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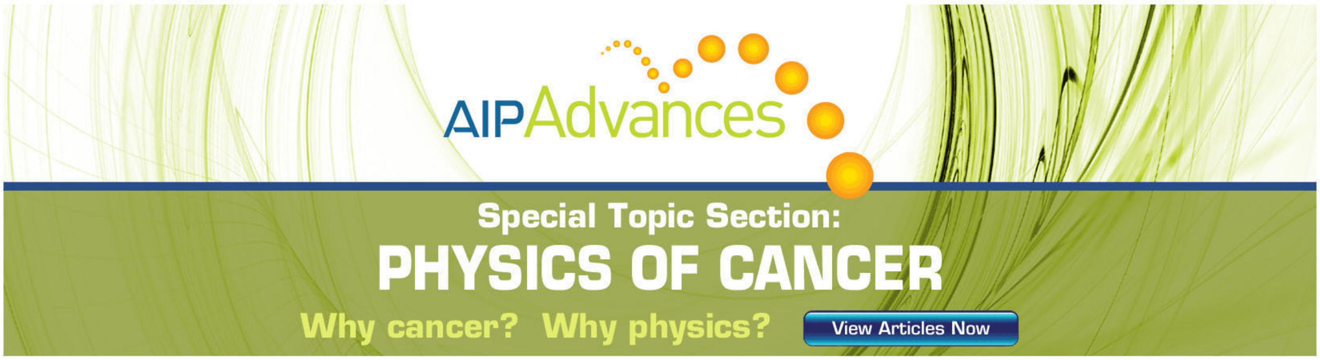

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Biologically inspired humidity sensor based on three-dimensional photonic crystals

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This letter presents a biomimetic humidity sensor inspired by the humidity-dependent color change observed in the cuticle of the Hercules beetle. A thin-film-type humidity sensor with nanoporous structures (three-dimensional photonic crystals) mimicking the spongy multilayer in the beetles was designed and fabricated using the colloidal templating method and a hydrophilic surface treatment. The visible color of the fabricated humidity sensor changes from blue-green to red as the environmental humidity increases. The wavelength of reflected light that is predicted by Bragg's equation considering the effect of water absorption shows a good agreement with experimental results. © *2010 American Institute of Physics*. [doi:10.1063/1.3486115]

Nature provides remarkably effective and optimal mechanism and design of sensing and actuation. The development of microelectromechanical systems and nanotechnology has made it possible to realize the micro/nanodevices that mimic optimal functions or structures found in nature. Many groups have reported various types of biomimetic devices by emulating biological systems such as hair cells, lateral lines, odour recognition mechanism, etc.[1] Structural coloration in nature, such as butterfly wings, beetle cuticles, fish, and peacock feathers, has attracted considerable attention in various research fields, and it has inspired optical devices.[2,3] Structural color is caused by the interaction of light with periodic microstructures rather than pigments. Recently, Rassart *et al.*,[4] analyzed the structural mechanism for the optical response of a tropical beetle, *Dynastes hercules*, which can be changed by its exposure to humidity. The elytra from the beetle appear khaki-green in a dry atmosphere and turn into black under high humidity levels as shown in Fig. 1. The visible dry-state greenish coloration originates from a open porous layer located at 3 μm below the cuticle surface. This layer has three-dimensional photonic crystal structures, which are a network of filamentary strings, arranged in layers parallel to the cuticle surface [Fig. 1(d)]. In dry state, nanosized holes in the layer are occupied with air (refractive index 1) but the empty holes are filled with water (refractive index 1.33) under high humidity. The change in refractive index with respect to the humidity level induces the variation in the visible color.

In this study, we present a biomimetic humidity sensor based on the principle and design of the structural coloration in the cuticle of the beetle and analyze the characteristics of the proposed humidity sensor. Generally, humidity sensors are widely used in measurements and control applications, including process control, meteorology, agriculture, and medical equipment.[5,6] Many humidity sensors have been developed with various physical principles, such as capacitive,[7] resistive,[8] mechanical,[9] and oscillating type.[10,11] These conventional sensors need externally wired electronics for measurements, causing electrical noise and complicated fabrication process. However, the proposed humidity sensor measures directly the level of humidity using the spectrum of visible light without electrical transducers. Moreover, the simple fabrication process and visible measurement technique make the humidity sensor applicable to various areas. Previously, a few researchers reported humidity sensing using photonic crystal hydrogel[12,13] but their sensing mechanism mainly depends on the quantity of expansion in hydrogel structures according the absorption level of environmental humidity. The photonic crystal based humidity sensor reported by Barry and Wiltzius[12] showed the narrow bandgap shift, 31 nm, which makes it difficult to detect the color change with the human eyes. The senor by Tian *et al.*[13] used a complex fabrication process and showed the large volume change over 200%, which can induce the decrease in durability.

