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A controlled approach to iron oxide nanoparticles functionalization for magnetic polymer brushes

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ABSTRACT

In this article, we report a detailed study of surface modification of magnetite nanoparticles by means of three different grafting agents, functional for the preparation of magnetic polymer brushes. 3-Aminopropyltriethoxysilane (APTES), 3-chloropropyltriethoxysilane (CPTES), and 2-(4-chlorosulfonylphenyl)ethyltrichlorosilane (CTCS) were chosen as grafting models through which a wide range of polymer brushes can be obtained. By means of accurate thermogravimetric analysis a good control over the amount of immobilized molecules is achieved, and optimal operating conditions for each grafting agent are consequently determined. Graft densities ranging from approximately 4 to 7 molecules per nm^2 are obtained, depending on the conditions used. In addition, the surface-initiated atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA) carried out with CTCS-coated nanoparticles is presented as an example of polymer brushes, leading to a well-defined and dense polymeric coating of around 0.6 PMMA chains per nm^2.

1. Introduction

In the last few years, magnetic nanoparticles (MNPs) have attracted increasing interest thanks to their ability to react in response to an external magnetic field. Among their potential applications, the most promising ones are probably in the biomedical field, as contrast enhancement agents for magnetic resonance imaging [1,2], as drug deliverers into specific targets [3], and as localized magnetic hyperthermia agents for cancer therapy [4]. Beyond the biomedical area, interesting studies have been reported on the use of MNPs for ferrofluids [5,6], data storage [7], and catalysis [8].

Since bare MNPs tend to aggregate into bigger clusters which have modified properties with respect to the single nanocrystals, a surface modification able to prevent self-aggregation is necessary for most of the applications. Their stabilization with hydrophilic or lipophilic coating allows to prepare MNP dispersions in a liquid medium and to keep them stable for long time without any aggregation. In addition, the coating can be used to add specific functionalities to the MNPs, such as fluorescent dyes or biological markers. In these circumstances, polymers play an important role both as dispersants and as linkers between the MNP and the external function. The two main strategies that can be followed to modify the MNP with a polymer brush coating are the *grafting to* and the *grafting from* approach. In the former, a pre-synthesized polymer with a suitable end-group is attached to the MNP by specific reaction between the end-group and a grafting agent anchored on the MNP. In the latter, the polymer chain is grown directly from an initiator which is pre-grafted to the MNP surface. In either case, a fine control of the surface functionalization with the grafting agents is essential.

Even though several studies on MNP surface modification are described in the literature [9], finding the right working conditions for a specific grafting agent is far from easy. In fact, reported data are generally affected by a wide variability, especially concerning reaction time and concentration that must be used to achieve the desired extent of grafting.

We focused our attention on the study of three different grafting agents of common use for the surface modification of Fe_3O_4 MNPs, with the aim of obtaining well-controlled functionalized nanocrystals. We have chosen 3-aminopropyltriethoxysilane (APTES), 3-chloropropyltriethoxysilane (CPTES), and 2-(4-chlorosulfonylphenyl)ethyltrichlorosilane (CTCS) as three grafting models through which a wide range of polymer brushes can be obtained. For all of them, the surface modification is based on the affinity of silane groups for the hydroxyls present on Fe_3O_4 surface, leading to the formation of Si—O bonds and leaving the terminal functional groups available for further steps. In particular, APTES and CPTES are suitable precursors of clickable coatings, which can be used in a *grafting to* approach, after transformation into azide of the amino and chloride groups, respectively [10,11]. The sulfonyl chloride moiety of CTCS is a universal initiator for the atom transfer radical polymerization (ATRP). It was reported

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Table 1
Amounts of grafting agents anchored on magnetite nanoparticle surface, determined by TGA.

Sample	Solvent	Grafting agent amount (mmol/g MNP)	Reaction conditions	TGA weight loss (%)	Calculated grafting success (mmol/g MNP)	Calculated grafting density (molecules/nm^2)
MNP@APTES-a-20	EtOH	20	2 h sonication	3.8	0.33	3.4
MNP@APTES-b-20	EtOH	20	2 h sonication + 6 h stirring	4.5	0.42	4.3
MNP@APTES-c-20	EtOH	20	2 h sonication + 6 h stirring + 10 h stirring at 60 °C	5.1	0.50	5.1
MNP@APTES-c-5	EtOH	5	2 h sonication + 6 h stirring + 10 h stirring at 60 °C	4.3	0.39	4.0
MNP@APTES-c-100	EtOH	100	2 h sonication + 6 h stirring + 10 h stirring at 60 °C	7.0	0.74	7.6
MNP@CPTES-a-20	CH_2Cl_2	20	2 h sonication	4.4	0.33	3.4
MNP@CPTES-b-20	CH_2Cl_2	20	2 h sonication + 6 h stirring	5.0	0.39	4.0
MNP@CPTES-c-20	CH_2Cl_2	20	2 h sonication + 6 h stirring + 10 h stirring at 60 °C	7.6	0.68	6.9
MNP@CPTES-c-5	CH_2Cl_2	5	2 h sonication + 6 h stirring + 10 h stirring at 60 °C	5.4	0.43	4.4
MNP@CPTES-c-100	CH_2Cl_2	100	2 h sonication + 6 h stirring + 10 h stirring at 60 °C	6.8	0.59	6.0
MNP@CTCS-a-5	Toluene	5	2 h sonication	11.6	0.52	5.3
MNP@CTCS-a-20	Toluene	20	2 h sonication	12.6	0.57	5.9
MNP@CTCS-a-100	Toluene	100	2 h sonication	14.4	0.68	6.9

