Preperation of Monodispersed SiO₂ Particles for Electrostatic Self-assembly of SiO₂/PEI Thin Film with Structural Colors on Polyester Fabrics

Guangqing Zhuang[1], Yun Zhang[1], Yanrong Jia[1], Dongming Qi[1], Qinguo Fan[1,2], and Jianzhong Shao[1]*

[1]*Engineering Research Center for Eco-Dyeing & Finishing of Textiles, Ministry of Education, Zhejiang Sci-Tech University, Hangzhou 310018, China*
[2]*Department of Bioengineering, University of Massachusetts Dartmouth, North Dartmouth, MA 02747, USA*

Abstract: The monodispersed SiO₂ particles with perfect sphericity and desired particle sizes were synthesized by an improved Stöber method. The particle sizes and size distribution of colloidal silica could be regulated by adjusting reaction temperature, reaction time, and the concentrations of NH₄OH, H₂O and TEOS. Dynamic light scattering particle size analysis and SEM analysis confirmed a narrowly distributed particle size and good sphericity of the synthesized SiO₂ nanoparticles. The structural colors of silica/polyethyleneimine (SiO₂/PEI) thin film fabricated on polyester fabrics were governed by SiO₂ particle size, assembly cycles and viewing angles, and the origin mechanism of the structural colors was based on the thin film interference theory. The resultant polyester fabrics showed vivid structural colors changing with the change in viewing angles, displaying a biomimetic variable coloration effect on textiles.

Keywords: Stöber, SiO₂ particles, Electrostatic self-assembly, Thin-film, Structural color, Textile

Introduction

Textile coloration is conventionally achieved by using chemical colorants. However, many creatures in nature show bright colors arising from special physical structures, referred to structural colors [1-3]. The formation of structural colors does not require any chemical colorants, and it is, in fact, a visual perception to the selectively reflected light by a special physical structure interacting with incident light, such as dispersion, scattering, interference and diffraction [4,5], exhibiting high brightness, high saturation and iridescent effect (color changes with change in view angles) [5-7].

Thin film interference is one of the most significant ways to produce structural colors in nature, such as wing of the butterfly, dragonfly and so on. There are various methods to construct thin films, such as chemical deposition [8], gravitational sedimentation [9,10], spin coating [11], electrostatic self-assembly [12-14] and so on. The electrostatic self-assembly technique is the most convenient method to create charged microstructures without complicated chemical reactions, and it has provided an effective approach to fabricate a variety of thin films using oppositely charged species. Nevertheless, it was hardly reported that this technique has been applied into textiles for generating thin films with structural colors.

Colloidal SiO₂ is a kind of common material to construct thin films, and Stöber method [15] is the most common method to synthesize SiO₂ colloidal particles by the hydrolysis and condensation reactions of tetraethyl orthosilicate (Si(OC₂H₅)₄, abbreviated as TEOS) in ethanol co-solvent in the presence of water and ammonia as a base catalyst. Although Stöber method has been almost thoroughly investigated, the control of particle size and size distribution

of SiO₂ spherical particles is still attracting much attention for broadening the realm of potential applications. For instance, the particle size and size distribution of SiO₂ colloidal particles should be controlled for fabricating thin films with structural colors by electrostatic self-assembly. Obviously, the thin film would not achieve brilliant structural colors unless it could keep a suitable thickness that was closely related to particle size and assembly cycles.

In this work, the size controlled and monodispersed SiO₂ particles were prepared by adjusting reaction time, reaction temperature, ammonia concentration, deionized water concentration and TEOS concentration with Stöber method, and silica/polyethyleneimine (SiO₂/PEI) thin films with structural colors were fabricated on polyester fabrics using the synthesized SiO₂ colloidal particles and oppositely charged PEI polymer with electrostatic self-assembly technique. The resultant polyester fabrics displayed brilliant and vivid structural colors, which varied with various SiO₂ particles size and various assembly cycles. And various hue and brightness were observed at various viewing angles, which achieved a charming color effect for textiles such as clothing, household items, decorative items and so on.

