



# Assessing the extent, stability, purity and properties of silanised detonation nanodiamond



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## ABSTRACT

The functionalisation of nanodiamond is a key step in furthering its application in areas such as surface coatings, drug delivery, bio imaging and other biomedical avenues. Accordingly, analytical methods for the detailed characterisation of functionalised nano-material are of great importance. This work presents an alternative approach for the elemental analysis of zero-dimensional nanocarbons, specifically detonation nanodiamond (DND) following purification and functionalisation procedures. There is a particular emphasis on the presence of silicon, both for the purified DND and after its functionalisation with silanes. Five different silylation procedures for purified DND were explored and assessed quantitatively using inductively coupled plasma-mass spectrometry (ICP-MS) for analysis of dilute suspensions. A maximum Si loading of 29,300  $\mu\text{g g}^{-1}$  on the DND was achieved through a combination of silylating reagents. The presence of 28 other elements in the DND materials was also quantified by ICP-MS. The characterisation of Si-bond formation was supported by FTIR and XPS evaluation of relevant functional groups. The thermal stability of the silylated DND was examined by thermogravimetric analysis. Improved particle size distribution and dispersion stability resulted from the silylation procedure, as confirmed by dynamic light scattering and capillary zone electrophoresis.

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## 1. Introduction

There is a growing interest in the properties and applications of ultra-dispersed matter, specifically nanodiamonds (ND), which are produced by a variety of synthetic methods. Some popular production methods include cavitation and laser production, chemical vapour deposition, crushed high-pressure high-temperature (HPHT) diamond, and detonation synthesis for the production of detonation nanodiamond (DND) [1]. The method of production can have a significant impact on the resultant diamond's properties, and DND is known to have higher impurity levels than those

present in other synthetically derived diamonds [2]. The type and level of impurities present in DND can vary quite dramatically, and they depend on both the production and purification methods utilised [3].

DND has shown significant promise for application in a wide variety of areas, including materials synthesis within polymer and carbon-based nano-composites [4–6], coating technologies [7], separation science/chromatography [8], and biomedical applications such as drug delivery and bio-imaging [9–12]. The purity of DND is of the utmost importance in biomedical applications in terms of furthering research outputs and reaching the ultimate goal of using these particles in human patients. It is therefore vital that reliable methods of elemental analysis and evaluation for DND are available. Furthermore, the control of DND surface properties and functionalities will be a key step in ensuring their continued progress in real world applications. It is imperative that there is full understanding and control over the surface chemistry of DND to allow its dispersion in solvents, or bonding to solid matrices, while simultaneously preventing the problem of agglomeration. Silylation can be very useful as a tool to tailor diamond nanoparticles for use as composite ingredients [13–15], or to adjust the surface

*Abbreviations:* BET, Brunauer–Emmett–Teller; BGE, background electrolyte; CE, capillary electrophoresis; CZE, capillary zone electrophoresis; DMODCS, dimethyloctadecylchlorosilane; DND, detonation nanodiamond; EOF, electroosmotic flow; HMDS, hexamethyldisilazane; ICP-MS, inductively coupled plasma mass spectrometry; TGA, thermogravimetric analysis; TMCS, trimethylchlorosilane.

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properties of prospective diamond-based sorbents for chromatography [8,16,17]. It offers a method for surface homogenisation prior to bio-conjugation. It is important to note the de-agglomeration of primary DND particles is highly important before proceeding with surface modification, and silylation has proven to be an effective route to improving dispersion stability and reducing aggregate size as demonstrated by Krueger et al. where the silylation of nanodiamond with (3-aminopropyl)trimethoxysilane and further with biotin was carried out for bioapplications such as labelling and drug delivery [18], and with 3-acryloxypropyl(trimethoxysilane) in combination with beads-assisted sonication for improving dispersion quality and stability [19]. Jeong et al. also reported on the silylation of ND for improving dispersion stability, prior to its inclusion in development of transparent composites where aggregate size directly affected the composite material's performance [20]. Dolmatov described a silylation procedure for nanodiamonds aimed at composites based on elastomer and polymer matrices, however there was no characterisation of the actual degree of silylation [21].

In the preparation of such stabilised, homogenised or modified particles, it is also vital that there are reliable characterisation methods allowing an understanding of the surface chemistry and impurities present in DND, as well as evaluating the stability of such particles under different conditions. Until as recently as 2013, there was a lack of comprehensive information on the presence of metal and non-carbon impurities in DND as a whole. Controlling and quantifying the heteroatom content in DND is a key step towards fully understanding and ensuring a high degree of purity before applying this variable material. There was an absence of suitable reliable analytical methods for this specific nanocarbon; an issue that was recently addressed in our laboratories. The direct aspiration of very dilute DND suspensions into a sector field inductively coupled plasma mass spectrometer (ICP-MS) has proven to be a reliable and sensitive method for the determination of impurities in DND [22,23]. Herein we demonstrate the application of this method to the quantification of purposely introduced elements (like Si) to the surface of DND. This analysis was performed on silylated DND, Si-contaminated DND and DND that underwent different deep purification routes in order to clearly assess the effect of silylation on the DND. Although requiring expensive instrumentation and experienced operators, the method is relatively fast and reduces the reliance on more time-consuming and less informative methods such as thermogravimetric analysis (TGA), FTIR, and others [24–26], which require further analysis to allow quantification of heteroelements in DND. In this instance, TGA and FTIR were used to further characterise the surface chemistry and thermal stability of the modified DND. In addition, the stability of modified DND was investigated using capillary zone electrophoresis (CZE), which has proven to be an informative technique with regard to nanoparticle size distributions, dispersion quality and stability or propensity to form aggregates, which is reflected in the peak shape obtained by a voltage-induced separation [27].

