Self-Assembled Monolayers of Dendron Thiols for Electrodeposition of Gold Nanostructures: Toward Fabrication of Superhydrophobic/Superhydrophilic Surfaces and pH-Responsive Surfaces

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Received October 11, 2004. In Final Form: December 17, 2004

This paper describes the fabrication of surfaces with different wettability, superhydrophobic/superhydrophilic, and pH-responsive properties. We used a self-assembled monolayer (SAM) of a dendron thiol as the underlying surface for electrodeposition of gold nanostructures. After this modification with a SAM of n-dodecanethiol or 11-mercaptoundecanol, the surface shows remarkable superhydrophobic properties with a contact angle of about 155° and a tilt angle of less than 2° or superhydrophilic properties with a contact angle of about 0°, respectively. Moreover, a large-scale pH-responsive surface was obtained by modification with 2-(11-mercaptoundecanamidom)benzoic acid (MUA). The pH-responsive behavior was amplified by using rough surfaces.

1. Introduction

Since the origin of the self-cleaning property of lotus leaves has been revealed, the possibility to mimic lotus leaves and artificially make self-cleaning surfaces has generated increasing interest. A self-cleaning surface is a superhydrophobic surface with a contact angle (CA) larger than 150° and a tilt angle (TA) of less than 5°. Numerous methods have been used to create such a superhydrophobic surface, including plasma fluorination,1 chemical vapor deposition,2 reconformation of polymers,3 electrodeposition on polyelectrolyte multilayer,4 sol–gel method, and others.5–7 In particular, from these methods we find that both the chemical modification (low surface free energy) and the surface structure (surface roughness) are very important factors determining the surface wettability properties. Consequently, the versatility of these methods makes them attractive for a number of areas including protective coating8 and microfluidic devices.9

Up to now, there have been many types of substrates with different functionality used to fabricate such self-cleaning surfaces. We wished to determine if a self-assembled monolayer (SAM) of a dendron thiol on gold could be used as an underlying surface for fabricating gold surfaces with different wettability, since dendrimers,10–12 regular branched macromolecules with structures precisely controlled at the molecular level, are promising candidates and building blocks for nanofabrication and nanodevices on a surface. In our previous work, we have reported a series of surface-bound dendron thiols and studied the factors that control the surface morphology of SAMs of those dendron thiols on a Au surface.13–18 Herein, we attempt to use the SAM of dendron thiols as a matrix of electrodeposition for the fabrication of gold nanostructures. And as-prepared gold surfaces prepared by such an approach and the availability of a large number of thiol molecules with different chemical properties might represent an easy way to study the wetting of surfaces, combining modification of low surface free energy coating and surface roughness.

In addition, a stimuli-responsive surface, which can change its surface property depending on the external stimuli of environment at different conditions, e.g., electric...
field, thermal treatment, etc., has attracted great interest of scientists. The stimuli responsiveness will be essential to control the surface physical properties, such as surface friction and surface wettability. Feng et al. and Sun et al. have reported that a ZnO2 rough surface and a PNIPAAm-modified rough surface undergo a wettability transition from superhydrophobicity to superhydrophility upon UV illumination and thermal treatment, respectively. Controlling the macroscopic physical properties of a surface, particularly the surface wettability by altering the pH, is especially interesting and fundamentally important for many material and biomaterial applications. Therefore, we designed and synthesized 2-(11-mercaptoundecanamido)benzoic acid (7) (MUABA) and investigated if it can be used for fabricating pH-responsive surfaces by the manipulation of surface free energy with pH.

2. Experimental Section

Materials. Decanethiol (C10–SH, Fluka), dodecanethiol (C12–SH, Fluka), 11-mercaptoundecanoic acid (HOOC–C11–SH, Aldrich), and 11-mercaptoundecanol (HO–C11–SH, Aldrich) were commercially obtained and used as received. Other chemicals were analytical-grade reagents and were used as received. The Fréchet-type dendron bromide was synthesized according to the literature. The carboxyl-terminated dendron thiol was prepared from the reaction of the corresponding dendron bromide 1, by using thioacetic acid, followed by hydrolysis of both the focal point and the terminal group (Scheme 1). Dendron thiol 3 was characterized by 1H NMR, 13C NMR, LC-TOF-MS, and FT-IR. The synthesis of mercaptoalkyl derivative 2-(11-mercaptoundecanamido)benzoic acid (7) (MUABA) is shown in Scheme 2, which can be used for modification of pH-responsive wettability.