Experimental

Reagents and Materials

Tetraethyl orthosilicate (TEOS) was purchased from Aldrich. Ammonia (NH₃) and absolute ethanol were purchased from Hangzhou Gaojing fine chemical Co., Ltd. Polyethylenimine (PEI) (Mw=70,000, 50 %) was purchased from Aladdin reagent Co., Ltd. Detergent 209 (a sulphonated acryl amine, anionic surfactant) was purchased from Zhejiang TransFar Co., Ltd. Deionized water (>18 MΩ.cm, Millipore Milli-Q) was used in all the polymerization processes in this study,

---

*Corresponding author: jshao@zstu.edu.cn

and all the other chemical reagents used were of analytical grade and used without further purification. Plain woven polyester fabrics with a fiber diameter of 13-14 microns were derived from Hangzhou Sijiqing Fabric Market.

Preparation of SiO₂ Nanoparticles

Stöber method was applied to synthesize SiO₂ colloidal particles. Typically, the synthesis [16-19] was carried out in a 250 m*l* three-necked round-bottom flask. For example, the synthesis of SiO₂ colloidal particles in 100 nm of particle size was as follows: 130 m*l* absolute ethanol, 8 m*l* deionized water and 1.5 m*l* ammonia were added into the three-necked round-bottom flask and stirred at around 1000 rpm for 10 min, and then 6.7 m*l* TEOS was subsequently injected into the above solution and quickly stirred for another 2 min. Finally, the mixed solution was slowly stirred at around 10 rpm for 20 h with a water bath at 25 °C until the reaction was completed.

Electrostatic Self-assembly of SiO₂/PEI Thin Films on Polyester Fabrics

(1) The preparation of precursor solutions: The monodispersed spherical SiO₂ nanoparticles with the size of 70 nm, 100 nm and 160 nm were respectively diluted with deionized water in the speed of one drop every second to avoid the cluster; The PEI (50 wt%, Mw=700,000) was adjusted to the concentration of 0.5 wt% using deionized water (>18 MΩ.cm).

(2) The pretreatment of polyester fabrics: Each black polyester fabric was divided into several pieces with a size of 50×25 mm (length×width) and cleaned in a Detergent 209 solution (1 g/*l*) for 10 min by an ultrasonic washing to ensure all the impurities possibly existed on the fabric surface to be removed, and then rinsed with plenty of deionized water, dried in a dust sealed container.

(3) Fabrication of the SiO₂/PEI films on polyester fabrics: The SiO₂/PEI films with structural colors were fabricated on polyester fabrics by electrostatic self-assembly technique using a three dimensional automatic control system (Asymtek D-580, USA). In a typical process, the pretreated polyester fabric was immersed in 0.5 wt% PEI aqueous solution for 5 min to get a positively charged substrate, followed by three times of two-minutes rinse in deionized water. Then the fabric was dipped in SiO₂ (0.1 %) colloidal solution for another 5 min to achieve a negatively charged surface, and also rinsed three times again, each for 2 min. The above procedure was defined as one cycle of the electrostatic self-assembly, and SiO₂/PEI thin films were obtained after n cycles of electrostatic self-assembly. Finally, the samples were dried at room temperature.

Characterization of the Particle Size and Size Distribution of SiO₂

The particle size and size distribution of SiO₂ were measured by a dynamic light scattering nanoparticle size analyzer (Delsa™ Nano C, Beckman Coulter, America) at room temperature. This data is the size of the SiO₂ nanoparticles in a colloid solution, while the absolute size of the nanoparticles should be smaller than that obtained in the experiment.

Scanning electron microscopy (SEM) images of the samples were taken by using a field emission SEM (ULTRA55, Carl Zeiss AG, Germany) at 2.0 kV working voltage. The colloidal SiO₂ particles were dispersed by absolute ethanol and dripped onto a silicon disc, not coated with gold before the SEM analysis.

