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Preparation and characterization of Y_2O_3 hollow spheres

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Y_2O_3 hollow spheres are prepared by coating the anionic poly (styrene-methyl acrylic acid) (PSA-A) latex with an amorphous yttrium layer and subsequent calcining at elevated temperatures in air. The aging temperature, aging time, the concentrations of Y(III) and urea are systematically varied to establish the optimum conditions for the formation of the coating shell. Zeta potential measurement, transmission electron microscopy, scanning electron microscopy, X-ray diffraction and infrared measurements are used to characterize the PSA-A latex, core-shell spheres and Y_2O_3 hollow spheres. A mechanism for the formation of the PSA-A/yttrium compounds core-shell spheres is suggested. The key factor to prepare smooth-coated spheres is obtained. © *2006 Springer Science + Business Media, Inc.*

1. Introduction

Mesoscale hollow spheres of inorganic materials have been used in many areas, such as capsule agents, fillers and coatings because of their low densities, high surface area and optical properties [1]. In recent years, many inorganic hollow spheres [2–9] including TiO_2, Fe_2O_3, CdS and Ag/TiO_2 have been prepared by templating directly against the polymer latex. Kawahashi [10,11] prepared Y_2O_3 hollow spheres by templating directly against cationic PS latex and indicated that the positively charged latex could be readily coated with yttrium basic carbonate, while the negatively charged polymer colloid could not [10]. In this paper, Y_2O_3 hollow spheres were prepared successfully by coating the negatively charged PSA-A latex with yttrium basic carbonate and subsequent calcining in air. A mechanism for the formation of the coating shell was suggested.

2. Experimental section

2.1. Materials

Yttrium oxide (its purity is 99.999%); nitric acid (AR, Tianjing Bodi Chemical Reagent of China); urea (AR, Yantai Sanhe Chemical Reagent of China); polyvinylpyrrolidone (PVP, average molecular weight 5000–700000, Hengda Chemical Reagent of China). The chemicals for the preparation of PSA-A latex can be found in report [12]. All the chemicals are used as received without further purification.

2.2. Preparation of particles

2.2.1. Poly (styrene-methyl acrylic acid) anionic (PSA-A) latex

PSA-A latex used as core particles is prepared by radical copolymerization with ammonium persulfate as initiator [12]. The obtained PSA-A latex is anionic because carboxyls are loaded on its surface.

2.2.2. Core-shell spheres

PSA-A particles are coated with uniform layers of yttrium compounds by adding yttrium nitrate (dissolving Y_2O_3 in nitric acid), urea and PVP to the PSA latex with subsequent aging process at 90°C for 3 h. Repeating the coating process two or three times can make the coating shell thicker. Yttrium basic carbonate small particles can be obtained by aging yttrium salt solutions at elevated temperature in the presence of urea [13]. PSA-A latex is coated with the new formed $Y(OH)CO_3$ small particles and core-shell spheres are obtained. The coated spheres are dried at 60°C in an oven.

2.2.3. Y_2O_3 hollow spheres

The Y_2O_3 hollow spheres are prepared by calcining the dried core-shell spheres in an oven in air at various tem-

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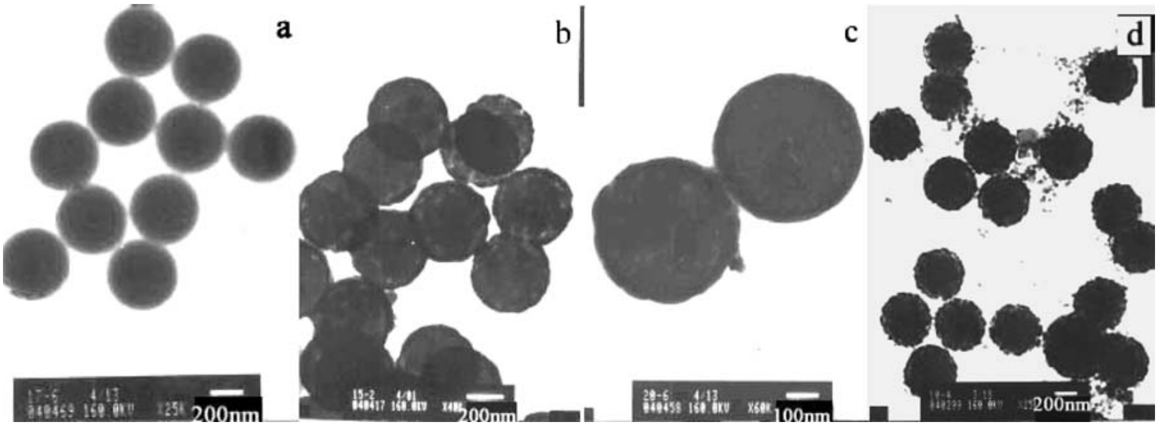

