Sensors and Actuators A xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Sensors and Actuators A: Physical

journal homepage: www.elsevier.com/locate/sna

Investigation of the spatial resolution of a laser-based stimulation process for light-addressable hydrogels with incorporated graphene oxide by means of IR thermography

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ARTICLE INFO

Article history:
Received 13 July 2017
Received in revised form
15 November 2017
Accepted 16 November 2017
Available online xxx

Keywords:
Responsive hydrogels
Light-addressable actuator
Graphene oxide
Lab-on-chip system
Spatial resolution

ABSTRACT

The development of lab-on-chip (LoC) devices has led to a demand of new microactuator technologies. Light-responsive hydrogels are promising candidates as actuator materials for this type of applications. These are polymers that change their water content and volume significantly upon illumination with a light source. For proper operation, the spatial resolution of the stimulation process is an important parameter. To investigate this resolution, poly(N-isopropylacrylamide) (PNIPAAm) hydrogels with incorporated graphene oxide (GO) were monitored with an infrared (IR) camera during illumination with a laser source. The GO nanoparticles convert the absorbed light energy into heat and for temperatures above the lower critical solution temperature (LCST), the polymer collapses. Therefore, the desired actuated area has to have a temperature above the LCST. A mathematical model was used to fit the recorded spatial temperature profiles in order to obtain the width at the LCST and to evaluate the temporal progression of the stimulated area. The results enable the development of new stimulation strategies and enhance the understanding of the spatial resolution of light-addressable hydrogels. Furthermore, the required stimulation time for different laser powers is presented.

1. Introduction

To accomplish the vision of having personalized medical devices in the future, there is an ongoing process to develop new and innovative products in the field of life sciences by the miniaturization of analytical techniques. The concept of integrating functions and tasks of a large-scale analytic laboratory into an analysis platform on chip level with outer dimensions in the centimeter range has led to the development of lab-on-chip (LoC) systems also referred to as micro total analysis systems (μTAS). Although these systems have not yet been established in everyday diagnostic as it was predicted a decade ago, their impact is significantly growing especially in the academic world [1–3]. Because of the variety of possible functionalities such as mixing, separation and detection of analytes, flow control, drug release and so on, LoC devices have to consist of a large number of different parts including mechanical, electronic and fluidic units [4–6]. Unfortunately, the elements for fluidic handling and actuators within the microfluidic system make up one of the biggest contributions to the fabrication costs, which is especially a drawback for disposable μTAS and LoC systems [7]. Therefore, the design of affordable LoC systems is closely related to the development of low-cost actuators.

Stimulus-responsive hydrogels are in focus for the development of sensor and actuator structures at the microscale due to their ability to change their volume and geometry significantly when triggered by a large number of possible environmental quantities such as pH value, ionic strength, temperature, electric and magnetic fields and light [8–13]. The stimulation with light allows to control the dimensions of the material without direct contact, which is of distinct importance to obtain sterile conditions in the field of biological and medical environments. Furthermore, light as stimulus can be applied easily without being limited by thermal diffusion as for temperature-sensitive hydrogels with heating structure or by ion diffusion as for pH-sensitive hydrogels [10]. In addition, the input of photon energy can be controlled with high spatial and tem-

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https://doi.org/10.1016/j.sna.2017.11.031
0924-4247/© 2017 Published by Elsevier B.V.

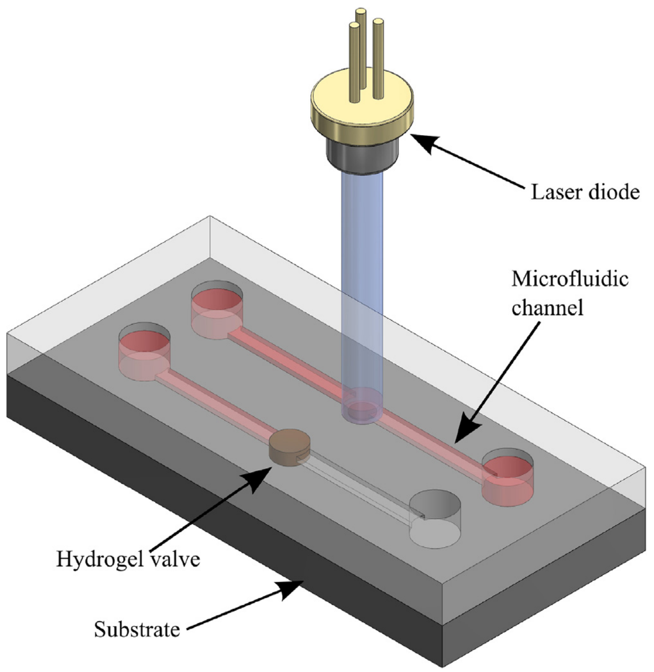

Fig. 1. Sample application of a light-sensitive hydrogel actuator within a LoC device: the hydrogels are integrated as light-driven valves. For the swollen state of the hydrogel on the left hand side, the channel is blocked and by stimulating the hydrogel with light (right channel), the channel is opened.

poral resolution so that the impact on the surrounding is decreased to a minimum [14]. Due to those advantages, light-sensitive materials are a very promising option for LoC applications.

