# A Shortcut To Organize Self-Assembled Monolayers of Cobalt Ferrite Nanoparticles on Silicon

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*Received July 27, 2007. Revised Manuscript Received September 24, 2007*

We report a successful synthetic strategy to covalently assemble a monolayer of $CoFe_2O_4$ nanoparticles on a silicon substrate using undecanoate as molecular linker. The nanocrystals of ferrite are coated with a protecting layer of undecanoate which beyond stabilizing the nanoparticles allows their organization on silicon directly reacting with Si–H surface through its vinyl end group. The organic coat was obtained during the synthesis of cobalt ferrite using sodium undecanoate as protective agent. This synthetic strategy avoids the exchange monolayer reaction generally required to bind the NPs on the substrate. The structural and magnetic characterizations of monolayer self-assembled nanoparticles on silicon surface are reported.

## 1. Introduction

Self-assembled monolayers (SAMs) are ordered molecular assemblies that are spontaneously formed by the adsorption of a surfactant with a specific affinity of its headgroup to a substrate.[1] In order to exploit the SAMs versatility, often inorganic nanoparticles (NPs) are coated with organic monolayers[2] in hybrid systems which can be used as fundamental building blocks in nanotechnology. The nanoscopic size of the inorganic core can provide novel physical properties (optical, magnetic, conductive, etc.); moreover, new molecular scale properties are introduced into systems of nanoparticles by the linking of specific bifunctional molecules to the nanoparticles surface as a monolayer, allowing for the creation of highly functional systems.

In order to fully exploit the opportunities outlined above, the controlled attachment of nanoparticles to specific sites on a given surface is an essential requisite. Improvements toward film stability can be obtained by designing appropriate organic bifunctional self-assembled monolayers as a molecular linker in order to obtain strong chemical bond between the nanoparticles and the substrate. In this contest the self-assembled monolayers technique represents one of the most promising routes due to the great advantage of structural stabilization via multiple covalent and hydrogen bonds.[3]

An attractive application of assembled nanoparticles on solid substrate is the new generation of high-density magnetic storage media.[4] Promising candidates are iron oxides[5,6] (magnetite and maghemite), cobalt ferrite,[7] and bimetallic alloys such as iron–platinum (FePt),[8–10] cobalt–platinum ($CoPt_3$),[11,12] and samarium–cobalt (Sm–Co).[13,14] Magnetic anisotropy and coercivity of these nanomaterials are strongly dependent on the size of the particles and justify any effort to produce size tuned magnetic nanoparticles with diameters ranging from the superparamagnetic threshold to the critical single domain size. In addition, organic coating, on the nanoparticles surface, avoids coalescence phenomena, and it could allow NPs to self-assemble in an ordered way on large areas of the substrates.

In a previous work, we reported[15] a method to obtain a monolayer of monodisperse superparamagnetic NPs onto a silicon surface. Monodisperse oleic acid-stabilized $Fe_3O_4$ nanoparticles with an average diameter of 7 nm were prepared by the high-temperature solution phase synthesis. Since the organic coating of the as-synthesized particles was not able to react with hydrogen-terminated silicon substrate,

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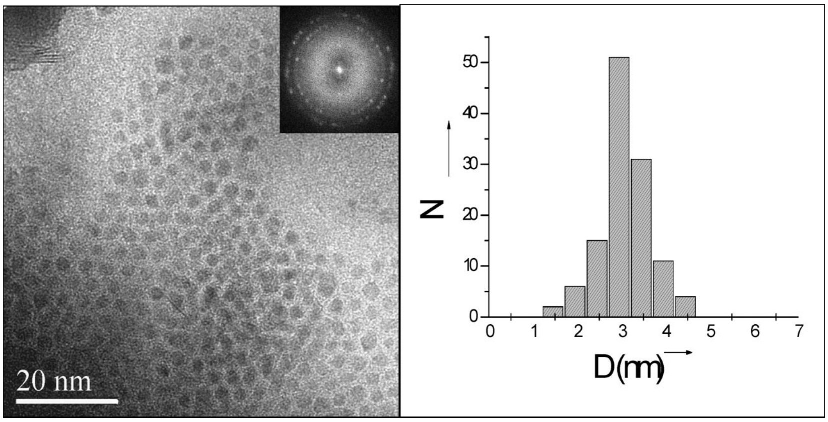

**Figure 1.** Left: TEM image of $CoFe_2O_4$ nanoparticles obtained by heating undecanoate complexes of iron and cobalt at 150 °C in octadecyl ether under a nitrogen atmosphere. The corresponding electron diffraction pattern is shown in the inset. Right: size distribution histogram obtained by measuring the inorganic core diameter of 100 nanoparticles.

