THE SURFACE MODIFICATION OF NANOPARTICLES COMPRISED OF MAGNETIC IRON OXIDE

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Abstract:
Iron oxide nanoparticles that have been functionalized are very interesting since they have several uses, particularly in nanomedicine. However, obstacles such fast aggregation, oxidation, etc. limit their potential uses. These limitations may be overcome by iron oxide nanoparticles with increased physicochemical characteristics after adequate surface modification. Recent developments in the surface modification of iron oxide nanoparticles using tiny organic compounds, polymers, and inorganic materials are summarized in this study. Various materials' surface-modified iron oxide nanoparticle production techniques, working principles, and applications are described. Finally, the development trends and possibilities are reviewed along with the technological challenges faced by iron oxide nanoparticles and their limits in real-world applications.
Keywords*: magnetic nanoparticles; nanomedicine; iron oxide nanoparticles; surface modification*

Introduction

Due to its many uses in a variety of sectors, including catalysis, data storage, environmental cleanup, magnetic fluids, electronic communication, and biomedicine, magnetic nanoparticles are now a hot topic of research. Due to their simplicity in surface modification, ease of production, and low toxicity, iron oxide nanoparticles are the most well-known and often utilized forms of magnetic nanoparticles in the area of biomedicine. The use of magnetic iron oxide nanoparticles in cancer treatment, magnetic resonance imaging agents, bioseparation, gene delivery, biosensors, protein purification, immunoassays, and cell labeling has been confirmed by recent studies and published literature.

However, owing to their enormous surface area, chemical reactivity, and high surface energy, iron oxide nanoparticles suffer from two key problems that cause them to lose their magnetic. These problems include fast aggregation and oxidation into the physiological milieu of tumors. Iron oxide nanoparticles must thus undergo the proper surface modification in order to make them biocompatible. The most popular technique for surface modification that couples organic or inorganic elements to iron oxide nanoparticle surfaces is the coating method. This technique not only stops iron oxide nanoparticles from oxidizing and clumping together, but it also offers the potential for further functionalization. Magnetic iron oxide nanoparticles may be functionalized to enhance their physicochemical characteristics, making them excellent candidates for use in biomedicine and catalysis.

Different IONP properties, including size, shape, morphology, and dispersability, may influence how they are used in biomedicine. As a result, scientists are concentrating on creating MNPs by employing various methods to regulate their morphology, size, and form in order to give them changeable and desired qualities. There have been numerous reported synthesis methods used to create magnetic iron oxide nanoparticles, including co-precipitation, hydrothermal, thermal decomposition, microemulsion, electrochemical deposition, laser pyrolysis, solvothermal methods, sonochemical methods, chemical vapor deposition, the microwave assisted method, and aerosol pyrolysis.

We briefly discuss the reasons why surface modification of MNPs is fundamentally necessary in this review before introducing the architectures of magnetic iron oxide nanocomposites. Inorganic and organic materials are the two types of materials utilized in surface modification. Small molecules and polymers make up the molecules of organic materials, while silica, carbon, metals, and metal oxides/sulfides make up the molecules of inorganic materials. The surface coating mechanisms of IONPs, current developments, and their uses in diverse sectors are discussed in the following section.

Surface Modification of Magnetic Iron Oxide Nanoparticles and Applications

There are four main purposes of surface modification of NPs:

(1) To improve or change the dispersion of MNPs;

(2) To improve the surface activity of MNPs;

(3) To enhance the physicochemical and mechanical properties; and

(4) To improve the bicompatibility of MNPs. There are mainly four magnetic iron oxide nanocomposites.

Surface Coating with Inorganic Materials

Silica

The most popular and commonly used substance for altering the surface of iron oxide nanoparticles is silica. The benefits of silica coating include less clumping, improved stability, and a decrease in the cytotoxic effects of MNPs. As a result, it has shown high stability, hydrophilicity, and biocompatibility. The process to adjust the size and thickness of the silica coated NPs has recently been disclosed by researchers. There are four primary methods to produce IONP@SiO_2.