Characterization of Structural Colors

Photographs of the structural colors on polyester fabrics were captured by Digital Single Lens Reflex Camera (EOS600D, Canon, Japan). The camera was installed on a tripod that was prior to adjusting the height. A set of samples were attached on a black art paper, and the photos of structural colors were recorded with the camera in the mode of auto intelligent scene and in the highest resolution at various view angles.

Results and Discussion

Preperation of Monodispersed Colloidal Silica

Effect of Reaction Time on SiO₂ Particle Size and Size Distribution

Based on a basic formula of Stöber method, the effect of reaction time on SiO₂ particle size and conversion rate of TEOS was firstly investigated and the results were shown in Figure 1.

Figure 1(a) showed that, there was an apparent increase in diameter of SiO₂ particles with increasing reaction time, and the conversion of TEOS linearly increased with increase in reaction time. When the reaction was carried out for 8 h, SiO₂ particle size distribution tended to be stable, and the average particle size remained about 40 nm. When the reaction time extended to 20 h, the conversion reached nearly 100 %, suggesting that whatever the growth of the SiO₂ particle or the generation of new SiO₂ particles were basically completed, thus 20 h was chosen as the optimized reaction time.

Effect of Reaction Temperature on SiO₂ Particle Size and Size Distribution

The effect of reaction temperature on the SiO₂ nanoparticle size and content percent was shown in Figure 2.

As seen in Figure 2, SiO₂ particle size was inversely proportional with the reaction temperature, that is, with the increase of reaction temperature, the particle size decreased. It could be explained that the nucleation rate increased in geometric series as reaction temperature raised, and thus promoted the formation of small size SiO₂ particles. It should be noted that a higher nucleation rate was not conducive to the system stability, while lower temperatures
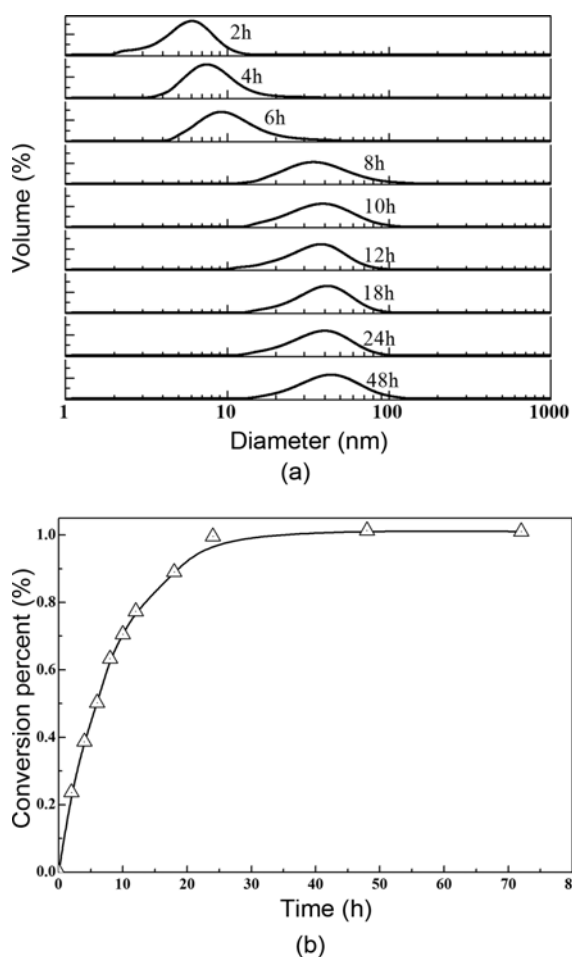
Figure 1. Effect of reaction time on the size distribution and conversion rate.
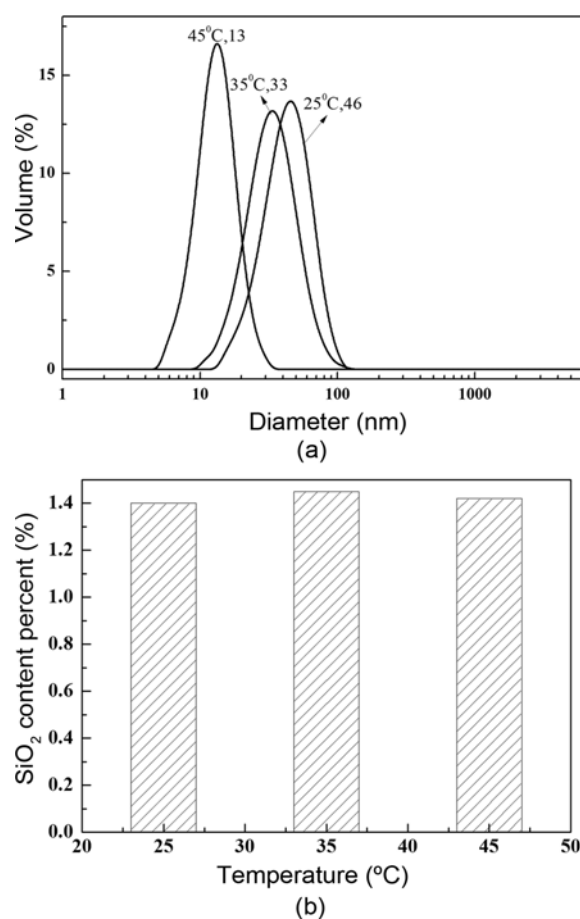

