Preparation of Polymer Hollow Microspheres Covered by Polymer Solid Particles via Two Polymerization Steps

Yongliang Zhao, Guannan Yin, Zheng Zheng, Haitao Wang, Qiangguo Du

Key Laboratory of Molecular Engineering of Polymers of Ministry of Education, Department of Macromolecular Science, Fudan University, Shanghai 200433, People’s Republic of China
Correspondence to: H. Wang (E-mail: wanght@fudan.edu.cn)

Received 2 August 2011; accepted 10 September 2011; published online 26 September 2011
DOI: 10.1002/pola.25002

ABSTRACT: A novel surface modification method for titania nanoparticles is provided via the surface-initiated photocatalytic polymerization with the aid of acrylic acid (AA) or sodium styrene sulfonate (NaSS). The properties of modified titania nanoparticles are investigated with aqueous electrophoresis measurements, dynamic light scattering (DLS), and transmission electron microscopy (TEM). Then the modified titania is used as Pickering stabilizer for further polymerization and the morphology of the resulted polymer microspheres is characterized by TEM and field-emission scanning electron microscopy. It is proven that the addition of AA or NaSS for the surface-initiated polymerization can obviously affect the structure and morphology of the final polymer composite microspheres. The formation mechanism of several kinds of polymer particles is also proposed. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 5257–5269, 2011

KEYWORDS: chemical grafting; emulsion polymerization; microstructure; stabilization; surface-initiated polymerization

INTRODUCTIOm Instead of molecular surfactants (small molecular surfactants or amphiphilic copolymers), solid particles, such as silica, metals, quantum dots, apatite, clays, and titania, are also used to stabilize emulsions, which is often called Pickering emulsion. The solid particles spontaneously self-assemble on an oil-water interface, forming a core-shell structure to impede coalescence of the two adjacent droplets. The attachment energy of solid particles on the interface is especially higher than that of molecular surfactants, which can ensure a long-term stability of emulsions for storage. Based on this merit, Pickering emulsions are extensively applied in fields such as cosmetics, food, petrochemicals, oil refining, and ore purification. As a crucial component in Pickering emulsions, the surface properties of solid particles are extremely significant, for example, charge, size, shape, wettability and the interaction between particles. Particles with appropriate hydrophobicity and weak flocculation are thought to can effectively stabilize emulsions.

Solid particles can also be used as stabilizer during polymerization. Polymer microspheres armored with clay and titania and silica have been successfully prepared by Bon using Pickering emulsion or miniemulsion polymerization. Armes and his group used commercially available silica particles to fabricate polymer/silica nanocomposites. Tiarks et al. have made a pioneering work on silica-stabilized polymer latex via miniemulsion polymerization. However, not every solid particle can be used to stabilize the emulsions, due to their extreme hydrophilicity or hydrophobicity. Recently, synergistic stabilization effect of solid nanoparticles and molecular surfactants in the formation and stability of emulsions have attracted extensive research. As we know, the wettability of particles can be easily modified by the small molecular surfactants, for example, nonionic, anionic, and cationic surfactants in aqueous phase via electrostatic adsorption and other interactions. In our previous paper, sodium oleate and oleic acid were used to improve the hydrophobicity of titania nanoparticles so as to stabilize emulsions effectively. The synergistic stabilization of solid particles and molecular surfactant is effective and this modification method is easy to realize. However, the stabilization mechanism is still under further research, for example, the contact angle θ increases when the hydrophobicity of particles is improved, and therefore the attachment energy E increases according to $E = \pi r^2 \gamma (1 - \cos \theta)^2$. Differently, the addition of molecular surfactants decreases interfacial energy γ, which is harmful to the increase of E. Therefore, it is not only synergistic but competitive between particles and surfactants. Other methods have also been reported to modify the wettability of nonsurface active particles via physical treatments such as ion exchange and chemical treatments. Some papers by Armes and Wu found that surface-functionalized silica particles as Pickering stabilizer preferred the formation of stable polymer-silica composite particles. The silica particles were modified by silane coupling agents such as...
3-(trimethoxysilyl) propyl methacrylates, 27 γ-glycidoxypropyl trimethoxysilane and γ-glycidoxypropyl methyldiethoxysilane. 28, 29 Voorn reported the preparation of polymer colloidal particles via inverse Pickering emulsion polymerization using organically modified clay platelets as stabilizer. 30 Recently, Zhao’s group has made a lot of researches on the fabrication of polymer microspheres stabilized by inorganic particles with polymer brushes. 31–33 In our previous paper, we used sodium oleate and oleic acid modified titania as Pickering stabilizer to prepare hollow and solid polystyrene (PS) microspheres via photocatalytic polymerization. 24 Herein, graft of PS chains on the surface of titania nanoparticles is used to improve their hydrophobicity via surface-initiated polymerization. Then the modified titania is utilized as Pickering stabilizer to fabricate PS/titania composite particles. Hexadecane (HD) is used to track the movement and distribution of monomer in initial droplets during the polymerization. Meanwhile, acrylic acid (AA) or sodium styrene sulfonate (NaSS) is used to increase grafting amount of PS chains on titania surface and improve the stability of the oil droplets. In this article, we provide a convenient modification method for titania particles and a new route to control the morphology and structure of resulted polymer microspheres. Several possible formation mechanisms of polymer particles are also proposed.

