



The Syntheses of New Type Janus Intelligence Nanometer Microsphere Oil Displacement Agent

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The shells of polystyrene hollow microspheres were impregnated with three-(methacryloyloxy) propyltrimethoxsilane (MPS), aminopropyltriethoxsilane (APTES) and ethyl orthosilicate (AEOS). The lipophilic and hydrophilic groups were introduced into the polystyrene matrix and the Janus structure is formed through aqueous phase by self-assembly on the surface of the shell by sol-gel process. In order to obtain the silica-based composite Janus nanomaterials, wedissolve and remove polystyrene, we can regulate the microstructure of Janus nanomaterials through changing the pH value of the reaction system and the amount of monomer, and then the Janus hollow spheres and nanosheets can be obtained.

1. Introduction

Janus material refers to the two chemical compositions in the same system, which has a clear partition structure, and thus has a dual nature such as hydrophilic / hydrophobic, polar / non-polar. This material is an important research direction of materials science. How to achieve the universality, controllability and mass production of these complex colloids is one of the key issues. The development of polymer microspheres has had a great impact on human economy and life, for example: polymer microspheres play an important role in coatings, cosmetics, photographic materials and biomedicine. The most important factor affecting the application of polymer microspheres is their morphology and size characteristics. Therefore, the study of morphological control of polymer microspheres has been a topic of concern to scientists. With the deepening of the research, microspheres with different morphologies and structures were prepared. One of the most interesting ones was anisotropy. Janus microspheres and porous polymer microspheres. Janus microspheres have morphological or chemical composition of the asymmetric nature. However, the synthesis of ordinary polymer microspheres is almost arbitrary, and the preparation of Janus microspheres is more difficult. Because for a microsphere, the thermodynamic stability of the surface free energy tends to be the lowest, resulting in the fact that the final microspheres can easily become a uniform surface and the lowest energy of the regular spherical. Therefore, it is difficult to obtain Janus microspheres through the use of traditional synthetic polymer microspheres. The preparation and morphology control of Janus microspheres is a challenging task in the field of materials science. The preparation process is controlled from thermodynamics and dynamics. In addition, porous polymer microspheres have attracted the attention of materials scientists because of their low density and high specific surface area. Since the preparation of Janus microspheres is closely related to the formation of porous polymer microspheres in thermodynamics and kinetics, the morphological control of Janus microspheres and porous polymer microspheres is studied in both basic and theoretical studies.

Controllable preparation of Janus materials with special microstructures is an important part of new material research. Since de Gennes firstly used Janus to describe the surface with different chemical properties of particles, the surface has a dual nature of the material research, which becomes a hot topic in the field of materials (De Gennes, 1992). At the same time, the surface of the Janus particles with dual properties imparts the properties of two different or even opposite (hydrophilic/hydrophobic, polar/nonpolar, positive charge/negative charge, etc.), which is effective in solving the functionalization and dispersibility of nanomaterials way. The dual nature of integration will have a new nature and play an important role in promoting the development of new materials. Janus materials have demonstrated excellent performance and

attractive application prospects in solid particle emulsifiers, assembly, optical probes and catalysis (Perro et al., 2005; Yang et al., 2008; Walther et al., 2013; Wang et al., 2009; Jiang et al., 2010; Lattuada and Hatton, 2011; Liang et al., 2014; Zhang et al., 2012; Zhang and Yang, 2011).

