The superlative properties of diamond make it a choice material for making nanoscale devices over a broad range of applications. Diamond devices are conventionally made using "top-down" processing, following the seeding and growth of nanocrystalline diamond (NCD) thin films, however, due to the great resilience of diamond, fabricating nanoscale devices is technologically demanding and nanoscale patterning requires expensive and lengthy processing such as electron beam lithography (EBL). In recent years, colour-vacancy centres in diamond that exhibit optically accessible and / or spin-dependent fluorescence, such as nitrogen- and silicon-vacancy centres, have inspired many new sensing and quantum information technologies. For many of these technologies, the precise nanopositioning of such colour centres is of utmost importance.

diamondDNA set out to develop a novel, inexpensive, rapid and scalable methodology to fabricate nanoscale diamond devices using "bottom-up" processing, with a promised feature resolution that would surpass current state-of-the-art processing techniques such as EBL. To achieve this goal, the technique of DNA Nanotechnology was proposed to create self-assembled DNA patterns of any desired shape, which would then be decorated with nanodiamond or diamondoid particles. Given the diameter of DNA is ca. 2 nm, structures with nearly 2 nm feature resolution should be achievable, especially when seeding the structures with molecular diamondoid particles.

During diamondDNA, a series of goals were set out to accomplish DNA-directed self-assembly of nanoscale nanodiamond devices. Two routes to success were proposed: 1) electrostatic self-assembly of positively charged nanodiamond with negatively charged DNA nanostructures, and 2) the covalent ligation of DNA strands with nanodiamond for subsequent incorporation into DNA nanostructures. It became clear during the early part of the outgoing period that route 1 was impractical. Instead, route 2 – covalent ligation – was much more promising.

To give some background, for a nanoparticle to participate in DNA self-assembly, it must be sufficiently small and of negative charge as to not interfere with the electrostatics of self-assembly. Furthermore, it must be functionalisable with probe DNA that is capable of intertwining with DNA nanostructures. In the return period diamondDNA, a novel process was successfully developed to functionalise detonation nanodiamond (DND) (or other diamond nanoparticles) to give nanoparticles with negatively charged zeta potentials; a small monodispersed size; and chemically-accessible functional groups (amino) to allow subsequent biomodification with DNA or other probe molecules. This was achieved by developing a mixed silanization ultrasonic milling chemistry using two silanes to create self-assembled monolayers (SAM) around DNDs. “THPMP” imparted a negative charge via phosphonate groups, and “APTES” imparted chemically reactive amino groups for subsequent functionalisation. By varying the stoichiometry of these two silanes, it was possible to tailor the surface properties of DND as desired. In conjugation to mixed silane functionalisation, bead-assisted sonication disintegration (BASD) processing was employed simultaneously with silanization in order to disintegrate and then instantly form a SAM around the dispersed DNDs, thereby avoiding re-aggregation of DND that can be typically seen post-disintegration. The apparatus used for in-situ silanization BASD can be seen in Figure 1a, and the reaction scheme in Figure 1b&c.

