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具有智能表面的工程混合材料可有效减轻石油源污染物

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摘要

受碳氢化合物污染的工业废水的产生及排放是一个重要的环境问题。污水以稳定的乳状液形式浮在水面,有时需要不同的技术来有效缓解或分离。原油乳状液和碳氢化合物污染的废水都含有悬浮固体、油/油脂、有机物、有毒元素、盐和难以处理的化学物质。一直以来,由于原油乳状液性质复杂及其产生大量的废物,如何适当处理原油乳状液是一大重要挑战。此外,从废物中回收石油将有助于满足人们对石油及其衍生物日益增长的需求。在此背景下,具有智能表面和可切换润湿性的功能性纳米结构材料因其在油水乳状液分离方面的优异性能而受到越来越多的关注。最近聚合物纳米结构材料在设计、组成、形态和微调方面的改进提高了其破乳功能。本文中,我们综述了受原油乳状液和碳氢化合物污染的废水流出物的环境影响。通过恰当的事例说明了受原油乳状液和碳氢化合物污染的废水流出物可以使用具有润湿性的智能聚合物纳米结构材料进行有效处理。本文举例讨论了油水乳状液有效分离的基本机制,并且探讨了智能材料的未来发展前景。

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1. 引言

乳状液是通常不混溶的两种或多种液体的混合物。然而,在某些情况下,乳化剂用于形成稳定的乳状液。油包水乳状液经久耐用,常用于石油工业[1]。由于其严重的环境后果和不利影响,来自石油工业的乳状液和被碳氢化合物污染的废水流出物是非常不受欢迎的。原油乳状液更危险,会在炼油厂操作中引起与腐蚀相关的问题。腐蚀问题也会给石油运输和工业石油产品的重加工造成困难[2]。

化学、物理和生物这三种方法通常用于分离油包水乳状液。这些技术的有效性取决于它们在发生分离之前降低乳状液稳定性的能力[3–5]。在石化工业中,乳状液首先经过分离处理,然后被送到炼油厂。化学表面活性剂是最常见的乳状液分离破乳剂[6]。油包水乳状液和水包油乳状液的显微照片示例如图1所示。在稳定的乳状液中,内相称为分散相,而外相称为连续相[7–8]。乳状液按液滴大小可分为:①微乳状液(10~100 nm);②细乳状液(20~1000 nm);③粗乳状液(0.5~1000 μm)。乳化剂、界

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面张力、体积特性和固体的存在等因素强烈影响乳状液液滴的大小[9]。然而，表面活性剂（如沥青质）的存在使乳状液在较长时间内保持动力学稳定[10]。由于乳状液电导率低和水滴尺寸小，合理开发且稳定的乳状液的结构既不取决于其合成也不随时间变化[11]。然而，乳状液的稳定性受到连续相和分散相的密度、黏度、表面活性剂和电解质浓度、水滴尺寸、界面张力和薄膜压缩性的强烈影响[10]。Bancroft法则决定了乳状液的稳定性，即乳化表面活性剂应溶于乳状液的连续相中。因此，如果表面活性剂显示出在分散相（水）中溶解的趋势，它将形成水包油乳状液。相反，如果表面活性剂在连续相（油）中显示出溶解性，则会形成油包水乳状液[12]。不幸的是，在原油勘探、加工和运输过程中会遇到两种乳状液（水包油或油包水）的形成。油水乳状液的这种普遍存在使基于乳状液的系统成为研究的重要课题。

具有成本效益的Janus、覆盆子和核壳状结构的磁性纳米复合材料已被广泛应用于乳状液分离[13–15]。油水分离过程与界面流变学改变密切相关，但其完整机制尚待阐明[16]。因此，阐明轻质原油乳状液破乳剂和碳氢化合物污染废水的油水分离机制及破乳剂的选择原则，对于化学表面活性剂的合理应用具有重要意义[6]。此外，这将为研究人员设计和开发具有疏水和亲水特性的新型两亲材料[17]和具有响应外部刺激的智能表面的聚合物提供基础[18]。不同的具有响应表面的材料已经被制备出来，它们不仅可以响应温度、pH值和紫外线（UV），而且对湿度也有响应[19–20]。这些具有刺激响应表面的智能材料在各种应用中表现出优异的性能，如油水混合物的分离[21]、药物输送[22]、生物传感器[23]和组织工程[24]。

