Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

2D and 3D Vanadium Oxide Inverse Opals and Hollow Sphere Arrays

*Eileen Armstrong, Michal Osiak, Hugh Geaney, Colm Glynn, and Colm O'Dwyer**

Department of Chemistry, University College Cork, Cork, Ireland
and
Micro &Nanoelectronics Centre, Tyndall National Institute, Lee Maltings, Cork, Ireland

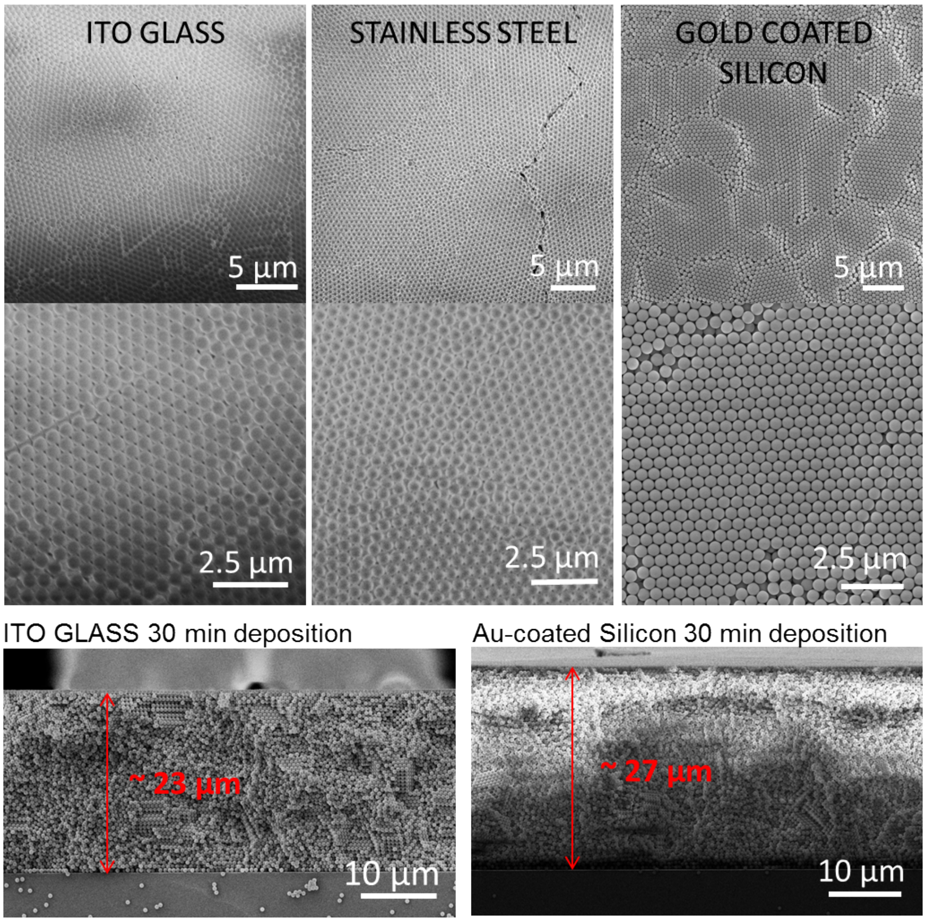


Fig. S1. SEM images of sphere templates deposited by electrophoretic deposition at 3V for 30 min on (a) ITO coated glass (b) Stainless Steel and (c) gold-coated Silicon showing domains of spheres arranged with the (111) plane parallel to the substrate. Bottom images indicating high level of thickness achieved for both ITO glass and Au-coated Silicon substrates

NOTE S1: SDS Model

The basis of the model is to determine if Derjaguin, Landau, Verwey and Overbeek (DLVO) theory can predict if single or multiple layers of spherical micelles form between SDS-functionalized PMMA spheres in water that accounts/predicts for the inter-sphere separation when deposited as an ordered assembly.

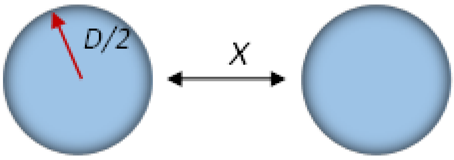
Assumptions:

- That SDS in micellular form is present between PMMA spheres (after removal from solution). The analysis assumes that only SDS causes a ‘gap’ between two sphere that would ordinarily touch, so that the distance between the sphere centres d = 2(D/2), where d is the centre-to-centre distance between two identical spheres and D is the diameter of a sphere, increases to d' = 2(D/2) + 2(2r_m), where r_m is the radius of a SDS micelle.

- That colloidal stability is present due to balance of vdW attractive forces and electrostatic and steric repulsions caused by presence of micellular SDS. With an SDS monomer functionalised PMMA (or PS) surface in water, the sphere colloidal is a sterically stabilised colloid. At the meniscus, just prior to deposition, the balance of forces is guided by evaporative self-assembly.

