

Fabrication of Carbon/Refractory Metal Nanocomposites as Thermally Stable Metallic Photonic Crystals

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Supplementary Information

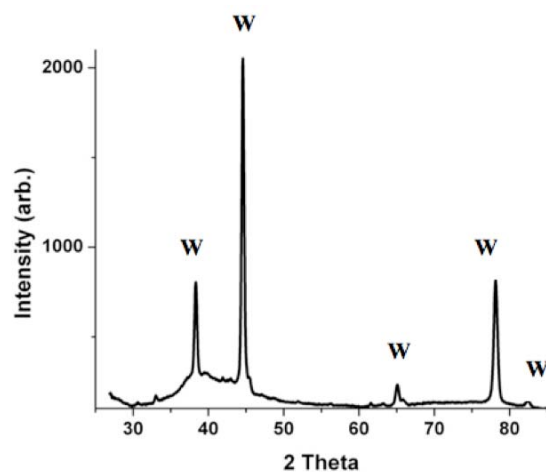


Fig. S1 XRD pattern of a tungsten-coated 3DOM carbon film. Peaks originating from *fcc* tungsten are labeled. The broad peak around 40° 2θ originates from the carbon scaffold.

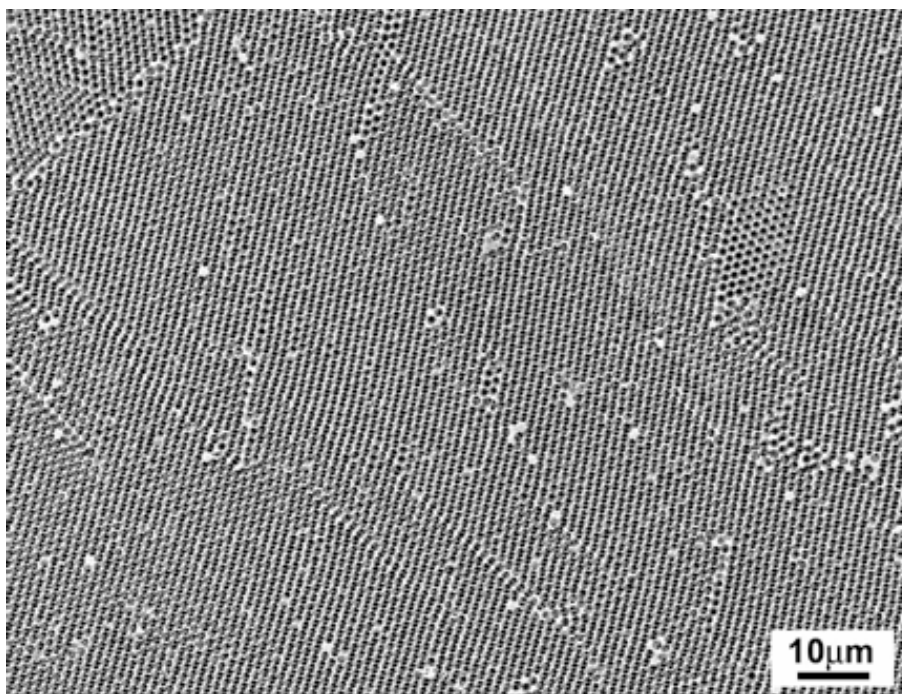


Fig. S2 Large-area, relatively defect-free MPhC film consisting of tungsten-coated 3DOM carbon.