At present, commonly used methods in the preparation of Janus materials include interface protection, phase separation, micro-processing and self-assembly. Pickering Emulsion Auxiliary Synthesis is a widely used method for the preparation of Janus granules in large quantities. Janus particles are distributed at the oil / water interface and the Janus particles are prepared by selective modification of the surface (Hong and Jiang, 2006; Liu et al., 2009; Wang et al., 2011; Wang et al., 2010), which is suitable for larger sized particles. For the nanoparticles, the adsorption energy at the interface is low, and the capillary force generated by the interaction between the particles leads to the emergence of the fold structure, and the monolayer structure cannot be obtained. Therefore, it is difficult for pickering emulsion assisted synthesis to prepare nanoscale Janus particles (Cheung and Bon, 2009; Cheung and Bon, 2009). Giersig et al. (1997) prepared nanoscale Janus materials use phase separation of inorganic/metal, but the method is limited by the specific chemical composition and structural morphology. The universality is poor. Chen et al. obtained magnetic Janus hydrogel particles using the micromachining techniques (Chen et al., 2009), Walther et al. and Erhardt et al. prepared a nanoscale discoid, rod-like and granular form using the self-assembly of the triblock copolymer, but the material size of the material prepared by micromachining was large and the submicron and nanoscale materials were not obtained (Erhardt et al., 2003). The method requires precise control of the molecular weight and molecular weight distribution of the block copolymer and requires harsh synthesis conditions. Therefore, the preparation of nanoscale Janus materials and the precise control of microstructure are still a challenge.

Liang et al. proposed a method for the preparation of Janus materials by an emulsion interface. In this method, the sol - gel reaction of the silicon precursor at the oil / water interface was carried out with the emulsion droplets as the template, and the organic / inorganic composite of the raspberry shape with the protruding structure was prepared by the seed emulsion polymerization. Microspheres (Liang et al., 2011).

In this paper, the polymer microspheres were used as seed, and the sol-gel reaction of the silicon precursor on the surface of the seed was induced and self-assembled to obtain Janus nanomaterials. As shown in figure 1, a pre-emulsion was prepared by mixing emulsions of two silane coupling agents, ethyl orthosilicate, water with emulsifier having lipophilic hydrophilic groups and it was added to a polymer hollow microsphere seed emulsion system. The organic/inorganic hybrid microspheres were prepared by sol - gel reaction and self - assembly of silicon precursor on the surface of seed. The lipophilic group containing double bond and the hydrophilic group containing amino group (-NH₂) were respectively directed to the seed ball matrix and the aqueous phase, and the seed ball was removed by solventing to obtain Janus hollow sphere and Janus nanosheets. To achieve the evolution of Janus nanomaterials from continuous shells to porous shell structures.

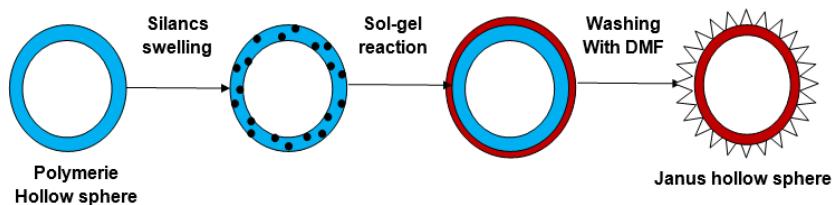


Figure 1: Synthesis of Janus Materials by Seed Emulsion Swelling Sol-gel Process

2. Experimental part

2.1 Reagents and Instruments

Polystyrene hollow microspheres (HP-433), Rohm and Haas Company; Ethyl orthosilicate (TEOS), analytical grade, Beijing Chemical Plant; 3-(methacryloyloxy) propyltrimethoxysilane (APMA), analytically pure, Alfa Aesar, Inc., prepared by the method described in (Chen et al., 2009) to prepare a pre-hydrolyzed styrene maleic anhydride copolymer (HSMA, mass), & It; RTI ID = 0.0 > (10%); N, N-dimethylformamide (DMF), hydrochloric acid (37% by mass), ammonia (25% by mass), anhydrous ethanol, chloroauric acid (HAuCl₄), citric acid Sodium and sodium borohydride (NaBH₄), analytical grade, Beijing chemical plant.

JEM-100CX Transmission Electron Microscope (TEM), Japan J.EOL Corporation; S-4800 Field Emission Scanning Electron Microscope (SEM), Japan Hitachi Corporation; Equinox 55 Infrared Spectrometer (FTIR), Germany Bruker; Pyris Heavy Tester (TGA), Perkin-Elmer, USA; Zetasizer NanoZS Granularity and Zeta Potentiometers, Malvern Instruments, UK.

