1

Introduction

1.1 Introduction of Amorphous Materials

Amorphous material is a type of substance in which basic units do not exhibit long-range order (LRO) in space but maintain some ordered characteristics only in the range of several atomic scope. Different from the traditional crystalline materials with regularly arranged basic units, amorphous materials are characterized by atomic short-range (<1 nm) order and long-range (>1 nm) disorder [1]. Compared with anisotropic crystalline materials, amorphous materials exhibit macroscopic homogeneity and isotropy. Based on this internal structure, amorphous materials do not have crystal defects such as dislocations, grain boundaries, etc., which endows the amorphous materials with some excellent mechanical properties such as high strength, high hardness, high wear resistance, high fatigue resistance, etc. At the same time, amorphous surface exhibits a high degree of unsaturated atomic sites or dangling bonds, which made it desirable as a model catalyst or a practical catalyst. Thus, the special disordered surface structure can provide more active sites than traditional crystal nanomaterials and further improve the catalytic performance. Apart from that, the special atomic arrangement of amorphous structures can effectively regulate the electronic state of the material, leading to optimized transmission of electrons or ions in catalysis. Therefore, the intensive study of amorphous materials has important implications for theoretical and practical exploration of solid materials.

In the order of aggregates, modern physics classifies conventional materials as solid, liquid, gaseous, and plasma states (Figure 1.1), which are considered to be the basic material forms that make up our surroundings. In addition to the three states of solid, liquid, and gas, which are common in our perception, the plasma state consists of gaseous molecules after ionization (thermal ionization, photoionization, impact ionization, etc.), and its behavior is mainly controlled by the Coulomb interaction between ions and electrons. The four basic states are stable under some certain conditions, and the transformation of physical states from one to another is due to the change of thermodynamic states such as temperature, volume, enthalpy, and entropy.

Compared to the stable basic states, the amorphous materials are considered to be a metastable intermediate state of liquid-to-solid transition. Its precursor is

Amorphous Nanomaterials: Preparation, Characterization and Applications, First Edition. Lin Guo.

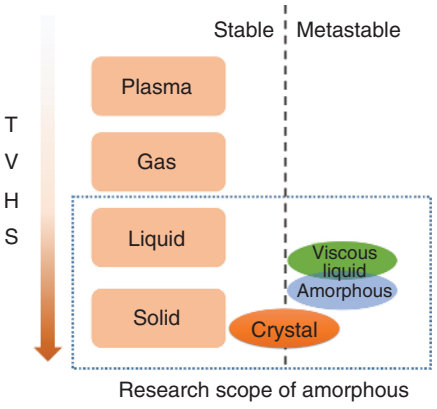

Figure 1.1 The research scope of amorphous materials. *T*, *V*, *H*, and *S* are the abbreviation of temperature, volume, enthalpy, and entropy, respectively.

a viscous liquid (supercooled liquid) that has begun to undergo agglomeration transformation. In addition, the next stage of an amorphous structure is a crystal with a stable periodic arrangement of the constituent elements. Amorphous materials have a phase similar to that of solid, which is embodied as a solid shape. Meanwhile, it has a disordered atomic arrangement similar to that of liquid. Without the fixed atomic pattern as crystal, or the dynamic equilibrium as liquid and gas, amorphous materials are intervened formatted solid with unstable state.

Few materials researches in the past hundred years discussed the amorphous system, most of the studies have used crystal models to construct their perceptions about the formation of materials. A sufficiently sound theoretical system has been established for crystals owing to its accurately and constantly regular atomic arrangements. Compared with these traditional crystalline materials, amorphous materials only have short-range order (SRO) in 1–2 atomic scope, without translational symmetry or rotational symmetry (Figure 1.2). This disordered state makes the amorphous material extremely difficult to be studied both experimentally and theoretically. For example, even though the spherical aberration correction technique and cryo-electron microscopy technique have achieved great development today, the most basic structural or the atomic arrangement of amorphous materials has not been effectively solved.

In both experimental observation and theoretical reasoning, the systematical arrangement and the regular morphology are the basis of scientific research, which

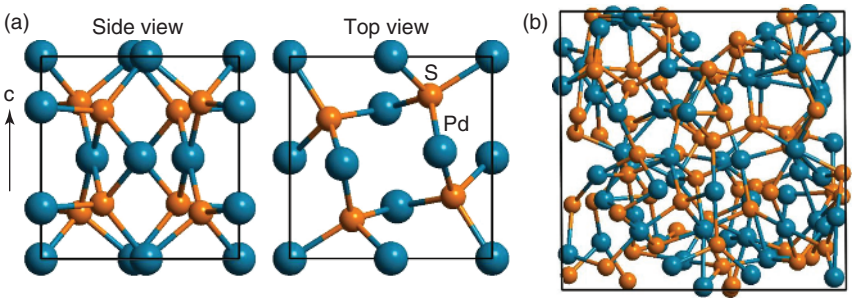

Figure 1.2 (a) The unit cell of PdS from different views. (b) Amorphous structure of eight cells of PdS with a quench cooling in dynamic simulation.

can greatly simplify people's cognitive process. The establishment of crystallography relies heavily on a theoretical system based on mathematics. However, among all the substances that make up the world, the ones with the perfect and regular arrangement are the only very special cases. The chaotic and disordered state is the real cornerstone of the whole condensed matter. From the water on which life depends, to the life itself, to the vast universe, to clusters of atoms tens of thousands of times smaller than bacteria, they are not arranged in regular form. Meanwhile, even though scientists have a complete and systematic understanding on crystal materials, researches are necessary to be carried out with the amorphous counterparts, such as glass, plastics and rubber, to further explore their irreplaceable role in many key areas.

Therefore, increasing attention has been received to the study of amorphous materials. In 1995, *Science* published a special issue: *Through the Glass Lightly*. It invited dozens of top scientists to put forward the ideas for the future of science in the twenty-first century. *Philip Warren Anderson* of Princeton University, who won the 1977 Nobel Prize in Physics for his fundamental theoretical research on the electronic structure of magnetic and disordered systems, believed that the deepest and most interesting unsolved problem in solid states theory is probably the theory of the nature of glass and glass transition. This can be the next breakthrough in the coming decade [2].

Ten years later in 2005, at the commemoration of the 125th anniversary of *Science*, another special issue named *What Don't We Know* invited many of the most influential scientists in various fields to raise 125 scientific problems that need to be solved urgently in this new century. Amorphous material was still listed among them: *What is the nature of the glassy state?* [3] Molecules in a glass are arranged much like those in liquids but are more tightly packed. Where and why does liquid end and glass begin?

At the 9th International Conference on bulk amorphous alloys, held in Xiamen University in 2012, *Takeshi Egami* from Oak Ridge National Laboratory and Tennessee State University, one of the most famous scientists in the field of amorphous materials and physics, concluded the conference by saying, the amorphous field is an area without textbooks, and aspiring young people should actively engage in research areas where textbooks are not yet available.

1.2 Structural Differences between Amorphous Materials and Crystals

According to the arrangement of atoms, modern science classifies solid materials into three categories: crystals, quasicrystal and amorphous materials (Figure 1.3).