### EXPERIMENTAL

#### Materials

Titanium (IV) chloride (TiCl₄; ≥98.0%), styrene (St; ≥99.0%), hexadecane (HD; ≥98.0%), acrylic acid (AA; ≥98.0%), sodium styrene sulfonate (NaSS; ≥98.0%), methanol (≥98.0%), and ethanol (EtOH; ≥99.7%) were all purchased from Sinopharm Chemical Reagent (China). St and AA were distilled under vacuum before use and other reagents were used as received. Deionized water was used throughout the experiments.

### Surface Modification of Titania Nanoparticles via Surface-Initiated Polymerization

The transparent anatase titania hydrosol was prepared by a controlled nonhydrolytic sol-gel method as mentioned in our previous work. 34 A small amount of hydrophobic PS chains were grafted onto the surface of titania nanoparticles via surface-initiated photocatalytic polymerization. As shown in Table 1, a certain amount of styrene and coupling agent (AA or NaSS) was added into a 25 mL glass flask with 15.0 g 1.0 wt % titania hydrosol. A constant magnetic stirring was conducted in the dark for 1 h at room temperature until the adsorption equilibrium. Then the flask was exposed to the XQ 500 W Xe lamp (the distance from the flask to the Xe lamp was 20 cm) with a constant magnetic stirring for 6 h at room temperature. The obtained turbid hydrosol was centrifuged (13,000 rpm, 30 min) by the TGL-16G centrifuge and washed with water and methanol for three times to remove free titania and oligomers. The surface-modified titania nanoparticles were dried or redispersed in water for the following measurements and experiments.

### Preparation of PS Microspheres via Photocatalytic Pickering Polymerization

PS microspheres were fabricated via a photocatalytic polymerization using titania as Pickering stabilizer and photocatalyst. In a typical preparation, the PS-modified titania particles (sample 5, 9, and 13) were redispersed in aqueous to obtain 15 g of 1.0 wt % titania hydrosol and mixed with 0.9 g oil phase (0.60 g St + 0.30 g HD) in a 25 mL glass flask. The mixture was emulsified by the FJ200-S homogenizer at 14,000 rpm for 10 min and the resulted emulsion was deoxygenated by bubbling with N₂ for 5 min. The polymerization was then conducted by exposing the flask to the XQ 500 W Xe lamp (the distance from the flask to the Xe lamp was 20 cm) with a constant magnetic stirring for 24 h at room temperature. The polymer microspheres were centrifuged (13,500 rpm, 15 min) from the emulsions by the TGL-16G centrifuge and redispersed in water or dried for

### Table 1 Recipes in 15 g of 1.0 wt % Titania Hydrosol for the Surface Modification via Surface-Initiated Photocatalytic Polymerization

<table>
<thead>
<tr>
<th>Sample</th>
<th>Titania (g)</th>
<th>AA (1.0 wt %) (g)</th>
<th>NaSS (1.0 wt %) (g)</th>
<th>St (g)</th>
<th>H₂O (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.15</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>15.0</td>
</tr>
<tr>
<td>2</td>
<td>0.15</td>
<td>–</td>
<td>–</td>
<td>0.0075</td>
<td>15.0</td>
</tr>
<tr>
<td>3</td>
<td>0.15</td>
<td>–</td>
<td>–</td>
<td>0.0150</td>
<td>15.0</td>
</tr>
<tr>
<td>4</td>
<td>0.15</td>
<td>–</td>
<td>–</td>
<td>0.0225</td>
<td>15.0</td>
</tr>
<tr>
<td>5</td>
<td>0.15</td>
<td>–</td>
<td>–</td>
<td>0.0300</td>
<td>15.0</td>
</tr>
<tr>
<td>6</td>
<td>0.15</td>
<td>0.375</td>
<td>–</td>
<td>0.0075</td>
<td>15.0</td>
</tr>
<tr>
<td>7</td>
<td>0.15</td>
<td>0.375</td>
<td>–</td>
<td>0.0150</td>
<td>15.0</td>
</tr>
<tr>
<td>8</td>
<td>0.15</td>
<td>0.375</td>
<td>–</td>
<td>0.0225</td>
<td>15.0</td>
</tr>
<tr>
<td>9</td>
<td>0.15</td>
<td>0.375</td>
<td>–</td>
<td>0.0300</td>
<td>15.0</td>
</tr>
<tr>
<td>10</td>
<td>0.15</td>
<td>–</td>
<td>0.375</td>
<td>0.0075</td>
<td>15.0</td>
</tr>
<tr>
<td>11</td>
<td>0.15</td>
<td>–</td>
<td>0.375</td>
<td>0.0150</td>
<td>15.0</td>
</tr>
<tr>
<td>12</td>
<td>0.15</td>
<td>–</td>
<td>0.375</td>
<td>0.0225</td>
<td>15.0</td>
</tr>
<tr>
<td>13</td>
<td>0.15</td>
<td>–</td>
<td>0.375</td>
<td>0.0300</td>
<td>15.0</td>
</tr>
</tbody>
</table>
the following characterizations. Meanwhile, three control experiments were designed and the details were shown in Table 2. It should be noted that there was only one polymerization step in these three experiments.

