Chapter 13
Preparation of Element-Block Materials Using Inorganic Nanostructures and Their Applications

Naokazu Idota and Yoshiyuki Sugahara

Abstract The evolution of organic-inorganic hybrids is highly desirable for the further acquisition of functionalities not achievable with conventional polymer materials in terms of mechanical, electronic, optical, and magnetic properties. Element-blocks, which are heterogeneous structures consisting of organic and inorganic components mixed at the element level, and their highly ordered polymeric derivatives, element-block polymers, are highly useful for overcoming a number of difficult problems. Among the various approaches to establishing element-blocks, this review focuses on surface modification of inorganic nanostructures with organic molecules to control interactions at the interfaces between organic and inorganic components in the organic-inorganic hybrids. For the design of surface-modified inorganic-nanostructure-based element-blocks, the dimensional features of inorganic nanostructures and the methods of modifying organic molecules on the surfaces are discussed from the viewpoint of nanomaterials. Finally, various applications using surface-modified inorganic-nanostructure-based element-blocks are introduced in terms of polymer-based hybrids and hierarchal architectures to provide successful examples, which are important to the development of polymeric materials based on element-blocks.

Keywords Nanostructure · Surface modification · Polymer-based hybrid · Hierarchical architecture

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13.1 Introduction

Organic-inorganic hybrid materials have been routinely developed to improve various properties of organic compounds, including their optical, thermal, electrochemical, and mechanical properties, by incorporation of inorganic compounds into organic compounds [1]. This concept is based not only on their complementary abilities to supply each other with lacking properties but also on the generation of new functionality with no loss of the intrinsic characteristics of either of their components. Since the functionalities often appear at the interfaces between organic and inorganic components, increasing the ratio of interfaces by reducing their domain sizes and mixing these components homogeneously is an important issue [2]. Phase separation or aggregation occurs easily, however, with decreases in the sizes of organic and inorganic components due to differences in their intrinsic compatibility, resulting in reduced performance compared with the original materials. Thus, a new technology is highly desirable to break through the concept of traditional organic-inorganic hybrid materials. Recently, heterogeneous structures consisting of organic and inorganic components mixed at the element level have been developed as a new family of functional materials, whose structural units are referred to as element-blocks [3]. These element-blocks and their highly ordered polymeric derivatives, element-block polymers, are expected to encourage the development of functional materials with various properties which are not achievable with conventional strategies for preparation of organic-inorganic hybrid materials.

The development of many types of element-blocks has been proposed using well-defined molecular design of organic and inorganic structures, such as polyhedral oligomeric silsesquioxanes (POSS) [4], size-controlled metal clusters [5], and silicon-bridged bithiophenes [6]. While the preparation procedures of these element-blocks are bottom-up approaches based on molecular design, another strategy is the use of inorganic nanostructures, which are preprogrammed nanomaterials with size-dependent properties. Inorganic nanostructures have been studied for decades because of their unique size-dependent characteristics, and the preparation methods and functionalities of various inorganic nanostructures, such as metal (oxide) nanoparticles [7], carbon nanotubes [8], and graphene nanosheets [9], have been investigated. This approach to preparing element-blocks is advantageous for creating predetermined functionalities based on the properties of the inorganic nanostructures, and the preparation of highly ordered element-block polymers is possible by introducing polymerizable groups or sites into element-block structures derived from inorganic nanostructures. Since it is difficult to achieve precise control of hierarchical structures using inorganic nanostructures and organic components with different intrinsic properties as mentioned above, a key technology for realizing element-blocks based on inorganic nanostructures is surface modification with organic molecules [10]. Surface properties are among the most essential factors in all organic-inorganic hybrid materials, because their interfaces play a crucial role in determining the microscopic and mesoscopic structures of final organic-inorganic hybrid materials. The use of element-blocks prepared via surface modification of inorganic nanostructures with organic molecules is thus an attractive strategy for adjusting their surface properties to achieve affinity with the conjugated organic components to prevent the phase separation or aggregation. Although a variety of surface coupling reagents have been extensively studied in academic as well as industrial settings, organic coupling molecules for surface modification of inorganic nanostructures should be properly selected to achieve desirable structures for potential applications. Therefore, innovative new element-blocks have been developed through an approach that differs from the molecular bottom-up approach, as demonstrated in Fig. 13.1.

This review focuses on the surface modification of inorganic nanostructures with organic molecules for preparation of element-blocks. The various inorganic nanostructures are classified into categories such as nanoparticles, nanotubes, and nanosheets to understand their dimensional characters. We then review the surface modification techniques used for inorganic nanostructures, especially the nanoparticles and nanosheets of transition metal oxides, employing organic molecules for the design of element-blocks. Based on currently available knowledge, recent possible applications using the modified inorganic nanostructures are discussed, mainly with respect to polymer-based hybrids.

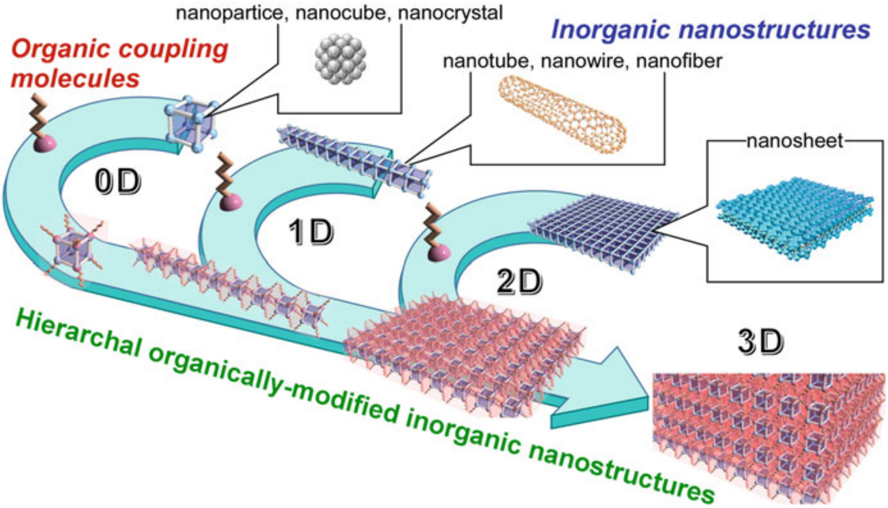

Fig. 13.1 Schematic concept for element-block materials comprising hierarchal organically modified inorganic nanostructures

