Review

Advances in nature-guided materials processing

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Abstract

The center of excellence (COE) titled ‘The Creation of Nature-Guided Materials Processing’ has been established in Nagoya University as the 21st Century COE Program supported by Ministry of Education, Culture, Sports, Science and Technology. In the Nature COE, various activities on the education and research are being performed through learning the laws of nature, namely, methods of attaining ‘appearance of the maximum function under the minimum substance and energy consumption’, which the nature and living organisms have acquired through their evolution in long period. Together with such educational programs for PhD students as research incentive, oversea training, and external evaluation programs, an ‘Open-Cluster Program’ was originated for promoting researches proposed by research groups consisting of young researchers in and out of the university and also for fostering them.

The researches are being advanced on materials used for living bodies, mimicking structures which nature or living bodies are forming, and producing materials by mimicking processes to form the structures observed in the nature or the living bodies. In this COE, these researches are conducted by four groups to extend the processes observed in the natural world to a new type of processing, that is, thoroughly examined and rationalized by plunging a scalpel of engineering and to establish a new academic field of materials science and engineering.

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1. Introduction

In the natural world, structures having extraordinary functions which were created in accordance with the laws of nature, are observed regardless of organic and inanimate. Living organisms have acquired methods of attaining ‘appearance of the maximum function under the minimum substance and energy consumption,’ through their evolution in long period. If essentials of the structures or the methods in the natural world can be applied for the industrial materials and their processing which we are now using, great advances in the field of materials research and also big contributions to the society will be expected.

In order to develop a new academic field of material processing by learning the laws of nature and build a world-leading center of the education and research, a center of excellence (COE) on ‘Nature-Guided Materials Processing’ has been established in Nagoya University as the 21st Century COE Program supported by Ministry of Education, Culture, Sports, Science and Technology. In the Nature COE, under collaboration with researchers and students in seven departments relating to the fields of chemistry and materials science in Nagoya University, and also with researchers in the outside of the university, various activities of education and research are being performed with a new view of learning the laws of nature.

In this paper, the outline of the education and research in the COE and the recent advance in the main researches are discussed.

2. Outline of the nature COE

The COE has both faces of education and research in the activity. Although the research activities conducted by four research groups form the foundation of the COE, priority of investment is put on the education programs for the students in PhD course and young researchers.

As one of characteristics in the activities of the COE, an ‘Open-Cluster Program’, which has both faces of the education and research, was originated for promoting the researches proposed by research groups consisting of young researchers and students and also for fostering them. In the fiscal year 2003, 20 groups were selected, consisting of 123 members, in total including 23 PhD students, 26 researchers from foreign countries. The 45 persons in total are from the outside of the university, because the Open-Cluster Program is opened for the outside. It is expected for the 20 groups to conduct their researches on world-highest level with their own originalities and to foster themselves through the practice of researches.

As another specific characteristic in the COE, all the research funds are invested not in ‘goods’ but in ‘matters’ in this COE. That is, the funds are spent not for purchasing experimental equipments at all, but for encouraging young persons who try to accomplish researches in earnest and in educating students who try to challenge in this new field.

2.1. Aim of the COE

In the 21st century, a new paradigm is required for reducing the use of resources, saving energy, relief and safety, and preservation of the environment. The materials are desired to transfigure so as to meet the new paradigm. For the breakthrough, with a basic concept of ‘the creation of nature-guided materials processing’ and on the basis of the superior potentials which the participating members have, this COE will try to establish a new academic field of materials science and engineering to which the smart methods in the natural world are introduced, to produce world-highest intelligent fruits and to foster a gathering of young minds for leading the new field and the sustainable development.

In order to utilize the superior functions woven by the nature for human life, it is not enough only to learn the apparent forms in the nature world, but it is necessary to create new processing of the structures to make the functions appear, by fully utilizing the scientific knowledge which has been cultivated up to now in the field of science and engineering. Thus, the basic concept for establishing this COE is to extend the processes observed in the natural world to a new type of processing, that is, thoroughly examined and rationalized by plunging a scalpel of engineering.

On accomplishing the task of this COE, it is necessary not only to do new developments where the wisdom of nature has to be injected into the science of nanotechnology, for example, in relation to functional materials, but also to lead the processing of structural materials today towards a new direction in accordance with minimizing energy consumption and keeping the environment earth-friendly. The new academic field developed by this COE will be able to promote the growth of embryos for new industries and the industrial conversion from the manufacturing in the 20th century, which is often not friendly to the nature and living things, to new manufacturing easily accepted by people in the 21st century. For these social meanings and contributions, the COE has big possibility and responsibility to realize them.

2.2. Research activities

As characteristic structures observed in the objects formed in the natural world, the followings are specified; (1) organic and inorganic interface structure, (2) hierarchical structure, (3) multi-functional structure, and (4) metabolic and information structures. It is important to gain insights from the unique structures demonstrated by the objects and from the processes that form these objects, for creating new manufacturing processes of materials that are useful for the human life. Therefore, the fields of research conducted in this COE have been decided as follows:
1. Researches of materials used for living bodies.
2. Researches for mimicking structures which nature or living bodies are forming.
3. Researches for producing materials by mimicking processes to form the structures observed in the nature or the living bodies.

The research themes in the three fields are studied by the following four research groups relating with the four characteristic structures mentioned above.

1. **Organic and inorganic interface structure formation processes.** With the aim of establishing the processes to form the organic and inorganic interface structure by learning synthesis processes in the natural world, such processes as synthesis of inorganic materials on organic-molecular assembly, arrangement of organic molecules on inorganic crystal plates and synthesis of inorganic and organic composites are studied.

2. **Control of hierarchical structures of soft materials.** For the development of polymerization techniques which can reproduce the very precise hierarchical structures created in the natural world and also for the creation of the control processes of hierarchical structures, three-dimensional and microscopic structure control of molecular gathering, the design of hybrid supermolecules and the recycling processes are studied.

