

Review

Polymer@SiO₂ Core–Shell Composite Particles: Preparation and Application

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Abstract: In recent years, core–shell composite particles with organic polymer as the core and inorganic SiO₂ as the shell have attracted widespread attention and prompted robust scientific endeavors. The encapsulation of SiO₂ can endow the polymer core with a variety of important properties, and is of great significance for the synthesis of multi–functional materials, having favorable application prospects in coating, polishing, medical, optical, magnetic, lubrication and other fields. In this paper, the recent advances in the preparation of core–shell polymer@SiO₂ composite particles are reviewed. From the perspective of interface bonding mechanisms between the core and the shell, this paper mainly focused on the following five aspects: Pickering stabilization, acid–base interaction, charge interaction, bridging of coupling agent, hydrogen bonding, and other actions. Additionally, applications of core–shell polymer@SiO₂ particles are also discussed. It is expected that this article can provide scientific guidance for the preparation of polymer@SiO₂ core–shell particles, further enriching their species and broadening their applications.

Keywords: polymer@SiO₂; polymer core; SiO₂ shell; core–shell composite particles; bonding mechanisms; preparation; application



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1. Introduction

In recent years, with the rapid growth of nano–synthesis technology, the investigation of nanocomposites has gradually changed from traditional physical blending to the tailoring of new chemical structures [1–4]. In order to meet the performance requirements of various fields, reasonably increasing the complexity of polymer structures in order to achieve multi–functionality has become the mainstream focus of research, in the context of which core–shell structures stand out. By attaching the shell materials onto the core surface by means of chemical/physical methods, composite particles characterized by a core–shell structure can be obtained. It is believed that coating it with the shell can greatly improve the surface properties and stability of the core material, and affording comprehensive properties not possessed by any single component [5]. Due to their unique performance advantages, core–shell nanocomposites have become a research hotspot in the areas of coatings [6,7], adhesives [8,9], optics [10–12], electronics [13,14], biomedicines [15–18], and lubrication [19,20], and also present great potential in the future field of new materials.

The successful synthesis of organic–inorganic nanocomposites comprised of organic polymers as the core and inorganic nanoparticles as the shell has become an important field of research and area of technological development due to their excellent properties [21]. In a typical construction, the organic polymer possesses good functionality (e.g., flexibility, ductility and dielectric properties) and workability, while the inorganic nanoparticles

provide superior chemical and mechanical properties (e.g., optical, thermal, load-carrying resistance and surface activities) [22,23]. In particular, owing to their good surface activity, excellent wear-resistance, and cost effectiveness, as well as the ease of performing synthesis and structural control in situ, extensive attention has been directed towards nano-SiO₂. Firstly, it is well known that organic polymers usually exhibit lipophilicity or possess poor hydrophilicity; therefore, it can be taken for granted that the wettability of the polymer can be significantly improved by coating it with SiO₂. Furthermore, since the surface energy of nano-SiO₂ is very high, causing it to agglomerate easily, the formation of core-shell structure can not only prevent the agglomeration of nano-SiO₂, but also enhance the dispersibility of the polymer spheres. Therefore, a noticeable improvement in mechanical and chemical properties can be achieved, compared with a simple physically mixed polymer/SiO₂ sample, making them attractive for prospective application in coating, polishing, optics, lubrication, medicine, and other fields.

However, to the best of our knowledge, no researchers have reviewed the preparation of polymer@SiO₂ core-shell composite particles consisting of a polymer as the core and SiO₂ as the shell, especially from the perspective of the binding mechanism between the core and the shell. Moreover, little research has addressed the unique application values of such composite particles.

Therefore, in this review, recent research progress regarding polymer@SiO₂ core-shell composite particles is summarized, and the potential applications of these particles are also briefly summarized. In terms of the interface bonding mechanisms between the core and the shell, five main strategies are discussed in this review: Pickering stabilization, acid-base interaction, charge interaction, bridging of the coupling agent, and hydrogen bonding and other actions, with each mechanism being elaborated in detail. In addition, the preparation of microporous or mesoporous SiO₂ spheres using polymer@SiO₂ core-shell particles as templates is also discussed in this paper. It is hoped that this work will provide a variety of ideas for researchers investigating polymer@SiO₂ core-shell composites, further promoting the development of core-shell preparation systems for wide application in various fields.

2. Synthesis Strategies

2.1. Pickering Stabilization

Pickering emulsion refers to an emulsion that is stabilized by solid nanoparticles at the interface between two incompatible phases. Binder [24] pointed out that the interface between two incompatible liquids was an ideal place for nanoparticles to self-assemble. In Pickering emulsion, solid particles are arranged spontaneously at the oil and water interface, thus stabilizing the monomer droplets, and enabling the subsequent formation of core-shell structured particles by initiating polymerization (see Figure 1). Studies have indicated that Pickering emulsion only takes place when the SiO₂ nanoparticles have a moderate degree of hydrophobicity, with stable emulsion not being possible in the case of nanoparticles that are either too hydrophobic or too hydrophilic [25,26]. Generally, there are two approaches to hydrophobize the SiO₂ surface: one is to graft a silane coupling agent onto its surface, and the other is to adsorb the polymer. Since the work done by the latter method is relatively few [27], the method of using a silane coupling agent to regulate the surface wettability will be primarily discussed. In this method, the modified-SiO₂ particles can exist stably in the water-oil interface, and the core-shelled nanocomposites are formed by initiating the polymerization. Additionally, the efforts on obtaining the core-shell polymer@SiO₂ particles directly using the alcoholic silica sol or pure SiO₂ will also be reviewed [28,29].

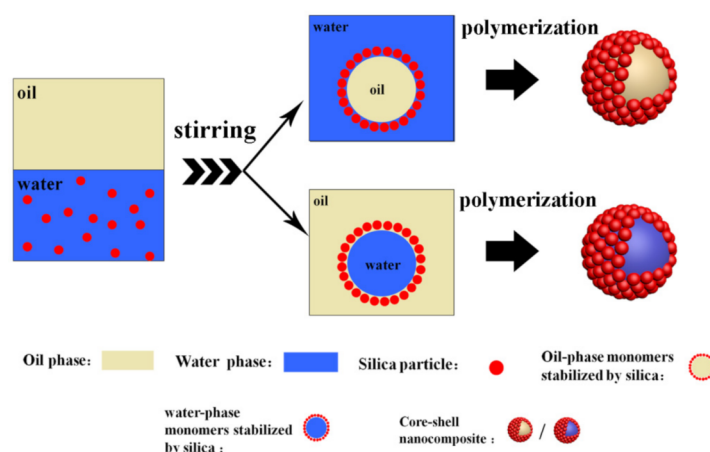


Figure 1. Mechanism of Pickering stabilization method.

Qi et al. [30] prepared P(MMA-BA)@SiO₂ core-shell nanocomposite by using SDS and MOA-9 as surfactants, and the influence of hydrophilic-lipophilic properties of SiO₂ on the morphology of nanocomposites was investigated. It can be seen from Figure 2 that the morphology of prepared nanoparticles changed from raspberry-like to guava-like with increasing the grafting density of MPS. The author believed that the distribution of SiO₂ nanoparticles in the emulsion system was subjected to the grafting density. Typically, when the grafting density was low, SiO₂ tended to assemble on the oil/water interface, forming raspberry-like particles (see Figure 2a). Whereas when the grafting density was relatively higher, SiO₂ would be more likely to stay in the monomer droplet due to its strong hydrophobicity, and a large number of pure polymer particles were produced during homogeneous nucleation and micelle nucleation stages (see Figure 2d). However, the guava-like morphology could only be formed when MPS was moderately grafted, in this case, the SiO₂ was located in micelles and encapsulated into the polymer during polymerization (see Figure 2b,c). Yang et al. [31,32] considered that there was an energy barrier to determine whether the SiO₂ particles were dispersed in water or adsorbed on the oil-water interface. Only when this barrier was overcome, could SiO₂ be adsorbed on the oil-water interface. The author believed that the partially wetted SiO₂ particles reduced this energy barrier and made it easier to adsorb closely on the oil-water interface compared with un-wetted particles. In addition, dispersing SiO₂ particles in an acid environment could also reduce this energy barrier, since the surface electricity of SiO₂ was weakened in acid environment, thus easing the electrostatic repulsion/energy barrier between particles. Elkalla et al. [33] had prepared PS@SiO₂ core-shell composite particles in an oil-in-water system by using hydrophobic SiO₂ nanoparticles as the stabilizer. From the viewpoint of thermodynamics, hydrophobic SiO₂ could not effectively stabilize the oil-in-water system due to the local energy. However, the author believed that this problem could be settled by simple ultrasonic treatment, and the three-dimensional network formed between SiO₂ particles could also play a good role in stabilizing the emulsion. However, obviously the size uniformity of the composite particles obtained in this article was very poor. Yin et al. [34] found that the nucleation mechanism and morphology of composite particles were greatly affected by the concentration of SiO₂. When the content of SiO₂ was low, a small number of monomers and initiators would diffuse into the water, and the continuous phase nucleation of droplets was enough to affect the morphology of products. Whereas when the amount of SiO₂ was increased or NaNO₃ was served as an inhibitor, the continuous phase nucleation would be restrained, so that the dispersed microspheres with high SiO₂ coverage could be obtained. The same regularity was also reported by Zhang et al. [35], it was found that the droplet nucleation occurred when SiO₂ content was higher, while the continuous phase nucleation dominated when the content of SiO₂ was lower, indicating that the content of SiO₂ had a great influence on the nucleation mechanism of the final products.

