Electronic Supporting information (ESI)

For

Instantaneous formation of polyoxometalate-based cerium vanadium oxide gels

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1. Instrumentation

FT-IR spectroscopy: FT-IR spectroscopy was performed on a Bruker FT-IR Spectrometer IFS113v. Samples were prepared as KBr pellets. Signals are given as wavenumbers in cm^{-1} using the following abbreviations: vs = very strong, s = strong, m = medium, w = weak and b = broad.

⁵¹V-NMR spectroscopy: ⁵¹V NMR spectra of the samples were measured on a 500 MHz Agilent NMR system using a 6 mm T3 HXY MAS Solids Probe. As the samples were liquid or gel-like, the observed ⁵¹V NMR lines were narrow, so no sample spinning was required. Chemical shifts are given according to the δ -scale in ppm and are referenced against VOCl₃ as internal standard.

UV-Vis spectroscopy: UV-Vis spectroscopy was performed on a Jasco V-670 spectrophotometer. Standard emission cuvettes (d = 10.0 mm, V = 3 ml) were used.

High-resolution transmission electron microscopy (HRTEM) and high-angle annular dark field-scanning transmission electron microscopy (HAADF-STEM): images were acquired using a Tecnai S-Twin30, 300 keV, GIF-TRIDIEM. Sample preparation was carried out as follows: two well-mixed solutions (A) and (B) were prepared. Solution (A) contained 5 ml of epoxy resin EMBED 812 + 8 ml Epoxy embedding medium, hardener Dodecenylsuccinic anhydride (DDSA). Solution (B) contained 8ml EMBED 812 + 7 ml Nadic Methyl Anhydride (NMA). Solutions (A) and (B) were combined under vigorous magnetic stirring followed directly thereafter 0.56 2,4,6-tris(dimethylaminomethyl)phenol (DMP-30). by ml The $(nBu_4N)_3[H_3V_{10}O_{28}]$ hydrogel sample was placed in a mold that was then filled with the A+B epoxy resin mixture. The entire process was carried out in a fume hood at room temperature.

Scanning electron microscopy (SEM): images were acquired using a field emission SEM Inspect F50 with an EDX system INCA PentaFETx3 (FEI Company, Eindhoven, Netherlands) in an energy range between 0-30 keV. To obtain the SEM images, the $(nBu_4N)_3[H_3V_{10}O_{28}]$ hydrogel was washed for three days in MilliQ water to remove excess DMSO. Briefly, on the first day water was added to a gel sample in a glass vial and each day the solvent was removed from the

gel-water suspension by pipette and replaced with fresh water. The gel was then partially dried in an open vial in the fume hood for 24 h. This semi-dried sample was then coated with Cr to improve the contrast of the images.

General remarks: All chemicals were purchased from Sigma Aldrich, ABCR or VWR and were of reagent grade. The chemicals were used without further purification. $(nBu_4N)_3[H_3V_{10}O_{28}]$ was prepared according to reference S1. $(nBu_4N)_4[V_4O_{12}]$ was prepared according to reference S2.

2. Synthesis and characterization of the DMSO-based gel

Synthesis: The standard gel samples were prepared as followed and used without further modification for all application studies: a solution of $(nBu_4N)_3[H_3V_{10}O_{28}]$ (92 mg, 0.06 mmol) and CeCl₃x7H₂O (40 mg, 0.11 mmol) in DMSO (5 ml) was heated to 80 oC. To this solution, a methanolic solution of TBAOH (1.5 M, 0.3 ml) was added dropwise under stirring. The clear solution was stirred for at 80 °C for 5 min and H₃PO₄ (9 M, 0.45 ml) was added dropwise, leading to an intensification of the deep orange-red colour. Upon addition of the last drop of H3PO4, instantaneous gelation occurred and a mechanically stable gel was obtained. The gel retains the shape of the respective reaction vessel and can be mechanically removed from the reaction vessel and cut into the desired shape using a scalpel. FT-IR (characteristic bands in cm⁻¹): 3425 (vs), 2956 (s), 2870 (m), 2351 (s), 1640 (s), 1467 (s), 1381 (s), 732 (w), 665 (w), 610 (w), 501 (w).



Figure S 1: FT-IR spectrum of the DMSO-based gel prepared by the standard procedure described above, recorded as KBr pellet.



Figure S 2: Photograph of gel formed following the above synthetic procedure.



Figure S 3: Gel formation as a function of Ce^{3+} / cluster molar ratio, showing that gel formation is observed between 1:4 to 1:12. Solvent: DMSO, cluster: $(nBu_4N)_4[V_4O_{12}]$. The standard synthetic procedure given above was used. Higher or lower ratios lead to partial gelation and mechanic instability.

Use of other solvents for gel preparation:

The above gel synthesis can be carried out in other polar organic solvents also. Tests where the DMSO in the original synthesis was replaced by solvents such as N,N-dimethyl formamide (DMF), acetonitrile, N,N-dimethyl acetamide (DMA) all gave gels, however, the gels generally showed lower mechanical stability, therefore this study is focused on DMSO-based gels.

