Reversible Attachment of Nanostructures at Molecular Printboards through Supramolecular Glue

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Received September 18, 2007. Revised Manuscript Received March 3, 2008

Regenerable surfaces and reversible attachment of nanostructures onto them is an important aim in nanotechnology. Reversible attachment of nanostructures at molecular printboards was illustrated by the adsorption and desorption of β-cyclodextrin (β-CD)-functionalized nanoparticles onto and from stimuli-responsive preadsorbed ferrocenyl-functionalized poly(propylene imine) dendrimers at a β-CD self-assembled monolayer (SAM). Electrochemical oxidation of the ferrocenyl endgroups was employed to induce desorption of nanostructures from the β-CD SAMs. A combined surface plasmon resonance spectroscopy and electrochemistry setup was used to monitor the in situ adsorption and desorption of ferrocenyl dendrimers and β-CD-functionalized Au nanoparticles (CD-Au, $d\sim$ 2.8 nm) onto and from the molecular printboard. In the case of the larger β-CD-functionalized silica nanoparticles (CD-SiO$_2$, $d\sim$ 60 nm), ultrasonication was used to reduce the desorption time. By electrochemical oxidation applied to a specific area of a nanoparticle layer, local desorption of nanoparticles was observed. In the nonoxidized area, nanoparticles remained robustly attached to the surface, whereas nanoparticles on the electrochemically oxidized area were completely removed.

Introduction

Assembly of nanostructures on surfaces is an active research field owing to the increasing demand for miniaturization of microelectronic and optical devices. In addition, the ability to reversibly adsorb and desorb nanostructures from the surface is crucial,[1] as structural manipulation or modifications are often needed on a specific area of a nanostructure. General coupling chemistries, e.g., electrostatic interactions,[2] covalent bonding[3] and thiol-based[4] self-assembly, result in strong but irreversible functionalized nanostructures on (patterned) surfaces. Hence, biomolecular and supramolecular systems involving DNA,[5,6] biotin−streptavidin,[7] supramolecular hydrogen bonding,[8] and ligand−receptor[9,10] interactions have been described as they offer highly specific and/or reversible binding of nanoparticles. Supramolecular chemistry is particularly attractive as it possesses controllable molecular recognition abilities with the possibility for error correction.[9] Our group has developed the concept of the "molecular printboard," i.e., β-cyclodextrin (β-CD) self-assembled monolayers (SAMs) on gold or glass that possess receptor properties.[11] Complementary adamantyl-functionalized dendrimers were employed as "nonreversible molecular glue" to construct self-assembled organic/inorganic multilayers with β-CD-functionalized gold and silica nanoparticles (CD-Au and CD-SiO$_2$ NPs) at the molecular printboard employing multivalent supramolecular interactions.[12,13]

The redox behavior of ferrocene is well-known for its reversibility in host−guest systems.[14–16] Kaifer and Stoddart et al. have described the interfacial monovalent ferrocenyl (Fc) complexation at a per-6-thio-β-CD monolayer.[17] We have demonstrated that multivalent Fc dendrimers can be reversibly adsorbed and removed from β-CD SAMs by electrochemical oxidization of the redox-active Fc end groups.[17–20]

