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A novel spherical carbon

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Abstract We developed a novel spherical carbon material. The spherical carbon is composed of a high density of carbon nanotubes or nanofilaments, and includes an oxidized diamond particle as a core. Syntheses of this carbon in high volume with high selectivity may be possible. It is expected that this carbon will be useful as a catalyst material for fuel cells, electric double-layer capacitors, etc.

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Introduction

Recently, the production and utilization of carbon nanotubes have attracted much attention [1–3]. A wide range of potential applications for carbon nanotubes have been proposed, including use in molecular electronic devices, field emission materials, and actuators. For this reason, much effort has been devoted to the synthesis of carbon nanotubes of high quality via simple and reliable techniques. Selective and controlled growth of carbon nanotubes is desirable, especially for applications in electronic devices and composite materials.

Although numerous methods for the synthesis of carbon nanotubes have been proposed, no effective method has been established. For example, arc discharge is an extremely inefficient synthesis method. The production of carbon nanotubes by arc discharge invariably results in the production of nanoparticles and other graphitic debris as byproducts. Removing the many byproducts has proven difficult, and has prevented progress in testing the bulk properties of carbon nanotubes [1].

A catalytic thermal chemical vapor deposition (CCVD) synthesizing method was extensively investigated as a promising method for large-scale production of nano-carbon materials, such as carbon nanotubes or nanofilaments. Comprehensive reviews of CCVD have been compiled [4–7]. The CCVD is attractive because it allows low temperature synthesis and large-scale production of carbon nanotubes or nanofilaments and enables control over the length, density, purity, and diameter of carbon nanotubes and carbon nanofilaments.

Oxidized diamond has recently drawn attention as a new unique material phase as a solid carbon oxide. The diamond surface is easily oxidized by oxidative acids such as HNO_3, HClO, H_2O_2, etc., and is also oxidized with oxygen at an elevated temperature to form C–O–C ether-type structures and C=O carbonyl-type structures [8]. Until now, no carbon-oxide solid phase has been found; however, the surface of oxidized diamond is considered to be a pseudo-carbon-oxide solid phase. The oxidized diamond surface is expected to behave as a carbon oxide for specified surface reactions such as catalytic, electrochemical reactions. Because such reactions must be controlled by the interaction between molecules and surfaces, the bulk structures of solids are less important.

Activated carbon has been widely utilized as a support material for metal or metal oxide-loaded catalysts. Activated carbon is composed of amorphous sp^2 carbon atoms. No carbon material constituted of pure sp^3 carbon atoms (diamond) has been examined as a catalyst-support material. However, our recent study of oxidized diamond-supported metal or metal oxide catalysts exhibited excellent catalytic activity for the light alkanes activated reactions [9, 10]. In these reactions, weak but significant interactions between loaded metal catalysts and support surfaces seemed to play important roles in enhancing and prolonging the activity of the respective catalysts. Oxidized diamond behaved as solid carbon oxide material and presents an excellent support material for catalysts.

In this study, we developed a novel spherical carbon material, and assessed its performance as a material for electrochemical capacitors. Spherical carbon was obtained by the decomposition of hydrocarbons using an oxidized diamond particle for the core. This composite carbon material of diamond (sp^3 carbon) and carbon nanotubes or filaments (sp^2 carbon) is expected to be as a novel composite carbon material.

Experimental

Oxidized diamond-based catalysts were prepared by impregnating an aqueous solution of metal nitrates or chlorides onto oxidized diamond (diameter of particles: 10–500 nm; surface area: 12.6 m^2/g). Oxidized diamond-supported metal catalysts (containing 5 wt% of metal) were prepared by impregnating an aqueous solution of $Fe(NO_3)_3 \cdot 9H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $RuCl_3 \cdot nH_2O$, $RhCl_3 \cdot 3H_2O$, $Pd(CH_3COO)_2$, $IrCl_4$, $(NH_4)_2[PtCl_4]$ (Wako Pure Chemical Industries, Ltd., Osaka, Japan) into the suspended oxidized diamond, followed by evaporation-to-dryness. Supported catalysts were dried and calcined at 673 K for 3 h in air prior to the reaction.

