Special Review

Review

Nanostructured Materials in Biological and Artificial Systems

Yoshiaki Fukushima

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ABSTRACT Selected research examples from the last decade at the TOYOTA CRDL, INC. for nanostructured materials were reviewed using the comparison introduced at the 11th Toyota Conference held in 1997. The results of mesoporous materials, characterizations using neutron scattering, approaches to an artificial enzyme, a photosynthesis system and bio-mineralization were included. The results were discussed from the viewpoints of true nanostructured material and the relationship between the characteristics and properties.

KEYWORDS 11th Toyota Conference, Mesoporous Materials, Neutron Quasi-elastic Scattering, Fuel Cell Membrane, Artificial Enzyme, Artificial Photosynthesis System, Bio-mineralization, Yohen-Temmoku bowl

1. Introduction

We organized the 11th Toyota Conference entitled "Nanostructured Materials in Biological and Artificial Systems" on November 5–8, 1997, sponsored by TOYOTA MOTOR CORPORATION. The conference covered modeling, analyses, syntheses and applications of mesoporous materials, nanoparticles, colloids, films and layers produced in natural or artificial processes. The reports at the conference were published as a special issue of Supramolecular Science Volume 5, Number 3–4, 1998. When we were planning the conference, one of the members of the organizing committee, Professor T. J. Pinnavia of Michigan State University, proposed that we define "nanostructured" materials. He asked us what NANOSTRUCTURED materials are. He wrote me the following letter. "Historically a number of nanosized materials have been reported to date such as colloids, nanocrystals and cluster compounds. Although they have exhibited interesting properties, most of them are simply nanosized particles. Their properties are invariant when the sizes are changed from atomic to conventional scales. True nanostructured materials, which we would like to define here, are ones whose structures and compositions can neither be described nor characterized by anything else than terms of a nanometer-length scale". As this statement was full of profound meaning, we accepted his comment and quoted it in the preface of the special issue.[1] However, the latter part of this statement, where he tried to define a true nanostructured material, was hard to interpret. One of the motivations for this review is to try to answer again his question, what is true nanostructured material.

The nanostructured materials and their related subjects are still studied in the world and also at Toyota Central R&D Labs., Inc. (TOYOTA CRDL, INC.). In this review, I selected some topics that were proposed in the 11th Toyota Conference as an origin of study with comparisons of some recent outcomes of TOYOTA CRDL INC. I would like to discuss the problem of the true nanostructured material from the viewpoint of my own interest. The performances of materials for automobile bodies, electric wires or catalysts are directly concerned with their properties, such as mechanical strength, electric conductivity or catalytic activity. For understanding and controlling the properties, it is necessary to know their characteristics, such as crystal structure, morphology of grains, electrical and magnetic structures, diffusion constant, and surface morphology and structure. Although the differences between "performance", "properties" and "characteristics" are not clear, I would like to define them in this review. As my interest has been the relation of properties and atomic architecture, the question for "true nanostructured material" could be replaced by the "necessity of the nanometer-scale structure for realizing a specific property", which is a viewpoint of this review.

2. Characterization Methods

In the research of materials, we should always follow the design-synthesis-characterization (DSC) cycle. Information regarding application needs should be one of the most important tasks for the design step. As part of this cycle, property and performance checks are included in the material development processes. Structural analyses using quantum beams from X-rays, electrons, light or neutrons are the principal methods of characterization. We focused on structure on the nanometer scale, as well as small-angle scattering[2,3] and electron diffraction and electron microscopy[4] techniques at the Toyota conference.

