

· 综述(明日之星专栏) ·

## 乳液聚合制备 Janus 颗粒研究进展

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**摘要** Janus 颗粒因其独特的表面分区结构, 在多相多组分复合体系界面调控和功能化方面展现出重要作用. 然而, Janus 颗粒结构相对复杂, 其微结构精确调控和批量化制备一直是限制其更多应用探索的瓶颈问题. 本综述从 Janus 颗粒结构构筑原理出发, 简述了 Janus 颗粒制备技术的重要发展历程, 重点介绍了乳液聚合方法在 Janus 颗粒制备方面优势, 并从传统乳液聚合、种子乳液聚合、Pickering 乳液聚合和乳液界面聚合四个方面总结了乳液聚合制备 Janus 颗粒的最新研究进展. 传统乳液聚合方面主要介绍了一步构筑 Janus 乳液的体系特点, 以及介绍了种子乳液聚合的原理、Pickering 乳液聚合的发展和乳液界面聚合中调控 Janus 颗粒形貌和结构的影响因素, 最后探讨了 Janus 颗粒制备技术的未来发展方向.

**关键词** Janus 颗粒, 乳液聚合, 种子乳液, Pickering 乳液, 界面

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与普通颗粒相比, Janus 颗粒因表面分区集成了两种及以上的化学组分和功能而具有更加复杂的结构, 其可控制备更具挑战. 通过简便、经济、高效的易于工业化方法实现 Janus 颗粒的精确可控合成, 是探索并实现 Janus 颗粒广泛应用的关键和前提. 早在 1989 年, Casagrande 等人就通过将玻璃微球浸没在二维平面中对裸露的部分进行改性, 制备了两亲性微球<sup>[1]</sup>. 1991 年诺贝尔物理学奖得主, 法国科学家 Pierre-Gilles de Gennes, 在以“Soft Matter”为题的诺贝尔奖报告中, 介绍了“Janus 颗粒”这一概念, 并指出了其在界面稳定调控方面的应用潜力, 引发了 Janus 材料研究的热潮<sup>[2]</sup>. Janus 颗粒因化学组成和形貌的各向异性, 在复合体系表界面的稳定和功能化方面具有显著优势, 在 Pickering 乳液稳定<sup>[3–5]</sup>、非均相催化<sup>[6–8]</sup>、共混增容<sup>[9–11]</sup>、填料分散<sup>[12]</sup>、功能涂层<sup>[13,14]</sup>和自组装<sup>[15]</sup>等领域展现了独特作用. 例

如: 磁响应性 Janus 颗粒作为可回收的固体乳化剂, 实现了油水分离和污染物降解过程的协同作用<sup>[16]</sup>; 微量的 Janus 片添加即可良好促进共混聚合物界面增容, 在增韧复合材料的同时大幅提高气体阻隔性能<sup>[17]</sup>; 又如, 将软硬复合 Janus 颗粒引入柔性涂层中, 可构筑刚柔并济的网络, Janus 颗粒作为分散剂诱导导电填料分层, 实现了高灵敏性功能自分层涂层构筑<sup>[18]</sup>; 在口腔医学方面, 相较于常规牙敏感治疗手段, 草莓半球形 Janus 颗粒加速了牙本质小管的封闭, 为牙本质超敏反应治疗提供了新的治疗方案<sup>[19]</sup>.

过去的三十多年中, 研究人员相继开发了嵌段共聚物自组装<sup>[20]</sup>、种子乳液聚合<sup>[21]</sup>、微流控<sup>[22,23]</sup>、Pickering 乳液界面保护法<sup>[24]</sup>和界面诱导相分离<sup>[25]</sup>等方法来制备 Janus 颗粒, 不断推动着 Janus 颗粒合成方法学和技术的发展(图 1). 对 Janus 颗粒的结构设计和化学合成, 需综合考虑

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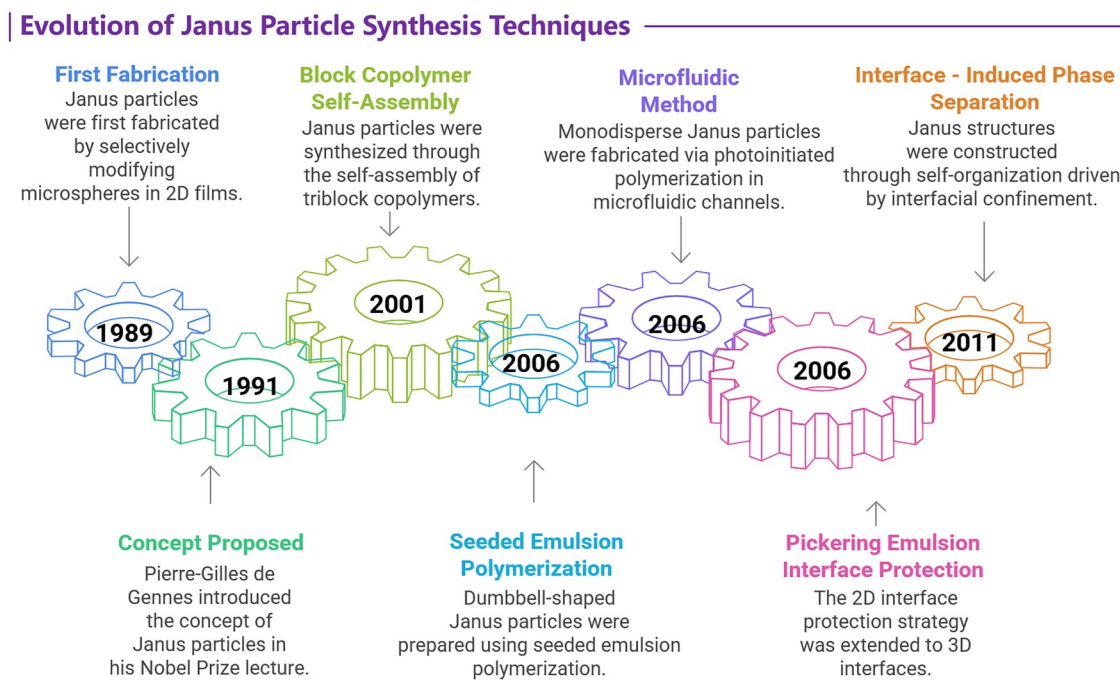


Fig. 1 Development history of Janus particle synthesis methods.

制备技术难易程度,是现代科学研究的重要前沿领域.作为交叉学科研究的典型,Janus颗粒合成对催化剂设计,智能材料开发和生命医学系统学习都有重要意义<sup>[26,27]</sup>.同时,在推动材料科学、能源化工及生物学工程技术的融合与创新等方面展现出广阔的应用前景.

其中,种子乳液聚合和界面诱导相分离策略基于乳液聚合技术,是制备Janus颗粒的重要方法,更具工业化潜力.在本综述中,我们总结了Janus颗粒合成方法学的发展过程和最新进展,重点介绍和讨论基于乳液聚合制备Janus颗粒方法,总结Janus颗粒合成进展及存在的挑战,并展望未来发展.

## 1 乳液聚合法合成Janus颗粒

乳液聚合作为一种制备高分子胶体颗粒的常用水性聚合技术,利用表面活性剂将不溶于水的单体分散为小液滴并稳定形成乳液,在引发剂的作用下进行自由基聚合<sup>[28]</sup>.由于聚合反应在水介质中进行,具有良好的散热效率和聚合效率,能够可控合成不同分子量和粒径的胶体颗粒<sup>[29,30]</sup>.同时,是一种低成本和环境友好型的生产技术,广泛应用于各种高分子材料的制备中<sup>[31]</sup>.

