

Layered Chromogenic Films for pH Sensing

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ABSTRACT

Robust, flexible alternatives are being sought to the classic glass pH electrode. Of particular interest are those based on optical means of signal transduction. Indicator molecules have been widely explored for pH monitoring when dispersed in solutions and more recently quantum dot materials have been shown to produce narrow bandwidth fluorescence emission. Herein we have placed both types of materials into polymeric films and demonstrated a simple yet effective way of measuring changes in pH through colorimetric monitoring of the films.

Keywords: luminescence, sensing, quenching, quantum dots, nanocrystals

1 INTRODUCTION

Monitoring pH has is crucial in a broad variety of applications and is becoming an ever more prominent parameter of interest nowadays as it plays a key in the function of many processes. For examples, pH is crucial in biological systems, with variations affecting many physiological processes. A broad range of industrial chemical processes are also strongly dependent on pH, with undesired values affecting production output and ultimately costs. In the food processing industry it also plays a key role in quality control. It is a critical parameter in the monitoring of industrial trade waste and water discharge, as regulators worldwide nowadays place tight controls on the pH of effluent.

Yet despite the apparent ubiquity of both its need and use, there still remains much research activity in this area, particularly in the development of smaller, more robust, less expensive pH monitoring devices which can be applied in many novel ways. Consequently, the development of inexpensive, flexible, robust pH sensors remains a key challenge.

Having established that monitoring pH is a critical capability, it is well noted that in most lab applications pH monitoring is carried out using the electrochemical glass electrode developed decades ago. This electrode, despite its well established accuracy and reliability, it does have limitations that make it ill-suited for many real-world applications. Such applications include in-vivo biomedical, clinical or where there may be size limitations or need for

deformability [1]. Another example comes from the food industry, where glass materials are highly undesired and this has led to a push in fabricating pH sensors based on polymeric materials that are food grade and do not suffer from the ability to break and release glass shards into the process. As a result, research into novel pH sensing systems continues to be an active area.

Sensors with an optical mode of operation have gained prominence, particularly those based on chromogenic and luminescent molecules. Such molecules work by either changing their color according to a pH transition (absorption based), changing the color at which they produce light (luminescence based), or cease producing light with pH (quenching based). pH indicator molecules, such as organic dyes, do have several advantages over conventional electrochemical pH sensors, however, they tend to be specific to a narrow pH range. Fortunately the breadth of molecules that fulfill this function is such that the pH range from 1 to 12 can be covered.

Recently fluorescent semiconductor quantum dots (QDs), which exhibit strong, narrow band fluorescence emission, have been shown to be applicable to a variety of sensing applications [2]. One of the attractive features of semiconductor quantum dots is that they can absorb light over a broad range of wavelengths yet only emit light a fixed narrow band. They have been demonstrated as sensors whereby their luminescence intensity decreases in the presences of a quencher, however the downside is that this quenching is mostly irreversible.

Here we report the development of flexible, water permeable, chromogenic films loaded with pH sensitive dyes whose optical properties have been tailored to those of the QDs. The QD itself may be embedded into either the same film as the dye or into a second impermeable film. These systems can be used for reversibly sensing pH changes by monitoring the QD's fluorescence emission.

Our approach involves coupling the optical properties of QDs with those of the pH indicator dye molecules. Under defined conditions, the dye in absorbing mode is chosen to either block the incoming light that stimulates the QD fluorescence, or to absorb the QDs outgoing fluorescence emission. By incorporating multiple dye/QD couples, it is possible to obtain high intensity signals for a wide range of pH.

The films can be easily cast onto a variety of substrates, including optical fiber tips, making them quite robust.

2 EXPERIMENTAL

Two types of CdSe/ZnS core-shell QDs were synthesized, each of different size and hence optical absorption and fluorescence properties. A colloidal synthesis approach was taken where the CdSe cores were first formed, followed by successive shelling with ZnS, thus yielding the core/shell QDs. Each type of QD was selected so that its fluorescence emission overlapped with the defining absorption band of a corresponding pH dye molecule.

