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Review

Surface Modification and Functionalization of Metal and Metal Oxide Nanoparticles by Organic Ligands

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Summary. Metal or metal oxide nanoparticles possess unique features compared to equivalent larger-scale materials. For applications, it is often necessary to stabilize or functionalize such nanoparticles. Thus, modification of the surface of nanoparticles is an important chemical challenge. In this survey, various possibilities are discussed how nanoparticles can be protected by organic ligands and how these ligands can be used to introduce functionalities. The preparative possibilities include grafting of an already functionalized ligand on the nanoparticle surface, exchanging part or all existing ligands on the nanoparticle surface, or grafting of a ligand on a nanoparticle followed by modification by organic chemical reactions.

Keywords. Nanostructures; Nanochemistry; Carboxylic acids; Ligands; Monolayers.

Introduction

Properties of nanoparticles are different to those of matter of the same chemical composition on a larger scale. Therefore, research on nanoparticles is increasing rapidly, and numerous applications are anticipated. Although some nanomaterials have excellent physical and chemical bulk properties, they do not possess suitable surface properties for specific applications. Consequently, it may be necessary to modify the surface of such materials [1]. The most common way to do so is to attach suitable organic groups to the surface atoms.

First, surface modification can stabilize nanoparticles against agglomeration [2–4]. A second aspect for modifying nanoparticles is to render them compatible with another phase. For example, metal particles can be made water-soluble when appropriate groups are attached [5]. Another example is the use of modified inorganic (nano-)fillers in organic polymers. The modification can avoid homogeneity and compatibility problems between the two phases and thus improve the mechanical properties of the composite [6]. A third interest in nanoparticles modification is to enable their self-organization [2]. A relatively unexploited additional possibility is the functionalization by the organic groups. While simple organic groups are sufficient to protect nanoparticles against agglomeration, functional organic groups on the particle surface may allow deliberate interaction of the nanoparticles with molecules, other nanoparticles, surfaces, or solids. The mentioned possibilities are synergetic. For example, surface functionalities also protect the nanoparticles against agglomeration and may be required to enable their self-organization.

In this survey the modification of two groups of nanoparticles will be discussed exemplarily, *viz.* noble metal nanoparticles and metal oxide nanoparticles. In both parts, general approaches of modifying the surface by organic groups will be outlined without attempting to cover all available literature comprehensively. We will first discuss some general

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aspects of introducing organic groups on the particle surface and will then highlight selected examples, where this modification was used for the functionalization of nanoparticles.

Surface modification of metal or metal oxide nanoparticles by means of metal or metalloid chloro or alkoxy derivatives is beyond the scope of this review article. Such a modification leads to the coverage of the nanoparticle surface by an oxide film and is used for protecting the surface or for controlling the acidity of the surface. For example, modifying a SiO_2 surface by titania enhances the basicity of the particle, but maintains some acidic sites [7, 8]. Similarly, the partial coverage of a silica surface by alumina will vary the density of the surface OH groups. Consequently a low proportion of $Al(OR)_3$ decreases and a high $Al(OR)_3$ proportion increases the surface OH density [9, 10]. Since this article deals with the surface modification of nanoparticles, only the composition of the outer inorganic shell of multi-shell particles is relevant.

Modification of Metal Nanoparticles

The literature on noble metal nanoparticles is already very dense, with gold nanoparticles being particularly well investigated. They already found various applications, such as catalysis, chemical sensing, bio-labeling or photonics [11, 12]. Bio-applications of gold nanoparticles are due to their very good oxidation resistance, easy synthesis and optical properties. Gold nanoparticles with appropriate ligands can be tolerated by organisms [11, 12]. For example, gold nanoparticles are good vehicles for tracers, and silver nanoparticles are very strong light absorbers and light scatterers.

Noble metal nanoparticles were mainly modified by thiols [2, 5, 11–14], disulfides [15], amines [5, 11, 12, 16, 17], nitriles, carboxylic acids and phosphines [12, 17, 18]. Selected examples will be provided in the following sections.

Thiols and Disulfides

The use of organosulfur compounds for modifying noble metal nanoparticles is one of the more developed methods, because organosulfur groups strongly coordinate to various metals, such as Ag, Cu [19], Pt, Hg, Fe, or Au. Sulfur possesses a huge affinity for metal surfaces, and organosulfur compounds thus will adsorb spontaneously [20]. The metal-sulfur interaction is strong enough to immobilize the thio groups on the surface of metal nanoparticles. For example, the chemisorption energy between gold and sulfur is estimated at $126\,kJ \cdot mol^{-1}$ [21]. When the thiol function is oxidized to sulfate or sulfonate the interaction with gold decreases [22].

Thiol- or disulfide-capped nanoparticles can be prepared by two methods. First, the sulfur compounds can be grafted on the surface of presynthesized nanoparticles [13, 23] covered by solvent molecules which are thus replaced by the sulfur-containing ligands [11, 14, 22, 24]. The second approach is to synthesize an organosulfur-capped nanoparticle in a one-step process, where the metal precursor and the protective ligand are reacted simultaneously. In this case, two processes compete with each other. The first is the growth of the particles leading to a reduction of the total surface. At some point, coordination of the ligands to the surface atoms of the clusters becomes more favorable and stops further growth. The choice of the organosulfur ligand and the variation of its concentration lead to a control of the particle size. For example, a good gold nanoparticle size control between 2 and 5 nm was achieved by varying the dodecanethiol concentration [25]. It was shown that varying the reaction conditions, notably the alkanethiol:Au ratio from 1:1 to 1:12 yields alkanethiolate-protected gold nanoparticles, for example Au particles covered by a hexadecanethiolate monolayer, with core sizes ranging from 0.7 to 5.2 nm [25]. When the same reduction method, using aqueous sodium borohydride, was used to synthesize silver nanoparticles covered by mercaptosuccinic acid, particles in the range 1.4–5.7 nm were obtained [26]. Reduction of $HAuCl_4$ by sodium borohydride in the presence of mercaptopropionic acid lead to particles with diameters ranging from 1.0 to 3.4 nm when the ligand:Au ratio was varied from 2.5:1 to 0.5:1 [27]. It is well known that the optical and electrical properties of metal nanoparticles are size-dependent [28]. Since the size of the nanoparticles can be controlled by varying the ligand concentration, an important influence of the nature and concentration of the ligand on the nanoparticle properties exists.