3. **Multi-functional materials processing.** For creating new processes to produce structures revealing multi-functions by controlling the structures of nano- to meso-scales in artificially fused materials, hybrid materials of ceramics and polymers produced by applying external magnetic or other fields and the simulation of its structure formation processes are studied.

4. **Metabolic/information structure formation processes.** For creating the processing of artificial materials having functions of information and reversible reactions under the control of nano-scale structures, self-repairing or multi-response materials, construction of metabolic reaction system analogous to biological behaviors, and recycling and circulation of the materials are studied.

In the central district in Japan where the Nagoya University is located, not only research institutes like National Institute of Advanced Industrial Science and Technology, National Institute for Materials Science, Japan Fine Ceramics Center and Okazaki National Research Institutes, which have high achievement in researches of chemicals, steels and ceramics are accumulated. This COE will make efforts for making networks of collaboration with the industries and the institutes. The sustainable development of this COE will be expected by applying patents useful for the industries and acquiring the intellectual property rights, together with getting competitive research funds.

### 2.3. Education programs

Through the research activities in the COE on the creation of the nature-guided materials processing, the education for the PhD students is being build up and improved constantly. It is aimed to train the students up to excellent young researchers, who are not locked into a narrow field of materials or chemistry, but have a broad perspective and specialties, brimming creativity, and can promote their researches on the world-highest level.

The education emerged from the usual style of instructing knowledge is promoted by executing the following five programs.

**Research Incentive Program.** In this program, the COE adopts excellent students as ‘COE Doctor’ and gives opportunity for them to deepen and enlarge their specialties and originalities through devoting themselves to their proposed researches. An attractive environment of research will be prepared for capable researchers to gather to this COE widely from both the inside and the outside of Japan. The students are recommended to progressively join the Open-Cluster organized by young researchers and students. It is aimed to enlighten the students on high capability of accomplishing research, by supplying them the competitive research environment where they can collaborate with excellent young researchers.

**Research Support Program.** Researches which the young researchers and students propose with their ideas are intensively promoted with the use of the research fund in this COE. The typical example is the support for the researches in the Open Cluster. It is expected to foster their minds for challenging difficult subjects and at the same time to bring up their originality and capability on proposing new ideas.

**International Lodging Seminar and Overseas Training Programs.** In the Lodging Program, the students are given a chance to discuss on their researches with prominent foreign researchers. In the Overseas Training Program, the students have chance to visit prominent research institutes in overseas and to touch researches on world-level. By performing these programs for internationalization, it can be promoted to form a wide international network of research and to do active exchanges of knowledge and personnel.

Through the education programs mentioned above, it is possible to promote the interactions with researchers having different ideas and the exchange of intellectual stimulation, and to cultivate the ability of students to undertake research with a ‘bird’s eye’ perspective. Under better performance of these programs, a comfortable environment for the students to study will be realized.

**External Evaluation Program.** The researches performed by the students and the performance of the educational
programs are evaluated by a committee adding top-level researchers in and out of Japan. By applying the external evaluation for independent planning of research seminar and the presentation of research results, self-consciousness of the students will be enhanced and an environment in which the students can try to raise their quality and ability with consciousness of the world level will be prepared. In the evaluation, qualitative items like originality and challenge mind should be considerably evaluated.

As this COE stands on several fields having different specialties, it is convenient for the students to gain knowledge in multiple fields. A new system of curriculum for the students to gain knowledge in different fields is being constructed under full support of the Graduate School of Engineering, Nagoya University. From the fiscal year 2003, a new curriculum lecture on ‘The Nature-guided Materials Processing’ has started in the seven departments relating to this COE.

After the end of the 21st Century COE Program, the educational programs will be continued by utilizing favorable policies offered by the Institute for Advanced Research in Nagoya University and the exchange program of young researchers, and also indirect expenses obtained by acquiring competitive research funds. The excellent researchers who are fostered by the educational program will lead the next generation and brew a next new environment where excellent students grow up, and finally not only sustainable progress in the researches but also a desirable circulation for constantly improved education will be realized.

3. Recent advances in the researches

Human beings have made possible efforts to build unrealistic circumstances that cannot be found anywhere on the surface of the earth in order to create stronger materials. Some of the examples of such man-made materials are stainless steel, tungsten alloys and super engineering plastics. As compared with the strategy of human beings, the strategy of the activity in nature and the evolution of living bodies are classified into (1) the law of the jungle (the world where the weaker are victims of the stronger [1]) and (2) trial and error for a very long time (100 million years and more). The jungle law is effective in the industrial society of human beings as in nature, but there is quite a difference in terms of the long-term trial and error experience. The method, trial and error, has been regarded as an inferior procedure to create something that characterizes the species of human beings.

The activity of human beings may appear to be purely logical and systematic. This recognition has been accepted as true for a long time. But one must concede that the numerous important advancements were made upon trial and error if one carefully observes the history of invention. For example, few of the numerous scientific progresses such as superconductivity, quantum mechanics, DNA and bioscience, the airplane, electrical equipments, atomic energy, integrated circuit, computer and laser would have been realized, if human beings had depended only on logical consideration and their creative power to advance their science in the 1900s [2]. It is one of the reasons why its research effort on materials synthesized in nature is focused.

3.1. Organic and inorganic interface structure formation processes

A variety of inorganic materials are synthesized in living creatures, and its process called biomineralization is known to be based on the concept that the appropriate material with required shape and size possessing useful functions is formed at the right time and arranged in the right place. To realize this concept, biomineralization usually occurs on the template which is composed of biopolymers, such as protein and polysaccharide, controlling the nucleation and growth of a solid phase at the organic/inorganic interfaces.

