Interaction of Phosphorus Dendrimers with Pre-Existing Metal Nanoparticles

Subjects: Nanoscience & Nanotechnology

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Nanoparticles are defined as matter that has at least one dimension between 1 and 100 nm, and that generally has different properties from its bulk. This is particularly the case for metal nanoparticles, such as gold nanoparticles (NPs), which have a different color depending on their size and differs from the color of bulk gold, in connection with their surface plasmon resonance. Gold NPs are widely used for diagnostics and therapy. Dendrimers are monodisperse hyperbranched polymers of nanometric size, very different from classical polymers, as they are synthesized step-by-step and not by bulk polymerization reactions. Most dendrimers are synthesized by a divergent process, starting from a multifunctional core, possessing 2 to 8 functions in most cases. Such a divergent process frequently involves two steps. Among the different types of dendrimers, polyphosphorhydrazone (PPH) dendrimers have been chosen.
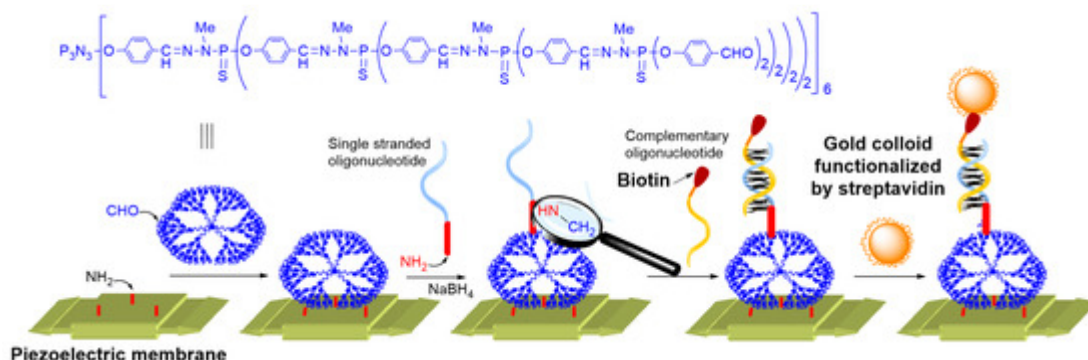
dendrimers   nanoparticles   hybrid materials

1. Gold Nanoparticles

Gold nanoparticles display a wide range of properties, depending on their size and the stabilizer used, and have been reviewed [1][2]. They have been used as catalysts [3]; as chemical and biological sensors [4]; and in medicine [5][6][7] for diagnosis, imaging, therapy [8], and drug delivery [9]. Two types of functionalized commercially available gold nanoparticles have been used in the interaction with phosphorus PPH dendrimers. A review has gathered the examples of the interplay of gold with phosphorus dendrimers, but focusing essentially on discrete complexes [10].
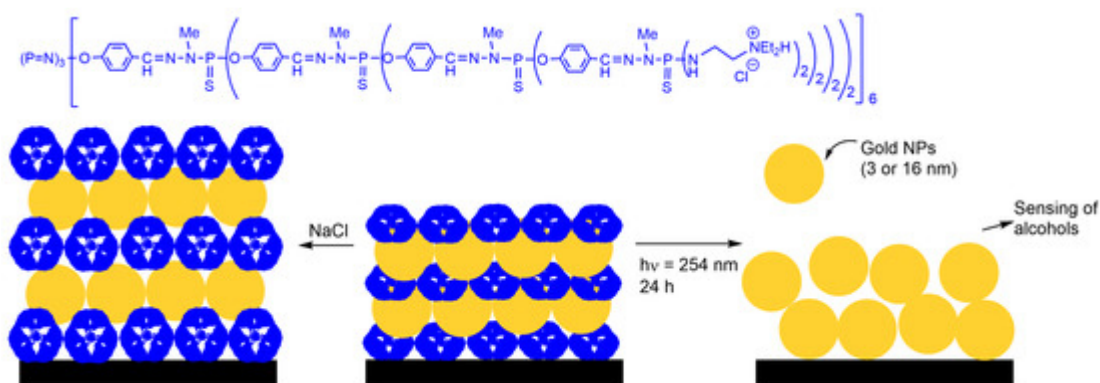
A fourth-generation phosphorhydrazone dendrimer has been covalently grafted to a piezoelectric membrane, preliminarily functionalized with γ-aminopropyltriethoxysilane (APTS); then, a single-stranded oligonucleotide functionalized on one end with a primary amine was covalently grafted, using a known procedure [11][12]. The resulting imine bonds were reduced with $NaBH_4$ to afford stable secondary amines, and the remaining aldehydes on the surface of the dendrimers were reduced to alcohols. A complementary oligonucleotide functionalized on one end with biotin was then hybridized. The presence of dendrimers as 3D linkers between a solid surface and an oligonucleotide is known to favor the hybridization, as it occurs away from the solid surface, almost like in solution, contrarily to classical linkers that fall onto the surface [13]. This system was used as a very sensitive sensor for monitoring the real-time kinetics of the absorption of gold colloids functionalized with streptavidin (diameter 40 nm) on the functionalized membrane (Scheme 1) [14]. This method was chosen to profit from the well-known strong association of biotin with streptavidin [15][16][17]. The mass sensitivity of the device, estimated as −3.9 Hz/pg, was

