Selectively Assembled Co Nanoparticle Stripes Prepared by Covalent Linkage and Microcontact Printing

Sung-Soo Bae,[‡] Do Kyung Lim,[‡] Jong-Il Park,[‡] Woo-Ram Lee,[§] Jinwoo Cheon,*,[§] and Sehun Kim*,[‡]

Department of Chemistry and School of Molecular Science (BK 21), Korea Advanced Institute of Science and Technology, Daejeon 305-701, Republic of Korea, and Department of Chemistry, College of Science, Yonsei University, Seoul 120-749, Republic of Korea

We introduce a novel strategy to fabricate a bifunctional monolayer assembly of Co nanoparticles on a Si-(111) surface via the covalent linkage of terminal functional groups between the Si surface and the nanoparticles. The Br-terminated Co nanoparticles that are assembled on the aminopropyl-terminated Si surface show an individual and random distribution over an entire surface. Furthermore, we have fabricated a selective patterned monolayer assembly of Co nanoparticles using a combination of microcontact printing and covalent linkage: the Br-terminated Co nanoparticles attached on only aminopropyl-terminated regions but not on the octadecyl-terminated regions that consist of nonfunctional alkyl groups.

Introduction

In recent years, the synthesis and materialization of nanoparticles has become a focus of research because of their potential use as nano building blocks that can provide nano electronic devices with specific electrical, optical, and magnetic properties.[1] Most research has focused on the development of novel synthetic methods for nanoparticles and on the characterization of their physical properties.[2−6] Also, various studies have been made on two-dimensional monolayers of nanoparticles through a simple self-assembly process.[7−9] However, to utilize the advantageous properties of nanoparticles within novel nanodevices, the controlled attachment of nanoparticles to specific sites on a given surface is required. With the aim of achieving this control, Alivisatos et al. proposed a strategy that uses a bifunctional self-assembled monolayer as a molecular linker that immobilizes CdS nanoparticles in monolayers on metal surfaces with chemical covalent linkages.[10] This strategy involves a hybrid system of nanoparticles, a molecular linker, and a solid surface. Further investigation of this strategy has now been carried out by several research groups, resulting in the fabrication of monolayers of nanoparticles on various solid surfaces.[11−19] However, the assembly of nanoparticle monolayers using molecular linkers has so far been restricted to noble metal and some metal oxide nanoparticles such as those of Au or Ag because of limitations in the chemical modification of nanoparticles or substrates. Consequently, these limitations have raised the unstable assembled systems of nanoparticles, which was based on weak nanoparticle−substrate interactions such as Coulombic force or van der Waals interaction. The assembly of monolayers of transition metal nanoparticles (e.g., Co or Fe nanoparticles) on Si surfaces through *strong covalent linkages* appears to be a promising method for overcoming these limitations.

In this study, we report a novel strategy for the fabrication of a Co nanoparticle monolayer on a Si(111) surface by using chemical covalent linkages between terminal functional groups attached to both the Si surface and the nanoparticles. This approach involves attaching a different functional group to each of the Co nanoparticle and the Si substrate, and then linking the two functional groups covalently. The nature of the resulting assembly of nanoparticles is dependent on the kind of functional group attached to the Si surface, and the number density of nanoparticles is found to be controllable by changing the time of immersion of the Si surface in the nanoparticle solution. Hence, the covalent linkage strategy using immersion enables the selective fabrication of a nanoparticle assembly on surfaces, the control of the distribution of nanoparticles on surfaces, and the enhancement of the thermal stability and adhesion property of the adsorbed layer of nanoparticles. We combine this approach with the conventional microcontact printing (*μ*-CP) method for obtaining selective assemblies of nanoparticles on micropatterned functional group terminated surfaces.[20,21] The combination of the two techniques results in patterned magnetic nanoparticle assemblies on Si surfaces that can be utilized in the production of prototypes of magnetic nanodevices.