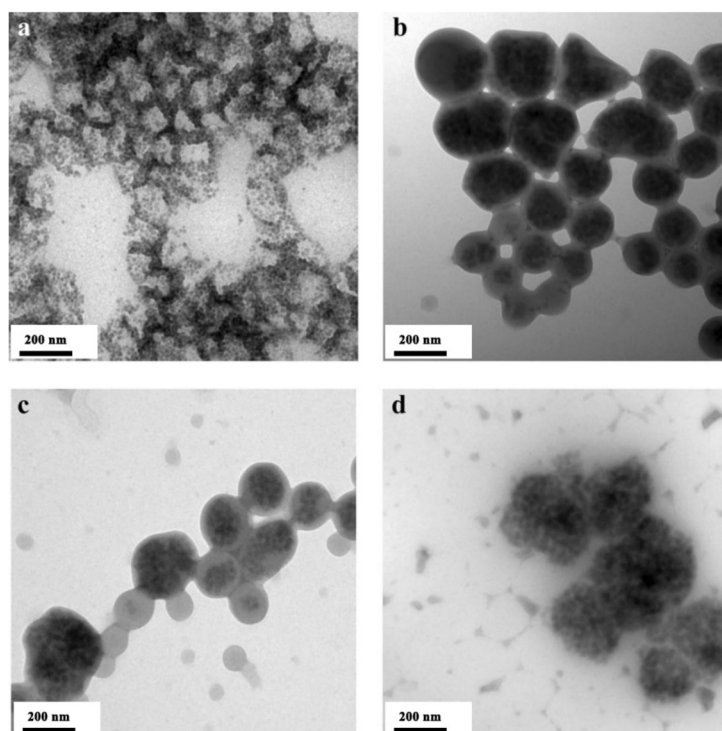


Figure 2. TEM images of poly(MMA-co-BA)@SiO₂ nanocomposite particles prepared by in situ emulsion polymerization (the surface MPS coupling densities of SiO₂ nanoparticles are as follows: (a), 1.44 $\mu\text{mol}\cdot(\text{m}^2 \text{SiO}_2)^{-1}$; (b), 2.24 $\mu\text{mol}\cdot(\text{m}^2 \text{SiO}_2)^{-1}$; (c), 2.97 $\mu\text{mol}\cdot(\text{m}^2 \text{SiO}_2)^{-1}$; (d), 3.52 $\mu\text{mol}\cdot(\text{m}^2 \text{SiO}_2)^{-1}$). Reproduced from [30] with permission from Springer Nature.

In addition to the wettability and concentration of SiO₂ particles, the *pH* value of the solution, as well as the types of initiators and emulsifiers, all affect the final morphology of the composite particles. Zhou et al. [36] thought that the concentration of nano-SiO₂ particles—as well as the type of initiator—had a synergistic effect on the morphology of the final product. Zhang et al. [37] found that the type of initiator had an important effect on the nucleation mechanism of composite particles. Tiarks et al. [38] studied the effects of monomer ratio, emulsifier type, and *pH* value on the morphology of composite particles, and concluded that the stable emulsion could only be obtained when the St monomer was copolymerized with 4-VP/VPy under the basic condition (*pH* = 10). It is worth mentioning that the micro-emulsion polymerization adopted in their work promised the high aggregation efficiency of SiO₂, but special equipment was required to guarantee the small and dispersed monomer droplets, which greatly increased the preparation cost. Besides, a large number of secondary SiO₂ particles that did not combine with the polymer core were also produced, which would severely compromise the film-forming performance of the products.

Some researchers had also applied pure SiO₂ particles or alcoholic silica sol as the sole stabilizer to prepare the core-shell polymer@SiO₂ nanocomposites. Armes's team [39,40] reported the preparation of PS@SiO₂ core-shell nanocomposites by dispersion polymerization with alcoholic silica sol as the stabilizer, and found that the size of PS@SiO₂ particles was almost independent of the initial concentration of SiO₂. Subsequently, the P2VP@SiO₂ core-shell nanoparticles were firstly prepared by emulsion polymerization, in which the aggregation efficiency of SiO₂ could reach 99% [41]. However, considering the expensive and unpleasant smell of 2-VP monomer, they further prepared PS@SiO₂ nanocomposites using glycerol functionalized silica sol without any assistance of emulsifier or auxiliary monomer [42], and the corresponding polymerization mechanism was proposed: firstly, the cationic initiator would be adsorbed onto the surface of SiO₂ under the action of electrostatic force, inducing a small amount of St in water to initiate on its surface. Then, the formed PS

oligomeric chains would enhance the hydrophobicity of SiO_2 and lead to its nucleation in aqueous phase. As the polymerization proceeded, the nucleated aggregates were further swelled by St monomers, resulting in an increase in aggregate size and a decrease in the coverage of SiO_2 particles. Therefore, the anionic SiO_2 particles in an aqueous phase would be continuously adsorbed onto the exposed surface of the positively charged aggregates, thus eventually forming the core-shelled PS@SiO_2 microspheres. Colver et al. [43] explored the influences of monomer ratio and pH value on the morphology of composite particles and the corresponding polymerization mechanism was put forward: firstly, during the homogeneous nucleation stage, when the wettability of SiO_2 particles was comparable to that of polymer chains, the polymer chains tended to precipitate on the SiO_2 surface and formed small polymer particles on its surface. As the reaction progressed, the polymer particles grew up gradually and the interfacial area between polymer particles and water increased. In order to prevent the aggregation of polymer particles, SiO_2 particles with negative electricity would adsorb onto the polymer surface and play the role of Pickering stabilizer, thus forming the composite particles with PMMA as the core and SiO_2 as the shell (see Figure 3a). Besides, the multilayered core-shell nanocomposites with well-defined morphology were also synthesized on this basis. It can be seen from Figure 3b,c that the outermost shell of the particles was composed of PAN and PBA, respectively. Zhang et al. [44] had successfully prepared raspberry-like PS@SiO_2 composite particles using MPS as an auxiliary monomer, and it was believed that the hydrolysis and condensation interaction between SiO_2 nanoparticles and MPS distributed on monomer droplet surface made the emulsion stable. However, it is worth noting that Satoh et al. [45] provided a simple and innovative method to prepare the SiO_2 -encapsulated core-shell composite particles. In the typical process, the SiO_2 aqueous solution was mixed with THF solution containing amino-functionalized PB microspheres, and the core-shelled $\text{PB-NH}_2\text{@SiO}_2$ composite particles could be easily prepared by evaporating THF. Obviously, this method was simple to operate and did not require an additional modification of SiO_2 , but the shortcoming is that the size uniformity of composite particles was difficult to control. Anyway, this work provides us with a new perspective for the preparation of organic@inorganic core-shell composites.

In summary, the preparation of polymer@ SiO_2 composite particles by Pickering emulsion polymerization has obvious advantages of environmentally friendly and low-cost versus traditional emulsion polymerization. In Pickering emulsion, due to the absence of a large number of surfactants, the recycling process is saved, and the foaming problem caused by traditional emulsifiers can also be largely avoided. However, some successful syntheses of composite particles still need the assistance of special dispersing equipment, which greatly increases the difficulty and cost of the preparation. Therefore, exploring a simple method for preparing polymer@ SiO_2 core-shell composite particles with uniform particle size distribution and good dispersion as well as no secondary particles will be the research focus for Pickering emulsion polymerization in the future.

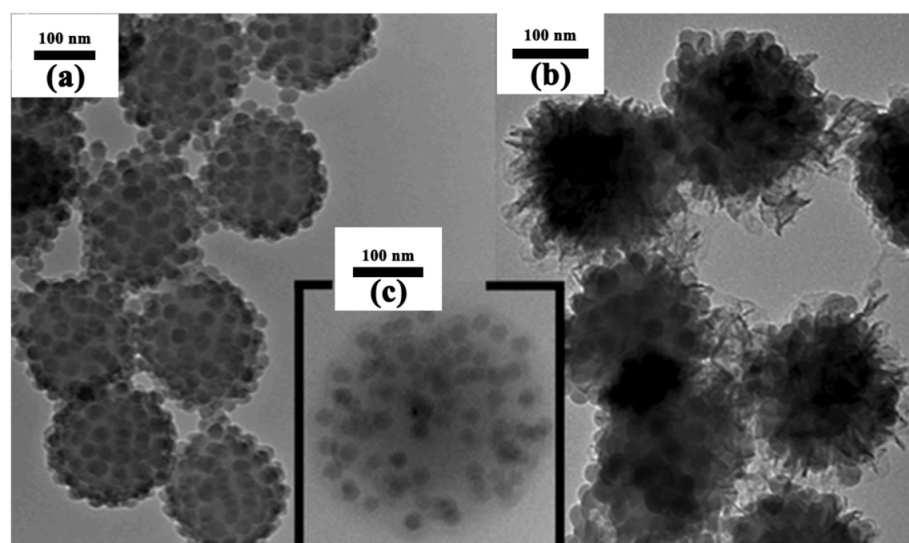


Figure 3. TEM images of (a) PMMA latex armored with SiO₂ nanoparticles obtained by Pickering emulsion polymerization. Multilayered nanocomposite polymer colloids with (b) a “hairy” outer-layer of poly(acrylonitrile) and (c) a soft shell of poly(n-butyl acrylate). Reproduced from [43] with permission from the American Chemical Society.

2.2. Acid–Base Interaction

Generally, SiO₂ particles prepared by the classical Stöber method [46] behave as acidic because of the presence of hydroxyl groups. Whereas when the monomer or the polymer itself shows alkaline, the acidic SiO₂ can be absorbed automatically onto the polymer surface, in which the acid–base interaction between SiO₂ and polymer plays the main role (see Figure 4). In the following content, the monomers that can induce the acid–base interaction between SiO₂ and polymer are summarized, mainly including the following three categories: pyridine, imidazole, and amine. We will discuss them, respectively.

