REVIEW

CHEMICAL BONDS IN MOLECULAR AGGREGATION – FROM DRINKING WATER TO NANOCOMPOSITES

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Abstract: Atoms in a small molecule are assembled by covalent bonds. Small molecules or ionic species tend to aggregate to larger units like macromolecules or crystals *via* various attractive forces categorized as noncovalent bonds (nonCBs). No living creatures can exist without water, whose moleculs are aggegated *via* hydrogen bonds, one of the most important nonCBs. Interfacial phenomena are associated with adsorption, mostly mediated by nonCBs at the boundaries between dissimilar counterparts. Aggregation of biomolecules is the origin of living organisms. Unfavorable aggregation states of biomolecules lead to diseases. Functions of nanocomposite materials depend on the states of molecular and/or ionic aggregation with nonCBs. Crystal engineering aims at controlling aggregation of organic and inorganic components to enable innovative nanostructured materials. This tutorial review focuses on some typical aspects of crossdisciplinary features of nonCBs in an attempt to trigger new insights in materials-oriented chemical science and engineering.

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1. Introduction

`All matters comprise atoms. An interatomic interaction within a simple molecule is explained by sharing one or more electrons in the outermost or valence orbitals surrounding participating nuclei. The atomic interaction in such a small molecule is defined as covalent bonding [1, 2]. All other atomic interactions belong to noncovalent interactions or noncovalent bonds (nonCBs). Among many nonCBs, van der Waals interaction and hydrogen bonds (HBs) are strictly defined by IUPAC [3, 4]. However, categorization of nonCBs are so broad and diverse that not all of them are defined unequivocally [5-7]. Strength of a chemical bond, regardless of covalency or noncovalency, is conventionally ranked by the enthalpy of atomization of associated aggregates [8, 9]. Actually, the physicochemical content of bond strength is much more complicated than those definable by thermodynamic terminology [10] as extensively discussed [11-15]. Basics of chemical bonds are not fixed at the textbook level when we strictly account the roles of electronegativity and atomic size [16]. The concept of chemical bonds is based on quantum mechanics and discussed in terms of the bonding and antibonding electrons [17, 18]. By the same token, there is an exact definition of bridge bonds in terms of the electron distribution function [19]. Detailed discussion of the theoretical aspects of nonCBs based on quantum physics will not be covered in the present text.

Aggregation of small molecules into larger units occurs in many different ways, e.g., clusters, supra- or macromolecules, biological cells, colloidal dispersing units or crystals. Interactions necessary for any molecular aggregation are dominated by nonCBs [20, 21]. Concepts of molecular aggregates discussed in this text play a crucial role on our daily life, including cooking (generally in food preparation), medical care, or materials technology for high-tech products such as microelectronic devices. Associative processes of small chemical construction units frequently proceed *via* a self-assemblage along with the principles of thermodynamic stabilization [22-25]. The concept of nonCBs is also significantly associated with coordination chemistry, centered by the concept of ligands [26-28]. Simplest inorganic ligands are oxide (O^{2-}) or hydroxide (OH^{-}) ions, when we observe conventional oxide crystals as the aggregates of inorganic coordination units, e.g., SiO_4 in SiO_2 solids, or TiO_6 in TiO_2 crystals. Ionic bonds dominating many popular crystals like NaCl are also categorized to nonCBs [15, 29].

The specific topics with nonCBs will be displayed in the next chapter. Introduction to many other working nonCBs are discussed by referring to interfacial phenomena, colloids and polymers as well as heterogeneous catalysis in chapters 3 and 4. Biomolecular aggregates like proteins are discussed in chapter 5. Chapter 6 exhibits crystal engineering and nanocomposite materials with extended discussion on the roles of nonCBs. In this last chapter, emphasis is laid on the interaction among inorganic and organic components, which may lead to more sustainable materials and their processing.

2. Noncovalent bonds

Noncovalent interactions are described in terms of electrostatics and polarization, in conjunction with Coulombic interaction of molecules [5, 6, 30]. Whether or not all the noncovalent interactions are defined as chemical bonds is controversial, particularly for van der Waals interaction. Microscopically, nonCBs are also understood as an interaction between energetics of σ- and π-hole and the "surface" of molecules [31]. Hydrogen bonds are compared

with other similar nonCBs like chalcogen-, halogen-, or tetrel bonds in terms of electron donor and acceptor in a periodical table [5, 6, 20, 30]. Tetrel bonds, centered by Group 14 atoms like C, Si, Ge [20] are similar to HBs and can be distinguished from genuine HBs only by detailed spectroscopic studies [32].

