

Preparation and Characterization of Porous Titanium Dioxide Sulfonated Polystyrene Composite Microspheres with Amphiphilicity

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ABSTRACT: Porous particles with amphiphilicity were prepared by a nonpolymeric pore-formation process with the sulfonation of polystyrene microspheres. Nano titanium dioxide (TiO_2) particles were then grafted onto the surface via a sol-gel method to finally form the composite particles. The effects of the mass ratio of ethanol (EtOH) to water, temperature, and solubility parameter on the pore-formation process is discussed in detail. The morphology, porous structure, and wetting properties of the particles were studied by scanning electron microscopy, transmission electron microscopy, Fourier transform infrared (FTIR) spectroscopy, and contact angle measurement. The results show that porous sulfonated polystyrene (SP) microspheres could be fabricated at 60°C with a 1 : 1 mass ratio of EtOH-water and a solubility parameter of $29.69 \text{ MPa}^{1/2}$. The TiO_2 particles were determined to be grafted onto the SP microspheres by physical-bond interaction on the basis of FTIR analysis. The contact angles for both water (aqueous-phase) and various organic solvent (oil-phase) droplets with different polarities on the surface of compressed tablets of TiO_2 -SP powder were all lower than 30° ; this indicated excellent amphiphilicity in the composite particles. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000-000, 2013

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INTRODUCTION

Porous polymer microspheres with amphiphilicity are of industrial and academic value because of their distinctive properties, including great dispersability in various solutions,¹ excellent adsorptivity, self-assembly ability,² and so on. Generally, these polymers are composited with an inorganic shell for specific purposes. Nano titanium dioxide (TiO_2) particles have properties such as a strong hydrophilicity, photocatalysis, and anti-ultraviolet capability and are frequently used as the shell layer. With their porous structure and amphiphilicity, the composites are broadly involved in many applications, including controlled release delivery,^{3,4} amphipathic adsorption,⁵ supported catalysis,⁶ membrane protein carrier,⁷ and heat insulation purposes.⁸ They especially have advantages in photocatalysis for the treatment of pollutants and functionalization for cosmetics. For example, water polluted with organics or inorganics can be purified under lighting conditions because of the high-efficiency photocatalysis of nano- TiO_2 particles fixed on polymer microspheres in the case of agglomeration, and the excellent amphiphilicity of the polymer offers their great dispersability in various types of polluted solutions. Simultaneously, the microspheres,

with a porous structure, as a support of TiO_2 particles can achieve outstanding pollutant-adsorption and catalytic efficiency with their great surface areas and convenient reusability after specific treatments. In functionalized cosmetics, the composites show superiority by offering great adsorption and slow-release effects for various active ingredients from hydrophobic to hydrophilic; these include vitamins or whitening agents because of the amphiphilicity and porous structure, whereas the attached nano- TiO_2 particles on the surface of microspheres may provide effective anti-ultraviolet capabilities.⁹

To fabricate porous composite particles with amphiphilicity, the first step is generally to create a porous structure by suspension polymerization, the stepwise alkali-acid method,¹⁰ seed swelling,^{11,12} or multiple emulsion polymerizations.¹³ The hydrophilicity of the polymer microspheres is then modified for a better connection with inorganic nanoparticles before the composite process by the introduction of hydrophilic groups such as surfactants or sulfonic or nitro groups into the microspheres. The sulfonic groups especially can offer excellent modification of the hydrophilicity. After modification, with active groups and a quantity of electricity, the polymer can firmly bond with

inorganic particles via the sol–gel method,¹⁴ reversible addition–fragmentation chain-transfer polymerization in supercritical CO₂,¹⁵ and so forth. However, many of these methods have certain limitations, for instance, toxic materials, complex processes, severe conditions, and poor amphiphilic effects. In addition, most methods for pore formation belong to polymerization, and the simple nonpolymeric pore-formation process has rarely been discussed. In fact, the process may show advantages in allowing the use of low-toxic porogens, such as *n*-heptane; less use of porogens; and the retention of a stable particle size during pore formation. In this article, a nonpolymeric approach for fabricating cage-like, porous TiO₂–sulfonated polystyrene (SP) composite microspheres with amphiphilicity is proposed. The porous particles with amphiphilicity were first prepared by a nonpolymeric pore formation process with the sulfonation of polystyrene (PS) microspheres. Nano-TiO₂ particles were then grafted onto the surface via the sol–gel method to finally form the composite particles, and the wetting properties of the composites for a variety of solvents with different polarities were examined in detail to demonstrate the amphiphilicity.

