Synthesis and Characterization of Diazonium Functionalized Nanoparticles for Deposition on Metal Surfaces

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Silica nanoparticles were surface-functionalized with diazonium groups. The reaction steps leading to the formation of the diazonium functionality were followed with IR and XPS, and the structure of the diazonium-functionalized nanoparticle was confirmed with solid state NMR. Nanoparticle size distribution was determined with DLS, SEM, and TEM. The nanoparticles were then covalently bonded to gold and iron surfaces. Their spatial distribution over the metal surface was analyzed by SEM. Diazonium modification of nanoparticles represents a new method for the covalent attachment of nanoparticles to metal surfaces.

Introduction

Metal and semiconductor surfaces are frequently modified with nanoparticles (np) in order to add new properties and functions, including superhydrophobicity[1,2] and corrosion protection.[3] Furthermore, surface attachment of nanoparticles is also an important step in the construction of photonic band-gap materials,[4] catalysts,[5] colloidal lithography, and devices such as biosensors.[7] Stability and performance of the nanostructured surface depends in part on the nanoparticle-substrate binding strength. As a consequence, various techniques have been developed to bind nanoparticles to metal or semiconductor surfaces, and most of them result in weak nanoparticle−surface interaction.[8−11] Recently, nanoparticles have been covalently bonded to substrates via the modification of both the substrate and the nanoparticle surfaces with functional organic groups that in a latter step react with each other.[12−14] Although this is a convenient manner to increase the strength of the np−surface interaction, it requires three controlled steps: (i) np modification; (ii) surface modification; and (iii) np−surface attachment. It would, of course, be welcomed to reduce the number of steps.

Molecular species can be covalently bonded to surfaces via the spontaneous or electrochemical reduction of organic moieties containing diazonium functionalities.[15,16] This reaction was first reported by Delamar et al. in 1992.[17] The accepted mechanism for this reaction has been demonstrated using a wide variety of substituted aryl diazoniums,[18] and it involves the generation of an aryl radical and the formation of a covalent bond with a surface species. Thus, organic molecules containing diazonium functionalities could be covalently bonded to many surfaces including Au, Fe, C, Si, GaAs, and Pd.[18,19] Furthermore, diazonium-functionalized proteins have been electrodeposited over Au, semiconductors,[20] and C substrates.[21,22]

Since diazonium salts are easily and rapidly prepared in one step from a wide range of anilines and its reduction takes place within seconds to minutes, it offers a simple and versatile way of modifying metal surfaces.[15] Therefore, nanoparticles functionalized with diazonium groups could, in principle, be covalently bonded to metal surfaces.

In this work, we synthesized silica nanoparticles surface-modified with diazonium groups using a four-step functionalization route. Although it is known that metal[23,24] and silica[25,26] nanoparticles can be functionalized with a variety of organic functional groups, this is the first time that nanoparticles were surface-modified with diazonium groups. Steps involved subsequent np−surface modification to give (i) amine, (ii) carboxylic

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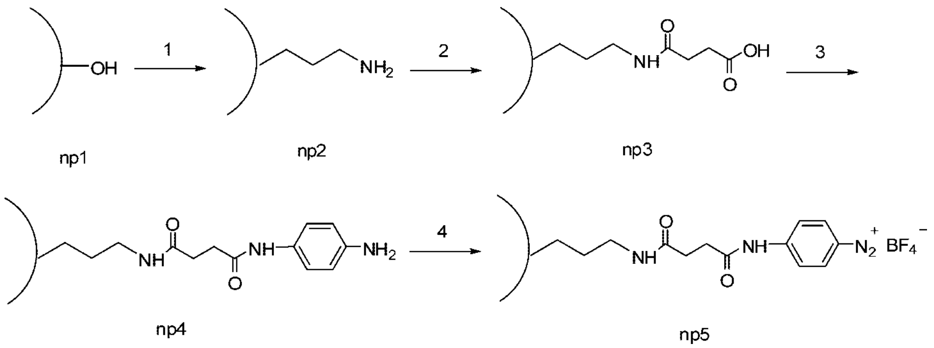
Scheme 1. Reaction Route Employed to Functionalize SiO_2 Nanoparticles[a]



[a] Reagents: (1) (a) NH_3, EtOH, H_2O; (b) APS; (2) succinic anhydride, THF; (3) (a) EDC, NHS, DMAP/ CH_2Cl_2, DMF; (b) *p*-phenylendiamine; (4) HBF_4, isoamyl nitrite/ EtOH.

acid, (iii) aniline, and (iv) diazonium organic functionalities. All reaction steps were followed with IR and XPS and the structure of the diazonium-functionalized nanoparticle was confirmed with solid state NMR. Finally, nanoparticles were bonded to gold and iron surfaces via electroreduction or spontaneous reduction of the diazonium functionality, respectively. Nanoparticle surface attachment was confirmed by XPS and SEM. Therefore, surface modification of SiO_2 nanoparticles with diazonium groups can be used to covalently bind nanoparticles to metal surfaces via the reduction of the diazonium functionality. This method represents a new convenient method for the covalent attachment of nanoparticles to metal surfaces.

