Sensor technologies based on a cellulose supported platform†

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A simple approach to sensor development based on encapsulating a probe molecule in a cellulose support followed by regeneration from an ionic liquid solution is demonstrated here by the codissolution of cellulose and 1-(2-pyridylazo)-2-naphthol in 1-butyl-3-methylimidazolium chloride followed by regeneration with water to form strips which exhibit a proportionate (1 : 1) response to Hg(II) in aqueous solution.

Modern society produces an enormous amount of chemical waste, *e.g.*, in the production of polymers, pharmaceuticals, *etc.*, and radioactive and biological wastes or byproducts continue to cause concern. Many of these compounds are released to the environment, and pose a threat to the health of living organisms. Thus, from contaminants, to light barriers, to blood sugar detection, the applications of sensing technologies are ubiquitous.

There is currently a growing need for new sensing devices, and this growth is likely to continue[1] as new analytes and new applications are studied. Recent major emphasis in this area can be found in the developments of the so called "chemical nose" and "chemical tongue".[2,3] There is a drive, therefore, to develop inexpensive, reusable, and portable sensors and sensor platforms that can detect specific compounds (*e.g.*, DDT, dioxin, *etc.*), or an entire class of compounds, such as heavy metals.

Cellulose is an abundant biorenewable resource that has been utilized as a support for sensing agents both in the past and in new applications. Cellulose is a prime candidate for a sensor support due to its hydrophilic nature and its ability to resist chemical attack and degradation.[4] Many useful sensing molecules are hydrophobic and thus not compatible with the cellulose support, thus, the sensing agent is often attached covalently to the surface,[5] or additional chemical treatments are required,[6] both increasing the cost or modifying the performance of the sensor.

Ionic liquids (ILs) are a class of salts that exhibit low melting points often paired with other favorable properties, such as wide electrochemical windows, high flexibility, and moderate viscosity, while usually retaining typical properties of salts, such as negligible vapor pressure.[7] Because of these favorable properties, ILs themselves are being studied for their potential use in new sensing applications, for example ion-sensors,[8] gas-sensors,[9] and sensors for water[7] and ethanol.[10] Nonetheless, ILs may be too expensive for routine use as a disposable sensor.

We[11,12] and others[13] have shown that several ILs directly dissolve cellulose and a wide range of compounds that are difficult to dissolve in traditional solvents.[14–16] We[11] have demonstrated previously that the cellulose in IL solution can be regenerated using a non-solvent into a variety of physical forms, and the IL recycled. Given that many functional probe molecules and cellulose can be dissolved in an IL at the same time, we hypothesized that an inexpensive route for the manufacture of a variety of new and simple sensing applications with very different sensing molecules could be developed through solution processing. We present here a proof of this concept with a class of sensors based on Hg(II) sensing agents physically encapsulated in a cellulose matrix. These cellulose-based sensors have several advantageous features, including low cost, high flexibility, a huge diversity of physical forms that can be realized, and easy preparation and handling. Additionally important, they can be environmentally benign if the probe is chosen wisely and the sensor is disposed of properly.

The issue of heavy metal pollution, especially by mercury, has generated a great deal of concern in recent years, and thus the detection of Hg(II) was chosen for a proof of concept. The effects of mercury, an extremely toxic element, are visible within living cells. Mercury binds well to sulfur-containing proteins and enzymes, thus inactivating important cell functions.[17] Despite its proven toxicity, mercury and its salts are extensively utilized in a large number of industrial applications. For example, many mercury-containing compounds are used in electrical equipment, catalysts, and paints, and are produced in processes involved in mining.[18] Thus, while many currently available methods for Hg(II) detection rely on electrochemistry and spectrophotometry, an inexpensive, portable, and quick device is needed for field testing.

We observed that the hydrophobic dye/metal complexant 1-(2-pyridylazo)-2-naphthol (PAN) is readily dissolved in the IL 1-butyl-3-methylimidazolium chloride ([C_4mim]Cl), and that it can be dissolved in the absence or presence of dissolved cellulose. PAN has been reported as a valuable extractant and indicator for metal ions,[19] and its incorporation in a wide array of substrates for metal ion detection is well studied.[20–23] Here we demonstrate the use of [C_4mim]Cl for the co-dissolution of PAN and cellulose to rapidly prepare inexpensive sensors for Hg(II) detection.

PAN in cellulose composites were prepared by first dissolving the cellulose in [C_4mim]Cl, and then adding PAN as a weight percent with respect to the mass of the cellulose in the IL solution.

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The resultant solution was vigorously stirred to ensure a homogenous distribution of PAN throughout the cellulosic solution, and cast into a thin film using a coating rod. The film was rinsed with deionized water to dissolve the water soluble [C_4mim]Cl. The film was free from visible particles, orange in color, and opaque (Fig. 1). After washing was complete, strips (1.5 cm × 3 cm) were cut from the sheet.