Occurrence of HBs is basically associated with charge transfer between dipoles [33-35]. There are wide variety of bond strenth among HBs, as Dejiraju pointed their borderless nature under the concept of hydrogen bridge [36]. As guided in Fig. 1, a balance of electrostatics, van der Waals nature, and covalency determins the charactger of HBs. Hydrogen bonds are expressed more generally as hydrogen bridges, X-H-A, where the hydrogen atom (H) abridges two neighboring atomic species, X, and A. The X-H-A bridging bond is explained by introducing three limits of HBs, i.e., covalent limit (40 kcal/mol), electrostatic limit (15 kcal/mol) and van der Waals limit (0.5 kcal/mol) [36]. Corpinot later introduced this concept in a wider framework in his tutorial review [37].
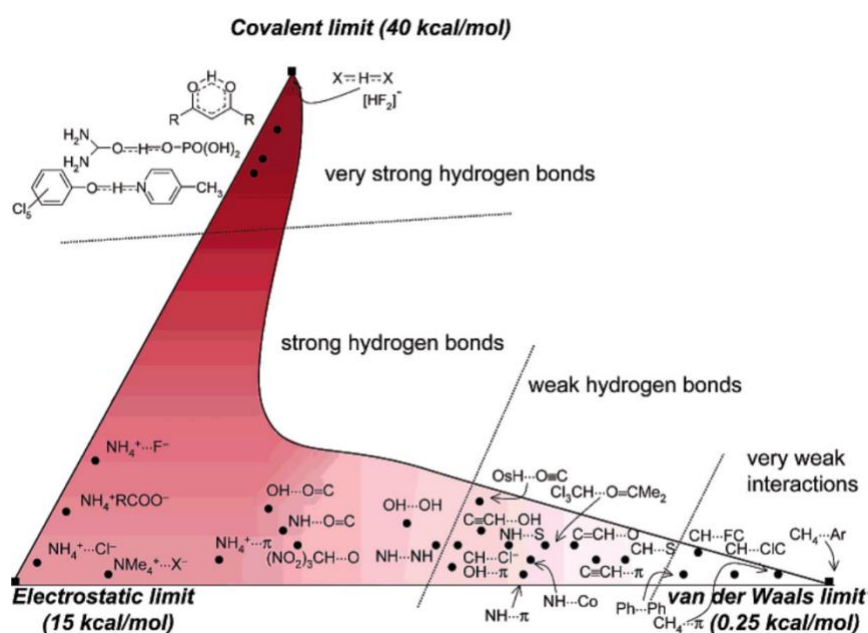
Fig. 1. Categorization of hydrogen bonds [29] (see text for details)

Figures 2a and 2b also demonstrates that HBs are not only simple bonds between two small molecules by s-electrons [38] but also p-electrons can participate. Hydrogen bonding form networks as well, which play an important role on the natural polymers like starch or cellulose [39, 40]. Multiple HBs bring about supramolecular complexes as shown in Fig. 2c [41]. In an aqueous solution containing ionic species, HBs play a particularly important role [42]. Excellent reviews by Scheiner [43] and Pairas et al. [38] exhibit physicochemical details of HBs. The unusually high boiling point of water, 373.2 K, with its atomic mass unit (amu) as small as 18.0 Da, compared with those of organic molecules at around similar molecular size, e.g., 111.6 K with 16.0 Da. The difference symbolizes the role of HBs in our daily life due to the high density of HBs in condensed phases (liquids and solids). The role of HBs

in our daily life is diverse, for instance, gelation of the colloids [44]. A non-flowable gel is formed even with a water content more than 97% in the case of edible jellies (dessert). Their smooth texture would be impossible without HBs.
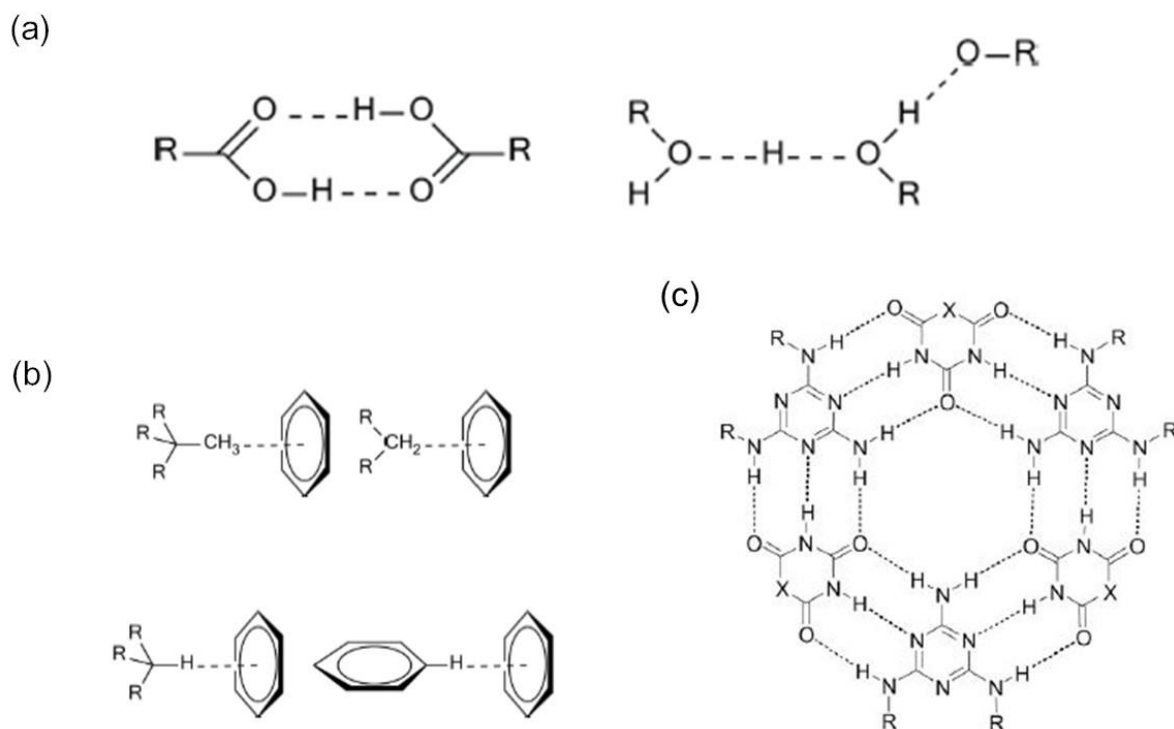
Fig. 2. Representative features of HBs. (a) HBs between same or different molecules [38]; (b) CH–p HBs [38]; (c) Multiple HBs to supramolecular structure [41]

What we observe in kitchen during cooking and baking is predominated by structural change of starch and denaturization of proteins. For both processes, reconstruction of the HBs plays a chief role. The subunits of starch, i.e., amylose and amylopectin [45] are rearranged during cooking to make row grains edible. Associative forces within and between these subunits are based on HBs [46, 47]. Most of the meat is heated in the kitchen to denature proteins with widely varying amount of liquids in the pot or pans. What is happening there is the changes in the three-dimensional structure of the polypeptide chains. This is usually coined as denaturation of proteins [48, 49]. Basics of HBs with their related materials are discussed in tutorial reviews [50-52]. Molecular crystals and their design are closely related to HBs [37]. Related issues will be discussed in depth in Chapter 6.