The QDs were coupled to p-nitrophenol (4-hydroxynitrobenzene) and propyl red (2-[4-(Dipropylamino)phenylazo]benzoic acid). In alkaline and neutral pH, p-nitrophenol is a vivid yellow color and absorbs strongly near 400nm, and is in its deprotonated, anionic form. At lower pH it is colorless, with a transition at around pH 4.5. Propyl red on the other hand shows a strong absorption band at around 550nm and exhibits a transition from red to yellow when going from acidic to alkaline conditions. The dye/QD couples were embedded into polymeric matrices which themselves are optically transparent and water permeable. The resultant mixtures were then solvent cast onto glass substrates thus forming the film.

The films were prepared by mixing polyvinyl chloride (PVC) powder with 2-nitrophenyl octyl ether as a plasticizer in tetrahydrofuran (THF) and the appropriate additions of the dye molecule. To prevent any possible leaching from the PVC film, the dyes were also chemically modified. This typically involved the conjugation of an alkyl chain to the dye molecule itself, thus not only rendering it less water soluble, but also more amenable to being incorporated within the PVC matrix.

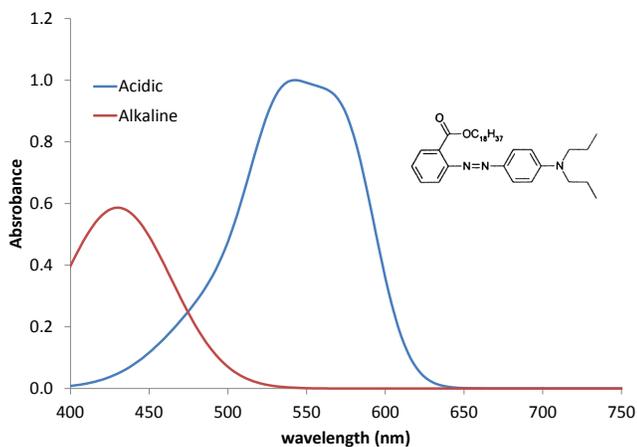


Figure 1: absorbance spectrum of modified propyl red in acidic and alkaline pH, molecule shown in inset.

An example can be seen in the inset Figure 1, which shows the addition of a long alkyl chain near the carboxylate functionality of the molecule. The figure also

shows the absorbance properties of the modified propyl red dye molecule. Under alkaline conditions a single absorption peak is present at around 440nm with a FWHM of around 90nm and the rest of the spectrum is flat. Acidic conditions see a significant change in the absorption properties, with the 440nm peak becoming suppressed and the new, broad peak emerges at around 550nm.

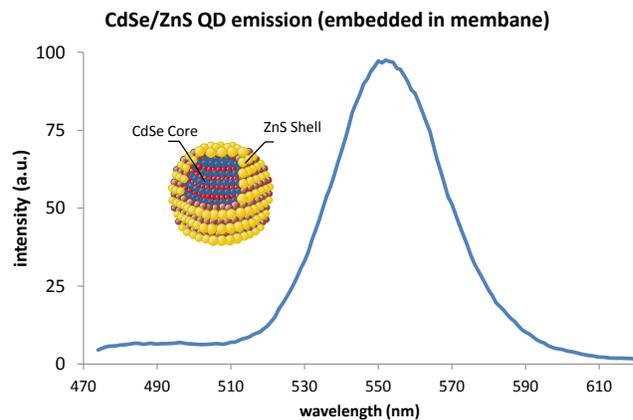


Figure 2: CdSe/ZnS QD fluorescence emission whose wavelength overlaps with the modified propyl red absorption (QD schematic shown in inset).