Experimental Section

Materials. A Si(111) (n-type, Sb-doped, $R = 0.008−0.02$ Ω·cm) substrate was obtained from Virginia Semiconductor. (3-Aminopropyl)diethoxymethylsilane (AP-DEMS), octadecyl-trichlorosilane (OD-TCS), and all solvents were purchased from Aldrich and used as received. Deionized water (18 MΩ·cm) was obtained using a Millipore 4-bowl purification system. Poly-(dimethylsiloxane) (PDMS) elastomer (Sylgard 184) was obtained from Dow Corning.

Synthesis of Co Nanoparticles. A 0.05 mmol sample of sodium bis(2-ethylhexyl)sulfosuccinate (NaAOT) and 0.05 mmol of 11-bromoundecanoic acid were dissolved in 36 mL of toluene at 110 °C. After 30 min, 4 mL of 0.5 M $Co_2(CO)_8$ in toluene solution was injected into the reaction vessel, and reaction was continued for 6 h at 110 °C. The solution color

* Corresponding authors. S.K.: e-mail, sehun-kim@kaist.ac.kr. J.C.: e-mail, jcheon@alchemy.yonsei.ac.kr.
‡ Korea Advanced Institute of Science and Technology.
§ Yonsei University.

changed from orange brown to brownish black. The resulting nanoparticles were purified by centrifugation after addition of excess ethanol.

Preparation of Functionalized Si Surface. For preparation of the aminopropyl (AP)-terminated Si surface as a functionalized substrate, first of all, the hydroxyl (OH)-terminated Si surface was prepared by the wet-chemical method. The Si(111) surface was cleaned by dipping in piranha solution (H_2SO_4: H_2O_2 = 7:3) at 90 °C for 1 h followed by washing with deionized water.[22] After cleaning, the sample was sonicated in basic hydroxide solution ($H_2O:H_2O_2:NH_3$ = 5:1:1) for 30 min, then sonicated in acidic peroxide solution ($H_2O:H_2O_2:HCl$ = 6:1:1) for 30 min followed by washing with deionized water, and kept in an oven at 120 °C for 10 min. And then, the OH-terminated surface was immersed in a toluene solution (10 mL) containing AP-DEMS (0.05 mL) at room temperature (RT) for 3 h under an Ar atmosphere. After the reaction, the sample was washed with toluene and kept in an oven at 120 °C for 30 min to promote strong Si—O—Si bonding.

Assembly of Nanoparticles on Functionalized Si Surface. The AP-terminated Si surfaces and a solution (0.2 mL) of Br-terminated Co nanoparticles were introduced into a toluene solution (10 mL) and the mixture was held at RT for 20 min to 18 h under an Ar atmosphere. After reaction, all samples were sonicated in toluene for 60 s to remove the physically deposited nanoparticles.

Preparation of Micropatterned Si Surface. A hexane solution of OD-TCS (10 mM) was wetted onto the PDMS stamp using a photoresist spin-coater (Headway Research Inc.) at 3000 rpm for 30 s. The OD-TCS wetted PDMS stamp was dried with N_2 gas for 10 s and then placed onto the OH-terminated Si surface by hand and held in place for 60 s. The sample was kept in an oven at 120 °C for 30 min and therefore the OH-OD-patterned surface is formed. For preparation of the AP-OD-patterned Si surfaces, the OH-OD-patterned Si surfaces were immersed in a toluene solution (10 mL) containing AP-DEMS (0.05 mL) at RT for 3 h under an Ar atmosphere. After immersion, the sample was washed with toluene and kept in an oven at 120 °C for 30 min.

Assembly of Nanoparticles on Micropatterned Si Surface. The AP-OD-patterned Si surface and a solution (0.2 mL) of Br-terminated Co nanoparticles were introduced into toluene (10 mL), and the mixture was held at RT for 6 h under an Ar atmosphere. After reaction, the sample was sonicated in toluene for 30 s.

