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## Antifogging antireflective thin films: Does the antifogging layer have to be the outmost layer? †

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**Unusual antifogging antireflective thin films with the maximum transmittance of 98.9% have been realized surprisingly by depositing a hollow silica nanoparticles layer on top of an antifogging polymer layer, which was considered as an irrational design according to the previous knowledge.**

Fog causes image distortion and reduces light transmittance. In practical applications, antireflective thin films simultaneously with antifogging property are highly desired in daily used eyeglasses, goggles, lenses, mirrors, analytical and medical optical instruments and so forth<sup>1</sup>. Superhydrophilic thin films, with water contact angle less than 5° within 0.5 s, attribute their excellent antifogging behavior to the rapid spreading of condensing water droplets on the surface<sup>2</sup>, but generally require complicated procedures to fabricate surface structures or TiO<sub>2</sub> thin films which however require UV illumination<sup>3</sup>. Moreover, the antifogging property derived from superhydrophilicity usually fades with time due to the loss of superhydrophilicity. Rubner and Cohen recently found that a thin film does not have to be superhydrophilic to be effectively antifogging<sup>4</sup>. Very recently, we reported a facile one-step approach to construction of self-healing antifogging thin films on the basis of partly cross-linked poly(vinyl alcohol)(PVA) and poly(acrylic acid)(PAA)<sup>5</sup>. When water molecules in moist air from a warmer environment start to condensate on the antifogging surface, the water molecules are rapidly absorbed into the hydrophilic domains of the polymer<sup>6</sup> by hydrogen bonding and dipole-dipole interaction, preventing microdroplets from forming on the thin film surface. Because of the hydrophilicity and hygroscopicity of the polymer thin film, the polymer film demonstrates excellent long-term antifogging property.

Many efforts have been devoted to the construction of multifunctional thin films that exhibit antifogging and antireflective

properties, including constructing superhydrophilic inorganic surfaces<sup>1,7</sup>, combining polymers with low reflective inorganic materials<sup>8</sup>, and constructing porous or moth-eye structures of polymers<sup>9</sup>. The identical feature among them is that the antifogging layer always acts as the outmost surface. This traditional notion may pose a major obstacle to the design of many multifunctional materials. For example, the application of antifogging layer on top of antireflective layer was found to significantly lower the transmittance of coated substrate. It is also difficult to fabricate antifogging conductive thin films because both layers are supposed to be placed at the outmost surface. In the current work, we first constructed an antifogging thin film of partly cross-linked poly(vinyl alcohol)(PVA) and poly(acrylic acid)(PAA), and then deposited hollow silica nanoparticles on the polymer thin film by dip-coating. Surprisingly, we attained a composite thin film with both antifogging and antireflective properties. To our best knowledge, no artificial surfaces have been reported so far to have an inner antifogging layer but simultaneously possess highly antireflective and excellent antifogging properties. These results may circumvent the obstacle that “the antifogging layer has to be the outmost layer”, and would significantly promote the device of multifunctional materials by rational arrangement of varied functional components in nano-dimensional space.

The formation process of thin films is schematically illustrated in Fig. 1a. Following coating the polymer thin layer, hollow silica nanoparticles were deposited upon the polymer thin film. By changing the number of dip-coating from the hollow silica nanoparticles suspension, we obtained polymer coated glass and hollow silica nanoparticles (HSNs)/polymer coated glasses (including 1HSNs/polymer, 2HSNs/polymer, 3HSNs/polymer coated glasses). High transmittance of 98.9% was attained simultaneously with excellent antifogging property. The surface morphology of 2HSNs/polymer coated glass was observed by scanning electron microscopy (SEM) (Fig. 1b). It is noted that hollow silica nanoparticles are closely packed on the polymer thin film. And, there are many voids, pores and cracks in the hollow silica nanoparticles layer, which allow access of water molecules to the hydrophilic and hygroscopic polymer layer. The average outer and inner diameters of hollow silica nanoparticles were estimated to be 41 nm and 19 nm, respectively, from transmission electron microscopy (TEM) observations (Fig. 1c). The average thickness of the inner polymer layer is about 7.1 μm from the side view SEM image (Fig. 1d). The adhesion between the polymer layer and the nanoparticles layer should mainly derive from Wan der Waals force and hydrogen bonding interaction.