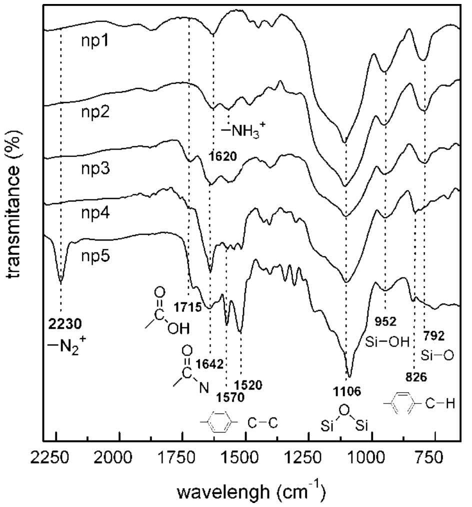


Figure 1. DRIFT spectra of nanoparticles as a function of reaction steps: silica **np1**; amino-terminated **np2**; carboxylic acid-terminated **np3**; aniline-terminated **np4**; diazonium terminated **np5**.

Experimental Section

Reagents and Materials. The following chemicals were of analytical grade and used as received from the manufacturer: tetraethoxysilane (TEOS, Acrôs), aminopropyltriethoxysilane (APS, Aldrich), *p*-phenylenediamine (Aldrich), tetrafluoroboronic acid (Aldrich), *N*-dimethylaminopyridine (DMAP, Fluka), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC, Fluka), succinic anhydride (Fluka), *N*-hydroxysuccinimide (NHS, Aldrich), and isoamyl nitrite (Sigma). Aqueous solutions were prepared with 18 MΩ Milli-Q (Millipore) water.

Synthesis of Bare (np1) and Amino Terminated (np2) Silica Nanoparticles. Bare and amino terminated SiO_2 nanoparticles were synthesized through a modified Stöber procedure.[27,26] Briefly, a mixture of 13.5 mL of ammonia 28%, 1.5 mL of Milli-Q H_2O and 6 mL of TEOS in 200 mL of ethanol was stirred at room temperature under nitrogen atmosphere for 5 h. A 300-μL portion of APS in 5 mL of ethanol was added, and the mixture was left to react overnight. Ammonia was removed by reduced pressure evaporation and the volume was reduced to 20 mL. The resulting **np2** nanoparticles were separated and cleaned by three cycles of washing with water-recollecting by centrifugation. Bare silica nanoparticles **np1** were synthesized under the same conditions without addition of APS. Ninhydrin test of **np2 (np1)** was positive (negative) indicating the presence (absence) of amine groups in **np2 (np1)**.

Synthesis of Carboxylic Acid Terminated Silica Nanoparticles (np3).[28] A 1.150-g portion of **np2** was suspended in 90 mL of tetrahydrofurane (THF). A 250-mg portion of succinic anhydride was added, and the mixture was stirred overnight at room temperature under nitrogen atmosphere. The mixture was left to precipitate, decanted, centrifuged, and the solid obtained was washed with ethanol to obtain **np3**. A ninhydrine test of **np3** was negative, indicating the absence of amine functions in **np3**.

Synthesis of Aniline Terminated Silica Nanoparticles (np4). The aniline group was added by an amide formation reaction of **np3** with *p*-phenylenediamine. Carboxylic acid groups were activated by formation of the *N*-hydroxysuccinimidyl ester. A 500-mg portion of **np3** was suspended in a mixture of 10 mL of dichloromethane (CH_2Cl_2) and 30 mL of *N*,*N*-dimethylformamide (DMF). A 155-mg portion of EDC, 180 mg of NHS, and a catalytic amount of DMAP were added. The mixture was stirred for an hour at room temperature under nitrogen atmosphere. Condensation with the amine was carried out in situ by adding 100 mg of *p*-phenylenediamine to the previous mixture and stirring overnight. The **np4** nanoparticles were separated by centrifugation and washed with ethanol.

Synthesis of Diazonium Salt Terminated Silica Nanoparticles (np5). The aniline **np4** was converted into its diazonium salt using a known procedure. A 220-mg portion of **np4** was partially dissolved in 6.3 mL of ethanol. A 160-μL portion of HBF_4 was added, and the mixture was cooled to 5 °C in an ice water bath. A 94-μL portion of isoamyl nitrite was added and the mixture was stirred for 1 h. Nanoparticles were precipitated with diethyl ether, filtered, and washed with diethyl ether. To confirm the presence of diazonium groups, a sample of **np5** was treated with β-naphtol in 0.1 M NaOH. The suspension immediately turned to a deep red color. It should be noted that the same procedure was repeated with a sample of **np4** with negative results.