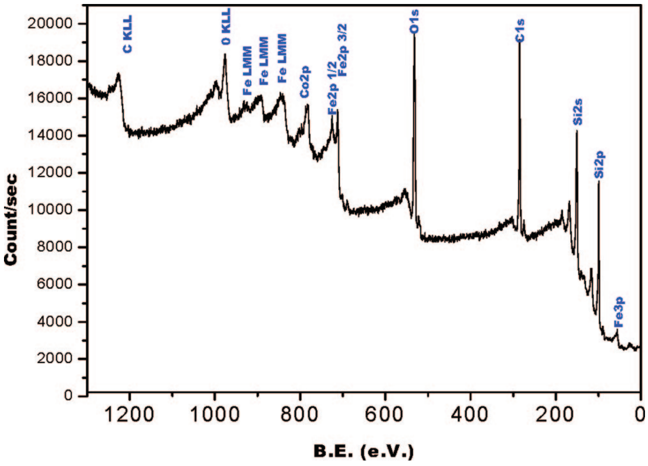

**Figure 2.** XPS wide spectrum of silicon wafer treated with toluene dispersion of undecanoate–cobalt ferrite nanoparticles.

we modified it through a monolayer exchange reaction, based on the incorporation of trimethoxy-7-octen-1-ylsilane into the oleic acid coating. In this process, nanoparticles were coated with molecules containing free vinyl end groups. Unsaturated functional groups are, in fact, suitable to covalently bind the iron oxide nanoparticles onto unoxidized silicon surface. Self-assembled monolayers of magnetite NPs were thus obtained.

Cattaruzza and co-workers also reported covalent assemblies of magnetite nanoparticles onto silicon substrate using as molecular linker the 10-undecanoic acid. The reactive coating was obtained, also in this case, with an exchange reaction between original oleic acid coating of the NPs and the unsaturated carboxylic acid.[16]

In this paper we report a new synthesis to obtain monodisperse magnetic nanoparticles directly covered by a bifunctional molecule containing free vinyl end groups able to link onto silicon substrate, without the need of ligand exchange reaction, thus resulting in a strong simplification of the synthetic procedure.

As starting material we have selected cobalt ferrite because of its higher anisotropy energy barrier for the magnetization reversal in comparison to iron oxide, which allows to reach lower temperatures before reaching the superparamagnetic limit.

## 2. Experimental Section

**2.1. Synthesis of $CoFe_2O_4$ Nanocrystallite.** $FeCl_2 \cdot 4H_2O$ (99+%), $CoCl_2 \cdot 6H_2O$ (99%), NaOH (pellets 97%), undecanoic acid (98%), and octyl ether were obtained from Aldrich Chemical Co. and used without further purification. To prepare sodium undecanoate, NaOH (15 mmol) was dissolved in 5 mL of deoxygenated water (nitrogen gas bubbling for 30 min) and mixed by vigorous stirring with undecanoic acid (15 mmol).

To prepare the metal–undecanoate complexes, $FeCl_2 \cdot 4H_2O$ (5 mmol) and $CoCl_2 \cdot 6H_2O$ (2.5 mmol) were dissolved in deoxygenated water, and the resulting solution was added to sodium undecanoate (15 mmol) under a nitrogen atmosphere, at room temperature, and vigorously stirred for 2 h. The pink precipitate was separated by filtration and doubly washed with deionized water to remove sodium and chlorine ions. During filtration the precipitate color changed to orange-brown. After drying, the iron/cobalt–undecanoate complexes (2 g) were transferred into a three-neck flask (100 mL) and octyl ether (20 mL) was added. The mixture was slowly heated from room temperature to 150 at 5 °C/min heating rate. After reaching the desired temperature, it was held at 150 °C for 2 h and then cooled to room temperature. The dispersion color changed to black, indicating that $CoFe_2O_4$ nanocrystallites were formed. The addition of ethanol to the dispersion cooled to room temperature yields a black precipitate. The product was washed with ethanol and centrifuged (8000 rpm), and finally it was dissolved in 40 mL of octyl ether, forming a dispersion stable over long period.