EXPERIMENTAL

Materials

The chemicals, including phenylethylene (St), 2,2-azobisisobutyronitrile (AIBN), sulfuric acid, *n*-heptane, tetrabutyl titanate, ethanol (EtOH), and hydrochloric acid (HCl), were all analytical grade and were purchased from Guangdong Guanghua Sci-Tech Co., Ltd. (Guangzhou, China). Poly(vinyl pyrrolidone) (PVP), also analytical grade, was from Shanghai Hengyuan Biochemical Reagents Co., Ltd. (Guangzhou, China). St, PVP, and AIBN were used as the starting materials in the preparation of the PS microspheres. Concentrated sulfuric acid was used as the sulfonating agent, and deionized water was needed as a solvent.

Preparation of the Porous SP Microspheres

In this experiment, PS microspheres were synthesized by dispersion polymerization. Typically, St (31.85 g), AIBN (0.32 g), and PVP (1.274 g) were dispersed in EtOH solution under ultrasound for 10 min. Polymerization was carried out at 70°C for 24 h with stirring at 300 rpm. The product was repeatedly washed in water and EtOH after filtration and dried *in vacuo*.

The previously synthesized PS microspheres (2 g) were dispersed in concentrated sulfuric acid (50 g) under ultrasound for 10 min. The sulfonation reaction was carried out at 40°C for 6 h with stirring at 300 rpm. After it was diluted by deionized water, the sample was repeatedly centrifuged and washed with EtOH–water and then dried *in vacuo* for 24 h.

The SP microspheres obtained previously were dispersed with EtOH–water mixtures (50 g) with different mass ratios, and *n*-heptane (10 g) was added to the mixture with stirring at a specific temperature for 6 h. The SP microspheres were then swollen and partly dissolved by the mixture of *n*-heptane and EtOH–water during this process, and the *n*-heptane was subsequently removed by repeated washing with water and EtOH after filtration. After further drying *in vacuo*, the porous SP microspheres were obtained.

Preparation of the Porous TiO₂–SP Microspheres with Amphiphilicity

The obtained porous SP microspheres (0.3 g) and tetrabutyl titanate (1 g) were added to EtOH (16 g) to obtain a solid–liquid mixture, whose pH was adjusted to below 4.5 by the addition of HCl. Then, a mixture of deionized water (0.5 g) and EtOH (16 g) was slowly dropped into the solid–liquid mixture at room temperature for 5 h under agitation.

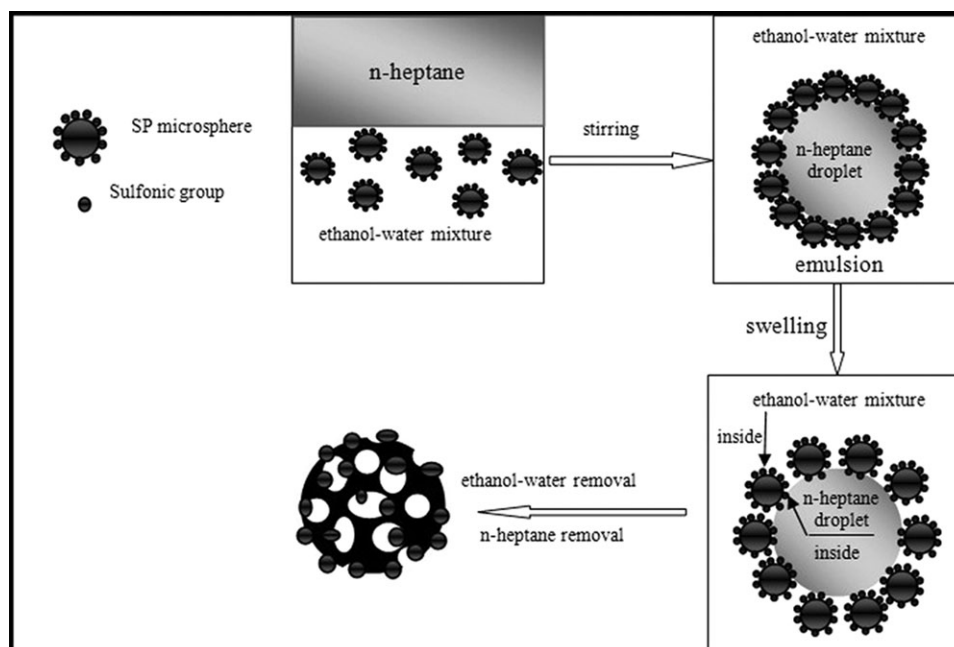


Figure 1. Schematic illustration of pore formation.

Table I. Particle Size and Size Distribution

Particle type	Average size (nm)	Polydispersity index
PS particles	1805	0.115
Porous SP microspheres	1792	0.168
TiO ₂ -SP composites	1995	0.163

The SP microspheres were electronegative because of the graft of sulfo groups and could adsorb the TiO₂ particles that were generated electropositively under acidic conditions via electrostatic adhesion.