DRIFT Measurements. Diffuse reflectance infrared Fourier transform (DRIFT) spectra were collected using a Nicolet 5700 FT-IR spectrometer (Nicolet Corporation) equipped with a cryogenic MCT-A detector and a diffuse reflectance accessory. Potassium bromide was employed as reference, and the spectra were collected with a spectral resolution of 4 cm^{-1} accumulating 32 scans.

XPS Measurements. X-ray photoelectron spectroscopy (XPS) measurements were obtained using a Specs Sage 150 spectrometer equipped with a dual anode Mg/Al X-ray source and an hemispherical

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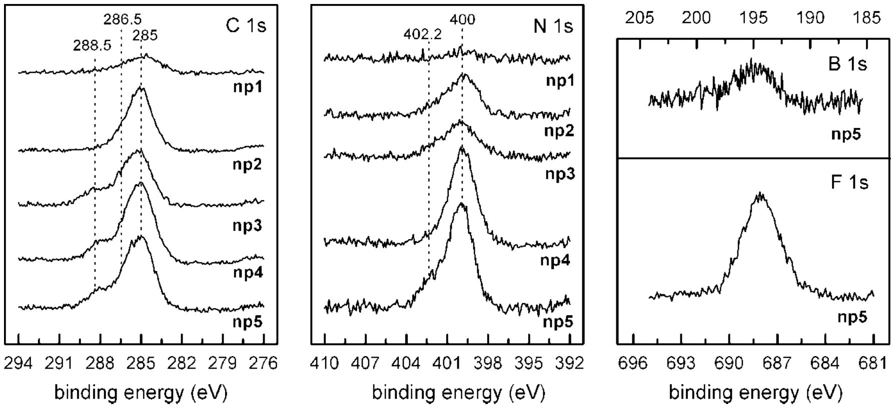
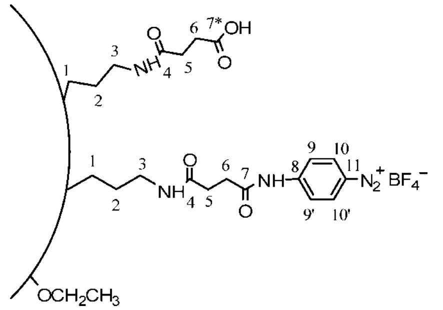


Figure 2. C 1s and N 1s XP spectra as a function of reaction steps (**np1**−**np5**). B 1s and F 1s XP spectra of the diazonium functionalized nanoparticles (**np5**).

Table 1. Assignment of ^{13}C CPMAS NMR of Diazonium Functionalized Nanoparticle np5

NMR signal (ppm)	assignment
10	1
18	$\underline{C}H_3CH_2O$
23	2
32	5,6
43	3
60	$CH_3\underline{C}H_2O$
109	11
124	9,9′
136	10,10′
141	8
175	4,7
179	7*

Scheme 2. Structure of the Diazonium Functionalized Nanoparticle np5 as Determined by ^{13}C NMR



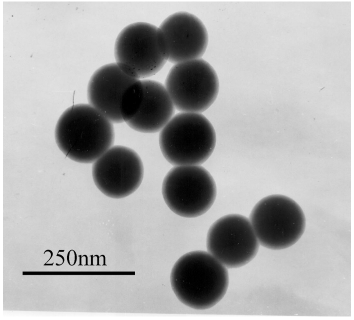


Figure 3. Representative TEM image of diazonium functionalized nanoparticles **np5**.

electron energy analyzer. Spectra were acquired using an unmonochromatic Mg Kα (1253.6 eV) source with a 90° detection angle. Quoted binding energies (BEs) are referred to the adventitious C 1s emission at 285 eV. Measurements conducted over powdered samples were made by placing a drop of a concentrated suspension of colloidal particles on a gold surface and drying in air. Atomic ratios were calculated from the integrated intensities of core levels after instrumental and photoionization cross-section corrections.

NMR Measurements. Cross polarization magic angle spinning ^{1}H−^{13}C nuclear magnetic resonance (CPMAS NMR) spectra were taken in a BRUKER MSL-300 spectrometer. A spinning speed of 7000 Hz was employed. The cross polarization contact time was 2 ms and TPPM proton decoupling mode was used. A total of 2400 scans were accumulated with 41 ms of acquisition time and a delay time between pulses of 5 s.