The second technique is the microemulsion technique, which has two subtypes: oil-in-water (O/W, reversed micelles) and water-in-oil (W/O, micelles). The microemulsion method, which combines water, oil, and surfactant, may be used to create sillca-coated iron oxide nanoparticles with high crystallinity. By using a microemulsion technique, Du et al. were able to create an antiseptic compound called cetyl trimethylammonium bromide to further functionalize the silica-encapsulated V core-shell structure. Their findings demonstrated that the water/surfactant molar ratio of the microemulsion system affects the core size of Fe_3O_4 NPs. Monodisperse dendritic mesoporous silica-encapsulated magnetic nanospheres with pore sizes of around 5.7 to 10.3 nm and shell thickness of 40 to 100 nm were created by Yang et al. using an oil-water two-phase multilayer coating method.

The third technique is called aerosol pyrolysis, which is very creative, extremely effective, and often done in a flame setting. Large-scale manufacture of carbon black, ceramic goods including fumed silica and titania, as well as zinc oxide and alumina powders, often use flame aerosol technology. The research team led by Professor Pratsinis has produced some very excellent results in this area. In his laboratories, he created the flame spray pyrolysis method for the production of aerosol films and particles at rates of up to 5 kg/h. In his experiments, he has shown how to precisely regulate the size, crystallinity, and morphology of aerosol particles, ranging from perfectly spherical to extremely ramified fractal-like formations. In a recent publication, his team studied the effects of humidity on the shape and size distribution of silica nanoparticle agglomerates.

The silica layer's many reactive silanol groups may also be used for further surface functionalization. The most often utilized binding ligands are 3-aminopropyl)triethoxysilane (APTES), 3-Mercaptopropyl)triMethoxysilane (MPTS), triethoxy vinyl silanes (VTES), and aminosilane. MNPs made of functionalized Fe3O4@SiO2 have several uses in the biomedical and environmental domains.

Carbon

Inorganic compounds with carbon-based compositions are also employed to coat the surface of IONPs to improve their stability, biocompatibility, and dispersivity. The Fe3O4@C nanocomposites have a variety of uses, including anode materials for lithium-ion batteries, electrode supercapacitors, microwave absorbers, and catalysts. Fe_3O_4@C nanocomposites have been shown by several research teams to be the best materials for supercapacitors. For example, Liu et al. created carbon-coated Fe_3O_4 nanorods by hydrothermal processes and a carbon-thermal reduction method, and they showed that the Fe_3O_4/C nanorods had greater specific capacitance and better cycle performance than pure Fe_3O_4. Typically, a carbon layer that keeps the particles intact and increases the electrodes' electrical conductivity causes this phenomena to occur.

Sinan et al. effectively synthesized multilayer porous Fe_3O_4/C nanocomposites with high specific surface area by hydrothermal carbonization and the MgO template technique after initially synthesizing Fe3O4 NPs using a co-precipitation approach. This demonstrated the great potential for Fe_3O_4/C nanocomposites as a negative material for asymmetric supercapacitors. According to studies, the addition of activated carbon with a three-dimensional (3D) network structure may improve Fe3O4's cycle stability and conductivity.

Metal

Metallic materials applied to the surface of IONPS may create an inert layer that generally has a core-shell, core-satellite, or dumbbell structure. To further functionalize the IONPS and increase stability and compatibility, metallic coatings are made possible.