2.2 Janus materials and preparation

A solution of 0.5g of TEOS, 0.086g of APTES, 0.119g of MPS, 0.125g of a solution was prepared by dispersing 2.0g of polystyrene hollow microspheres in 40.0g of water and uniformly dispersing the seeds to obtain a seed emulsion; adjusting the pH to 3.0 with 2 mol/Emulsifier HSMA and 12.5g of water after mixing, high-speed shear emulsification 2min to get precursor emulsion. The precursor emulsion was added to the seed emulsion and heated to 70°C for 2 h at room temperature. The pH was adjusted to 11 with ammonia (1 mol/L) for 8h. The product was washed with ethanol/water to give organic/inorganic composite microspheres. The polystyrene in the organic/inorganic composite microspheres was removed by DMF to obtain Janus material (hollow ball or nanosheets).

2.3 Janus structure tag

The citrate-protected Au nanoparticles were prepared by reference. Add 5mL of 1% aqueous solution of chloroauric acid in 500mL water and 2mL of sodium citrate aqueous solution with 1% mass fraction, and stir for 10 min at room temperature. Add 0.75mL of NaBH₄ aqueous solution with 0.075% mass fraction, and stir for 2h. Citrate-protected Au nanoparticles were obtained with an average particle diameter of about 6 nm. The amount of Janus nanosheets was dispersed in water, and 1mL citrate-protected Au nanoparticles dispersion was added for 5 min and allowed to stand for 10 min. The granules were centrifuged and washed three times with water to obtain Au nanoparticles labeled Janus nanosheets. The same method is used to mark Janus hollow ball.

3. Results and discussion

3.1 Preparation of Janus hollow ball

The development of polymer particles has great influence on our economy and life. For example, polymer particles have increasingly become an important subject with desirable physical properties applied as coatings, light-sensing materials, bio-medicine, and so on. Since the morphology and size of particles is the key factors to determine potential applications of polymer particles, great interest has been focused on the morphology control of polymer particles. Various of morphological particles have been prepared. Amongst, Janus particles and multihollow polymer particles have received considerable attention over the last decade. Because its anisotropic surface chemical composition is compared with a homogeneous shape, Janus particles have some unique properties. However, due to the asymmetric feature in the particles, the preparation of Janus particles remains challenging for a long time. The final morphology is determined by the competition between thermodynamic and kinetic factors. Multihollow polymer particles have a unique advantage in a low density and high specific surface area. Because the formation mechanism of Janus and multihollow particles involves the interactions between thermodynamic and kinetic factors, the preparation and morphology control of Janus and multihollow polymer particles have great significance not only in enriching the theory in interface and colloid surface science, but also in expanding their practice application fields. This paper aims at the preparation of Janus and multihollow polymer particles with controllable morphologies from different emulsion systems (seed emulsion, miniemulsion, Pickering emulsion) based on the interface physical chemistry theory.

Janus material refers to the same particle on both sides with different chemical composition or nature, which is a typical composite material and has become a new material research hotspot. The most notable feature of the Janus material is the zoning of chemical composition/function. The currently reported Janus colloids are mostly spherical or rod colloid, and the different components of the division are in the outer surface of the colloid, with non-central symmetrical structure. We propose a new structure of the Janus colloid-Janus hollow sphere: the spherical shell of the inner and outer surfaces of the chemical composition of the different hollow sphere. Although these particles have a centrosymmetric structure, because of the inner and outer surface of the shell chemical composition of different asymmetry, this kind of hollow ball is called as Janus hollow ball. We carry out a series of studies around Janus hollow ball macro control, chemical composition and functional zoning control methodology, partition microstructure control, and material batch preparation and application. A new method for the synthesis of Janus hollow ball was developed, and a new idea was proposed to adjust the structure of the shell structure by adjusting the surface of the emulsion. The Janus hollow ball composition/functional partition and microstructure were precisely controlled and expanded. Janus hollow ball in oil and water separation, controllable release and other applications.