For a system in which the QDs outgoing fluorescence was to be blocked by the dye layer, the QDs emission should overlap with either of the absorption peaks in the dye. For this case the 550nm peak was selected and the respective QDs emission was matched to this wavelength, as seen in Figure 2.

A similar approach was taken for the p-nitrophenol system. p-nitrophenol shows strong absorbance in the blue region centered around 400nm at pH above 7, therefore it could be used to block the incoming excitation to the QDs. Consequently these two systems were explored herein. The films were fabricated by layering either dye film over a second film containing the QDs.

2.1 Testing Chamber and Experimental Conditions

To test the layers, a cell was constructed which consisted of an LED excitation source of appropriate wavelength for each membrane, a reservoir for the liquid, a window/slot into which the dye/QD film was placed and behind the film a photodiode with appropriate blocking filters to collect the light signal from the QDs. Throughout the experiments the pH was adjusted and the signals recorded following each pH adjustment. A schematic representation of the system is shown in Figure 3.

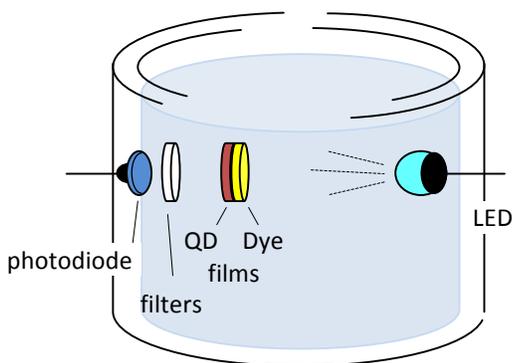


Figure 3: Schematic representation of the optical testing system.

3 RESULTS

Figure 4 shows the photographs of the modified dyes in films after having been exposed to alkaline and acidic conditions. The films are quite robust and can be peeled and stretched without tearing. The figure also shows the fluorescence of the QDs in solution and also in thin film form. Placing either the dyes or the QDs into the films did not affect their optical properties.

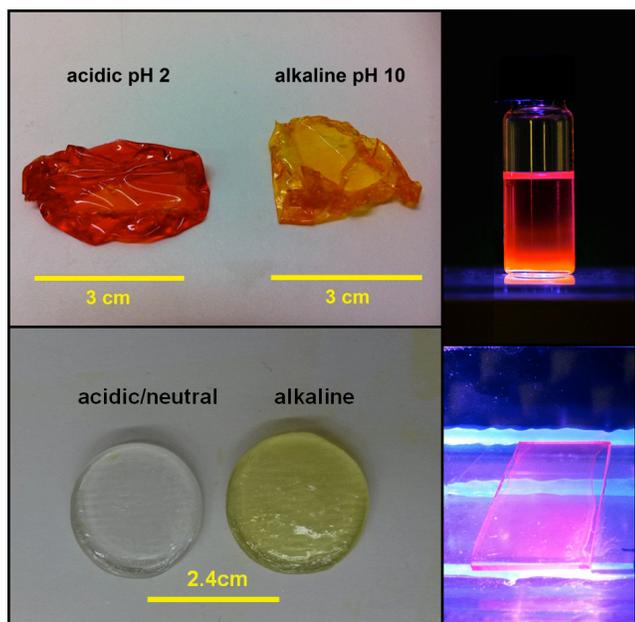


Figure 4: Optical images of the modified propyl-red (top left) and p-nitrophenol (bottom left) sensing films at different pH. Fluorescent colloidal QDs (top right) and QDs in polymer matrix (bottom right)

Figure 5 shows the response of the p-nitrophenol dye/QD systems at different pH. Fluorescence spectra were recorded following the films being exposed to the aqueous solutions of differing pH for 30 seconds. Excitation was carried out at 400nm. As seen from the figure, under

alkaline conditions the dye successfully absorbs the incoming 400nm excitation thus preventing the QDs from fluorescing. In acidic conditions the dye film is optically transparent and hence the light from the LED is able to excite the QDs. The optical transitions were repeatable.