## 2. Experimental

### 2.1. Materials and reagents

The detonation nanodiamond (DND) was obtained from YTM ARGE A.S. (Istanbul, Turkey; product code NDG.11.02.28.01). Additionally, raw detonation soot (DS) was supplied by the same producer; in the form of a black-coloured powder. A 1% aqueous suspension of the DS had a pH of 9.43.

Milli-Q deionised water (Millipore, Bedford, MA, USA) with resistivity 18.5 M $\Omega$  cm (at 298 K) was used throughout this work. All reagents used were of analytical grade quality: 95–97% H<sub>2</sub>SO<sub>4</sub> and 48% HF, 70% HNO<sub>3</sub> were all obtained from Chem-Supply,

Gillman, SA, Australia. In addition, 37% HCl from Merck, Kil-syth, Australia, and 70% HClO<sub>4</sub> from Univar, Ingleburn, Australia were used. The silylation reagents: trimethylchlorosilane (TMCS), dimethyloctadecylchlorosilane (DMODCS), hexamethyldisilazane (HMDS), and toluene were of analytical grade quality, and were purchased from Sigma Aldrich, Castle Hill, NSW, Australia. Sodium tetraborate (99.998%) and NaOH were used in the preparation of background electrolytes (BGE) for CZE, and were also obtained from Sigma Aldrich, Castle Hill, NSW, Australia. Buffers were prepared by dilution of a stock solution of sodium tetraborate, and the pH was adjusted using 1 M NaOH.

### 2.2. Modification of detonation nanodiamond

#### 2.2.1. Initial purification procedures

The raw DS obtained from YTM ARGE A.S. had been purified by the supplier prior to shipment, whereby a sulphuric acid/potassium dichromate wet graphite digestion method was utilised [19]. This material was additionally purified on-site using a procedure previously described by our research group [28] for preparation of NSFPA type of purified DND. Briefly, NSFPA was purified from the DS using acidic oxidation with a mixture of HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, HF and HClO<sub>4</sub> (where % ratio was 44:44:6:6). Subsequent washing steps were performed to reduce the digested impurities and residual acids. It is important to note that Si contamination of DND can occur through everyday processing of DND materials in borosilicate glassware [28] and as a precaution, special attention was paid to handling procedures for DND within this study wherein only polypropylene containers were used for storage of DND samples. Obviously, contamination does not occur in glassware when non-polar organic solvents like toluene are used as the modification medium, as described below for modification of DND.

#### 2.2.2. Hydrophobisation of detonation nanodiamond using silanisation

The NSFPA type of purified DND was used in all experiments on hydrophobisation.

*Sample 1.* 0.451 g of DND, and 5 mL TMCS were added to 45 mL of as-stored toluene in a triple-neck flat-bottomed flask. The reaction was kept under constant magnetic stirring and the reaction flask was fitted with a reflux condenser and a thermometer. The temperature was set to 376 K, at which time an additional 1 mL of TMCS was added to the flask. The mixture was then stirred at 376 K for 21 h. The subsequent additions of 2 mL of TMCS and 2 mL pyridine were made, and the reaction was allowed to continue for a further 5 h.

*Sample 2.* DND was firstly dried under vacuum at 673 K overnight. Then 0.218 g of dried DND and 0.207 g DMODCS were added to 50 mL of dehydrated toluene in a triple-neck flat-bottomed flask. The reaction flask was fitted with a reflux condenser and a thermometer, as above, and was kept under constant magnetic stirring. The temperature was then set to 373 K, at which time an additional 0.313 g DMODCS dissolved in 5 mL of toluene was added. The reaction mixture was refluxed under stirring for 19 h.

*Sample 3.* 0.264 g of dried DND (vacuum dried, 673 K overnight), 4 mL of HMDS and 8 mL of TMCS were added to 188 mL of dehydrated toluene in a triple-neck flat-bottomed flask. The reaction mixture was refluxed under stirring for 19 h.

*Sample 4.* 0.189 g of dried DND (vacuum dried, 673 K overnight), 0.534 g DMODCS and 2.2 mL of HMDS were added to 58 mL dehydrated toluene in a triple-neck flat-bottomed flask. The reaction mixture was held under the same conditions as described above for sample 3.

*Sample 5.* 0.220 g of dried DND (vacuum dried, 673 K overnight) and 10 mL TMCS were added to 50 mL dehydrated toluene in a

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