**Characterization**

The morphologies of prepared titania/PS microspheres were characterized with the Hitachi H-600 transmission electron microscopy (TEM) and Hitachi S-4800 field-emission scanning electron microscopy (FE-SEM). They were dropped onto the carbon-coated lacy substrates for observation. The amount of PS grafted on the surfaces of the titania particles was measured by thermogravimetric analysis (TGA) using a Perkin–Elmer Pyris 1 thermogravimetric analyzer at a heating rate of 20 °C/min under air atmosphere. Before TGA tests, the samples were dried at 80 °C for 24 h. The titania content of the polymer microspheres was also investigated by TGA with the same heating condition. The particle size distribution of the titania hydrosol was determined by means of dynamic light scattering (DLS), performing at 25 °C on the Malvern Autosizer 4700 at a scattering angle of 90°. The hydrosol was diluted 10 times with a concentration of 0.1 wt % in a PS cell for the measurement. The zeta potential of the titania hydrosol was measured with the Malvern Zetasizer Nano ZS instrument at pH 4.0. Microscopy images of initial emulsion droplets were taken with the aigo EV5680 Optical Microscope. The emulsions were diluted and dropped onto a glass slide. The morphologies of the PS microspheres were also observed by the TESCAN 5136MM SEM. The dispersions of the PS microspheres were diluted with ethanol and dried on a glass slide followed by sputter coating with gold. FTIR spectra were taken on the Nicolet Nexus-470 FTIR spectrometer. The surface-modified titania nanoparticles were centrifuged and washed with ethanol and water, dried in a vacuum oven for 24 h, and then pressed into KBr pellets for FTIR measurements.

**RESULTS AND DISCUSSION**

**Surface Modification of Titania Hydrosol via Surface-Initiated Photocatalytic Polymerization**

It is well known that the surface chemistry of inorganic particles is significant in Pickering emulsions. The stability of the initial emulsion droplets and the morphology and structure of the final polymer particles are both affected by it. Hence, aqueous electrophoresis is used to characterize the zeta potential of the modified titania hydrosols, as shown in Figure 1. The zeta potential of the intrinsic cationic titania is +51.2 mV at pH 4.0. Titania colloidal particles are well dispersed in water by a strong electrostatic repulsion. The zeta potential has a slight decrease when 2.5 wt % (relative to titania) of AA or NaSS is added. Differently, the decrease is more obvious when NaSS is used because NaSS molecules tend to adsorb on the surface of cationic titania nanoparticles via an electrostatic attraction. The interaction shields partial charges of titania and results in an obvious decrease. However, AA can just adsorb onto the surface of titania particles via a coordination between titanium centers and the carboxylic groups. A slight decrease of zeta potential is observed for titania hydrogel without the coupling agent after the surface-initiated photocatalytic polymerization. It only decreases about 2.6 mV even when adding 20 wt % of styrene. Interestingly, the decrease of zeta potential is obvious when AA or NaSS is added. It decreases about 5.5 and 6.5 mV, respectively after the photocatalytic polymerization when styrene is 20 wt %. Based on these results, we ascribe the differences to the surface property of titania nanoparticles. It is difficult for styrene molecules to adsorb onto the highly hydrophilic surface of titania, so the amount of PS chains attached on the surface of particles is quite limited. This low efficiency of surface modification can’t improve the hydrophobicity of titania sufficiently, which makes a slight decrease of zeta potential. Differently, the addition of AA or NaSS can effectively increase the adsorbed styrene molecules and induce the chemical graft of PS chains on the surface of titania particles. The highly efficient polymer graft leads to an obvious improvement in hydrophobicity and flocculation of titania particles, as well as the decrease of zeta potential.

**FIGURE 1** Comparison of the zeta potentials of 1.0 wt % modified titania hydrogel at a pH value of 4.0, as a function of styrene/titania mass ratio.