To mimic the nanoporous structures found in the cuticle, the colloidal templating method was used as shown in Fig. 2. Colloidal crystals based on silica nanoparticles (diameter:

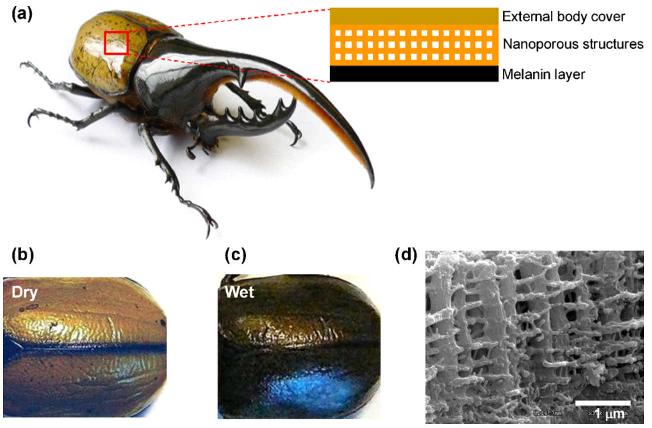

FIG. 1. (Color online) (a) Photograph of a Hercules beetle. The exoskeleton of the Hercules beetle changes from (b) khaki-green in a dry atmosphere to (c) black in high humidity level. (d) SEM image of the cuticle of Hercules beetle.

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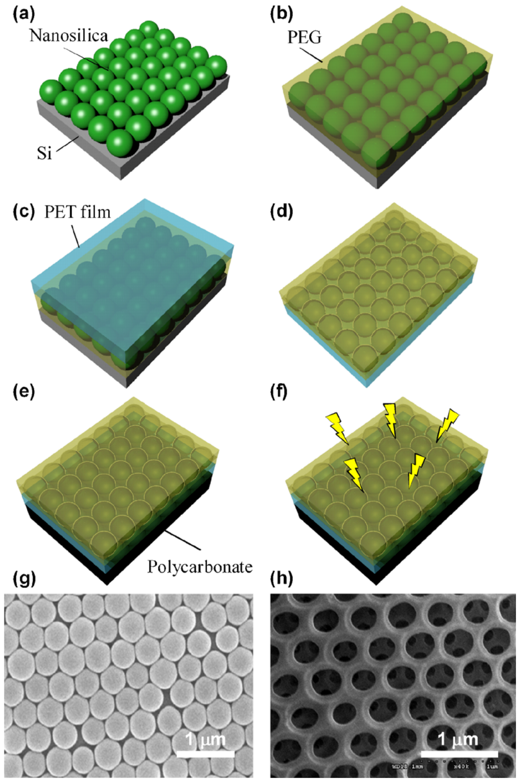

FIG. 2. (Color online) Fabrication process of the proposed humidity sensors and resultant SEM images.

275 nm) were assembled on Si substrates from colloidal solution using dip-coating deposition [Fig. 2(a)].[14] After drying is complete, the colloidal crystals were immersed into photocurable poly (ethylene glycol)-diacrylate (PEG-DA) solution for 5 min [Fig. 2(b)]. PEG-DA solution was prepared from 99 wt % PEG-DA [Aldrich, molecular weight (MW) 258] and 1 wt % of a water-soluble photoinitiator 2-hydroxy-2-methylpropiophenone photoinitiator (Aldrich).[15] Then, a polyethylene terephthalate (PET) film was covered on it and the sample was exposed to UV (250–400 nm) for a few tens of second 90 mW/cm^2 [Fig. 2(c)]. Since the surface of PET film was modified with urethane groups to increase adhesion to the acrylate-containing monomer, the polymerized PEG-DA layer with the PET film was peeled off from Si substrate using a tweezer. The resultant inverse opal structures were obtained by wet etching of the silica nanoparticles in buffer oxide etchant [Fig. 2(d)]. As shown in Fig. 1(a), the cuticle is composed of the external body cover, nanoporous structures and a black melanin layer. Similarly, a black polycarbonate film was bonded with the PET film [Fig. 2(e)]. A PEG based copolymer with the flat surface is hydrophilic but it becomes hydrophobic when its surface has the patterned nanostructures.[16] Therefore, in order to make the fabricated inverse opal structures hydrophilic, O_2 plasma surface treatment was applied [Fig. 2(f)]. This surface treatment process is essential step to humidify the empty nanosized holes easily. Figures 2(g) and 2(f) show the scanning electron microscopy (SEM) images for the colloidal crystals and its inverse structures after wet etching, respectively. This fabricated period nanoporous structures show similar three-dimensional configuration with the porous layer found in the cuticle of the Hercules beetle.

