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Synthesis and organic functionalization approaches for magnetite (Fe₃O₄) nanoparticles

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ABSTRACT

Several new techniques are invented in recent years to attach organic, bio-organic functionalities to the nanostructures such as the nanoparticles. This approach of adding surface reactivity to the particles enables to tune the properties and reactivity of the resulting hybrid monolayer protected nanoparticles. Magnetic iron oxide nanoparticles of various sizes are reported which bears different organic or polymeric groups. In the present note we have revised the important methods of synthesis of magnetite (Fe₃O₄) nanoparticles and highlighted the most common strategies for the functionalization of these nanoparticles with organic compounds from very recent literature. This short note will help the students and researchers to screen and choose methods for the synthesis and functionalization of magnetite nanoparticles. Copyright © 2012 VBRI Press.

Keywords: Iron oxide (Fe₃O₄); synthesis of iron oxides; functionalization of iron oxides.

Introduction

Shell of organic compounds, surfactants or polymers are constructed around nanoparticles of various materials in order to add stability to them preventing their aggregations and minimizing surface energies [1a-b]. But in recent years newly invented experimental procedures and synthetic methods of constructions of monolayers onto the surface of nanoparticles has completely changed the initial impression of these coatings. Nanoparticles of gold, silver, silica, iron oxides, and various other materials bearing different organic functional groups are reported to the date. When bi-functional organic compounds of the type “X-(spacer)_n-FG” are used for formation of monolayers around nanoparticles the resulting nanoparticles are called as *functional nanoparticles* or *functional nanocolloids*. In the general formula FG = organic functional group and X = interacting group that helps to attach the molecule onto the surface of nanoparticles. Very recently a new term “*Organic nanocompounds*” [1c] is coined for such reactive nanoparticles bearing various organic functional groups on which any of the organic reactions can be carried out.

Iron oxide nanoparticles are of various types, some commonly synthesized and versatile iron oxides are magnetite (Fe₃O₄), hematite (α -Fe₂O₃), Maghemite (γ -Fe₂O₃), Goethite (α -FeOOH). [2] The common methods of the synthesis of iron oxide nanoparticles are listed in Table 1. In situ surface modification (monolayer formation for stabilization) and post synthetic surface modification are the two main strategies used for the tailoring of the surface properties of iron oxide nanoparticles [3]. Once the organic

or polymeric functionality gets attached to the surface of iron oxide nanoparticles these surface functional groups are then used to carry out various organic reactions. The functional groups can be utilized for attachment of bio molecules, covalent immobilizations of drugs and complex formations in detecting systems, creation of surface patterns or for constructions of layer by layer assemblies [4]. A huge number of reports on the synthesis and functionalization of magnetite nanoparticles appear in the literature. In the present short note we have revised some very latest reports on synthesis and functionalization of iron oxide (magnetite nanoparticles) so that this note will be handy for the researchers to get up to date knowledge about the happenings in this field of research.

Synthesis of magnetic iron oxide (Fe₃O₄) nanoparticles

Various chemical methods can be used to synthesize magnetic nanoparticles for medical imaging and other applications and they are: microemulsions, co-precipitation, sol-gel syntheses, sonochemical reactions, hydrothermal reactions, hydrolysis and thermolysis of precursors, flow injection syntheses and electrospray syntheses. The synthesis of superparamagnetic nanoparticles is a complex process because of their colloidal nature. The first main chemical challenge consists of defining experimental conditions, leading to a monodisperse population. Below is a list of most commonly used methods for synthesis of magnetite nanoparticles with their recent advancements.