**2.2. Preparation of Silicon Substrate.** Oriented silicon wafers (100) were provided by ST Microelectronics of Catania (Italy). The substrates were cut into 1 × 1 $cm^2$ pieces, ultrasonically cleaned in toluene, acetone, and doubly distilled water for 15 min periods, and then soaked in piranha solution $H_2SO_4$ (98%)/$H_2O_2$ (30%) (1:3 by volume). To remove the native oxide layer, the substrates were dipped in a buffered solution of a 1:7 mixture of HF (48%) and $NH_4F$ (40%) (v/v) at room temperature for 2 min. The silicon samples (5 pieces) were washed with distilled and deoxygenated water (nitrogen gas bubbling for 20 min) and immediately introduced in the reactor system to obtain the nanoparticles monolayer.

**2.3. Deposition of Nanoparticles on Silicon Substrate.** Cobalt–ferrite nanoparticles dispersion (2 mL of octyl ether solution)

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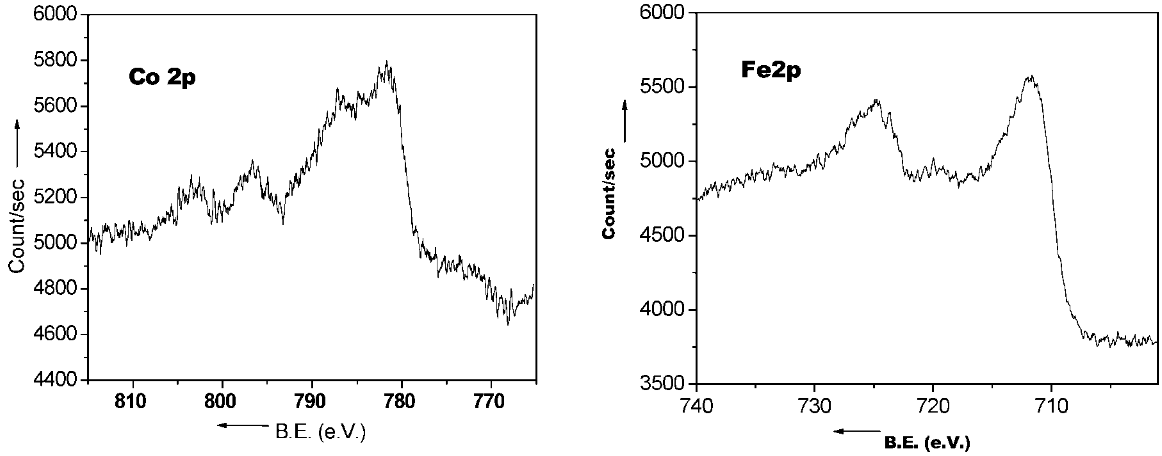

**Figure 3.** Co 2p and Fe 2p photoionization regions of silicon wafer treated with toluene dispersion of undecanoate–cobalt ferrite nanoparticles.

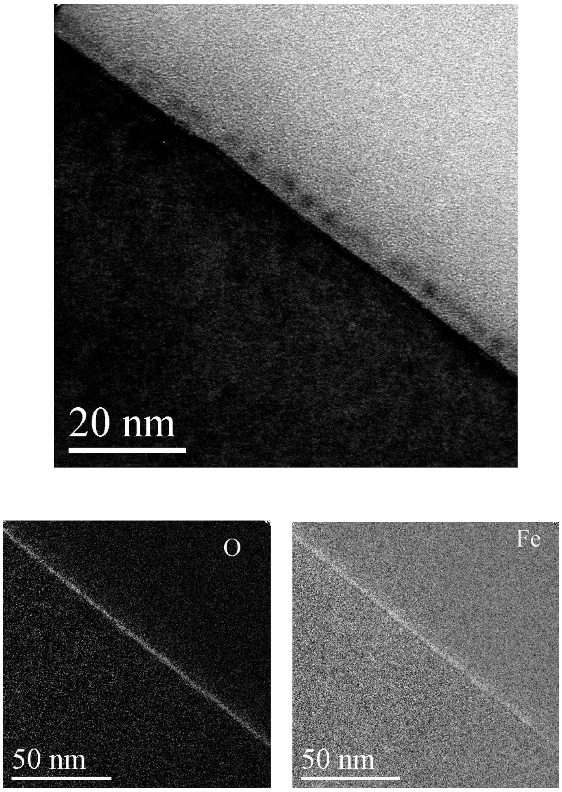

**Figure 4.** Cross section TEM image of cobalt ferrite NP monolayer on silicon wafer. On the lower side the composition image maps of O and Fe measured by EELS are reported.

was transferred into three-neck flask (100 mL), and toluene (20 mL) was added. The oxygen in the dispersion was removed by nitrogen bubbling for 20 min, and the silicon samples were introduced in the reactor. The system was refluxed for 1 h. Finally, all the samples were rinsed by ultrasonication in toluene for 5 min, dried with clean $N_2$, and stored in a dust-free nitrogen atmosphere.

