The Universe is My Nano-fab: Scanning Transmission Electron Microscopy of Nanomaterials from Space

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Although nanoscience is a relatively new field of study, nanomaterials have existed for billions of years. Technologically important materials, such as graphene, nanodiamond, and SiC formed first not in clean-room fabrication facilities, but in the outflows of ancient dying stars. In the laboratory, the atomic-scale ordering, impurity and defect content of these materials can be optimized by manipulating the thermodynamic and kinetic growth conditions for specific optical, electrical or other properties. In space, the same principles of thermodynamics and kinetics apply; the atomic-scale structure is a function of pressure, temperature, etc.. However, here the impurities are fortuitously incorporated from the ambient environment, and serve as witness to the presolar or other cosmic origin rather than a commercial purpose. Aberration-corrected scanning transmission electron microscopy (AC-STEM) can reveal the structure of these nanomaterials, often down to the individual impurity atom.

One of the most historically important nanomaterials from space is nanodiamond. It was the first phase identified as a carrier of an isotopically anomalous component that originated outside our solar system [1]. These isotopic anomalies are the products of supernova nucleosynthesis, and are present as trace (ppb to ppt) components of nanodiamond residues chemically isolated from primitive meteorites. The supernova components include noble gasses such a He, Ar, Ne, Kr, and Xe, as well heavier elements such as Te. How and where the nanodiamonds formed, and how the impurity atoms were incorporated remains a matter of significant debate. The small size of individual diamonds, only 3 nm on average, precludes accurate isotope composition analysis at the single particle scale, except possibly of the major element C. At the bulk scale, the C and N isotopic compositions of the nanodiamonds are within solar system values. The noble gas isotope compositions are only measured at the bulk scale, due to the low concentration, and thus only a tiny minority of the individual nanodiamonds is necessary formed from supernova material. The majority may have formed within the solar system.

By studying the impurity distribution in meteoritic nanodiamonds at the single-atom scale with AC-STEM, we hope to simultaneously constrain the possible origins of the meteoric nanodiamonds, and to gain insight into potential new synthetic doping mechanisms for nanodiamonds and other refractory nanoparticles. We recently demonstrated a flexible doping method for nanodiamonds, under high pressure / high temperature conditions with a laser-heated diamond anvil cell [2]. Our method allows for incorporation of impurities into an amorphous carbon aerogel and subsequently transforms the aerogel into diamond, while maintaining the nanoscale particle size with a pore-filling noble gas pressure medium. The distribution of dopants, such as N, Si, or even Ar, can be analyzed with AC-STEM imaging and spectroscopy. Our demonstration of Ar doping in synthetic nanodiamond by this method suggests that some of the meteoritic nanodiamonds may have formed by conversion of amorphous organic ices with adsorbed noble gas atoms in the outer solar system under HT/HP conditions. It also suggests a way for incorporation of dopants with applications in quantum information, without relying on ion implantation.

While not every nanomaterial from space has useful applications, and not every technologically interesting synthetic nanoparticle has a natural space-formed analog, the study of other nanomaterials from space can provide access to expanded thermodynamic phase space, and proof of durability on cosmological timescales. We seek inspiration for advanced materials development from the natural nanofabrication facilitates otherwise known as stars, through the detailed understanding provided by single-atom sensitivity electron microscopy imaging and spectroscopy.

[1] Lewis R. et al. Interstellar diamonds in meteorites. *Nature* (1987) 326:162-165. [2] Crane M.J., et al. High-pressure, high-temperature molecular doping of nanodiamond. *Science Advances* (2019) 5, eaau6073.