Electronic Supplementary Material (ESI) for Journal of Materials Chemistry

Supporting Information

Sol-gel synthesis of hierarchically porous TiO_2 beads using calcium alginate beads as sacrificial templates

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Surface Hydroxyl Group (OH) Determination. Thermogravimetric testing was conducted on calcined TiO_2 beads to determine OH content using a procedure developed by Mueller *et al.*[1] The heating profile was set as follows under a nitrogen atmosphere: the materials were stabilized at 25 ºC for 5 min before being subjected to a heating ramp of 10 ºC min^{-1} to 120 ºC before further stabilization at that temperature for 30 min. The materials were then heated to 500 ºC with a heating ramp of 20 ºC min^{-1}. The surface hydroxyl group density was calculated based on the weight loss (g) between 120 ºC and 500 ºC using Equation S1 as follows:

$$OHnm^{-2} = \alpha\left(\frac{wt_{T_1} - wt_{T_2}}{wt_{T_1}}\right)\frac{2N_{\mathrm{A}}}{SA_{\mathrm{BET}} \times Mw_{\mathrm{H_2O}}} \quad \text{(S1)}$$

where α is a calibration factor with the value 0.625, T_1=120 ºC and T_2=500 ºC, N_A is Avogadro's number and SA_{BET} is the BET surface area in nm^2 g^{-1} and Mw_{H2O} is the molecular weight of water. Also,