Synthesis of Second Generation Dendron Thioacetate (CH3OOC)–[G-2]–SCOOCH3 (2). Dendron 1 (0.20 g, 0.19 mmol) was dissolved in 10 mL of dichloromethane, and the solution was cooled in an ice bath. The solution was stirred while triethylamine was dissolved in 10 mL of dichloromethane, and the solution was

![Scheme 2](https://example.com/scheme2.png)

* Key: (A) N(Et)3, CH3COSH; (B) (a) NaOH, (b) HCl.

Scheme 2. The Synthetic Process of the pH-Responsive Molecule

2-(11-Mercaptoundecanamido)benzoic Acid (7) (MUABA)
differentiate the different types of carbon atoms in $^{13}$C NMR. LC-TOF-MS: $[M - \text{H}]^+ (m/z)$ found 935.549, calcd 935.97. FT-IR ($\nu_{\text{wave/cm}^{-1}}$, CaF$_2$) 2916, 2848 (CH$_2$), 1691 (C=O) ($\text{Ar-C=C}$), 1450 (CH$_2$), 1159 (Ar=O), 1053 (C-O).

**Synthesis of Methyl 2-Undec-10-enamebolbenzoate (5).** Methyl anthranilate (4) (3.5 g, 23 mmol) and triethylamine (3.5 g, 35 mmol) were dissolved in dichloromethane (80 mL). 10-Undecenoyl chloride (6.6 g, 28 mL) was added slowly to the above solution under constant stirring. The solution was further stirred at room temperature during 1 h. The solvent was evaporated under reduced pressure, and the residue was dissolved in diethyl ether (80 mL). The organic layer was washed with brine ($2 \times 50$ mL), dried over magnesium sulfate, and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel using dichloromethane as the eluent yielding a white powder (6.2 g, 85%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ (ppm) 11.06 (s, 1H, NH), 8.74 (d, $J = 7$ Hz, 1H, 6-H), 8.02 (d, $J = 7$ Hz, 1H, 3-H), 7.54 (t, $J = 7$ Hz, 1H, 4-H), 7.06 (t, $J = 7$ Hz, 1H, 5-H), 5.84-5.74 (m, 1H, $=\text{CH}$), 5.03-4.91 (m, 2H, $=\text{CH}_2$), 3.92 (s, 3H, CH$_3$), 2.44 (t, $J = 7.3$ Hz, 2H, COCH$_2$), 2.07-2.00 (m, 2H, $=\text{CH}_2$CH$_2$), 1.78-1.70 (m, 2H, COCH$_2$CH$_2$), 1.37-1.31 (m, 10H, rest CH$_2$). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ (ppm) 172.7, 169.1, 142.1, 139.5, 135.1, 131.2, 129.2, 127.0, 115.1, 114.5, 52.7, 39.1, 34.2, 29.69, 29.66, 29.58, 29.46, 29.29, 25.9. MS (CI): $[M + H]^{+}$ (m/z) found 318, calcd 318.43.