Figure 2. Effect of reaction temperature on the size distribution and content percent; (a) effect of reaction time on the size distribution and (b) effect of reaction time on content percent.

could induce mild reaction and produce stably dispersed SiO$_2$ particles. It was difficult to obtain a straightforward correlation between reaction temperature and SiO$_2$ amount from Figure 2, and there was no obvious change in the conversion that have reached nearly 100 % as temperature increasing. So, 25 °C was selected as the optimized reaction temperature in this study.

Effect of Reactant Concentration on SiO$_2$ Particle Size and Size Distribution

The effect of reactant concentration on the SiO$_2$ nanoparticles size and content percent was investigated and the results were shown in Table 1.

Table 1 represented that the variation in SiO$_2$ particle size was mainly influenced by the concentrations of NH$_4$OH and H$_2$O. The particle size and size distribution of colloidal SiO$_2$ increased with increasing ammonia concentration, while the particle size of SiO$_2$ increased firstly and then decreased with increasing the amount of deionized water. However, the amount of SiO$_2$ particles was significantly influenced by TEOS concentration. The reasons for above phenomena were

Table 1. Effect of reactant concentration on particle size and content percent

Factor	The amount of material (M)	The average SiO$_2$ particle size (nm)	The content percent of SiO$_2$
NH$_4$OH	0.25	9	1.41
	0.50	35	1.46
	0.75	56	1.68
	1	77	1.72
TEOS	0.2	35	1.46
	0.4	42	2.60
	0.6	42	3.85
	0.8	45	4.92
H$_2$O	2	19	1.49
	4	37	1.46
	8	64	1.53
	12	61	1.64
	16	61	1.54

mainly related to the role of each substance in the reaction, which could be explained using the following reaction equations:
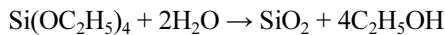
(1) The hydrolysis of tetraethyl orthosilicate:

$$Si(OC_2H_5)_4 + 4H_2O \rightarrow Si(OH)_4 + 4C_2H_5OH$$
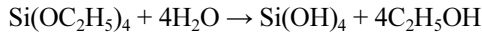
(2) The condensation of tetraethyl orthosilicate:

$$Si(OH)_4 \rightarrow SiO_2 + 2H_2O$$

(3) Total reaction:

$$Si(OC_2H_5)_4 + 2H_2O \rightarrow SiO_2 + 4C_2H_5OH$$
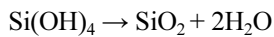
where, ammonia is used as a catalyst in the reactions. It was generally recognized that the formation of SiO₂ particles was, in fact, a complicated competition process among hydrolysis, nucleation and grain growth in the synthesis reaction of SiO₂ nanoparticles by Stöber method, and the hydrolysis reaction was a controlling step in the whole reaction, while nucleation occurred at the early stages of the reaction. Because ammonia acted as a basic catalyst in this reaction, both hydrolysis rate and nucleation rate were accelerated as ammonia concentration was increased [20], but the increase in hydrolysis rate was more significant than the increase in nucleation rate, so that the nucleus number was decreased and the particle size of colloidal SiO₂ was increased.

When the amount of the TEOS was fixed, there was a critical concentration of deionized water. Before the critical value, the colloidal particle concentration increased with increasing the amount of deionized water, and the particle size became larger through the reunion of crystallite nucleation. After the critical value, TEOS hydrolysis was accelerated significantly and the nucleation was faster as the amount of deionized water was further increased. The faster the nucleation rate was accelerated, the more the nucleus number was increased, then the obtained SiO₂ particle size would be decreased [21]. When the amount of ammonia and deionized water were fixed, and the nucleation was basically completed at early stages of the reaction, the effect of TEOS concentration on the particle size could be neglected. While TEOS, as silicon source, was increased, more new nucleus produced due to the hydrolysis of TEOS, and then the amount of the resultant SiO₂ particles was increased. However, the new nucleus was not proportionally increased, therefore, a high silicon source concentration would lead to a decrease in the conversion of TEOS.

In summary, the successful control of SiO₂ particle size and size distribution was achieved by adjusting the reaction conditions using Stöber method. It was reconfirmed that the most important factor determining the particle size and size distribution of SiO₂ particles in the reaction process was ammonia concentration, therefore, the size of SiO₂ particles used for fabricating thin films to generate structural colors should be prepared under specific conditions.

Size Distribution of SiO₂ Nanoparticles

Due to the requirement of follow-up research involved in the effect of different particle sizes of SiO₂ nanoparticles on the fabric structural colors, three kinds of particles sized in
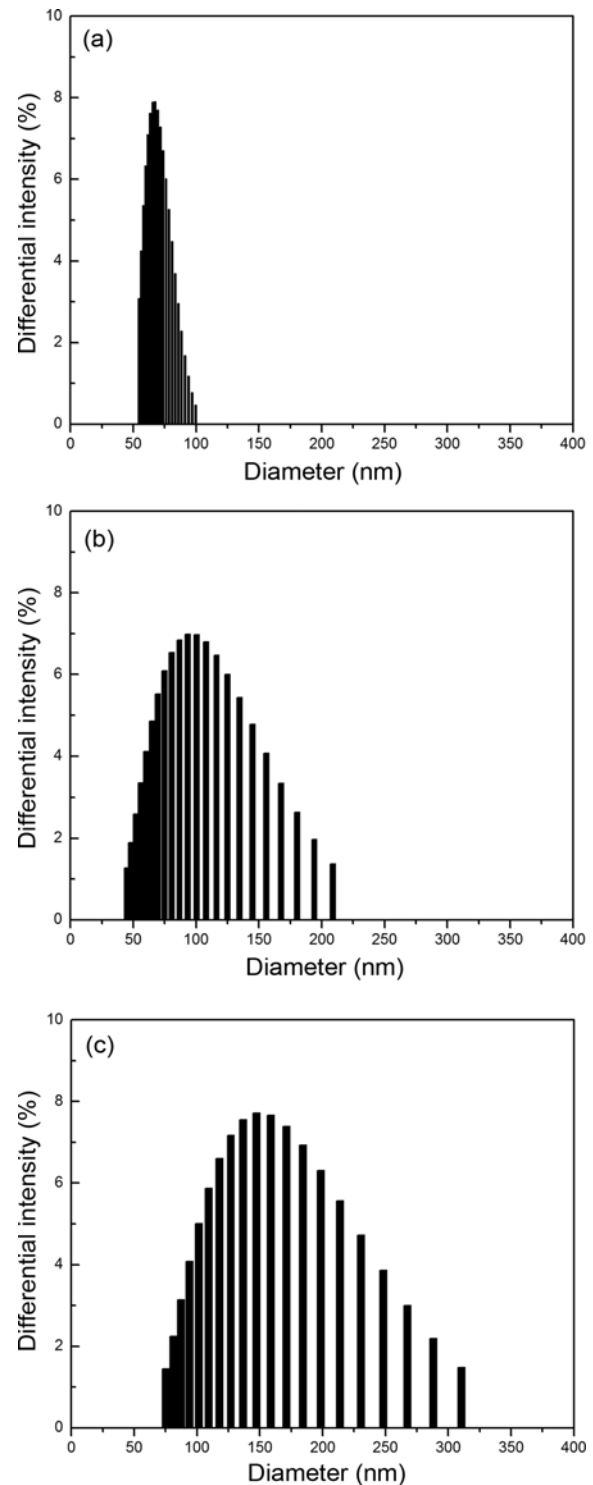