**2.4. Characterization Techniques.** TEM micrographs were obtained using a JEOL JEM 2010 electron microscope operating at 200 kV. XPS measurements were carried out using a PE-PHI/SAM5600 monochromator system spectrometer. AFM (tapping mode) and MFM images were obtained with a Nanoscope IIIa (Digital Instruments). Height images were flattened to remove background slopes. No other filtering procedures were performed on these images. Magnetic measurements were performed using a Cryogenic S600 SQUID magnetometer. The diamagnetic contribution of the silicon wafer was separately measured and then subtracted from the magnetic data.

## 3. Results and Discussion

Monodisperse undecanoate-stabilized $CoFe_2O_4$ nanoparticles with an average diameter of 3 nm were prepared by solution phase synthesis. The synthesis involves the reaction of sodium undecanoate with iron(II) and cobalt(II) ions, the formation of the corresponding metal complexes, and their subsequent decomposition at relatively low temperature (150 °C) in an organic solvent under an inert atmosphere.

The morphological and structural properties of the as-prepared particles were characterized by transmission electron microscopy (TEM) analyses. TEM images revealed the formation of uniform particles that, once deposited over a copper grid, tend to self-organize in a regular hexagonal layer. The size distribution, obtained from a statistic analysis over 100 nanoparticles, is shown in Figure 1 (right side). The average diameter of the inorganic core is $d = 3.1$ nm with a $\sigma = 0.6$ nm. The corresponding electron diffraction pattern confirms the nanocrystals cobalt ferrite nature.[17]

To obtain a nanocrystals monolayer on silicon substrate, we used a diluted toluene dispersion of the nanoparticles coated by undecanoate. The unoxidized silicon substrate was dipped in the dispersion deoxygenated by nitrogen bubbling, and the system was refluxed for 2 h at 112 °C. In these conditions the vinyl groups of organic coating react with hydrogen-terminated silicon groups forming strong covalent Si–C bonds between nanoparticles and substrate. These samples were washed and analyzed by X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and atomic force microscopy (AFM). The magnetic characterization was performed by a superconducting quantum interference device magnetometer (SQUID).

The XPS wide spectrum of silicon wafer treated with toluene dispersion of cobalt ferrite nanoparticles is shown in Figure 2. The presence of C 1s, O 1s, Co 2p, Fe 2p, Si 2s, and Si 2p core photoionization signals and of C KLL, O

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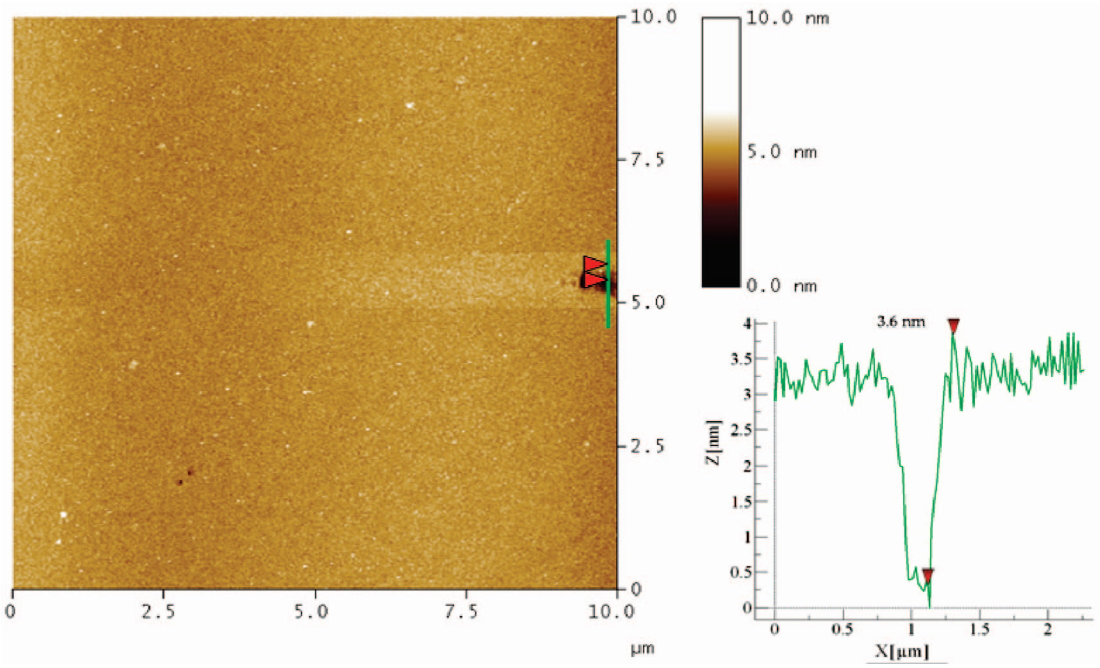

