Electronic Supplementary Information

Periodic Arrays of Structurally Complex Oxide Nanoshells and Their Use as Substrate-Confined Nanoreactors

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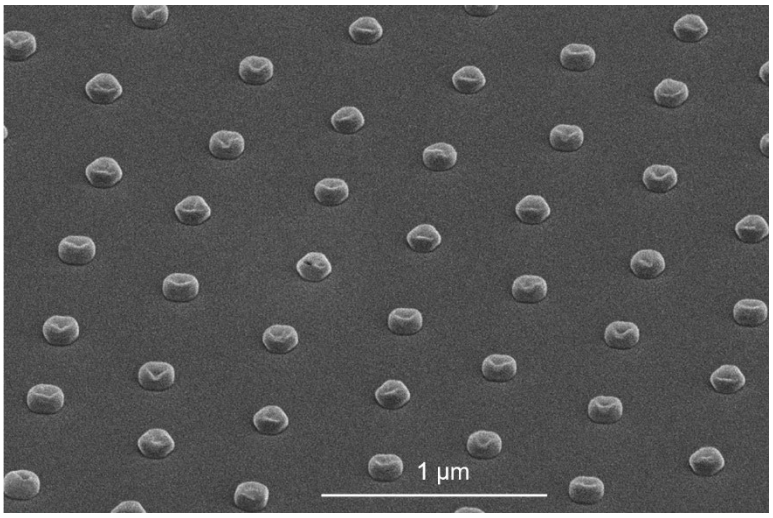

Fig. S1. SEM image of HfO_2 nanoshells that have collapsed because they lack the structural rigidity needed to withstand the capillary forces present when the nanoshells are removed from the etchant, rinsed, and then dried.

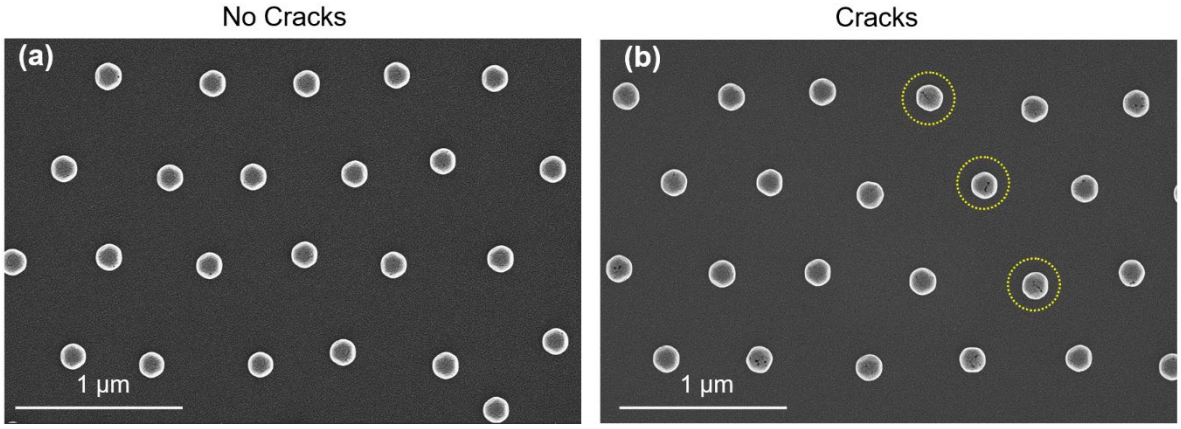

Fig. S2. SEM images of HfO_2 nanoshells where nanopores were induced using 770 °C anneals lasting (a) 30 and (b) 120 min. It should be noted that while both anneal times realize nanoshells in high yield, the longer anneal time gives rise to a significant number of shells with sizeable cracks (denoted by dashed yellow circles).

