

### Fine and Nanoparticle Adhesion and Aggregation Behaviour Characterisation and Control<sup>†</sup>

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The control of adhesion and aggregation behaviour in gases, liquids, and solids is important for the application of inorganic nano- and fine particles in various fields, such as functional materials and devices, pharmaceuticals, cosmetics, and pigments. We have developed original methods for the characterisation of interfacial molecular- and nanometre-scale structures and interactions between particles and substrate materials. The surface molecular-structure design by an organic surfactant, commonly called a "ligand," was investigated with different molecular structures for nanoparticle-dispersion stability control in various organic solvents and polymer solid materials. First, we introduce various approaches for controlling the interfacial molecular structure of nanoparticles to disperse nanoparticles in various liquids. Next, aggregation- and adhesion-behaviour characterisation methods, such as colloid probe atomic force microscopy and the control of fine powders and microcapsules in the ceramic and pharmaceutical fields, are reviewed. Finally, the characterisation and control of the adhesion behaviour of fine ash particles at high temperatures in energy generation and environmental systems are investigated. Original



**Review Paper** 

characterisation devices and a model of an ash-particle preparation method from pure silica were developed by adding small amounts of elements, such as alkali metals and phosphates, to analyse the increase mechanism of the ash-adhesion force at high temperatures. Based on the results of the analysis, the adhesion behaviour can be controlled by the addition of various materials. **Keywords:** particle surface interaction, interface structure design, ligand and dispersant, dispersion/aggregation control, high temperature effect

### 1. Introduction

Nanoparticles, which are smaller than 100 nm in diameter, have various functional properties such as quantum, optical, electromagnetic, and chemical catalytic properties. Recently, mass-production processes for nanoparticles and nanomaterials have been developed, and cost reduction is progressing. For example, the mass production of carbon nanotubes has been developed at the commercial level using a fluidised bed process (Li et al., 2021) and a new reactor design (Yoko et al., 2020). Technologies for controlling the size, shape, composition, and crystallinity of various nanoparticles and materials in gas and liquid phases have also been developed (Park et al., 2004). However, the aggregation- and adhesion-behaviour control of fine and nanoscale particles remains important for the application of nanoparticles in functional material processing, pharmaceuticals, cosmetics, and pigments. For example, when hydrophilic nanoparticles such as metal oxides are dis-

persed in a nonpolar solvent, a surfactant or ligand comprising a hydrophobic organic chain and an adsorbent group or coupling agent is adsorbed or reacts on the surface of the nanoparticles. The theory required to obtain the optimum molecular size and structure of the ligand and coupling agent for nanoparticle aggregation control in various solvents has not yet been completed. For nanoparticle dispersion, a ligand that is not too large compared with the polymer is typically used. In contrast, for fine particles and microcapsules, which are larger than 100 nm in diameter, a polymer dispersant with a size of approximately 10,000 g/mol is typically adsorbed on the particles for dispersion (Kamiya et al., 1999). In the gas phase, a nanometre-scale surface treatment was developed to reduce the adhesion force of fine particles. In particular, at high temperatures, the increase in ash adhesion causes various problems in power generation using coal and in environmental plants for biomass and waste combustion. The control of adhesion and aggregation behaviours in air is also an important subject.

This paper discusses the fundamentals of fine and nanoscale particle behaviours such as the reason for the difference in surface activity and structure, focusing on the



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dispersion and aggregation control of nanoparticles in various solvents. The combination of the materials, size, shape, and surface structure of nanoparticles with solvent properties is an important factor in the selection of a molecular design structure for nanoparticles. Two approaches are proposed to disperse nanoparticles: one is the development of ligands with universal dispersibility in different solvents, and the other is ligand-exchange technology for particle synthesis and dispersion control in the final desired solvent. Next, we focus on fine-particle and microcapsule aggregation- and adhesion-behaviour characterisation and control in liquid. By Ducker et al. (1992), the surface interactions between fine particles were determined using colloidal probe atomic force microscopy, AFM and other characterisation methods. Based on the characterisation results, the optimum polymer and surface molecular structure required to control the surface interaction and dense suspension behaviour is determined. Finally, some original characterisation methods for fine-ash particle-adhesion behaviour at high temperatures have been developed. Based on the characterisation results of the surface interaction, the mechanism of the adhesion-increasing behaviour is investigated, and new methods for controlling ash adhesion at high temperatures have been also developed and introduced in this paper.