A possible application of a light-driven actuator within a microfluidic system is depicted schematically in Fig. 1. The hydrogels within the channels act as valves which control the flow. For the swollen state (left channel), the hydrogel blocks the channel and no flow occurs. Upon illumination (right channel), the hydrogel collapses and the channel is opened. Therefore, the liquid can pass by and is pumped through the channel.

One possible approach to achieve light-responsive hydrogels is the integration of a functional group into the hydrogel, which exhibits a photoswitching effect, like photoisomerization under illumination. These light-sensitive groups are azobenzene, spiropyran, etc. For example, the isomers of spiropyran have a high difference in polarity leading to a change in hydrophilicity. The hydrophilic protonated merocyanine causes a swollen material, whereas the hydrophobic spiropyran leads to a de-swollen state. First microactuators for LoC devices have been realized with hydrogels containing these functional groups [14–17].

Another promising idea to realize the stimulation of hydrogels with light is the integration of nanoparticles into temperature-sensitive hydrogels so that these materials can be heated optothermically. Most of these materials are based on poly(N-isopropylacrylamide) (PNIPAAm) gels, which belong to the group of temperature-responsive hydrogels showing lower critical solution temperature (LCST) behavior. Below this critical temperature limit of typically 32 °C, the hydrophilic amide groups of PNIPAAm are dominant because the enthalpy of the hydrogen bonds formed between water molecules and the polar groups of the polymer has a bigger influence on the free energy compared to the entropy term. Hence, the material swells in aqueous solutions and increases in size due to the absorbed water. Above the temperature limit, the isopropyl groups are dominant because the entropy term has an increased contribution to the free energy leading to phase separation once the free energy change becomes positive [18–20]. The hydrogel collapses and decreases in size due to the diffusion of stored water into the environment. A variety of different nanoparticles has been applied to increase the light absorption of PNIPAAm-based hydrogels including metallic nanoparticles such as gold [21] or iron oxide [22,23], polypyrrol particles [24], and variations of carbon such as carbon nanotubes [25,26] or graphene oxide [27–31]. These nanoparticles absorb the photon energy within the polymer network, convert it into heat and the hydrogel collapses when the transition temperature is exceeded. For example, the electrons within the conjugated π-system of GO nanoparticles are promoted to an excited state by absorption of UV and blue light photons and transfer their energy to phonons leading to a heating of the material.

Because of the continuous miniaturization efforts for LoC devices and µTAS, it is important to gain knowledge about the spatial limitations and benefits of this light-induced actuators as well as their limitations due to thermal diffusion. To the best of our knowledge, the spatial resolution of this light-induced stimulation process has not been investigated in detail yet. In this work, the spatial resolution was investigated by monitoring the temperature distribution of PNIPAAm-based hydrogels modified with graphene oxide (GO) under illumination of a laser beam via infrared (IR) thermography. At first, the beam properties of the laser source were characterized to know, e.g., the beam radius at the location of the hydrogel. After that, the hydrogels with incorporated GO were heated up locally by laser radiation and the raise in temperature as well as the spatial temperature profile were monitored for different laser powers. The measurement data was fitted with an appropriated model to achieve the size of the area above the critical temperature limit of the hydrogels. These results gain knowledge of the local heating process within the hydrogel in order to further improve the stimulation process and the spatial resolution for the succeeding actuator functionality.

2. Experimental

2.1. Materials

N-isopropylacrylamide (NIPAAm, 99%; Sigma–Aldrich), 2-hydroxy-4-(2-hydroxyethoxy)-2-methylpropiophenone (Irgacure 2959; Sigma–Aldrich) as photoinitiator and N,N′-methylenebis(acrylamide) (MBAm, 98%; Sigma–Aldrich) as cross-linking agent were utilized as they were provided by the sources without any further purification process. The base for the photopolymerization process was a monomer solution containing 100 mmol monomer (NIPAAm), 1 mmol crosslinker (MBAm) and 0.45 mmol photoinitiator (Irgacure 2959) dissolved in 60 ml deionized (DI) water. After stirring for 2 h, the solution was degassed with nitrogen for 1 h. The pre-polymer solution was mixed with GO dispersions with a concentration of 4 mg ml^{-1} in a ratio of 1:1 for hydrogels with GO leading to an amount of 2 mg ml^{-1} within the gels. To increase the adhesion of the polymer to the underlying substrate, a 0.5 wt.% solution of 3-(dimethyl chlorosilyl) propyl methacrylate (Sigma–Aldrich) in ethanol was applied as adhesion promoter to precoat the substrates.

2.2. Fabrication processes

To ensure that no light is absorbed by the substrate, the hydrogel samples were fabricated on top of standard microscope slides made of “non-absorbing” glass (Carl Roth). Prior to the polymerization of the hydrogels, the glass slides were treated in a plasma cleaner (Femto PCCE, Diener electronic) for 2 min at a pressure of 0.3 mbar and power of 100 W and then immersed in the adhesion-promoter solution for at least 24 h prior to further steps. After that,

Please cite this article in press as: L. Breuer, et al., Investigation of the spatial resolution of a laser-based stimulation process for light-addressable hydrogels with incorporated graphene oxide by means of IR thermography, Sens. Actuators A: Phys. (2017), https://doi.org/10.1016/j.sna.2017.11.031