13.2 Classification of Inorganic Nanostructures

Attention has recently been paid to inorganic nanostructures in a wide range of research fields with attention to the inorganic synthesis and control of the physicochemical properties of inorganic materials. Inorganic nanostructures consist mainly of metals and metal oxides, and the size-dependent properties of inorganic nanostructures are often discussed in terms of classifications according to their shape; nanoparticles, nanotubes/nanofibers, and nanosheets are categorized as zero-dimensional (0D), one-dimensional (1D), and two-dimensional (2D) inorganic nanostructures, respectively (Fig. 13.2) [11]. Among them, one of the most important characteristics for inorganic nanostructures is the quantum size effect. Decreasing metal and semiconductor materials to sizes smaller than a de Broglie wavelength induces significant restrictions on the electron motion by quantum confinement in all three spatial dimensions, resulting in a decrease in the energy level number and widening of the bandgaps. Such changes in the bandgaps provide unique properties compared with conventional bulk materials. For example, semiconductor nanocrystals showed particle-size-dependent control of adsorption and emission wavelengths by the quantum size effect [12]. The quantum size effect can also be obtained by anisotropic decreases in the sizes of inorganic components, including nanotubes and nanosheets. In this section, the characteristics of inorganic nanostructures are introduced based on their dimensional characters.

13.2.1 0D Inorganic Nanostructures

Among the typical inorganic nanostructures exhibiting the quantum size effect are nanoparticles categorized as 0D inorganic nanostructures. A decrease in all the axial lengths of the bulk materials to smaller than the wave number of electrons leads to immobile electrons of any dimension in the materials, resulting in zero dimension for electrons (so-called quantum dots) [13]. Semiconductor quantum dots have been

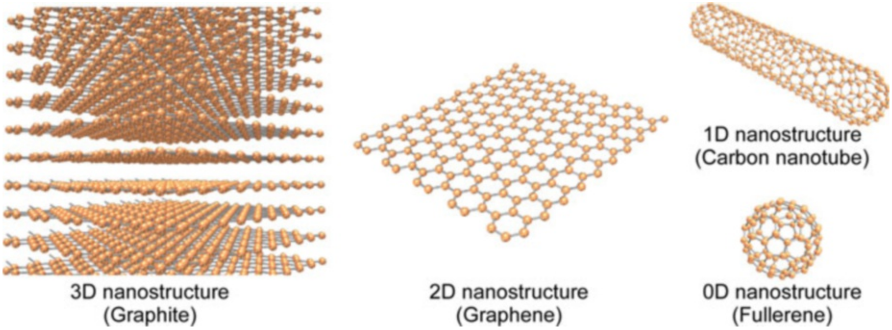

Fig. 13.2 Dimensional classification of nanostructures as an example of carbon compounds

extensively studied in a variety of fields with respect to their numerical theories and physical and chemical features, and a desire has emerged to use them for optical information communication systems and quantum cipher communication devices because of their huge information storage capacity. The quantum dots also possess a number of size-dependent properties, such as high electron density and strong optical absorption (e.g., Au nanoparticles [14]), photoluminescence (e.g., CdSe nanoparticles [15]), phosphorescence (e.g., Y_2O_3 nanoparticles [16]), and magnetic moments (e.g., iron oxide nanoparticles [17]). Procedural techniques for controlling the functions of nanoparticles have advanced over recent decades. The preparation of nanoparticles typically involves either a direct synthetic route of physical (e.g., vapor deposition, laser ablation) or chemical (e.g., sol-gel, micelle, pyrolysis) processes [18]. Reduction methods using metal salts with stabilizers are well known for synthesizing metallic nanoparticles in chemical liquid processes. The size, shape, and polydispersity of metallic nanoparticles can be controlled by varying the reaction conditions, including the concentration, use of reducing agents, and addition of capping ligands, which act as inhibitors to particle growth. In metal oxide nanoparticles, the common methods are coprecipitation, thermal decomposition, and hydrothermal synthesis, which allow synthesis of high-quality nanoparticles [19]. The other route to preparation of nanoparticles is the use of milling to reduce the size of large particles. It has been shown that wet milling using fine ceramic beads below 30 μm in diameter enables a decrease in the particle size to as low as 1–10 nm [20]. The 0D nanoparticle serves as a foundation for various inorganic nanostructures, and higher-ordered inorganic nanostructures can be precisely constructed by self-organization of assembled nanoparticles [21]. The self-assembly of nanoparticles can be controlled by balancing the attraction forces between them, leading to a generation of various highly ordered inorganic nanostructures, including chains, sheets, vesicles, and 3D architectures.