better than state-of-the-art values for piezoelectric mass-sensing devices by a factor of several hundred at that time (2005) [14].

Scheme 1. Step-by-step modification of a piezoelectric membrane for sensing gold nanoparticles [14]. Covalent bonding between dendrimer and oligonucleotide shown inside the magnifying glass.

Besides the covalent grafting of dendrimers to the surface shown in the previous paragraphs, they can also be deposited layer-by-layer by electrostatic interactions on positively charged surfaces. Such positive surfaces were obtained by first coating the surface with 3-(diethoxymethylsilyl) propylamine (3-APDMES). Using alternate negatively and positively charged dendrimers, both of generation 4, enabled the step-by-step increase in the thickness of the coating by electrostatic interactions [18]. An analogous process was carried out with anionic gold nanoparticles (Au NPs), instead of the anionic dendrimers. These Au NPs equipped with anionic carboxyl functional groups were synthesized according to published procedures [19][20], and had diameters of approximately either 3 or 16 nm, as determined by TEM (transmission electron microscopy). These Au NPs and fourth-generation cationic phosphorus dendrimers (48 ammonium terminal functions) were deposited alternately on 3-APDMES-coated substrates (silicon wafer or quartz of a micro-balance) [21]. The deposition was carried out by immersing the substrates into Au NP colloidal suspensions for several minutes, followed by a rinsing step to remove any physically adsorbed NPs, and blow-drying with nitrogen. The same process was also carried out with the positively charged dendrimers, and each step was monitored by UV-vis spectroscopy. Up to 10 bilayers (Au NPs/dendrimers) were deposited. Upon addition of salt (NaCl), the dendrimers were swollen, probably due to reduced electrostatic repulsion between neighboring identically charged species [22], leading to an increase in the average distance between Au layers. The films were also exposed to deep UV light with a wavelength of 254 nm for 24 h, with the aim of removing the dendrimers (Scheme 2). Indeed, the dendrimer strongly absorbs at this wavelength and is destroyed by prolonged irradiation, as already observed in MALDI-Tof spectrometry, which used a UV-laser for desorption [23]. These films composed of Au nanoparticles (and a few remaining dendritic residues) were investigated in the sensing of five alcohols with different refractive indices, which were methanol, ethanol, 1-propanol, 1-butanol, and 1-pentanol, whose refractive indices are 1.329, 1.361, 1.385, 1.399, and 1.410, respectively. The absorbance peak (λ_{max}) of Au multilayer films exhibited a moderate red-shift as the refractive index of the solvents increased, showing their potential as chemical sensors [21].

Scheme 2. Structure of fourth-generation dendrimer functionalized with ammoniums on its surface, and its use for the layer-by-layer elaboration of a multilayer with negatively charged gold nanoparticles [21].

