Active Control of Wetting Using Applied Electrical Potentials and Self-Assembled Monolayers[1]

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We have used applied electrical potentials, in combination with self-assembled monolayers (SAMs) of alkanethiolates supported on gold films, to control the wettability of a surface over wide ranges. A surface can be transformed from nonwetting to wetting, or the reverse, with time constants of seconds. The method is based on a competition between reductive electrochemical desorption of a hydrophobic SAM and its re-formation from alkanethiol in solution. Self-assembled monolayers formed from either $CH_3(CH_2)_{15}$-SH or $CH_3(CH_2)_2SH$ were hydrophobic ($80° < \theta < 110°$, θ = contact angle) toward aqueous solutions of electrolyte at neutral potentials but became hydrophilic ($\theta \sim 10°$) at reducing potentials ($E < -1.3$ V vs Ag wire). Contact angles of aqueous solutions containing $CH_3(CH_2)_2SH$ returned to their initial values ($\theta \sim 80°$) after the reducing potentials were removed. Because the change in wettability was dependent on the structure of the organic molecule in the monolayer, it was possible to prepare patterned SAMs in which certain regions were transformed from hydrophobic to hydrophilic by changing potential, while other regions were inert.

We report a method for active control of the wetting of gold surfaces, using applied electrical potentials and self-assembled monolayers of alkanethiolates (SAMs). The study of wetting has, in the past, largely concentrated on static systems and the use of thermodynamic analyses;[2–4] studies of dynamic systems have focused on the irreversible spreading of liquids on solids.[4] The method outlined here moves to active control of wetting and provides a procedure for transforming a surface from nonwetting to wetting, or the reverse, with time constants of seconds, using a competition between reductive electrochemical desorption of a SAM[5] and its re-formation from alkanethiol in solution. We believe that this method will be useful in fundamental studies both of wetting and of SAMs and lead to applications that require active control of wettability.[6]

This method is based on two observations. First, Porter has shown that it is possible, by electrochemical reduction, to remove a hydrophobic SAM from a gold surface;[5] an aqueous drop of electrolyte spreads spontaneously as this reductive desorption occurs. Second, when an appropriate alkanethiol is included in the aqueous solution of electrolyte, the SAM re-forms spontaneously when the electrical potential is lowered below that required to desorb the SAM; as the SAM re-forms, the drop of electrolyte spontaneously retracts. Thus, the surface is wettable when the applied potential is reducing and nonwettable when the potential is close to zero. The flexibility of the method is enhanced by the observation that different electrochemical potentials are required to desorb SAMs

derived from alkanethiols of different chain lengths;[5] it is, therefore, possible to prepare patterned SAMs[7,8] in which certain regions are readily transformed from hydrophobic to hydrophilic while others remain hydrophobic.

Figure 1 shows the effect of reducing electrical potentials on the wettability (contact angle, θ, of an aqueous solution of 0.1 M $NaClO_4$, 5 mM K_2HPO_4, 5 mM KH_2PO_4, at pH 7) of gold films[9] supporting SAMs formed from either $CH_3(CH_2)_2SH$ or $CH_3(CH_2)_{15}SH$.[10] Both gold surfaces were hydrophobic ($80° < \theta < 110°$) at neutral potentials and became hydrophilic ($\theta \sim 10°$) at reducing potentials; the surfaces differed from each other, however, in (i) the magnitude of the reducing potential (E) required to cause the transformation from hydrophobic to hydrophilic and (ii) the sharpness of the transition (ΔE) from hydrophobic to hydrophilic. The observation that gold surfaces supporting alkanethiolates with short chains are transformed to hydrophilic surfaces at less reducing potentials than are long-chain alkanethiols is consistent with the influence of chain length on the potential required for the reductive desorption of SAMs reported by Porter.[5]

The increase in wettability observed upon reductive desorption of the SAMs was reversed by removal of the

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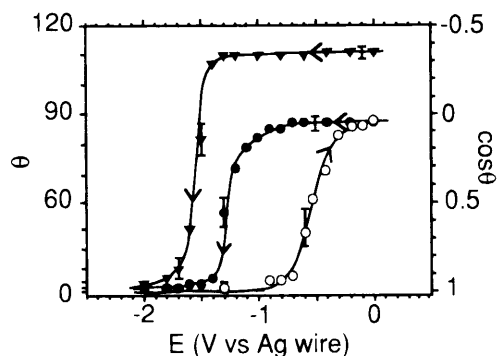
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(10) Self-assembled monolayers were formed from ethanolic solutions (~1 mM) of either $CH_3(CH_2)_2SH$ or $CH_3(CH_2)_{15}SH$.

(11) Receding contact angles of aqueous solutions of 0.1 M $NaClO_4$ were irreproducible when measured by the procedure used for advancing contact angles. The reproducibility of receding contact angles was made good, however, by using an experimental procedure (see caption in Figure 1) that minimized the length of time the aqueous solution wet the gold surface. The reproducibility of the receding contact angles was sensitive to the nature of the electrolyte; aqueous solutions of 0.1 M ammonium formate (NH_4HCO_2) were cycled back and forth between 0.0 V and −1.5 V in steps of 0.1 V with reproducible advancing and receding contact angles over four cycles—in the case of ammonium formate, however, the change in contact angle with electrical potential was less than with $NaClO_4$ (~82° at 0.0 V and 28° at −1.5 V).