**Synthesis of Methyl 2-(11-Mercaptoundecanamido)benzoate (6).** Compound 5 (0.95 g, 3.0 mmol), thioacetic acid (0.95 g, 13 mmol), and AIBN (50 mg, 30 mmol) were dissolved in methanol (700 mL) under argon atmosphere. The solution was irradiated for 8 h with a mercury lamp through Duran glassware. After evaporation of the solvent under reduced pressure, the product was purified by column chromatography on silica gel with dichloromethane as the eluent yielding 5 (C$_6$H$_4$NO$_2$) as a white powder (1.0 g, 13 mmol). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ (ppm) 11.06 (s, 1H, NH), 8.74 (d, $J = 7$ Hz, 1H, 6-H), 8.00 (d, $J = 7$ Hz, 1H, 3-H), 7.72 (t, $J = 7$ Hz, 1H, 4-H), 7.04 (t, $J = 7$ Hz, 1H, 5-H), 2.91 (s, 3H, CH$_3$), 2.41 (t, $J = 7.3$ Hz, 2H, COCH$_2$), 2.34 (t, $J = 7.3$ Hz, 2H, NO$_2$), 1.30 (s, 3H, COCH$_3$), 1.77-1.71 (m, 10H, rest CH$_2$). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ (ppm) 196.1, 172.5, 160.0, 142.1, 134.9, 131.1, 122.6, 120.6, 115.0, 52.6, 39.0, 30.9, 29.4, 29.83, 29.70, 29.63, 29.50, 29.44, 29.41, 29.12, 25.8. MS (CI): $[M + H^+]^{+}$ (m/z) found 394, calcd 394.55.

**Synthesis of 2-(11-Mercaptoundecanamido)benzoic Acid (7) (MUABA).** Thioacetic acid 6 (0.12 g, 3.1 mmol) was dissolved in a mixture of methanol (3 mL) and THF (1 mL). After argon was bubbled through the mixture for 10 min, an aqueous NaOH solution (1 M, 1 mL) was added. The mixture was stirred under argon atmosphere at room temperature for 1 h. After addition of aqueous HCl (1 M, 1 mL) under argon atmosphere, the solution was extracted with dichloromethane (10 mL). After being dried with magnesium sulfate, the salt was removed under reduced pressure and the crude product was purified by column chromatography on silica gel with dichloromethane/ethylmethanol (70:30 v/v) as the eluent yielding a white powder (78 mg, 76%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ (ppm) 10.96 (s, 1H, NH), 8.77 (d, $J = 7$ Hz, 1H, 6-H), 8.13 (d, $J = 7$ Hz, 1H, 3-H), 7.52 (t, $J = 7$ Hz, 1H, 4-H), 7.12 (t, $J = 7$ Hz, 1H, 5-H), 2.54-2.45 (m, 4H, COCH$_2$, CH$_2$SH), 1.79-1.29 (m, 16H, rest CH$_2$). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ (ppm) 198.90, 198.42, 173.07, 172.43, 170.98, 142.55, 136.08, 132.13, 125.01, 121.00, 114.23, 39.31, 39.30, 29.84, 29.75, 29.69, 29.54, 29.45, 29.34, 25.60, 25.04. MS (ES): $[M + Na^+]^{+}$ (m/z) found 360.3, calcd 360.47.

**Preparation of the Gold Substrates.** After a thorough cleaning, a quartz or glass substrate was precoated with 6 nm Au(111) terraces, often extending over thousands of angstroms.

**Preparation of the Self-Assembled Monolayer (SAM) on Gold.** The gold-coated substrates for electrodeposition measure-ments were dipped into the dendron thiol (HOOCC$_1$-G-2)-SH solution at room temperature for at least 24 h, while the gold-coated substrates for STM measurements, after flame-annealing and cooling to room temperature, were dipped into an ethanolic solution of dendron thiol (HOOCC$_1$-G-2)-SH (1 mM) at 50 °C for at least 8 h. Then the SAMs on gold substrate were rinsed extensively with pure ethanol and dried in a stream of dry nitrogen before characterizations. For COOEt SAMs, they were rinsed sequentially with pure ethanol, 10% acetic acid, and ethanol and then dried with a stream of nitrogen.

**General Techniques.** $^1$H NMR and $^{13}$C NMR spectra were recorded with CDCl$_3$ and DMSO solutions on a Bruker Advance 500 spectrometer using TMS as the internal reference. FT-IR spectra and infrared reflection–absorption spectroscopy (IR-RAS) were collected with a diamond ATR crystal using a Mattson 400 Fourier transform spectrometer. X-ray photoelectron spectroscopy was performed on a VG ESCALAB MK II spectrometer with a Mg K$_x$ X-ray source (1253.6 eV). The base pressure in the analysis chamber during spectral acquisition was $3 \times 10^{-7}$ Pa. The spectra were collected using the pass energy of 50 eV with SAM-covered gold slides as the substrate and calibrated by referencing to the binding energy of C$_1$s.