# 2. Interface-structure design of nanoparticles for aggregation-behaviour control in liquid

## 2.1 Interface structure and behaviour of nanoparticles

Nanoparticles have large specific surface areas and high surface energies. To discuss the effect of the particle size on the surface energy and structure, a simple crystal structure was assumed as in a simple cubic and one-atom basis. The relationship between the surface atom ratio,  $R_i$ , and the particle size, which is determined by the number of atoms per side, *i*, is calculated using the following equation (see **Fig. 1(a)**):

$$R_i = \frac{i^3 - (i-2)^3}{i^3} = 1 - \left(\frac{i-2}{i}\right)^3 \tag{1}$$

When i = 1 or 2, all atoms exist on the surface; when i = 3, only one atom exists inside, and the surface atom ratio is 8/9, which is approximately 90 %. With an increase in *i*, the surface atom ratio  $R_i$  decreases; however, for i < 10, the surface atom ratio and surface energy are still high, as shown in **Fig. 1(b)**, which displays the relationship between *i* and  $R_i$ . The particle size was calculated; because the atomic radius is 0.124 nm, the particle is not stable, and is formed as a cluster. When particle growth reaches i > 10, the surface atom ratio is smaller than 50 %, cubic particlesurface energy is reduced, and the cubic particle is "stable" as a nanoparticle. Another example of the effect of the particle diameter on the surface molecular structure is shown in the surface silanol structure of alkoxide-derived silica particles, which was determined using FT-IR, as shown in Fig. 2(a) (Kamiya et al., 2000). The spectrum peak of free silanol at  $3750 \text{ cm}^{-1}$  decreased with increasing particle diameter and disappeared, and almost all the silanol was hydrogenbonded when the particle size reached 260 nm. This change in the silanol group structure may be related to the distance between the neighbouring silanol groups, as shown in Fig. 2(b).

The estimated distance between the O and H atoms of the neighbouring silanol groups increased with decreasing

<ul> <li>Surface atom</li> <li>Inside atom</li> </ul>	0	8			
umber of atoms per one side, i	1	2	3	4	5
otal number of atoms	1	$2^3 = 8$	3 <sup>3</sup> = 27	$4^3 = 64$	5 <sup>3</sup> = 125
umber of surface atoms	1	8	$3^3 - 1 = 26$	$4^3 - 2^3 = 56$	$5^3 - 3^3 = 99$
atio of surface atoms, R <sub>i</sub> [%]	100	100	26/27 = 96.2	87.5	79.2
	Surface atom Inside atom umber of atoms per one side, <i>i</i> tal number of atoms umber of surface atoms atio of surface atoms, <i>R<sub>i</sub></i> [%]	Surface atom Inside atom	Surface atom       Surface atom         Inside atom       Inside atom         umber of atoms per one side, i       1       2         tal number of atoms       1 $2^3 = 8$ umber of surface atoms       1       8         atio of surface atoms, $R_i[\%]$ 100       100	Surface atom Inside atom umber of atoms per one side, $\begin{vmatrix} 1 & 2 & 3 \\ 1 & 2^3 = 8 & 3^3 = 27 \\ 1 & 3^3 - 1 = 26 \\ 1 & 8 & 3^3 - 1 = 26 \\ 1 & 0 & 100 & 26/27 = 96.2 \\ 1 & 0 & 0 & 0 & 26/27 = 96.2 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0$	Surface atom       Surface atom <t< td=""></t<>



Fig. 1 Estimated effect of simple cubic particle size on surface atom ratio. (a) Conceptual diagram and table for calculation of surface atom ratio. (b) Relationship between number of atoms per one side and surface atom ratio estimated by Eqn. (1).



**Fig. 2** Effect of silica particle diameter on surface silanol structure. **(a)** FT-IR diagram of silica with different diameter. **(b)** Estimated surface silanol structure. Adapted with permission from Ref. (Kamiya et al., 2000). Copyright (2000) Wiley.

particle diameter. This difference in the surface molecular structure affects the reaction density of the silane coupling agent on the silica surface. Because of the large distance between the O and H atoms and the low surface silanol density of the nanoparticles, the amount of chemisorbed silane coupling agent per unit surface area on the nanoparticles (30 nm in diameter) was lower than that on the fine particles (200 nm in diameter), as shown in **Fig. 3** (Iijima et al., 2007).

