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Design of ZnO hollow nanosphere arrays for UV absorbing transparent glasses

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Abstract We present ZnO hollow nanosphere (HNS) arrays on glass substrate for high-efficient UV absorbing transparent glasses. Diffraction efficiencies of the proposed ZnO HNS arrays were calculated using a rigorous coupled wave analysis method. The results show the effect of design parameters, such as diameter, aspect ratio, and fill factors, on the optical characteristics. The analysis based on effective medium theory also supports the calculation results. Detailed design guidelines for optimum geometry are also discussed.

Keywords UV shielding · Hollow spheres · Nanostructure · Zinc oxide

1 Introduction

Excessive exposure to ultraviolet (UV) rays in sunlight causes deterioration of physical/chemical properties in glasses, polymers, and wooden substrates. Prolonged exposure of solar UV radiation to human body also result in acute and chronic health problems on the skin, eye and immune system (Diffey 1998). Shielding from UV irradiation based on inorganic UV absorbers (i.e., zinc oxide (ZnO), cerium oxide (CeO_2), and titanium dioxide (TiO_2), etc.) have been extensively studied for applications in cosmetics, automobiles, and

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bio-medical tools (Jaroenworaluck et al. 2006; Hanley et al. 2008; Morimoto et al. 1999). For automobile or window applications, various methods have been reported to develop transparent UV-absorbers, such as thin-film coating of single or complex oxides on transparent materials, synthesis of micro- or nano-sized oxide particles, multilayer coatings, and bandgap engineering of these materials (Morimoto et al. 1999; Hwang et al. 2003; Lima et al. 2012). By contrast, less attention has been paid to the optical design of such structures for improving optical properties. Although currently available transparent UV-absorbers provide strong UV absorption and comparable clarity in visible ranges, important details related to the transmittance/absorbance were not optimized. For instance, ZnO coated glasses show inherent low transmittance in the visible ranges due to high refractive index discontinuity at air/ZnO/glass interfaces. Control of ZnO density and thickness of coated layer is also very crucial to obtain both strong absorption and high transmission in the UV and visible region, respectively. Other materials have similar tendencies.

Recent advancement on the synthesis of ZnO nanoparticles allows preparation of ordered, monolayer hollow structures with controllable sizes and shapes (Deng et al. 2008; Chen et al. 2011; Yin et al. 2012; He et al. 2013). Such ZnO hollow nanosphere (HNS) arrays have gained much attention due to their high surface/volume ratio, which could be used in energy storage, sensing and biomedical devices (Wang et al. 2012; Dong et al. 2012; Fang et al. 2011). In this paper, we introduce ZnO HNS arrays, instead of conventional ZnO thin-films or nanoparticles, for highly transparent UV absorbing glasses. Based on the rigorous coupled-wave analysis (RCWA) method, we calculate diffraction efficiency of ZnO HNS arrays on glass substrates with different diameter, aspect ratio, and fill factor. We also discuss the optimum geometries in order to obtain high transmittance without scattering in the visible wavelength ranges while sustaining strong UV absorption.

2 Simulation results and discussion

Figure 1 shows schematic illustrations (left) and refractive index (RI) profiles (right) of (a) a conventional ZnO thin film and (b) proposed ZnO HNS arrays on a glass substrate. UV absorbing oxide materials including ZnO has a refractive index of $\sim$2.1, which is much higher value than that of glass substrate ($n_g \sim 1.5$), resulting in strong Fresnel reflection. Such negative effect can be minimized by introducing ZnO HNS arrays with an adequate aspect ratio (i.e. pore size over diameter of HNS). Since the effective RI of subwavelength structures is determined by the volume weighted average refractive index of air and structures, the ZnO HNS could provide the effective RI of $\sim$1.5, which is similar to that of glass substrate, as indicated in right of Fig. 1b. Such hollow sphere generate two peaky points in the effective index distribution, however, it does not affect the optical characteristics, because the thicknesses are very small.