Hydrogen bonds are most important in biosciences [38, 53]. No living creatures can exist without water and associated HBs [54]. Indeed, water molecules with their intrinsic attractive interaction by HBs are active constituents of biological cells [53]. Their roles include those of solvent, hydration and "joints" in many biomolecular units. It is important to note that similar chemical issues need consideration in medicine or pathology [55, 56]. Related topics will further be referred to Chapter 5. Basics of functional materials are intensively associated with HBs with various interaction of other chemical bonds. Mechanically interlocked molecular frameworks and larger structural units, called metal organic frameworks (MOFs), are the

concepts related to functional materials associated with HBs [57, 58]. These topics will be discussed in more detail in Chap. 6 with the interests in the functional materials processing.

3.   Adsorption and interfacial phenomena

Adsorption is one of the fundamental phenomena in surface and interface chemistry. It plays a crucial role in diverse categories from environmental issues to chemical industry. The interaction between the adsorbate, the chemical guest species which are going to the host substrate species, i.e., adsorbent is generalized as adsorption. It is divided into two categories. One is physical adsorption (physisorption) driven by van der Waals force, and the other is chemical adsorption (chemisorption), where chemical bonds are formed between adsorbate and adsorbent [59, 60]. While van der Waals interaction is occasionally categorized as a weak bonding, the role of the electrons is only a very weak interaction due to their synchronized movement belonging to corresponding atomic parties. The interaction is either due to weak London dispersion forces or a bit stronger dipole-dipole forces [61] without participation of chemical bonds in a conventional context. Therefore, only chemisorption is considered further in this chapter.

Basics of chemisorption have been intensively studied particularly for neutral gas molecules on metal single crystals [60]. The intensity of the host – guest interaction is evaluated by the adsorption energy, i.e., the energy needed to separate the adsorbate from the adsorbent. It can be quantified as the heat released during adsorption and measured by calorimetry [62] from the combination of atoms on single crystal with defined surface described by Miller indices. Such a basic study is important for the application to much more complicated organic molecules on the "dirty" substrates, e.g., defective powder surfaces [63]. The interaction or bonding between adsorbents and adsorbates varies from covalent to a variety of nonCBs [60]. One of the representative mechanisms, the Langmuir-Hinshelwood type, is based on the energetically equilibrated states between the guest and host species by forming a kind of nonCBs. As a consequence, adsorbed species may be deformed or dissociate due to mismatches of molecular bond length and the interatomic spacing on the substrate. This frustrated state of the adsorbed species is less stable and more active, so that it triggers heterogeneous catalytic reactions [64].

Surface active agents or surfactants are associating two nonfriendly materials species, i.e., water affinitive (hydrophilic) and water repelling (hydrophobic) ones [65]. The latter property, coined as hydrophobicity, means that the molecule or its local does not strongly interact with water, but only exhibiting van der Waals interactions. Surfactants play an important role in many fields in our daily life, including foods, clothes or paints. Surfactant molecules form micelles (micellization) when their concentration exceed a critical value, called critical micelle concentration, abbreviated as ccc [66]. Micellization results from hydrophobic interaction when participating molecules possess hydrophilic and hydrophobic elements (amphiphilic molecules) simultaneously [63, 67]. Micellization generally occur in many other amphiphilic molecules like peptide, and lead to various functionalization [68]. Associated aspects will further be discussed in Chap. 5 in conjunction with biomaterials. One of the main mechanisms of the surfactant is the removal of oily dirt from textiles by virtue of encapsulation by micelles [44, 69, 70]. The process is not restricted to washing textiles [71] or foods [72], but extended to broader environmental issues like soil decontamination [73, 74].

Adsorption is a leading principle of heterogeneous catalysis, which predominates many chemical engineering processes [60]. As historically summarized by Fechte et al [75], the topic was almost always spotlighted in chemical industry, historically lead by petroleum industry [76, 77] and polymer technology [78, 79]. One of the most significant mechanisms involved in heterogeneous catalysis is dissociative adsorption, i.e., a neutral molecule is dissociated upon its adsorption on the substrate. This would seem that a covalent bond stabilizing an adsorbing molecule is weaker than nonCBs enabling adsorption. This puzzling question will be solved when we consider quantum states of the adsorbing species [80] (Fig. 3) or heterogeneity of the host substrate [81-83] (Fig. 4).
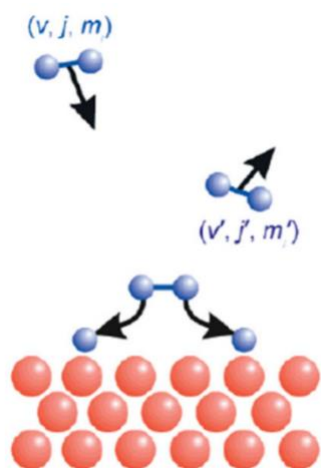

**Fig. 3.** Quantum state controlled dissociative adsorption [80]
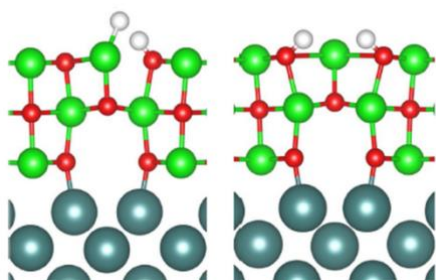
Fig. 4. Substrate controlled dissociative adsorption [81]