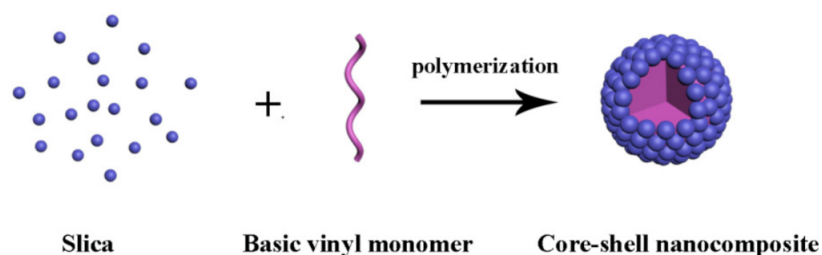


Figure 4. Schematic diagram of the acid–base interaction.

Percy et al. [47] successfully synthesized P4VP@SiO₂ nanocomposites with ‘currant-bun’ morphologies by dispersion polymerization without any emulsifier. Further investigation indicated that copolymerizing 4-VP with MMA and St could also bring about this morphology, whereas only MMA and St could not be successfully synthesized, indicating that the acid–base interaction between 4-VP and SiO₂ played a significant role in the polymerization. Zou et al. [48] prepared the polymer@SiO₂ nanoparticles by sol–gel method using PVP as an emulsifier and 4-VP as an auxiliary comonomer. The author believed that the successful encapsulation of SiO₂ was the result of the synergy of 4-VP and PVP, and the hollow SiO₂ spheres could also be fabricated by the subsequent dissolution of the polymer core. Cheng et al. [49] found that PMMA@SiO₂ composite particles with different morphologies (such as conventional core–shell structure, multi-core–shell structure, and raspberry-like structure) could be well obtained by changing the polymerization conditions. Barthet et al. [50] investigated the effect of monomer types (4-VP, 2-VP,

DEMEA) on the morphology of core-shell particles. Studies have shown that although all of these monomers were alkaline, only 4-VP could successfully bring about core-shell nanoparticles, indicating that the existence of alkaline vinyl monomer was a necessary but not sufficient condition, whereas, it is worth mentioning that 4-VP/2-VP has obvious disadvantages, such as low initiation efficiency, smelliness, and high cost, so it is not an ideal candidate for industrial use.

Chen et al. [51,52] = firstly prepared raspberry-like PMMA@SiO₂ core-shell nanoparticles using 1-VID as the auxiliary monomer. The author proved that the composite structure could only be successfully synthesized under alkaline conditions, especially when the *pH* value of the environment was eight, and the coverage of SiO₂ could reach the maximum. Zhang et al. [53] fabricated PS@SiO₂ core-shell microspheres by micro-emulsion polymerization with SDS as surfactant and 1-VID as an auxiliary monomer. The influences of dosage parameters such as SiO₂, 1-VID, and SDS on the polymerization stability, particle size, and morphology of core-shell particles were studied, and the formation mechanism was preliminarily explored. Wang et al. [54] applied SMA spheres as templates and DEA as a catalyst to synthesize rambutan-like SMA@SiO₂ nanocomposite particles, and SMA/SiO₂/Ag⁺ hierarchical structure was also prepared by reducing Ag⁺ on the surface of SMA@SiO₂ microspheres. Cai et al. [55] studied the influence of different types of amine catalysts on the morphology of P(St-AA)@SiO₂ composite particles. It can be seen from Figure 5 that almost all of the amine catalysts could obtain the well-defined core-shell/raspberry-like morphology except for NaOH. The author believed that the acid-base interaction between -COO⁻ / -N⁺ / -SiO⁻ induced the encapsulation of SiO₂ on the polymer surface, and the presence of PAA could provide steric-hindrance, which was more effective for the nuclei-growth-controlled process. In addition, the study also found that the structure of core-shell particles could be easily regulated by adjusting the types of alkalis and the volume ratio of ethanol/water. Not only that, the water contact angle could also be well adjusted by hydrophobic the core-shell particle surface with dodecyltrichlorosilane.

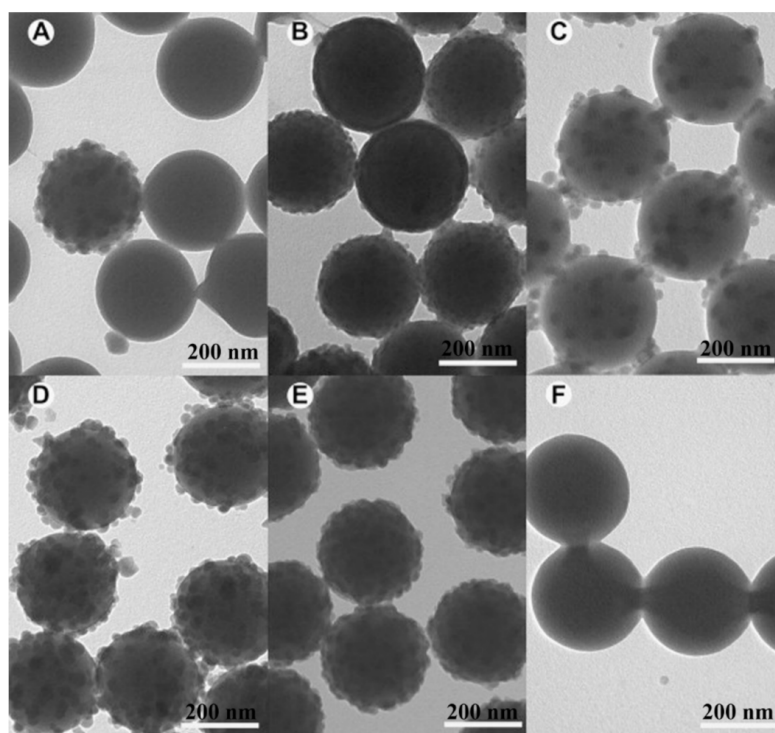


Figure 5. TEM images of PS/SiO₂ composite particles prepared with different alkali as catalyst. (A) DA 1.0 g, (B) EDA 1.0 g, (C) TEA 1.0 g, (D) NH₃ H₂O 1.0 g, (E) DEA 1.0 g, (F) NaOH 1.0 g (*V*_{ethanol}/*V*_{water} is 40 mL/5 mL). Reproduced from [55] with permission from the Elsevier.

As previously mentioned, the core-shell nanoparticles prepared by Pickering emulsion polymerization will inevitably produce secondary SiO_2 particles, which will certainly damage the integrity and transmittance of the product films. However, these problems can be largely avoided by using acid-base interaction to synthesize the composite particles. Even so, it cannot be ignored that there are still relatively few studies using imidazole and amine as catalysts to induce the acid-base interaction, indicating that there is still a lot of work to do in this field, and need further exploration.

2.3. Charge Interaction

The charge interaction is nothing more than the mutual attraction between particles through the electrostatic interaction (see Figure 6). To the best of our knowledge, the surface of SiO_2 particles prepared by the Stöber method generally shows a negative charge, and if we want to produce core-shell nanocomposite particles by electrostatic interaction, the surface of the polymer core must be positively charged. Normally, there are four ways to make the polymer core surface positively charged. Here, these methods will be discussed in detail.

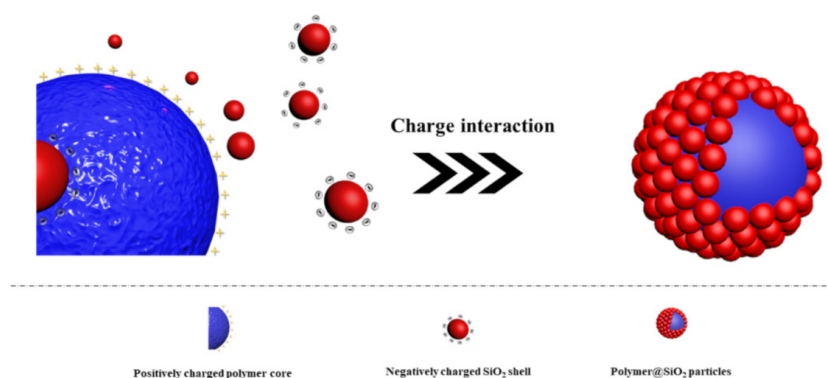


Figure 6. Schematic diagram of the charge interaction.

(1) Functionalizing the polymer beads (i.e., by modifying the positively charged groups onto the polymer core).

In some literature, sulfonation or ammonia functionalization was often used to modify the polymer core. Cornelissen et al. [56] deposited a layer of SiO_2 on the PS surface by functionalizing the PS surface with an amino/amphoteric group, but the repeatability of the experiment was proved to be poor by using sodium silicate as a SiO_2 source. Yu et al. [57] coated PS spheres with SiO_2 using the Stöber method. The results showed that when the PS surface was decorated with sulfonate group, that is, the surface was negatively charged, it was not easy to obtain the core-shell structure. Whereas when the PS surface was amino-functionalized, the PS surface behaved neutral or slightly positively charged at this point, which would lead to the automatic adsorption of SiO_2 , thus forming the PS@SiO_2 particles with a core-shell structure. Fan et al. [58] applied anionic sulfonated PS beads (see Figure 7a) as the core and cationic aniline monomer as the assembly medium to prepare PSS@SiO_2 core-shell nanoparticles (see Figure 7b), and synthesized the hollow microcapsules (see Figure 7c) through subsequent calcination. The author found that the dual functions of electrostatic and swelling between aniline and PSS spheres played the main role in the adsorption of SiO_2 , and the assembly of aniline was directly affected by the sulfonation degree of PSS particles. Yang et al. [59] prepared amine-functionalized APS-PL@SiO_2 core-shell nanoparticles using ammonia-functionalized PS microspheres as a template via lysine adsorption and TEOS hydrolyzation, and the hollow SiO_2 microspheres were also prepared by the calcination or solvent dissolution. Since the functionalized polymer microspheres were commercially available, the cost of the preparation process was greatly saved.

