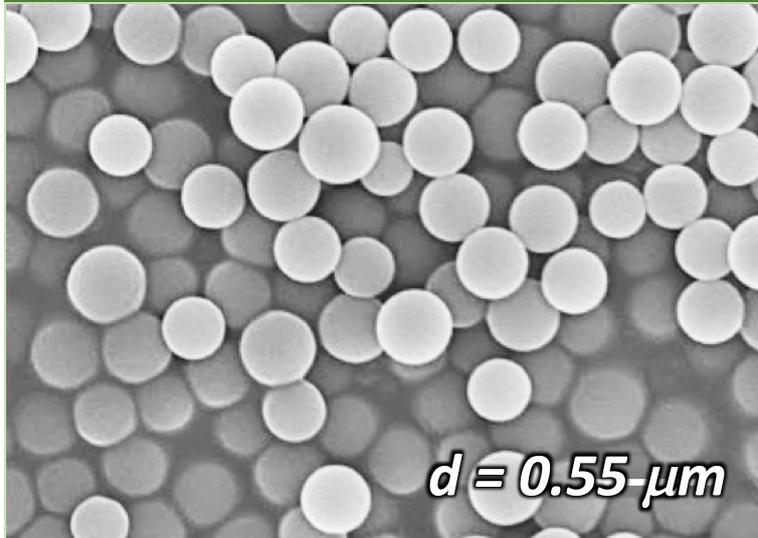


黒色ポリマー美粒子

カーボンブラックに替わる新材料



製造

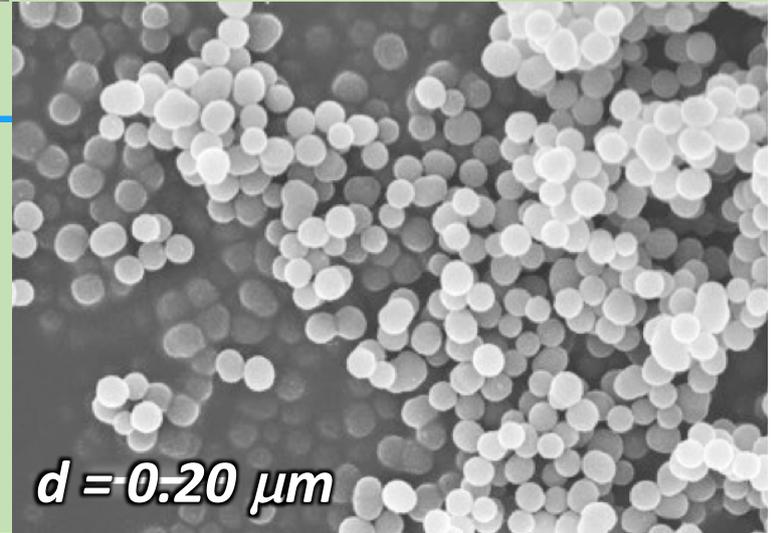
- ◆ 真球状かつ単分散
- ◆ ナノからマイクロサイズまで
- ◆ 褐色から黒色まで