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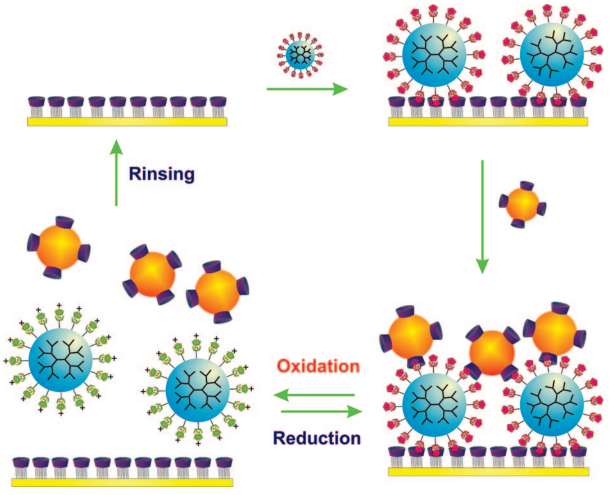
(1) Tang, C. S.; Schmutz, P.; Petronis, S.; Textor, M.; Keller, B.; Voros, J. *Biotechnol. Bioeng.* **2005**, *91*, 285.
(2) Decher, G. *Science* **1997**, *277*, 1232.
(3) Paraschiv, V.; Zapotoczny, S.; de Jong, M. R.; Vancso, G. J.; Huskens, J.; Reinhoudt, D. N. *Adv. Mater.* **2002**, *14*, 722.
(4) Kiely, C. J.; Fink, J.; Zheng, J. G.; Brust, M.; Bethell, D.; Schiffrin, D. J. *Adv. Mater.* **2000**, *12*, 640.
(5) Alivisatos, A. P.; Johnsson, K. P.; Peng, X. G.; Wilson, T. E.; Loweth, C. J.; Bruchez, M. P.; Schultz, P. G. *Nature* **1996**, *382*, 609.
(6) Mirkin, C. A.; Letsinger, R. L.; Mucic, R. C.; Storhoff, J. J. *Nature* **1996**, *382*, 607.
(7) Haes, A. J.; Van Duyne, R. P. *J. Am. Chem. Soc.* **2002**, *124*, 10596.
(8) Labande, A.; Ruiz, J.; Astruc, D. *J. Am. Chem. Soc.* **2002**, *124*, 1782.
(9) Reinhoudt, D. N.; Crego-Calama, M. *Science* **2002**, *295*, 2403.
(10) Lahav, M.; Shipway, A. N.; Willner, I.; Nielsen, M. B.; Stoddart, J. F. *J. Electroanal. Chem.* **2000**, *482*, 217.
(11) Beulen, M. W. J.; Bügler, J.; Lammerink, B.; Geurts, F. A. J.; Biemond, E.; van Leerdam, K. G. C.; van Veggel, F.; Engbersen, J. F. J.; Reinhoudt, D. N. *Langmuir* **1998**, *14*, 6424.
(12) Crespo-Biel, O.; Dordi, B.; Reinhoudt, D. N.; Huskens, J. *J. Am. Chem. Soc.* **2005**, *127*, 7594.
(13) Mahalingam, V.; Onclin, S.; Peter, M.; Ravoo, B. J.; Huskens, J.; Reinhoudt, D. N. *Langmuir* **2004**, *20*, 11756.
(14) Beer, P. D.; Tite, E. L.; Ibbotson, A. *Dalton Trans.* **1991**, 1691.
(15) Plenio, H.; Aberle, C. *Chem.−Eur. J.* **2001**, *7*, 4438.
(16) Willner, I.; Doron, A.; Katz, E.; Levi, S.; Frank, A. J. *Langmuir* **1996**, *12*, 946.
(17) Rojas, M. T.; Koniger, R.; Stoddart, J. F.; Kaifer, A. E. *J. Am. Chem. Soc.* **1995**, *117*, 336.
(18) Nijhuis, C. A.; Huskens, J.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **2004**, *126*, 12266.
(19) Nijhuis, C. A.; Yu, F.; Knoll, W.; Huskens, J.; Reinhoudt, D. N. *Langmuir* **2005**, *21*, 7866.
(20) Valerio, C.; Fillaut, J. L.; Ruiz, J.; Guittard, J.; Blais, J. C.; Astruc, D. *J. Am. Chem. Soc.* **1997**, *119*, 2588.

10.1021/cm703597w CCC: $40.75

Scheme 1. Illustration of the Adsorption and Desorption of β-CD-Functionalized NPs onto and from β-CD SAMs with Fc Dendrimers as a Reversible Supramolecular Glue



Here, it is demonstrated that, by using Fc dendrimers as supramolecular reversible glue, β-CD-functionalized nanoparticles (NPs) can be reversibly adsorbed and desorbed from the molecular printboard (Scheme 1). Our aim is to practically realize the concept of reversible immobilization of nanostructures, with the focus on: (i) the electrochemical addressability of the reversible glue, when sandwiched between the SAM and NP interfaces, (ii) optimization of the conditions for disassembly of the reversible glue and the NPs off the interface, and (iii) possible size effects of the NPs on the reversibility. The repeated adsorption and desorption of β-CD-functionalized gold (CD-Au) NPs onto and from the surface were monitored in situ by a combined surface plasmon resonance spectroscopy (SPR) and electrochemistry setup.[19] For easy visualization and for studying potential size effects on reversibility, experiments were repeated by using larger β-CD-functionalized silica (SiO_2−CD) nanoparticles of 60 nm in diameter.

