

Pickering乳液的稳定性研究及其在食品领域的应用进展

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Pickering 乳液的稳定性研究及其在食品领域的应用进展

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摘要:皮克林(Pickering)乳液是一种由固体颗粒代替传统乳化剂形成的新型乳液体系,具有稳定性强、对环境友好、安全性高等天然优势,在食品、化妆品、化工材料、生物医药等多个领域一直备受青睐。本文阐述了 Pickering 乳液的稳定机制,在其基础上从六个方面主要讨论影响 Pickering 乳液稳定性的相关因素,分别为固体颗粒的类型、形状、浓度、表面电荷、油水相体积分数及湿润性;同时,总结了近几年 Pickering 乳液用于制备智能食品薄膜、防止脂质氧化、递送生物活性物质、合成分子印迹聚合物、实现双相催化、构建 4D 打印食品原材料的国内外研究成果,旨在为食品工业及其他相关领域的多元化发展提供理论依据和技术支撑。

关键词:Pickering 乳液,稳定机制,影响因素,功能性,食品应用

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Research on the Stability of Pickering Emulsion and Its Application in Food Field

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Abstract: Pickering emulsions is a new emulsions system formed by replacing traditional emulsifiers with solid particles, which has some advantages such as strong stability, environmentally-friendly, high safety and so on. It has been highly favored in the fields of food, cosmetics, chemical materials and biomedicine. Based on the stability mechanism of Pickering emulsions, this review mainly discusses relevant factors affecting its stability from six aspects, including the type of solid particles, shape of solid particles, concentration of solid particles, surface charge of aqueous phase, volume fraction of oil-water phase and the wettability. Meanwhile, the achievements of domestic and overseas on Pickering emulsions are also summarized, including preparing the intelligent food films, preventing the lipid oxidation, delivering the bioactive substances, synthesizing the molecularly imprinted polymers, achieving biphasic catalysis, and constructing 4D printed food raw materials in recent years. This paper aims to provide theoretical basis and technical support to a certain extent for the diversified development of food industry and other related fields.

Key words: Pickering emulsions; stability mechanism; interfering factors; function; food application

乳液一般由互不相容的两相组成,一相(内相或分散相)以液滴形式分散到另一相(外相或连续相)中。传统乳液一般通过物理化学方式(如聚结、絮

凝、奥氏熟化等)迫使油水相分离,属于热力学不稳定体系,因此,需借助乳化剂(吐温、司盘、双亲性高分子聚合物等)作用于油水界面来保持乳液稳定,然

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而这种乳化剂稳定性低、成本高、毒性强,使乳液在生产加工中受到了严重的限制。20 世纪初,科学家 Pickering^[1] 证明由无机固体颗粒稳定的石蜡油乳液,较传统乳液具有更好的稳定性,并以姓氏命名。固体颗粒不同于传统乳化剂,能够不可逆地吸附在两相界面中形成稳固的机械屏障(如图 1 所示),得到的乳液体系具有稳定性高、毒性低、环保性强、生物相容性好等优势,目前已被广泛应用于化妆品、医药、食品、化工、材料等多个领域。

目前,关于 Pickering 乳液食品领域发展前景十分可观,但关于稳定机制的研究仍然欠缺,本文在阐述 Pickering 乳液体系稳定机制的基础上,重点从固体颗粒的类型、形状、浓度、表面电荷、油水相体积分数、湿润性六个方面分析影响其稳定性的因素。同时,结合国内外食品领域发展现状,总结了 Pickering 乳液在制备智能食品薄膜、防止脂质氧化、递送生物活性物质、合成分子印迹聚合物、实现双相催化、构建 4D 打印食品原材料的应用进展,为 Pickering 乳液在食品工业领域的发展提供参考和依据。

1 Pickering 乳液的稳定机制

Pickering 乳液的稳定性是通过颗粒在两相界面上的吸附形成机械屏障,改变颗粒间的空间位阻而实现的,是一个热力学不可逆过程^[2]。根据经典 Bancroft 定律^[3]:

$$\Delta G_d = \pi r^2 \gamma_{ow} (1 - |\cos(\theta)|)^2 \quad \text{式 (1)}$$

式中, ΔG_d 为解吸自由能(J), r 为颗粒半径(m), γ_{ow} 为油水界面张力(N/m), θ 为三相接触角($^\circ$)。

从式(1)看出,解吸自由能和三相接触角、颗粒半径、界面张力密切相关。从热力学角度分析得出,当 r 和 γ_{ow} 越大, θ 越接近 90° 时,颗粒脱离界面的解吸能远大于热能,从而使乳液体系越稳定。相对于传统乳液,当位于界面间的固体颗粒吸附发生形变时,产生的横向毛细管压力可以防止颗粒分解并形成一种界面膜,位于界面间相邻却形状方向各异的颗粒产

生的毛细管压力越强,界面能量也随之增强^[4-5]。界面膜的形成是来自颗粒与颗粒之间以及颗粒与两相之间的相互作用力。颗粒与液滴之间在范德华力、静电、疏水等作用力下形成多层吸附层或凝胶网络,并使吸附层具有一定的刚性、粘弹性和机械强度,降低颗粒的迁移速率,阻碍液滴絮凝和聚结,从而提供一道物理屏障促进了乳液的稳定性^[2-3,6]。