**TABLE 2 Three Control Experiments via One Polymerization Step**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Titania (g)</th>
<th>AA (1.0 wt %) (g)</th>
<th>NaSS (1.0 wt %) (g)</th>
<th>(St + HD) (g)</th>
<th>H₂O (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>0.15</td>
<td>–</td>
<td>–</td>
<td>0.6 ± 0.3</td>
<td>15.0</td>
</tr>
<tr>
<td>15</td>
<td>0.15</td>
<td>0.375</td>
<td>–</td>
<td>0.6 ± 0.3</td>
<td>15.0</td>
</tr>
<tr>
<td>16</td>
<td>0.15</td>
<td>–</td>
<td>0.375</td>
<td>0.6 ± 0.3</td>
<td>15.0</td>
</tr>
</tbody>
</table>
DLS measurements are taken to characterize the size and size distribution of the three titania hydrosols, as shown in Figure 2. Titania hydrosol without modification presents a relatively narrow size distribution and an average size of 26.2 nm. A slight increase in size and size distribution is observed after the addition of AA or NaSS [Fig. 2(a)]. We ascribe it to the weak flocculation of titania caused by the adsorption of the coupling agent. A big difference in size and distribution is observed after the surface-initiated polymerization of styrene. For the modification system with AA and NaSS [Fig. 2(c,d)], the average size increases obviously and a bimodal distribution appears. One peak is from 20 to 60 nm and the other is in the range of 100 to 300 nm. The peak intensity ratio of the latter to the former increases with increment of styrene content and the size distribution of the latter doesn’t broaden. However, a quite broad size distribution (20–1000 nm) is found when the pure titania hydrosol initiates the polymerization of styrene [Fig. 2(b)]. The distribution below 200 nm doesn’t change much when increasing the styrene amount, but the part above 200 nm shifts to a larger size. We ascribe the increase of the size to the flocculation of inorganic particles. In the system without AA or NaSS, the broad distribution means a nonuniform modification. As mentioned earlier, because the titania particles are highly hydrophilic and the monomer and polymer are hydrophobic, the interaction between them cannot happen in the homogeneous phase. Only a small amount of adsorbed monomer can be initiated and generate hydrophobic oligomers. These attached hydrophobic polymer chains destroy the colloidal stability of titania and induce a slight flocculation. Meanwhile, the improved hydrophobicity of inorganic particles facilitates the further adsorption of monomer molecules for polymerization. More polymer chains are attached onto the surface and a more obvious flocculation is induced. It well explains that the two distributions have different responses to the variety of monomer content. In a word, the broad distribution is in relation to the nonuniform surface modification. For the titania hydrosol with AA or NaSS, the coupling agent can effectively bridge the two immiscible phases because the hydrophilic groups interact with the surface of titania particles and the hydrophobic double bonds copolymerize with styrene monomers, which can improve the adsorbed amount of polymer chains and ensure a uniform graft on each titania particle. Importantly, the slightly flocculated titania (20–60 nm) can be further flocculated (100–300 nm) when increasing the initial amount of styrene. Therefore, the modification and resulted flocculation is relatively uniform, which presents a more narrow size distribution.

**FIGURE 2** Size distribution of the titania particles (a) before and (b–d) after surface-initiated photocatalytic polymerization with different styrene content.
distribution than that in the modification system without AA or NaSS.

Herein, the TEM tests are conducted to more directly observe the morphology and size distribution of titania particles after surface-initiated photocatalytic polymerization. It is seen from Figure 3(a) that the size of unmodified titania is about 20 nm and the distribution is quite uniform. After the polymerization of 20 wt % styrene, most of titania particles don’t change significantly except for a few aggregates of the modified titania [Fig. 3(b)]. Differently, when AA is used, a large amount of aggregates of titania are observed after the polymerization from Figure 3(c) and the size is quite uniform. A similar result is obtained when NaSS is used [Fig. 3(d)]. TEM observation is accordant with the DLS results, indicating that the coupling agent makes the surface modification more uniformly.

FTIR spectra are used to clarify the interaction between PS chains and the titania nanoparticles after surface-initiated polymerization, as shown in Figure 4. The surface-modified titania nanoparticles have been washed by ethanol and water completely before test. The characteristic absorption peaks at 1601, 1580, 1558, and 1491 cm\(^{-1}\) in Figure 4(a) confirm the successful synthesis of PS by the photocatalysis of the self-made titania hydrosol.\(^{36}\) The broad peak at 3400 cm\(^{-1}\) is caused by the stretching vibration of \(-\text{OH}\) groups in the titania particles and the peak at 1633 cm\(^{-1}\) is assigned to the bending vibration of adsorbed water molecules on the surface of titania.\(^{37}\) The obvious rise of the baseline below 1100 cm\(^{-1}\) is due to the strong absorption of Ti=O on the titania lattice.\(^{38}\) FTIR results reveal the fact that PS has been successfully grafted onto the surface of titania via a certain interaction in the modification systems, which is consistent with the previous inference. Moreover, a weak peak at 1715 cm\(^{-1}\) for stretching vibration of C=O is seen from the magnified spectrum of sample 9 [Fig. 4(b)], which indicates the successful incorporation of AA into the modified titania, although the amount of AA introduced is as low as 2.5 wt % relative to titania. It is important for the chemical graft of PS chains onto the surface of titania particles via surface-initiated polymerization.