In the present sub-theme, learning from and being inspired by the optimized biomineralization processes, it will be attempted to create novel materials processing technology through the formation of organic/inorganic interface structures at ambient temperature under the normal pressure. This nature-symbiotic and environment-friendly technology would lead to cultivating a novel field, ‘bio-inspired and bio-surpassing materials science’, hopefully giving rise to new electronic/photonic nanotechnology of the 21st century and developing advanced medical engineering and biotechnology.

Studies on the following three major areas are being undertaken: (a) organic molecules assembling and nano-/micro processing on solid substrates, (b) synthesis of inorganic materials and devices on organic molecular-assembly templates, and (c) inorganic/organic composite synthesis and its application to cancer cure.

Nano/micro processing of self-assembled monolayers (SAM) is being investigated. The first goal is to develop a two-dimensional microprocessing technique for SAM’s and polymer surfaces. It has been succeeded to develop an apparatus for ultra-short wavelength UV light exposure and monolayer photoresists, and to establish a technique to fabricate molecular microstructures with high spatial resolution of μm to sub-μm order (Fig. 1) [3,4]. Secondly, a nanoprocessing technique employing a scanning probe
microscope and a focused ion beam has been developed, and a nano-pattern of SAM has been successfully realized [5].

Investigations on the inorganic solidification on the organic SAM templates have been extensively carried out for the past 10 years mainly in western countries, while the study on the micro/nano patterning of functional ceramics in terms of device applications has been actively conducted in Nagoya University. Simple and convenient techniques for nano/micro patterning of inorganic materials are intensively required in various fields, and their bio-inspired patterning methods being developed are attracting much attention from industries. They have so far succeeded in fabricating micropatterns of thin films of functional oxide materials, such as TiO$_2$ [6], ZnO [7], SnO$_2$ [8], and SrTiO$_3$ [9] (Fig. 2), and also developed a few processes to produce micropatterns of metal and ceramic fine particles [10–12]. Although the mechanism of micropatterning through site-selective deposition of a solid phase is specific for each case, it has been found that it could be generally classified into several categories based on the manner how the interfacial interactions take place. Further creation of novel patterning processes and integration techniques would give rise to the invention of fundamental technology for the future microelectronics, optoelectronics, functional ceramic manufacturing and so on.

Fabrication of temperature stable semiconductor light emitting devices by formation of nanostructure, due to natural chemical reaction, in semiconductor active layer has been intensively conducted. Rare-earth elements as a dopant in semiconductors exhibit their characteristic, sharp and temperature stable, spectrum. Utilization of these properties as the light emitting devices driven by current injection is quite attractive for devices in optical communication where temperature stability of wavelength and a sharp spectrum is essentially important in the future wide band information networks. They grow those semiconductors by all organometallic chemical vapor deposition, especially rare-earth doped III−V compounds where control of conductivity and formation of double heterostructure are well established. It has been demonstrated that codoping of Er and O into GaAs makes a single molecular structure Er−2O (two As atoms and two O atoms surrounding Er) and this structure restricts the crystal field around Er in one symmetry, and then the spectrum is well arranged, resulting in an extreme enhancement, by 100 times, of the peak intensity (Fig. 3).

Using this codoped GaAs as the active layer of GaInP/GaAs:Er/GaInP double heterostructure, they have successfully observed light emission by current injection from this device. At the same time, they have obtained an extremely large optical excitation cross section (by 5–6 orders in magnitude larger than those in Er doped SiO$_2$ fibers) [13–15].

Organic/inorganic composites are useful materials which can be expected to generate new functions combining those of each component. A process has been developed for a composite formation based on the surface modification of metal nanoparticles with organic molecules [16] and the formation of microparticles within the organic vesicles (Fig. 4). The composite particles can accumulate specifically within a tumor and generate heat under the alternative magnetic field. Increased temperature killed the tumor and also stimulated expression of heat shock protein. The increased expression of heat shock protein induced...
the tumor-specific immunogenicity. Complete tumor regression was observed in 90% in an in vivo study of mouse B16 melanoma [17]. Similar results were obtained in a needle-type magnetite composite [18–20].

We will further attempt to clarify the organic/inorganic interfacial interactions seen in the nature, specifically biological systems, from the viewpoint of materials science, extract its basic principles, and realize them in our artificial materials processing technology.

3.2. Control of hierarchical structures of soft materials

Polymeric materials are typical examples to show hierarchy in both space and time. The studies on clarification of hierarchical feature of soft matters are being conducted. The major subjects consist of (1) synthesis of bioinspired helical polymers and (2) multiphase hierarchical structures of block and graft copolymers. The essence of these two subjects is shown below.

(1) Helical polymer synthesis inspired by natural biopolymers. The macromolecular helicity is the most important chirality that shows a sophisticated and fundamental function in nature, where ‘chirality’ means handedness from Greek ‘cheir’ like hands, in which the molecules are not superposed with their mirror images. The synthesis of helical polymers and helical assemblies as well as the control of their helix-sense has been attracting considerably not only to mimic such unique biological macromolecular structures, but also to develop novel chiral materials for the use as liquid crystals, enantioselective catalysts, and chiral selectors [21]. Besides these helical polymers, they recently succeeded in inducing a conceptually new helicity on optically active polyacetylenes upon complexation with optically active small molecules capable of interacting with the polymers [22].