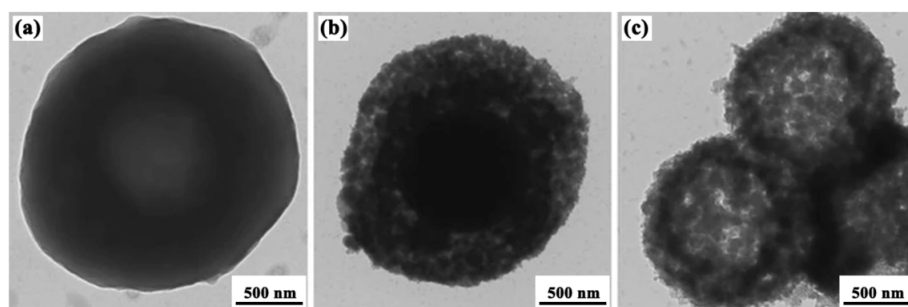


Figure 7. TEM images of (a) PSS particle, (b) composite particle, and (c) SiO₂ microcapsules in samples of 8 h sulfonation. Reproduced from [58] with permission from the Springer Nature.

(2) Using a cationic initiator to initiate the polymerization.

Adopting a cationic initiator to initiate the polymerization can directly make the polymer surface positively charged, among them, a water-soluble azo-initiator is commonly used, i.e. AIBA. For example, Xu et al. [60] prepared the positively charged polymer microspheres using AIBA as an initiator. By simply blending the negatively charged SiO₂ with positively charged polymer nanoparticles, raspberry-like polymer@SiO₂ nanocomposites could be prepared through electrostatic interaction. Zou et al. [61] synthesized the PS@SiO₂ core-shell composite particles using sodium silicate, PVP, and AIBA as the silicon source, stabilizer, and initiator, respectively. Balmer et al. [62] successfully prepared P2VP@SiO₂ core-shell composite particles using AIBA as an initiator. The single-layer adsorption of SiO₂ was explored, and the calculation formula of packing efficiency P was established. Narongthong et al. [63] prepared a novel hybrid hollow latex particle with P(St/AA), PDVB, and SiO₂ as the inner polymer shell, outer polymer shell, and outermost layer, respectively. In this typical polymerization process, P(St/AA), DVB and AIBA were employed as the seed, swelling, and crosslinking monomers as well as the initiator. As shown in Figure 8, it could be obtained that the primary free radicals produced by AIBN were adsorbed on the SiO₂ surface electrostatically and further reacted with a small amount of DVB in water to produce the oligomers (stage I–II). Due to the limited water solubility, the SiO₂–oligomers particles would adsorb onto the P(St/AA) surface automatically (stage III). With increasing the reaction time, DVB swelled in P(St/AA) particles gradually migrated to its surface, and participated in polymerization. As the polymerization proceeded, the poor compatibility between PDVB and P(St/AA) as well as the strong capillary force generated between SiO₂ nanoparticles made the carboxylate and sulfate hydrophilic end groups of P(St/AA) diffuse to the water interface for adsorption, thus forming a pore inside of the polymer sphere (stage IV). After the polymerization, hybrid hollow particles with large void and non-collapse structure was finally obtained (stage V). In this process, no core removal, solvent evaporation or surface modification was adopted, and no secondary nucleation had been found.

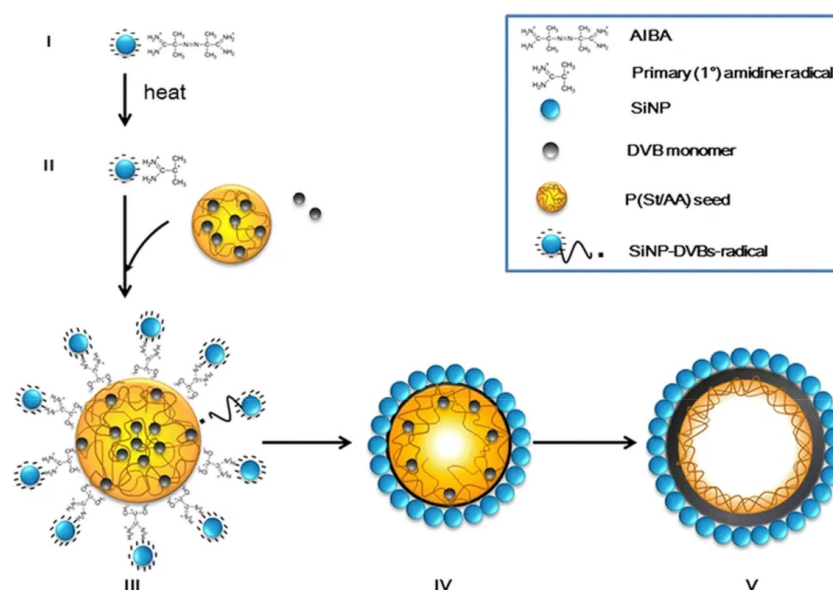


Figure 8. Proposed mechanism of the formation of hybrid HL-SiNPs particles prepared using seed/DVB. Reproduced from [63] with permission from Springer Nature.

(3) Copolymerization with cationic monomer.

Compared with toxic and expensive 4-VP, using non-toxic and cost-effective cationic monomer MTC as the auxiliary monomer is more beneficial to environmental protection and industrialization. Chen et al. [64] prepared raspberry-like PMMA@SiO₂ composite particles by free-radical copolymerization with MTC. Fan et al. [65] found that the electrostatic attraction brought by MTC was of vital importance for the adsorption of SiO₂ and the formation of raspberry-like morphology, and the amount of AIBA had little effect on the SiO₂ content as well as the core-shell morphology. Zhang's team [66–68] synthesized polymer@SiO₂ core-shell composite particles under different systems (such as emulsion polymerization, microemulsion polymerization, and dispersion polymerization) by employing MTC as the auxiliary comonomer. Hwang et al. [69] coated a layer of SiO₂ on P(MMA-MTC) surface by the Stöber method, and further synthesized the superhydrophobic particles by coupling P(MMA-MTC)@SiO₂ particles with fluoroalkyl silane. Chen et al. [70] prepared P(St-MTC)@SiO₂ core-shell composite particles in microemulsion with the assistance of non-ionic surfactants, and the results showed that the synthesized composite particles had excellent acid/base endurance.

Certainly, core-shell structured complexes can also be successfully synthesized by using SiO₂ microspheres or polymers that are themselves positively charged [71,72]. However, there are relatively few works on this aspect, so we have not done much discussion here.

(4) Adopting cationic surfactant to carry out the emulsion polymerization.

It is known to all that cationic emulsifier has positive charges at its hydrophilic end. During the emulsification process, the hydrophobic end of the cationic emulsifier will adsorb onto the polymer surface, and its hydrophilic end will interact with the negatively charged SiO₂. Here, the cationic emulsifier serves as a structure-directing agent to bridge and anchor SiO₂ particles. In the literature, the most commonly used cationic emulsifier is CTAB. Pakdel et al. [73] successfully synthesized PMMA@SiO₂ core-shell nanocomposites using both CTAB and SiO₂ to stabilize the MMA monomers. Zhang et al. [74] found that the size, morphology, and SiO₂ content of composite microspheres were greatly affected by the amount of CTAB, SiO₂, and monomer. Ge et al. [75] prepared P(St-MAA)@SiO₂ core-shell nanocomposite particles using P(St-MAA) as a template and CTAB as a structure-directing agent. It can be seen from Figure 9 that when P(St-MAA)@SiO₂ hybrid was prepared at room temperature, the structure of the SiO₂ shell was loose, and hollow SiO₂ beads with micropore structure could be formed by calcination. Whereas when the prepared composite was aged at 150 °C, the high temperature would promote the polycondensation

reaction of SiO_2 , resulting in a dense SiO_2 shell, so the hollow SiO_2 spheres with continuous mesoporous structure could be fabricated.

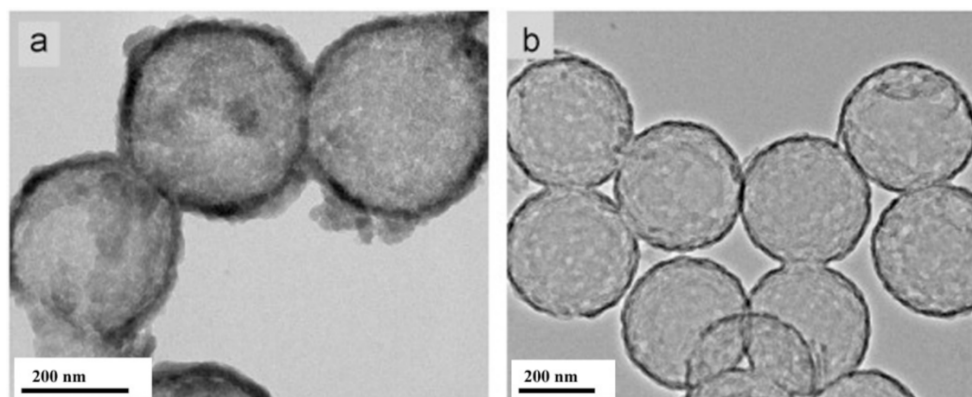


Figure 9. TEM images of the hollow SiO_2 samples, prepared by removing the latex templates from SiO_2 -coated PS-methyl acrylic acid latex composites by calcination. The SiO_2 -coated latex composites were prepared (a) at room temperature and aged (b) at 150 °C. Reproduced from [75] with permission from the Elsevier.

However, there are few reports about using cationic emulsifiers to prepare core-shell structured nanoparticles, and most of them remain in the preparation stage. The parameter regulation of this method as well as the accurate control of the core-shell structure still need to be further studied.