Recently, application of heterogeneous catalysis expanded toward environment techniques seeking sustainability. As shown in Fig. 5 [84], the catalysis-centered closed system enable the life cycle toward carbon neutrality. Smart utilization of biomass resources is one of the related top issues. To convert cellulosic resources to biofuels like ethanol, there are many steps, where heterogeneous catalyses play a crucial role [85-87]. Elimination of hazardous substances, like volatile organic species, is one of the central positions of environmental issues [88].
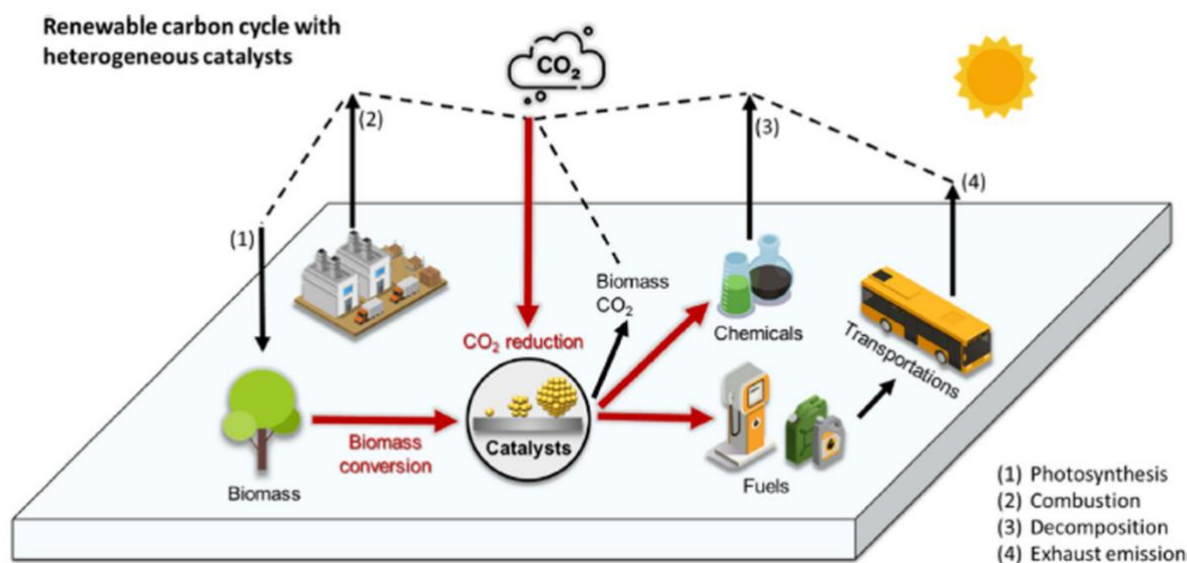
Fig. 5. A scheme of working heterogeneous catalyst. Proposed renewable carbon cycle with heterogenous catalysts to convert biomass and CO2 into renewable fuels and chemicals simultaneously [89]
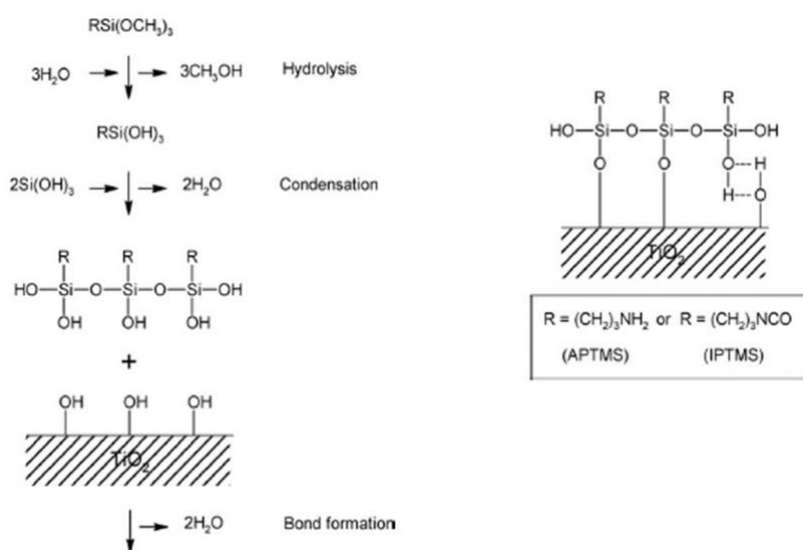
**Fig. 6** Chemical grafting of organosilanes onto TiO2 nanoparticles surface [90]

There is a fundamental phenomenon on the surface of metal oxides with water. Oxide ion, O^{2-} on the surface is particularly affinitive to protons and hence leads water adsorption. In most cases, adsorbed water does not remain as a neutral molecule but tends to polarize toward dissociation to H^+ and OH^- whose tendency depends on the state of surface [91]. In case of silica, where the structure is described as a network of siloxane (Si-O-Si) bonds, dangling bond on the surface turns adsorbed water into a surface silanol group, Si-OH. The process has been investigated in detail by experiments [92] or molecular dynamic calculations [93]. Thus, the surface of typical oxides are rich in surface OH groups under the ambient conditions. Surface

modification with coupling agents mostly occurs *via* a chemical interaction with such surface OH groups, resulting in the surface grafting, as exemplified in Fig. 6 [90]. Related techniques are used for enhancing catalytic activity [94] or corrosion protection of metal surfaces [95] . One of the industrially important related genres is a color material, i.e., paints and inks. They are dispersion systems, where small solid pigment particles are dispersed in liquids called vehicles. Until recently, vehicles are mostly hydrophobic organic solvents while pigments are hydrophilic oxides or sulfides, so that the resulting paints are unstable, prone to quick sedimentation. In line with avoiding volatile organic species mentioned above, water-based vehicles are preferentially used nowadays. Depending on the vehicle polarity, pigment particles need to be either hydrophilic (water affinitive) or lyophilic (oil affinitive). Thus, surface modification of pigments need to be flexible. Use of various surfactants including amphiphilic (both affinitive) have been developed [96, 97]. Coupling agents are also important for surface modification. While their structures are similar to those of surfactants, they are grafted on the surface, with more stable and irreversible nonCBs [90, 98].