Instrumentation. Field emission-scanning electron microscopy (FE-SEM) images were obtained using an XL30SFEG (Philips). Water contact angles of the functionalized Si surfaces were measured with a Model G2 contact angle meter (KRÜSS GmbH). X-ray photoelectron spectroscopy (XPS) data were obtained using a VG ESCA2000 with an Mg (Kα) source. The XPS measurement was made with a takeoff angle 45° and the bulk Si peak at 99.3 eV was used as a reference for calibration of the energy scale.

Results and Discussion

Co nanoparticles have been recognized as ideal building blocks for self-assembled magnetic monolayers for two main reasons: the narrow size distribution that can be easily attained, and the ease with which specific functional groups can be introduced into the outer parts of attached surfactants. Figure 1a shows the transmission electron microscopy (TEM) image of the resulting Co nanoparticles, which have average diameters of 10 nm (σ < 10%). The Co nanoparticles are well dispersed
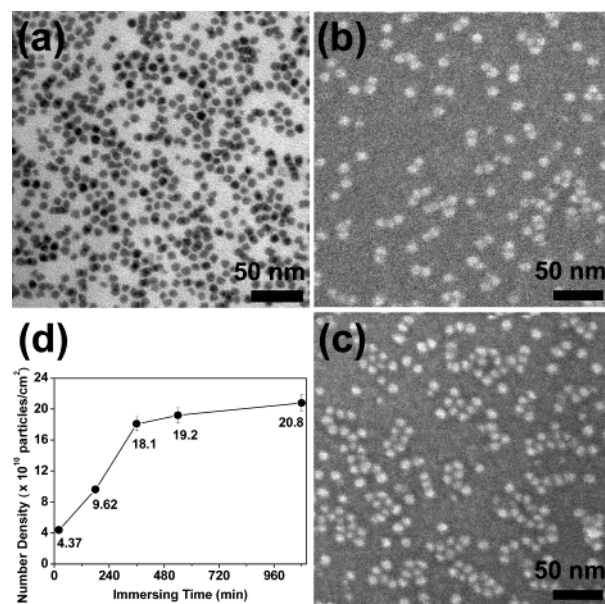

Figure 1. (a) TEM image of 10 nm Co nanoparticles capped with 11-bromoundecanoic acid. FE-SEM images showing an assembly of Co nanoparticles on an AP-terminated Si surface after immersion for (b) 3 h and (c) 9 h, respectively. (d) Variation of the number density of Co nanoparticles adsorbed on the AP-terminated Si surfaces as a function of immersion time.

in toluene and capped with 11-bromoundecanoic acid. The attachment of the acid groups to the surface of the Co nanoparticles was confirmed by energy-dispersive X-ray spectroscopy (EDS) and XPS.[5,9,23]

For qualitative confirmation of the functionalization of the Si surface, we measured the water contact angles of the functionalized Si surfaces used in this study. The measured contact angle for AP-terminated surface was 65−68°. These values are consistent with previously reported results.[24,25] When nanoparticles were deposited on the AP-terminated Si surfaces, the measured contact angles increase to 85° because the alkylbromine group in the surfactant is more hydrophobic than the AP groups. Therefore, the substantial change in the contact angle caused by nanoparticle deposition means that contact angle measurements can be utilized to indirectly confirm the self-assembly of Co nanoparticles on the AP-terminated Si surfaces.

Parts b and c of Figure 1 show FE-SEM images of the distributions of Co nanoparticles on the AP-terminated Si surfaces obtained after immersion for 3 and 9 h, respectively. The distributions of nanoparticles are dependent upon the immersing reaction time: after immersion for 3 h, the nanoparticles show an individual distribution with low number densities of particles (Figure 1b). After immersion for 9 h, the nanoparticles have a random distribution over the entire AP-terminated surface (Figure 1c).