DLS Measurements. Particle size distribution was measured by dynamic light scattering (DLS) using a Brookhaven 90Plus analyzer. Samples consisted of very dilute suspensions of nanoparticles in ethanol.

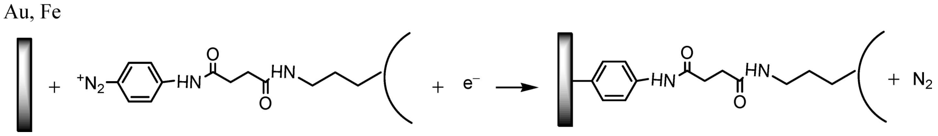
TEM and SEM Measurements. Transmition electron microscopy (TEM) observations were made using a Philips EM-301 TEM microscope. TEM samples were prepared by placing a drop of a diluted dispersion of nanoparticles in ethanol directly on a carbon-coated copper grid (200 mesh). Scanning electron microscopy (SEM) observations were made using a Philips XL-30 SEM microscope under an acceleration voltage of 25 kV.

Surface Modification. Electroreduction of diazonium nps on Au surfaces was performed as follows: Silicon (100) substrates were coated with a 200-nm gold layer on a 20 nm titanium and 20 nm palladium adhesion layer by thermal evaporation with an Edwards Auto 306 vacuum coating system at $P < 1\ 10^{-8}$ bar and employed as electrodes. Au electrodes were cleaned in an ultrasonic bath with purified acetone and electrochemically cleaned in 2 M H_2SO_4, until a well-defined voltammetry was achieved. All electrochemical measurements were performed with an Autolab PGSTAT 30 potentiostat (Eco Chemie, Holland) using a purpose-built three-electrode cell comprising a gold working electrode, a platinum counter electrode, and a Ag/AgCl (3.0 M NaCl) reference electrode operated at room temperature. Electroreduction of diazonium salt **np5** was carried out using a suspension of nps in ACN (1 mg/ml) with 0.1 M Bu_4BF_4 as supporting electrolyte. Cyclic voltammetry measurements showed a peak at −1.23 V (vs Ag/AgCl) due to the reduction of the diazonium salt. Fe samples were polished with a 1 μm diamond slurry, immersed in a 1:1 CH_2Cl_2: acetone mixture and washed by sonication for 5 min prior their use. Spontaneous grafting was carried out by placing the Fe samples horizontally on the bottom of an Erlenmeyer flask containing a suspension of 1.5% of diazonium functionalized **np5** nanoparticles in acetonitrile. The Erlenmeyer was shacken for 10 min at 200 rpm. Following deposition, all samples were washed with ACN and then ultrasonicated in acetone for 10 min to remove any species adsorbed onto the surface.

Results and Discussion

Scheme 1 shows the four-step reaction route employed to synthesize the diazonium surface-functionalized SiO_2 nanoparticles from **np1**. Step 1 involved functionalization of the silica

Scheme 3. Surface Attachment of Diazonium Functionalized Nanoparticles to Metal Surfaces



nanoparticle with amine groups by reaction with APS. The elongation of this functionality by reaction with succinic anhydride led to the formation of a carboxylic acid function (step 2) which was then subjected to amidation conditions with *p*-phenylenediamine to obtain an aniline (step 3). This compound was finally converted to its diazonium tetrafluoroborate derivative via reaction with isoamyl nitrite and tetrafluoroboronic acid (step 4). Detailed reaction conditions are given in the Experimental Section.