Productivity

性質

- ◆ 高分散性
- ◆ 耐熱性・耐光性・耐薬品性
- ◆ 絶縁性

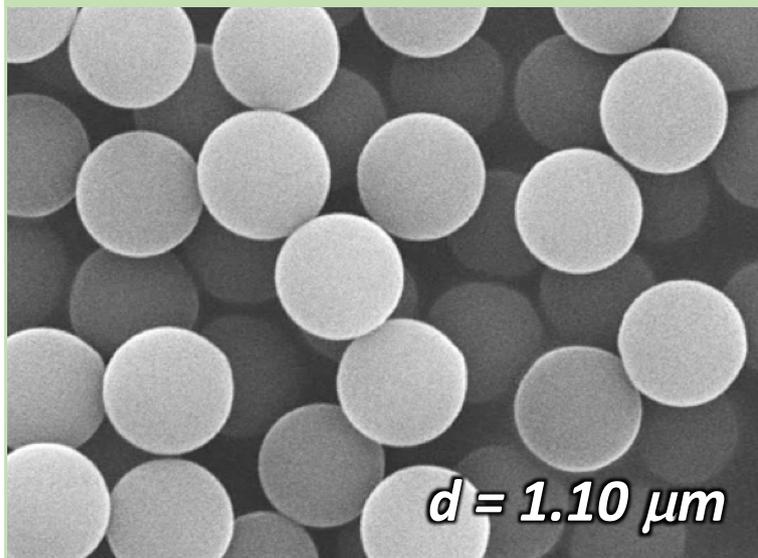
Surfactant-free



用途

高分散性が生み出す無限の展開力
機能性フィラー 光散乱材 隠蔽材
高解像度黒色トナー 液晶スペーサー
近赤外吸収・反射材 構造色主材・助材

Various Applications





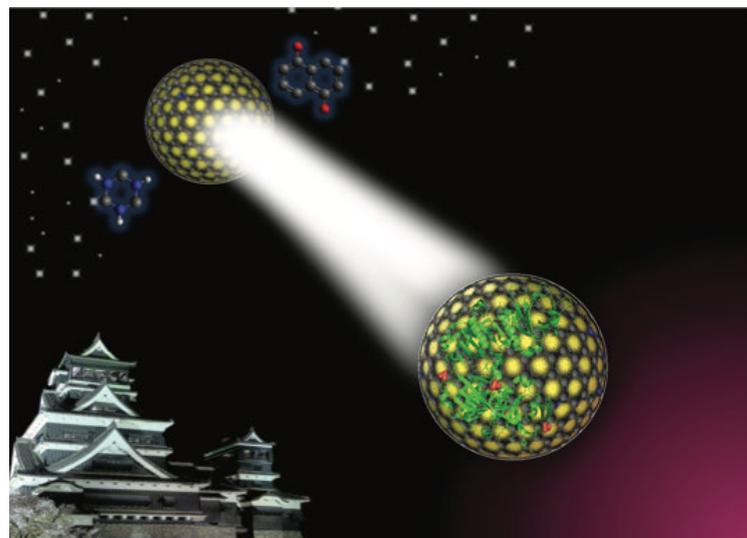
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Amphiphilic spherical nanoparticles with a nitrogen-enriched carbon-like surface by using β -lactoglobulin as a template†

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Showing research from Professor H. Ihara's laboratory, Department of Applied Chemistry and Biochemistry, Kumamoto University, Kumamoto, Japan.

Amphiphilic spherical nanoparticles with a nitrogen-enriched carbon-like surface by using β -lactoglobulin as a template

Amphiphilic spherical nanoparticles having N-enriched carbonised surface prepared by a facile one-pot polymerization of conjugated molecules with β -lactoglobulin aggregates as template with tunable size (70–750 nm) and mild heat-treatment to extend π -conjugated structures.



Non-conductive, Size-controlled Monodisperse Black Particles Prepared by a One-pot Polymerization and Low-temperature Calcination

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This paper introduces a new class of size-controlled and non-conductive black particles based on the preparation of monodisperse spherical polymer particles from 1,5-dihydroxynaphthalene and 1,3,5-trimethylhexahydro-1,3,5-triazine and subsequent low-temperature calcination. The versatility of our method can be emphasized by one-pot polymerization in a simple solvent system without any surfactant, and size controllability from submicron to micron orders in the diameter. High non-conductivity can be kept by calcination even at higher temperature.

Keywords: Carbon black | Amorphous carbon | Monodisperse spherical particle

Carbon-based fine particles have been widely used as fillers for enhancing the reinforcement for bulk materials.^{1–3} In addition, the excellent physical stability and unique chemical properties of these fine particles expand their potential utility in electroconductive materials,^{4–7} carriers for catalysts,^{8–10} packing materials for column separation,^{11–15} etc. For example, carbon black has been widely used as black materials such as pigment and colorant for inks, paints, and resins. In these applications, electroconductivity is an important physical factor: non- or high electroconductivity should be selected depending on the intended use.

