

## Heterogeneous colorimetric sensor for mercuric salts†

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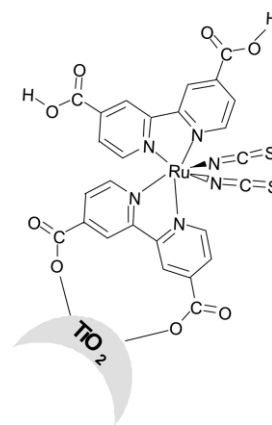
A novel chemical sensor for the colorimetric detection of mercuric salts is described. The sensor is based on a mesoporous nanocrystalline TiO<sub>2</sub> film sensitised with a ruthenium dye; immersion of this film in an aqueous solution of Hg<sup>2+</sup> results in a rapid colorimetric response, with both a high selectivity and a sub-micromolar sensitivity.

Sensing harmful species is critical to environmental monitoring, in the control of chemical processes and in medical applications. The selective detection of mercury is of particular importance, it being both biologically highly toxic (damaging the central nervous system and creating neuropsychiatric disorders in humans) and a common environmental pollutant. Elementary mercury and Hg<sup>2+</sup> salts are released in the environment by various processes while methyl mercury, which is the most dangerous for human health, appears in a second step owing to microorganisms activity. Existing chemical sensors for the detection of Hg<sup>2+</sup> include devices based on thin films of gold,<sup>1</sup> environmentally-sensitive organic molecules,<sup>2,3</sup> polymeric materials<sup>4,5</sup> and bio-composites.<sup>6</sup> Devices based on thin-film gold layers operate at high temperatures (150–300 °C) and require, for substantial sensitivity, complicated electronic circuits. On the other hand polymer composites exhibit limited sensitivity, while sensors based on simple organic luminophores<sup>3,7</sup> can usually only function in organic solvents, and often need long equilibrium times for quantitative detection. Similarly, limitations are encountered with biosensing of Hg<sup>2+</sup> which requires the use of buffering solutions and long equilibration times before the reading can be carried out.<sup>6</sup>

Mesoporous nanocrystalline TiO<sub>2</sub> films are potentially interesting materials for the development of optical sensors due to their high surface area and excellent optical transparency in the visible region of the spectrum ( $\lambda > 400$  nm). The adsorption of molecular dyes to the surface of these films has led to applications such as electrochromic windows,<sup>8</sup> solar cells,<sup>9</sup> biosensors,<sup>10</sup> heterosupramolecular devices<sup>11</sup> and, as we have recently reported, the heterogeneous sensing of anions down to micromolar concentrations.<sup>12</sup> Herein, we report the realization of a colorimetric and spectrophotometric chemical sensor based on a dye sensitised mesoporous TiO<sub>2</sub> film capable of detecting sub-micromolar concentrations of toxic mercuric salts.

In particular, we have investigated the ability of the TiO<sub>2</sub>/N719 [N719 = bis(2,2'-bipyridyl)-4,4'-dicarboxylato)ruthenium(II) bis-tetrabutylammonium bis-thiocyanate] films to act as a colorimetric and spectrophotometric sensor for the detection of metal cations in aqueous solutions (Scheme 1). To do so, the ruthenium complex (N719) was adsorbed onto a 4  $\mu$ m thick TiO<sub>2</sub> film by soaking the film in 1 mM solution of the dye in a 1:1 mixture of acetonitrile/*tert*-butanol at room temperature overnight. The cation sensing experiments with the TiO<sub>2</sub>/N719 films were carried out in distilled water (pH ~ 5)<sup>13</sup> by exposing the films to micromolar solutions of the metal cations under study (*i.e.* Ca<sup>2+</sup>, Mg<sup>2+</sup>, Mn<sup>2+</sup>, Fe<sup>2+</sup> and all of the metal cations catalogued by the Environmental Protection Agency<sup>14</sup> as “drinking water contaminants”, namely Cd<sup>2+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, Hg<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup> and Zn<sup>2+</sup>). Remarkably, as illustrated in Fig. 1, the TiO<sub>2</sub>/N719 film demonstrated a change in its colour only in

the presence of Hg<sup>2+</sup>. Fig. 2 shows the corresponding spectral shift, with Hg<sup>2+</sup> immersion resulting in a hypsochromic shift of the N719 visible absorption band from 535 to 481 nm. No optical changes of the films were observed with any other of the metals under study even when the films were exposed to millimolar concentrations.<sup>15</sup> The kinetics of the color change in the presence of Hg<sup>2+</sup> were



Scheme 1

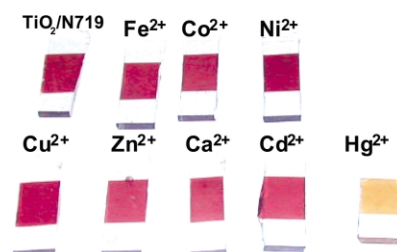


Fig. 1 Color changes observed after the TiO<sub>2</sub>/N719 film was dipped for 10 min in a 20  $\mu$ M aqueous solutions of the indicated metals.