- The evaporation step is not assumed here to alter the final inter-sphere distance found at maximum flocculation of the colloid in the SDS-containing solution above the SDS CMC.

The vdW pair potential describing interactions between two hard spheres separate by a distance x can be simplified from the full interaction pair potential in the case where spheres are close, to:



$$U_{vdW} \sim -\frac{[A_{11}\left(\frac{D}{2}\right)]}{12x}$$

where A_{11} is the Hamaker constant between PMMA sphere ~ 6.3 × 10^{-20} J (~ 15 k_BT). PS has a similar value of 6.5-9 × 10^{-20} J.

In the case of SDS functionalised spheres, x is the distance between two sphere surfaces, i.e. thickness of film caused by micelles is present, i.e. $x = \alpha r_m$, where $\alpha \in R$. If we can estimate x, it will be some factor of r_m and thus we can estimate the number of micelles between spheres.

The electrostatic repulsion of SDS coated PMMA, which are not considered as charged spheres once SDS-functionalized, is given by

$$2\pi\varepsilon\varepsilon_0\left(\frac{D}{2}\right)\psi_\delta e^{(-\kappa x)}$$

where ε is the relative permittivity of PMMA ~78-82 ε_0 (value of 80 used), and κ^{-1} is the Debye-Hückel screening length or double layer thickness given by

$$\kappa^{-1} = \sqrt{\frac{\left(2z^2e^2N_AC_0\right)}{\left(\varepsilon\varepsilon_0k_BT\right)}}$$

wherez is the net charge (z = 1 for a single negative charge of an SDS molecule in solution, and C_0 is its concentration (>CMC in this case). More simply, it can be approximated quite well by $\kappa^{-1} = 0.3041/(\mathrm{mod}(z)\sqrt{C_0})$ ~ 3.4 nm using C_0 as the SDS concentration used, e.g. 8 × 10^{-3} mol.

The exponential can be expanded through Maclaurin series and limited to its first order, thus the balance of electrostatic/steric and vdW forces is

$$\frac{A_{11}(\frac{D}{2})}{12x} = 2\pi\varepsilon\varepsilon_0\left(\frac{D}{2}\right)\psi_0{}^2(1 - \kappa x)$$

Rearranging, and obtaining the required root of x,

$$x \sim \frac{1}{2\kappa} \pm \left[\frac{\sqrt{1 - 4\kappa N}}{2\kappa}\right],$$

where

$$N = \frac{A_{11}D}{24\pi\varepsilon\varepsilon_0 D\psi_0{}^2}\,(N = 1.356\ \times 10^{-9}\,JmF^{-1}V^{-1})$$

$x = 1.7 \pm 1.3 \times 10^{-9}$ m.

The diameter of an SDS micelle is fundamentally given by 3.5 to 4 nm corresponding to estimated micelle radius of approximately 1.75 to 2 nm.[1, 2]

For either prolate or oblate shaped micelles, the average diameter is here assumed to account for either extensions beyond spherical at 298 K, and $r_m \sim 1.8$ nm. Essentially, the model predicts a film that is approximately a single micelle thick between the spheres at maximum packing just above CMC.

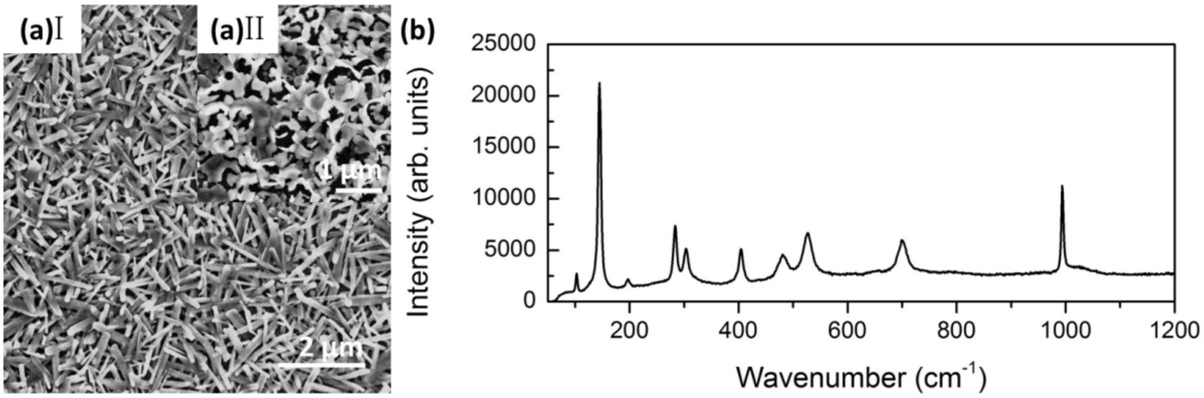


Fig. S2 (a)I SEM image of 100:1 IPA:$OV(OCH(CH_3)_2)_3$ precursor solution drop-cast with 20 s sonication, and then allowed to hydrolyse in air, and heated at 450 °C for 5 hours in a furnace oven (a)II SEM image of another area on same sample highlighting the non-uniformity of infiltration and crystallization by this method (b) Raman spectrum of (a) showing peaks at 103, 145, 197, 285, 304, 405, 483, 526, 703, and 994 cm^{-1} indicating the formation of crystalline orthorhombic V_2O_5.

