

FTIR (KBr): $\nu = 2245, 2180, 2115, \text{ and } 1024 \text{ cm}^{-1}$. ^{13}C CP MAS NMR (resonance frequency 100.61 MHz, spinning rate 12 kHz): $\delta = 80.6, 69.4, 64.6, 56.7, 52.4, 26.3 \text{ and } 10.9$. Elemental analysis: calcd for $\text{ZrC}_{12}\text{H}_{18}\text{O}_4$: Zr 28.75, C 45.39, H 5.67, O 20.19; found: Zr 33.50, C 41.35, H 5.35.

Ta(OEt)₅ and Ti(OⁱPr)₄: Prepared similarly using **3** (7.54 mmol, 0.83 g) and a mixture of Ta(OEt)₅ (3.89 mmol, 1.58 g) and Ti(OⁱPr)₄ (3.37 mmol, 0.96 g), and isolated as a light brown powder (3.23 g). FTIR (KBr): $\nu = 2245, 2180, 2124, \text{ and } 1028 \text{ cm}^{-1}$. ^{13}C CP MAS NMR (resonance frequency 100.61 MHz, spinning rate 12 kHz): $\delta = 78.9, 69.5, 60.7, 50.7, 26.0, \text{ and } 19.5$. Elemental analysis: calcd for $\text{TiTaC}_{24}\text{H}_{37}\text{O}_9$: Ti 6.86, Ta 25.94, C 41.31, H 5.30, O 20.59; found: Ti 6.80, Ta 24.30, C 41.02, H 4.97.

Preparation of 5: $\{\text{Co}_2(\text{CO})_6\}_2(\mu_2\eta^2\text{-}\mu_2\eta^2\text{-HOCH}_2\text{-C}\equiv\text{C-C}\equiv\text{C-CH}_2\text{OH})$ **4** was prepared as described in [13]. **4** (0.53 g, 0.78 mmol) was reacted with Ti(OⁱPr)₄ (0.23 g, 0.8 mmol) following the procedure described above. **5** was isolated as a deep-brown solid (0.76 g). FTIR (KBr): $\nu = 2102, 2083, 2061, 2027 \text{ cm}^{-1}$. Elemental analysis: calcd for $\text{TiCo}_4\text{C}_{24}\text{H}_{18}\text{O}_{18}$: Ti 5.45, Co 26.85, H 2.07; found: Ti 6.20, Co 29.40, H 2.10.

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Self-Assembly of an Operating Electrical Circuit Based on Shape Complementarity and the Hydrophobic Effect**

By Andreas Terfort and George M. Whitesides*

Self-assembly is a principle that is widely followed in biology to build up large molecular structures from smaller, simpler units;^[1] it is now being actively explored for use in fabrication of complex assemblies of non-biological molecules.^[2,3] Self-assembly is massively parallel, reversible, and self-repairing; it can, in principle, generate large numbers of correctly associated aggregates rapidly and conveniently. These characteristics make self-assembly a conceptually attractive strategy for mass fabrication of small (micrometer- to millimeter-sized) devices, and for the fabrication of mesoscale devices that cannot be assembled directly.

