SILVER-NANOPARTICLE ENHANCED PVA THIN-FILM COLORIMETRIC HUMIDITY SENSOR

Yangxi Zhang[1], Ouyang Xia[1], Kwun Hei Ho[2], Zengtian Liang[1], Dangyuan Lei[2], A. Ping Zhang[1] and Hwa-Yaw Tam[1]*

[1] Photonics Research Centre, Department of Electrical Engineering, The Hong Kong Polytechnic University, Hong Kong SAR, China

[2] Department of Applied Physics, The Hong Kong Polytechnic University, Hong Kong SAR, China

ABSTRACT

In this paper, a fast-response colorimetric humidity sensor based on silver-nanoparticle (AgNP) enhanced polyvinyl alcohol (PVA) thin-film interferometer is reported. The AgNPs are directly printed on a titanium dioxide (TiO_2) capped quartz substrate via precision photoreduction technology. Compared with a single layer of PVA film, this PVA-AgNP-TiO_2 structure displays more brilliant and abundant colors. The colorimetric sensor can rapidly respond to humidity change in air, and the measured rise time of response is 87 ms. Such fast-response colorimetric sensors have great potential for many applications, such as breath analysis and smartphone camera-based biochips.

KEYWORDS

Silver nanoparticles, colorimetric sensor, humidity sensor, thin-film interferometer

INTRODUCTION

Colorimetric analysis is a well-established sensing method by comparing the color of samples. Thanks to the human eye's spectral color sensitivity, colorimetric analysis is one of the most convenient methods in biomedical analysis and industrial purposes, due to the simplicity and low detection limit [1]. Recently, modern smartphones with high-resolution RGB cameras and ultra-high signal processing capability facilitate new progress in colorimetric analysis and showed significant advantages over traditional platforms, such as high speed, large data management ability, and friendly user interfaces [2]. The development enables high-speed real-time monitoring and raises new need for fast-response colorimetric sensors.

One of promising technologies for colorimetric analysis is structural color approaches, which have advantages over traditional ones in terms of response-range tuning and label-free sensing [3]. Many photonic structures and devices, such as 1D (dimensional) gratings, 2D and 3D photonic crystals, holographic structures, and Fabry–Pérot resonant cavity have been demonstrated for colorimetric sensing [3]. However, the response of the sensors with multilayer sensing film is typically slow due to diffusion nature, while complex nanostructured photonic sensors are commonly expensive and hard to fabricate. A potential solution to these technical bottlenecks is thin-film interferometers, which uses a single layer of responsive hydrogel to form a thin-film interference for color generation [4]. However, to achieve discernible color change, a considerable thickness is required for thin-film interferometers, which thus still limits response time within certain level.

In this paper, we report a fast-response colorimetric sensor based on a nanoparticle-enhanced thin-film interferometer. A directly printed thin layer of AgNP is used to enhance the color of a humidity-responsive PVA film. This combination can not only provide a means to adjust the color spectrum without change in film thickness, but also increase the sensitivity of the colorimetric sensor. In the experiments, a colorimetric sensor array based on AgNP enhanced responsive PVA thin-film was fabricated for humidity sensing. Testing results showed that the color became more brilliant with the addition of AgNPs, and the colors can fast respond to the change of humidity for real-time monitoring.

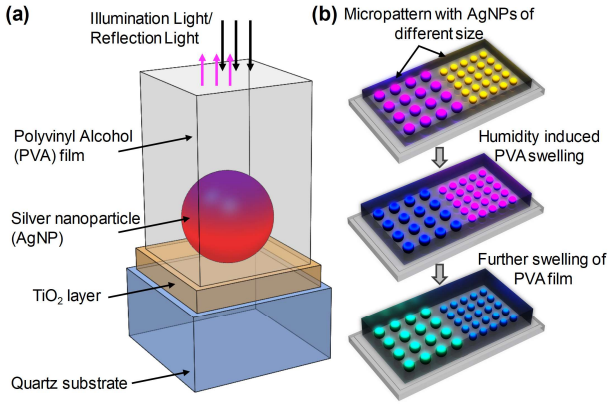

Figure 1: Schematics of the PVA-AgNP-TiO_2 structure of the colorimetric humidity sensor (a) and its working principle (b).

METHOD

For a thin-film colorimetric sensor, the diffusion of target substances in responsive film is the key factor of response time. From the diffusion theory, Fick's second law described that the diffusion time for a specified concentration is proportional to the square of diffusion depth, which thus requests a thin film for fast-response applications. However, the film thickness of a thin-film interference sensor is constrained by the color generation at visible range.

To reduce film thickness in thin-film interference sensor, we designed a nanoparticle enhanced thin-film structure for sensing and fabricated an AgNP enhanced colorimetric humidity sensor array. The structure of the sensor is illustrated in Fig.1. The sensor contains a quartz substrate with TiO_2 layer, a single-particle layer of AgNPs for plasmon-based color enhancement, and an ultra-thin layer of PVA for humidity sensing. When the humidity of

the external environment increases, the PVA film absorbs moisture from air and then its thickness increase and refractive index slightly reduces. Therefore, an obvious color change will be induced because of the shift of its reflection spectrum. In particular, the particle size of AgNPs can be used to tune the reflection spectrum of the thin-film interference. Therefore, micropatterns array of silver particles with different sizes can be fabricated for colorimetric analysis. The color of the sensor can be collected by a Bayer filter image sensor on commercial camera for signal demodulation and analysis.