1.2.1 Crystals and Quasicrystals

For crystal materials, the atomic arrangement has both translational symmetry and rotational symmetry. In real space, its structural elements (atoms or molecules) are arranged periodically in three-dimensional space according to certain rules. Therefore, periodicity is considered as the most essential characteristic of a crystal

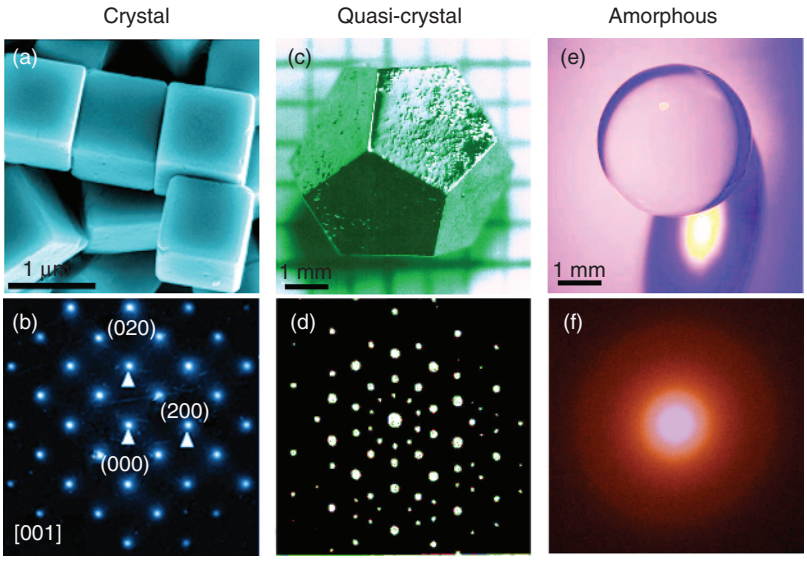

Figure 1.3 The morphologies of three different kinds of solid materials, as well as their corresponding electron diffraction patterns. (a, b) Crystal, (c, d) quasicrystal, and (e, f) amorphous materials. Source: Panels (a, b) Reproduced with permission from Zhang et al. [4]. Copyright 2009, Royal Society of Chemistry. Panel. (c) Reproduced with permission from Fisher et al. [5]. Copyright 2000, Elsevier Inc. Panel. (d) Reproduced with permission from Zhang et al. [6]. Copyright 1985, Taylor and Francis Group. Panel. (f) Reproduced with permission from Yue et al. [7]. Copyright 2015, Science China Press.

structure. Its morphology is mostly manifested as a highly symmetrical polyhedron (Figure 1.3a). In reciprocal space, the periodically arranged structural units of a single crystal material would produce diffraction spots with translation and rotation repeatability. The diffused diffraction spots form diamond patterns centered on the transmission spot (Figure 1.3b). The diamond angle and edge length are the direct transformation of crystal lattice parameters. For polycrystalline materials, the diffraction patterns are sharp diffraction rings centered on the transmission spot.

For quasicrystal materials (Figure 1.3c), the atomic arrangement has rotational symmetry but does not have translational symmetry. Its biggest feature is the symmetry that is incompatible with the traditional crystal space lattice (e.g. fifth symmetric axis). In reciprocal space, it also exhibits similar diffraction patterns as the crystals with regular and diffused diffraction spots (Figure 1.3d). The difference is that there is only rotation regularity and no translation regularity.

Because crystals and quasicrystals have great consistency in structure, modern solid-state physics is also accustomed to classifying quasicrystals together into crystals, i.e. materials with sharp diffraction spots (i.e. periodic arrangement of atoms in real space) as crystals, which have the following characteristics:

(1) The atomic arrangement of crystal units has long-range symmetry and regularity.

(2) Crystals show self-limitation, which means natural-grown crystals without external interference will eventually grow into regular morphologies with high symmetry. It is the geometric basis for the determination of crystals.
(3) Crystals obey the law of constancy of interfacial angles, which is the first law of geometric crystallography, and is also the basis for judging crystals in morphology. It states that the angles between two corresponding faces on the crystals of any solid chemical or mineral species are constant and are characteristic of the species. The law holds for any crystals, regardless of size, locality of occurrence, or whether they are natural or man-made.
(4) Single crystals are anisotropic.
(5) Crystal material has a fixed melting point, and its temperature remains unchanged during the phase transition process.
(6) Crystals can produce X-ray diffraction with specific regularity: It is the basis for modern crystallography to judge whether a substance is a crystal or not.

1.2.2 Amorphous Materials

For amorphous materials, the arrangement of atoms does not have long-range symmetry, neither rotational symmetry nor translational symmetry. In real space, it is generally believed that amorphous materials have SRO only in a few angstroms but do not have LRO. It cannot spontaneously embody regular morphology (except spherical), so amorphous materials are generally known as formless (Figure 1.3e). In reciprocal space, the diffraction pattern does not have any diffraction spots or sharp rings but a circular diffraction halo (Figure 1.3f).

Compared with crystalline materials, the features of amorphous materials can be summarized as follows:

(1) Atoms in amorphous materials only have fixed atomic arrangement rules in the nearest and the next neighbor (<1 nm). The order of the longer range is still unclear.
(2) Because of the long-range disorder of the atomic arrangement, the regular morphology of amorphous materials cannot be obtained by natural growth under non-limited conditions. Therefore, amorphous materials always embody as formless or spherical, driven by surface energy.
(3) Amorphous material is physically and chemically isotropic: the homogeneity of the atomic environment determines that they are not as anisotropic as crystals;
(4) Compared with crystal, the amorphous material is metastable. The amorphous structure will relax to crystalline state at a high-temperature/high-pressure processing.
(5) There is no fixed melting point for amorphous material. It only showed a glass transition temperature. There is no unchanged temperature platform during the phase transition process.
(6) Amorphous material does not produce regular X-ray diffraction. The typical X-ray diffraction pattern of amorphous material is a hump at a specific location, rather than a series of peaks in crystal. Its typical electronic diffraction pattern is diffraction halos.

It can be found that the essential difference between amorphous structure and crystals lies in the LRO, and the similarity lies in the high SRO.

SRO means that amorphous atoms only have a high degree of local correlation, which is the result of the strong chemical bonds between the nearest neighbor (including the next neighbor) atoms to maintain as a fixed component solid. This makes the short-range structure of amorphous materials similar to that of crystals, so the SRO is considered as the structural feature of amorphous materials. A large number of simulations and experiments show that the short-order scale of amorphous crystals should be less than 1 nm.

Common diffraction methods, such as X-ray diffraction and selective electron diffraction, are based on LRO. Therefore, it is difficult to directly obtain short-range informations and images of amorphous material. To investigate the average structure information such as the radial distribution function (RDF), the analysis of atomic ordering of amorphous structures is generally based on the fitting results of diffraction (electron, neutron, etc.) or spectroscopy (X-ray fine structure absorption spectroscopy, nuclear magnetic resonance spectroscopy, etc.).

In 2011, *Chen Mingwei* and *Akihisa Inoue* [8] of Northeastern University used the most advanced spherical aberration correcting transmission electron microscopy (AC-TEM) technology to reduce the diameter of the coherent electron beam to 3 Å for nanobeam electron diffraction (NBED) analysis to replace traditional selective area electron diffraction (SAED). It was found in the experiment that under the 3.6 Å electron beam, the diffraction pattern of amorphous material showed obvious patterning (Figure 1.4). For the first time, the order of the atomic neighbor and the next-nearest neighbor structure of the amorphous alloy was observed.