In the presence of optically active compounds capable of interacting with the polymer’s functional groups, a dynamic, one-handed macromolecular helicity can be induced in the polymer backbones, resulting in a characteristic, induced-circular dichroism (ICD) in the UV–Visible region of the polymer main chain (Fig. 5). For example, a poly(4-carboxyphenyl) acetylene (poly-1) forms an acid–base complex with chiral amines through noncovalent interaction and the complexes showed a split-type ICD in the UV–Visible region in organic solvents. The split type of the cotton effects, namely manifestation in circular dichroism of the absorption of circular polarized radiation, can be used as a novel probe for determining the chirality of amines [23]. Moreover, the macromolecular helicity induced on poly-1 can be ‘memorized’ when chiral amines were completely replaced by various achiral amines in solution [24]. Poly(phenylacetylenes) bearing a phosphono group are highly sensitive to the chirality of a variety of biomolecules including amino acids, aminosugars, and peptides; the assay of 19 of the common free l-amino acids produced ICDs with the sign reflecting the absolute configurations [25]. Poly-2 with the bulky crown ether as the pendant can respond to an extremely small enantiomeric imbalance in amino acids (less than 0.005% enantiomeric excess of alanine for example) and exhibits ICDs with a strong positive non-linear effect [26].

Optically active poly(phenylacetylenes) bearing an optically active pendant also have a helical conformation and show interesting functions. Poly-3 bearing a β-cyclodextrin(β-CyD) residue as the pendant exhibits a macro-molecular helicity inversion accompanied by a color change responding to temperatures, solvents, and molecular and chiral recognition events that occurred at the remote side chain [27]. An optically active, C60-based helical poly(phenylacetylene) (poly-4) prepared by the copolymerization of an achiral fullerene monomer

Fig. 5. Schematic representation of helicity introduction on achiral poly(phenylacetylenes) upon complexation with chiral compounds and structure of helical poly(phenylacetylene) derivatives.
with an optically active phenylacetylene exhibits an ICD in the fullerene chromophore region, indicating that the achiral C₆₀ pendants arrange in a helical array with a predominant screw-sense along the polymer backbone [28].

(2) Multiphase hierarchical structures of block copolymers. Microphase-separated structures formed by block copolymers are typical class of hierarchical structures. They exhibit various nanoscopic patterns depending on their molecular parameters such as molecular weight, composition and chain connectivity and so on [29]. Thermodynamic equilibrium structures of several block copolymers with various architectures are compared here.

Fig. 6 shows tricontinuous Gyroid structure formed by a poly(isoprene-b-styrene-b-2-vinylpyridine) triblock copolymer of the ABC type [30], where Gyroid structure is a mathematically predicted structure with ‘minimal surface’ whose mean curvature is constantly zero. This structure has been found to include two equivalent but totally independent surfaces derived from genuine Gyroid minimal surface [31]. Three polymer phases divided by these two surfaces are all three-dimensionally continuous and have very high periodicity. Furthermore, this structure must show chirality between 10 and 100 nm length scale and could bring a novel nanoscopic manufacturing material.

The second model polymer is two-component cyclic block copolymer composed of polystyrene and polyisoprene [32,33]. The molecular weight dependence of microdomain spacing has been investigated and it has found that chain elongation along the direction perpendicular to lamellar interface is suppressed considerably because of all loop conformation of cyclic molecules whose both ends are tethered to microdomain interface.

Fig. 7 compares periodic but essentially quite different multi-phase structures from two kinds of tetra-block copolymers, i.e. ABCA and ABCD. Fig. 7a shows three-phase lamellar structure whose repeating unit is -black-white-gray-. It is noticed that it has the feature of non-centrosymmetric structure which contains neither symmetry plane nor rotational axis [34]. This highly useful structure was observed for pure block copolymer system for the first time. On the other hand, very periodic four phase structure from four component block copolymer is shown in Fig. 7b.
The repeating unit is –black(A)–white(B)–gray(C)–white(D)–gray(C)–white(B)–, namely it is four-phase six-layer structure. One notices here that this structure contains several symmetry planes and hence it is generally known centrosymmetric structure from four component polymeric material.

3.3. Multi-functional materials processing

Multiple functions are very common in plants and animals grown naturally. For example, bone has important functions of supporting body, moving muscle and making blood and so on. It is indeed a natural inorganic/organic composite made of hydroxyapatite (HAp) and collagen. This study aims to develop new processes of producing artificial nano- or meso-scaled composites with multiple functions. To accomplish this aim, adopted in this study are various methods including the chemical solution, the magnetic-field materials processing and the process simulation, all of which have been developed in Nagoya University. It is stressed here that such a multiple-functional material is one of the new-type of materials, since most of previous materials investigations have been devoted to the search for one extreme property (e.g. superconductivity) rather than multiple properties. The engineering innovation of multi-functional materials will clear the way for a new field in materials science and engineering.

For innovation of nano-crystal/polymer composites using chemical solution method, the functional ceramic materials have been studied at a molecular level in view of basic science and a novel material processing technology [36–39]. By controlling the starting molecular structures and the reaction scheme in this process, some dielectric and optical materials have been synthesized successfully at the temperatures much lower than the conventional process temperatures.

Hybridization of inorganic functional materials with organic molecules was developed for processing a novel material under mild conditions observed commonly in nature. A barium titanate-organic precursor molecule system was selected as a candidate for a new functional material. The crystallization of barium titanate was achieved as nano-sized particles in the organic matrix below 130 °C, as shown in Fig. 8. Further studies on the size control of the hybrid and its response for the applied electric field are now in progress.

Growth of artificial bones and teeth under a high magnetic field is actively investigated. The recent development of superconducting magnet technologies has enabled to provide a rather large space with a high magnetic field. In such a high magnetic field, magnetization force, which is familiar as the force attracting iron to a magnet, works in not only magnetic materials but also non-magnetic materials such as paramagnetic and diamagnetic ones. The magnetization force makes crystal orientation in materials align to a magnetic field direction as a compass rotates to the north direction. HAp is a main component in bones and teeth of vertebrates and has an excellent biocompatibility. Bioactive phenomena are different between the a-, b- and the c-plane of HAp crystals. Furthermore, HAp crystals in an organism are highly orientated to exert chemical durability and physical strength. Thus, the control of the crystal orientation of HAp crystals has strongly been desired in the biomaterial field. Nowadays, this control becomes possible by using a high magnetic field, though HAp is a non-magnetic material.