Characterization

The particle size analysis was achieved by Malvern ZS Nano S analyzer (London, United Kingdom), and the elemental contents were analyzed by an Elementar Vario EL III (Hanau, Germany). The surface and cross-sectional morphology of the microspheres were observed by scanning electron microscopy LEO 1530VP (Oberkochen, Germany) and transmission electron microscopy Hitachi H-7650 (Tokyo, Japan). The wettability of the porous particles was measured by a Dataphysics OCA-20 contact angle analyzer (Stuttgart, Germany). This instrument consisted of a charge-coupled device video camera with a resolution of 768 × 576 pixels and up to 50 images per second, multiple dosing/microsyringe units, and a temperature-controlled environmental chamber. The drop image was processed

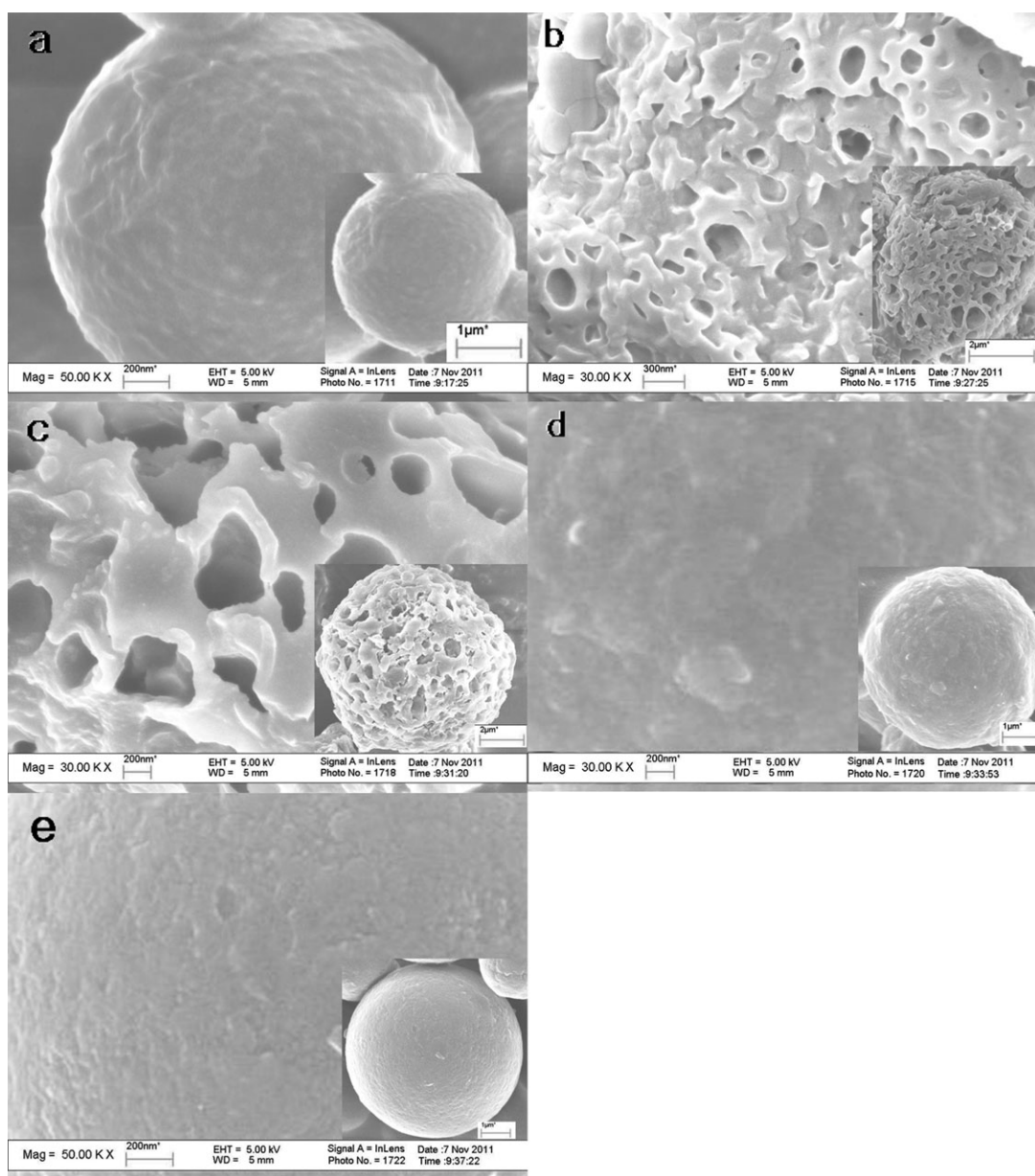


Figure 2. Surface morphology of microspheres prepared EtOH–water solutions with different mass ratios: (a) 0 : 50, (b) 15 : 35, (c) 25 : 25, (d) 35 : 15, and (e) 50 : 0.