For crystal materials, the most essential feature is the orderly arrangement of structural elements. It enables crystal research to be based on mathematics and established standard models. The structural or compositional changes could be fully studied rely on the established model. It can also introduce various defects on the basis of the model and establish a material–structure–property relationship to adjust the performance by tuning materials. This kind of systematic research can not only ensure the continuous follow-up of the theoretical research to the explanation of experimental phenomena but also make medium- and long-term predictions of experimental results. The experimental data will be fed back to the theoretical system at the same time, making it complete and more accurate, forming a perfect closed loop between theory and experiment.

Most of the modern structure detection was built based on crystal models. Thus, for amorphous materials without the LRO, the existing analysis methods can only give average atomic information in the statistical category, which is difficult to get the accurate structural information. Therefore, we have not been able to accurately establish the structural model of amorphous materials to sort out the complex long-range interactions beyond the atomic scale. The existed amorphous research studies have established the relationship between materials, kinetic units, and properties in metallic glass systems. Apart from it, many other research studies are still individual results that are only in the experimental observation stage to

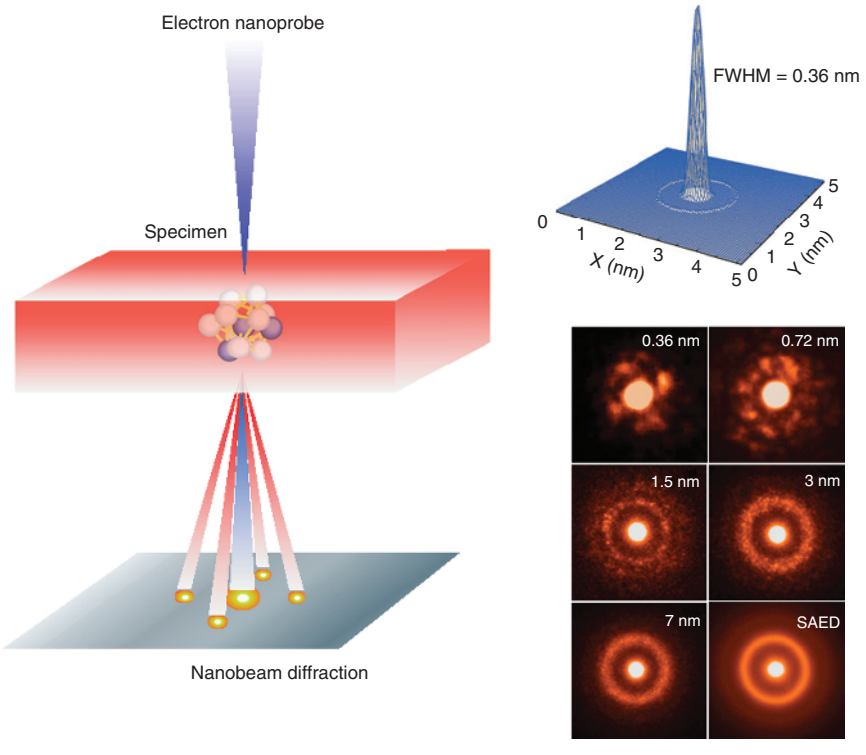

Figure 1.4 The ordered diffraction patterns of amorphous material under coherent electron nanobeam with different diameters. Source: Reproduced with permission from Hirata et al. [8]. Copyright 2011, Nature Publishing Group.

summarize the phenomenological rules. This situation may be improved with the development of the basic physics and experimental characterization technique.

1.3 History of Amorphous Materials

Throughout the history of human science and technology, the breakthrough of new technologies is always accompanied by the discovery of new materials. From ancient bone, stone, porcelain, metal materials to modern high-performance plastics, alloys, micro–nanomaterials, which are still developing, all of them have left a deep imprint in the history of science development. Along with the progressing of scientific theory, the ways of exploring new materials have changed significantly (Figure 1.5). For example, it took thousands of years for human beings to distinguish and adjust the composition of substances. From original bone and stone tools to synthetic bronze and iron tools, we finally obtained engineering materials based on precisely controlled alloys and composites. All of them provide the strong support for the industrialization process of human beings. On the other hand, it took decades to achieve material design and control from macroscale to nanoscale, then to atomic scale, laying a structural foundation for discovery of modern high performance energy storage

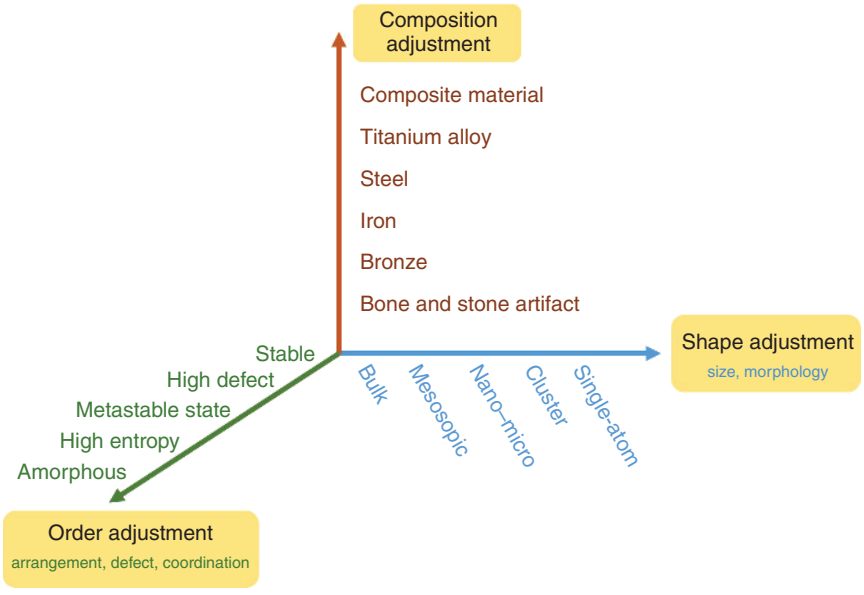

Figure 1.5 The development of materials research in different research orientations.

and conversion materials. This accelerated proceeding was strongly supported by various physical and chemical theories and methods and also supported by the rapid development of characterization methods. On the basis of these development, scientists continue to focus on atomic ordering of the materials, which was expected to further improve the mechanical or catalytic properties of traditional crystal materials. With the help of the most advanced characterization methods, such as spherical AC-TEM and synchrotron radiation X-ray fine absorption spectroscopy, scientists try to adjust the atomic arrangement to obtain new structural materials, such as metastable materials, high-entropy alloys, metallic glass, and amorphous materials.

1.3.1 Establishment of Crystallography

The concept of amorphous is defined in the comparison of crystallography in solid physics. Therefore, the history of amorphous materials should be compared with that of crystallography.

On 25 June 2012, *the General Assembly of the United Nations* adopted a resolution, which proclaiming the year 2014 as the *International Year of Crystallography*. It was named to commemorate *Max von Laue*, who won the Nobel Prize in Physics of 1917, about 100 years ago for characterizing the crystal structure by X-ray. At the same time, it was also commemorated *Johannes Kepler* proposed the famous article *A New Year's Gift of Hexagonal Snow* 400 years ago (1611). He was regarded as the first one to conceptualize the symmetry of crystals which were formed by a regular accumulation of spherical elements. It was considered to be the beginning of the establishment of traditional crystallography.