乳液聚合构筑非对称Janus结构的核心原理在于对新相形成和两相相分离过程的调控.在乳

液中引入两种或多种单体的组合,引发聚合诱导相分离,就能够制备具备组成分区特征的Janus颗粒<sup>[32,33]</sup>.相分离是否完全,决定了Janus颗粒是否具备明显界面分隔,也进一步影响其表面的功能.决定相分离程度的主要参数包括两种聚合物的不相容性(用Flory-Huggins相互作用参数 $\chi$ 表示)、相对于两种聚合物的溶剂质量和两种聚合物的聚合度差异等.其中,聚合物相互作用参数是评估两相组分是否有足够高的界面能来抵抗融合,相互作用参数越小,代表两相相容性越好,因此相分离越不容易发生<sup>[32,34]</sup>.此外,当某一相存在温度或pH响应单元时,通过温度来调节分子链的舒展状态,改变体系pH值控制质子化和去质子化过程就可以实现颗粒形貌调控,获得温度、pH响应性的功能Janus颗粒<sup>[35-37]</sup>.研究表明,乳液体系的配方调控和聚合工艺控制是调控Janus颗粒结构的两个重要途径<sup>[38,39]</sup>.

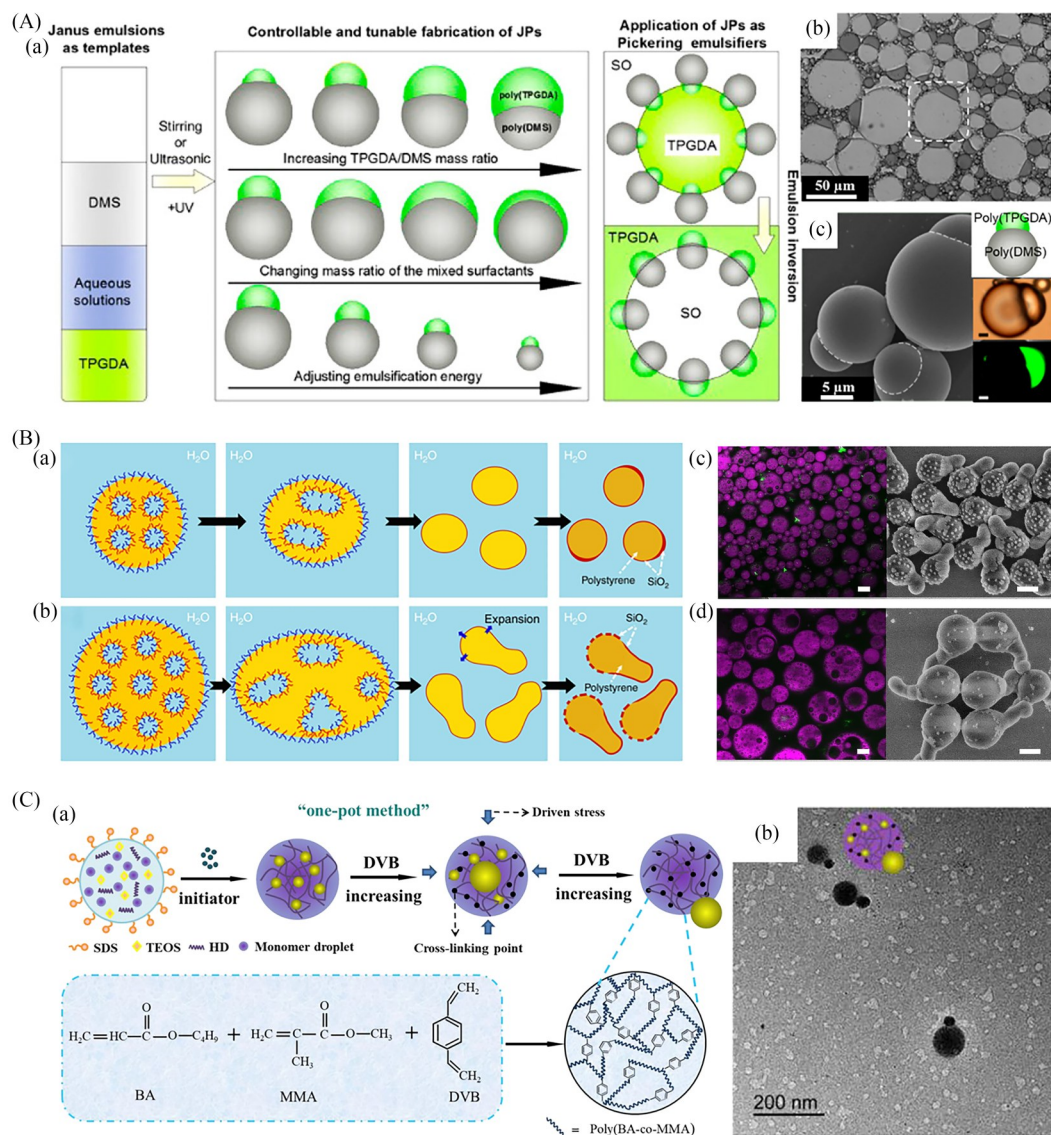
因此,乳液聚合为制备Janus颗粒提供了一种经济、高效、易于工业化的方法.具体而言,用于制备Janus颗粒的乳液聚合方法可分为以下几种:Janus乳液聚合、Pickering乳液合、种子乳液聚合和乳液界面聚合,本文将进一步展开介绍.

### 1.1 Janus乳液聚合

当选取两种及以上单体作为乳液分散相,通过单体相容性和聚合诱导相分离过程控制,能够

实现一步聚合直接获得具有相分离结构的 Janus 颗粒. Guo 和 Ge 等<sup>[40,41]</sup>通过设计 Janus 结构乳液体系, 制备了多种不同组成和结构的 Janus 颗粒. 以二缩三丙二醇二丙烯酸酯(TPGDA)和甲基丙烯酰氧基丙基二甲基甲氧基硅烷(DMS)两种可聚合单体作为油相, 以含表面活性剂的水溶液作为水相, 超声乳化形成分散相油相为 Janus 结构的乳

液, 进一步通过紫外引发聚合获得了聚 TPGDA/DMS Janus 颗粒. 单体比例、表面活性剂用量和乳化方式等因素均可调控 Janus 颗粒的形貌和分区, 实现了由雪人到哑铃型 Janus 颗粒形貌的精确控制(图 2(A)). Möller 等<sup>[42]</sup>将聚硅酸四乙酯 (PEOS)用作稳定 W/O/W 双乳液的内部和外部油水界面的活性分子, 制备纳米级的双微乳液, 通