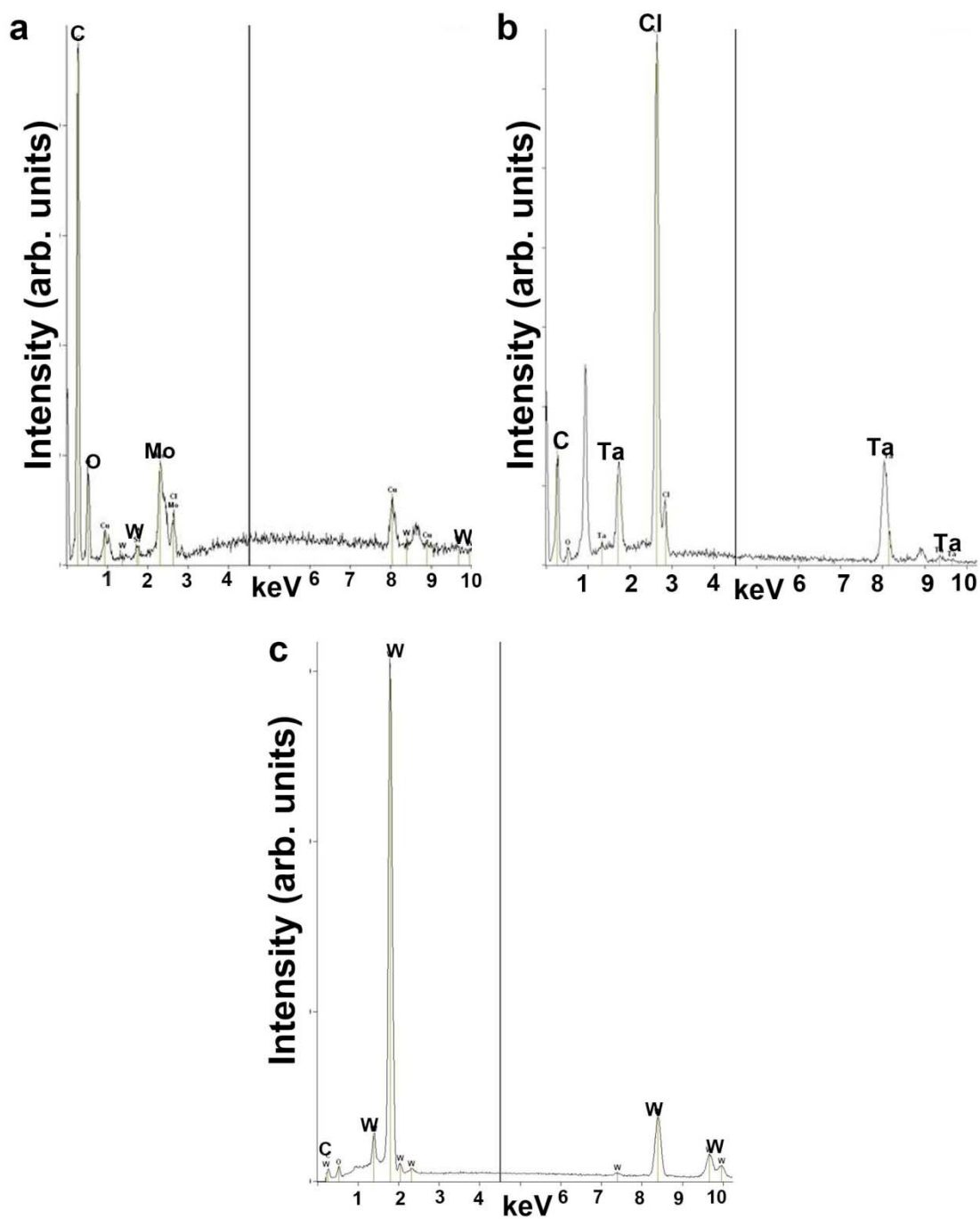


Fig. S3 EDS spectrum obtained from a (a) molybdenum (b) tantalum (c) tungsten-coated 3DOM carbon thin film.

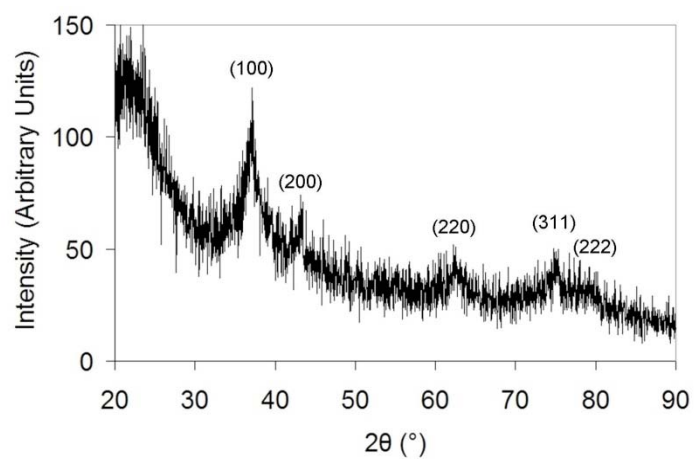


Fig. S4 XRD pattern of fcc cubic tungsten coated onto 3DOM carbon monolith.