### 2.2 Simultaneous design of nanoparticle synthesis and dispersion in nonpolar solvent

Using a metal oleate complex as the raw material, oleylgroup surface-modified nanoparticles were synthesised in a nonpolar solvent under high temperature and pressure conditions. The synthesised nanoparticles were dispersed and stabilised in a nonpolar solvent and self-assembled to form a close-packed structure via the coating and drying process using the nanoparticle suspension by Park et al. (2004). The size and shape of nanoparticles could be controlled by varying the synthesis conditions. In the normal hydrothermal synthesis process, oleic-group surfacemodified nanoparticles were synthesised by adding an organic surfactant with an oleic chain. For example, the particle size and morphology of titanium oxide (Dinh et al., 2009) and iron oxide (Cara et al., 2015) nanoparticles were controlled by adding different ratios of oleic acid and oleic amine in the hydrothermal process. The synthesis of nanoparticles in the presence of oleic acid and amine enabled control of the particle structure and functional behaviours of metal, metal oxide, and sulphide nanoparticles. This method has been detailed in review articles by



Additive amount of SC agent [µmol/m<sup>2</sup>]

**Fig. 3** Chemisorbed amount of silane coupling agent on silica particles measured using an organic element analyzer. Adapted with permission from Ref. (Iijima et al., 2007). Copyright (2007) Elsevier B.V.

#### Mourdikoudis et al. (2022).

Oleic-group modified nanoparticles are effective for dispersion stability in nonpolar solvents such as toluene. However, if the solution properties are changed by a small amount of a hydrophilic solvent, such as methanol, the dispersion stability decreases and nanoparticle aggregation is promoted. To obtain nanoparticles dispersed in a polymer composite, a hydrophilic polymer resin monomer was added to nanoparticles dispersed in a nonpolar solvent. Because of the change in solvent polarity, white turbidity due to nanoparticle aggregation was observed. If the solvent, solution, or matrix solid selected for application cannot maintain dispersion stability with oleic-group modified nanoparticles, the following two approaches may be used:

- 1) Development of ligand molecular-structure design for dispersion in various solvent and solid materials.
- Ligand exchange to change in surface-modified molecular structure from the synthesis process used to obtain the optimum surface organic structure for dispersion in different solvents and solid matrix.

The details of each approach will be introduced in the following sections.

### 2.3 Development of ligand-structure design for dispersion of nanoparticles in various solvents

To select organic ligands to disperse nanoparticles in the target solvent, the optimum organic chain in the ligand should be selected and synthesised; however, the theory for optimum ligand selection has not yet been completed. To disperse nanoparticles in various organic solvents, various commercial ligands and surfactants with different molecular structures, including hydrophilic and hydrophobic groups in one molecule, were added to the nanoparticle suspension. Iijima et al. (2009) discovered the optimum surfactant by examining the stability of each dispersion, as shown in Fig. 4(a). This surfactant included PEG and a hydrocarbon chain in the molecule. Titanium-oxide nanoparticles modified with this surfactant were dispersed in various solvents, ranging from methanol to toluene. Furthermore, ligand-modified TiO<sub>2</sub> nanoparticles were dispersed in a PMMA resin, and this polymer composite exhibited shape-memory properties against temperature changes.

Because this ligand has an anionic phosphonic group for adsorption on nanoparticles, metal-oxide nanoparticles, such as titanium and aluminium oxide, can be dispersed in various solvents by the adsorption of this ligand. However, noble-metal nanoparticles, such as gold and silver, as well as silica nanoparticles, cannot disperse in solvents without the adsorption of these ligands. A two-step adsorption method was developed in which a polymer dispersant with amine groups, such as polyethyleneimine, is first adsorbed, followed by ligand adsorption (Iijima and Kamiya, 2010). Because amine polymer dispersants have multiple cationic



**Fig. 4** Ligand molecular structure and photo of transparent suspension, (a) Commercial ligand, adapted with permission from Ref. (Ijima et al., 2009). Copyright (2009) American Chemical Society. (b) Synthesised ligand, adapted with permission from Ref. (Okada et al., 2018a). Copyright (2018) Wiley.



Before AgNP modification

After AgNP modification

**Fig. 5** SEM and TEM observation of aramid nanofiber before and after surface modification of silver nanoparticle, AgNP, with surface treatment. Adapted with permission from Ref. (Iijima and Kamiya, 2015). Copyright (2015) Elsevier B.V.

amino groups in one molecule, the nanoparticle surface is positively charged, and the anionic ligand can be adsorbed. Using the two-step adsorption process, gold, silver, and silica nanoparticles were universally dispersed in various solvents. For application in conductive and antistatic polymers, surface-modified silver nanoparticles using this process were attached and distributed on aramid nanofibers (ANFs). Because the ANFs formed aggregates, surfacemodified silver nanoparticles promoted the uniform dispersion of ANFs, as shown in **Fig. 5** (lijima and Kamiya, 2015). The surface-modified silver nanoparticles coated with ANFs were uniformly distributed in the epoxy resin.

The number of organic molecules on the surface increased owing to multilayer adsorption, and the final concentration of organic compounds in the inorganic nanoparticles reached approximately 10–30 wt% because of the high specific surface area of the nanoparticles. Furthermore, the dispersed suspension and composite turned yellow because the commercial ligand contained impurities.