In order to control the crystal orientation in HAp, the slurry of HAp was poured into a crucible and a slip casting that is widely utilized as one of ceramics shaping methods, was carried out under the high magnetic field of 12 T [40, 41]. The dried HAp was sintered under no magnetic field. X-ray diffraction patterns of the sintered body are shown in Fig. 9. It is noticed that only the c-plane is seen in the case with the imposition of the magnetic field and both the a-, b- and c-plane appear in the case without it. That is, the slip
casting method under a high magnetic field can produce the highly crystal orientated HAp block.

As described earlier, bones and teeth of vertebrates are composed of HAp and collagen, which provides mechanical strength and mechanical toughness to HAp body, and are structured so as to align the c-axis of HAp in parallel to the axis of collagen. It is planed to make the crystal aligned composite of HAp and collagen in the same orientation as seen in an organism.

In addition, another target is concerned with the development of implant materials for the bone substitution which is coated with the HAp on the high strength titanium alloy by using the hydro-process, as shown in Fig. 10 [42–46]. Simultaneous coating was carried out with HAp, calcium carbonate and collagen on the titanium alloy by the thermal substrate method in an aqueous solution, and then in vitro evaluation was performed with the coated specimens. Also, the composite film coating with HAp and collagen by the cathodic electrolysis was conducted in the aqueous solution containing H₂O₂. It is now in plan to do in vivo evaluation performed with the coated specimens. Also, the composite film coating with HAp and collagen by the cathodic electrolysis was conducted in the aqueous solution containing H₂O₂. It is now in plan to do in vivo evaluation of the bone substitutional materials coated with the HAp, calcium carbonate and/or collagen by various hydro- processes. Furthermore, attention will be directed toward the fixation of the calcium phosphate compounds in the waste fluid and its application to the recovery of the environment.

Regarding simulation of microstructural evolution and process design, an intelligent method for the design of metals and ceramics has been proposed on the basis of molecular orbital calculations. Recently, the simulation for the microstructural evolution in some alloys has been carried out by the phase-field method [47]. It is aimed to trace the evolutionary process of microstructures in multifunctional materials by using both the phase-field method and the first-principles electronic structure calculation method. Firstly, the evolutionary processes of microstructures are examined experimentally in several polymer-blends (e.g. polystyrene (PS)-poly(vinyl methyl ether) (PVME)), and the experimental results are compared with the simulated results by the phase-field method. Secondly, iron nano-clusters dispersed in a polymer matrix is made by mixing an iron complex with a polymer, and the properties are examined, while paying attention to their interfacial dynamics and microstructural evolution. Then, the process for producing such composite materials is designed with the aid of the simulations.

3.4. Metabolic/information structure formation processes

By learning from the evolution of nature for a very long time (100 million years and more), three approaches of the research on the metabolic/information structures formation processes (1)–(3) are being conducted.

1) The research work on man-made materials with metabolism, which is introduced in this journal [48], is focusing on the self-repairing reaction, the metabolic reaction and the activities based on the information of DNA in a living body. Generally speaking, man-made materials are deteriorated irreversibly. Therefore, hitherto the initial strength of the man-made materials has been ‘overdesigned,’ taking the deterioration factor into account. The protection system of such man-made materials can be called ‘passive protection’. The passive protection system in polymers is illustrated in Fig. 11a [48]. In this system, the cause of the deterioration is due to the direct attacks on the additives in place of the polymer. Therefore, there is no protection system after almost all molecules of the additives are damaged. On the other hand, the criteria of selecting materials that compose a living body in nature so as to guard its body as a carrier of DNA, are the assumption of the materials’ deterioration, continuous repair and abandonment of decisive damage. Namely, a living body has an ‘active protection system’ by which the deterioration site is constantly repaired. The additives do not react with the deterioration factor directly but is a bystander during the deterioration process. The active protection system is illustrated in Fig. 11b. The concept of man-made self-repairing materials has been discussed for several decades. However, there is no material in which the self-repairing reaction is clearly observed. The problem is how to find the materials and to survey their characteristics, then clarifying the problems to overcome to apply them to industrial uses.

From the point of this issue, the three methods shown below for active protection are studied:

(a) Active protection using relatively simple reactions.
(b) Application of metabolic reactions accompanied by energy transfer in man-made materials.
(c) Protection of complexes, especially sophisticated metabolic/information structures formation processes.

As an example of the researches on the type (b), the self-repairing reaction in polyphenylene-ether (PPE) is shown in Fig. 12 [48]. PPE is also damaged by heat, light, oxygen and mechanical strength. The scission, the oxidation and the transposition occur subsequently. A hydrogen donor can stabilize the radicals that are generated through the process.
and both the ends recombine with copper. Cu(II) forms a complex with the end groups and withdraws an electron from the end. The chains recombine and the copper changes to Cu(I). Deactivated Cu migrates in the polymer and two molecules of Cu react with an oxygen molecule to be oxidized to Cu(II). The oxygen ionizes and reacts with two hydrogen ions to form a water molecule. It goes out from PPE as a waste of the metabolic reactions.

(2) With a view of learning the laws of nature, such particle/fluid separation as filtration, membrane filtration, expression, centrifugation and coagulation is being studied to be more widely accepted in diversified fields, for example, in the dairy and food industry, biotechnology, medicine and waterworks. The materials to be separated are also diversified as protein, ultrafine particle and emulsion. These technologies are selected because they are energy efficient, simple and friendly to the environment. A leading role is intended to be played in the researches of particle/fluid separation on the basis of the promising results so far published in scientific journals, etc.