Table II. Effect of the Mass Proportion of EtOH to Water on the Porous Structure and Morphology

EtOH-water (g/g)	Temperature (°C)	n-Heptane (g)	Porous structure and morphology
0 : 50	70	10	Convex surface, no pores
15 : 35	70	10	Rough surface, porous
25 : 25	70	10	Rough surface, porous
35 : 15	70	10	Smooth surface, no pores
50 : 0	70	10	Smooth surface, no pores

by an image analysis system, which calculated both the left and right contact angles from the shape of the drop with an accuracy of $\pm 0.01^\circ$. Fourier transform infrared (FTIR) spectra were conducted on a 380 FTIR spectrometer (Nicolet Instruments Co., Wisconsin, USA) in the range from 4000 to 400 cm^{-1} in transmission.

RESULTS AND DISCUSSION

Process of Pore Formation

The sulfonating process is critical to the pore-formation process. As sulfonic groups with a strong hydrophilicity are grafted to microspheres, the microspheres become partly hydrophilic but remain lipophilic because of the PS chains; this results in an excellent amphiphilicity. Thus, the SP microspheres obtain a

similar function like an emulsifier because of the amphiphilicity. Because of the hydrophilic effect of the sulfonic groups, strong osmotic pressure is, therefore, generated inside the SP particles,¹⁶ which acts as the swelling power in pore formation when the SP particles are placed in a properly polar solvent.

The process of porous structure formation is shown in Figure 1. The solvent is made up of aqueous and oleic phases. The SP microspheres were first dispersed at the interface between water–oil phases, and they formed a stable Pickering emulsion system.¹⁶ They could be swollen by an oily monomer after emulsification. Under stirring conditions, the oily monomer was dispersed into droplets and further swelled the SP microspheres. Moreover, the SP particles were permeated by water droplets at the same time, with the help of water osmotic

