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A Novel Preparation Method of Raspberry-like PMMA/SiO$_2$ Hybrid Microspheres

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ABSTRACT: This paper presents a novel method for preparation of raspberry-like organic−inorganic hybrid microspheres with PMMA as core and nanosilica particles as shell. A cationic monomer, 2-(methacryloyl)ethyltrimethylammonium chloride (MTC), was used as an auxiliary monomer, and nanosilica particles were deposited onto the surfaces of organic particles in aqueous medium via electrostatic interaction between nanosilica particles and MTC. The whole process required neither surface treatment for nanosilica particles nor additional surfactant or stabilizer. TEM indicated that electrostatic interaction between negatively charged silica and positively charged MTC was strong enough for the formation of colloidally stable hybrid microspheres with raspberry-like morphology. The average particle sizes and the final silica contents of the hybrid microspheres ranged from 180 to 600 nm and 15 to 60 wt %, respectively. A possible formation mechanism of the raspberry-like hybrid microspheres was proposed on the basis of the effects of some influencing parameters, for instance, diameters and amount of the silica particles, MTC and APS concentration on the polymerization stability, diameters, silica content, and morphology of the hybrid microspheres.

Introduction

In recent years, the strategy to fabricate nanocoating or shell on colloidal particles is of burgeoning interest, principally because such particles can display novel and enhanced properties (e.g., mechanical, chemical, electrical, rheological, magnetic, and optical) by independently altering the composition, dimension, and structure of the cores and shells.[1−10] Among the coating materials, silica is the most popular candidate since it has great potential applications in many industrial areas such as paints, catalysis, drug delivery, composite materials, and so on.[11−15] Although a number of processes have been reported to successfully synthesize hybrid microspheres with core−shell structure using silica as shell, two of them are particularly interesting for the formation of homogeneous, dense coating of silica on different types of template particles. In the first process,[16,17] the surfaces of the core particles (gold, silver, or polymer colloids) are modified with surfactant, stabilizer, or some reactive coupling agent, which encourages the silica shell to deposit on them. For instance, Imhof[15] prepared polystyrene/silica (PSt/SiO$_2$) core−shell nanocomposite particles by using poly(*N*-vinylpyrrolidone) (PVP) as a coupling agent. First, PVP were adsorbed onto PSt colloids and then directly transferred into an ammonia/ethanol mixture, in which a sol−gel process of tetraethoxysilane (TEOS) was carried out. Smooth and homogeneous silica shells of variable thickness could be obtained by adjusting the concentration of TEOS. The second process, termed the layer-by-layer (LbL) self-assembly technique,[1,9,18−22] has become an very attractive topic of investigation since the pioneering work done by Caruso.[1] The basis of this process is the electrostatic association between alternately deposited, oppositely charged species. Multilayered shells were assembled onto submicrometer-sized PSt latex by the sequential adsorption of silica nanoparticles and poly(diallyldimethylammonium chloride) from aqueous solutions.[23]

However, the surface treatment in the former process and the repeated centrifugation/water wash/redispersion cycles in the latter one made the two processes very tedious and energy-consuming. Most recently, Armes[24−28] and co-workers and our previous work[29] used 4-vinylpyridine (4-VP) and 1-vinylimidazole (1-VID) as auxiliary monomers to successfully prepare raspberry-like PMMA/SiO$_2$ organic−inorganic hybrid microspheres, respectively. In their method, the acid−base interaction between hydroxyl groups (acidic) of silica surfaces and amino groups (basic) of 4-VP or 1-VID promoted the formation of nanocomposite particles. It turned out that at least 10% 4-VP or 1-VID based on monomer mass was essential for successful nanocomposite particles formation; nevertheless, this kind of auxiliary monomer was very expensive and malodorous.

