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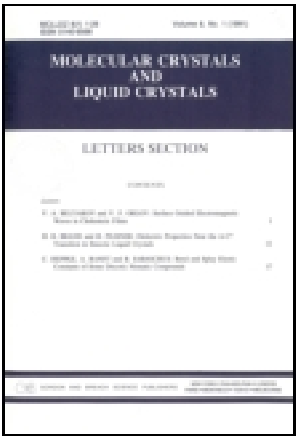

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Synthesis of Macro-Porous Anti-Reflective Materials from the TEOS-PS System for a Solar Cover Glass

No-Kuk Park [a] , Do Hyeong Kim [a] , Min-Jung Kim [a] , Tae Jin Lee [a] , Seung Hyun Lee [b] & Seung Hun Lee [a b]
[a] School of Chemical Engineering, Yeungnam University , 214-1, Daedong, Gyeongsan , Gyeongbuk , 712-749 , Korea
[b] YoungChang Chemical Co. Ltd. , 365-11, Yuseo-ri, Seonnam, Seongju , Gyeongbuk , 719-831 , Korea
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Synthesis of Macro-Porous Anti-Reflective Materials from the TEOS-PS System for a Solar Cover Glass

NO-KUK PARK,[1] DO HYEONG KIM,[1] MIN-JUNG KIM,[1]
TAE JIN LEE,[1,*] SEUNG HYUN LEE,[2]
AND SEUNG HUN LEE[1,2]

[1]School of Chemical Engineering, Yeungnam University, 214-1, Daedong, Gyeongsan, Gyeongbuk 712-749, Korea
[2]YoungChang Chemical Co. Ltd., 365-11, Yuseo-ri, Seonnam, Seongju, Gyeongbuk 719-831, Korea

A mixed polystyrene (PS) and tetra-ethyl-ortho-silicate (TEOS) colloidal solution (TEOS-PS mixture solution) was synthesized for the formation of an anti-reflective layer over glass substrates. Macro pores were formed in the silicon oxide layer due to the decomposition of PS spheres for treatment at high temperatures. The macro pores were approximately 167 nm in size, which is well matched to the size of the PS spherical beads. This anti-reflective agent has the advantage, which can be applied to the simple large area coating process. On the other hand, a TEOS-PS mixture solution was not a stable solution due to its gelation by the hydrolysis of TEOS. Therefore, the macro porous silica layer on a glass substrate can be coated with the TEOS-PS-IPA system for anti-reflection in this study.

Keywords Anti-reflection; macro porous silica; polystyrene nano-beads; TEOS

1. Introduction

The constantly increasing demand for renewable and nonpolluting energy production methods has made solar cells one of hottest research areas. More cost-effective fabrication is one of the key issues in solar cell research [1–3]. Many applications, such as miniaturized chemical analysis systems, would also benefit greatly from low-cost surfaces with low and uniform reflectivity [1,4]. Typically, the suppression of Fresnel reflection is achieved using anti-reflective coatings, but they suppress reflection efficiently only in a narrow wavelength range. The suppression of reflection over a broad spectral range can be achieved using nano-textured surfaces that form a graded transition of the reflective index from air to the substrate. A variety of materials have been used as anti-reflective materials, such as an etched silicon wafer, embossing type polymer, TiO_2 and SnO_2 nano-particles, and ZnO and Si nano-wires etc., and have been developed by many researchers [1,5–6]. On the other hand, the processes for the commercialization of these research products are quite difficult, which is a homogeneous coating, crystal growth, etching and the synthesis of a polymer over a large surface area substrate for anti-reflectance [5,7]. Therefore, this study evaluated

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[*] Address correspondence to Tae Jin Lee, School of Chemical Engineering, Yeungnam University, 214-1, Daedong, Gyeongsan, Gyeongbuk 712-749, Korea. E-mail: tjlee@ynu.ac.kr

