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Molecular Memory Circuits Using a Virus as a Template

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Introduction: Significant challenges exist in constructing and manipulating the building blocks of a nanoscale device. After such a device is assembled, it is an additional challenge to electronically address or measure responses at the molecular level. We demonstrate the usefulness of individual virus particles as scaffolds to enable design, construction, and measurement of nanoscale molecular electronics memory devices. Such devices are of great interest for their potential to enable lightweight, low-cost, and low-power technologies such as handheld electronic sensors and inexpensive disposable molecular memories. Taking advantage of molecular electronics requires developing novel techniques for organizing nanosized materials into usable devices. As biological interactions are better understood, there has been great interest in using the specificity and strong interactions present in biology for this purpose. By combining the structural specificity provided by biological systems with the material properties of synthetic systems it is possible to develop novel devices on the nanoscale. Using viruses as nanoscale scaffolds for devices offers the promise of exquisite control of positioning on the nanoscale, using a particle that can either interface with lithographically defined structures, or undergo further self-assembly into extended structures by itself. We use cowpea mosaic virus (CPMV) as a nanoscale scaffold for constructing molecular electronic circuits for use in memory applications.[1]

Nanocircuit Assembly: Using genetically engineered CPMV allows the generation of specific patterns of functional amino acids, which provide a means to assemble complex structures with high spatial specificity on the nanometer scale. To construct nanoscale circuits, the amino acid cysteine was inserted in a specific predetermined pattern on the virus surface. Gold nanoparticles were bound to the inserted cysteine thiol groups. To make electronic circuits, the nanoparticles were then interconnected using conjugated conducting molecules, resulting in three-dimensional networks called viral nanoblocks (VNBs). Network properties were engineered by using molecular connectors with different properties. Networks consisting of just molecular wires were compared with networks containing bipyridyl-dinitro oligophenylene ethynylene dithiol (BPDN), a molecule with two conductance states which has been shown to behave as a molecular switch.[2]

Measuring Molecular Circuits: The conductance of the molecular network self-assembled on isolated single VNBs was measured using scanning tunneling microscopy (STM). Although STM characterization is a well-established technique for determining the conductance of isolated molecules, our measurements are the first demonstration of a self-assembled molecular network on the nanometer scale. To carry out these measurements, a self-assembled monolayer of undecanethiol (C11) on a gold-on-mica substrate was used to isolate virus-based networks from each other. This substrate was exposed to virus-templated nanocircuits to produce isolated viruses bound to the underlying gold substrate via the inserted conducting molecules that can be interrogated individually by the STM (Fig. 7(a)). Control samples exposed to unmodified viruses show dark areas that do not contain bright spots (Fig. 7(b)). These high contrast areas do not appear in films that have not been exposed to virus (not shown). Substrates exposed to viruses with attached gold nanoparticles show characteristic dark areas containing brighter spots (Fig. 7(c)). Within these darker areas are bright spots that are likely to be 5-nm gold nanoparticles attached to the virus. Substrates exposed to conductive VNBs show large bright features that are highly enhanced and prominent (Fig. 7(d)). The distinct change in VNB appearance after exposure to conductive molecules suggests that functionalization with molecular wires opens a pathway for charge transport across the molecular network templated on the viral scaffold.

Tunneling spectroscopy measurements were also made on VNBs after imaging to examine the conductance of the molecular networks. For tunneling spectroscopy, the STM tip was held over the VNB with the feedback turned off. The bias voltage was swept while recording the tunneling current (current vs voltage = I/V). Individual molecular wire networks show no discontinuities, hysteresis, or other non-linear behaviors over a voltage range of 0 to 2 V (Fig. 8(a)). In contrast to this linear I/V behavior measured for control molecular wire networks, STM measurements of isolated BPDN-containing networks (Fig. 8(b)) show pronounced hysteretic behavior.[1] BPDN-containing networks show a discontinuity in the measured I/V behavior that is similar to that observed in individual BPDN molecules.[2] Furthermore, the stepped features that appear at ~1.5 V and 2 V suggest that there are multiple conductance states accessible to the molecular network. These steps may occur when different molecules in the network change conductance state, and are in good agreement with calculated models of the molecular networks.

Discussion: We have produced conductive networks on the nanoscale using CPMV as a template

for self-assembly and demonstrated that the network properties depend on the properties of the nanoscale components. Thus, we can engineer the behavior of nanoscale templated devices by selecting appropriate molecular components. Building such electronic circuits from molecular building blocks is an area of great interest. The CPMV scaffold uses the chemical specificity present in biological systems to organize inorganic components with great precision in three dimensions. In using molecules that can act as bistable molecular switches, we built switchable molecular networks with a 28 nm footprint. Such CPMV-based bit storage devices have a theoretical density of 1 petabit/cm^2, with the potential for increased storage density due to the availability of more than two conductance states on each virus. Future work in this area could produce additional functional templated devices such as biosensors or nanostructured light harvesters. By using bottom-up programmed self-assembly to produce a free-standing nanodevice, we showed that biological nanoparticles can be used in materials engineering.

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References

[1] A.S. Blum, C.M. Soto, C.D. Wilson, C. Amsinck, P. Franzon, and B.R. Ratna, "Electronic Properties of Molecular Memory Circuits on a Nanoscale Scaffold," *IEEE Trans. NanoBio.* **6**, 270-274 (2007).