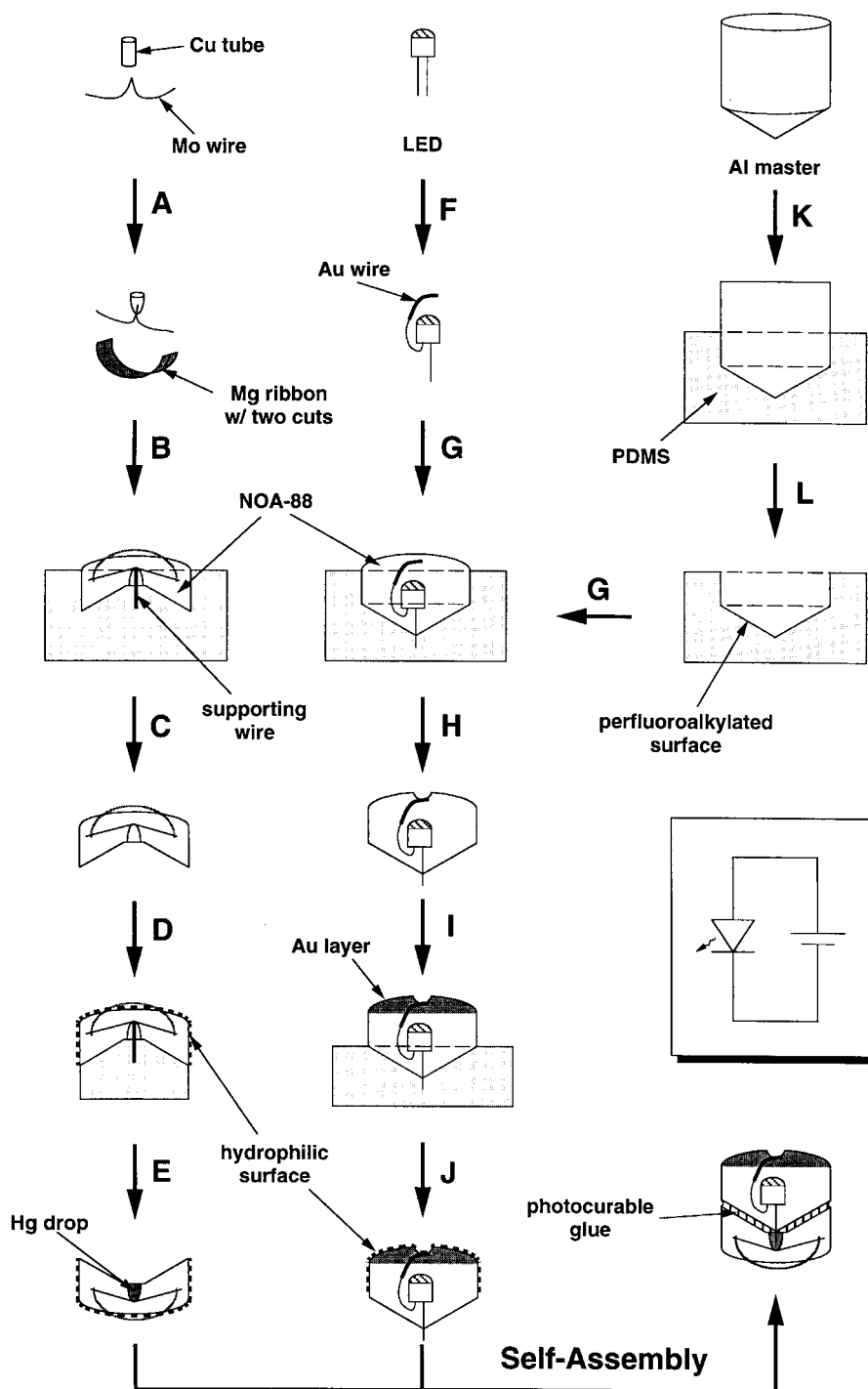
We have described processes in which three-dimensional, millimeter-sized objects assembled themselves, either from a number of identical parts or from two different, complementary parts.^[5] The driving force for those self-assemblies was the minimization of exposed hydrophobic surface in an aqueous environment;^[5] the organizing principle was shape selection. This paper describes the self-assembly of two different non-functional subunits having shape-complementary, hydrophobic surfaces into an electrically functional aggregate (Scheme 1). The recognition results from recognition of conically shaped, hydrophobic sites (one concave, the other convex, in a "lock and key" manner) in an aqueous medium. The surfaces of each element that were designed to be non-interactive were hydrophilic. To enhance self-alignment and freeze the parts in place after self-assembly, a hydrophobic, photocurable lubricant was assembled on the surfaces that mated during recognition. Correct assembly of the two subunits formed an electrical circuit containing a light-emitting diode (LED); this circuit exposed a gold cathode and a magnesium anode and constituted an electrochemical cell when the assembled system was immersed in a suitable electrolyte.