to be particularly effective in the polymerization of styrene [12], methylacrylates [13] and acrylates [14]. Therefore, CTCS can easily give rise to polymer brushes on the MNPs, in a typical *grafting from* approach [15–18].

To overcome the lack of reproducibility which often affects this kind of studies, mostly due to the differences in shape and size of MNPs obtained by different authors, we utilized commercial nanocrystals of naked Fe_3O_4. A drawback of naked MNPs is that they easily form aggregates, thus they need to be sonicated long to give a homogeneous dispersion in liquid medium. On the other hand, they are chemically ready-to-use since they have no ligands to be removed/exchanged, consequently the grafting process is clean and direct. Thermogravimetric analysis (TGA) allowed us to carefully monitor the grafting process, so that well-controlled surface grafted MNPs were obtained. In this article we discuss the immobilization of APTES, CPTES, and CTCS on magnetite MNP surface, giving an outline of the results obtained in different conditions, in comparison with already published data. Results concerning the growth of PMMA brushes from the same modified MNPs are also reported. The report aims at providing a general and versatile method for the stabilization and functionalization of Fe_3O_4 MNPs with polymeric brushes.

2. Experimental

2.1. Materials

Fe_3O_4 MNPs (average size: 20 nm, surface area > 60 m^2/g) were purchased from Aldrich. APTES and CPTES were purchased from Aldrich. CTCS (50% solution in CH_2Cl_2) was purchased from ABCR. Methyl methacrylate (MMA) was purchased from Aldrich and distilled under reduced pressure over CaH_2 before use. Toluene was distilled over Na before use. CH_2Cl_2 and EtOH were purchased from Riedel-de Haën and used as received. CuBr, *p*-toluenesulfonylchloride (TsCl), 2,2′-bipyridine (bpy), and HF aqueous (47%) solution were purchased from Aldrich and used as received.

2.2. Measurements

FTIR spectra were recorded by a Bruker TENSOR27 spectrophotometer. Gel Permeation Chromatography (GPC) measurements were carried out on a Waters SEC system equipped with a 2414 RI and a 490 UV detectors, 2 PL gel Mix C columns, THF as solvent and PMMA as reference. GC analysis were performed using a Agilent Technologies 6890 N GC System. Atomic force microscopy (AFM) investigations were performed using a NT-MDT NTEGRA apparatus in tapping mode under ambient conditions. Samples for AFM were prepared by casting a 0.5 mg/mL $CHCl_3$ solution on top of a Si substrate, hence the morphology of resulting film was studied. Transmission electron microscopy (TEM) measurements have been performed with a Zeiss HTEM Libra200. Samples for TEM were prepared by casting a diluted (0.1 mg/mL) MNP solution in $CHCl_3$ on top of a TEM copper grid, so that the only material attached to the grid edges was analyzed. TGA were carried out on a Perkin Elmer TGA-7 instrument at a scan rate of 20 °C/min in nitrogen atmosphere at a flow rate of 50 ml/min. TGA and derivate thermogravimetry (DTG) curves were recorded from 50 up to 700 °C.

2.3. Surface modification on Fe_3O_4 MNPs

MNPs surface was modified by reaction of APTES, CPTES and CTCS with hydroxyl groups located on Fe_3O_4 external surface. To evaluate the extent of functionalization the reaction was performed using different conditions, which are reported in Table 1.

In a general procedure, 20 mg of naked magnetite MNPs were put in a Schlenk flask containing 10 mL of the required solvent and kept in ultrasonic bath for 30 min to obtain a homogenous dark solution. After this time, required amounts of APTES or CPTES were added drop by drop through a microsyringe without stopping the sonication. CTCS was added as 50% CH_2Cl_2 solution in the same way, but keeping the system under nitrogen atmosphere.