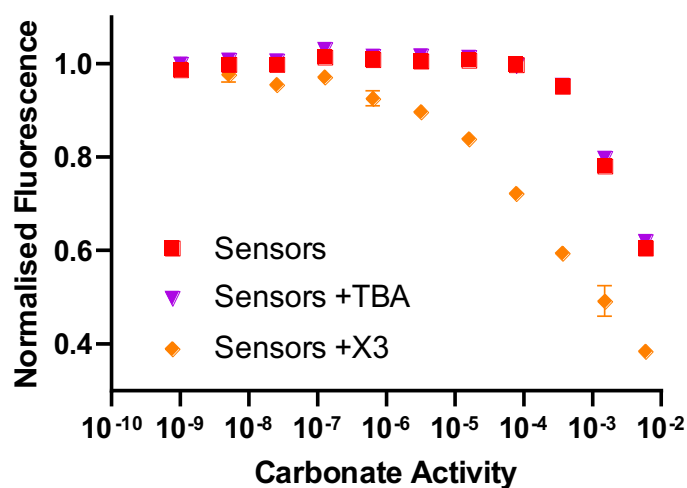


Figure 1. Solvatochromic carbonate sensor response modulated by the addition of a second dye, X3, to the sample solution.

[1] X. Xie, M. Pawlak, M. Tercier-Waeber, E. Bakker, *Anal. Chem.*, **2012**, *84*, 3163-3169.