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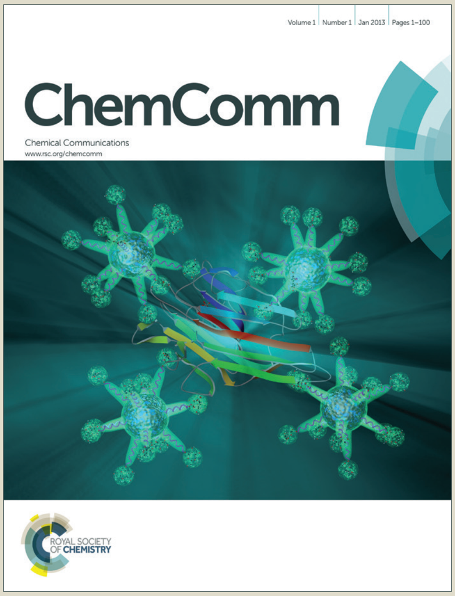

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Size Tunable Synthesis of Solution Processable Diamond Nanocrystals

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Diamond nanocrystals were synthesized catalyst-free from nanoporous carbon at high pressure and high temperature (HPHT). The synthesized nanocrystals have tunable diameters between 50 and 200 nm. The nanocrystals are dispersible in organic solvents such as acetone and isotropic in nature as seen from dynamic light scattering technique.

Diamond is the hardest known material with a hardness of ~ 120-130 GPa for synthetic highly pure single-crystalline diamond.[1] It is used in various applications such as cutting, grinding, machining. In 1955 synthetic diamond was first made at high pressure and high temperature (HPHT) by Bundy et al.[2] Soviet scientists first introduced detonation method during 1960s, which produced diamond nanocrystals of few nanometers in diameters detonating an oxygen-deficient explosive mixture of TNT/RDX in a closed chamber.[3] Diamond produced by the detonation method is heavily contaminated and requires expensive processing to obtain pure diamond nanocrystals. Even then, the diamond nanocrystals do not have well defined faces and edges which is important for applications as abrasives. Chemical vapor deposition (CVD) was introduced to synthesize diamond as thin film.[4] Other routes for the synthesis of nanodiamond are hydrothermal synthesis,[5] chlorination of carbides,[6] ultrasound cavitation,[7] laser ablation,[8] and microplasma dissociation of ethanol.[9] Irifune synthesized nanopolycrystalline diamond using graphite as starting materials without aid of any catalyst at a pressure of 21 GPa and 2000 °C.[10] Recently new route of producing nanopolycrystalline diamond has emerged by using mesoporous carbon materials as precursor.[11] In this method, a mesoporous carbon CMK-8 (which is inverse replica of KIT-6 silica) was used as carbon precursor and the diamond was produced at temperatures as low as 1300 °C. The synthesized diamonds are mesoporous and monolithic in nature. The precursor carbon material was produced in a multi-step nanocasting method. These syntheses conditions (pressure and temperature) were later extended to produce nanocrystalline diamond aerogels using chemically inert solid Ne as a hydrostatic pressure medium.[12] However, in the latter study laser (rather than resistive) was used for heating purpose. In all of these cases the diamond nanocrystals were aggregated and no processible individual phase pure (contaminant free) diamond nanocrystals were obtained.

Herein, we report on the catalyst-free bulk synthesis of single-crystalline diamond nanocrystals from soft-templated periodic mesoporous carbon at 14 GPa and 1300 °C-1400 °C. The mesoporous carbon material can be synthesized in a one step process. The high reactivity of precursor material is believed to be due to high surface area and homogeneous porosity of the material. The diamond nanocrystals are nearly monodisperse with diameters that can be tuned between 50 and 200 nm. They are colorless, and exhibit well-defined faces and edges. Colloidal solutions of the diamond nanocrystals with 100 and 200 nm diameters can be produced without agglomeration of the nanocrystals.