The exact nature of the metal-sulfur interaction is not completely resolved in most cases [13, 15, 24, 29–31]. It was found by elemental analysis and theoretical calculations that approximately two gold atoms are required on the surface per thiol [21]. In the special case of aromatic thiols it was shown that the thiol head group can occupy various adsorption sites on the metal surface, with very small energy differences. The difference consists in the additional electrostatic interaction between the aromatic ring and the surface, depending on the ring orientation relative to the gold surface [32].

Thiols can interact with metal nanoparticles in two different ways. The first possibility is the adsorption of the intact RSH molecule on the surface [33]. The second possibility is chemisorption of thiols or disulfides on metal surfaces which generates SR groups [25, 28]. Chemisorption of thiols on the metal surface occurs with concomitant cleavage of the S–H bond. Spectroscopic and theoretical investigations of the interaction of chemisorbed methylthiolate with gold surfaces were entirely consistent with a picture of methylthiolate radicals covalently bound to Au with essentially no metal-molecule charge transfer [34]. Intact disulfide are not adsorbed as such, but are split in two thiolate moieties upon chemisorption [33].

The immobilization of organosulfur molecules on the metal surface occurs in two stages. The first is very rapid and depends on the concentration of the organosulfur compound solution. The second stage consists in anchoring the last molecules, typically 10% of the total number. During this step the organic groups bonded to the sulfur atoms reorganize themselves to enhance the total stability. Consequently the kinetics of this second step is linked to ligand–ligand interactions [15].

Once the metal particle surface is capped by thiols or thiolates, the organic shell can be modified by thiol–thiol exchange. This procedure is interesting for the functionalization of nanoparticles, especially if the organic function to be introduced is not compatible with the conditions for the synthesis of the nanoparticles. Thiol–thiol exchange mostly requires a considerable excess of incoming ligand to render exchange complete, but deliberate partial exchange may also be useful. Nevertheless, the resulting layers will invariably be composed of both the previous and the incoming ligands in a certain ratio. For this reason, it may be preferable to use first a more weakly bonded ligand (see below) which then can be completely and easily displaced by a thiol ligand, leading to a monolayer consisting of only the incoming ligand [35]. The rate of exchange decreases as the chain length and/or steric bulk of the initial protecting ligand shell is increased [12, 36]. Unfortunately, a partial desorption of thiolated species and/or a partial replacement by ligand exchange are commonly observed during the aging or in biological media. This phenomenon, if it is not controlled, is detrimental for the colloid stability [13, 20].

The grafted organic molecules may influence the nanoparticle properties. For example, a study on gold nanoparticles stabilized by different thiol ligands with or without a functional organic group showed that the optical properties of the thiol-stabilized gold nanoparticles depend strongly on the composition of the ligand shell. This dependence is a result of the ligand shell influence on the electronic structure of the particle core [18]. Moreover, ligand/particle interactions can occur upon coordination of ligands on particles. An example are electron transfer phenomena between a pyrene-substituted thiol as the chromophore and gold nanoparticles, outlined in the next section of this review [37].

Amines and Ammonium Ions

Modification of metal nanoparticles by adsorbing amines is generally done to stabilize the particles [12]. For example, coverage of Pd nanoparticles by hexadecylamine leads to a better dispersion and stability of the particles provided that the hexadecylamine coverage is sufficient [17]. The main difference between modification by means of thiols or amines is the stability of the nanoparticles. The interaction between amino groups and metal nanoparticle surfaces is much weaker than that of thiolate groups. One consequence of the weaker bonding is that amine-modified nanoparticles are bigger than their organosulfur-modified equivalents [11, 12]. Both methods can be complementary. For example, peptides are linked to silver nanoparticles through both the thiol and amine functions [5].

A wide-spread method to stabilize noble metal nanoparticles is by adsorption of tetraalkylammonium halides. Long chain ammonium ions, such as tetraoctylammonium ions, are often used because of their amphiphilic properties allowing either creation of emulsions or compatibilization of nanoparticles in a particular medium. Hydrophobic metal nanoparticles stabilized with functionalized long chain ammonium ions can turn to be hydrophilic. This is, for example, a necessary condition for bio-applications

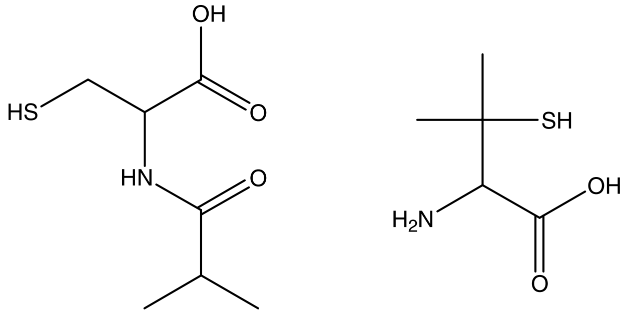

Fig. 1. *N*-isobutyryl-L-cysteine (*left*); penicillamine (*right*)

[16]. Nevertheless, ammonium ions, having shorter chain lengths of 4–8 carbons, have also been used to stabilize transition metal nanoparticles. When the metal nanoparticles were synthesized electrochemically, the ammonium surfactant served as electrolyte as well as stabilizer. The obtained nanoparticles were perfectly size-controlled and monodisperse, ranging from 1.2 to 5 nm [38–40].

Carboxylic Acids

Infrared spectroscopy as well as theoretical calculations revealed that the metal surfaces interact with negatively charged carboxylate groups, obtained by deprotonation of carboxylic acids [5, 41–45].