The decomposition of methane or ethane was carried out in a flow reactor. Using 50–100 mg of catalyst, 20 mL/min CH_4 or C_2H_6 was introduced at temperature ranges of 673–973 K. The reaction time was varied in the range of 0.5–5 h.

Scanning electron microscopy (SEM) results was performed using a HITACHI S-4500. Transmission electron microscopy (TEM) was performed using a JEOL JEM-2010 (200 kV) on catalyst samples so that the morphology of the deposited carbon could be determined. Scanning transmission electron microscopy (STEM) was performed using a HITACHI HD2000 STEM.

X-ray photoelectron spectroscopy (XPS) results were obtained on an X-ray photoelectron spectrometer (VG Sigma Probe) using Al$K\alpha$ radiation as the energy source.

To determine the properties of the electric double layer formed on the electrode, a configuration of electrode/electrolytic solution/electrode was selected. The test cell was composed of a pair of electrodes which prepared from spherical carbon or active carbon. A pair of electrodes was sandwiched as a separator. Electrodes were facing each other. Samples used spherical carbon or active carbon mixed with 10 wt% of poly-tetrafluoroethylene (PTFE; DU PONT-MITSUI Fluorochemicals Co., Ltd., Tokyo, Japan) as a binder. The prepared electrodes had a dimension of 10 mm in diameter and around 1 mm in thickness. The prepared electrodes were characterized in 1 M H_2SO_4 by a constant current method using a charge–discharge apparatus (HJ-201B; Hokuto Denko) under the following conditions. The current density was kept constant at 2.4 mA/cm^2 on charge, and varied over the range of 0.8–24 mA/cm^2 on discharge. The voltage varied over the range of 0.2–0.8 V.

Results and discussion

Figure 1 is the proposed model of oxidized diamond. The diffuse reflectance FT-IR spectrum oxidized diamond contained bands in the region of 1650–1850 cm^{-1}, which were ascribed to C=O stretching vibrations (νC=O), and absorptions at 1150 and 1250 cm^{-1} were assigned to C–O–C stretching vibrations (νC–O). These results indicate that oxygen species were introduced onto the diamond surface [8, 9].

Group VIII metal-loaded oxidized diamond catalysts were tested for decomposition of methane and ethane. Table 1 shows the catalytic activity for the decomposition of methane and ethane over oxidized diamond-supported catalysts. The catalytic decomposition of methane and ethane occurred at 723 K. The order of the catalytic activity of metal species at a reaction temperature of 823 K was as follows: Ni > Co > Pd. The oxidized diamond-supported Ni catalyst showed the highest rate of hydrocarbon conversion. On the other hand, Fe, Ru, Rh, Ir, and Pt-loaded oxidized diamond catalysts did not show catalytic activity for decomposition of methane and ethane. Ni and Pd loaded on oxidized diamond catalysts have been reported to be active species for decomposition of methane