**Figure 5.** AFM topographic image of cobalt ferrite NP monolayer on silicon wafer with a scanning area of 10 μm × 10 μm. The mean roughness ($R_a$) in this area is 0.226 nm. The monolayer mean height is 3.6 nm as shown in the profile on the right side of the figure.

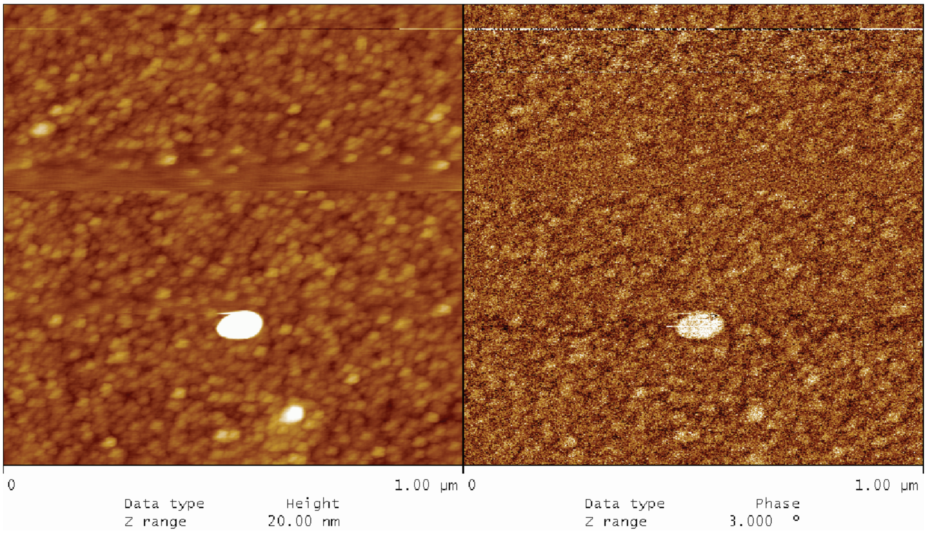

**Figure 6.** AFM topographic (left) and magnetic (right) images of cobalt ferrite NP monolayer on silicon wafer with a scanning area of 1 μm × 1 μm. The mean roughness ($R_a$) is 0.221 nm.

KLL, and Fe LMM Auger signals clearly indicates that the deposition of cobalt ferrite nanoparticles occurred on the surface.

Figure 3 (left) shows the XPS spectrum in the binding energy region between 765 and 815 eV. The peaks at binding energies 781.5 eV (fwhm = 3.0 eV) and 796.8 eV are attributed to spin–orbit splitting of the Co 2p photoelectron lines.[18] Strong satellite structures at 5.6 eV on the higher binding energy side of the main peaks were also observed and confirmed that Co is present as $Co^{2+}$.[19] The Fe 2p photoionization region is also reported (see Figure 3, right). The signal of Fe $2p_{3/2}$ at BE 711.6 eV with separation spin–orbit of 13.3 eV by Fe $2p_{1/2}$ is characteristic of $Fe^{3+}$.[20] The absence of Fe(II) signals confirms the oxidation of the Fe(II) to Fe(III) during washing of undecanoate precursors described in the Experimental Section.

