Colloidal crystals have attracted considerable attention due to their deterministic three-dimensional (3D) structures, interesting optical properties and ease of assembly.[1–5] The use of colloidal crystals as templates to impart periodic patterns into various materials has been broadly employed to create, for example, unique optoelectronic devices,[6–7] sensors,[8–12] and energy storage devices.[13–14] The general motivation for templating is to utilize the opals’ interconnected 3D structure to define the 3D structure of a material which is inherently difficult to form into a highly regular 3D structure on its own. A single replication yields a structure which is an inverse of the colloidal template, and a double replication yields the original structure of the template. This process is only successful if the colloidal template can withstand the deposition conditions of the material to be templated and there exist conditions whereby the original template can be removed without damaging the templated material. Given that the most popular template, silica, can only be removed with hydrofluoric acid or strong base, chemicals that dissolve many materials, this can be challenging. Polymer templates (e.g. polystyrene or poly(methyl methacrylate)) are easy to remove, but cannot withstand high temperature deposition strategies, limiting their use.[2] Thermally-stable colloids which could be removed under orthogonal conditions, i.e., conditions that do not damage the templated material, would allow currently inaccessibilities materials templating strategies. Additionally, if the templates contained additional desirable structural complexities (e.g. a high surface area) which are replicated in the templated material, additional applications may emerge; for example, dye sensitized solar cells require high-surface area electrodes,[15] as do many other catalytic devices. In this communication, we first demonstrate the fabrication of high-quality colloidal crystals from mesoporous carbon colloidal crystals which meet these requirements by tailoring the surface charge on the mesoporous carbon colloids. We then demonstrate the use of these colloidal crystals as high-surface area templates for traditionally difficult to template materials, employing carbon removal processes that are not destructive to the deposited material, creating unique, nanostructured inverse opal structures.

As a first attempt to make a carbon opal, monodispersed starburst carbon spheres (MSCS), synthesized as previously reported,[31] were dispersed into ethanol and deposited on a substrate via convective deposition.[7,32,33] Even though the polydispersity of the MSCS was very low (only 1.038), the result was a disordered film, probably because the zeta-potential of the as synthesized MSCS was only –14 mV. This compares to a zeta-potential of –31 mV measured for typical opal-forming silica particles. It has been shown that partial oxidation of carbon fibers introduces ionizable oxygen species (e.g., carboxylic acid).[34] These species would increase the surface charge. Heating the MSCS in air at 300 and 400 °C increased the surface charge.
with no significant size change; see Table 1 and Figure S1 for zeta-potential and SEM analysis. Significant size reduction occurred at 500 °C, and by 600 °C, the MSCS sample disappeared due to complete oxidation of the carbon.[34] To verify the porous structure of the MSCS remained through the oxidations, nitrogen adsorption measurements were conducted (Figure 1); the pore volume, size, and specific surface area are included in Table 1. The structural characteristics of the MSCS oxidized at 300 and 400 °C change very little. There is only a minor decrease in pore volume and a slight increase in pore size due to partial collapse of micropores, with the surface area remaining over 1300 m² g⁻¹. Oxidation at 500 °C resulted in significant decreases in both pore volume and surface area, and there is now no clear mesopore size distribution. To investigate the surface chemical effects of oxidation, X-ray Photoelectron Spectroscopy (XPS) was conducted on the as-synthesized and 400 °C treated samples (Table S1 and Figure S2). The surface of the oxidized carbon contained significantly more oxygen containing moieties, i.e., hydroxyls, quinones, and carboxylic acids (C-OH, C = O, C-OOH). The presence of these functional groups agree well with the increased surface charge measured for the oxidized MSCS and is consistent with other results.[34] Opal formation was then attempted using the MSCS with the increased surface charge. Both the 300 °C and 400 °C oxidized samples formed colloidal crystals, with the sample oxidized at 400 °C producing the highest quality (shown in Figure 2). The higher quality of the opals fabricated using the 400 °C oxidized MSCS can be attributed to the increased stability of the suspension due to the higher surface charge compared to the as-synthesized and 300 °C oxidized (−46 mV vs. −14 and −26 mV, respectively). Although opals produced this way show high degree of order in the Scanning Electron Microscopy (SEM) micrographs, due to the strong absorption of carbon, a low optical reflectivity and transmission was observed (Figure S3).