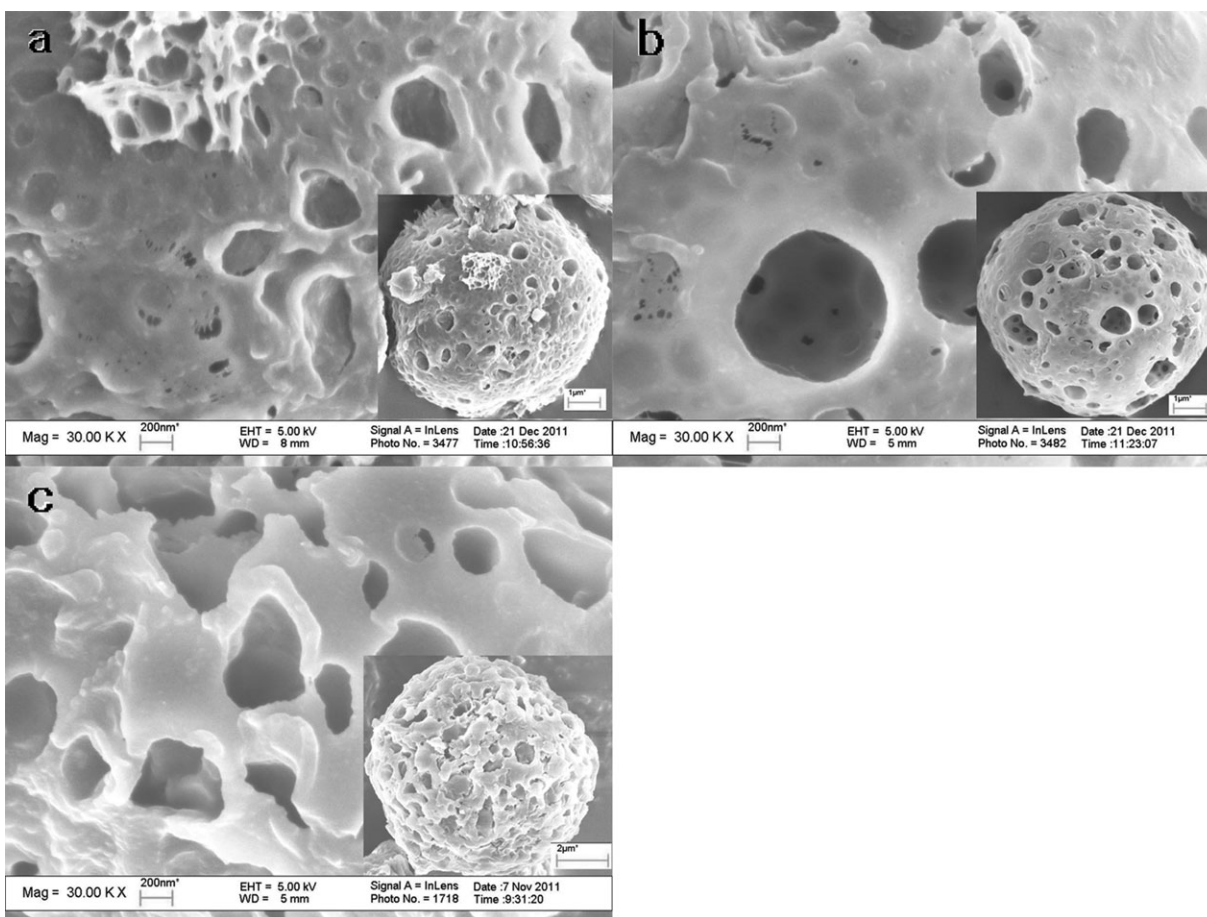


Figure 3. SEM images of porous SP microspheres prepared at (a) 50, (b) 60, and (c) 70°C.

Table III. Effect of the Temperature on the Porous Structure and Morphology

Temperature (°C)	EtOH-water (g/g)	<i>n</i> -Heptane (g)	Porous structure and morphology
50	25 : 25	10	Superficially porous, no holes inside
60	25 : 25	10	Cagelike porous, relatively smooth surface
70	25 : 25	10	Rough surface, porous

pressure; this was due to the hydrophilicity of sulfonate groups. The SP particles were hence internally dissolved by the porogen *n*-heptane. Pores were formed after *n*-heptane, EtOH, and water were removed by repeated washing and drying. The porous microspheres were finally obtained by the previous procedure. We easily discovered two key factors in the pore formation based on this specific process: the amphiphilicity of the microspheres and the polarity of the solvents. The former offered the osmotic power, and the latter constructed the environment for generating osmotic pressure. The amphiphilicity could be obtained by sulfonation. Various kinds of monomers, including methyl methacrylate and St, or the solvent *n*-heptane could be used to dissolve the microspheres with some polar substances, such as water and *n*-butylacrylate, added to adjust their polarity. A closed polarity implies a similar solubility parameter, and a small difference in the solubility parameter between the solvents and polymer microspheres can lead to an excellent dissolution effect.

Particle Size and Content of Sulfonic Groups

Three types of microspheres, PS particles, porous SP microspheres, and TiO₂-SP composites, were dispersed in EtOH for particle size characterization, and the average sizes were 1805, 1792, and 1995 nm with polydispersity indices of 0.115, 0.168, and 0.163, respectively; these imply a great monodisperse performance. We also found that the particle sizes changed little during the pore-formation and composite processes. The content of sulfonic groups on the PS particles was measured by elemental analysis. The mass fractions for C, H, S, and O were

89.82, 7.47, 1.05, and 1.65%, respectively, and the C/H/S/O ratio was 220 : 220 : 1 : 3 in the atom number proportion form; this indicated the introduction of sulfonic groups (Table I).

Effect of the Mass Ratio of the EtOH–Water Mixture

EtOH–water mixtures with different mass ratios were used as solvents in the pore-formation process. Whether the microspheres could be prepared as porous was decided by the specific mass ratio of EtOH to water. Five parallel experiments with mass ratios of EtOH to water of 0 : 50, 15 : 35, 25 : 25, 35 : 15, and 50 : 0 were carried out at 70°C to study the effects. The SEM observations of the porous structure are shown in Figure 2. It was clear that the porous structure was highly related to the EtOH–water mass ratio. Three runs, in which the mass ratios were 0 : 50, 35 : 15, or 50 : 0, did not successfully result in porous microspheres, and the surfaces of the microspheres were relatively smooth. Both of the remaining runs, with EtOH–water mass ratio of 15 : 35 and 25 : 25, resulted in porous microspheres with rough surfaces (Table II and Figure 2).

In this specific process, *n*-heptane acted as an oleic phase, and the EtOH–water mixture acted as an aqueous phase to adjust the solution polarity. The solubility of both EtOH and *n*-heptane for PS was poor at room temperature, whereas it could be improved with an increase in the temperature. The existence of EtOH contributed to better swelling of the SP particles for *n*-heptane. Under heating conditions, the SP particles were easier to swell with *n*-heptane and EtOH. With a 0 : 50 mass ratio of EtOH to water, that is, without the help of EtOH, *n*-heptane could not disperse in water and lacked the osmotic power to swell the SP particles. When the EtOH mass increased, the solution polarity was close to that of SP particles; this favored the swelling process. However, as EtOH was added in excess, a great polarity difference could occur; this led to a relatively poor solubility for the SP microspheres. As a result, the particles could not form porous structures under a 35 : 15 mass ratio of EtOH to water. For the 50 : 0 mass ratio of EtOH to water, *n*-heptane was totally dispersed in EtOH and could not form droplets at all without water; this led to a deficiency of osmotic power, and hence, no porous microspheres could be fabricated. With a proper EtOH–water mass ratio, such as 25 : 25 or 15 : 35, the osmotic power and a limited small polarity difference