The number density of adsorbed nanoparticles can be controlled by varying the immersion time of the Si surface in the constant concentration solution of nanoparticles. The number densities of particles on the functionalized Si surfaces were determined from the FE-SEM images and changed to the coverage. The number densities linearly increase with immersion time for the surfaces, as shown in Figure 1d. After immersion for 6 h, however, the number density does not increase and the AP-terminated surface becomes saturated. If we assume that the size of the nanoparticles including surfactant shells is 12.0 nm, we estimate that the number density of nanoparticles required for the full coverage of 1 monolayer (ML) is about 6.90×10^{11} nanoparticles/cm^2. In the saturated region (from 6

Selectively Assembled Co Nanoparticle Stripes

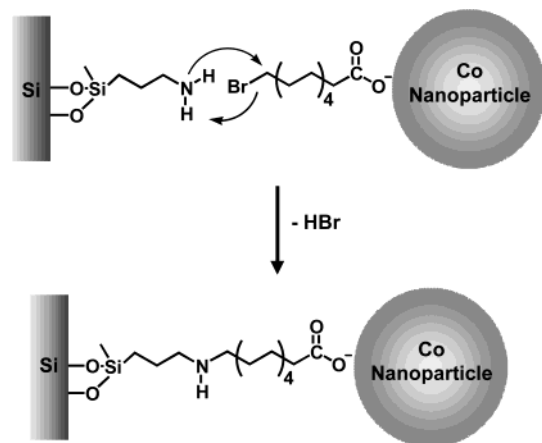*J. Phys. Chem. B, Vol. 108, No. 8, 2004* **2577**

Figure 2. Direct nucleophilic substitution reaction between the terminal Br group of the Co nanoparticle and the NH$_2$ group on the Si surface.

to 18 h), the number density was found to be less than half a monolayer (2.08 × 10^{11} nanoparticles/cm^2). We conclude that the Co nanoparticle assembly produced on the AP-terminated Si surface is approximately 0.3 ML in coverage. Although at high number densities saturation behavior was observed, multilayers of nanoparticles were not observed on either functionalized Si surface.

In contrast to the highly ordered phases obtained by dropping nanoparticle solutions onto carbon grid substrates, we find that Co nanoparticles form randomly distributed arrays on the functionalized surface. The formation of ordered phases is known to be governed by the interactions between the nanoparticles on the substrate. The observed random distribution is therefore attributed to the hindered interactions between nanoparticles. This is due to the rapid and strong chemical reaction that occurs between the functional groups of the nanoparticles and the functionalized Si surfaces, leading to irreversible anchoring of the nanoparticles to the surfaces through covalent linkages. Also, we think that the disordered distribution of nanoparticles may be due to the disordered absorption of AP-DEMS, linker molecules, on Si surface. As far as we know, in the literature, the detailed atomic level adsorption structure of AP-terminated Si surface is not available and a further study is needed in future. Therefore, it seems reasonable to conclude that the disordered array of the AP-DEMS molecules is another cause of the random assembly of nanoparticles.

The covalent linkage of Co nanoparticles onto the AP-terminated Si surfaces proceeds via the direct nucleophilic organic substitution reaction of the terminal Br groups of surfactants with the NH$_2$ groups on the Si surface according to Figure 2. To confirm the formation of covalent bonds between the nanoparticles and the functionalized surface, we performed a control experiment that attempts assembly of Co nanoparticles on a nonfunctionalized surface, i.e., on an H-passivated Si(111) surface prepared by etching the native surface oxide of the Si surface with 40% NH$_4$F solution.[26] An FE-SEM image of the H-passivated Si surface after immersion for 18 h in a toluene solution of Br-terminated Co nanoparticles showed the absence of adsorbed nanoparticles (not shown here); we conclude that Br-terminated nanoparticles do not bond to an H-passivated Si surface. This experiment provides important evidence for the formation of a strong covalent linkage between the terminal Br group of surfactants in nanoparticles and the Si surfaces functionalized with NH$_2$ groups.