The amount of the grafted polymer is measured by TGA. The results are listed in Table 3. \(W_{\text{loss}}\) is the total weight loss of particles and \(W_{\text{cont}}\) is the content of grafted PS. \(W_{\text{loss}}\) for pure titania particles prepared via a controlled nonhydrolytic sol-gel process is 11.55 wt %. Therefore, \(W_{\text{cont}}\) for each sample can be calculated via eq 1:

\[
W_{\text{cont}} = \frac{(W_{\text{loss}} - 11.55)}{(100 - 11.55)} \times 100
\]

It is clearly seen that a certain amount of PS are grafted onto the titania particles, and the grafted polymer chains
increase with the amount of styrene monomer. It is noteworthy that the adsorbed amount of PS is quite low (3.28 wt %) even when styrene is as much as 20 wt % in the modification system without the coupling agent. Differently, the amount of PS is greatly enhanced when the coupling agent is used with the same dose of styrene monomer. We ascribe this to the coupling effect of AA and NaSS between polymer chains and inorganic particles. It provides a good explanation for dramatic increment of grafted polymer chains on the surface of titania nanoparticles.

Pickering Emulsions Stabilized by Surface-Modified Titania

Binks has reported that it is not effective to form oil/water emulsions when extremely hydrophilic inorganic nanoparticles are used as Pickering stabilizer. Improvement in hydrophobicity of nanoparticles and weak flocculation are thought to be important in stabilizing oil/water emulsions. The graft of PS chains has already been proven to have an obvious influence on hydrophobicity and flocculation of titania nanoparticles by the results of DLS and TEM. Thus, the abilities of these surface-modified titania particles to stabilize Pickering emulsions are investigated with an optical microscope, as shown in Figure 5. The diameter of initial droplets stabilized by titania without undergoing the polymerization is in a range of 10 to 20 μm whether adding coupling agent (2.5 wt % relative to titania) or not [Fig. 5(a–c)]. Meanwhile, the droplets are observed with a quite low stability to coalescence during the characterization. This situation is changed when titania is modified by PS chains via surface-initiated polymerization. However, the surface-modified titania particles obtained in the three systems exhibit different ability to stabilize the emulsion droplets. Specifically speaking, the size of the droplets is in the range of 4–15 μm when surface-modified titania particles without coupling agent is used as stabilizer [Fig. 5(d)]. A much more uniform size distribution of the emulsion droplets of approximately 3–5 μm is obtained when AA is added [Fig. 5(e)]. The emulsion is observed with long-time stability over 3 months. Just as expected, a similar result is obtained when NaSS is used except for a slightly larger size [Fig. 5(f)]. We ascribe these results to the surface chemistry of titania particles. The titania without polymer chains on the surface has a poor ability to stabilize the emulsion for its high hydrophilicity no matter if coupling agent is added, although the homogenization provides energy for partial particles to adsorb provisionally onto the oil-water interface. The attachment energy, which has been shown to be correlative with the stability of solid-stabilized emulsions, is not high enough to overcome the Brownian motion of particles on the interface. Thus, the titania nanoparticles are prone to redisperse in aqueous phase, resulting in a coalescence of initial droplets and a further phase separation of the oil and water. The improved hydrophobicity by the graft of the polymer chains and homogenization treatment facilitate the adsorption of particles onto the interfaces and provide high attachment energy. Therefore, the desorption of particles and coalescence of droplets are restrained. For the modification system without coupling agent, titania with sufficient

### TABLE 3 Amount of Adsorbed PS after Surface-Initiated Polymerization

<table>
<thead>
<tr>
<th>Sample</th>
<th>$W_{\text{loss}}$ (%)</th>
<th>$W_{\text{cont}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11.55</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>11.78</td>
<td>0.26</td>
</tr>
<tr>
<td>3</td>
<td>12.15</td>
<td>0.68</td>
</tr>
<tr>
<td>4</td>
<td>13.56</td>
<td>2.27</td>
</tr>
<tr>
<td>5</td>
<td>14.45</td>
<td>3.28</td>
</tr>
<tr>
<td>6</td>
<td>14.80</td>
<td>3.67</td>
</tr>
<tr>
<td>7</td>
<td>19.12</td>
<td>8.56</td>
</tr>
<tr>
<td>8</td>
<td>24.72</td>
<td>14.89</td>
</tr>
<tr>
<td>9</td>
<td>27.23</td>
<td>17.73</td>
</tr>
<tr>
<td>10</td>
<td>12.06</td>
<td>0.58</td>
</tr>
<tr>
<td>11</td>
<td>20.02</td>
<td>9.58</td>
</tr>
<tr>
<td>12</td>
<td>21.50</td>
<td>11.25</td>
</tr>
<tr>
<td>13</td>
<td>28.49</td>
<td>19.15</td>
</tr>
</tbody>
</table>
modification can stabilize emulsions well while little or none modified particles exhibit poor stabilization for droplets. It is the reason why a broad size distribution appears in Figure 5(d). Contrarily, the addition of AA or NaSS for the surface-initiated polymerization makes the graft of PS more effectively and uniformly, leading to the emulsion with long-time stability.

