Recent Progress on Preparation of Amphiphilic Janus Particles

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Abstract. Janus comes from the Roman mythology of the double god. In his Nobel Prize acceptance speech in 1991, De Gennes first proposed the concept of Janus particles, which is used to describe two sides of the same particle having different chemical composition and/or morphological structure. Janus particle surfaces can have different hydrophilic and hydrophobic properties at the same time. Similar to traditional molecular surfactants, Janus particles can spontaneously adsorb onto the fluid interface, thus effectively stabilizing the multiphase system (emulsion or foam). Janus particles of various forms can be obtained according to different preparation processes. The organic polymer Janus particles mainly include spherical, disk, column and hollow shape. Due to the asymmetry of morphology and chemical composition of Janus particles, the conventional methods for preparing uniformly modified particles, such as suspension polymerization and emulsion polymerization, cannot be generally adopted. Over the past two decades, many methods for the preparation of Janus particles have been developed, including interface protection modification, phase separation and self-assembly of block copolymer.

1. Interface Protection Modification
The interfacial protection modification mainly includes selective protection and protection of modified particles for subsequent local surface modification, mainly including two-dimensional plane and three-dimensional emulsion template modification, namely two-dimensional plane protection modification and three-dimensional Pickering emulsion template modification [1-3].

1.1 Two dimensional conservation modification
The strategy to prepare Janus particles by this method is to spread the modified particles on the surface of the two-dimensional substrate. Due to the space arrangement, the lower side of the particle surface is protected, and the upper end of the exposed is modified, so that Janus particles can be easily prepared.

Ling et al. prepared Janus particles by embedding silica particles into PMMA substrates through PMMA cover and plasma etching and chemical modification on the surface of unprotected particles, as shown in Fig. 1 [4]. Lin et al. embedded one end of silica particles into a two-dimensional substrate, adsorbed gold nanoparticles to the surface of exposed silica particles through electrostatic action, and then removed the substrate to obtain the prepared Janus particles [5]. Cayre et al. obtained Janus particles by dispersing polystyrene microspheres on glass sheets and by modifying one side of them using a combination of polydimethylsiloxane moulding and reverse charge electrostatic action (microcontact printing) [6].
The drawback of the two-dimensional planar protection modification method is that the particle size of the particles to be modified is uniform, and the limitation of the single layer distribution on the surface of the two-dimensional substrate greatly limits the mass preparation of Janus particles. Compared with the two-dimensional planar protection modification, the Pickering emulsion template method can effectively overcome the above problems [7].

1.2 Pickering emulsion form method

By Pickering emulsion template of Janus particles prepared by modified particle dispersion strategy is to stay in oil/water interface, part of the particles in oil phase, the other part is in the water phase, when introduced in the oil phase and/or water phase reaction with granular material, in this phase of the surface of the particles will be modified, which were on both sides of the structure and/or chemical composition of different Janus particles [8]. Pickering emulsion template method, which is widely used in the preparation of Janus particles, has its unique advantages. Organic particles, inorganic particles and metal particles can all be used as modified particles. In addition, the Pickering emulsion template method can provide large interfacial reaction space in the process of preparing Janus particles, which is beneficial to increase the yield of Janus particles [9].

D. Suzuki and others using the precipitation polymerization of block copolymer microgels in hexadecane/water boundary surface adsorption and Pickering emulsion system was prepared, then hydrophilic ethylenediamine to join Pickering emulsion system, exposing the amino grafting microgel in the water phase, reaction by elevating temperature again after the release of the modified particles, amino, end up with a side to the other side of carboxyl of Janus particles [10]. But during this process, the rotation of particles at the oil/water interface affects the formation of Janus particles. Therefore, Hong et al. used solidified paraffin to solidify modified particles to avoid their rotation at the interface, and then prepared amphiphilic Janus particles through paraffin/water Pickering emulsion system [11]. The silicon dioxide particles were added to the mixture of paraffin and water to prepare the Pickering emulsion, which was then cooled to solidify the paraffin. The silane coupling agent is dissolved in water to react with the surface of silica particles exposed to paraffin. Although the method is simple, it has some limitations in the subsequent modification process, which needs to maintain the appropriate temperature and select the appropriate solvent. The advantages of using paraffin as oil phase in Pickering emulsion template method are as follows [12,13]: During the modification process, the rotation of particles on the interface is the biggest problem in Pickering emulsion template method; The solidified paraffin can effectively protect part of the surface of the particles covered in paraffin, and the subsequent modification reaction has little interference to it, so that the exposed particle surface can be fully modified; uring paraffin is easily removed by solvent or ultrasound.
2. Phase Separation Process

Phase separation method of preparation of Janus particles is incompatible or part of a compatible system of two or more in some kind of driving force under the condition of phase separation, with normally with core-shell inorganic nanoparticles as precursor, inorganic particles with core-shell structure generally consists of two phase system, through the chemical reaction or physical change that one phase concentration or growth so as to realize the separation of particles Janus particles is obtained [14].