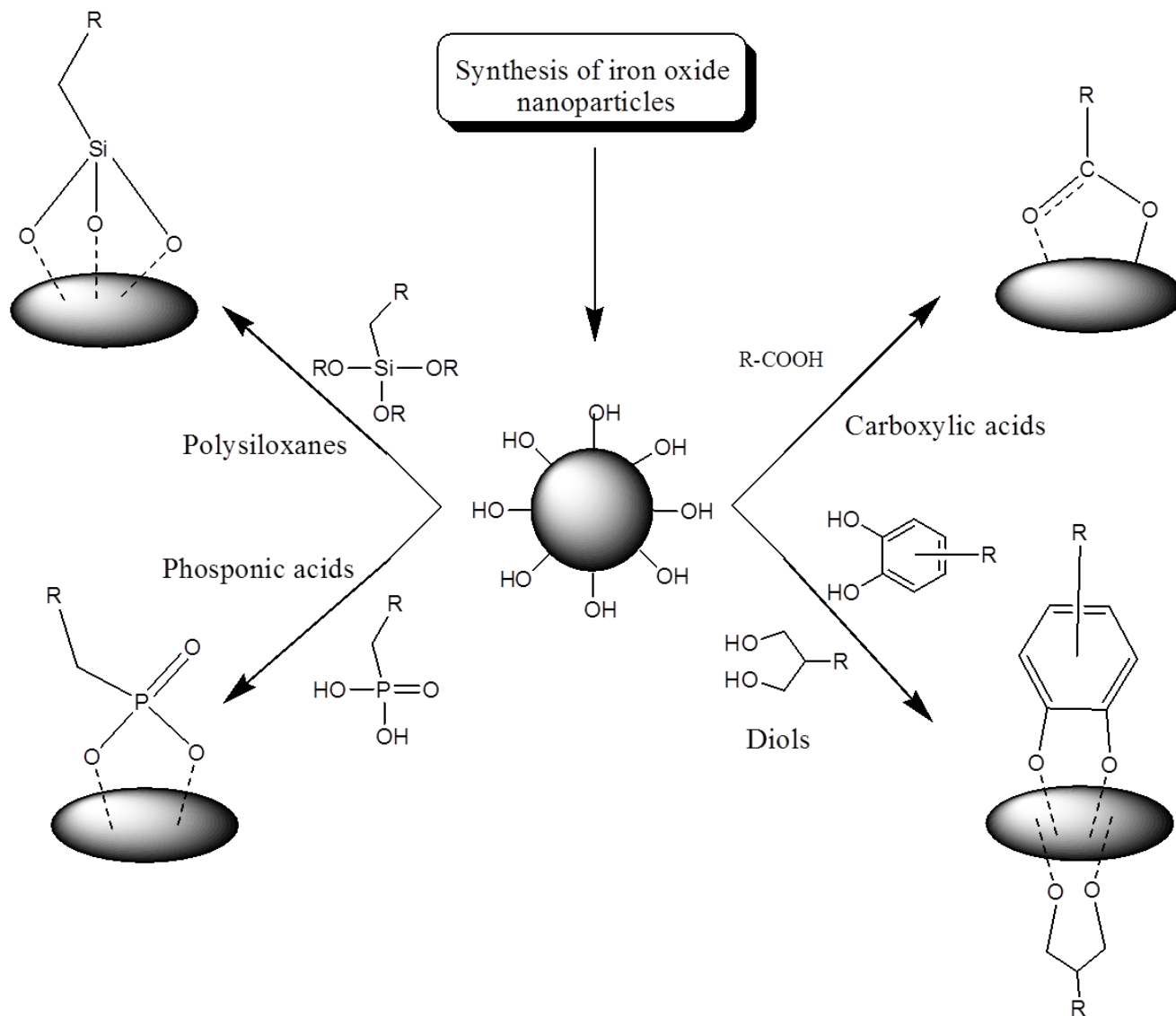
Table 1. Common synthesis methods for iron oxide nanoparticles.