Experimental Section

Materials. β-CD heptathioether[11] and ferrocenyl poly(propylene imine) dendrimers of generation 3 (G3-PPI-$(Fc)_{16}$)[18] were synthesized as described before. β-CD-functionalized Au (CD-Au, $d \approx$ 2.8 nm) and silica nanoparticles (CD-SiO_2, $d \approx$ 60 nm) were prepared according to published procedures.[12,13] Poly(dimethylsiloxane) Sylgard 184 and curing agent were obtained from Dow Corning. Milli-Q water with a resistivity greater than 18 MΩ cm was used in all our experiments.

Substrate and Monolayer Preparation. All adsorbate solutions were prepared freshly prior to use. Round glass-supported gold substrates for SPR and electrochemistry (2.54 cm diameter; 50 or 200 nm Au) were obtained from Ssens BV (Hengelo, The Netherlands). Gold substrates were cleaned by immersing the substrates in piranha (conc. H_2SO_4 and 33% H_2O_2 in a 3:1 ratio; **Warning!** piranha should be handled with caution; it is a highly corrosive oxidizing agent) for 10 s and leaving the substrates for 5 min in absolute ethanol. The substrates were subsequently immersed into a 0.1 mM β-CD heptathioether adsorbate solution in EtOH and $CHCl_3$ (1:2 v/v) for 16 h at 60 °C. The samples were then rinsed with substantial amounts of $CHCl_3$, EtOH, and Milli-Q water. The adsorption of G3-PPI-$(Fc)_{16}$ was achieved by immersing the β-CD SAM substrates in a solution of 1 mM G3-PPI-$(Fc)_{16}$ for 30 min, followed by rinsing with 10 mM aqueous β-CD at pH 2 and Milli-Q water.

Microcontact Printing. Poly(dimethylsiloxane) (PDMS) stamps were prepared by casting a 10:1 (v/v) mixture of Sylgard 184 elastomer and curing agent against a patterned silicon master. After curing of the stamps overnight, they were mildly oxidized in an ozone plasma reactor (Ultra-Violet Products Inc., model PR-100) for 60 min to render their surfaces hydrophilic. Subsequently, they were inked by soaking them in a 1 mM aqueous solution of the G3-PPI-$(Fc)_{16}$ for 20 min. The stamps were blown dry in a stream of N_2 before printing. The stamps were brought in conformal contact with β-CD SAM for 10 min and then carefully removed. The substrates were thoroughly rinsed with water.

Assembly of a Dendrimer-Au Nanoparticle Structure. The assembly of a Au nanoparticle sandwich layer was performed in an SPR flow cell setup by first flowing 0.1 mM G3-PPI-$(Fc)_{16}$ (0.1 mM Fc functionality) dendrimers in 10 mM β-CD, pH 2 solution through the SPR cell, followed by introducing CD-Au (5.8 μM in β-CD functionality) NPs in a background solution of 10 mM β-CD in HEPES buffer. Between the adsorption steps, the substrate was rinsed with the respective background solution to remove any physisorbed material. All adsorptions were performed at a flow rate of 0.5 mL/min.

Preparation of a Dendrimer-SiO_2 Nanoparticle Structure. A monolayer of CD-SiO_2 NPs was deposited onto a β-CD SAM with preadsorbed (from solution) or microcontact printed G3-PPI-$(Fc)_{16}$ by using a convective assembly setup.[21] The nanoparticle layer was then ultrasonicated for 20 s, rinsed with Milli-Q water of pH 2, and Milli-Q water, and gently blown dry with N_2 before electrochemical testing.