Figure 1 TEM images of (a) PSA-A latex particles, (b) smooth-coated spheres of sample 4 and (c) sample 5, (d) mixed systems of sample 9.

peratures (500°C, 600°C and 700°C respectively) with heating rate of 1°C min^{-1}.

2.3. Analysis

The average size of the dispersions and the hollow spheres is determined by transmission electron microscopy (TEM) of JEM-2000EX (JEOL) and scanning electron microscopy modeled JSM-6700 F. The hollow particles are examined by X-ray diffraction (XRD) using a D/Max r-B. Zeta potential measurements (Zeta sizer 3000 HS, MALVERN) of PSA-A latex, yttrium basic carbonates small particles and core-shell spheres are carried out as a function of the pH in distilled water. The core-shell spheres and hollow spheres are examined by infrared (IR) using a Bruker Vector-22 infrared spectroscopy.

3. Results and discussion

3.1. Preparation of core-shell spheres

The TEM of PSA-A latex is shown in Fig. 1a. The PSA-A latex is in uniform size and its diameter is about 450 nm on average. Typical TEM images of the smooth PSA-A/yttrium compounds core-shell spheres are shown in Fig. 1b and c, in which the inorganic shell appeared as a dark ring around the PSA-A latex core and no secondary particles are found. Intact and smooth core-shell spheres are prepared and the diameter of core-shell particles is about 500 nm. So the thickness of the shell is about 50 nm.

The aging temperature, aging time and the concentrations of Y(III) and urea are systematically varied to establish the optimum conditions for the formation of core-shell spheres. The results of the experiments are summarized in Table I. It is evident that successful coating is dependent on the four parameters in Table I. When the aging temperature was 90°C and the aging time was 3 h, smooth-coated spheres are obtained, while no coating or mixed systems are formed if the aging temperature is lower (70°C or 80°C), even the aging time is much longer (4 ∼ 6 h). Fig. 1d shows the TEM photograph of mixed systems.

TABLE I Properties of coated spheres obtained in dispersions containing 5 g/L PSA-A latex and 10 g/L PVP under corresponding experimental conditions

Sample	*T* (°C)	*T* (h)	Y (III) (10^{-2}mol/L)	Urea (mol/L)	System characterization
1	90	3	0.1	1.2	S
2	90	3	0.1	2.0	S
3	90	3	0.1	0.70	S
4	90	3	0.5	0.90	S
5	90	3	0.5	2.0	S
6	90	3	1.5	1.2	S
7	90	3	1.5	2.25	S
8	90	3	1.8	1.5	S
9	90	3	0.08	1.8	M
10	90	3	0.5	2.25	M
11	90	3	0.5	0.45	M
12	80	4	0.5	0.90	M
13	70	6	0.5	0.90	N
14	90	3	1.8	2	M
15	90	3	2.0	0.90	M

S: smooth-coated spheres; N: no coating on the PSA-A spheres; M: mixed systems showing both film formation and adhesion of particles homogeneously precipitated in solution.