PS Microspheres Stabilized by Unmodified Titania

As described in our previous paper,24 the surface properties of titania determine the stability of the initial droplets and polymerization routes it adopts. Specifically, there are mainly two polymerization routes during the solid-stabilized emulsion polymerization. If the solid-stabilized emulsion has a poor stability, the particles will drop from the oil/water interface to aqueous phase and result in the rupture of the initial droplets. Thus homogeneous nucleation is prone to occur on the surface of inorganic particles and the increasing polymer/water interface needs to be stabilized by the solid particles dispersed in aqueous phase via collision40 or electrostatic interaction.28 It has been proven that the stabilization of solid particles for droplets is played step by step during the polymerization and the initial solid-stabilized monomer droplets are not the nucleation location. The size and distribution of initial droplets don’t correspond to that of final polymer particles. If the stability of the solid-stabilized droplets is high enough, the solid particles can exist on the oil/water interface with high attachment energy. The nucleation and growth of polymer chains occur in the initial droplets which serve as the reaction vessels during the polymerization. Therefore, the size and distribution of the final polymer particles are consistent with the initial droplets. In this article, a photocatalytic polymerization route is used to prepare PS particles using PS-modified titania as photocatalyst and Pickering stabilizer. A certain quantity of HD is mixed with the monomer to tail the change of droplets during the polymerization, which is used to clarify the modification and stabilization effect of solid particles. Three control experiments are designed to better understand how PS-modified titania particles influence the stability of emulsions and the polymerization process. The formulation details are listed in Table 2. The difference from the systems with surface modification is that the titania is directly used in the Pickering polymerization process. The structure and morphology of the final polymer microspheres are shown in Figure 6.

Solid PS microspheres are prepared when native titania without PS modification is used as Pickering stabilizer. The size is ~1 μm and the distribution is broad. Titania nanoparticles sparsely distribute on the surface of microspheres [Fig. 6(a)].

FIGURE 5 Optical microscopy images of the oil/water emulsions stabilized by titania particles (a) before and after treated by (b) AA and (c) NaSS, as well as surface-modified titania via photocatalytic polymerization for sample (d–f) 5, 9, and 13. The scale bar is 30 μm.
The TGA result shows the titania content of the microsphere is only 2.88 wt % [Fig. 7(a)]. Solid polymer microspheres with size of nearly 200 nm and more narrow distribution are obtained when AA is introduced. As shown in Figure 6(b), titania particles densely distribute on the surface of polymer microspheres. The titania content reaches 13.52 wt % [Fig. 7(b)], which is much more than that in the microspheres without AA. A similar result is obtained when NaSS is used, except for a little larger size (300 nm) and a little lower titania content (12.69 wt %) [Figs. 6(c) and 7(c)]. The slight difference between AA and NaSS on the size and titania content of polymer microspheres may be induced by their interaction with titania nanoparticles. HD is observed staying on the upper layer of the final emulsions in three control experiments, indicating the rupture and coalescence of initial droplets during the polymerization. The low stability of droplets leads to the transference and redistribution of the monomer and HD. In contrast with the OM results [Fig. 5(a–c)], it is found the size and distribution of initial droplets have nothing to do with the final polymer particles.

Based on the above results, the specific polymerization routes adopted during the control experiments are shown in Scheme 1. In our photocatalytic polymerization process, no other initiator is used, and thus the surface of titania nanoparticles is the main reaction locus at the early stage of the polymerization. When unmodified titania is used as Pickering stabilizer, the small amount of monomer dissolved in water prefers to adsorb on the surface of titania nanoparticles for their large surface area and active surface chemistry. Active radicals generate on the surface during the radiation of UV light followed by the surface polymerization of the adsorbed styrene. The produced hydrophobic oligomers attach on the surface of titania nanoparticles and make them hydrophobic. The improvement in hydrophobicity induces the aggregation of titania to produce nuclei, which can be quickly swollen by monomers. With further polymerization, the nascent nuclei grow in size. The increasing interfacial area needs to be stabilized by the titania remaining in aqueous phase via heterocoagulation. However, this process is not efficient because the only driving force for the adsorption of titania nanoparticles is

**FIGURE 6** FE-SEM images of PS microspheres for sample (a–c) 14–16. The insets show the TEM images for each corresponding sample.
provided by the improved hydrophobicity. Once a certain amount of nuclei are formed, the monomer is more prone to diffuse into them for their solubilization, leading to a mass of titania nanoparticles unmodified or little modified. These titania nanoparticles dispersed in aqueous lack enough driving force to adsorb onto the interface and stabilize the polymer particles. It well explains the formation of polymer microspheres with large size, broad distribution and low titania content. It is also clearly found from Figure 6(a) that excess free titania particles disperse in the emulsions after the polymerization.

The addition of AA or NaSS makes the adsorption of styrene monomer quickly for their coupling effect. As the polymerization starts, the resulted oligomers can adsorb onto the surface of titania particles uniformly, inducing the quick aggregation of titania. With further polymerization, the titania particles which do not participate in the nucleation process can be driven to the interface quickly and efficiently to stabilize the polymer particles because of the improved hydrophobicity. Thus, polymer microspheres with small size, narrow distribution and high titania content are prepared with little titania left in the emulsions [Fig. 6(b,c)].