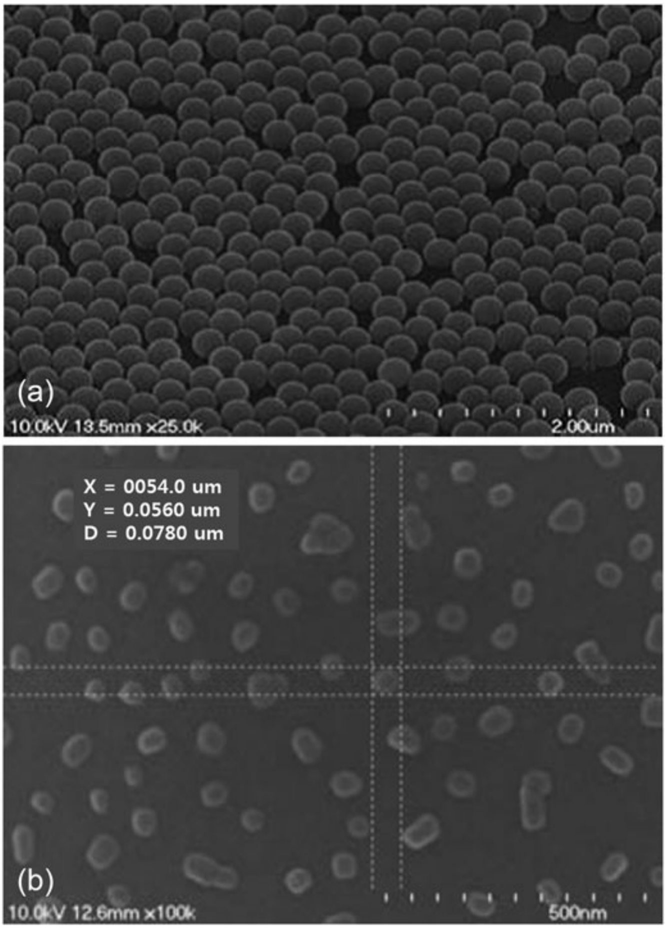

Figure 1. SEM images of PS nano-beads controlled by the styrene monomer content, (a) adding 0.235 mol/L styrene, (b) adding 0.124 mol/L styrene.

a liquid phase agent, a TEOS-PS based solution, to develop a high processing anti-reflective coating system for the anti-reflective of a large surface area substrate. Tetra-ethyl-ortho-silicate (TEOS) was used as a precursor for the formation of a silica layer over the glass substrate. Polystyrene (PS) nano beads were used as an additive for making pores in the silica layer. This technology can be used for the high anti-reflective effect with a coating of a macro-porous silica layer over the glass substrate, and is also a different method compared to a high roughness layer by etching, crystal growth etc. In this study, polystyrene, in which its size is controlled by polymerization, was added to the silica source material for the formation of a macro-porous silica layer as an anti-reflective layer. The solvent of the TEOS-PS system was selected to enhance the stability of the anti-reflective solution.

2. Experimental

2.1 Synthesis of the Polystyrene Colloidal Solution

TEOS (Sigma-Aldrich, $C_8H_{20}O_4Si$, MW: 208.33) as the raw material was used for the formation of a SiO_2 layer over a glass substrate. A PS colloidal solution was also used as

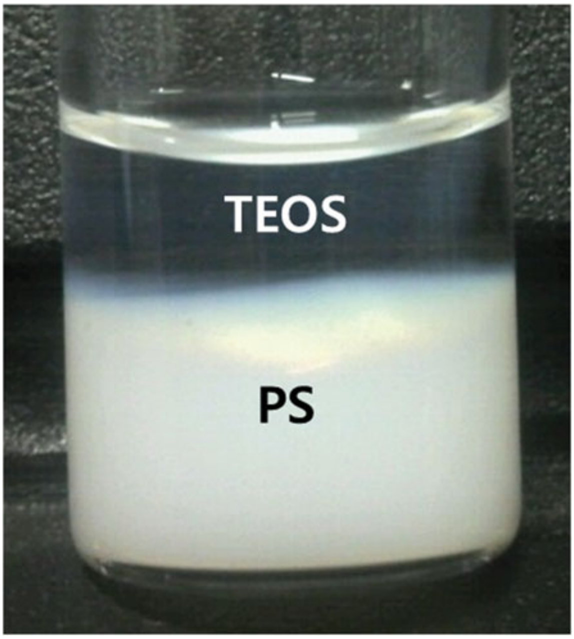

Figure 2. Image of the separating phase between the TEOS and PS solutions.