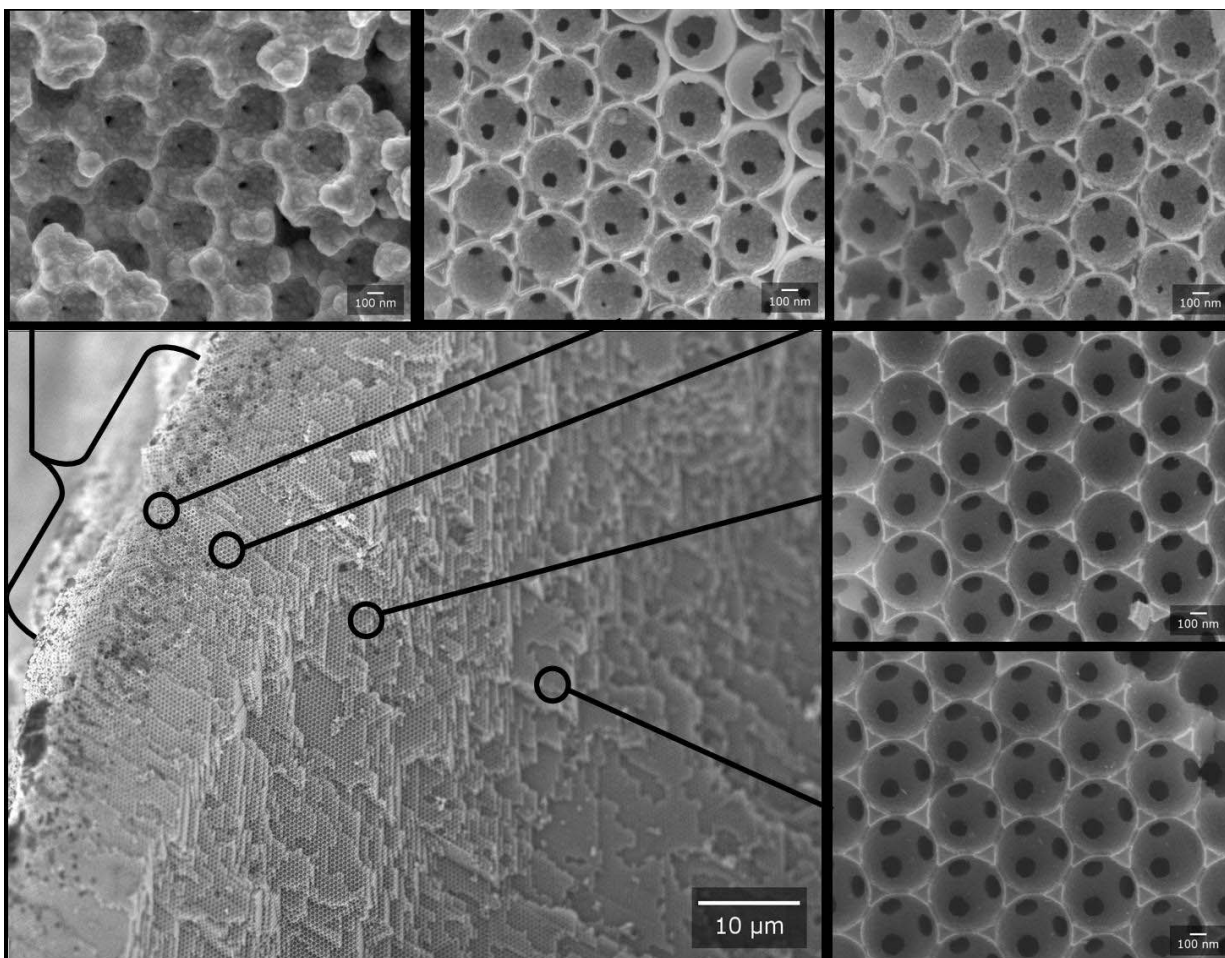


Fig. S5 SEM images of the cross section of sample 3DOM C/W2 (without a hafnia interlayer). From top-left going clockwise: images at depths of 0 μm , 1 μm , 8 μm , 43 μm , and 97 μm . The bottom-left image is an overview showing the respective position of the other images with the surface of the material appearing in the top-left of the image.

