Inkjet Printed Hollow Silica Nanoparticles for Anti-Reflective Coatings

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Abstract

Patterned anti-reflective (AR) film using hollow silica nanoparticles (HSNPs) was achieved by inkjet printing technology. Various refractive indices for optimizing AR coating on different substrates were controlled by tuning the void space and wall thickness of HSNPs. Highly enhanced mechanical resistance could also obtained by combining HSNPs and its binder.

Introduction

Hollow silica nanoparticles (HSNPs) are regarded as a promising material for anti-reflective coating (ARC) due to their tunable void space and cage-structured shells. Various coating techniques such as spin coating and dip coating have been applied to ARC films on the multiple substrates. However, these methods would not satisfy the patterning the films and coatings on the curvature substrates. Inkjet printing with accurate control the film thickness is introduced to obtain uniform films in diverse substrates. For example, a multiplayer anti-reflective film with 3.2% out of 4% enhancement in visible range could be obtained by controlling the film thickness. Inkjet printer can also enable the computer-designed patterns in millimetre scale print onto substrates like phone screen. Therefore, inkjet printing has become increasingly attractive for various applications such as thin-film transistors[1,2,3]. solar cells[4,5], sensors[6], biological and pharmaceutical engineering[7].

In this study, HSNPs were synthesized by a fed batch reaction utilizing polyacrylic acid (PAA) and tetraethyl orthosilicate (TEOS) as the template and precursor, respectively. Subsequently, inkjet printer was used both to control the ARC film thickness and to obtain the designed patterns; especially a feasible and stable HSNPs ink for inkjet printer with high adaptability to multiple applications is developed. Finally, we investigated the transmittance and mechanical resistance of the printed HSNPs thin film, and then optimized the reflective indices of ARC thin films.

Experimental

Chemicals Tetraethyl orthosilicate (TEOS, reagent grade, Sigma-Aldrich), poly(acrylic acid) (PAA, MW=5000, Polysciences), ammonium hydroxide (28-30%, MACRON), sodium hydroxide (ACS, MACRON), isopropyl alcohol (ACS, MACRON), ethanol (ACS, MACRON), acetone (ACS, MACRON), and ethylene glycol (Mallinckrodt chemicals) were used as purchased without further purification.

Synthesis of hollow silica nanoparticles (HSNPs) HSNPs were synthesized by a fed batch reaction[8]. 0.12 g of PAA was dissolved into 1.5 mL of NH_3OH, which was then mixed with 30 mL of ethanol. In a separated bottle, 0.75 mL of TEOS was dissolved in 10 mL of ethanol. TEOS solution was pumped into the solution containing PAA and NH_3OH at a flow rate of 0.03 mL min^{-1} with a peristaltic pump (REGLO Digital, Ismatec). The mixed solution was stirred at room temperature for 5 hrs to grow the silica shell on the surface of PAA polyelectrolyte emulsion. Finally, the PAA templates were washed away with deionized water.

Inkjet Print The ink was prepared by adding 20% volume ethylene glycol into as-prepared HSNPs to adjust the viscosity in a printable range. Silica binder in 30% volume was mixed with the ink to bond the nanoparticles together and stick the film onto substrates. The adding of this binder was aiming to enhance the mechanical resistance of the final antireflective thin film after 5 hrs baking at 60 °C. Glass and silicon wafers were used as substrates. The silicon wafers were oxidized so that the surface behaved similarly to the amorphous glass surface. The 2 cm × 2 cm glass and silicon substrates were treated by 1M sodium hydroxide for 4 min, then cleaned with acetone, *iso*-propanol and nitrogen gas by sequence. A Dimatix Materials Printer 2831 was used for the printing experiment at room temperature and 60 °C. Three nozzles out of sixteen ones were used under controlled voltage and waveform of the signal for the stable droplets.

Characterization The UV-Vis transmittance spectra were measured by JASCO V-670 spectrometer. The morphology and size of nanoparticles were characterized by FEI QUANTA 600F scattering electron microscope (SEM) and FEI Titan 80-200 transmission electron microscope (TEM). The mechanical resistance was tested by the Abrasion Test machine with 710 g weight for 100 cycles. Fourier transform infrared spectroscopy (FTIR) was used to measure the remaining PAA after washing by deionized water.

Results and Discussion

Figure 1 shows the TEM and SEM images of as-synthesized HSNPs with an average size of ~30 nm and with a shell thickness of ~10 nm. It can be seen that the inside void space was successfully created by washing away PAA templates with deionized water at room temperature.

FT-IR spectrum (Figure 2) shows that pure PAA has a characteristic peak at 1697.1 cm^{-1} which can be indexed to the carbonyl asymmetric stretching band of unneutralized -COOH[9]. This peak shifted to 1710.7 cm^{-1} due to the bonding with the -OH bond on silica surface when PAA embraced in silica shell. This peak was diminished after washing as shown in Figure 2.