Combined SPR Spectroscopy and Electrochemistry Setup. The SPR setup was obtained from Resonant Probes GmbH. The instrument consists of a HeNe laser (JDS Uniphase, 10 mW, λ = 632.8 nm) whose light passes through a chopper that is connected to a lock-in amplifier (EG&G 7256). The modulated beam is directed through two polarizers (OWIS) to control the intensity and the plane of polarization of the light. The light is coupled via a high-index prism (Scott, LaSFN9) in the Kretschmann configuration to the backside of the gold-coated substrate, which is optically matched through a refractive-index-matching oil (Cargille; series B; n_D^{25} = 1.700 ± 0.002) at the prism, mounted on a $\theta-2\theta$ goniometer in contact with a Teflon cell with a volume of 113 mm^3 and a diameter of 6 mm. The light that leaves the prism passes through a beam splitter; subsequently, the s-polarized light is directed to a reference detector, and the p-polarized light passes through a lens which focuses the light onto a photodiode detector. Laser fluctuations are filtered out by dividing the intensity of the p-polarized light (I_p) by the intensity of the s-polarized light (I_s). The SPR experiments were performed in a flow cell system. Rates of 0.5 and 4.0 mL/min were set as typical flow rates for adsorption and desorption, respectively. Upon completion of an experiment, the flow rate was adjusted back to 0.5 mL/min, such that a proper comparison of SPR intensity changes can be made between before adsorption and after desorption.

Electrochemistry was performed with an AUTOLAB PGSTAT10 in a three-electrode setup with the Au SPR substrates at the prism as the working electrode, a Ag/AgCl ($V_{Ag/AgCl}$ = +0.21 V_{NHE}) reference electrode and a platinum wire as counter electrode. The cyclic voltammetry (CV)-induced desorption processes on gold were detected by monitoring reflectivity changes as a function of time at a fixed incidence angle, θ. CV was performed on a bare β-CD

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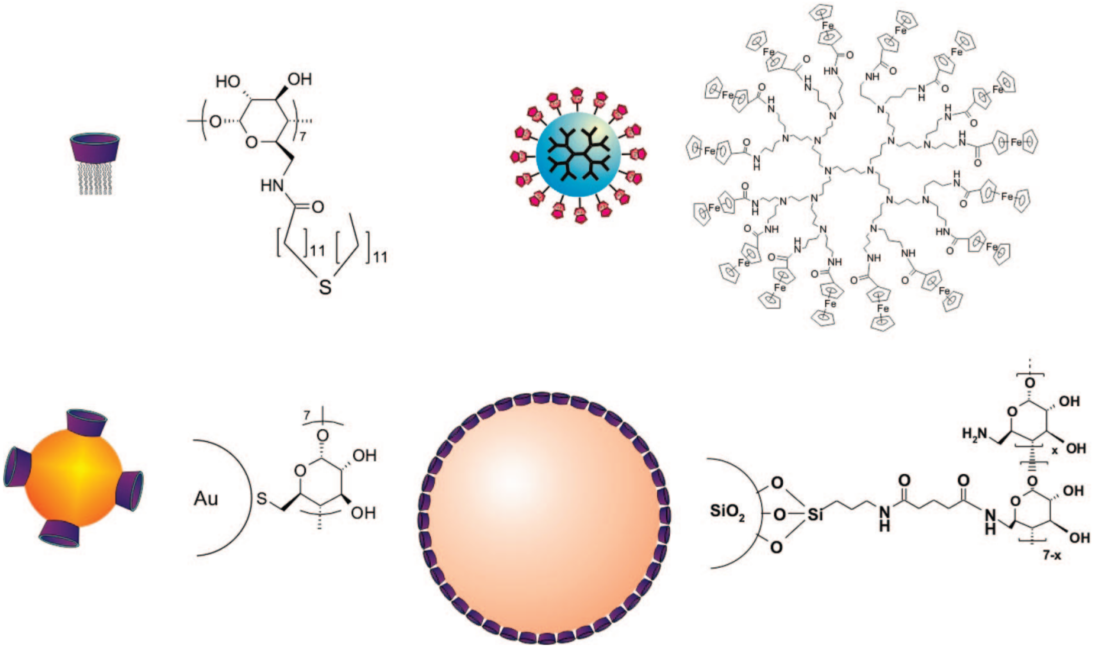
(21) Maury, P.; Escalante, M.; Reinhoudt, D. N.; Huskens, J. *Adv. Mater.* **2005**, *17*, 2718.

Chart 1. Chemical structures of β-CD heptathioether, ferrocenyl poly(propylene imine) dendrimer of generation 3, β-CD-functionalized Au, and silica nanoparticles



SAM, showing the SPR signal remained unchanged during CV, indicating that all SPR intensity changes can be attributed fully to adsorption and desorption processes. Chronoamperometry (CA) was performed by holding the potential at +0.65 $V_{Ag/AgCl}$.