13.2.2 1D Inorganic Nanostructures

Although completely confined electrons are present in quantum dots, as mentioned above, one-dimensionally confined electrons are present in inorganic nanostructures called quantum wires [13], in which electrons can move freely only in one direction. Quantum wires surrounded by a material with a large bandgap confine electron and holes in one dimension (carriers can only move in one dimension) due to the larger bandgap. Since quantum wires exhibit a unique conductivity behavior which does not follow Orme's law, it is desirable to develop their applications for single-electron transfer devices. Carbon nanotubes are considered to be among the typical 1D inorganic nanostructures, and these have been evolving continuously in response to investigation of their synthesis, theory, characterization, and applications [22]. Carbon nanotubes consist of graphitic sheets rolled into cylindrical shapes with nanometer diameters. The properties of carbon nanotubes can be varied as a function of their helicity and tube diameter, and carbon nanotubes behave like metals or semiconductors according to the arrangement of the hexagon rings along their tubular surfaces [23]. In addition to the unique properties derived from the 1D structure, carbon nanotubes exhibit effective release of electrons from their tips, even with low voltages applied, due to the electric field concentration [24], leading to applications as cantilevers for probe microscopy and nanoactuators. Other one-dimensional inorganic nanostructures, such as metal nanorods (e.g., Au, Ag, Si), metal oxide nanowires (e.g., Al_2O_3, ZnO, TiO_2), nitride nanotubes (e.g., BN, AlN), and semiconductor nanowires (e.g., GaAs, InP), have attracted considerable attention [25, 26]. Chemical processes, such as chemical vapor deposition (CVD), precursor decomposition, and solvothermal, hydrothermal, and carbothermal processes, have been employed in the preparation of 1D inorganic nanowires. In these processes, nucleation and nuclear growth are important for controlling the crystallization processes that determine their properties [27]. Sufficiently high concentrations of the raw materials facilitate aggregation into small clusters through homogeneous nucleation, and larger clusters are subsequently formed by further growth of these small clusters. In order to control the crystallization, various methods have been widely investigated, such as the introduction of solid-liquid interfaces, use of templates or capping agents to direct the one-dimensional formation, and hierarchical self-assembly from 0D inorganic nanostructures. Compared to solid nanowires, inorganic nanotubes have more complex hollow structures, and the use of carbon-like hexagonal boron nitride [28] and template techniques for other inorganic materials [29] have been reported to form nanotube structures.

13.2.3 2D Inorganic Nanostructures

In quantum chemistry, two-dimensionally confined electrons are known to be present in quantum wells [13], which are used as semiconductor lasers to develop blue light-emitting diodes for large-capacity information storage. Graphene nanosheets exfoliated from graphite are representative of two-dimensional inorganic nanostructures [30], though their behavior is expected to differ from those of the quantum wells in semiconductor interfaces. The differences are caused by the unique electronic properties of graphene nanosheets, which exhibit electron-hole degeneracy and disappearance of carrier mass near the neutral charge point [31]. Since the structure of graphene nanosheets is a plane of sp^2 carbon atoms, their fundamental properties are similar to those of carbon nanotubes, whose structure consists of graphene nanosheets rolled into cylindrical shapes. On the other hand, the typical preparation procedure for graphene nanosheets (e.g., mechanical or chemical exfoliation from graphite) is easier than that for carbon nanotubes. Other methods of synthesizing graphene nanosheets include CVD, annealing at high temperature, unzipping of nanotubes, and microwave synthesis [32]. Graphene nanosheets exhibit good electrical conductivity, high thermal conductivity, strong mechanical properties, and optical transmittance due to their 2D quantum effects, and their electronic and thermal properties can be controlled by adjusting the number of layers [33].

Other types of inorganic nanosheets can be prepared, meanwhile, by exfoliation from some ion-exchangeable inorganic layered compounds, which accommodate guest species to form intercalation compounds. Typical inorganic layered compounds include clay minerals, such as montmorillonite and kaolinite, but other synthetic compounds, including zirconium phosphates, layered double hydroxides (LDHs), layered metal oxyhalides, layered titanates, layered niobates, and layered perovskites, can also be employed [34]. Although smectic clay minerals exfoliate spontaneously in water because of their low layer charge densities [35], the exfoliation of inorganic layered compounds with high layer charge densities, such as layered titanates and layered perovskites, is mainly induced by intercalation reactions or interlayer surface modification in appropriate combinations between the host and guest species [36]. Among examples, the interlayer distance of ion-exchangeable layered compounds is expanded by substituting the original interlayer ions with bulky organic ones (e.g., tetrabutylammonium cations (TBA^+)). The expansion can decrease the electrostatic interactions at the interlayers, resulting in exfoliation with the aid of mechanical shaking. In neutral layered compounds such as transition metal chalcogenides, intercalation of guest species proceeds after weakly charging the interlayers by reduction [37]. Exfoliated nanosheets can be obtained as dispersions, and applications using deposited nanosheets have been investigated by the Langmuir-Blodgett method and layer-by-layer technique [38].

13.3 Surface Modification of Inorganic Nanostructures with Organic Molecules

Surface modification with organic molecules is an effective technique for controlling the surface properties of inorganic materials that has been used routinely in not only scientific research but also in industrial applications [10]. In inorganic nanostructures, grafting of organic molecules as monolayers is an essential factor in preventing drastic changes in their well-defined size for maintaining the intrinsic properties of the inorganic nanostructures. Appropriate selection of surface coupling reagents based on the shape and quality of the inorganic nanostructures is therefore important. In this section, the focus is on surface modification of inorganic nanoparticles and nanosheets, and the applicability of various surface coupling reagents is discussed.

13.3.1 Surface Modification of Nanoparticles

Since nanoparticles have large specific surface areas compared with bulk materials, interactions between nanoparticles such as the van der Waals force, electrostatic interactions, and hydrogen bonds are significantly strengthened by differences in the surface energies between the nanoparticles and dispersion media, easily resulting in phase separation or aggregation [39]. The dispersion technique is therefore important for maintaining the size-dependent properties of the nanoparticles. Although the use of electric repulsion between surface-charged nanoparticles achieved by adjusting the pH of the dispersion medium is a simple method, surface modification with organic molecules can be an effective technique for controlling the polarity of the nanoparticle surfaces according to solvent properties. Typical coupling reagents for metal nanoparticles are thiol derivatives, which can react with metal atoms to modify them into monolayers [40]. For example, alkanethiols form a commensurate $\sqrt{3} \times \sqrt{3}$ R30° structure on Au(111) surfaces, resulting in all-trans alkyl chain formation with a tilt angle of ca. 30°. The tilt angle depends on the type of metal atoms, as exemplified by $16 \pm 2°$ for palladium, 12° for copper, ca. 10° for silver, and $\approx 0°$ for mercury [41]. The sulfur atoms in the alkanethiols can bind with metal atoms in stable quasi-covalent bonds, and van der Waals forces between their alkyl groups lead to decreases in the surface free energy. Longer alkyl chains in the alkanethiols contribute to restricting their molecular rotations, and the surface modification becomes more stable consequently. Since the headgroups of alkanethiol can be replaced with various functional groups, preparation of modified nanoparticles has been developed using thiol derivatives with hydrophilic and polar headgroups to improve water dispersibility [42].