Tanaka et al. dissolved the incompatible PMMA and polystyrene (PS) in toluene, dispersed the toluene drops in the surfactant aqueous solution, emulsified and evaporated solvent, and separated the PMMA and PS, thus producing the snow humanoid Janus particles [15]. Phase separation is a competitive process, which is combined by thermal drive and dynamic drive. By adjusting the content of sodium dodecyl sulfonate, the balance between dynamic drive and thermal drive can be changed, thus producing Janus particles with different shapes, such as concave and acorn. Mulvaney et al. made use of SiO$_2$/Ag nanoparticles with nucleo-shell structure as precursors, and generated AgI through the chemical reaction between SiO$_2$ in the shell and Ag in the core [16]. As the reaction went on, the generated AgI continuously enriched on the shell surface of particles, and eventually formed SiO$_2$/AgI Janus materials in the shape of snowman. Gu and others will iron nanoparticles dispersion of platinum alloy, then amorphous cadmium sulfide under the condition of heat dispersion in iron platinum nanoparticles surface form a layer of transparent uniform film, forming a core-shell structure, because the two substances in the solvent with incompatible lattice, recrystallization occurs when phase separation into a snowman Janus particles, as shown in Fig. 2, the granules have paramagnetism and fluorescence at the same time [17].

![Fig. 2 One-pot prepare snowlike CdS-FePt Janus particles](image)

Although Janus particle size of the preparation of phase separation is larger, phase separation can use a variety of complex microstructure is incompatible in the preparation of complex structure of Janus particles, for example in the field of some complex targeted drugs, the respect such as catalysis, electromagnetism has broad application prospects [18].

3. Self-assembly of Block Copolymers

A block copolymer is a copolymer that consists of two or more repeating units, each of which forms a long sequence chain segment and is covalently linked to each other. The molecular structure of the block copolymer which can self-assemble into highly ordered microphase structure is usually highly ordered [19]. The block copolymer can be self-assembled or dissolved in different solvents to the molecular level. The selective solvent can be used to form micelle microstructure, which forms the nucleus from the less water-soluble part of the block copolymer, and the shell around the nucleus is formed by highly swollen and water-soluble blocks [20]. Micelle of different shapes can be formed according to the degree of shell swelling and the proportion of block copolymer. The self-assembly method of block copolymer is diversified, and the size, shape and composition of Janus particles can be designed in advance, and the preparation conditions are mild and easy to control. This method has a
relatively solid theoretical foundation and the potential of mass preparation, so it has attracted more and more attention and in-depth research from more and more scholars. Self-assembly of block copolymer mainly includes self-assembly, interface self-assembly and solution self-assembly.

4. Conclusion

Other methods of preparing Janus granules have been reported in recent years. Isojima et al. prepared magnetic Janus particles sensitive to pH and temperature by using the electrostatic interaction between particles with different charges to protect the hemispherical surface of particles [21]. Ahmad et al. used poly (n-isopropyl acrylamide) temperature-sensitive microgel to shrink above the phase transition temperature and gather on the hemisphere of the water-borne liquid droplet formed by the microfluidic device, and then made the hydrophilic monomer (acrylamide) on the other half of the sphere to polymerize, to get the temperature-sensitive Janus microgel [22]. Cheng et al. used inorganic nanotubes adsorbed by hydrophilic-hydrophobic diblock polymers as asymmetric tools to prepare amphiphilic polymer Janus particles in one step, which could form monodisperse supermicelles by self-assembly and build Janus particles based on amphiphilic triblock polymers [23,24]. Janus particles formed by microphase separation in the micellar formed by block polymers can be self-assembled into tubular superstructure and nano-sheet structure. Lu et al. prepared amphiphilic organic-inorganic hybrid Janus particles in one step by means of phase separation and ultrasound-induced polymerization in the droplet microreactor formed by microemulsion [25]. However, due to the harsh preparation conditions and high cost, these methods are difficult to make large-scale preparation, and the Janus particle size distribution is wide.

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