

Synthesis of Fluorine-Doped Hydrophilic Carbon Nanoparticles from Hexafluorobenzene by Femtosecond Laser Pulses

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Highlights	フッ素を高密度に含み、かつ水に親和性のある炭素ナノ粒子の簡便な合成法の開発に成功しました。
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Discription

《研究の背景》

酸素と水素の反応によって発電する燃料電池は、水以外を排出しないクリーンエネルギー源として注目されています。燃料電池の普及には、耐久性に優れ、再生利用が可能であり、酸素を効率よく還元する触媒が必要です。現在、希少金属である白金が触媒に用いられていますが、これに代るものとして、ヘテロ原子(窒素、ホウ素、リンなど)を組み込んだ炭素材料が有望視されています。

2013年には、フッ素を含む触媒が白金触媒に匹敵する性能を示すことが報告されました。この触媒は高温(1000℃)での焼成によって得られました。また、放電により5%までのフッ素を含む触媒も2015年に報告されています。しかし、フッ素原子をさらに高い密度で炭素材料に導入するためには、取扱いが困難な毒物(フッ化水素酸)や極めて反応性が高いガス(フッ素)を用いる必要があります。

そこで、私たちの研究チームは、フッ素をより高い密度で組み込んだ炭素材料を、レーザーを用いて簡便に生成する手法の開発に取り組みました。

《研究の内容》

今回、有機溶媒(ヘキサフロロベンゼン)にフェムト秒レーザーを照射することで、フッ素原子を含んだ炭素ナノ粒子(約50nm)を極めて簡便に合成することに成功しました。

通常のフッ素導入法とは異なり、本手法では加熱の必要がなく室温で実施可能です。また、反応溶液を不活性ガスで保護するなどの特別な処置は不要であり、空気が存在しても反応が起こります。さらに、水が過剰に存在する条件でも粒子が生成されます。

このフッ化炭素ナノ粒子を分析したところ、表面におけるフッ素/炭素比が40%に達していることが分かりました。また、従来のフッ素導入法では素材の内部にフッ素を十分に導入することは困難ですが、今回合成した粒子全体のフッ素/炭素比は30%と高い値を実現できました。

さらに特筆すべき特徴として、今回合成した粒子が長期間にわたって水に安定した状態で分散することが挙げられます。この粒子は水を多く含む細胞や生体などになじみやすいことが期待されますので、医療等の分野でさまざまな用途が考えられます。

《期待される効果》

今回の発見は、今後の燃料電池開発に際して貴金属を含まない高効率酸素還元触媒の実現のための設計・開発に大きく寄与すると考えられます。また、フッ素を高密度に含み、かつ水に分散する粒子の特性を活かし、医学(¹⁹F MRI 造影剤等)分野等への応用も期待できます。

“フッ素を高密度に含む! “親水性” 炭素ナノ粒子合成法の開発に成功 ~燃料電池、¹⁹F MRI 造影剤等への応用に期待~”. 大阪市立大学. <https://www.osaka-cu.ac.jp/ja/news/2016/160908>. (参照 2016-09-08)

Synthesis of Fluorine-Doped Hydrophilic Carbon Nanoparticles from Hexafluorobenzene by Femtosecond Laser Pulses

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Abstract: We report on the preparation and characterization of fluorine-doped hydrophilic carbon nanoparticles by the exposure of hexafluorobenzene or a water/hexafluorobenzene bilayer solution to femtosecond laser pulses. Uniform atom distributions were achieved not only on the particle surface but also inside the particles. The semi-ionic character of C-F bonds and the non-aggregating feature of the nanoparticles play key roles in the water dispersible character of fluorine-doped carbon nanoparticles. The building-up process of carbon nanoparticles, i.e., the fragmentations of hexafluorobenzene initiated by the electrons generated in laser-induced plasma followed by the reconstruction of a carbon framework of nanoparticles, is suggested.

