臨界点近傍及び超臨界ベンゼン中における、有機金属化合物を用いた自己組織化による炭素ナノ構造物の創生

著者	Yasuhiro Hayasaki
学位授与大学	東洋大学
取得学位	博士
学位の分野	工学
報告番号	32663甲第417号
学位授与年月日	2017-03-25
URL	http://id.nii.ac.jp/1060/00008969/

氏　　名（本籍地）	早　﨑　泰　弘（鹿児島県）
学 位 の 種 類	博士（工学）
報告・学位記番号	甲第417号（甲工第109号）
学位記授与の日付	平成29年３月25日
学位記授与の要件	本学学位規程第３条第１項該当
学 位 論 文 題 目	Creation of carbon nanostructures via self-assembly using organometallic compounds in benzene under near- and super-critical conditions （和訳：臨界点近傍及び超臨界ベンゼン中における、有機金属化合物を用いた自己組織化による炭素ナノ構造物の創生）
論 文 審 査 委 員	主査　教授　工学博士　前　川　透
	副査　教授　博士（工学）　森　本　久　雄
	副査　特任准教授　博士（理学）　内　田　貴　司

【論文審査】Review of the thesis

There are carbon allotropes such as graphite, graphene, diamond, lonsdaleite, fullerene, carbon nanotubes, carbon coils and carbon onions. Those allotropes have their own unique mechanical, electrical, optical and chemical properties. The densities of two phases; gas and liquid, become identical and the size of molecular clusters increases as the fluid systems approach the critical points. Fluid over the critical point is called super-critical fluid. Near-critical and super-critical fluids are often used in nanotechnology as well as chemical, electrical, environmental science and engineering. In the present doctoral study, carbon nanostructures such as single component magnetic particle-containing carbon nanoparticles, binary alloy-containing carbon nanoparticles and carbon coils are synthesised via self-assembly in near- and super-critical benzene.

The thesis entitled “Creation of carbon nanostructures via self-assembly using organometallic compounds in benzene under near- and super-critical conditions” consists of 5 chapters; i.e., “Chapter 1: Introduction”, “Chapter 2: Equipment and methods for materials characterisation”, “Chapter 3: Creation of metal-containing carbon onions via self-assembly in metallocene/benzene solution irradiated with an ultraviolet laser”, "Chapter 4: Synthesis of magnetic alloy-containing carbon nanoparticles in super-critical benzene irradiated with an ultraviolet laser", "Chapter 5: Creation of carbon coils in near-/super-critical benzene" and "Chapter 6: Conclusions".

Chapter 1 Introduction

This chapter focuses on some introductory explanation of "Carbon and carbon nanostructures", "Near- and super-critical fluids", "Benzene", "Metallocenes" and "Metal nanoparticles", which are all related to the present doctoral study, and shows the "Objective and outline of the thesis". Each substance has its own critical pressure, critical temperature and critical density. At the critical point, the densities of two phases; gas and liquid, become identical and the size of molecular clusters increases and becomes comparable to the wavelength of light. Fluid is not transparent at the critical point; known as critical opalescence. Fluid over the critical point is called super-critical fluid. In terms of non-equilibrium transport phenomena, perturbations of the temperature, pressure and density propagate as acoustic waves due to low thermal diffusivity and high compressibility, which is known as the piston effect, and strong buoyancy convection is induced due to the low thermal diffusivity and high temperature coefficient of volume expansion. Near-critical and super-critical fluids are often used in nanotechnology as well as chemical, electrical, environmental science and engineering. Chemicals are extracted, semiconductors are washed and cleaned and nanomaterials and nanostructures are efficiently created in near-critical and super-critical fluids.

In the present doctoral study, magnetic nanoparticles, which are covered with carbon layers, and carbon coils are synthesised via self-assembly in super-critical benzene, in which organometallic compounds are dissolved, irradiating a UV laser beam into the fluid.