Silane coupling reagents are used extensively for surface modification of transition metal oxide nanoparticles. Surface modification with silane coupling reagents, or silanization, was initially developed in surface functionalization of silica particles [43]. Common silane coupling reagents bear alkoxysilyl (≡Si-OR) or chlorosilyl groups (≡Si-Cl), which can be hydrolyzed and subsequently reacted with hydroxyl groups on transition metal oxide surfaces through condensation (Fig. 13.3a), and various organic functional groups are available in the other terminated side of silane molecules. Inter- and intramolecular condensation reactions of silyl groups (the so-called homocondensation), on the other hand, also occur during the silanization, resulting in multilayered modification. Thus, the selection of appropriate reaction conditions, particularly with respect to water content, is important for surface modification of inorganic nanostructures while maintaining their original size [44]. Silanization proceeds not only in liquid-phase reactions but also in vapor-phase deposition, and the vaporization enables it to proceed under vacuum conditions at low temperature with the use of silane coupling reagents with large molecular weights [45]. A variety of silane coupling reagents is commercially available, and the dispersibility of modified TiO_2 nanoparticles in organic solvents can be controlled by managing the mixing ratio of silane alkoxides [46].

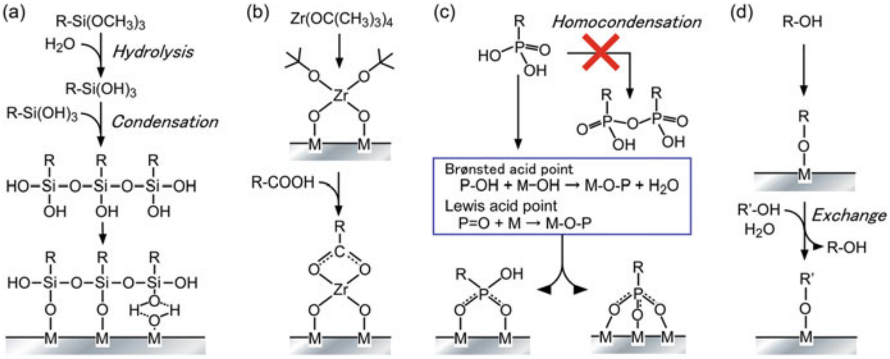

Fig. 13.3 Modification process with organic groups onto metal oxide surfaces. (**a**) Silanization, (**b**) carboxylic acids via zirconium tetra-*tert*-butoxide [47], (**c**) phosphorus coupling, and (**d**) alcohol-exchange-type reactions

Transition metal oxide nanoparticles are covered with hydroxyl groups, which play important roles in solid catalysts and modification with coupling molecules. Since these surface hydroxyl groups can serve as Brønsted acid sites, carboxylates and phosphonates can be modified onto the surfaces through acid-base reactions. Although organocarboxylic acids can easily react with the transition metal oxide nanoparticles, stable surface modification using organocarboxylic acids is often difficult because of the relatively weak and reversible interactions. In order to overcome this issue, the deposition reaction of zirconium tetra-*tert*-butoxide ($Zr(O^tBu)_4$) onto transition metal surfaces has been reported [47]. Organocarboxylic acids can be stably and irreversibly reacted with ZrO_2 surfaces to form strong bidentate bonds, and modification with carboxylic acids is also applicable to native oxide surfaces, such as hydroxylated alumina, by pretreatment with $Zr(O^tBu)_4$ (Fig. 13.3b). TiO_2 nanoparticles were also reported to permit bidentate binding with carboxylic acid moieties in a fashion similar to ZrO_2 [48].

Phosphorus coupling reagents have been attracting attention recently for their ability to modify transition metal oxides stably as self-assembled monolayers. The phosphorus coupling reagents form covalent M-O-P bonds, which are relatively stable with respect to hydrolysis, by reacting with hydroxyl groups of transition metal oxide surfaces (Fig. 13.3c) [49]. It is worth noting that no homocondensation of phosphorous coupling reagents proceeds under mild conditions [50]. Thus, surface modification of phosphorus coupling reagents is a suitable technique for functionalization of transition metal oxide nanoparticles. Phosphoric acid esters are also attractive for use in surface modification because of their high solubility in organic solvents and easy preparation from commercially available phosphoric acid and alcohol [51]. Other organic acids involving sulfonic acids have been used to introduce functional groups onto nanoparticle surfaces [52].

13.3.2 Surface Modification of Nanosheets

A variety of metal oxide nanosheets prepared by the deposition method or exfoliation from layered materials can be modified using coupling reagents in a way similar to nanoparticles. Graphene nanosheets, on the other hand, are inert with respect with organic coupling reagents, since graphene nanosheets consist of two-dimensional sp ^{2}-hybridized carbon atoms arrayed in a honeycomb pattern. The surface modification of graphene nanosheets with organic molecules is mainly achieved by two general routes: free radical or Diels-Alder reaction with C=C bonds of pristine graphene [53] or formation of covalent bonds with oxygen groups of graphene oxides (GO) [54]. Highly reactive free radicals generated by heating a diazonium salt can attack the sp^2 carbon atoms of graphene nanosheets forming a covalent bond, and dienophile derivatives are also bound to these though a cycloaddition reaction. GO is a single graphitic monolayer partially containing oxidized aliphatic regions (sp^3 carbon atoms), such as hydroxyl, epoxy, carbonyl, and carboxyl functional groups. Using these oxidized species, organic molecules can be covalently bound through formation of ester and amide bonds. The deactivation of the instinct properties of graphene nanosheets by surface modification is relatively low, and a chemical reduction of GO can remove the oxygen atoms to recover the pristine graphene, although the recovery is incomplete. Among other modification methods, direct attachment of hydrogen and halogen atoms to graphene surfaces by plasma treatment and heat-induced halogenation has been reported [9].