Doping fluorine atoms into carbon materials such as graphene,^[1] graphite,^[2] carbon black,^[3] fullerene,^[4] and single-wall carbon nanotube^[5] dramatically changes the material's electronic, mechanical, and chemical properties, such as redox,^[6] surface friction,^[3] solubility,^[5] and catalytic activity,^[7] making such materials useful.^[8] Furthermore, the hydrophilic functionalization of nanocarbon materials makes them useful for biological and medical applications: fluorescent biomarkers suitable for living cell imaging,^[9] ¹⁹F MRI *in vivo* imaging,^[10] and drug delivery.^[11]

Generally speaking, however, fluorine doping cannot be consistent with water dispersibility of carbon materials, such as polyethylene, graphene,^[1] and graphite.^[2] Basically, high fluorine doping is accomplished under severe synthetic conditions using very reactive reagents such as F₂ and HF.^[2-5,12] Furthermore, the production of hydrophilic carbon materials also requires long-term oxidative acid treatments with heating to introduce OH and/or COOH groups to the surface.^[13] The addition of hydrophilic functional groups to the highly fluorinated carbons, such as carbon blacks (F/C=0.89^[3]) and graphite (F/C=0.83^[2]), would not be useful under acidic condition due to the liberation of fluorine atoms. The need for simpler synthetic methods for the simultaneous functionalization of both fluorine incorporation and hydrophilicity in carbon materials is important for broader application of nanocarbon materials.

In 2015, the different synthetic methods of fluorinated carbon

nanoparticles (CNPs) were reported.^[12,14-15] Panomsuwan et al. reported the incorporation of fluorine (F/C = 0.05 on surface) in CNPs by solution plasma in C₆H₅CF₃.^[14] The affinity of these CNPs to water was not mentioned. Alekseev et al. carried out an electrochemical synthesis of carbon fluorooxide nanoparticles (F/C = 0.19 in whole particles), which were dispersed in water after the hydrolysis of their ester groups in aqueous NaOH solution.^[12] On the other hand, Lyth et al. reported the solvothermal synthesis of superhydrophobic NaF-encapsulated fluorinated CNPs (F/C = 0.23 on surface; F/C = 0.028 in whole particles) from fluorinated alcohol treated with sodium at elevated temperature.^[15] The opposite affinity to water deduced from the latter two reports, independent of the fluorine content, are indicated by the presence or absence of hydrophilic OH and/or COOH groups on the surface of the CNPs.

Herein we report a simple procedure to synthesize fluorine-doped (F/C > 0.3) hydrophilic CNPs from hexafluorobenzene (HFB) facilitated by the solvated electrons that femtosecond laser pulses generate. The atomic composition of fluorine in the CNPs as well as on their surface was higher than in previously reported methods. In addition, our procedure works under room temperature, aqueous, and aerated conditions without any harsh reagents.

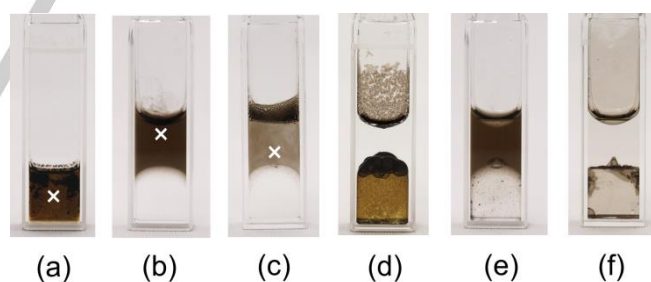


Figure 1. (a–c) The cuvette after 25-min laser irradiation to (a) HFB, (b, c) W/HFB bilayer solution. The laser beam was focused on (b) the water layer immediately after sample preparation, (c) the water layer saturated with HFB (1 day after sample preparation.) Laser focusing position is indicated by x. (d–f) The cuvette after shaking (a–c) by hand. The bilayer solution (d) was prepared by adding 1 mL water to (a) before shaking.

