

## Polyelectrolyte Multilayer as Matrix for Electrochemical Deposition of Gold Clusters: Toward Super-Hydrophobic Surface

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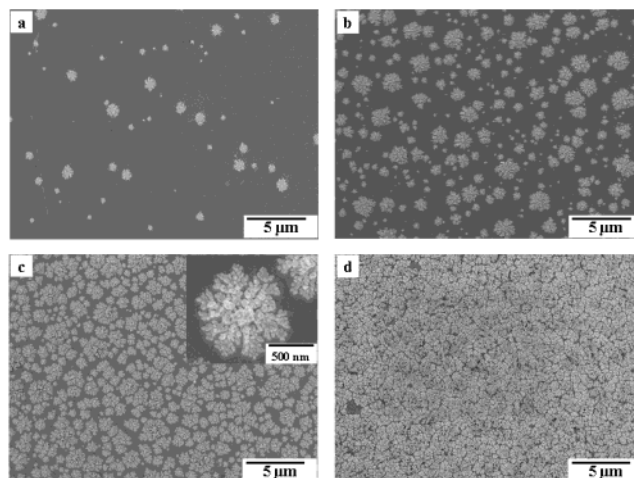
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This communication describes the use of a polyelectrolyte multilayer as a preformed matrix in electrochemical deposition to adjust the morphology of gold clusters, leading to the fabrication of a super-hydrophobic surface. The polyelectrolyte multilayer is fabricated by layer-by-layer (LbL) self-assembly technique, as introduced first by G. Decher.<sup>1</sup> The LbL technique has proved to be a versatile method to assemble layered nanostructures with tailored composition and architecture,<sup>2</sup> and it has been shown to have promising applications in areas such as chemical sensors or biosensors,<sup>3</sup> enzyme immobilization,<sup>4</sup> hollow capsules,<sup>5</sup> surface patterning,<sup>6</sup> separation membranes,<sup>7</sup> microporous films,<sup>8</sup> light-emitting diodes,<sup>9</sup> erasable films,<sup>10</sup> and nanocomposites.<sup>11</sup> Recently, it has been exciting to see that the related research is not restricted to fundamental aspects but is extended from laboratories to commercial production, e.g. coating for contact lenses. However, to the best of our knowledge, there are few reports that combine LbL and electrochemical deposition for the formation of metal clusters.

We demonstrate that the surface covered with dendritic gold clusters, which is formed by electrochemical deposition onto an indium tin oxide (ITO) electrode modified with a polyelectrolyte multilayer, shows super-hydrophobic properties after further chemisorption of a self-assembled monolayer of *n*-dodecanethiol. Since the origin of the self-cleaning property of lotus leaves has been revealed to be a cooperative effect of microstructures and nanostructures at the surface, to mimic such surface structures and to tune finely the wetting property have attracted significant attention. Until now, a few interesting lotuslike films with super-hydrophobic properties have been reported, including arrays of carbon nanotubes,<sup>12</sup> polyacrylonitrile nanofibers,<sup>13</sup> fluoropolymer surfaces,<sup>14</sup> and others.<sup>15</sup> Herein, we combine the LbL self-assembly technique with electrochemical deposition for controlling the density and morphology of gold clusters and develop a way for fabricating a super-hydrophobic surface.

Figure 1 shows scanning electron microscopy (SEM) images of gold clusters that are formed by electrochemical deposition onto the modified ITO electrode. We modified the ITO electrode with six bilayers of poly(diallyldimethylammonium chloride) (PDDA) and poly(4-styrene sulfonate) (PSS) for its high stability in water solution. After the ITO electrode was modified by PDDA/PSS multilayer, it was immersed in a mixture of the H<sub>2</sub>SO<sub>4</sub> (0.5 M) and KAuCl<sub>4</sub> (1 mg/mL), and electrochemical deposition was conducted at -200 mV by single potential time base mode, using a platinum electrode as the counter-electrode and Ag/AgCl as the reference electrode. From Figure 1, we can see clearly that gold



**Figure 1.** SEM images of dendritic gold clusters formed on an ITO electrode modified with a polyelectrolyte multilayer by electrochemical deposition at -200 mV (vs Ag/AgCl) (single potential time base mode). Deposition time is 2 s (a), 50 s (b), 200 s (c), 800 s (d).

clusters are formed under these conditions, exhibiting interesting dendritic structures with nanoscale protuberances. The deposition process has been observed carefully: a few dendritic structures form at the very beginning of the electrochemical deposition; thereafter, with extension of the deposition time, the surface density of the gold clusters increases with a slight augmentation of the size. The enlarged view of a gold cluster in Figure 1c shows that it is a three-dimensional dendritic structure.

