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Grafting of diazonium salts on oxides surface: formation of aryl-O bonds on iron oxide nanoparticles

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ABSTRACT: Combining *ab initio* modelling and ⁵⁷Fe Mössbauer spectrometry, we characterized
the nature of the chemical linkage of aminoalkyl arenediazonium salt on the surface of iron oxide
nanoparticles. We established that it is built through a metal-oxygen-carbon bonding and not a
metal-carbon one, as usually suggested and commonly observed in previously studied metal or
carbon-based surfaces.

TEXT

Magnetic nanoparticles (NPs) provide many exciting opportunities in biomedical applications if high-quality materials, mainly regarding size and size distribution, crystallinity, magnetic features, and surface functionalization, can be elaborated. (Gao, Gu, et Xu 2009; Mornet et al. 2004; Corot et al. 2006, Laurent et al. 2011) For instance, their notoriety as heating agents for magnetic hyperthermia, contrast agents for magnetic resonance imaging (MRI) or magnetically guided vectors for specific drug delivery is essentially related to a satisfying compromise between a relevant magnetization and a medical suitable size. These magnetic NPs are mainly maghemite iron oxide, known as γ -Fe₂O₃. They have a spinel cubic structure, the oxygen forming a fcc lattice and iron cations occupying the tetrahedral (A) and octahedral (B) interstitial sites as follows (Fe³⁺)[Fe³⁺_{1.67}Fe²⁺_{0.33}]₄O₄, where the round and square brackets represent A and B sites, respectively. This structure confers them magnetic properties with a ferrimagnetic ordering at room temperature and a magnetization reaching about 74 emu g⁻¹ in their bulk form. (Valenzuela 2005 ; Cullity et Graham 2011) Under a critical size, these NPs exhibit a superparamagnetic behavior with a size dependent blocking temperature, most of the time lower than room temperature, which can be very useful for the aforementioned applications. This critical size ranges around 30 nm for almost isotropic in shape particles produced by chemical wet routes (Lévy et al. 2008, Krishnan 2010, Laurent et al. 2011) . Besides, iron naturally occurs in the human body (the average adult possessing ca. 5 g), thus the discussed NPs may be considered biocompatible (Wu, He, et Jiang 2008) and relatively safe at reasonable doses.

To ensure effective control over their colloidal stability in water and physiological medium, they usually have been functionalized using organic ligands bearing chelating groups such as

carboxylates,(Tadmor et al. 2000 ; Rosensweig, Kaiser, et Miskolczy 1969) amines and hydroxyls, (Rockenberger, Scher, et Alivisatos 1999) phosphates and phosphonates, (Yee et al. 1999) and sulfonates and thiols. (Lu et al. 2003 ; Kataby et al. 1998). The anchoring of the chelate type groups may fail on metal oxide surfaces in aqueous or protic media due to the hydrolytic instability of the surface attachment and/or the dynamic nature of the interaction. Therefore, developing efficient functionalization chemical strategies to obtain strong and stable linkages between the iron oxide NPs surface and the organic coating still remains challenging, particularly when this anchoring serves as a platform to conjugate biomolecules such as drugs and/or targeting agent for specific *in vivo* applications.

For this purpose, the grafting method based on diazonium salts chemistry has been used for the surface modification of the magnetic nanoparticles (Chehimi 2012 ; Belanger et Pinson 2011 ; Mahouche-Chergui et al. 2011, Hurley et McCreery 2004). Aryl diazonium salts have been shown to be useful organic reagents for the surface modification of metallic (Au, Pt, Pd, Ru, and Ti) substrates, (Mahouche et al. 2009 ; Jiang, Sumpter, et Dai 2006 ;Matrab et al. 2007) as well as carbon-based ones, (Matrab et al. 2006 ;Golosova, Papadakis, et Jordan 2011) affording strong metal-carbon and carbon-carbon linkages, respectively. Raman was also used successfully to establish the Au-C nature of the bonding between an aryl group and gold nanoparticles (Laurentius et al. 2011). In the case of metal or carbon based NPs, the resulting hybrids, dispersed in different media, evidenced a great stability confirming the robustness of the built links. Grafting of diazonium salts on the surface of oxides has also been reported on indium tin oxide (ITO) by electrochemical reduction with different diazonium salts; -Ar-R, -R=NO₂, -CO₂H, -F, (Maldonado et al. 2006; Chung et al. 2012 ; Mirkhalaf et al. 2011) phosphonic acid, (X. Chen et al. 2011) -CHO (Haque et Kim 2011; Chiou, Tsai, et Wang 2014) but also on

fluorine tin oxide (FTO) (Lamberti et al. 2013), titanium (Merson et al. 2004) and iron oxide (Griffete et al. 2011) nanoparticles. In these papers the presence of the organic group on the surface was carefully characterized but no indication was given on the nature of the bond involved. It was possible by X-Ray Photoelectron Spectroscopy (XPS) examination of a copper surface modified spontaneously by different diazonium salts to obtain strong evidence of a Cu-O-aryl bonding. (Hurley et McCreery 2004) More recently, the surface of aluminum NPs derivatized with a diazonium salt was examined by Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS). These spectra allowed to demonstrate the existence of both Al-aryl and Al-O-aryl bonds. (Atmane et al. 2013). MnO₂ nanorods have been modified with aryl groups and a aryl carbon-oxygen bond was evidenced by XPS (Bell et al. 2014).