Figure 1 shows DRIFT spectra of products **np1**−**np5**. All spectra show peaks at 3430 and 952 cm^{-1} corresponding to Si−OH stretching,[29] and peaks at 1106 and 792 cm^{-1} assigned to Si−O−Si and Si−O vibrations, respectively.[29] C−H stretching vibrations for alkyl groups is observed in all measurements at 2930 cm^{-1}.[30] The presence of the C−H stretching in the case of the nonfunctionalized nanoparticles **np1**, indicates incomplete hydrolysis of TEOS during **np1** synthesis and hence the presence of ethoxy groups.[31] The peak at 1620 cm^{-1} could be due to water adsorption[29] and can also be found in all cases. The aminopropyl functionalized nanoparticles **np2** spectrum should have a peak corresponding to the N−H stretching at 3200−3500 cm^{-1}.[32] This peak could just be seen due to its overlap with the SiOH signal. Furthermore, we observe a peak at 1568 cm^{-1} assignable to the ammonium cation.[32] This later observation suggests that silanol surface groups can interact with amine groups forming zwitterions[33]and resulting in ammonium groups. The carboxy-functionalized nanoparticle **np3** spectrum shows two peaks due to the C=O stretching of carbonyl groups. The peak at 1715 cm^{-1} confirms the presence of the carboxylic acid functionality[32] and the peak at ~1642 cm^{-1} (overlapping the adsorbed water signal), confirms the formation of amide bonds.[32] The DRIFT spectrum of aniline-modified nanoparticles **np4** shows a strong peak at 1642 cm^{-1} that, in line with the reduction of the 1715 cm^{-1} carboxylic peak, suggests the amidation of most of the carboxylic groups. This spectrum also suggests the presence of an aniline group with two peaks at 1520 and 1570 cm^{-1} corresponding to the aromatic C−C stretching vibrations. Furthermore, we observe a peak at 826 cm^{-1} corresponding to the C−H bending vibrations in the para-disubstituted aromatic group. The spectrum corresponding to the diazonium functionalized nanoparticles **np5**, shows a peak at 2230 cm^{-1} which is not present in any of the other spectra (**np1**−**np4**) and that corresponds to the stretching vibration of the diazonium N_2^+ group.[34] This demonstrates the success of the diazotation reaction. Peaks corresponding to the BF_4 group overlap with the Si−O−Si stretching vibration at 1106 cm^{-1}. Overall, Figure 1 shows the appearance and disappearance of the different organic functions from the surface of the np as the reaction proceeds according to Scheme 1. Therefore, the DRIFT data indicates that the reaction route proceeds as expected with subsequent (1) amine, (2) carboxylic acid, (3) aniline, and (4) diazonium organic functions surface terminating the silica nanoparticles. This observation is further confirmed by the XPS data discussed below.

Nanoparticles **np1**−**np5** were analyzed with XPS. Broad scans (not shown) show the presence of Si, O, and C in all samples (**np1**−**np5**). Nanoparticles containing amine, amide, or diazonium groups (**np2**−**np4**) also showed the presence of N, whereas the diazonium salt **np5** was the only sample showing a signal for F and B as expected. Figure 2 shows C 1s and N 1s XP spectra as a function of reaction steps, i.e., **np1**−**np5,** and B 1s and F 1s spectra for **np5**. C 1s XP spectra show three main contributions at ~285, ~286.5, and ~288.5 eV, corresponding to CμC bonds,[35] a CμN bond, and XμC=O (X is N or O), respectively.[37] A small C signal in the bare silica sample **np1** is observed and is probably due to ethoxy groups in line with the DRIFT results discussed above. The C1s spectrum corresponding to **np2** shows two contributions at ~285 and ~286.5 eV, as expected on the basis of the molecular structure of the propylamine group. Carboxylated nanoparticles **np3** show a new contribution in the C 1s XP spectrum at ~288.5 eV due to the presence of amide and carboxylic group, as expected. This peak is also observed in the following reaction steps, as can be seen in the spectra corresponding to **np4** and **np5**, in good agreement with the respective molecular structures.

Silica nanoparticles **np1** show no signal in the N 1s region as expected. Amino (**np2**) and carboxylic acid (**np3**) nanoparticles show a main N 1s peak at ~400 eV, which is due to the amine[38] and amide[39] groups, respectively. Note that a small peak at ~401.8 eV is also observed and is probably due to protonated amine groups,[38] in line with the 1568 cm^{-1} peak found in the DRIFT measurement (see above). Furthermore, the intensity of the N 1s signal remains constant in going from **np2** to **np3** (step 2) as expected. Aniline functionalized nanoparticles **np4** show a N 1s peak at ~400 eV due to the amide[39] and aniline[38] functionalities present on the nanoparticle. Furthermore, the N-integrated area increases by a factor of 2.2, which suggests that the amidation of the carboxylic groups to yield the aniline functionality (step 3) is not complete. The spectrum of the diazotized nanoparticles **np5** shows a new peak at 402.2 eV, consistent with the presence of a diazonium group.[40] This coincides with the appearance of the 2231 cm^{-1} peak in the **np5** DRIFT spectrum and demonstrates the presence of the diazonium functionality. B and F are only observed in the diazonium functionalized nanoparticles **np5**. The B 1s peak at 194.5 eV and the F 1s peak at 688 eV are consistent with the presence of the BF_4^{μ} anion in **np5**;[41] furthermore, the F/B ratio is 3.8, in very good agreement with the expected value (4).