On the other hand, precise control of the size and shape of carbon-based fine particles is strongly desired because their monodispersity allows for highly dense filling. A typical example is often seen in the column systems used for high-performance liquid chromatography. In a silica-based stationary phase, the particles show high sphericity and monodispersity (diameter: 1–5 μm), which results in the best performance in terms of chromatographic resolution.

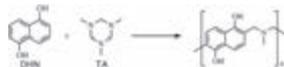
With this background, we developed a versatile method for preparing size-controlled spherical carbon-like, but non-conductive black particles having high sphericity and monodispersity. Also we focused on non-conductivity because non-conductive black materials are required in many industrial fields such as pigments, toners, paints, and shielding industries while carbon blacks remain conductive. Our method involves the one-pot polymerization of 1,5-dihydroxynaphthalene (DHN) and 1,3,5-trimethylhexahydro-1,3,5-triazine (TA) in ethanol and/or related solvents such as ethylene glycol (EG) and water, without any additive (dispersant), and subsequent calcination at relatively low temperature. The diameters of the resultant black particles can be controlled in the range of submicron to a couple of microns.

The typical preparation procedure is as follows: 30 mM each of DHN and TA was mixed and dissolved in ethanol at room

Table 1. Preparation condition and average diameter of the polymer particles^a

Name	Composition ratio of solvent		Conc. /mM	Reaction temp. /°C	Calcination temp. /°C	Average particle diameter / μm	CV	
	EtOH	EG						H ₂ O
E ₁₀ -80	1.2	100	0	75	80	2.31	0.09	
E ₁₀ -80 L1	100	0	0	50	80	1.71	0.08	
E ₁₀ -80	100	0	0	30	80	1.33	0.07	
E ₁₀ -80 S1	100	0	0	15	80	1.06	0.1	
E ₁₀ -80/200	100	0	0	30	80	200	1.20	0.08
E ₁₀ -80/400	100	0	0	30	80	400	1.13	0.1
E ₂ G ₂ -80	70	30	0	30	80	—	0.54	0.09
E ₂ G ₂ -80	50	50	0	30	80	—	0.32	0.09
E ₂ G ₂ -80	30	70	0	30	80	—	0.25	0.12
G ₁₀ W ₁₀ -80	0	100	0	30	80	—	0.13	0.16
G ₁₀ W ₂₀ -80	0	100	0	30	180	—	0.12	0.16
E ₂ G ₂ W ₂₀ -80	50	50	0	30	80	—	0.72	0.17

^aConc.: Initial concentrations of DHN and TA. Coefficient of variation (CV) was calculated as standard deviation divided by average particle diameter. All particle size was determined from SEM images. The estimated reaction mechanism is as follows:



temperature and heated to 80 °C under gentle stirring. The solution was stirred for 6 h, during which time the color changed gradually via light green to dark green. Microscopic observations indicated that the initial precipitation of the spherical solid particles commenced within 30 min and that the color change of the solution was due to the produced solid component. The solid component (E₁₀-80) was obtained by filtration, sufficient washing with ethanol, and drying in vacuo. Table 1 summarizes the reaction conditions and results.