**3. Results and Discussion**

3.1. Electrodeposition of Gold Nanostructures. The formation of gold nanostructures can be adjusted by controlling the time of electrodeposition. Figure 1 shows SEM images of the gold nanostructures formed on the SAM of the dendron thiol (HOOCC$_1$-G-2)-SH by electrodeposition at $-200$ mV in a HauCl$_4$/H$_2$SO$_4$ mixture electrolyte for different electrodeposition time. As indicated by SEM observation shown in this figure, a few uniform gold nanostructures form at the very beginning of the electrodeposition; thereafter, with extension of the electrodeposition time, the surface density of the gold nanostructures increases with a gradual augmentation of the particle size. As a result, the surface roughness also becomes larger with the increase of the time of electrodeposition. In addition, the morphology of the electrodeposited gold nanostructures formed is found to be potential controlled. We have changed the potential for electrodeposition and found that upon electrodeposition at $-400$ mV discrete gold particles were formed, as shown in Figure 2a, which is obtained under the same conditions except the electrodeposition potential, but their shape is quite different from that shown in Figure 1d.

There are reasons why the dendron thiol has been chosen as the underlying surface for electrodeposition.
However, in the case of dendron thiol (HOOC)₄ surface after the same electrodeposition time (Figure 2c). nanostructures did not cover completely the underlying gold results in high resistance. As a consequence, the gold SH SAMs, is slower, because such an ordered SAM on hydrophilic Surfaces.

Therefore, a kind of self-cleaning surface has been fabricated successfully by combination of electrodeposition (surface structure) and postmodification (chemical modification).

To understand the origin of the observed superhydrophobicity, we have described the CA in terms of the Cassie equation,

$$\cos \theta = f_1 \cos \theta - f_2 ,$$

in which $f_1$ and $f_2$ are the fractions of solid surface and air in contact with liquid, respectively. $\theta$, and $\theta$ are the CAs on the SAM of n-dodecanethiol with a rough surface covered with electrodeposited gold nanostructures (155°) and with a smooth gold surface (107°), respectively. Since $f_1 + f_2 = 1$, $f_1$ and $f_2$ are calculated to be 0.13 and 0.87. The high value of $f_2$ suggests that the very large fraction of air trapped in the interspaces among the electrodeposited gold nanostructures is responsible for the superhydrophobicity.

Figure 3a shows that a value of 149° has already been reached for CA after an electrodeposition time of 300 s. The surface cannot, however, be termed as a self-cleaning surface, because the TA is beyond 60°. In other words, the water droplet does not roll off easily (Figure 3c), though the surface is superhydrophobic. For a electrodeposition time of 800 s, the CA is already as high as 155°, but the TA is still beyond 10°. As discussed above, when the electrodeposition time is 1600 s, the formed gold nanostructures show a CA of 155° and a TA less than 2°, thus with gold nanostructures with low surface free energy chemicals, e.g., n-dodecanethiol (C₁₂−SH), the surface CA increases gradually with the increase of electrodeposition time, reflecting the evolution from less hydrophobic to superhydrophobic (Figure 3a). When electrodeposition time is as high as 1600 s, the surface shows a CA of about 155° (Figure 3b) and a TA of below 2°, using water as an indicator (4 μL droplet size). TA reflects the difference between the advancing and receding CA (CA hysteresis), and the low TA indicates that water droplets roll off easily. Therefore, a kind of self-cleaning surface has been fabricated successfully by combination of electrodeposition (surface structure) and postmodification (chemical modification).
meeting the requirement of a self-cleaning surface. The fact that TA becomes smaller and smaller with the extension of electrodeposition time is consistent with the gradual increase of surface roughness. It also agrees well with the simulation work of Johnson and Dettre showing that the CA hysteresis on hydrophobic surfaces increases with increasing surface roughness in the low roughness region but decreases drastically when the roughness becomes large.