Oleic acid and oleylamine are often present in the solution as a capping agent in the organic synthesis pathway. In the presence of oleic acid and oleylamine, Freitas et al. employed 1-hexadecanol to decrease $Fe(acac)_3$ for amine-functionalized Fe_3O4 NPs. A reducing agent is another function of oleylamine. These amine groups are able to bind Au3+. Then, in three Fe3O4:HAuCl4 molar ratios (1:1, 1:4, and 1:7), they created core-shell Fe_3O_4@Au MNPs. According to their findings, Fe3O4@Au produced in a 1:4 ratio performs best, whereas a 1:1 gold shell cannot entirely encapsulate the Fe_3O_4 core. As an iron precursor and a gold precursor, respectively, Li and colleagues utilized FeO(OH) and HAuCl4, respectively. By reducing FeO(OH) and $HAuC_{l4}$ in 1-octadecene solvent, octahedron-like Au/Fe_3O_4 NPs were created in the presence of oleic acid. The ratio of the raw components determines the size of the produced particles.

On the other hand, due to their distinct antibacterial properties, silver-coated magnetic nanocomposites are regarded as potential multifunctional materials as well. However, hybrid Fe_3O_4@C@Ag nanocomposites are the most common kind due to their vast use in several research fields. Fe_3O_4@C@Ag nanocomposites were created by Xia et al. They came to the conclusion that adding a carbon layer improved the antibacterial activity of the nanocomposites over Fe_3O_4@Ag. As a result, the hybrid Fe_3O_4@C@Ag may be employed as adsorbents, magneto-optical probes, antibacterial agents, catalysts, and more. As a bi-functional probe for MRI and two-photon fluorescence (TPF) imaging methods as well as for near-infrared light sensitive drug delivery, Chen et al. developed a multifunctional system based on Fe_3O_4@C@Ag hybrid NPs.

Metal Oxides/Sulfides

In the functionalization of IONPs, distinct physicochemical characteristics of metal oxides and metal sulfides are quite interesting. Generally, by examining the structure, the metal oxides are categorized into six basic groups such as M2O (Cu_2O, Ag_2O etc.), MO (ZnO, MgO, CoO, ZnS, CdS etc.), $M2O_3$ (Al2O3, Y_2O_3, Bi_2S_3 etc.), MO_2 (TiO_2, SnO_2 etc.), M_2O_5 (V_2O_5 etc.) and MO_3 (WO_3, MoO_3 etc.). By using the sonochemical approach, Saffari created superparamagnetic Fe_3O_4-ZnO nanocomposites with 10% ZnO content and found that the Fe_3O_4/ZnO nanocomposite exhibits good photocatalytic characteristics. The degradation of eight different types of organic dyes was examined, and it was discovered that the Fe_3O_4/ZnO nanocomposite possesses adequate photocatalytic characteristics. A novel variety of magnetically separable Fe_3O_4/ZnO/$CoWO_4$ nanocomposites with a distinct $CoWO_4$ ratio was recently created by Shekofteh-Gohari et al. The nanocomposites had outstanding photocatalytic activity when the $CoWO_4$ content was 30%.

Surface Coating with Organic Materials Polymers

nanoparticles of iron oxide Additionally, Hauser et al. discovered that when using synthetic techniques, the dextran concentration has a significant impact on the iron oxide nanoparticles' size, stability, crystallinity, and magnetic. Dextran-coated IONPs are regarded as attractive prospects for biomedical applications due to their biosafety, bioactivity, biocompatibility, and minimal cytotoxicity. By adding dextran and cisplatin hyaluronic acid to iron oxide nanoparticles, Unterweger et al. created a unique drug delivery method. The iron oxide nanoparticles that were drug-free shown high biocompatibility and no harmful effects after being tested in the Jurkat cell line and the PC-3 cell line, however the iron oxide nanoparticles that had been combined with cisplatin were able to cause apoptosis. In two-step and one-step processes, Osborne et al. created dextran-coated iron oxide nanoparticles that may be employed as clinical MRI contrast agents. This approach is straightforward, adaptable, economical, and repeatable. As a result, the manufacturing processes' complexity is significantly reduced, enabling the commercial production of surface-modified iron oxide nanoparticles.