In 1699, *Nicolas Steno* observed a large number of ores and proposed that the angle between two identical crystal planes of a crystal is always constant, regardless of the size and shape of the crystal plane [9]. It was called *the law of constant angles of the crystal plane*, which was generally recognized as *the first law of crystals*. Prior to the discovery of X-ray, the law laid the foundation for crystal identification, and the word *Crystal* began to be used to describe substances with regular morphologies and fixed angles.

In 1784, *Rene Just Hayuy* proposed that each crystal plane was simply composed of blocks of the same size and shape. The crystal structure was described as a regular three-dimensional arrangement, which was an infinite repetition of cells in the three-dimensional directions. On this basis, *William Hallowes Miller* proposed in 1839 that each crystal plane can be described by three simple integers (h, l, k). That was the *Miller Index*, as was still used today.

At the end of the nineteenth century, from a mathematical point of view, scientists put forward 32-point groups to describe the symmetry of crystal shape and 230 space groups to nominate the symmetry of microelements. Until now, all the geometric structure characteristics of crystallography have been basically perfected.

In 1912, on the basis of *Laue*'s work, *William Lawrence Bragg* proposed the famous *Bragg Formula*, which laid the foundation for the establishment of modern crystallography and the characterization of crystal structure. Later, together with his father *William Henry Bragg*, he quickly characterized the crystal structure of various substances, and established modern crystallography soon [10].

From the development history of crystallography, we can find that the confirmation of crystal structure characteristics depends on the discovery of X-ray, but the establishment of geometric theory in crystallography was far before the characterization of its crystal structure. All the elements in the definition of crystals (crystals are solids with regular periodic repetitive arrangement of internal particles in three-dimensional space) are determined before X-ray discovery. The establishment of crystallography depends more on the mathematics-induced theoretical system and physics-drove technique.

1.3.2 Enlightenment of Amorphous Materials

The use of natural amorphous materials can be traced back to prehistoric times when *Obsidian* was used as a cutting tool. It was a kind of natural glass, formed by the sudden cooling of magma from volcanic lava. With a sharp fracture surface, people used it for cutting as knives.

Because of the simplicity of preparation, glass has become the first amorphous material to be prepared on a large scale. The history of glass preparation can be traced back to the ancient *Babylonians* and *Greeks* 5000 years ago, but it was not until the twelfth century that glass began to be manufactured in batches as an industrial material. Subsequently, the large-scale preparation of transparent glass rapidly promoted the development of science and technology at that time. For example, *Galileo Galilei*'s home-made telescope discovered the uneven surface of the moon in 1609, refuted *Aristotle*'s theory of perfect celestial bodies, and opened the curtain

of modern astronomy; *Isaac Newton* observed the dispersion of light with a prism in 1666. A year later in 1676, *Antonie van Leeuwenhoek*, the father of the microscope, reported observations of red blood cells and microbes, which laid the foundation of modern bacteriology and protozoology in biology. This transparent, stable, and processable material provided fully technical support for the development in many disciplines.

1.3.3 Modern Amorphous Materials 1-Disordered Elementary Substance

The research on amorphous materials is still centered on the comparison with crystals. There are three most used names of disorder materials. *Amorphous* is the earliest and most widely used expression approach. *Glass* is another name of disorder material, especially in the metallic glass field. *Non-crystal* is used in the field of biomineralization.

Amorphous, the most common English expression of disordered materials, originated from Greek, where a is a prefix, indicating no; morphous comes from morph, referring to morphology. The original meaning of this word is material without morphology. It can be seen that before the establishment of modern crystallography, people have known the morphological differences between amorphous materials and crystalline materials to distinguish them.

In 1840, *Justus von Liebig*, the German organic chemist and father of mineral nutrition, described in his classic book *Organic Chemistry in its Application to Agriculture and Physiology* that when sulfur is heated to 160 °C, and then quickly pouring into cold water, sulfur does not crystallize but turns soft and transparent. In this chapter, he wrote "such solid bodies are called amorphous". This may be the earliest report that compared morphologies between amorphous and crystalline materials. *Liebig* then published in the famous medical journal *Provincial Medical and Surgical Journal* in 1840, pointed out that in the extraction of quinine (the main component of antimalarial drugs), quinine obtained from quinoline tincture mainly exists in the form of amorphous [11]. It does not affect its medical value but can greatly enhance the natural quinoline. In 1862, *G. Gore* pointed out in *On the Properties of Electro-Deposited Antimony* that when antimony was electrodeposited, different deposition conditions would lead to two kinds of antimony monomers with different structures, i.e. crystalline antimony and amorphous antimony [12]. He also reported that amorphous antimony showed different physical and chemical properties.

Before the twentieth century, the research on amorphous materials was still in the enlightenment stage. The amorphous materials were mainly found in the preparation of traditional crystal materials. The morphology and properties of this "novel" material were fully compared with traditional crystal materials. Because X-ray has not been discovered and modern crystallography has not been developed, the essential characteristics of the disordered structure have not been discovered. However, these studies are very important for the development of amorphous and crystal. For example, in the study of amorphous sulfur, *Liebig* argued that the softness of amorphous sulfur proved a remarkable fact that the smallest particles that make

up a solid are movable to some extent and not perfectly connected. Modern X-ray crystallography verified that the structure of amorphous sulfur should be a spiral chain structure changed from the S_8 ring of crystal sulfur, endowed it with the same elasticity as rubber. There is no doubt that, the recognition at that time has a great significance in the research of solid science.

The amorphous state of phosphorus is the same as that of sulfur. Similar to the octahedral ring structural unit of sulfur crystal, the structural unit of phosphorus crystal is a regular tetrahedral structure composed of phosphorus atoms (P_4). When the crystal of white phosphorus is melted at a high temperature, P_4 tetrahedron transforms into a chain-connected structure. Then, the amorphous red phosphorus could be obtained by quenching, maintaining its chain-like structure. Recently, amorphous phosphorus has showed great applications in lithium-ion batteries and sodium-ion batteries because of their superhigh theoretical capacity. Similarly, in some polymer materials, when the asymmetry of the atoms connected changes irregularly, the polymer will form a random stereomer, which will behave as an amorphous state. Because of the complexity of the molecular structure of ultralong chains, the atomic arrangement modes of amorphous nonmetallic elements such as amorphous sulfur, red phosphorus, and amorphous polymers are not clear yet. However, they all have glass transition temperatures similar to those of glass, so they belong to the category of amorphous.

1.3.4 Modern Amorphous Materials 2-Metallic Glass

Metallic glass is the most abundant and widely used material in modern amorphous scientific research. Because its main synthetic process and property are similar to traditional glass, it is usually just named as glass.

Learn from the quenching technology in glass and smelt, the earliest attempts were made to condense high-temperature metal vapors (Bi, Ga, Sn, etc.) on ultra-low-temperature (2–4 K) substrates and use large instantaneous temperature differences to stabilize disorder structure. In 1934, German scientist *Krammer* used vapor deposition to obtain the first systematic preparation of amorphous alloys. Subsequently, a variety of metals, including semiconductors such as As and Te, were produced by gas-phase quenching [13]. However, these reports have not attract much attention to amorphous materials because the preparation process is more limited and cannot be extended to other materials.