The use of ligands for nanoparticle modification, with more than one functionalities, as the ones shown in Fig. 1, may lead to a multifunctional adsorption on the surface. DFT calculations revealed a bifunctional attachment of *N*-isobutyryl-L-cysteine on gold nanoparticles through the thiol and carboxylate functions, and a trifunctional coordination of penicillamine with simultaneous interaction of the thiol, amine and carboxylate groups with the particle surface. The stability of the resulting system can be dramatically increased owing to the multiple attachments [5, 46, 47]. FTIR study of the interactions between these ligands and the surface indicated that the coordination of the carboxylic acid group occurs largely through carboxylate chemisorption even if a small part occurs by interaction with the protonated carboxylate. Concomitantly, the amine coordination occurs essentially by interaction of NH_3^+ [46].

Phosphines

The modification of metal nanoparticles by phosphines is easy to achieve and consequently very interesting [12]. For example, gold nanoparticles were protected by triphenylphosphine [18]. The drawback of this method compared to the previous ones is that phosphine interaction with the metal nanoparticle is very weak and thus results in a very poor stability of the nanoparticles [12, 18]. The lack of stability results in an easy exchange with other ligands, which are more strongly bonded to the metal surface [12]. A very noticeable feature of such exchange reactions is that, contrary to the thiol–thiol exchange, every phosphine ligand is exchanged. The exchange of phosphine ligands by thiol ligands is accompanied by a higher stability of the resulting nanoparticles [12, 18]. In the case of phosphine-amine exchange, less stable gold particles are obtained. However, an interesting aspect of this exchange is that the particles are growing during the modification [12].

The lack of stability of phosphine ligands can be overcome by the use of polyphosphine ligands. Thus, palladium nanoparticles were stabilized with di- or triphosphines, such as bis(diphenylphosphino)-decane or bis(diphenylphosphinoethyl)phenylphosphine. It was demonstrated that the multiphosphine ligands were firmly coordinated at the surface of the palladium particles [17].

Modification of Metal Oxide Nanoparticles

The interest in metal oxide nanoparticles is also increasing, for example because of very interesting optical or magnetic properties [4, 48–54]. Various organic compounds are potential metal oxide modifiers, among them, as for metal nanoparticles, thiols, carboxylic acids and amines [30, 55, 56]. However, amines and thiols are relatively rarely used, an example is thiourea to modify SnO_2 surfaces [30]. The main compounds used for modifying metal oxide nanoparticles are phosphonates or silanes.

Ligand exchange at a metal oxide nanoparticle surface is only possible without rearrangement of the particle or particle surface, if the incoming and outgoing ligands have the same charges and occupy the same number of coordination sites. For example, when a monodentate ligand is exchanged by an equally charged bi- or tri-dentate ligand, the metal oxide surface has to rearrange to accommodate the additional ligand centers. Consequently such reactions are not favorable and examples are rare [2]. For this reason, the introduction of a multidentate ligand occurs generally directly. In general, reaction control of the modified nanoparticle synthesis is better with the one-step method. Moreover a one-step method is generally easier and cheaper [13, 17, 22, 55, 57].

Carboxylates

Carboxylate ligands, especially fatty acids, are often used for modifying metal oxide nanoparticles [15, 58]. The binding of carboxylate ligands on the surface of titania nanoparticles with various controlled sizes in the range 0.7–6.0 nm has been investigated by using the transient molecular probe all-*trans*-retinoic acid, where the excited triplet-state probe molecule generated by a photoinduced interfacial charge recombination for the adsorbed monolayer acted as a reporter for the different surface binding forms. This study revealed that the surface binding forms are size-dependent. Adsorption decreases, as the size of the nanoparticle gets smaller, whereas the proportion of the chemisorption forms (Fig. 2) increases [59].

Silanes

Silanes are the most often used modifiers for metal oxide surfaces. This includes alkoxysilane, ≡Si–O*R* (*R* = alkyl), hydrogenosilane, ≡Si–H, or chlorosilane, ≡Si–Cl, reagents. As a matter of fact, there is a broad variety of commercially available silanes, and others are readily synthesized or modified. One of the main advantages of silanes is that they can bear numerous functionalities, for example amino, cyano, carboxylic acid, epoxy groups, *etc.* [6, 55, 60–66]. The post-synthesis grafting of silyl groups on a metal oxide surface is quite easy. Moreover, silanes can also be used for the one step method, where the silane is introduced at the same time as the metal oxide precursors [2]. This method is applicable to numerous metal oxides such as SiO_2, Al_2O_3, TiO_2, SnO_2, ZrO_2, V_2O_5, *etc.*

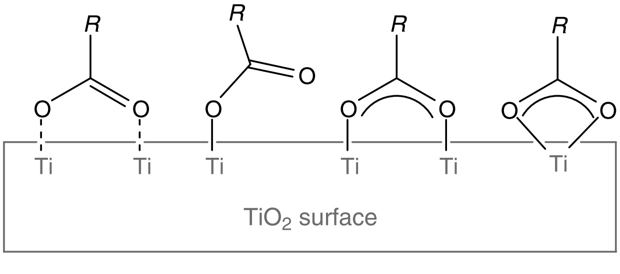

Fig. 2. Adsorption and chemisorption forms of carboxylic acid/carboxylate ligands on titania nanoparticles. *Left to right* physical adsorption, monodentate coordination, bridging chemisorption, chelating chemisorption

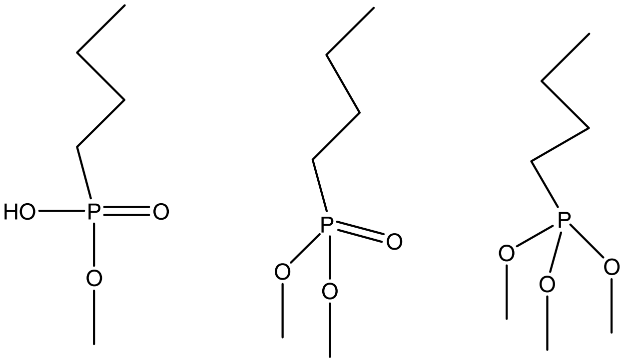

Fig. 3. Mono-, bi-, or tridentate anchorage of a phosphonate ligand on a metal oxide surface