To confirm the optical properties of these HNS structures, we first calculated transmitted diffraction efficiencies in the wavelength range of 300–800 nm, based on RCWA method (DiffractMod, RSoft Design Group, USA). RCWA represents the electromagnetic fields as a sum over coupled waves (Moharam 1988). A periodic permittivity function is represented using Fourier harmonics. Each coupled wave is related to a Fourier harmonics, allowing the full vectorial Maxwell's equations to be solved in the Fourier domain. The diffraction efficiencies are then calculated at the end of simulation in order to obtain the total reflectance. In this calculation, we used monolayer of ZnO HNS with a sixfold

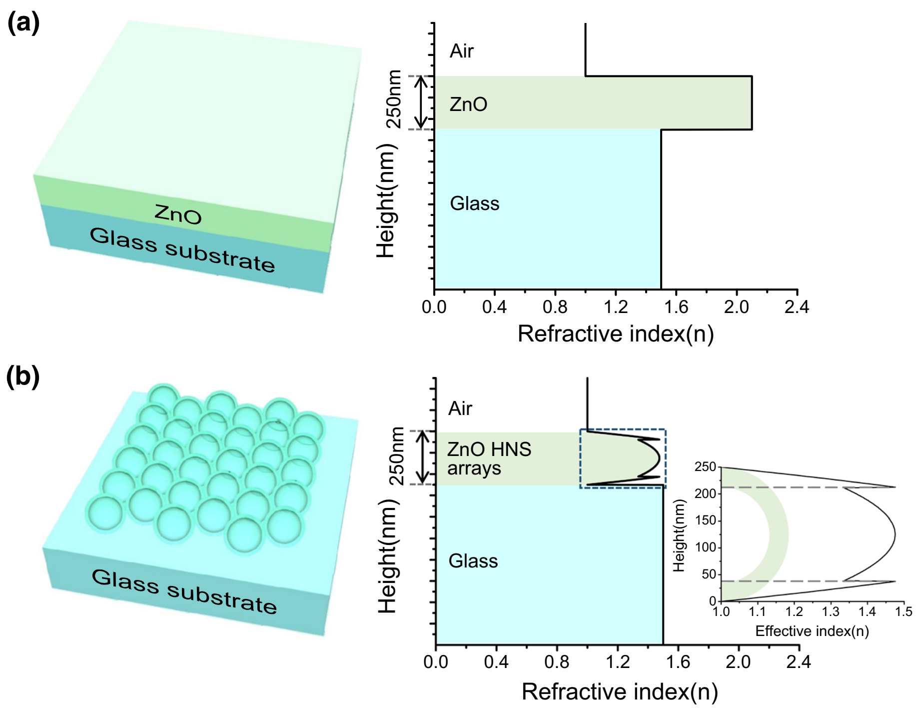

Fig. 1 Schematic illustrations (*left*) and refractive index (RI) profiles versus height (*right*) of UV absorbing transparent glasses with **a** a conventional ZnO thin-film and **b** ZnO hollow nanosphere (HNS) arrays. RI of each material at 450 nm were considered. The effective RI of ZnO HNS was calculated from the packing fraction of ZnO

hexagonal symmetry. Fifth diffraction order and grid size of 5 nm were used to calculation the diffraction efficiency, which is enough to stabilize the results numerically. The RI value for the ZnO and borosilicate glass were taken from the literature and SCHOTT optical glass data sheets, respectively (Yoshikawa and Adachi 1997, SCHOTT http://us.schott.com/sgt/english/products/catalogs.html). Materials dispersion with Sellmeier formulae are as below:

$$n^2 - 1 = \frac{1.03961212\lambda^2}{\lambda^2 - 0.00600069867} + \frac{0.231792344\lambda^2}{\lambda^2 - 0.0200179144} + \frac{1.01046945\lambda^2}{\lambda^2 - 103.560653} \quad (1)$$

$$n^2 = 2.81418 + \frac{0.87968\lambda^2}{\lambda^2 - 0.3042^2} + 0.00711\lambda^2 \quad (2)$$

for the borosilicate glass (1) and the ZnO (2), respectively. Extinction coefficients were also considered for obtaining exact outputs.

The UV protection effect is given by high extinction coefficient of ZnO at UV region, as depicted in Fig. 2a. On the other hand, the presence of extinction coefficient at 400–500 nm generate an adverse effect on the transmittance in this region, together with index discontinuity between ZnO and glass substrate. Figure 2b, c shows the calculated transmittance spectra for (b) the conventional ZnO thin-film and (c) the ZnO sphere arrays with and without pores. As depicted in Fig. 2b, the coating of ZnO thin-film on glass

