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An evaluation of the distribution of metal ions in otherwise uniform titania sol-gel layers designed for optical sensing using laser ablation inductive coupled plasma mass spectroscopy

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ABSTRACT

Free-base porphyrins are bound to titania sol-gel layers deposited on glass slides. The porphyrin-containing titania layers show the UV-VIS spectra of the porphyrin and are found to be uniformly and evenly distributed. By addition of a metal salt to the titania layer, it was possible to metallate the free-base porphyrin within and change the UV-VIS absorbance of the porphyrin. The metalloporphyrins based on Cu and Zn ions could be detected by laser ablation inductive coupled plasma mass spectroscopy (LA-ICP-MS). Aggregation of metals is observed indicating that metal ions are also attaching directly to the titania. In samples where already metalized porphyrins are used little or no aggregation is observed, indicating that the titania sol gel is non-uniform in its affinity for metal ions.

Keywords: Sol-gel, titania, porphyrin, detection, thin layer, metal sensors, optical sensing, chemical sensors

1. INTRODUCTION

Titania micron-thickness layers fabricated by sol-gel condensation have been extensively studied, with their spectroscopy and elemental composition characterized in detail, including within optical fibres; for example see [1]. Titania possesses remarkable chemical and bioactive properties, and has affinity for binding to a range of commonly used sensor sites and ligands such –OH and –COOH containing organic compounds. Titania itself has little absorption of visible light, has a high refractive index and high porosity that allows for gases and liquids to enter the structure - seemingly an all round material ideal for optical sensing in waveguide or fibre form, for example. These properties allow for any compound bound with the titania layer to react with reactants present in its environment. Previously, titania sol-gel layers of this kind were utilized for the construction of a simple optical fibre sensor by binding a free-base porphyrin onto the titania layer [2]. Upon contact with acidic gas, the porphyrin changed its UV-Vis spectra and this change was detected by fibre evanescent field spectroscopy.

Porphyrins have been extensively investigated given their general robustness and their chemical design flexibility as well as the unusual electronic distribution that allows for sensitive electronic and excitonic bandgap engineering. For example, a particularly important area of research involves the use of free-base porphyrins that exhibit UV-Vis changes upon metallation. The incorporation of a metal ion within its macrocycle makes for an ideal metal impurity sensor, increasingly important for water, environmental and industrial sensing. The integration of such metal sensing species with titania is therefore of great interest [3]. Despite this interest, very little detailed analysis has been carried out to determine the practicality of such sensors including the distribution of both porphyrin and metal onto the titania layer. In previous work, we employed various techniques, including FTIR to explore the improvement in sol gel layer fabrication under cold processing and demonstrated a specially uniform layer when high speed spin coating (>6000 rpm) was used [1]. In this work, we examine the uptake of metal ions (Cu^{2+} and Zn^{2+}) by a porphyrin-laced titania layer along with the distribution of both porphyrin and metal intake across the layer using laser ablation inductive coupled plasma mass spectroscopy (LA-ICP-MS). LA-ICP-MS uses a laser to ablate surfaces to generate aerosols, which are collected for elemental analysis. It has previously been successfully used for the detection of metallated pthalocyanines [4]. LA-ICP-MS has also been used to successfully detect the presence of trace quantities of zinc and copper [5], and given that phthalocyanines have a similar chemical structure to porphyrins, LA-ICP-MS was chosen to detect metals bound within the porphyrin.

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2. EXPERIMENTAL METHOD

To fabricate the sol gel layer, tetraisopropyl titanate (1.0 mL) was added to isopropanol (19.0 mL) to make a TPT isopropanol solution (5% v/v). The mixture was left overnight for aging prior to use. Cleaned glass slides were secured onto a spin coater and set to spin at 1000 RPM for 60 seconds. TPT solution was added upon starting the rotation. The substrates were washed with isopropanol and dried under nitrogen. Metallation was done differently for each sample using four distinct processes, two of which involved dual combination of reagents onto the sol gel layer (simulating real sensing) and two of which involved direct deposition after the metal has been bound to the porphyrin. Table 1 summarises this whilst Figure 1 summarises the chemical pathways used.

Sample	Compounds added	Metallation site
Sample 1	Free-base hydroxyphenyl porphyrin, followed by $Zn(OAc)_2.2H_2O$ solution	On titania sol-gel layer
Sample 2	Free-base hydroxyphenyl porphyrin, followed by $Cu(OAc)_2.H_2O$ solution	On titania sol-gel layer
Sample 3	Zinc(II) hydroxyphenyl porphyrin	External metallation
Sample 4	Copper(II) hydroxyphenyl porphyrin	External metallation

Table 1. The compound added to each sample and its site for metallation.

