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Controllable Synthesis of Hexagonal Hollow Silica Plate Particles and their Low Refractive Index in Polymer Nanocomposite Films

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1. Introduction

Hollow silica particles have attracted tremendous interests in recent years due to their remarkable properties and great potential for widespread applications, but the precise design and control of their structure remains a significant challenge.

In this work, hexagonal hollow silica plate (HHSP) particles were successfully synthesized through a sol–gel method by utilizing the reaction condition at room temperature, using tetraethyl orthosilicate (TEOS) as a silica precursor and zinc oxide (ZnO) particles as a colloid template. The structure and morphology of HHSP particles were controlled by examining samples taken at different reaction time and the thickness of silica shell can be adjusted by varying the TEOS/ZnO molar ratios. Furthermore, the polymer/HHSP composite thin films were prepared using poly(methyl methacrylate) (PMMA) matrix and surface modified HHSP particles by grafting silane coupling agents. The composite films exhibited high visible and UV light transmittance over than 95%. In addition, the HHSP particles having a refractive index as low as 1.28 were obtained, which may result in a new generation of film materials.

2. Experimental Method

In a typical procedure, ZnO particles were dispersed into a mixture of ethanol, ultrapure water and ammonia solution (28 wt%) prior to stirring for 10 min. TEOS was slowly added to the solution and the mixture was stirred for 4 h at room temperature. The precipitate was isolated from the solution by centrifugation followed by washing and vacuum drying. Removal of ZnO was achieved by etching in HCl solution, generating the HHSP particles. The HHSP particles after surface modification were dispersed in methyl isobutyl ketone (MIBK) and cooled to -20ºC. PMMA was diluted in the MIBK to yield a 5 wt% PMMA solution and mixed with a desired amount of HHSP particles before stirring for 3 h at 80ºC. The HHSP particles suspension was coated onto cleaned glass substrates using a bar coating machine, forming the PMMA/HHSP composite films.

3. Results and Discussion

Fig. 1(a) displays TEM image of the HHSP particles, showing hexagonal plates with an average diameter (edge-to-edge) of about 531 nm. The shell thickness (L_s) of the HHSP particles can be precisely tailored by simply controlling the amount of TEOS precursor. The L_s comparison for experimental and theoretical calculations is shown in Fig. 1(b). The particle L_s increased from 12.2 to 43.2 nm with a gradual increase of the TEOS/ZnO molar ratio from 0.15 to 1.00. The observed experimental results are in good agreement with the theoretical calculations up to a TEOS/ZnO molar ratio of 0.60.

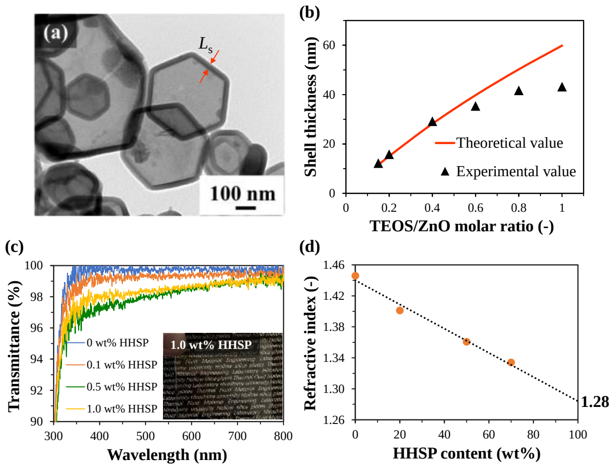

Fig. 1. (a) TEM image of HHSP particles, (b) Effect of HHSP particle L_s at different TEOS/ZnO molar ratios, (c) Optical transmittance spectra, and (d) Refractive index of PMMA/HHSP composite films prepared with different amounts of HHSP particles.

As the HHSP content was increased from 0.1 to 1.0 wt%, the transmittance of the PMMA/HHSP composite films slightly decreased (Fig. 1(c)). High transmittance values were observed (>95%) for the composite thin films in the UV and visible regions, indicating that highly transparent composite films were fabricated. As seen in Fig. 1(d), the refractive index of PMMA/HHSP composite films decreases from 1.45 to 1.33 with an increasing amount of HHSP particles from 0 to 70 wt%. By further increasing the HHSP particle content, the refractive index decreases and approaches a value of approximately 1.28, which is significantly lower than dense silica (n = 1.46 at 589 nm). The versatility of HHSP particles with low refractive index show bright prospect as a promising material for potential applications in the fields of electronics and optical devices.

References

1) Ogi, T. *et al*., Nanostructuring Strategies in Functional Fine-Particle Synthesis towards Resource and Energy Saving Applications, Adv. Powder Technol., **25**, 3−17 (2014).
2) Cao, K.L.A. *et al*., Precisely Tailored Synthesis of Hexagonal Hollow Silica Plate Particles and their Polymer Nanocomposite Films with Low Refractive Index, J. Colloid Interface Sci., **571**, 378−386 (2020).

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