Fabrication of Large-Area Photovoltaic Crystal with Modified Surface Using Trimethoxysilyl Propyl Methacrylate (TMSPM) for Solar Cell Protection

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ABSTRACT: Protection of solar cell surface is important to prevent from dust, pollen, sand, etc. Therefore, development of large area antifouling film is urgent for high performance of solar cells. The surface of silica spheres was modified to fabricate large area antifouling film. The surface of monodisperse silica spheres has been modified with 3-(trimethoxysilyl) propylmethacrylate (TMSPM) to fabricate large area photonic crystal. Although the surface modification of silica spheres with TMSPM has been failed for the base catalyst, the second trial using acid catalyst showed the following results. The FTIR absorption peak at 1721 cm^{-1} representing C=O stretching vibration indicates that the TMSPM was attached on the surface of silica spheres. The methanol solution comprised of the surface modified silica spheres (average diameter of 380 nm) and a photoinitiator was poured in the patterned silicon wafer with the dimension of 10 cm x 10 cm and irradiated UV-light during the self-assembly process. The result showed large area crack and defect free nanostructures.

Key words: Large Area Photonic Crystal, Silica spheres, TMSPM, Surface modification

1. Introduction

Photonic crystals have great promise for the integrated photonic circuits and numerous useful photonic devices including sensors[1], detectors[2], resonators[3] and waveguides[4]. The characteristic structure of the photonic crystals has a periodic modulation of the refractive index[5]. Therefore, the photonic crystals can be fabricated with periodically arranging materials with highly different refractive indices. The electron beam lithography has been most frequently used technique for the fabrication of photonic crystals due to the design flexibility and highly accurate control of the structure. However, the electron beam lithography technique is extremely slow process and expensive method, which is impractical for the fabrication of the large area photonic crystal. Laser interference lithography and holographic lithography can generate the uniform and periodic submicrometer patterns in the order of cm^2. Self-assembly of microspheres is another simple and easy technique to fabricate two and three dimensional photonic crystals. However, in this technique, the defects between the crystal lattices still need to be improved. Recently, these defects have been removed by the surface modification of the silica spheres and in situ photo-crosslinking technique during the self-assembly process[6]. In this paper, we report the surface modification process of the silica spheres and fabrication method of the large area photonic crystal. We have observed the critical problem during attaching the 3-(trimethoxysilyl) propyl methacrylate (TMSPM) to the surface of the silica spheres with a base catalyst. Discussions of the problems with the spectroscopy and with the surface images, and the method to overcome the problems are the main topics in this manuscript.

2. Experimental

Ammonium hydroxide (NH_4OH, 28 %), tetraethylorthosilicate (TEOS, 98%), TMSPM (98%), 2-propanol (99%) and methanol (HPLC grade) were purchased from Sigma Aldrich Co. The monodisperse silica spheres were prepared using Stöber method. The 2-propanol (100 ml) and the NH_4OH (100 ml) were placed into the 250 ml round bottom flask. Approximately 4.5 g of TEOS was added to the flask and stirred for 6 h. The first attempt to attach the TMSPM on the surface of the silica

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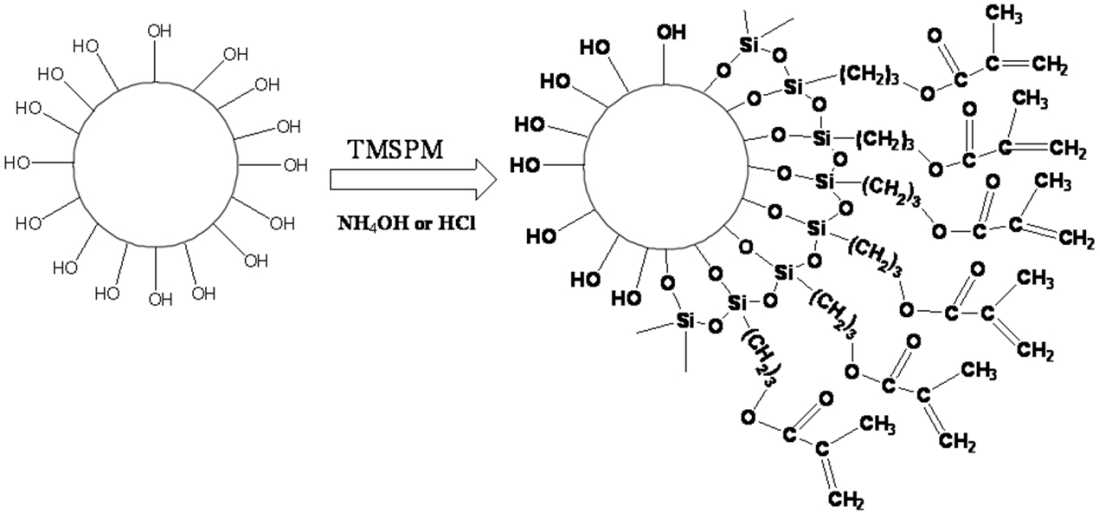