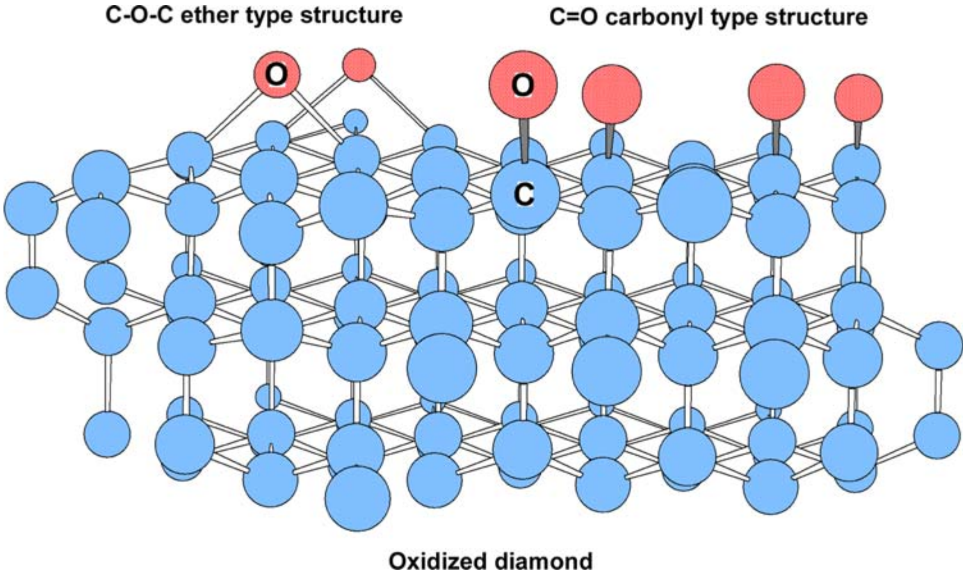

Fig. 1 Proposed model of oxidized diamond

Table 1 Effect of temperature on the carbon yield over oxidized diamond-supported catalysts

Catalyst	Temperature (K)	Carbon yield (%)	
		Methane	Ethane
Co	723	1.0	0.8
	773	8.8	1.8
	823	6.4	4.8
	873	0	0
Ni	723	3.9	10.7
	773	8.8	20.8
	823	17.0	17.2
	873	0	0
Pd	723	0.4	0.7
	773	1.5	2.6
	823	4.0	4.2
	873	8.5	6.3

Reaction conditions—Metal loading level: 5 wt%; flow rate: 20 mL/min; reaction time: 3 h; catalyst: 0:05 g; space velocity: 24,000 h^{-1} mL/g-cat

[9, 10]. The oxidized diamond-supported Co catalyst also demonstrated catalytic activities. Ni- and Co-loaded catalysts did not exhibit catalytic activities above 873 K. In contrast, Pd-oxidized diamond catalyst exhibited a high catalytic activity with increasing reaction temperature. From XPS measurement, the ratio of Ni and Co species on oxidized diamond surfaces at 873 K decreased compared with that for fresh catalysts, respectively (Table 2). Additionally, Ni and Co might diffuse into oxidized diamond at high temperature.

Figure 2 shows SEM image of Ni (5 wt%)/oxidized diamond catalyst. Ni particles are seen as white areas on the surface of the oxidized diamond particles. Ni particles with diameters of 6–16 nm are homogeneously dispersed on the oxidized diamond. The average diameter was approximately 10 nm. High dispersion of Ni species on oxidized diamond would indicate high catalytic activity for decomposition of hydrocarbon.

Table 2 Estimate of chemical concentration

Catalysts	Elements	Fresh atomic %	873 K[a]
Ni/oxidized diamond	Ni2p	3.72	2.15
Co/oxidized diamond	Co2p	2.07	1.01

[a] Catalysts were calcined at 873 K for 1 h in Ar

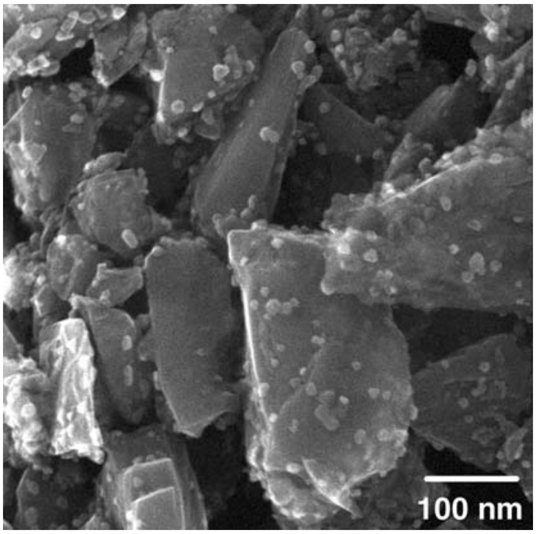

Fig. 2 Ni/oxidized diamond catalyst. Ni loading level: 5 wt%. Prior to reaction, catalyst was calcined at 673 K for 3 h in air