In the XPS spectra of samples prepared in the same conditions but at deposition temperature of 90–95 °C the photoionization signals of cobalt and iron are absent. The driving force of formation of nanoparticles layer is the deposition temperature: the hydrosililation reaction between silicon substrate and vinyl group occur only if the temperature is high enough (>105 °C) to allow the formation of covalent bond Si–C.

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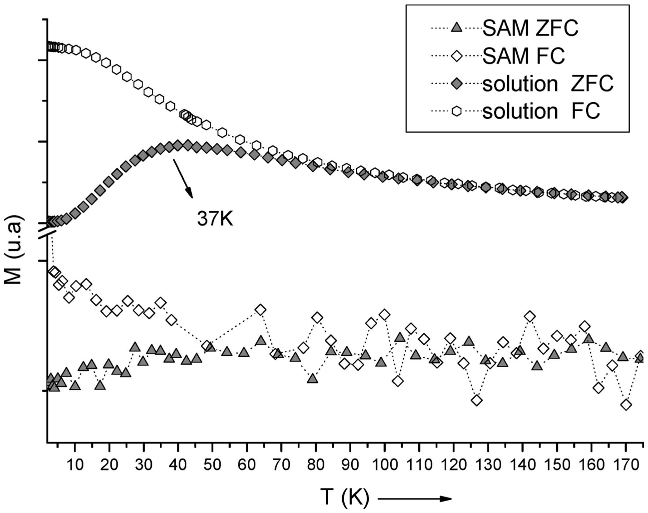


**Figure 7.** Temperature dependence of the ZFC (full symbols) and FC (open symbols) magnetizations of a SAM of $CoFe_2O_4$ nanoparticles on a silicon surface (bottom curves) and of the same particles dispersed in a toluene solution (upper curves). Both measurements were performed with an applied field of 0.01 T.

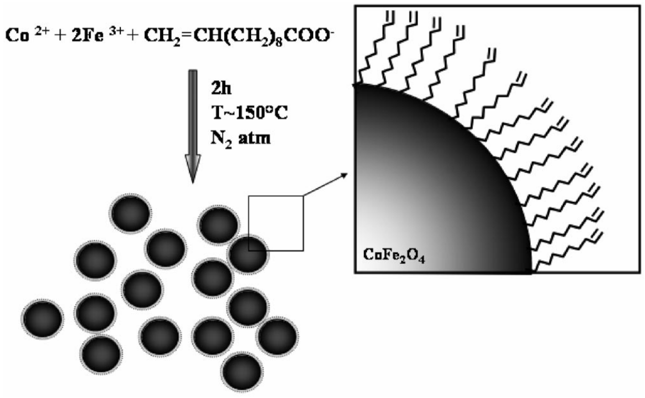
Cross sections of some samples were analyzed by TEM to evaluate the number of nanoparticles layers anchored on silicon surface. The TEM image (see Figure 4) clearly shows that only one layer of nanoparticles covers the silicon wafer confirming the efficiency of the SAM technique and of the synthetic strategy. The compositional analysis of film was investigated by EELS equipped in TEM, and the compositional image maps of O and Fe are also reported (Figure 4, lower side).

The topography and the roughness and the magnetic domains of the film were investigated by atomic force microscopy. One of the AFM images collected on an area of 10 $\mu m^2$, in tapping mode, of silicon sample after deposition of nanoparticles is reported (see Figure 5). The sample is homogeneously covered and has a mean roughness ($R_a$) of 0.226 nm. It has been possible to measure the height of the film (3.6 nm) taking advantage of an imperfection that uncovers the silicon surface in a small area clearly visible on the right side of Figure 5. This result, in agreement with that of TEM measurements, has confirmed that only one nanoparticles layer has been deposited on the silicon wafer.

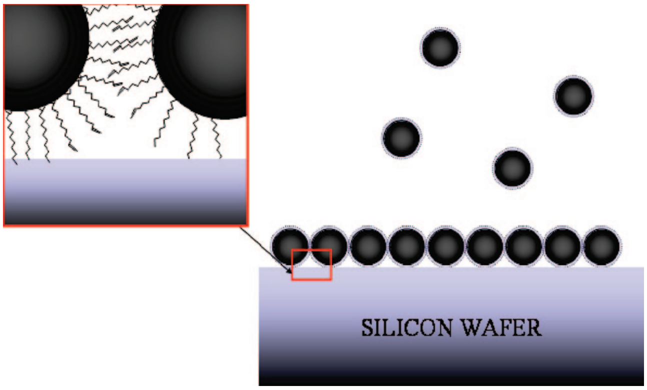
To confirm the magnetic nature of SAM, we investigated a smaller area (1 $\mu m^2$) in the same region and we acquired images in tapping mode and in magnetic mode. The results are reported in Figure 6. The magnetic image (right side) reproduces the topographic one (left side). This indicates that the silicon surface is homogeneously covered by magnetic nanoparticles.