2.4. Bridging of Coupling Agent

At present, there are only a few researches have been reported on the preparation of polymer@ SiO_2 core-shell nanoparticles by coupling agent bridging method [76,77]. Unlike the previous strategies, this method can combine the polymer core with SiO_2 particles in the form of chemical bonding. It can be obtained from Figure 10 that when the surface of the polymer is decorated with alkoxy groups, SiO_2 particles can be anchored onto the polymer surface tightly by hydrolysis and condensation. This anchoring is robust and is largely independent of pH , temperature, or surfactant. However, this does not mean that SiO_2 can be loaded under any conditions. Bourgeat et al. [76] explored the stability of PS colloids functionalized by MPS. It was found that the stability of colloidal suspension highly depended on the properties of pH and surfactant, especially when the pH value was 7, the colloidal particles exhibited optimal stability, and no condensation product was generated. Tissot et al. [78,79] also observed this regularity. It was found that MPS was hardly hydrolyzed or condensed in a neutral condition, which should be responsible for the good stability of colloidal particles as well as the successful coating of SiO_2 . Yang et al. [80] found that the thermal properties of PB could be well improved after being functionalized by MPS. Besides, Lin et al. [81] discovered that the thermal stability of the core-shelled SiO_2 @PMMA particles was better than that of PMMA@ SiO_2 particles. Particularly, hybrid hollow or bowl-shaped polymer@ SiO_2 composite particles were prepared by Zhang et al. [82]. The study indicated that the morphology of composite particles depended on the content of MPS. Recently, Zhao et al. [83–86] prepared polymer@ SiO_2 core-shell nanoparticles using polymer precursor by one-pot synthesis (see Figure 11), and the corresponding polymerization mechanism was proposed: before the reaction started, PS and PEOS could be miscible. As the reaction proceeded, PEOS were hydrophilic enough to separate it from the PS phase and migrated to the surface of PS. After the reaction, the PEOS dissolved in PS was completely consumed and finally formed a layer of SiO_2 on the PS surface. The study also showed that the content of SiO_2 and the size of composite particles could be well controlled by changing the PEOS content and the pH value of the solution.

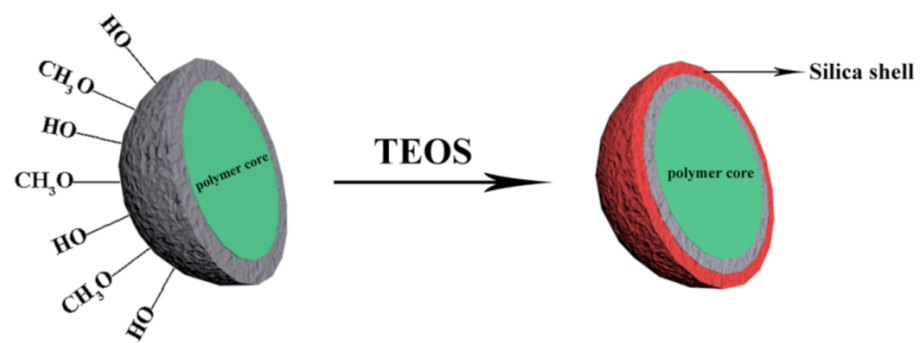


Figure 10. Schematic diagram of the bridging of coupling agent.

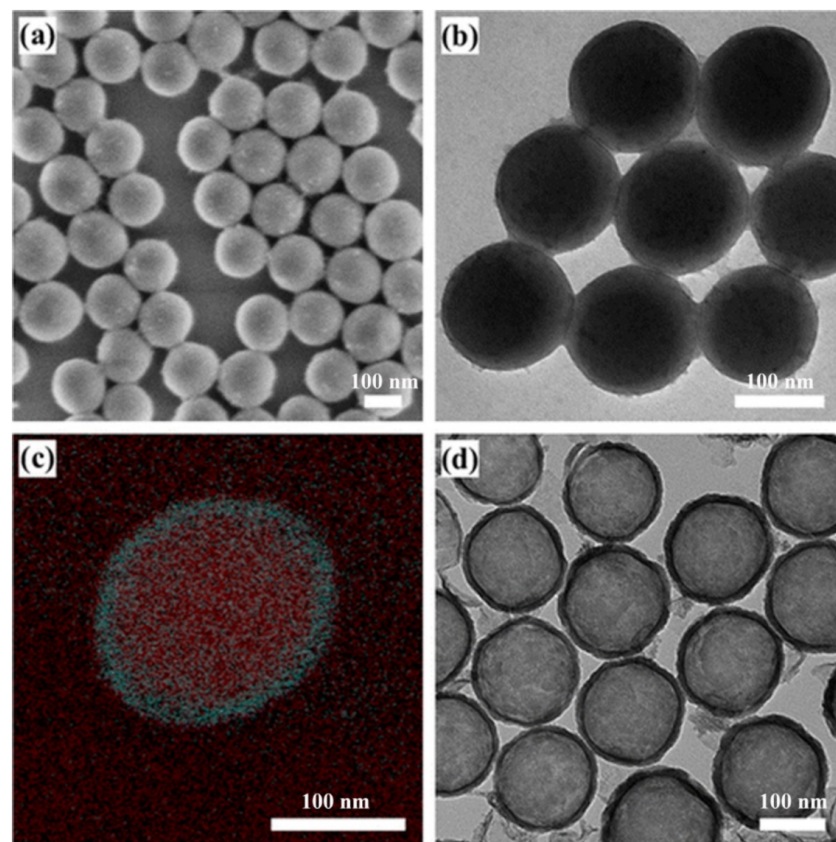


Figure 11. FE-SEM (a), TEM (b), and EDX-STEM mapping micrographs (c) of PS@SiO₂ core-shell particles prepared by emulsifying a mixture of St (1.2 g) and PEOS (1.2 g) in the water of *pH* 7 via ultrasonication and subsequent heating at 70 °C. (d) TEM image of SiO₂ hollow particles obtained by calcination of the core-shell particles. Blue color indicates the presence of silicon atoms, and red color corresponds to carbon atoms. Reproduced from [83] with permission from the American Chemical Society.

By means of bridging of coupling agent, polymer@SiO₂ nanoparticles can be synthesized in strong chemical bonding using a single reaction vessel, and the effective utilization rate of material is greatly improved, which is not available for other synthesis strategies. However, although the preparation process is simple, the requirements for some reaction conditions are strict, such as the *pH* value of the solution, as well as the time and temperature of the reaction.

2.5. Hydrogen Bonding and Other Actions

Hydrogen bonding interaction occurs when the hydrogen atom approaches a strongly electronegative atom with lone pair of electrons [87] (see Figure 12). Although the force is relatively weak, hydrogen bonds can undoubtedly be used as a driving force to promote the adsorption of SiO_2 onto the polymer surface.

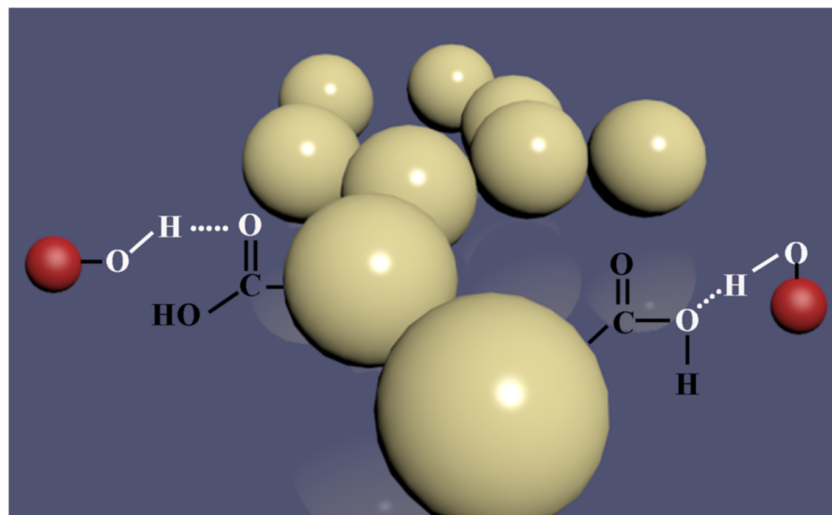


Figure 12. Schematic diagram of the hydrogen bonding.

You et al. [88] prepared $[\text{P}(\text{St-BA-AA})]@\text{SiO}_2$ core-shell nanoparticles by emulsion polymerization. Research on rheological properties and morphology showed that the successful coating of SiO_2 was attributed to the hydrogen bonding interaction between silanol groups of SiO_2 and carboxyl groups on the surface of the polymer. Liu et al. [89] had first synthesized PAA and $\text{P}(\text{EGDMA-co-VPy})$ particles by distillation precipitation polymerization, then adsorbed PAA on the surface of $\text{P}(\text{EGDMA-co-VPy})$ by hydrogen bond, and finally coated SiO_2 on the outermost layer by Stöber method. Wen et al. [90] coated a layer of SiO_2 on the PVAc surface with anionic reactive surfactant and HAPS as stabilizers. The author believed that it was the hydrogen bond between the silanol group and the hydroxyl group rather than the hydrogen bond between the silanol and carbonyl group that played a major role in the formation of the raspberry-like core-shell nanocomposites. However, Zhai et al. [91] insisted that there was a hydrogen bond between the silanol group and the carbonyl group. Qiu et al. [92] explored the effect of ammonia concentration on the assembly efficiency of SiO_2 particles. It was found that increasing the ammonia content hindered the assembly of SiO_2 on the PS template while decreasing the concentration of ammonia resulted in a high assembly of SiO_2 . Graf et al. [93] used PVP as a stabilizer to prepare the $\text{PS}@\text{SiO}_2$ core-shell microspheres. The study indicated that the length of the PVP molecular chain strongly affected the stability of the colloids, and the uniformity of the SiO_2 shell depended on the adsorption mode of PVP molecules on the PS surface. Percy et al. [94] prepared $\text{polymer}@\text{SiO}_2$ nanocomposite particles by using ultrafine alcoholic SiO_2 sol, in which the hydrogen bond between carbonyl ester and silanol group played a significant role in the formation of core-shell structure.