4. Crosslinking in colloidal dispersion and polymers

Crosslinking in colloidal system changes a free-flowing dispersion (sol) into solid-like states (gel). The process is generally called as a sol-gel process. This expands from a recipe of sweet jerry in kitchen to a processing of solid functional materials [99]. Most of the related science and technology is based on the hydrogel, solidified by HBs [100]. As shown in Fig. 7, network structure in hydrogel is often accompanied by hydrophobic associative force [101]. Structuring of hydrogel is predominated by the concentration of coexisting salts and pH, and mostly associated with self-assembly [102]. Such a structured hydrogel is applied intensively to tissue engineering, as will be mentioned in the next chapter.
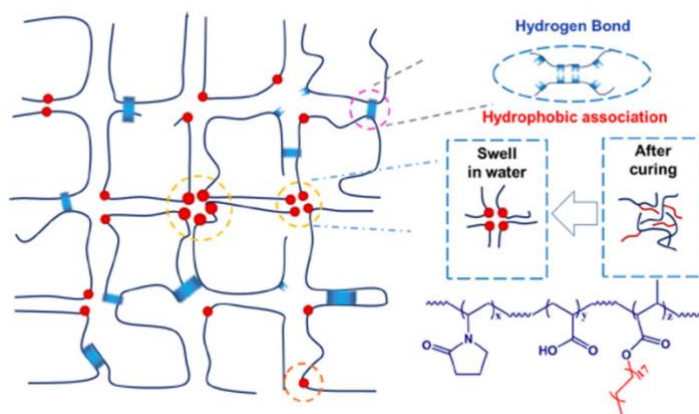

Fig. 7. Network structure of hydrogen bond and hydrophobic associating cross-linked hydrogels [100]

Linear polymers drastically changes their mechanical properties by three-dimensional crosslinking. Crosslinking of elastomer is one of the traditional technologies in rubber industry under the concept of vulcanization of natural rubber or cis- and trans-polyisoprene [103]. Mechanical properties of the rubber – clay composites are known to be improved by HBs [104]. Difference in the thermoset plastics from thermoplastic is due to the covalently crosslinked structure of the former [105]. This is out of the scope of this article. However, it is important

to note that covalent and noncovalent crosslinking are almost always mixed within a single polymeric material as shown in Fig. 8 [106]. Non-covalently crosslinked polymers or hydrogels are now under spotlight, particularly in conjunction with tissue engineering [107, 108]. Role of HBs on engineering nanocomposites was discussed in detail by Lu et al [109]. The concept of dynamic bonding, which reversibly break and reform, will give many attractive properties particularly in nanocomposite hydrogels.
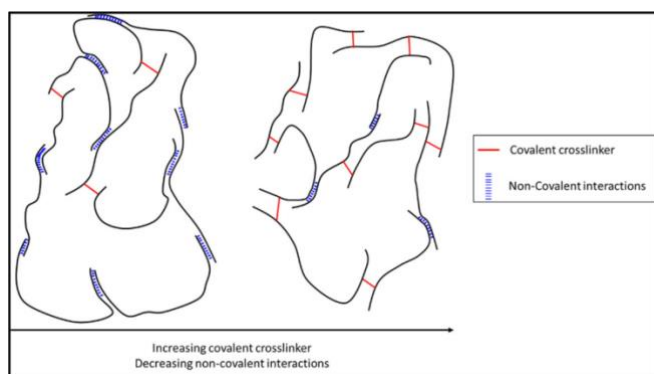

Fig. 8. Polymer network depicting covalent as well as noncovalent interactions [106]
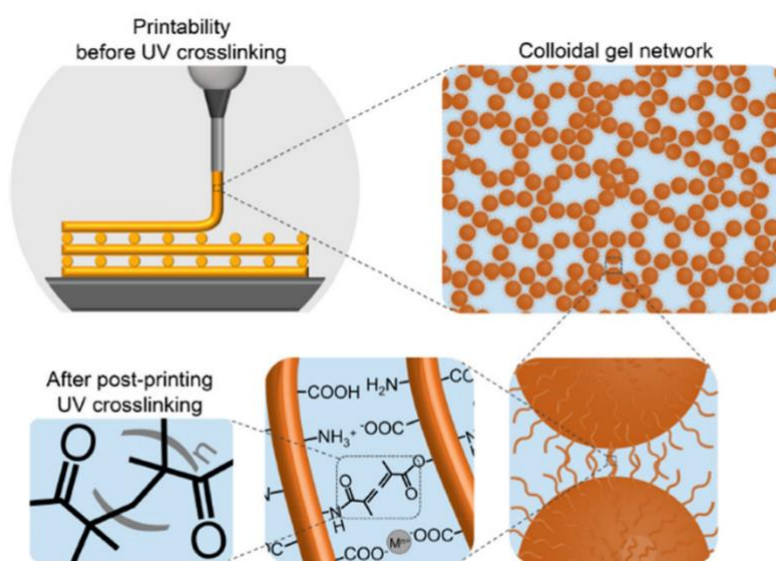
Fig. 9 Schematic illustration of extrusion-based 3D printing of gelatin-based colloidal inks [110]

