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Ultrathin Cantilevers Based on Polymer–Ceramic Nanocomposite Assembled through Layer-by-Layer Adsorption

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ABSTRACT

An ultrathin cantilever based on nanoorganized film from six alternating monolayers of clay plates, polycations, and magnetite nanoparticles was developed. The 170-nm thick clay–polymer–magnetite cantilever is a magnetic free-standing microstrip with a root anchored on a substrate. Hundreds of such cantilevers can be produced on a solid substrate within one processing cycle and, therefore, to provide sensor arrays or an adjustable surface with synchronized cantilever movements using an external magnetic field.

The growth of ordered, composite, and functional thin films containing building blocks such as polymers, nanoparticles, and enzymes organized with nanometer precision has been attracting research attention in the fields of optoelectronics, catalysis, and biochemistry.[1−8] By exploiting a nanoassembly technique called layer-by-layer self-assembly (LbL), new nanocomposites have been created and integrated into devices.[9−12] LbL self-assembly is based on alternate electrostatic adsorption of charged components (linear polyions, nanoparticles, and proteins).[13−19] The thin films are adsorbed onto a substrate from an aqueous solution via a sequential dipping process. The oppositely charged monomolecular layers are adsorbed on each other and locked via electrostatic binding. The multilayer growth step can be 1−2 nm, and the multilayers of any composition can be designed.

The bendable cantilever beam is widely used in sensing components.[20−22] A conventional cantilever is made from silicon by micromachining techniques. Here we present a new type of cantilever which is a free-standing, layer-by-layer (LbL) nanocomposite of a polymer and montmorillonite clay. In this work, we solved three fabrication problems: first, to find a multilayer composition with proper elastic properties; second, to perform micropatterning on LbL-multilayers; and third, to release one part of a nanocomposite film while keeping its "root" fixed on the substrate. The technique to pattern and detach the multilayer is critical in the cantilever fabrication. Recently, Hammond's group has developed microstamp patterning of LbL self-assembled thin films.[23,24] In another approach, patterning of LbL multilayers on silicon wafers was demonstrated with traditional microlithography.[12] The releasing of LbL self-assembled multilayers and the formation of free-floating or free-standing films has also been reported.[17−19] In this paper, a process based on traditional lithography and LbL self-assembly was demonstrated to produce single or multiple polymer−ceramic microcantilevers on a solid substrate.

The LbL cantilever is magnetic free-standing microstrip with a root anchored on the substrate (Figure 1). The cantilever is a LbL assembled multilayer of poly(dimethyldiallyl ammonium chloride) (PDDA), montmorillonite clay, and black iron oxide magnetic nanocrystals. Cationic PDDA serves as a polyelectrolyte glue to hold negative clay and magnetite nanoparticles together. Montmorillonite clay is a laminated flake of 1 nm thick and 300−400 nm wide. Its six monolayers alternated with polymer layers made the cantilever structure more steadfast. Fe_3O_4/Fe_2O_3 magnetic nanoparticles were also integrated into the cantilever. This design introduces new features to cantilever devices because they are much thinner and more flexible than existing solid silicon or metal cantilevers and their composition may be optimized with nanometer precision. Thickness, flexibility, and functionality of LbL multilayers can be adjusted by changing the number of monolayers of clay, polymers, and nanoparticles, and including other nanoblocks (such as DNA and enzymes) with the same LbL-assembly technique. Magnetic nanoparticles were integrated into a cantilever so that they are able to detect magnetic fields. A magnetometer may be based on this structure. The possibility to easily produce multiple polymer−clay cantilevers may be extended to a new field: a group of cantilevers may be implanted in a fluidic channel and a one-directional magnetic field sweeping at a regular frequency may result in micropumping.

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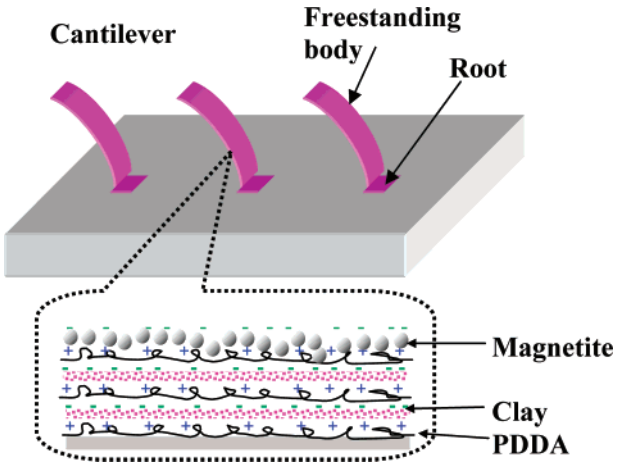

Figure 1. Schematic of the magnetic thin film cantilever which is composed of 6 tetralayers of PDDA/clay/PDDA/magnetite.