2. 1 Design-synthesis-characterization (DSC) Cycle in Research of Mesoporous Materials

We have been collaborating with Prof. Terasaki, who proposed a strategy for characterizing nanostructured materials using electron diffraction, electron microscopy and modeling.[4] We could follow the characterization (C) of mesoporous silica,[5] by following a design (D) of the noble material and attempting synthesis (S). Besides the DCS cycles, we also found characteristic properties of mesoporous silica, such as catalysis,[6-10] by collaboration with Prof. Ichikawa, who reported the catalytic behaviors of the nanostructured materials at the Toyota conference, along with adsorption properties,[11-12] stabilized enzymes[13-15] and organic molecules included in the nano-spaces.[16,17] Some interesting properties led to proposals for new applications such as a catalysts for a fuel cell[18] or an adsorption heat-pump.[19] Continuous research following the DSC cycle achieved the innovative result of a periodic mesoporous organosilica (PMO),[20,21] which was recognized in one of the core papers to open a new chemistry and materials science front and promote new research work in the world. The noble properties[22] of the hybrid mesoporous materials are expected to have innovative applications.

2. 2 Complementary Approaches in Material Characterization

At the 11th Toyota Conference, two examples of small-angle neutron scattering for emulsions and polymer gels were introduced. Prof. Kanaya of Kyoto University proposed the complementary approach using wide-angle neutron scattering, small-angle neutron scattering, ultra-small-angle neutron scattering and light scattering to advance the nanostructure .[3] Since 1997, the super photon ring at the 8 GeV (SPring-8) facility was opened for common use, and consequently the world's strongest X-rays have been available for characterization of the materials. The complementary use of X-rays and neutrons is a powerful method for structural analysis. The Kanaya group confirmed the unique Shishi-kebab structure (**Fig. 1**) of flow molded polyethylene by using small- and wide-angle X-ray scattering, small-angle neutron scattering, light scattering and an optical microscopy.[23-25] The information of a wide-scale structure from 0.1 nm to 0.1 mm made it possible to understand the abnormal strength: about 300 kg•mm^{-2} of polyethylene fiber. The nanosize of the kebab part with the crystal lamellae and their nm scale periodically arrayed along the shish part with the stretched molecular chain micro fibrils contributed to their mechanical properties. Here we have a typical example of nanostructured material whose property or performance was realized by its nanometer-scale structure.

2. 3 Connection of Character with Property: Neutron Scattering

Understanding the structure of matters is the basis for material research. However, the characteristics cannot

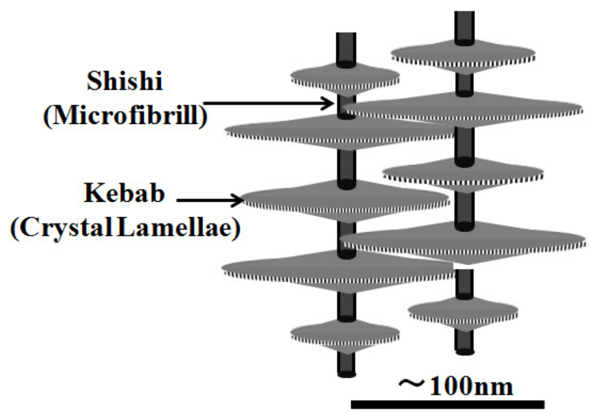

Fig. 1 Shishi-kebab model for the structure of the melt drawing polyethylene.[23]

directly be connected with properties without our own imagination or modeling using computer simulations and calculations. We can measure the properties of bulk materials such as electric conductivity, thermal conductivity, magnetization or mechanical strength, and also check performances of a catalysts, fuel cell, battery or automobile body. However, there is still a significant gap between the micro- or meso-scale character and the intrinsic properties of the materials due to the influences of measuring methods, impurities, defects and interfaces. Recent development in computer modeling methods is one of the most helpful tools for our imagination. I am expecting that the most advanced neutron scattering and the X-ray free electron laser will connect the nanostructure and intrinsic properties.

