

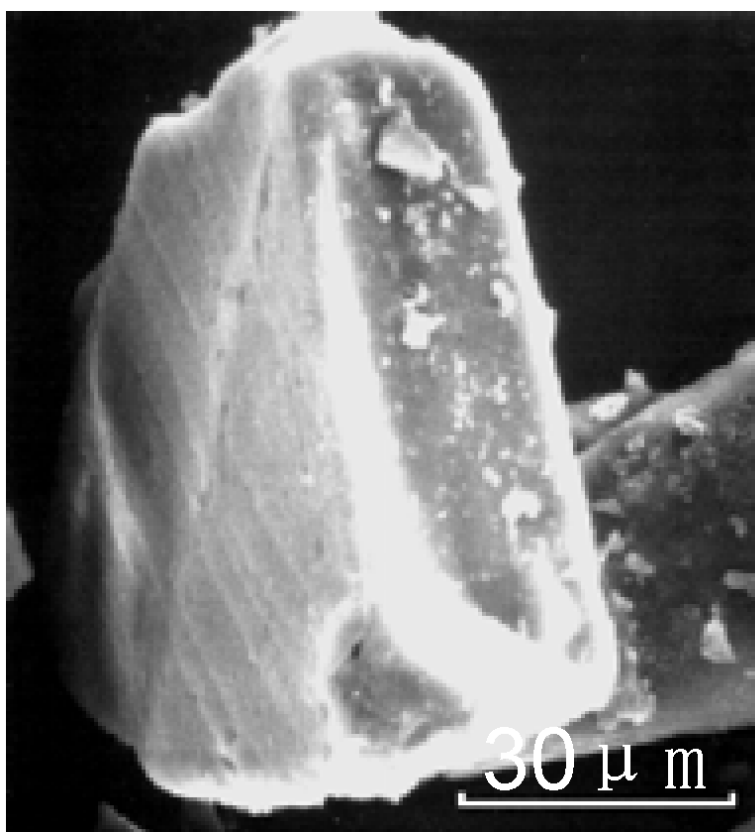
Communication

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Diamond Formation by Reduction of Carbon Dioxide at Low Temperatures

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Because of its abundance on earth and of the role it plays in life processes, activation of carbon dioxide arouses considerable interest. Among other modes of activation, the reduction of carbon dioxide has been extensively studied using electrochemical^{1,2} and photochemical^{3,4} reactions in light of the problems of global warming and depletion of fossil fuels.^{5–7} Although research to optimize the reaction products is active, CO is often the main reduction product, while formate may also be formed depending on the reaction condition.^{8,9} Diamond is a material with uniquely attractive physical, thermal, and optical properties used in applications ranging from abrasives, tool coating, bearing surfaces, microelectronics, and optics to corrosion protection.^{10–13} Here, we first report on the synthesis of high-quality large-size diamond microparticles reaching up to 250 μm by reduction of dense CO₂ with metallic sodium at a temperature as low as 440 °C.

The reaction was carried out in a stainless steel autoclave (10 mL), in which a sufficient amount of solid CO₂, freshly made from high purity CO₂ gas (99+%), was placed in an autoclave to ensure that the CO₂ was in supercritical states at high temperatures. A typical reaction used 8.0 g of CO₂ and 2.0 g of metallic Na, in which CO₂ was in excess for the oxidation of metallic Na.

If it is not specifically mentioned, most of the reactions were conducted at 440 °C, 800 atm for 12 h. The products were washed with ethanol, 2 mol/L HCl, and then distilled water, respectively. No residual metallic Na was found present in the product due to the excessive use of CO₂; hence the washing process of the product is for safety. The pressure was autogenic depending on reaction conditions. Under the most reducing conditions, the main products identified were diamond, graphite, Na₂CO₃, and residual CO₂ gas. Figure 1 shows the XRD pattern of a powder sample from one autoclave. The reflection peaks, indexed with 111, 220, and 311, correspond unambiguously to cubic diamond with a lattice constant $a = 3.568 \text{ \AA}$. It was also found that there was a weak peak at 26.2°, indicating small amounts of graphite present in the sample. The Raman spectrum of the product exhibits an intense first-order peak at 1332 cm⁻¹ [Figure 2], which is the characteristic signature of the cubic diamond, indicating the formation of well-crystallized diamond. The full-width at half-maximum (fwhm) of the peak is 4.7 cm⁻¹, close to that for natural diamonds (1.5–2.5 cm⁻¹), indicating less strain and crystal defects in our synthetic diamond.¹³