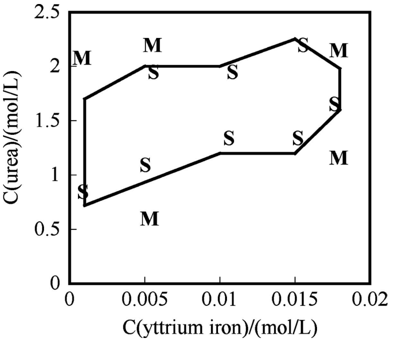

Figure 2 Precipitation domain for systems containing varied amounts of $Y(NO_3)_3$ and urea in the presence of 5 g/L PSA-A latex and 10 g/L PVP, aged at 90°C for 3 h. S: smooth-coated spheres; M: mixed systems.

The concentrations of Y (III) and urea also have profound effects on the coating results see Table I. Fig. 2 shows the precipitation domain for systems containing varied amounts of Y(III) and urea in the presence of

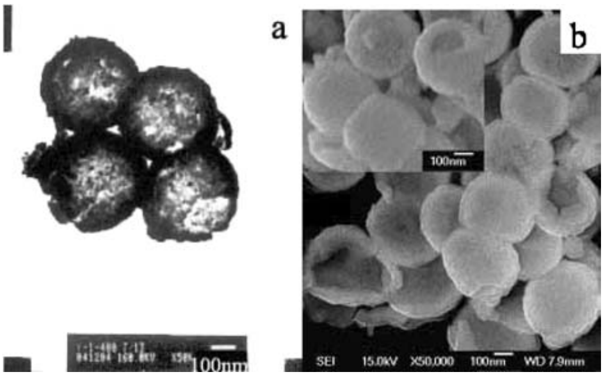

Figure 3 (a) TEM images and (b) SEM images of hollow spheres calcined at 600°C of sample 4.

5 g/L PSA-A latex and 10 g/L PVP, aged at 90°C for 3 h. Smooth-coated spheres (S of Table I) are formed in the full boundary delineate conditions and mixed systems showing both film formation and adhesion of particles homogeneously precipitated in solution.

3.2. Preparation of Y_2O_3 hollow spheres

To prepare Y_2O_3 hollow spheres, it is necessary to remove the PSA-A latex from the core-shell particles. We prepare Y_2O_3 hollow spheres by calcining the core-shell particles at elevated temperature in air.

Fig. 3 shows the TEM and SEM images of Y_2O_3 hollow spheres, broken spheres appear in some of them, showing that the particles are hollow spheres. Fig. 3 also shows that the diameter of the hollow spheres is less than 500 nm indicating that hollow spheres are a little bit shrunk during the calcining process.

The IR data for the hollow spheres of sample 4 calcined at 600°C and coated particles are shown in Fig. 4a and b respectively. Curve b obtained from sample 4 reveals the peaks of 701, 761, 1075 and 3027 cm^{-1} for the phenyl group; the peaks of 2958 and 2932 cm^{-1} for –CH– group in polystyrene; the peak of 1724 cm^{-1} for the –COO– group; the peaks of 3000 to 3500 cm^{-1} for the OH stretching vibrations; the peaks of 1400–1500 cm^{-1} and 843 cm^{-1} for carbonate bands of yttrium basic carbonate. There are no spectra characteristic bands of PSA on curve a, confirming that the polymer cores are decomposed completely.

Fig. 5 shows the XRD patterns of Y_2O_3 hollow spheres calcined at 500°C, 600°C and 700°C respectively. It indicates that the Y_2O_3 crystalline phase is formed at calcining temperatures of higher than 500°C and the Y_2O_3 hollow spheres are body-centered cubic composition.

3.3. The mechanism for the formation of the core-shell spheres

The zeta potentials of dispersions consisting of PSA-A latex (line a), the formed yttrium basic carbonate small particles (line b) and the core-shell spheres (line c) as a function of pH in distilled water are shown in Fig. 6. It reveals that the isoelectric points (i.e.p.) of PSA-A latex, yttrium basic carbonates particles and core-shell particles are at pH values of about 3.2, 4.3 and 5.6 respectively.