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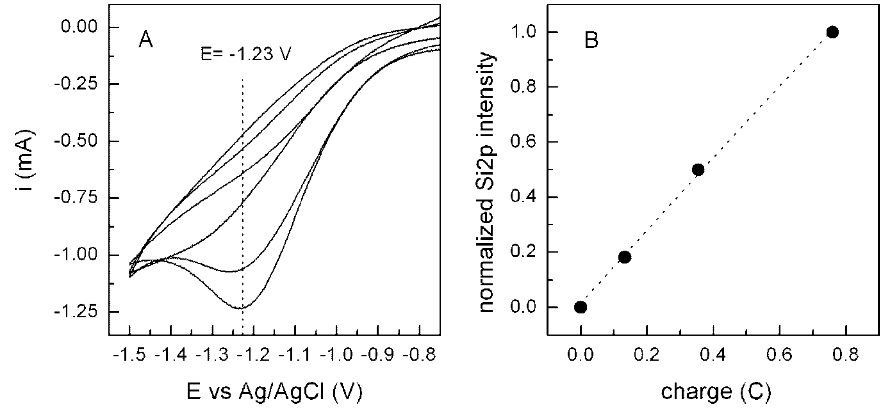

Figure 4. (A) Cyclic voltammograms corresponding to the electroreduction of the diazonium-functionalized nps over a Au electrode. (B) Normalized Si 2p integrated XPS intensity as a function of charge for the electrodeposition of diazonium-nps over Au electrodes at $V = -1.45$ V (vs Ag/AgCl).

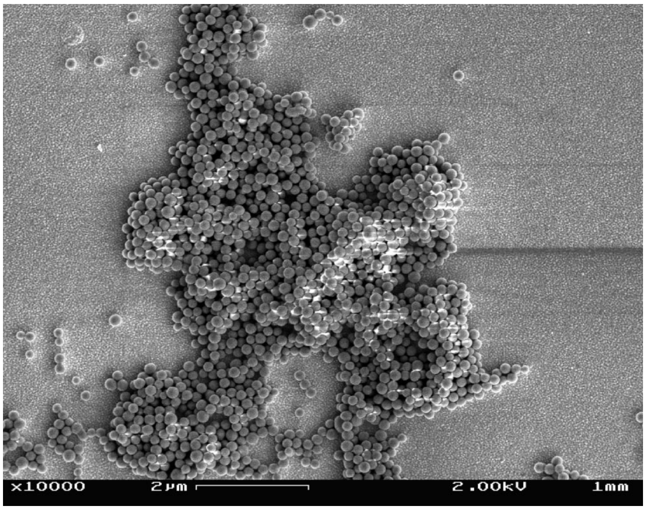

Figure 5. Representative SEM image of the Au electrode after electrodeposition of **np5** ($C \approx 0.8$ C).

The structure of the diazonium salt **np5** was confirmed by ^{13}C CPMAS NMR (see Table 1 and Scheme 2). Signals at 18 and 60 ppm were assigned to carbon atoms from ethoxy groups that remain in the nanoparticle,[31,42] in agreement with the DRIFT and XPS measurements (see above). Signals due to the presence of both diazonium and carboxylic acid terminated groups were found. This observation is in agreement with DRIFT and XPS measurements discussed above, as it indicates that the amidation of carboxylic groups to yield aniline (step 3) is incomplete. No differences are expected in the signals corresponding to C1 to C6 and they were assigned as follows. The C1 peak was found at 10 ppm in line with literature values for aminopropyl-bounded silica nanoparticles.[42] The 32 and 43 ppm peaks were assigned to C2 and C3, despite the fact that they show an upfield shift with respect to analogous carbons in aminopropyl-bounded silica nanoparticles.[42] This assignment is possible because the same shift is observed in the acetylation of butylamine.[43] A peak at 32 ppm is assigned to C5 and C6, in good agreement with values calculated for succinamide metilene carbons.[44] Signals at 175 and 179 ppm are assigned to amide (C4, C7) and carboxylic acid (C7*) carbons, respectively. Two signals can be seen in the aromatic zone with maxima at 124 and 136 ppm, consistent with the calculated values for the diazonium salt (122 for C9 (and 9′) and 132 for C10 (and 10′)). Calculations[44] for aromatic peaks of aniline **np4** show values that can not be found in the NMR spectra, in particular the peak corresponding to C10 (and 10′) at 117 ppm. This suggests that the diazotation reaction (step 4) is complete (there is no aniline left). DRIFT, XPS, and NMR measurements indicate that the structure of **np5** is close to the one shown in Scheme 2 with a majority of diazonim surface groups.

The diazonium functionalized nanoparticlesʼ (**np5**) average particle size was evaluated by SEM, TEM, and DLS. Analysis of SEM images yields an average nanoparticle diameter of 134 ± 12 nm. TEM measurements (see Figure 3 below) showed an average diameter of 133 ± 10 nm, whereas DLS experiments gave an effective diameter value of 149 ± 2 nm. It is known that scattering and microscopy measurements yield different average particle sizes,[26] as DLS measures the hydrodynamic diameter which is always larger than the geometric diameter of the particles.