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† Electronic Supplementary Information (ESI) available: methods to prepare partly cross-linked poly(vinyl alcohol)(PVA) and poly(acrylic acid)(PAA), hollow silica nanoparticles and thin films; characterization of the thin films: Fig. S1 Images of water contact angles on (a) blank glass, (b) 2HSNs coated glass, (c) polymer coated glass, and (d) 2HSNs/polymer coated glass; Fig. S2 ATR-FTIR spectrum of the polymer thin film. See DOI: 10.1039/x0xx00000x

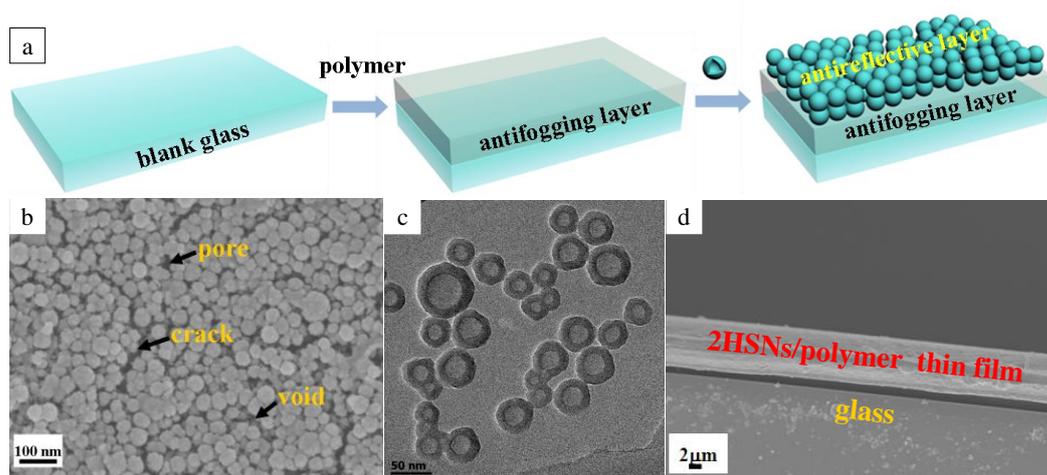


Fig. 1 (a) Schematic illustration of the formation process of antifogging antireflective thin films, (b) SEM image of the 2HSNs/polymer thin film coated glass, (c) TEM image of the HSNs, and (d) side view SEM image of the 2HSNs/polymer thin film coated glass.

Transmission spectra of blank glass and glasses coated, respectively, by polymer, 1HSNs/polymer, 2HSNs/polymer, 3HSNs/polymer are shown in Fig. 2a. Clearly, the deposition of polymer thin film only slightly changed the transmittance of glass substrate, but the further deposition of hollow silica nanoparticles significantly changed the transmittance. Therefore, the antireflective property is derived from the HSNs layer with low refractive index. As shown in Fig. 2e (Table), the 2HSNs/polymer coated glass has, among the listed specimens, the highest maximum transmittance of

strong light scattering of tiny water droplets. In contrast, the polymer coated part (Fig. 3b) and 2HSNs/polymer coated part (Fig. 3c) remained highly transparent, the words below being clearly visible. Therefore, the antifogging property of 2HSNs/polymer coated glass does not derive from HSNs, but is attributed to the polymer thin layer although it is not located at the outmost surface. Thus, the polymer coated glass and 2HSNs/polymer coated glass exhibit excellent antifogging behavior in sharp contrast to blank glass and the 2HSNs coated glass.