We are using two aspects of quantum beams, wavelength and energy, for the characterizations of the materials. As the wavelength of an X-ray is several angstroms, which is comparable to the distance between atoms or the lattice periodicity in condensed matter, it is suitable to characterize the static structure of matter by using wave interference. Energy changes between an incident and a scattering beam provide us with information about a dynamic structure, such as vibration or diffusion. As the energy of infrared or visible light is comparable with the vibration mode of the usual chemical bonds in condensed matter or molecules, infrared and Raman spectroscopies are powerful tools to characterize the dynamic structures. The γ-ray, X-ray, ultraviolet, visible and infrared rays are electromagnetic waves that follow Plank's rule, as shown in **Fig. 2**. Figure 2 also shows the relation between energy and wavelength for particle rays such as electron and neutron beams, which follow the de Broglie rule. Neutron beams with wavelengths of several angstroms are suitable for characterizing the static structure of solids and liquids. Neutron beams have an energy of several tens to hundreds meV, which is suitable for dynamic structures. Cold and thermal neutron scattering has been expected to provide the vibration or diffusion properties within the region of nanometer size and the pico-second time scale. The vibration or diffusion behaviors within regions of this size and time scale would be useful to understand the relation of the static structure and the intrinsic properties such as catalytic activities or ion diffusion. Recent developments of the neutron facility in the Japan Proton Accelerator Research Complex (J-PARC) make possible a high flux of cold and thermal neutrons, which can apply neutron scattering for the characterization of materials.

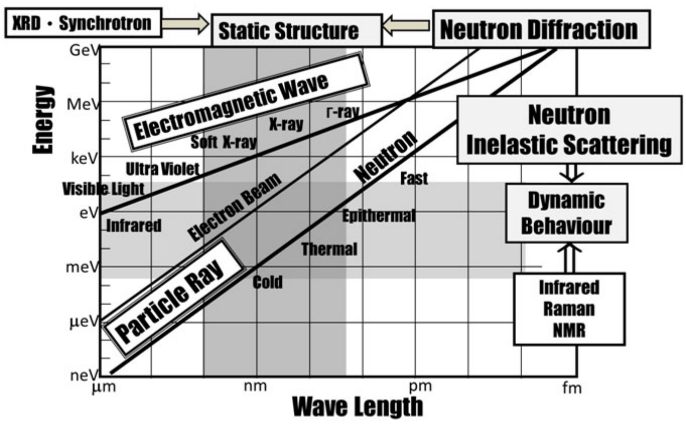

Fig. 2 Characterizations of static and dynamic structure using neutron.

Besides the energy-wavelength relationship, neutrons have the characteristic of hydrogen or proton scattering. As the incoherent scattering length of neutrons for hydrogen or protons is about ten times larger than that for other atoms, neutron scattering is suitable to analyze the dynamics of hydrogen and molecules containing hydrogen. The quasi-elastic neutron scattering (QENS) spectrum is related to self-diffusion and local jump motion. When water, hydroxide or protons in a sample are tightly bound to solid surfaces and their movement is restricted, incident neutron energy is not modified by the scattering and only the same profiles of scattering neutrons with an incident neutron beam are observed. This is called elastic scattering. The movements of the hydrogen modify the neutron spectrum and diffuse the quasi-elastic spectra around the elastic peak, as shown in **Fig. 3**. The ratio of the elastic peak and the quasi-elastic peak corresponds to the ratio of restricted and moving molecules. The spectrum for the adsorbed water in the mesoporous silica shows that water molecules in the first layer on the silica surface could not move, although other water molecules in the mesopore-space could move. Further precise curve-fitting analyses of the broad quasi-elastic peak provided the averaged staying time at trapping sites, the jumping length between neighboring trapping sites and the self-diffusion constant of the water molecules. The jumping mechanism and diffusion constant of the water molecule in the nano-spaces were different from those of bulk water.