Fig. 1. Schematic view of the surface modification process

spheres, various amounts of TMSPM were directly added to the silica spheres and stirred for 6 h. The spheres were separated from the solution by repeated centrifuge and washing processes. For the acid catalyst process, the synthesized spheres were separated by centrifuge and washed with methanol. The spheres were re-dispersed to the methanol, and TMSPM and HCl were added to the sphere solution. Hydrolysis and condensation reactions of the TMSPM were performed by stirring the mixture solution at room temperature. The surface modified silica spheres were separated by centrifuge and washing with methanol. The spheres were dispersed to the methanol and added approximately 2 wt.% (with respect to sphere weight) of Irgacure-184 as a photoinitiator. The mixture of the spheres and the photoinitiator was filled in a square pattern with the dimension of 10 cm x 10 cm. Deep ultraviolet light (254 nm) was irradiated to the sphere solution during the self-assembly process. The field emission scanning electron microscope (FESEM) images and Fourier transform infrared (FTIR) spectra of the spheres were obtained with JEOL JSM-7401F microscope and Nicolet iS5 spectrometer, respectively.

3. Results and discussion

Attaching versatile hybrid materials to the surface of the silica spheres has huge advantages to fabricate diverse photonic devices. The schematic view of the hydrolysis and condensation reactions is shown in Fig. 1. The first trial is the direct addition of the TMSPM to the Stöber synthetic process to simplify the reaction process. The NH_4OH acts as a base catalyst. According to the FTIR spectra and FESEM images, there is no evidence

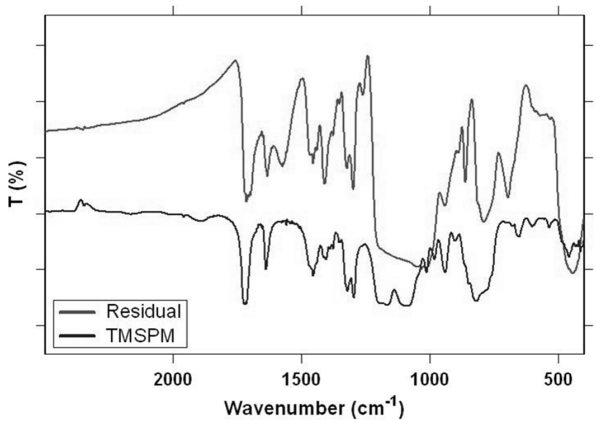

Fig. 2. FTIR spectra of silica spheres and the dried solid from the reaction solution for the base catalyst process

that the TMSPM is incorporated on the surface of the spheres[6]. The spheres and reaction solution are separated by centrifuge to find out the cause of the absence of the TMSPM on the surface of the silica spheres. The reaction solution is dried and collected the residual solid. Fig. 2 shows the FTIR spectra of the TMSPM and residual solid. The FTIR spectrum of the residual solid is very similar compared with that of the pure TMSPM. This result implies that the major part of the TMSPM is still remained in the solution after the reaction.

For the acid catalyzed reaction, a few drops of HCl was used as a catalyst. The surface modified spheres were separated by centrifuge and washing with methanol several times. Fig. 3(a) and 3(b) show the modified spheres before and after washing with methanol, respectively. Aggregated spheres are appeared as shown in the Fig. 3(a), which is due to the residual gel before washing process. After washing process, aggregated spheres are