Chapter 2 Equipment and methods for materials characterisation

The materials synthesised and/or dealt with in the present doctoral research were thoroughly characterised and analysed using the following microscopes and spectroscopic analysers; scanning electron microscopes (SEMs), transmission electron microscopes (TEMs), energy dispersive X-ray spectroscopy (EDS), vibrating sample magnetometer (VSM), superconducting quantum interference device (SQUID), X-ray diffractometer

(XRD), Raman spectrometer and thermogravimetric analyser (TGA).

Chapter 3 Creation of metal-containing carbon onions via self-assembly in metallocene/benzene solution irradiated with an ultraviolet laser

Nanostructures are commonly created by so-called top-down ultra-fine fabrication techniques such as photolithography, X-ray lithography and etching, whereas they can also be formed via bottom-up self-assembly processes learning from biological systems. In this chapter, a bottom-up method of producing metal-containing carbon onions is demonstrated using benzene under their sub- and super-critical conditions. Metallocene such as ferrocene ($Fe(cp)_2$) or cobaltocene ($Co(cp)_2$) is mixed with benzene and an ultraviolet laser is irradiated into the metallocene/benzene solution. It is found that iron- and cobalt-containing carbon onions are formed via self-assembly in benzene under sub- and near-critical conditions. The dependence of the structural and magnetic characteristics of the nanoparticles produced in benzene on the temperature of the benzene/metallocene solution is clarified.

The number and diameter of metal-containing carbon onions are the same irrespective of the difference in the temperature and the saturation magnetisation of iron- and cobalt-containing carbon onions increases with the mass concentration of metallocenes mixed with benzene. The present metal-containing carbon onions may well be utilised particularly in biomedical fields as well as in the fields of nano/micro electronics, magnetics and electro mechanics.

Chapter 4 Synthesis of magnetic alloy-containing carbon nanoparticles in super-critical benzene irradiated with an ultraviolet laser

Magnetic nanoparticles have attracted a lot of attention in recent years considering particularly their application to biomedical studies; e.g., they can be used as nano agents for the enhancement of magnetic resonance imaging, nano media for hyperthermic treatment of cancer cells, nano vehicles for drug delivery and nano robots for the encouragement of biochemical reactions and surgery on target cells. Heat is generated in magnetic nanoparticles by applying alternating magnetic fields to them via either the Néel or hysteresis loss heating effect depending on the magnetic nature of nanoparticles; i.e.,

superparamagnetism or ferromagnetism. Hyperthermic treatment of cancer cells using magnetic nanoparticles subjected to alternating magnetic fields has been actively studied in recent years since only target cells can be locally heated and killed without damaging any other normal cells. Biocompatibility of nanoparticles, however, becomes a crucial factor when they are used for medical treatment, noting that metallic particles are in general cytotoxic. The size of particles is also important when the particles are used for biomedical purposes. It should also be noticed that the efficiency of hyperthermic treatment of cells depends on the magnetic nature of the particles and the magnetic properties; that is, the saturation and remnant magnetisation, and coercivity. Magnetic materials such as iron, cobalt and nickel are appropriate candidates for hyperthermic treatment of cells, but the biocompatibility, size and magnetic properties of the particles become crucial factors as mentioned. Carbon materials are generally speaking chemically stable and biocompatible compared to metal particles and therefore it is demanded to produce biocompatible magnetic nanoparticles covered with carbon layers.
The gas-liquid coexistence curves terminate at the critical points, where large molecular clusters are formed and several critical anomalies such as divergence of the physical properties and fast propagations of temperature, pressure and density perturbations occur. It has also been demonstrated that nano materials can be efficiently synthesised in near-critical and super-critical fluids such as carbon dioxide, benzene and acetone under their near- and super-critical conditions, by irradiating ultraviolet (UV) laser beams into the fluids.