Alkoxy- and chlorosilanes react with −OH groups on the metal oxide surface through a condensation reaction. In the case of chlorosilanes R_2SiCl_2 or $RSiCl_3$, the reactivity is so high that no water or catalyst is needed. This high reactivity of the di- and trichlorosilanes implies that they will not only react with a single M–OH at the surface but may also react with adjacent M–OH groups resulting in multidentate attachments (see Fig. 3 for a similar situation with phosphonates) or may form oligosiloxane structures by homocondensation reactions. In consequence, the structure of the resulting organosiloxane layer is often ill-defined. This is the reason why monochlorosilanes are more often used than di- or trichlorosilanes even if they need an activation by a base such as amines [15, 58, 67].

It is also important to note that surface modification by chloro- or alkoxysilanes leads to HCl or alcohol byproducts, which can alter the nanoparticle. For example, magnetic ferrite nanoparticles were found to disintegrate immediately because of the liberation of HCl, which is known to dissolve ferrite materials [68].

The use of organosilicon hydrides for surface modification can also be of great interest since it produces nanoparticles in a clean reaction, by-products being limited to hydrogen or water. Such silanes were successfully used for SiO_2, ZrO_2, TiO_2, or HfO_2 modification [69].

Phosphonates

Modification of a metal oxide surface by phosphonate groups creates M–O–P bonds. Phosphonate groups can be introduced by P–OH, P–OR (*R* = alkyl) or P–O$^-$ containing precursors. For example, reactions of phosphonic acids with TiO_2 surfaces result in covalent Ti–O–P bonds in a large pH range [70–72]. Contrary to the modification of titania particles by means of silanes, which creates unstable Ti–O–Si bonds, Ti–O–P bonds are very stable toward hydrolysis. Another important difference to silanes is that phosphonates only undergo reactions with surface OH groups, but do not undergo homocondensations, *i.e.*, do not form P–O–P bonds. Surfaces of alumina, stannia, zirconia, magnetite, *etc*., can also easily be functionalized by phosphonate groups [57, 71, 73–75].

A major features of the attachment of a phosphonate group on a metal oxide surface is that the anchorage can be mono-, bi-, or tridentate (Fig. 3). For example, a recent investigation of the binding of (11-hydroxyundecyl)phosphonic acid or (12-carboxydodecyl)phosphonic acid on a SnO_2 surface by solid state ^{31}P NMR showed a bi- and tridentate attachment of phosphonate ligands [76]. The multidentate attachment is another stabilizing factor for the modified nanoparticles [2, 71, 77]. In the case of the bifunctional (11-hydroxyundecyl)phosphonic acid it is interesting to note that the phosphonate group and not the carboxylate group was bonded to the stannia surface.

Phosphonate modification is very powerful for metal oxide surfaces such as alumina or titania, but Si–O–P bonds created by interaction of a phosphonate with a silica surface are not very stable. As a matter of fact, the Si–O–P bond is sensible to hydrolysis, contrary to other M–O–P bonds. The use of phosphonate modification of metal oxide surfaces is consequently limited to non-siliceous particles [71, 77].

Thus, for some applications, like the immobilization of proteins, it can be very advantageous to modify a surface with a phosphonate group instead of a silyl group, because of the higher stability of the resulting layer under physiological conditions as well as the fact that there is no need of a preliminary surface conditioning [70].

Chemical Functionalization of Nanoparticles

So much work was already done on the modification of nanoparticles that it is no longer possible to describe all systems exhaustively. We therefore restrict ourselves to some representative examples of nanoparticle functionalization, highlighting the previous discussion and making clear the richness of such chemistry.

There are two strategies for the introduction of functional groups (Fig. 4). The first method ("method 1") consists in introducing the whole functional ligand in a single step. This requires bifunctional organic compounds, where one functionality (*X*) is used to attach to the nanoparticle surface and the second group (*Z*) is the group by which the nanoparticle is functionalized. In "method 2", a bifunc-

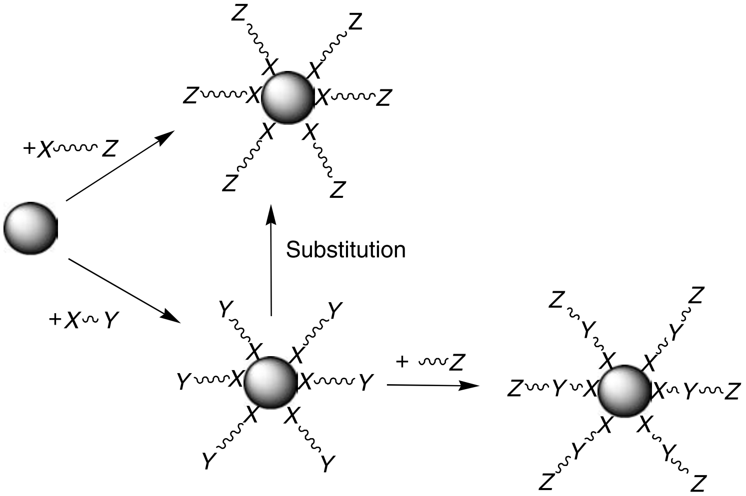

Fig. 4. Two ways to functionalize nanoparticles. Method 1 (*top*) Ligands with the *Z* functionality react directly with the nanoparticle; method 2 (*bottom*): a ligand with a *Y* functionality reacts directly with the nanoparticle and is, in a second step, converted in another functionality *Z*

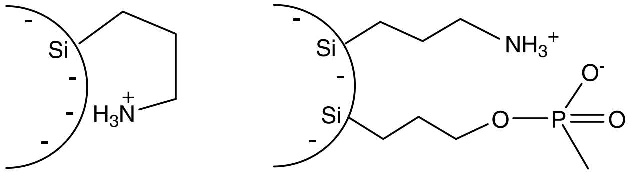

Fig. 5. Stabilization of nanoparticles by interaction between amine and phosphonate groups

tional compound *X–Y* is reacted first, where the group *Y* acts as a coupling site and can be converted, in a second step, in the final functionality *Z*. Method 1 is preferred whenever possible because there is one step less. The main reason not to use the first method is incompatibility of the functional group Z with the preparation process, for example if the group Z can also react with the particle surface. Another reason for a step-wise procedure could be steric hindrance.