Due to the MSCS porosity and potential for complete removal by oxidation in air, the carbon colloidal crystals are ideally suited as templates to create unique nanostructures after inversion. Employed here are two gas-phase deposition techniques that allow deep infilling of the mesopores: atomic layer deposition (ALD) of hafnia (HfO₂) and alumina (Al₂O₃) and static chemical vapor deposition (CVD) of silicon (Si). SEM

Table 1. MSCS surface properties after heat treatment for 30 min.

<table>
<thead>
<tr>
<th>Heat treatment °C</th>
<th>Diameter [nm]</th>
<th>Zeta Potential [mV]</th>
<th>Pore volume [mL g⁻¹]</th>
<th>Pore size [nm]</th>
<th>Specific surface area [m² g⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>As prepared</td>
<td>484 ± 19</td>
<td>−14 ± 6</td>
<td>1.00</td>
<td>1.67</td>
<td>1670</td>
</tr>
<tr>
<td>300</td>
<td>475 ± 7</td>
<td>−26 ± 6</td>
<td>0.92</td>
<td>1.74</td>
<td>1490</td>
</tr>
<tr>
<td>400</td>
<td>473 ± 7</td>
<td>−46 ± 4</td>
<td>0.92</td>
<td>1.87</td>
<td>1360</td>
</tr>
<tr>
<td>500</td>
<td>244 ± 10</td>
<td>−34 ± 4</td>
<td>0.37</td>
<td>-</td>
<td>420</td>
</tr>
<tr>
<td>600</td>
<td>-</td>
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Figure 1. (a) Nitrogen adsorption (solid circles) and desorption (open circles) isotherms of as prepared MSCS (black curve), and MSCS oxidized at 300 °C (red), 400 °C (blue), and 500 °C (green). (b) Calculated pore size distribution from (a).

Figure 2. SEM micrographs showing cross-section (a,b) and oblique (c) views of 5 layer opals, and (d) cross-section micrograph of 7 layer opal, all fabricated from 400 °C oxidized MSCS.
Measurements reveal the HfO$_2$ infiltrates approximately the structure of the HfO$_2$ in the as-deposited state. The top of the MSCS removal. Since carbon can be readily removed through carbon, grain growth and sintering in the HfO$_2$ occur simultaneously. It appears that during the MSCS thermal removal process, a smooth, instead of granular, nanostructure is observed. Carbon, due to its low atomic number, appears darker than the HfO$_2$ in the SEM micrograph. The micrograph shows a bright HfO$_2$ shell and spokes of HfO$_2$ penetrating the MSCS. Measurements reveal the HfO$_2$ infiltrates approximately 80 nm. ALD is known to fill deep vias and other high aspect ratio structures, and thus deep infiltrating of the MSCS was not a surprise.

After a brief Reactive Ion Etch (RIE) to open the top HfO$_2$ surface, carbon was thermally removed at 600 °C for 1 h. Unlike wet or deep RIE etching required for silica template removal, this thermal removal process does not remove HfO$_2$, so all the deposited HfO$_2$ remains. Figure 3b shows the HfO$_2$ inverse opal SEM and TEM micrographs. In these, a granular HfO$_2$ structure exists, perhaps due to the HfO$_2$ crystallizing during the thermal MSCS removal. Since carbon can be readily removed through oxygen plasma at room temperature, it was possible to evaluate the structure of the HfO$_2$ in the as-deposited state. The top of the HfO$_2$-coated MSCS opal was opened via RIE etching, followed by an oxygen plasma etch to remove the MSCS. The resulting inverse opal (Figure 3c) contrasts sharply with the thermally removed MSCS: a smooth, instead of granular, nanostructure is observed. It appears that during the MSCS thermal removal process, grain growth and sintering in the HfO$_2$ occur simultaneously with carbon removal. Once the MSCS support is removed, the HfO$_2$ is free to crystallize and coarsen, while the as-deposited HfO$_2$ better replicates the ultra-high surface area MSCS.