an additive for the formation of pores in the SiO_2 layer, and was synthesized as spherical type particles by the polymerization of a styrene monomer (Sigma-Aldrich, $C_6H_5CH{=}CH_2$, MW: 104.15). Their size was controlled with the amount of styrene monomer added. The PS latex was prepared in the experimental setup equipped with a 500 ml jacketed glass vessel, magnetic stirrer, condenser, vacuum system, nitrogen flow system and thermocouple. The temperature was controlled using a PID controller and kept within ±0.1 °C. The narrowly dispersed latex was prepared by the surfactant-free emulsion polymerization of styrene. Millipore water (468 ml) and styrene (0.058 and 0.11 mol) were charged in the reactor. The reactor was purged with alternate cycles of nitrogen and vacuum, and finally left under a nitrogen atmosphere. After heating the reaction mixture to 70 °C with stirring at 400 rpm, the initial solution (0.42 g, 1.5 mmol of KPS in 10 ml of water) was injected into the reactor through a syringe. The reactor was allowed to run under these conditions for 12 h.

2.2 Preparation of Anti-Reflective Solution

To prepare the liquid solution type, anti-reflective agent for the formation of macro porous silica layer was prepared using TEOS as a precursor and PS nano spheres as the template for the formation of pores in the silica layer. The precursor and template solutions were mixed, and various alcohols, such as methanol, ethanol and iso-propyl alcohol (IPA), were added for the successful mixing of these solutions. The alcohols at 10 volumetric percentages were added to the mixture solution. The mixing property of the two solutions was examined with the addition of alcohols. The solvent of the PS colloidal solution, which is distilled water, was replaced with iso-propyl alcohol after removing the water solvent by rotary vacuum evaporation. The IPA of the content corresponding to the amount of water removed from the PS colloidal solution was recharged. The mixing ratio of the TEOS and PS colloidal solution was fixed to 2:8.

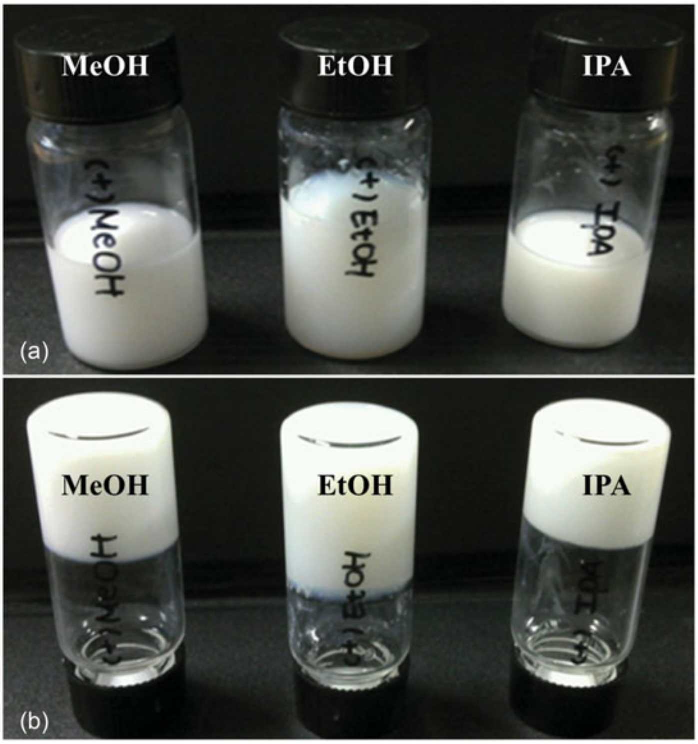

Figure 3. Image of the TEOS-PS mixture solutions prepared with the addition of alcohols, such as methanol, ethanol and IPA; (a) mixing state of TEOS and PS, (b) gelation state of the TEOS-PS mixture solutions after 24 h.