The miniature LED (Lumex Inc., Part # SSL-LX203CSRT) used in this circuit turned on at about 1.5 V, and had a nominal operating voltage of 1.6 V. In order for the electrochemical element to exceed this potential under load, an oxidizing electrolyte (potassium ferricyanide, $\text{K}_3[\text{Fe}(\text{CN})_6]$, 60 mM) was used in conjunction with the

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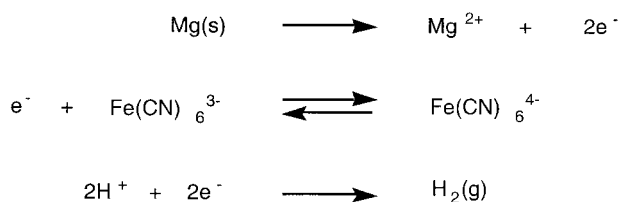
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Scheme 1. The fabrication scheme for the self-assembling circuit. The fabrication of the PDMS mold is representative of all four molds used in this project. A Mo wire was kinked and inserted into a Cu tube and held in place by crimping the tube (A). Then the ends of the Mo wire were inserted into two cuts in a bent Mg ribbon and the assembly was placed in the mold (B); the prepolymer was cast and cured by UV irradiation; after removal from the mold (C) the “lock” part was placed in the sample holder, where it was treated with oxygen plasma to make its outer surface hydrophilic (D). The Cu cup was finally amalgamated, and a drop of Hg was placed in it. The mercury was held in place by capillary forces (E). This drop assured the electrical contact between the two parts after self-assembly. For the “key” part, the anode wire of an LED was bent up and the last millimeters were replaced by a Au wire (F); after sticking it into the PDMS mold, NOA-88 was cast on it and cured (G). The polymer above the Au wire was removed (H), before Au (1000 Å) was evaporated onto it. The Au layer was reinforced by electroplating another 1 μm, then the part was put into the holder (I), where it was treated with oxygen plasma. To hydrophilize the Au layer, a hydrophilic SAM was formed on it. The molds used in this project were cast from Al masters produced in a machine shop by casting them into PDMS (K). After removal of the master, the molds were subsequently treated with oxygen plasma and vapors of a perfluoroalkyl trichlorosilane to achieve a very lipo- and hydrophobic surface (L). The “lock” and “key” parts self-assemble in an aqueous suspension in the presence of a hydrophobic, photocurable lubricant to form the complete electrical circuit. A schematic representation of the circuit is given in the highlighted box.

gold–magnesium element. The electrolyte also contained disodium ethylenediamine tetraacetate (EDTA, 60 mM)—a complexing reagent for magnesium ions—and acetic acid (added to achieve pH 4) to reduce the internal resistance of the electrochemical cell by preventing passivation of the magnesium surface by oxide formation. The overall reaction powering the LED involved dissolution of the magnesium(0) at the anode and reduction of ferricyanide to ferrocyanide at the gold cathode; the major undesirable side reaction was the formation of H₂ at the magnesium surface, see Scheme 2.



Scheme 2.

The pH was chosen as a compromise between minimizing electrical resistance and minimizing the evolution of H₂. Initial experiments showed that the maximum attainable current was approximately proportional to the surface area of the gold electrode and was not limited significantly by the surface area of the magnesium. The area of the gold electrode was therefore maximized by evaporation of gold (100 nm, with 5 nm of titanium as an adhesion promoter) over the entire top surface of the “key” unit. To ensure good electrical contact between this layer and the gold wire at the anode of the LED, the thickness of the gold film was increased to 1 μm by electroplating using a commercial bath (Orotemp 24 from Technic, Providence, RI).