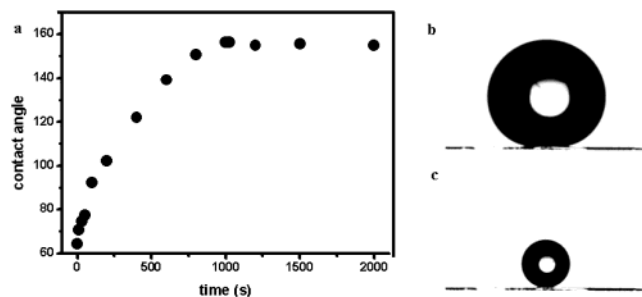
When the above modified ITO surface with gold clusters is immersed in an ethanol solution of *n*-dodecanethiol ( $1 \times 10^{-3}$  M) overnight, the surface-active molecule can chemisorb onto the surface of gold clusters and form a self-assembled monolayer. After rinsing with pure ethanol, we have studied the wetting property of the modified surface by contact angle measurement. As shown in Figure 2a, the contact angles of the surface, using water droplet as an indicator (drop weight 5 mg), are remarkably different, depending on the duration of the electrochemical deposition of the gold clusters. The contact angles increase gradually with the time of electrochemical deposition. When the deposition time exceeds 1000 s, the contact angle reaches a constant value, as high as 156°, suggesting that our method can lead to the formation of a super-hydrophobic surface. The change of the contact angle for the modified surface is consistent with the different surface density of gold clusters formed at different times of electrochemical deposition, as indicated in Figure 1. The shape of a water droplet on the surface of modified gold clusters, with contact angle of 156° is shown in Figure 2b. The contact angle can change from 156° to 173° after 40 min of exposure to ambient environment, as shown in Figure

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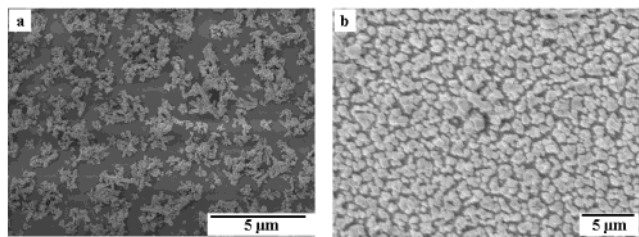
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**Figure 2.** (a) Dynamic contact angle measurements on the surface of dendritic gold clusters as a function of the duration of electrochemical deposition at  $-200$  mV (vs Ag/AgCl) by single potential time base mode. (b) Shape of a water droplet on the surface of dendritic gold clusters (drop weight 5 mg). (c) Shape of (b) after 40 min of exposure to ambient environment.



**Figure 3.** (a) SEM image of the gold aggregates formed on a bare ITO electrode by electrochemical deposition at  $-200$  mV (vs Ag/AgCl) (single potential time base mode; deposition time 500 s). (b) SEM image of the gold aggregates formed on a polyelectrolyte multilayer modified electrode by electrochemical deposition at  $-500$  mV (vs Ag/AgCl) (single potential time base mode; deposition time 200 s).

2c. On one hand, the apparent enhancement in super-hydrophobicity is related to the shrinkage of the water droplet due to the evaporation and the reduction of gravitational effect. On the other hand, the phenomenon suggests that the super-hydrophobic surface fabricated in the way is rather stable. Further evidence for the super-hydrophobicity of the surface is given by its low tilt angle, which reflects the difference between advancing and receding contact angle. The tilt angle of the surface is around  $1.5^\circ$ , indicating that water droplets roll off easily.

For the smooth gold surface modified with *n*-dodecanethiol, we have found that the contact angle is only about  $95^\circ$ , suggesting that the surface morphology is necessary for super-hydrophobicity. To thoroughly understand the super-hydrophobicity of the surface of dendritic gold clusters modified with *n*-dodecanethiol, we describe the contact angle in terms of the Cassie equation.<sup>13</sup> We therefore realize that the super-hydrophobicity originates from the contribution of the air trapped in the interspace of rough surface (see details in the Supporting Information).

The polyelectrolyte multilayer is crucial for the formation of the dendritic structure of gold clusters. As shown in Figure 3a, the gold aggregates can form on a bare ITO electrode under similar conditions of electrochemical deposition, but they do not show dendritic structures. Moreover, the adhesion between the bare ITO electrode and the formed gold aggregates is not strong enough, and the formed gold aggregate can fall off easily.

The morphology of gold aggregates formed in single potential time base mode is potential-controlled, including two processes of enrichment and reduction of anion at the electrode surface. We have changed the potential for electrochemical deposition and confirmed

that the dendritic structure of gold clusters can only form at a potential around  $-200$  mV. For different potentials of the electrochemical deposition, e.g. at  $-500$  mV, it can increase the process of enrichment of the anions to the electrode interface and leads to the formation of discrete gold aggregates, as shown in Figure 3b. After modification of these nondendritic aggregates with *n*-dodecanethiol, the contact angle is only about  $110^\circ$ , which provides further evidence that the dendritic structure of gold clusters plays an important role in fabricating the super-hydrophobic surface.

In conclusion, we have proposed a new way for the fabrication of a super-hydrophobic surface, by combination of LbL technique and electrochemical deposition. We think a similar concept could be applied to make other interesting nanostructures of noble or heavy metals, used in, for example, matrices for surface-enhanced Raman spectroscopy, surface catalysis, which would open new promising applications for the work in the LbL community.