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The HFB turned dark yellow upon femtosecond laser irradiation and was accompanied by black particles (Figure 1a). Those particles did not show hydrophilicity at all: the particles did not move to the water layer (upper layer, Figure 1d) but stayed in the HFB layer (lower layer) after the addition of water followed by shaking. It was noted that no particles were appeared from benzene,^[16] whereas CNPs were formed from aqueous benzene under the same experimental conditions.^[17] In addition, the yield of CNPs were enhanced by using

benzene/water (B/W) bilayer solution.^[17] We concluded that the production of dense CNPs in B/W bilayer solution was due to the continuous supply of benzene into water layer through B/W interface.^[17] Furthermore, we investigated that the affinity of CNPs to water was determined by the concentration of benzene in water.^[17] Therefore, we prepared water/HFB (W/HFB) bilayer solution with the different concentration of HFB in the water layer. As in the case of B/W bilayer solution,^[17] hydrophilic CNPs were formed when the concentration of HFB in water was low, i.e., the water layer was exposed to laser pulses immediately after the preparation of W/HFB bilayer solution: The black particles that appeared in the water (upper layer, Figure 1b) did not move to the HFB by shaking (Figure 1e). In order to prepare the water layer saturated with HFB (3.25×10^{-3} mol dm⁻³),^[18] the W/HFB bilayer solution was left standing for 1-day. Most of the resultant particles were initially condensed on the air/water interface (Figure 1c) and moved to the HFB after shaking (Figure 1f). It is evident that hydrophobic CNPs are formed when the water layer is saturated with HFB; however, the yield of CNPs seems to be lower than that in neat HFB. Therefore, we next characterize the hydrophobic and hydrophilic particles, namely CNPs(HFB) and CNPs(W) produced from HFB (Figure 1a) and W/HFB (Figure 1b), to clarify the origin of their opposite affinities to water.

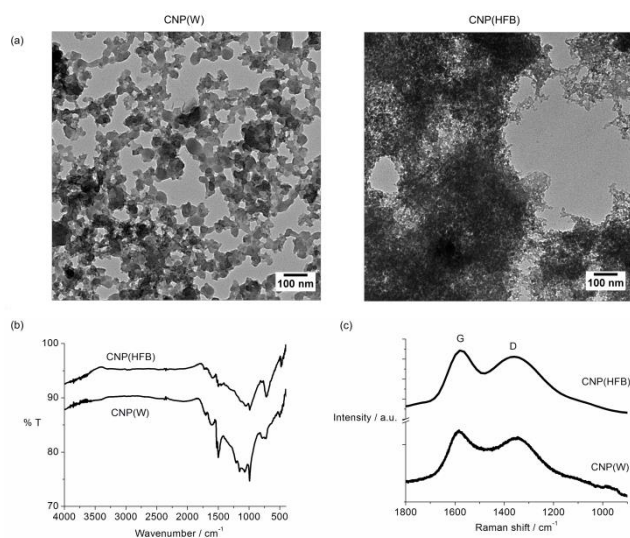


Figure 2. (a) TEM images, (b) IR, (c) Raman spectra of CNPs(W) and CNPs(HFB).

Despite their different morphologies, CNPs(W) and CNPs(HFB) did not differ significantly in the spectrometric analysis. Most of the CNPs(W) were loosely agglomerated (Figure 2a, Figure S1a), but the individual particles were less than 50 nm in diameter (Figure S1c), which seemed to be well isolated compared to the CNPs synthesized by solution plasma in C₆H₅CF₃.^[14] In contrast, the CNPs(HFB) seemed to be highly aggregated (Figure 2a, Figure S1b), and none of the particles were isolated even after the 100-fold dilution with HFB (Figure S1d). IR spectra (Figure 2b) showed typical peculiarities of amorphous fluorocarbons at around 1100 cm⁻¹ in both cases.^[19] Unlike the case of hydrophilic CNPs produced from B/W bilayer

solution,^[17] CNPs(W) did not have a hydrophilic group such as OH. It is noted that CNPs(W) showed rather strong peaks at 1000 and 1500 cm⁻¹ corresponding to C-F and C-C ring stretching.^[19] Judging from the appearance of the D band (1360 cm⁻¹) and G band (1580 cm⁻¹) in Raman spectra (Figure 2c), and the intensity ratio of those bands ($I_D/I_G = 1$), both CNPs should have disordered structures. Further, X-ray diffraction (XRD) patterns of CNPs (Figure S2) showed broad diffraction peaks ($2\theta \approx 22^\circ$ and 41°) corresponding to amorphous carbon by analogy to the previous report.^[14]