Since proton diffusion is one of the most important properties for fuel cell development, proton, water and hydronium diffusion behavior in solid proton conductive materials[26,27] and hydrated polymer films[28-30] have been analyzed by QENS. Perovskite ($SrCe(Yb)O_3$) has attracted attention as a proton conductive solid.[26] Models for the proton motions around the –OH group in the solid shown in **Fig. 4** were proposed[27] and analyzed by quasi-elastic and inelastic neutron scattering.[31,32] The quasi-elastic spectrum suggested the four jumping modes of H^+: rotating around Ce^{4+} -O (τ_R), trapping at the Ce^{4+} -O site for τ sec followed by jumping about 0.3 nm to the neighboring Ce^{4+} -O site, trapping at the Yb^{3+} -O site for τ_0 sec followed by jumping about 0.3 nm to the Ce^{4+} -O site, and trapping at the Yb^{3+} -O site for τ_1 sec followed by jumping about 1 nm to the Yb^{3+} -O site. The research studies proposed that the proton diffusion constant in this oxide was related to the jumps between Yb^{3+} -O sites, and the combination of jumps between Ce^{4+} -O sites with lower activation energy is attributable to the high proton conductivity.

The water content in an organic polymer membrane changes with relative humidity, which changes the nanometer-scale structure of the water clusters. The molecular motions and vibrations of the matrix polymer chains also affect the diffusion of protons (H^+), water (H_2O), hydronium ions (H_3O^+) and hydronium cluster ($H_7O_3^+$). The structure, vibration and diffusion properties have been analyzed by X-ray and small-angle neutron scattering, infrared, and inelastic neutron and quasi-elastic neutron spectroscopy.[28-30] As shown in **Fig. 5**, the following five modes of protons and proton movement were proposed.

a) Tightly bound H^+ to SO_4^- group on the surface of the polymer membrane.
b) Jumping between the neighboring trap sites.
c) Moving in the water clusters hydrated with SO_4^- groups.
d) Moving in the water domains surrounded by the polymer chains.
e) Jumping between the water domains.

It is necessary for understanding the proton diffusion mechanism to analyze the static and dynamic structure in the space range from several angstroms to several hundreds of μm, and in the time range from several pico-sec to several tens of nano-seconds. Although the phenomena are too complicated to realize an acceptable model, this has been challenging and important work.

Increasing acid density is expected to increase the proton diffusivity even in a low humidity environment. However, increasing the SO_4^- groups in the polymer chain also raises excess swelling with water to weaken

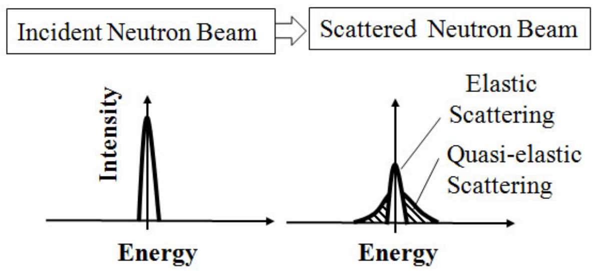

Fig. 3 Energy spectrum of incident and scattered neutron in quasi-elastic neutron scattering experiment.

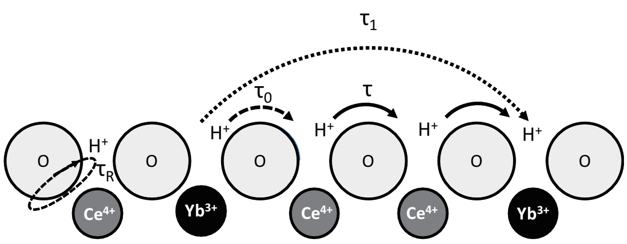

Fig. 4 Model for jumping diffusion modes in a perovskite oxide.