Recently, aryl diazoates were grafted at the surface of iron oxide NPs working in a basic aqueous medium (Griffete et al. 2011; Podvorica et al. 2009). The chemical bonding nature between the aryl group and the oxide surface was not established in those papers, but the formation of a metal-oxygen-carbon bonding was strongly supposed.

From a general point of view, very few experimental techniques exist to evaluate the adsorbates chemical bonding. All of them are based on a spectroscopic analysis of the organic species such as FTIR (PM-IRAS), (Risse et al. 2003; Borasio et al. 2005) Raman (SERS) (Nilsson et Pettersson 2004; Vericat et al. 2006) and XPS. (S. Chen et Liu 2006; Fleger et al. 2009) Surprisingly, tools based on the analysis of the substrate were seldom considered. Focusing on magnetic iron oxide NPs, ⁵⁷Fe Mössbauer spectrometry appears as the best non-destructive technique able to discriminate, as the surface is enhanced, core and surface Fe species through their electronic and magnetic hyperfine characteristics. Coupled to *ab initio* modelling, with a special emphasis on the surface, relevant information on the electronic transfer between

the molecules and the outer layer of NPs can be obtained. To the best of our knowledge, this approach was used only once to characterize dopamine-maghemite nanohybrids. (Fouineau et al. 2013)

For such a purpose, were prepared maghemite $\gamma\text{-Fe}_2\text{O}_3$ NPs using the polyol process as previously described. (Basti et al. 2010; Hanini et al. 2011) The particles consist of roughly spherical and almost uniform in size particles with an average diameter of 10 nm as illustrated in the recorded Transmission Electron Microscopy (TEM) micrograph given in Fig 1a. They exhibit a typical superparamagnetic behavior with a saturation magnetization at the body temperature of $65 \text{ emu}\cdot\text{g}^{-1}$ very close to that reported for bulk maghemite (see supporting information section). They were subsequently functionalized by hydrophilic 4-alkylaminophenyl groups derivative using arenediazonium salt chemistry. Typically, 4-(*tert*-butyl ethylcarbamate)benzenediazonium tetrafluoroborate salt, $[\text{BF}_4^-, \text{N}_2\text{-C}_6\text{H}_4\text{-C}_2\text{H}_4\text{-NH-Boc}]$ was prepared and grafted on the maghemite NPs according to the procedure described elsewhere (Griffete et al. 2011). The Boc protecting group was then removed by acidic cleavage (see the additional information).

The adsorption of the aryl diazonium salt at the surface of maghemite NPs was investigated by different tools. First, TEM images were recorded on the as-produced hybrids dispersed in water and compared to those obtained on bare NPs. They didn't unambiguously prove the organic coating of NPs by a thin and a dense aryl-based molecular layer however they evidenced their better dispersion. Indeed, hybrid NPs are clearly less aggregated (Fig 1b) than their bare counterparts (Fig 1a). Interestingly, the particle size of both kind of NPs, inferred from a

statistical analysis of their TEM micrographs (see supporting information section) were found equivalent about 10 nm.

FTIR spectra of the hybrids NPs before and after Boc deprotection were also recorded and compared to those of bare iron oxide NPs and free $[\text{BF}_4^-; \text{N}_2\text{-C}_6\text{H}_4\text{-C}_2\text{H}_4\text{-NH-Boc}]$ (Fig 2). The spectrum of NP-C₆H₄-C₂H₄-NH₂ appears to be a combination of the spectra of pure NPs (band below 800 cm⁻¹ attributed to the different vibration modes of the Fe-O skeleton (Salah 2006, Waldron 1955, White et DeAngelis 1967)) and that of the aromatic ring vibrations deformation (bands at 1600 cm⁻¹), confirming the presence of a phenyl grafting on the surface of NPs. We note that the relative band of aryl group was shifted from 1582 cm⁻¹ in the free aryl diazonium salt to 1600 cm⁻¹ in the hybrid particles. This shift can be explained by the liberation of electron withdrawing group -N₂⁺ during the cleavage of the diazonium moieties. N₂ release is usually evidenced by the disappearance of the N≡N stretching mode near 2280 cm⁻¹. (Mahouche-Chergui et al. 2011) This is exactly observed when one compares the FTIR spectrum of free $^+\text{N}_2\text{C}_6\text{H}_4\text{-C}_2\text{H}_4\text{-NH-Boc}$ to those of its hybrid counterpart. Thermogravimetry analysis carried out up to 800 °C on both bare and deprotected hybrid NPs evidenced a weight loss of about 22 and 5 wt.-%, respectively (see supporting information). This weight discrepancy agrees with a high grafting density of the aryl-based moieties on the NPs surface as suggested by TEM images.