Both subunits were fabricated from NOA-88 (Norland, New Brunswick, NJ), a stiff, photocurable polyurethane with excellent adhesion to the metals used. To build the “lock” part, the center of a short molybdenum wire (0.13 mm diameter) was crimped into a copper cup (made by closing one side of a 1.6 mm diameter copper tube) and then connected to the ends of a bent magnesium ribbon before casting with the polyurethane prepolymer in a mold made of poly(dimethylsiloxane) (PDMS). After curing the polymer with UV light, the copper cup was treated with a drop of concentrated aqueous Hg(NO₃)₂ solution to preform a thin layer of copper amalgam on its surface. After amalgamation, the cup was washed with water and absolute ethanol, dried, and filled with mercury (~2 μL) using a syringe. Capillary forces held the drop in the cup, while the molybdenum wire prevented the mercury from creeping into the magnesium (amalgamation reduced the maximum attainable electrochemical potential).^[6] The “key” part was fabricated by bending the anode of the LED up and replacing the last few millimeters by a piece of gold wire. This construction was cast in the polymer to a thickness that just covered the gold wire. After curing, some polymer was re-

moved to re-expose the gold wire, leaving the exposed part recessed from the rest of the surface. This design protected the mechanically sensitive area in which the wire came into contact with the upper gold layer from damage during self-assembly, a process that produced some mechanical stress as a result of tumbling. The extended gold layer was then formed by evaporation and electroplating as described above.

Before self-assembly, the exposed surfaces of both “lock” and “key” elements were differentiated into hydrophilic and hydrophobic regions. The surfaces that were designed to interact (the hydrophobic surfaces) were protected physically by putting them into molds with complementary shapes and exposed to an oxygen plasma. This exposure rendered the exposed surfaces hydrophilic. The “key” parts were also immersed for several minutes in an ethanolic solution of HS(CH₂)₁₁(OCH₂CH₂)_nOH (*n* ≈ 7.2);^[7] this procedure formed a hydrophilic self-assembled monolayer (SAM) on the exposed gold surface. An equal number (~8) of the “lock” and “key” parts were then suspended in water in the presence of a small amount of photocurable lubricant. When the mixture was gently agitated by tumbling, the “lock” and “key” elements assembled. Subsequent irradiation with UV light froze the parts in place. This self-assembly usually yielded correctly assembled pairs quantitatively.^[8] When these assembled circuits were transferred to the ferricyanide electrolyte solution, the gold–magnesium element provided the LED with enough power to light up (Fig. 1). Due to mechanical stress and to corrosion,

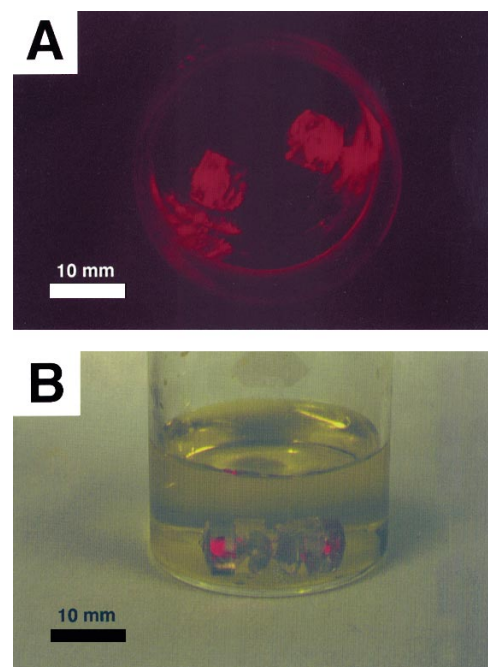


Fig. 1. A) Two of the self-assembled circuits in the electrolyte. The red light is from the LED. B) The same units in daylight: the glow can still be seen. The construction of the aggregates is visible. The hydrogen bubbles formed at the magnesium electrode are due to the direct reaction with acetic acid.

the yield of functional circuits was limited to about 80%. More robust constructions should help to circumvent this problem in the future.