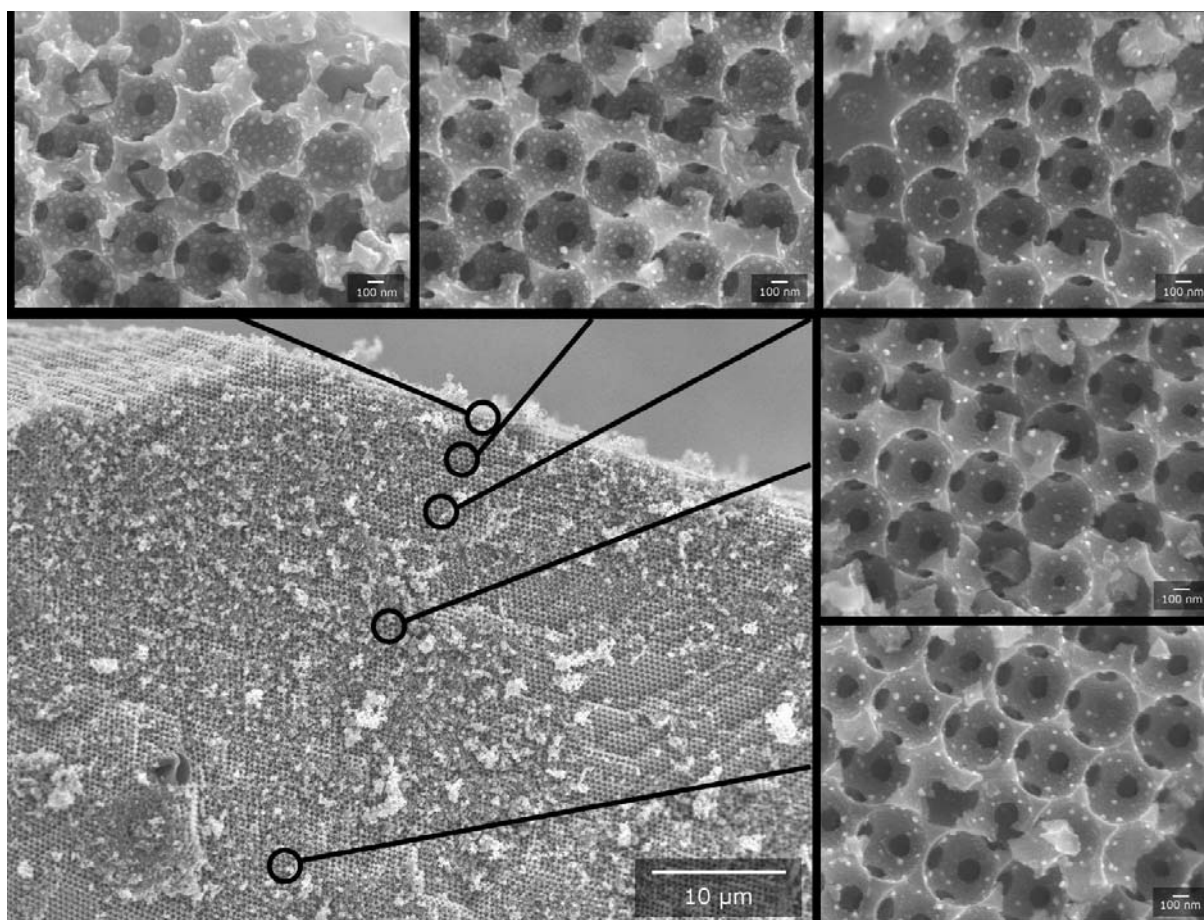


Fig. S6 SEM images of sample 3DOM C/W1 (without a hafnia interlayer) after vacuum-thermal treatment at 1000 °C for 1 h. Clockwise from top left: images at depths of 1 μm, 8.5 μm, 20 μm, 40 μm, and 83 μm. The bottom-left image is an overview showing the respective position of the other images with the surface of the material appearing in the top-right of the image.

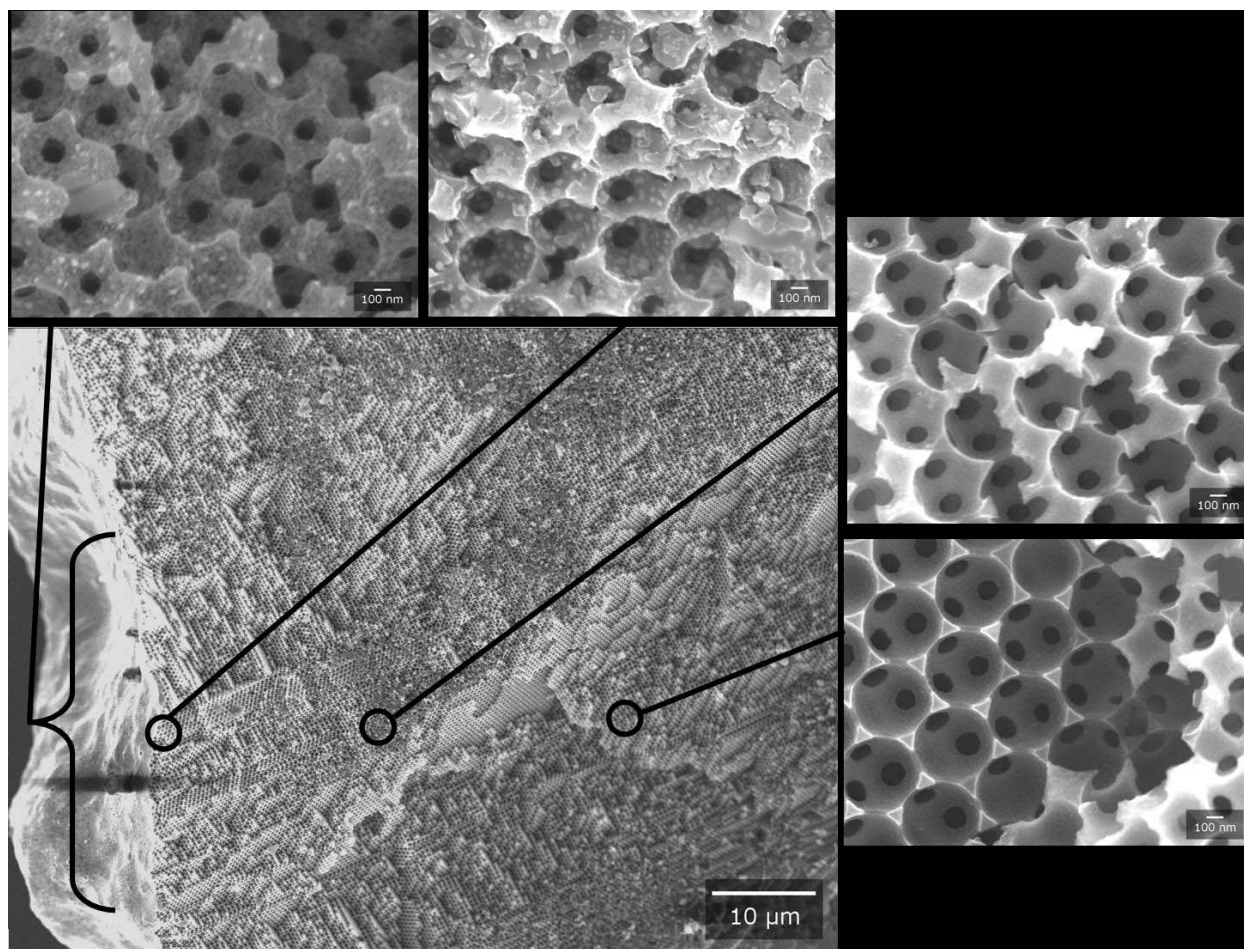


Fig. S7 SEM images of sample 3DOM C/W2 (without a hafnia interlayer) after thermal treatment. Clockwise from top left: images at depths of 0 μm , 1 μm , 23 μm , and 46 μm . The bottom left is an overview showing the respective position of the other images with the surface of the material appearing on the left of the image. The images at depths of 23 and 46 μm (right corner) show no penetration of hafnia or tungsten CVD layer (smooth 3DOM C scaffold). This indicates while using more metal precursor per deposition results in smoother metal coating, it leads to blocking of scaffold windows with metal deposition, and hence thinner metal deposition deeper into the sample.