In this work, we would like to present a novel process to prepare raspberry-like hybrid microspheres by using a cheap, commercially available cationic monomer MTC and electrostatic interaction of MTC with aqueous silica particles, and only around 3% MTC based on monomer mass was copolymerized with MMA in the presence of aqueous silica particles which were simultaneously electrostatically adsorbed onto the surfaces of the organic particles. Since the surface hydroxyl groups of silica particles were hydrophilic, they could act as emulsifier to stabilize the organic particles. The whole process required neither surface treatment for nanosilica particles nor addition of surfactant or stabilizer. The electrostatic interaction between negatively charged silica and positively charged MTC was strong enough for the formation of long-stable hybrid microspheres with raspberry-like morphology. We believe there has been no report to date using electrostatic interaction of positively charged monomer and negatively charged silica to prepare organic−inorganic hybrid microspheres in soapless aqueous medium.

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Table 1. Summary of PMMA/SiO_2 Hybrid Microspheres Obtained at Different Conditions

runs[a]	silica diameter (nm)	SiO_2 (g)	MTC (%)[b]	APS (%)[c]	particle size[d] (nm)	SiO_2 (wt %)
1	20	14	2	1	296	16.4
2	20	14	2.5	1	247	22.6
3	20	14	3	1	218	33.9
4	20	14	3.5	1	180	40.8
5	20	12	3	1	208	32.6
6	20	16	3	1	223	34.7
7	20	18	3	1	214	35.6
8	10	14	3	1	576	20.4
9	10	14	4	1	340	27.1
10	10	14	5	1	285	39.4
11	10	14	6	1	253	47.5
12	10	12	6	1	266	47.3
13	10	16	6	1	260	44.9
14	10	18	6	1	270	49.2
15	10	16	5	1.4	276	28.2
16	10	16	5	1.0	268	38.6
17	10	16	5	0.8	287	50.2
18	10	16	5	0.5	290	58.6

[a] Reaction conditions: given MMA, MTC, SiO_2 sol, and APS were diluted to 100 g with deionized water, and polymerizations were carried out at 60 °C for 24 h. MMA was fixed at 8 g for all syntheses. [b] Based on MMA mass. [c] Based on MMA mass. [d] As determined by DLS.

Experimental Section

Materials. Methyl methacrylate (MMA) was purchased from Shanghai Chemical Reagent Co. (China) and purified by treating with 5 wt % aqueous NaOH to remove the inhibitor. 2-(Methacryloyl)ethyltrimethylammonium chloride (MTC, 76.7 wt %) aqueous solution was supplied by YanCheng Medical Chemical Co. (China). The silica sols BINDZIL 30/80 (40 nm, pH 9.5, 30 wt %), NYACOL 20/40 (20 nm, pH 10.0, 40 wt %), NYACOL 830 (10 nm, pH 10.5, 30 wt %), and BINDZIL 15/500 (6 nm, pH 10.0, 15 wt %) were supplied as aqueous dispersions by Eka Chemicals Co. (Sweden) and used as received. 2,2′-Azobis(isobutyronitrile) (AIBN) was purchased from Shanghai Chemical Reagent Co. (China) and used as received. Ammonium persulfate (APS) was purchased from Shanghai Gaoqiao Petrochemical Co. (China) and purified by recrystallization.

Preparation of Hybrid Microspheres. A typical preparation process was carried out as follows: a known amount of MTC (2−6 wt % based on MMA), various aqueous silica sols with diameter of 10 nm (40−60 g) or 20 nm (30−45 g), and deionized water (32−62 g) were charged into a 250 mL round-bottom flask equipped with mechanical stirrer, thermometer with a temperature controller, an N_2 inlet, a Graham condenser, and a heating mantle and stirred at room temperature for 1 h. The reaction mixture was then slowly added by MMA (8 g) and heated to 60 °C, followed by addition of APS (1.0−1.4 wt % based on MMA) aqueous solution. The mixture was diluted with deionized water to 100 g. The reaction was carried at 60 °C for 24 h under a slow stream of N_2. The resulted milky-like dispersions were purified by centrifugation−redispersion cycles for several times until no free silica particles were observed by TEM. Each time successive supernatants were removed and replaced with deionized water. A series of hybrid microspheres were prepared using different reaction conditions, as summarized in Table 1.

Characterization of PMMA/SiO_2 Hybrid Microspheres. *Particle Size Analysis*. Dynamic light scattering (DLS, Beckman Coulter Co.) measurements were carried out on the diluted reaction solutions to obtain the intensity-average diameters of the particles. Each analysis was repeated three times to give the average particle size.