For the synthesis of diamond under HPHT conditions a mesoporous carbon material with cylindrical pores (SBA-15 type) was used as a precursor. The nanoporous carbon material was synthesized through polycondensation of resorcinol and formaldehyde under acidic conditions in the presence of Pluronic F127 block copolymers as structure directing agents following a published procedure with some modifications (Details in Supporting Information).[13] The mesoscale order of the synthesized porous carbon material was verified by small angle X-ray scattering (Figure S1). The material had a NLDFT pore size of 5.3 nm, a BET surface area of ~ 650 m^2/g, and a pore volume of 0.60 cm^3/g as determined from nitrogen gas adsorption measurement (Figure S1). The chemical composition of the carbon material was determined by EDX and Raman analysis, which supports that the mesoporous carbon contains about 95% carbon and 5% oxygen with some C-H functionalities on the pore surface of the carbon (See Table S1 and Figure S2). This mesoporous carbon was subjected to a pressure of 14 GPa and a temperature of 1300 ^oC for 3 h using a multi-anvil apparatus. The mass yield of nanodiamond was ~ 73% (See Supporting Information for Experimental Details and calculation).

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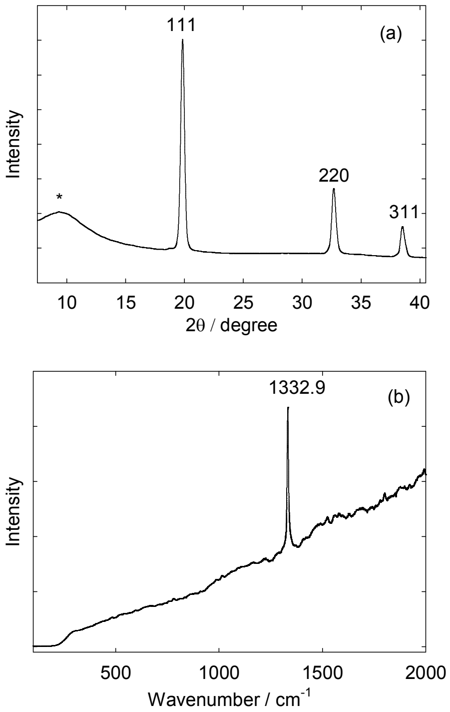

Fig. 1 (a) XRD pattern (Mo Kα) and (b) UV-Raman (λ_{ex} = 325 nm) spectrum of synthesized diamond nanocrystals. Asterisk (*) in (a) indicates amorphous carbon.

The product material was examined by XRD analysis (Figure 1a). The reflections of the XRD pattern could be indexed as 111, 220, and 311 on a cubic lattice of diamond (Figure 1a). The synthesized diamond has a lattice constant of 3.5728 Å. An additional broad peak at ~ 9.6 degrees may be due the presence of some amorphous carbon.[5] Nonetheless, the high intensity of the main diamond peak (111) compared to amorphous carbon peak is indicative of high yield conversion into diamond. In order to understand the yield of the product material, TGA analysis under air was carried out (Figure S3). TGA showed a single weight loss at ~ 630 ^{o}C, indicating that the product material contained only diamond. Previously similar weight loss was observed for purified nano diamond produced by detonation technique.[14]

Additionally, the formation of diamond was confirmed by Raman spectroscopy (using 325 nm UV laser, which was found effective for diamond samples with high degree of fluorescence) at ambient conditions.[15] An intense band at 1332.9 cm^{-1} was observed indicating the presence of diamond (Figure 1b). This band is corresponding to the A_{1g} mode of vibrations.

The morphology of the synthesized diamond was characterized by TEM and SEM. TEM of the as-synthesized diamond showed faceted diamond nanocrystals, with diameters in the range of ~ 200 nm (Figure 2a). Some smaller and larger nanocrystals were also observed. The selected area electron diffraction (SAED) pattern of the diamond shows distinct diffraction spots. This indicates the presence of multiple crystals in the selected area. The EDX pattern from the area shown in TEM image shows the presence of carbon further supporting that the material is diamond (Figure S4). The synthesized diamond crystals were further characterized by SEM, which showed that the diamond crystals with diameters of ~ 200 nm (Figure 2b) corroborating the nanocrystals sizes seen by TEM. The HR-TEM and SAED clearly confirms the single crystallinity of the diamond nanocrystals. Lattice spacing was calculated from HR-TEM (d_{111} = 0.206 nm), which matches that of diamond (Figure 2c).