Table IV. Effect of the Solubility Parameter on the Pore Formation

Runs	EtOH-water (g/g)	Temperature (°C)	δ_{water} (MPa ^{1/2})	w_{water}	δ_{ethanol} (MPa ^{1/2})	w_{ethanol}	$\delta_{\text{n-heptane}}$ (MPa ^{1/2})	$w_{\text{n-heptane}}$	δ_m (MPa ^{1/2})	Morphology
Figure 2(a)	0 : 50	70	46.42	0.77	23.93	0.00	13.89	0.23	38.93	No pores
Figure 2(b)	15 : 35	70	46.42	0.50	23.93	0.27	13.89	0.23	32.86	Porous
Figure 2(d)	35 : 15	70	46.42	0.20	23.93	0.58	13.89	0.22	26.21	No pores
Figure 2(e)	50 : 0	70	46.42	0.00	23.93	0.81	13.89	0.19	22.02	No pores
Figure 2(c)	25 : 25	70	46.42	0.35	23.93	0.44	13.89	0.21	30.19	Porous
Figure 3(b)	25 : 25	60	47.04	0.35	24.44	0.44	14.16	0.21	29.69	Porous
Figure 3(a)	25 : 25	50	47.65	0.35	24.94	0.44	14.42	0.21	30.67	Porous

Here, δ_{water} , δ_{ethanol} , and $\delta_{\text{n-heptane}}$ are the solubility parameter of water, ethanol and *n*-heptane respectively. w_{ethanol} and $w_{\text{n-heptane}}$ are the volume fraction of ethanol and *n*-heptane.

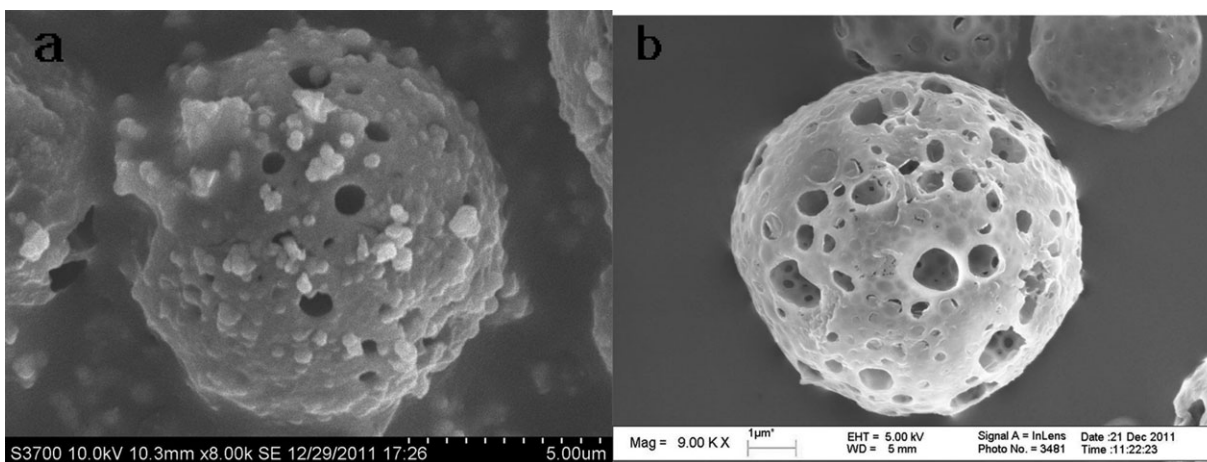


Figure 4. SEM image of the (a) TiO₂-SP and (b) SP microspheres.

were obtained; therefore, the pore formation could be successfully achieved as a consequence.

Effect of the Temperature

The solubility played a key role during the whole pore-formation process. As we know, both EtOH and *n*-heptane are poor in solubility for PS at room temperature; however, it can be improved by increasing the temperature. In this part of the study, we adjusted the solubility by controlling the temperature and successfully fabricated porous microspheres. The pore-formation process was carried out at 50, 60, and 70°C, respectively. The results are shown in Figure 3.

EtOH and *n*-heptane were poor solvents and could not swell the SP microspheres well at 50°C; the prepared SP microspheres were externally porous but had no internal holes. As the temperature rose to 60°C, cage-like porous microspheres could be successfully fabricated because of the improved solubility of EtOH and *n*-heptane. However, some SP microspheres seemed to be partly dissolved in solvents and were superficially rough when they were swollen at 70°C (Table III).