Scanning electron micrographs of some diamond particles of the product were shown in Figure 3a,b. The particles with sizes larger than 100 μm can be clearly seen. The size of some large particles reaches up to 250 μm (not shown). Under an optical microscope, the diamonds appear to be transparent and colorless. Combined with the narrow fwhm of the Raman peak, it is suggested that the process yielded high-quality diamonds. It was found that the diamond particles are octahedral when their sizes are around 10 μm [Figure 4] and the increase of the particle size leads to the disappearance of the octahedral shape. The amount of graphite increases, while the diamond decreases along with a decrease of

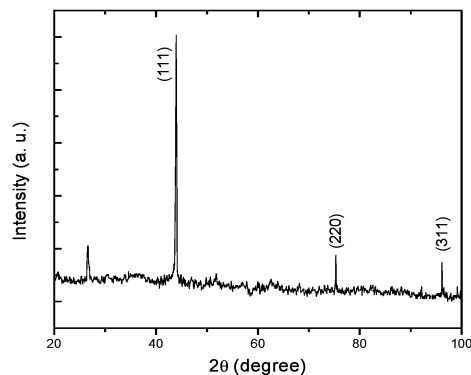


Figure 1. X-ray diffraction pattern of the sample formed by reduction of dense CO₂ with metallic Na at 440 °C, 800 atm.

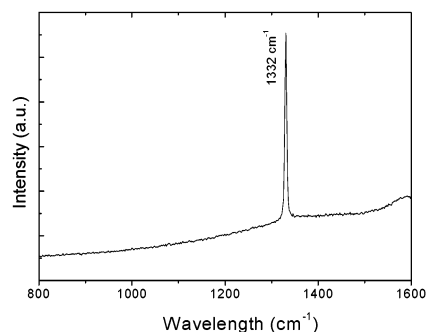


Figure 2. Raman spectrum of a diamond particle, using an excitation wavelength of 514.3 nm. The measurements were performed on a LABRAM-HR Confocal Laser MicroRaman spectrometer.

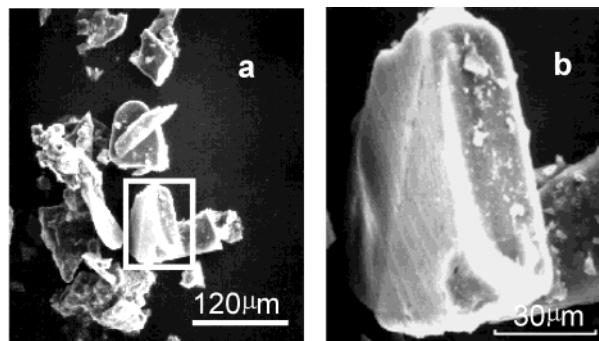


Figure 3. Scanning electron micrographs of diamond microparticles synthesized in a high-pressure CO₂ reduction process (a). The area of rectangle is shown enlarged in (b).

reaction temperature. No diamond was detected by XRD analysis when the reaction was conducted at 400 °C, and the amount of CO₂ decreasing to 4.0 g yields only graphite, which reveals CO₂ reduction to diamond is sensitive to the temperature and pressure of the system. At 440 °C and 800 atm, the total yield of diamond