To reduce the concentration of organic compounds in the surface-modified nanoparticles as well as impurities in the ligand, Iijima et al. (2009) synthesised various ligands based on the clarification of which structure in the commercial ligand, shown in Fig. 4(a), contributes to universal dispersibility in various solvents. Finally, they discovered the serial structure of simple alkyl and PEG chains for the universal dispersibility of nanoparticles in various solvents, as shown in Fig. 4(b) (Okada et al., 2018a). By purifying each ligand-synthesis process, the yellow colour disappeared. For silica and noble-metal nanoparticles that could not be adsorbed by phosphonic groups, ligands with amino groups as the adsorbing group were synthesised and adsorbed on each nanoparticle (Maeta et al., 2018). Using the characterisation method for adsorption strength described later, the adsorbed group was selected for different nanoparticle materials, and the optimum ligand for dispersion in various solvents was synthesised.

#### 2.4 Ligand exchange for various applications

Because the adsorbed strength of the exchanged ligand must be higher than that of the ligand during the synthesis process, characterisation of the adsorbed strength of the ligand for the nanoparticle materials is important (Zeininger et al., 2016). Examples of adsorption groups for inorganic nanoparticles are shown in **Fig. 6**. By combining one adsorptive group with a modified organic chain structure, a designed ligand is synthesised for the dispersion of nanoparticles. The optimal modified organic chain structure for the final dispersion in solvents and solids should be combined with the strongest adsorption group.

One characterisation method for the adsorption strength is a simple visual method, and the other is an instrumental method using NMR. A visual observation method was applied by utilising the properties of a mixed solvent of cyclohexane and methanol, which were separated at room temperature and uniformly mixed at temperatures higher than 40 °C. For example, as shown in Fig. 7, the first ligands combined with a hydrophilic organic chain with a PEG group and catechol were adsorbed onto iron-oxide nanoparticles (Okada et al., 2018b). The two phases were separated, and the surface-modified iron-oxide nanoparticles were dispersed in methanol. Upon heating to 40 °C, the two solvents were mixed uniformly and a second ligand with an oleyl chain and phosphite group was added to the suspension. Finally, the suspension was cooled to room temperature for 3 h, and the two solvents were separated. Because oleic ligands with phosphite groups were ex-



Fig. 6 Examples of adsorption groups.



**Fig.** 7 Direct observation to determine for the adsorption strength on iron-oxide nanoparticles, adapted with permission from Ref. (Okada et al., 2018b). Copyright (2018) Wiley.

changed on the surface of iron oxide, the nanoparticles were dispersed into the upper phase, a hydrophobic solvent. Based on this result, we determined that the phosphite group had a higher adsorption strength compared with catechol for the iron-oxide nanoparticles. This method was applied to different combinations of organic chains and adsorbed groups, and the ranking of adsorption strength was determined for each nanoparticle material.

The second method using NMR is also a popular method for observing ligand exchanges. Compared to the NMR signal of the free dissolved ligand in the solvent, the NMR peak of the adsorbed ligand on the nanoparticles was broadened (Aiello et al., 2021; Hens et al., 2013; Schechtel et al., 2019; Yamashita et al., 2021). Different ligands were added to the suspension, and the ligands with broadened peaks exhibited higher adsorption strengths. This method required the synthesis of high-purity ligands with uniform molecular structures.

Recently, crown ether-associated ligands with different salts led to the stripping of oleic acid on  $Fe_3O_4$  nanoparticles, which were used during the nanoparticle-synthesis process, and different ligands could be re-grafted onto the nanoparticles (Shirmardi Shaghasemi et al., 2017). If crown ethers have the same function for stripping different ligands from nanoparticles, this approach may be applied to ligand exchange on various nanoparticles.

### 2.5 Analysis of dispersion mechanism and advanced behaviours of surface-modified nanoparticles

The detailed mechanism describing why the abovedescribed oleyl, alkyl-PEG chain structures exhibited dispersion stability of nanoparticles in nonpolar or various solvents are not clear. Various approaches, such as a thermodynamic analysis of the effect of the organic chain structure (branched or linear) and a molecular-dynamics simulation of the adsorbed ligand structure on the nanoparticle surface, have been proposed (Elimelech et al., 2022; Saito et al., 2021; Yang et al., 2016). The action mechanisms of each ligand were elucidated by combining various analyses and simulation methods. Yamashita et al. (2022) discovered an attracting phenomenon, which was the temperature dependence of the dispersion behaviour of surfacemodified nanoparticles in solvents. This phenomenon was similar to the solubility of the molecules in the solvent, and the dispersibility of the nanoparticles increased with increasing temperature. The boundary temperature between aggregation and dispersion depended on the molecularchain length and ligand structure. For a simple straight alkyl chain in the ligand, the optimum chain length for maintaining dispersion over a wide temperature range is shown in Fig. 8. The range of optimum chain lengths for dispersion over a wide temperature range appeared to depend on the particle diameter and material.

