

The role of positron annihilation lifetime studies and nuclear sensors for characterising porous materials

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Abstract. A series of nuclear sensors were designed to assess the chemistry within the nanopores of a porous material. The nuclear sensors of varying size, charge, and hydrophobicity were exposed to hollow silica shells (HSS) at varying pH. Uptake and release kinetics were studied over a 24 h period at room temperature. Preliminary study indicate positively charged nuclear sensors were selectively and rapidly (within 10 min) absorbed by the HSS at pH 7 to 9. PALS showed there were two types of pores (1.7 and 0.7 nm) present. The data suggest the nuclear sensors sit within the larger pore of the HSS. Both PALS and nuclear sensors are required to obtain an accurate insight into the nanoporosity of the hollow silica shells.

1. Introduction

A breakthrough in the synthesis of mesoporous silica materials with controlled particle size, morphology and porosity has enabled new applications in medicine, environment and industry.[1-2] The silica matrices are particularly attractive because of their chemical stability and biocompatibility. They can be readily internalised by plant and animal cells when functionalized and show no significant cytotoxicity.[3]

For many mesoporous silica nanoparticles, absorption on the surface of the pores can be controlled by size or morphology of the pores.[4] However it is difficult to predict under what condition the cargo molecules can be loaded and released. Small Angle Neutron Scattering (SANS), X-Ray Spectroscopy (SAXS), nitrogen gas adsorption-desorption, Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Brunauer Emmett Teller (BET) measurements and Positron Annihilation Lifetime Spectroscopy (PALS) all provide information about porosity in materials.[5] However, these tools provide little information about the chemistry within the nanopores of the silica shells. Understanding how to optimise the number of available pores and determining the physical properties within these pores continues to challenge the field. This study reports a preliminary investigation on how we use positron annihilation lifetime spectroscopy (PALS) and nuclear sensors (radiotracers) (see Figure 1) to probe the chemistry in these pores.

2. Preparation

2.1. Preparation of HSS

The HSS were prepared as described previously.[6] Poly(1-methylpyrrol-2-ylsquaraine) (PMPS) were prepared by refluxing equimolar amounts of 1-methylpyrrole and squaric acid in butan-1-ol for 18 h. The PMPS beads were filtered off and then transferred to a crucible and held at 660°C for up to 3 h, after which time the sample was removed and cooled to ambient temperature.

2.2. Synthesis of Nuclear Sensors (NS)

The hexaaza cages ligand (Figure 1a) that consist of 6 secondary nitrogen donor groups that have an ability to encapsulate metal ions were synthesised in a similar method to that described in the literature.[7] The Ligands were radiolabelled with either Cu^{2+} or Co^{2+} metal ion solutions doped with $^{57}\text{Co}^{2+}$ or $^{64}\text{Cu}^{2+}$ radioisotopes, respectively. A typical procedure involved exposing equimolar amounts of the Ligand (dota, diamsar, or sarar-NCS) at 1.5×10^{-2} M with the radioisotope solution in sodium phosphate buffer (PBS) pH 7. The complexation reactions were monitored at 23 °C by instant thin layer chromatography (ITLC-SG) until complete (> 95%).

2.3. Binding of NS to HSS

A typical procedure involved mixing 10 mg (accurately weighed in triplicate) of HSS in 1480 μL of appropriate buffer (pH 3-9) at 23 °C. The resulting mixture was then vortexed for 5 s and left to agitate for 5 min. The HSS were then exposed to either free $^{57}\text{natCo}^{2+}$ or $^{64}\text{natCu}^{2+}$ (1×10^{-3} M) or $^{57}\text{natCo}$ -Ligand (1×10^{-4} M) in 20 μL . Uptake of the metal ions and $^{57}\text{natCo}$ -Ligand were monitored until equilibrium was reached. The radioactivity associated with the HSS was measured using the gamma counter. The moles of nuclear sensors associated with the HSS were calculated in the following manner, $A = B \times \%$ activity associated with HSS/weight (mg) of HSS. Where A = mole of metal ion or metal complex bound to HSS per milligrams and B = initial moles of metal ion or metal complex.

2.4. Co^{2+} -doped HSS

HSS (300 mg) was swelled in 0.1 M potassium dihydrogen phosphate (PBS) solution (5 mL) for 5 min. Cobalt(II) chloride (0.82g) in PBS was added to the suspension and agitated for 24 h at 23 °C. The Co^{2+} doped HSS was isolated after centrifugation (1000 rpm for 1 min) washed with Milli-Q water (3 x 1 mL) and then dried in air.