Additive manufacturing using 3D printer requires quick crosslinking of the gelatin-based colloidal inks ejected from jet nozzle. Irradiation or photo-induced crosslinking is suitable for those purposes [110, 111]. Figure 9 displays the process from macroscopic to microscopic view of the related chemical issues involved [110]. Crosslinking is also leading adhesive technology. Modern robust hydrogel adhesive, frequently used for do-it-yourself activity, dual hydrogen bonding network play a significant role [112, 113]. Formation and development of HBs during preparation of hydrogel-based adhesive is shown in Fig. 10 [113].
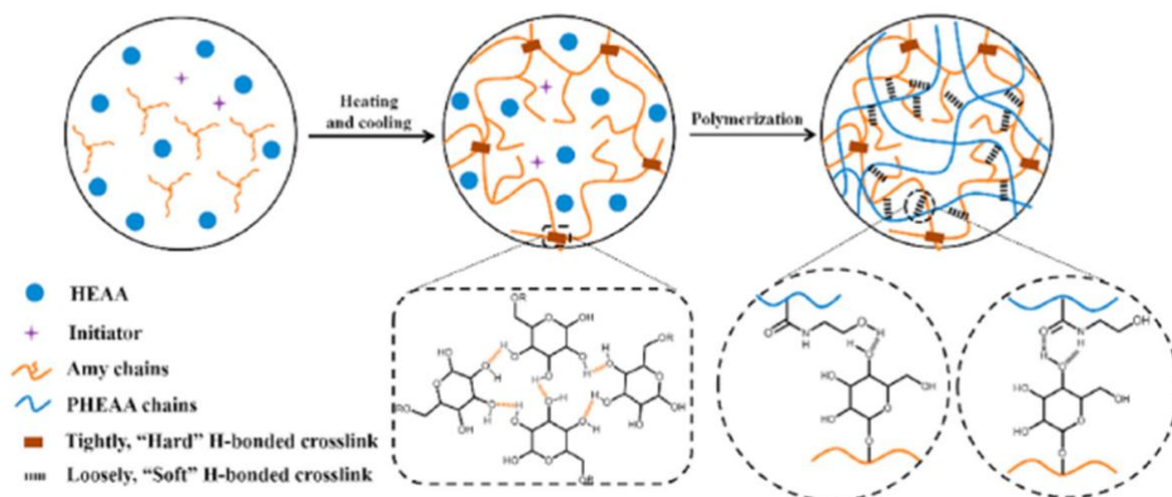
Fig. 10. Scheme of preparation of Amylopectin (Amy)/poly(N-hydroxyethyl acrylamide) (PHEAA,) double network (DN) hydrogels via a one-pot heating-cooling-thermal polymerization method [113]

5. Protein and biomaterials

Proteins are products of life, from microorganisms to human beings. They are ensembles of amino acids. To be more exact, the basic unit of proteins is a polypeptide chain of various amino acids covalently bound by peptide bonds [114]. Bio-related functions emerge, however, from the higher order structure where primary peptide chains are combined by HBs, suggested at first by Pauling and his coworkers [115, 116]. In addition to HBs, salt bridges, to be understood as a kind of nonCBs, play an important role as well [12]. Higher order protein structures are diverse. The first step, formation of secondary level structures in the form of α-helices and β-sheets is displayed in Figs. 11, where the red dotted lines are an indication of the presence of hydrogen bonds between two peptide strands [117]. The change from secondary to quaternary structure is illustrated in Fig.12 [118]. Those higher structures are then examined from various viewpoints [119, 120]. One of the top issues with protein is associated with diseases due to misfolding of higher order protein structure, called prions [121], like Alzheimer symptom [122] or bovine spongiform encephalopathy (Mad cow disease) [123]. It is really interesting but still remains mysterious how the prions are generated, despite their importance of life science [117, 124]. For these reasons, protein engineering tend to direct to therapeutics and pharmaceutics [119, 125]. One of the latest protein technologies is also associated with vaccines against Covid-19 pandemics [126, 127]. Our brain memory storage is associated with multiple HBs pattern in complicated neuronal synapses [128, 129]. Brain science is rapidly developing area even at the molecular level, where the role of HBs is discussed on various bases [130-132]. Ambitious attempts on the synthesis of synapse organizers might pave the way to combat brain diseases such as Alzheimer's [129].
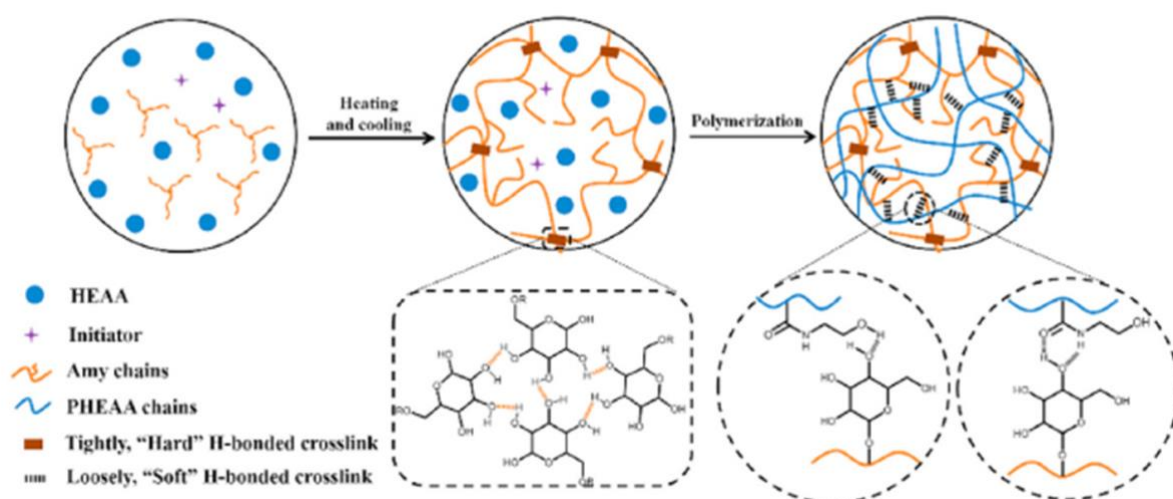
Fig. 11. Formation of secondary level structures or protein in the form of α-helices and β-sheets [117].
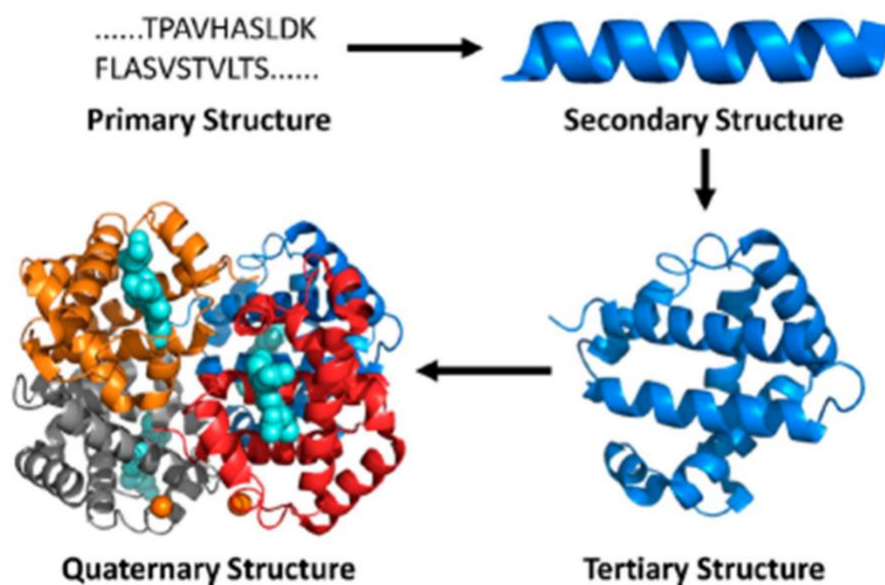
Fig. 12. Four orders of protein structure exemplified by human deoxyhemoglobin [118]