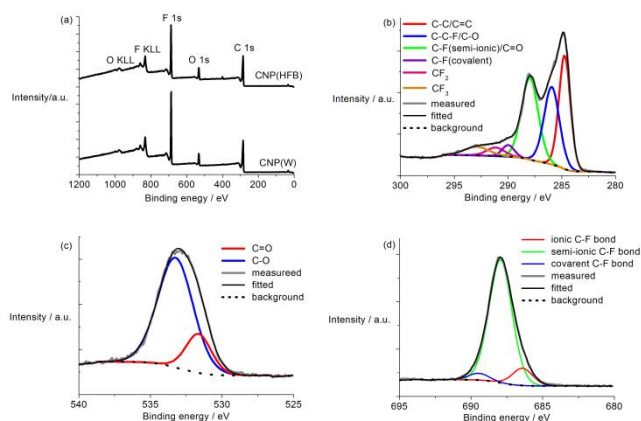


Figure 3. XPS spectra of CNPs. (a) survey scan of CNP(W) and CNP(HFB), (b) C 1s, (c) O 1s, (d) F 1s region of CNP(W).

Table 1. Atomic composition (at%) and their relative ratios of CNPs obtained by XPS and SEM-EDS measurements

		C	O	F	O/C	F/C
CNP(W)	XPS	65.5	7.1	27.4	0.11	0.42
	EDS	69.9	8.8	21.3	0.13	0.30
CNP(HFB)	XPS	67.4	7.9	24.7	0.12	0.37
	EDS	72.2	8.1	19.7	0.11	0.28

Large numbers of C-F bonds were incorporated into the surface as well as inside of the CNPs. The X-ray photoelectron spectra (XPS) survey scan revealed the evident peaks of carbon, oxygen, and fluorine on the surface of the CNPs (Figure 3a). Furthermore, the elemental mapping (line-scan) analysis using a scanning electron microscope equipped with an energy-dispersive X-ray spectrometer (SEM-EDS) showed the nearly uniform distribution of each element in CNP clusters (<500 nm, Figure S3) as well as micro-scaled agglomerates (>10 μm) (Figure S4). Taking the diameter of a single particle (about 50 nm, see Figure 2) and the penetration depth of electron beam into account, we can say that carbon, oxygen, and fluorine are homogeneously distributed in CNPs. Table 1 summarizes the atomic composition of the surface (XPS) and whole CNPs (SEM-EDS). We emphasize three important findings: 1) large fluorine incorporation (F/C > 0.3), 2) identical O/C and F/C

values for both CNPs, 3) F/C 1.3 times larger on the surface than the whole particles. Furthermore, the chemical bonding states of the elements on the surface were determined by XPS (Figure 3b-d, CNPs(W); Figure S5, CNPs(HFB)). We did not find any noticeable differences between CNPs(W) and CNPs(HFB) in the binding energy or the population of the bonding state of each element (Tables S1 to S3). The major components of CNPs found in the C 1s spectrum were C-C (C=C), C-C-F (C-O), and C-F (C=O). We cannot discriminate the overlapped peaks in C 1s at ca. 288 eV assigned as C-F or C=O bonds; however, this peak is considered a semi-ionic C-F bond, judging by the absence of C=O bonds in the IR spectra. It should be mentioned that the prominent peak found at 288 eV, was nearly absent in other fluorinated CNPs reported in 2015.^[14,15] Based on the assignments of O 1s and IR spectra, it is suggested that the oxygen incorporation is not important for the hydrophilic nature of CNPs because 1) the O/C values of CNPs(W) and CNPs(HFB) were similar, 2) oxygen was dominantly involved in CNPs as C-O bond. The candidates sources of oxygen incorporated in CNPs may be O₂ and/or water because they appear in comparable concentrations in HFB: the concentrations of O₂ and water are 4.4×10^{-3} ^[20] and 1.7×10^{-2} mol dm⁻³,^[21] respectively. The assignment of the F 1s peak appearing at ca. 688 eV is ambiguous because it depends on the structure of the carbon materials: covalent C-F;^[15] semi-ionic C-F.^[1, 2, 7, 14] We deconvoluted the F 1s peak into semi-ionic (>80%) and ionic (>10%) C-F bonds based on the findings in the C 1s spectra.