The silane coupling agents containing different groups can spontaneously orientate hydrophilic groups and lipophilic groups towards the aqueous phase and the oil phase when the sol-gel reaction occurs at the interface of the emulsion oil-water. The sol-gel reaction resulted in a different group of shells with a Janus structure. In addition, the sol-gel product after swelling of the silane coupling agent in polystyrene

microspheres is incompatible with polystyrene, and phase separation occurs on the surface of the seed microspheres to obtain composite microspheres with convex structure on the surface [25]. The silica-phase structure formed by the sol-gel is controlled by pH. Under acidic conditions, the hydrolysis rate of the precursor is greater than the condensation rate, so that the shell obtained by sol-gel is dense and smooth, with different functional groups on both sides. Under alkaline conditions, the condensation rate is greater than the hydrolysis rate, resulting in rough shell.

Polystyrene hollow microspheres have a diameter of 400 nm. When the pH of the reaction system is 4, the surface of the organic/inorganic composite microspheres is slightly rough. The granules of the polystyrene seed were removed by DMF, and the Janus hollow sphere was obtained by centrifugal separation. The shell was dense and continuous, and the inner and outer surfaces were smooth, whose thickness was 10 nm. When the pH of the reaction system is 11, the surface of the organic/inorganic composite microspheres becomes rough. The hollow shell thickness is still 10 nm, but it has become a porous structure. The outer surface is rough and the nanoparticles are tightly packed. The pH value of the reaction system was further increased to 12, and the morphology of the composite microspheres did not change significantly, and the porosity and porosity of the porous shell experienced a further increase. But at this time bath gel - gel reaction rate is too fast, there is freedom in the body phase. Thus, the pH of the reaction system is fixed at 11.

The composition of organic/inorganic composite microspheres was characterized by infrared spectroscopy. The characteristic peaks at 1632 cm⁻¹ corresponding to the C=C group at the end of MPS; the characteristic peaks at 1800, 1870 and 1940 cm⁻¹ corresponding to the doubling and frequency bands of hydrogen on the benzene ring; the absorption peaks at 756 cm⁻¹ corresponding to the polystyrene benzene ring hydrogen atoms on the surface deformation vibration peaks; 1087 and 1050 cm⁻¹ corresponding to the Si-O bond in the silica stretching vibration peaks. After removal of polystyrene by DMF, the characteristic peaks disappear; the characteristic peaks of silica and C=C and -NH₂ groups still exist.

Compared with the sol-gel reaction, the Zeta potential of polystyrene microspheres was shown to be -33 mV, and the Zeta potential of the composite microspheres after sol-gel reaction was 42 mV, indicating that a silica shell having an amino group on the outside was formed on the surface of the polystyrene microspheres.

To further characterize the different chemical groups on both sides of the inner and outer sides of the polystyrene hollow microspheres, we select the surface of the shell with a negatively charged citric acid-protected Au nanoparticles (6m in diameter) to label the surface amino group (-NH₂). The hollow ball was crushed with an ultrasonic cell shredder to obtain a response of the nanosheets. By SEM observation, it was found that the roughness on both sides of the nanosheets was different. The roughened side corresponds to the outer surface of the hollow sphere, and the smooth side corresponds to the inner surface of the hollow sphere. EDX element analysis showed that the system did not contain Au elements. When labeling with citric acid-protected Au nanoparticles, the negatively charged Au nanoparticles were selectively adsorbed on the roughened side of the nanosheets and the smooth side had no nanoparticles. The Au nanoparticles were adsorbed on the surface of the microspheres, and the EDX element analysis (Table 1) showed that the Janus hollow microspheres. There was an N element with a mass fraction of 3.62%. Au nanoparticles were adsorbed onto the Janus nanosheet with the -NH₂ group side, while the side without the -NH₂ group did not adsorb Au nanoparticles. It is proved that the prepared hollow spherical shell has a Janus structure.