Electrochemistry. Electrochemical measurements were performed in a three-electrode setup equipped with a platinum counter electrode, a mercury sulfate reference electrode ($V_{MSE} = +0.61\ V_{NHE}$) and a screw cap holding the gold working electrode with surface area of 0.44 cm^2. Cyclic voltammetric tests were performed in an aqueous solution 0.1 M K_2SO_4, between −0.35 V_{MSE} and +0.30 V_{MSE}, at the given scan rate. CA was performed by holding the potential at +0.15 V_{MSE}, and the changes in the oxidation current with time were recorded. The samples after electrochemistry were sonicated for 100 s, rinsed with pH 2 Milli-Q water and blown dry with N_2.

Scanning Electron Microscopy (SEM). All SEM images were taken with a HR-LEO 1550 FEF SEM.

Results and Discussion

Scheme 1 describes the build-up and breakdown of nanoparticle assemblies on a molecular printboard via a reversible supramolecular glue. A monolayer of NPs was formed by stepwise adsorption of aqueous ferrocenyl (Fc) dendrimers and β-CD-functionalized NPs onto the β-CD SAM via multivalent supramolecular host−guest interactions (Chart 1). Ferrocenyl poly(propylene imine) dendrimer of generation 3 (G3-PPI-$(Fc)_{16}$) serves as a "reversible supramolecular glue" for the binding and unbinding of nanoparticles or nano-objects to and from the molecular printboard.[19] Intentional desorption of the NPs from the surface can be achieved by electrochemical oxidation of the Fc groups of the dendrimers to ferrocenium cations, such that the assembled nanostructures are removed from the surface.

A combined SPR and electrochemistry setup[22] was used to monitor in situ the adsorption and desorption of G3-PPI-$(Fc)_{16}$ and CD-Au nanoparticles (NPs) onto and from a β-CD SAM on gold, while monitoring the SPR and *IV* responses simultaneously. CV was performed on a bare β-CD SAM, showing that the SPR signal remained unchanged during CV in the absence of electroactive dendrimers (data not shown), indicating that the SPR intensity can be completely attributed to the adsorption and desorption processes.[18,19] The adsorption of G3-PPI-$(Fc)_{16}$ in 10 mM β-CD in pH 2 water and CD-Au NPs in 10 mM β-CD in HEPES buffer were adsorbed at a flow rate of 0.5 mL/min. To assist desorption of the nanostructures from the surface, the flow rate was increased to 4.0 mL/min during desorption. After the experiment, the flow rate was adjusted back to 0.5 mL/min for proper comparison of the SPR intensities before adsorption and after desorption.

Figure 1 shows the sequential adsorption and electrochemically induced desorption of G3-PPI-$(Fc)_{16}$ and CD-Au (*d* 2.8 nm) onto and from the molecular printboard, as studied by SPR spectroscopy. G3-PPI-$(Fc)_{16}$ was used because it yields thermodynamically and kinetically stable complexes at the β-CD SAM, even when rinsing with 10 mM β-CD.[19] G3-PPI-$(Fc)_{16}$ was applied in a pH 2 solution, while the CD-Au NPs were applied in a HEPES buffer, both for stability reasons.[12] To evaluate the SPR signal changes accurately, the SPR flow cell was flushed with the corresponding buffer before the introduction of the respective adsorbing component and rinsed afterward with the same buffer.[12] After adsorption of G3-PPI-$(Fc)_{16}$ (0.1 mM in Fc functionality), a CD-Au NP solution (5.8 μM in CD functionality) was introduced, and rinsing led to removal of physisorbed NPs. When the adsorption of dendrimers is omitted, the CD-Au NPs do not adsorb at the β-CD SAM.[12]

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(22) Nijhuis, C. A.; Sinha, J. K.; Wittstock, G.; Huskens, J.; Ravoo, B. J.; Reinhoudt, D. N. *Langmuir* **2006**, *22*, 9770.

(23) Bruinink, C. M.; Nijhuis, C. A.; Peter, M.; Dordi, B.; Crespo-Biel, O.; Auletta, T.; Mulder, A.; Schonherr, H.; Vancso, G. J.; Huskens, J.; Reinhoudt, D. N. *Chem.−Eur. J.* **2005**, *11*, 3988.