Tissue engineering is one of the rapidly developing technological genres associated with nonCBs. Development of preparing artificial bones [133] and skin [134] is remarkable. While those artificial tissues are synthesized purely chemically, as shown in Fig. 13 as an example of artificial skin synthesis [134], such tissues are also embodied from the concept of biomimetic technology [135, 136]. As mentioned in the previous chapter, most of the related materials belong to the hydrogels [100, 101, 137]. For more practical application of those materials to regeneration medicine, we have to overcome biocompatibility, which depends on the critical balance with our immune system [138, 139].
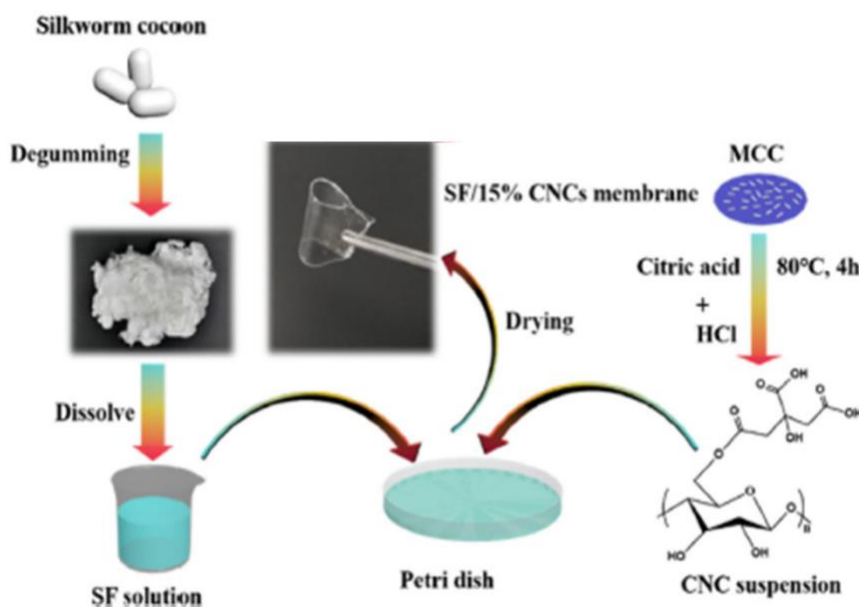
Fig. 13. Schematic diagram of preparation of artificial skin from natural silk fibroin (SF) and cellulose nanocrystals (CNC) [134].

