

## Preparation of Janus colloidal particles via Pickering emulsion: An overview

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### HIGHLIGHTS

- ▶ Janus colloidal particles (JCPs) have catchy asymmetric morphological structures.
- ▶ All preparation methods of JCPs are mainly based on phase separation strategy.
- ▶ Pickering emulsion (PE) is promising efficient technique for preparation of JCPs.
- ▶ PE consists of stabilized liquid phases by solid particles at their interfaces.
- ▶ Morphology, size and functionality of JCPs can be easily controlled by using PE.

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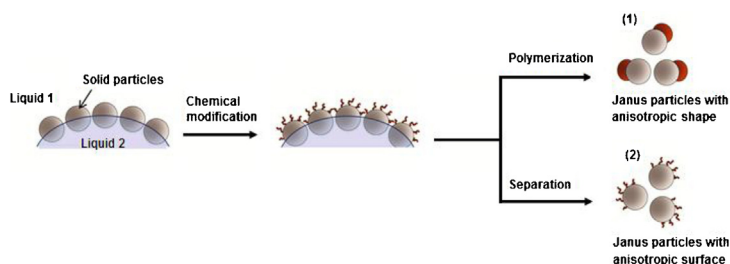
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### GRAPHICAL ABSTRACT

Preparation of Janus colloidal particles using Pickering emulsion method.



### ABSTRACT

Janus colloidal particles (JCPs), compartmentalized colloids with two sides of different chemistry or polarity, have attracted significant attention in recent years due to their novel morphologies and diverse potential applications in materials science, biomedicine and in the field of highly specific biosensors. Due to these fascinating features, the synthesis of Janus particles remains a big challenge. However, major progress concerning their preparation in useful amounts has been achieved in recent years. Among the used synthetic approaches, Pickering emulsion, bearing solid nanoparticles at the interface between two liquid phases as the stabilizing agent, is one of the elegant methods used for the synthesis of Janus colloidal particles with controllable morphology in a wide range of size and surface functionality. A monolayer of organic and inorganic nanoparticles can stabilize an emulsion droplet only when their hemispherical surface is chemically modified, while the remaining surface is protected. This approach offers the possibility to alter the surface of nanoparticles with a variety of functional groups which lead to Janus particles with complex structure.

In this review article, we represent an overview on the state of the art for producing Janus colloidal particles based on Pickering emulsion strategy. The pioneer and recent respective works of Janus colloidal particles with anisotropic in surface and/or in structure were also described.

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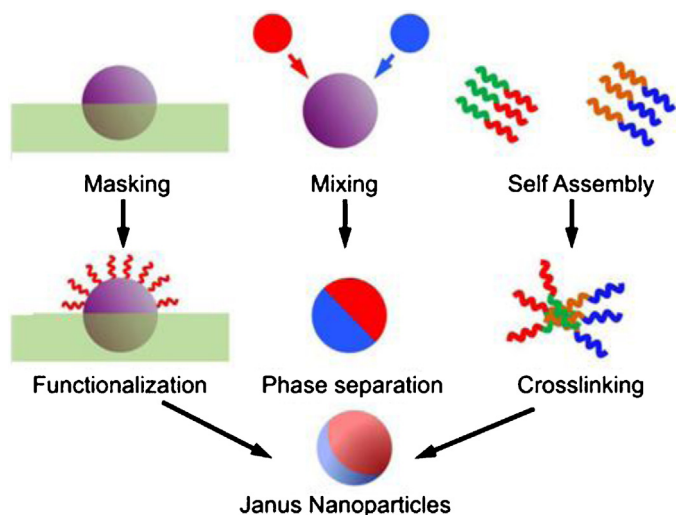
## 1. Introduction

Colloidal particles have attracted considerable attention in life science as solid supports of biomolecules for cell separation [1], as contrast agents in detection tools for in vivo biomedical diagnostic [2], as support for sample preparation of nucleic acids extraction [3], and as nanocapsules for active biomolecules in drug

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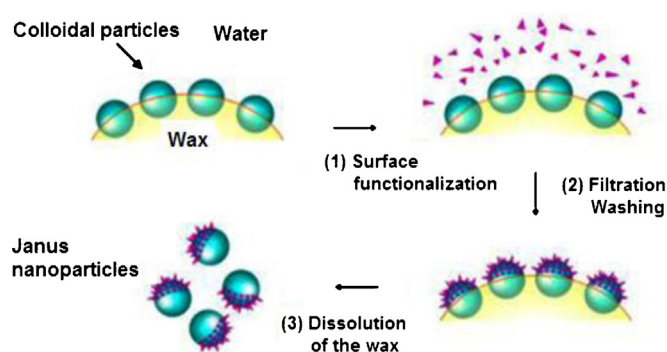