The time course of the particle diameter in ethanol was evaluated by dynamic light scattering (DLS). As shown in Figure 1, the particle diameter of E₁₀-80 increased until 3 h and reached saturation at around 1.3 μm , which is nearly equal to that in DLS monitoring. No such particle precipitation was observed when the reaction solvent was changed from ethanol to dimethylformamide (DMF), although prolonged (a couple of days) reaction led to gelation. However, E₁₀-80 did not dissolve in DMF but also showed any swelling in DMF. Similar participation and non-solubility to DMF was also confirmed in E₂G₂-80 and E₂G₂W₂₀-80, which were prepared in mixed solution systems containing 50 vol% of ethylene glycol and water,

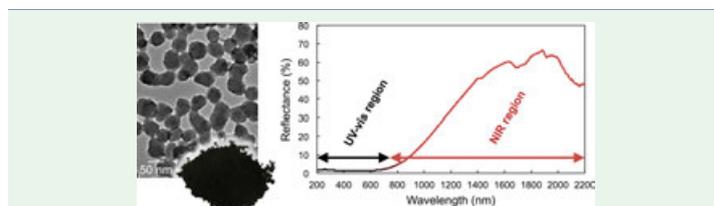
Monodisperse Surface-Charge-Controlled Black Nanoparticles for Near-Infrared Shielding

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Supporting Information



ABSTRACT: A simple and quick preparation of black polymer nanoparticles by the microwave-assisted polymerization of 1,5-dihydroxynaphthalene and 1,3,5-trimethyl-1,3,5-triazine under high temperature and pressure was demonstrated. The average diameter of the nanoparticles ranged from 20 to 700 nm, depending on the preparation conditions such as reaction solvent, monomer concentrations, and monomer ratio in the seed mixture. The surface charge of the nanoparticles was also determined by the monomer ratio used in the seed mixture. The nanoparticles could be dispersed in polar solvents such as water, methanol, and ethanol, probably because the phenolic hydroxyl groups and primary/secondary amine groups remained on the surface of the nanoparticles. The reflectance spectroscopic measurements from 200 to 2200 nm showed that the nanoparticles expressed selective reflectivity of NIR wavelengths. The absorption and reflectance properties could be tuned by microwave-assisted calcination of the nanoparticles. The particles were initially dark green, but when the particles were heated at 250 °C for 10 min in ethylene glycol, they absorbed light in the UV–visible region (reflectance was less than 3% from 200 to 750 nm), indicating the color of the particles had become perfectly black. Reflection in the NIR region from 1250 to 2150 nm, however, remained more than 50% after calcination. The calcinated nanoparticles could be dispersed in water, and the surface charge was positive at lower pH and negative at higher pH. The isoelectric point shifted slightly from 5.3 to 4.4 after wet calcination at 250 °C. The amount of nitrogen in the nanoparticles decreased remarkably after calcination; therefore, the phenolic hydroxyl groups must have remained on the surface of the calcinated nanoparticles preferentially to the amine groups. These black nanoparticles with selective reflectance in the NIR region could be applied to black heat-shielding materials such as paints for buildings and automobiles.

KEYWORDS: microwave synthesis, π -conjugated polymer, dispersion polymerization, amphiphilic surface, selective reflectance of NIR, heat-shielding materials, heat-insulating materials

1. INTRODUCTION

Recently, heat shielding and heat insulation have become important issues for energy efficiency and global warming. Various heat-shielding materials have been developed for suppressing the internal temperature increase of buildings and automobiles caused by sunlight.^{1–3} Because approximately one-half of sunlight is heat rays, which includes the electromagnetic radiation from near-infrared (NIR) to infrared (IR), materials with high reflectivity in the NIR–IR region can be used as heat-shielding materials. Heat-shielding coatings have been increasingly used for the roofs and walls of

buildings, as well as the bodies of automobiles, because of their excellent convenience. The heat-shielding coatings usually contain inorganic pigments which selectively reflect wavelengths in the infrared region in addition to reflecting some visible light.^{4–8} The color of an IR-reflective pigment is characterized by its reflectivity and absorptivity; therefore, it is possible to control the color of the pigments by changing the

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Novel Black Organic Phase for Ultra Selective Retention by Surface Modification of Porous Silica

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This paper demonstrates that novel composites of porous silica with carbon-like black materials are different from conventional carbon black. The obtained black composites maintained high porosity of the base silica and exhibited extremely high molecular shape selectivity, especially for geometrical isomers.