Challenges arise in promoting the application of surfacemodified nanoparticles in liquids, some of which are summarised in **Table 1**. First, the critical particle-solid concentration in suspensions with high fluidity is considerably lower than that in submicron-particle suspensions. In the field of fine-ceramic processing, the critical solid fraction of submicron-particle suspensions is higher than 60 vol%; however, the critical concentration of nanoparticle suspensions is approximately 30 vol%.

Another problem is that the surface-modified organic ligand mass fraction is approximately 20-30 % of that of the nanoparticles to ensure complete coverage of the nanoparticle surface, owing to the high specific surface area. Ligand molecules are similar in size to the nanoparticles. From a different perspective, surface-modified inorganic nanoparticles are almost considered organic-inorganic composite materials. After coating silicon oligomer on silica nanoparticles in an aqueous suspension, additional silicon oligomer was added to the suspension, which was polymerised, and coated on the base; thus, silicone sheets with dispersed silica nanoparticles were prepared by Iijima et al. (2013). This composite sheet was considerably more flexible than a silicone sheet without a silica-nanoparticle dispersion, and adding other functional nanoparticles is simple. New applications for silicon with optical and electrical functional properties are expected.



**Fig. 8** Relationship between mean particle diameter determined by DLS and carbon length in ligand at temperature ranging from 5 to 55 °C. Adapted with permission from Ref. (Yamashita et al., 2022). Copyright (2022) Wiley.

3. Characterisation of aggregation and adhesion behaviour and control of submicron-sized fine particles in liquid and gas phases

Submicron fine particles and microcapsules with diameters larger than 100 nm have been used as raw materials and products in various fields, such as ceramics, batteries, pigments, pharmaceuticals, and cosmetics. The characterisation of the aggregation and adhesion behaviour of these particles and their control in the liquid and gas phases are also important for the development of each application field. In the energy generation and environmental fields, ash adhesion and growth phenomena at high temperatures are important for the stable operation of coal, biomass and waste combustion, and gasification processes. Direct characterisation methods for the surface interactions between particles and materials have been developed using various original methods in the gas and liquid phases. Surface-modification and structure-design methods have also been developed for the control of surface interactions based on the characterisation and analysis of surface interactions. In this section, the characterisation and analysis methods for surface interactions in the liquid and gas phases are reviewed.

### 3.1 Characterisation of surface interactions between particles, microcapsules, and various substrates in the liquid phase using colloid probe AFM

### 3.1.1 Ceramics processing

In the fine-ceramic preparation process, the raw materials of fine particles are dispersed in water or organic solvents, and a suspension with high fluidity and solid concentrations higher than 50 vol% is prepared. Foamed powder bodies are obtained via a shaping process, such as coating and drying, or drying/granulation followed by dry pressing the powder into a mould and applying cold isostatic pressing. The final ceramic materials are then prepared by sintering. To obtain a high-fluidity suspension with a high solid content, the surface interaction between fine particles is generally controlled using a polymer dispersant. The particles are larger than 100 nm in diameter, and the van der Waals forces start to act at a surface distance of several nanometres. This surface distance

 Table 1
 Summary of key challenges for nanoparticle applications.

Subject	Main application fields	Example of solutions, approaches	
Low solid content in fluid suspension	Advanced ceramics, polymer composite for functional materials	Small molecules for surface modification	
High organic content caused by high surface area	Polymer composite, ceramics and functional sensor	Pre-coating by monomer or oligomer of polymer source, decreasing before sintering	
High surface reaction activity	Composite, catalyst, DDS	Surface coating and treatment	



**Fig. 9** SEM observation of colloid probe prepared by different methods. (a) Spray dried and sintered granule probe, adapted with permission from Ref. (Iijima et al., 2007). Copyright (2007) Elsevier B.V. (b) Carbon nanoparticle coating on spherical resin particle by mechanical process, adapted with permission from Ref. (Hanada et al., 2013). Copyright (2013) Elsevier B.V.

decreases with decreasing particle size. For the dispersion of submicron particles, the molecular weight of the polymer dispersant is approximately 10,000 g/mol, which is larger than that of the ligand for the nanoparticles (Kamiya et al., 1999).