It is challenged to develop a new material processing guided by phenomena and structures observed in the nature or the living thing from the standpoint of separation. Fig. 13 shows a conceptual diagram of the research on the application of membrane filtration, one of most advanced separation technologies, to the material processing. Membrane filtration is a noble technique to form a structure easily, which is produced as an accumulated layer of particles or molecules on the membrane surface. In this process, it is important to control the microscopic properties of components (size, shape, orientation, etc.) and the microscopic interactions (affinity, coagulation, adsorption, etc.). Using the information observed at micro level, the control of the structure of accumulated layer would be possible at macro level. Moreover, this macroscopic control can be applied to the development of the materials with microscopic separation functions, such as affinity separation media with selective function. Thus, new and more efficient material processing can be established by the effective combination of particle/fluid separation technology and nature-guided information.

The latest researches on the separation process are as follows:

(a) Development of material process using affinity: when ligand is added to a solution including racemic body and filtered by a membrane, optical separation is possible due to the fact that one type is rejected by the membrane along with the ligand and another type is passed through the membrane.

(b) Development of material process using osmotic pressure: dewatering of a semi-solid material without damaging its structure can be performed by use of the osmotic pressure instead of the mechanical pressure.

(c) Development of process for forming gelatinous materials: a new method has been developed for preparing the gel emulsions highly concentrated by filtration-consolidation of oil-in-water emulsions.

Fig. 11. Comparison of (a) ‘passive’ and (b) ‘active’ protections in polymer materials.

Fig. 12. Self-repairing reaction in polyphenylene-ether (PPE).
(3) On the metabolic/information structure formation processes, it is also intended to study the structural materials. The large structures are made mainly of metallic materials and most of them suffer from mechanical damages. Aircraft, bridge, vessel and/or power plant cannot avoid fatigue damage in service. In those structures, non-destructive inspection and repair for danger section are repeated in order to keep their integrity.

One of the positive approaches for mechanical damages in service is the idea of self-repairing materials. The materials with self-repairing property are strongly required for the engineering structural materials, if possible. One example of excellent structural materials with self-repairing property is a lived plant. A tree in the windy area spontaneously transforms its inside structure. A plant can sense the mechanical incitement and can flexibly recover its weak and/or damaged positions through its metabolism. Even in metallic material, the idea of self-repairing has been previously proposed. The small capsules embedded in material could break due to the matrix cracking and the repairing material inside of the capsules would be supplied to the crack. This is, however, just an idea and this type of material has not really been developed. The self-repairing behavior similar with this idea is observed in a ceramics material [49]. Many small cracks are usually induced in ceramics at machining and they reduce the strength. In the ceramics with SiO2 binder, the molten binder due to an annealing fills up the cracks. This mechanism can recover the strength deterioration after machining. A plant can locally yield the repairing material with the elements movement, that is, still different from the metal with repairing capsules. Because diffusion rate of elements is quite slow in the metallic material, it is quite difficult in metal to realize self-repairing effect similar with a plant. In the metallic materials and the ceramics, it is necessary to set a contrivance that is ambushed for the damage.

An increase of the resistance for crack propagation during crack extension is one of the ideas for self-repairing effect, even though the crack itself is remained. The fiber-metal laminate plate can typically show this behavior [50]. In this material, thin sheet of glass fiber/epoxy or aramid fiber/epoxy is sandwiched between aluminum alloy skin plates. Fatigue crack easily propagates in the aluminum skin sheets. The inside fiber layer, however, does not show the fatigue damage. Fatigue crack propagates just on the skin sheets and the fiber layer remains, bridging across the crack. The remained fiber layer can act as a crack closer. The bridged fiber sheet induces the larger crack closing force during crack extension. As the fatigue crack propagation
rate is controlled by the crack opening displacement, the bridging fiber layer strongly suppresses the propagation rate, shown in Fig. 14. In the materials whose crack closing force is enhanced by the residual stress in fiber layer, fatigue crack propagation rate slows down during crack extension and finally stops. This behavior is not complete self-repairing effect, but it is the suppression effect for damage expansion.

4. Conclusions

The COE titled the Creation of Nature-Guided Materials Processing has been established in the Nagoya University to perform the education and research under a new view of learning the laws of nature. In the COE, together with such educational programs for PhD students as research incentive, research support, international lodging seminar, overseas training, and external evaluation programs, an Open-Cluster Program has been originated to promote the researches proposed by research groups consisting of young researchers and students and also to foster them. The Open-Cluster Program is opened for the outside of the university and recommended to collaborate with research institutes in and out of Japan.

By gaining insights from the unique structures observed in the natural world and from the processes that form the structures to create new manufacturing processes of materials that are useful for the human life, the researches in the COE are performed on the materials used for living bodies, mimicking structures which nature or living bodies are forming and producing materials by mimicking processes to form the structures observed in the nature or the living bodies. The researches are being advanced on the formation processes of the organic and inorganic interface structure, the hierarchical structure, the multi-functional structure, and the metabolic and information structures.

Through the activities of the education and researches in the COE, it will be expected to establish a new academic field of materials science and engineering which is introducing the smart methods in the natural world, to produce world-highest intelligent fruits and to foster a gathering of young minds for leading the new field and the sustainable development.

