Diamond Synthesis

Reply to Comment on "Growth of Large Diamond Crystals by Reduction of Magnesium Carbonate with Metallic Sodium"[**]

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Stichwörter:
chemical vapor deposition · correspondence · diamond synthesis · high-pressure chemistry · Raman spectroscopy · synthetic methods

First, thanks to Professor Hermann Sachdev who has commented on our work. The comments were thoughtful.

We should have cited reference [1] paper in our communication in reference [2] because the latter paper reported progress related to the former, we apologize for having not done so. We also apologize for a mistake made during handing the X-ray diffraction data for reference [2]. The original XRD paper was recorded on chart paper, which was then scanned into the computer as a BMP format file and subsequently digitized. In this process, our technician responsible for treating the X-ray data made an error and used, after polishing, a similar BMP format file obtained from a another sample synthesized in our lab.

We appreciate the analysis of Sachdev: diamonds might be generated from carbon monoxide or formed in a C/H/O system. In our synthesis, diamond was not found in the $K_2C_2O_4$/Na and CoC_2O_4/Na systems (not published), and carbon nanotubes were formed by using carbon suboxide as carbon source.[3] In both of these cases, carbon monoxide is present during the reaction.

Chemical vapor deposition (CVD) is a low-pressure synthetic process, which normally requires that the substrate be maintained at a temperature in the range of 1000–1400 K and that the precursor gas be diluted in an excess of hydrogen (typical CH_4 mixing ratio ≈ 1–2 vol%).[4] In our process, diamond particles about 250 μm long formed in the CO_2/Na system; the volume of hydrogen in the gas phase could not have reached the levels required to produce diamonds in the CVD system, even though traces of water are present in dry ice. In addition, the $MgCO_3$/Na system, which has considerably less water present, also produces diamonds. The intense, sharp peaks found in the Raman spectra at 1332 cm^{-1} show that the diamonds are highly crystalline. [1,2]

Indeed, most diamond particles generated in our process appear with irregular morphologies (see Supporting Information). The particles in the scanning electron micrographs (SEM) images were picked up from products under an optical microscope, which were already confirmed to be diamond by Raman analysis. Sachdev observed that Figure 3 of reference [1] displayed solid material that was not facetted and resembled dissolutive material, whereas Figure 4 in reference [1] clearly showed facetted material of growth type. In fact, we have no idea what the appearance of our diamond should be. We are also aware of this difference as discussed in reference [1]: Octahedral diamond particles were observed in the CO_2/Na system when the particles were rather small (only several micrometers), and an increase in the particle size led to the disappearance of the octahedral shape. Octahedral particles of around 4.3 μm were also observed in CO_2/Li system under SEM and TEM, which were confirmed to be diamonds by electron diffraction.[5] It is true that energy-dispersive spectroscopy (EDS) analyses can provide information of elemental composition, and can further confirm whether a particle is diamond, as suggested by Sachdev. We have performed EDS analysis under SEM on a particle that was produced in the $MgCO_3$/Na system followed by treatment with aqueous HF solution to remove α-SiO_2, which shows that the particle contains 93.05% carbon with F, Na, Mg, and Si contaminations (see Supporting Information).

Graphite and amorphous carbon were removed by treating the solid precipitate with aqueous perchloric acid ($HClO_4$; 4.0 M) at 140°C for about 10 hrs.[6] In some cases, large particles were picked out from the treated sample for Raman and SEM analysis. A particle separated by this process is shown in the inset of Figure 1. This particle has an irregular shape, but it was confirmed to be diamond by Raman spectroscopy (Figure 1).

