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:

$$
OH_{mm}^{-2} = \alpha \left( \frac{wt_{T_1} - wt_{T_2}}{wt_{T_1}} \right) \frac{2N_A}{SA_{BET} \times M_{H_2O}}
$$

(S1)

where $\alpha$ 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 $M_{H_2O}$ is the molecular weight of water. Also,

$$
OH_g^{-1} = OH_{mm}^{-2} \times SA_{BET}
$$

(S2)
Figure S1. N₂ 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 Ca²⁺ bath and a curing time of 2 h and (b) TiO₂ beads prepared using CaAlg beads synthesized from (1) 1 wt% or (2) 2 wt% NaAlg solution, a 0.27 M Ca²⁺ bath and a curing time of 2 h. The templated beads were calcined at 450 °C. Nitrogen sorption isotherms of the TiO₂ 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 Ca²⁺ 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, °C). Beads were subjected to a linear heating ramp of 10 °C 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 °C. The exothermic peak occurring at ~850 °C (with no mass loss) was likely due to further crystallization occurring within the metal oxide, whereas the endothermic process occurring at ~100 °C 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.

<table>
<thead>
<tr>
<th>NaAlg - Ca$^{2+}$ (wt% - M)</th>
<th>Atomic Percent (%)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ti</td>
</tr>
<tr>
<td>1- 0.14</td>
<td>30.28</td>
</tr>
<tr>
<td>1- 0.27</td>
<td>32.14</td>
</tr>
<tr>
<td>1- 0.42</td>
<td>36.22</td>
</tr>
<tr>
<td>2- 0.14</td>
<td>33.31</td>
</tr>
<tr>
<td>2- 0.27</td>
<td>37.25</td>
</tr>
<tr>
<td>2- 0.42</td>
<td>33.22</td>
</tr>
</tbody>
</table>

$^a$Values obtained are indicative only; as obtained from EDX analysis of the central region of the beads.
Figure S3. XRD patterns of TiO\textsubscript{2} beads calcined at 450 °C. 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\textsuperscript{2+} or 1 wt% NaAlg solution and (d) 0.42 M, (e) 0.27 M or (f) 0.14 M Ca\textsuperscript{2+} with a curing time of 2 h. Patterns have each been shifted upwards by 200 a.u.

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