In preparation of surface-modified inorganic-nanosheet-based element-blocks, the use of ion-exchangeable layered compounds is attractive for simultaneous employment of interlayer surface modification with coupling molecules and weakening of the electrostatic interactions at the interlayer for subsequent exfoliation to surface-modified inorganic nanosheets as well as intercalation. Grafting reactions of the interlayer surfaces of layered perovskites, $HLaNb_2O_7{\cdot}xH_2O$ (HLaNb), using various *n*-alcohols via so-called alcohol-exchange-type reactions have been reported (Fig. 13.3d) [55]. In this type of reaction, alkoxy groups that are bound covalently to the $[LaNb_2O_7]$ units can be exchanged with other alkoxy groups upon reaction with alcohols in the presence of a small amount of water via a hydrolysis-reesterification mechanism. The technique is available for subsequent modification with larger alcohols by using layered perovskites modified with smaller alcohols as intermediates. That is to say, alcohol-exchange reactions in less reactive hosts can be employed for grafting reactions with larger *n*-alcohols after direct reaction with methanol. This approach also induces decreases in the electrostatic interactions at the interlayers, and *n*-alkoxy-modified nanosheets can consequently be obtained by an exfoliation process through ultrasonication. The *n*-alkoxy groups on the HLaNb surface form all-trans conformations as bilayers at the interlayers with a tilt angle of ca. 57° [56]. The title angle is independent on the alkyl chain length in the *n*-alkoxy groups, and the increase in the interlayer distance is 0.214 nm per one carbon atom. The title angle and increase ratio of the interlayer distance in the *n*-alkoxy groups depend significantly on the type of host compounds, such as 41° and 0.166 nm for

$HCa_2Nb_3O_{10}{\cdot}xH_2O$ [57] and 75° and 0.244 nm for $H_2La_2Ti_3O_{10}$ [58]. In addition to *n*-alcohols, branched and fluorinated alcohols can also be bound though alcohol-exchange reactions [59, 60]. Although the alkoxy groups on inorganic nanosheets exhibited high thermal stability, hydrolysis occurred under alkaline conditions to remove the *n*-alkoxy groups easily from the surfaces.

In addition to inorganic nanoparticles, phosphorus coupling reagents are also powerful tools for preparation of surface-modified inorganic-nanosheet-based element-blocks from layered compounds of transition metal oxides by forming self-assembled monolayers. The monolayered modification provides clear regularity of the interlayer distances in the host compounds determined by XRD patterns, and the exfoliated products can be used as well-defined element-blocks. Organophosphonic acids can react with the *n*-decoxy derivative of HLaNb as an intermediate [61]. The phosphorus environment of the organophosphonic acid moieties is monodentate with a phosphoryl group and P-OH group remaining, although the phosphorus environment is mainly bidentate or tridentate for transition metal oxide nanoparticles. Since organophosphonic acids are relatively strong acids, on the other hand, the reactions with organophosphonic acids often resulted in dissolution of the host compounds. When kaolinite was reacted with phenyphosphonic acids with the intention of intercalation, for example, lamellar aluminum phenylphosphonate was crystallized after a part of the kaolinite had dissolved [62]. In surface modification of layered compounds with organophosphonic acids, a mechanical exfoliation process such as ultrasonication is also required for obtaining surface-modified nanosheets in a way similar to that of *n*-alkoxy-modified layered compounds. Another approach to preparing surface-modified nanosheets is surface-initiated polymerizations at the interlayers of the host compounds. Such polymerization can be achieved using interlayer modification with organophosphonic acids comprising atom transfer radical polymerization (ATRP) initiators, resulting in spontaneous exfoliation from the organically modified layered compounds in solution by the excluded volume effects of grafted polymer chains [63].

A remarkable layered compound for preparation of interesting nanosheets is potassium hexaniobate, $K_4Nb_6O_{17}{\cdot}3H_2O$, since creation of single- or double-layered nanosheets can be achieved by utilizing its unique structure [64]. $K_4Nb_6O_{17}{\cdot}3H_2O$ has alternately stacked hydrated and anhydrous interlayers with different reactivities. Some large guest molecules can recognize the difference in reactivity and preferentially intercalate into the hydrated interlayers. Based on this structural feature, two types of intercalation compounds can be prepared: intercalation compounds bearing guest species in every other interlayer (A-type) and intercalation compounds whose interlayers are occupied completely by guest species (B-type). It is also possible to create two types of organophosphonate derivatives separately by using two types of intercalation compounds as intermediates (Fig. 13.4). As a consequence, single- or double-layered nanosheets can be obtained by exfoliation upon ultrasonication from the organophosphonate-modified derivatives.

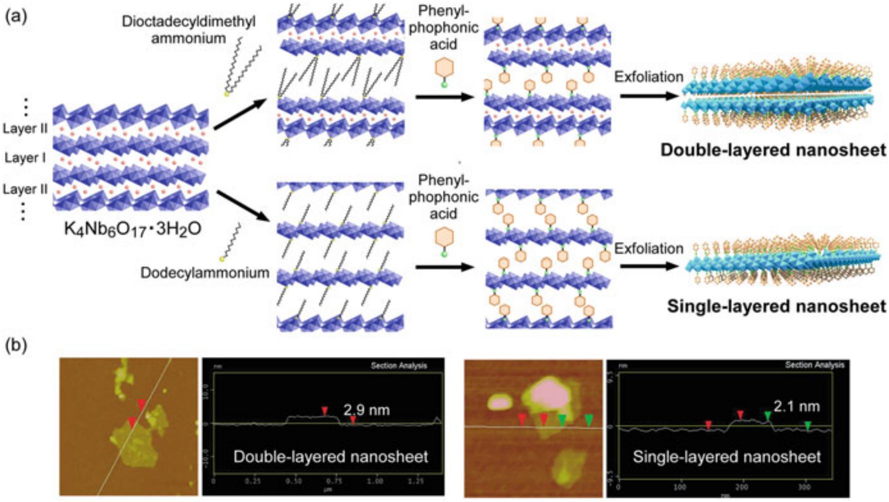

Fig. 13.4 Selective surface grafting of layered potassium hexaniobate, $K_4Nb_6O_{17}\cdot3H_2O$, for preparation of single- or double-layered nanosheets [64] (© 2014 American Chemical Society). (**a**) $K_4Nb_6O_{17}\cdot3H_2O$ are intercalated with dioctadecyldimethylammonium ions in every other interlayer (A-type) or occupied completely by dodecylammonium ions (B-type), and single- or double-layered nanosheets can be prepared via selective grafting with phenylphosphonic acids followed by exfoliation by ultrasonication. (**b**) AFM top-view and cross-sectional images for single- (left) and double-layered (right) nanosheets