In three polymerization systems, the initial droplets have a low stability to coalescence and an endless diffusion of monomers from oil droplets or aqueous phase to the nascent nuclei has taken place. Here, the distribution of monomers among the three phases (aqueous phase, polymer particles and monomer droplets) is assumed to reach a thermodynamic equilibrium until the termination of polymerization. As we know, HD is highly hydrophobic and its solubility in water is five orders of magnitude lower than that of styrene at room temperature. Importantly, HD is not a good solvent for PS. Therefore, as monomer diffusion and polymerization proceeds, it has no other choice but to be excluded to the upper layer of final emulsions. Therefore, we deduce that the unstable initial droplets are not the polymerization locus, but acting as monomer storages.

PS Microspheres Stabilized by Surface-Modified Titania

![TGA curves of PS microspheres for sample (a–c) 14–16.](image)

The obtained PS-modified titania has a good ability to stabilize initial droplets, which can be concluded from the results of OM [Fig. 5(d–f)]. It is interesting to explore if the stability is kept throughout the whole polymerization process and affects the polymerization routes, that is, whether the droplet nucleation happens and hollow PS microspheres are formed. Herein, three polymerization systems stabilized by the modified titania are investigated and the obtained polymer microspheres are shown in Figure 8.

Two kinds of PS microspheres with completely different structures are prepared when PS-modified titania without coupling agent is used as stabilizer after Pickering polymerization. One is hollow PS microspheres with a size of about 4 μm and a relatively smooth surface [Fig. 8(a)]. It is clearly seen that the individual titania nanoparticles evenly cover the surface of the polymer microspheres from Figure 9(a). The titania content is as high as 12.51 wt % according to TGA result as shown in Figure 10(a). The other is solid microspheres with the average size of 200 nm and narrow size distribution [Fig. 8(b)]. The size of these solid microspheres is much smaller than those obtained in the unmodified system [Fig. 6(a)] and the titania content is 5.58 wt % [Fig. 10(b)]. The two kinds of microspheres are in the top and bottom of the centrifuge tube respectively after high speed centrifugation. We think that the formation of the two kinds of microspheres is in relation with the nonuniform attachment of PS chains on the surface of titania particles. Based on the DLS and TGA results, a preliminary conclusion is made that most of the titania particles are attached by a small amount or none of PS chains and very few are fully modified. Therefore, the improvement in hydrophobicity of titania is not uniform and these particles have the different stabilization for emulsions. That is why droplets with two sizes (big size of 15 μm and small size of ca. 4–5 μm) are found during the observation by optical microscopy [Fig. 5(d)].

Titania particles with sufficient modification have an obvious improvement in hydrophobicity and adsorb onto the oil/water interface stably after high shear homogenization, which is propitious to form droplets with small size. Hence,
each titania-stabilized droplet serves as an independent ves-

cel, which is named a colloidosome by Dinsmore et al.41 The

monomer adsorbed on the surface of titania is firstly initiated

and then the chain propagation occurs with a continuous

feeding of styrene from the oil droplets. Because HD is not a

good solvent of PS, phase separation happens during the poly-

merization, leaving HD trapped in the center of the micro-

spheres and resulting in the formation of hollow structure.

Titania particles with a small amount of PS chains on the

surface have a limited improvement in hydrophobicity and low

attachment energy on the oil/water interface even if a

high shear force is used. They are not effective for stabilizing

the emulsions, so droplets with big size are observed in Fig-

ure 5(d). The formation mechanism of solid microspheres is

similar to the aforesaid mechanism in the unmodified sys-

tems, but there are still some differences. Firstly, although

insufficiently modified titania is not effective for stabilizing

initial droplets to prepare hollow microspheres, it has a

slight improvement in hydrophobicity and a weak floccula-

tion. Hydrophilic groups on the surface of titania expose

to the external water phase and hydrophobic PS chains

entangle each other internally, forming a similar structure as

micelle. Therefore, these aggregates are soon swollen by

monomer from the initial droplets or dissolved in water.

The nucleation step is quick and uniform. Secondly, as the

polymerization is evoked by the generated radicals on the

surface of titania, the further growth of primary nuclei con-

tinuously increases the oil/water interface, which also needs

to be stabilized. Fortunately, the titania particles are less

modified by PS chains and have slight improvement in

hydrophobicity even if they don’t participate in nucleation,

which provides driving force to absorb onto the increasing
interface to stabilize the polymer particles. Therefore, titania
content of solid particles stabilized by sample 5 [Fig. 10(b)]
is higher than that by unmodified system [Fig. 7(a)] and no
free titania is observed from Figure 8(b). Simply, the nuclea-
tion is relatively uniform and quick and the subsequent sta-
bilization for polymer particles by PS-modified titania is

effective, which warrants the formation of PS microspheres

with smaller size and narrower distribution. In a word, poly-

mer microspheres with two different structures are obtained

in one reaction system, indicating two polymerization routes

FIGURE 8 SEM or FE-SEM images of PS microspheres stabilized by sample (a,b) 5, (c) 9, and (d) 13. (a) Hollow and (b) solid microspheres are obtained when sample 5 is used as stabilizer. The insets show the TEM images for each corresponding sample.
are used. Naturally, we ascribe this to the different stabilization effects for Pickering emulsions of the PS-modified titania via surface-initiated polymerization.