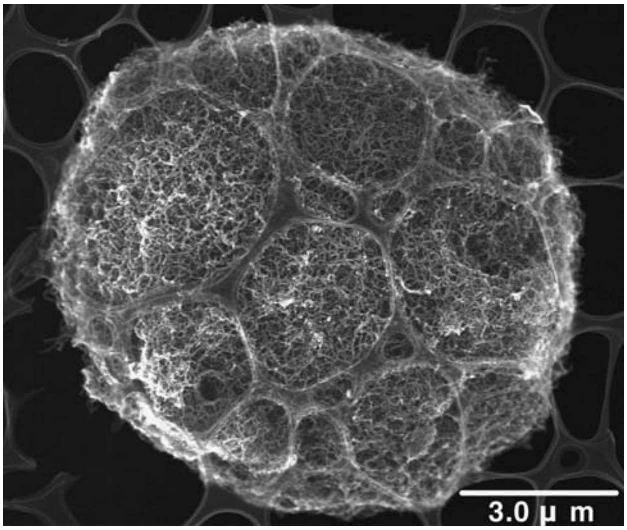

Fig. 3 SEM image of spherical carbon. Reaction conditions—Ni loading level: 5 wt%; CH_4 flow rate: 20 mL/min; reaction temperature: 823 K; reaction time: 3 h; catalyst: 0:05 g; space velocity: 24,000 h^{-1} mL/g-cat

Figure 3 shows a SEM image of carbon nanomaterials over oxidized diamond-supported Ni catalyst. The carbon nanomaterials were prepared by the decomposition of methane at 823 K. Globular solidification is apparent in Fig. 3. Figure 4 shows SEM images of carbon nanomaterials over oxidized diamond-supported Co and Pd catalysts. The carbon nanomaterials were prepared by the decomposition of methane at 823 K. Carbon products similar to those obtained using Ni/oxidized diamond catalyst were obtained by using Co and Pd-loaded oxidized diamond catalysts.

From Fig. 5, it is observed that the globular solidification is composed of carbon filaments. Carbon nanomaterials that are produced by arc discharge invariably contain a large amount of soot. Removing many side-products has proved difficult, and has prevented progress in testing the bulk properties of carbon nanomaterials. On the other hand, in this new process, a large amount of carbon nanofilament could be produced on oxidized diamond with high selectivity and without soot.

The spherical carbon has diamond particle in its core, and carbon nanofilaments radiating outward from diamond core analogous to micelle. To help the unique structure of spherical carbon, Fig. 6 shows a possible model of this novel composite carbon material. The oxidized diamond particle plays the role of the core in spherical carbon. The loaded metals are controlled by the oxidized diamond support at a nanoscale (Fig. 2). The sintering of loaded metals during the reaction can be avoided, and loaded metals can be controlled to high dispersion. In addition, the carbon nanofilaments can be grown to high density in a short period of time using a metallic catalyst. This is possible because the size of the spheroidal particles can be controlled like the reaction temperature and time, it became possible. Uniform secondary particles can be synthesized in large quantities at a micron scale, and such precise, automatic control of the grain size distribution would represent a major advantage to the use of spherical carbon as a composite material. Moreover, it is believed that the catalyst support will be useful as a core for globular carbon products, because it uses nano-sized diamond particles as a catalyst support material.