Chemical Composition Analysis. About 5 mg of dried hybrid microspheres was analyzed by thermogravimetric analysis using a Perkin-Elmer (TGA-7 USA) instrument in air and heated from room temperature to 800 °C at a scan rate of 20 °C/min. The SiO_2 contents of the hybrid microspheres were calculated after subtracting losses due to surface moisture.

Morphology of Hybrid Microspheres. Transmission electron microscopy (TEM Hitachi H-600 instrument, Hitachi Co., Japan) was used to observe the morphologies of obtained hybrid microspheres. The dispersions were diluted and ultrasonized at 25 °C for 10 min and then dried onto carbon-coated copper grids before examination.

Results and Discussion

Effect of Nanosilica Diameter on Polymerization Stability. In this research, nanosilica particles were adsorbed onto the surfaces of the organic particles via electrostatic interaction and stabilized the organic particles as emulsifier. In this case, one may be curious to know how the diameters of the nanosilica particles influence the polymerization stability. In this experiment, different nanosilica particles with mean diameters of 6, 10, 20, and 40 nm were tried. DLS and TEM indicated that only the hybrid microspheres prepared with 10 and 20 nm silica particles had rather narrow size distribution in the experimental range and kept stable for more than 6 months, suggesting that these nanosilica particles had relatively high stabilization power under the present reaction conditions. In contrast, large amounts of coagulum were obtained for those formulations using 6 and 40 nm silica particles, indicating their poor stabilization power.

To gain insight into the mechanism of coagulation, the same amount of coagulum obtained from the formulations using 6 and 40 nm silica particles were collected and calcined at 800 °C to determine the compositions. Assuming all the incombustible residues were pure silica, it was found that 85 wt % of the coagulum were pure silica for 6 nm silica while only 20 wt % for 40 nm silica. This was possibly because for a given PMMA core, too many 6 nm silica particles were available while too few 40 nm silica particles were available on the surface via adsorption of electrostatic interaction, which destabilized the nanocomposite particles.

Effect of the MTC Comonomer Concentration. The effect of the MTC comonomer concentration on the hybrid microspheres was investigated and summarized in Table 1 (runs 1−4 and 8−11). For 20 nm silica, 2 wt % MTC based on MMA was enough to ensure the polymerization stability while at least 3 wt % MTC was required for 10 nm silica. This could be explained as follows: for each individual silica particle, a 20 nm silica particle has 4 times the surface area as a 10 nm silica particle. Thus, to reach the same surface coverage degree, more 10 nm silica particles were required than 20 nm particles during the adsorption process. Since nanosilica particles were adsorbed via electrostatic interaction between MTC and silica particles, more MTC was needed to adsorb enough silica particles to ensure the polymerization stability when using 10 nm silica sols comparing with using 20 nm silica sols.

Figure 1 illustrated the changes in both size and SiO_2 content as a function of MTC amount for the hybrid microspheres prepared with 20 nm silica. It was found that the average particle size decreased from 290 to 180 nm, and the final silica content of the hybrid microspheres increased from 16.4% to 40.8% as MTC amount increased from 2% to 3.5%. This was because increasing the MTC amount meant more nanosilica could be adsorbed and acting as emulsifier, which decreasing the average particle size. Similar results were found for

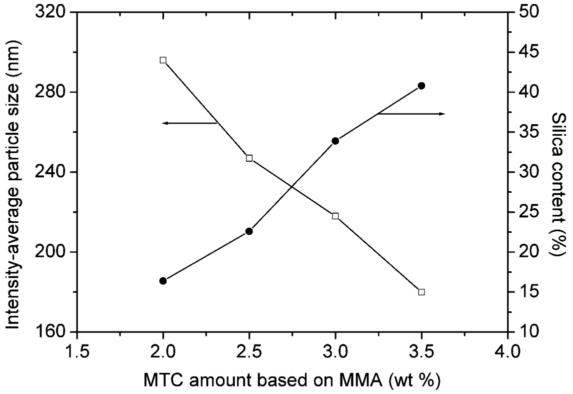

Figure 1. Dependence of particle size and silica content on MTC concentration for hybrid microspheres prepared with 20 nm silica (runs 1−4 in Table 1).