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References

[1] C.R. Darwin, On the Origin of Species by Means of Natural Selection, or the Preservation of Favored Races in the Struggle for Life, John Murray, London, 1859.
[2] R.H. Brown, The Wisdom of Science, Cambridge University Press, Cambridge, 1986.
[3] N. Saito, K. Hayashi, H. Sugimura, O. Takai, Decomposition mechanism of p-chloromethylphenyltrimethoxysilane self-assembled monolayers on vacuum ultra violet irradiation, J. Mater. Chem. 12 (2002) 2684–2687.
[4] A. Hozumi, T. Masuda, K. Hayashi, H. Sugimura, O. Takai, T. Kameyama, Spatially defined surface modification of poly(methyl methacrylate) using 172 nm vacuum ultraviolet light, Langmuir 18 (23) (2002) 9022–9027.
[5] H. Sugimura, T. Hanji, K. Hayashi, O. Takai, Surface modification of an organosilane self-assembled monolayer on silicon substrates using atomic force microscopy: scanning probe electrochemistry toward nanolithography, Ultramicroscopy 91 (1–4) (2002) 221–226.
[6] Y. Masuda, T. Sugiyama, K. Koumoto, Deposition mechanism and site-selective deposition of anatase-type TiO₂ from an aqueous solution, J. Mater. Chem. 12 (2002) 2643–2647.
[7] N. Saito, H. Haneda, T. Sekiguchi, N. Ohashi, I. Sakaguchi, K. Koumoto, Low-temperature fabrication of light-emitting zinc oxide micropatterns using self-assembled monolayers, Adv. Mater. 14 (6) (2002) 418–421.
[8] N. Shirahata, Y. Masuda, T. Yonezawa, K. Koumoto, Control over film thickness of SnO₂ ultrathin film selectively deposited on a patterned self-assembled monolayer, Langmuir 18 (26) (2002) 10379–10385.
[9] Y.F. Gao, Y. Masuda, T. Yonezawa, K. Koumoto, Site-selective deposition and micropatterning of SrTiO₃ thin film on self-assembled monolayers by the liquid phase deposition method, Chem. Mater. 14 (2002) 5006–5014.
[10] Y. Masuda, M. Itoh, T. Yonezawa, K. Koumoto, Low-dimensional arrangement of SiO₂ particles, Langmuir 18 (10) (2002) 4155–4159.
[11] Y. Masuda, T. Koumura, T. Okawa, K. Koumoto, Micropatterning of Ni particles on a BaTiO₃ green sheet using a self-assembled monolayer, J. Colloid Interface Sci. 263 (2003) 190–195.
[12] T. Yonezawa, H. Genda, K. Koumoto, Cationic silver nanoparticles dispersed in water prepared from insoluble salts, Chem. Lett. 32 (2) (2003) 194–195.
[13] A. Koizumi, H. Moriya, N. Watanabe, Y. Nonogaki, Y. Fujiwara, Y. Takeda, Luminescence properties of Er,O-codoped InGaAs/GaAs multi-quantum-well structures grown by organometallic vapor phase epitaxy, Appl. Phys. Lett. 80 (9) (2002) 1559–1561.
[14] J. Yoshikawa, S. Okubo, H. Ohta, T. Koide, T. Kawamoto, Y. Fujiwara, Y. Takeda, ESR study of heavily doped GaAs:Er grown by organometallic vapor phase epitaxy, in: A. Kawamori, J. Yamauchi, H. Ohta (Eds.), EPR in the 21st Century: Basics and Applications to Material, Life and Earth Sciences, Elsevier, Amsterdam, 2002, pp. 302–305.
[15] Y. Takeda, Y. Fujiwara, A. Koizumi, JST semiconductor layer structures doped with rare-earth elements for light emitting diodes, light emitting diodes, semiconductor lasers and semiconductor optical amplifiers and their production techniques, Japanese Patent 2002-265488 (2002.09.11) pending.
[16] A. Itoh, M. Shinkai, H. Honda, K. Yoshikawa, S. Saga, T. Wakabayashi, J. Yoshida, T. Kobayashi, Heat shock protein 70 expression induces an antitumorimmunity during intracellular hyperthermia using magnetic nanoparticles, Cancer Immun. Immunother. 52 (2) (2003) 80–88.
[17] M. Suzuki, M. Shinkai, H. Honda, T. Kobayashi, Anti-cancer effect and immune induction by hyperthermia of malignant melanoma using magnetite cationic liposomes, Melanoma Res. 13 (2) (2003) 129–135.
[18] M. Shinkai, K. Ueda, S. Ohtsu, H. Honda, K. Kohri, T. Kobayashi, Effect of functional magnetic particles on radiofrequency capacitive heating: an in vivo study, Jpn. J. Cancer Res. 93 (1) (2002) 103–108.

[19] M. Shinkai, K. Ueda, S. Ohtsu, H. Honda, K. Kohri, J. Inoue, T. Kobayashi, Characteristics of particulate heating mediator in RF capacitive heating, Jpn. J. Hyperthermic Oncol. 18 (1) (2002) 33–40.

[20] M. Shinkai, K. Ueno, H. Honda, T. Kobayashi, Magnetite needle as heating mediator for intracellular hyperthermia of tumor, Jpn. J. Hyperthermic Oncol. 18 (4) (2002) 191–198.

[21] Y. Okamoto, T. Nakano, Synthetic helical polymers: conformation and function, Chem. Rev. 101 (2001) 4013–4038.

[22] E. Yashima, Chiral and chirality discrimination on helical polyacetylenes, Anal. Sci. 18 (2002) 3–6.

[23] E. Yashima, T. Matsushima, Y. Okamoto, Chirality assignment of amines and amino alcohols based on circular dichroism induced by helix formation of a stereoregular polyy-carboxyphenylacetylene through acid–base complexation, J. Am. Chem. Soc. 119 (1997) 6345–6359.

[24] E. Yashima, K. Maeda, Y. Okamoto, Memory of macromolecular helicity assisted by interaction with achiral small molecules, Nature 399 (1999) 449–451.

[25] H. Onouchi, K. Maeda, E. Yashima, J. Am. Chem. Soc. 123 (2001) 7441.

[26] R. Nonokawa, E. Yashima, Detection and amplification of a small enantiomeric imbalance in α-amino acids by a helical poly(phenylacetylene) with crown ether pendants, J. Am. Chem. Soc. 125 (2003) 1278–1283.