Finally, X-ray diffraction (XRD) analysis of bare and hybrid NPs, confirmed that the aryl grafting does not affect *a priori* the crystal structure of the iron oxide phase. XRD patterns recorded before and after surface treatment are similar and composed of broadened peaks typical of pure spinel maghemite (not shown here).

The mechanism for the grafting reaction in aqueous basic medium is supposed to involve the formation of diazohydroxides and diazoate species (Hegarty 2010) which dediazonize along an homolytic pathway to give the aryl radicals. (Pazo-Llorente, Bravo-Diaz, et Gonzalez-Romero 2004) This radical might react directly on an iron or oxygen surface particle atoms. The chemical linkage can be built through a carbon-iron or a carbon-oxygen-iron bound. In the first case a surface carbide-like bond is formed while in the other an alkoxyde-like one is obtained. To discriminate between these two extreme situations, we used the Fe local probe analysis route, namely ^{57}Fe transmission Mössbauer spectrometry, to determine the charge density variation on surface iron atoms before and after grafting. As illustrated in Fig 3, the 300 K Mössbauer spectra exhibit broadened lines resulting typically from the presence of superparamagnetic relaxation phenomena: the lack of resolution makes impossible the estimation of the proportions of iron cations located in A and B sites, respectively. However, the mean values of the isomer shift, which are unchanged before and after grafting, are typical of Fe^{3+} species, namely $\langle \delta_{\text{BareNPs}} \rangle = \langle \delta_{\text{HybridNPs}} \rangle = 0.33 \text{ mm.s}^{-1}$. In addition, the weak difference between the mean values of hyperfine field estimated at 300 K ($\langle B_{\text{hf-BareNPs}} \rangle = 34.2(5) \text{ T}$ and $\langle B_{\text{hf-HybridNPs}} \rangle = 33.0(5) \text{ T}$), can be explained by the change of the mean distance between NPs because of the grafting of aryl group at their surface, favoring a decrease of dipolar interactions and making the relaxation phenomena faster, thus decreasing the hyperfine field values. When cooling the samples at 77 K, the Mössbauer hyperfine structures split into asymmetrical sextets (see Fig 3) and the spectrum recorded at 77 K on the hybrid NPs remained close to that of bare $\gamma\text{-Fe}_2\text{O}_3$ ones. The asymmetry allows the spectra to be decomposed into two components, which should be attributed to octahedral and tetrahedral Fe sites on the basis of the largest and the smallest isomer shift values, respectively. It is important to note that an accurate estimation of their proportions should require an external

magnetic field spectrum at low temperature, that allows to split the 77K-sextet into two well resolved components, because of the ferrimagnetic behavior of present powders. The measured average isomer shift and hyperfine fields (together with those of each component) are very close to each other in both samples and typical of Fe³⁺ cations (Table 1), thus confirming previous results obtained at 300 K. These results are very important because they show that Fe-C like links cannot be formed but only oxygen-mediated bonds are produced. Indeed, surface iron Fe atoms involved in carbide like Fe-C bonds should exhibit a closer to zero isomer shift (typically, $\delta = 0.019$ mm/s in Fe₃C bulk cementite carbide at room temperature (Ron et al. 1966) with an iron atom oxidation state close to that of metal (Ron et al. 1966 ;Fang, van Huis, et Zandbergen 2009). Besides, surface iron Fe²⁺ or Fe³⁺ ions involved in Fe-C hydrocarbon bonds like in alkyl, alkynyl, carbene, vinylidene or allenylidene complexes must exhibit an isomer shift significantly smaller than that in Fe-O oxide bonds. (Guillaume et al. 1998) Typically, iron(II) centers connected to a η^1 -bond carbon ligand exhibit an isomer shift ranging between 0.15 and 0.25 mm/s depending on the nature of the ligand while iron(III) centers exhibit an isomer shift closer to 0.25 mm/s at 300K.(Guillaume et al. 1998 ; Roger et al. 1991)

The existence of such iron species should induce a significant decrease of the average iron isomer shift in the whole hybrid NPs, compared to their bare counterparts, which is not the case. Indeed, according to the geometrical model of (Binder et Weinstabl 2007) the atomic fraction of iron localized at the surface of about 10 nm sized spherical maghemite spinel particles can be estimated at around 7 at.%. Assuming a dense amine aryl derivative grafting at the surface of these nanoparticles, where one molecule is attached to one iron surface cation, the organic weight content of the resulting hybrids reaches about 15 wt.-%, which is very close to the measured weight loss on these objects by thermo-gravimetric (TG) analysis. Moreover, the

electronic density change of 7 at.-% of iron atoms in the case of their carbide or organometallic like bonding, where each surface iron is linked to one carbon, should induce a largely measurable iron isomer shift decrease in the Mössbauer hybrid spectrum.