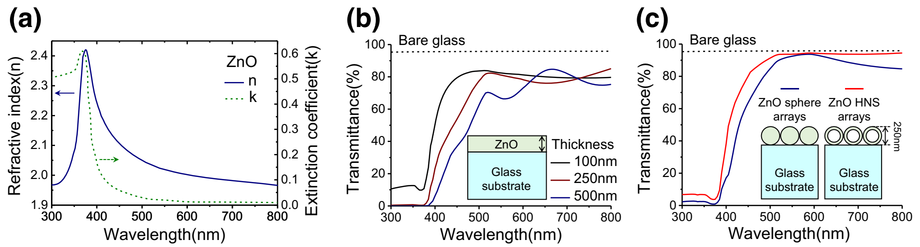

Fig. 2 **a** Refractive index and extinction coefficient spectra of ZnO as a function of wavelength, and transmittance spectra of glasses with **b** a ZnO thin-film with three different thicknesses (i.e., 100, 250, and 500 nm), and **c** ZnO sphere arrays and ZnO HNS arrays with an aspect ratio of 70 %. The diameter of both sphere and HNS are 250 nm

substrate affords strong UV absorption, while it shows much lower transmittance (~80 %) compared to that of bare glass (~96 %, single side), regardless of the thickness variation. On the other hand, ZnO HNS arrays with a diameter of 250 nm and aspect ratio of 70 % exhibit transmittance of ~92 % in the whole visible region, maintaining UV transmission of less than ~8 %. The ZnO nanospheres also improve the transmittance, but it has lower transmittance than that of ZnO HNS due to mild change of effective RI.

In order to optimize the geometry of ZnO HNS, we conducted calculations with different diameters, pore sizes, and packing fractions, all of which are in the reasonable ranges on the fabrication side. Figure 3a shows the effect of thickness variation (from 100 to 500 nm) of ZnO HNS arrays (with an aspect ratio of 70 %) on the transmittance. The aspect ratio is defined by the ratio between the pore size and diameter. As indicated, smaller diameter of HNS have a relatively low absorption, resulting in higher transmission in the UV wavelength ranges. This low absorption can be improved with an increment of diameter. However, over a diameter of ~300 nm, transmission band tends to decrease as the diameter increases. This negative effect is caused by higher order diffraction as well as increased absorption. Figure 3b shows the electrical field intensity distribution of ZnO HNS arrays with a diameter of 250 and 500 nm, respectively, at a wavelength of 500 nm. Since ZnO HNS arrays with a diameter of 250 nm is in the subwavelength regime, the plane wave passes smoothly through the structures without any scattering (Leem et al.

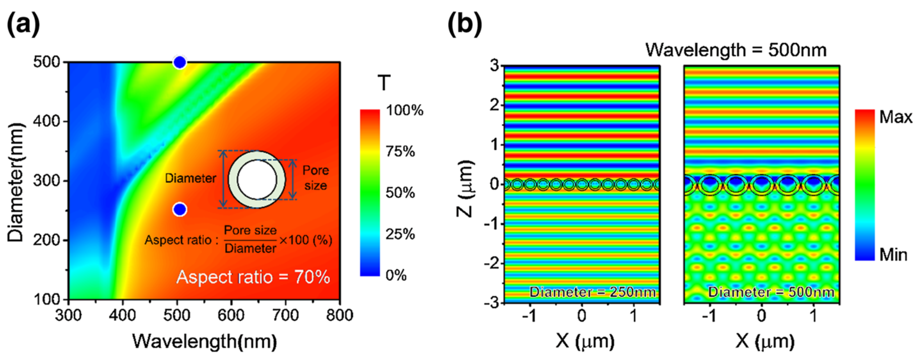

Fig. 3 **a** Contour plot of the transmittance variations for ZnO HNS arrays as a function of diameter and wavelength, and **b** Electrical field intensity distributions of ZnO HNS arrays with a diameter of 250 and 500 nm, respectively, at a wavelength of 500 nm. The aspect ratio of HNS is 70 %

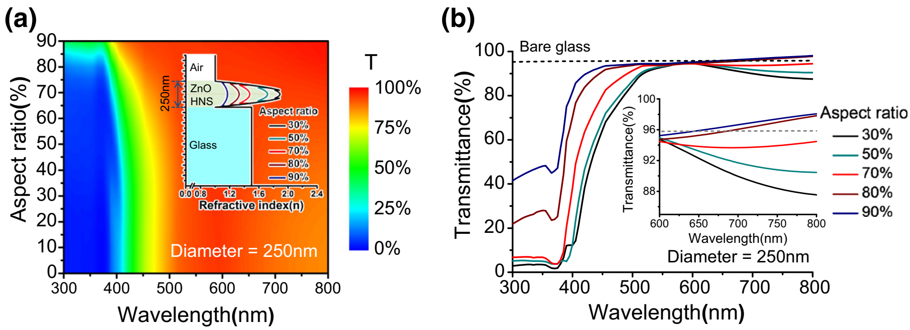

Fig. 4 **a** Contour plot of the transmittance of ZnO HNS arrays with 250 nm diameter, as a function of aspect ratio and wavelength. The inset shows refractive index profiles of ZnO HNS arrays with five different aspect ratios (i.e., 30, 50, 70, 80, and 90 %). **b** Transmittance spectra of ZnO HNS arrays with 250 nm diameter for 30, 50, 70, 80 and 90 % aspect ratios. The *inset* shows the enlarged transmittance spectra at 600–800 nm