It should be noted that, in principle, some degree of nanoparticle coupling could be expected in the synthesis of **np4** by reaction of both amine moieties of *p*-phenylenediamine with acid groups of different nanoparticles. However, since we do not observe changes in the hydrodynamic average ratio and particle size distribution measured with DLS as a function of synthesis steps (going from **np1** to **np5**) and we never observed a multinomial particle size distribution (over 7 days), we excluded this possibility from 250nm taking place.

Diazonium functionalized nanoparticles were deposited over Au and Fe surfaces by reduction of the diazonium functionality followed by surface attachment of the organic molecule (see Scheme 3).[15] It has been previously demonstrated that the reaction needs to be driven by an applied potential in the case of Au, whereas it can proceed spontaneously without any electrochemical assistance over Fe surfaces.[45]

Figure 4A shows subsequent cyclic voltammograms corresponding to the electroreduction of the diazonium functionalized nps over a Au electrode. The wave shows a reduction peak at −1.23 V (vs Ag/AgCl) due to the reduction of the diazonium moiety. Repetitive voltammograms show a decrease in the reduction peak and its total disappearance in agreement with

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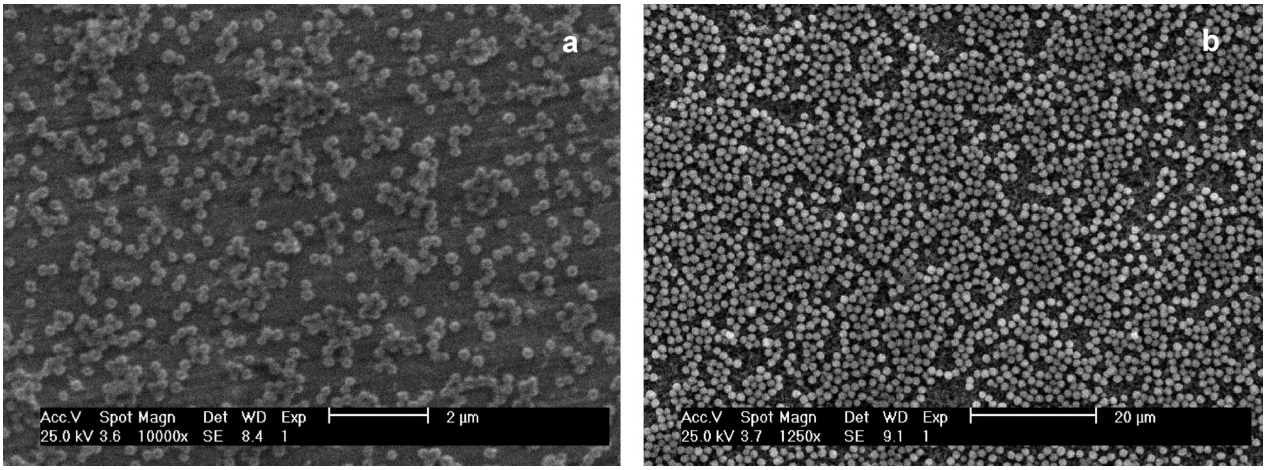

Figure 6. Representative SEM images for the deposition of diazonium-particles of different diameters (a) ∼150 nm and (b) ∼1.4 *µ*m over Fe.

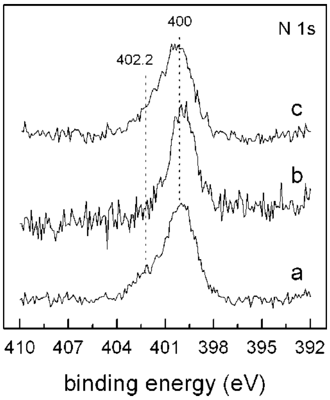

Figure 7. N 1s XP spectra corresponding to (a) diazonium functionalized nanoparticles **np5**, (b) **np5** electrodeposited over Au surfaces, and (c) **np5** deposited over Fe surfaces.

previous observations.[46] It should be noted that the diazonium reduction potential depends on the nature of the substituents of the aromatic ring. Indeed, deactivating substituents, such as nitro groups,[19] lead to a positive reduction peak (0.24 V vs SCE) while activant substituents, like alkyles,[19] lead to negative potential peaks (−0.36 V vs SCE). In our case, the amide group is a highly activating aromatic substituent, and therefore, the diazonium reduction peak is observed at more negative potentials (−1.23 V vs Ag/AgCl). Figure 4B shows the normalized Si 2p integrated XPS intensity as a function of charge for the electrodeposition of diazonium-nps over Au electrodes at $V = -1.45$ V (vs Ag/AgCl). Clearly, as the charge increases, the coverage of nps over the electrode surface increases as expected. The same trend was observed when the electrodeposition was carried out at a fixed current. It should be noted that if no voltage was applied to the Au electrode, then no nanoparticle deposition over the substrate was observed, confirming that the observed surface nanoparticles are electrodeposited over the Au surface.