Fig. 6 indicates that the new formed $Y(OH)CO_3$ small particles have opposite surface charge to the core in the pH range of 3.2–4.3 and the core-shell spheres in pH range of 4.3–5.6 respectively. Therefore, the formation and growth of PSA-A latex/$Y(OH)CO_3$ core-shell spheres should be caused by their charge attraction.

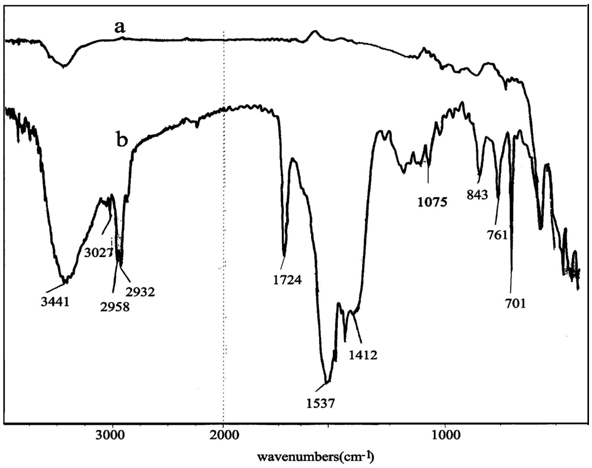

Figure 4 IR spectra of (a) the core-shell spheres and (b) hollow spheres.

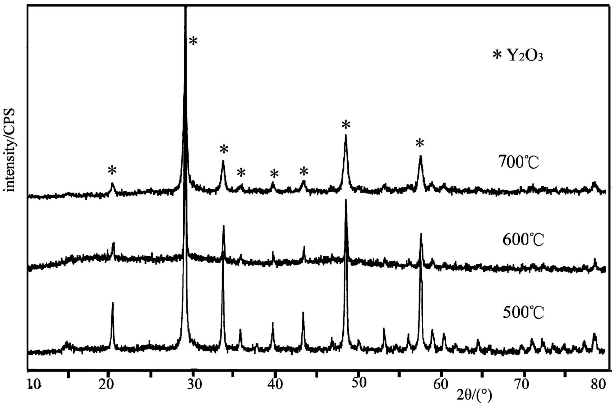

Figure 5 XRD patterns of sample 4 calcined at 500, 600 and 700°C

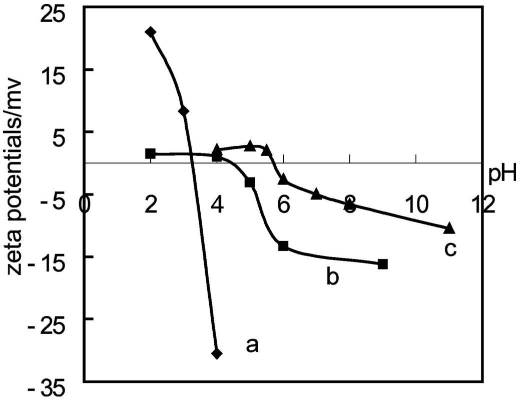

Figure 6 Zeta potentials of dispersions consisting of (a) PSA-A latex, (b) $Y(OH)CO_3$ particles, and (c) core-shell spheres as a function of pH values in distilled water.

We infer that the formation process of core-shell spheres might contain three steps: firstly, pH value increases because of the hydration of urea, and $Y(OH)CO_3$ small particles are formed at the same time [13]; then, the new formed $Y(OH)CO_3$ small particles are coated on the core surface because of their opposite surface charge in the pH range of 3.2–4.3; and last, the thin coating layer grows thicker because the surface charge on the formed core-shell particles are also opposite to that of $Y(OH)CO_3$ small particles in the pH range of 4.3–5.6.