2 影响 Pickering 乳液稳定性的因素

2.1 固体颗粒类型

2.1.1 无机颗粒 无机颗粒是目前制备 Pickering 乳液使用最广泛的一类,如二氧化硅(Silica, SiO_2)、二氧化钛(Titanium Dioxide, TiO_2)、蒙脱土(Montmorillonite, MMT)、碳纳米管(Carbon Nanotubes, CNTs)等。 SiO_2 具有易改性、耐酸碱、形态清晰、尺寸范围广等特点^[7-8]。由于 SiO_2 表面带有 Si-OH 基团^[9],从而产生很强的亲水性,处于酸碱条件下则易聚集,乳液体系不稳定。因此,天然 SiO_2 通常经由化学改性后使用^[3]。 TiO_2 是一种金属氧化物,且易加工、成本低。作为新型绿色高效的光催化和传感器材料之一^[10-12],具有良好的化学稳定性、安全性和半导体性能。研究证明 TiO_2 可增强油水界面覆盖率,形成更厚的界面吸附层,高效防止液滴间碰撞和聚结^[13]。MMT 由两片四面体 SiO_2 和八面体 $\text{Al}(\text{OH})_3$ 或 $\text{Mg}(\text{OH})_2$ 组成^[14],是一种粘土颗粒,储量丰富,具有良好的吸附性、表面积特异性和分散性能^[15-16]。与 SiO_2 相似,天然的 MMT 亲水性很强,也需将其改性才可使用^[17],当与海藻酸钠(SA)复合后,该 Pickering 乳液表现出良好的分散性和稳定性^[14]。CNTs 因具有高机械强度、较大的比表面积以及良好的电气性能^[18],使其成为一种理想的纳米材料。但由于疏水性较强,需改性使其更亲水来稳定油水界面,常见的改性方法是利用氧等离子体处理,引入亲水性官能团(羟基和羧基)^[19-20],而 Quynh 等^[21] 利用动态共价平衡改性,通过 3,5-二硝基苯基引入官能团作用

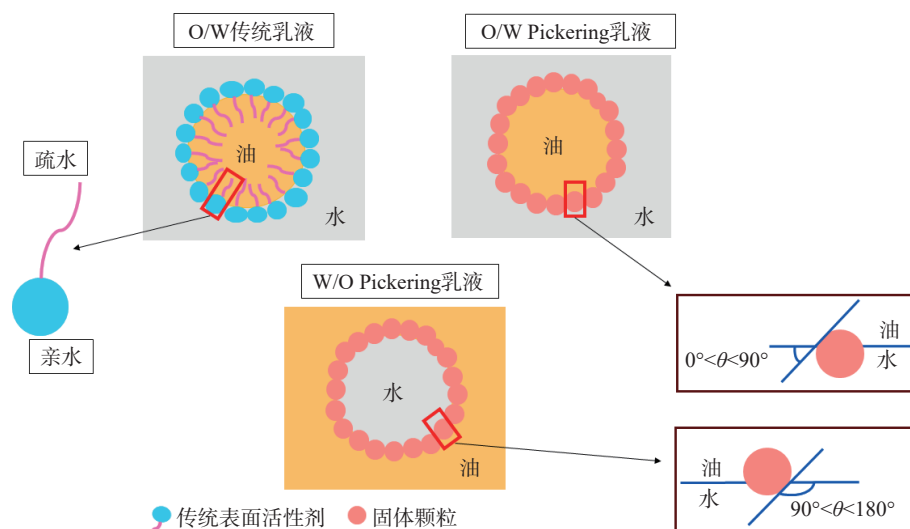


图 1 传统乳液和 Pickering 乳液示意图^[2]

Fig.1 Schematic diagram of the traditional emulsions and Pickering emulsions^[2]

于 CNTs 表面,一步制备稳定的 Pickering 乳液。

2.1.2 有机颗粒 有机颗粒中大多数为天然大分子物质,常常被用作制备食品级 Pickering 乳液,如蛋白质基颗粒、多糖基颗粒、多酚基颗粒、脂质基颗粒等。

2.1.2.1 蛋白质基颗粒 蛋白质基颗粒,如醇溶蛋白^[22-26]、大豆蛋白^[27-29]、乳清蛋白^[30-31]、明胶^[32]等,富含多种氨基酸,拥有良好的界面空间和乳化活性,其结构、可持续性、生物降解性及相容性深受研究者关注^[33]。作为 Pickering 乳液稳定剂的优质原料,可通过氢键、范德华力、静电相互作用形成刚性物理屏障,还可通过不同的制备方法对蛋白质改性从而得到

更稳定的 Pickering 乳液(见表 1)。

2.1.2.2 多糖基颗粒 多糖基颗粒也常用于稳定 Pickering 乳液(见表 2)。淀粉作为一种天然植物多糖,由线性直链淀粉和分枝支链淀粉组成,具有生物降解、无刺激和无毒性等优势。然而天然的淀粉颗粒不适合直接稳定 Pickering 乳液,原因是淀粉颗粒中含有较多羟基结构,导致其疏水性较差^[34-35]。因此,可通过辛烯基琥珀酸酐(Octenyl Succinic Anhydride, OSA)改善两亲性^[36-37]。纤维素由 β -1,4-D-吡喃葡萄糖的重复环组成,属于一种线性大分子,可再生性强^[38]。将其经过强酸水解,去除无定形区得到的纤维素纳米晶(Cellulose Nanocrystals, CNCs),呈宽

表 1 部分蛋白质基颗粒稳定 Pickering 乳液的研究

Table 1 Study on several protein based particles for stabilizing Pickering emulsions