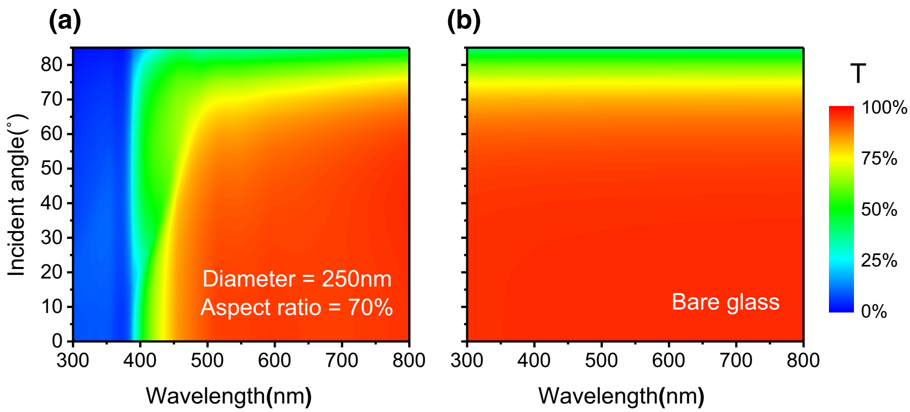

Fig. 5 Contour maps of angle dependent transmittance of **a** ZnO HNS arrays with an optimized geometry (i.e., 250 nm diameter and 70 % aspect ratio) on a glass substrate and **b** bare glass (as a reference). In this calculation, non-polarized light transmittance was calculated through the averaging of the transmittances for p and s linear polarizations, respectively

2011). By contrast, ZnO HNS with a diameter of 500 nm generate distinct higher order transmission, which leads low haze in window applications.

Figure 4 shows the influence of the aspect ratio of ZnO HNS on the transmittance for diameter of 250 nm. As indicated in Fig. 4a, UV protection effect can be attained with ZnO HNSs with the aspect ratio of <70 %. The aspect ratio also has a trade-off between UV absorption and transmission at visible wavelength. Depending on the aspect ratio, effective refractive index is remarkable changed from ~1.1 (at 90 %) to ~1.9 (at 30 %), as depicted in the inset of Fig. 4a. These variations strongly affects to the transmission characteristics, especially at longer wavelength ranges (Inset of Fig. 4b). In case of aspect ratio of over 80 % even provide higher transmittance than that of base glass because the HNS acts as an antireflection coating. However, these designs are not adequate for UV protection due to deterioration of UV absorption. The ZnO HNS arrays with an aspect ratio of ~70 % exhibit best optical performance at both UV and visible wavelength ranges.

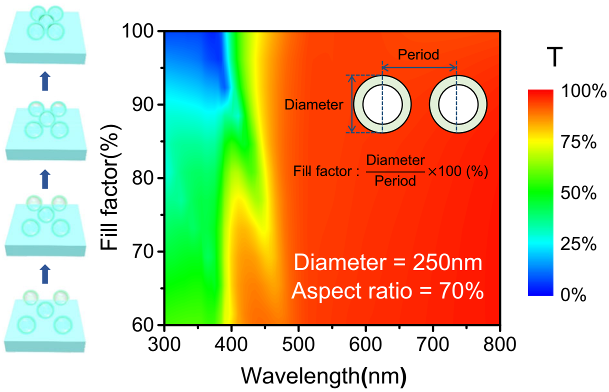

Fig. 6 Contour plot of the variation of transmittance of ZnO HNS arrays with different fill factors from 60 to 100 %. The diameter and aspect ratio was fixed to 250 nm and 70 %, respectively

The influence of the incident angle of light on the transmittance is crucial for the transparent glass applications. The HNS arrays with an optimized geometry (i.e., diameter of 250 nm, aspect ratio of 70 %, closely packed structure) shows omni-directional high transmittance in the visible region, which is comparable to that of bare glass, while sustaining UV absorption, as shown in Fig. 5. Slight degradation of transmittance near 430 nm at an incident angle of 40°–70° is attributable to the extended optical path length. Figure 6 shows the effect of fill factor of HNS arrays, which is also controllable during the fabrication, on the transmission characteristics. The fill factor is defined by the ratio between the period and diameter. As the fill factor decreases, it reduces the amount of blocking the UV light due to the reduced probability of UV absorption. Since the lower fill factor means the higher period, high order transmission of visible light can occur at a low fill factor. With the fill factor of >90 %, the UV shielding performance of ZnO HNS arrays provides comparable to that of closely packed structure (i.e., fill factor of 100 %).