Colloid probe AFM has been applied to characterise the change in interaction owing to various surface modifications to analyse the action mechanism and determine the optimum condition of the polymer dispersant structure and surface modification, such as silane coupling agents or thiols. An example of a colloid probe is shown in Fig. 9, where a fine spherical particle attached to the top of a commercially available tip was prepared for AFM. A system combining a high-resolution optical video system and micromanipulator was also developed for probe fabrication by Kamiya et al. (2006). Preparing a fine particle probe with a size smaller than 1 µm by optical microscope is difficult; therefore, a spherical particle of several micrometres was prepared using spray drying granulation and sintering (Fig. 9(a), Iijima et al., 2007) or coating nanoparticles on spherical resin particles via a mechanical compounding method (Hanada et al., 2013). By using colloidal probes with different materials, the effect of the polymer structure and silane coupling surface-modification conditions on the surface interaction between particles and dispersion behaviour in suspensions has been discussed for aqueous solutions and organic solvents (Mori et al., 2016).

Polymer dispersants are generally used to increase the fluidity of slurries by dispersing fine-particle aggregates. In the case of cast moulding of slurries, shape-retention agents are used to provide strength to the formed bodies. Recently, a new functional polymer was discovered, which acts as a dispersant during slurry preparation, followed by time-dependent gelation to maintain the shape of the formed bodies (Yang et al., 2013). The action mechanism of this polymer over time was discussed using the colloidal probe AFM method (Yamamoto et al., 2019).

#### 3.1.2 Pharmaceutical application

To characterise the interfacial structure and properties of

microcapsules for drug-delivery systems, a colloid probe or substrate was prepared from a granule of microcapsules, and surface interactions were measured via probe AFM in aqueous solutions with different pH conditions. For example, microcapsules with modified pH-sensitive gel surfaces have been used in oral-delivery medicine. Under the acidic conditions in the stomach, the pH-sensitive surface gel shrank and protected the incorporated peptide drug. Under the neutral pH conditions in the small intestine, the pHsensitive gel swelled and released the peptide drug. Using the colloidal probe AFM method (Iijima et al., 2008), the surface interaction between the microcapsule and mucinlayer substrate was determined under different aqueous pH conditions. The mucin layer that formed on the mica surface mimicked the mucosa of the small intestine and stomach. A long-range adhesive force was measured at neutral pH owing to the swollen surface of the pH-sensitive gel, and the microcapsule remained in the small intestine. Under low-acidic pH conditions, a short-range attractive force was detected because the surface gel layer shrank and had a rigid structure. Furthermore, using carbon-nanotube probe AFM, the interaction between chitosan-modified liposome capsules and the mucin layer under different pH conditions was investigated (Yamamoto et al., 2018).

### 3.1.3 Surface-nanostructure control for toner and cosmetic applications

To improve the image quality of electronic copying, a mechanical surface-treatment technology for a surfacemodified silica nanoparticle-coated toner was developed, and the adhesion force was determined using colloid probe AFM (Tanaka et al., 2008a). The surface structure was characterised by the fractal dimension, and the relationship between the adhesion force of the toner and the fractal dimension was determined using colloid probe AFM (Tanaka et al., 2008b). Experiments confirmed that the inclusion of the silica nanoparticles increased the fractal dimension and reduced the adhesion force.

The effect of surface-adhered nanoparticles and nanoporous structures on particle–particle interactions was investigated using colloid probe AFM for cosmetic applications. The adhered nanoparticles decreased cosmetic particle–particle interactions. With the nanoporous structure, the formation of liquid bridges was enhanced; thus, the adhesion force did not increase with humidity (Kani et al., 2007).

### 3.2 Fine-particle adhesion-behaviour characterisation under high-temperature conditions

For the inorganic-compound properties in the pulverised-coal combustion process, the target temperature range was higher than 1500 °C because the viscosity of molten ash is important. However, because ash deposition

occurred on the surface of the superheater and heat exchanger, and dust was collected by a ceramic filter, the target temperature was lower than 1000 °C. Thus, it was necessary to characterise the adhesion properties of solid ash particles.

Two methods have been developed to characterise the adhesion force at high temperatures of up to 1000 °C. One method is the measurement of a direct single-particle adhesion force, which uses the same method as the AFM force curve. Another method is the powder-bed strength method. The main targets were ash particles generated during coal, biomass and waste combustion, and gasification processes.

### 3.2.1 Interaction-measurement system between a single ash particle and substrate

A schematic of the adhesion-force measurement system is shown in **Fig. 10** (Gao et al., 2020). A single ash particle that adhered to the top of a pure alumina rod was pressed onto a substrate prepared from a superheater material on a high-purity quartz glass leaf spring. A small area of the ash particles and substrate was heated to 900 °C using an infrared condensing heater. The compression force was measured by the displacement at the top of the leaf spring. As it reached the maximum compression value, a single ash turned and reduced the compression force, as shown in **Fig. 10**. The movement of the alumina rod was controlled by a high-resolution linear motor. If an adhesion force acted between the ash and substrate, the leaf spring warped



Fig. 10 Measurement system for adhesion force between single particle and metal substrate at high temperature, adapted with permission from Ref. (Gao et al., 2020). Copyright (2020) American Chemical Society.

to the tension side. When the tensile force of the leaf spring balanced the adhesion force between the ash particle and the substrate, the ash particle separated from the substrate surface. The maximum tensile force was determined to be the adhesion force.