$$OHg^{-1} = OHnm^{-2} \times SA_{\mathrm{BET}} \quad \text{(S2)}$$

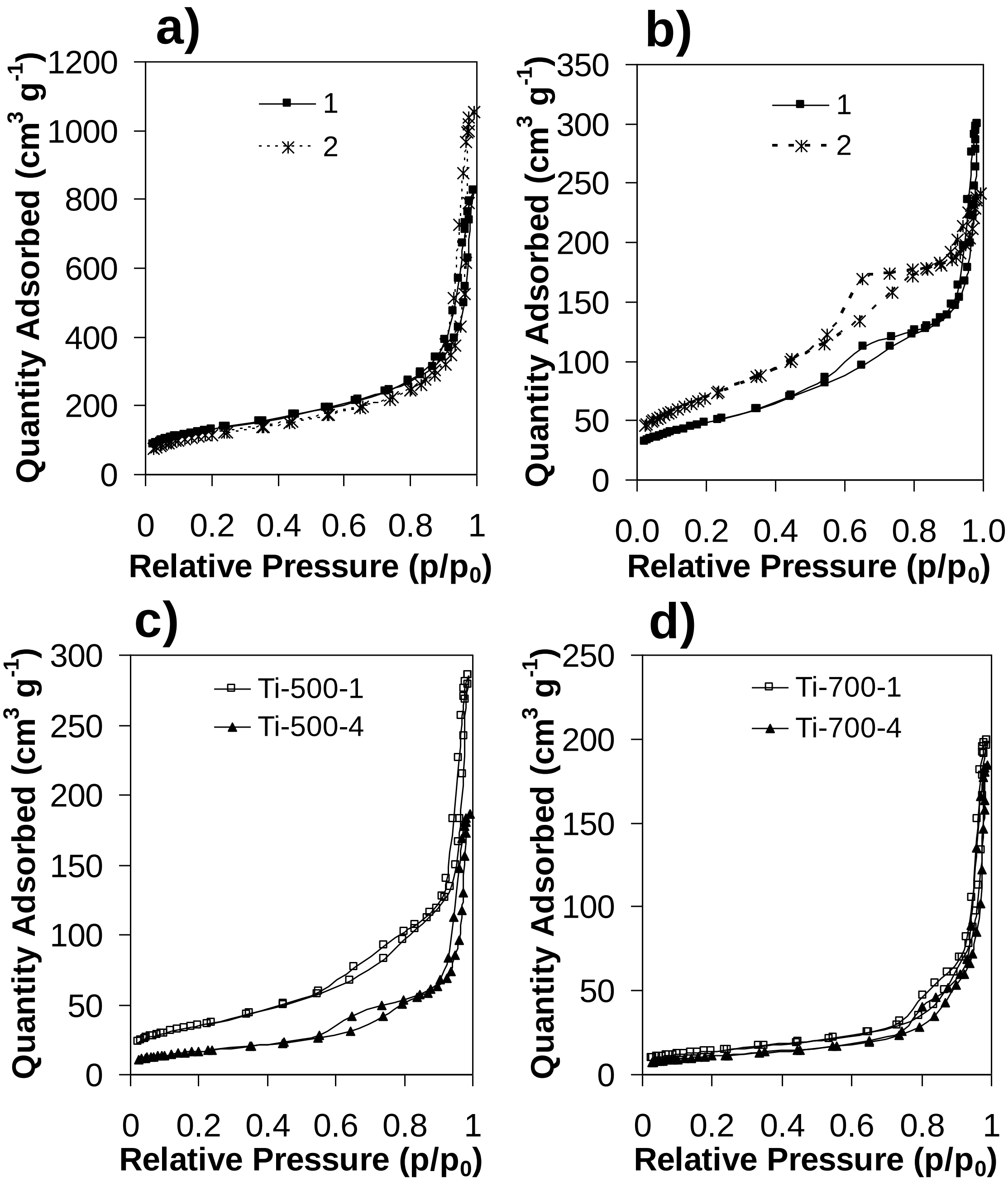

Figure S1. N_2 sorption isotherms of (a) critical point dried CaAlg template beads prepared using (1) 1 wt% or (2) 2 wt% NaAlg solution, a 0.27 M Ca^{2+} bath and a curing time of 2 h and (b) TiO_2 beads prepared using CaAlg beads synthesized from (1) 1 wt% or (2) 2 wt% NaAlg solution, a 0.27 M Ca^{2+} bath and a curing time of 2 h. The templated beads were calcined at 450 °C. Nitrogen sorption isotherms of the TiO_2 beads originally calcined at (c) 500 °C and (d) 700 °C, and functionalized with 0 wt% (Ti-500-1 and Ti-700-1) or 1 wt% (Ti-500-4 and Ti-700-4) Alen . The CaAlg template beads employed for this study were produced from 1 wt% NaAlg, a 0.27 M Ca^{2+} bath and cured for 24 h. Isotherms have *not* been offset.

All sorption isotherms were of Type IV, indicative of the presence of a mesoporous structure and featured two hysteresis loops that can be associated with the presence of small mesopores and meso-macropores, at lower and higher relative pressures, respectively.

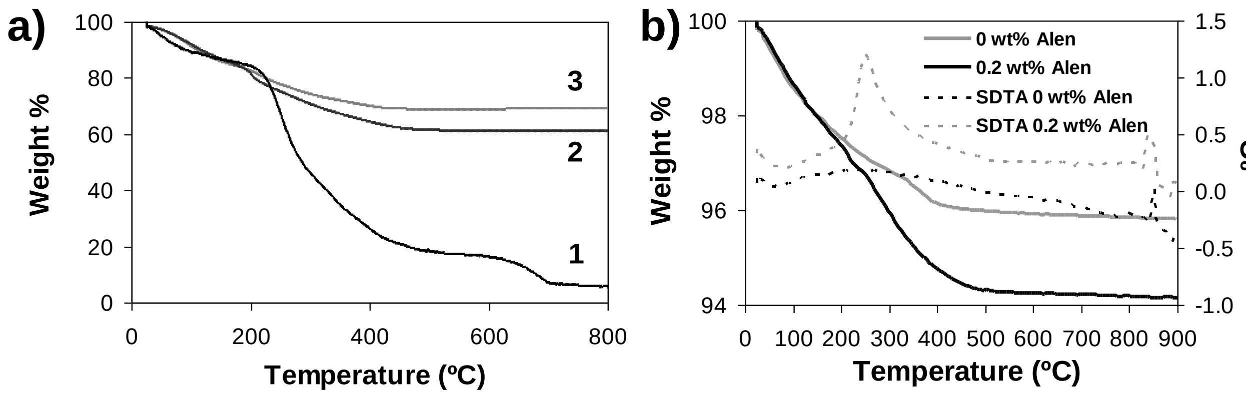

Figure S2. (a) Thermograms of (1) critical point dried CaAlg template beads prepared using 1 wt% NaAlg solution, a 0.27 M Ca^{2+} bath and cured for 2 h. Hybrid alginate/TiO_2 beads prepared using CaAlg template beads prepared from (2) 2 wt% or (3) 1 wt% NaAlg solution, 0.27 M Ca^{2+} bath with a curing time of 2 h. (b) Thermograms of Ti-500 beads loaded with 0 and 0.2 wt% Alen at pH 2.01. CaAlg template beads used were produced from 1 wt% NaAlg solution, 0.27 M Ca^{2+} and cured for 24 h. Solid lines represent thermogravimetric profiles related to the mass loss in percentage (Left axis, Weight %) whereas dashed lines represent single differential temperature profiles (SDTA) (Right axis, ºC). Beads were subjected to a linear heating ramp of 10 ºC min^{-1} under an oxygen atmosphere.

