Microfabrication of Self-Oscillating Gel by Photolithography

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Introduction: We have been studying the self-oscillating gel coupled with the oscillating reaction (the Belousov-Zhabotinsky (BZ) reaction)¹. The gel consists of the crosslinked poly(N-isopropyl-acrylamide (NIPAAm)) to which ruthenium tris(2,2'-bipyridine) (Ru(bpy)₃), a catalyst for BZ reaction, is covalently bonded. In this study, we have attempted microfabrication of self-oscillating gel by photolithography for application to micro-devices such as MEMS and µTAS. Two photolithographic methods, (1) using photoinitiator and (2) using the polymer with azidophenyl groups, were employed to control the gel structure. Optimal conditions for microfabrication have been discussed by changing the concentration and composition of monomer solution and the intensity and time of photo-irradiation.

Experimental: (1) Microfabrication using photoinitiator. NIPAAm, Ru(bpy)₃ monomer, N,N’-methylenebisacrylamide (MBAAm, 1.25mol%), and 2,2-dimethoxy-2-phenylacetophenone (photoinitiator) were dissolved in methanol. After purged with nitrogen gas, the solution was injected between glass plate and photomask plate separated by Teflon sheet (0.5mm). Polymerization was carried out by irradiating monochromatic light (370nm).

(2) Microfabrication using photosensitive polymer. At first, poly(NIPAAm-co-acrylic acid-co-Ru(bpy)₃) (molar ratio was 97:2:1) was synthesized in methanol (5mL, total monomer concentration 2.0M) containing 2,2’-azobisisobutyronitrile (AIBN, 1mol% of total monomers) at 60°C for 24h. The resulting mixture was dialyzed against methanol and water, and then freeze-dried. Subsequently, this copolymer (100mg), 4-azidoaniline (30mg) and water-soluble carbodiimide (64mg) were dissolved in PBS (pH 7.0, 20mL), and the mixture was stirred at 4°C for 24h. The azidophenyl-amidated copolymer was obtained by dialyzing resulting mixture for 3 days against water and freeze-drying (Fig.1). Then this copolymer was dissolved in methanol (40mg/mL). The polymer solution was coated on glass or polystyrene plate and dried up. The plate was then covered with a photomask and UV light was irradiated.

Results and discussion: By both microfabrication method (1) and (2), several shapes of micrometer-sized gels with the same pattern as photomask were synthesized. As monomer and photoinitiator concentrations increase, the gelation time became shorter. Optimal condition for microfabrication (1) was obtained when the monomer concentration was 2.0M and light intensity was 1.5kW/cm². Fig.2 shows the lattice-shaped gel prepared by microfabrication (2). In oxidized state, the gel swelled more than in reduced state (Fig.3). Self-oscillation occurred and chemical wave propagation was observed as these gels were immersed in the substrate solution of BZ reaction. The self-oscillating behavior of the microgels was analyzed with comparing that of bulk gel.

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Abstract

We have been studying the self-oscillating gel coupled with the oscillating reaction (the Belousov-Zhabotinsky (BZ) reaction). The gel consists of the crosslinked poly(N-isopropyl-acrylamide (NIPAAm)) to which ruthenium tris(2,2Õ-bipyridine) (Ru(bpy)₃) catalyst for BZ reaction, is covalently bonded.

In this study, we have attempted microfabrication of self-oscillating gel by photolithography for application to micro-devices such as MEMS and µTAS. Two photolithographic methods, (1) using photoinitiator and (2) using the polymer with azidophenyl groups, were employed to control the gel structure. Optimal conditions for microfabrication have been discussed by changing the concentration and composition of monomer solution and the intensity and time of photo-irradiation.
Mechanism of Self-Oscillation for Polymer Gel

Belousov-Zhabotinsky (BZ) reaction

**Reactants:** MA, NaBrO₃, HNO₃
**Catalyst:** Ru(bpy)₃²⁺

**Poly(NIPAAm-co-Ru(bpy)₃) gel**

**Swelling curve**

- **Oxidized state, Ru(III)**
- **Reduced state, Ru(II)**

**Difference of swelling ratio**

**Transduction circuit**

- Ru(bpy)₃³⁺
- Ru(bpy)₃²⁺
- NIPAAm
- Ru(bpy)₃

**Transducer**

**Heart muscle-emulating materials.**
**Self-oscillating micropump or microactuator.**

Microfabrication of Gels

Miniaturization of the gel

- Improvement of response time
  (The response time of gel is proportional to the square of gel size)
- Application to the micro-devices
  (ex. Microactuator, µTAS, MEMS)

Technology of miniaturization

-Synthetic technique-
- Suspension polymerization
- Emulsion polymerization
  (ex. Preparation of micro/nano gel particles)
  etc.