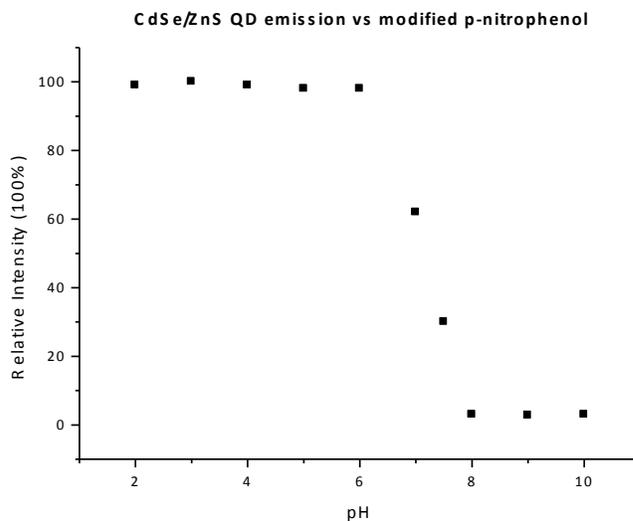


Figure 5: Fluorescence emission of the layered QD/dye p-nitrophenol film couple at different pH.

The response of the modified propyl red/QD system is shown in Figure 6. Excitations were carried out at 350nm. The dye successfully absorbs the QD emission during acidic condition, whereas in alkaline its 550nm absorption is suppressed, thus being transparent to the QD's emissions.

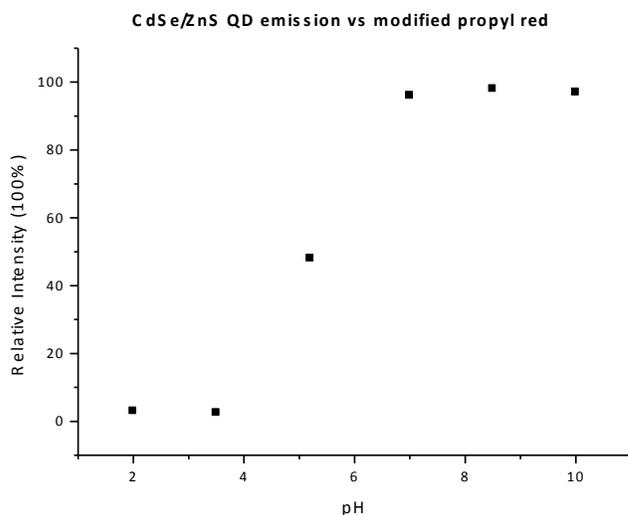


Figure 6: Fluorescence emission of the layered QD/propyl red dye film couple at different pH.

4 CONCLUSION

Embedding pH sensitive molecules into and quantum dot nanocrystals is an exciting prospect for the fabrication of simple, inexpensive and even disposable sensors. The robustness of the films and their ease of deposition makes them promising candidates for direct fabrication onto optical fibers and thus serve as optodes for pH sensing. By couple dye molecules to QDs having different fluorescence emissions and hence different colors enables the discrete color of the QD emission to be associated with a different pH range. The concept can be extended to not only sensing pH, but also to sensing other analytes.

REFERENCES

- [1] W-D Huang, H. Cao, S. Deb, M.Chiao, J.C. Chiao, "A flexible pH sensor based on the iridium oxide sensing film", *Sensors and Actuators A*, 169, 2011 1-11
- [2] M.F. Frasco and N. Chaniotakis, "Semiconductor Quantum Dots in Chemical Sensors and Biosensors", *Sensors* 2009, 9, 7266-7286
- [3] X. Zhang, A. Fakler, U.E. Spichiger "Design of pH microelectrodes based on ETH⁺ 2418 and their application for measurement of pH profile in instant noodles", *Analytica Chimica Acta* 445 2001, 57-65