In this chapter, magnetic alloy-containing carbon nanoparticles (MA@C NPs) are synthesised via the following two-step procedure; (1) irradiation of a laser beam of 266 nm wavelength into super-critical benzene, in which both ferrocene ($Fe(cp)_2$) and cobaltocene ($Co(cp)_2$) are dissolved, at 290 °C; and (2) annealing of the particles at 600 and 800 °C. It is found that the core particles are composed of cobalt (Co), iron (Fe) and oxygen (O) and covered with carbon layers. The structure of the core particles as-synthesised and annealed at 600 and 800 °C is, respectively, amorphous, $CoFe_2O_4$ and FeCo. The viability of L929 cells in the presence of MA@C NPs is investigated and it is found that there is no serious advert effect of the MA@C NPs on the cell viability thanks to the carbon layers covering the core particles. The magnetic properties are well characterised. The saturation and remnant magnetisation and coercivity increase and as a result, the hyperthermic efficiency becomes higher with an increase in the annealing temperature. The further modification of the surface of the present particles with several functional molecules becomes easier due to the carbon layers, which makes the present particles more valuable. It is therefore supposed that the presently synthesised MA@C NPs may well be utilised for nanotechnology-based biomedical engineering; e.g., nano bioimaging, nano hyperthermia and nano surgery.

Chapter 6 Creation of carbon coils in near-/super-critical benzene

Various types of carbon nanostructures such as fullerenes, carbon onions, carbon nanotubes, graphene, carbon coils, metal-containing carbon onions and metal-containing carbon nanotubes have been discovered and synthesised and the application of those nano materials to various fields have been intensively investigated. Several innovative methodologies for synthesising the above carbon nanostructures have been invented, modified and improved and now high quality carbon nano materials can be synthesised by several sophisticated methods such as arc discharge, laser ablation and chemical vapour deposition. The shape of carbon coils is really unique among those carbon nanostructures. Carbon coils have high elasticity, high electric conductivity and high electromagnetic wave absorption.

In this chapter, carbon coils are created using a chemical catalyst; bis (t-butylacetoacetato) copper (II):$Cu(tbaoac)_2$, which is dissolved in critical benzene, with UV laser irradiation. The second (532 nm wavelength), third (355 nm) and fourth (266 nm) harmonic photons generated from an Nd:YAG laser are irradiated into near-critical benzene, in which $Cu(tbaoac)_2$ is dissolved, at 290 °C and it is found that carbon fibres and coils are created via the interactions among the incident photons, catalytic nanoparticles and benzene molecules captured in large clusters formed under near-critical conditions. The size of carbon fibres and coils is dependant on the wavelength of the incident photons. When $Cu(tbaoac)_2$ is dissolved in benzene under near-critical conditions, irradiation of 355 and 266 nm wavelengths efficiently creates carbon coils. The operational temperature of the present synthetic method is much lower than that of the conventional synthetic methods of nano materials and what is more, the laser power density can be as low as 5.2 mW mm^{-2}.

Chapter 7 Conclusions

The results obtained in the doctoral study are summarised in this chapter.

(a) A UV-laser beam is irradiated into super-critical benzene, in which ferrocene or cobaltocene are dissolved. Iron-containing and cobalt-containing carbon onions are formed. The iron- and cobalt-containing carbon nanoparticles possess superparamagnetic characteristics. The effect of the concentration of ferrocene and cobaltocene on the magnetic properties of the metal-containing carbon nanoparticles is clarified. The number and diameter of metal-containing carbon nanoparticles were the same irrespective of the difference in the temperature.

(b) A laser beam of 266 nm wavelength is irradiated into super-critical benzene, in which both ferrocene and cobaltocene are dissolved, and the materials produced after laser irradiation are annealed at 600 and 800 °C. It is found that particles are composed of carbon (C), iron (Fe), cobalt (Co) and oxygen (O). Particles as-synthesised and annealed at 600 and 800 °C are, respectively, amorphous and $CoFe_2O_4$ covered with carbon layers ($CoFe_2O_4$@C) and FeCo covered with carbon layers (FeCo@C). The mechanism of the formation of the particles is clarified. The viability of cell line L929 in the presence of MA@C NPs as-synthesised, and annealed at 600 and 800 °C are investigated using an Alamar blue assay. The cell viability is over 80 %. It is supposed that the cell viability is not seriously deteriorated thanks to the carbon layers covering the core particles. The hyperthermic performance of the nanoparticles is also investigated. The hyperthermic efficiency of these nanoparticles dispersed in ethanol is increased with an increase in the annealing temperature.