In addition, for gold nanostructures electrodeposited at −200 mV (vs Ag/AgCl) for 1600 s and modified with 11-mercaptoundecanol (HO–C\textsubscript{11}–SH), the surface was found to exhibit superhydrophilic properties with a CA of close to 0°. The water droplet dispensed on the surface spreads immediately. To understand the origin of the superhydrophilicity, we describe the CA in terms of the Cassie hemiwicking model,

\[ \cos \theta = f_1 \cos \theta_1 + f_2 \cos \theta_2, \]

in which \( f_1 \) and \( f_2 \) are the fractions of solid surface and liquid in the interspaces among the electrodeposited gold nanostructures in contact with water, respectively. \( \theta_1 \) and \( \theta_2 \) are the CAs on the SAM of HO–C\textsubscript{11}–SH with a rough surface, assuming a sketchy value of 5° and of 25° on a smooth surface, respectively. It can be deduced from this equation that increasing the fraction of liquid \( f_2 \) decreases the CA of the rough surface \( (\theta) \). According to the equation, the \( f_2 \) value of the rough surface with gold nanostructures is estimated to be as high as 0.96, resulting in the superhydrophilic surface.

### 3.3. pH-Responsive Wetting Properties

It is reported that polyethylene films can show a pH responsive wettability after modification with acylated anthranilate moieties through surface reaction. Inspired by this work, we designed and synthesized the mercaptoalkyl derivative, 2-(11-mercaptopundecanamido)benzoic acid (7) (MUABA, Scheme 2). After modification of the rough surface with this compound, the rough surface of gold nanostructures exhibited a pH-responsive behavior (Figure 4A) with an exceptionally large change in CA as a function of the pH, from nearly superhydrophobic (CA of about 145°) to superhydrophilic (CA of near 0°) (Figure 4A). Though given the fact that the carboxylic acid groups at low pH can be protonated and relatively hydrophobic (−COOH) and at high pH present as carboxylate anions and more hydrophilic (−COO\textsuperscript{−}), the change of conformation may be essential for the large change of CA with pH. Moreover, this change on rough surface (Figure 4A) is much larger than the one observed on flat gold surfaces (Figure 4B). Therefore it seems reasonable to conclude that the roughness of the gold nanostructures likely enhances the pH-responsive properties and, hence, results in the observed large-scale pH-responsive behavior, while leaving the morphology of the surface constant.

#### 4. Conclusions

In conclusion, we have demonstrated that the SAM of dendron thiols can be used as an underlying surface for electrodeposition of gold nanostructures at the same time allowing the control of their size and shape by electrodeposition time and electrodeposition potential. Moreover, further modification of the gold nanostructures with either n-dodecanethiol or 11-mercaptopundecanol results in good superhydrophobic or superhydrophilic properties, respectively. It is anticipated that this research may open a route for fabrication of nanostructured materials and provide a way for mimicking lotus leaves, leading to the production of self-cleaning coatings. Furthermore, a large-scale pH-responsive surface was obtained by modification of gold with 7. Compared to a flat gold surface, the roughness of the gold significantly enhanced the responsiveness of the anthranilic monolayer. These findings demonstrate that surface structure plays a significant role in the amplification of pH-responsive behavior, and this concept is expected to be also valid for other types of stimuli-responsive systems such as electrical potentials.

**Acknowledgment.** The authors thank the Major State Basic Research Development Program (Grant. No. G2000078102), 863 High-tech R&D Program (2003AA302140), Ministry of Education (key project, and 20020010006), and National Natural Science Foundation of China (20334010, 20473045) for financial support. The Flemish government is thanked for a bilateral grant (BIL02/03). M.S. thanks the F.W.O. Vlaanderen for a postdoctoral fellowship.

**Supporting Information Available:** Further details of preparation and characterization of self-assembled monolayers of dendron thiol (HOOC\textsubscript{4}G2–SH on gold. This material is available free of charge via the Internet at http://pubs.acs.org. LA047491B

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