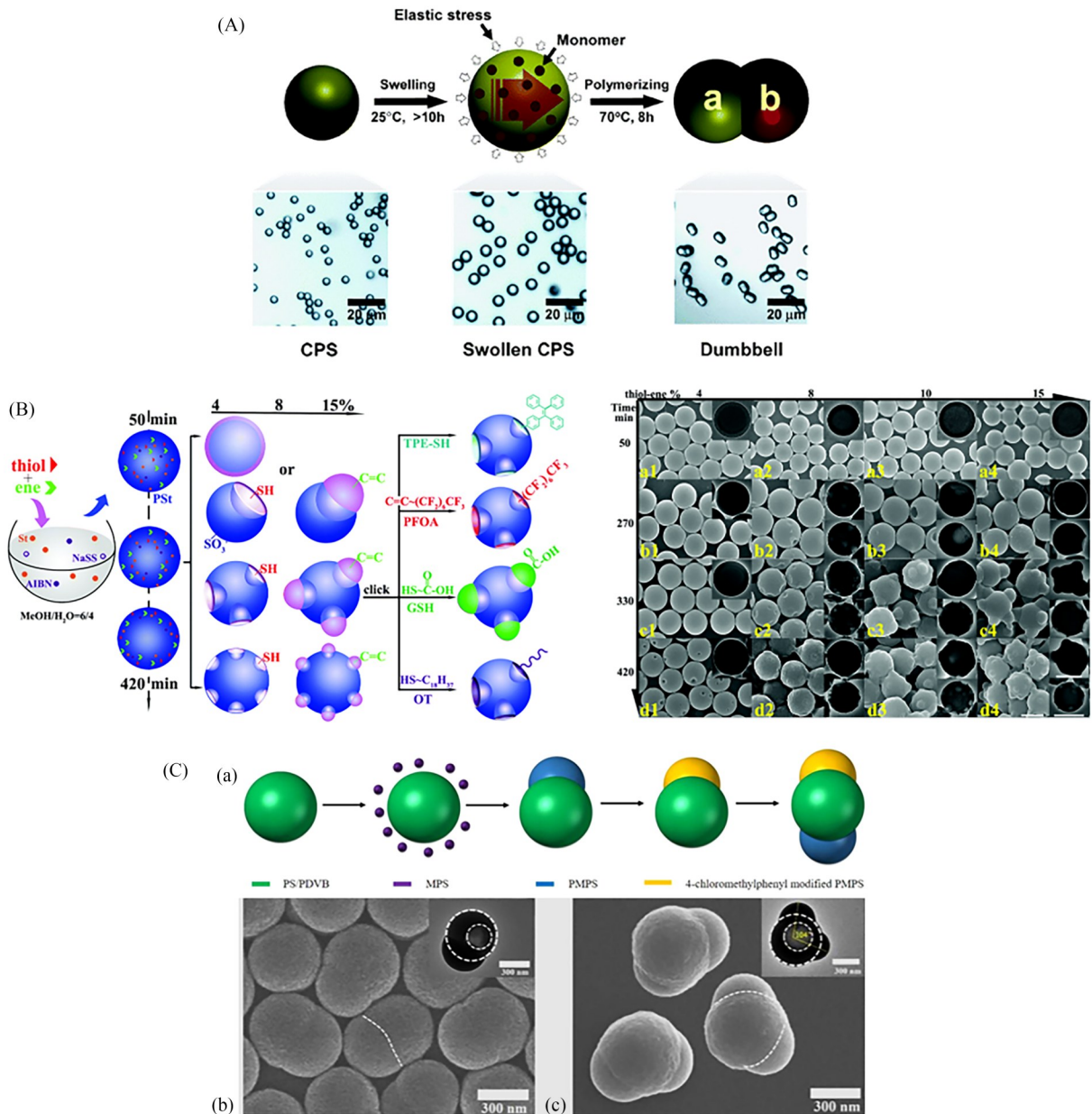
**Fig. 2** (A) Schematic synthesis of anisotropic Janus particle (a), micrographs of Janus emulsion droplets (b) and SEM images of the resultant particles (c). (Reproduced with permission from Ref.[40]; Copyright (2017) American Chemical Society). (B) Oval-shaped polystyrene@SiO<sub>2</sub> particles are formed from relatively small emulsion droplets that cannot be deformed significantly by magnetic stirring (a). Relatively big emulsion droplets that are largely elongated by magnetic stirring are fragmented into anisotropic particles, and the recovery of the liquid core to a spherical shape induces the breakage of the already formed silica shell (b). Multiple emulsions are prepared using a rotor-stator homogenizer operated at 9000 and 4000 r/min, respectively (c, d). The left shows fluorescence micrograph (scale bars=10 μm) of the emulsion and the right displays the FESEM image of the particles (scale bars=200 nm). (Reproduced with permission from Ref.[42]; Copyright (2018) Springer Nature). (C) Synthetic mechanism (a) and TEM image (b) of Janus C-PA/SiO<sub>2</sub> CLPs. (Reproduced with permission from Ref.[43]; Copyright (2022) Wiley).

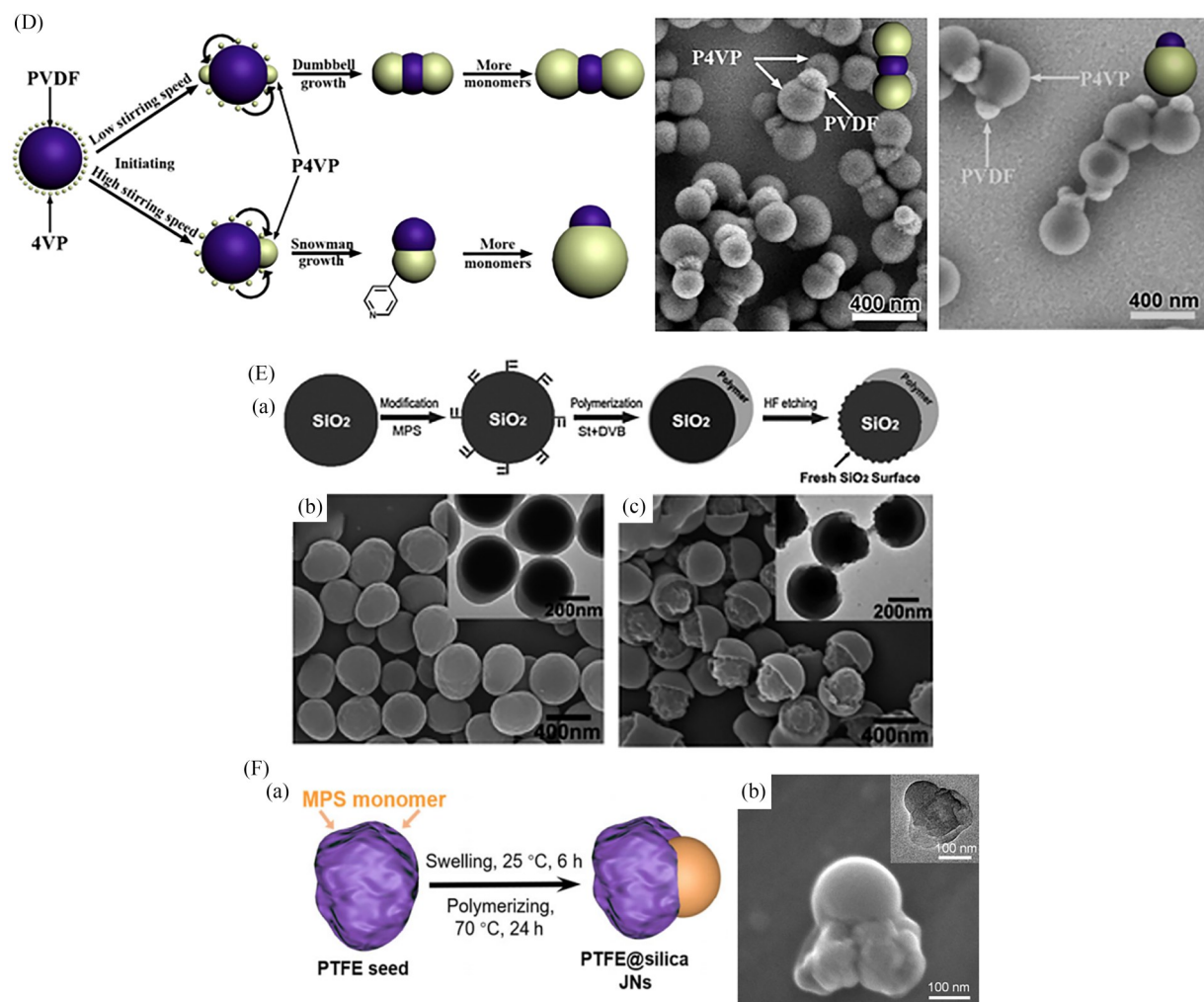
过油相的聚合和 PTEOS 的转化获得具有蘑菇形态的 Janus 纳米颗粒(图 2(B)). Ma 和 Gao 等<sup>[43]</sup>报导了由乳液聚合法一步获得聚丙烯酸酯/二氧化硅 Janus 复合胶乳粒子(图 2(C)).