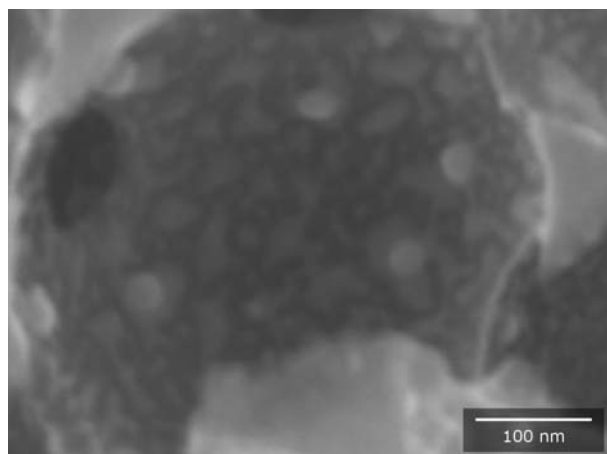


Fig. S8 High magnification SEM image of sample 3DOM C/W1 (without a hafnia interlayer) at a depth of 20 μm after thermal treatment. The image shows lighter tungsten grains against a darker carbon background.



Fig. S9 SEM cross-section of a 3DOM carbon monolith with a coating of hafnium oxide. The oxide can be seen as a bright layer against the darker carbon background.

Table S1 Variation in window sizes of samples 3DOM C/W1 and 3DOM C/W2, without a hafnia interlayer, after thermal treatment as a function of depth in the 3DOM C structure.

Sample 3DOM C/W1		Sample 3DOM C/W2	
Depth	Window Size	Depth	Window Size
(μm)	(nm)	(μm)	(nm)
1	142 ± 10	0	129 ± 8
8.5	140 ± 14	1	142 ± 13
20	133 ± 13	23	136 ± 15
40	138 ± 10	46	135 ± 11
83	141 ± 11		

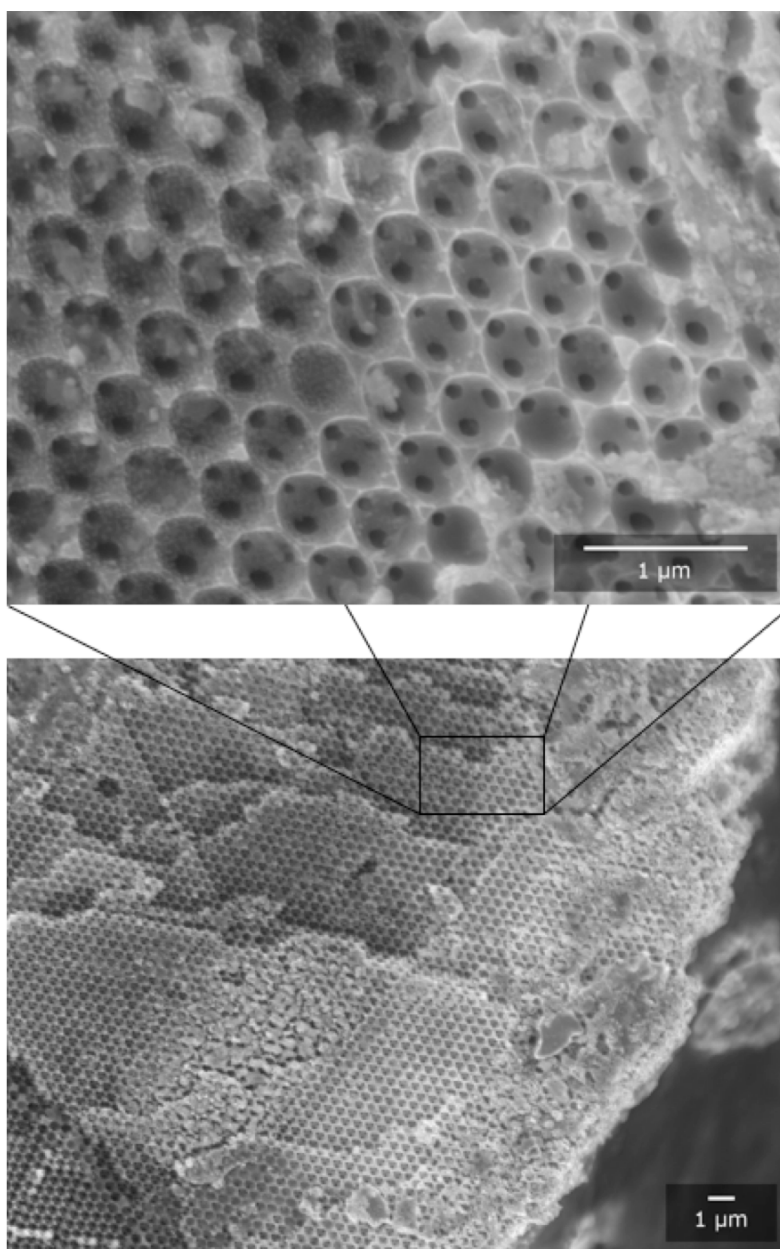


Fig. S10 SEM images of another region in the 3DOM C/W2H monolith, with a hafnia interlayer, after vacuum thermal treatment at 1000 °C for 1 h. The extent of hafnia penetration is clearly visible by the change in sample brightness, the brighter region on the right being closer to the external surface of the monolith where it was preferentially coated with hafnia. The expanded view on the top shows a smooth tungsten layer in the hafnia-coated area and tungsten agglomerates in the non-coated area. (Note that the surface of this sample had not been modified by oxygen plasma treatment.)