XPS measurements were carried out to gain more insight into the chemical covalent linkages between the nanoparticles and
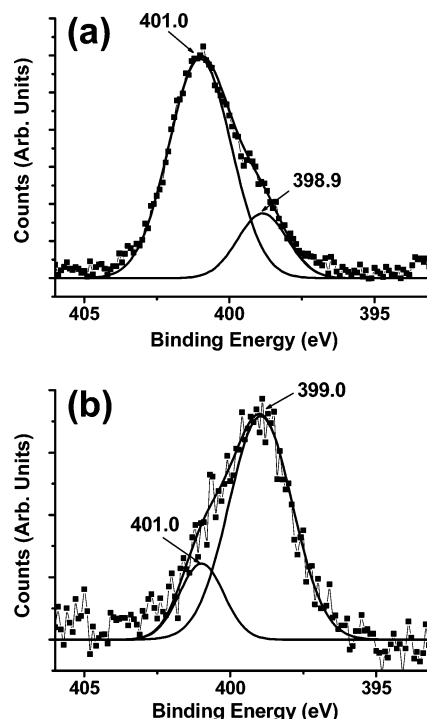

Figure 3. N(1s) XPS data for (a) the AP-terminated surface and (b) the AP-terminated surface with adsorbed Co nanoparticles.

the substrates. The XPS spectra of the functionalized surfaces and of those surfaces with adsorbed Co nanoparticles were fitted with Gaussian functions and deconvoluted. In the XPS spectra of the AP-terminated Si surface (Figure 3a) and of the AP-terminated Si surface with adsorbed Co nanoparticles (Figure 3b), the N(1s) spectra can be deconvoluted into two peaks, one at 401.0 eV for protonated amine (−NH$_3^+$) and the other at 398.9 eV for the free amine (−NH$_2$ or −N(H)−).[27] Some of the free amine groups in the AP-terminated surface are transformed into protonated amine by adsorption of trace amounts of water. Therefore, the intensity of the protonated amine peak is larger than that due to the free amines. However, the intensity of the peak due to protonated amines is reduced after the adsorption of Co nanoparticles in comparison with that due to the free amines by the transformation of protonated amines into secondary amines (−N(H)−). This change in intensity indicates that Co nanoparticles are attached to the AP-terminated surface by covalent N−C bonds.

To illustrate the selectivity of the functionalized Si surface, we fabricated a 2D micropatterned assembly of Co nanoparticles attached to the Si surface by chemical covalent linkages using μ-CP as shown in Figure 4. The μ-CP method is a soft lithographic method developed by Whitesides et al. that has been used to prepare high-quality self-assembled patterns with well-defined lateral dimensions.[20,21] A patterned surface with alternating stripes of OH and OD group termination was prepared by μ-CP method using OD-TCS, as shown in Figure 4a. Then, we prepared an AP-OD-patterned surface through selective self-assembly of AP groups on the OH-terminated regions by treating the micropatterned Si surface with AP-DEMS in toluene (Figure 4b). Finally, the treatment of the AP-OD-patterned Si surface with the Co nanoparticle solution led to the selective assembly of nanoparticles covalently bound to the AP-terminated regions (Figure 4c).

Figure 5 shows FE-SEM images of the patterned assemblies of Co nanoparticles on the micropatterned Si surface. The FE-SEM image of the striped patterns that consist of assembled
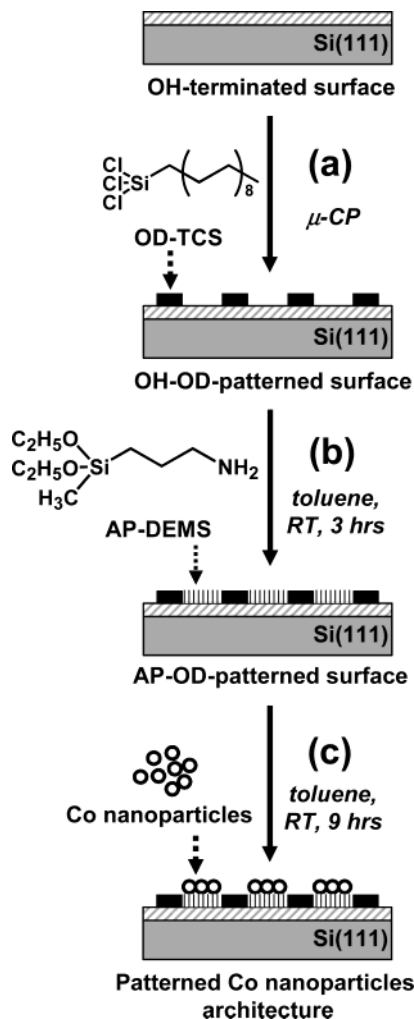
2578 *J. Phys. Chem. B, Vol. 108, No. 8, 2004*

Bae et al.

