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Aerogel materials have myriad scientific and technological applications due to their large intrinsic surface areas and ultralow densities. However, creating a nanodiamond aerogel matrix has remained an outstanding and intriguing challenge. Here we report the high-pressure, high-temperature synthesis of a diamond aerogel from an amorphous carbon aerogel precursor using a laser-heated diamond anvil cell. Neon is used as a chemically inert, near-hydrostatic pressure medium that prevents collapse of the aerogel under pressure by conformally filling the aerogel’s void volume. Electron and X-ray spectromicroscopy confirm the aerogel morphology and composition of the nanodiamond matrix. Time-resolved photoluminescence measurements of recovered material reveal the formation of both nitrogen- and silicon-vacancy point-defects, suggesting a broad range of applications for this nano-crystalline diamond aerogel.

**Synthesis and characterization of a nanocrystalline diamond aerogel**

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Aerogels are a fascinating class of high surface-area continuous solids with a broad range of both commercial and fundamental scientific applications (1–8). Both crystalline and amorphous structures have been synthesized. Amorphous carbon aerogel in particular has received a considerable amount of attention in recent years owing to its low cost, electrical conductivity, mechanical strength, and thermal stability (9). Numerous applications have been explored for this material including water desalination (10), electrochemical supercapacitors (11), as well as both thermal (12) and optical (13) insulation. Impressive advances have been made in the case of polycrystalline aerogels through the oxidative aggregation of chalcogenide quantum dots that preserve spectral signatures of quantum confinement (14). Furthermore, recent high-pressure, high-temperature (HPHT) experiments with mesoporous silica and periodic carbon have been employed to produce mesoporous coesite (15, 16) and diamond (17) structures.

Despite much progress in achieving phase transitions in mesoporous materials, the transition from an amorphous to a crystalline phase in carbon aerogel materials has remained a challenge. The extremely low density and irregular pore structure in aerogel materials make preventing pore collapse a formidable obstacle. Such a nondestructive transition would nevertheless be desirable, because a porous, three-dimensional self-supporting structure consisting of diamonds would have unprecedented optical, thermal, and chemical properties while still maintaining the inherent advantages of aerogel morphology. For instance, diamond aerogel promises a widely tunable optical index of refraction (≈1 < n ≈ 2.4) for antireflection coatings, biocompatibility, chemical doping, potentially enhanced thermal conduction, as well as electrical field emission applications while still maintaining the low-density, high surface area and self-supporting aerogel morphology. Such a material is particularly intriguing in light of the numerous scientific and technological applications of conventional nanodiamonds, which range from optical quantum bits (18) to cellular biomarkers (19). Here we demonstrate the experimental feasibility of maintaining the morphology of a carbon aerogel through an induced HPHT amorphous-to-crystalline phase transition.

**Results and Discussion**

In order to affect the transition to diamond we first pressurize the amorphous precursor material sufficiently to enter the diamond stability range of the carbon phase diagram (20) and then heat the sample to overcome kinetic barriers. This is accomplished experimentally using a laser-heated diamond anvil cell (LHDAC) (Fig. 1A).

The amorphous precursor aerogel (of density 0.040 g/cm³; see SI) was placed into the diamond cell sample cavity (Fig. 1A), which was then filled with supercritical neon at approximately 22,000 psi. We note that while the precursor is self-supporting it is still relatively delicate at least on length scales larger than a few micrometers. Finger pressure, for example, is enough to visibly collapse it. Because our nominal aim was to preserve the aerogel’s structure on all length scales larger than the interatomic, it was vital to ensure it was as near as possible hydrostatically supported at the pressures chosen for synthesis. Ideally, the pressure on the inside and outside of the material should be equal and there should be a uniform pressure across the entire sample. Neon is a commonly used pressure transmitting medium in diamond anvil cell experiments and provides a reasonable approximation to a hydrostatic environment at even quite high pressures. At room temperature neon freezes at approximately 4.7 GPa (21), which is well below the pressures chosen here for synthesis; however, it is expected to remain relatively soft. Also, because it was in the supercritical state during the initial high-pressure gas loading of the diamond cell (SI Text) it was assumed to completely fill the aerogel without encountering resistance due to for example surface tension. Furthermore, neon’s inertness made chemical reactions with the sample extremely unlikely while its transparency facilitates optical microscopy, Raman spectroscopy, and laser heating.