蛋白质名称	材料	油相	制备方法	乳液表现特征	参考文献
玉米醇溶蛋白	玉米醇溶蛋白/果胶	玉米油	反溶剂法,油体积比80%,10000 r/min,高速剪切2 min	突出粘弹性和氧化稳定性	[22]
	玉米醇溶蛋白/可溶性大豆多糖	大豆油	70%乙醇溶液中溶解不同浓度Zein,8000 r/min,高速剪切3 min	在25 ℃下具有较高的稳定性	[23]
	玉米醇溶蛋白/亚麻籽胶	玉米油	反溶剂法,超声波处理,15000 r/min,高速分散3 min	良好的储存稳定性	[24]
	玉米醇溶蛋白/纤维素纳米晶	中链甘油三酯	溶剂蒸发法,18000 r/min,均化5 min	界面性质保持良好,乳液表现出良好的储存稳定性	[25]
麦醇溶蛋白	麦醇溶蛋白/阿拉伯胶	玉米油	一步法,70%乙醇溶液溶解,调节pH4.9,12000 r/min,高速剪切2 min	稳定的表现粘度,储能模量更高	[26]
大豆蛋白	大豆蛋白	大豆油	酸诱导自组装法,12000 r/min,高速剪切2 min	界面间保持稳定,聚集程度良好	[27]
	大豆蛋白/花青素	大豆油	颗粒之间共价复合,调节pH为7.0后10000 r/min,高速剪切2 min	良好的储存稳定性	[28]
	大豆蛋白/细菌纤维素纳米纤维	中链甘油三酯	以2:8的油水体积比制备,16000 r/min,高速均化2 min	良好的储存稳定性	[29]
乳清蛋白	乳清蛋白/乳清蛋白原纤维	大豆油	湿法磷酸纯化WPI,然后制备与WPI复合物溶液混合为油分数25%的乳液,8000 r/min,高速均化2 min	弹性凝胶状和高稳定性	[30]
	乳清蛋白/植物甾醇	大豆油	抗溶剂法,8000 r/min,均质3 min	弹性凝胶状和高稳定性	[31]
明胶	明胶	大豆油	两步去溶剂法,13500 r/min,混合均质1 min	良好的储存稳定性	[32]

表 2 部分多糖基颗粒稳定 Pickering 乳液的研究

Table 2 Study on several polysaccharide based particles for stabilizing Pickering emulsions

糖类名称	材料	油相	制备方法	乳液表现特征	参考文献
淀粉	大米淀粉	中链甘油三酯	涡流混合将淀粉分散在水相中,添加油相,20000 r/min,高速剪切1 min	增强乳液稳定性	[45]
	高粱淀粉	大豆油	用不同的油体积比和淀粉浓度制备乳液,16000 r/min 剪切油水混合物2 min	良好的储存稳定性	[46]
纤维素	CNCs/姜黄素	红棕榈油	将姜黄素粉末溶解于油相中并在30 ℃下磁力搅拌12 h制备。采用两步法,油水比为1:4的Pickering乳液	良好的稳定性	[47]
壳聚糖	阿拉伯胶/白芦藜醇	橄榄油	离子凝胶法,将橄榄油缓慢加入纳米颗粒分散体,13500 r/min,均化5~7 min	增强乳液稳定性	[48]
	海藻酸钠	棕榈油	将棕榈油精添加到壳聚糖颗粒分散液(pH6.9)中,5000 r/min,均化5 min	增强乳液稳定性	[49]
阿拉伯胶	大麦醇溶蛋白	辛癸酸三酰甘油酯	抗溶剂沉淀法,pH5.0,10000 r/min,高速均化8 min	能够长期储存	[50]
	卵清蛋白	植物油	将紫苏籽油添加到复合物悬浮液中,复合物与油的质量比达到1:4,17000 r/min,分散5 min。	较强的稳定性和良好的分散性	[51]
	壳聚糖	橄榄油	固定复合物浓度为1.5%(w/v),质量比为1:1,13500 r/min,高速均化7 min	良好的储存稳定性	[52]
果胶	卵清蛋白/姜黄素	橄榄油	复合物pH4.4,15000 r/min,1 min高速剪切制备	增强乳液稳定性	[53]
	玉米醇溶蛋白	玉米油	抗溶剂沉淀法,pH4.0,将玉米油缓慢添加到复合物悬浮液中,12000 r/min高速均质3 min	增强乳液稳定性	[54]

棒状或针状,具有高结晶度、高纵横比等特点^[39],通过改性还可提高其乳化能力^[40],Chen 等^[41]研究证明,改性后的 CNCs 即使存在于颗粒浓度非常低的水相中,也能制备出稳定的高内相 Pickering 乳液。壳聚糖(Chitosan, CS)是由无规则分布的脱乙酰基(β -(1 $\rightarrow$ 4)-D-葡萄糖胺)和乙酰化单元(N-乙酰基-D-葡萄糖胺)组成的多糖^[42],也是天然多糖中唯一的阳离子多糖。在碱性条件下,壳聚糖的氨基基团去质子化,表面电荷降低,使壳聚糖自组装成胶体颗粒,吸附在油水界面,阻碍液滴聚集,成功稳定 Pickering 乳液^[43]。另外,由于它独特的抗菌性、粘性、生物降解和生物相容性,在生物医药领域具有高开发前景^[44]。

2.1.2.3 多酚基颗粒 多酚基颗粒^[55]是普遍存在于自然界中的植物次生代谢产物,具有不同数量芳香羟基环。利用多酚基颗粒制备 Pickering 乳液,可以提高多酚化合物的生物可及性,同时赋予 Pickering 乳液更多抗氧化、抗菌、抗炎等功能特性^[28,48,55]。然而多酚基颗粒稳定 Pickering 乳液食品方面的研究目前不多见。Zhao 等^[56]制备松子油 Pickering 乳液,发现单宁酸和没食子酸两种酚类化合物均表现出最佳乳化能力,提高乳液氧化稳定性。由于单宁酸含有较多数量羟基基团,乳液稳定性方面表现更为显著。Noon 等^[57]制备芦丁水合物稳定的 Pickering 乳液,发现芦丁既可作为常规 Pickering 乳液稳定剂,还可作为抗氧化剂提高乳液氧化稳定性。