[2] A.S. Blum, J.G. Kushmerick, D.P. Long, C.H. Patterson, J.C. Yang, J.C. Henderson, Y. Yao, J.M. Tour, R. Shashidhar, and B.R. Ratna, "Molecularly Inherent Voltage-controlled Conductance Switching," *Nature Materials* **4**, 167-172 (2005).

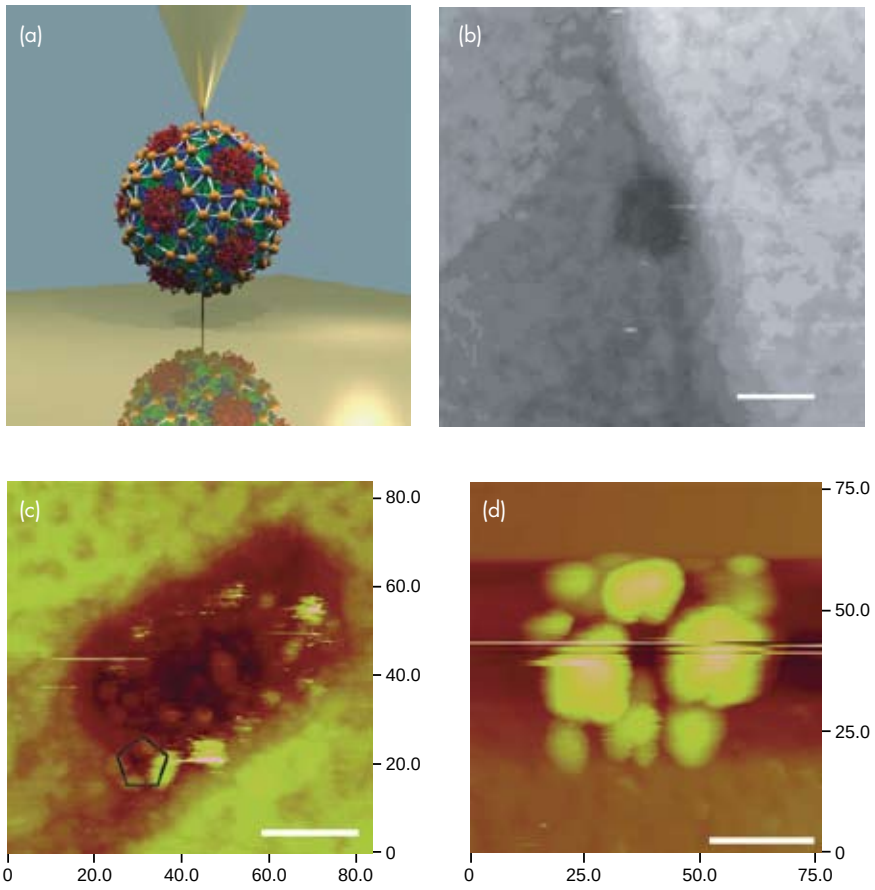

FIGURE 7
STM studies of viral nanoblocks. I_t = 2.5 pA, V_{bias} = 1 V. (a) Schematic of STM experiment, showing isolated conductive VNB attached to gold substrate through a conducting molecule inserted in an insulating C11 matrix. (b) STM image showing isolated CPMV virus (dark patch). Scale bar indicates 30 nm. (c) STM image of CPMV with 5-nm gold nanoparticles. The size and shape indicate that there are likely two viruses in this image. Pentagon indicates likely 5-fold axis. Scale bar indicates 20 nm. (d) STM image of conductive VNB in C11 alkane matrix. Scale bar indicates 20 nm.

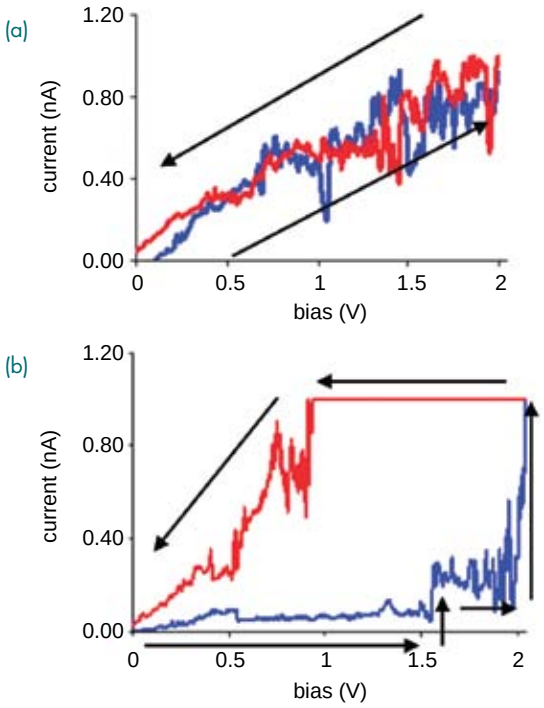

FIGURE 8
(a) Current vs voltage (I/V) for an isolated CPMV VNB network. This molecular wire network does not display non-linear behaviors. (b) Current vs voltage (I/V) measurement for isolated CPMV-BPDN network showing steps in conductance and multi-state behavior.