Hollow PS microspheres with the size of about 4–5 μm are obtained when PS-grafted titania with coupling agent is used as stabilizer, as shown in Figure 8(c,d). An interesting result is observed that these hollow microspheres have a rough surface, which is different from the hollow ones using the PS-modified titania particles as stabilizer without coupling agent. Solid particles with a size of 100–200 nm densely distribute on the surface of the hollow microspheres seen from the SEM and TEM images. FE-SEM and local enlarged images with high resolution [Fig. 9(b,c)] further indicate that the hollow microspheres and solid particles are covered by individual titania nanoparticles and titania contents are as high as about 17 wt % according to TGA results as shown in Figure 10.

Form the TGA results listed in Table 3, it is clearly seen that the amount of grafted PS chains is much more when AA or NaSS is used for surface-initiated photocatalytic polymerization. As reported earlier, solid particles with improvement in hydrophobicity and weak flocculation are thought to be important in stabilizing oil/water emulsions. Therefore, the size of final polymer hollow microspheres is approximately 4–5 μm, which is basically consistent with that of initial droplets. It gives a further support that these droplets are

![Figure 9](image9.png)  
**FIGURE 9** FE-SEM images of PS hollow microspheres stabilized by sample (a–c) 5, 9, and 13. The insets are local enlarged images for each corresponding sample.

![Figure 10](image10.png)  
**FIGURE 10** TGA curves of PS microspheres stabilized by sample (a,b) 5, (c) 9, and (d) 13. (a) Solid and (b) hollow microspheres are obtained when sample 5 is used as stabilizer.
stable enough to act as reaction vessels during the whole polymerization process.

Herein, we think that the coupling agent (AA or NaSS) participating in the surface-initiated polymerization can obviously improve the hydrophobicity of titania and induce the following formation of aggregates with the size of nearly 100–300 nm. These aggregates with a similar "micellar" structure not only stabilize the initial emulsion droplets effectively but are easily swollen by monomer. Therefore, both droplet and micellar nucleation happens simultaneously during the polymerization. The distribution of styrene in the initial droplets achieves a dynamic equilibrium between the two until the end of the polymerization to produce hollow spheres with a size of 4–5 µm and solid spheres on the surface. A small amount of titania particles with inadequate surface modification also adsorb on the surface of polymer particles due to their improved hydrophobicity. Therefore, most of titania particles are incorporated into the final polymer microspheres. It well explains why the titania content is much higher than previously described polymerization system.

According to the above results, formation procedures of the polymer microspheres with different structures using titania particles as stabilizer after two polymerization steps are shown in Scheme 2. For the modification system without coupling agent, the attachment of PS chains on the surface of titania particles is limited and nonuniform. Titania nanoparticles with sufficient surface modification can well stabilize initial droplets and result in droplet nucleation to obtain hollow microspheres covered by individual titania nanoparticles. Less modified titania participates in the homogeneous nucleation in aqueous phase to prepare PS solid microspheres. Because some PS chains have already attached on the surface of titania via a surface-initiated polymerization, it facilitates the quick and uniform nucleation and following adsorption to the polymer/water interface, which result in a small size and narrow distribution of polymer solid microspheres. The coupling effect of AA or NaSS can obviously increase the amount and uniformity of the grafted polymer chains, which induces a sufficient improvement in hydrophobicity and following formation of titania aggregates with a size of 100–300 nm. These aggregates have good stabilization for initial droplets and Pickering emulsions with the size of 4–5 µm are easily formed. Meanwhile, they have a similar structure as micelle and can also easily be swollen by monomer in initial droplets. Finally, hollow PS microspheres covered by solid microspheres with a size of 100–200 nm are prepared by Pickering polymerization.

**CONCLUSIONS**

The surface-initiated photocatalytic polymerization is adopted for the surface modification of titania nanoparticles. The addition of coupling agent, such as AA or NaSS obviously increases the amount and uniformity of the grafted polymer chains on the surface of titania particles. Polymer microspheres with different structures are prepared after further Pickering polymerization when modified titania is used as stabilizer and photocatalyst. The way adopted in the polymerization is determined by the stabilization effect of titania for the initial droplets, which also finally influences the morphology and structure of PS microspheres. The polymer hollow microspheres covered by polymer solid particles are obtained due to the coexistence of droplet and micellar nucleation during the polymerization. The formation mechanisms of several kinds of polymer microspheres are also provided in this article.

This work was funded by the National Natural Science Foundation of China (NSFC) (No.20704007).

**REFERENCES AND NOTES**