2.3 Formation of a Macro Porous Silica Layer Using the Template Method

The anti-reflective agent solutions were prepared by the mixing the TEOS and PS colloidal solution, and the volumetric mixing ratio of these solutions was fixed to TEOS/PS = 1/4. The anti-reflective agent was coated on a glass substrate using a spray coating technique

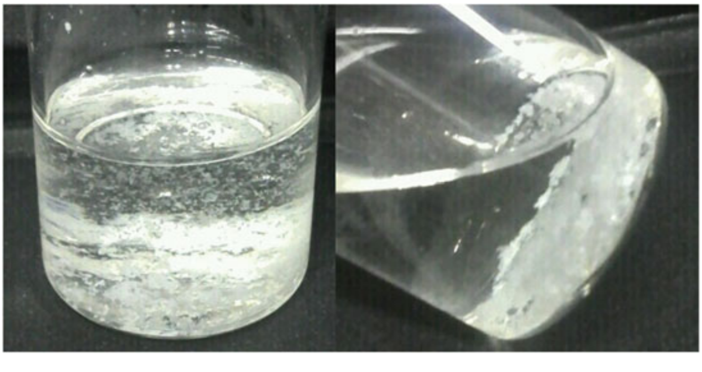

Figure 4. Image of PS-MeOH and PS-EtOH solutions prepared by mixing the PS-powder and alcohols, such as methanol and ethanol.

Figure 5. Image of the PS-IPA solution prepared by the mixing of PS-powder and IPA

and the spray nozzle (0.5 mm of nozzle size) was used to spray the solution. The TEOS-PS mixture solution was sprayed on the glass substrate at three times for each 1 sec at every time and the pressure of N_2 supplied from the gas cylinder was maintained at 2 atm. The glass substrate coated with the anti-reflective agent was dried at 150 °C for 12 h and treated thermally at 700 °C for 1 h. The thermal treatment process was carried out in a quartz tube with an external diameter of 5 inches in a 3-zone horizontal tube type furnace. The glass substrate, which is coated with the anti-reflective agent, on an alumina boat was placed in the inlet of the quartz tube before the thermal treatment. When the furnace temperature reached at the thermal treatment temperature, the alumina boat was moved to the center of the quartz tube and the thermal treatment was performed for 1 h. After the thermal treatment, the alumina boat was moved to the inlet of the quartz tube.

2.4 Characterization of the PS Beads and Silica Layer

The size and morphology of the PS particles suspended in the colloidal solution were observed by field emission scanning electronic microscopy (FE-SEM, Hitachi Ltd., S-4800). The pores in the silica layer coated over the glass substrate were also examined by FE-SEM. The reflectance of the macro porous silica layer in the wavelength ranges of 350–800 nm was measured using an ultraviolet/visible (UV-Vis) spectrophotometer (Agilent, cary 5000).

3. Results and Discussion

3.1 Synthesis of PS Spherical Beads

PS nano spherical beads were used as the template for the formation of macro pores in the silica layer. In this study, a PS colloidal solution was synthesized with a low concentration of styrene monomer for the formation of nano sized spherical beads. The size of the PS spherical beads synthesized by other researchers was above 300 nm [8,9]. In this study, the particle size of the PS spherical beads was controlled by the styrene content, as shown in Fig. 1. The morphology of the PS beads was a spherical type when the content of styrene added for polymerization was above 0.235 mol/L, as shown in Fig. 1(a). The particle size was approximately 150 nm. On the other hand, non-spherical type PS with a particle size of 50 nm was synthesized when 0.124 mol/L of styrene was added, as shown in Fig. 1(b). Because the reaction rate can be dependent on the monomer concentration