2. ZnCdSe Quantum Dots

Based on the method shown in Scheme 2, layer-by-layer electrostatic deposition inside the porous alumina membrane, of 400 nm in diameter with a pore depth of 80 μm, was carried out with positively and negatively charged phosphorus dendrimers. After removal of the template, such a process afforded nanotubes made of dendrimers [18]. The same process inside porous alumina was applied to quantum dots (QDs), which are fluorophores based on metallic nanoparticles such as ZnCdSe alloys, instead of the negatively charged dendrimers. In fact, three bilayers of positively and negatively charged dendrimers were first deposited inside the pores, previously functionalized with 3-APDMES (**Figure 1**). Five bilayers of positively charged dendrimers and negatively charged QDs with a luminescence maximum at λ = 561 nm (QD^{561}, green) were then deposited, followed by five bilayers of the same type, based on QD^{594} (orange), and finally five analogous bilayers based on QD^{614} (red). A graded-bandgap was observed with these nanotubes composed of dendrimers and quantum dots, as they exclusively show an emission peak centered at λ = 614 nm, originating from QD^{614}. On the top of this perfectly controlled multilayer, a 15-mer probe DNA (p-DNA) was immobilized and used for hybridization with Cy5-labeled complementary DNA (t-DNA) (**Figure 1**). Detection through fluorescence/Förster resonance energy transfer (FRET) displayed an increase in the Cy5 emission, which received an energy transfer of approximately 3.2% from the quantum dots. Although the energy transfer efficiency from the QDs to Cy5 is relatively low, it is sufficient to ensure the sensitive detection of DNA hybridization, with an enhancement factor of, ca. 15, indicating that such devices have potential utility for the detection of trace amounts of DNA [24]. Such devices were also elaborated on Au-coated glass surfaces, but not tested for DNA hybridization [25]. The work concerning the layer-by-layer modification of materials with dendrimers has been reviewed [26].
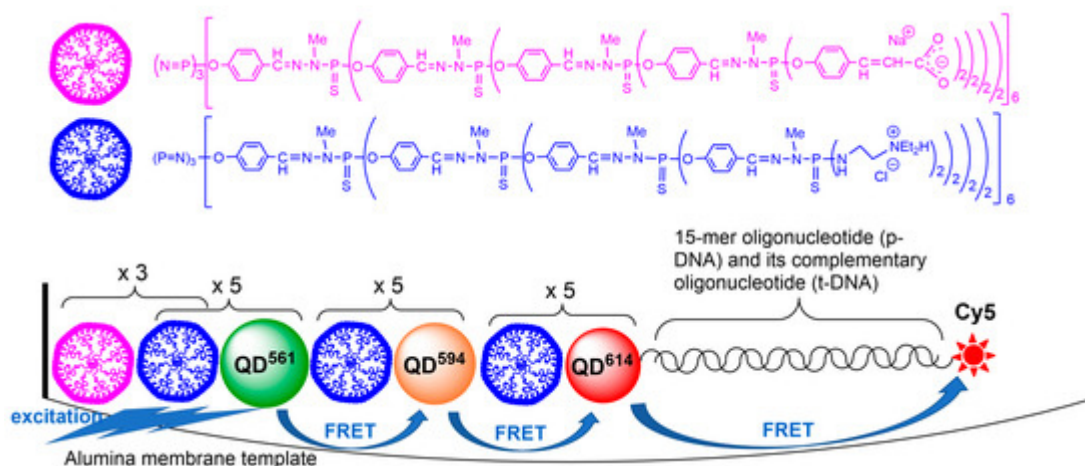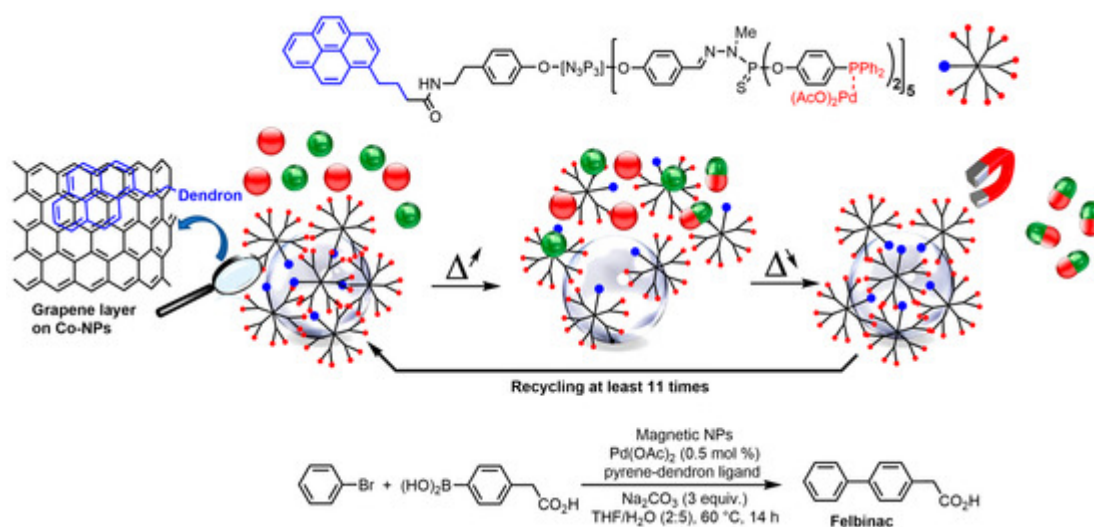
Figure 3. Schematization of a device comprising charged dendrimers and quantum dots associated with electrostatic interactions, for the sensitive detection of DNA [24].
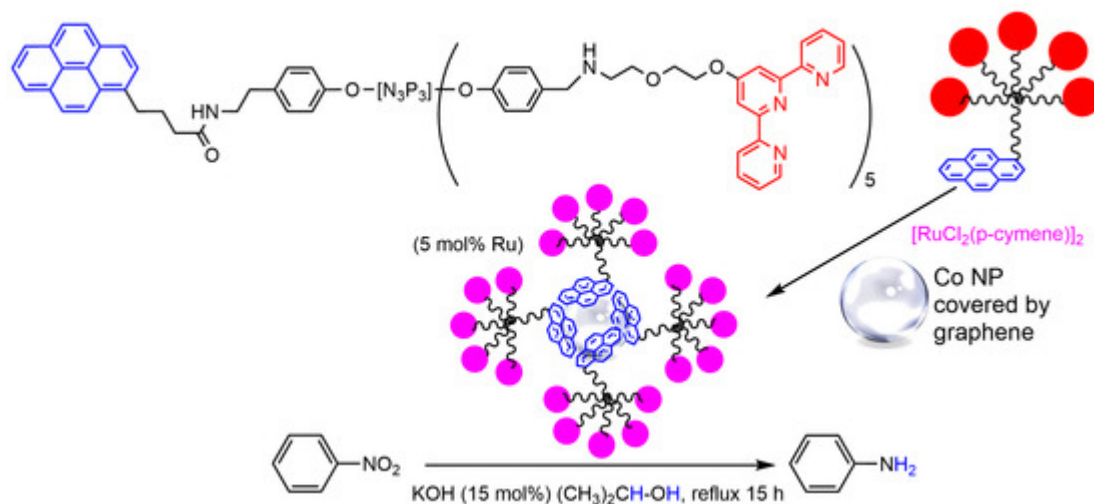
3. Cobalt Nanoparticles