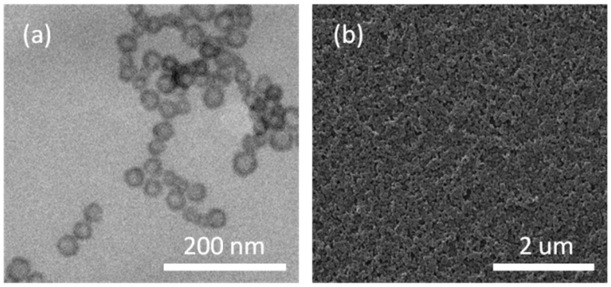

Figure 1. (a) TEM and (b) SEM images of HSNPs.

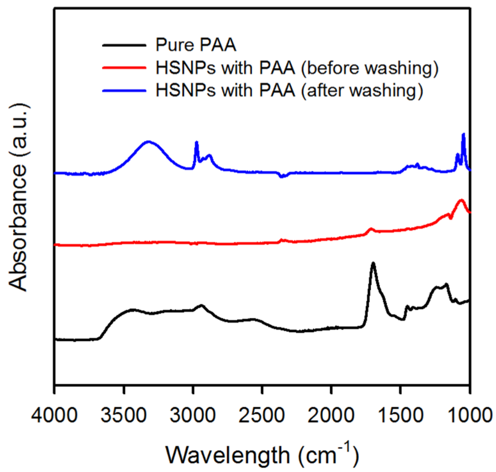

Figure 2. FT-IR spectra of pure PAA and HSNPs before and after washing.

According to the Fresnel equation (eq.1), the reflectance of normal incidence highly depends on the refractive index (RI) which is derived from the light speed in the specific medium with respect to that in vacuum. n_{air}, n_s and n are the refractive indexes of air, substrate, and anti-reflective film, respectively. The HSNPs used in our experiment have a lower RI than solid silica NPs due to their high fill factor of air inside core. This RI is much closer to the value of $\sqrt{n_{air}n_s}$ in which the reflectance is theoretically zero[10].

$$r = \left(\frac{n_{air}n_s - n^2}{n_{air}n_s + n^2}\right)^2 \qquad (1)$$

Additionally, Raut et al.[10] also indicated that the destructive interference could cancel two reflected lights and therefore diminish the reflectance if its thickness is equal to $\lambda_0/4n$. λ_0 is quantified by $\frac{2\lambda_1\lambda_2}{\lambda_1+\lambda_2}$ where λ_1 and λ_2 are the wavelengths to defining the spectral range (the visible range used in this paper is 400-800 nm). In this case, well controlled film thickness also contributes to attenuating the reflectance. Since tailoring the RI of HSNPs is not the main focus of this research, the following discussion would concentrates on the film thickness control by inkjet printer.

To create a smooth and continuous AR coating, drop spacing is one of the important parameters. Figure 3a & 3b show that the high drop spacing at 50 μm generated parallel lines because the drop prints were too far away from each other to form a successive film. In contrast, small drop spacing at 30 μm led to the pile and distorts the pattern. Suitable drop spacing at room temperature was found to be at 35 μm with a smooth and continuous film (Figure 3c). When the substrate temperature was raised to 60 °C for constantly curing the film, the drop spacing should be reduced to 30 μm as the HSNPs migration in the film has been decreased whereas the fast solvent evaporates under high temperature.

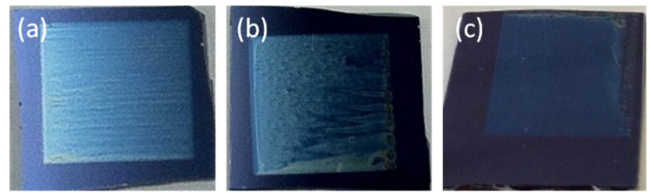

Figure 3. Photograph of printing (a) at 50 µm, (b) at 30 µm, and (c) at 35 µm drop spacing. Lines induced by printing.

After six-cycle inkjet printing at drop spacing of 35 μm on the glass substrate, the transmittance has been enhanced almost 2.5% in average as shown in Figure 4. However, according to the numerical model in our previous work[11], two layers of HSNPs were able to increase the transmittance of glass by 3.8% out of 4%. The inset SEM image in Figure 4 shows that the substrate after 6 cycle printing was not even fully covered by HSNPs which cause the lower transmittance than the model prediction. To build up the film thickness, the HSNPs binder is an essential component to prevent the first-layer nanoparticles redissolving into the solvent of the second layer. Different from the method using opposite charge to create multilayer thin film, our process is to firstly fix each layer onto the substrate by 2 hrs baking at 60 °C. The bonded layer has been covered by -OH bond and subsequently is ready to be coated by a new layer. Herein, as Figure 5 shown, the transmittance from build-up thickness can reach 3.2% in average.