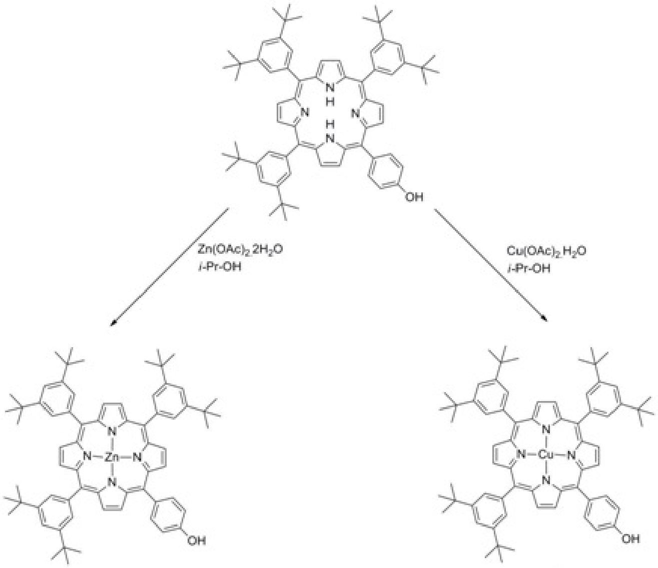

Figure 1. The reaction scheme for the metallation of the hydroxyphenyl porphyrin used (top) to zinc(II) porphyrin (bottom left) and copper(II) porphyrin (bottom right).

3. RESULTS AND DISCUSSION

UV-VIS spectra using samples 1 – 4 are shown in Figure 2. A shift in the Soret band observed with samples (1) and (2) indicated that metallation occured by absorbing metal into the sol-gel, where it reacted with the porphyrin within. Samples (3) and (4), which contained the externally metallated metalloporphyrins, were compared with samples (1) and (2), and exhibited the same shift in the Soret band. Thus, in both cases metallated porphyrins are attached to the titania. The UV-VIS spectra confirmed that the pathway of sample (1) and (3) formed the same final product, and likewise with sample (2) and (4).

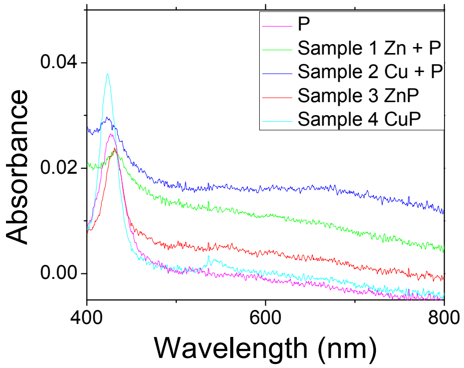

Figure 2. UV-VIS transmission spectra of the titania sol-gel slide with the porphyrin starting material (P) and its equivalent metalloporphyrins from samples (1 – 4).

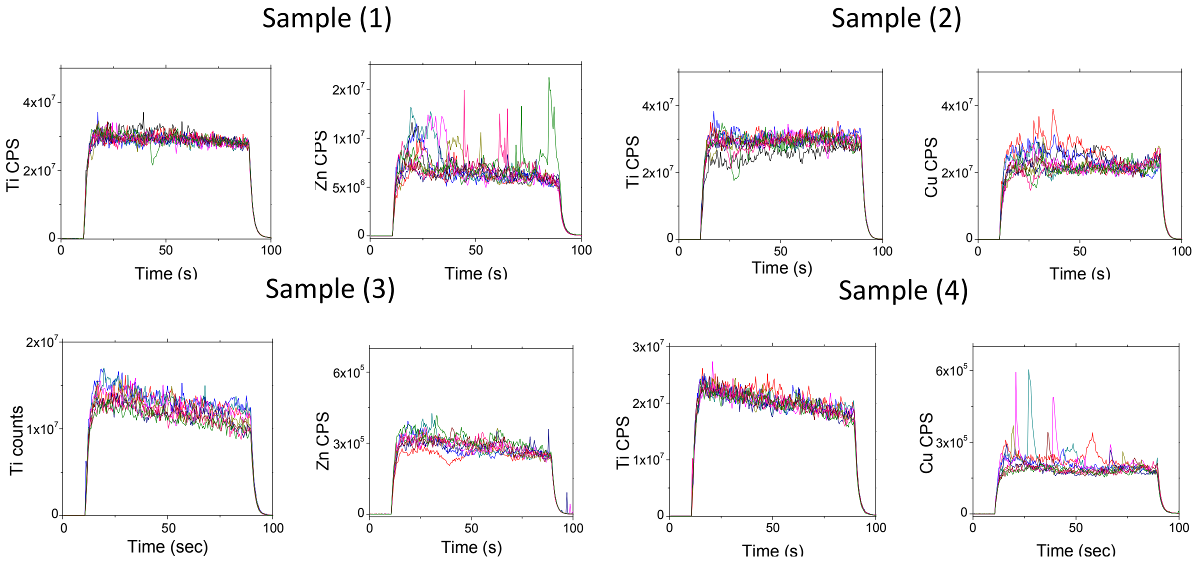

Figure 3. LA-ICP-MS of samples (1 – 4), indicating the Ti/Zn/Cu quantity for multiple lines scans across each sample as a function of time (where time signifies a different position on the sample).