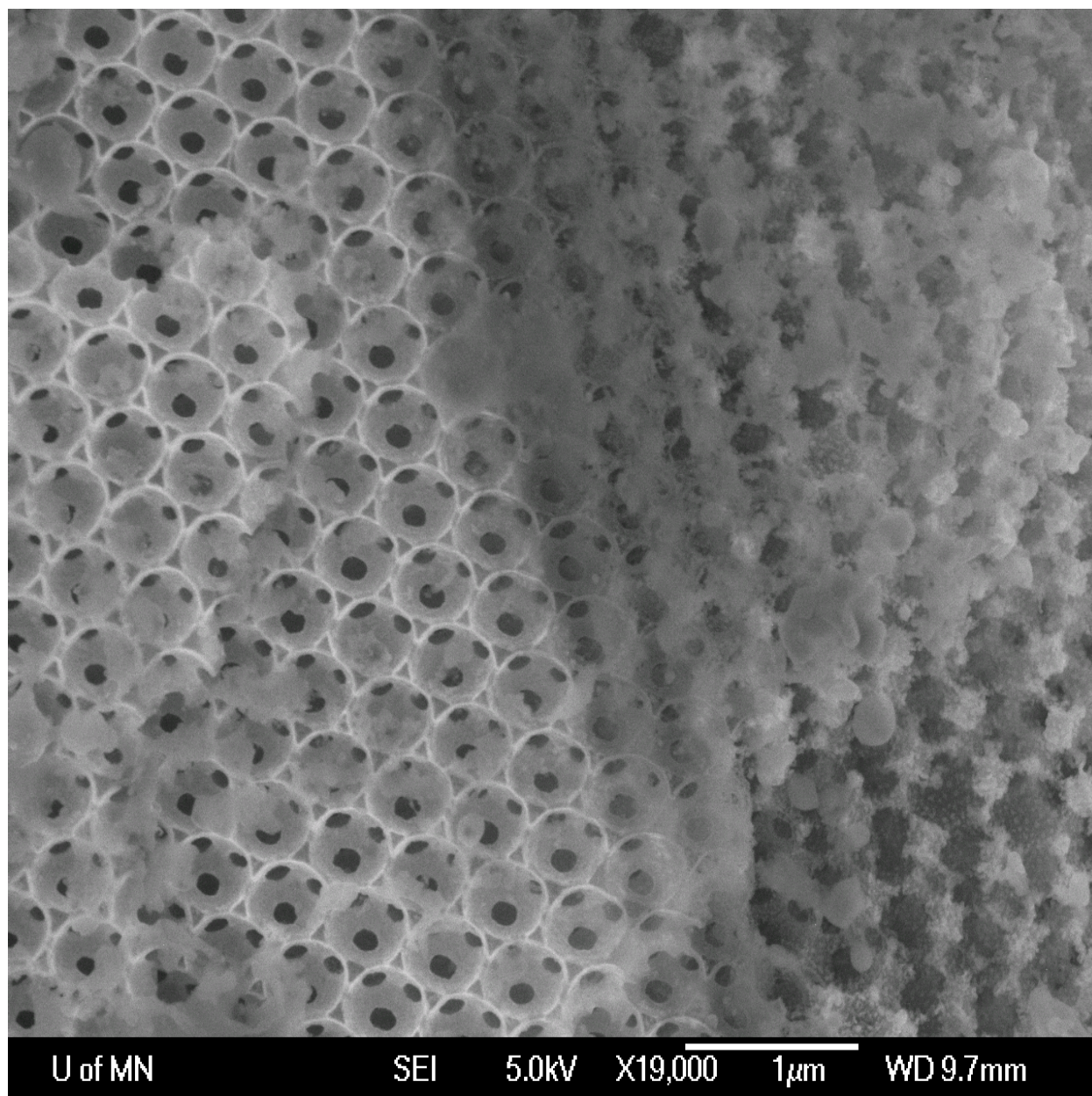


Fig. S11 SEM image of a cross-section of the 3DOM C/W2H monolith shown in Fig. S10 (with a hafnia interlayer), after vacuum thermal treatment at 1000 °C for an additional 5 h. The extent of hafnia penetration is clearly visible by the change in sample brightness, the brighter region on the left being closer to the external surface of the monolith where it was preferentially coated with hafnia. The tungsten coating on the hafnia interlayer (left) remained relatively smooth after thermal treatment, whereas the tungsten agglomerated in the region lacking a hafnia interlayer (right). The monolith remained intact on the bulk scale after this thermal treatment.