2.5. PALS

Positron annihilation lifetime spectroscopy (PALS) was used to determine the microporosity within the HSS. The positron lifetimes were analysed using the Laplace inversion technique and fitted assuming three annihilation modes or components [i.e. free positron : β^+ ; *para*-positronium: *p*-Ps; *ortho*-positronium : *o*-Ps]. The third component, associated with the pick-off annihilation or *o*-Ps is used to determine the lifetime and relative intensities of the micropores. Eqn (1) shows the relationship between the lifetime spectrum of positrons, $S_{\text{LT}}(t)$ and the lifetime components. The observed spectra were analysed with a time resolution of about 170 ps (full-width-at-half-maximum, FWHM) by using the RESOLUTION computer program.[8]

$$S_{\text{LT}}(t) = \sum \lambda_i I_i \exp(-\lambda_i t), \quad (1)$$

where λ_i and I_i are respectively the *i*-th components of the annihilation rate of positrons and its intensity. The lifetime of the positrons, τ_i , is given by $1/\lambda_i$.

3. Results and Discussion

The HSS were prepared by the overcoating of sacrificial polymeric template particles with silicon precursor followed by thermal calcination in a furnace at 660 °C.[6] Ligands were synthesized in a

similar manner to that described elsewhere [7] or purchased from a commercial supplier. Each ligand was then radiolabelled with $^{57}\text{nat}\text{Co}$ at a metal ion (M) to ligand ratio of 1:1 at pH 7 at 23 °C and micromolar concentrations as previously described. ITLC was used to ensure the complexation of the $^{57}\text{nat}\text{Co}$ was complete (>95%) [see Figure 2]. Uncomplexed ^{57}Co and ^{64}Cu were used to monitor the absorption of Co^{2+} and Cu^{2+} , respectively. HSS were exposed to each NS in buffered solution at pH 3 to 9. Solutions were sampled at varying time intervals (up to 24 h) to determine unbound NS. Figure 3 show the similar binding profiles for Cu^{2+} and Co^{2+} with significantly higher absorption (1.5 higher) for the former. The rate of absorption for the Cu^{2+} ion was also considerably faster than those for the Co^{2+} ion, reaching their maximum absorption within 10 minutes and 90 minutes, respectively.

The uptake of NS (Co-dota, Co-diamsar and Co-sarar-NCS) by the HSS was also monitored over time (up to 24 h) or until equilibrium was reached at pH 7. Figure 4 compares the binding of a series of NS (Co-dota, Co-diamsar and Co-sarar-NCS) to the HSS at pH 7. The data show that subtle changes in the structure has a significant effect on the binding properties of the HSS. The positively charged NS [the free metals, metal-ligand complexes] of varying size are preferably taken up by the HSS at higher pHs. Notably, negatively charged NS (Co-dota) was weakly absorbed compared to the positively charged NS (Figure 4), suggesting the pores of HSS are negatively charged at high pH.

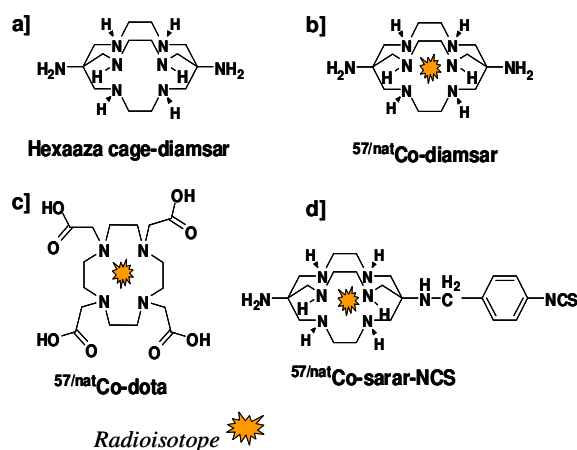


Figure 1. Ligands were radiolabelled with $^{57}\text{nat}\text{Co}^{2+}$ to form the nuclear.

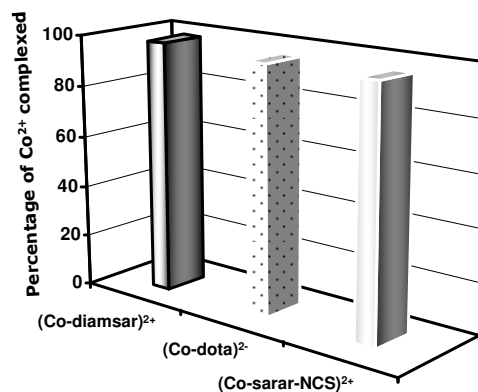


Figure 2. Percent of $^{57}\text{nat}\text{Co}^{2+}$ complexed by dota, diamsar and sarar-NCS after 1 h.^a

^a $[\text{M}^{2+}] = 10^{-3} \text{ M}$; Buffer : 0.1M PBS pH 7; Temp = 23°C; Time = 1 h.

