Optical Materials 80 (2018) 241–246

Contents lists available at ScienceDirect

Optical Materials

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

Ultra-thin, conformal, and hydratable color-absorbers using silk protein hydrogel

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ARTICLE INFO

Keywords:
Metal-insulator-metal resonator
Silk protein
Hydrogel
Ultra-thin color absorber
Refractometric sensor

ABSTRACT

Planar and multilayered photonic devices offer unprecedented opportunities in biological and chemical sensing due to strong light-matter interactions. However, uses of rigid substances such as semiconductors and dielectrics confront photonic devices with issues of biocompatibility and a mechanical mismatch for their application on humid, uneven, and soft biological surfaces. Here, we report that favorable material traits of natural silk protein led to the fabrication of an ultra-thin, conformal, and water-permeable (hydratable) metal-insulator-metal (MIM) color absorber that was mapped on soft, curved, and hydrated biological interfaces. Strong absorption was induced in the MIM structure and could be tuned by hydration and tilting of the sample. The transferred MIM color absorbers reached the exhibition of a very strong resonant absorption in the visible and near infra-red ranges. In addition, we demonstrated that the conformal resonator could function as a refractometric glucose sensor applied on a contact lens.

1. Introduction

Photonics-based wireless technology has revolutionized the fields of biochemical sensing [1–4], imaging [5–7], and color displays [8–10] by manipulating light-matter interactions within a broad spectral range. For practical applications, lithography-free planar photonic devices such as a metal-insulator-metal (MIM) resonator based on a Fabry-Perot etalon are highly desirable since they possess the characteristics of a cost-effective production, high efficiency, and tenability, all at the same time [11–15]. However, conventional planar photonic devices are almost exclusively fabricated on rigid substrates with little mechanical flexibility and thus difficult for application to uneven, humid, and soft surfaces like biological tissues. By imparting mechanical flexibility, planar photonic devices possess an enormous application potential in epidermal sensing, artificial ocular prostheses, and bio-imaging. To date, flexible planar photonic devices have exclusively used synthetic polymers such as polyethylene terephthalate (PET) [16,17], polyimide (PI) [18,19], and polydimethylsiloxane (PDMS) [20,21] which provide weak light-matter interactions due to their low refractive indices, poor biocompatibility, and low water-permeability which all are undesirable traits for biological applications. As far as the application to biological tissues is concerned, both thinning the flexible photonic devices for high conformability and the use of bio-friendly hydrogels for better biotic-abiotic interfaces are exigent requirements.

Silk protein is an attractive material in bio- and nanophotonics due to its favorable traits such as optical transparency, mechanical stability, biocompatibility, and biodegradability [22–26]. Such high-technological features of silk protein led to the replacement of conventional dielectric materials for engineering photonics devices [27,28]. To date, various silk-based photonic devices exist, including lasers [29,30], photonic crystals [31,32], and metamaterials [33]. Moreover, incorporating noble metals in silk nanostructures leads to fully biocompatible photonic devices because of the biocompatibility and the strong adhesion between them [34–36]. The crystallization of silk films by organic solvents or water vapor treatments induces nanochannels of the cross-linked silk molecules (silk hydrogel) [37,38] and subsequently allows for hydratable photonics devices where analytes in aqueous solutions can be permeable [35,36]. This means that the silk hydrogel photonic devices can communicate with fluidic environments like body fluid, desirable for them in their epidermal and human-implantable forms. These properties of the silk film meet the criteria for the fabrication of an ultra-thin MIM resonator that can transform their optical properties according to the operating environment and random surfaces.

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https://doi.org/10.1016/j.optmat.2018.04.054
Received 16 February 2018; Received in revised form 6 April 2018; Accepted 30 April 2018
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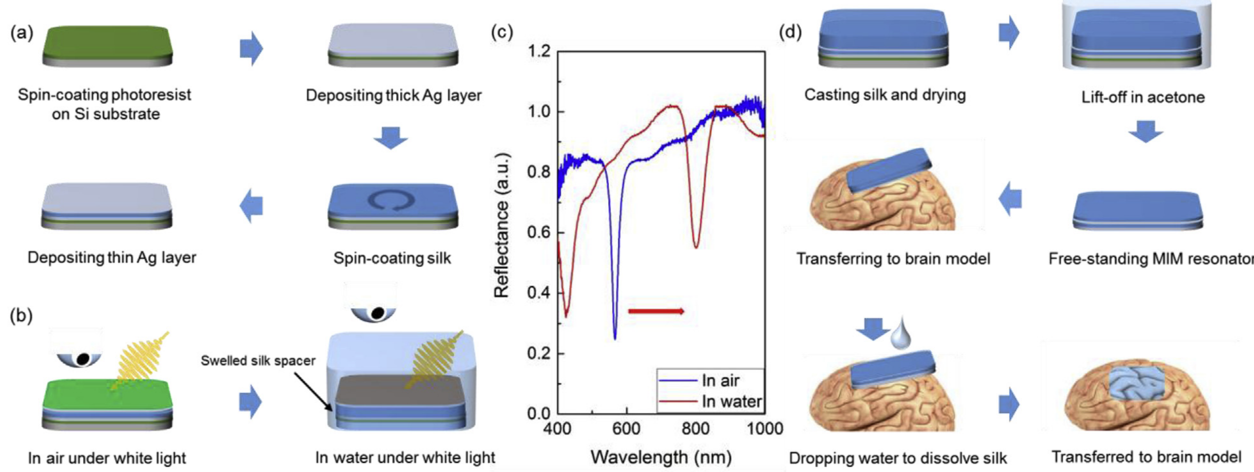