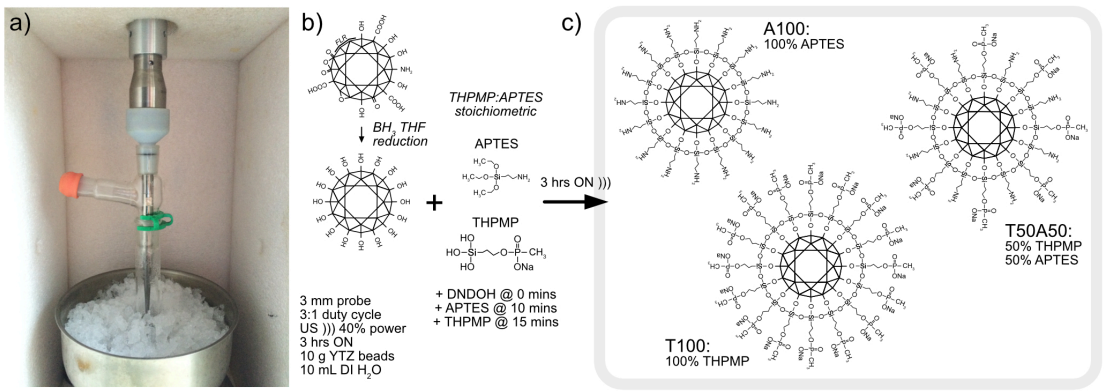

Figure 1 ***: a) in-situ silanization BASD apparatus b) reaction scheme and c) example products of functionalized nanodiamonds.***

Having established a robust method to disperse and functionalise DND, the remainder of diamondDNA was devoted to the self-assembly of DND-DNA conjugates with DNA origami structures. DND-DNA conjugates were synthesized with subsequent standard bioconjugate techniques (amino-SSMCC-thiol coupling) to have DNA strands that would incorporate into DNA origami structures in various configurations. A DNA origami pattern of Rothemund's sharp triangle was used as a test pattern. Despite DNA origami structures assembling in solution as can be seen in Figure 2, ultimately, DND-DNA-origami structures could not be obtained. Considerable insight was gained on the surface properties of DND, and with further modification and experimentation, it could be possible to obtain assembled structures.

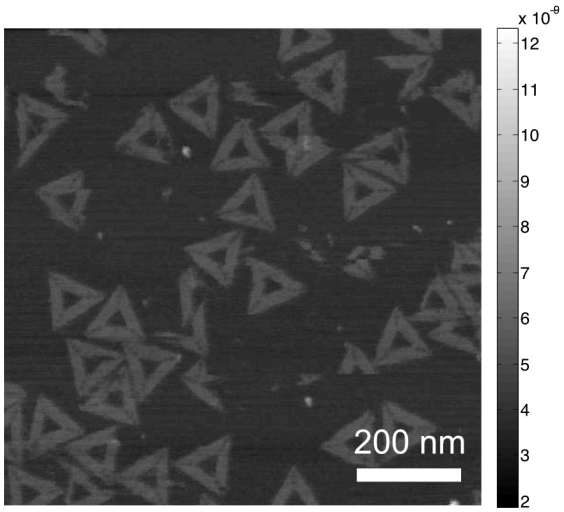

Figure 2: DNA origami triangles imaged with AFM

Although decorated DNA origami structures remained elusive during diamondDNA, beyond diamondDNA, the chemical preparatory method developed herein is of great interest for applications in other bioconjugate fields such as bio labeling (fluorescent nanodiamond conjugated to selective antibodies), or as a ligation method to attach nanodiamond particles to bio-scaffolds or biosensors. In general, any application that requires multifarious functionality of soluble nanodiamond particles could benefit from the mixed silanization BASD process developed in diamondDNA.

Alongside core efforts within diamondDNA, the project was fruitful in producing pristine colour-centres nanodiamonds from ultrapure diamondoid seeds during the outgoing phase at Stanford University. This work resulted in a patent ("Formation of diamond nanoparticles with color centers from diamondoids as seeds", Filed: 5/12/2015 Appl. No.: 62/160281).

In summary, diamondDNA has succeeded in part by developing a robust novel method to functionalize nanodiamond with an unprecedented level of control, versatility and performance. This method stands to impact many research fields that involve the functionalisation of nanodiamond materials, and initial dissemination of the project to related research groups has been accomplished. Furthermore, the work product described within the diamondoid colour-centre patent has provided a high quality route for producing nanoparticles with non-quenching, bright near infrared fluorescence (silicon-vacancies) and/or magnetic/electrical field sensitivity (nitrogen-vacancies), which are in high demand for bio-imaging and magnetometry applications, respectively. The former will allow for high-speed and long-term imaging of nanoscale biological events, which could result in novel medical therapies or diagnoses. The latter could allow for highly sensitive nanosensors, or pristine accessible qubits for quantum information processing.

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