Figure 5 shows a representative SEM image of the Au electrode after the electrodeposition of diazonium-nps ($C \approx 0.8$ C). It is clear that the gold surface was partially covered with nanoparticles which mainly form clusters. Different electrodeposition conditions, such as concentration of np, potential, and deposition times were assayed but clusters were always found on the electrografted Au surfaces.

There are two possible explanations for the formation of np-clusters over the Au surface: (i) nps form clusters in solution without electrochemical assistance and are therefore electrodeposited as clusters and (ii) nanoparticles remain as individual entities in solution and clusters are formed as the diazonium-nps are electroreduced over the Au surface. DLS measurements as a function of time show that the nanoparticle average diameter remains constant. Furthermore, a monodisperse particle size distribution was measured in all cases, demonstrating that np clusters are not formed in solution without electrochemical assistance. Therefore, we propose that the np clusters are formed as the nps are electrodeposited over the Au surface. It has been previously reported[47] that multilayer films of substituted phenyl moieties can be formed by the electrolysis of diazonium salts. A mechanism has been proposed involving the reaction of aryl radicals with a surface-bound phenyl group. This mechanism can explain the electrochemically assisted cluster formation observed. According to the accepted mechanism, when a nanoparticle approaches the Au surface, diazonium groups are electroreduced and free radicals are formed. These radicals can attach to the surface forming Au−C covalent bonds or they can react with aromatic groups that form C−C bonds and link different nanoparticles, leading to cluster formation.

In order to test this hypothesis, we deposited the diazonium functionalized nanopaticles over Fe surfaces, where it is known that bonding takes place without electrochemical assistance,[45] and therefore, we could expect no cluster formation. Figure 6 shows representative SEM images for the deposition of diazonium-particless of different diameters (a) ∼150 nm and (b) ∼1.4 *µ*m. It is clear that in both cases, we observe a homogeneous surface coverage with a very small tendency for particles to form clusters reinforcing our hypothesis. On the basis of previous studies,[15] we expect the formation of a covalent bond between the functionalized nanoparticles and the metal surfaces. Au and Fe samples were subjected to exhaustive rinsing with acetone, isopropyl alcohol, CH_2Cl_2, and ethanol after deposition of the diazonium functionalized particles. They were also sonicated in acetone and shacked overnight in a 5% NaCl solution. In all cases, no changes were observed in the SEM images, and therefore, we propose that a sufficiently strong bond is formed between the nanoparticle and the metal surface.

As a caveat, we note that codeposition of nano- and micro-diazonium functionalized particles over Fe surfaces creates a dual surface roughness that when made hydrophobic resulted in a superhydrophobic Fe surface with a water contact angle of ∼163°.[48]

A final question remains regarding the fate of the very reactive diazonium groups after the functionalized nanoparticles have been deposited over Au or the Fe surfaces. In order to find the answer, the np-functionalized surfaces where characterized with XPS. Figure 7 shows N 1s XP spectra corresponding to (a) diazonium functionalized nanoparticles **np5**, (b) **np5** electrodeposited over Au surfaces, and (c) **np5** deposited over Fe surfaces. All spectra show a peak at ∼400 eV due to the amine and amide groups present in the nanoparticle. The 402.2 eV contribution due to the diazonium group is clearly distinguished in the spectrum corresponding to **np5** (a) and its presence can not be fully ruled out in the case of np deposition over Fe. However, the XPS signal due to the diazonium group is clearly absent from the spectrum corresponding to the electrodeposition of diazonium functionalized nanoparticles over Au. We propose that the diazonium groups react while electrodeposited bonding to other functional groups or with solvent molecules. This observation is in line with the proposed mechanism for clustering formation: electroreduction of the dizonium groups is very efficient, resulting in the formation of very active free radicals that either bind to the Au surface or react with organic groups forming clusters.

Conclusions

We present a new method for the covalent attachment of nanoparticles to metal surfaces. Diazonium functionalized silica nanoparticles were synthesized following a four-step functionalization route. DRIFT, XPS, and NMR measurements indicate the successful functionalization of the SiO_2 nanoparticles in each reaction step. Diazonium functionalized nanoparticles were covalently bonded to gold surfaces via electro-reduction of the diazonium group with no previous metal modification. Nanoparticles form clusters over the Au surface and the diazonium groups are lost after electrodeposition. Although the nanoparticles' surface coverage can be controlled electrochemically, clusters are observed in all cases. Alternatively, spontaneous deposition of diazonium functionalized nanoparticles over Fe surfaces without electrochemical assistance results in a homogeneous surface coverage with no cluster formation.

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