## 1.2 种子乳液聚合

种子乳液聚合是利用预先形成的乳胶颗粒(种子)作为模板, 通过控制单体扩散和聚合过程, 实现对聚合物颗粒的尺寸、形貌、组成及微结构的精准调控. 该方法目前常用于制备具有核壳、雪人和 patchy 形貌等复杂结构的聚合物-聚合物或聚合物-无机颗粒<sup>[44]</sup>. 与常规乳液聚合方法相比, 其优点在于分步聚合能够更精准地调控颗粒结构, 且尺寸更均一. 2006 年, Weitz 等<sup>[21]</sup>首

次提出了以(聚苯乙烯)PS 颗粒作为种子, 通过种子乳液聚合制备了 PS/PMMA、PS/(聚乙炔亚胺)PEI 等一系列哑铃型 Janus 颗粒(图 3(A)). 反应性单体对交联聚合物种子的溶胀过程和聚合过程, 可以有效诱导相分离, 获得具有分区结构的聚合物-聚合物 Janus 颗粒. 基于上述种子乳液聚合机制, 研究人员进一步探究了多种形态和组成的各向异性聚合物-聚合物 Janus 颗粒结构. Yang 和 Liu 等<sup>[45]</sup>将间歇生长硫代烯聚合与苯乙烯(St)的链生长聚合相结合, 因为硫代烯聚合物和聚苯乙烯链结构和亲水性方面的差异, 复合颗粒中的硫代烯聚合物和聚苯乙烯发生了相分离, 形成了核壳结构和凹陷或凸起结构, 制备出具有坚硬主体和柔





**Fig. 3** (A) Scheme for synthesis of anisotropic nonspherical dumbbell particles by using the seeded polymerization technique. Bright-field microscope (BFM) images exemplify the synthesis of PS/PBMA dumbbell particles. (Reproduced with permission from Ref.[21]; Copyright (2006) American Chemical Society). (B) One-pot synthesis of the clickable core-shell, dimple- or bulge-patched particles by thiol-ene click reaction concurrent with the polymerization of St in a dispersion system (a), SEM and TEM images (the upper right inserts) of particles produced when various amounts of TMPMP/TTT were added after different time, scale bars are 500 nm (b). (Reproduced with permission from Ref.[45]; Copyright (2017) The Royal Society of Chemistry). (C) Illustrative synthesis of the triblock Janus particle by seeded emulsion polymerization (a), SEM and inset TEM images of (b) the Janus particle by seeded emulsion polymerization against the as-synthesized PS/PDVB-silica Janus particle, (c) the triblock Janus particle against the 4-chloromethylphenyl modified PS/PDVB-silica Janus particle. (Reproduced with permission from Ref.[48]; Copyright (2019) American Chemical Society). (D) Schematic of preparing process of PVDF/PS Janus particles (a), SEM micrograph of PVDF seed particles and PVDF/PS composite particles (b, c). (Reproduced with permission from Ref.[49]; Copyright (2015) American Chemical Society). (E) Schematic synthesis of Janus colloids by wet etching the anisotropic composite colloids formed by polymerization induced dewetting (a), before (b) and after (c) etching the anisotropic composite colloids. (Reproduced with permission from Ref.[50]; (2010) The Royal Society of Chemistry). (F) Schematic of preparing process of PTFE@silica JNs (a), SEM and TEM images of PTFE@silica JNs (b). (Reproduced with permission from Ref.[51]; Copyright (2024) Springer Nature).

软、可点击的凹陷或凸起斑块状微粒(图3(B)). 这种方法的优势在于可以一锅制备单分散、稳定、具有反应活性的Janus颗粒.

种子乳液聚合制备Janus颗粒方法具有普适性, 除上述聚合物-聚合物Janus颗粒, 还能够用

于制备聚合物-无机复合Janus颗粒. 常见聚合物颗粒如聚苯乙烯、聚丙烯腈、丁苯胶乳、苯丙胶乳等均能作为种子, 通过硅烷偶联剂溶胀后并进一步聚合诱导相分离, 制备有机-无机复合的Janus颗粒. 我们以中空的聚苯乙烯颗粒作为种

子, 采用种子乳液聚合技术, 使用 3-(甲基丙烯酰氧)丙基三甲氧基硅烷作为活性单体对聚苯乙烯进行溶胀, 添加引发剂引发聚合, 通过 pH 和单体用量调节在种子表面形成一个或多个凸起, 然后溶解 PS 得到 Janus 颗粒, 实现了从亚微米级到纳米级连续可调的 Janus 颗粒制备<sup>[46]</sup>. 当构成 Janus 颗粒的种子相和新相相容性较差时, 线性颗粒作为种子也能够制备形貌均匀的 Janus 颗粒, 但交联的聚合物种子赋予 Janus 颗粒更好的耐溶剂性<sup>[47]</sup>. 同时, 种子颗粒本身的微结构也是调控 Janus 颗粒新相生成的有效方法. 例如, 我们利用种子乳液聚合技术首先制备具有不同偏心结构的中空种子微球, 能够在聚合物种子表面依次生长两个不同的氧化硅凸起<sup>[48]</sup>. 根据偏心度变化, 两个氧化硅凸起轴线之间的角度可在  $0^{\circ}$ ~ $180^{\circ}$  范围内调控. 三嵌段 Janus 粒子的两个氧化硅凸起和 PS/PDVB 区域可以选择性地进行分别改性, Janus 颗粒的形貌和组分都得到进一步丰富(图 3(C)). 同时, 一个有趣的发现是第一个氧化硅凸起的表面疏水改性决定了第二个氧化硅凸起的生长位置.

除了上述种子溶胀聚合诱导相分离方法制备 Janus 颗粒, 不易被溶胀的半结晶性聚合物胶体, 甚至无机颗粒也能够作为种子, 通过种子乳液聚合制备 Janus 颗粒. Pan 等<sup>[49]</sup>选择聚偏二氟乙烯(PVDF)颗粒作为种子, 苯乙烯(St)作为单体, 通过无皂种子乳液聚合, 在 PVDF 种子颗粒表面引发单电子转移自由基聚合(SET-RP)制备了具有可控形貌的不对称聚偏二氟乙烯/聚苯乙烯(PVDF/PS)复合胶乳颗粒. 这种复合胶乳颗粒的形貌可以通过 St/PVDF 投料比、反应温度和催化剂铜丝的长度等因素调控, 提出了 PVDF 种子和 PS 凸起组分不相容介导的表面成核机制(图 3(D)). Yang 等<sup>[50]</sup>用硅烷偶联剂修饰直径约 400 nm 的单分散二氧化硅胶体, 在其表面引入乙烯基. 添加苯乙烯和二乙烯基苯在颗粒表面聚合后, 刻蚀复合胶体上的弱有机薄层露出新鲜的二氧化硅表面, 得到了  $\text{SiO}_2$ -PS 复合 Janus 胶体(图 3(E)). 近期, 我们以 PTFE 纳米颗粒作为种子, 通过硅烷前驱体在种子颗粒表面吸附并进一步聚合, 制备了 PTFE@Silica Janus 颗粒(图 3(F)). 该 Janus 颗粒具有优异润滑性, 以其作为水基润滑添加剂, 摩擦系数(COF)和磨损体积分别降低了 63.8% 和

94.2%<sup>[51]</sup>.