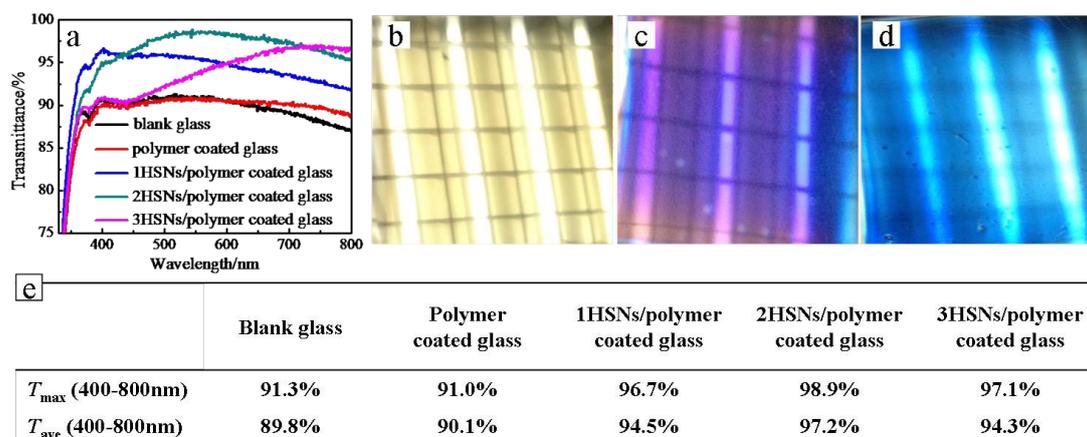


Fig. 2 (a) Transmission spectra of blank glass and glasses coated, respectively, by polymer, 1HSNs/polymer, 2HSNs/polymer, and 3HSNs/polymer. Digital images of the interface reflection toward a fluorescent lamp on the surface of 1HSNs/polymer coated glass (b), 2HSNs/polymer coated glass (c), and 3HSNs/polymer coated glass (d). (e) Table | Maximum transmittance ( $T_{\max}$ ) and average transmittance ( $T_{\text{ave}}$ ) in the wavelength range of 400-800 nm of blank glass and glasses coated, respectively, by polymer, 1HSNs/polymer, 2HSNs/polymer, and 3HSNs/polymer.

98.9% and the highest average transmittance of 97.2% in the wavelength range of 400–800 nm, while blank glass has the maximum transmittance of 91.3% and the average transmittance of 89.8% in the identical wavelength range. Digital images of the interface reflection toward a fluorescent lamp on the surface of 1HSNs/polymer, 2HSNs/polymer, 3HSNs/polymer coated glasses are shown in Fig. 2b-d. Thus, the optical performance and interface reflection color could be effectively tuned<sup>10</sup>.

As shown in Fig. 3, when the substrates partly coated by 2HSNs, polymer and 2HSNs/polymer, respectively, were cooled at  $-6^{\circ}\text{C}$  for 24 h in a refrigerator, and then exposed to humid laboratory air (relative humidity (RH): 20%-40%), the uncoated and 2HSNs coated part (Fig. 3a) fogged immediately, the words below being blurred by

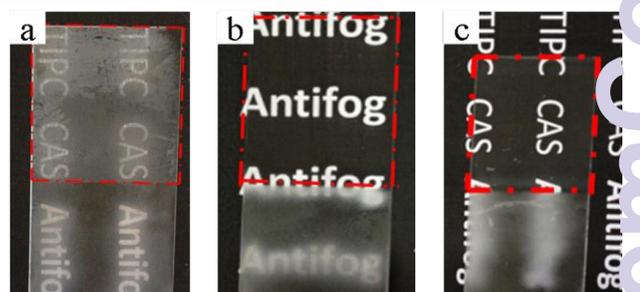
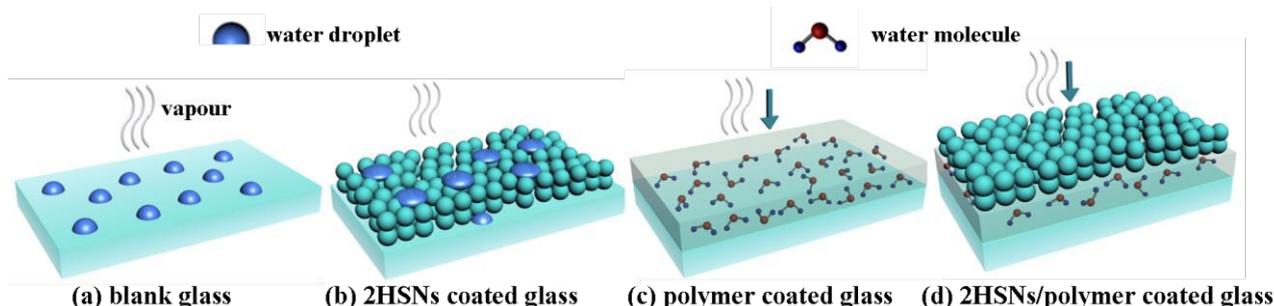


Fig. 3 Digital images exhibiting the antifogging property of (a) 2HSNs, (b) polymer, and (c) 2HSNs/polymer coated glasses (upper part) and blank glasses (lower part).