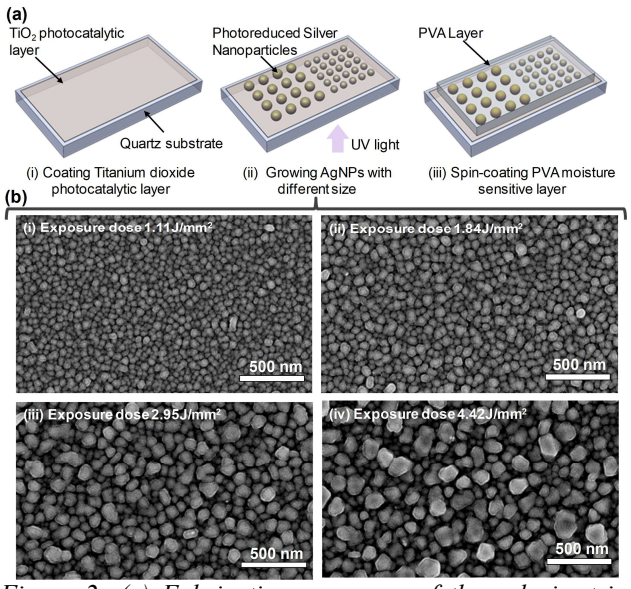

Figure 2: (a) Fabrication processes of the colorimetric humidity sensor. (b) SEM images of the AgNPs grown via precision photoreduction. As the exposure dose increases, the particle size also increases. All those samples are printed on the same substrate.

Figure 2 shows the fabrication processes of the sensor array. First, AgNPs are directly printed on a substrate via a precision photoreduction process with an in-house optical 3D μ-printing platform [5]. The advantage of this printing process is that it can simultaneously produces particles with different sizes on one substrate. The dimension of AgNP (typically 10~100 nm) can be precisely customized by UV exposure dose, as shown in Fig. 2 (b). This AgNP was grown upon TiO_2 photocatalytic layer (~10 nm) which is spin-coated on a quartz sheet by sol-gel method. Second, 5% PVA aqueous solution is spin-coated upon the plasmonic substrate as a humidity sensitive film (typically 60~100 nm), to form the particle-film composite structure.

RESULTS

PVA films with different thicknesses by adjusting spin-coating speed were used to evaluate the individual effects of particle size and film thickness in a particle-film composite structure, as shown in Fig. 3. All data were measured on 50% relative humidity (RH) and 25°C room temperature with microscope and spectrometer on microscope. The spectra of the samples both depends on the dimension of AgNPs and the thickness of PVA film. With the increase of the exposure dose for larger AgNPs (see Fig. 2(b)), the spectral dip shifted to the longer wavelength direction, and the contrast was significantly increased. The result indicates that the introduction of AgNPs can enhance the color of the thin-film interferometer and the modulation of the color response of the PVA-AgNP-TiO_2 structure. When the thickness of PVA film is increased by reducing spin-coating speed (Fig. 3(b)), a clear color change from yellow to blue was observed.

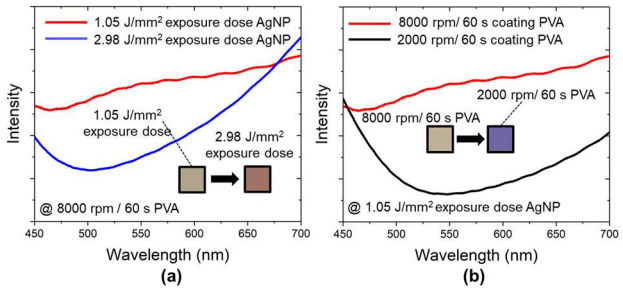

Figure 3: Comparison of reflection spectra and colors of different samples with different size (increase with exposure dose in growth) of silver nanoparticles (a) and different thicknesses (decrease with spin-coating speed) of PVA film (b).

Moreover, a colorimetric sensor array with a 65.6-nm thick PVA film (thickness was measured by SEM in vacuum) was fabricated and tested, as shown in Fig. 4 and Fig. 5, respectively. Each sensor has a distinct micropattern of AgNPs, whose average size is different to the AgNPs of other sensors. Hence, the sensor array provides abundant color data for colorimetric analysis. The high resolution of our micro-printing process greatly reduces the overall size of the device. A sample with gradually changed color, in which particles of different sizes were printed on one micropattern to improve visible color contrast for direct human eye detection, as shown in Fig. 4(a). Such gradually changed color pattern provides a clear and easily distinguishable color change for humidity analysis. The measured colors of the sensor array with respect to humidity change are summarized in Fig. 4(b). It shows that the color changes significantly in the range of 70 %~100 % RH. Compared to the sample with only PVA-TiO2 film coated on quartz substrate (i.e. the last row with 0 exposure dose in Fig. 4(b)), the samples with AgNPs exhibited more significant color changes. Such a sensor array can provide multidimensional color information through inter-comparison.