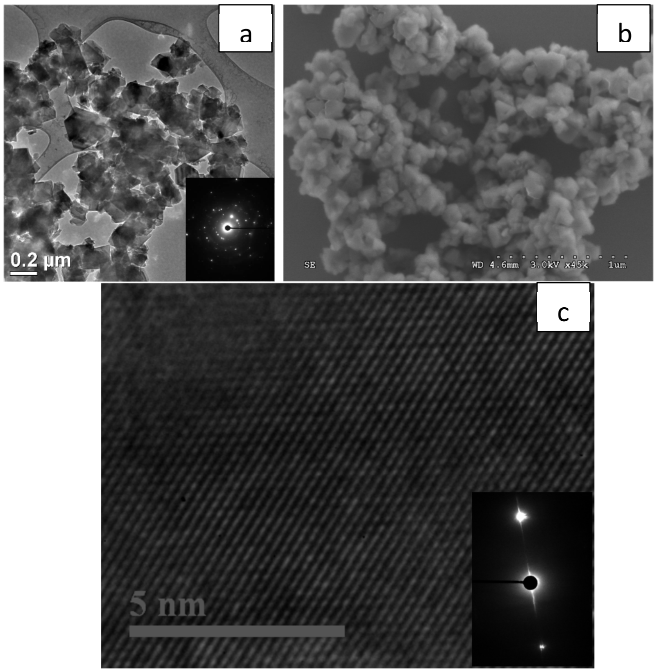

Fig. 2 a) TEM, SAED (inset of a), b) SEM, and c) HR-TEM, SAED (inset of c) of synthesized diamond nanocrystals

From the TEM and SEM images it was ambiguous if the diamond nanocystrals were agglomerated to form a polycrystalline material or existed as individual nanocrystals. To decide this, the diamond nanocrystals were dispersed in acetone by sonication for 1 min and dynamic light scattering (DLS) measurements were performed at different scattering angles (in between 45 to 100 degree) to measure the average size and size distributions of the diamond nanocrystals. The photographic image showed that the diamond nanocrystals form a clean suspension in acetone (Figure 3, inset). The hydrodynamic radius (R_h) was determined by the CONTIN analysis method (Figure 3). By extrapolating R_h to 0^{o} scattering angle, the R_{h0} value was calculated.[16] The average hydrodynamic diameter of the nanocrystals was in the range of 195 ±10 nm with a polydispersity of 1.27 as measured from the DLS. This value is in accordance with the results obtained from TEM and SEM measurements, which show that the diamond nanocrystals exist as individual nanocrystals. As seen from Figure 3, the angular dependence of the R_h value was very weak, indicating that the nanocrystals are quite anisotropic. It is important to note that so far only detonated diamond with particle size ~ 5 nm are known to be dispersible in solution by sonication or laser irradiation.[17, 18] However, this behavior is not known for faceted diamond nanocrystals with diameters larger than 100 nm, except aggregated diamond nanocrystals composed of smaller nanocrystals.[19] The diamond solution was fluorescent as seen from photoluminiscence spectroscopy (Figure S5). The peak between 575-800 nm could be related to nitrogen vacancy point defects in the diamond nanocrystals.[12, 20]

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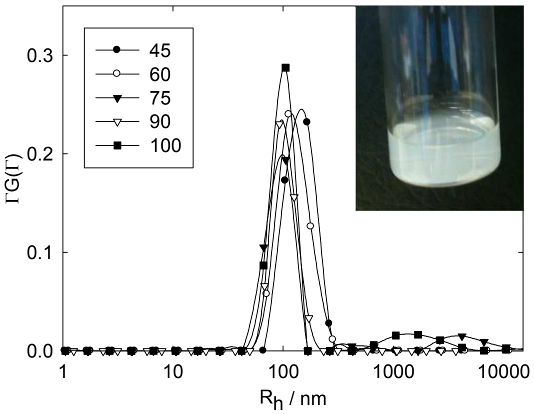

Fig. 3 CONTIN analysis of Dynamic light scattering measurements at different scattering angles (45 to 100 degree) of diamond nanocrystals dispersed in acetone (inset shows diamond solution).