Fig. 1. Ultra-thin, conformal, and hydratable metal-insulator-metal (MIM) resonator. (a) Fabrication steps for the MIM resonator. (b) Schematic images showing water swelling of the silk spacer in the MIM resonator. (c) Reflectance spectra of the MIM resonator in air (blue line) and water (red line). (d) Schematics of the free-standing MIM resonator's preparation and its transfer to an arbitrary surface. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Here, we report conformal, ultra-thin, and water-permeable (hydratable) MIM color absorbers that can be transferred to humid, soft, and/or rough biological surfaces. To create a MIM resonator, the cross-linked silk layer was sandwiched by two planar silver mirrors with a thickness of 200 nm at the bottom and 30 nm at the top. Incident light was strongly localized in the silk layer and absorbed at a resonant wavelength, adjustable by controlling the silk layer's thickness. On the hydrated surface, the resonant wavelength was largely red-shifted due to the swollen silk layer for which the reduced refractive index (RI) and the increased thickness were assessed. We performed experimental and computational wavelength-tuning investigations with the hydration and the angular dependence of the resonance. By adding a sacrificial layer and a carrying silk layer, the ultra-thin MIM color absorber can be transferred to any arbitrary substrate. As a proof-of-concept experiment, the ultra-thin MIM resonator conformed on a contact lens and a human brain model with curved and wrinkled surfaces. The reflectance patterns effectively changed, according to the investigated position. In addition, by taking advantage of the strong light-matter interaction in the swollen silk layer, the MIM color absorber on the contact lens was applied as a refractometric sensor to gauge the glucose concentration in water. Additionally, the good permeability of the silk to gas and water molecules [24,39,40] can enhance the application area of hydrogel silk film when applied to the biological surfaces by adopting a proper device design.

2. Results and discussions

The schemes of the fabrication process and the working principle are shown in Fig. 1. A thin silk film was sandwiched between two Ag layers with a thickness of 200 nm for the bottom layer and 30 nm for the top one to yield a MIM resonator structure on a photoresist-coated silicon substrate. This photoresist layer was used as the sacrificial layer to lift the MIM layer from the substrate. To determine the high absorbance of the resonators, the bottom Ag layer's thickness was set at 200 nm to block a transmission effect, while the optically thin Ag top layer with 30-nm-thick efficiently balanced the localizing and coupling of incident light within the insulating layer. Before depositing the top Ag layer, the silk-insulating layer was hydrogelated by treating it with a methanol solution. An aqueous solution could infiltrate the silk hydrogel layer, subsequently induce swelling, equivalent to the layer's expansion, and reduce the effective refractive index (RI) following which the phenomena drastically changed the resonator's optical

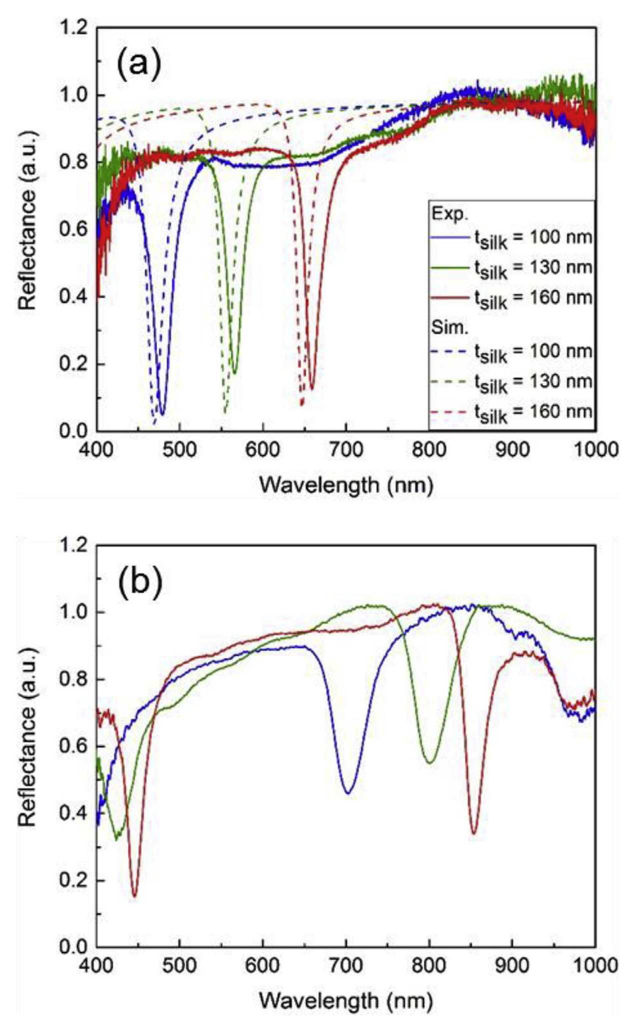

Fig. 2. Optical response of the MIM color absorber. (a) Measured (solid line) and simulated (dashed line) reflectance spectra of the MIM color absorber in air with t_{silk} = 100 nm, 130 nm, and 160 nm. (b) Measured reflectance spectra of the MIM color absorbers in water. The estimated thicknesses of the swollen silk films were 190 (blue line), 230 (green line), and 250 nm (red line), respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)