Inorg. Chem. **2008**, *47*, 1898−1900

Inorganic Chemistry
Communication

Grafting a Monolayer of Superparamagnetic Cyanide-Bridged Coordination Nanoparticles on Si(100)

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Received November 27, 2007

The grafting of a monolayer of 6 nm superparamagnetic cyanide-bridged CsNiCr nanoparticles was achieved on a Ni(II)-functionalized Si(100) substrate; magnetic studies reveals that the grafted nanoparticles are nearly magnetically isolated within the monolayer.

Processing nanoparticles as monolayers on substrates is of technological importance (optical, magneto-optical, and electronic devices, sensors, etc.) as well as of fundamental interest in nanotechnologies.[1–8] Controlling the concentration of the objects on a given surface is a prerequisite to exploring the properties of a reduced assembly and eventually the properties of a single object. This is the first step for devices relevant to the emerging field of molecular spintronics.

The recent interest in the behavior of cyanide-bridged nanoparticles stems from the diversity of the properties observed in the bulk materials (magnetism, magneto-optics, photomagnetism, electrochromism, ion selective membranes, catalysis, charge transfer, etc.).[9–18] Cyanide-bridged nanoparticles have been shown to behave as superparamagnets and photomagnets.[19–29] Recently, light-induced blocking of the magnetization was evidenced in trimetallic $\mathrm{Mo(CN)_8NiCu}$ 3 nm particles.[27] The recent stabilization of CsNiCr coordination nanoparticles in water without the need of any organic agent opened the possibility of manipulating these objects in solution.[21]

The aim of this work was to achieve the 2D grafting on Si(100) of the superparamagnetic $\mathrm{Cs_{0.7}Ni[Cr(CN)_6]_{0.9}}$ (Cs-

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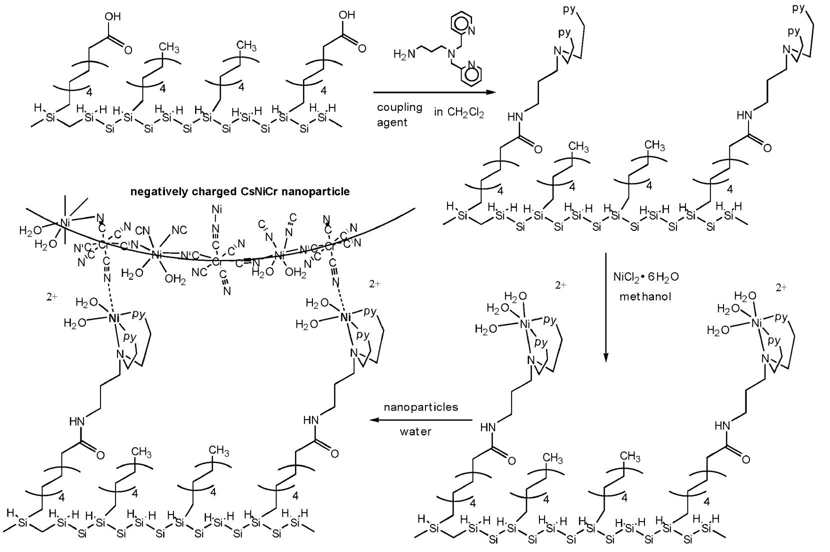

Figure 1. Schematic view of the three-step reaction leading to the nanoparticles monolayer,

NiCr) nanoparticles that were spontaneously stabilized, avoiding as much as possible dipolar interactions. The strategy consists of functionalization of the substrate with a group that has the ability to anchor the nanoparticles. In order to reduce the surface coverage, the anchoring group was diluted with an innocent one during the functionalization process (see below). One of the best surfaces to achieve such dilution is the hydrogen-terminated silicon one.[30,31] Talham and co-workers have already addressed the growth of extended Prussian blue analogues on different substrates.[32] Our aim here is to obtain nanostructured monolayers by using already preformed particles and avoid coordination bonds between the particles.