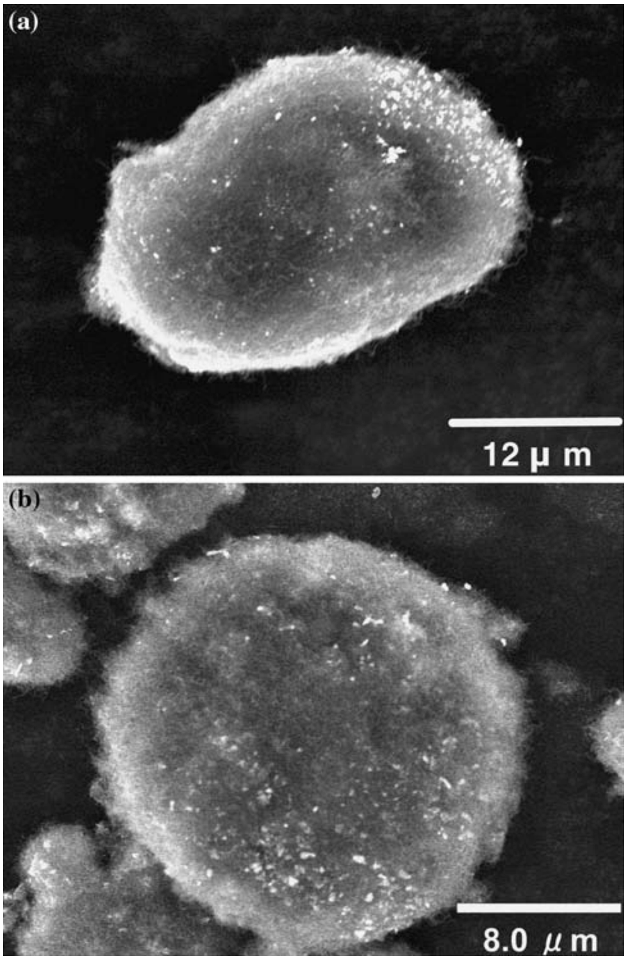

Fig. 4 SEM images of spherical carbon. **a** Co/oxidized diamond catalyst and **b** Pd/oxidized diamond catalyst. Reaction conditions—metal loading level: 5 wt%, CH_4 flow rate: 20 mL/min, reaction temperature: 823 K; reaction time: 3 h; catalyst: 0:05 g; space velocity: 24,000 h^{-1} mL/g-cat

Spherical carbon was obtained using oxidized diamond-supported Ni, Co, and Pd catalysts. Figure 7 shows transmission electron microscope (TEM) image of spherical carbon over oxidized diamond-supported Ni catalyst. As can be seen in the TEM image, primarily the nanostructured carbon was multi-walled carbon nanotubes (MWCNT), and partially cup-stacked carbon nanofilaments that are also observed over the oxidized diamond-supported Ni catalyst.