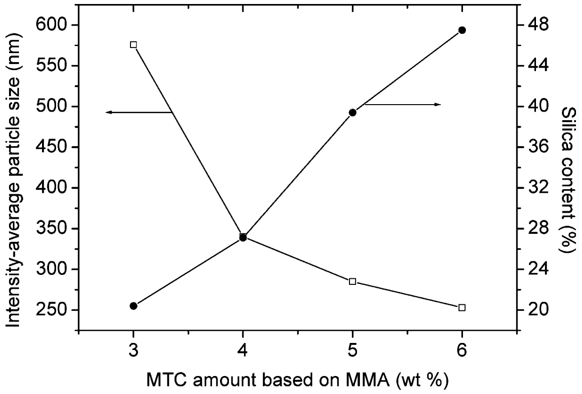

Figure 2. Dependence of particle size and silica content on MTC concentration for hybrid microspheres prepared with 10 nm silica (runs 8−11 in Table 1).

those hybrid microspheres prepared with 10 nm silica sols for runs 8−11 in Table 1, as shown in Figure 2.

Comparing the change in particle sizes of nanocomposite particles prepared with 20 and 10 nm silica was very interesting: the particles obtained by 20 nm silica had considerably smaller particle sizes than those prepared using 10 nm silica under the same condition. This was probably because larger silica particles (20 nm) could hinder more MMA monomer diffused from microdroplets entering the oligomeric radicals to propagate compared with 10 nm silica particles, which decreased the mean size of the hybrid microspheres, based on the possible formation mechanism of the microspheres discussed below.

Effect of the Nanosilica Amount. The effect of initial nanosilica amount on the properties of nanocomposites were also investigated and individually listed in Table 2 from the related runs in Table 1 for clear comparison. It could be seen that the diameters and final silica contents of the microspheres were almost independent of the initial silica amount. This was not difficult to understand: during the soapless one-step process, since nanosilica particles were adsorbed onto the surfaces of the organic particles via electrostatic interaction with MTC, the amount of adsorbed nanosilica and the particle size should be constant at a given MTC concentration.

Effect of the Initiator Amount. Figure 3 illustrates the diameters and final silica contents of the hybrid microspheres as a function of initiator concentration. It appeared that the mean particle diameters did not change within the experimental error when the APS concentration increased from 0.5 to 1.4 wt %, since more APS meant generating more oligomeric radicals. However, the final silica contents of the hybrid microspheres evidently decreased from 58.6 to 28.2 wt %. The question seemed to be related to the charge on the initiator fragment. In the present work, the fragment derived from the decomposition of APS was anionic sulfate radicals; thus, more APS meant more negatively charged fragments, which could prevent more negatively charged silica particles depositing onto the organic particles due to static repulsion.

Table 2. Summary of PMMA/SiO$_2$ Hybrid Microspheres Obtained at Different Conditions

runs[a]	silica diameter (nm)	SiO$_2$ (g)	MTC (%)[b]	particle size[c] (nm)	SiO$_2$ (wt %)
5	20	12	3	208	32.6
3	20	14	3	218	33.9
6	20	16	3	223	34.7
7	20	18	3	214	35.6
12	10	12	6	266	47.3
11	10	14	6	253	47.5
13	10	16	6	260	44.9
14	10	18	6	270	49.2

[a] Reaction conditions: given MMA, MTC, SiO$_2$ sol, and APS were diluted to 100 g with deionized water, and polymerizations were carried out at 60 °C for 24 h. MMA was fixed at 8 g for all syntheses. APS was fixed at 1 wt % based on MMA mass. [b] Based on MMA mass. [c] As determined by DLS.

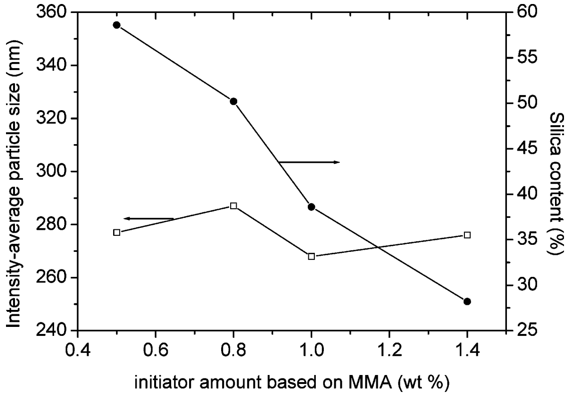

Figure 3. Dependence of particle size and silica content on the initiator concentration (runs 15−18 in Table 1).