13.4 Applications Using Surface-Modified Inorganic-Nanostructure-Based Element-Blocks

Functional organic-inorganic hybrid materials derived from inorganic nanostructures via surface modification with organic groups are playing important roles in various applications, such as catalysts, separation materials, electronic materials, and biomedical materials. The unique features of inorganic nanostructures such as a photothermal effect in Au [14] and superparamagnetism in Fe_3O_4 [17] are used in innovative ways, and surface modification with organic groups generates synergistic effects, in particular, for biological processes with the addition of biocompatibility and stimuli responsibility [7]. Another attractive capability is the control of interactions between organic and inorganic components in organic-inorganic hybrids using the surface-modified inorganic-nanostructure-based element-blocks to improve their performances. Since inorganic nanostructures aggregate easily in organic solvents or polymer matrices, surface modification of inorganic nanostructures with organic groups is an essential technique for well-defined dispersion in organic components to provide the instinct properties of the inorganic nanostructures [2]. Based on the strategic designs of modified organic structures, graft architectures, and certain types of inorganic nanostructures, possible applications using organic-inorganic hybrids with inorganic nanostructures have been demonstrated across a wide range one after another. This section focuses on recent applications of organic-inorganic hybrids using surface-modified inorganic-nanostructure-based element-blocks.

13.4.1 Polymer-Based Hybrids

Inorganic nanostructures have been routinely used for polymer-based hybrids as nanofillers to improve the thermal, mechanical, and optical properties of polymer matrices. It is critical for polymer-based hybrids to maintain the instinct properties of polymer matrices, such as transparency, lightweight, excellent formability, and low cost, even after incorporation of inorganic nanostructures. The aggregation or phase separation of inorganic nanostructures in polymer-based hybrids could, however, cause a reduction of the properties of polymer matrices. Even using small nanoparticles, for an example, Rayleigh scattering at the interfaces between the aggregated inorganic nanoparticles and the polymer matrices occurs when the aggregate size increases to above 40 nm, leading to a decline in the transparency of polymer-based hybrids [65]. Since the aggregation is caused mainly by differences in compatibility between the surface properties of inorganic nanostructures and polymer matrices, surface modification of inorganic nanostructures with appropriate organic groups is important for suppressing their aggregation. Although functionalized polymers have recently been developed through molecular design, demand remains for improvement of the properties of commercially available polymers by incorporating inorganic nanostructure for various industrial applications. The use of inorganic nanoparticles with high refractive indices as nanofillers is attractive for improving the refractive indices of common optical polymers such as poly(methyl methacrylate) (PMMA) and epoxy resins, since they have a restricted range of refractive indices of from 1.3 to 1.7 [66]. Surface modification of rutile-type TiO2 nanoparticles, which have high refractive indices ($n = 2.5$–2.7), has been demonstrated in the application of transparent polymer-based hybrids with high refractive indices. In these applications, *n*-octylphosphonic acid [67] and oleyl phosphate [68] are covalently bound to the surfaces of TiO_2 nanoparticles to form a monolayer, and the homogeneous dispersion of the nanoparticles in organic solvents and polymer matrices is achieved by varying the surface properties of the nanoparticles. The polymer-based hybrid thin films with surface-modified nanoparticles exhibit excellent transparency, and their refractive indices increase with increases in the TiO_2 content. Such ex situ approaches are suitable for preparing optical hybrid thin films with thicknesses of less than several μm, because of significant effects of the dynamic structural changes occurring during solvent evaporation for thick hybrid films [69]. For preparation of bulk optical hybrids such as photovoltaic devices and ophthalmic lenses, in situ polymerization of monomer dispersions containing surface-modified nanoparticles without solvent evaporation is a useful technique, and grafting polymer chains used in the matrices of the bulk hybrids onto the nanoparticles help to prevent their aggregation during in situ polymerization [70]. In addition, it was reported that modification of the polymer chain lengths on the nanoparticles was critical for dispersion in the polymer matrices (Fig. 13.5a). Surface-initiated living polymerization processes [71] such as ATRP, nitroxide-mediated polymerization (NMP), and reversible addition fragmentation chain transfer (RAFT) are therefore effective in modifying well-defined polymer chains on inorganic nanostructures for preparation of transparent bulk hybrids with high refractive indices.