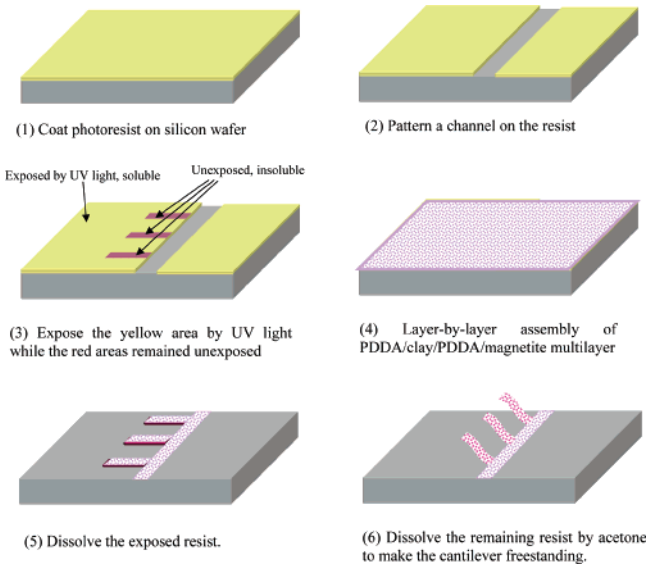

Figure 2. Schematic of the fabrication of the LbL film cantilever.

Microcantilever Preparation. Poly(dimethyldiallyl ammonium chloride), MW 200−300K (PDDA, Aldrich), and sodium poly (styrene sulfonate), MW 70,000 (PSS, Aldrich), were used at a concentration of 1.5−3 mg/mL. Montmorillonite clay (Sigma) and magnetite powder were dispersed in DI water at concentrations of 5 mg/mL. These suspensions were stirred up and sonicated for 30 min. Magnetite nanoparticles (Fe_3O_4/Fe_2O_3, 14 nm in diameter) were from PolySciences Inc.

A 4-in. silicon wafer was placed in a sulfuric acid and hydrogen peroxide solution (volume ratio 3:7) at 70° C for 1 h. The wafer was completely rinsed by DI water and baked on a hotplate at 150° C for 3 min. Two layers of positive resist (PR1813) were coated at a speed of 1000 rpm for 40 s. The wafer with photoresist was baked on a hotplate at 150° C for 80 s. The resist was subsequently exposed by UV light through the first mask for 20 s. Next, it was immersed in a developer solution (MF-319). At this point, the channel was transferred onto the resist. After that, the resist was irradiated again by UV light through the second mask to project the images of cantilever beams on the resist. LbL assembly of clay and magnetite nanoparticles was performed on such a prepared silicon wafer.

Before depositing multilayers, a surface potential of used nanoparticles was measured with the help of the Brookhaven ZetaPlus instrument. The zeta-potential of aqueous montmorillonite clay and magnetite at pH 6.5 was -50 ± 2 and -40 ± 1 mV, respectively. Therefore, the positively charged PDDA was alternated with these anionic nanoblocks. Two precursor bilayers of PDDA and PSS were deposited to provide a well-charged and uniform surface. The subsequent coating of clay was optimized to make the multilayer strong and flexible. The sequence of the alternate immersion to the component solutions was the following: [PDDA (10 min) + PSS (10 min)]$_{2\ \text{cycles}}$ + [PDDA (10 min) + $Fe_3O_4-Fe_2O_3$ (15 min) + PDDA (10 min) + clay (8 min)]$_{6\ \text{cycles}}$. The intermediate rinsing and drying after each immersion was necessary. The sample was rinsed by immersing the wafer in DI water for 1 min and then dried in a nitrogen stream. Subsequently, the wafer was soaked in a developer solution to remove the resist and the multilayer above it, with the assistance of sonication. Then, the wafer was placed in acetone until the cantilever was free-standing.

To optimize the assembly, the quartz crystal microbalance technique (9-MHz QCM, USI-System, Japan) was employed to monitor the growth rate of the LbL multilayer. In average, one tetracycle of clay/PDDA/$Fe_3O_4-Fe_2O_3$/PDDA adsorption gives a film thickness increase of 25 nm as was determined from corresponding QCM frequency shifts.[15] The total thickness of the cantilever was 170 nm, which agrees well with the measurement of the resulting micropatterns with a surface profiler (Tencor Profilometer).