Anchoring on Si–H substrate magnetite particles already functionalized by groups bearing terminal alkene has been reported.[33,34] This interesting strategy, however, does not allow control of the surface coverage and in some cases leads to the formation of double layers that are difficult to avoid. An alternative route is, thus, to functionalize the substrate prior to grafting. Such a strategy is suitable for particles that are stable in solution without the presence of any agent (organic polymer, ligand, etc.), as is the case for the negatively charged CsNiCr coordination nanoparticles.[21] The approach we use here consists of the preparation of a Si(100) surface terminated by a cationic *metal complex* that plays the role of the *anchoring group* for the particles.

After functionalization of the hydrogen-terminated Si(100) surface with a monolayer of undecanoic acid diluted in decane (1/100) using well-known procedures,[30,35,36] the substrate was reacted with the organic ligand *N*,*N*-bis[(pyridin-2-yl)methyl]propane-1,3-diamine[37] in the presence of *N*′-[3-(dimethylamino)propyl]-*N*-ethylcarbodiimide hydrochloride, leading to the ligand grafting via amide groups (synthetic procedures in the Supporting Information and Figure 1). The substrate bearing the dangling chelating ligands was subsequently immersed for 15 min in a 10^{-3} mol L^{-1} $NiCl_2 \cdot 6H_2O$ methanolic solution and then sonicated for 30 s in methanol (Figure 1). The chelating effect of the tridendate ligand leads to the formation of a cationic $N_3Ni(H_2O)_3$ species pointing out of the substrate. Finally, the wafer functionalized by the Ni complex was soaked in an aqueous colloidal solution containing the CsNiCr particles. The colloidal solution was obtained as described in ref 20. Half of the solution was used to graft the particles. To the other half was added poly(vinylpyrrolidone) (PVP; 300 equiv/Ni) to isolate a highly diluted sample that was fully characterized [by X-ray powder diffraction (XRPD) and IR; Figures S1 and S2, respectively, in the Supporting Information]. Elemental analysis for the PVP diluted sample leads to the same stoichiometry for cesium, nickel, and chromium as that for the already reported particles.[20] Found: Cs, 2.33; Ni, 1.5; Cr, 1.23; C, 51.38; H, 7.52; N, 11.71. Calcd for $Cs_{0.7}Ni[Cr(CN)_6]_{0.9} \cdot 26C_6H_9NO \cdot 24H_2O$: Cs, 2.52; Ni, 1.56; Cr, 1.27; C, 52.56; H, 8.44; N, 11.92. The magnetic behavior reveals the superparamagnetic behavior expected but with a blocking temperature for the present sample of around 5 K [χ' and $\chi'' = f(T)$, Figures S3 and S4 in the Supporting Information]. After 15 min, the wafer was removed from the solution, washed several times with deionized water and methanol, and then dried under vacuum.

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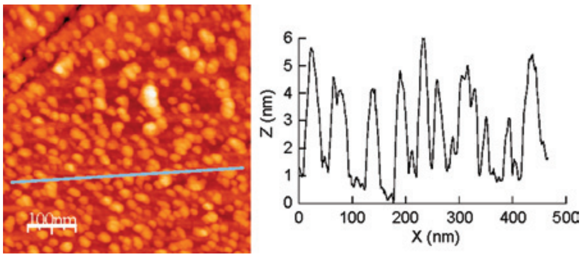

Figure 2. (left) AFM image of the monolayer of nanoparticles and (right) topography along a 0.5 μm line.

Attenuated total reflection infrared spectroscopy shows the same band at 2172 cm^{-1} corresponding to bridging cyanides as that for the nongrafted particles (Figure S5 in the Supporting Information). The analysis of the XPS spectra (Figure S6 in the Supporting Information) at the nickel, chromium, and cesium edges leads to atomic ratios of 0.9 and 0.66 for Cr/Ni and Cs/Ni, respectively, which correspond within experimental error to the unit formula found for the nanoparticles. In order to ensure that the particles are grafted on the silicon surface thanks to the presence of the N_3Ni groups, a drop of the colloidal solution was cast on a wafer functionalized only with decane. The wafer was then rinsed exactly as the one functionalized with the nickel complex, and its XPS spectrum was recorded. No metallic atoms were present, demonstrating that the nickel-terminated surface is needed to induce a strong interaction with the nanoparticles.