An example for the interference of functional groups with the particle surface is the back bonding of amino or ammonium groups to interact with charged surfaces (Fig. 5, left). In the case of silica particles covered by 3-aminopropyl groups (from the reaction with 3-aminopropyl-triethoxysilane) the zeta potential and thus the particle agglomeration was controlled by co-reaction with 3-(trihydroxysilyl)-propylmethylphosphonate. Back bonding of the NH_2 groups on the particle surface was thus suppressed by interaction between the amino and phosphonate groups (Fig. 5, right) [78].

Examples for Method 1

The capping ligands that allow introducing various functionalities on metal nanoparticles are thiols. The functions most often introduced by thiol ligands are COOH, NH_2 or OH. These groups can undergo further chemical reactions once attached to the particle surface [4, 13–16, 22–24, 33, 79–82]. The functional groups can also provide compatibility with the environment of the nanoparticles. For example, the grafting of carboxylate-terminated alkanethiols results in water-dispersible nanoparticles [5, 13, 83].

An example of modified gold nanoparticles using a functional thiol is shown in Fig. 6. In this example the functionality is a bipyridine group capable of binding metal cations [84, 85].

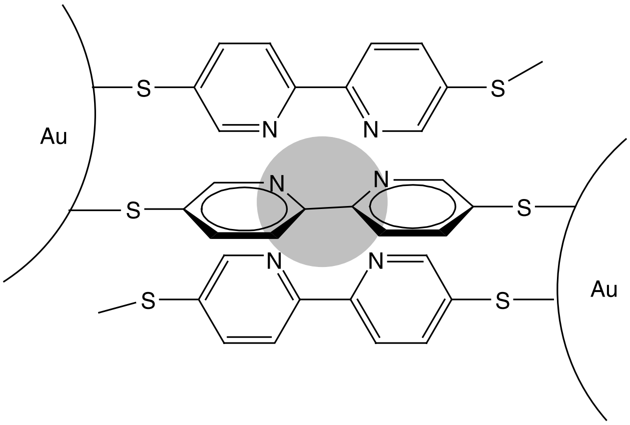

Fig. 6. Modified gold nanoparticles as cation scavengers

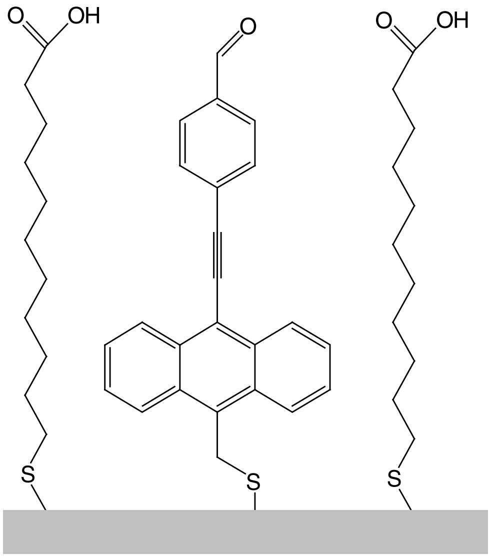

Fig. 7. Modifiable functional ligands on gold nanoparticles

As mentioned before, one of the very interesting features of gold nanoparticles is that they are tolerated by organisms. Consequently, a large field of applications for gold nanoparticle is their use as vehicles in biological systems. Furthermore, gold nanoparticles can bear sensor, marker or bio-molecule anchoring sites, as shown in Fig. 7 [70, 86]. Ligands with long alkyl chains are used to provide stability to the ligand layer, and the aldehyde group at the end of the chain can be used for further reaction.

In the first part of this review, the ligand influence on the nanoparticles properties was mentioned. An example are electron transfer phenomena between a pyrene-substituted thiol, the chromophore, and gold nanoparticles, leading to a dramatic increase in the emission yield. In this example the authors reduced the gold nanoparticle precursor, $HAuCl_4$, with $NaBH_4$ in the presence of pyrenylalkanethiol [37]. An alternative synthesis method was to stabilize first the gold nanoparticles using tetraoctylammonium bromide and in a second step to exchange the bromide ligand toward 1-methylaminopyrene [37].

A well-known example of modifying metal oxide nanoparticles with functional carboxylic acids is the modification of TiO_2 for dye-sensitized solar cells. In such devices, ruthenium complexes are commonly used as dyes, which are often modified with carboxylate groups to provide a stable interaction with the TiO_2 nanoparticles [87, 88]. The surface binding of the chromophores on TiO_2 is highly influenced by the number of carboxylate groups and is the most decisive factor in controlling the sensitization efficiency. An example of a dye with more than one carboxylate group is shown in Fig. 8 [89–91].

An example for bonding of a chromophore with conjugated linkers through carboxylate groups on a titania or zirconia surface is shown in Fig. 9 [92].

Coordinating nanoparticles to polymers is a very interesting way to synthesize hybrid organic-inorganic composites with synergetic properties [93].