2.1.2.4 脂质基颗粒 脂质基颗粒具有高熔点和良好的界面活性,通常由熔融-冷却法制备而成。但因其疏水性较强,在制备乳液时,需加入少量表面活性剂或其它乳化剂,改善两亲性减少液滴聚结^[58]。相关研究表明,由脂质基颗粒制备的 Pickering 乳液,相比传统乳液,表现的物理稳定性更强^[59-61]。然而,截至目前脂质基颗粒应用于 Pickering 乳液的研究还较少,需在其类型、制备方法和稳定机制等方面加深探索。

2.1.2.5 植物甾醇 植物甾醇^[31,62]也能稳定 Pickering 乳液体系,其主要来源于油脂含量高的植物性食物^[63],是植物中特有的活性成分,也是细胞膜的基本成分,结构与胆固醇相关。Lan 等^[64]制备 Pickering 乳液中发现,将干燥的植物甾醇颗粒以微晶形式分散到油相中,这种界面结晶的形式能够高效促进乳液稳定。

2.2 固体颗粒形状

颗粒形状(球形和非球形)也是影响 Pickering 乳液稳定性的一个关键因素。球形颗粒,如 SiO₂、TiO₂、多孔微球等,不仅易于制备,而且很容易吸附到油水界面,形成良好的空间位阻效应,提高乳液的稳定性;棒状颗粒与球形颗粒不同,颗粒间会因排列重叠形成一种毛细管作用力^[65],而另一种波动导向力是由流体界面处能量激发毛细管波所引起的^[66],因此,随着纵横比增加,颗粒间强烈的碰撞纠缠使其形成无序的网络结构^[67],这成为稳定 Pickering 乳液的决定性因素;片状颗粒与 2D 界面相似,有相关研究表明,添加电

解质或改变 pH 可降低片状颗粒的 Zeta 电位,使其更容易吸附到界面,形成稳固的凝胶网络,提高乳液的稳定性^[68];盘状颗粒可通过液滴表面覆盖率来判断,覆盖能力越强,界面作用力越强,从而影响乳液的稳定性^[69]。

2.3 固体颗粒浓度

固体颗粒浓度直接影响 Pickering 乳液体系的微观结构和流变学特性^[2],如液滴尺寸、乳液粘弹性、颗粒堆积密度等。随着颗粒浓度增加,液滴表面粒子的吸附率增强,相应液滴的尺寸逐渐减小,液滴间的吸附层从最初稳定的融合状态逐渐形成单层颗粒吸附层,当液滴尺寸减小到一定值并保持不变时,此时液滴间形成多层吸附层或凝胶网络,这种凝胶网络有助于固定液滴,阻碍液滴碰撞聚结,提高乳液稳定性^[3,6,58]。

2.4 表面电荷

Zeta 电位一般可作为评定颗粒表面电荷能力的指标。乳液水相中的盐离子会对颗粒产生静电屏蔽作用,导致颗粒在界面间不可逆地吸附力和表面电荷发生改变,从而影响乳液的稳定性。当盐离子浓度过高时,存在较多反向离子,表面电荷会屏蔽并减小颗粒间的静电斥力,导致乳液体系不稳定^[70-71];当盐离子浓度降至很低时,所产生的静电斥力可忽略不计。除了改变颗粒在界面间的作用力外,离子强度还能改变颗粒的疏水性使乳液体系保持稳定^[72-73]。另外,pH 也会使颗粒表面电荷发生变化,影响其静电相互作用,出现分散或絮凝现象,使乳液失稳^[74]。

2.5 油相的选择及油水相体积分数

Sakiko 等^[75]研究 N-异丙基丙烯酰胺颗粒与多种油类型(十六烷、庚烷和三氯乙烯)制备的 Pickering 乳液,结果证明这些油相均与水相表面形成连贯的颗粒层,表面覆盖率达到 75%~100%,具有很强的吸附力,形成的 O/W 型 Pickering 乳液室温储存达到 3 个月以上。Zhang 等^[76]通过显微镜观察癸烷或十六烷制备的 Pickering 乳液发现,与使用癸烷相比,由十六烷制备的乳液液滴明显更大、更均匀。Liu 等^[77]和 He 等^[78]从制备的 Pickering 乳液中发现,当增加油相体积分数时,乳液类型可从 O/W 转相成 W/O,因此,油相的选择以及油水相比比例决定了油水界面张力,并影响其与颗粒间的相互作用,从而影响乳液的稳定性。

2.6 湿润性

油水界面间的三相接触角(θ)通常作为 Pickering 乳液的湿润性及类型的评价指标。

$$\cos\theta = \frac{\gamma_{p/o} - \gamma_{p/w}}{\gamma_{o/w}} \quad \text{式(2)}$$

式中, $\gamma_{p/o}$ 、 $\gamma_{p/w}$ 和 $\gamma_{o/w}$ 分别表示油、水以及油/水界面上的张力。

从杨氏方程^[3]式(2)看出, θ 与界面张力直接相关,并能决定乳液的类型和性质。当 $\theta < 90^\circ$ 时,颗粒

亲水, 倾向 O/W 型 Pickering 乳液; $\theta > 90^\circ$ 时, 颗粒疏水, 倾向 W/O 型 Pickering 乳液^[68]; 当 θ 接近 90° 时, 此时颗粒呈两亲性, 油水界面达到良好的稳定状态, 同时颗粒吸附到界面的能量最高; 当 θ 为 0° 或 180° 时, 颗粒可能会全部分散在水相或者油相中, 导致絮凝或沉淀, 乳液难以达到稳定状态, 使乳液失稳^[7,68]。