This demonstration of fabrication of a complex, electrically and electrochemically functional system uses self-assembly in four ways: i) in recognition of the “lock” and “key” components, by exploiting hydrophobic interactions between surfaces with complementary shapes; ii) in tailoring the surface properties of the subunits, by forming a hydrophilic SAM on the exposed surface of gold to prevent coating with the liquid adhesive; iii) in joining the subunits, by selectively forming a thin film of adhesive on the hydrophobic surfaces by interaction of these surfaces with droplets of this adhesive suspended in water; iv) in containing the mercury drop as a coherent structure in the copper cup. The success of this process depends on forming the surfaces of the subunits designed to interact into precise, complementary shapes, and on patterning these surfaces into hydrophobic and hydrophilic regions. To achieve electrical contact reproducibly, some degree of mechanical freedom was required. The liquid mercury provided the system with the required flexibility: as long as the cathode wire of the LED touched the mercury, electrical contact was maintained.

Simple shape complementarity, in combination with fluidic shear and gravitational forces, has been used by Smith and co-workers in an elegant demonstration of the filling of shaped depressions in a planar substrate by small micro-electronic devices.^[9,10] The forces underlying this work are gravitational: the devices settle into depressions with complementary shapes. The process our work describes is biomimetic: it occurs with the interacting objects moving unconstrained in three dimensions; the major interaction holding these objects together is hydrophobicity. Wide variation in the pairwise selectivity of interacting subunits can easily be achieved by choosing among complementary shapes for surfaces designed to interact.

Although the demonstrations described here were carried out with only two objects, and relatively large ones at that, the principles used apply to much smaller objects, and to larger numbers of them. We believe that the principles of design illustrated by these devices will ultimately be applicable to a wide range of functional devices, and opens the door to exploration of self-assembly as a new fabrication technique for complex, three-dimensional, functional systems.

Experimental

To self-assemble the circuits, the “lock” and “key” parts, eight pieces of each, were placed in a 100 mL round bottom flask with two indentations. The pieces were 5 mm long and cylindrical in cross section, with a diameter of 8 mm. The photocurable lubricant (200 μ L, consisting of 96 wt.-% dodecylmethacrylate, 2 wt.-% benzoin isobutyl ether, and 2 wt.-% 1,6-hexanediol diacrylate) and 500 μ L of ethanol were added. After gently shaking the mixture by hand to wet all the surfaces of the parts, the flask was completely filled with water and a stopper was inserted. The flask was rotated horizontally with a motor at 50–100 rpm, until the assembly was complete; self-assembly took about 0.5–2 h. The flask was exposed to UV light (500 W

high pressure mercury lamp) for 1 h to freeze the parts in place. When the assembled parts were transferred into the electrolyte, approximately 80% of the LEDs turned on.

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Controlled Mineralization and Assembly of Hydrolysis-Based Nanoparticles in Organic Solvents Combining Polymer Micelles and Microwave Techniques

By Joachim Spatz, Stefan Mößmer, Martin Möller,*
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In the past decade research on nanoparticulate materials has developed into an important interdisciplinary field of materials science.^[1–4] Size reduction of metals and semiconductors to the range of a few nanometers leads to novel and peculiar properties, for example, because of quantum size effects, the giant oscillation strength of metal particles, and also the surface effects in chemical reactions.^[2] Concepts in polymer science are directed towards formation of metal or semiconductor nanocrystals of well-defined size, which are arranged regularly in an optically transparent polymer matrix.^[5–8] Incorporation of small particles into polymers allows nanoparticulate films to be cast onto various substrates and provides particle stabilization.

For a polymer composite, absorption of light is dominated by scattering and the extinction coefficient of the particles, provided that the polymer itself is transparent in the visible light range. Both contributions are affected by the size of nanoparticles.^[2] Semiconductors are good candidates for tuning both scattering and extinction coefficient parameters simply by controlling the size of the particles.

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