-Lithography-
- Shape of gel can be easily changed.
  - Photolithography
    Easy synthesis and simple device
  - X-ray lithography (LIGA)
    3D Microfabrication
We have attempted microfabrication of self-oscillating gel by photolithography for application to micro-devices such as MEMS and µTAS. Two photolithographic methods were employed to control the gel structure.

1. **Photolithography**
   
   (1) Microfabrication using photo-initiator
   
   (2) Microfabrication using photosensitive polymer

   Optimal conditions for microfabrication have been discussed by changing the concentration and composition of monomer solution and the intensity and time of photo-irradiation.

2. **X-ray lithography (LIGA)**

   Preparation of Ciliary motion actuator made of self-oscillating gel (Artificial Cilia)
Microfabrication Using Photo-Initiator

Monomer solution (concentration; 2M)

- NIPAAm
- Ru(bpy)$_3$ monomer (5 wt%)
- MBAAm (cross-linker) (1.25 mol%)
- Photo initiator (10 wt%)
- Methanol

Monochromatic light (370 nm)

- Photomask
- Spacer (thickness: 0.5 mm)
- Glass plate

Optimal conditions;
Intensity: 1.0~1.5 mW/cm$^2$
Irradiation time: 3~5 min.

The monomer solution was poured between the photomask and the glass.

1 - (1) Photolithography using photo-initiator

2,2,-Dimethoxy-2-phenylacetophenone
Micropatterning of Poly(NIPAAm-co-Ru(bpy)$_3$) Gel Using Photo-Initiator.

Photolithography using photo-initiator

Reduced state (in Ce(III) / HNO$_3$)

Oxidized state (in Ce(IV) / HNO$_3$)
Microfabrication Using Photosensitive Polymer

1 - (2) Photolithography using photosensitive polymer

**Molar ratio**

![Molar ratio diagram](image-url)

- **Polymer coating on a plate.**
- **Photomasking**
- **UV irradiation**
- **Washing**
- **Gel pattern fixed on PS plate**
- **Detached microgels from glass plate**

**Chemical Reaction**

- **Water soluble carbodiimide pH 7.0, 4°C, 24 hours**

**4-azidophenylamidated poly(NIPAAm-co-Ru(bpy)₃)**

**Nitren reaction was occurred. -N₃ groups bonded any carbon chain near it.**
Micro-patterning of Poly(NIPAAm-co-Ru(bpy)$_3$) Gel Using Photosensitive Polymer [1]

The minimum size for this microfabrication method = several µm
Micro-patterning of Poly(NIPAAm-co-Ru(bpy)$_3$) Gel Using Photosensitive Polymer [2]

Photomask (lattice-shaped)  
Prepared gel (on PS plate)
AFM Image of Lattice-shaped Microgel

1 - (2) Photolithography using photosensitive polymer

3D image of AFM

Thickness Å700 nm
Redox Changes of Poly(NIPAAm-co-Ru(bpy)$_3$) Microgels Prepared by Photosensitive Polymer.

1- (2) Photolithography using photosensitive polymer
Chemical Wave Propagation of Poly(NIPAAm-co-Ru(bpy)$_3$) Microgel Prepared by Using Photosensitive Polymer

Outer solution:
[MA]=0.09 M, [NaBrO$_3$]=0.1 M, [HNO$_3$]=0.4 M

BZ reaction was occurred inside of the gel, and the chemical wave was propagated through the patterned gel arrangement.
The PMMA mold was too hard to takeout the gel, so the PDMS mold, the softer one, was prepared.

2. X-ray lithography

**Preparation of Artificial Cilia by X-ray Lithography**

**Photolithography**
- 2D-microfabrication
- 3D-microfabrication

**X-ray lithography**

**Concept of Artificial Cilia**
- The propagation of chemical wave
- Lean the projections successively

**Moving deep X-ray lithography technique**
- Exposure
- Development
- Au Evaporation
- Ni Electroplating
- PDMS molding
- De-molding

The propagation of chemical wave

Poly(NIPAAm-co-Ru(bpy)$_3$) gel

Moving the photomask, X-ray was irradiated.

The PMMA mold was too hard to takeout the gel, so the PDMS mold, the softer one, was prepared.
The motion of the gel projection on BZ reaction was analyzed by image processing based on the video image.

The circular motion like a cilia

Summary

< Microfabrication of self-oscillating gel >

1. Photolithography
Several shapes of micrometer-sized gels were synthesized. Redox change of self-oscillating gel was observed and swelling change was measured. In the aqueous solution containing BZ substrates, self-oscillation accompanied by the propagation of chemical wave was achieved.

2. X-ray lithography (LIGA)
The gel array with projections on surface was prepared. Following the propagation of chemical wave, the motion like a cilia was observed. (Realization of artificial cilia.)