To verify these hypotheses, experiments were conducted to crystallize the HfO$_2$ prior to MSCS template removal. A sample, the HfO$_2$ is amorphous. To crystallize the HfO$_2$ prior to carbon removal, the sample was annealed in forming gas (5% H$_2$ in Ar) at 600 °C for 1 h. This replicates the thermal removal process time and temperature; however, the forming gas limits MSCS oxidation. Crystallization of the HfO$_2$ prior to template removal is only possible due to carbon's high thermal stability and inert nature with respect to HfO$_2$. After annealing, the MSCS was removed through oxygen plasma. Cross-sectional SEM (Figure 3d) of this sample is strikingly similar to the as-deposited, oxygen plasma removed samples (Figure 3c). It appears the MSCS provided a support and template during HfO$_2$ crystallization, limiting sintering and grain growth, preserving the templated nanostructure. X-ray diffraction (XRD) on the as-deposited and annealed samples was used to confirm the amorphous nature of the as-deposited HfO$_2$ and its crystalline nature after annealing. For this experiment, it is important that the majority of the HfO$_2$ is deposited in the pores of the MSCS and not on the MSCS surface (the x-ray experiment does not distinguish between HfO$_2$ on the surface of the MSCS surface and in the pores), and so the number of ALD cycles was reduced to 60, depositing nominally 6 nm of HfO$_2$. Most of the HfO$_2$ will be inside the MSCS, and only a few nm will be on the surface of the carbon colloids. XRD shows the as-deposited HfO$_2$ is amorphous, while the annealed sample is crystalline (Figure S4). From the Scherrer Equation (Equation S1), the average crystallite thickness was found to be 8.4 nm, substantially greater than the 1.87 nm MSCS pore size but significantly less than the total length infiltrated into the pores (≈80 nm), indicating the HfO$_2$ crystallites may be rod-like. Transmission electron microscopy (TEM) (Figure 3d, top) and selected area electron diffraction (SAED, Figure S5) confirmed the crystalline nature of HfO$_2$.

100 cycles (10 nm nominally) of ALD Al$_2$O$_3$, with the MSCS thermally removed, is shown with a FIB cut in Figure 4a. As with the HfO$_2$, the thermal removal process is completely orthogonal to Al$_2$O$_3$ removal. In most of the MSCS, the Al$_2$O$_3$ infiltrates into the center; however, ‘defects’ of partially unfilled MSCS occur (top right MSCS in Figure 4a). The TEM micrograph of the Al$_2$O$_3$ inverse colloid in Figure 4b shows the solid Al$_2$O$_3$ shell and porous center. Unlike for HfO$_2$, the Al$_2$O$_3$ inverse opal did not crystallize, and its mesostructure did not appear to Oswald ripen during thermal carbon removal at 600 °C (XRD in Figure S4). This may not be surprising, as 1100 °C is a typical crystallization temperature for alumina.