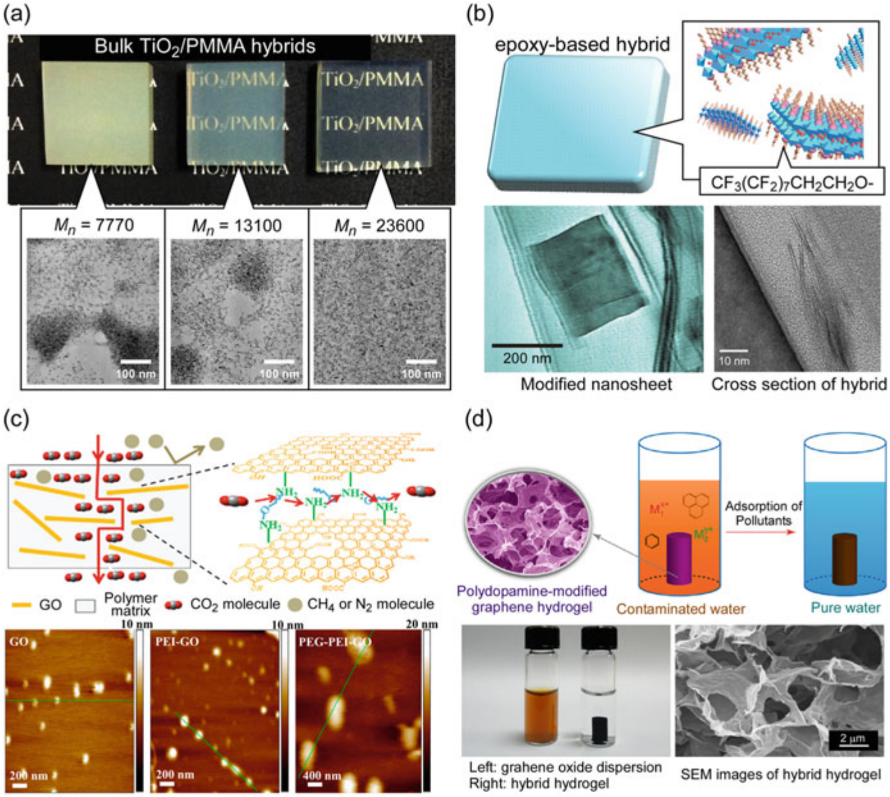

Fig. 13.5 Polymer-based hybrids using organically modified nanostructures. (**a**) Photographs and TEM images of bulk PMMA hybrids containing PMMA-modified TiO_2 nanoparticles with different chain length [70] (© 2016 American Chemical Society), (**b**) overview of epoxy-based hybrids with layered perovskite nanosheets bearing hydrophobic fluorinated alkoxy groups and its microscopic images (left, TEM image of the modified nanosheets; right, cross-section FE-TEM image of the hybrid) [75] (© 2014 Royal Society of Chemistry), (**c**) overview of CO_2 permselective polymer-based hybrid membrane incorporating graphene oxide nanosheets functionalized with PEG and PEI and AFM images of the modified nanosheets [76] (© 2015 American Chemical Society), and (**d**) overview of functional hydrogels containing polydopamine-modified graphene nanosheets as a reusable adsorbent of heavy metal ions for water purification and its images (left, photographs of the products; right, SEM images of the hybrid) [78] (© 2013 American Chemical Society)

Other improvements in the properties of polymer-based hybrids using inorganic nanostructures have been experimentally and theoretically investigated. The mechanical properties of synthetic polymers, including tensile strength, flexural strength, hardness, Young's modulus, and stiffness, can be improved by the incorporation of surface-modified inorganic nanostructures via reinforcement mechanisms [72]. The well-dispersed inorganic nanostructures in the polymer-based hybrids also act as thermal insulators and mass transport barriers to the volatiles generated during decomposition, enabling them to exhibit stable thermal properties [73]. Along with such advantageous properties for polymer materials, inorganic nanosheets have additional superior barrier properties with respect to gas penetration, including penetration by oxygen, carbon dioxide, and organic gases, due to their two-dimensional high aspect ratios. The incorporated nanosheets in polymer matrices create tortuous pathways for the diffusion of gaseous molecules passing through the polymer-based hybrids. Although gaseous molecules can penetrate perpendicularly through a bare polymer film, diffused molecules navigate around impenetrable platelets and through interfacial zones, which have permeability characteristics [74]. These properties are useful for food packaging and flame-retardant materials. These properties of the polymer-based hybrids are also further improved by enhanced dispersibility through surface modification of inorganic nanostructures with organic molecules. In addition, the surface-modified nanosheets allow control of affinities for specific molecules to the polymer-based hybrids according to the type of coupling reagent. Epoxy-based hybrids with layered perovskite nanosheets bearing hydrophobic fluorinated alkoxy groups, $CF_3(CF_2)_7C_2H_4O$, on the surface exhibited not only improved mechanical and thermal properties but also reduced water uptake compared to neat epoxy resins due to the surface-modifying hydrophobic groups (Fig. 13.5b) [75]. CO_2 permselective hybrid membranes can be fabricated by incorporating graphene oxide nanosheets functionalized with polyethylene glycol (PEG) and polyethylenimine (PEI) into commercially available polymers (Fig. 13.5c) [76]. In these modified nanosheets, oxyethylene groups in modified PEG and various types of amine groups in PEI showed excellent affinity and reversible reactivity to CO_2, respectively. The hybrid membranes with modified nanosheets thus had selective properties of catch and release for CO_2. Titanate nanosheets functionalized with sulfonic acids were used as nanofillers to improve the proton conductivity of Nafion® [77]. The sulfonic acid groups on the nanosheets simultaneously assisted the proton transfer and dispersion in the polymer matrices, and the methanol permeability of hybrid membranes, which caused a decline in their proton conductivity, was decreased by the tortuous pathways of dispersed nanosheets in the membranes. Functional hydrogels containing polydopamine-modified graphene nanosheets were reported to act as reusable adsorbents of heavy metal ions for water purification (Fig. 13.5d) [78]. The dopamine residues on the nanosheets play the role of reducing agents for graphene and the active sites for heavy metals ions through electrostatic, bidentate chelating, or hydrogen-bonding interactions. Surface modification with organic molecules can thus provide polymer-based hybrids with additional functionalities and synergistic effects.

13.4.2 Construction of Hierarchical Architectures

A next generation of organic-inorganic hybrids is being developed by constructing hierarchical architectures using organic modification of inorganic nanostructures through self-assembly. Although the aforementioned polymer-based hybrids exhibit various improved and added properties depending on the surface-modifying organic groups and inorganic nanostructures, a paradigm shift to further advances in organic-inorganic hybrid materials is required for assembling modified inorganic nanostructures displaying new properties as a result of interactions between the excitons, magnetic moments, or surface plasmons of individual inorganic nanostructures [21]. It will be important for achieving this purpose to construct hierarchical architectures comprising modified inorganic nanostructures as element-blocks through precise control of the spacing and alignment of individual inorganic nanostructures. The well-defined alignment of inorganic nanostructures has been investigated using self-assembly through a balance between attraction and repulsion forces [79], and surface modification of the inorganic nanostructures leads to binding of their hierarchical architectures. A possible technique for preparing self-assembled high-order architectures is site- or area-selective surface modification of inorganic nanostructures, in which the patterned organic groups act as links between modified inorganic nanostructures. In Au nanoparticle surfaces modified with thiolated molecules, there are two diametrically opposed singularities that are present at the particle poles, at which modified molecules are not optimally stabilized by intermolecular interactions with their neighbors, resulting in replacement with other thiolated molecules through place-exchange reactions [80]. Use of this characteristic enables the reactive organic groups to be introduced at only the two polar positions of the Au nanoparticles, and linear chains comprising the modified nanoparticles can be fabricated by linkage between the reactive organic groups. In addition, Ag nanorods have different reactivities between the {100} and {111} facets in their crystalline planes [81]. Individual surface modification of the Au nanorods with cetyltrimethylammonium bromide (CTAB) and polystyrene was led to the construction of a variety of hierarchal architectures such as chains, rings, spheres, and vesicles by changing the solvent composition (Fig. 13.6a) [82]. Such hierarchical organization based on patterning modification can also be achieved by using Janus nanoparticles, with the surfaces of both hemispheres modified with different organic groups [83].