The key factors to prepare smooth-coated spheres are controlling aging time properly in the pH ranges of 3.2–4.3 and 4.3–5.6. Firstly, if the aging time at the pH range of 3.2–4.3 is too short, the $Y(OH)CO_3$ small particles are partly coated on the PSA-A latex surface; while if it's too long, $Y(OH)CO_3$ particles will grow to big particles because of the same surface charge of $Y(OH)CO_3$ particles and the thin coating layer. They will separate from the system to form the mixed systems. Secondly, the aging time at the pH range of 4.3–5.6 should be controlled for a while to make the thin coating layer thinker and smooth-coated spheres are formed. In addition, the aging time at the pH ranges of less than 3.2 or higher than 5.6 also should be controlled properly. If it is too long, the $Y(OH)CO_3$ particles will grow to big particles and separate from the system because their surface charge is the same as that of other particles. Thus, the aging time at different pH ranges should be controlled properly for the preparation of smooth-coated spheres.

In a word, the pH value as a function of time during the coating process in system is a main factor for a successful preparation of smooth-coated spheres and it is mainly affected by three parameters: aging temperature, concentrations of Y(III) and urea. The pH value as a function of time can be controlled properly by controlling the three parameters to prepare smooth-coated spheres. Those are accordance with the experiment results of Table I.

Kawahashi studied the mechanism for the formation of PS-C latex/$Y(OH)CO_3$ core-shell spheres [10] and he thinks that the core-shell particles can be prepared by making the pH value in the system higher than the i.e.p of $Y(OH)CO_3$ particles because of the charge attraction between $Y(OH)CO_3$ particles and PS-C latex. Therefore, the preparation of cationic latex/$Y(OH)CO_3$ core-shell particles is easier than the preparation of anionic latex/$Y(OH)CO_3$ core-shell particles and Kawahashi only obtained the former.

The mechanism and optimum conditions for the formation of the above two kinds of core-shell spheres are different because of the different surface charge of polymer core. Thus, the surface charge of polymer core is also one main factor for a successful preparation of smooth-coated spheres.

4. Conclusion

Y_2O_3 hollow spheres are prepared by templating directly against PSA-A latex. The aging temperature, the concentrations of Y(III) and urea are systematically varied and the optimum conditions of coating are obtained. A mechanism for the formation of the PSA-A/yttrium compounds core-shell spheres is suggested. Surface charges on the polymer core and pH value of dispersions are the main factors as a function of time for a successful preparation of smooth-coated spheres.

References

1. J. K. COCHRAN, *Curr. Opin. Solid State Mater. Sci.* **3** (1998) 474.
2. S. EIDEN and G. MARET, *J. Coll. Interf. Sci.* **2250** (2002) 281.
3. H. SHIHO and N. KAWAHASHI, *J. Colloid Polym. Sci.* **278**(3) (2000) 270.
4. H. BAMNOLKER, B. NITZAN, S. GURA and S. MARGEI, *J. Mater. Sci. Lett.* **16**(16) (1997) 1412.
5. H. SHIHO and N. KAWAHASHI, *J. Coll. Interf. Sci.* **226** (2000) 91.
6. C. SONG, G. GU, Y. LIN, H. WANG, Y. GUO, X. FU and Z. HU, *J. Mater. Res. Bull.* **38** (2003) 917.
7. C. SONG, D. WANG, G. GU, Y. LIN, J. YANG, L. CHEN, X. FUN and Z. HU, *J. coll. Interf. Sci.* **272** (2004) 340.
8. R. A. CARUSO, A. SUSHA and F. CARUSO, *J. Chem. Mat.* **13**(2) (2001) 400.
9. Y. LU, Y. YIN and Y. XIA, *Adv. Mater.* **13** (2001) 271.
10. N. KAWAHASHI and E. MATIJEVIC, *J. Coll. Interf. Sci.* **138**(2) (1990) 534.
11. *Idem.,ibid.***143** (1991) 103.
12. Y. GUO, G. GU, Y. JIAO, F. XUN and Z. HU, *J. Poly. Mater. Sci. Engng. (China)* **19**(4) (2003) 40.
13. B. AIKEN, W. P. HSU and E. MATIJEVIC, *J. Amer. Ceram. Soc.* **71** (1987) 845.

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