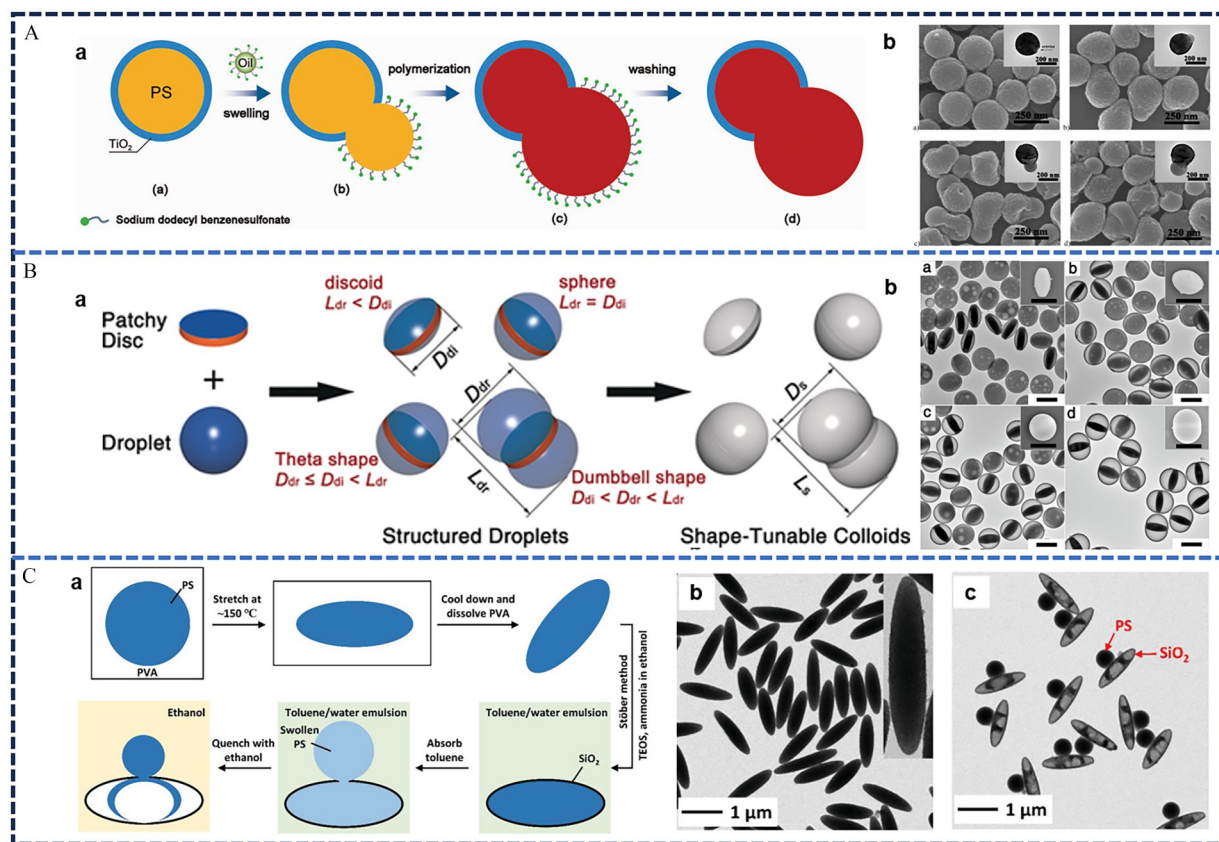
在可反应单体溶胀种子及聚合成核过程中, 通过对种子和单体的比例进行精确控制, 可以实现 Janus 颗粒不同分区比例调控. 对于易溶胀的聚合物胶体颗粒, 单体可以进入聚合物网络内部导致种子溶胀, 然后通过光或热引发聚合, 聚合物与种子相容性差异驱动相分离, 最终形成非对称的 Janus 结构. 对于结晶性或无机种子颗粒, 吸附在种子表面的反应单体随着反应进行在种子颗粒表面逐渐成核最终形成 Janus 颗粒.

通过种子乳液聚合法, 可以制备尺寸均匀、形状多样、微结构可调的 Janus 颗粒. 以核壳结构的颗粒作为种子, 也是获得 Janus 颗粒的有效方法. 该方法通过破坏核壳种子颗粒的对称性或形成新相来构筑 Janus 结构. 如图 4 所示, 以  $\text{PS}@TiO_2$  核壳颗粒作为种子, 以甲苯为油相的水包油乳液溶胀种子, 由于甲苯乳液对 PS 内核的溶胀, PS 向外膨胀产生渗透压破坏  $TiO_2$  壳层, 形成凸起, 获得了可控形态的雪人状 Janus 颗粒<sup>[52]</sup>(图 4(A)). 进一步引入交联剂 DVB, 可以增加颗粒的耐溶剂性.

除了种子组成和结构, 种子乳液界面张力和分子间相互作用在 Janus 颗粒的形成中也发挥重要作用<sup>[53]</sup>. 因此, 研究人员探究了构成乳液的溶剂、单体及表面活性剂等因素对 Janus 颗粒形貌结构的影响. 例如, Liu 等提出一种利用复合盘状聚苯乙烯/聚甲基丙烯酸乙基己酯(PS/PEHMA)复合胶体颗粒作为种子制备 Janus 颗粒的策略<sup>[54]</sup>. 制备的 Janus 颗粒的形状由吸附在种子表面的乳液液滴演化而来, 获得了多种形态的 PS/PEHMA- $\text{SiO}_2$  Janus 颗粒(图 4(B)). 该研究也进一步证实, 不同形状的复合种子颗粒表面具有不同润湿性, 影响单体液滴的吸附, 进而可以对 Janus 颗粒的结构进行精细调控.

在核壳颗粒种子乳液聚合的基础上, Xia 等<sup>[55]</sup>以非球形核壳结构颗粒作为种子制备 Janus 颗粒. 通过溶胀椭球形  $\text{PS}@SiO_2$  核壳结构, PS 内核从椭球的赤道处挤出, 成功制备了 T 形 Janus 颗粒. 通过简单的调节溶剂的浓度和种类, 就可以很好控制 PS 和  $\text{SiO}_2$  的分区比例(图 4(C)).

总之, 在种子乳液聚合制备 Janus 颗粒过程中, 种子颗粒的选择对于相分离行为与最终结构形成具有重要影响. 一般而言, 需同时考虑其化



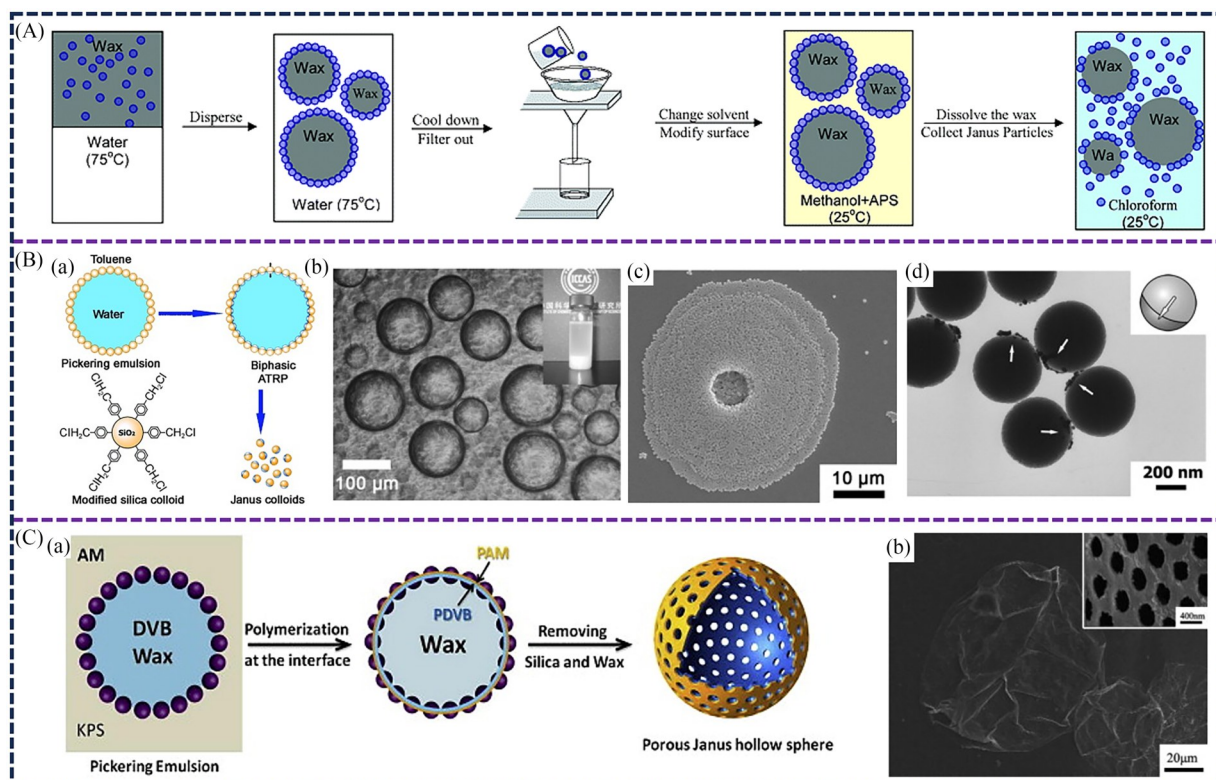
**Fig. 4** (A) Schematic synthesis of anisotropic Janus particle by emulsion swelling the core-shell structure (a), and some representative anisotropic composite particles by emulsion swelling at varied toluene/particle weight ratio (b). (Reproduced with permission from Ref.[52]; Copyright (2012) American Chemical Society). (B) Synthesis of colloidal particles with tunable shapes (a), TEM and SEM images of theta-shaped and discoid silica colloids obtained from liquid droplets at various methanol/water ratios (b). (Reproduced with permission from Ref.[54]; Copyright (2018) Wiley). (C) Schematic showing the formation of a T-shaped Janus particle by swelling a PS@SiO<sub>2</sub> spheroid with a toluene/water emulsion to punch a hole in the SiO<sub>2</sub> shell at the equatorial position (a), TEM image of PS@SiO<sub>2</sub> spheroids with a shell thickness of 20 nm prepared using the Stöber method (b), and TEM image of T-shaped Janus particles fabricated by swelling the PS@SiO<sub>2</sub> spheroids with a toluene/water emulsion (1% by volume) for 6 h (c). (Reproduced with permission from Ref.[55]; Copyright (2022) Wiley).