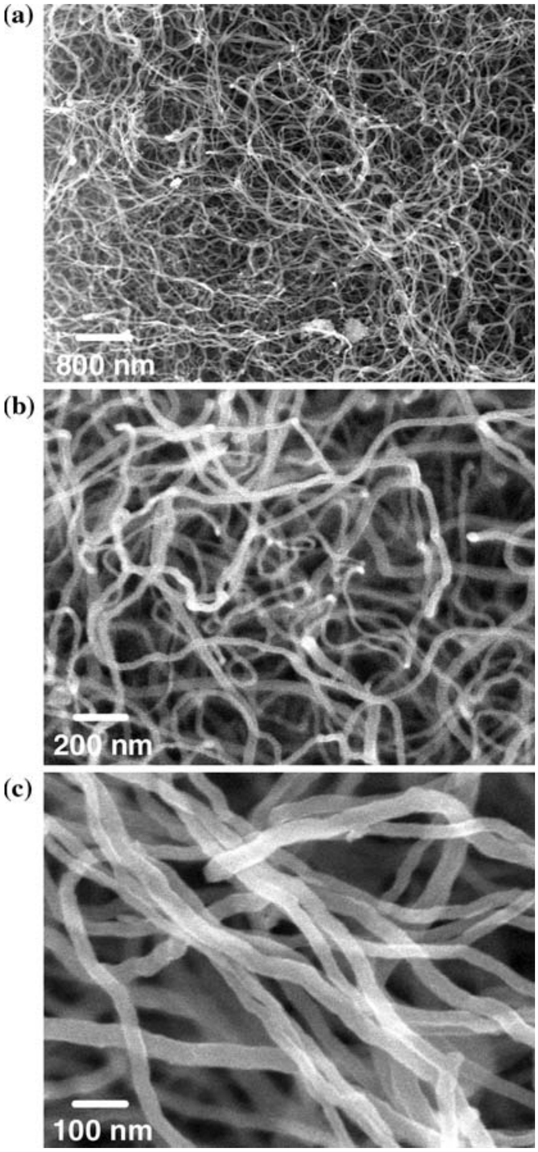

Fig. 5 SEM images of carbon nanomaterials over Co/oxidized diamond obtained by decomposition of methane. Reaction conditions—Co loading level: 5 wt%; CH_4 flow rate: 20 mL/min; reaction temperature: 823 K; reaction time: 3 h; catalyst: 0:05 g; space velocity: 24,000 h^{-1} mL/g-cat

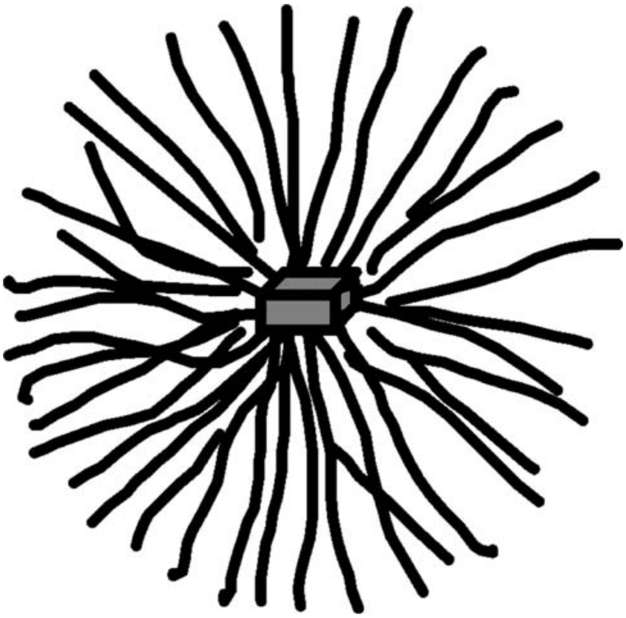

Fig. 6 Model of spherical carbon

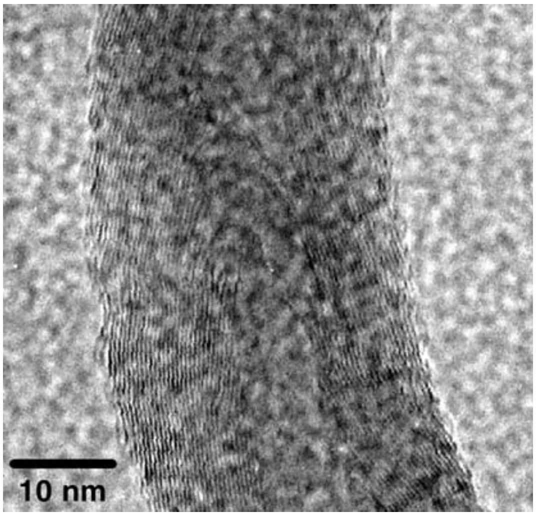

Fig. 7 TEM image of spherical carbon. Reaction conditions—Ni loading level: 5 wt%; CH_4 flow rate: 20 mL/min; reaction temperature: 823 K; reaction time: 3 h; catalyst: 0:05 g; space velocity: 24,000 h^{-1} mL/g-cat

In the catalytic growth of carbon nanofilaments, the structure of carbon nanofilaments has been shown to be strongly depended on the catalyst composition and the nature of the metal-support interaction [3, 11, 12]. The SEM and TEM images revealed the presence of carbon nanomaterials on the diamond surface. Although it is premature to discuss the role of metal particles or species, these observations suggest that the formation mechanisms and characteristics of carbon nanomaterials. The support of Ni by the carbon nanomaterials that were formed over the oxidized diamond was highly dependent on the metal species employed. In addition, highly dispersion of active Ni species on oxidized diamond would indicate high catalytic activity for the decomposition of hydrocarbon.