A customized humidity chamber was designed in order to provide and control the humidity to the sample and to help measuring the reflectance spectra through a bifurcated optic fiber by removing the external light. The bifurcated optic fiber was used to illuminate the sample and to collect the backscattered light. Using this fiber, measurements were carried out in a backscattering conformation at normal incidence, that is, the incidence of light is normal to the surface of the sample and measurements were also taken at normal to the surface. The humidity level was measured with high-precision miniature humidity/temperature transmitter (EE80 series, E+E elektronik) in real-time and it was installed near the sample in the customized humidity chamber. Spectrum data were acquired using an optical spectrum analyzer (AQ6315B, Ando), which was connected with the bifurcated optic fiber. The sample was illuminated by a white light source (AQ4303B, Ando).

The resulting reflected wavelength in the fabricated film type sensor can be predicted by Bragg's equation for normal incidence as follows:[17]

$$\lambda = 2dn_{\text{eff}}, \tag{1}$$

where λ is the peak wavelength of reflected light, $d=0.816D$ is the interlayer spacing in the [111] direction, $D=275\ \text{nm}$ represents the diameter of nanoporous holes, and η_{eff} is the effective refractive index of the sample. The effective refractive index of a two-phase structure can be estimated as follows:[18]

$$n_{\text{eff}} = fn_{\text{air}} + (1-f)n_{\text{PEG}}, \tag{2}$$

where $f=0.74$ is the void fraction of the porous structures for an ideal fcc package, and $\eta_{\text{air}}=1$ and $\eta_{\text{PEG}}=1.49$ represent the refractive index of air and PEG-DA materials, respectively. When water penetrates into nanoporous structures, the effective refractive index becomes

$$n^*_{\text{eff}} = fn_w + (1-f)n_{\text{PEG}}, \tag{3}$$

where $n_w=1.33$ is the refractive index of water. The photonic bandgap shift (the change in the peak reflected wavelength) due to the water penetration can be calculated as $\Delta\lambda=2d(n^*_{\text{eff}}-n_{\text{eff}})$.

If we assume that there is no swelling in PEG-DA material (interlayer spacing d is fixed), the bandgap shift from the dry state to wet state can be estimated as $\Delta\lambda=109.6\ \text{nm}$ where the reflective wavelengths in dry and wet states are 505.97 nm and 615.57 nm, respectively.

Figure 3(a) shows the reflectance spectra of the proposed humidity sensor when it is exposed to various humidity conditions. The peak wavelength of the reflective light increases as the humidity becomes higher. The initial color of the sensor was blue-green when the humidity was 25% and the color change from green, yellow, orange to red when the relative humidity increased from 40%, 80%, 90% to 98%, respectively. Figure 3(b) represents the effect of plasma surface treatment that makes the nanoporous structure hydrophilic. Without this surface treatment, the bandgap shift in the sample was only 14 nm when the relative humidity was changed from 25% to 98%. However, after plasma surface treatment, the shift increased with 137 nm dramatically under the same condition. This bandgap shift is about 20% larger than the estimated theoretical value, $\Delta\lambda=109.6\ \text{nm}$. This discrepancy seems to be mainly due to the ignorance of the swelling in PEG-DA materials in analytical model. In order to minimize the swelling effect of PEG-DA backbone,