学组成与物理特性. 在化学组成上, 种子颗粒需具备与目标单体之间适当的不相容性. 若相容性好, 易导致单体包覆整个种子表面而抑制 Janus 结构形成<sup>[56]</sup>. 对于聚合物种子而言, 交联程度和单体种类选择可以影响相分离程度与第二相的生长位置<sup>[57]</sup>. 在物理特性上, 颗粒的表面性质, 如亲疏水性和电负性, 也能进一步引导单体的选择性聚合, 控制第二相的生长位置与形貌. 如通过不同表面活性剂来调节界面张力, 可实现从核-壳结构到非对称 Janus 结构的可控转变<sup>[58]</sup>.

### 1.3 Pickering 乳液聚合

纳米颗粒能够通过吸附来减少高能表面的接触从而降低体系的表面能, 在界面聚集稳定乳液, 被称为 Pickering 乳液<sup>[59,60]</sup>. 由于从界面脱附到体相所需的能量是跟表面活性剂分子半径相关

的函数, 相比于传统表面活性剂(小分子), 固体颗粒脱附所需能量比小分子表面活性剂高 3~5 个数量级, 普遍认为这种吸附通常是不可逆的, 因此利用固体颗粒代替传统的表面活性剂稳定的乳液体系更稳定<sup>[61]</sup>. 利用这种方法, 固体颗粒吸附在油水界面上形成稳定的物理屏障, 活性单体可以分散在油相或水相中, 从而实现单侧的改性. 与二维界面法保护相比, 该方法制备 Janus 颗粒效率更高<sup>[62~64]</sup>. Granick 等<sup>[24]</sup>首次提出使用 Pickering 乳液法合成 Janus 颗粒, 使用 SiO<sub>2</sub> 颗粒将熔融状态下的相变石蜡乳化后快速冷却形成固-液界面以达到部分保护颗粒表面的目的, 通过调控固体颗粒的在石蜡中的嵌入深度来控制颗粒被保护的区域, 进一步通过选择性修饰使颗粒的两侧具有不同化学组成和物理性质(图 5(A)).



**Fig. 5** (A) Schematic procedure to create Janus particles by functionalizing particles adsorbed onto an emulsion of water and oil and then cooling the sample so that the oil crystallizes to form a wax. (Reproduced with permission from Ref.[24]; Copyright (2006) American Chemical Society). (B) Schematic synthesis of Janus colloids by biphasic grafting at a Pickering emulsion interface (a), optical microscope image of the W/O Pickering emulsion stabilized by CMPTS-modified SiO<sub>2</sub> colloids (b) (inset: the emulsion appearance), SEM image of one emulsion drop after drying (c), TEM images of Janus colloids with adsorbed Au NPs. (Reproduced with permission from Ref.[65]; Copyright (2008) Wiley). (C) Schematic synthesis of the Janus polymeric cages with uniform transverse holes across the shell (a), SEM image of polymeric cages after removal of the silica particles and wax (inset magnified surface structure) (b). (Reproduced with permission from Ref.[67]; Copyright (2012) Elsevier).

类似地, 选择性修饰也可以在液-液界面直接进行, 不同性质的前驱体分别在溶解在两种溶剂中, 两相可以同时反应进行聚合物修饰. Yang等<sup>[65]</sup>使用亲脂改性后的单分散二氧化硅球作为固体表面活性剂, 稳定油包水型 Pickering 乳液. 通过原子转移自由基聚合(ATRP)将不同的聚合物刷分别接枝在液-液界面处的二氧化硅颗粒两侧, 获得 Janus 颗粒(图 5(B)). Zhao 等也利用这一方法将二氧化硅颗粒用作固体颗粒表面活性剂, 通过表面引发的聚合反应, 成功制备了两面半球上分别带有疏水性聚苯乙烯(PS)和亲水性聚甲基丙烯酸钠(P SMA)刷的 Janus 粒子<sup>[66]</sup>.

Pickering 乳液方法与乳液界面聚合相结合, 可以制备具有中空结构的多孔 Janus 笼<sup>[67]</sup>. 改性二氧化硅颗粒单层排布在界面处形成稳定乳液, 油溶性单体和水溶性单体在界面上的二氧化硅颗粒