The magnetic characterization of the sample was also performed using a SQUID magnetometer. In Figure 7 the temperature dependence of the zero field cooled (ZFC) and field cooled (FC) magnetizations of the cobalt ferrite particles deposited on the silicon wafer is shown and is compared to that measured for the coated nanoparticles dispersed in toluene. The latter displays the behavior characteristic of single domain magnetic nanoparticles: at room temperature all the particles are in the superparamagnetic regime, consistent with the very small size of the nanoparticles, while below ca. 80 K, $T_{sep}$, thermal irreversibility occurs. Below this temperature the ZFC curve exhibits a round maximum at $T_{max} = 37$ K, while the FC curve continues to increase down to 8 K and then saturates to a constant value. The relatively small difference between $T_{max}$ and $T_{sep}$ and the low-temperature saturation of the FC curve can be taken as an indication of a narrow energy barrier distribution, if compared to most of the systems reported in the literature. A rough estimation of the anisotropy energy constant, $K_{eff}$, can be obtained from $T_{max}$ using the Néel–Brown model[20,21] for the relaxation, $K_{eff} = 25k_BT_B/V$, where $V$ is the particle volume, $k_B$ is the Boltzmann constant, and $T_B$ is the blocking temperature, i.e., the temperature at which the average reversal time of the magnetization equals the experimental time scale, which for this kind of measurements can be assumed to be 100 s. As a first approximation $T_B$ can be identified with $T_{max}$, and thus from the previous relation we obtain $K_{eff} = 9 \times 10^5$ J/m$^3$. This is a large value, but it is

**Scheme 1. Synthesis of Monodisperse Cobalt Ferrite Nanoparticles Coated with Undecanoate**



**Scheme 2. Cobalt Ferrite Nanoparticles SAM Covalently Linked on Hydrogen-Terminated Silicon (100) Surface**[a]



[a] Silicon is introduced in the reactor system containing the dispersion of cobalt ferrite nanoparticles in dehydrated and deoxygenated toluene. The solution is refluxed (112 °C) for 2 h under $N_2$ flow. Through a thermal hydrosilylation reaction, the vinyl group of nanoparticles organic coating reacts with Si–H and strongly binds the nanocrystals to silicon substrate.

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consistent with those already observed for cobalt ferrite particles with nanometric size.[22] Moreover, this $K_{\mathrm{eff}}$ value explains the very large coercive field obtained from the hysteresis loops of the dispersion recorded at 2.5 K of 1.58 T. The hysteresis loop shows also a reduced remnant magnetization of ca. 0.5, indicating the particles have a uniaxial magnetic anisotropy[23] .

The ZFC and FC magnetization curves of the same nanoparticles deposited on a silicon wafer are much more noisy due to the very low amount of particles measured, close to the instrumental sensitivity. However the two curves resemble those of the same particles in solution, confirming that the particles are effectively deposited to the Si surface and that no large modifications of the particle magnetic properties occurred.

The saturation magnetization of the SAM, obtained after the removal of the substrate contribution, which particularly in the high field region dominates the sample magnetization, is of the same order of magnitude of that expected for a regular, close-packed monolayer of 3 nm coated nanoparticles ($2 \times 10^{-4}$ emu/cm$^2$).

## 4. Conclusions

We have presented a new approach for the preparation of monolayers of magnetic nanoparticles covalently linked to unoxidized silicon substrate. With respect to previously reported methods, our method avoids the exchange monolayer reaction required to bind the NPs on substrate. In fact, sodium undecanoate, used as protective agent during the synthesis of nanocrystals, is able to react directly with Si–H surface to its vinyl end group and permits to covalently assembly only one layer of magnetic nanoparticles on silicon wafer. XPS, TEM, AFM, and magnetic characterizations of the samples confirmed the efficacy of this chemical approach to nanoparticles assembly.

**Acknowledgment.** The authors thank C. Bongiorno for TEM images and Prof. G. Marletta and Prof. G. Zhavnerko for AFM and MFM characterizations.

CM702042J

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