For metals and alloys, the traditional manufacturing process has long been melting and colling. Because the difference of local structure and density between metal liquids and their solids is very small, it has been thought that metal liquids cannot be overcooled. However, in 1952, *Turnbull David* discovered that metals can be supercooled to 20% of their melting temperature, breaking this conclusion and providing a theoretical basis for the development of amorphous alloys [14]. In 1960, *Pol Duwez* et al. [15] reported in *Nature* that a band-shaped amorphous Au–Si alloy was synthesized by quenching for the first time. He improved the rapid quenching process with a quenching rate of 10^6 K s^{-1}, made the disordered atoms in the metal melt unable to rearrange to crystal, and obtain amorphous material. Since then, metallic glass

has quickly attracted widespread attention, and quenching has also become a basic method for synthesizing amorphous materials.

Especially since 1988, *Inoue* et al. [16] summarized three experimental rules for obtaining bulk amorphous alloys:

(1) The alloy should be composed of more than three alloy elements;
(2) There should be more than 12% atomic size difference between the main elements;
(3) The mixing heat between the elements should be negative.

The preparation of metallic glass were then promoted from low-dimensional materials to bulk amorphous materials. Many excellent characteristics are fully utilized, so it has become a research field with important application prospects.

Metallic glass showes a unique disordered structure, without defects such as dislocations and grain boundaries in the crystal, endowing them with many unique superior properties. For example, in terms of mechanical properties, metallic glasses exhibit high strength, high hardness, high wear resistance and corrosion resistance, high fatigue resistance, low elastic modulus, large elastic strain limit, etc. Thus, metallic glass possesses broad potential applications in the fields of engineering mechanics, biological sciences, and aerospace. For example, the amorphous alloys in almost every alloy system have achieved several times higher strength than the crystalline material. In 2011, *Zhang Tao* et al. [17] developed a CoTaB ternary alloy with a compressive strength of 6.0 GPa and a specific strength of 650 Nm g^{-1}, which reached the highest record for the strength of metal materials.

At the same time, the introduction of micro/nanoscale heterogeneous structures or the second phase in bulk amorphous materials could significantly improve the toughness of amorphous materials. In 2007, according to Poisson's ratio criterion, *Wang Weihua* et al. [18] adjusted the composition of the Zr–Cu–Ni–Al metallic alloy and prepared an amorphous alloy system with a multilevel microscale heterogeneous structure, which showed high strength (1.7 GPa) and very large compressive plasticity (strain > 150%). These amorphous alloys can even be bent to 90° at room temperature (Figure 1.6a–d). In 2008, *WL Johnson* et al. [19] improved the composition of the amorphous alloy and controlled the content of each component to synthesize the Zr–Ti–Nb–Cu–Be metallic alloy with a micron-scale precipitated second phase. For the first time, the fracture deformation has been increased to more than 10%, and up to 14%. At the same time, the fracture toughness of the amorphous alloy reached 170 MPa $m^{0.5}$, indicating an excellent toughness (Figure 1.6e–g).

In addition to the mechanical properties, another key point for amorphous materials attracting widespread attention is the application in catalysis. Amorphous materials exhibit high activity surface with unsaturated coordination sites and unique local environment with uniform chemical states and atomic structures. Whether in theoretical research as a model catalyst or performance exploration as a practical catalyst, the study of amorphous materials is significant. For example, in 1925, *Constable* systematically discussed the difference between amorphous materials and crystalline materials during the process of catalytic decomposition by calculating the active center and pointed out that amorphous materials may

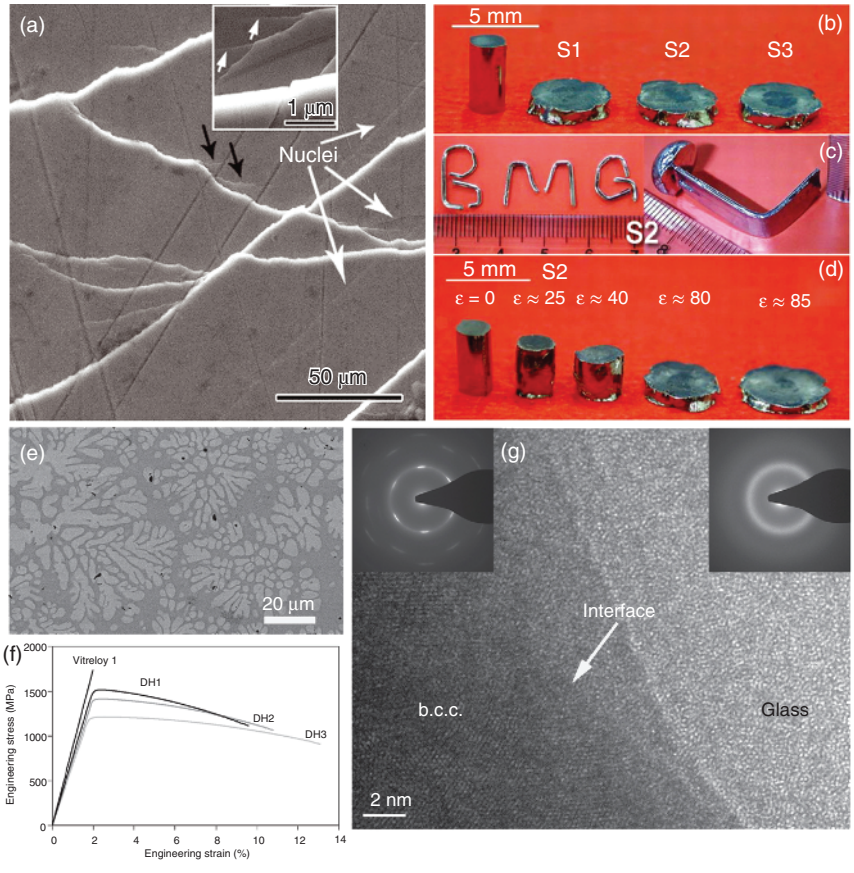

Figure 1.6 Amorphous metal with micro/nanomicrostructure. (a–d) Amorphous alloy with micron-scale heterogeneous structure and its mechanical properties and (e–g) amorphous alloy with micron-scale second phase and its mechanical properties. Source: Panels (a–d) reproduced with permission from Liu et al. [18]. Copyright 2007, AAAS. Panels (e–g) reproduced with permission from Hofmann et al. [19]. Copyright 2008, Nature Publishing Group.

have higher performance [20]. In 1980, at the Seventh International Conference on Catalysis, *Gerard V. Smith* of the University of Southern Illinois at Carbondale [21] firstly demonstrated amorphous alloys as a new system for catalytic reactions. In 1983, *Brower* et al. reported in *Nature* that Pd-based metallic glass has a higher selectivity than crystalline Pd in hydrogenation reactions [22], which gradually opened the prelude to the research of amorphous alloys in the field of catalysis.

However, because of the low specific surface area, amorphous alloys always failed to fully realize the true activity. For example, in the degradation of direct blue, the degradation ability of iron-based amorphous alloy (46 h) is not significantly improved, compared to pure iron (>50 h). However, after grinding the amorphous alloy to the micron level, it can completely degrade the same concentration of

dye in a short period of 1 h [23], showing the important application prospects of micro–nanoamorphous materials in the field of catalysis.