3 Pickering 乳液在食品领域的应用

3.1 制备智能食品薄膜

在食品包装行业中, 一般选择薄膜来隔离分解微生物细菌和外来污染物的侵入。近年来, 智能食品包装激发了研究者的兴趣, 其优势在于利用生物传感器对食物新鲜度的监测和追踪, 为食品安全和人体健康提供有效保障^[79]。Wang 等^[80] 利用明胶颗粒通过两步去溶剂法制备 Pickering 乳液, 并制备成双功能智能食品包装膜。结果表明, 该膜表现出优异的抗菌、抗氧化性以及良好的机械性和避光性。该方法对 pH/NH₃ 快速准确、可逆的响应以及对颜色敏感的切换(黄色→红色), 与监测富含蛋白质食物新鲜度的标准方法(TVB-N)相比, 成功抑制其微生物生长, 达到了延长保质期的目的(如图 2 所示)。Liu 等^[81] 将肉桂油 Pickering 乳液和姜黄素(Curcumin, Cur)加入明胶/壳聚糖膜基质中, 制备一种智能生物复合膜。相关研究结果表明, 该膜具有良好的机械性、优异的抗菌、抗氧化活性、以及水蒸气和紫外线阻隔性; 利用 TVB-N 监测 Cur 样品膜对猪肉的保鲜效果, 颜色从亮棕色切换成暗棕色, 延缓了猪肉的腐败程度, 这些结果为肉类食品包装应用提供一种新策略。Liu 等^[82] 将负载 Cur 的 Pickering 乳液与玉米淀粉和聚乙烯醇基质结合, 制备了智能食品包装膜。结果表明, 该膜具备的抗氧化活性, 可以减少 Cur 在制备和储存过程中的分解。随着时间的变化, 负载 Cur 的 Pickering 乳液所制备的薄膜比 Cur 溶液制备的薄膜颜色变化更明显(黄色→红色)。食品新鲜度监测是食品加工生产中备受重视的问题, 利用改性的

天然生物材料制备的 Pickering 乳液和智能包装结合既满足了低成本、绿色环保等发展理念, 同时, 对食品安全和营养健康具有重要意义。

3.2 防止脂质氧化

脂质氧化过程是一种自由基链式反应, 常常伴随初级(氢过氧化物)和次级氧化产物(醛和酮)的形成, 这些有毒物质严重影响食品的外观口感和营养健康^[83]。Pickering 乳液体系中, 由固体颗粒构成的界面层是控制脂质氧化的有效方法。利用界面间固体颗粒相互作用形成的致密层充当保护屏障, 可以有效防止氧化剂的攻击^[84]。Wang 等^[85] 研究了明胶与儿茶素之间相互作用制备出的 Pickering 乳液(如图 3 所示)中, 利用氢键、疏水键和共价键的结合能够稳定吸附在油水界面, 经氧化剂作用 12 d 后, 初级氧化产物含量仅为 $1.39 \pm 0.12 \mu\text{mol/L}$, 与脂质过氧化抑制率整体变化趋势一致, 为保护功能成分免受氧化攻击提供一种新方法。Wang 等^[86] 采用米糠改性小麦面筋纳米粒子制备的 Pickering 乳液, 在 37°C 储存 20 d 后, 该 Pickering 乳液界面间形成的物理屏障使初级氧化物含量从 $1059.0 \pm 35.5 \text{ mmol/kg}$ 降至 $726.6 \pm 66.9 \text{ mmol/kg}$, 次级氧化物含量从 $278.6 \pm 6.2 \mu\text{mol/kg}$ 降至 $132.2 \pm 7.5 \mu\text{mol/kg}$, 成功延缓脂质氧化。Huang 等^[87] 利用 CS 和酪蛋白磷酸肽制备的高内相 Pickering 乳液(High Internal Phase Pickering Emulsions, HIPPEs), 所形成致密的界面层, 使乳液在储存和消化过程中抑制了脂质氧化。结果表明, 初级氧化产物含量和次级氧化物含量分别为 13 和 1 mmol/kg, 经 60°C 储存 10 h 后, 初级氧化产物含量远低于 20 mmol/kg。如今, 关于控制食物中脂质氧化速率的问题仍是一项重大挑战, 可利用 Pickering 乳液体系开发更多不同方法, 为加工延长保质期的食品提供实际应用。

3.3 递送生物活性物质

生物活性物质, 如类胡萝卜素、脂肪酸、植物甾醇、多酚和维生素等, 极易受到光、酶、极端 pH、高温和氧气的影响, 在食品加工中受到限制。Pickering 乳液体系经研究证实可提高生物活性物质的稳定性, Han 等^[88] 制备壳聚糖/阿拉伯胶纳米颗粒稳定的 Pickering 乳液用于评估对 Cur 的输送情况, 该乳液利用颗粒间的静电相互作用使油水界面保持稳定, 体外模拟胃液和小肠对 Cur 的控制释放得出 94% 的高包封率, 成功证明 Pickering 乳液可作为 Cur 的递送系统。Wei 等^[89] 利用颗粒-生物聚合物-表面活性剂混合制备新型 Pickering 乳液用于递送 β -胡萝卜素。结果表明, 该乳液中三种不同乳化剂的共存可诱导界面处竞争性位移、多层沉积和颗粒间网络形成。在紫外照射条件下, β -胡萝卜素的保留率增加了 2 倍且持续 8 h, 实现了高效递送。Lv 等^[90] 用高压诱导法制备一种 Pickering 乳液凝胶(如图 4 所示), 用于评估番茄红素的体外释放情况。结果表明, 在模拟胃肠期阶段前 30 min 快速释放番茄红素, 并