Results presented here were mostly obtained from three separate experiments in which amorphous precursor samples were compressed to approximately 21.0 GPa, 22.5 GPa, and 25.5 GPa. The samples were then laser heated in order to drive the transition to diamond. We chose this pressure range in order to favor the formation of diamond, but we did not attempt to establish a
minimum synthesis pressure, or more generally the required minimum combined conditions of pressure and temperature. Furthermore, precise determination of temperature was complicated by a number of factors including sample motion during heating in the melted neon. In a single separate experiment in argon in which sample motion was reduced, and on the basis of measured thermal emission data, we concluded that synthesis temperature likely exceeds $1,580 \pm 40$ K (see SI Text for important details).

Raman spectroscopy was used to characterize the state of the sample and monitor the transition from amorphous to crystalline diamond. The amorphous carbon aerogel sample appears completely opaque before heating, owing to its strong broadband absorbance (13). The material becomes highly transparent following laser heating and was observed to transmit a large amount of incident light in comparison with the amorphous precursor (Fig. 1A). Raman spectra were acquired from the carbon aerogel after pressurizing and before heating (Fig. 1C and Fig. S1) and were found to be similar to prior reports on amorphous carbon from pressure-induced shifts. This observation rules out the possibility of a superhard graphite phase helping to prevent pore collapse, which has been hypothesized for mesoporous carbon (17) given that the spectrum still appears amorphous after pressurizing. Spectra obtained following laser heating (Fig. 1D and Fig. S1) revealed a new sharp peak between approximately $1,390 \text{ cm}^{-1}$ and $1,404 \text{ cm}^{-1}$ (depending on the pressure) and the pressure dependence of this mode was consistent with cubic crystalline diamond (Fig. S2). Furthermore, intense fluorescence was visible during Raman measurements from the laser-heated material, which was retained at ambient conditions (Fig. 1D Inset), suggesting the potential formation of luminescent point defects in the newly formed diamond phase. Aside from the fact that diamond is favored thermodynamically, we also note that recent theoretical and experimental reports have demonstrated hydrogen-catalyzed synthesis of diamond nanocrystals (22).

Transmission electron microscopy (TEM) of recovered material (Fig. 2A and B) revealed that the highly porous aerogel morphology of the precursor appears well preserved in the recovered material, while electron diffraction (Fig. 2C and D) confirms the conversion from amorphous carbon to cubic diamond. The presence of the diamond phase is confirmed further through high resolution TEM images (Fig. 2E and F). The amorphous starting material consists of interconnected graphitic domains with sizes of approximately 10 nm, in agreement with previous reports for...
carbon aerogel (9). In contrast, the recovered diamond aerogel material consists of nanocrystalline grains connected through what appears to be thin surface coatings of graphitic carbon. Individual grains range in size from 2.5 to 100 nm and at high resolution show sharp lattice fringes with a d-spacing of approximately 2.06 Å corresponding to the (111) plane of cubic diamond (Fig. 2F). We assume this size distribution is due to the extent of heating, which depends on how well incident laser light is absorbed by different regions of the sample. Also, melting of the neon medium may facilitate agglomeration and crystal growth. High resolution SEM analysis (Fig. S4) is consistent with TEM observations. The measured Raman spectra after heating are likely dominated by the presence of the larger diamond grains because the corresponding frequencies and line shape are consistent with diamonds of grain size >10 nm (see ref. 23).

Electron energy loss spectroscopy spectra (Fig. S5), obtained from this material with 1.8-eV resolution, show the characteristic second gap of diamond at 302.5 eV as well as a small sp² graphite π* absorption shoulder at 285.5 eV. The sp² absorption is consistent with the diamond nanocrystals having thin surface coatings of graphitic carbon; however, this energy resolution is insufficient to completely resolve pre-edge features.