1.3.5 Modern Amorphous Materials 3-Nontraditional Amorphous Nanomaterials

The polymerized amorphous structure represented by amorphous sulfur and polymers, and the multielement metallic amorphous structure represented by metallic glass together constitute the traditional amorphous materials. They demonstrate the standard structure characteristics of amorphous represented by glass, which is the existence of glass transition temperature. The former amorphous structure is formed due to the complexity of the basic chain structure, the flexibility and the homogeneous site would confuse the connection of monomer. The construction of latter amorphous structure is due to the hindrance of multiple components during quenching, which prevent the atoms to move to the regular position in crystal.

In addition to these two strategies, by manipulating the synthesis step and introducing additional factors to disrupt the regular arrangement, it is possible to obtain amorphous nanomaterials whose compositions are basically the same as their crystals, but whose structure is chaotic. These materials also have a random atomic arrangement. Here we simply summarize some methods and will describe them in chapter 4 to chapter 8.

1. For most metal, the amorphous structure of a single elemental metal cannot be easily obtained by quenching. By means of chemical synthesis in solution, the strong reducing agent $NaBH_4/KBH_4$ could be used to rapidly reduce the transition metal from the solvent. This process is similar to the fast quenching of metallic glass in which metal atoms are frozen at the disordered arrangement in solution. Apart from it, the residual small atoms B hinders the nucleation and regular arrangement of metal atoms, producing amorphous M–B nanomaterials.
2. For Si and Ge, which are the most important materials in the semiconductor field, their industrial amorphous materials cannot be obtained by the quenching method. That was because of the distinct difference between the six-coordinated structure in the liquid phase and the four-coordinated structure in the solid phase. Therefore, the preparation of amorphous silicon relies on gas-phase synthesis methods. However, the directly obtained amorphous silicon from gaseous Si exhibit a high concentration of dangling bonds. The product with abundant defects shows no practical industrial value. Thus, amorphous Si always replace to amorphous silicon–hydrogen alloy obtained from the decomposition of the precursor silane (SiH_4) by the vapor deposition method or the glow discharge method. Hydrogen atoms can saturate the dangling bonds, thereby reducing the concentration of the paramagnetic center by four to five orders of magnitude. In addition to the advantage of simple and convenient, the amorphous silicon can be easily adjusted to a p-type or n-type semiconductor mixing a small amount of borane (BH_3) or phosphane (PH_5).
3. Amorphous nanomateriasl could also be achieved in solution by adjusting the decomposition process of the precursor to obtain a partially decomposed product

in which the obtained amorphous structure is stabilized by the remaining atoms/coordination groups. For example, as the most polar solvent, water molecules can easily coordinate with cations to form ionic hydrates, which is widely used in the formation of amorphous oxides, hydroxides, et al. For example, in the preparation of titanium dioxide in solution, the amorphous hydrated oxidation state is usually obtained first. In the field of biomineralization, amorphous calcium carbonate is the most important intermediate state in the mineralization process. Its formation also depends on the water carried out from the solution. Its composition is mostly understood as hydrated calcium carbonate. The addition of Mg ions, polyacids, amino acids, etc., which mimic the biological environment, can effectively improve the stability of its amorphous structure.

4. In addition to the introduction of additional components, taking away the structural atoms to construct an unsaturated environment can also destroy the regular atomic arrangement of the original structure to obtain an amorphous structure. For example, the classic semiconductor material titanium dioxide can change to black/blue titanium dioxide with a large number of oxygen atoms missing under a strong reducing atmosphere. Due to the abundant oxygen defects, its surface usually exhibits an amorphous structure. This is a universal method for many transition metal oxides like ZnO, CeO_2, SnO_2.
5. For ultrasmall/ultrathin nanomaterials, the position of the atoms on the surface could be affected by surface ligand. The design of surface ligands could reduce the order of atoms to construct amorphous structures. A large number of amorphous noble metal particles and amorphous ultrathin two-dimensional materials could be achieved through this method.

1.4 Growth Mechanisms of Amorphous Nanomaterials

1.4.1 Classical Nucleation Theory

In classical nucleation theory, the formation of solid particles in solution underwent two phases: nucleation and growth. In 1950, *Lamer* proposed a nucleation mechanism in the energy category based on the sulfur colloid synthesis process in solution, which is still one of the most significant self-consistent nucleation mechanisms [24].

At the nucleation stage, the transition from the liquid phase to the solid phase occurs. There are two kinds of energy changes during this transition. One is the volume free energy (ΔG_V), which is defined as the decrease of the free energy of atoms during the transition from the free state in the solution to the crystal nuclei. The other is the surface free energy (ΔG_γ), which demonstrates the increasing of the system's free energy from the generated new interfaces. If the newly generated nucleus is regarded as a sphere, the former is a positive correlation function of volume (the cube of the radius r), $\Delta G_V = 4/3\pi r^3 \cdot \rho RT \ln(c/c_0)$, where c_0 is the concentration of the supersaturated solution. The latter is a positive correlation function of the surface area (the square of r), $\Delta G_\gamma = 4\pi r^2 \cdot \gamma_{s-l}$. This makes a critical radius r^* in the nucleation process, which exhibit a negative correlation with the

concentration of the supersaturated solution. Therefore, a higher concentration supersaturation lead to smaller nucleation radius.

Taking the formation of metal materials as an example. During the nucleation stage, the original precursors are reduced to metal atoms with external stimulation (reductive agent adding, heating, irradiating, etc.). These atoms will be the modular units for the subsequent construction of the crystal structure. With the decomposition of the precursor, the concentration of metal atoms increases. Once the atomic concentration exceeds the minimum supersaturation point, the atoms exhibit a tendency to aggregate spontaneously to reduce surface energy (surface energy is higher than volume energy before the critical radius). In somewhere of the solution, affected by thermodynamic fluctuations, initial nuclei would instantaneously aggregate by atoms and separate from solution. Once the initial clusters are formed, these seeds then accelerate their growth by adsorbing free atoms in the solution, leading to the decrease of the concentration of atoms in the solution. At this time, the decomposition of the precursor is still continuing and the free atom is continuously added. If the atomic concentration drops rapidly below the minimum supersaturation, no additional nucleation will occur and the resulting product will exhibit a monodisperse size. With the continuous supply of atoms through the precursor decomposition, the initial nucleus will grow into nanocrystals with an increasing size, until achieving an equilibrium state between the surface atoms on the nanocrystals and the free atoms in the solution.

Once the seed is formed, its size would increase by continuous addition of free atoms. From the perspective of chemical deposition, when atoms are added to a solid surface, the atoms diffuse on their surface until they encounter a step position where they can be incorporated. At the same time, as particle size increases, the volume free energy reduces (favorable for growth) and surface energy increases (favorable for dissolution). The dynamic interaction of growth and dissolution leads to the formation of anisotropic nanocrystal with specific morphology. With the development of in-situ electron microscopes, the structure and shape of seeds and nanocrystals produced at different stages could be observed. Therefore, a large number of studies have reported to explore the relationship between the initial seed and the final nanocrystal. After the nucleation and growth of the seed, the generated new nanocrystal will still go through complex evolution, such as Ostwald ripening, Kirkendall diffusion, oriented attachment, etc. Finally, nanoparticles with specific structure and morphology are obtained.

A typical synthesis method developed under the guidance of this theory is the hot injection method proposed by *A. P. Alivisatos* and *Peng Xiaogang* of the University of California [25]. Cold stock solution is quickly injected into the rapidly stirred, hot solvent, and a large number of crystal nuclei are instantaneously generated. The monomer concentration is rapidly reduced below the supersaturation threshold, and further nucleation is suppressed. This method separates the nucleation from growth, yielding particles of one size. It is a classic method for preparing monodisperse nanoparticles, especially quantum dots.