With regard to diamond characterization, the synthesized diamonds were usually characterized by electron diffraction,[7] X-ray diffraction (XRD), Raman spectroscopy, and SEM.[8] These common tools for diamond character-

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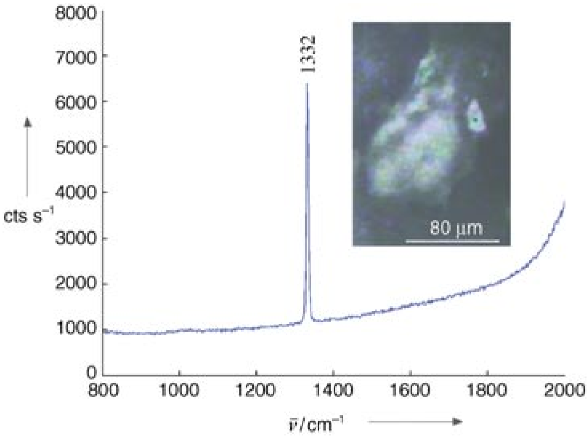

Figure 1. Raman spectrum and image of a diamond particle produced in $MgCO_3$/Na system, the image was taken by an optical microscope attached to a Raman spectrometer. Cts = counts.

ization were also used in our characterization, which provides enough evidence that diamonds were indeed produced in our synthesis.

In the early stage of this research, it was our aim to get pure diamonds, therefore the XRD patterns were measured on the products after appropriate treatments. In reference [2] graphite and other crystalline impurities were completely removed by treating the sample with ethanol, HCl (2.0 M), distilled water, and $HClO_4$ (4.0 M). As the reaction was performed in a new cell, no significant amount of silicon oxide and iron-based compounds were detected. Therefore, the XRD pattern only shows peaks from diamond, although there are some amorphous impurities. These details should have been included in reference [2].

We agree with Sachdev that the characterization of reaction intermediates is important for a new process and could help us to understand the diamond-growth process in the system. It was found that impurities were also formed during the reaction, which depend upon the material of the cell wall (that is, whether a new cell or old cell was used), the starting materials, and reaction conditions. For example, $FeCO_3$ and graphite were found to be present as by-products in CO_2/K system.[5] In addition to graphite, Na_2CO_3, MgO, α-SiO_2, and iron-based compounds were also found in the product mixture along with diamonds in $MgCO_3$/Na system when the reaction was carried out in an old cell (see Supporting Information). Some impurities (Si, Fe) may originate from the wall of the stainless-steel cell.

In Figure 2 of reference [1], the Raman spectrum displays a strong peak at 1332 cm^{-1}, which is characteristic peak of cubic diamond. It also contains an additional broad feature at about 1600 cm^{-1} (between 1582 cm^{-1} of E_{2g} mode of graphite and 1620 cm^{-1} of microcrystalline graphite). We agree that this one may be assigned to sp^2 hybridized carbon atom. We also wished to know whether this feature arises from an sp^2 hybridized carbon atom present as inclusion in the diamond particles or originates from surface reconstruction. In reference [2], the feature at about 2000 cm^{-1} might originate from strong fluorescence of carbon materials, which has also been observed in the spectrum of other diamond materials.[9] However the above features do not appear in the Raman spectrum of high-pressure high-temperature (HPHT) and CVD diamonds referred to by Sachdev, which also indicates that our diamonds have different origins. The detail reason about these features needs to be investigated.

Our reaction cell was not commercial and was heated in an oven. The temperature was measured by a temperature controller linked to a thermocouple, while the pressure is autogenic and calculated for high temperatures. The growth of diamonds is dependent on many parameters, some of which are: temperature, pressure, cell material, and starting reactants. Therefore, the reproduction experiments need to be carried out in a careful manner. Even so, we could produce diamonds from time to time with the $MgCO_3$/Na and CO_2/M (M = Li, Na, K) systems.

Please note: Minor changes have been made to this manuscript since its publication in *Angewandte* Early View. The Editor.

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[10] The Raman measurements were performed on a LABRAM-HR confocal laser microRaman spectrometer with an excitation wavelength of 514.3 nm. Optical photograph of diamonds taken from a LABRAM-HR Confocal Laser MicroRaman Spectrometer, the spot size is about 8 µm and scanning time is 3 seconds. X-ray diffraction patterns were performed on a Rigaku D/max-rA X-ray diffractometer with CuKα radiation.