Electrical Devices

Fully Plastic Actuator through Layer-by-Layer Casting with Ionic-Liquid-Based Bucky Gel

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Printable electrical devices[1,2] are attractive for the development of microelectromechanical systems (MEMS) including sensors, switches, and micromachines. In particular, printable actuators that can infinitely operate in air at low voltages would give a breakthrough in the design of miniaturized mechanical devices. Conjugated polymers can be regarded as potential materials for the fabrication of such soft actuators.[3–7] Although a few examples of conjugated polymer actuators that can work in air have been reported,[8] their complicated configurations require multistage processing that involve, for example, sputter deposition of metallic layer electrodes and electrochemical deposition of polymer layers. Herein we report the first dry actuator that can be fabricated simply through layer-by-layer casting with "bucky gel", a

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gelatinous room-temperature ionic liquid that contains single-walled carbon nanotubes (SWNTs).[9] Our actuator adopts a bimorph configuration with a polymer-supported internal ionic liquid electrolyte layer sandwiched by bucky-gel electrode layers which allows quick and long-lived operation in air at low applied voltages.

Baughman et al. reported that SWNT sheets, laminated together with double-sided Scotch tape, show an electrochemical actuation in aqueous electrolyte solutions, where the SWNT sheets not only serve as electrodes but also undergo elongation/contraction upon charge injection into the nanotubes.[10] We were motivated to apply bucky gels to the fabrication of soft actuators with the expectation that such actuators with built-in ionic-liquid components can operate in air without external electrolytes. Bucky gels can be readily prepared by grinding SWNTs in imidazolium ion-based ionic liquids; the heavily entangled nanotube bundles are exfoliated by a possible cation–π interaction[11] on the SWNT surfaces to give much finer bundles. Ionic liquids are nonvolatile and characterized by their high ionic conductivities and wide potential windows, which are advantageous for rapid responses in actuation and high electrochemical stabilities of the components, respectively.[12]

The configuration of our bucky-gel actuator is illustrated in Figure 1 a. The actuator film was fabricated through layer-by-layer casting of the electrode (SWNTs) and the electrolyte (ionic liquid) components in a gelatinous mixture of poly (vinylidene fluoride-co-hexafluoropropylene) (PVdF(HFP); Figure 1 b) as a polymer support and 4-methyl-2-pentanone (MP). In a typical example, the bucky-gel electrode layers include 13 wt % of SWNTs, 54 wt % of 1-butyl-3-methylimidazolium tetrafluoroborate ($BMIBF_4$; Figure 1 b) and 33 wt % of PVdF(HFP), whereas the internal ionic-liquid electrolyte layer[13] contains 67 wt % of $BMIBF_4$ and 33 wt % of PVdF(HFP). In sharp contrast with previous conjugated polymer actuators, the fabrication process includes neither deposition of metallic layers nor electrochemical polymerization. Scanning electron micrograph of a cross-section of the actuator strip showed that the electrode and electrolyte layers are seamlessly connected with one another (Figure 2), thereby facilitating intra- and interlayer ion transport, which is essential for quick response.

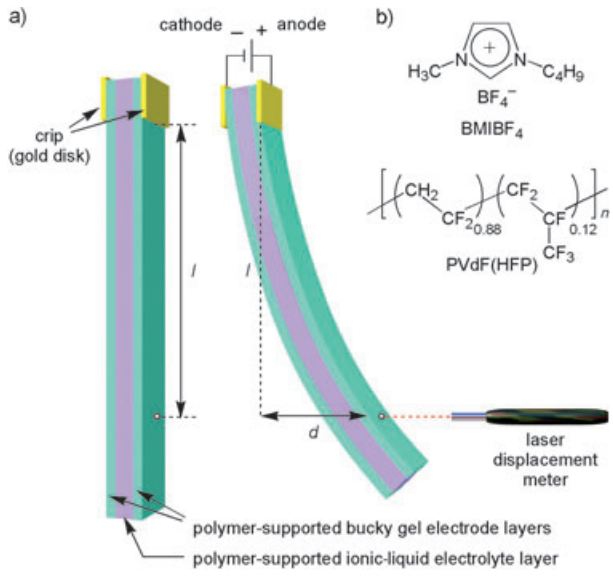

Figure 1. Bucky-gel-based bimorph actuator fabricated through layer-by-layer casting. a) Schematic structure of the actuator strip composed of a polymer-supported ionic-liquid electrolyte layer sandwiched by bucky-gel electrode layers, and experimental setup for cantilever oscillation. The displacements (δ) at a point 10 mm ($=l$) away from the fixed position were continuously measured by a laser displacement meter. b) Molecular structures of $BMIBF_4$ and PVdF(HFP).