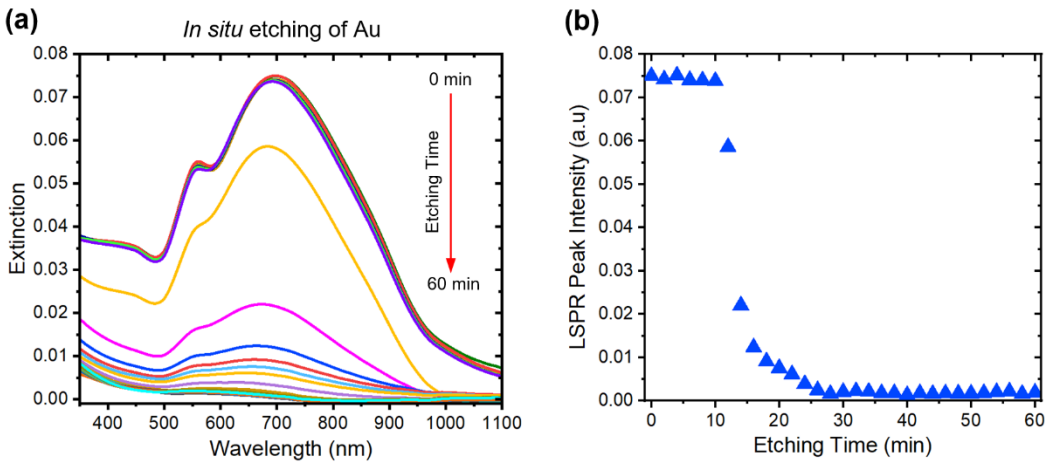

Fig. S3. (a) Extinction spectra measured *in situ* showing the time progression of the plasmon resonance for annealed Au@HfO_2 core–shell structures that are exposed to *aqua regia* etch. Spectra were taken every 2 min for 60 min. (b) Dependency of the maximum plasmon peak intensity plotted as a function of etching time. It should be noted that there exists a 10 min delay before appreciable etching occurs. The data is supportive of the fact that the *aqua regia* etch plays a role in forming nanopores on the annealed HfO_2 shells from which the Au is removed.

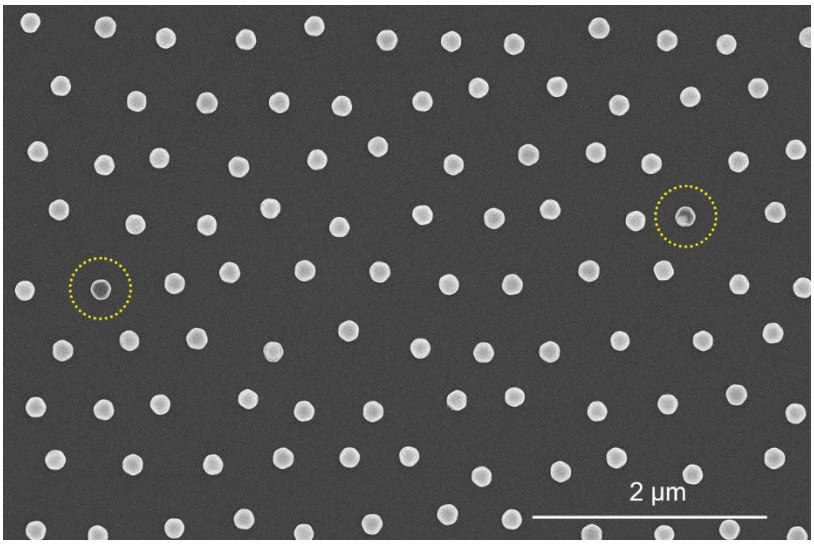

Fig. S4. SEM image of unannealed Au@HfO_2 core–shell structures that were exposed to *aqua regia* overnight. With only two structures appearing hollow or partially hallowed (denoted by dashed yellow circles), there is near 100% survivability. This data provides proof that the 770 °C anneal is essential for forming nanopores in the HfO_2 shell in a timely manner.

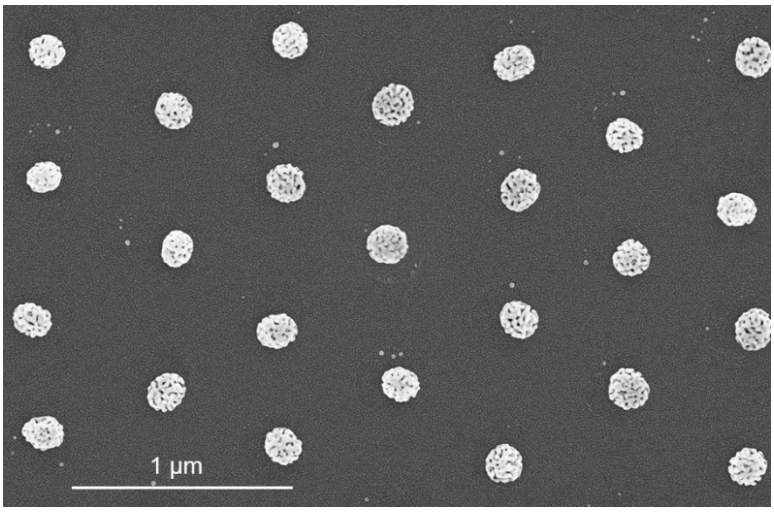

Fig. S5. SEM image of an array of porous Au structures formed by dealloying Ag from near-hemispherical AuAg alloyed nanostructures. It should be noted that these structures are quite similar to those produced within the confines of a HfO_2 nanoshell.