Methods	Key features	Reference
Co-precipitation	This is the most conventional method and is also used by several commercial production plants for the synthesis of magnetic or black iron oxides. This method consists of mixing ferric (Fe-III) and ferrous ions (Fe-II) in strong basic conditions. P ^H of the medium, ionic strength and ratio of salts are the factors which affect the quality of nanoparticles prepared. However recently various suitable modifications of this process are observed where a good control over size and magnetic properties is obtained. Surfactant or stabilizers can also be added in the reaction media to generate stabilized nanoparticles.	[5-7]
Thermal decomposition	An organic solution phase decomposition route is used in this method. Iron (II) oleate, Fe (Cup) ₃ , Fe(CO) ₅ , Fe(acac) ₃ are the complexes commonly used for thermal degradation. This method produces monodispersed nanoparticles. Guardia et al. have reported their studies on effect of various parameters that affect the thermal decomposition synthesis of iron oxides.	[8-10]
Microemulsion	Water in oil micro emulsions are very famous for the synthesis of iron oxide nanoparticles. In situ coating of the stabilizers is obtained in this method preventing the particles from aggregations. Darnabdi <i>et al.</i> recently have reported on the synthesis of iron oxide nanoparticles of 4 to 9 nm by microemulsion method which is a fast and reproducible method which has the virtues of simplicity, reproducibility, and high yield. By varying the preparation conditions, the size of the nanoparticles has been tailored.	[11,12]
Hydrothermal synthesis	Highly crystalline and pure iron oxide nanoparticles can be obtained by this method. This method can be also combined with other methods mentioned in order to first synthesis the nanoparticles and use hydrothermal method to coat them with stabilizers as reported by Bae et al. A simple, environmentally friendly hydrothermal stripping route for synthesizing highly size controlled spherical ferric oxide nanoparticles is also reported recently. Purity of the particles and crystals obtained greatly influence the magnetic properties.	[13,14]
Sonochemical synthesis	Sonication of solutions of Fe (II) or Fe (III) complexes or salts under inert atmosphere or ultrasonic decomposition of iron carbonyl precursors leads to amorphous nanoparticles of narrow particle size distribution. Amount of water and rate of sonication are two important factors that found to affect the final particle size and magnetic properties.	[15,16]

An untreated iron oxide nanoparticle put into water or complex aqueous environments to get hydrolysed and bears large number of hydroxyl groups. The interactions of these hydroxyl groups with various compounds/polymers used for their surface modifications determine the stability of the resulting monolayer around them.

Surface functionalization by organic materials

For real world applications of metal oxide nanoparticles it is often necessary that they should be coated with stabilizers or to functionalize them. Iron oxide nanoparticles have enormous number of application which includes using of them in aqueous suspensions or water



Scheme 1. Common synthetic strategies adopted for the attachment of organic / polymeric molecules to the surface of iron oxides.

organic solvent mixtures. Iron oxide put into such solvent systems containing water bear large number of hydroxyl (-OH) groups on their surfaces. Functional groups, including carboxylates, phosphates, and sulfates, are known to bind to the surface of magnetites (Fe_3O_4). Furthermore, this stabilization can be tailored for dispersibility into oil/hydrocarbon carrier fluids or aqueous media. The reactivity of surface hydroxyl groups is different towards different interacting groups. An organic compound or polymer of type interacting group-Functional groups when used for formation of monolayers it imparts functionality to the nanoparticles.

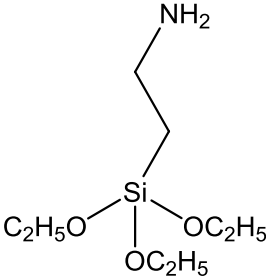
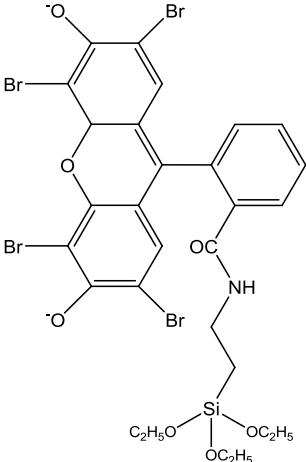
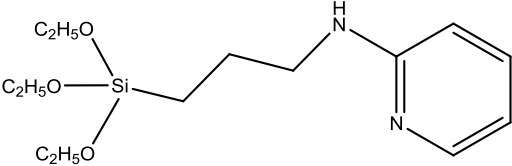
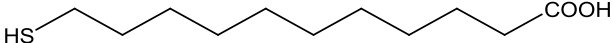
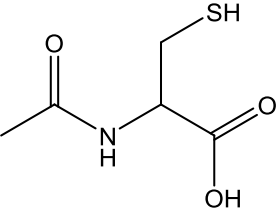
Scheme 1 shows the main interacting groups from organic compounds surfactants/polymers and biomolecules with iron oxide surface while, **Table 2** enlists the most recent functional group attachments to the iron oxide nanoparticles. The list gives an idea about their reactivity towards different organic groups and biomolecules. When organic functionalities are attached to the nanoparticles the resulting metal-organic hybrids system becomes new ω -functionalized monolayers. These monolayers bearing

various groups greatly alter the properties of nanoparticle underlying them.