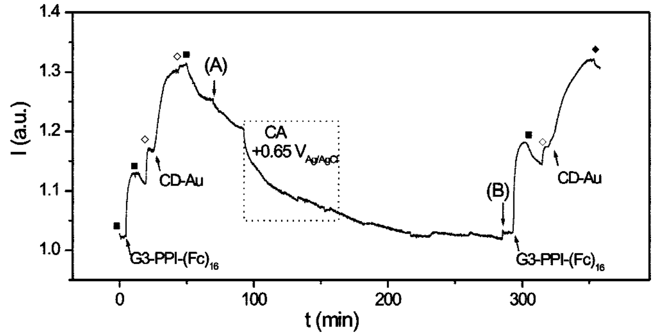

Figure 1. SPR sensogram of the sequential adsorption of 0.1 mM G3-PPI-(Fc)$_{16}$ dendrimers and CD-Au NPs (5.8 μM in β-CD functionality) onto a β-CD SAM, followed by rinsing and CA-induced desorption. The substrate was then reused for another buildup of G3-PPI-(Fc)$_{16}$ dendrimers and CD-Au NPs. (A) Change of flowrate to 4.0 mL/min; (B) change of flow rate to 0.5 mL/min. Symbols (■) and (◇) indicate rinsing with 10 mM β-CD in pH 2 water and with HEPES buffer, respectively.

Increase of the flow rate (Figure 1A) led to some additional removal of dendrimers and/or NPs.

The oxidation of the Fc groups was induced by CA at a potential of +0.65 V$_{Ag/AgCl}$ for 1 h. CA is used for the complete desorption of the NPs (and dendrimers) from the molecular printboards because it allows control over the oxidation potential and duration. CV appeared to be not beneficial here because it involves repeated oxidation and reduction cycles, which led to reformation of the supramolecular bonds before detectable desorption occurred (data not shown). Upon CA, a reduction in SPR intensity was observed once oxidation started. Although desorption occurred, the desorption rate was rather small, in particular when compared to the desorption of the dendrimers in absence of NPs.[18,19] The desorption rate appeared to be dependent on the flow rate through the SPR flow cell. The desorption rate observed here (Figure 1; about 50% coverage decrease per hour) was obtained at a fairly high flow rate; at lower flow rates, desorption was (much) slower (data not shown). Nonetheless, the SPR intensity was restored to its original starting intensity at point B, indicating a (near) complete removal of dendrimers and NPs.

To assess the reusability of a β-CD SAM after prolonged electrochemistry, another stepwise adsorption of G3-PPI-(Fc)$_{16}$ and CD-Au was performed after the desorption process on the same substrate (Figure 1), at $t = 300$ min. The increase in intensity was similar to the previous adsorption process, proving the robustness of the β-CD SAM after prolonged electrochemistry.[7] This is important, as it indicates that the β-CD SAM can be reused. By consideration that desorption assisted by flow is time-consuming, desorption in the experiment thereafter was performed by ultrasonicating the substrates in water for 2 min after electrochemistry, as 2 min ultrasonication appeared sufficient to assist the removal of the nanoparticle layer from the surface.

To determine possible NP size effects on the reversibility of the nanostructure attachment, larger NPs, i.e., β-CD-functionalized silica nanoparticles (CD-SiO_2 NPs) of 60 nm, were used.[9] Figure 2A shows a densely packed CD-SiO_2 layer on G3-PPI-(Fc)$_{16}$ at the molecular printboard. The layer was repeatedly oxidized and reduced during 50 CV cycles between −0.35 and +0.30 V$_{MSE}$ at a scan rate of 500 mV/s. The sample was sonicated in water to remove any physisorbed particles. Figure 2B shows that the SiO_2 NP layer remained nearly unchanged after electrochemistry, indicating the robust attachment as a result of strong multivalent supramolecular interactions. The CVs show highly reversible oxidation and reduction scans (Figure 2C). The total coverage of Fc moieties of G3-PPI-(Fc)$_{16}$ sandwiched between the β-CD SAM and the CD-SiO_2 NPs was comparable to the coverage of G3-PPI-(Fc)$_{16}$ on a β-CD SAM, without the NPs attached,[18] indicating that all Fc moieties were electrochemically addressable. However, the system with only dendrimers on the β-CD SAM showed a gradual decrease in intensity of oxidation current with increasing scan number, which indicates a gradual desorption and diffusion of dendrimers from the β-CD SAM.[18,19] With addition of CD-SiO_2 NPs onto the surfaces of G3-PPI-(Fc)$_{16}$ on β-CD SAMs, the current reduction was nearly negligible, probably due to the inhibited diffusion of oxidized dendrimers from the interface as a result of slow mass transport of the CD-SiO_2 from the interface at the electrochemical time scale. During the subsequent reduction sweep, the dendrimers remain close to the substrate to be reduced back to their neutral form leading to rebinding to the host surface and the CD-SiO_2 NPs.