CNP production is initiated by solvated electrons that the ionization of water or HFB generates through femtosecond laser pulses. In the case of W/HFB bilayer solution, the primary reaction should be the ionization of water, as in the case of aqueous benzene.^[17] By the exposure of water to femtosecond laser pulses, reactive species such as e⁻_{aq}, H[·], ·O⁻, and OH[·] are generated. The primary reaction in aqueous benzene is the OH[·] addition ($k = 7.6 \times 10^9$ dm³ mol⁻¹ s⁻¹) rather than reduction with e⁻_{aq} ($k = 1.2 \times 10^7$ dm³ mol⁻¹ s⁻¹).^[17] In contrast, HFB reacts with e⁻_{aq} ($k = 2.0 \times 10^{10}$ dm³ mol⁻¹ s⁻¹) 10 times faster than with OH[·] ($k = 2.0 \times 10^9$ dm³ mol⁻¹ s⁻¹).^[22] The reduction of HFB was confirmed by the detection of F⁻ and the decrease in pH in W/HFB (Figure S6). Based on the experimental findings and rate constants, it is concluded that the key reactive species for the production of CNPs in this study is, instead of OH[·], e⁻_{aq} generated from water (W/HFB) as well as from HFB. Beyond the primary reactions between HFB and solvated electrons followed by the liberation of F⁻, the chemistry of CNP formation is uncertain due to its complexity. It is, however, plausible to speculate that the successive reduction as well as the ionization and photoreactions in the laser focal spot lead the initial products to be polymerized, carbonized, and finally graphitized to form graphitic and disordered carbon structures incorporating fluorine as C-F and oxygen as C-O forms on the surface as well as inside the CNPs.

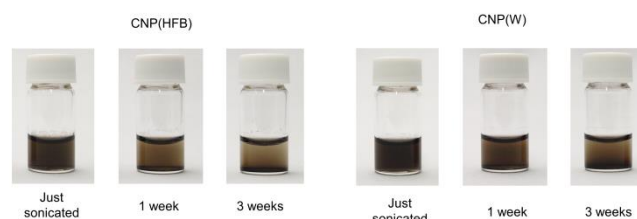


Figure 4. Images of CNPs in water 1 and 3 weeks after 30-min ultrasonication.

As the only major difference between CNPs(W) and CNPs(HFB) is their morphology in TEM and SEM images, we examined the stability of a colloidal solution of CNPs in water. Dried CNPs(HFB) and CNPs(W) were redispersed in 2 mL water by 30-min ultrasonication and left for 3 weeks (Figure 4). Although some precipitation could be observed, it is obvious that the CNPs were stable during the 3 weeks, and no difference is found between CNPs(HFB) and CNPs(W). The CNPs(HFB) observed by TEM after the above mentioned post-treatments were well isolated as was CNPs(W). We now conclude that the hydrophobicity of CNPs(HFB) is due to the unavoidable aggregation occurring in neat HFB. Thus the role of water is very simple: the dispersal of CNPs in water prevents their aggregation. Once the concentration of HFB in water is saturated, the advantage will be lost resulting in hydrophobic CNPs as shown in Figure 1f. Thus, aggregation should be avoided by keeping the HFB concentration in water low enough to yield hydrophilic CNPs without post-treatments.