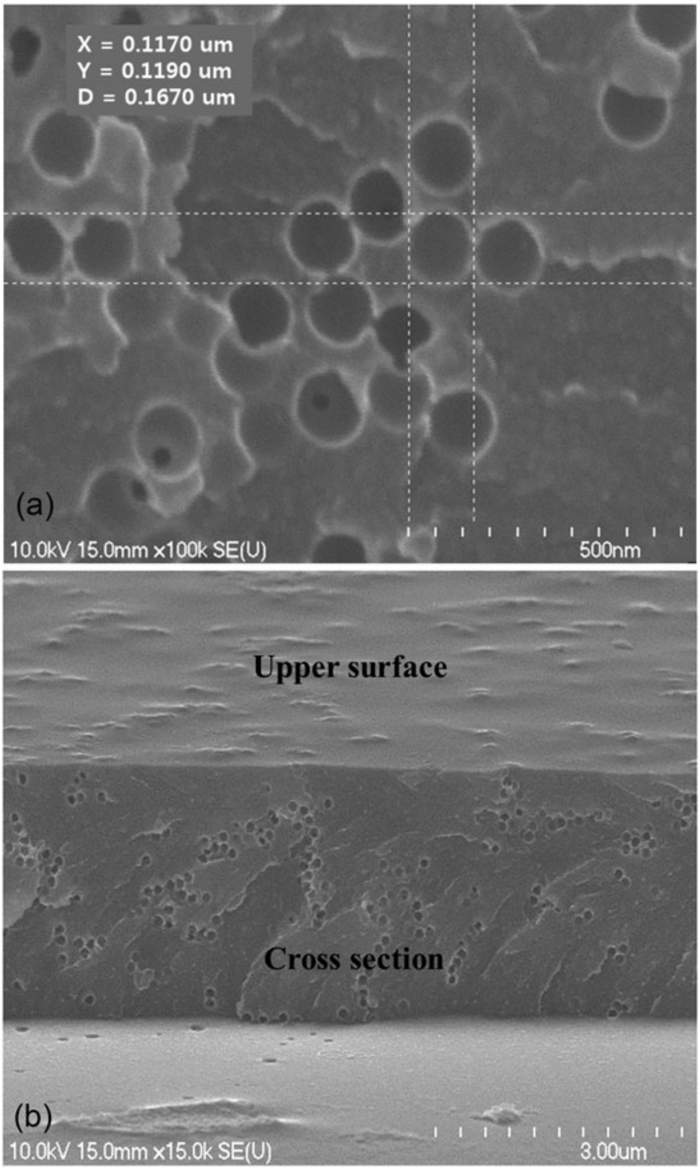

Figure 6. SEM images of the macro porous silica layer on a glass substrate, (a) cross section and (b) upper surface.

in the polymerization process, the size of the polystyrene spherical beads can be reduced with decreasing concentration of the styrene monomer. Because these spherical beads were regular in size, macro pores of an ordered structure could be formed in the silica layer.

3.2 Preparation of Anti-Reflective Solution

TEOS and PS beads were used as the precursor and template for the macro porous silica layer, respectively. On the other hand, the two solutions were not mixed because TEOS is a

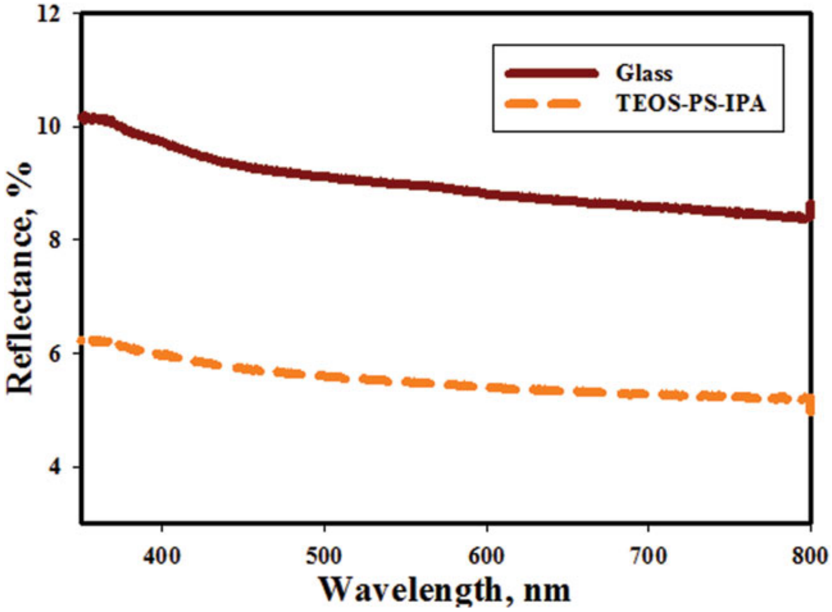

Figure 7. Reflectance of the glass substrates coated with and without a macro porous silica layer.

hydrophobic solution, as shown in Fig. 2. Therefore, alcohols (methanol, ethanol and IPA) were added to improve the mixing of the TEOS and PS colloidal solutions. The TEOS and PS colloidal solutions were well mixed with the addition of alcohols, as shown in Fig. 3(a). On the other hand, these mixture solutions were stiffened after 12 h due to its gelation by the hydrolysis of TEOS, as shown in Figure 3(b). The hydrolysis of TEOS occurred with the influence of H_2O in the PS colloidal solution contained as the solvent.