By adopting Stöber or modified Stöber method, SiO_2 could be encapsulated on the polymer surface in a simple way. However, before that, there must be an interaction between SiO_2 and polymer, otherwise, a large number of secondary particles that were not combined with the polymer core would be generated, thus polluting the final product. Wan et al. [95] synthesized $\text{PAA}@\text{SiO}_2$ core-shell microspheres with controllable size and shell thickness using the modified Stöber method in high yield. It was pointed out that the interaction between the polymer chain and the hydroxyl group of SiO_2 particles induced the deposition of SiO_2 nanoparticles on aggregates. Hotta et al. [96] adsorbed a layer of

SiO₂ on a polymer surface using the Stöber method. The study showed that the growth rate and maximum film thickness of the SiO₂ shell were closely related to the reaction time and the *pH* value of the solution and the deposition thickness was independent of the number of PS spheres. Zhou et al. [97] prepared the raspberry-like P(St-BA-AA)@SiO₂ composite particles as well as a composite film by sol-gel method. It was found that there were improved properties in thermal, flame retardancy, mechanical, and water resistance of the film, and its transmission was almost unaffected due to the uniform distribution of SiO₂.

Generally, the successful preparation of core-shell composite particles does not only rely on a single interaction, but the result of multiple interactions, that is, synergism. For example, Dupin et al. [98] prepared P2VP@SiO₂ colloidal nanocomposite particles by emulsion polymerization. The obtained particles exhibited an unambiguous morphology with core-shell structure, and the aggregation efficiency of SiO₂ could reach to 99%. The dual effects of charge interaction and acid-base interaction might play an important role. Li et al. [99] successfully synthesized core-shell composite particles with different shapes by changing the content of SiO₂, monomer, and surfactant, as well as the particle size of SiO₂, in which the Pickering stabilization and the bridging of silane coupling agent might be the key to synthesis. Armes's group [100] prepared polymer@SiO₂ core-shell nanoparticles by using commercial glycerol-functionalized SiO₂ sol without the aid of an emulsifier, non-aqueous co-solvent, or auxiliary monomer (see Figure 13a,b). Their experiment confirmed the importance of the combined use of cationic AIBA initiator and glycerol functionalized Bindzil CC40 SiO₂ sol for the successful synthesis of nanocomposite particles (see Figure 13c,d), in which the Pickering stabilization, charge interaction as well as the hydrogen bond between the hydroxyl group of glycerol and carbonyl group of acrylates seemed to be the most likely explanations. On this basis, P(MMA-BA)@SiO₂ nanoparticles with core-shell structure were successfully synthesized in their succeeding work by using AIBA as an initiator [101]. Certainly, the heart of these two efforts was the combination use of glycerol-functionalized SiO₂ sol and AIBA.

However, the hydrogen bond is relatively weak compared with other interactions, and composite particles formed by this interaction appear to have poor stability. For example, on the basis of the surface thermodynamics argument [102], the morphology of the composite particles will change after film formation, and SiO₂ would migrate to the film surface [94].

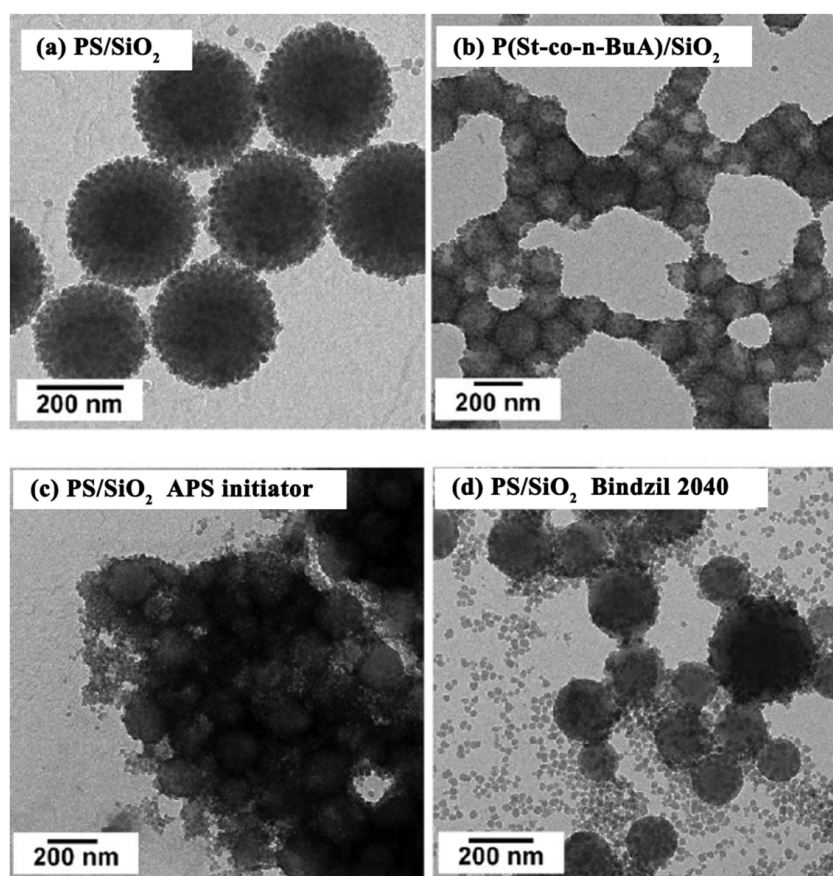


Figure 13. TEM images of: (a) PS/SiO₂ nanocomposite particles and (b) poly(styrene-co-n-butyl acrylate)/SiO₂ nanocomposite particles prepared by emulsion (co)polymerization using a cationic AIBA initiator at 60 °C in the presence of a commercial glycerol-functionalized SiO₂ sol; (c) the identical styrene homopolymerization in the presence of the same SiO₂ sol with an anionic APS initiator did not produce colloiddally stable particles; (d) if AIBA-initiated styrene homopolymerization is conducted in the presence of a non-functionalized SiO₂ sol (Bindzil 2040), well-defined nanocomposite particles are not obtained and there is substantial excess SiO₂ sol. Reproduced from [100] with permission from John Wiley and Sons.

3. Applications

3.1. Coating

Through copolymerization of EMA and MTC, and then blending with commercial SiO₂, Pan et al. [77] obtained the raspberry-like PEMA@SiO₂ composite nanoparticles via electrostatic interaction. By further grafting hydrophilic block copolymer P(MPC-b-MPS) onto the SiO₂ surface, the P(MPC-b-MPS)-PEMA@SiO₂ microspheres were synthesized. It had been proved that the coating prepared by these hybrid spheres exhibited excellent underwater superoleophobic and anti-biofouling performances as well as self-repairing ability (see Figure 14). Amalvy et al. [102] prepared polymer@SiO₂ core-shell nanocomposites with 4-VP as comonomer. The research indicated that using MPEGMA as a steric stabilizer could improve the stability of colloidal particles and the absorption content of SiO₂. Besides, it was also found that the structure of composite particles was changed after film formation, the copolymer components were migrated to the film surface, which would make it a new substitute for wear-resistant coating. Polakiewicz et al. [103] had prepared superhydrophilic coatings using polymer@SiO₂ core-shell composite materials, and the hydrophilicity, chemical composition, surface morphology as well as the durability of accelerated environmental exposure of coatings were studied. The results indicated that these synthesized particles would have great potential in the fields of super-hydrophilic, durable

and transparent coatings. Shen et al. [104] prepared the polyacrylate@SiO₂ core-shell nanoparticles using PVA as stabilizer and MPS as auxiliary monomer. It was found that the uniform distribution of SiO₂ shell in the matrix had critical impact on the film-forming properties of polymer, and due to the existence of uniform cross-linked SiO₂ network, the thermal stability, stiffness as well as the water resistance of polyacrylate@SiO₂ film were proved to be better than those of pure polyacrylate film.

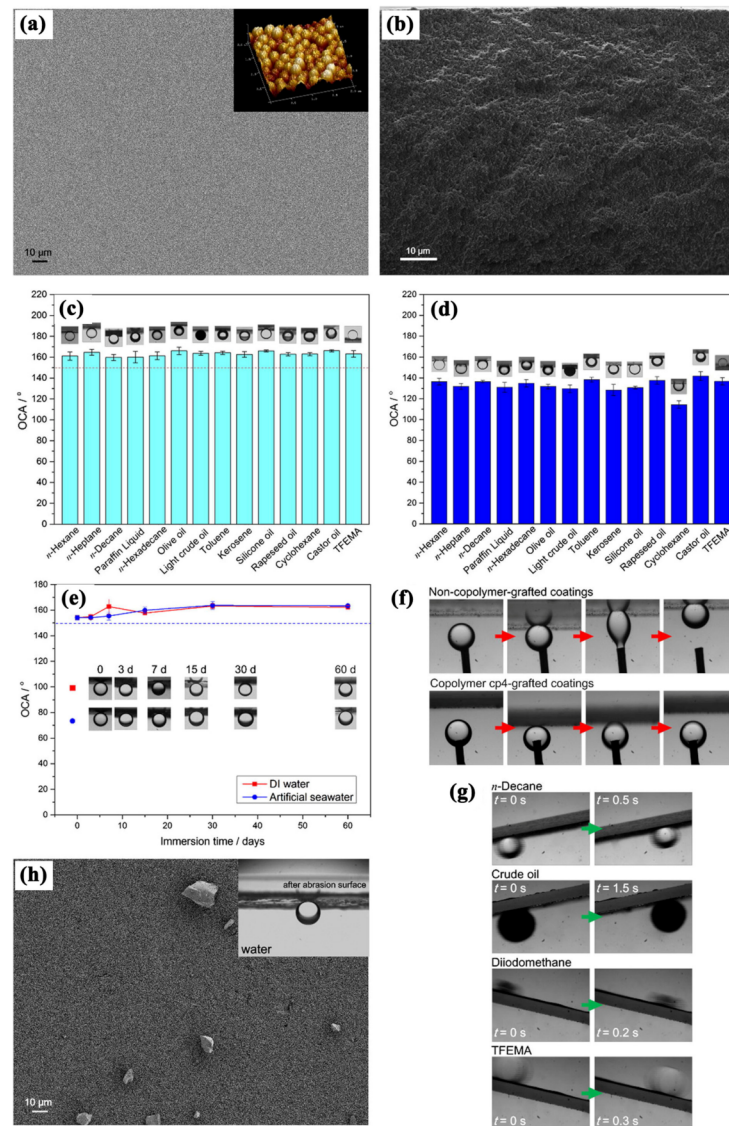


Figure 14. (a) FESEM and AFM images of the surface of copolymer-grafted hybrid sphere-based coating. (b) Cross-sectional FESEM images of copolymer-grafted hybrid sphere-based coating. (c) Underwater OCAs of the typical copolymer-grafted hybrid sphere-based coating. (d) Underwater OCAs of pure hybrid sphere-based coating. (e) OCAs of coating immersed in DI water and artificial seawater for different days. (f) Oil adhesion on coatings. (g) Oil droplets rolling on the surfaces of coating. (h) Surface morphology and OCA of typical copolymer-grafted hybrid sphere-based coating after sand abrasion test. Reproduced from [77] with permission from the Elsevier Inc.