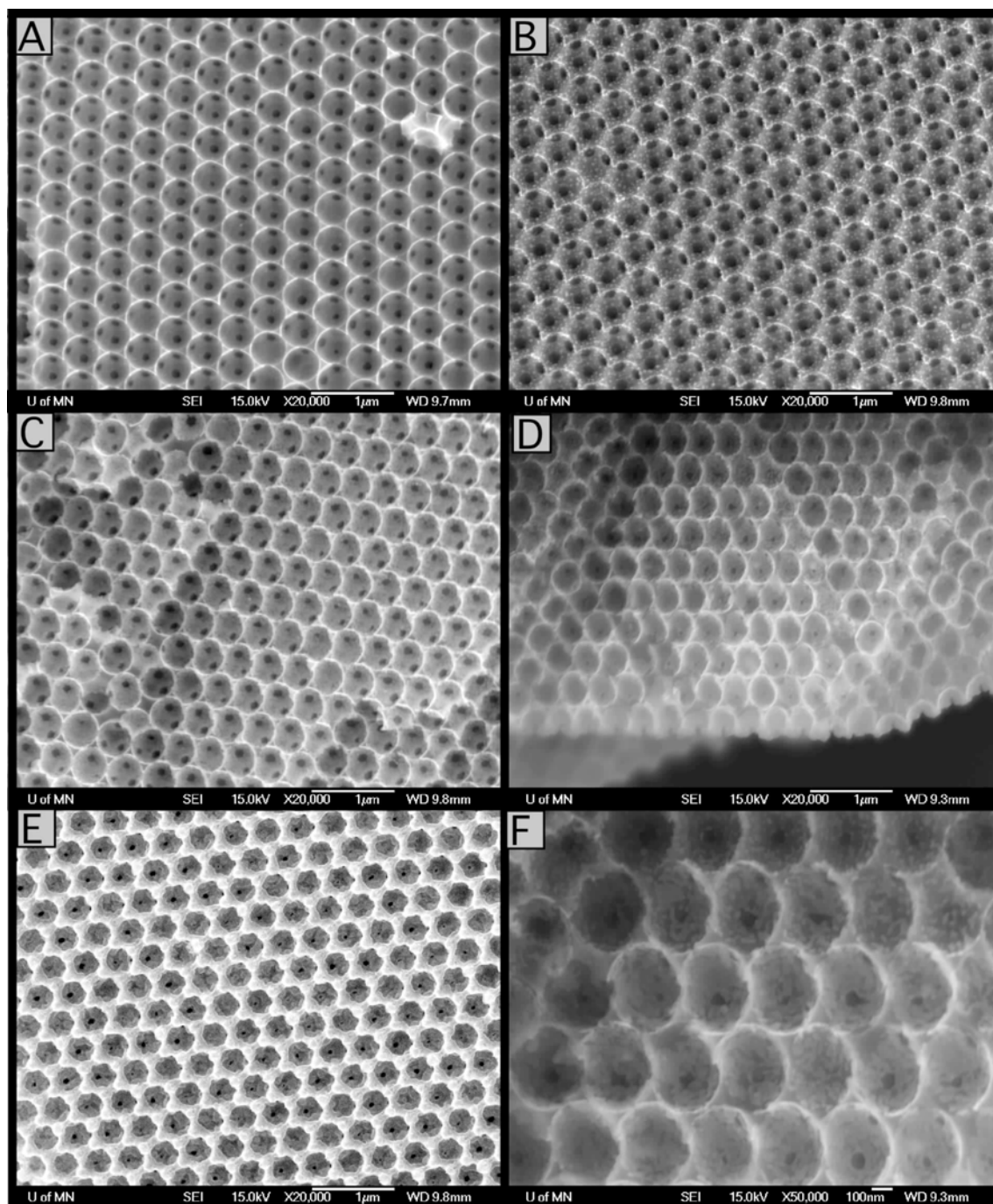


Fig. S12 SEM images showing the texture gradient across the 3DOM C/W2H monolith shown in Fig. S11, which had been heated in vacuum at 1000 °C for 1 h and later for an additional 5 h. (A) Region near the center of the monolith, which had not been coated with hafnia or tungsten. (B-E) Regions with increasing amounts of tungsten. No hafnia interlayer was present in (B) and little in (C). Image (D) shows a region where the boundary for hafnia penetration becomes apparent from differences in brightness (increased charging where the hafnia layer insulates tungsten from carbon). Image (E) shows a surface layer. (F) Expanded view near the hafnia boundary in (D).