Figure 4. Procedures for patterning Co nanoparticle assemblies on the functional group patterned Si surfaces.
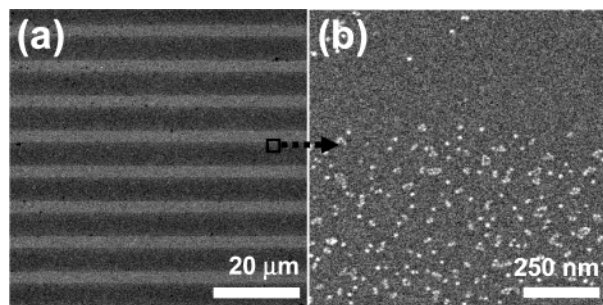

Figure 5. FE-SEM images of the patterned assembly of Co nanoparticles on the AP-OD-patterned Si surface at (a) low magnification and (b) enlarged magnification.

nanoparticles (dark regions) and OD-terminated regions (light regions) is shown in Figure 5a. The contrasting regions in the striped patterns arise from their difference in the secondary electron emissions.[21] The enlarged FE-SEM image in Figure 5b shows that the Co nanoparticles assemble on the patterned AP-terminated regions but not on the patterned OD-terminated regions in the patterned AP-OD-terminated surfaces. This result indicates that selective covalent bonding occurs between the Br-terminated Co nanoparticles and the AP-terminated surfaces. Consequently, the patterned assembly of the Co nanoparticles is predetermined by the functional-group pattern on the Si

surface, which acts as a template for the assembly of the nanoparticles.

The combination of the μ-CP and covalent linkage methods can be utilized to control the number density of the nanoparticles and the position of the nanoparticles on a surface. We showed the fact that the number density of the nanoparticles can be varied by controlling the reaction conditions such as the immersion time of the functionalized Si surface. Furthermore, the positioning of nanoparticles on a surface can be controlled by the μ-CP method for formation of uniformly patterned self-assembled monolayers over wide areas. Although considerable study on the fabrication of patterned structures with nanoscale dimension is still required, it is important to note that the nanoparticle patterning methods presented here have the potential to enable the controlled assembly of nanoparticles in arbitrary patterned architectures.

Conclusion

We have reported a novel and versatile strategy for the fabrication of assemblies of Co nanoparticles on Si surfaces through the use of covalent linkages between terminal functional groups attached to the Si substrate and the Co nanoparticles. The distribution and number density of adsorbed nanoparticles can be controlled by varying the immersion time. Furthermore, by using the μ-CP method the selective assembly of nanoparticles on micropatterned surfaces with different functional groups can be achieved. We believe that the two strategies presented here provide a foundation for the development of systems of nano building blocks for use in future transition metal nanoparticle-based architectures.

References and Notes

(1) Fendler, J. H. *Nanoparticles and Nanostructured Films: preparation, characterization and applications*; Wiley-VCH: Wienheim, 1998.

(2) Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706.

(3) Sun, S.; Murray, C. B. *J. Appl. Phys.* **1999**, *85*, 4325.

(4) Puntes, V. F.; Krishnan, K. M.; Alivisatos, A. P. *Science* **2001**, *291*, 2115.

(5) Park, J.-I.; Kang, N.-J.; Jun, Y.-W.; Oh, S. J.; Ri, H.-C.; Cheon, J. *ChemPhysChem* **2002**, *3*, 543.