The patterning and releasing of the nanocomposite cantilever is realized by traditional MEMS surface micromachining. Figure 2 displays the schematic of the cantilever fabrication. Positive photoresist is coated on the silicon wafer. The first lithography and development create a channel on the resist, as shown in the second step of Figure 2. Then, the second UV irradiation exposes the entire resist, except those masked areas that will form the body of the cantilevers. The exposure of UV light leads to photochemical reactions in the resist to make it soluble in developer while the unexposed area remains insoluble. At this step, the exposed and nonexposed resists are both kept on the wafer without being developed. Next, the LbL-adsorption process described above begins. The LbL-multilayer finally sticks to three areas: the channel on the wafer, the unexposed resist, and the exposed resist. After this, the wafer is soaked in a resist developer to dissolve only the exposed resist. When this portion of resist is quickly dissolved, the LbL-multilayer above it will be peeled off, as shown in step 5 of Figure 2. Finally, an unexposed resist is slowly dissolved in acetone solution and the multilayer film above it becomes free-standing.

Figure 3a shows the top view of the free-standing cantilever. The other images of Figure 3 show the deflection of the cantilever in water under a changing magnetic field by moving a permanent magnet of 400 Oe 0.5 cm above the

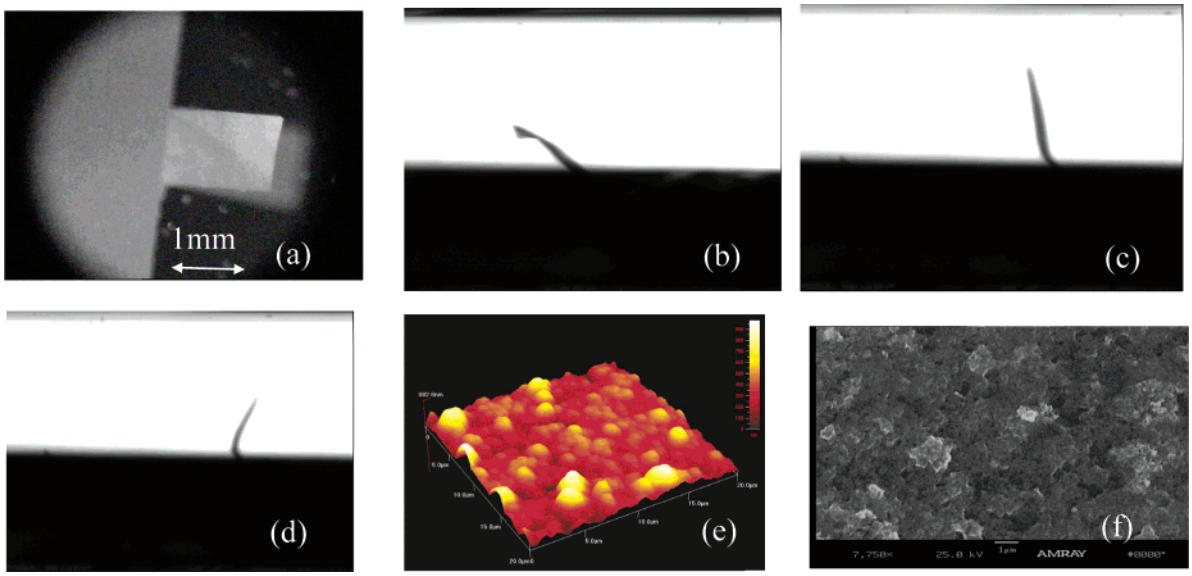

Figure 3. Images of free-standing LbL cantilever in water, (a) top-view, and (b−d) the response of the cantilever to changing magnetic field. (e) Atomic force micrographs of the cantilever surface; (f) a scanning electron microscopy image of the cantilever surface.

cantilever. The cantilever can be bent to angles exceeding 90 degrees in the presence of a magnetic field and can restore immediately when the magnetic field disappears. Such up−down movement of the cantilever can last for a long time without showing any fatigue failure or damage in the structure (we made 200 such bendings without any signs of destruction). The LbL cantilever is very steadfast and flexible. We believe that it is due to the interlayer connections of montmorillonite that has a shape of laminated sheets. Without montmorillonite layers, the free-standing polycation/polyanion cantilevers were weak and unstable. Figure 3e−f shows images of the cantilever surface. It consists from mosaic of many montmorillonite microsheets, and the film surface roughness is ca. 30 nm which is ca. 18% of its thickness. In the extension of this work, we made an array of 30 LbL-cantilevers with smaller dimensions of 100 μm wide, 200 μm long, and 100 nm thick.

In summary, we have developed a synthetic technique for a layer-by-layer self-assembled ultrathin microcantilever of clay/polymer nanocomposites. Its thickness, functionality, and strength can be adjusted in a wide range. It may find applications in sensors and actuators if appropriate functional nanoparticles are integrated. Hundreds of such cantilevers can be produced on a solid substrate within one processing cycle and, therefore, to provide sensor arrays or an adjustable surface with synchronized cantilever movements using an external magnetic field.

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Supporting Information Available: Movie of the cantilever movement under the influence of magnetic field. This material is available free of charge via the Internet at http://pubs.acs.org.

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