However, the theory is still an ideal model under extreme conditions, while the actual reactions and processes that occur in solution are far more complicated.

Professor *David W. Oxtoby* of the University of Chicago, author of the famous Chemistry textbook "*Principles of Modern Chemistry*" in 1998 [26] stated that "Nucleation theory is one of the few areas of science in which agreement of predicted and measured rates to within several orders of magnitude is considered a major success" to comment the deficiencies of the classic nucleation growth theory.

For example, apart from decomposition to metal atoms, the precursors could also firstly assemble to aggregation and directly decompose to clusters. In the growth stage of the nucleus, the atomic adding mode is not the only growth way. The nucleus and nanocrystals can also directly merge into larger particles through attachment.

1.4.2 Multistep Transformation Mechanism with Amorphous Participation

In the traditional growth mechanism, the formation and growth of amorphous structures could not be explained, and a suitable new mechanism is desired. The rapid development of biomineralization research provides a theoretical basis for explaining the formation of amorphous materials in solution.

Biomineralization is a natural synthesis process, which use organic templates to control the growth of the inorganic phase. For example, amorphous calcium carbonate (ACC) have been particularly well studied as precursor in the biomineralization of invertebrates, such as mollusk shells and sea urchin spines (Figure 1.7). The high degree of crystallographic control is achieved from amorphous precursor in the biologically formed crystals. Scientists hope to be able to extrapolate the knowledge gained from such model systems and apply it to other inorganic systems to regulate crystallographic properties for advanced materials applications.

A large number of observations on biomineralization have found that the formation of many biomineral go through an amorphous precursor, which cannot be explained by the classical crystallization theory. Thus, the biomineralization pathway may be inconsistent with the traditional nucleation theory. *Laurie B. Gower* of the University of Florida and *Helmut Cölfen* of the University of Constance have proposed a multistep growth mechanism based on biomineralization for this problem.

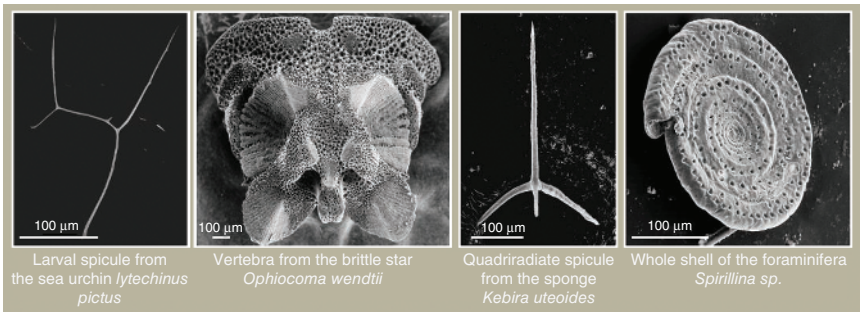

Figure 1.7 Different organisms likely use the same strategy to generate diverse skeletal parts from crystals that arise from a transient amorphous calcium carbonate phase. Source: Reproduced with permission from Weiner et al. [27]. Copyright 2005, AAAS.

Gower pointed out [28] that the formation of solids in solution requires a multistep process, with multiple metastable states in it. The *Ostwald–Lussac* rule specifies that if a solution is supersaturated with respect to more than one phase, the more soluble (least stable) phase is often the first phase to form. Therefore, a highly unstable liquid precursor (polymer-induced liquid precursor) is formed first in the solution, and then it transform into an amorphous phase with unstable structure, followed by successively crystalline phases with decreasing energy and gradually increasing stability.

Cölfen proposed the theory of stable prenucleation cluster concept [29]. He pointed out that when the supersaturation of the solution reached a certain threshold, the ions meet in solution based on stochastic collisions and formed a stable pre-nucleation cluster. He experimentally showed that the clusters can be understood as a solute in the solution, without a phase interface. Its structure may not be related to the macroscopic bulk. In this process, the entropy increase caused by the release of ion hydration water is the driving force for the formation of the cluster. Crystalline could be directly nucleated from stable pre-nucleation clusters under certain conditions.

In general, the possible continuous phase transition of the biomineralization process from solution to crystal was shown in Figure 1.8. The process of biomineralization generally involves the participation of amorphous precursors, which makes its research very important for the formation mechanism of amorphous materials. The entire formation process of crystal $CaCO_3$ is clearly divided into two phases: the termination of the liquid phase and the generation of the solid phase. This process may provide an answer for the former question in the commemoration of the 125th anniversary of *Science*, where and why does liquid end and amorphous begin? If our target product is amorphous rather than crystalline, the reaction needs to be truncated at some stage in the process.

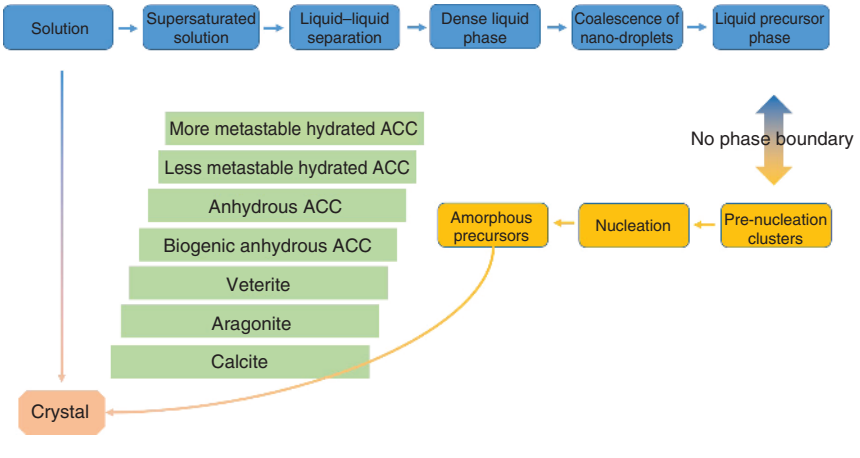

Figure 1.8 A reported growth mechanism of amorphous nanomaterials in solution.

1.4.3 Complex Growth Process in Solution

Using in-situ imaging techniques (scanning electron microscope, transmission electron microscope, and atomic force microscope) to characterize the growth process, *James J. De Yoreo* of Pacific Northwest National Laboratory summarized the existing crystal growth modes and proposed the crystallization by particle attachment (CPA) theory [30]. He pointed out that, in addition to the monomer-by-monomer addition described in classical models, crystallization by addition of particles, ranging from multi-ion complexes to fully formed nanocrystals, is now recognized as a common phenomenon. Crystallization can occur by attachment of a wide range of species more complex than simple ions. These higher order species are collectively named as particles. They are broadly defined to include multi-ion complexes, oligomers (or clusters), and nanoparticles, whether crystalline, amorphous, or liquid. Compared to traditional growth models, the growth, assembly, and transformation of these particles seem to be the actual route in the formation of crystal particles.