Figure 3. Different size distribution of SiO₂ nanoparticles; (a) 70 nm, (b) 100 nm, and (c)160 nm.

70 nm, 100 nm and 160 nm were prepared, and the mono-dispersity of SiO$_2$ nanoparticles was studied.

Under the condition of same amount of TEOS, 70 nm, 100 nm, and 160 nm of SiO$_2$ nanoparticles were obtained by adjusting the amount of water and ammonia respectively, and the average particle size and its coefficient of variation were confirmed by dynamic light scattering particle size analyzer. No doubt that, the narrower the particle size distribution, the better the monodispersity of SiO$_2$ nanoparticles. As shown in Figure 3, the monodispersities of the three kinds of SiO$_2$ particles were all satisfied, but the coefficient of variation values tended to increase with the increase in SiO$_2$ particle size. Due to the increase in the amount of deionized water and ammonia during the preparation of larger nano-particle size, not only the hydrolysis and polymerization rate increased, but also the concentration of microcrystals increased accordingly. Under the certain concentration of microcrystalline nuclear, new nuclear reunion could be generated as well as the new nuclear surface electrostatic repulsive force growing on the surface was overcome, so

that the particle size became larger, and the particle size distribution was also broadened.

SEM Analysis of the SiO$_2$ Nanoparticle Morphology

SEM was used for observing the morphology of the prepared SiO$_2$ nanoparticles. Colloidal SiO$_2$ were dripped onto a silicon disc to position the SiO$_2$ nanoparticles in the experiment. As Figure 4 showed, the uniform SiO$_2$ nanoparticles with spherical shape and smooth surface were obtained using the above optimized preparation conditions. The uniformity of particles in Figure 4(b) was better than that in Figure 4(a) and (c), while the sphericity of particles in different particle sizes was similar. It seemed that the particle size distribution was narrower if the particle size became smaller. In this study, SiO$_2$ nanoparticles in above three diameters were used to fabricate thin films on polyester fabrics with structural colors (see the next section).