The adhesion force was measured at different high temperatures and maximum compression forces, and the results of the relationship between the maximum compression and adhesion force at different temperatures is shown in **Fig. 11**. When the temperature increased to 900 °C, the adhesion force increased with an increase in the maximum compression force. At 750 °C and 850 °C, the adhesion force was similar for different maximum compression forces. It appears that plastic deformation at the contact point increased the adhesion force at 900 °C; this was analysed using Hertz's deformation theory at the contact point. A fitting line was obtained using this theory, as shown in **Fig. 11**.

### 3.2.2 Powder-bed method

Using the principle of a room-temperature measuring device, a split-type tensile-strength tester of powder beds for high temperatures was developed, and the schematic of the measurement device is shown in Fig. 12(a) (Kamiya et al., 2002a). Fused silica glass with a low thermal-expansion coefficient was used as the material for the suspended cell for measurements at high temperatures. Because the metal cell has a higher thermal-expansion coefficient than that of an inorganic powder bed, the powder bed breaks owing to the thermal expansion of the cell at elevated temperatures. The tensile strengths of the ashes, coal, biomass, and waste increased sharply at a particular temperature, depending on the ash. An increase in the



**Fig. 11** Example of relationship between maximum compression compressive force and adhesion force at different temperatures, adapted with permission from Ref. (Gao et al., 2020). Copyright (2020) American Chemical Society.



Fig. 12 Principle of measurement system for tensile and shear strength of powder bed. (a) Tensile strength tester of powder bed, adapted with permission from Ref. (Kamiya et al., 2002a). Copyright (2002) American Chemical Society. (b) Shear strength test at interface between powder bed and metal, adapted with permission from Ref. (Aoki et al., 2020). Copyright (2020) American Chemical Society.

adhesion force at high temperatures has been shown to cause various problems in different plants.

Tensile stress was applied to the ash layer on the substrate metal surface to measure the surface interaction between the ash powder bed and the surface of the superheater and/or heat-transfer tube (Liu et al., 2023). However, measuring strength by creating a fracture surface between the metal surface and ash powder layer is difficult. As the fluid flows inside the superheater and heat exchanger, the temperature from the inside to the surface changes in a complex manner, as shown in **Fig. 12(b)** (Aoki et al., 2020; 2022). The temperature distribution was reproduced by air at a controlled flow rate under a metal plate. The shear strength between the ash layer and metal surface and the corrosion behaviour of the metal surface by the ash layer at high temperatures were also observed under different temperature distributions.

### 3.2.3 Analysis and control of ash adhesion behaviour at high temperatures

The increase in the adhesion force at high temperatures has been attributed to the formation of a small amount of liquid phase from low-melting-point eutectic compounds. To observe liquid-phase formation, the ash particles were observed at the high-temperature heating stage using a field emission scanning electron microscope (FE-SEM). However, because the generated liquid phase was volatilised under high-vacuum conditions in the FE-SEM, analysing the elements in the generated liquid phase was difficult. Therefore, after recording the observation image and ash-sample coordinates under a high vacuum, the ash samples were moved to a separate chamber under high-vacuum conditions and crossed the threshold to the FE-SEM, as



Fig. 13 FE-SEM observation system of fine particles before and after heat treatment. Adapted with permission from Ref. (Tsukada et al., 2003). Copyright (2003) Elsevier B.V.



**Fig. 14** FE-SEM observation of ash particles before and after heat treatment at 900 °C. Adapted with permission from Ref. (Horiguchi et

al., 2018). Copyright (2018) American Chemical Society.

shown in Fig. 13 (Tsukada et al., 2003). Air was introduced into the chamber to raise the pressure to a normal value, and the ash samples were heated in an infrared condensing furnace to a predetermined temperature. After being cooled to room temperature under high-vacuum conditions in the chamber, the ash samples were returned to the FE-SEM, and the morphology change was observed before and after the heat treatment. As an example, Fig. 14 shows the results of the observations of the pulverised coal combustion ash (Horiguchi et al., 2018). Before and after the heat treatment, morphological changes due to liquid-phase formation were observed in some parts. Using energydispersive X-ray spectroscopy at the deformed parts, a high content of alkali metal and aluminium was confirmed, and low-temperature melting based on thermodynamic calculations was discussed. In the case of sewage slag ash, the phosphate content in the morphologically changed part was higher than that in the other unchanged parts, and the phosphate generated a low-melting-point eutectic phase with other elements.