Morphology of the Hybrid Microspheres. TEM had been proved to be a very effective tool for the observation of hybrid microspheres with raspberry-like or other morphologies in our previous studies[29] and other reports.[26−28] Figure 4 displayed the TEM images of the hybrid microspheres obtained with 20 nm silica and various MTC amount (runs 1−4 in Table 1). From the images one could see a distinct raspberry-like morphology with PMMA as core and silica particles as shell. The hybrid microspheres obtained at above 2 wt % MTC were approximately spherical and had a very narrow size distribution. But when MTC decreased to 2 wt %, there was some tendency for flocculation and/or coagulation tendency between hybrid microspheres, since less MTC adsorbed onto fewer silica particles, which was insufficient to stabilize the hybrid microspheres.

The TEM images of the samples prepared with 10 nm silica and different initiator concentration (runs 15−18 in Table 1) were demonstrated in Figure 5. Significant flocculation of the hybrid microspheres was observed when the initiator amount was 0.5 wt % based on MMA, but as initiator amount increased, those hybrid micro-

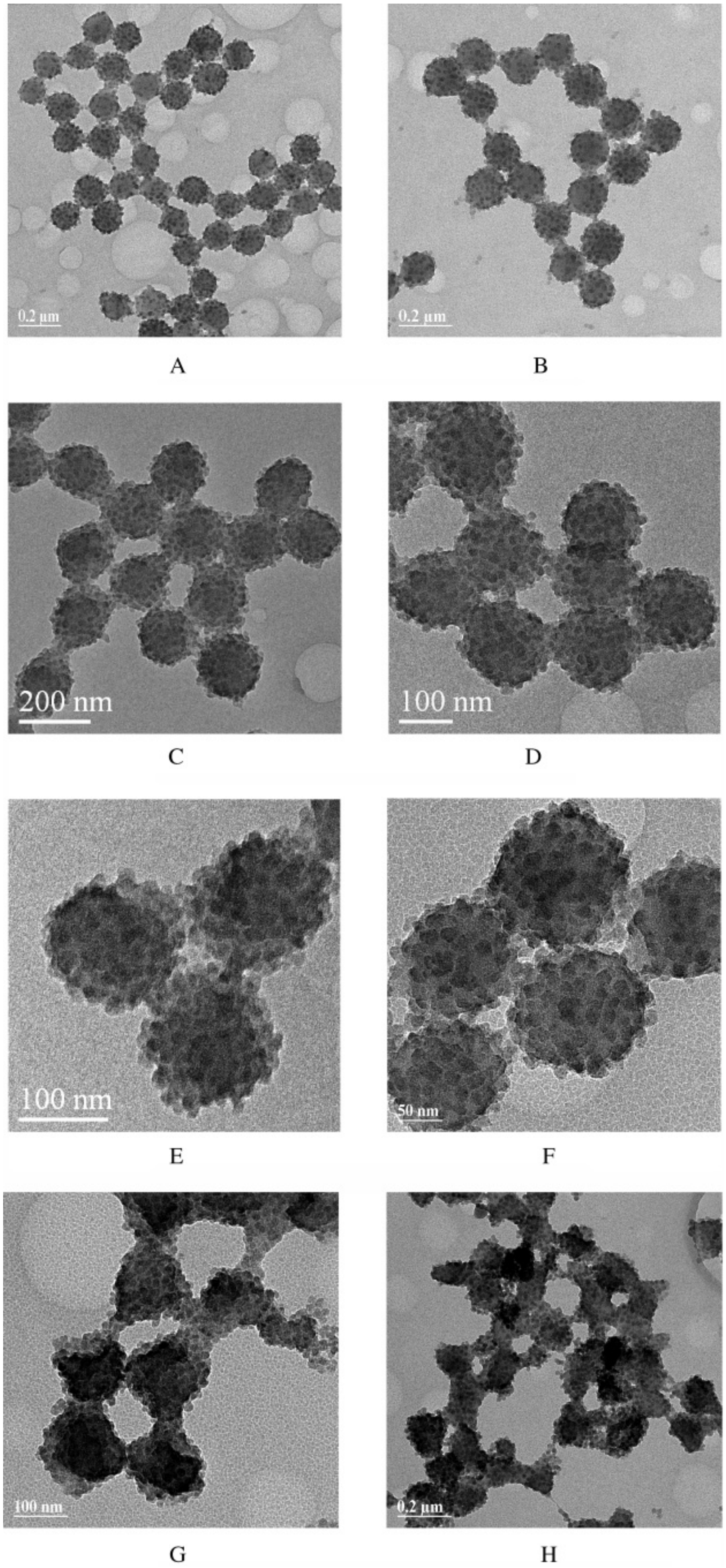

Figure 4. TEM images of the hybrid microspheres prepared with 20 nm silica at various MTC concentrations: (A, B) 3.5%, run 4; (C, D) 3.0%, run 3; (E, F) 2.5%, run 2; (G, H) 2.0%, run 1. Other reaction conditions were fixed for all syntheses as listed in Table 1.

spheres showed spherical and reasonably uniform sizes. The hybrid microspheres prepared at 0.5 wt % initiator had the highest silica content of 58.6 wt %, as indicated in Table 1 and Figure 3. Furthermore, the sample of