**Fig. 1.** Schematic diagram illustrating the three main strategies for the preparation of Janus nanoparticles: masking, phase separation and self-assembly. Reproduced with permission [6]. Copyright 2011, Elsevier.

delivery systems [4]. Nowadays, various particle morphologies can be prepared using well defined processes and chemistry. Recently, colloidal particles with anisotropic shape and/or surface properties (Janus colloidal particles, JCPs) have attracted significant attention due to their novel morphologies and diverse potential applications in various domains including materials science, biomedicine and in the field of highly specific biosensors. The name “Janus” derived from the double-face Roman God “Janus” was launched on these particles which have two sides of different chemistry or polarity [5–7]. The fascinating properties of JCPs, derived from their asymmetric structure, allow for their controlled self-assembly and surface activity. As a result of the simultaneous presence of two different regions in JCPs, which can be designed to have different hydrophobicity and thereby mimic the behavior of surfactants, they can form stable clusters with defined size, and substantially reduce the interfacial tension between two different phases. Additionally, JCPs can bring together different materials in a segregated manner at the nanoscale, thus combining widely different properties in a single entity, as in the case of heterodimers [6,8–12]. Furthermore, Janus nanocomposites with spatially separated functionalities, uniform size, tunable composition, and efficient stimuli-responsive features are highly needed in various potential applications, e.g. catalysis, biosensing, and drug delivery [13–17]. However, the rapid development in the applications of JCPs requires sophisticated controls over their inherent properties, which usually rely on the composition, size and shape of the particles, as well as their appropriate surface modification. Due to these fascinating features, the synthesis of Janus particles is still a major challenge which requires ingenious strategies [6].

Recently, major progress concerning their preparation has been achieved. Generally, two important issues need to be addressed to develop anisotropic colloids particles of less than one micrometer in dimension via bulk approach. The first one is the ability to control the geometry with fine control over the particle surface potential and surface chemistry. The other is the ability to produce Janus particles in large quantities, which will be necessary for technological applications. In this regard, there are three main strategies for the preparation of Janus nanoparticles (Fig. 1) including masking, phase separation and self-assembly using various techniques such as microfluidic systems, surface modification, Pickering emulsion, etc [6].

Although the microfluidic methods based on phase separation strategy can be scaled-up to produce large amount of Janus



**Fig. 2.** Schematic representation of the step-by-step fabrication of Janus colloidal particles through Pickering emulsion process. Reproduced with permission [30]. Copyright 2009, Elsevier.

particles in a continuous fashion [18–21], the resultant particles are typically rather large due to the relatively large size of fluidic channels. Thus, the main problem is that the size of these colloidal particles ranges from one to hundreds of micrometers. The toposelective surface modification (immobilization) method is the most intuitive route to elaborate site-specific functionalized Janus particles [22–25]. Based on this technique, a part of the homogeneous colloidal particles is masked (shielded) and the other unshielded part is modified with chemical or physical agents providing Janus particles with anisotropic in surface as well as in bulk properties. The immobilization process has been typically achieved by trapping the nanoparticles at the interface between two liquid phases, or on a solid surface which is the most feasible process [26,27]. This approach is virtually applicable to any type of material, and offers the possibility to modify the surface of nanoparticles with a wide variety of functional groups. Although the functionalization of nanoparticles deposited on flat solid substrates offers the broadest range of functionalization groups, only a few milligrams of particles are produced in one batch. In addition, the use of nanoparticles trapped on liquid droplets to provide the surfaces functionalization is a viable alternative to obtain controllable geometry and scalable in gram-sized quantities of Janus colloidal nanoparticles [28–30]. The process used for synthesis of Janus colloidal particles by partial shielding of the homogeneous nanoparticles between liquid/liquid interfaces and then chemically modifying these particles in an aqueous phase is so called Pickering emulsion method. Recently, this method is considered as one of the elegant ways to prepare Janus colloidal particles with controllable geometry in a wide range of size, functionality and in gram-sized quantities, as can be seen from the various recently published reviews and research articles [6,31–33].

Thus, this review profoundly focuses on state of the art for fabrication of Janus colloidal particles through the Pickering emulsion strategy, including theoretical behavior of the colloidal particles, commonly explored roots, pioneering works and the recent published articles on Janus colloidal particles. The fabrication of Janus colloidal particles through the Pickering emulsion route is schematically represented in Fig. 2.

## 2. Pickering emulsion

In the classic solid particles-stabilized emulsion, typically referred to as Pickering emulsion, particles accumulate at the interface between two immiscible liquids and stabilize the droplets against coalescence by forming a mechanically robust monolayer at the two liquids interface (Fig. 3A) [34–37]. The supracolloidal structures obtained by Pickering stabilization are also called colloidosomes. The solid particles can be organic, e.g., polymer latex,

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