(6) Park, J.-I.; Cheon, J. *J. Am. Chem. Soc.* **2001**, *123*, 5743.

(7) Motte, L.; Lacaze, E.; Maillard, M.; Pileni, M. P. *Langmuir* **2000**, *16*, 3803.

(8) Lin, X. M.; Jaeger, H. M.; Sorensen, C. M.; Klabunde, K. J. *J. Phys. Chem. B* **2001**, *105*, 3353.

(9) Hong, Y.-K.; Kim, H.; Lee, G.; Kim, W.; Park, J.-I.; Cheon, J.; Koo, J.-Y. *Appl. Phys. Lett.* **2002**, *80*, 844.

(10) Colvin, V. L.; Goldstein, A. N.; Alivisatos, A. P. *J. Am. Chem. Soc.* **1992**, *114*, 5221.

(11) Grabar, K. C.; Freeman, R. G.; Hommer, M. B.; Natan, M. J. *Anal. Chem.* **1995**, *67*, 735.

(12) Grabar, K. C.; Smith, P. C.; Musick, M. D.; Davis, J. A.; Walter, D. G.; Jackson, M. A.; Guthrie, A. P.; Natan, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 1148.

(13) Paraschiv, V.; Zapotoczny, S.; de Jong, M. R.; Vancso, G. J.; Huskens, J.; Reinhoudt, D. N. *Adv. Mater.* **2002**, *14*, 722.

(14) Zhu, T.; Fu, X.; Mu, T.; Wang, J.; Liu, Z. F. *Langmuir* **1999**, *15*, 5197.

Selectively Assembled Co Nanoparticle Stripes

J. Phys. Chem. B, Vol. 108, No. 8, 2004 **2579**

(15) He, H. X.; Zhang, H.; Li, Q. G.; Zhu, T.; Li, S. F. Y.; Liu, Z. F. *Langmuir* **2000**, *16*, 3846.

(16) Zheng, J.; Zhu, Z.; Chen, H.; Liu, Z. F. *Langmuir* **2000**, *16*, 4409.

(17) Sato, T.; Hasko, D. G.; Ahmed, H. *J. Vac. Sci. Technol. B* **1997**, *15*, 45.

(18) Sato, T.; Ahmed, H.; Brown. D.; Johnson, B. F. G. *J. Appl. Phys.* **1997**, *82*, 696.

(19) Bhat, R. R.; Fischer, D. A.; Genzer, J. *Langmuir* **2002**, *18*, 5640.

(20) Xia, Y.; Mrksich, M.; Kim, E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1995**, *117*, 9576.

(21) Jeon, N. L.; Finnie, K.; Branshaw, K.; Nuzzo, R. G. *Langmuir* **1997**, *13*, 3382.

(22) ***Caution!*** *Piranha solutions are extraordinarily dangerous, reacting explosively with trace quantities of organics. They should be handled in very small quantities with the utmost care.*

(23) Analysis of the Co and Br peaks in the EDS spectra confirmed the presence of Co nanoparticles capped with 11-bromoundecanoic acid. The C(1s) XPS spectra for the functionalized Si surfaces with adsorbed Co nanoparticles have three distinct peaks at 284.6, 286.3, and 288.4 eV, which were assigned to alkyl carbons, sulfonate carbons, and the carboxyl carbons in the surfactants of nanoparticles, respectively.

(24) Kim, H. J.; Moon, J. H.; Park, J. W. *J. Colloid Interface Sci.* **2000**, *227*, 247.

(25) Oh, S. J.; Cho, S. J.; Kim, C. O.; Park, J. W. *Langmuir* **2002**, *18*, 1764.

(26) Linford, M. R.; Fenter, P.; Eisenberger, P. M.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1995**, *117*, 3145.

(27) Moon, J. H.; Kim, J. H.; Kim, K.-J.; Kang, T.-H.; Kim, B.; Kim, C.-H.; Hahn, J. H.; Park, J. W. *Langmuir* **1997**, *13*, 4305.