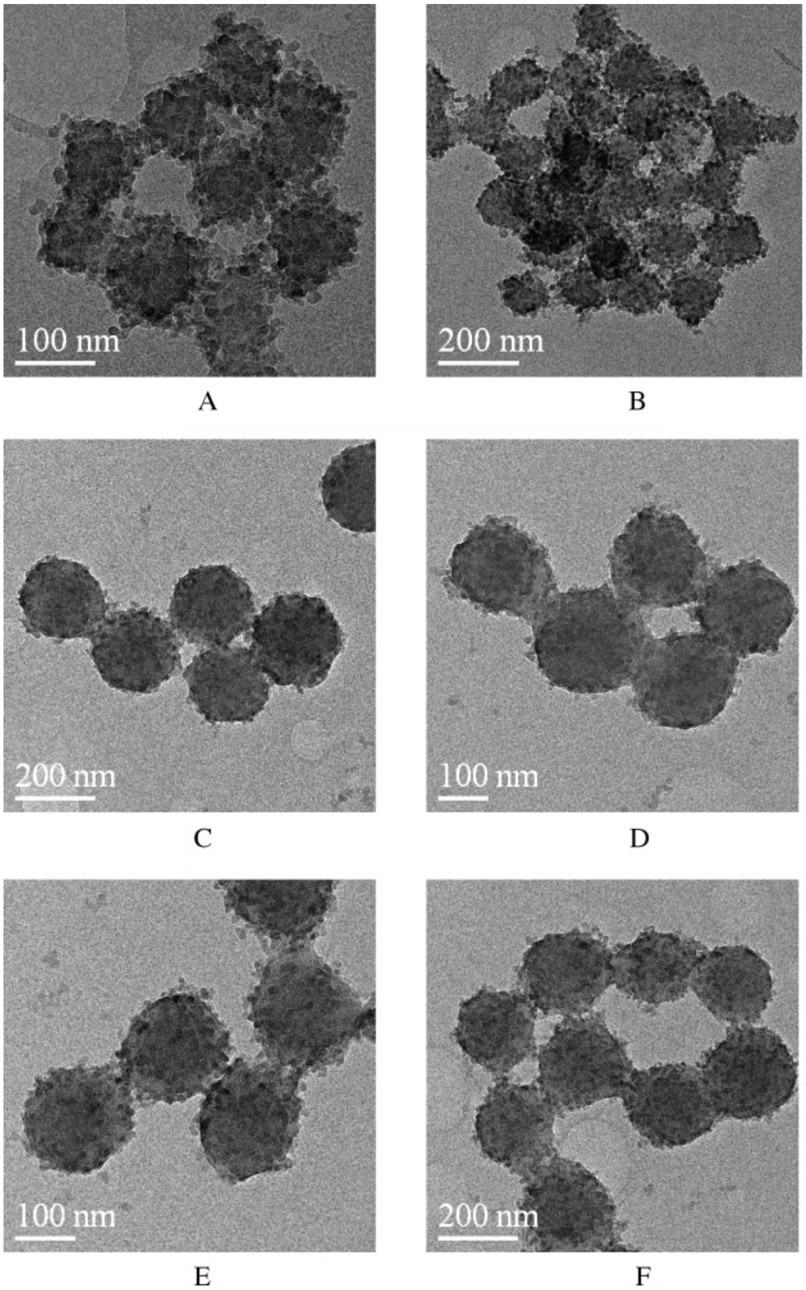

Figure 5. TEM images of the nanocomposite particles prepared with 10 nm silica at various initiator concentrations: (A, B) 0.5%, run 18; (C, D) 1.0%, run 16; (E, F) 1.4%, run 15. Other reaction conditions were fixed for all syntheses as listed in Table 1.

Figure 5A,B had a diameter of 290 nm from DLS while 110 nm from TEM images, which was due to the existence of flocculation between hybrid microspheres. This flocculation could be cleaved again under intense mechanical stirring, which showed the typical thixotropic properties, confirming that supramolecular crystals formed in the concentrated silica suspension according to the literature.[30]

Formation Mechanism of the PMMA/SiO$_2$ Hybrid Microspheres. To understand the formation mechanism of raspberry-like PMMA/SiO$_2$ hybrid microspheres, control experiments without either silica or MTC were carried out. It was found that macroscopic precipitates were obtained in the absence of silica sol, while in the absence of MTC, a metastable milky-like dispersion was obtained, which became unstable after storage for only 1 day. TEM indicated only some bare PMMA particles without any encapsulated or adsorbed nanosilica particles. In addition, since colloidally stable dispersions were obtained for all the formulations listed in Table 1 when the water-soluble APS initiator was used, we tried to use the oil-soluble initiator AIBN to determine the loci of initial reaction in the polymerization system. However, only large amounts of macroscopic precipitate were obtained.

Therefore, on the basis of all the experimental results and discussions, we deduce a possible formation mechanism of raspberry-like PMMA/SiO$_2$ hybrid microspheres based on the scheme shown in Figure 6 as follows: Before the polymerization was carried out, in part I, free silica particles, nanosilica particles adsorbing MTC, free MMA molecules dissolved in the water, and microdroplets of monomers stabilized by silica particles, meanwhile, silica particles acted as pickering emulsifier,[31] composed the reaction solution. After addition of APS, in part II, initiator decomposition occurred in the