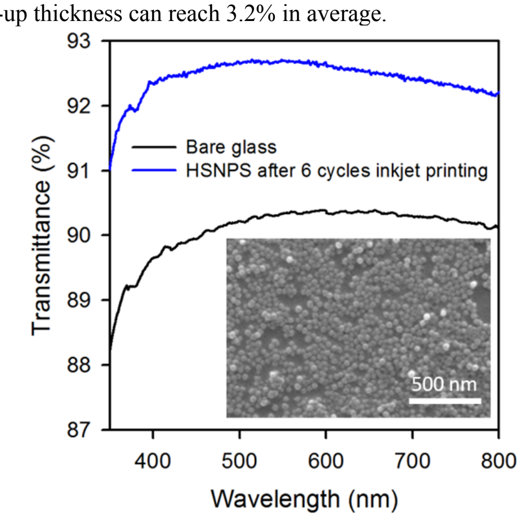

Figure 4. Transmittance 5 cycles inkjet printing of HSNPs on glass (inset of SEM image).

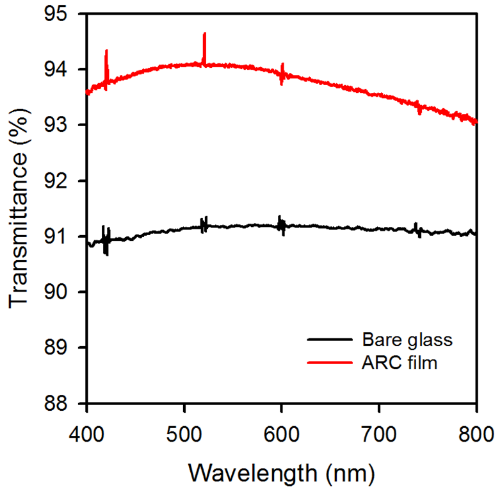

Figure 5. Change in total light transmittance across the visible spectrum of the sample in build-up thickness. Bumps on the spectra are from instrumental errors.

Furthermore, the ink containing 30% vol. binder is able to endure mechanical abrasion. After 100 cycles of abrasion with 710 gram weigh, only 0.3% transmittance in average has been diminished (Figure 6).

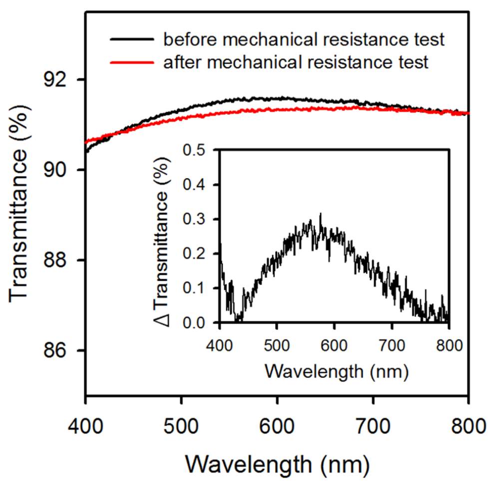

Figure 6. Transmittance of 5 cycles coated sample before and after mechanical resistance test. Insert shows change in total light transmittance across the visible spectrum.

Inkjet printer owns an important advantage is to create computer-designed pattern with the as-prepared ink. In our case, an "OSU" pattern in millimeter was successfully fabricated onto the silicon substrate (Figure 7). A good shape of the pattern was observed by SEM in Figure 7b, however the fuzzy edge and printed lines were noticeable. At high magnification (Figure 7c), the ripple pattern was observed, which is result in the "coffee ring" effects from the Marangoni flow during the evaporation of solvent[9, 12, 13, 14]. To prevent this pattern and increase the printing resolution, a plan to use the mixture of the different solvents in various vapor pressures would be carried out in future.

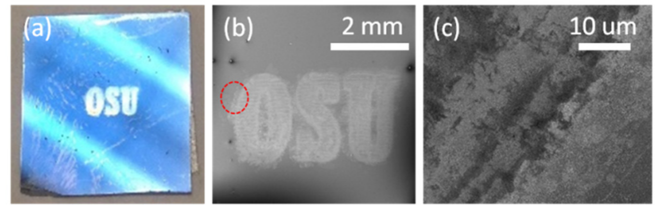

Figure 7. (a) Photograph and (b) SEM image of the "OSU" print of HSNPs. (c) SEM image of the amplified edge of letter "O" dotted by circle in Figure 7b.

Conclusion

HSNPs for ARC film were coated by computer-designed inkjet printing. The transmittance has been enhanced by 3.2% in average with a good mechanical resistance in which the transmittance only decreased 0.3% after the abrasion test. As the current resolution can pattern to sub-millimeter accuracy, we are subject to ongoing investigations on curvature substrates such as lens.

Acknowledgement

The authors grateful thank to Seung-Yeol Han for information and guidance relevant to the binder of silica thin films and the mechanical abrasion test. This project is partially supported by NSF I-Corps IIP-1439485 and NSF STTR phase II award IIP 1230456.

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Chih-Hung (Alex) Chang. Dr. Chang is currently a Professor of Chemical Engineering at Oregon State University. He has more than 80 refereed publications, 8 issued patents, and 4 pending patents in the areas of thin films electronics, nanomaterials, and microreaction technology. He is a co-founder and acting chief science officer of start-up venture CSD Nano, Inc.

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