Structural Colors of SiO$_2$/PEI Thin Films Assembled on Polyester Fabrics

Figure 5 showed the structural colors of polyester fabrics with SiO$_2$/PEI thin films fabricated with the above three sizes of SiO$_2$ particles by electrostatic self-assembly technique and observed at same viewing angle under natural light. A distinguished phenomenon can be seen from Figure 5 that the fabric samples assembled with same assembly cycles but
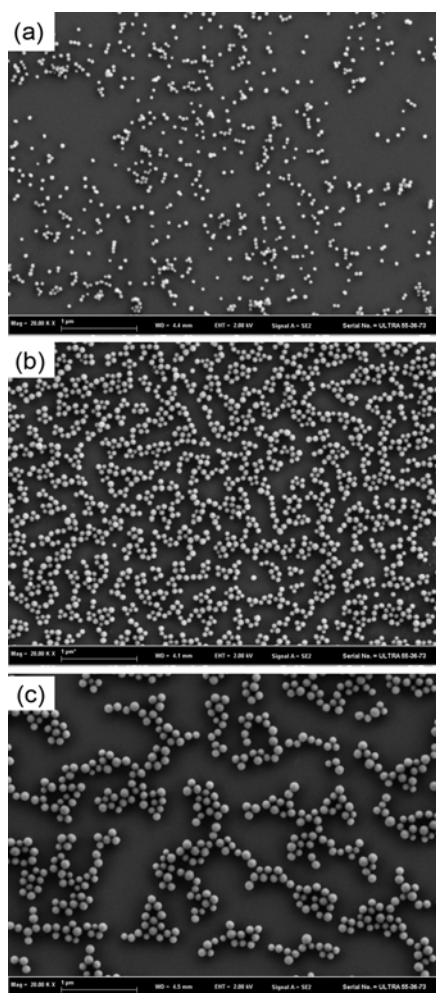

Figure 5. The structural colors in 7 cycles on polyester fabrics with various SiO$_2$ particle size in (a) 70 nm, (b) 100 nm, and (c) 160 nm.
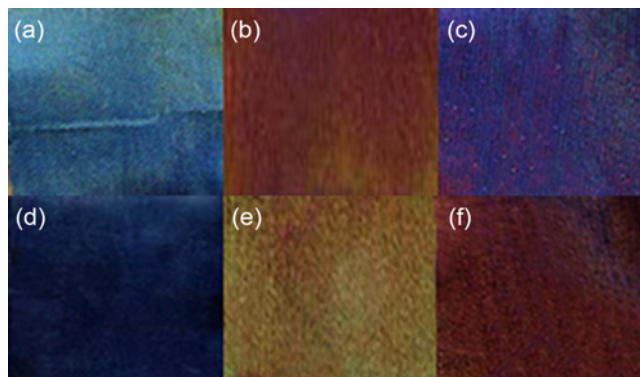

Figure 6. The structural colors of various cycles on polyester fabrics with 100 nm SiO$_2$ particle size observed in two different viewing directions (a), (d) 8 cycles; (b), (e) 10 cycles; (c), (f) 11 cycles.

Figure 4. SEM images of SiO$_2$ nanoparticles of different particle size; (a) 70 nm, (b) 100 nm, and (c) 160 nm.

with different SiO$_2$ particles sized in 70 nm, 100 nm, and 160 nm respectively showed different structural colors, which varied from dark blue to blue, then to red, suggesting that the structural color changed with the change in particle size when the number of assembly cycles was fixed.

As shown in Figure 6, photographs of the polyester fabrics assembled with 100 nm SiO$_2$ nanoparticles were captured at various viewing angles. Apparently, the fabrics with various assembly cycles showed distinct structural colors at the same viewing angle. And, the structural color of a same fabric varied with various viewing angles, as shown in Figure 6(a), (b), (c), (d), (e) and (f).

Structural colors are principally shifted according to the optical path length in a function of the film thickness and index of refraction [22]. In terms of thin film interference theory, the phenomena of Figure 5 and Figure 6 can be explained using the following equation:

$$2n_bd\cos\theta_b=(2m+1)\frac{\lambda}{2}$$

Here, n_b is the refractive index of thin film; θ_b is the light incidence angle; m is integer; λ is the biggest reflected light wavelength. The structural color from thin film interference is mainly controlled by λ. According to the equation, when n_b and θ_b were fixed, λ varied with film thickness, and there were two ways to change the thickness of a thin film, one of which was to change the diameter of SiO$_2$ particles as Figure 5 showed, the other was to change the assembly cycles as Figure 6(a), (b) and (c) showed. When n_b and d were fixed, the structural color of a same fabric could vary with the incidence angle. Furthermore, the optical behaviors showed in Figure 5 and Figure 6 were well satisfied with the theory of the thin film interference. The assembly process and the structural coloration mechanism will be discussed further in our other publications.