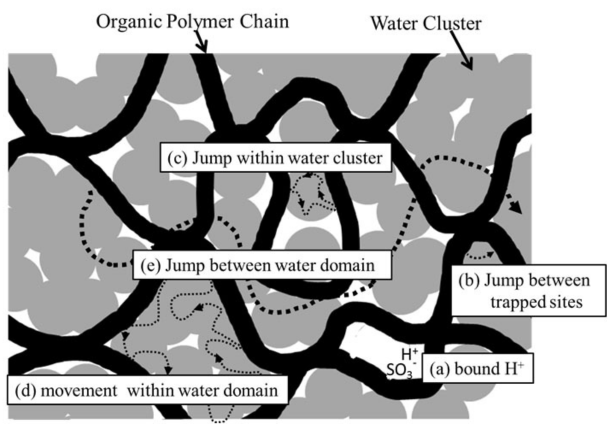

Fig. 5 Proton diffusion modes in a swollen polymer membrane.

the mechanical properties and durability. Although mesoporous silica with SO_4^- groups on the inner surface (**Fig. 6**) is expected to be a suitable material to control the acid density without modification of the swelling property, intrinsic proton conductivity could not be evaluated due to the powder morphology. Complementary analyses of quasi-elastic neutron scattering, X-Ray diffraction, electron microscope observation and proton conductivity measurement confirmed the direct jump between the acid sites even in the low humidity environment.(33) The characteristics and the properties of this material were well established to propose the possibility of excellent performance for a fuel cell membrane. Besides the proton dynamics, those of other ions such as lithium and sodium ion were also analyzed by QENS(34,35) and offered valuable information for secondary battery development. Following the opening of the neutron facilities in J-PARC and the X-ray facilities in SPring-8, muon-spin rotation and muon-spin relaxation (μ^+SR) facilities and the X-ray free electron laser facility, the SPring-8 Angstrom Compact free electron Laser (SACLA) has been opened for public use and offered us dynamic structure(36,37) and nanoscale structure(38) information. Developments of the characterization method are expected to broaden our knowledge of materials.

3. Nanostructured Materials in Biological Systems and Bio-inspired Research

In the natural system, highly selective and high-speed proton diffusions are realized by controlling the pore size and the surface properties of the channels, as shown in **Fig. 7**. It was proposed that the pinpoints of narrow spaces with a hydrophilic surface and the relatively wide channels with a hydrophobic surface would contribute to the excellent proton transfer property in proteins.(39) In the design process of the materials, assemblies of the parts with specific functions are necessary for obtaining excellent materials for useful systems, which was proposed as a closing remark of the 11th Toyota Conference. In the case of the proton channel in Fig. 7, combinations of a hydrophilic part and a hydrophilic part should be mimicked in artificial developments.

3. 1 Artificial Enzymes

A biological catalyst, an enzyme, has the remarkable ability of selectivity and provides a lower activation energy (higher reaction rate constant). We confirmed the excellent performance of an enzyme by preparing an enzyme fuel cell, in which the suitable enzymes for anode and cathode reactions and a porous carbon electrode with suitable pore size to include the enzymes were assembled.(40) Application of the enzyme fuel cell was limited due to the poor durability and low

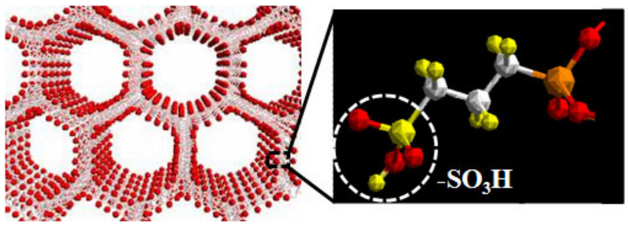

Fig. 6 Structure model of a mesoporous silica modified with $-SO_3H$ group.