Figure 1. Potential-dependent contact angles (θ) of aqueous solutions of electrolyte (0.1 M NaClO$_4$, 5 mM K$_2$HPO$_4$, 5 mM KH$_2$PO$_4$, pH 7) on films of gold: Monolayer of CH$_3$(CH$_2$)$_2$S (●, advancing contact angle; ○, receding contact angle); SAM of CH$_3$(CH$_2$)$_{15}$S (▼). The contact angles were measured using a telescope and goniometer, and a Pt wire (counter electrode) and Ag wire (reference electrode) inserted into ∼25 μL of aqueous solution. Advancing contact angles: First, the contact angle was measured at 0.0 V. Second, the potential was ramped to −0.1 V over a 1 to 5 s interval of time and held there. The advancing contact angle was measured after the drop had stopped spreading (typically 10−15 s). The potential was then changed by −0.1 V and the procedure repeated. Receding contact angles: Approximately 10 mM CH$_3$(CH$_2$)$_2$SH was dissolved in the aqueous solution of electrolyte. First, the potential was ramped to −1.3 V and the drop wet the surface of the gold. Within 5 s, the potential was reduced to the desired value.[11] The receding contact angle was measured after the drop retracted to its steady state (typically 5−10 s). The measurements of advancing and receding contact angles represent the average of three samples. Error bars show maximum deviations about the average.

reducing potentials when the aqueous solutions of electrolyte contained CH$_3$(CH$_2$)$_2$SH: Contact angles were observed to return to their initial values (85−90°)[12] as the monolayer of CH$_3$(CH$_2$)$_2$S re-formed on the surface of the gold (Figure 1, open circles).

Figure 2 illustrates active control of the wettability of a gold surface patterned with a triangular area of CH$_3$-(CH$_2$)$_2$S;[13] the area outside the triangle supported a SAM of CH$_3$(CH$_2$)$_{15}$S (Figure 2a). At neutral potentials the aqueous electrolyte (which contained 10 mM CH$_3$(CH$_2$)$_2$-SH) formed a hemispherical drop on the hydrophobic monolayer of CH$_3$(CH$_2$)$_2$S (Figure 2b). An applied reducing potential of $E = -1.4$ V (vs Ag wire) selectively transformed the area within the triangle from hydrophobic to hydrophilic; the drop of electrolyte spread spontaneously over the area of the triangle and was bounded by the hydrophobic SAM of CH$_3$(CH$_2$)$_{15}$S (Figure 2c). Subsequently, the surface was returned to a neutral potential, the hydrophobic monolayer of CH$_3$(CH$_2$)$_2$S re-formed spontaneously on the area within the triangle, and the drop of aqueous electrolyte retracted toward the center of the triangle (Figure 2d). Figure 2d shows that the drop of liquid did not retract completely from the top-left corner of the triangle. Regions of surface where the SAM changed from CH$_3$(CH$_2$)$_2$S to CH$_3$(CH$_2$)$_{15}$S often pinned the edges of receding drops.[14]

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(12) The hysteresis observed in the contact angle at 0 V (<5°) is less than the hysteresis measured by advancing and receding a drop of water across a monolayer of CH$_3$(CH$_2$)$_2$S (∼10°).

(13) We used a Staedtler pen containing neat (liquid) CH$_3$(CH$_2$)$_{15}$-SH, clamped to a X-Y micrometer, to "write" the borders of the triangle.[8] The gold film outside of the triangle was derivatized by reactively spreading a 1 mM ethanolic solution of CH$_3$(CH$_2$)$_{15}$SH across the gold; the border of the triangle, formed from the neat CH$_3$(CH$_2$)$_{15}$SH, was not wet by the ethanolic solution. The interior of the triangle was derivatized with a monolayer of CH$_3$(CH$_2$)$_2$S by immersing the gold film in a 1 mM ethanolic solution of CH$_3$(CH$_2$)$_2$SH for 30 s.

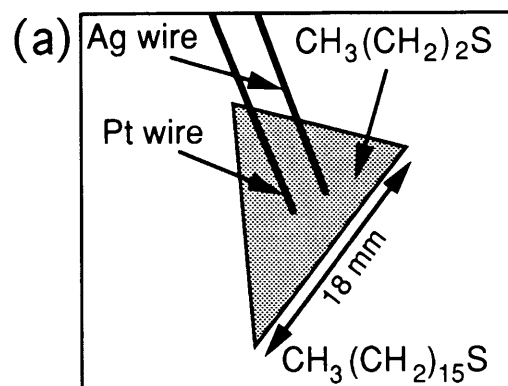**Figure 2.** Potential-dependent wetting of an aqueous solution of electrolyte (10 mM CH$_3$(CH$_2$)$_2$SH, 0.1 M NaClO$_4$, 5 mM K$_2$-HPO$_4$, 5 mM KH$_2$PO$_4$, pH 7) on a gold film patterned with self-assembled monolayers of CH$_3$(CH$_2$)$_2$S and CH$_3$(CH$_2$)$_{15}$S: (a) schematic illustration of the patterned surface; photograph (top view) of liquid at (b) $E = 0$ V (Ag wire), (c) $E = -1.4$ V, and (d) $E = 0$ V. The photographs in the sequence (b−d) were taken approximately ∼30 s apart. The reference electrode was a 0.5 mm diameter Ag wire and the counter electrode was a 0.25 mm Pt wire.

Applied electrical potentials, in combination with self-assembled monolayers of organic molecules on gold films, can be used to control *in situ* the wettability of surfaces.

Because the change in wettability is dependent on the structure of the organic molecule in the monolayer, applied electrical potentials can be used to amplify differences in the properties of patterned surfaces. Reversible control

of wettability, achieved by including an alkanethiol in the electrolyte, makes possible active control over shapes formed by liquids on surfaces and, we believe, can form the basis of methods for patterning surfaces with areas of SAMs having contrasting properties.

(14) In contrast, aqueous solutions containing $CH_3(CH_2)_2SH$ showed little hysteresis at 0 V on surfaces of gold that were not patterned with SAMs (Figure 1).