6. **Crystal engineering and nanocomposite materials**

This chapter discusses two important nonCBs related items, i.e., crystal engineering and metalloxane bonds. Crystal engineering is based on the molecular crystals. Only a few inorganic substances like water, carbon dioxide or iodine form molecular crystals. In contrast, nearly all the organic molecules form molecular crystals when they order in a long range. Crystal engineering is based on the combination of HBs [29, 37]. Crystal engineering is also a part of computational chemistry, seeking appropriate combination of the element structures by nonCBs, by virtue of the database sources like the Cambridge Structural Database (CSD) toolbox [140].
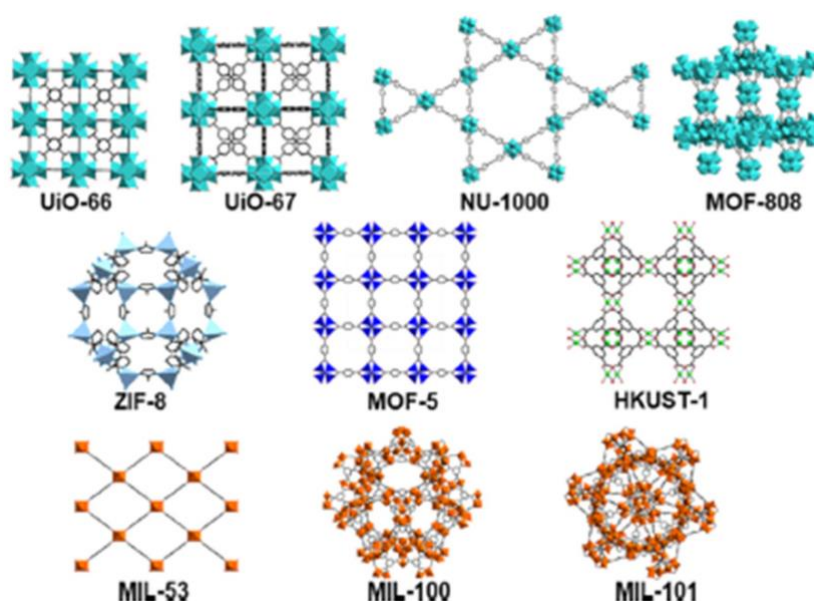
Fig. 14. Crystal structures of MOFs [141]

In last decades, interests in the metal organic frameworks (MOFs) have remarkably increased [29, 57, 142]. MOFs are organic−inorganic hybrids assembled from metal ions or clusters and organic ligands [143]. As shown in Fig. 14, we know various species of MOFs [141]. Metal organic frameworks (MOFs) are reticular solids consisting of inorganic nodes (such as metal atoms) and organic linkers. Due to its microstructure, their internal specific surface area is very large up to 7000 m^2. Most popular inorganic nodes are transition metal oxy-hydroxides, such as $Zr_6O_4(OH)_4$. When this is combined with an organic linker, benzene-1,4-dicarboxylic acid, it is named as UiO-66. For other nodes and linkers with the names appeared in Fig. 14, it is recommended to refer Table 1 of ref. [141]. They are developed in the course of improving heterogenous catalysis starting from basic solids, due to their unique properties like high thermal stability, discrete ordered structure, ultra-low densities and large internal surface area [144]. It is to be emphasized that MOFs and related materials are closely related to HBs [145, 146]. MOFs were developed in the interests of materials applications, e.g., for energy storage devices such as lithium ion batteries [147], particularly for solid-state electrolytes, the core material for all-solid rechargeable batteries [148-152]. They were also developed for medical biomaterials [153], or environmental issues such as CO_2 fixation [154]. Due to their unique structures, MOFs are also used as various templates for material syntheses [155]. MOFs are generally prepared in the framework of coordination chemistry and mainly via sol-gel processes [143]. However, other more facile and green methods are rapidly developing, among others via mechanochemical routes [156-158]. Liquid crystals, playing a key role in modern display technology, have also much to do with nonCBs and crystal technology [159, 160]. Their electrical conductivity and luminescence efficiency are also improved by designed introduction of HBs [161].

In our daily life, we have many bridging bonds, i.e., Ca-O-Si for calcium silicates in cement clinker, or Ba-O-Ti for barium titanate used in microelectronic devices. When two cationic species, M_1 and M_2 are abridged by an electronegative atoms, notably oxygen, the formed bridging bond, M_1-O-M_2, is called a metalloxane bond [162-165]. They play a crucial role in heterocationic complexes, notably complex oxides. When $M_1 = M_2 = Si$, it is called a siloxane bond, which plays a particularly significant role in silica chemistry [166, 167]. For the metalloxane bond formation, lattice imperfection plays particularly an important role, since bond distortion or vacancy enhances electron maldistribution and hence polarization of chemical species of concern. This was demonstrated by the change in the electronic overlap population with decreasing coordination number of a pair of atoms abridged by an oxygen atom [164].

Two genres of nonCBs with metallic atoms are introduced, where they are either hinging with other metallic species, or organic species forming metal – carbon bonds. The latter plays an important role in organometallic compounds, serving as catalysts for organic syntheses [168, 169]. In metallocene compounds, an important group of organometallics, two coplanar aromatic rings are bridged by a metallic atom *via* a special coordination [170, 171]. Both of these groups belong to the former category. Representatives of the latter category is metals abridged by electrophilic atoms. They are coined as hetero-bridging bonds were already referred in this journal [172] and play a crucial role for complexing inorganic compounds like metal oxides. Their role is particularly important in the synthesis via sol-gel alkoxide, chemical solution deposition or mechanochemical syntheses, often shortened as mechanosynthesis as already mentioned in conjunction with MOFs synthesis.

7. Concluding remarks

Despite huge diversity, nonCBs possess several general features, i.e., i) they dominate all the properties of molecular aggregates, natural or artificial, ii) they accompany general physicochemical principles, i.e., and stabilization [38, 43], often with charge transfer [42, 173]. Hunting for new, functional materials is nothing but to rationalize and design the order of nonCBs. This is in line with seeking green processes to meet sustainable development goals. Concerted action of unconventional processes like electrochemical, photochemical, sonochemical, magnetochemical or mechanochemical ones, can also be assisted by the formation of particular nonCBs. More broadly, nonCBs not only aggregate chemical species, but hinge concepts of many different genres of chemical technology, making languages of different branches understandable, for instance, those in organic synthesis and inorganic materials sciences. Systematic combination and optimization of nonCBs are in line with sustainability, a leading concept throughout the chemical technology to date and in future.

Acknowledgments

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