The final successful material investigated for template inversion was Si, which as grown using static CVD. SEM and TEM micrographs are shown in Figure 4c,d. To prevent Si oxidation, MSCS were removed via room temperature oxygen plasma after removing the top Si over layer via RIE. The conformal Si static CVD deposition infiltrates the MSCS template, creating...
at a wavelength of 840 nm. A MSCS opal was also coated with 300 cycles HfO\textsubscript{2} (30 nm nominally). The optical measurements are shown in Figure 5b after the MSCS were removed. 30 nm of HfO\textsubscript{2} is below the pinch-off point (when the colloid interstitials fill and block further precursor deposition) of 37 nm for the 479 nm colloids. For the thicker HfO\textsubscript{2} deposition, the reflection peak red-shifts to 1.0 \( \mu \text{m} \) and increases to 35% with well-defined Fabry-Perot fringes. Since the mesopores are already full after 100 ALD cycles, the extra 200 cycles simply increase the thickness of solid HfO\textsubscript{2} shell around each MSCS particle, leading to the red-shift and increases in intensity of the reflection peak. The Al\textsubscript{2}O\textsubscript{3} optical measurements are shown in Figure 5c. Interestingly, no reflection peak is observed; this could be the result of the infilling ‘defects’, where a portion of the colloids have large voids in the center. These defects perhaps act as strong scattering centers. Optical measurements of the Si inverse structure are shown in Figure 5d; the main reflectance peak is at 940 nm with 19% reflectance. The transmittance measurement shows a primary dip of 63% corresponding with the reflectance peak; the remaining 18% of the light is either absorbed or scattered. Interestingly, the Si inverse structure has a transmittance of near 95% at longer wavelengths, compared to only \( \sim 55\% \) for a typical Si inverse opal. The high transmittance (low reflectance) is evidence that the effective refractive index of the porous Si structure is much lower than pure Si (\( \sim 3.5 \)).

In conclusion, we have shown that by tailoring the surface charge of carbon colloids, high-quality carbon colloidal crystals can be fabricated and that these high-surface area colloidal crystals can be used as templates for a variety of materials, a porous-Si interior. As expected, XRD (Figure S4) reveals the as-grown Si is amorphous, as Si crystallization requires heating to 1000 °C for several hours. Platinum ALD in the MSCS was also attempted. However, due to oxygen being a reactant in the ALD growth, the MSCS opal oxidizes and loses its well-defined order.

Optical measurements were conducted on HfO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, and Si inverted opals (Figure 5). Figure 5a shows the 100 cycle ALD HfO\textsubscript{2} inverse structure with a primary reflection peak of 16%
creating unique, high-surface area nanostructured inverse opals. These materials, HfO₂, Al₂O₃, and Si, penetrate deep into the mesopores of the MSCS. Importantly, the carbon removal process is completely orthogonal to the deposited material removal, preserving the fine-scale mesostructure of the MSCS in the templated materials. Because MSCS removal is orthogonal to the etching of many materials, MSCS provide a general approach for templating materials which currently cannot be templated by conventional opals.

**Experimental Section**

**Synthesis:** Monodisperse Starburst Carbon Spheres (MSCS) were synthesized as previously reported.[1] The MSCS were oxidized in a Lindberg furnace using a 30 min ramp, 30 min hold, and cooled to room temperature. Foropal fabrication, Piranha-cleaned substrates (glass or quartz) were placed at a 20° angle in a 20 mL scintillation vial with 0.7 g colloidal suspension (0.5–2 wt% in ethanol). The vials were placed in an incubator (Fisher, Isotemp 125D) and held at 40 °C overnight.

**Infiltration and Template Removal:** HfO₂ and Al₂O₃ ALD, using a Cambridge Nanotech ALD system, were done at 200 °C and 80 °C, respectively, on fabricated carbon opals with both recipes having a growth rate of 1 Å cycle⁻¹. Si static CVD was done to expose the MSCS for thermal or oxygen plasma removal. Thermal removal was done at 600 °C for 1 h with a 30 min ramp. Oxygen plasma removal was done using 200 W at 400 mTorr, 20 W, for 2 h.

**Characterization:** Nitrogen physisorption isotherms, BET specific surface area, and pore volume were measured and calculated as previously described.[2] Scanning electron microscopy (SEM) was done on Hitachi S-4700 or S-4800. Transmission electron microscopy (TEM) was done on a JEOL 2100LA at an accelerating voltage of 200 kV. Focus ion beam (FIB) milling was done on a FEI Beam 235 FIB. Zeta-potential measurements were conducted in Millipore water on a NICOMP 380 ZLS Particle Sizer.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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