3.2. Polishing

Chen et al. [105,106] prepared a PS composite with a mesoporous CTAB/SiO₂ shell by the Stöber method, and a composite particle with a sponge-like or worm-like shell was also synthesized by adjusting the stirring speed in the synthesis process. The polishing testing showed that the composite with mesoporous shell (CTAB removed) had lower surface

roughness and higher MRR than the composite without CTAB removed (see Figure 15), indicating that the mesoporous SiO_2 shell contributed to the reduction of indentation depth and the improvement of MRR. Zhang et al. [107] used AIBA as an initiator to prepare PS microspheres with a positive charge and then coated the SiO_2 shell on the PS surface by hydrolysis and condensation of TEOS. Compared with the traditional SiO_2 abrasive, the root mean square roughness of the copper wafer was reduced from 4.27 nm to 0.56 nm when applied PS@ SiO_2 as abrasive, and MRR was also proved to be slightly higher than that of SiO_2 abrasive. Armini et al. [108] prepared two types of polymer@ SiO_2 core-shell composite particles through silane coupling agent and electrostatic interaction, respectively. The effects of polishing time and solid content of abrasive on the chemical mechanical polishing process were studied. The results showed that the defects caused by chemical mechanical polishing of core-shell composite particles were much shallower than those caused by conventional SiO_2 , and the number of defects increased with the increase of polishing time. In addition, increasing the solid content of abrasives could also contribute to the growth of defects number.

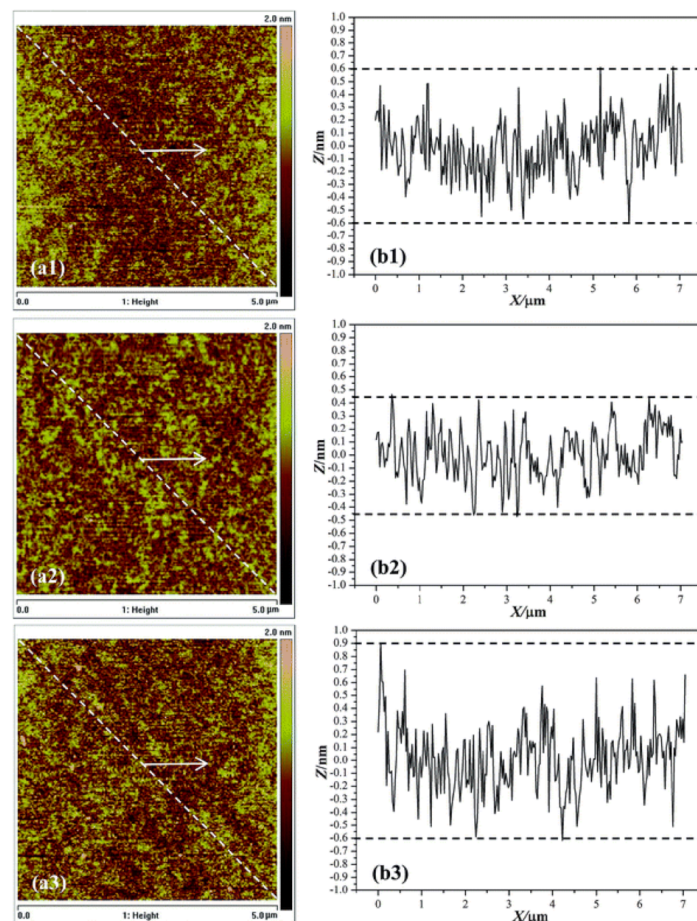


Figure 15. Two-dimensional AFM images and corresponding line scan profiles of the substrates after finishing with composites—A (a1,b1), —B (a2,b2), and —C (a3,b3), in which the line scan profiles in (b1), (b2), and (b3) are obtained by scanning the dashed line positions in (a1), (a2) and (a3), respectively. Reproduced from [105].

3.3. Medicine

Ma et al. [109] successfully prepared the temperature-sensitive PS@PNIPAAm@ SiO_2 nanospheres using water-soluble V-086 as initiator, and the mechanisms of homogeneous coagulative nucleation as well as droplet nucleation in the early stage of Pickering emulsion polymerization were proposed. The results indicated that the as-prepared

PS@PNIPAAm@SiO₂ nanospheres could be taken up by prostate cancer cells (PC3-PSMA), which would have important applications in the field of drug transportation. Ito et al. [110] adsorbed a layer of SiO₂ particles onto the PAH/PLGA surface through electrostatic interaction. Compared with pure PLGA particles, PAH/PLGA@SiO₂ particles encapsulated with pyrene could not only maintain the fluorescence characteristics for a long time but also had excellent release behavior, which would have great application values in medical and biological imaging fields. Li et al. [111] adopted SiO₂-MPS particles as templates to prepare SiO₂-PMAA-SiO₂ double-shell composite microspheres via distillation precipitation polymerization and sol-gel method, and the *pH*-responsive monodisperse PMAA hollow microspheres with flexible (deformable) shell were further synthesized by selectively removing the SiO₂ core. The *pH* response behavior of PMAA hollow microspheres in different *pH* solutions was studied. As shown in Figure 16, it was found that the diameter of PMAA hollow microspheres increased significantly with the increase in *pH* value, and the morphology of PMAA hollow microspheres could reversibly change from collapse to swollen at different *pH* values. Considering that the polydispersity of hollow PMAA microspheres was independent of *pH* value, the synthesized hollow PMAA microspheres were expected to be used in drug delivery systems as well as other biological systems requiring uniform *pH*-response characteristics. Tan et al. [112] had prepared hollow SiO₂ spherical particles with hexagonal ordered mesoporous shells using CTAB and unmodified PS latex microspheres as templates, which was expected to play a potential role in the fields of drug delivery, controlled release, adsorption, and catalysis. However, compared with the concentrated ammonia solution used by Tan et al., Qi et al. [113] successfully synthesized monodispersed HMS capsules with adjustable particle size and shell thickness in a weakly alkaline ethanol/water solution. The CO₂ capture capability of HMS impregnated with tetraethylenepentamine was evaluated. The results showed that the amine-impregnated HMS-400 exhibited excellent capture capability of up to 6.6 mmol CO₂/g of sorbent at 75 °C and 1 atm CO₂, and the amine efficiency for CO₂ capture was up to 353 mg CO₂/g of amine, which was about 50% higher than that of microspheres prepared by Xu et al. [114]. Given that the preparation method used in this work was simple, controllable, and easy to industrialize, this monodispersed capsule might have potential values in drug delivery, catalysis, separation, or as a biological and chemical microreactor.

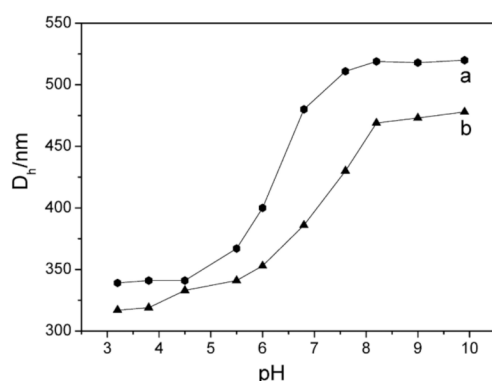


Figure 16. Hydrodynamic diameter (*D_h*) of PMAA hollow microspheres as a function of *pH* in the (a) absence and (b) presence of added NaCl to maintain a constant ionic strength at 0.01 M. Reproduced from [111] with permission from the American Chemical Society.