[27] E. Yashima, K. Maeda, O. Sato, Switching of a macromolecular helix for visual discrimination of molecular recognition events, J. Am. Chem. Soc. 123 (2001) 8159–8160.

[28] T. Nishimura, K. Takatani, S. Sakurai, K. Maeda, E. Yashima, A helical array of pendant fullerenes on an optically active polyphenylacetylene, Angew. Chem. Int. Ed. 41 (2002) 3602–3604.

[29] Y. Matsushita, Studies on equilibrium structures of complex polymers in condensed systems, J. Polym. Sci., Part B, Polym. Phys. Ed. 38 (2000) 1645.

[30] J. Suzuki, M. Seki, Y. Matsushita, The tricontinuous double-gyroid structure from a three-component polymer system, J. Chem. Phys. 112 (2000) 4862.

[31] M. Seki, J. Suzuki, Y. Matsushita, Small-angle X-ray scattering analysis of the periodic tricontinuous network structure of symmetric ABC triblock copolymers, J. Appl. Crystallogr. 33 (2000) 285.

[32] A. Takano, A. Nonaka, O. Kadoi, K. Hirahara, S. Kawahara, Y. Isono, N. Torikai, Y. Matsushita, Preparation and characterization of cyclic polystyrene with short polyy-(2-tert-butylbutadiene) sequence, J. Polym. Sci., Polym. Phys. Ed. 40 (2002) 1582.

[33] A. Takano, O. Kadoi, K. Hirahara, S. Kawahara, Y. Isono, J. Suzuki, Y. Matsushita, Preparation and morphology of ring-shaped poly-styrene-block-polyyisoprenes, Macromolecules 36 (2003) 3045.

[34] A. Takano, K. Soga, J. Suzuki, Y. Matsushita, Non-centrosymmetric structure from a tetrablock copolymer of the ABCA type, submitted for publication.

[35] A. Takano, K. Soga, T. Asari, S. Arai, H. Saka, Y. Matsushita, Observation of four phase lamellar structure from a tetrablock copolymer of the ABCD Type, submitted for publication.

[36] Y. Ikuhara, Y. Iwamoto, K. Kikuta, S. Hirano, Precursor derived LiMn2O4 thin films as ionic conductor, Ionics 6 (2000) 156–160.

[37] W. Sakamoto, Y. Horis, T. Yogo, S. Hirano, Synthesis and properties of highly oriented (Sr,Ba)(Nb,Ta)2O6 thin films, Jpn. J. Appl. Phys. 40 (9B) (2001) 5599–5604. Pt 1.

[38] K. Ueno, W. Sakamoto, T. Yogo, S. Hirano, Synthesis of conductive LaNiO3 thin film by chemical solution deposition, Jpn. J. Appl. Phys. 40 (10) (2001) 6049–6054. Pt 1.

[39] S. Hirano, T. Yogo, W. Sakamoto, S. Yamada, T. Nakamura, T. Yamamoto, H. Uki, Y. Ando, In-situ processing of nano crystalline oxide particles/polymer hybrid, J. Sol–Gel Sci. Tech. 20 (2003) 35–41.

[40] K. Inoue, K. Sassa, Y. Yokogawa, Y. Sakka, M. Okido, S. Asai, Control of crystal orientation of hydroxyapatite by using a high magnetic field, Proceedings of the 15th International Symposium on Ceramics in Meeting of the International Society for Ceramics in Medicine, Bioceramics 15 (2002) 513–516.

[41] K. Inoue, K. Sassa, Y. Yokogawa, Y. Sakka, M. Okido, S. Asai, Control of crystal orientation of hydroxyapatite by imposition of a high magnetic field, Mater. Trans. 44 (2003) 1133–1137.

[42] K. Kuroda, R. Ichino, M. Okido, O. Takai, Hydroxyapatite coating on titanium by thermal substrate method in aqueous solution, J. Biomed. Mater. Res. 59 (2002) 390–397.

[43] K. Kuroda, R. Ichino, M. Okido, O. Takai, Effects of ion concentration and pH on hydroxyapatite deposition from aqueous solution onto titanium by the thermal substrate method, J. Biomed. Mater. Res. 61 (2002) 354–359.

[44] K. Kuroda, Y. Miyashita, R. Ichino, M. Okido, O. Takai, Preparation of calcium phosphate coatings on titanium by the thermal substrate method and in vitro evaluation, Mater. Trans. 43 (2002) 3015–3019.

[45] M. Okido, K. Kuroda, M. Ishikawa, R. Ichino, O. Takai, Hydroxyapatite coating on titanium by means of thermal substrate method in aqueous solutions, Solid State Ionics 151 (2002) 42–57.

[46] M. Okido, K. Nishikawa, K. Kuroda, R. Ichino, Z. Zhao, O. Takai, Hydroxyapatite film coating process on titanium cathode by EQCM technique, Mater. Trans. 43 (2002) 3010–3014.

[47] Y. Murata, T. Koyama, M. Morinaga, T. Miyazaki, Prediction of the phases phase morphology in Fe–Cr–W–C quaternary steels with the aid of system free energy concept, ISIJ Int. 42 (2002) 1423–1429.

[48] K. Takada, M. Tanahashi, H. Unno, Self-repairing mechanism of plastics, submitted for publication.

[49] K. Ando, M.C. Chu, S. Matsushita, S. Sato, Effect of crack-healing and proof-testing procedures on fatigue strength and reliability of Si3N4/SiC composites, J. Eur. Ceram. Soc. 23 (2003) 977–984.

[50] T. Miyata, T. Tagawa, F. Takahashi, H. Hira, Fatigue crack propagation behavior of fiber metal laminate—-influences of initial notch length and pre-stretching, J. Soc. Mater. Sci. Jpn 45 (1996) 334–339.