Table S1 Comparison of the bond lengths calculated for the V = O bond from each Raman spectra shown in the main text, confirming V_2O_5 formation.

Sample (Figure)	Frequency (cm^{-1})	Bond Length R (Å)
Fig.3 (a) wider walled region	995.904	1.5984
Fig.3 (b) thin walled region	994.796	1.5989
Fig.4 (Dip Coated)(dominant other phase)	991.472	1.6007
Fig. 5 (2)	1001.55	1.595
Fig. 5 (5)	995.87	1.598
Fig. 5 (6)	993.654	1.5996
Fig. 5 (9)	993.654	1.5996
Fig. 5(12)	993.654	1.5996
Fig. 5(14)	1006.94	1.5927
Fig. 8 Dropcast (Basins)	994.796	1.5989
Fig. 8 DipCoated (hollow spheres)	995.904	1.5984
Fig. 9 (dipcoated/after heating)	995.904	1.5984

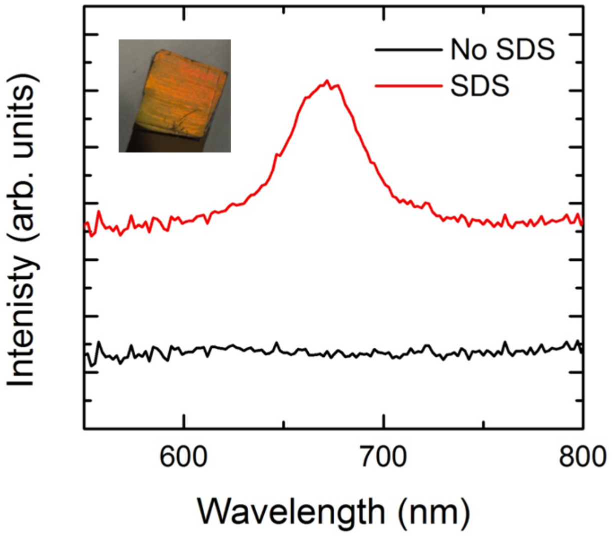


Fig. S3 Light scattering normal to the surface (i.e. angle of diffraction = 0°) for light incident at 60° on a 2D monolayer photonic crystal template of PMMA spheres formed with SDS (red) and a disordered photonic glass formed when SDS is not added to the solution of PMMA spheres.

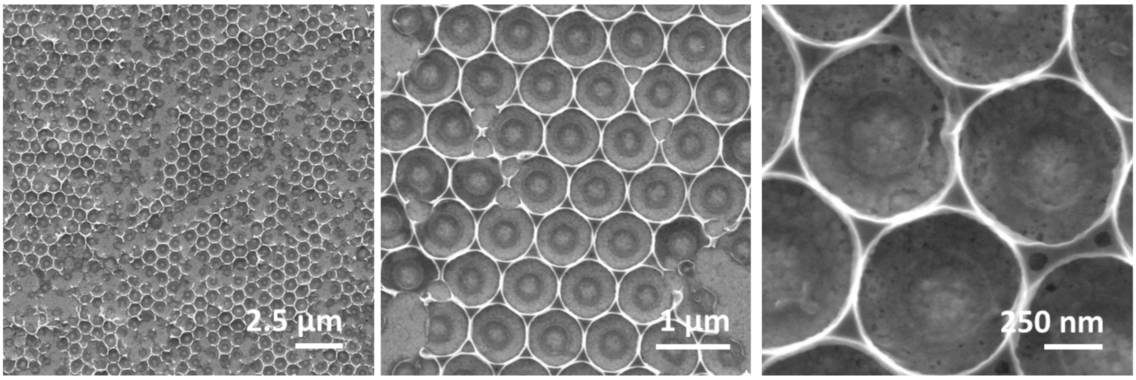


Fig. S4 SEM images at different magnification of the IO structure formed from dip coating a monolayer template in the 100:1 IPA:$OV(OCH(CH_3)_2)_3$ precursor solution, only once, at the rate of 150 mm/min showing the effects of low filling factor.

References

[1] M. Molero, R. Andreu, D. González, J. J. Calvente, G. López-Pérez, *Langmuir* **2000**, *17*, 314-322.

[2] C. D. Bruce, M. L. Berkowitz, L. Perera, M. D. E. Forbes, *The Journal of Physical Chemistry B* **2002**, *106*, 3788-3793.