Keywords: π -Conjugated structure | Porous material | Amorphous carbon

To address the growing demand for enhanced separation selectivity in column technology, a variety of functional molecules have been designed and immobilized on porous carriers to meet this demand, as exemplified by successful applications of macrocyclic-grafted silica,^{1–3} where high selectivity is achieved by macrocyclic ordering of heteroatoms as interaction points. On the other hand, non-macrocyclic compounds can also achieve selectivity enhancement if weak interaction points are integrated and oriented. Typical examples include integrated carbonyl group systems like side-chain ordered polymers containing ester bonds,^{6–8} alternating phthalimide-based copolymers,⁹ and polypeptide,¹⁰ and molecular-gel-based ordered organic phases,^{11–13} which provide higher selectivity than conventional hydrophobized silica, especially for separating geometrical isomers. These successful applications are directly related to the promotion of multiple carbonyl- π interactions¹⁴ with guest molecules.

π -Electron-rich organic phases are also attractive for selectivity enhancement. Although π - π interactions are considerably weaker than carbonyl- π interactions,^{14,15} integration of aromatic π -moieties enables selectivity enhancement, as exemplified by polymers with aromatic side chains,^{16,17} imidazolium-based ionic liquids,^{18,19} polycyclic aromatics like pyrene and coronene,²⁰ aromatic foldamers,²¹ fullerenes,^{22,23} carbon nanotubes,²⁴ and graphite carbon.^{25,26}

Herein, we introduce a new class of π -electron-rich organic phases (Figure 1) for ultra-selective adsorption, which are based on carbon-like black materials different from conventional carbon black and graphite. The designed materials exhibit the following advantages. (1) The pre-black organic thin layer can be created on porous silica microspheres by direct copolymerization of 1,5-dihydroxynaphthalene (DHN) and 1,3,5-trimethylhexahydro-1,3,5-triazine (TMTA)²⁷ in a simple solvent system. The amount of immobilized material is easy to adjust while preserving the large surface area of porous silica, since polymerization occurs on the silica surface in a semi-quantitative fashion. Additionally, polymer growth does not require silica to be surface-treated. (2) Copolymerization is accompanied by crosslinking; therefore, no elution is observed after washing with solvents. (3) The adhered polymer can be converted into carbon-like black materials by heat treatment at a suitable temperature,

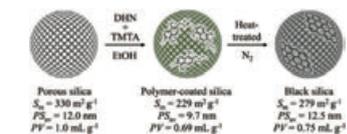


Figure 1. Schematic preparation of black silica by direct copolymerization of 1,5-dihydroxynaphthalene (DHN) and 1,3,5-trimethylhexahydro-1,3,5-triazine (TMTA) on porous silica, showing the typical specific surface area (S_s), average pore size (P_p), and pore volume (P_pV). The estimated structures of a copolymer intermediate and black component are illustrated in each picture.

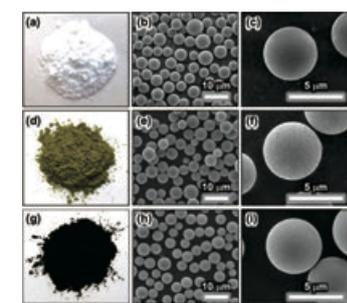


Figure 2. Bulk and SEM images of non-modified silica (a–c), P₁₇-78 (d–f), and P₁₇-78/560 (g–i).

allowing the adsorptivity and selectivity of the column system to be flexibly tuned.

Copolymerization was carried out at a fixed molar ratio (1:1) of DHN and TMTA. The original milky white mixture of these monomers with YMC silica as porous carrier in ethanol turned green after 1 h stirring at reflux temperature (78 °C). Optical microscopy imaging indicated that the above change was due to the coloration of silica and not that of the solvent. As shown in Figure 2d, a moss green product was obtained after 4 h stirring.