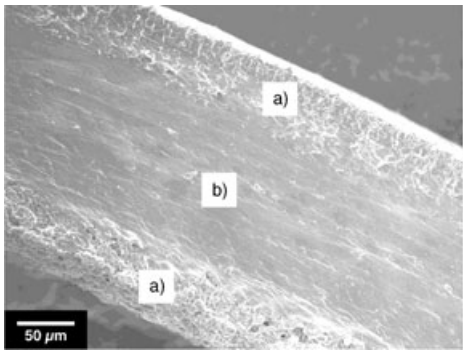

Figure 2. Scanning electron micrograph of a cross section of a bucky-gel actuator strip (0.25 mm in thickness); a) and b) represent the polymer-supported bucky-gel electrode and the ionic-liquid electrolyte layers, respectively.

We confirmed that the bucky-gel actuator with such a simple three-layered configuration indeed operates quickly in air in response to low applied voltages. The actuation experiments were conducted by applying alternating square-wave voltages to a $15 \times 1\text{-mm}^2$-sized actuator strip (0.28 mm in thickness) clipped by working/counter gold disk electrodes; the displacement at a point 10 mm away from the fixed position was continuously monitored from one side of the actuator strip by using a laser displacement meter (Figure 1 a). For example, when an electric potential of ± 3.5 V was applied with a frequency of 0.01 Hz, an actuator strip underwent a bending motion toward the anode side (Figure 3 a) with a maximum displacement of 5 mm. Upon increment of the frequency of an applied voltage of ± 3.0 V from 0.01 to 0.1 Hz, 1.0–10 Hz (Figure 4), and 30 Hz, a perfect response of the actuator strip resulted. As the applied voltage was changed from ± 1.0 to ± 2.0 and then ± 3.0 V (0.1 Hz), the displacement of the actuator strip was increased from 0.36 to 0.76 and 1.8 mm, respectively. The electric current profile of the actuation (Figure 3 b) displayed only charging and discharging, thus indicating that the bucky-gel electrodes act as an electric double-layer capacitor. We found that the double-layer capacitance of the bucky-gel electrode has a value of 48 F (g of SWNTs)$^{-1}$, which is more than twice as large as those of a SWNT sheet dipped in ionic liquids (18–24 F g^{-1}).[14] Such a large double-layer capacitance of the bucky-gel electrode is believed to originate from highly dispersed carbon nanotubes. The strain and stress generated in the bucky-gel electrode layer, when estimated from the displacement (Figure 3 a) at an applied voltage of ± 3.5 V

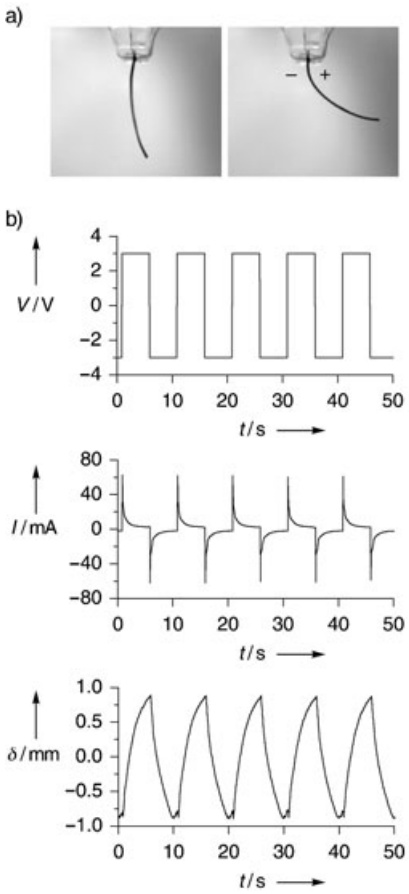

Figure 3. Performances of a bucky gel actuator (15 mm in length, 1 mm in width, 0.28 mm in thickness) in response to alternating square-wave electric potentials. a) Bending motion of the actuator strip at an applied voltage of ±3.5 V with a frequency of 0.01 Hz. b) Input signals (*V*), currents (*I*), and displacements (δ) of the actuator strip at an applied voltage of ±3.0 V with a frequency of 0.1 Hz.

(0.01 Hz), were 0.9% and 0.1 MPa, respectively. Of interest, the observed strain is comparable to or even larger than that of the SWNT sheet-based actuator,[10] in spite of the fact that the SWNT content in the bucky-gel electrodes is only 13 wt%. We consider that the bending motion of our actuator takes place by dimensional changes of the soft electrode layers in response to alternating voltages. When an electric potential is applied to the actuator, imidazolium (BMI^+) and BF_4^- ions of the built-in ionic liquid are thought to be transported to the cathodic and anodic sides, respectively, and form electric double layers with negatively and positively charged nanotubes. These ion transports most likely result in swelling of the cathode layer and shrinkage of the anode layer, as the former ion is larger than the latter. Consequently, the actuator bends toward the anode side (Figure 3a). Such a reversible change in the electrode dimensions takes advantage of the flexibility of the soft component materials. The SWNT-sheet-based actuator has been reported to bend toward the same direction, as it is operative by elongation and contraction of the nanotube bundles upon injection of negative and positive charges, respectively. Thus, these macroscopic and nanoscopic dimensional changes in the actuator strip do not compensate but can be synchronous with one another and may generate a large bending motion.