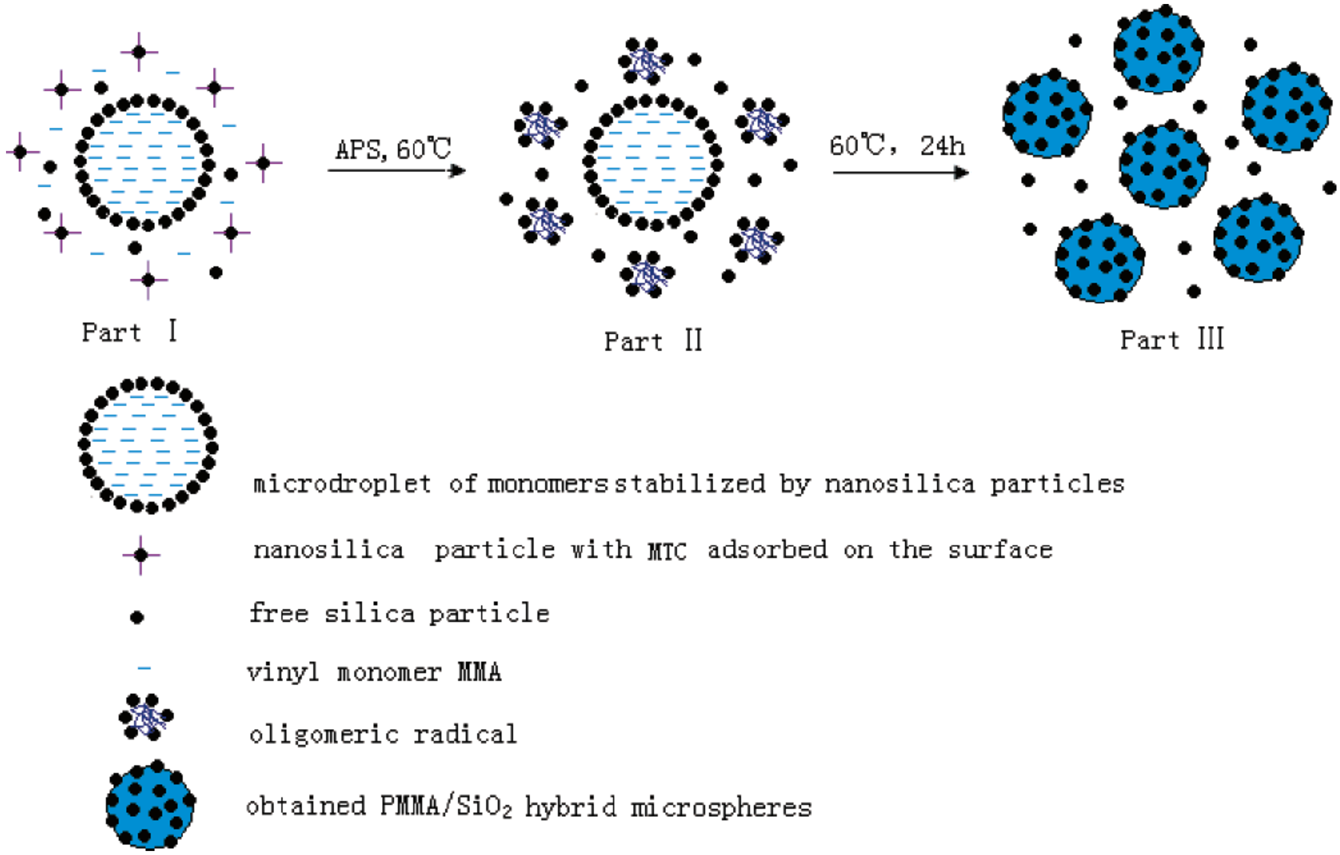

Figure 6. Schematic diagram of formation mechanism of the raspberry-like PMMA/SiO_2 hybrid nanocomposite particles.

aqueous phase. This generated free radicals, which initiated the polymerization of MMA dissolved in the water and MTC adsorbed on the surfaces of nanosilica to form oligomeric radicals. Subsequently the MMA monomer in the microdroplets continuously diffused and was captured by the oligomeric radicals, causing chain propagation and finally forming raspberry-like hybrid microspheres with PMMA as core and silica particles as shell. The termination of the growing chains occurred in part III when another free radical entered the particles.

Conclusions

A series of raspberry-like PMMA/SiO_2 hybrid microspheres were successfully prepared using a novel method, in which a cationic monomer (MTC) was used as auxiliary monomer and nanosilica particles were adsorbed onto the surfaces of organic particles via electrostatic interaction to form nanocomposite particles with a raspberry-like morphology. Neither surface treatment for nanosilica particles nor added surfactant or stabilizer was required. Different silica particle sizes were tried, and it was found that 10 and 20 nm silicas were suitable for the formation of colloidally stable raspberry-like PMMA/SiO_2 hybrid microspheres. The average particle sizes and the final silica contents of the hybrid microspheres ranged from 180 to 600 nm and 15 to 60 wt %, respectively, depending on the reaction conditions. The locus of the initial reaction in the polymerization system appeared to be in the aqueous phase, and a possible formation mechanism of the raspberry-like hybrid microspheres is proposed.

Since the compositions and properties of organic phase could be tuned by different monomers, and the inorganic nanoparticles could be SiO_2, Al_2O_3, Fe_3O_4, TiO_2, etc, in principle, one should be able to prepare various environmentally friendly hybrid microspheres or materials with the desired properties (abrasion-resistant, UV-shielding, reactive, catalytic, optical, electrical, etc.) using this method.

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