The removal of a complete NP layer from the surface has been shown to be feasible in Figure 1. In reality, one may not need to regenerate the entire substrate but only a small area. Hence, an individually addressable electrode is essential such that a certain area of a substrate can be selectively oxidized, and error correction can be made on that specific area. As a proof of principle, an intended desorption area was defined by an O-ring. The area within the O-ring was exposed to the electrolyte with the counter electrode, whereas the area outside the O-ring remained dry. The substrate was electrochemically biased at +0.15 V$_{MSE}$ (CA) until the oxidation current had decreased, indicating the complete oxidation of Fc endgroups to ferrocenium cations (Figure 3C). This result was further supported by CVs after CA (Figure 3D), which showed the absence of Fc oxidation and reduction peaks between −0.35 and +0.30 V$_{MSE}$, indicating a clean desorption of dendrimers and NPs. The SEM image in Figure 3A corresponds to the area exposed to electrochemistry after CA. The CD-SiO_2 NP layer had been completely removed in the area inside the O-ring. The coverage of CD-SiO_2 NPs in the area outside the O-ring remained unchanged (Figure 3B).

The concept of using ferrocenyl dendrimers as a reversible glue for building up nanostructures is not only limited to homogeneous substrates. The specific and directed assembly of nanostructures was achieved by selectively printing G3-PPI-(Fc)$_{16}$ onto a β-CD SAM by microcontact printing,[23] followed by selective deposition of CD-SiO_2 NPs onto the dendrimer areas of the surface, forming NP lines (Figure 4A). The NP lines could be "erased" by electrochemically biasing the substrate at +0.15 V$_{MSE}$ (Figure 4B), followed by ultrasonication of the substrate in water. This led to complete particle removal, similar to that shown in Figure 3A.

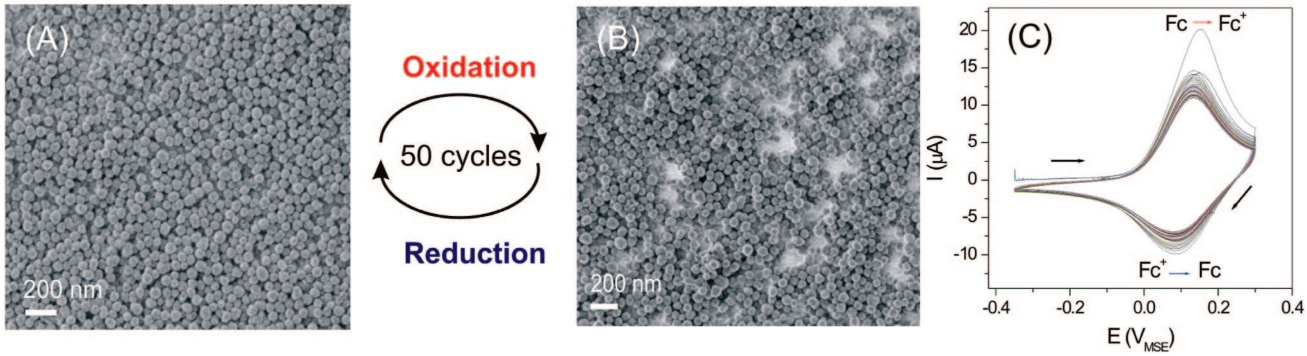

Figure 2. SEM images of CD-SiO_2 NP layer on β-CD SAM with preadsorbed G3-PPI-$(Fc)_{16}$ (A) and after 50 CV scans and 2 min sonication in water (B) and cyclic voltammograms in an aqueous solution 0.1 M K_2SO_4, between -0.35 V_{MSE} and $+0.30$ V_{MSE}, at scan rates of 500 mV/s (C).