Analysis of the Solubility Parameter

The solubility parameter of a mixture (δ_m) can be calculated by the following equation:¹⁷

$$\delta_m = \sum_{i=1}^n \delta_i w_i, \quad \sum_{i=1}^n w_i = 1$$

where δ_i is the solubility of single component *i* and w_i is the volume fraction of the single component. The calculated solubility parameters for a variety of mixtures of solvents are listed in Table IV.

The solubility parameter of the SP particles was preliminarily tested to be 29.34 MPa^{1/2} by the equilibrium swelling method.¹⁸ As we all know, a close solubility parameter between solvents and particles can achieve a good dissolution effect. As shown in Table IV, the run of Figure 3(b), corresponding to a solubility parameter of 29.69 MPa^{1/2}, which was the most similar solubility parameter to the SP particles (29.34 MPa^{1/2}) achieved a deeply porous structure with some small inside holes. The runs of Figures 2(b,c) and 3(a), with solubility parameters of 32.86, 30.19, and 30.67, respectively, only obtained superficially porous

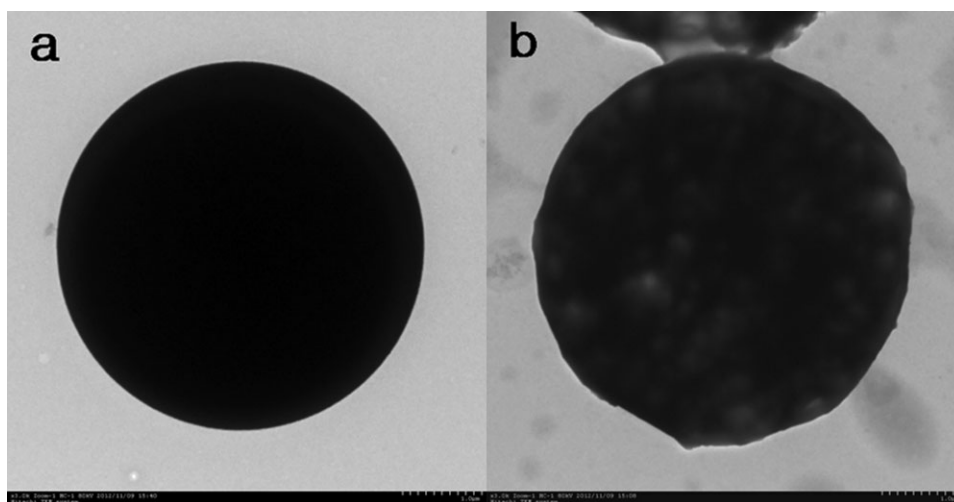


Figure 5. TEM images of the (a) PS and (b) porous SP microspheres.

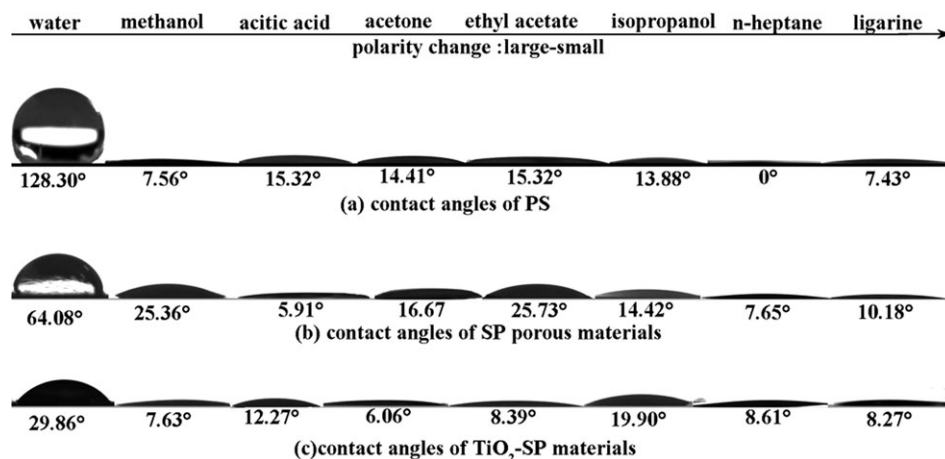


Figure 6. Contact angles for droplets of solutions with different polarities.

structures, and the pore paths did not extend much inside. Although the rest of runs shown in Table IV, with solubility parameters far away from $29.34 \text{ MPa}^{1/2}$, failed to form porous structures because of the large difference in solubility parameters between the SP microsphere and the solution mixtures.