To confirm these experimental results, we performed *ab initio* calculations to simulate the surface functionalization of maghemite by a phenyl C_6H_5 radical, in the framework of density functional theory (DFT) as implemented in the Quantum Espresso (Giannozzi et al. 2009) package. In case of the phenyl radical we checked two configurations, namely a C_6H_5 radical which we constrained to be closer to a surface oxygen atom or to a surface iron atom at the start of the structural optimization procedure. For the structural optimization of maghemite the general gradient approximation (GGA) density functional from (Perdew, Burke, et Ernzerhof 1996) was used, whereas the final optimization has been done by using the Hubbard corrected local density approximation (LDA+U) method with the (Perdew et Wang 1992) functional. The LDA+U parameters were set to $U = 4.5$ eV and $J = 0.367$ eV. A cutoff energy of 30 Ry and a 0.2 Ry mixing factor for self-consistency was used. We used a $3 \times 3 \times 3$ sampling of the first Brillouin zone and a Gaussian smearing factor of 0.02 Ry. The absolute pseudo-energies were determined and then the binding energies were computed by difference. Results, within an estimated accuracy of 1 mRy, show a binding energy of -0.1885 Ry and -0.1694 Ry for the phenyl group: carbon-iron bond and carbon-oxygen bond, respectively. From these values it is hard to tell which bond will be formed in a preferential way.

We computed also the change in Löwdin charges (projecting the final wavefunctions on the atomic wavefunctions used for pseudopotential generation) of each atom of the system during grafting. The results, presented in Fig 4, illustrate how there is indeed a partial reduction of Fe^{3+} atoms, the d orbitals being reduced, showing a marked increase in charge, especially around the

linking oxygen atoms in the case of the carbon-oxygen bond. In the case of the phenyl ligand, a change in the s orbitals is noticed, but the reduction of Fe^{3+} atoms is, as expected, more important than in the carbon-oxygen case. This shows, in link with the Mössbauer spectrometry results showing that Fe^{3+} dominates, that this carbon-oxygen mechanism is the dominant one. We also computed the reduced gradient of the electronic density according to the method described previously plotting the isosurface of the reduced gradient of the electronic density at a value of 0.5. At this value, this method allows to characterize whether chemical bonds are ionic or covalent. One can check from Fig 4 that the bonding of the atoms in the ligand is, as expected, covalent (no isosurface is present except at the center of the aromatic ring), and the bonding in iron oxide is strongly ionic (high presence of the isosurface). The welcome result is then that the bonding is covalent, which is a strong requirement for pharmaceutical applications of the considered nanohybrids. The accuracy of our results is additionally reinforced by the detailed data provided in Table 2. In particular, we give our estimations of the employed supercell dimensions, magnitudes of the maghemite surface bonds, as well as the bonds between phenyl radical and the maghemite surface. For the purpose of the physical relevancy of our results, they are compared with other theoretical predictions and with the experimental data, where available. We note, that obtained values are in good agreement with the reference data, suggesting plausibility of our simulations.

To conclude, in this paper, using a subtle combination of *ab initio* modelling and Mössbauer spectrometry, we could demonstrate the nature of aminoalkyl arenediazonium salt derivative attachment on iron oxide nanoparticles. It is constituted of a carbon-oxygen-iron linkage, where iron cations exhibit a +3 oxidation state. Typically, the radical aryl carbon reacts with the surface

oxygen atoms itself bonded to iron ferric oxide lattice The covalent and robust nature of this bonding thus offers interesting perspectives for applications of those nanoparticles.

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		This work	Other theoretical work	Experiment
Edge lengths	a	8.329 Å	8.359 Å	8.347 Å
	c	24.987 Å	24.854 Å (Grau-Crespo et al. 2010)	24.042 Å (Shmakov et al. 1995)
Surface bonds	Fe _{tetra} - O	1.8 Å	1.85 Å	1.84 Å
	Fe _{octa} - O	2.02 Å	2.06 Å (Benny 2010)	2.09 Å (Jørgensen et al. 2007)
C₆H₆-surface bonds	C - Fe	2.28 Å	-	-
	O - Fe	1.2 Å	-	-

Table 2 Comparison of the cell dimensions and bonds in different sites (octahedral and tetrahedral) of structure used in this study with other works.