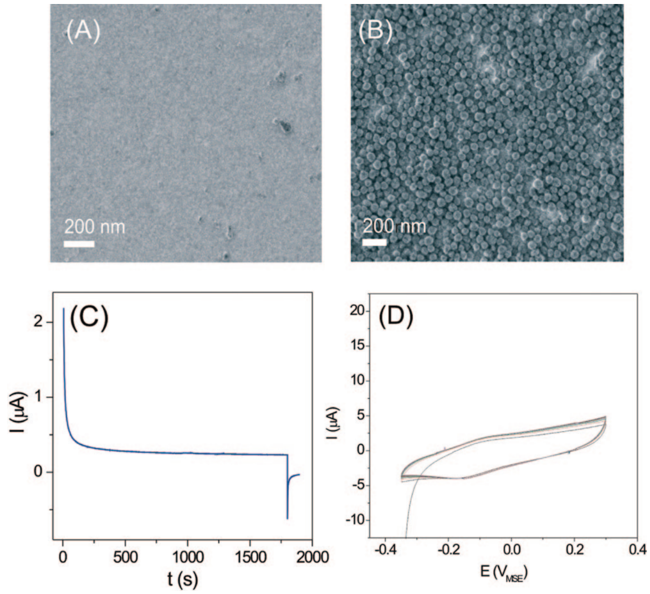

Figure 3. SEM images of a CD-SiO_2 NP layer on a β-CD SAM with preadsorbed G3-PPI-$(Fc)_{16}$ after 1800 s CA and 2 min ultrasonication inside (A) and outside (B) the electrochemically addressed area. CA scan in 0.1 M K_2SO_4 at $+0.15$ V_{MSE} for 1800 s (C), CV after 1800 s CA scan (D). CV was performed in an aqueous solution 0.1 M K_2SO_4, between -0.35 V_{MSE} and 0.35 V_{MSE}, at a scan rate of 500 mV/s.

Conclusions

In conclusion, reversible nanostructure attachment was demonstrated by using ferrocenyl dendrimers as multivalent "reversible supramolecular glue" for association and (electrochemical) dissociation of β-CD-functionalized NPs at the molecular printboard. It is a valid method for NPs of different core material and size; the only requirement is the surface functionalization of the NPs with β-CD receptors. The actual rate of desorption of the NPs after electrochemical oxidation of the supramolecular glue is governed by the inertia of the NPs as witnessed by the flow rate dependence and the accelerated desorption upon ultrasonic agitation.

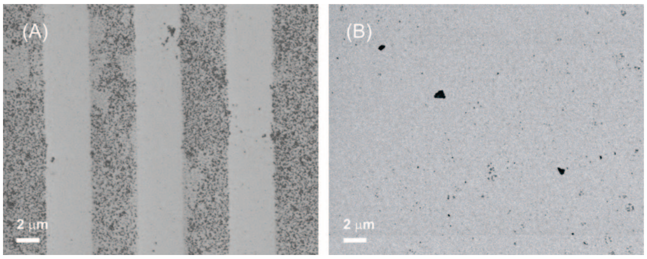

Figure 4. Selective deposition of CD-SiO_2 NPs onto microcontact printed lines of G3-PPI-$(Fc)_{16}$ at a β-CD SAM (A), followed by CA at 0.65 V for 20 min, followed by 2 min sonication in water (B).

The use of electroactive dendrimers as "reversible supramolecular glue" for building up and (electrochemically induced) breaking down nanostructures at molecular printboards may become generally applicable to the assembly of (bio)molecules and/or nanostructures onto β-CD SAMs via strong, specific and tunable multivalent host−guest interactions. Local surface modification may be achieved by individually addressed electrodes on a substrate, while the integrity and molecular recognition properties of the SAMs remain unchanged after modification. The limits regarding nanostructure size depend on the accuracy with which such electrode arrays, or the positioning of the electroactive dendrimers onto them, can be controlled. The concept holds potential for the construction and local modification of nanostructures, especially for multielectrode steered arrays.

Acknowledgment. Dr. O. Crespo-Biel is acknowledged for providing the CD-Au NPs. X.Y.L and J.H. thank the Council for Chemical Sciences of The Netherlands Organization for Scientific Research (NWO-CW) for financial support (Vidi Vemieuwingsimpuls grant 700.52.423 to J.H.).

CM703597W