The gelation of the TEOS-PS mixture solution means the low stability of the anti-reflective solution during the treatment of the product, such as a transport and storage etc. The hydrolysis of TEOS by the contact of H_2O, such as the moisture in atmosphere or water in solution, must be prevented to maintain the stability of the anti-reflective solution. Therefore, the water in the PS colloidal solution was removed completely using a rotary vacuum evaporator and PS nano-beads were dispersed in the alcohols. An ultra-sonic bath was used to disperse the PS beads in the alcohol solvents. On the other hand, the PS beads dispersed in methanol or ethanol aggregated, and the colloid state was not maintained, as shown in Fig. 4. The PS bead powder was well dispersed in IPA and the colloidal state was well maintained, as shown in Fig. 5. Therefore, PS beads dispersed in IPA were used as the template solution for the macro porous silica layer over the glass substrate in this study. The gelation of a mixture solution was not observed and the stability of TEOS mixed with the PS-IPA colloidal solution was confirmed.

The size-controlled polystyrene and TEOS solutions were mixed at a 1:1 ratio and the TEOS-PS mixture solution was coated on the glass substrate using a spin coater. The silica layer coated over glass substrate was treated at 700 °C for 1 h. To examine the formation of pores in the silicon oxide layer, a cross section of the silicon oxide layer was analyzed by SEM. PS spherical beads are removed by the oxidative thermal decomposition at high temperatures. Therefore, the TEOS-PS coating layer is converted to a TEOS layer, which is in turn oxidized to a SiO_2 layer under high temperature and atmospheric conditions.

The anti-reflective solution was coated over the glass substrate to reduce the reflectance. The morphology of the cross section and upper surface of the silica layer formed after the thermal treatment at 700 °C for 1 h was observed by FE-SEM, as shown in Fig. 6. The thickness of the silica layer coated on the silica layer was approximately 1.0–3.0 μm, as shown in Fig. 6(a). FE-SEM revealed macro-size pores, 167 nm in size, distributed homogeneously in the silica layer. The macro pores were formed in the silicon oxide layer due to decomposition of the PS spherical beads by a thermal treatment at high temperatures. The homogeneous distribution of macro pores in the silica layer was maintained because the PS nano-beads were dispersed in a colloidal state. The morphology of the upper surface over the silica layer was observed as a flat surface and pores were not formed over the surface of the silica layer, as shown in Figure 6(b). The flat surface over the silica layer for anti-reflectance can also reduce surface contamination. However, it was observed that the porous silica layer had the low uniformity and the density of pore. The control of TEOS/PS mixing ratio was need for changing the uniformity and the density of pore in silica layer.

3.3 Reflective Tests for the Macro Porous Silica Layer

The reflectance of the glass substrate coated with macro porous silica, which is formed with a TEOS-PS-IPA solution as the anti-reflective agent, was measured by UV-Vis spectroscopy over the wavelength range of 350–800 nm. The reflectance of the glass substrate was reduced with the formation of macro pores in the silica layer, as shown in Fig. 7. The coated and non-coated glasses had a different reflectance of approximately 3-4%. Therefore, the reflective index is reduced by the formation of pores in the silica layer coated over the glass substrate.

4. Conclusions

The TEOS-PS mixture solution was synthesized for the formation of an anti-reflective layer over a glass substrate. TEOS and PS were used for the formation of a silica layer and macro pores, respectively. The size of the macro pores was determined by the size of the PS spherical beads. The size of the PS beads could be controlled by the content of styrene added for polymerization. A suitable solvent was selected to achieve a high stability of a TEOS-PS mixture solution as an anti-reflective coating agent. A TEOS-PS-IPA-based solution was suggested in this study. This anti-reflective agent can be applied to a simple large area coating process.

Acknowledgment

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