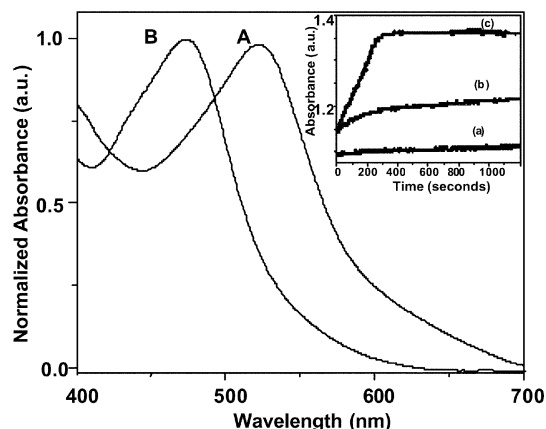


Fig. 2 Normalized absorption spectra of a TiO<sub>2</sub>/N719 before (A) and after (B) the film was immersed for 10 min in a 4 mL quartz cuvette containing a 20  $\mu$ M solution of Hg<sup>2+</sup>. The inset shows the kinetics of the change in absorption measured at  $\lambda = 480$  nm following immersion of the TiO<sub>2</sub>/N719 film in aqueous solutions with (a) 0 M, (b) 10<sup>-5</sup> M and (c) 10<sup>-4</sup> M Hg<sup>2+</sup>.

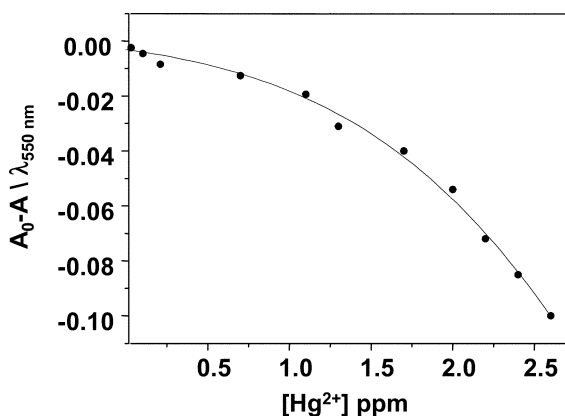
† Electronic supplementary information (ESI) available: Materials and methods. See <http://www.rsc.org/suppdata/cc/b3/b314138a/>

observed to be dependent upon the concentration of  $\text{Hg}^{2+}$  (see insert Fig. 2), ranging from seconds at millimolar concentrations to minutes at low concentrations. This colour change was found to be irreversible, persisting for several weeks and being insensitive to subsequent drying of the film and rinsing in  $\text{Hg}^{2+}$  free control solutions.

The color change in the presence of  $\text{Hg}^{2+}$  was found to be insensitive to interference by other metal cations. A  $\text{TiO}_2/\text{N719}$  film was exposed to a solution containing sub-micromolar amounts of  $\text{Hg}^{2+}$  and micromolar quantities of all the other metal cations under study. The optical changes of the film were identical to those observed for solutions containing only mercury, demonstrating the lack of interference by other cations. Similarly, the effect of anionic species was studied by adding to the  $\text{Hg}^{2+}$  solution micromolar amounts of  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{AcO}^-$ ,  $\text{NO}_3^-$  and  $\text{HSO}_4^-$  (as their tetrabutylammonium salts). No interference in the presence of these anionic species was observed.

The sensitivity of the  $\text{TiO}_2/\text{N719}$  film for the detection of  $\text{Hg}^{2+}$  cations was investigated by "naked eye" and spectrophotometric studies as a function of  $\text{Hg}^{2+}$  concentration. "Naked eye" detection was found to be possible down to 20  $\mu\text{M}$  of  $\text{Hg}^{2+}$ . Spectrophotometric detection allowed the sensing down to  $\sim 0.3 \mu\text{M}$  of  $\text{Hg}^{2+}$  (0.5 ppm of  $\text{Hg}^{2+}$ ), as illustrated in Fig. 3.