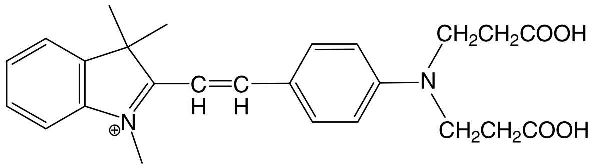

Fig. 8. A hemicyanine-based organic dye used to modify titania nanoparticles for organic solar cells

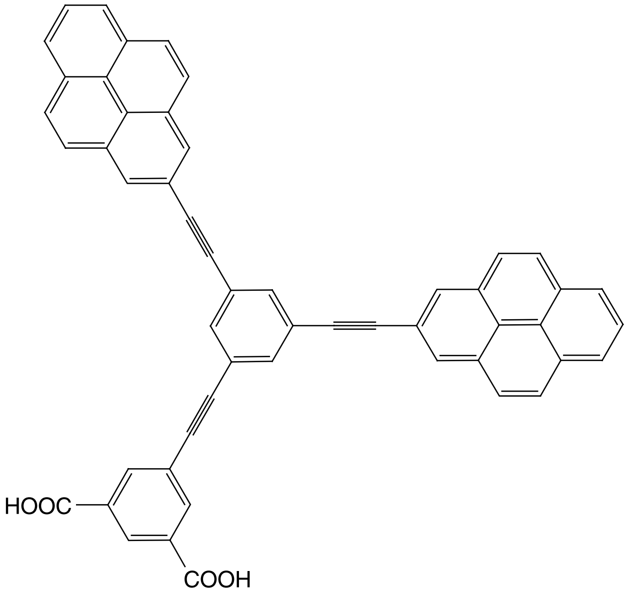

Fig. 9. A pyrene-substituted phenylenethynylene ligand

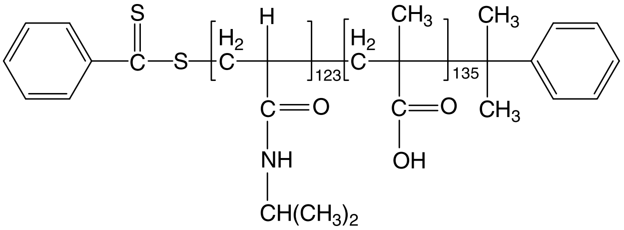

Fig. 10. Dithioester endcapped poly(methacrylic acid)-block-poly(*N*-isopropylacrylamide)

Looking at such systems from another point of view is that pending functional groups at the polymer serve as ligands to the nanoparticles. Studies on photovoltaic cells have investigated the impact of carboxylate group density for conducting carboxylated polythiophenes anchored onto titania. If the density of groups is just enough to attach the polymer, the benefits of the interface modifier can be exploited without substantially decreasing the performances [94].

Another example for an interaction between a functionalized polymer and a nanoparticle is shown in Fig. 10, where $HAuCl_4$ was reduced by lithium triethylborohydride in the presence of the block copolymer, poly(methacrylic acid)-block-poly(*N*-isopropylacrylamide) [95]. The dithioester endgroup of the starting polymer is reduced to a thiol simultaneously when reducing $HAuCl_4$, and the sulfur atom coordinates the nanoparticle surface. This resulted in gold nanoparticles protected with the pH and temperature-sensitive diblock copolymer.

Several groups developed nanoparticles modified by functional ligands, where the pending functionality was used as polymerization catalyst or initiator [96, 97]. Two functionalities as chain transfer agents for reversible addition fragmentation chain transfer polymerization attached to gold nanoparticles are shown in Fig. 11 [98].

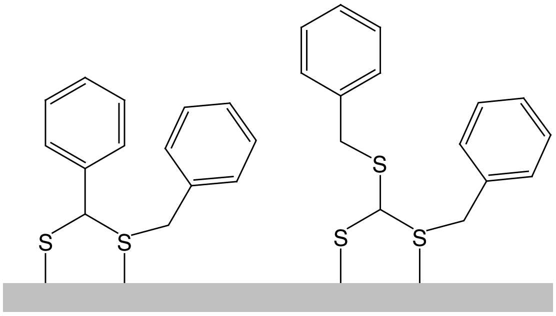

Fig. 11. Gold nanoparticles modified by reversible addition fragmentation chain transfer polymerization initiators

In building more complex nanoparticle-containing systems, it is often useful to attach the particles to another surface [2, 4, 16, 23, 64, 81]. This often requires the modification of the nanoparticles by functionalities capable of bonding to the other surface. For example, much work was devoted to the linkage of nanoparticles to carbon nanotubes, and several methods were developed [99]. An interesting example is the grafting of metal nanoparticles on the carbon nanotubes by means of *DNA* interactions. To this end, *DNA*-modified carbon nanotubes were linked to gold nanoparticles covered by complementary *DNA* to allow formation of *Watson-Crick* pairs [100].

Through the use of functional alkoxysilanes, metal nanoparticles can easily be functionalized by reactive Si(O*R*)$_3$ groups which allow subsequent bonding to metal oxide surfaces (Fig. 12) [101, 102]. This possibility is of course not applicable to metal oxide particles, because in this case the Si(O*R*)$_3$ groups would react with the oxide.

Examples for Method 2

It was already pointed out that the first method of nanoparticle functionalization, *i.e.*, the introduction of the functional ligand in one step, has several constraints. Consequently, many systems were developed following the second method, where the nanoparticles are first stabilized with a ligand the functional group of which can then be altered to achieve the desired final functionality. A very illustrative example on the stepwise formation of the final functionality is shown in Fig. 13. *Ding et al.* introduced an atom transfer radical polymerization catalyst on Fe$_3$O$_4$ nanoparticles by stepwise modification of an aminopropylsilyl ligand [2, 103]. In the first step, an olefinic group was introduced by reacting the NH$_2$ group of the aminopropyl ligand, which was then reacted with a triamine to eventually obtain a strongly chelating ligand for the coordination of copper bromide.