Thermal stability analysis

Standard thermal stability of the gel using thermogravimetric analysis did not give satisfying results, as during the heating process, the formation of gaseous solvent within the gel and subsequent rupture of the gel led to irreproducible data. Therefore, the gel degradation was inspected visually using a melting point apparatus and irreversible degradation of the gels were observed near the respective solvent boiling point, i.e. for the standard DMSO-gel, decomposition was noted at *ca.* 180-185 °C, for the DMF-based gels,

degradation was observed at *ca*. 145-150 °C, for the DMA-based gels, decomposition was observed at ca. 155-160 °C. These experiments were reproducible and carried out in triplicate.

3. Model pollutant removal study

The removal of the model dye pollutant basic blue 41 (BB41) by adsorption to a gel sample was investigated as follows. A cylindrical piece of gel (l = 1.0 cm, d = 0.85 cm, surface area: 3.8 cm², volume: 0.5 cm³, prepared according to the standard procedure above) was immersed in an aqueous BB41 solution (V = 3.0 ml, [BB41]₀ = 12 mM) and gently agitated by shaking in the dark to avoid light-driven dye degradation. Uptake of BB41 within the gel was followed by UV-Vis spectroscopy of the supernatant BB41 solution. Removal of *ca*. 87 % of BB41 over a period of 110 h was observed, see below.



Figure S 4: Removal of BB41 from an aqueous solution by the vanadium oxide gel. Solvent: H_2O , [BB41]₀: 12 mM, standard gel sample (surface area: 3.8 cm², volume: 0.56 cm³, prepared according to the standard procedure above).

4. Acid release in aqueous solution

Release of acid present in the gel (due to addition of H_3PO_4 during synthesis) into aqueous solution was followed using a pH meter. To this end, a cylindrical piece of gel prepared according to the standard conditions above (diameter 0.85 cm, height 1.0 cm, surface area: 3.8 cm², volume: 0.56 cm³) was immersed in water (5 ml) and the pH was followed as a function of time. To demonstrate the system tunability, two additional experiments were performed where the gel cylinder was cut in half and in quarters, respectively. The increased surface area led to faster proton release, see below.



Figure S 5: Acid release by gel pieces as a function of surface area. Solvent: H_2O , standard gel sample (surface area: 3.5 cm², volume: 0.5 cm³, prepared according to the standard procedure above).

The "re-charging" of a gel sample with acid (H3PO4) was examined as follows: the standard cylindrical DMSO gel sample as used above was prepared and immersed in water for acid release. After acid release was complete (120 min), the gel was recovered and immersed in a DMSO solution (5 ml) containing 0.45 ml H_3PO_{4conc} (thus reproducing the original gel synthesis conditions) for 5 h. The gel sample was then recovered and re-immersed in water under the standard acidity test conditions described above. The sample showed a similar acid release behavior as in the first run.



Figure S 6: Recyclability of the gel for acid release into aqueous solution using the standard test described in section 2.5. Solvent: H_2O , standard gel sample (surface area: 3.5 cm², volume: 0.5 cm³, prepared according to the standard procedure above).



Figure S 7: Representative HAADF-STEM images of the gel prepared by the standard method, showing the internal network of intertwined fibrillary structures stabilising the gel matrix.



Figure S 8: Representative HAADF-STEM images with corresponding EDS area scans of the standard gel, showing the presence of vanadium (K α 4.95 and L α 0.51 keV) and cerium (L α 4.84 and M 0.83 keV) in the intertwined fibres. Note that the strong copper signal (K α 8.04 keV) arises from the carbon-coated copper TEM grids on which the sample was deposited for imaging.

³¹P-NMR and ⁵¹V-NMR spectroscopies were performed to gain insight into the changes in P and V chemical environment upon gel formation, see below. For V, changes are observed as discussed in the main manuscript.

For P, a shift from the initial signal at $\delta = 10.4$ ppm (0.1 ml) to $\delta = 10.9$ ppm (0.2 ml) to a more complex composite signal (for 0.5 ml phosphoric acid added) with maxima at $\delta = 11.3$ ppm and 10.5 ppm and a shoulder at $\delta = 9.3$ ppm. All signals are in the range expected for ortho-phosphate ions.^{S3}



⁵¹V-NMR Chemical Shift δ / ppm

Figure 2: ³¹P-NMR data (top) and ⁵¹V-NMR data (bottom), showing the changes in chemical shifts observed during gel formation. Conditions: solvent: DMSO; precursor: $(nBu_4N)_3[H_3V_{10}O_{28}]$ hydrolyzed by addition of nBu_4NOH . H₃PO₄ (9 M).

3. Literature references

- S1 C. Streb, R. Tsunashima, D. A. MacLaren, T. McGlone, T. Akutagawa, T. Nakamura, A. Scandurra, B. Pignataro, N. Gadegaard and L. Cronin, *Angew. Chem. Int. Ed.*, 2009, 48, 6490–6493.
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- S3 I. L. Mudrakovskii, V. P. Shmachkova, N. S. Kotsarenko and V. M. Mastikhin, J. Phys. Chem. Solids, 1986, 47, 335–339.