### 3.2.4 Model of ash preparation from pure fine particles and discussion on adhesion-increase mechanism

Combustion ash includes many types of elemental components; therefore, analysing the increase mechanism of the ash adhesion force at high temperatures is difficult. With the development of the abovementioned devices for measurement and analysis, a model of an ash synthesis method from fine pure silica particles was developed by adding the estimated elements to increase the adhesion force at high temperatures. First, for pulverised coal combustion ash, a small amount of alkali metal, sodium or potassium, and oxalate aqueous solution were added to fine pure silica particles, followed by a heat treatment, grinding, and the classification of the modelled ash (Kamiya et al., 2002b). The tensile strength of the modelled ash beds was determined at different temperatures, ranging from room temperature to 900 °C. The increase in tensile strength of a real combustion ash bed was almost reproduced by the modelled ash, as shown in Fig. 15. The low-melting-point eutectic phase of silica and alkali metal was responsible for the increase in high-temperature adhesion. Based on this result, a similar method was applied to synthesise the modelled ash from waste- and biomass-combustion ash, such as sewage sludge, in which phosphorus was added to pure silica particles (Gao and Kamiya, 2020; Horiguchi et al., 2021a).

### 3.2.5 Ash adhesion-behaviour control at high temperatures

To solve the ash-adhesion problem and problems with the superheater and heat exchanger, various additives, such as kaolinite and dolomite for coal and biomass combustion (Duchesne et al., 2017), and iron oxide for sewage-sludge combustion, have been investigated to prevent ash deposi-



Fig. 15 Effect of temperature on tensile strength of real fly ash and model synthesised ash powder bed. Adapted with permission from Ref. (Kamiya et al., 2002b). Copyright (2002) American Chemical Society.

tion and reduce ash-layer growth in combustion plants (Horiguchi et al., 2021a). The changes in the liquid- and slag-phase formation temperature owing to composition were discussed using thermodynamic calculations to analyse the adhesion-behaviour control mechanism via the addition of various materials. The scientific selection of optimum additives to control ash behaviour has progressed with the development of characterisation and analysis methods.

Recent reports have shown that the addition of alumina nanoparticles effectively reduced the tensile strength of the ash powder layer (Gao et al., 2019; Horiguchi et al., 2018, 2022). All cases of the real and modified model of coal, biomass and waste combustion ash showed that the addition of alumina nanoparticles controlled the tensile strength of the particle layer at high temperatures. Because alumina nanoparticles have high reactivity, the addition of nanoparticles chemically suppressed the formation of a lowmelting-point eutectic phase. Furthermore, nanoparticle addition increased the porosity ratio of the ash-particle layer by forming porous aggregates between the ash particles. By increasing the liquid-phase formation temperature using chemical reactions and the physical suppression of the packing behaviour of the ash layer, the addition of nanoparticles controlled the tensile strength of the ash layer at high temperatures.

The increase mechanism of ash adhesion at high temperatures was estimated using liquid- and slag-phase formation and the liquid-bridge force of the small amount of generated slag. However, the adhesion increase at relatively lower temperatures (below 500 °C) was observed using pure calcium carbonate fine particles. In this temperature range, liquid- and slag-phase formation and sintering with volume changes were not observed (Horiguchi et al., 2021b). Therefore, investigating the mechanism of the adhesion force and developing adhesion-behaviour control technology are necessary.

### 4. Conclusion

Molecular and nanometre-scale surface-structure designs of particles were reviewed from the perspective of controlling the adhesion and aggregation of nanoscale and fine particles in gas and liquid. These control methods are indispensable for realising the various functions of nanoparticles and fine particles. However, real situations were implemented based on empirical knowledge; thus, developing scientific approaches for controlling adhesion and aggregation is necessary. With the recent development of mass production and cost reduction for various nanoparticles, the interface structure design of nanoparticles has also been developed. This is expected to establish a systematic interface-structure design method that can handle various combinations of particle characteristics, such as size, shape, materials, surface structure, and the matrix of the solid and solvent that disperse the nanoparticles. There are many challenges related to the practical use of functional nanoparticles, such as increasing the solid content in solution and reducing the number of adsorbed ligands. However, the development of fundamental research for interface-structure design will overcome these barriers. The control of fine-particle behaviour, such as hightemperature adhesion and the interaction between organic/ inorganic solid particles, microcapsules, and biomolecules, is also important for applying powder technology in various industrial fields, such as energy generation, environmental systems, and medical and health industries.

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