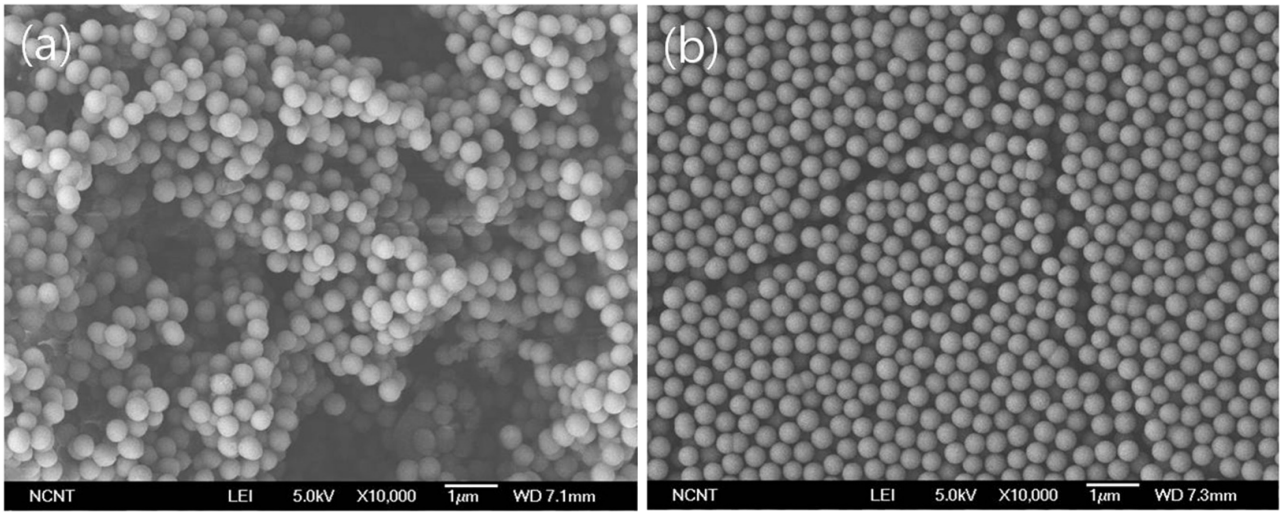

Fig. 3. FESEM images of spheres (a) before and (b) washing process

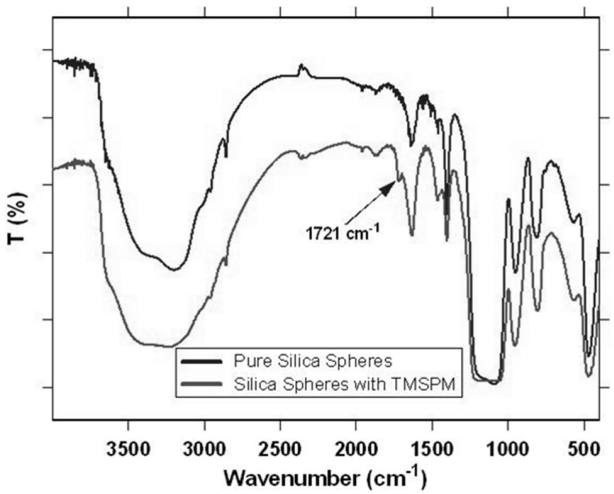

Fig. 4. FTIR spectra before and after surface modification

not formed as shown in Fig. 3(b). Fig. 4 shows the FTIR spectra of pure silica spheres and silica spheres modified with TMSPM. The absorption peak at 1721 cm^{-1} attributed the C=O stretching vibration of the ester group gives the evidence of the existence of the TMSPM on the surface of the silica spheres.

Self-assembly of nanoparticles has attracted enormous interest for potential large area bottom-up process to overcome the drawbacks of the conventional top-down process. However, these self-assembly process to fabricate large photonic crystal films has resulted several critical defects including the formation of cracks, colloid vacancies and domain boundaries. To overcome these defect problems we developed the in situ photo-cross-linking process during the self-assembly process. This process has been developed with the surface modified silica spheres with vinyltriethoxysilane and has been used base catalyst[7]. First of all, the silica spheres were washed with methanol several times. The spheres were redispersed to the methanol, and approximately 2 wt.% of Irgacure-184 was added to the solution. The solution was poured to the patterned silicon wafer with the dimension of 10 cm x 10 cm and exposed to the UV-light (254 nm) during the drying process. Fig. 5(a) and 5(b) show the self

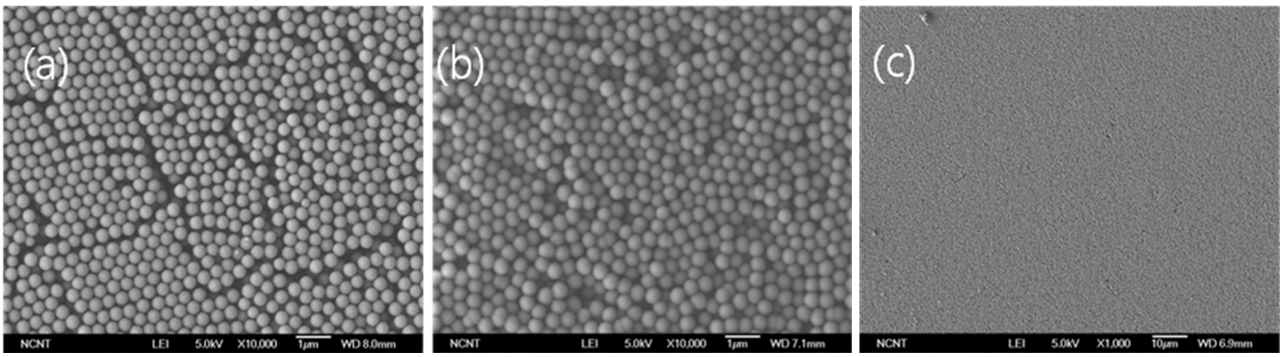

Fig. 5. FESEM images of the photonic crystal (a) without photo-crosslinking process, (b) with photo-crosslinking process and (c) of large area

assembled silica spheres without crosslinking process and with crosslinking process, respectively. As shown in Fig. 5(a), cracks are generated during the drying process. However, cracks are not observed in the self-asssemblied silica sphere film with this new method as shown in Fig. 5(b). The crack-free large area photonic crystal is shown in Fig. 5(c). This method demonstrates that the large area nanostructures can be fabricated without crack or any other defect.

4. Conclusions

Surface of silica spheres were modified with TMSPM to fabricate large area nanostructures to use the protection of solar cell surface. Although the surface modification of silica spheres with TMSPM was failed for the base catalyst, acid catalyst showed the corporation of TMSPM on the surface of silica spheres. The FTIR absorption peak at 1721 cm^{-1} representing C=O stretching vibration indicates the incorporation of TMSPM on the surface of the silica spheres. Large area nanostructures were fabricated with UIV irradiation during the self-assembly process.

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