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**Supporting Information Available:** Multilayer fabrication and characterization, the Cassie Equation description, and contrast experiment (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) Decher, G.; Hong, J. *Makromol. Chem. Macromol. Symp.* **1991**, *46*, 321.
- (2) (a) Decher, G. *Science* **1997**, *277*, 1232. (b) Zhang, X.; Shen, J. C. *Adv. Mater.* **1999**, *11*, 1139.
- (3) (a) Wang, B. Q.; Rusling, J. F. *Anal. Chem.* **2003**, *75*, 4229. (b) Sun, C. Q.; Sun, Y. P.; Zhang, X.; Xu, H. D.; Shen, J. C. *Anal. Chim. Acta* **1995**, *312*, 207.
- (4) (a) *Protein Architectures: Interfacing Molecular Assemblies and Immobilization Biotechnology*; Lvov, Y., Moehwald, H., Eds; Marcel Dekker: New York, 2000. (b) Sun, J. Q.; Sun, Y. P.; Wang, Z. Q.; Wang, Y.; Zhang, X.; Shen, J. C. *Macromol. Chem. Phys.* **2001**, *202*, 111.
- (5) (a) Lvov, Y.; Antipov, A. A.; Mamedov, A.; Moehwald, H.; Sukhorukov, G. B. *Nano Lett.* **2001**, *3*, 125. (b) Antipov, A. A.; Sukhorukov, G. B.; Donath, E.; Moehwald, H. *J. Phys. Chem. B* **2001**, *105*, 2281.
- (6) (a) Zheng, H. P.; Lee, H.; Rubner, M. F.; Hammond, P. T. *Adv. Mater.* **2002**, *14*, 569. (b) Yang, S. Y.; Rubner, M. F. *J. Am. Chem. Soc.* **2002**, *124*, 2100. (c) Shi, F.; Dong, B.; Qiu, D. L.; Sun, J. Q.; Wu, T.; Zhang, X. *Adv. Mater.* **2002**, *14*, 805.
- (7) (a) Balachandra, A. M.; Dai, J. H.; Bruening, M. L. *Macromolecules* **2002**, *35*, 3171. (b) Harris, J. J.; DeRose, P. M.; Bruening, M. L. *J. Am. Chem. Soc.* **1999**, *121*, 1978.
- (8) (a) Fery, A.; Scholer, B.; Cassagneau, T.; Caruso, F. *Langmuir* **2001**, *17*, 377. (b) Mendelsohn, J. D.; Barrett, C. J.; Chan, V. V.; Pal, A. J.; Mayes, A. M.; Rubner, M. F. *Langmuir* **2000**, *16*, 5017. (c) Zhang, H. Y.; Fu, Y.; Wang, D.; Wang, L.; Wang, Z. Q.; Zhang, X. *Langmuir* **2003**, *19*, 8497.
- (9) (a) Rogach, A. L.; Koktysh, D. S.; Harrison, M.; Kotov, N. A. *Chem. Mater.* **2000**, *12*, 1526. (b) Wang, Y.; Tang, Z. Y.; Correa-Duarte, M. A.; Liz-Marza'n, L. M.; Kotov, N. A. *J. Am. Chem. Soc.* **2003**, *125*, 2830.
- (10) (a) Xie, A. F.; Granick, S. *J. Am. Chem. Soc.* **2001**, *123*, 3175. (b) Zhang, X. Y.; Zhu, Y. X.; Granick, S. *J. Am. Chem. Soc.* **2001**, *123*, 6736.
- (11) (a) Kotov, N. A.; Dekany, I.; Fendler, J. H. *J. Phys. Chem.* **1995**, *99*, 13065. (b) Gao, M. Y.; Zhang, X.; Yang, B.; Shen, J. C. *Chem. Commun.* **1994**, 2229.
- (12) (a) Li, H. J.; Wang, X. B.; Song, Y. L.; Li, Q. S.; Jiang, L.; Zhu, D. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 1743. (b) Lau, K. K. S.; Bico, J.; Teo, K. B. K.; Chhowalla, M.; Amaratunga, G. A. J.; Milne, W. I.; Mckinley, G. H.; Gleason, K. K. *Nano Lett.* **2003**, *3*, 1701.
- (13) Feng, L.; Li, S. H.; Li, H. J.; Zhai, J.; Song, Y. L.; Jiang, L.; Zhu, D. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 1221.
- (14) Woodward, I.; Schofield, W. C. E.; Roucoules, V.; Badyal, J. P. S. *Langmuir* **2003**, *19*, 3432.
- (15) (a) Tsujii, K.; Yamamoto, T.; Onda, T.; Shibuichi, S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1011. (b) Nakajima, A.; Fujishima, A.; Hashimoto, K.; Watanabe, T. *Adv. Mater.* **1999**, *11*, 1365. (c) Tadanaga, T.; Morinaga, J.; Matsuda, A.; Minami, T. *Chem. Mater.* **2000**, *12*, 590.

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