The origin of the sub-micromolar sensitivity of this sensing system to  $\text{Hg}^{2+}$  requires careful consideration. The  $\text{TiO}_2/\text{N719}$  films employed in this study have an area of 1  $\text{cm}^2$  and bind approximately 300 nmol of ruthenium dye (determined from the film optical density, and employing a N719 extinction coefficient of  $12000 \text{ M}^{-1} \text{ cm}^{-1}$  at 535 nm). We observe that complete color change of the film from red-purple ( $\lambda_{\text{max}} = 535 \text{ nm}$ ) to yellow ( $\lambda_{\text{max}} = 481 \text{ nm}$ ) occurs at levels of mercury as low as 60 nmol (20  $\mu\text{M}$  in 3  $\text{cm}^3$ ), corresponding to an  $\text{Hg}^{2+}$  to N719 dye ratio of approximately 1 to 5. This observation suggests that the process responsible for the colour change of the N719 dye involves a chemical transformation catalysed by the  $\text{Hg}^{2+}$  ions rather than the formation of a 1:1 complex. The kinetic data shown in Fig. 2 are consistent with a catalytic mode of action, with the rate of colour change increasing as the  $\text{Hg}^{2+}$  concentration is increased. However we note that the saturation in the colour change observed for all  $\text{Hg}^{2+}$  concentrations at long times implies that the reaction is only partially catalytic, with the  $\text{Hg}^{2+}$  being rapidly consumed in the reaction.



**Fig. 3** Titration of the change in the absorption of a N719/ $\text{TiO}_2$  film measured at 550 nm vs. the concentration of added  $\text{Hg}^{2+}$  ions. Measurements were carried out 1 min after each addition of  $\text{Hg}^{2+}$  ions.

We assign the hypsochromic shift of the N719 absorption band observed in the presence of  $\text{Hg}^{2+}$  ions to a transformation of the NCS ligands of this dye. Previous studies have reported a blue shift of the N719 absorption in the presence of chemical oxidants (such as  $\text{H}_2\text{O}_2$ ) or after long period irradiation of the film; under these conditions this blue shift has been assigned to loss of sulfur from the NCS ligand leading to formation of coordinated cyanide. Our assignment of the hypsochromic shift observed here to transformation of the NCS ligands was further supported by FTIR and Raman spectra, which both showed that immersion of the film in  $\text{Hg}^{2+}$  solutions resulted in a disappearance of the  $2105 \text{ cm}^{-1}$  band assigned previously to the CN vibration of the NCS ligand.

It has been previously reported that  $\text{Hg}^{2+}$  can be used in the catalytic desulfurisation of organic moieties,<sup>4</sup> consistent with the results we report here. We note however that the nature of the ruthenium complex resulting from the catalytic reaction here proposed remains unclear. IR and Raman spectra of the  $\text{Hg}^{2+}$  treated  $\text{TiO}_2/\text{N719}$  films showed the appearance of a new band at  $\sim 2140 \text{ cm}^{-1}$ , distinct from the  $\nu\text{CN}$  band (at  $2080 \text{ cm}^{-1}$ ) reported previously for ruthenium cyanide complexes. Experiments are underway to understand the details of this interesting chemical process.

In conclusion, we have demonstrated a novel and practical heterogeneous system for the colorimetric sensing of  $\text{Hg}^{2+}$  in aqueous solutions at room temperature. The system exhibits a sub-micromolar sensitivity, attributed to a transformation of the thiocyanate ligands of the sensor dye induced by  $\text{Hg}^{2+}$  ions. The sensor is found to be highly selective, being insensitive to all other metal ions of concern as drinking water pollutants.

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- 13 We note that the use of more alkaline solutions resulted in poor binding stability of the N719 dye.
- 14 See: <http://www.epa.gov/eftpages/pollwaterpollutants.html>.
- 15 We also investigated the response of the  $\text{TiO}_2/\text{N719}$  films to other soft metals known to act as desulfurization agents such as  $\text{Pt}^{2+}$ ,  $\text{Pd}^{2+}$  and  $\text{Ag}^{2+}$ . In all cases, a hypsochromic shift of the  $\text{TiO}_2/\text{N719}$  film absorption was observed, consistent with the proposed desulfurisation of the N719 NCS ligands. We note that the EPA does not include these elements in the list of inorganic drinking water contaminants.