Morphology of the Composite Microspheres

The nano-TiO₂ particles were prepared electropositively in the sol-gel process¹⁹ and hence adhered to the electronegative SP microspheres to form the TiO₂-SP composite particles. As shown in Figure 4, the TiO₂-SP composite particles become much rougher [Figure 4(a)] with the grafted nano-TiO₂ particles on their surface compared to the original SP microspheres shown in Figure 4(b). Some TiO₂ particles adhered to the internal pores with small size and led to many plugged pores, and part of the holes were totally sealed by the TiO₂ particles. This

needs further improvement and will be addressed in our future studies.

As shown by the TEM images in Figure 5, the internal pores are shown by some light-colored parts in Figure 5(b) for the porous SP microspheres, whereas the totally dark color (without pores) shows the original PS microsphere in Figure 5(a).

Analysis of Amphiphilicity

Figure 6 shows the contact angles for water (aqueous-phase) and organic solvent (oil-phase) droplets with polarity orders from large to small on the surface of the compressed tablets of PS, porous SP, and TiO₂-SP powders, respectively. For all of the organic droplets used, the contact angles of the three powder materials were less than 30°; this indicated an outstanding lipophilicity. However, the water contact angles changed significantly, from 128.3° for the original PS powder to 64.08° for the porous SP after sulfonation to 29.86° for the TiO₂-SP composite powders and finally became hydrophilic with the introduction of sulfonic groups and TiO₂ particles. Therefore, two types of amphiphilic materials, porous SP and TiO₂-SP powders (the latter especially exhibited better amphiphilicity), were prepared.

FTIR Analysis

The FTIR spectra of the PS, porous SP, and TiO₂-SP composite particles are shown in Figure 7 for comparison. Table V lists the

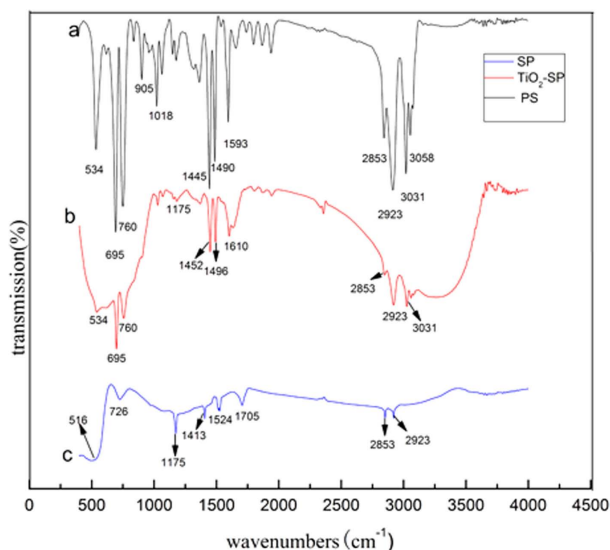


Figure 7. FTIR spectra of the PS (a), TiO₂-SP composite (b) and porous SP (c) particles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table V. Assignment of the FTIR Peak Positions

Assignment	Peak positions (cm ⁻¹)		
	PS	SP	TiO ₂ -SP
C-H(-C ₆ H ₅)	534, 695, 760, 905	516, 726	534, 695, 760, 3031
			1018, 3031, 3058
C-H(-CH ₂ -)	2853, 2923	2853, 2923	2853, 2923
C=C(-C ₆ H ₅)	1445, 1490, 1593	1413, 1524, 1705	1452, 1496, 1610
S=O(-SO ₃ H)	—	1175	1175

analyzed FTIR absorption peaks. Peaks in the ranges 500–1018 and 3000–3100 cm^{-1} corresponded to the absorption of C–H in the benzene ring, and peaks in the range 1400–1700 cm^{-1} were attributed to the C=C stretching absorption. Peaks at 2863 and 2923 cm^{-1} were from the stretching vibration band of the C–H of methylene. In addition, the peak at 1175 cm^{-1} , which resulted from the introduced S=O ($-\text{SO}_3\text{H}$), was present in the FTIR spectra of SP and TiO_2 -SP. It stayed the same after the TiO_2 was fixed on the SP microsphere surface, and this indicated that the TiO_2 particles were grafted onto the porous SP microspheres via a physical force instead of via chemical bonding.

CONCLUSIONS

In summary, we have proposed a method for fabricating porous TiO_2 -SP composite microspheres with amphiphilicity. The amphiphilicity and porous structure were acquired by sulfonation and the swelling process. In the pore-formation process, an EtOH–water mixture and *n*-heptane were used as swelling solvents. Adjusting the mass ratio of EtOH to water to achieve a proper polarity was demonstrated to be feasible, and a suitable swelling temperature was necessary to obtain a proper solvent dissolubility for this specific pore formation. TiO_2 nanoparticles were finally grafted onto the porous SP microspheres through electrostatic adhesion. In addition, the contact angle analysis implied excellent amphiphilicity of the fabricated porous composite particles, and this enabled the porous polymer, with potential for various fields.

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