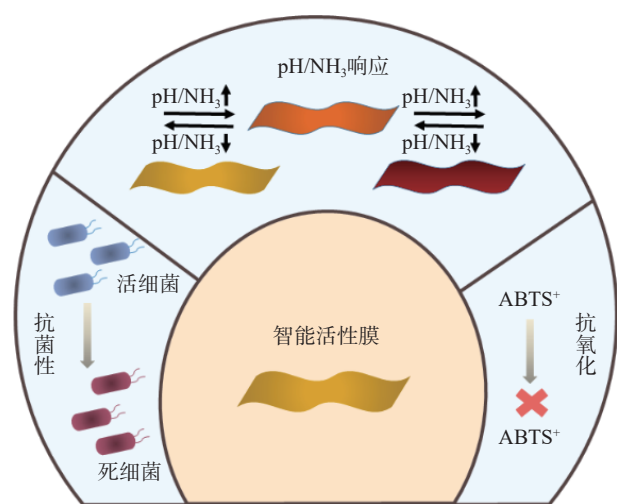
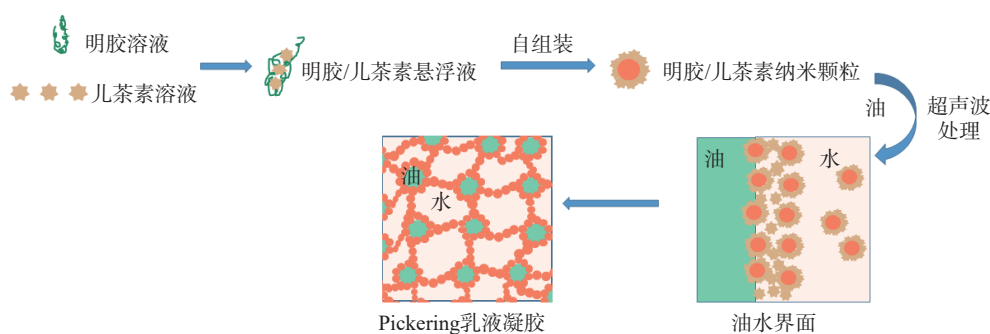
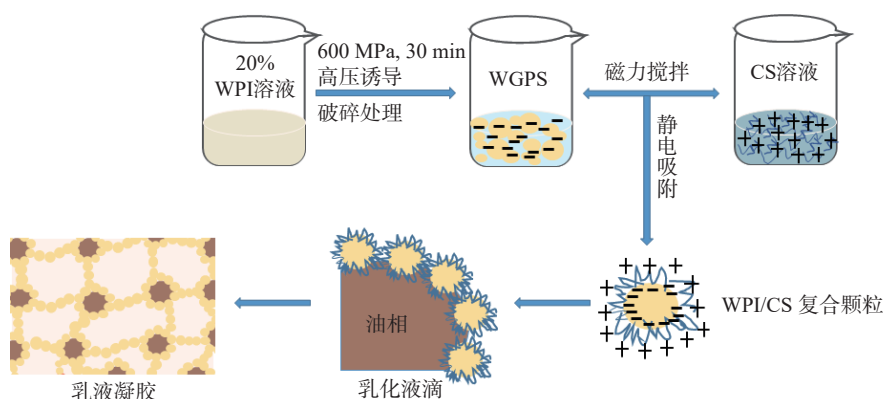


图 2 智能活性膜的示意图^[80]

Fig.2 Schematic diagram of the intelligent active film^[80]

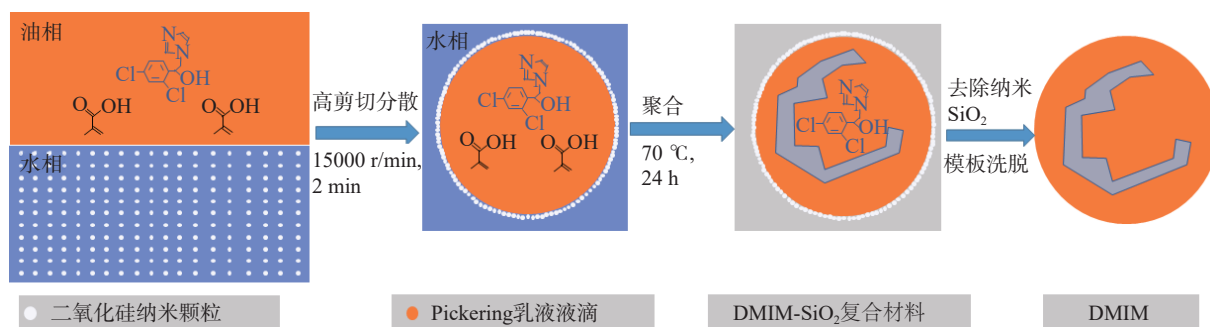
图 3 调节明胶和儿茶素之间的分子相互作用制备 Pickering 乳液示意图^[85]Fig.3 Schematic diagram of the Pickering emulsions prepared by regulating molecular interactions between gelatin and catechin^[85]图 4 乳清分离蛋白和壳聚糖制备 Pickering 乳液凝胶流程^[90]Fig.4 Process of the Pickering emulsions gel prepared by whey protein isolate and chitosan^[90]

在剩余时间内保持恒定的释放速率,由此证明该 Pickering 乳液凝胶作为递送系统具有一定的控释潜力。基于健康和绿色生活理念导向, Pickering 乳液在递送生物活性物质方面尚具有开发前景,进一步研究需深入探讨靶向递送生物活性物质的作用效果,实现理论与实践双突破。