Cobalt nanoparticles covered by a few layers of graphene were used as support for catalysts [27]. Cobalt nanoparticles (Co NPs) are magnetic; thus, they can be easily recovered using a magnet [28]. In the first experiment, two phosphorus dendrons (generations 0 and 1) bearing a pyrene at the core and 5 or 10 triphenyl phosphines as terminal functions were used for complexing palladium, as previously reported [29]. The specific reaction of one of the chlorides of the cyclotriphosphazene $N_3P_3Cl_6$, affording one function different from the five others, has been used for the synthesis of these dendrons. Such a possibility was previously used for the synthesis of dendritic structures, and has been reviewed [30]. The dendrons shown in Scheme 3 cover the Co-NPs at room temperature by π-stacking interactions between the pyrene at the core of the dendrons and the graphene layers on the NPs. Heating in solution fragilizes this interaction, and the dendrons go inside the solution, where they can perform catalysis. At the end of catalysis, cooling the reaction medium permits the dendrons to interact again by π-stacking with the NPs, which can be taken off the reaction medium using a magnet. In this way, the dendron can be easily recovered and reused. The concept was applied to the synthesis of Felbinac (an anti-inflammatory drug) by Suzuki coupling [31], using the zeroth-generation dendron (five phosphine complexes) (Scheme 3). The catalytic dendrons were recovered eleven times, displaying even at run 12 a 100% yield in Felbinac [27].