In order to understand the effect of temperature, an experiment at somewhat higher temperature (1400 ^{o}C) for 30 min was performed. The reflections on the XRD pattern could be indexed to diamond along with some minor impurities (Figure S6).[21] Additionally, formation of diamond was confirmed by Raman spectroscopy (Figure S7). When the synthesis was run for 3h at 14 GPa and 1400 ^{o}C, the product material was exclusively diamond as seen from XRD pattern and Raman spectroscopy (Figure S8 and Figure S9). Raman spectroscopy for both the materials shows a band at ~ 1335 cm^{-1} indicative of formation of diamond. TEM images show that these nanocrystals have clear facets and diameters of ≤ 50 nm and ~ 100 nm for 30 min and 3h respectively (Figure 4). The presence of diamond nanocrystals was further confirmed by SAED (Figure 4 inset) SEM showed micron-sized aggregates of the nanocrystals (Figure S10 and Figure S11). CONTIN analysis of the DLS measurements gave an average 100 nm diameter of the diamond nanoparticles produced at 1400 ^{o}C and 3h reaction time. This diameter is the same as the diameter seen in TEM demonstrating the presence of individual nanocrystals in the colloidal solution (Figure S12). For the nanocrystals made 1400 °C and 30 min CONTIN analysis revealed a diameter of ca. 800 nm. This is much larger than the particle diameter seen in TEM which suggests that in the diamond nanoparticles are agglomerated (Figure S13). Possibly, the higher surface energy of the 50 nm nanocrystals is responsible for the higher tendency of agglomeration.

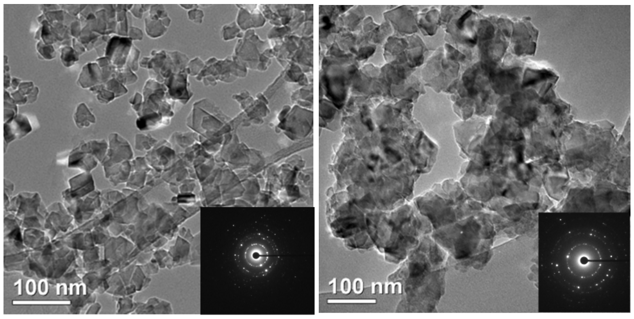

Fig. 4 TEM image and SAED pattern (inset) of product materials obtained at pressures of 14 GPa (left, 30 min), and (right, 3h) at a temperature of 1400 ^{o}C.

To better understand the effect of pressure on phase transformation, we performed experiments at somewhat lower pressure (e.g. 12 GPa) and similar temperature (e.g. 1300 ^{o}C for 3 h). In this case the final product material was black in color. The reflections of the XRD pattern could be indexed to graphite (Figure S14). The sharpness of the reflections resembles that of the commercially available polycrystalline graphite.[22] The result shows that the diamond nanocrystals only form at pressures > 12 GPa. Raman spectroscopy for the materials shows a band at ~ 1582 cm^{-1} which is due to the G band of graphite (Figure S15). TEM image shows that these materials have flake-like morphologies. (Figure S15). SAED shows diffraction spots which indicate that the graphite formed is polycrystalline in nature (Figure S16).[23] To compare our previous results, we performed experiment with the SBA-15 type mesoprorous carbon at 21 GPa that gave transparent mesoporous diamond (Figure S17). Therefore, we believe that the formation of nanocrystals could be related to the reduced pressure (14 vs. 21 GPa) and that the mesostructure (cubic vs. hexagonal) has minor influence.

In conclusion, we report the high yield synthesis of individual diamond nanocrystals in a HPHT synthesis. The diamond forms without aid of any catalyst at a mild temperature. The diamond nanocrystals are nearly monodisperse in size and their sizes are tunable between 50 and 200 nm by choice of temperature and reaction time. The nanocrystals form colloidal solutions in acetone. The high purity at which the nanocrystals are obtained as well as their well-defined shape and size make them a new alternative to diamond nanocrystals obtained by detonation synthesis, which can be produced only in low purity and with ill-defined crystal surface structures. The higher quality of the diamond nanocrystals reported in this work has potential to translate in better properties as abrasives for fine-polishing and sintered bulk polycrystalline diamonds for drilling and cutting tools.

Notes and references

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

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