Figure S2b shows the results obtained when Ti-500 beads were heated following functionalization with Alen at 0 and 0.2 wt% (pH 2.01). Alen loaded TiO_2 samples showed a distinct exothermic peak at ~250 ºC. The exothermic peak occurring at ~850 ºC (with no mass loss) was likely due to further crystallization occurring within the metal oxide, whereas the endothermic process occurring at ~100 ºC was due to the evaporation of physisorbed water. Hence the temperature range (120-800 °C) was used to assess the mass loss attributed to Alen loading.

Table S1. Atomic percent composition of TiO_2 beads prepared using varying CaAlg template beads prepared from 1 or 2 wt% NaAlg and 0.14, 0.27 or 0.42 M Ca^{2+} and a curing time of 2 h.

NaAlg - Ca^{2+} (wt% - M)	Atomic Percent (%)^a		
	Ti	O	Ca
1- 0.14	30.28	67.90	1.82
1- 0.27	32.14	65.79	2.07
1- 0.42	36.22	60.31	3.48
2- 0.14	33.31	63.80	2.89
2- 0.27	37.25	59.48	3.27
2- 0.42	33.22	61.79	4.99

^{a}Values obtained are indicative only; as obtained from EDX analysis of the central region of the beads.

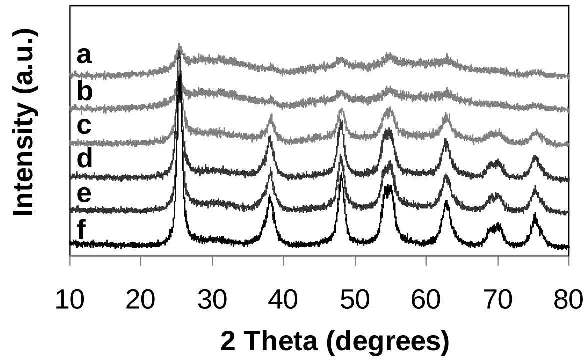

Figure S3. XRD patterns of TiO_2 beads calcined at 450 ºC. The CaAlg template beads used were prepared using 2 wt% NaAlg solution and (a) 0.42 M, (b) 0.27 M or (c) 0.14 M Ca^{2+} or 1 wt% NaAlg solution and (d) 0.42 M, (e) 0.27 M or (f) 0.14 M Ca^{2+} with a curing time of 2 h. Patterns have each been shifted upwards by 200 a.u.

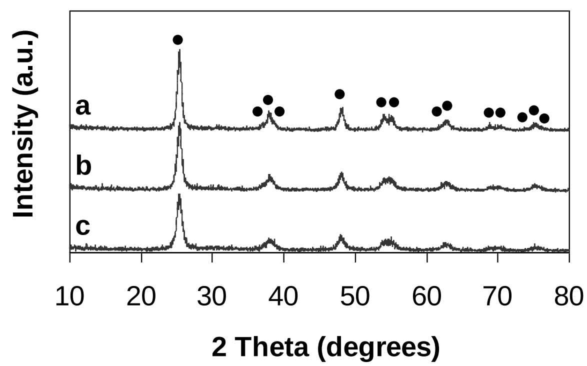

Figure S4. XRD patterns of TiO_2 beads calcined at (a) 500 ºC, (b) 600 ºC or (c) 700 ºC. The CaAlg template beads employed were produced using 1 wt% NaAlg solution and 0.27 M Ca^{2+} with a curing time of 24 h. Dots represent anatase reflection peaks. Patterns have each been shifted upwards by 200 a.u.

1 R. Mueller, H. K. Kammler, K. Wegner and S. E. Pratsinis, *Langmuir*, 2003, **19**, 160.