Scheme 1 Schematic illustration of the behavior of water vapour when encountering (a) blank glass, (b) 2HSNs coated glass, (c) polymer coated glass, and (d) 2HSNs/polymer coated glass, respectively. Water droplets formed on blank glass and the 2HSNs coated glass, while water vapour was absorbed into the polymer layer on the polymer coated glass and 2HSNs/polymer coated glass.

The water contact angles on blank glass, 2HSNs coated glass, polymer coated glass and 2HSNs/polymer coated glass are  $49.4^\circ$ ,  $18.0^\circ$ ,  $56.8^\circ$ ,  $37.5^\circ$  (Fig. S1), respectively. None of them are superhydrophilic. Therefore the antifogging property of 2HSNs/polymer coated glass does not derive from the traditional superhydrophilic antifogging mechanism. The antifogging mechanism of the polymer was investigated by attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) and quartz crystal microbalance (QCM). ATR-FTIR analysis (Fig. S2) of the polymer thin film shows two characteristic peaks, of which the broad band at  $3300\text{ cm}^{-1}$  is attributed to the hydroxyl group, and the band at  $1703\text{ cm}^{-1}$  originates from the carbonyl group of ester. Clearly, even after the esterification reaction, the polymer maintains sufficient free hydroxyl groups. As discussed above, there are many voids, pores and cracks in the hollow silica nanoparticles layer through which water molecules can transfer, and thus the water molecules can be rapidly absorbed into the hydrophilic domains of the polymer layer<sup>5</sup> by hydrogen bonding and dipole-dipole interaction, preventing microdroplets from forming on the composite thin film surface. The absorption of water molecules must give rise to a corresponding mass change. The mass change of polymer thin film arising from the antifogging test was monitored by quartz crystal microbalance (QCM). The QCM measurements indicate that the amount of water absorbed by the polymer ( $6.78 \times 10^{-9}\text{ g}$ ) was  $3.69 \times 10^{-10}\text{ g}$ . In other words, the thin film weight increased by nearly 5.45wt% because of the absorption of water. These experimental results are in accordance with the work we have recently reported<sup>5</sup> with only difference in the weight of absorbed water. Therefore, the antifogging property of 2HSNs/polymer coated glass derives from the hygroscopicity of the polymer layer although it is not located at the outmost surface.

When a surface encounters moist air of higher temperature, fog usually forms during the first few seconds of contact. Antifogging behavior at the first stage is extremely important, since the subsequent fogging may be less severe or even diminished because of the adaptation of surface to the environmental temperature and humidity in a while.<sup>6</sup> Scheme 1 illustrates the behavior of vapour in the antifogging test when encountering blank glass and the 2HSNs, polymer, 2HSNs/polymer coated glasses, respectively, during the first few seconds of contact. Water droplets formed on blank glass and the 2HSNs coated glass during the first few seconds of contact with vapour, while the vapour was absorbed into the polymer layer on the polymer coated glass and 2HSNs/polymer coated glass. The average thickness of polymer thin film is  $7.1\text{ }\mu\text{m}$  from the side view SEM image (Fig. 1d), meaning there is sufficient volume to accommodate water molecules. The hygroscopicity of the polymer thin film is the intrinsic driving force while the voids, pores, and cracks in the HSNs layer provide the passway for vapour, accounting for the excellent antifogging property. And the antifogging property of 2HSNs/polymer coated glass remains even after a storage of 1 year.

In conclusion, we successfully attained unusual antifogging-antireflective functional thin films. The antifogging property mainly derives from the hygroscopicity of the polymer layer which is located in the inner space rather than at the outmost surface, while the antireflective property is attributed to the low refractive index of the hollow silica nanoparticles layer. The hygroscopicity of the polymer thin film is the intrinsic driving force while the voids, pores, and cracks in the HSNs layer provide the passway for vapour, accounting for the excellent antifogging property. What is the most important finding is that the antifogging thin film is not necessarily to be at the outmost surface. To our best knowledge, no synthetic surfaces reported so far possess highly antireflective and excellent antifogging properties with the antifogging layer in the inner space. This work represents a breakthrough to the traditional design notion "The antifogging layer has to be the outmost layer". And the dramatic innovation and remarkable notion "The antifogging layer does not have to be the outmost layer" would promote the device of multifunctional materials in consideration of various components with rationally tailored orders in space.

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