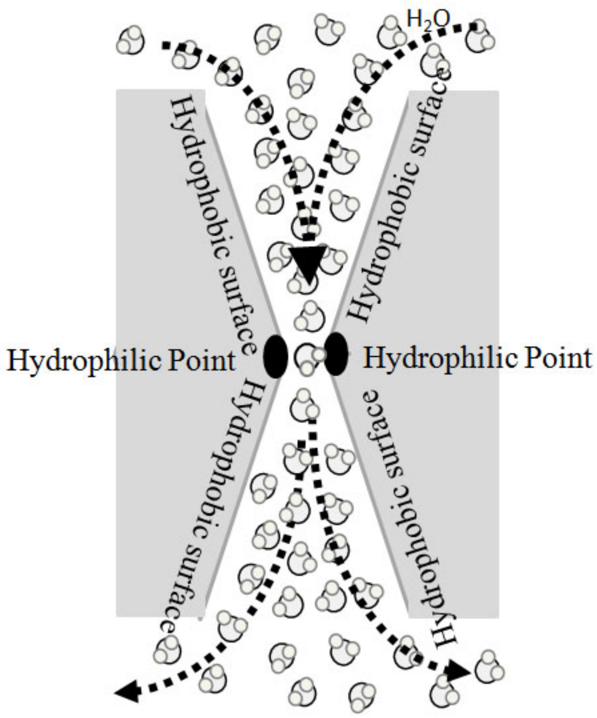

Fig. 7 Water transfer model in bio-membrane channel.(39)

active site density of the enzymes. However, the low activation energy for the fuel cell reaction was affirmed in this enzyme catalysis system, which is expected to be mimicked in an artificial system. The required parts for reaction, adsorption, introducing reactants, removing products and controlling the reaction are assembled in the enzymes. The molecules are self-assembled in nanometer spaces prepared by proteins, in which the nanometer scale is important for energy and electron transfer between the molecules and quick movement of hydrated molecules.

Chlorophyll a ($C_{55}H_{72}MgN_4O_5$) is one of the most important pigments in chloroplasts for the photosynthesis system in plants. Chlorophyll a cannot work alone but aggregates to form a light-harvesting complex antenna that realizes effective photoelectric conversion, durability for light radiation and a long-lived active state. A hydrophilic phytol ($C_{20}H_{39}OH$) group and a metal organic complex Mg-porphyrin were bound to form the chlorophyll a molecule. The porphyrin part is an active site for photoelectric conversion and the phytol group helps to self-assemble the arrangement of the antenna. When mesoporous silica with a suitable pore size and a suitable solvent for chlorophyll a is present, the chlorophyll was selectively adsorbed in the nano-space of the mesoporous silica. The adsorbed molecules were arrayed in the mesopores as shown in **Fig. 8**.[16] The arrangement where the porphyrin molecules are oriented face-to-face within 1 nm distance would allow energy transfer between the porphyrin molecules.[41] A metal porphyrin which is similar in structure to the chlorophyll a is used in natural enzymes such as hemoglobin or myoglobin. Although Heme, Fe^{2+} -porhyrin, was not adsorbed in the mesoporous silica and had little activity as a catalyst, the phytol modified Heme molecules were adsorbed in the mesoporous silica to form the same molecular arrangement shown in Fig. 8 with an analogous effect of the natural enzyme myoglobin.[17] These results suggest that the control of the local nanometer-sized environment around the activation site of Fe^{2+} was necessary to realize the excellent catalytic activities, which were brought by the arrangement of the protein globin in the natural enzyme and also by the molecular assemblies in the nano-spaces of the mesoporous silica. The artificial enzyme has been one of the most attractive approaches in nanostructured material science.[42]

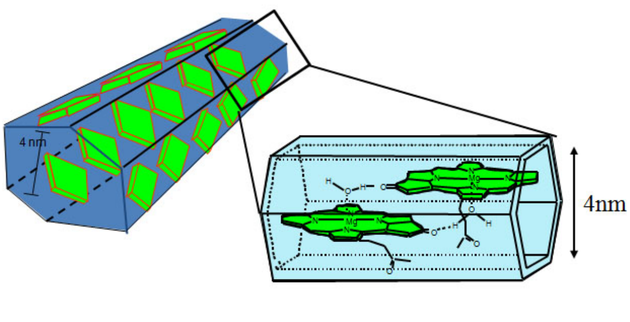

Fig. 8 Model of the arrangement of chlorophyll a in the mesoporous silica.[16]