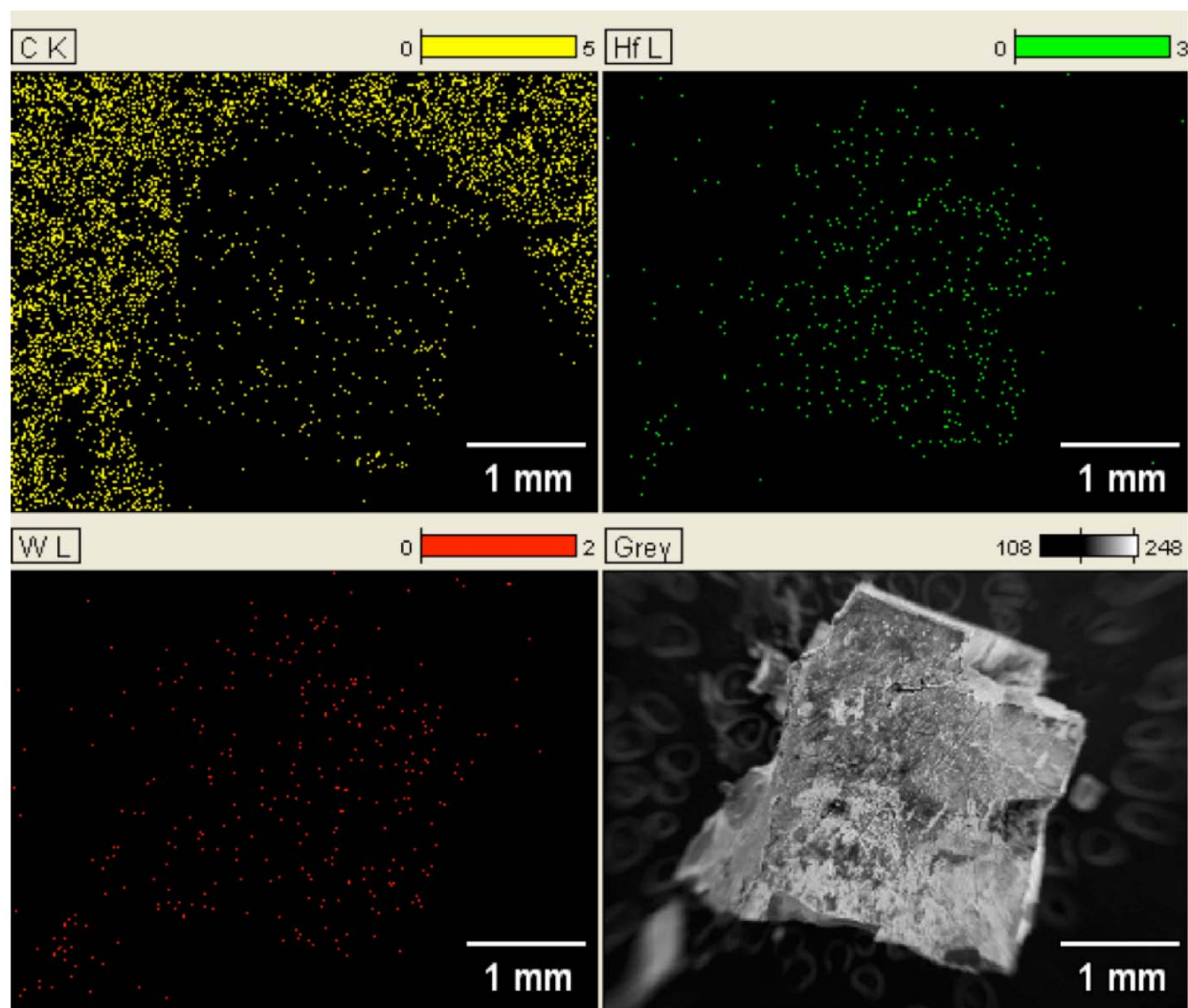


Fig. S13 EDS maps of the 3DOM C/W2H monolith, which had been heated in vacuum at 1000 °C for 1 h and later for an additional 5 h, showing the presence of both Hf and W in the near-surface region that was probed.

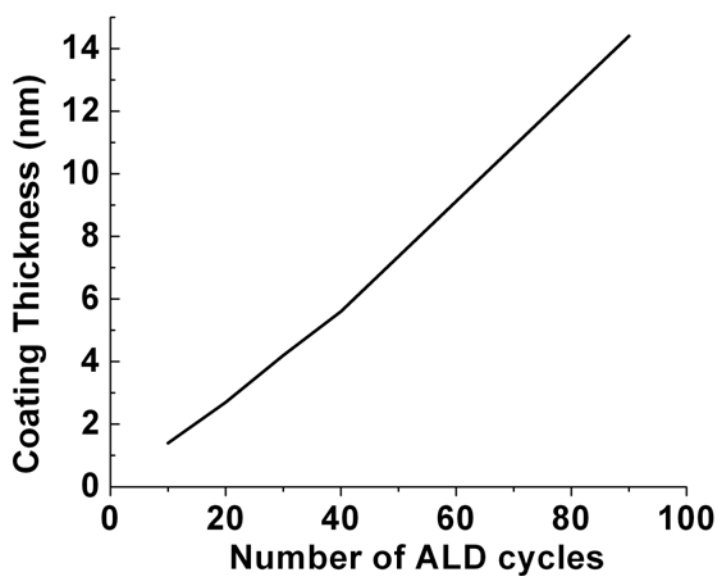


Fig. S14 Hafnium oxide coating thickness as a function of the number of ALD cycles on a flat silicon substrate. The same deposition conditions were used as for the 3DOM C samples. The thickness was estimated using optical ellipsometry after depositing a hafnia layer on a silicon wafer. Since a direct estimation of the hafnia coating thickness was not possible on the porous 3D surface, representative measurements were made on a flat wafer.