We applied the spherical carbon as a novel carbon material, the electrochemical double-layer capacitor (EDLC). The EDLC is a new type of capacitor or a new concept, it has been investigated for several years by now [13, 14]. The electrochemical storage of energy has been considered by using various carbon materials, such as activated carbon, carbon nanotubes, and carbon nanofilaments used as capacitor electrodes [15, 16].

Table 3 Capacitance of cells with spherical carbon and active carbon electrodes

Electrode	Method	[H_2SO_4] (M)	Surface area (m^2/g)	Specific capacitance (μF/cm^2)
Spherical carbon	CV	1.0	131	4.0
Active carbon	CV	1.0	1826	2.8

The spherical carbon showed a higher-specific capacitance despite having a specific surface area smaller than that of an activated carbon (Table 3). After the thousands of repeated test, very little degradation was observed. Activated carbon is a well-known material as a suitable material for capacitor electrodes. To indicate high performance for EDLC, effective surface area or pore size distribution, conductivity, and presence of electroactive species are required for carbon materials. The reason of the high performance for EDLC is still not clear. However, spherical carbon is composed of multi-walled carbon nanotubes, and partially cup-stacked carbon nanofilaments. Active carbon is an *amorphous* form of *carbon*. Structure of the spherical carbon may be related to the high performance and long durability for EDLC. Our results thus demonstrated that the spherical carbon has potential advantages as a novel material form for EDLC application.

Conclusion

Oxidized diamond is proposed as a useful novel catalytic medium for synthesis of spherical carbon nanomaterial, and it is suggested that oxidized diamond solids have potential for producing unique reactions in the field of nanomaterial synthesis. Spherical carbon was successfully synthesized using an oxidized diamond-supported catalysts. The possibility of using spherical carbon as an EDLC was also demonstrated.

References

1. Harris PJF (1999) Carbon nanotubes and related structures. New materials for the twenty-first century. Cambridge University Press, Cambridge, pp 1–15
2. Inagaki M (2000) New carbons-control of structure and functions. Elsevier Scientific Publications, Amsterdam, NY, pp 1–240
3. Tibbetts GG (2001) In: Biró LP, Bernardo CA, Tibbetts GG, Lambin Ph (eds) Carbon filaments and nanotubes: common origins, differing applications? Series E, vol 372. Kluwer Academic Publishers, Dordrecht, pp 1–11, 63–73
4. Baker RTK (1989) Carbon 22:315
5. Rodriguez NM (1993) J Mater Res 8:3233
6. Rodriguez NM, Chambers A, Baker RTK (1995) Langmuir 11:3862
7. Serp P, Corrias M, Kalck P (2003) Appl Catal A 253:337
8. Ando T, Yamamoto K, Ishii M, Kamo M, Sato Y (1993) J Chem Soc Faraday Trans 89:3635
9. Nakagawa K, Yamagishi M, Nishimoto H, Ikenaga N, Kobayashi T, Gamo MN, Suzuki MT, Ando T (2003) Chem Mater 15:4571
10. Nakagawa K, Gamo MN, Ando T (2005) Int J Hydrogen Energy 30:201
11. Anderson PE, Rodriguez NM (1999) J Mater Res 14:2912
12. Anderson PE, Rodriguez NM (2000) Chem Mater 12:823
13. Conway BE (1991) J Electrochem Soc 138:1539
14. Sarangapani S, Tilak BV, Chen C-P (1996) J Electrochem Soc 143:3791
15. Niu C, Sichel EK, Hoch R, Moy D, Tennent H (1997) Appl Phys Lett 70:1480
16. Frackowiak E, Béguin F (2001) Carbon 39:937