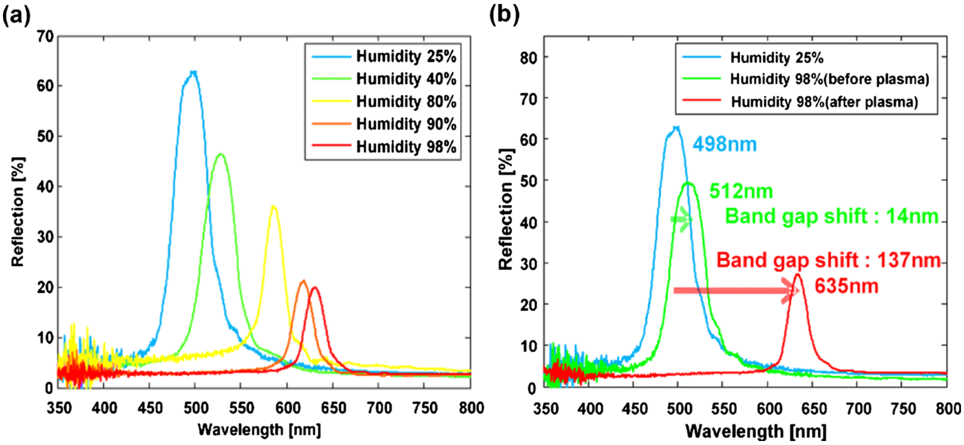

FIG. 3. (Color online) (a) Corresponding reflectance spectra of the humidity sensor under various humidity conditions. (b) Plasma surface treatment effect: The photonic bandgap shift increased dramatically from 14 to 137 nm in reflectance spectra of the humidity sensor after surface treatment, when the sensor is exposed to high humidity (98%).

we used PEG-DA with low MW (258).[19] It is noted that the main contribution of the bandgap shift is the water penetration into nanosized holes. We repeated the same experiments using various samples with different hole sizes and observed similar discrepancies (20%) between analytical predictions and experimental data.[20] These results support the principle of humidity-dependent color change found in the cuticle of beetle.[4] Figure 4 describes the photograph images [Figs. 4(a) and 4(b)] and microscope images [Figs. 4(c) and 4(d)]. The structural color change observed in the sample was clearly visible when it was exposed to the environmental humidity. The sample shows blue-green color in dry state and it turns into red color in high humidity level.[20] These photograph images indicated that the change in color in the sample can be detected and distinguished by the naked eyes. Moreover, the humidity-dependent color variation was valid over hundreds of cyclic experiments, showing its good durability and repeatability as a humidity sensor.

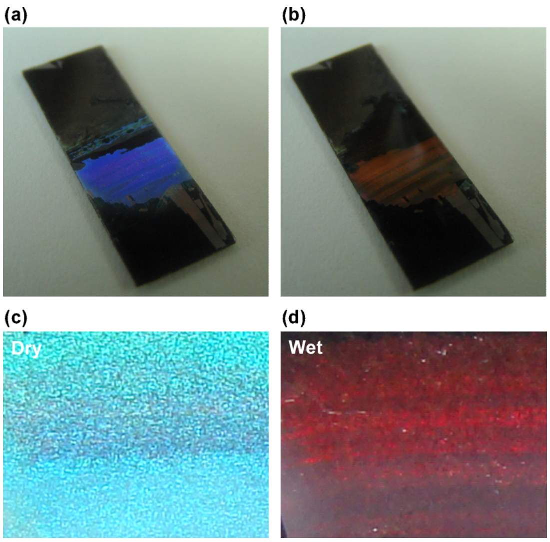

FIG. 4. (Color online) Photographs show the color change in the biomimetic sensors with relative humidity. (a) Light gray (blue-green) color in dry state turned into (b) dark gray (red) color in wet state (almost 100% relative humidity), which were taken on a digital camera. Microscope images show the dry state (c) and the wet state (d) of the presented film. Supplementary movie shows the *in situ* color change in the humidity sensor from the wet state to the dry state, which was observed under microscope (enhanced online). [URL: http://dx.doi.org/10.1063/1.3486115.1]

In conclusion, a film-type humidity sensor inspired by the photonic crystal structure of the cuticle of Hercules beetle was designed and fabricated. The reflective color of the fabricated sample changes from blue-green to red with the bandgap shift of 137 nm when increasing humidity, which could be discriminated by human eyes. The analytical prediction on the bandgap shift by Bragg's equation showed a good agreement with the experimental results. This proposed bioinspired artificial sensor offers alternative sensing mechanism to quantify the environmental humidity in a simple and effective way.

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[20] See supplementary material at http://dx.doi.org/10.1063/1.3486115 for description of another experimental case and the movie showing the color change from wet to dry state.