Chitosan is an alkaline hydrophilic

polymer that has been shown in published studies to have low toxicity, strong biocompatibility, and biodegradability. IONPs that have been coated with chitosan are often subsequently functionalized with additional polymers like PEG and PAA. For instance, Yan et al. developed magnetic composite microspheres coated with chitosan-PAA and discovered that the addition of PAA considerably improved the ability of Cu (II) to adsorb. 10-hydroxycamptothecin (HCPT) was used by Qu et al. to PEG-chitosan-Fe3O4 nanocomposites.

Small Molecules and Surfactants

The three basic categories of functionalized NPs are lipophilic, hydrophilic, and amphiphilic. These surface-coated NPs' various surface features serve as the foundation for this kind of division. In order to make bare MNPs suitable for various applications in a variety of research fields, different functional groups (e.g., -OH, -COOH, -NH2, -SH) can be bound to the surface of the MNPs. These functional groups can then be further conjugated with different biomolecules, metal ions, and polymers. Briefly, the most popular silane coupling agents employed in the surface modification of IONPs are 3-aminopropyltriethyloxysilane (APTES), mercaptopropyltriethoxysilane (MPTES), and triethoxyvinylsilane (VTES). In order to create the APTES-coated Fe3O4 NPs with a diameter of 8.4 2.1 nm, Wang et al. used the sonochemical approach. They came to the conclusion that the produced NPs displayed superparamagnetism and excellent dispersibility. These iron oxide nanoparticles were used to produce magnetorheological fluids, which had typical magnetorheological characteristics.

The actual use of these NPs is severely constrained since using lipophilic materials coated on IONPs in a biomedical setting is not a wise option. The goal of the study is to create hydrophilic or water-soluble iron oxide nanoparticles, which will improve the practical uses of iron oxide nanoparticles. By using various manufacturing techniques, various chemical compounds, including amino acids, citric acid, vitamins, cyclodextrin dopamine, lauric acid, and dimercaptosuccinic acid (DMSA), are often employed to change the surface of IONPs in order to significantly increase their water solubility. One method is to incorporate these tiny organic molecules right away when doing the synthesis.

Jin et al. each added arginine, lysine, and poly-L-lysine to Fe_3O_4 NPs in turn. In the pH range of 4 to 10, they discovered that these samples had a high bacterial capture effectiveness. Recently, Karimzadeh et al. created a brand-new technique based on CED for the manufacture of amino acid modified Fe_3O_4 NPs. Citric acid may adsorb on the surface of magnetite NPs by the coordination of one or two carboxylate functional groups, according to Sahoo et al. The liquid laser ablation approach was used by Durdureanu-Angheluta et al. to create spherical, citric acid-coated IONPs with an average size of around 60 nm. Their created NPs feature a core-shell structure and an exterior layer made of citric acid's hydrophilic substance, which aids in the NPs' stabilization in aqueous dispersions. On the other hand, the surface decorating of IONPs also makes use of a low-cost hydrophilic material containing lipophilic cavities known as -cyclodextrin. The Fe_3O_4 NPs modified by -cyclodextrin were made by Li et al. using N_2 plasma-induced grafting. It is possible to remove both organic and inorganic pollutants with this combination. Due to their water solubility and anti-oxidant properties, a few research groups also employed ascorbic acid (vitamin C) to modify the surfaces of IONPs. They came to the conclusion that these surface decorated NPs may be used as MRI contrast agents.

Conclusions

The surface modification of IONPs by various organic molecules, such as surfactants, polymers, and inorganic substances, such as silicon groups, carbon, metal, and metal oxides/sulfides, is summarized in this paper. The range of applications for IONPs is substantially increased by surface coating, which also increases the stability, biocompatibility, and even the solubility of IONPs. There was also discussion of various synthesis techniques, reaction processes, performance, advancements, and possible applications. The purpose of citing significant research results from recent years is to provide readers of this review the information they need to understand the logical coherence of the claims made in this study concerning the surface modification of IONPs.

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