LA-ICP-MS measurements, shown in Figure 3, were carried out by taking multiple line-scans on the titania layer, with 2 mm between each scan. Each line was acquired at 0.1 mm/second to give the elemental composition of the ablated areas. Multiple line-scans for each sample were compared to map the elemental composition of the surface. It was observed that the titania composition is relatively constant throughout the slide for samples (1) and (2) but linearly decreased in quantity from one end to the other in (3) and (4). The results indicate a similar quantity of titania overall, although a gradual decrease in (3) and (4) was observed, suggesting uniform layer formation with no obvious aggregation. The metal ions can be seen to have considerable fluctuation in samples (1) and (2) in contrast to (3) and (4). This is evidence that aggregation has occurred unevenly using the method of preparation of (1) and (2). The presence of metal ions in samples (3) and (4) confirms successful metallation of the porphyrin, as the sol-gel layer was never in any direct contact with the metal ion. The only source of metals it could possibly receive would be from the metalloporphyrins. The metal quantity detected by LA-ICP-MS was also compared and is shown in Figure 4. Samples (1) and (2), which had the porphyrin added first and then metal salt, are closer to a realistic sensor, and on these samples there was a much larger quantity of metals detected on the surface. This may be attributed to direct absorption of metal salts onto the titania, indicating that the activity of the titania itself may be higher than that of the porphyrin. Given the highly porous structure of the sol-gels, which imparts a large surface area, this would be quite likely. The number of moles of the metal solution should greatly exceed the amount of porphyrin, so there would be a large quantity of excess metal not needed for the metallation reaction that were not completely removed by physical washing. This would indicate that porphyrin intake is generally not high and that the metal affinity is non-uniform across the titania; which may in turn indicate that the porosity is non-uniform although the titania layer itself is.

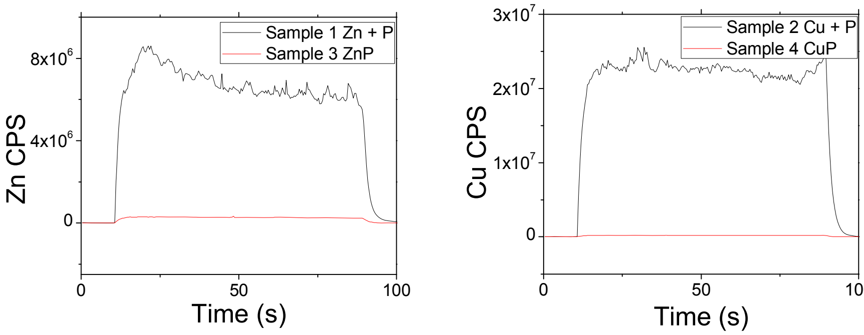

Figure 4. LA-ICP-MS results comparing the quantity of Zn on samples (1 – 3) and the quantities of Cu on samples (2 – 4).

4. CONCLUSION

Free-base hydroxyphenyl porphyrins bound onto titania sol-gel layers were successfully metallated within the sol-gel layers, with the Soret band shifting to confirm this reaction. Elemental analysis of the surfaces by LA-ICP-MS confirmed that the distribution of metal over the surface was fairly uniform when directly metalled porphyrins were used. In two samples, the competing interactions between porphyrins and metals when reagents are mixed directly on the surface sees significant intake of metal salts into the titania matrix which is strongly bound. Upon metal uptake, the porphyrin was subsequently metallated within the sol-gel layer and showed a shift of the Soret band. Aggregation of the metal indicates non-uniform affinity or porosity along the titania layer, in spite of its uniformity. In this work we have considered the porphyrin as a sensor itself to detect metals via uptake of metals within the sol-gel layer, and metallation of the porphyrin on the titania sol layers is feasible. Although the measurements were restricted to accessible films on slides, they provide useful insight into the likelihood of metal uptake and the challenges of separating out porphyrin and titania attachments either in film, waveguide or structured optical fibre, for example. Experiments (3) and (4) indicate that external metallation is necessary if unwanted metal-titania interactions are avoided (in some cases these may themselves be more useful). This is very much dependent on the type of chemical sensor being explored.

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