Scheme 3. Cobalt nanoparticle covered by a few layers of graphene, and by dendrons interacting by π-stacking (see the magnifying glass), used as easily recovered catalyst in Suzuki reactions [27].

A related work was carried out with a small dendron functionalized with a pyrene at the core and five terpyridines on the surface, suitable for the complexation of ruthenium. This complex was used for catalyzing the hydrogenation of nitrobenzene to aniline, using 2-propanol as the transfer hydrogen source (Scheme 4). In that case also, the dendron onto the cobalt NPs could be recovered using a magnet and reused at least seven times [32]. The efficiency of magnetic nanoparticles as versatile supports for catalysts has been reviewed [33].

Scheme 4. Transfer hydrogenation catalysis with dendrons interacting by π-stacking with Co-NPs [32].

The same type of π-stacking interaction was also applied to a dendron bearing a pyrene moiety at the core and 10 poly(vinylidene fluoride) (PVDF) chains on the surface. In order to maximize the efficiency of interaction with the Co-NPs, a long linker was used between the pyrene and the cyclotriphosphazene (**Figure 2**). The stability of the π-stacking interactions when the temperature increased and the reversibility of the process when the temperature decreased were studied. A partial release of the dendron from the surface of the Co-NPs was observed at 60 °C, but a partial reversibility to the π-stacking was observed on cooling to 20 °C. [34].
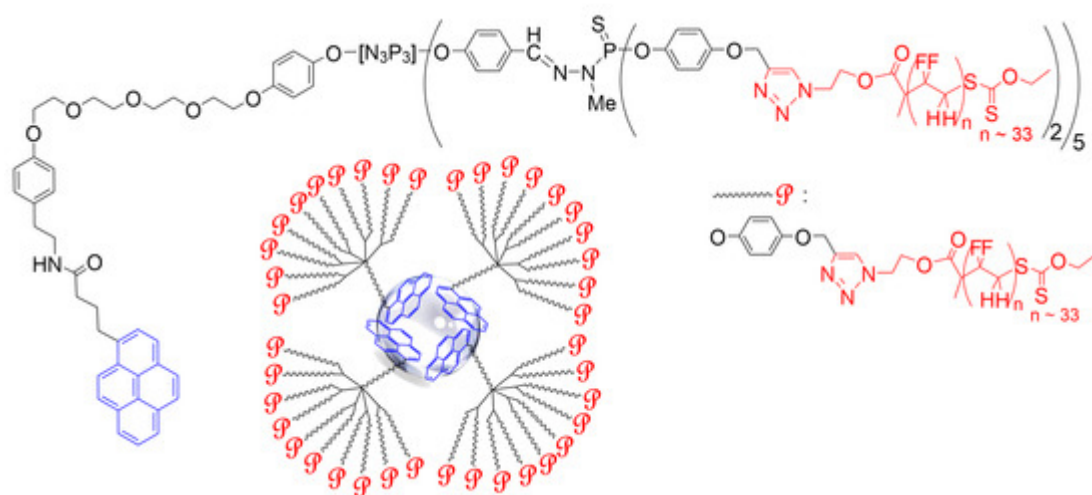
Figure 2. Dendron functionalized with 10 poly(vinylidene fluoride) chains, and interacting by π-stacking with Co-NPs [34].

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