In a real crystallization process, even if only considering the reaction mechanism of a specific system, multiple growth mechanisms can occur simultaneously. It depends on the values of global parameters such as supersaturation, local factors that include interface curvature, and materials parameters such as phase stability versus particle size. The growth process may include the traditional direct connection of atoms, the connection of crystal clusters, the connection of amorphous particles and the subsequent crystallization or maturation, and the oriented or non-oriented connection of crystal particles and recrystallization. Ostwald ripening can occur in all particles to provide free radicals for the main particles. At the same time, twins, stacking faults, and dislocations can result from the attachment of crystalline particles. It can be found that the predictive understanding of the theory of particle-connected crystallization is helpful for the further development of amorphous nanomaterial design and synthesis.

1.5 Summary and Outlook

Although many studies have confirmed the significance of amorphous nanomaterials, their development is still in their infancy. For example, it is widely believed that amorphous materials have SRO, but their atomic arrangement cannot be accurately defined, even with the help of AC-TEM. Intense debates regarding whether they could exhibit medium-range ordering at the nanometer scale or even LRO are still ongoing. In addition, compared with the highly ordered arrangement of atoms in crystals, the atomic disorder of amorphous materials endows them highly unsaturated centers on the surface. If the unsaturated centers were all active sites, the catalytic performance would be improved by an order of magnitude. However, the reported research has not achieved such an improvement. Therefore, as an emerging discipline, the study of amorphous nanomaterials is of great significance.

At the same time, the synthesis of amorphous nanomaterials is only in the exploration stage. Most of the as-reported synthesis method is incomprehensive and non-systematic, while systematical and universal methods are needed. Limited by the isotropic feature of amorphous structure, the morphology of naturally growing amorphous materials are spherical particles. If 1D materials are expected, an external force must be applied to confine the growth direction, for example, electrospinning and chemical vapor deposition. The preparation of 3D materials with regular morphology can only rely on the hard template method and then etching the template to obtain a polyhedron frame or shell. The template-free self-growth of amorphous materials with specific and programmed morphology is extremely difficult. Thus, researches on the design and synthesis of amorphous nanomaterial should be comprehensively reviewed to summarize the laws. In addition, the study of the relationship between structure and related properties of the amorphous nanomaterials and their potential applications will greatly promote the development of amorphous nanomaterials.

References

1 Hilden, L.R. and Morris, K.R. (2004). Physics of amorphous solids. *J. Pharm. Sci.* 93: 3–12.
2 Anderson, P.W. (1995). Through the glass lightly. *Science* 267: 1615–1616.
3 Couzin, J. (2005). What is the nature of the glassy state. *Science* 309: 83–83.
4 Zhang, D.-F., Zhang, H., Guo, L. et al. (2009). Delicate control of crystallographic facet-oriented Cu_2O nanocrystals and the correlated adsorption ability. *J. Mater. Chem.* 19: 5220–5225.
5 Fisher, I.R., Kramer, M.J., Islam, Z. et al. (2000). Growth of large single-grain quasicrystals from high-temperature metallic solutions. *Mater. Sci. Eng. A* 294: 10–16.
6 Zhang, Z., Ye, H.Q., and Kuo, K.H. (1985). A new icosahedral phase with m35 symmetry. *Philos. Mag. A* 52: L49–L52.
7 Yue, Y., Zheng, K., Zhang, L., and Guo, L. (2015). Origin of high elastic strain in amorphous silica nanowires. *Sci. China Mater.* 58: 274–280.
8 Hirata, A., Guan, P., Fujita, T. et al. (2011). Direct observation of local atomic order in a metallic glass. *Nat. Mater.* 10: 28–33.
9 Steno, N. (1669). *De solido intra solidum naturaliter contento Dissertationis Prodromus*. Florence: sub signo Stellae.
10 Bragg, W.L. (1913). The structure of some crystals as indicated by their diffraction of X-rays. *Proc. R. Soc. London Ser. A* 89: 248–277.
11 Liebig, B. (1840). On amorphous quinine: as it exists in the substance known in commerce as quinoidine. *Prov. Med. Surg. J.* 10: 265.
12 Gore, G. (1862). On the properties of electro-deposited antimony. *Proc. R. Soc. Lond.* 12: 323–331.

13 Buckel, W. and Hilsch, R. (1954). Einfluß der Kondensation bei tiefen Temperaturen auf den elektrischen Widerstand und die Supraleitung für verschiedene Metalle. *Zeitschrift für Physik* 138(2): 109–120.

14 Turnbull, D. (1950). The supercooling of aggregates of small metal particles. *JOM* 2: 1144–1148.

15 Klement, W., Willens, R., and Duwez, P. (1960). Non-crystalline structure in solidified gold–silicon alloys. *Nature* 187: 869–870.

16 Zhang, T., Inoue, A., and Masumoto, T. (1991). Amorphous Zr–Al–TM (TM=Co, Ni, Cu) alloys with significant supercooled liquid region of over 100 K. *Mater. Trans., JIM* 32: 1005–1010.

17 Wang, J., Li, R., Hua, N., and Zhang, T. (2011). Co-based ternary bulk metallic glasses with ultrahigh strength and plasticity. *J. Mater. Res.* 26: 2072–2079.

18 Liu, Y.H., Wang, G., Wang, R.J. et al. (2007). Super plastic bulk metallic glasses at room temperature. *Science* 315: 1385–1393.

19 Hofmann, D.C., Suh, J.Y., Wiest, A. et al. (2008). Designing metallic glass matrix composites with high toughness and tensile ductility. *Nature* 451: 1085–1094.

20 Constable, F.H. (1925). The catalytic action of copper. Part VII. A study of the effect of pressure on the rate of dehydrogenation of alcohols. *Proc. R. Soc. Lond.* 107: 279–286.

21 Smith, G.V., Brower, W.E., Matyjaszczyk, M.S., and Pettit, T.L. (1981). Metallic glasses: new catalyst systems. *Stud. Surf. Sci. Catal.* 7: 355–363.

22 Brower, W., Matyjaszczyk, M., Pettit, T., and Smith, G. (1983). Metallic glasses as novel catalysts. *Nature* 301: 497–499.

23 Wang, J.Q., Liu, Y.H., Chen, M.W. et al. (2012). Rapid degradation of azo dye by Fe-based metallic glass powder. *Adv. Funct. Mater.* 22: 2567–2570.

24 LaMer, V.K. and Dinegar, R.H. (1950). Theory, production and mechanism of formation of monodispersed hydrosols. *J. Am. Chem. Soc.* 72: 4847–4854.

25 Peng, X., Wickham, J., and Alivisatos, A.P. (1998). Kinetics of II-VI and III-V colloidal semiconductor nanocrystal growth: "focusing" of size distributions. *J. Am. Chem. Soc.* 120: 5343–5344.

26 Oxtoby, D.W. (1998). Nucleation of first-order phase transitions. *Acc. Chem. Res.* 31: 91–97.

27 Weiner, S., Sagi, I., and Addadi, L. (2005). Choosing the crystallization path less traveled. *Science* 309: 1027–1028.

28 Gower, L.B. (2008). Biomimetic model systems for investigating the amorphous precursor pathway and its role in biomineralization. *Chem. Rev.* 108: 4551–4627.

29 Gebauer, D. and Colfen, H. (2011). Prenucleation clusters and non-classical nucleation. *Nano Today* 6: 564–584.

30 De Yoreo, J.J., Gilbert, P.U., Sommerdijk, N.A. et al. (2015). Crystallization by particle attachment in synthetic, biogenic, and geologic environments. *Science* 349: 498.