3.4 合成分子印迹聚合物

食品加工过程中违规使用抗生素、农药残留超标、过量使用添加剂对人体健康和食品安全带来许多不良影响。分子印迹技术是一种对目标模板匹配并进行选择性识别^[91-92],合成分子印迹聚合物(Molecularly Imprinted Polymers, MIPs)的方法,已广泛应用于食品样品分析检测。MIPs 通常在有机溶剂中聚合,使用过多有机溶剂损失成本且对环境有害^[93],利用 Pickering 乳液体系聚合既简单高效又经济环

保,同时为食品检测提供新途径。Li 等^[94]通过 β -环糊精稳定 O/W 型 Pickering 乳液聚合制备球型 MIPs,用于红霉素的选择性识别和吸附。吸附动力学研究表明,该 MIPs 的快速吸附特性和模式遵循伪一阶模型,拟合良好,牛奶样品中红霉素的吸附容量为 51.45 mg/g,接近目标值(55.26 mg/g),成功证明该 Pickering 乳液聚合的 MIPs 具有良好的吸附能力,可以作为食品中红霉素残留检测的一项候选。Zhang 等^[95]利用 Pickering 乳液体系聚合成虚拟分子印迹微球(DMIM)(如图 5 所示),用于鱼类样品中三种唑类杀菌剂的预处理。静态吸附实验结果表明,该 DMIM 对克林巴唑(CBZ)、克霉唑(CMZ)和咪康唑(MNZ)可进行良好的识别,并作为一种固相分散萃取吸附剂对 CBZ、CMZ 和 MNZ 进行分离检测,高效液相色谱显示,在 225 nm 处 CBZ、CMZ 和 MNZ

图 5 Pickering 乳液聚合的虚拟压印示意图^[95]Fig.5 Schematic diagram of dummy imprinting by the Pickering emulsions polymerization^[95]

检出限分别为 0.045、0.036 和 0.033 $\mu\text{g/g}$, 这些结果证明, 该 DMIM 对鱼类中唑类杀菌剂的预处理具有良好的应用前景。陈波等^[96]利用 Pickering 乳液制备 MIPs 用于苹果中丁香菌酯的检测。结果表明, 该 MIPs 遵循伪二级动力学模型, 并作为固相分散萃取吸附剂分离检测苹果中的丁香菌酯, 高效液相色谱显示, 在 320 nm 处检出限为 0.02 mg/kg, 回收率达到 86.52%~103.28%, 成功为其在丁香菌酯的残留检测应用奠定基础。对于食品中蔬菜、水果、牛奶的生物残留, Pickering 乳液合成 MIPs 是一种极具潜力的分析工具, 未来应开发多类别、多分析物提取能力的方法, 以便更好、更快地适应商业化发展。

3.5 实现双相催化

为提高鲜奶油、人造黄油、复原乳等食品在生产加工过程中的催化效率^[97], Pickering 乳液体系可作为绿色化学转化成高级催化系统的必选途径, 利用其高界面层和高稳定性的内在优势与双相催化系统 (Biphasic Systems, BS)^[97-98]相结合, 有利于固体颗粒和催化剂的回收利用。Huang 等^[99]利用 CS 纳米凝胶制备的 Pickering 乳液用于评估其催化能力。结果表明, 脂肪酶与 CS 纳米凝胶的非共价结合, 经过水解、酯化、脱酸, 催化活性最高约 80%, pH6.5 时稳定性最强, 经 13 次循环后仍保持 55% 的催化活性。Yu 等^[100]利用乙基纤维素壳聚糖复合颗粒 (ECCPs) 制备 W/O 型 Pickering 乳液, 将其用于可循环式生物催化微反应器 (如图 6 所示)。结果表明, 随着水含量增加, 该乳液的类型可从 W/O 转相为 W/O/W 和 O/W, 酯化反应的转化率在 30 min 达到 64.6%, 120 min 达到 88.3%。以脂肪酶催化己酸己酯模型, 催化活性提高 6.3 倍, 经 15 次循环后仍保持 81% 稳定值。Xi 等^[101]利用酪蛋白酸钠颗粒结合 CO_2 响应

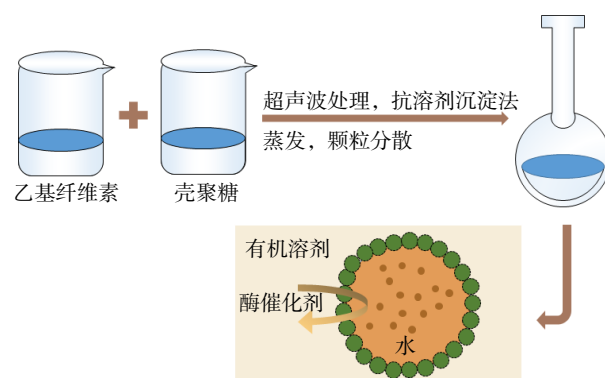


图 6 ECCPs 制备 W/O Pickering 乳液用于生物催化微反应器示意图^[100]

Fig.6 Schematic diagram of the W/O Pickering emulsions prepared by ECCPs for biocatalytic microreactor^[100]

制备 Pickering 乳液评估其催化能力。结果表明, 该乳液经交替循环 30 多次后, 回收的酶仍保持催化活性, 每个循环后转化率超过 90%, 表现出的高反应效率, 为食品转化工艺提供有利依据。先进的 BS 对于绿色可持续发展的食品工业具有潜在的应用前景, 需开发更多天然材料制备 Pickering 乳液的方法, 与 BS 的稳定性、功能性相结合, 为食品加工生产实现更实用和商业化的转化。