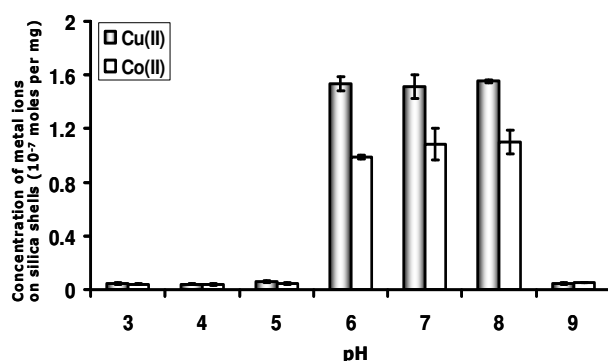


Figure 3. The effect of pH on metal binding properties of HSS at ambient temperature.^a

^a $[\text{M}^{2+}] = 10^{-3} \text{ mol/L}$; silica shell = 10 mg; Vol = 1.5 mL; Time = 10 min; Temp = 23°C; number of samples (n)=3.

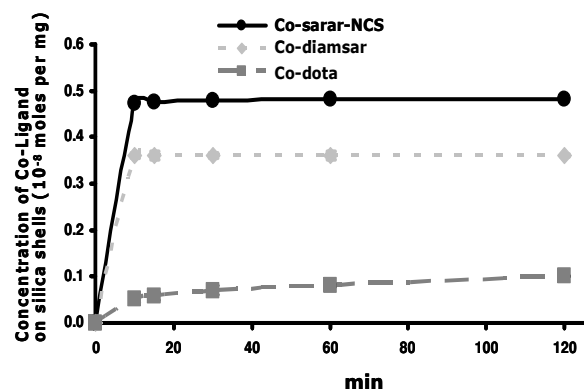


Figure 4. Moles of $[\text{M-Ligand}]^{2+}$ absorbed into HSS at pH 7 over time.^a

^a $[\text{M-Ligand}] = 10^{-4} \text{ mol/L}$; silica shell = 10 mg; Vol = 1.5 mL; Temp = 23°C; number of samples (n)=3.

In order to gain insight where the NS are located in the HSS, the HSS was loaded with Co(II) at physiological pH (7) and its PALS spectrum compared with that of the undoped HSS. Data were fitted using eqn (1) and results are summarized in Figure 5. Four lifetime components [τ_1 , τ_2 , τ_3 and τ_4] were present in the HSS sample and only three components were refined for the PALS spectrum of the doped with Co²⁺ HSS. The τ_3 and τ_4 components were fitted using the Tao-Eldrup model to determine the pore diameters.[9] Two pores sizes were evident in the HSS sample, a large pore 1.7 nm related to the τ_4 and a smaller pore at 0.6-0.7 nm defined by τ_3 . The loss of the τ_4 component suggests the metal ion is trapped in this pore. Conversely the pores with diameter of 0.6-0.7 nm or smaller do not contribute to the metal trapping.

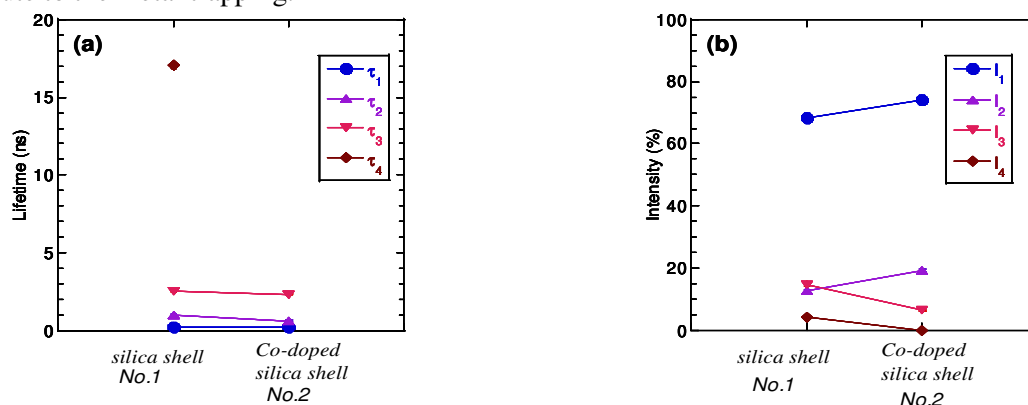


Figure 5. The lifetime and relative intensities of nanopores in the HSS.

4. Conclusions

Nuclear sensors are novel non-destructive tools for studying porosity of materials. Because of their high sensitivity (up to 10^{-5} ppb) only small quantities (e.g 10 milligrams) of material are required for analysis. Tailoring the shape, charge and hydrophobicity of the nuclear sensors provides information on the chemical reactivity of the pores within a porous material. PALS can be used to provide information on where the molecules might be absorbed in a material. Collectively, PALS and nuclear sensors have proven to be valuable tools to assess the chemistry and availability of micropores in materials. Further work will involve broadening the range of NS to gain a deeper understanding of the relationship between structure and function of novel porous materials.

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*Abbreviations: 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid (dota); 3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane-1,8-diamine (diansar); *N*^l-(4-isothiocyanatobenzyl)-3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane-1,8-diamine (sarar-NCS); Metal complexes of these ligands will be denoted as (M-ligand), e.g. ((Co-diansar)).