Atomic force microscopy (AFM) imaging was performed on the CsNiCr functionalized substrate (Figures 2 and S7 in the Supporting Information). The average height of the explored area (0.5 × 0.5 μm^2) was found to be equal to 5.5 nm (Figure S7 in the Supporting Information), which corresponds to what is expected from a monolayer of the nanoparticles present on top of the functionalized layer. The absence of heights close to mutiples of 6 nm excludes the formation of overlayers of particles on top of those directly linked to the surface.

The IR, XPS, and AFM results are consistent with a single monolayer of magnetic nanoparticles linked to the surface. The interaction between the functionalized layer and the negatively charged particles may be purely electrostatic or, in addition, due to the formation of a coordination bond. Indeed, the surface of the particles has N atoms belonging to the peripheral $Cr(CN)_6^{3-}$ molecules that may achieve such a bond with the nickel-terminated surface. However, at this stage, there is no definitive proof of the nature of the bond between the surface and the particles.

The magnetic behavior of a monolayer of nanoparticles was investigated. To do so, a 10 × 0.8 cm^2 silicon wafer was first functionalized with the nickel complex as described above. Then, it was partly masked, leaving only a central area of 0.8 × 0.8 cm^2 that was put in contact of the nanoparticles. Such a setup allows, during the SQUID measurement, avoidance of the contribution of the wafer to the whole signal so that only the magnetic signal due to the particles can be directly measured. This is of crucial importance in the case of a monolayer containing low concentrations of magnetic species. The field-cooled (FC) and zero-field-cooled (ZFC) magnetization measurements on the as-prepared substrate were carried out within an applied field of 100 Oe, and a signal of very good quality was obtained. The FC and ZFC magnetization curves are compared to those of the reference sample of particles diluted in a polymer matrix (PVP; Figure 3). The ZFC and FC curves for the two samples do not coincide at low temperature. For the particles diluted in PVP, the maximum of the ZFC curve is found at T = 4 K; it corresponds to the blocking temperature of the particles and is consistent with the alternating current studies (Figure S4 in the Supporting Information). The ZFC curve corresponding to the monolayer has its maximum at almost the same temperature as that of the particles diluted in PVP, leading to the conclusion that the same blocking temperature is found for the particles grafted on the surface. This result demonstrates that the nanoparticles keep their integrity when grafted on the nickel-terminated surface; otherwise, a different magnetic behavior would have been observed. Moreover, the unchanged blocking temperature is consistent with average interparticle dipolar interactions within the monolayer similar to those of the highly diluted PVP sample. This is consistent with rather large interparticle distances within the monolayer compatible with the low concentration of the anchoring groups.

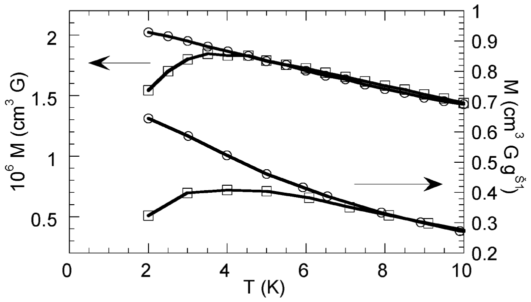

Figure 3. FC (○) and ZFC (□) magnetization curves for the CsNiCr nanoparticles diluted in PVP (bottom) and grafted onto Si(100) (top).

In this Communication, we validate the grafting of superparamagnetic coordination nanoparticles on the Si(100) surface functionalized by a metal complex that will be extended to other charged coordination nanoparticles. The low concentration of the anchoring groups precludes the aggregation of the nanoparticles and keeps their structural and magnetic integrity. This preliminary result is encouraging and opens the possibility of tuning the surface coverage and thus the magnetic response by the concentration of the anchoring groups.

Acknowledgment. We thank the CNRS (Centre National de la Recherche Scientifique), the Nanoscience Competence Center of Région Ile-de-France C'Nano IdF, and the European community for financial support (Contract MRTN-CT-2003–504880/RTN Network "QuEMolNa" and Contract NMP3-CT-2005-515767 NoE "MAGMANET").

Supporting Information Available: XRPD, IR spectrum, and $\chi', \chi'' = f(T)$ of diluted CsNiCr particles; IR, AFM, and XPS spectra of the monolayer; synthetic procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

IC702328W