Applications of functionalized iron oxide nanoparticles

The above mentioned synthetic procedures and strategies are used to synthesize iron oxide nanoparticles bearing various functional groups which were then further exploited to carry out various reactions onto them. The functional groups present on the surface of the nanoparticles are used for covalent immobilization of biomolecules, drugs and for trapping ions or molecules in detection processes. Magnetic resonance imaging is one the important applications of the magnetic iron oxide particles where they are used as contrasting agents. Recently it has been reported that the functionalization strategies used can affect the magnetic properties of resulting nanohybrids (nanoparticles bearing functional groups or polymers) so one should be careful

Table 2. Iron oxide nanoparticles bearing different organic functional groups for various applications.

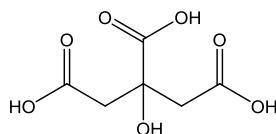
Interacting functional group	Functionality attached	Reference
Trialkoxy silane/Siloxane		[17]
		[17]
		[17a]
Carboxylic acid		[18]
		[18]

while choosing the functionalization strategies while targeting such applications.

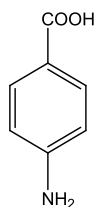
Apart from biomedical applications iron oxide possess various other applications which include use functionalized iron oxides for constructions of detector systems, as a pigments and as probes or adsorbates for removal specific substances from the mixtures, catalysts, or catalytic supports and fillers for nanocomposites preparations. There are many reports where magnetic iron oxides bearing

various groups, functionalized with polymers, amino acids, biomolecules in each case the interactions of molecules attached are always of those types which are mentioned in **Table 2 [3]**.

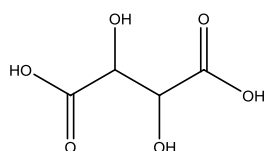
Carboxylic acids



[18]

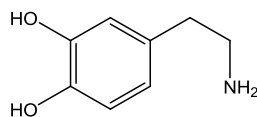


[18]

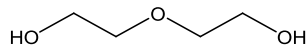


[19]

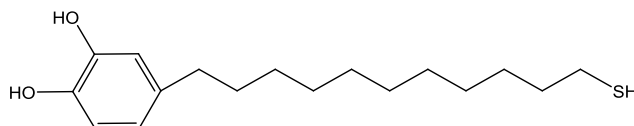
Diols



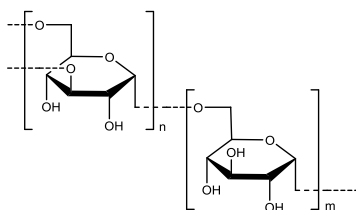
[18]



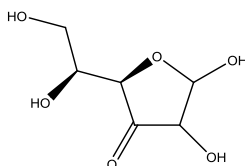
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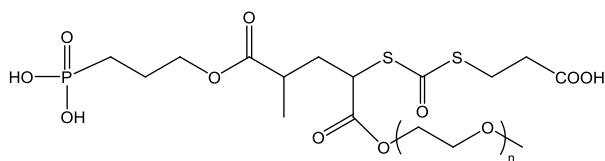
[20]



[19]



Phosphonic acid



[21]

Conclusion

In summary iron oxide nanoparticles can be functionalized with amines, carboxylic acids, alcohols, sugar molecules etc. and the resulting nanoparticles bearing these functional groups undergo various reactions by virtue of functional groups present on them. When organic groups present onto the surface of nanoparticles of any material are exploited for carrying out reactions the process becomes a heterogeneous type of surface reaction. The reactivity of functional groups attached to the nanoparticles depends upon type material and reactivity of the incoming group. The object of this note is to highlight the reactivity of iron oxide (magnetite) nanoparticles towards different interacting organic groups. Various analytical, surface spectroscopic and instrumental techniques have been developed in last few years which can monitor the organic reactions carried out onto the surface of nanoparticles. Especially functionalized gold nanoparticles and their reactions are well studied. If the initial monolayer of organic/polymeric compounds onto the nanoparticles is stable under various conditions which allows repeated drying and re-dispersion of the functional nanocolloids as that of organic compounds then functional nanoparticles can be called as *organic nanocompounds*.

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