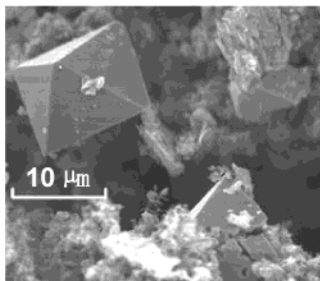


Figure 4. Field emission scanning electron micrograph of the product before washing with 2 mol/L HCl aqueous solution.

and graphite was around 16.2% (mol ratio), and the maximum transformation ratio for CO₂ to diamond was found to be as high as 8.9% (mol ratio). Interestingly, it was found that increasing the amount of metallic Na is favorable for CO₂ reduction to graphite; more graphite was detected by XRD analysis as the amount of metallic Na increased to 3.0 g. However, small brightness crystals of diamond embedded in black graphite powder can be clearly seen by the naked eye. At the beginning of the reduction, the pressure in the autoclave was relatively high. However, as CO₂ was reduced by metallic Na, the pressure in the autoclave decreased. A larger amount of metallic Na reacts with CO₂ in a relatively low-pressure environment, which should be responsible for the formation of more graphite. These results suggest that it is possible to increase the yield and particle size of diamond by optimizing the process.

Since the first report of diamond synthesis through a high-temperature high-pressure process,¹⁴ several approaches have been developed to synthesize diamond.^{15–18} The diamonds made with the TNT detonation process were composed of nanometer-sized spherical particles.¹⁵ Micrometer-sized diamonds have been grown in a hydrothermal process using carbon, metal, and water near 800 °C and at 1.4 kbar of pressure, but the diamond seeds were needed.¹⁶ Chemical vapor deposition (CVD) is a low-pressure synthetic process for the synthesis of polycrystalline diamond or diamondlike structure films with a crystal size of 0.1–10 μm.^{17,18} Recently, diamond powder was also synthesized through a metallic reduction–pyrolysis–catalysis route with the reaction of carbon tetrachloride and sodium at 700 °C.¹² However, the size of the diamonds is significantly less than 1 μm. As compared to the methods mentioned above, the present route exhibits an obvious advantage in terms of simple equipment, mild reaction conditions, use of cheap nontoxic low-energy CO₂ molecules as the carbon source, and large-size diamond product.

CO₂ is relatively inert toward single electron transfer. Indeed, the standard potential of the CO₂/CO₂^{•-} couple in an aprotic solvent such as *N,N'*-dimethylformamide (DMF) containing a counteranion (Net₄⁺) (tetraethylammonium), not giving rise to strong ion-pairing, is as negative as –2.2 V versus SCE. The potential for the redox couple Na⁺/Na (–2.7 V) is negative enough for the CO₂ reduction to CO₂^{•-}, evincing that the formation of the CO₂^{•-} radical anion is indeed highly likely in the system investigated here.^{19,20} Under supercritical conditions, the increased polarity of CO₂²¹ is favorable

for CO₂ adsorption on the surface of Na or the wall of the cell and may accelerate the electron transfer from Na to CO₂ or an intermediate. However, the mechanism of the reduction of CO₂ and connection of carbon atoms to form sp³ hybrid bonds is required for one to understand this process. Moreover, it is found that in our process the formation of diamond occurs at pressures much lower than its thermodynamic stable limit.²² There might be an unknown mechanism for the metastable formation of diamond involved, such as a cell wall surface-mediated process. It should be noted that the production of diamond by this process is reproducible, which will provide researchers an opportunity to establish the formation mechanism fully.

The above studies illustrate a low-temperature diamond synthesis technique, in which diamond (10–250 μm) can form at a temperature as low as 440 °C by reduction of dense CO₂ with metallic Na. For the synthesis technique, CO₂ was reduced to diamond in a simple reaction autoclave, which is clearly an interesting and important topic in both CO₂ and diamond chemistry. Carbon dioxide is a nontoxic low-energy molecule, abundant on earth. This novel reduction method could allow studies of large-size diamond production using CO₂ as the carbon source.

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Supporting Information Available: Micrograph of diamond octahedral (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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