Supplementary Material (ESI) for Soft Matter

Supporting Information for

Logic Swelling Response of DNA-polymer Hybrid Hydrogel

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Materials

Materials used for surface functionalization of fiber optic lightguide to covalently attach the hydrogel and for the synthesis of the oligonucleotide-acrylamide hybrid hydrogel were as follow: Acrylamide (prop-2-enamide, 99%, Sigma), bisacrylamide (N,N-methylene-bis-acrylamide, 99%+, Acros organics), single stranded oligonucleotides with methacrylate group at 5' end (5′-acrydite, Integrated DNA Technologies) (see sequences in Fig.1), Tris (2-Amino-2-hydroxymethyl-propane-1,3-diol, Sigma Aldrich, 99.8%+), EDTA (2,2',2",2'"-(ethane-1,2-diyldinitrilo)tetraacetic acid, Sigma Aldrich, 99%), NaCl (sodium chloride, Sigma Aldrich, 99%)), squalane (2,6,10,15,19,23-hexamethyltetracosane, 99%, Aldrich), photo initiator (hydroxycyclohexylphenylketone, 99%, Aldrich)

Instrumentation and signal processing

Changes in the swelling properties of the oligonucleotide-acrylamide hybrid hydrogel were determined employing a high resolution interferometric instrument setup consisting of an optical fiber with a hydrogel chemically bound at one end and a connector/adapter system at the other (connector: FOC2 STD-A600, Huber + Suhner, adapter: FOC2 FOC2-D001, Huber + Suhner). An optical fiber (108163/02 Huber + Suhner) was connected to the detector controlled by a computer. A LabView program (supplied by InvivoSense) was used for instrument readout. The semispherical hydrogel, with radius of about 50-60 μm deposited at

the end of the optical fiber, played a role of Fabry-Perot cavity for the infrared beam (1530-1560 nm). Changes in optical length (ΔL_{opt}) of the gel cavity were determined based on the change in the phase of the interfering waves reflected from the fiber-gel and gel-solution interfaces[1]. It is previously reported that a resolution of 2 nm in changes of the optical length within the hydrogel is achieved, and the sample rate is about 1 Hz[1]. Changes in optical length, ΔL_{opt}, were monitored until the hydrogels reached the new equilibrium swelling volume under the applied conditions. The initial swelling rates ($\Delta L_{opt}/\Delta t$) of the hydrogels following changes in the solvent conditions were estimated based on linear regression for the data collected up to 1000 seconds. Changes in equilibrium swelling degree were expressed as: $(\Delta L_{opt}/L_{opt})\bullet 100\%$ where L_{opt} is an optical length of the cavity equilibrated in buffer solution before experiments. Note however that the uncertainty in the determination of the overall optical length of the hydrogel from the amplitude of the interference wave (±2 μm)[1] respresent a $< 2\%$ error in the estimation of the absolutte swelling degree.

Preparation of optical fibers for covalent attachment of hydrogels at the end.

The end of the optical fiber were activated and prepared for covalent grafting the hydrogels to the fiber matrix as previously detailed.[1] In brief, freshly cut fibers were stripped and immersed 20 min. in 0.01 M HCl for surface activation. Next, cleaned and activated fibers were surface functionalized by immersion into 10 vol% solution of 3-(trimethoxysilyl)propyl methacrylate in hexane and left for 1 h in order to allow silanization and chemically bind the methacrylate groups to the fiber surface. The attached layer containing the methacrylate groups played a role of covalent binder for the droplet of a gel during and after polymerization.

Preparation of pre-gel solutions

Pregel solution was composed of 10 wt% of acrylamide, 0.6 mol% covalent crosslinker, bisacrylamide, 0.4 mol% A1-A2 complex (see sequences in Fig.1) of single stranded oligonucleotides with methacrylate group at 5' end (5′-acrydite) acting as reversible crosslinker in buffer solution (pH = 7.7, composed of 10 mM Tris, 1 mM EDTA, 150 mM NaCl). A photoinitiator (hydroxycyclohexylphenylketone) was employed. After preparation the solution was kept for 3 hours at room temperature to enable A1 and A2 strands hybridization prior to polymerization.

Oligonucleotide-polyacrylamide hybrid hydrogel synthesis

A small aliquot of the pregel solution was deposited at the end of methacrylate functionalized optical fiber using a pipet. To avoid water evaporation from the hydrogel droplet deposition and polymerization were carried out in a squalane solution. Polymerization was induced by UV light from Dymax Bluewave 50 source and carried out for 6 minutes. The optical fiber with the cured hydrogel was removed from squalane and the hydrogel rinsed in excess of buffer in order to remove possible unpolymerized monomers and equilibrate the gel.

Measurements

Optical fibers with chemically bound hydrogels were protected against mechanical damage with glass tubes with an inner diameter of 1mm filled with buffer solution. All experiments were carried out at 23°C in buffer solution (pH = 7.7, 10 mM Tris, 1 mM EDTA, 150 mM NaCl) after preequilibration of the hydrogel in the same buffer solution.

(1) Tierney, S.; Hjelme, D. R.; Stokke, B. T. *Anal. Chem.* **2008**, *80*, 5086-5093.