A Hg(II) stock solution was prepared by dissolving $Hg(NO_3)_2\cdot H_2O$ in 0.01 M HNO_3 and lower concentrations were prepared by dilution. Upon contact of the films with aqueous Hg(II) solutions, PAN–Hg(II) complex formation was achieved within 1–10 min, depending on the Hg(II) concentration. (Fig. 1-left shows the distinct color change from the orange unreacted PAN sensor to the dark purple reacted sensor.) At lower concentrations, a visual color change was observed after approximately 5 min; at higher concentrations, a visual color change could be observed almost immediately. For consistency, all measurements were made after 10 min contacts. UV–visible absorbance spectra (Varian Optical Cary 3C UV–visible spectrophotometer; Mulgrave, Australia) for the unreacted and reacted films were collected by mounting the films on glass microscope slides and subtracting the baseline absorbance of the microscope slide.

The heterocyclic nitrogen and the hydroxyl group in PAN have pK_a values (pK_{NH} = 1.9; pK_{OH} = 12.2) allowing for the complexation to be fine tuned simply by controlling the pH.[24] The pH dependence of the sensors was determined by contacting the sensor strips with 50 ppm aqueous Hg(II) solutions at pH values 3.4, 4.0, 4.5, 5.0, 5.5, 5.9, 6.5, and 7.2 and measuring the resultant UV–visible absorbance. At pH 6.5 and 7.2 (prepared using a NaOH–NaH_2PO_4 buffer) the films were too intensely colored to be accurately measured with the protocol used here. All subsequent studies were thus carried out in buffered solutions at pH = 5.5.

The spectra shown in Fig. 2 were collected after contact of fresh sensor strips with aqueous Hg(II) solutions of concentrations ranging from 5–100 ppm. The black line is the blank, the absorption of a cellulose strip with 5% (w/w) PAN as prepared and prior to any solution contact. Using this spectrum, it is possible to eliminate any interferences in the dye's response as a result of the cellulose substrate. The remaining spectra clearly show that as the concentration of Hg(II) increases, a peak indicative of the purple PAN–Hg(II) complex near 600 nm increases in intensity while the peak for the uncoordinated orange PAN near 400 nm decreases. This response is linear in the Hg(II) concentration range from 5–100 ppm with a computed regression coefficient value, *r*, of 0.9869 (Fig. 3).

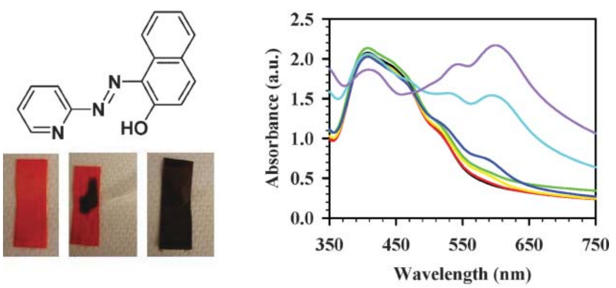

Fig. 1 (Left) Structure of 1-(2-pyridylazo)-2-naphthol (PAN) and from left to right: unreacted sensor, partially reacted sensor, fully reacted sensor. (Right) Absorption spectra of sensors after contact with various buffered pH solutions containing 50 ppm Hg(II) (black blank; red pH 3.4; green pH 4.0; yellow pH 4.5; blue pH 5.0; cyan pH 5.5; purple pH 5.9).

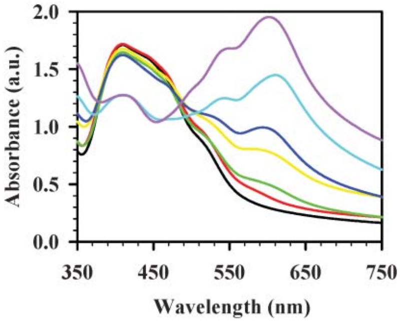

Fig. 2 Absorbance spectra after contact with solutions of varying concentration of Hg(II) (black blank; red 5 ppm; green 10 ppm; yellow 25 ppm; blue 50 ppm; cyan 75 ppm; purple 100 ppm).

Stripping of the sensors was studied by examining the peak at 600 nm after contact with 1 M NaCl (Fig. 4) and in a second experiment with 2 M acetic acid (HOAc) (Fig. 5). The red line in Fig. 4 was recorded for the PAN–Hg(II) complex in a cellulose strip contacted with 100 ppm Hg(II) solution. This strip was then allowed to soak in a 1 M NaCl solution for 10 min where it returned to its original orange color and its spectrum was again recorded (green line in Fig. 4). However, when this strip was subsequently introduced back into the Hg(II) solution, no Hg(II)-complexation was observed (yellow line).