Our bucky-gel-based actuator is long-lived upon operation in air. Figure 5 shows the cycle life in air under

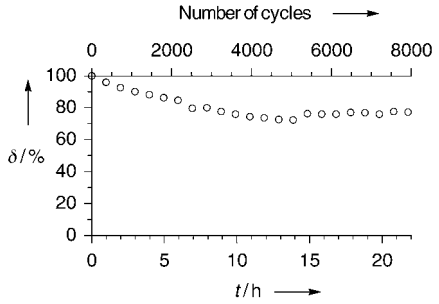

Figure 5. Cycle life of a bucky-gel actuator strip (15 mm in length, 1 mm in width, 0.28 mm in thickness) under continuous operation in air at an alternating square-wave electric potential of ±2.0 V with a frequency of 0.1 Hz.

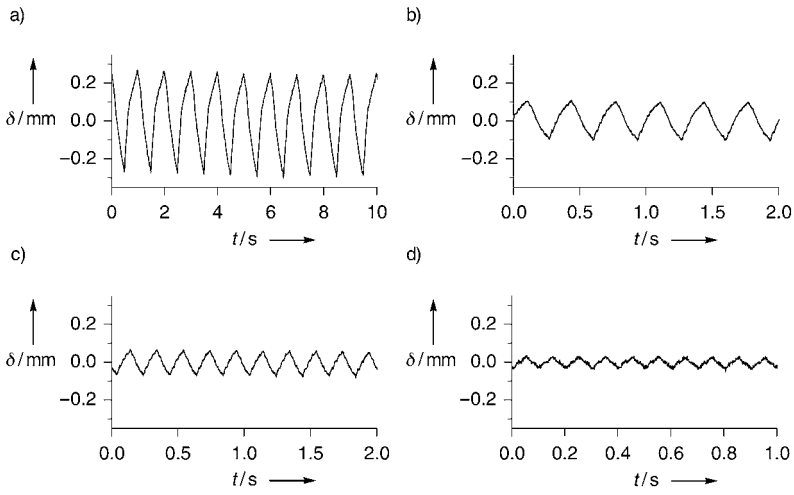

Figure 4. Performances of a bucky gel actuator (15 mm in length, 1 mm in width, 0.28 mm in thickness). Time-dependent displacements (δ) of the actuator strip at an applied square-wave electric potential of ±3.0 V with frequencies of a) 1.0; b) 3.0; c) 5.0; d) 10 Hz.

continuous operation in response to ±2.0 V square-wave input signals at a frequency of 0.1 Hz; the actuation could be repeated at least 8000 cycles, only with a 20% initial decrease in the actuator stroke, possibly as a result of the annealing of the material. We also confirmed that the actuator is usable periodically over a period of two months without any loss of performance.

The actuator reported herein has several advantages. First, the fabrication does not require any special apparatus but only an agate mortar and a hot plate. Such a simple layer-by-layer casting process can readily be extended to printing-based processing essential for miniaturization of machinery. Whereas the quick-responding actuators reported thus far require electro-

lyte solutions for operation, our bucky-gel-based actuator quickly operates in air for a long time owing to the built-in ionic-liquid component. The observed performance and durability are one of the highest among those reported for low-voltage driven, dry electromechanical actuators and may be further tuned simply by varying the ionic-liquid and supporting-polymer components. The present development provides an important step toward the realization of printing-based fabrication of miniaturized mechanical devices.

Experimental Section

Fabrication of actuator films by layer-by-layer casting: Typically, a suspension of SWNTs (high-purity HiPco SWNTs) (50 mg) in $BMIBF_4$ (205 mg) was ground for 15 min with an agate mortar. The bucky gel thus obtained was transferred to a mixture of PVdF(HFP) (126 mg) and 4-methyl-2-pentanone (MP) (2.5 mL). The mixture was heated at 80 °C for 20 min on a hot plate, and the resultant gelatinous material was then cast on an aluminum mold (4 cm in length, 1 cm in width, 0.17 mm in depth) and allowed to cool to room temperature, affording the first layer. Subsequently, a hot gelatinous mixture[13] of $BMIBF_4$ (253 mg), PVdF(HFP) (127 mg), and MP (0.8 mL) was cast onto the first layer. The resultant double-layered film was allowed to cool to room temperature after the thickness was adjusted by a 0.34-mm-thick spacer. The aforementioned hot gelatinous material derived from bucky gel was again cast onto the second layer and processed with a 0.17-mm-thick spacer. Finally, the three-layered (bimorph) film thus obtained was allowed to stand in air overnight and then dried under reduced pressure to remove the volatile fraction (MP), thus affording an actuator film with a thickness of 0.25–0.3 mm.

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