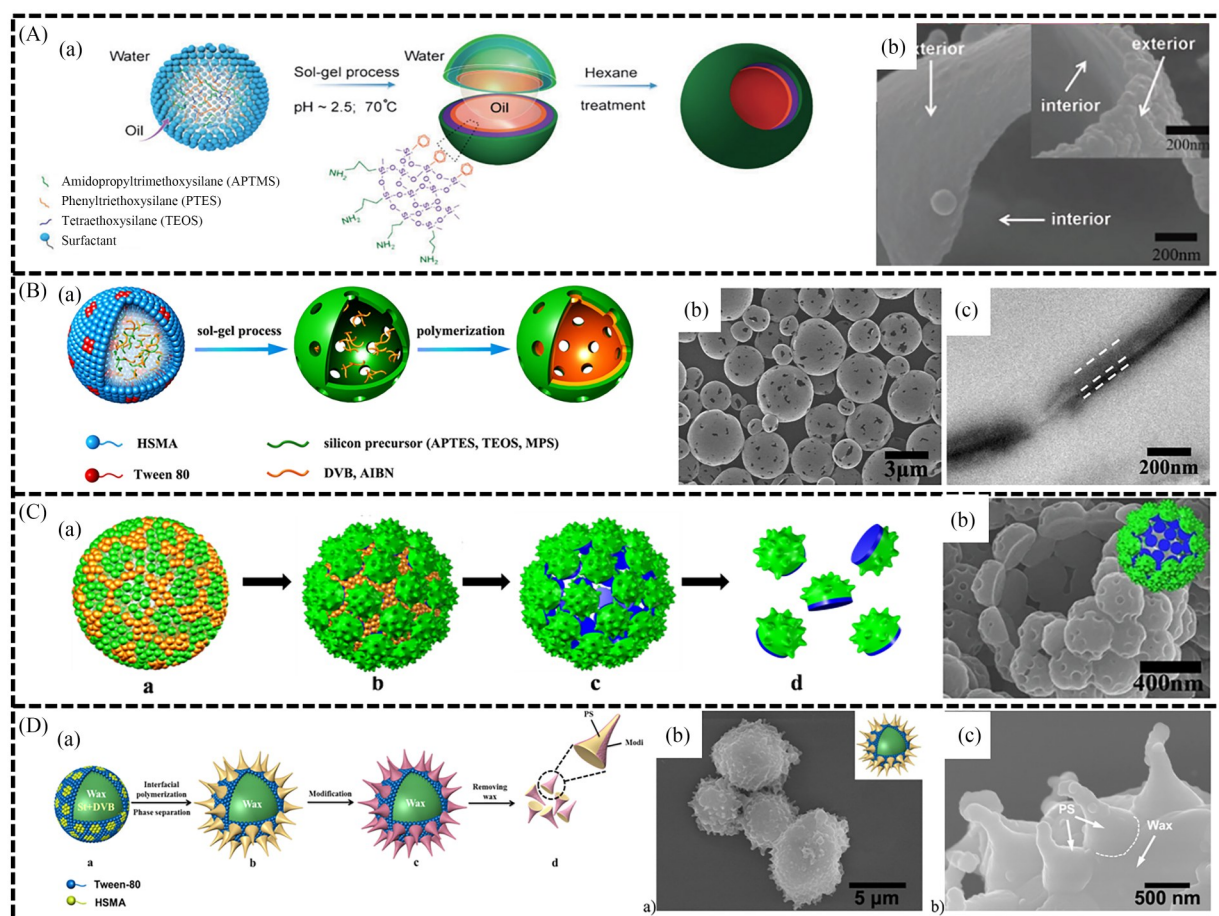
之间的空隙中共聚, 形成两亲性聚合物 Janus 外壳. 由于二氧化硅颗粒嵌入其中, 当去除二氧化硅颗粒后, 获得了孔洞均匀, 排列规则的 Janus 聚合物笼(图 5(C)). Pickering 乳液聚合不仅避免了小分子表面活性剂的使用, 还通过调控固体颗粒的吸附位置和界面性质, 实现了对 Janus 颗粒分区结构的精确控制. 然而, 为了确保 Janus 结构的均匀性, 颗粒在界面处的排布必须是单层的, 颗粒在界面处的旋转也可能导致改性的不均匀. 所以需要进一步发展提高产量和实现精确调控的方法.

#### 1.4 乳液界面聚合

上述提到的种子乳液聚合和 Pickering 乳液聚合涉及到多步反应途径, 发展更加简便的一锅制备 Janus 颗粒方法至关重要. 乳液界面的“Janus”环境能够诱导亲水和亲油基团自发地分别朝向水相和油相, 通过界面反应形成壳层并固

定取向结构, 能够直接获得壳层内、外表面具有不同化学组成的 Janus 中空球. 基于此, 我们利用油/水界面两侧化学环境不同形成的“静态 Janus”界面作为临时模板, 提出了乳液界面材料化和复配表面活性剂诱导界面相分离构建补丁结构制备 Janus 材料和调控微结构的方法<sup>[25]</sup>, 该方法适用于将具有不同功能基团的活性单体作为制备 Janus 颗粒的前驱体, 通常可以获得 Janus 中空球和二维 Janus 片<sup>[68]</sup>. 例如, 3 种硅烷偶联剂在乳液油水界面定向自组织并进行溶胶凝胶反应, 能成功制备内外表面基团不同的 Janus 中空球, 使用超声粉碎可以进一步将其破碎为对应的 Janus 片(图 6(A)). 这类二维的 Janus 片用作固体表

面活性剂时, 能够通过减少界面处的旋转从而提高稳定性. 当使用两种表面活性剂复配稳定乳液界面时, 通过三相界面张力调控能够实现乳液界面的微相分离, 再在特定表面活性剂区域进行化学反应, 则可以直接制备多孔 Janus 中空笼(图 6(B))<sup>[69]</sup>或草莓状 Janus 颗粒(图 6(C))<sup>[70]</sup>. 此外, 改变活性单体的类型, 如将硅烷偶联剂替换为乙烯类单体, 可通过调节水、油、聚合物等多相界面的界面张力调控 Janus 颗粒的形貌, 制备形状和结构兼具各向异性的飞碟形聚合物颗粒<sup>[71]</sup>、锥形 Janus 颗粒(图 6(D))<sup>[72]</sup>和多孔 Janus 纳米片<sup>[17]</sup>. 这种方法操作简单, 调控途径广泛, 尺寸在一定范围内可控, 是可以批量制备具有高表面活性和

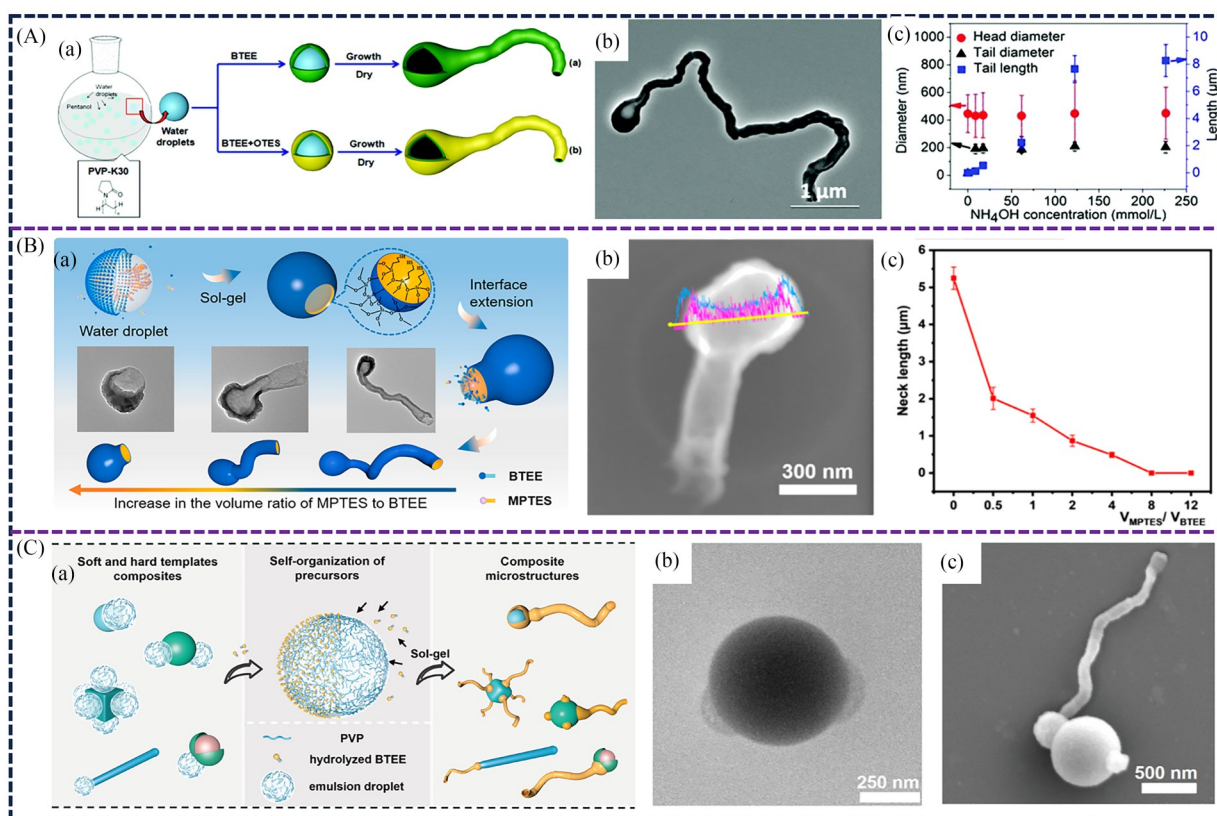


**Fig. 6** (A) Illustrative fabrication of the Janus hollow spheres by emulsion interfacial self-assembled sol-gel process (a), SEM image of the Janus hollow sphere (b). (Reproduced with permission from Ref.[25]; Copyright (2011) The Royal Society of Chemistry). (B) Schematic synthesis of a Janus cage with bilayered polymer-inorganic composites (a), SEM (b) and cross-section TEM images (c) of the Janus composite cage. (Reproduced with permission from Ref.[69]; Copyright (2013) American Chemical Society). (C) Schematic synthesis of the Janus colloidosomes and Janus particles with increasing Tween-80 content (a), SEM images of the representative colloidosome (b). (Reproduced with permission from Ref.[70]; Copyright (2015) Springer Nature); (D) Schematic synthesis of the conelike Janus particles at the patchy emulsion interface (a), SEM images of the paraffin spheres with the conelike PS particles grown at the surface (b, c). (Reproduced with permission from Ref.[72]; Copyright (2015) American Chemical Society).