Conclusion

Monodispersed SiO$_2$ nanoparticles with spherical shape and smooth surface could be synthesized by Stöber method, and the particle size and size distribution could be regulated by reaction time, reaction temperature, ammonia concentration, deionized water concentration and TEOS concentration. The structural colors of polyester fabrics with SiO$_2$/PEI thin films fabricated by electrostatic self-assembly varied with SiO$_2$ nanoparticles sizes, assembly cycles and viewing angles.

The structural coloration via thin film fabrication can be a new approach for textile coloration, though it is still in its infancy with many challenges.

Acknowledgments

References

1. M. Srinivasarao, *Chem. Rev.*, **99**, 1935 (1999).
2. C. W. Mason, *J. Phys. Chem. C*, **30**, 401 (1923).
3. A. R. Parker, V. L. Welch, D. Driver, and N. Martini, *Nature*, **426**, 786 (2003).
4. K. Q. Zhang, W. Yuan, and A. Zhang, *Functional Materials Information*, **7**, 39 (2010).
5. M. Sachiko and M. Shimomura, *Colloid. Surface. A.*, **284**, 315 (2006).
6. G. A. Tayeb, B. Gralak, and S. Enoch, *Optics and Photonics News*, **14**, 38 (2003).
7. R. C. McPhedran, N. A. Nicorovici, D. R. McKenzie, L. C. Botten, A. R. Parker, and G. W. Rouse, *Aust. J. Chem*., **54**, 241 (2001).
8. P. Mitra, A. P. Chatterjee, and H. S. Maiti, *J. Mater. Sci.: Mater. Electron.*, **9**, 441 (1998).
9. K. E. Davis, W. B. Russel, and W. J. Glantschnig, *Science*, **245**, 507 (1989).
10. H. Miguez, F. Meseguer, C. Lopez, A. Mifsud, J. S. Moya, and L. Vazquez, *Langmuir*, **13**, 6009 (2013).
11. J. Chen, P. T. Dong, D. Di, C. G. Wang, H. X. Wang, J. F. Wang, and X. Z. Wu, *Appl. Surf. Sci.*, **270**, 6 (2013).
12. H. T. Fu and K. Takaomi, *Desalination*, **264**, 115 (2010).
13. X. Chen, X. Zhang, W. S. Yang, and D. G. Evans, *Mater. Scie. Eng. C*, **29**, 284 (2009).
14. Z. P. Li, J. Q. Wang, X. H. Liu, J. F. Ou, and S. R. Yang, *J. Mater. Chem.*, **21**, 3397 (2011).
15. W. Stöber, A. Fink, and E. Bohn, *J. Colloid Interf. Sci.*, **26**, 62 (1968).
16. A. Y. Cai, S. L. Zhang, A. P. Zhu, and D. Sheng, *Polym. Compos.*, **31**, 807 (2009).
17. Y. Takeda, Y. Komori, and H. Yoshitake, *Colloid. Surface. A.*, **422**, 68 (2013).
18. G. H. Bogush, M. A. Tracy, and C. F. Zukoski, *J. Non-Cryst. Solids*, **104**, 95 (1988).
19. S. R. Kline and E. W. Kaler, *J. Colloid Interf. Sci.*, **203**, 392 (1998).
20. T. Matsoukas and E. Gulari, *J. Colloid Interf. Sci.* **124**, 252 (1988).
21. V. K. Lamer and R. H. Dinegar, *J. Am. Chem. Soc.*, **72**, 4847 (1950).
22. T. Fujie, Y. Okamura, and S. J. Takeoka, *Colloid. Surface. A.*, **334**, 28 (2009).