Supporting Information

Gradient porous materials by emulsion centrifuging

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**Experimental Details:**

**Chemical and reagents**

Ammonium persulfate (APS; 98%), acrylamide (AM; 99%), N,N’-methylene bisacrylamide (MBAM; 99%), N,N,N,N-tetramethylethlenediamine (TMEDA; 99.5%), titanium (IV) isopropoxide (Ti(OiPr)₄, 99.9%) Triton X-405 (70% solution in water), sodium dodecyl sulphate (SDS > 99%), poly(vinyl alcohol) (PVA; 80% hydrolyzed, Mw 9–10K), light mineral oil (>98%), cyclohexane (analytical grade), Oil Red, Nile Blue were purchased from Sigma-Aldrich and used as received. Distilled water was used throughout the experiments.

**Preparation of gradient porous PVA monolith**

A stock solution of 5 %wt PVA (Mw, 10K) was prepared. The emulsion was prepared by adding 3 ml Oil Red–cyclohexane slowly into 3 ml of the PVA solution with 0.15g SDS while stirring at 1000 rpm for 10 minutes using a digital overhead stirrer (IKA Eurostar). The formed emulsion (6 ml) was transferred into a glass vial (round bottom, dimension 10 mm x 80 mm) and centrifuged at 1000 rpm for 1 minute using EPPENDORF centrifuge 5415D. The same glass vials and the volume of the emulsions were used for the experiments below with centrifugation time kept for 1 minute. This produced the monolithic rods with height around 75 mm.

An image of the centrifuged emulsion is given here. The same cropped image also appears as Fig. 1a.
The formed gradient emulsions were rapidly frozen in liquid nitrogen and then transferred into a freeze dryer (Vis Advantage) with the shelf temperature set at –10 °C for 2 days to remove the solvents.

**Gradient porous Silica-PVA monolith**
The silica particles functionalised with $N$-(5-Fluoresceinyl) maleimide dye were prepared according to a similar procedure reported before. The formed particles were around 1µm in size. The as-prepared silica colloids were suspended in 5 wt% PVA solution to make silica concentrations at 5 wt% and 10 wt%. The emulsions were prepared by adding 3 ml Oil Red-cyclohexane solution slowly into 3 ml of the silica-PVA solution containing 0.15g SDS with stirring at 1000 rpm. The resulting emulsions were centrifuged at 800 rpm and then freeze dried.

**Silica-Titania composite**
The porous PVA-silica monolith (made from the emulsion containing 5wt % silica) was soaked in a solution of Ti(OiPr)$_4$ in isopropanol (0.3g isopropanol + 1ml Ti(OiPr)$_4$) for 6 hours at room temperature. The soaked monolith was filtered and soaked in isopropanol for 15 minutes twice to remove any excess precursor solution from the material. The resulting monolith was dried in air at room temperature and then transferred into an oven at 65 °C for 12 hours. The organic phase was removed by calcination at 550 °C for 5 hours with heating rate 1 °C/min and cooling rate 10 °C/min.

**Preparation of gradient porous polyacrylamide (PAM)**
A monomer stock solution was prepared by dissolving 14.4g AM and 3.6g MBAM in 20ml of 5 wt% PVA (Mw 10K) solution. The emulsion was prepared by adding 3 ml of Oil Red-light mineral oil slowly into 3 ml of monomer solution with 0.3 ml Triton X-405 and 100µl of 10 wt% APS. The emulsions were formed at stirring speed of 1500 rpm for 10 minutes. 20µl of TMEDA was added and stirred for 30 seconds. The obtained emulsions were centrifuged at 1000 rpm for 1 minute and started to polymerize at room temperature, but was heated at 60 °C for 24 hours to ensure complete polymerization. The internal oil phase was removed from the monolith by immersing in n-hexane for at least 24 hours, then washed ten times with a mixture of acetone and n-hexane. The washed samples were allowed to dry in air at room temperature.
**Characterisation**

Morphology of the porous structures was observed by a Hitachi S-4800 scanning electron microscope (SEM). Three small pieces were taken from the top, middle and bottom of the monoliths and then adhered to the stud in this order using Araldite resin and then coated with gold using a sputter-coater (EMITECH K550X) for 3 minutes at 30 mA before SEM imaging. The Brunauer–Emmett–Teller (BET) surface area and mesopore volume were measured using a Micromeritics ASAP 2020 adsorption analyzer by N₂ sorption at 77 K. Samples were degassed for 24 hours at 120 °C before N₂ sorption analysis. The mesopore size distributions were calculated from both desorption and adsorption data by the Barrett–Joyner–Halenda (BJH) method. Macropore volume and macropore size distribution were recorded by mercury intrusion porosimetry using a Micromeritics Autopore IV 9500 porosimeter over a pressure range of 0.10 – 60000 psia. Intrusion volume was calculated by subtracting the intrusion arising from mercury interpenetration in large spaces (pore size >150 µm) from the total intrusion. The porosity can be calculated from the intrusion pore volume when necessary:

\[
\text{Porosity} = \frac{M \cdot V_i}{(M/\rho) + M \cdot V_i}
\]

Where M is the mass of the sample, Vi is the intrusion pore volume of the sample, and ρ is the skeletal density of the material for the sample.

For gas sorption and Hg intrusion measurements, the monoliths were divided into three parts equally (bottom, middle, and top) which were directly used for analysis.
Table S1. The characterization data for the gradient porous PVA as shown in Fig. S1 (see next page)

<table>
<thead>
<tr>
<th>Section</th>
<th>Surface area</th>
<th>Intrusion volume (cm³/g)</th>
<th>Bulk density (g/cm³)</th>
<th>Macropore peak size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% PVA (1000 rpm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Top</td>
<td>~ 0</td>
<td>13.37</td>
<td>0.054</td>
<td>13.93</td>
</tr>
<tr>
<td>Middle</td>
<td>~ 0</td>
<td>9.89</td>
<td>0.067</td>
<td>11.33</td>
</tr>
<tr>
<td>bottom</td>
<td>17</td>
<td>6.50</td>
<td>0.14</td>
<td>0.82</td>
</tr>
</tbody>
</table>
Supporting Figures

Figure S1. Representative SEM images of gradient porous PVA prepared by freeze-drying the emulsion after centrifuging at 1000 rpm. The emulsion was formed from equal volumes
of cycohexane (containing Oil Red) and 5 wt% aqueous PVA solution with 0.05 SDS/ml aqueous solution.

Figure S2. This photo shows the appearance of the emulsion containing 5 wt% silica colloids after centrifuging at 1000 rpm for 1 minute.
Figure S3, PVA-silica composite made from the emulsion containing 5 wt% silica colloids (sample S1 in Table 1). SEM images show the pore structure of the materials at bottom (A), middle (B), and top (C) of the prepared monolith. Macropore size distributions for the different parts of the material measured by Hg porosimetry are shown in (D).
Figure S4. (A) The isotherms of calcined S1 by nitrogen sorption; (B) The corresponding pore size distribution calculated from desorption data by BJH method.
Figure S5. The gradient porous structure of silica-TiO$_2$ monolith (S6). (A) top, (B) middle and (C) bottom part of the monolith.
Figure S6. Characterization results for gradient porous silica-titania composite (sample S2 in Table 1). (A) Macropore size distribution measured by Hg intrusion. The isothermal curves (B), mesopore size distribution calculated from desorption data (C) and adsorption data (D) by the BJH method.