The hue degree of the sensor's color was quantitatively analyzed. Photographs of Fig. 4(a) and the original photos of Fig. 4(b) were taken by commercial cameras with microscope lens. Through the Bayer filter of the camera's digital RGB image sensor, the color information on visible spectrum is transformed into RGB (red, green, blue) components for calculation of HSL (hue, saturation, lightness). Experimental results revealed that the hue value can clearly represent the humidity change as the samples' color changes from yellow to purple to blue-green. The comparison between two samples with AgNPs of different sizes is given in Fig.4(c). In comparison with the commonly used high-refractive-index silicon substrate, as shown in Fig. 4(d), this plasmonic substrate (AgNP-TiO_2-

quartz) can provide higher hue sensitivity.

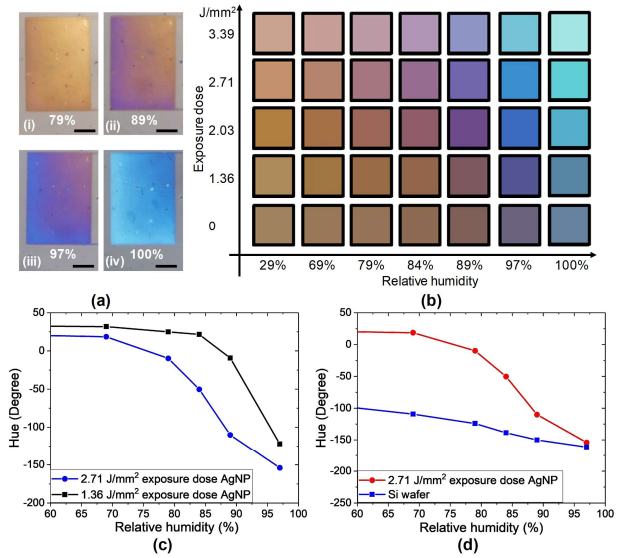

Figure 4: Testing results of a colorimetric humidity sensor. (a) Optical microscope photo of a micropattern with gradually changed color at different humidity enviorments (scale bar 50 μm). (b) Dependence of the colors on humidity and exposure dose in AgNPs growth. (c, d) Change of the color hue with respect to relative humidity, on different substrates.

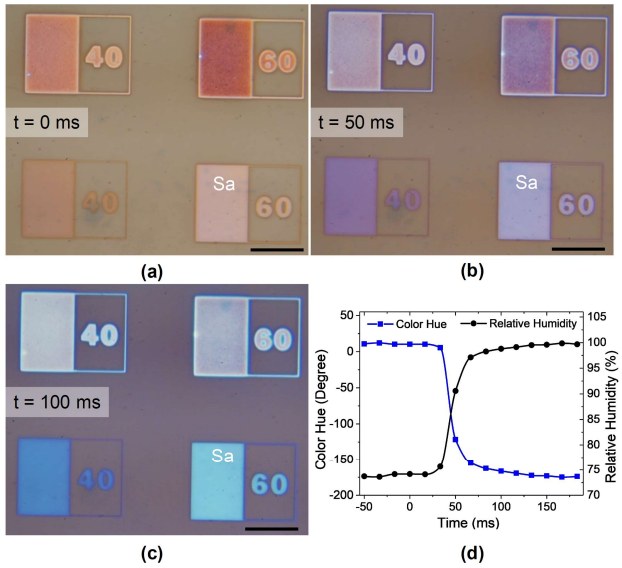

Figure 5: Measured responses of the colorimetric humidity sensor in human breathing gas testing. (a)~(c) Optical microscope photos of the sensor at diffent time points (scale bar 150 μm). (d) Measured color hue (from sample pattern Sa in (a)~(c)) and calculated relative humidity with respect to time.

Because of the thin PVA film, this sensor has fast response. To test the response speed of the fabricated sensor, optical microscope photos of the color change of the sensor during a very short period of time are shown in Fig 5(a)~(c). The images were taken by a commercial camera at the speed of 60 fps. After image processing, the change of hue with respect to time was obtained, and the measured humidity curve was calculated, as shown Fig.5 (d). The measured rise time of the sensor is as short as 87 ms. This sensor has faster response than the thin-film colorimetric humidity sensors with 100-ms-level response time [4, 6, 7], and is comparable with ultra-fast resistance humidity sensors based on graphene oxide or silicon-nanocrystal [8].

CONCLUTIONS

In this paper, we reported a fast-response colorimetric humidity sensor based on AgNP enhanced PVA thin-film interferometer. AgNPs can enhance color information of the thin-film sensor, and greatly improve the response speed by reduction of the film thickness. Such a sensor structure can be utilized not only in humidity sensing, but also for other thin-film colorimetric sensors based on responsive films. It is believed that such a colorimetric sensor is very promising for real-time monitoring and non-contact detection applications, such as breath analysis and smartphone camera-based biochips.

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CONTACT

* A.Ping Zhang, E-mail: azhang@polyu.edu.hk