3 Conclusion

By calculations of diffraction efficiencies of ZnO HNS arrays on glass substrate using RCWA method, we investigated the effects of geometrical parameters (i.e., diameters, aspect ratio, and fill factors) of ZnO HNSs on the optical performance of UV absorptive transparent glasses. From the calculation results, it is found that closely packed ZnO HNS arrays with a diameter of 250 nm and aspect ratio of 70 % provide superior optical characteristics. It is believed that the concept of ZnO HNS arrays and design guidelines would be helpful to various UV shielding applications.

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References

Chen, M., Hu, L., Xu, J., Liao, M., Wu, L., Fang, X.: ZnO hollow-sphere nanofilm-based high-performance and low-cost photodetector. Small **7**, 2449–2453 (2011)

Deng, Z., Chen, M., Gu, G., Wu, L.: A facile method to fabricate ZnO hollow spheres and their photocatalytic property. J. Phys. Chem. B **112**, 16–22 (2008)

Diffey, B.L.: Ultraviolet radiation and human health. Clin. Dermatol. **16**, 83–89 (1998)

Dong, Z., Lai, X., Halpert, J.E., Yang, N., Yi, L., Zhai, J., Wang, D., Tang, Z., Jiang, L.: Accurate control of multishelled ZnO hollow microspheres for dye-Sensitized solar cells with high efficiency. Adv. Mater. **24**, 1046–1049 (2012)

Fang, B., Zhang, C., Wang, G., Wang, M., Ji, Y.: A glucose oxidase immobilization platform for glucose biosensor using ZnO hollow nanospheres. Sens. Actuators B **155**, 304–310 (2011)

Hanley, C., Layne, J., Punnoose, A., Reddy, K.M., Coombs, I., Coombs, A., Feris, K., Wingett, D.: Preferential killing of cancer cells and activated human T cells using ZnO nanoparticles. Nanotechnology **19**, 295103–295122 (2008)

He, X., Yue, C., Zang, Y., Yin, J., Sun, S., Li, J., Kang, J.: Multi-hot spot configuration on urchin-like Ag nanoparticle/ZnO hollow nanosphere arrays for highly sensitive SERS. J. Mater. Chem. A **1**, 15010–15015 (2013)

Hwang, D.K., Moon, J.H., Shul, Y.G.: Scratch resistant and transparent UV-protective coating on polycarbonate. J. Sol–Gel. Sci. Technol. **26**, 783–787 (2003)

Jaroenworaluck, A., Sunsaneeyametha, W., Kosachan, N., Stevens, R.: Characteristics of silica-coated TiO2 and its UV absorption for sunscreen cosmetic applications. Surf. Interface Anal. **38**, 473–477 (2006)

Leem, J.W., Song, Y.M., Yu, J.S.: Broadband wide-angle antireflection enhancement in AZO/Si shell/core subwavelength grating structures with hydrophobic surface for Si-based solar cells. Opt. Express **19**, A1155–A1164 (2011)

Lima, J.F., Martins, R.F., Serra, O.A.: Transparent UV-absorbers thin films of zinc oxide: ceria system synthesized via sol–gel process. Opt. Mat. **35**, 56–60 (2012)

Moharam, M.G.: Coupled-wave analysis of two-dimensional dielectric gratings. Proc. SPIE **883**, 8–11 (1988)

Morimoto, T., Tomonaga, H., Mitani, A.: Ultraviolet ray absorbing coatings on glass for automobiles. Thin Solid Films **351**, 61–65 (1999)

SCHOTT'96 for Windows Catalog Optical Glass, Schott Glaswerke Mainz, Germany, 1996. Available from http://us.schott.com/sgt/english/products/catalogs.html

Wang, L., Lou, Z., Fei, T., Zhang, T.: Templating synthesis of ZnO hollow nanospheres loaded with Au nanoparticles and their enhanced gas sensing properties. J. Mater. Chem. **22**, 4767–4771 (2012)

Yin, J., Zang, Y., Yue, C., Wu, Z., Wu, S., Li, J., Wu, Z.: Ag nanoparticle/ZnO hollow nanosphere arrays: large scale synthesis and surface plasmon resonance effect induced Raman scattering enhancement. J. Mater. Chem. **22**, 7902–7909 (2012)

Yoshikawa, H., Adachi, S.: Optical constants of ZnO. Jpn. J. Appl. Phys. **36**, 6237–6243 (1997)