Comparison of the recovered aerogel with other types of nanodiamond aids in the characterization of the aerogel’s composition. Fig. 3 and Fig. S6 show high energy resolution (approximately 100 meV) C ls near-edge X-ray absorption fine structure (NEXAFS) data measured on the aerogel materials using scanning transmission X-ray microscopy (STXM) as well as total electron yield (TEY) mode on bulk diamond and detonation nanodiamonds of 4 nm diameter. While the precursor aerogel exhibits predominantly sp² carbon, the diamond aerogel spectrum distinctly resembles the predominantly sp³ detonation nanodiamond spectrum (24). This includes the characteristic second gap in the diamond band structure at 302.5 eV, which has been shown to become less pronounced with decreasing crystallite size in nanodiamond materials (25). The C ls Æ π* transitions at 285 and 287 eV in the spectra of the aerogel and detonation nanocrystals match remarkably well in both energy position and intensity. They are characteristic of sp² carbon and have been attributed to a fullerene-like surface reconstruction on the diamond nanoparticles (24). This agrees with TEM results (Fig. 2F), which show thin surface coatings consistent with graphitic carbon. The fundamental similarities between the spectra for STXM spectra of diamond aerogel and TEY spectra of detonation nanodiamonds give a clear indication from sampling many grains (>10³) that the diamond aerogel consists of nanodiamond crystallites of similar composition, morphology, and surface reconstruction as clean detonation nanodiamonds.

Another dramatic new property of the recovered diamond aerogel in comparison with the amorphous starting material is the presence of bright and photostable luminescence. Fig. 4A shows a bright-field TEM image from a segment of recovered diamond aerogel material that contains several different diamond grain sizes, from 2.5 to 100 nm. Two pronounced features are observed in the photoluminescence spectrum (Fig. 4B): a broad feature starting at approximately 639 nm and a sharper feature at approximately 739 nm. These wavelengths are comparable to those of the well known negatively charged nitrogen-vacancy (N − V)− (26) and neutral silicon di-vacancy (V-Si-V) (27) centers, respectively. These features were not observed in all recovered material and likely result from the unintended presence of both N and Si in the precursor aerogel. Confocal fluorescence images were collected from recovered diamond aerogel (Fig. 4C) in conjunction with time correlated single photon counting (TCSPC) of both small and large grains (Fig. 4D), which were spectrally filtered around the nitrogen-vacancy peak. The TCSPC data indicate that the emission lifetime from the aerogel in the 639-nm spectral region has an approximately 10-ns component (Fig. 4D, blue) characteristic of the negatively charged (N − V)− center (28), which is a prime candidate for future quantum information processing (29, 30). Furthermore, TCSPC data for the 739-nm spectral region (Fig. S7 and S8) shows a lifetime of approximately 1 ns, consistent with the (V-Si-V) center, which has been proposed as a biocompatible near-infrared fluorophore (31).
Conclusion

We present a general experimental approach for preserving the mass-fractal microstructure of an amorphous carbon aerogel through a phase change to a polycrystalline diamond aerogel. Novel scientific applications of diamond aerogel are expected as a consequence of the unique physical properties of diamond compared with amorphous carbon, as well as from the chemical flexibility of the amorphous aerogel's aqueous synthesis. This method is likely to be general and may be extended to produce previously unachieved crystalline aerogel phases (starting from, for example, amorphous SiO$_2$) with potential relevance as materials with enhanced energy storage and production capabilities (32). No attempt was made here to determine the minimum combined conditions of pressure and temperature required for synthesis, which might in fact be substantially less extreme and applicable on a larger scale, assuming a suitable candidate material to support the aerogel under pressure. Future work will be directed at establishing minimal thermodynamic conditions for the phase transition as well as tailoring the amorphous precursor to produce nanostructured diamond materials with novel compositions and unrealized three-dimensional morphologies (33).

Materials and Methods

Pressures were obtained in situ in the diamond cell using the technique based on ruby fluorescence. Carbon aerogel sample material was loaded into the diamond cell cavity using hand held needles in air. Neon (Airgas-Specialty Gases, UHP) was loaded into the cavity under high pressure (approximately 22,000 psi). Temperatures were not measured in the experiments in a neon medium. In an argon medium a lower limit on the transition temperature was obtained from measured thermal emission data. SI Text contains further details for aerogel synthesis, diamond anvil cell loading, Raman spectroscopy, laser heating, temperature estimation, TCSPC, STXM, and Tey techniques.

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