3.4. Lubrication

In the work of our research group, Wang et al. [115] coated polyacrylate on nano-PTFE spheres surface to obtain PTFE@polyacrylate core-shell composite particles. Research showed that the coating prepared by this composite could improve the wear resistance and bearing capacity of pure PTFE or pure polyacrylate coating noticeably. However, despite the amelioration of dispersibility, wear resistance, and bearing capacity brought by polyacrylate

shells, this improvement was still slightly inferior to that of polar inorganic nanoparticles. Therefore, on the basis of the synthesized PTFE@polyacrylate core-shell composite particles, Wang et al. [116] further prepared PTFE@SiO₂ core-shell composite particles by bridging of silane coupling agent, in which the SiO₂ shell was coated continuously and densely on the outermost layer, as shown in Figure 17a–d. The water lubrication tests showed that the encapsulation of SiO₂ could not only greatly improve the wettability and dispersibility of PTFE, but also significantly enhance the wear resistance on the basis of maintaining its good lubricity, which cannot be achieved by simple physical mixing of PTFE and SiO₂ particles (see Figure 17e–h). Furthermore, the experiments [117] of applying this new composite particle as an oil lubricating additive showed that PTFE@SiO₂ particles had good dispersibility and stability in PAO6 base oil, and the corrosion resistance, as well as extreme pressure performance, were better than those of ZDDP. The friction and wear tests showed that the lubricant containing PTFE@SiO₂ composite particles had excellent friction reduction and anti-wear properties compared with the lubricant added with PTFE, SiO₂, or physically mixed PTFE/SiO₂ particles, which was believed to be related to the existence of core-shell structure and the formation of high-quality organic-inorganic co-extruded transfer film. Moreover, in order to investigate the wear and transfer behaviors of core-shell composite particles, Wang et al. [118] further conducted a more detailed study on the morphology evolution as well as wear and transfer behaviors of PTFE@SiO₂ composite particles in the epoxy resin coating, and a series of meaningful viewpoints were obtained. This work provided good scientific guidance for the lubrication mechanism of core-shell composite particles, especially for soft@hard core-shell composite particles, further enriching the tribological theory of core-shell solid lubricants.

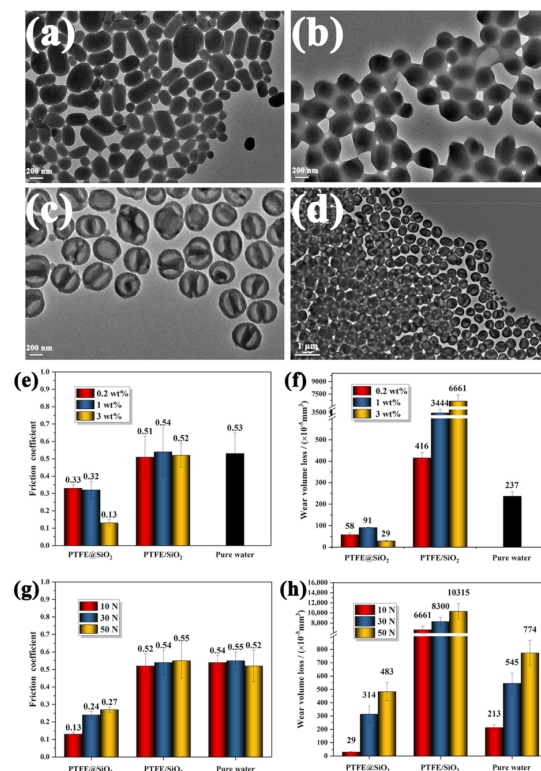


Figure 17. TEM and SEM images of pure PTFE (a), PTFE@P(MMA-co-MPS) (b), and PTFE@SiO₂ (c) high magnification, (d) low magnification). The changes of friction coefficient (e,g) and wear volume loss (f,h) for the samples with different amounts of addition and load, respectively. The error bar represents the standard deviation of the average value of three tests. Reproduced from [116] with permission from the Elsevier.

3.5. Other Fields

By inverse Pickering emulsion polymerization, Zhang et al. [119] prepared PAM@SiO₂ core-shell composite particles using MPS-modified SiO₂ as a stabilizer. The adsorption experiments of Hg²⁺ showed that the core-shell composite particles had higher efficiency and adsorption capacity as well as good recyclability compared with PAM and SiO₂ particles, which could be applied as a promising candidate for removing the heavy metal ions in wastewater. Yamamoto et al. [120] used PVP as a stabilizer to prepare PB@SiO₂ core-shell nanoparticles and synthesized PSA films by blending PB@SiO₂ nanocomposites with pure PB particles in different weight ratios. Probe tack tests at the standard probe rate indicated that the maximum stress of tack adhesion as well as the adhesion energy of PSA film increased 2.36 times and 1.39 times, respectively compared with pure PB film. It was believed that nanoscale mechanical deformation and energy dissipation ability of ‘soft-hard’ nanocomposites played a crucial role in improving the adhesion energy, which made the core-shell PB@SiO₂ particle a good candidate for pressure-sensitive adhesive. Chen et al. [121] reported a new type of organic@inorganic hybrid nanoparticles, whose core and shell were composed of optically active helical polyacetylene and SiO₂, respectively. The results showed that this hybrid nanoparticle not only exhibited high stability in emulsion but also could induce the enantioselective crystallization of alanine enantiomers, which would have potential applications in chiral separation. Gao et al. [122] synthesized polyacrylate@SiO₂ core-shell nanoparticles and employed them as binders for pigment printing. The results showed that the resistance to wet rubbing fastness and soaping fastness of these composite particles have improved by half a grade compared with those commonly used binders (see Figure 18). Duan et al. [123] successfully synthesized PNIPAAm@SiO₂ core-shell microspheres in a toluene solution. The preliminary research showed that PNIPAAm@SiO₂ particles had thermal-response behaviors similar to that of pure micro-gel at LCST of around 32 °C. The dye release performance indicated that the release rate of composite microspheres was affected by temperature as well as the size and surface characteristics of SiO₂ particles. The author believed that the new materials prepared based on this synthesis strategy would have attractive application prospects in catalysis, drug transportation, and other fields.

binder	rubbing fastness		soaping fastness	softness
	dry	wet		
None	–	–	–	7.65
Commodity binder	3–4	3	3–4	7.65
Pickering emulsion	3–4	3–4	4	7.65

Figure 18. The application results of pigment printing. Reproduced from [122] with permission from the Elsevier B. V.

4. Summary and Outlook

So far, facing the gradual development of synthesis technology and equipment, the research endeavors on core-shell composites with polymer as core and SiO₂ as shell are increasing with each passing day. In this paper, the synthetic progresses from the viewpoint of interface bonding mechanisms of polymer@SiO₂ core-shell nanospheres are mainly reviewed, and its applications are also briefly discussed. In particular, the bonding mechanisms we reported are elaborated extensively in five categories according to the interaction between the core and shell. However, it still needs a lot of basic research to deepen the understanding of existing synthetic methods, and further develop the new synthetic procedure. Besides, the literature on the preparation of high solid content dispersions is

relatively scarce, and the general, as well as precise control of the core-shell composite structure, has not yet been possible. Furthermore, how to effectively exert and control the synergistic effect between the core and shell, as well as to properly handle the interface relationship between the inner core and the outer shell also need to be further investigated. Moreover, some prepared polymer@SiO₂ core-shell composite particles may have potential applications in other fields and need further investigation, such as FTFE@SiO₂ core-shell composite particles may be a good substitute for antifouling and wear-resistant coating additives. Not only that, most of the research on polymer@SiO₂ core-shell nanoparticles is mainly focused on the single-shell layer materials, while the preparations of two-shell layers or multi-shell layer materials are still in their infancy. Finally, according to the literature summary in this paper, it is found that most of the innovative works are concentrated between 1990 and 2018. That is to say, there is still much room for improvement in the research of polymer@SiO₂ core-shell composite materials in the future.

It is hoped that the methods and ideas provided in this paper can bring readers convenience for seeking suitable methods to fabricate the polymer@SiO₂ core-shell composites, and further promote the research progress of core-shell composite materials.

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Abbreviations

1-Vinylimidazole, 1-VID; 2-Vinylpyridine, 2-VP; 4-Vinylpyridine, 4-VP/VPy; Acrylic acid, AA; 2,2-Azobis(2-amidinopropane) dihydrochloride, AIBA; Amine-functionalized polystyrene, APS; n-Butyl acrylate, BA; Cetyltrimethylammonium bromide, CTAB; Diethylamine, DA; Diethanolamine, DEA; 2-(Diethylamino)ethyl methacrylate, DEMEA; Divinyl benzene, DVB; Ethylenediamine, EDA; Ethyleneglycol dimethacrylate, EGDMA; Ethyl methacrylate, EMA; Field emission scanning electron microscope, FE-SEM; 3-Allyloxy-2-hydroxy-1-propanesulfonic acid sodium salt, HAPS; Hollow spherical particles with mesoporous shell, HMS; Low critical solution temperature, LCST; Methacrylic acid, MAA; Methyl methacrylate, MMA; Fatty alcohol-polyoxyethylene ether, MOA-9; 2-Methacryloyloxyethyl phosphorylcholine, MPC; Methacrylate-capped poly(ethylene glycol), MPEGMA; Methacryloxy propyl trimethoxysilane, MPS; Material removal rate, MRR; Methacryloxyethyl trimethylammonium chloride, MTC; Oil contact angle, OCA; Poly(2-vinylpyridine), P2VP; Poly(acrylic acid), PAA; Poly(allylamine hydrochloride), PAH; Polyacrylamide, PAM; Polyacrylonitrile, PAN; 1,2-Polybutadiene, PB; Poly(n-butyl acrylate), PBA; Poly(divinyl benzene), PDVB; Polyethyl methacrylate, PEMA; Polyethoxysiloxane, PEOS; Poly-L-lysine, PL; Poly(lactide-co-glycolide), PLGA; Poly(methacrylic acid), PMAA; Polymethyl methacrylate, PMMA; Poly(N-isopropylacrylamide), PNIPAAm; Polystyrene, PS; Pressure-sensitive adhesive, PSA; Sulfonated polystyrene, PSS; Polytetrafluoroethylene, PTFE; Polyvinyl alcohol, PVA; Poly(vinyl acetate), PVAc; Polyvinylpyrrolidone,

PVP; Sodium dodecyl sulfate, SDS; Silica, SiO₂; Poly(styrenealt-maleic anhydride), SMA; Styrene, St; Scanning transmission electron microscopy, STEM; Triethanolamine, TEA; Transmission electron microscope, TEM; Tetraethoxysilane, TEOS; Tetrahydrofuran, THF; 2,2-Azobis(2-methyl-N-(2-hydroxyethyl)propionamide, V-086; Zinc dialkylphosphorodithiolate, ZDDP.

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