Table 1: EDX Element Analysis of Janus Hollow Sphere after Being Labeled with Au Nanoparticles

Element	Si	O	C	N	Au
Mass fraction (%)	53.55	37.14	3.45	3.62	2.24

3.2 Preparation of Janus nanosheet

The results of previous studies show that the amount of monomer decreases; the degree of swelling of the seed ball decreases; the viscosity of the shell increases significantly; and the fusion of monomer or oligomer is seriously blocked. It provides a good confined space for the growth of nanoparticles. A single Janus particle provides a new idea. The results of thermogravimetric analysis showed that the silica content in the composite microspheres was linearly increased with the TEOS/seed mass ratio (Fig. 2).

The inner and outer surfaces of the shells of the hollow spheres were smooth by using the three kinds of silicon precursors under the condition of acid catalysis at room temperature, and the inorganic Janus hollow sphere was prepared by sol-gel at the emulsion interface. The temperature of the inner surface of the hollow sphere remains smooth. However, the inner surface becomes rough, and the outer surface of the hollow sphere is still smooth. The polymer/inorganic composite Janus nanosheets were obtained by mechanical grinding of the hollow spheres. The side of the nanosheets is an inorganic layer, which is relatively smooth; the other side is a polymer layer, which is relatively rough. The size of the nanosheets can be controlled by the strength and time of the grinding. In addition, the content of polymer and inorganic matter in the composite

Janus nanosheets and the thickness of the two layers can be controlled by the concentration of the reactants. The silicon precursor 3- (methacryloyloxy) propyltrimethoxysilane effectively connects the polymer layer and the inorganic layer together. The polymer/inorganic composite Janus nanosheets have amphiphilic properties and can be used as a granular emulsifier to obtain a stable emulsion system. The size of the emulsion droplets can be adjusted by the number of compound Janus nanosheets. In addition, simply changing the polymer content in the Janus nanosheets can effectively control structural stability and Janus equilibrium.

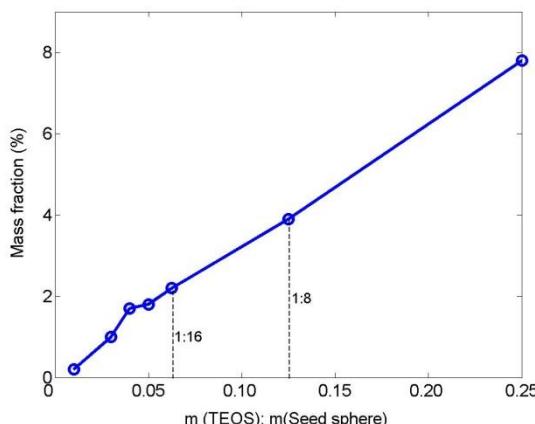


Figure 2: Dependence of Silica Content of the Composite Sphere on TEOS/Seed Sphere Ratio.

When the TEOS / seed mass ratio is reduced to 1/8, the porous structure of the Janus hollow spherical shell is more significant and the accumulation of nanoparticles becomes loose. As the mass ratio of TEOS / seed balls decreases further to 1/16, the shell of the Janus hollow sphere becomes incomplete and the discontinuous porous shell is broken into Janus nanosheets.

4. Conclusion

The microsphere shells were swollen with aminopropyltriethoxysilane, 3-(methacryloyloxy) propyltrimethylsilane and ethyl orthosilicate by using the polystyrene hollow microspheres as seed spheres. The organic/inorganic composite microspheres were prepared by sol - gel reaction control of inorganic phase separation and self-assembly. The lipophilic and hydrophilic groups of the silicon precursor were directed towards the polymer and the aqueous phase at the interface forms the Janus shell. Dissolve the seeds to remove the seeds, obtaining the Janus shell with amino and double bond located on the both sides. The Janus nanostructures can be controlled by adjusting the pH value and the number of precursors, and the Janus nanostructures can be controlled from the intact shell to the nanosheets. The Janus nanostructures have both amino and double bonds at the two ends in order to further functionalize the Janus nanomaterials, providing the basic conditions.

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