3.6 构建 4D 打印食品原材料

4D 打印是一种新兴附加制造技术, 具备 3D 打印传统方法的全部优势, 由 Tibbits 教授在 2013 年首次提出^[102]。如今, 4D 打印食品技术可能更具吸引力, 它可通过环境或人工刺激 (如温度、pH、水、紫外、光等) 的响应, 使 3D 打印对象 (第四维) 的状态随时间发生物理或化学变化^[103], 不仅增强 3D 打印食品的营养价值, 满足消费者饮食各异的偏好需求^[104], 还可定制功能营养食物维护健康和预防疾病^[105]。

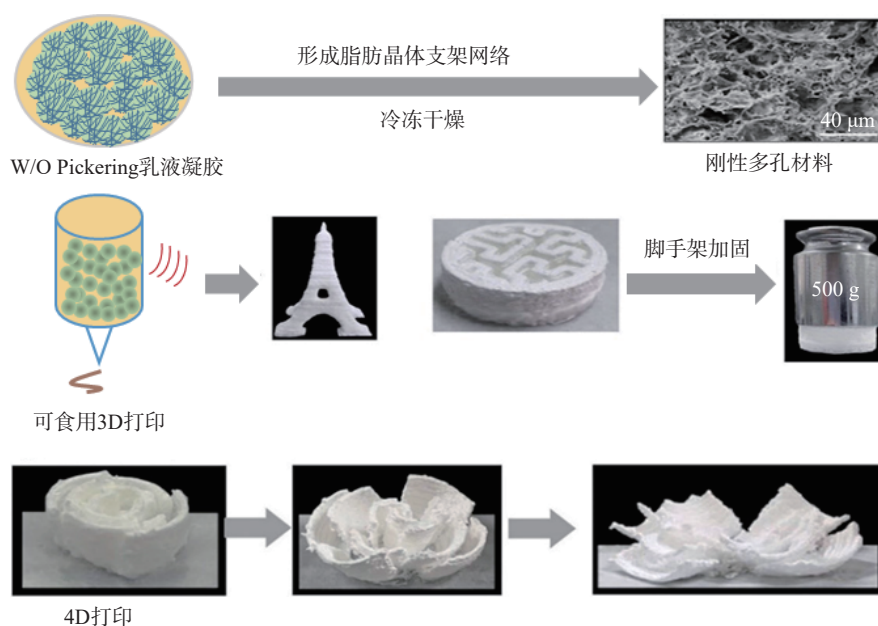


图 7 双支架网络调节 Pickering 乳液凝胶 4D 打印应用示意图^[107]

Fig.7 Schematic diagram of the Pickering emulsion gel 4D printing application with dual support network adjustment^[107]

Cen 等^[106]利用 pH 敏感的 Cur 制备 Pickering 乳液用于 4D 打印。当油相体积 65%, 复合物质量比 2:2, 浓度为 2% 时, 该乳液表现出强大的凝胶网络结构和高粘弹性, 满足 4D 打印的先决条件。加入 Cur 后, 通过温度刺激, pH 升高, 样品颜色的变化(黄色→红色)成功验证其 4D 打印性能。Jiang 等^[107]利用植物甾醇制备了具有双支架网络结构的 Pickering 乳液凝胶(如图 7 所示)。结果表明, 双支架网络分别由氢键和结晶形式构成。该乳液凝胶代替可可脂制备巧克力制品, 表现出的高粘弹性和低油含量成功为 4D 打印奠定基础。当热诱导目标底部时, 外壁逐渐熔化并掉落, 其形状的变化实现 4D 打印效果, 同时为加工低脂食品增添新的可能性。Li 等^[108]制备基于 β -环糊精的 HIPPEs, 用于实现 4D 打印的颜色转换。结果表明, 随着 β -环糊精浓度的增加, 小液滴紧密堆积, 乳液表现出更高的粘弹性和印刷性; 随着油相和水相分别加入 Cur 和 NaHCO_3 , 调节温度、时间、 NaHCO_3 浓度, 样品颜色从亮黄色转变为红棕色, 成功验证其 4D 打印性能。在目前的研究中, 3D 打印技术结合 Pickering 乳液制备的食品会受温度等环境因素影响无法轻易改变形状, 而 4D 打印结合 Pickering 乳液可以克服这种限制。随着时间的推移, 4D 打印技术通过对温度、湿度等变化做出响应, 根据消费者爱好需求改变食品感官特性, 带来不一样的用餐乐趣, 尤其对胃口不佳的儿童具有实际意义。

4 结论

Pickering 乳液作为一种新型乳液体系, 稳定性与固体颗粒、形状、浓度、表面电荷、湿润性、油相体积分数等因素密切相关, 为了控制这些因素, 进一步提高 Pickering 乳液稳定性, 经常利用多种因素协同稳定 Pickering 乳液的机制, 使其能够更稳定地存在于复杂的体系, 促进 Pickering 乳液在多方面领域的应用。

近年来, 消费者对健康养生的意识有所提高, 食品行业个性化营养需求强劲。Pickering 乳液在食品等方面的应用日益成熟, 其优良性能已被多项研究证实, 为精准营养、农残检测、绿色化学等领域的发展提供了更多可能。但因技术限制仍存在很多不足, 例如, 4D 打印食品加工时间长, 而随着 5D、6D 打印技术的发展或可弥补; 从乳液中递送营养物质的控释与保留还需深入探索, 尤其对特殊人群要避免引起不良反应, 应多评价其安全和有效性; MIPs 面对复杂的样品分析检测仍具挑战性, 应开发更多高选择性和高亲和力的分子印迹材料与 Pickering 乳液应用结合。总而言之, 未来应注重挖掘高新技术, 开发多种不同功能类型的 Pickering 乳液, 以期食品工业和其他相关领域实现多元化、商业化应用提供新思路。

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