Homogeneous surface modification of inorganic nanostructures also allows construction of higher-order architectures through control of self-assembly. Inorganic nanoparticles modified with block copolymers comprising hydrophilic and hydrophobic segments spontaneously exhibit vesicular or tubular formation by conformational changes of tethered polymer chains (Fig.13.6b) [84]. This mechanism is mainly based on rearrangements of the polymer conformation for minimizing the interfacial energy through partial hydration of the block copolymers, and the morphologies and geometries of these assemblies can be controlled by the

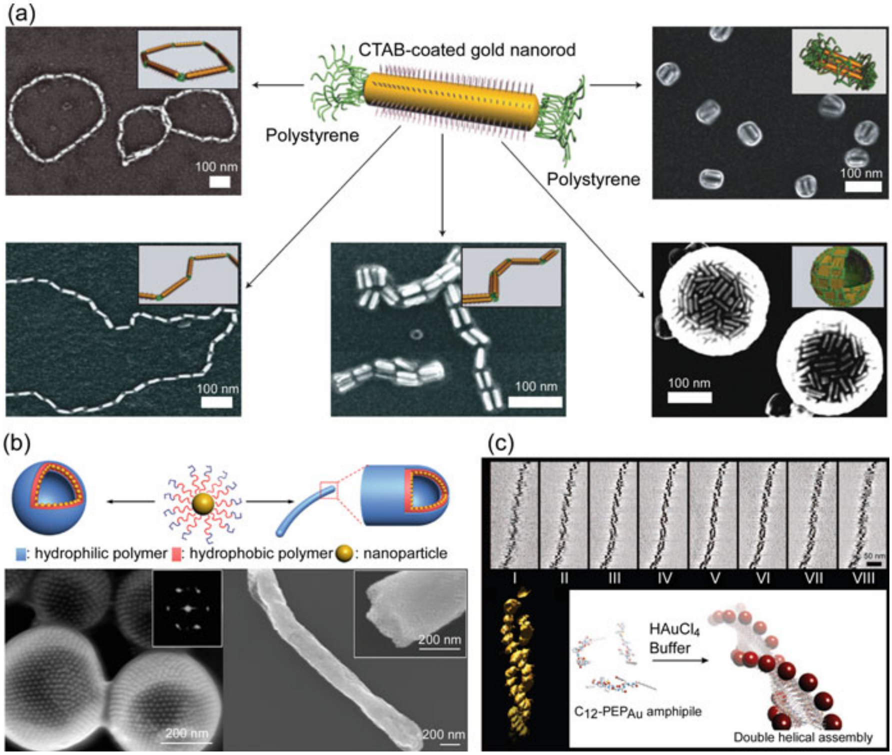

Fig. 13.6 Hierarchical architectures based on organically modified nanostructures. (**a**) Schematic images of self-assembly comprising polymer-modified gold nanorods in selective solvents and its SEM images (insets in the SEM images show corresponding schematic diagrams of the nanorod assemblies) [82] (© 2007 Nature Publishing Group), (**b**) schematic images of amphiphilic block copolymer-assisted self-assembly of nanoparticles into vesicles or tubules and its SEM images (left, vesicles with inset of the FFT pattern; right, tubules with inset of high-resolution image) [84] (© 2012 American Chemical Society), and (**c**) schematic images of forming gold nanoparticle double helices and its electron tomography data (X-Y computational slices (I–VIII) of 3D tomographic volume containing the double helical gold nanoparticle assembly) [86] (© 2008 American Chemical Society)

nanoparticle size and molecular weight of modified block copolymers. Assembly of Ag nanocubes have shown one-dimensional edge-to-edge and face-to-face orientations with modification of the nanocube surfaces with polymers of different chain lengths [85]. During solvent annealing processing of a polystyrene solution containing poly(*N*-vinyl-2-pyrrolidone)-grafted nanocubes, the nanocube-polymer hybrids underwent spontaneous self-organized phase segregation to form nanocube strings according to the balance between the chain lengths and effective surface energy of the Ag nanocubes. Biological self-assembly is a potential technique for building up hierarchical architectures. An interesting report was published on formation of double helices through peptide conjugation using Au nanoparticles with small peptides AYSSGAPPMPPF attached (Fig. 13.6c) [86]. The attachment of aliphatic carbon tails to the N-terminuses of the peptides would promote creation of various multidimensional supramolecular assemblies, such as 1D peptide amphiphilic structures.

13.5 Summary

This review introduces element-blocks prepared by surface modification of inorganic nanostructures with functional organic groups for the development of versatile organic-inorganic hybrid materials. Inorganic nanostructures are classified according to their dimensional characteristics, and the importance of selecting appropriate surface modification techniques for use of the instinct features of both nanostructures and modified organic groups is described. It is further demonstrated that feasible applications such as polymer-based hybrids and hierarchal architectures can be achieved by designing organically modified nanostructures. Since control of surface properties is an essential factor in every field of materials science, the surface design combined with interface design between organic and inorganic components at the molecular level is expected to contribute to advances in not only conventional organic-inorganic hybrid materials but also in element-block materials.

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