3. 2 Approach to Artificial Photosynthesis

Artificial photosynthesis is one of the most desired technologies to address global warming and to save future energy. Useful hydrocarbons are produced from CO_2 and H_2O by using the energy of sunlight in natural photosynthesis. Although ultraviolet light energy is suitable for the reaction, natural leaves prefer not to use the ultraviolet, but instead prefer to use visible light with lower energy due to the effective utilization of sunlight and protection of their own bodies and systems against light radiation. As the visible light energy is not enough to generate hydrocarbon from CO_2 and H_2O, the leaves prepare two photoelectric conversion elements called photosystems I and II, which are connected to obtain enough energy. We tried to assemble the artificial photosystems I and II. One photosystem is a complex[43] of organic photo-active molecules and molecular nano-sheets of quasi-TiO_2 proposed by Dr. Sasaki.[44] The other is a complex of visible light active organic molecules with mesoporous silica. We focused on the electron or hole transfer between the two model systems.[45,46] Although this assembly has not been developed as a useful photosynthesis system, the challenge for assembling photochemical active semiconductors, oxidation and reduction catalysts has been continued at the TOYOTA CRDL, INC. In the photosynthesis system, elements for light harvesting, photoelectric conversion and catalysis for oxidation of H_2O and reduction of CO_2 are used. The assembly of these elements with efficient electron, hole, and mass transfers, for which the arrangements on the nanometer scale hold the key, is one of the most important challenges. Periodic mesoporous organosilica (PMO) with a chromophore group in the framework is expected to be a candidate for the light-harvesting element. An efficient energy transfer from the framework chromophore to the guest dye[47] and CO_2 reduction catalysis[48] in the mesopore spaces were confirmed. In these assemblies, organic-inorganic hybrid frameworks served not only as a photoelectric conversion element but also as a protective covering for the functional organic molecules against radiation of ultraviolet light.[48] Another approach at the TOYOTA CRDL, INC., which demonstrated artificial hydrocarbon photosynthesis using only H_2O, CO_2 and visible light, is the preparation of a catalysis element for selective $HCOO^-$ formation in an aqueous system, hybridized with an inorganic semiconductor[49] and followed by the conjugate with H_2O oxidation photo catalysis.[50,51] We could have a typical example of a nanoscale assembly technology of nano-parts to obtain a useful system, and TOYOTA CRDL, INC. has been in the position to lead in this field.

3. 3 Bio-mineralization

Research on organic/inorganic hybrids or complex materials is inspired by the bio-mineralization process. In biological systems, organic/inorganic hybrids or complex materials have produced many interesting nano-magnets,[52] nano-hybrids in shells[53] and plant bodies.[54] An example of the nano-magnet particle is shown on the front cover of the proceedings of the 11th Toyota Conference. Calcium carbonate ($CaCO_3$) minerals are one of the most important minerals on our earth, because of their role of fixing CO_2 in the environment and serving as a source of material for shells, plant bodies, industrial concrete and plasters. Although bio-mimetic approaches to make unique composites were tried,[55] materials with excellent properties such as abalone shells have not been artificially obtained. We studied the influence of organic polymer films on the formation of $CaCO_3$ and obtained an organic $CaCO_3$ composite film.[56] The effects of the low molecular weight organic amines and aminoacids on $CaCO_3$ precipitation have been studied,[57,58] but the preparation of polyamide $CaCO_3$ hybrids is challenging. The process to make nanostructured materials inspired by bio-mineralization was developed in other directions to prepare ordered nano-hetero-metallic materials from organic block copolymers.[59]