复杂结构的 Janus 颗粒的经济方法。

通过改变溶剂和表面活性剂种类, 可以进一步降低乳液的粒径. 因此, 也常使用微乳液体系作为制备非球形的棒状、花状和纤维状等颗粒的模板<sup>[73-75]</sup>. 我们进一步拓展乳液界面材料化构筑 Janus 结构方法, 通过复制微乳液液滴运动的轨迹, 实现“动态 Janus”界面材料化, 制备了具有一维中空结构的形状高度各向异性蝌蚪状 Janus 颗粒<sup>[76]</sup>. 反应时间、催化剂浓度和水含量可

以分别调控蝌蚪结构尾部的长度和头部的直径(图 7(A)). 并且, 硅烷前驱体的有机基团对颗粒生长控制表现独特的“开关”作用, 实现了从单孔 Janus 颗粒到长颈瓶状 Janus 颗粒的可控制备(图 7(B))<sup>[77]</sup>. 进一步, 利用液滴在颗粒表面吸附行为差异, 将微乳液液滴软模板与颗粒硬模板复合, 实现了在颗粒表面选区生长, 制备了结构可控的 Janus 中空纤维, 同时制备了多种具有多级非对称结构的 Janus 颗粒(图 7(C))<sup>[78]</sup>.



**Fig. 7** (A) Schematic illustration of tadpole-like nanotubes and tadpole-like Janus nanotubes (a), TEM images of the tadpole-like nanotubes (b), the average tail length and tail diameter of the tadpole-like nanotubes with different reaction times (c), (Reproduced with permission from Ref.[76]; Copyright (2021) The Royal Society of Chemistry). (B) Schematic illustration of the preparation of Janus particles with tunable anisotropic hollow structures (a), EDS elemental mapping images of flask-like Janus particles (b), variation pattern of the neck length of flask-like Janus particles with  $V_{MPTES}/V_{BTEE}$  volume ratios (c). (Reproduced with permission from Ref.[77]; Copyright (2022) American Chemical Society). (C) Schematic illustration of the asymmetric growth mechanism for anisotropic multitentacle Janus particles with different morphologies (a), cryo-TEM and EDS image of the emulsion droplets anchored on the surface of SiO<sub>2</sub> nanoparticle seed (b), SEM images of multitentacle Janus particles synthesized with 450 μL of dispersion phases (c). (Reproduced with permission from Ref.[78]; Copyright (2024) Wiley).

## 2 总结与展望

乳液聚合作为制备 Janus 颗粒的重要手段, 包括 Janus 乳液聚合、种子乳液聚合、Pickering 乳液聚合以及界面聚合在内的方法, 极大地丰富

了 Janus 颗粒设计合成策略, 为实现 Janus 颗粒工业化生产提供了极具潜力的技术方案。

然而, 由于 Janus 材料本身具有复杂的非对称结构, 其制备过程中, 在形貌控制和多功能集成方面面临较大挑战, 尤其是结构可控性差、形

貌可预测性不足及批量化能力有限,成为制约其广泛应用的瓶颈问题。

未来的研究重点应该聚焦以下几个方面:一方面,亟需开发更高效、低成本且结构可控的 Janus 颗粒合成技术,尤其是在乳液聚合体系中探索超越成分相容性差异驱动的界面分区机制,发展可适用于多种材料体系的通用形貌调控方法;另一方面,结合界面工程、智能响应材料和自动化生产技术制备新型 Janus 颗粒,推动 Janus 颗粒在新兴多功能材料领域的实际应用,例如靶向药物递送、生物传感、界面催化以及能源存储

等.通过实现对 Janus 结构的精准调控与批量化制备,将有望打破当前的技术瓶颈,推动 Janus 颗粒从实验室走向规模化应用,真正发挥其独特优势.乳液聚合是一种低成本和环境友好的微球材料工业化生产方法,但产品微结构调控手段有限.因此,以乳液聚合生产技术为基础,突破基于组成相容性差异驱动的相分离机理,降低材料化学组成差异依赖的颗粒形貌和微结构调控方法至关重要.在结构可控性与批量生产方面的持续进步,将为 Janus 颗粒在应用研究中的推广提供可靠的工艺支撑和经济高效的产品基础。



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Review (Emerging Young Scientists)

## Research Advances in Janus Particles Prepared by Emulsion Polymerization

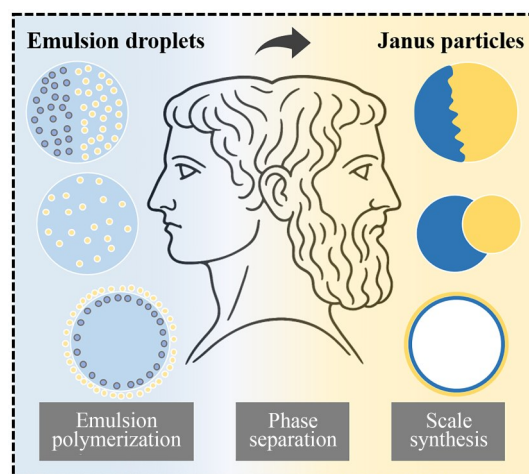
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**Abstract** Janus particles are commonly defined as colloidal structures with two distinct surface regions that differ in physical or chemical properties. They have been widely recognized for their multifunctionality in areas

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such as emulsion stabilization, targeted drug delivery, catalysis, and sensing. Due to their anisotropic nature, enhanced interfacial behavior and spatially selective interactions can be achieved. However, the precise control of their microstructures and the development of scalable fabrication techniques remain key challenges. To address these limitations, emulsion polymerization has been extensively employed as a versatile and controllable method. Its mild reaction conditions, compatibility with various monomers, and tunable polymerization pathways have enabled the successful preparation of a wide range of Janus particles. Four principal emulsion polymerization strategies have been developed and systematically studied: traditional emulsion polymerization, seeded emulsion polymerization, Pickering emulsion polymerization, and interfacial emulsion polymerization. In traditional approaches, Janus emulsions are typically formed in a one-step process, but fine control over morphology is often limited. In seeded emulsion polymerization, asymmetry is introduced by directional polymer growth on preformed seed particles, allowing greater precision in particle structure. In Pickering emulsion polymerization, emulsion droplets are stabilized by solid particles, and polymerization is selectively initiated at specific regions through masking effects or selective monomer affinity at interfaces, enabling precise control of particle morphology and composition. In interfacial emulsion polymerization, polymer growth is triggered at phase boundaries, permitting the fabrication of compartmentalized and well-defined Janus architectures. Although significant advancements have been achieved through these methods, difficulties in reproducibility, yield, and large-scale production continue to hinder their broader application. To overcome these issues, further improvements in interfacial stability, emulsion design, and polymerization kinetics are required. Overall, emulsion polymerization has been demonstrated as an effective technique for the fabrication of Janus particles, and continued progress in this field is expected to facilitate their transition from laboratory-scale synthesis in advanced materials research to industrial-scale production.



**Keywords** Janus particles, Emulsion polymerization, Seeded emulsion, Pickering emulsion, Interface