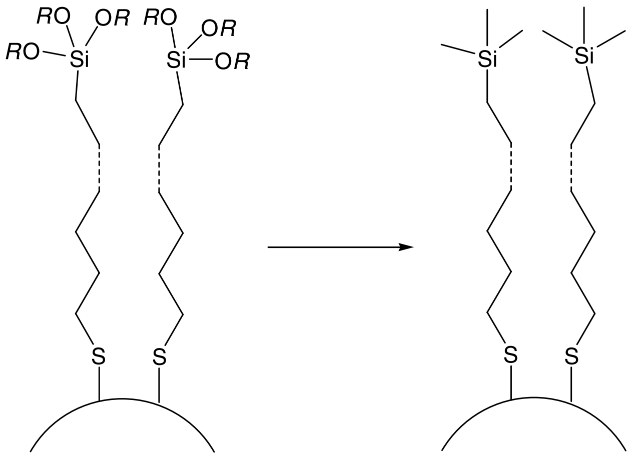

Fig. 12. Modification of silver nanoparticles by alkoxysilyl-substituted thiols

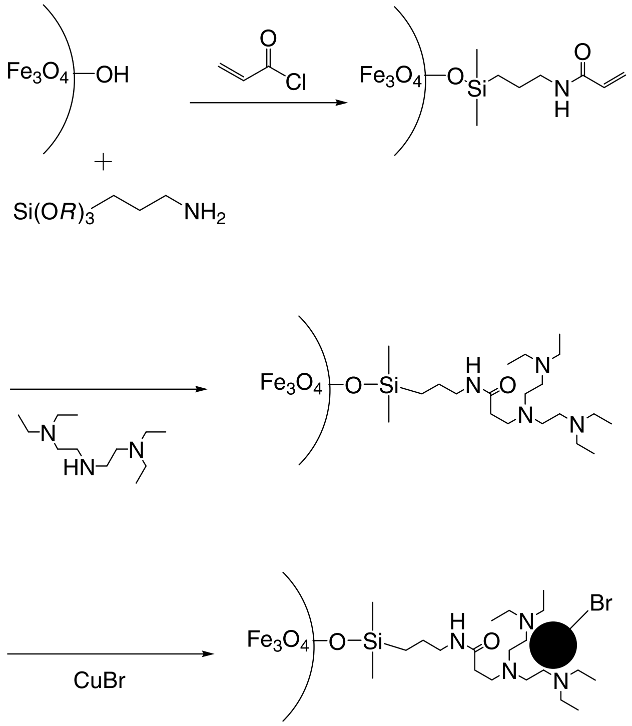

Fig. 13. Modification of a Fe$_3$O$_4$ surface to graft a catalyst for atom transfer radical polymerization

The use of functionalized trialkoxysilanes is widespread. As a matter of fact, many organic func-

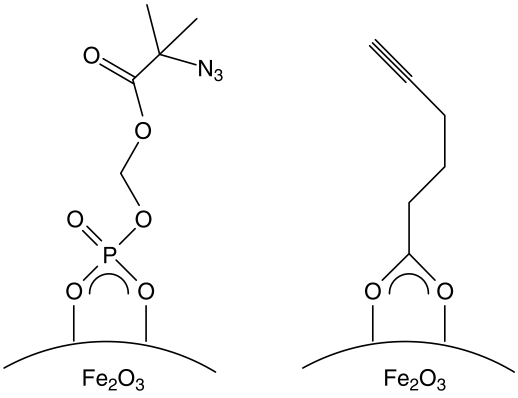

Fig. 14. An azide-substituted phosphonate (*left*) and alkyne-substituted carboxylate ligand (*right*) on Fe$_2$O$_3$ nanoparticles

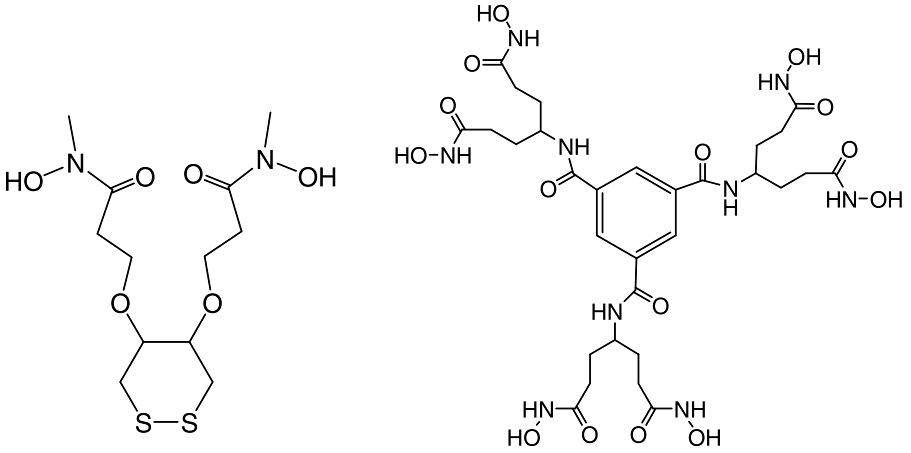

Fig. 15. Hydroxamate derivatives used for the formation of a dendrimeric shell around gold nanoparticles

tionalities can be attached to alkoxysilanes, such as vinyl, epoxy, amino, sulfur-containing, phosphonic acid groups, *etc.* [48, 55, 58, 60, 61, 63, 66, 104–107].

Azide- or alkynyl-substituted carboxylate and phosphonate ligands (Fig. 14) were used by *Turro et al.* to functionalize Fe_2O_3 nanoparticles by click reactions. The nanoparticles are first synthesized in the presence of oleic acid, and then the acid was replaced either by the phosphonic or carboxylic acid. The thus functionalized nanoparticles were then reacted with complementary click functional compounds, *viz.* the N_3-substituted particle with 5-chloropentyne, and the alkynyl-substituted particle with benzyl azide [74].