(c) The second (532 nm wavelength), third (355 nm) and fourth (266 nm) harmonic photons generated from an Nd:YAG laser are irradiated into near-critical benzene, in which bis(t-butylacetoacetato)copper: $Cu(tbaoac)_2$ is dissolved, at 290 °C and it is found that carbon fibres and coils are created via the interactions among the incident photons, catalytic nanoparticles and benzene molecules captured in large clusters formed under near-critical conditions. TEM observation and EDS analysis show that the carbon coils grow from copper nanoparticles, which are formed via pyrolytic and photolytic decomposition of $Cu(tbaoac)_2$. When $Cu(tbaoac)_2$ is dissolved in benzene under near-critical conditions, irradiation of photons of 355 and 266 nm wavelengths efficiently creates carbon coils. The size of carbon fibres and coils is dependant on the wavelength of the incident photons.

In the present doctoral research, carbon materials such as metal-containing carbon nanoparticles, alloy-containing carbon nanoparticles and carbon coils are synthesised dissolving organometallic compounds in near- and super-critical benzene, which is irradiated with a laser beam. It is supposed that the present methodology may well be utilised for the synthesis of different core particles-containing carbon nanoparticles by changing the organometallic compounds dissolved in solvent.

【審査結果】Summary and decision

The thesis entitled “Creation of carbon nanostructures via self-assembly using organometallic compounds in benzene under near- and super-critical conditions” focused on the synthesis of (a) single component magnetic nanoparticles covered with carbon onions; (b) binary alloy-containing carbon nanoparticles; and (c) carbon coils via self-assembly in super-critical benzene, in which organometallic compounds were dissolved, by irradiation of an ultraviolet laser beam. The results shown in the thesis are outstanding from an international point of view and the significant points in the present study are summarised below;

(1) Iron (Fe) or cobalt (Co) containing carbon onions can be self-assembled in super-critical benzene, in which either ferrocene or cobaltocene are dissolved, by irradiating an ultraviolet laser beam of 266 nm wavelength. The synthetic temperature is much lower than that of conventional methods. Both iron and cobalt containing carbon onions show superparamagnetic characteristics.

(2) Alloy (Fe and Co) containing carbon nanoparticles can be synthesised in super-critical benzene, in which both ferrocene and cobaltocene are dissolved, by irradiating an ultraviolet laser beam of 266 nm wavelength.

(3) The above alloy nanoparticles can be either $CoFe_2O_4$ or FeCo by annealing the nanoparticles at 600 or 800 °C. In other words, the components of the core nanoparticles can be controlled by altering the annealing temperature.

(4) The saturation and remnant magnetisation and coercivity dramatically increase after annealing the nanoparticles, as a result of which the hyperthermic performance of the nanoparticles is greatly improved.

(5) The above magnetic nanoparticles are biocompatible thanks to carbon layers covering the core particles. In other words, the present magnetic carbon nanoparticles can be utilised for hypertheric treatment for cancer cells.

(6) Carbon coils can be self-assembled in super-critical benzene, in which a copper

compound; Cu(tbaoac)$_2$, is dissolved, by irradiating a laser beam of 266, 355 and 532 nm wavelengths.

(7) The present results show that different multifunctional carbon nanostructures and nanomaterials may be self-assembled by dissolving different organometallic compounds in super-critical fluids, which may open up a new methodology for synthesising carbon nanostructures and nanomaterials at low temperature.

The results obtained by the present doctoral study have been highly appreciated by materials science societies; two first-authoring papers and one second-authoring paper have been published by international journals (The Institute of Physics and The Royal Society of Chemistry).

Judging by the results shown in the thesis and the number of international papers published so far, the level of the present research results is definitely high by international standards and the present results may well make a great contribution to the development of new methodologies for synthesising novel functional nanoparticles and nanostructures. The present results may also contribute to the development of advanced high precision biomedical devices and sensors. In conclusion, the thesis is considered to be a high quality, high standard one by international standards.