Fig. 5 shows that a reversible 'strip' was achieved by soaking the reacted films in 2 M HOAc for 10 min, after which the strips

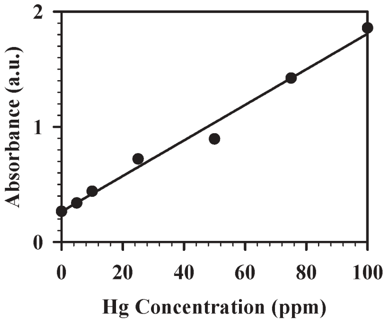

Fig. 3 Absorbance at 600 nm *versus* Hg(II) concentration indicating a linear sensor response (*r* = 0.9869).

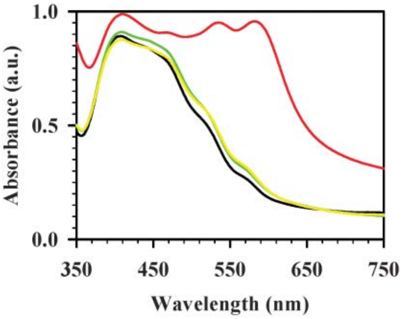

Fig. 4 Absorbance spectra related to tests of NaCl stripping: (black PAN film as prepared; red after contact with 100 ppm Hg(II) solution; green after stripping with 1 M NaCl; yellow after second contact with 100 ppm Hg(II) solution).

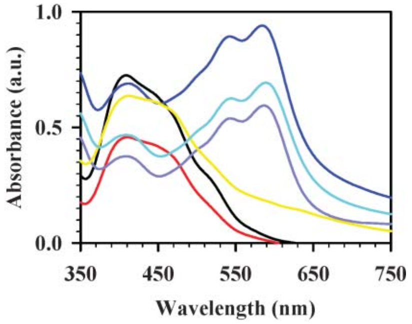

Fig. 5 Absorbance spectra of stripping with acetic acid (black PAN film as prepared; blue after contact with 75 ppm Hg(II) solution; red after stripping with 2 M HOAc; purple after second contact with 75 ppm Hg(II) solution; yellow after second stripping with 2 M HOAc; cyan after third contact with 75 ppm Hg(II) solution).

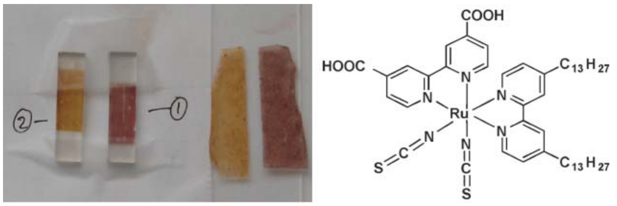

Fig. 6 (Left) TiO_2-based sensors (left) and cellulose-based sensors (right) containing N621. In each set, the sensor on the left was exposed to Hg(II) and the one on the right was not. (Right) Structure of the dye.

returned to their original orange color. These strips were rinsed with deionized water and re-contacted with 75 ppm Hg(II) solution, after which they were stripped again with 2 M HOAc.

The cellulose strips could be reused up to to five times, however, because the PAN is encapsulated in, rather than chemically bound to, the cellulose, leaching of the dye does occur. This leaching was observed visually in the acetic acid solution. After five uses of the sensor, too much dye had leached out for there still to be a visible color change. Control of leaching and batch-to-batch reproducibility will need to be optimized for each specific sensing agent utilized.

The selectivity of the sensors for Hg(II) was also investigated by exposing the films to aqueous solutions of Cu(II) and Zn(II). It was found that the PAN–cellulose sensors were not selective for Hg(II) in the presence of other metal ions. (Details and spectroscopic data from the selectivity testing can be found in the ESI.)

Having demonstrated the proof of concept with a non-selective dye, the interchangeability of the sensor probe encapsulated within the cellulose was investigated. The Hg(II) selective dye, *cis*-dithiocyanatobis-2,2′-bipyridine-4,4′-$(COOH)_2$-4,4′-tridecyl-2,2′-bipyridineruthenium(II) ([Ru(dcbpyH)(tdbpy)$(NCS)_2$]; N621), has been previously studied on a TiO_2 support.[25] Utilizing the cellulose platform, this dye was immobilized using a similar procedure to that used for PAN. Fig. 6 shows that this dye complexes with Hg(II) after encapsulation into the cellulose with essentially the same colorimetric response observed when the dye is bound to TiO_2.

We have demonstrated a versatile, inexpensive, and biodegradable sensor platform in which virtually any sensor probe molecule compatible with the cellulose matrix can be embedded. Such sensors can be tailor-made with relatively little effort and 'sensor kits' are envisioned where the sensing agent and support can be reconstituted and used on-site.§

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Notes and references

§ As we were submitting this manuscript, a paper[26] appeared describing the preparation of analogous PAN-in-cellulose sensors for Zn(II), Mn(II), and Ni(II) ions using an ionic liquid fabrication process. The results broadly support the general conclusions reported here, and a detailed comparison between the different techniques is likely to prove interesting in the development of more specific sensors.

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