Wanunu et al. built a dendrimeric shell on gold nanoparticles by stepwise chelation of Zr(IV) making use of the functional organic groups in the organic layer. The surface initiation sites for dendrimer growth were obtained by incorporating small proportions of bis-hydroxamate disulfide anchor ligands (Fig. 15, left) in the octanethiol surface layer. Alternate coordination of Zr(IV) ions to the pending hydroxamate groups followed by coordination of branched ligands (Fig. 15, right) to the Zr(IV) centers afforded surface-confined dendrimers of increasing generation when this sequence was repeated [108].

The first part of this review highlighted the fact that ligand exchange reactions are equilibria that depend on the bonds strengths of the involved ligands. Incomplete exchange results in nanoparticles bearing both ligands. This can be used to prepare multifunctional nanoparticles (Figs. 16 and 17) [12, 35, 109]. The functional groups introduced by such exchange reactions can be used for further modification, as shown in Fig. 17, where bromide is exchanged for azide groups followed by a click reaction.

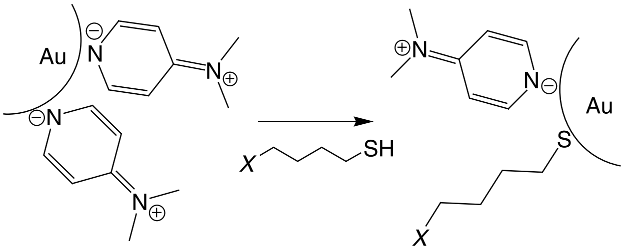

Fig. 16. Dimethylaminopyridine-thiol exchange on a gold nanoparticle

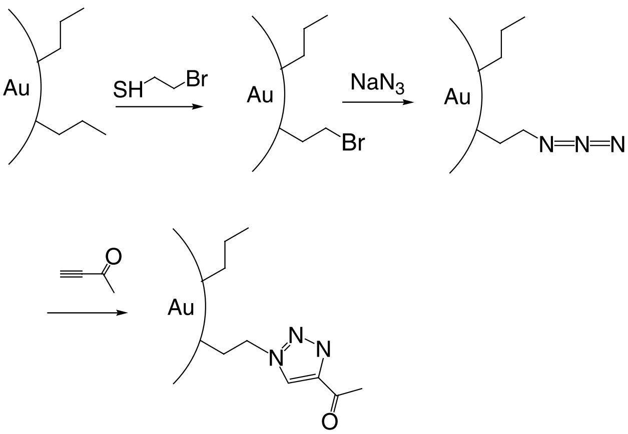

Fig. 17. Preparation of multifunctional gold nanoparticles by thiol exchange

A completely different approach of modifying thiol-stabilized nanoparticles was reported by *Brinker et al.* Since alkyl chains are chemically inert,

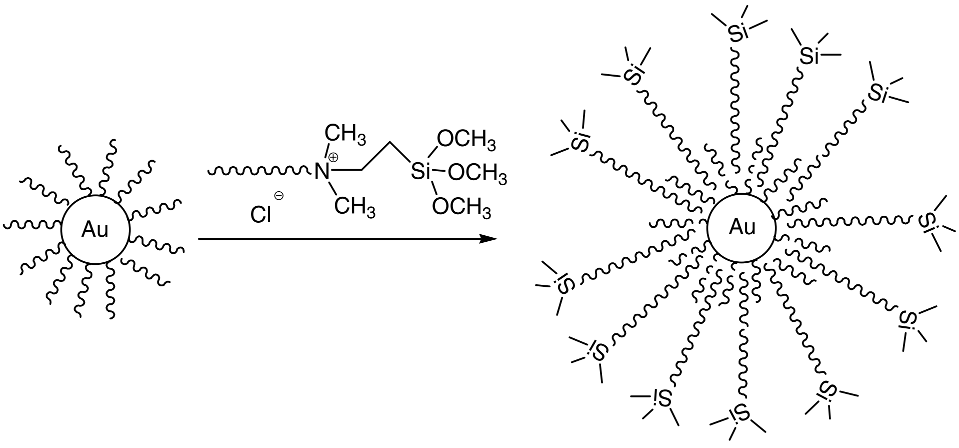

Fig. 18. Self-assembly of octadecyldimethyl(3-trimethoxysilylpropyl)ammonium chloride around dodecanethiol-stabilized gold nanoparticles

preventing further chemical functionalization, hydrophobic interactions between alkyl chains were utilized for functionalization. To this end, dodecanethiol-stabilized gold nanoparticles were reacted with octadecyldimethyl(3-trimethoxysilylpropyl)-ammonium chloride. The long alkyl chains of both the adsorbed thiol ligand and ammonium ligand are interacting with each other. The resulting self-assembled micelles around a gold core are thus formed by a primary layer of alkanethiol groups and a secondary layer of long chain ammonium groups bearing alkoxysilyl head groups outside, (see Fig. 18). The accessible outer silyl groups are still able of reacting in a subsequent reaction step, for example hydrolytic polycondensation [16].

Chlorohydrogenosilanes, such as $H(CH_3)_2SiCl$, are also powerful agents to introduce functional groups on a surface. Upon reaction of the chlorosilane, Si–H groups are introduced on the surface, which are very reactive toward alkenes, alkynes, triazonium salts, *etc.* [2]. The Si–H function can also be converted in Si–Cl groups by reaction with PCl_5 (Fig. 19) for further introducing another functionality [110–112].

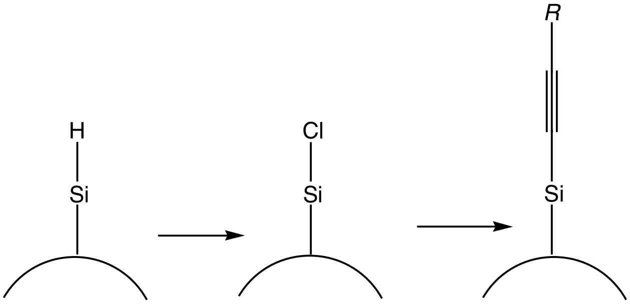

Fig. 19. Modification of hydrogenosilyl groups

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