4. Typical Nanostructure Material in Traditional Technology

In biological systems, we have many examples of nanostructured materials and assemblies, which arouse our interest but which are still hard to imitate artificially. I also found an example in traditional technology. Jian ware bowls created at the Song dynasty (10th–13th centuries) are known as Temmoku ware in Japan. The inner brilliant black glazing of the Yohen-Temmoku bowls is splashed with spots, and a sparkling lazuline border surrounds the spots. The color of the border varies depending on the incident light and viewing position. There are three examples of Yohen-Temmoku bowls in the world, and these three bowls are a Japanese National Treasure. Only a few rare samples with this kind of brilliant glaze effect have been found at the Jian kiln site. Fortunately, I had the opportunity to observe one of the shards by electron microscopy, electron diffraction and energy dispersive X-ray spectroscopy.[60] The glazing was the glass phase except for the magnetite polycrystalline of the surface layer, which was about 40 nm in thickness. Crinkle patterns of about 0.1 μm pitch, as shown in **Fig. 9**, play the role of surface grating for visible light diffraction, which contributes to the varied color change from the Yohen effect. A nanometer-scale iron oxide film was formed at the surface, followed by hardening of the inner glass phase during the cooling process. The crinkling patterns are formed during this process.

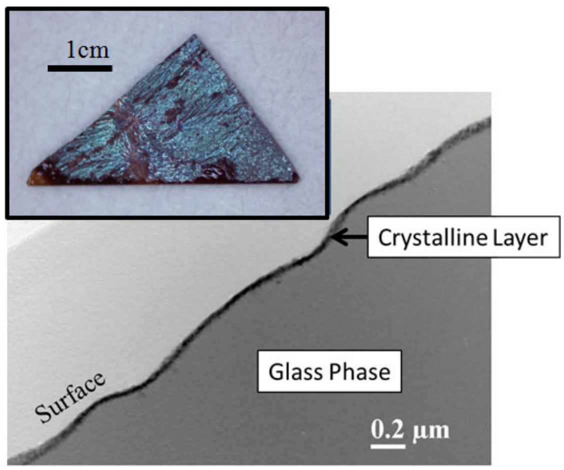

Fig. 9 TEM image of glazing layer of ancient china TENMOKU, prepared from a sample from the Jian kiln site.

Although many trials have tried to reproduce this brilliant pattern for more than a thousand years, no one has reached the technology of Yohen-Temmoku. Here we have another excellent nanostructured material, whose character was understood by recent technology.

5. Conclusions

We have many excellent examples of nanostructures in natural, biological, earth and cosmic sciences, and also in ancient and modern technology. We have been trying to understand their essence by using available research methods. The gap between natural system/artificial system, character/property/performance of materials, and noble discovery/application, has yet to be closed. However, we have made many considerable achievements, as shown in this review on both sides of science and technology, as a result of complementary works under interrelated influences. I had an interesting meeting at the 11th Toyota Conference over a broad range of scientific and engineering activities, of characterization, synthesis, assembling and applying of nanostructured materials in biological and artificial systems. Small but interesting and successful cases of true nanostructured materials in the latest decade were introduced in this review. I hope to be able to continue characterizations of organic/inorganic interactions and challenges to bio-mineralization mimics.

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Yoshiaki Fukushima

Research Fields:
- Organic and Inorganic Hybrids
- Bio-mineralization

Academic Degree: Dr.Eng.

Academic Societies:
- The Chemical Society of Japan
- The Japan Institute of Metals and Materials
- The Clay Science Society of Japan
- The Japanese Society for Neutron Science
- Japan Society of Powder and Powder Metallurgy

Awards:
- The Japan Society of Powder and Powder Metallurgy Award for Research Development, 1994
- The Ceramic Society of Japan Award for Ceramography, 1997
- The Secretary of Science and Technology Agency Award for Distinguished Reserch, 1998
- The Chemical Society of Japan Award for Technical Development, 2000
- The Clay Science Society of Japan Award, 2000
- Japan Fine Ceramic Association Award for Technical Development, 2005
- AIPEA(International Association for Study of Clays) Medal, 2009
- The Chemical Society of Japan Fellow, 2010