Unlike conventional CNPs, the most probable origin of the water dispersibility of CNPs(W) produced by the proposed method may be the presence of semi-ionic C-F bonds, which would be effective in dispersing the CNPs in water by hydrogen bonding.^[5] There are three possible reasons for the hydrophilicity of our CNPs: 1) the building-up process forms a nearly uniform atom distribution; 2) C-F bonds on the surfaces as well as disordered structures inside CNPs enable the CNPs to attract water; and 3) each CNP is well isolated (not agglutinated). By analogy with above suggestions, hydrophilicity could be expected for fluorinated carbon blacks, which have semi-ionic C-F bonds,^[3] if they are cracked into primary particles. However, agglutinated carbon black, primary particles connected tightly by chemical bonds, require a mechanical process such as bead milling in order to crack them into primary particles. On the other hand, it is found that our CNPs(HFB) are easy to segregate into primary particles for dispersion in water.

In summary, we synthesized and characterized fluorine-incorporated hydrophilic CNPs from HFB. The colloidal solution of CNPs was stable for several weeks due to the presence of the semi-ionic C-F bonds on the surface of the CNPs. Laser ablation in liquid is a quite powerful method to prepare nanoparticles from solid reactants.^[23-26] The method reported in this study also provides a useful and alternative way to prepare CNPs from any liquid reactants as well as solution involving other heteroatoms as well as metals. However, our proposed method has many difficulties for the engineering applications. The low production yield is originated in the very small reaction

volume (in a few tens of micrometers in diameter) although the electron density achieved in this study reaches 10^{18} cm^{-3} .^[27] In addition, laser pulses cannot penetrate deeply into solution when the optical density of the solution becomes high due to the formation of the black CNPs. The former disadvantage could be overcome by producing several hundreds of focusing spots using a fly's-eye lens array if sufficient energy is available. More cost effective and high productivity approach would be the use of a flow reactor^[28,29] instead of a batch reactor, and the replacement of femtosecond laser to the other plasma sources, if high density electron generation is possible. What are the functions and potential applications of highly fluorinated CNPs? This is an open question. Recently fluorinated CNPs, synthesized at high temperature ($>1000 \text{ }^\circ\text{C}$), showed excellent properties as metal-free oxygen reduction reaction catalysts for fuel cells, though the fluorine content is very low ($\text{F/C} > 0.0053$).^[7] We expect that CNPs with highly fluorinated surfaces and interiors hold great promise for oxygen reduction reaction activity in fuel cells as well as biological applications due to their hydrophilic character.

Experimental Section

Details of the laser experiments have been described elsewhere.^[17] Briefly, samples were ionized by focused femtosecond laser pulses from a Ti:Sapphire laser ($0.8 \text{ } \mu\text{m}$, 40 fs , 1 kHz) under aerated conditions at room temperature. We collected all particles formed in the cuvettes for spectroscopic analysis (IR, Raman, XRD, XPS, and SEM-EDS). After the 25-min laser irradiation to the HFB and/or W/HFB bilayer solution, the particles were washed repeatedly in distilled water in order to remove F- as well as fluorine atoms physically deposited on the surface of particles. For the preparation of specimens for TEM observations, sample solution was directly dropped onto a copper grids covered with amorphous carbon film followed by drying in air atmosphere at room temperature.

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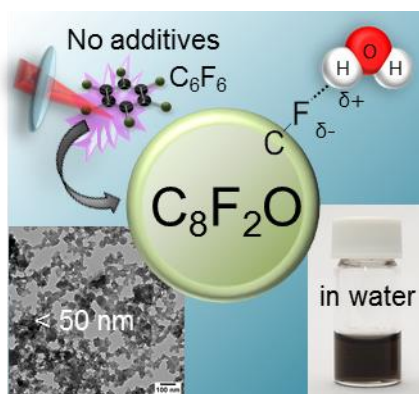
Keywords: Aggregation • Carbon materials • Femtosecond laser • Plasma chemistry • Solvated electrons

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COMMUNICATION

We report the simple synthesis of fluorine-doped ($F/C > 0.3$) hydrophilic carbon nanoparticles. The building-up process from hexafluorobenzene enables us to incorporate fluorine on the surface as well as inside the particles. The affinity to water is explained by the non-aggregating feature of the particles as well as the semi-ionic character of C-F bonds, which form hydrogen bonds with water.



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**Synthesis of Fluorine-Doped
Hydrophilic Carbon Nanoparticles
from Hexafluorobenzene by
Femtosecond Laser Pulses**