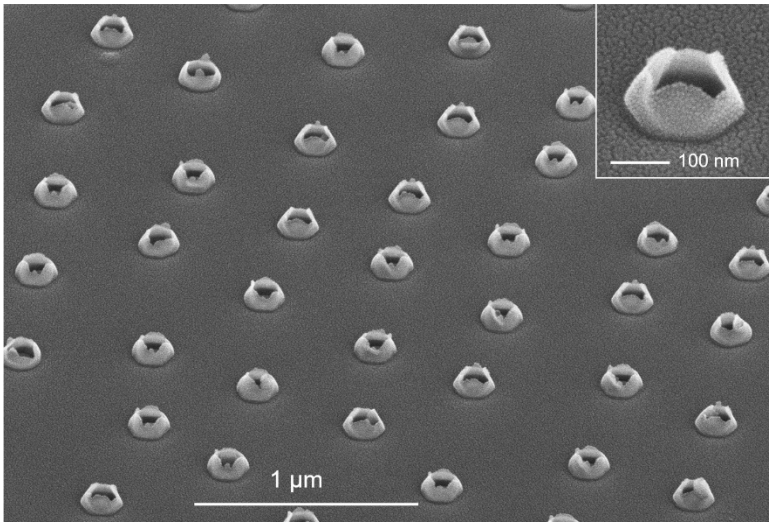

Fig. S6. SEM images of a periodic array of open-topped HfO_2 nanobowls formed by (i) fabricating Au@HfO_2 core−shell, (ii) Ar^+ ion milling at normal incidence to expose Au at just the top of the structure, and (iii) etching away the Au using *aqua regia*.

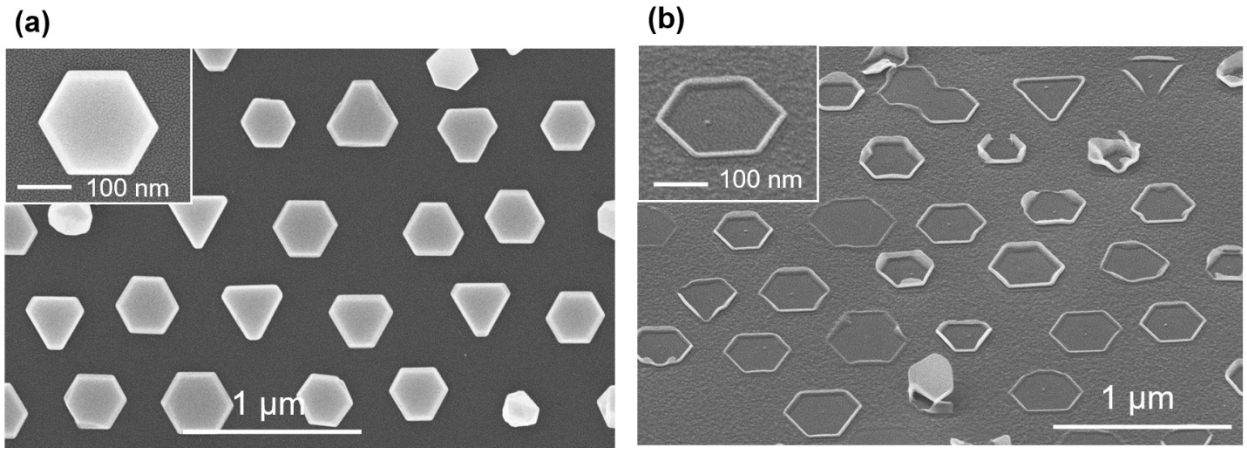

Fig. S7. SEM image of (a) hexagonal Au nanoplate templates and (b) the hexagonal HfO_2 nanorings formed when using the coating-milling-etching procedure shown schematically in Fig. 4a.