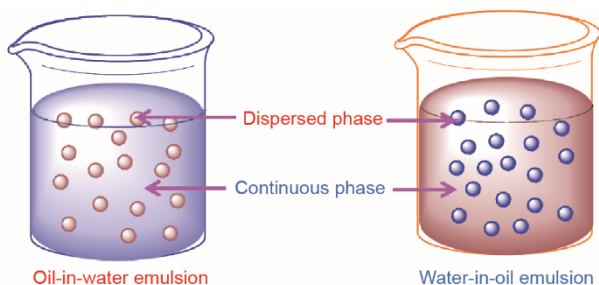


图1. 油包水乳状液和水包油乳状液的显微照片。

具有智能界面和超润湿性的材料的应用是一个新兴的研究方向[25]。具有切换润湿性的材料更适用于油水分离，可以除油（疏水/亲油）或除水（亲水/疏油）。由于其优异的分选效率和可回收性，具有智能润湿表面的材料优于用于处理碳氢化合物污染废水和分离油水乳状液的传

统分离材料。智能表面被定义为具有以下多功能特征的任何材料表面：①能够重新排列其形态；②能够保留其组成；③能够响应反应环境的变化而自我增强其功能。值得注意的是，独特的可切换润湿性在“除水”和“除油”实践中均有效。已经证明，根据外部条件改变其响应的刺激响应聚合物材料，可以有效地用于各种应用，包括水净化（如去除石油污染物、重金属离子和蛋白质生物污垢）[26–30]。刺激响应聚合物因其反应性和优异的加工性能而成为设计和制造具有独特表面和可切换润湿性的材料的有力候选对象。

本文总结了乳状液体系、乳状液对环境的影响，以及具有智能表面的聚合物混合材料在有效分离油水乳状液中的应用。通过以下部分概述了聚合物工程的新兴领域：①乳状液体系；②乳状液分离的背景；③油水分离的传统方法；④具有智能表面和切换润湿性的刺激响应聚合物和杂化材料，以及它们在油水分离中的应用；⑤不同纳米材料在可控油水分离中的应用比较。最后，本文对智能表面聚合物在油水分离中的应用进行了展望。

2. 油乳状液对环境的影响

原油和含碳氢化合物废水对环境具有严重影响，这主要取决于其生产工艺。此外，乳状液和废水受控或不受控地排放到许多水基质中也会造成环境危害。

2.1. 漏油对环境的影响

已经提出了几种机制来解释石油泄漏如何对环境造成危害，包括：

- (1) 由于摄入或吸入芳香族和脂肪族成分引起的刺激；
- (2) 油性产品表面的涂层；
- (3) 因细菌降解油分而引起的氧气消耗；
- (4) 由于细菌降解导致海产品中碳含量增加。

由于微生物通过吸收阳光的能量（光氧化）进行代谢，油主要因乳化作用而扩散到外部环境，形成稳定的乳状液、溶解、沉淀和化学氧化[29,31–34]。原油/轻质石油具有挥发性，含有许多水溶性化合物和漂浮物，并且可以在陆地或水面上迅速扩散。因此，新鲜油会造成更严重的环境影响，因为新鲜油中的碳氢化合物很容易被摄入、吸收和吸入[31,33]。

油的成分随时间不断变化，这可能会留下少量固体、不溶性残渣（称为焦油球），这些残渣中含有有毒的多环芳烃（PAH），对环境产生剧毒影响[33]。在这个风化过

程中, 重油与水混合形成稳定的乳状液, 相对来说更耐分离并能够减缓风化过程[33,35]。此外, 乳状液或乳化油更难以通过简单的分散、脱脂或刺激去除。重油和水乳状液在环境中停留的时间更长, 降解缓慢[33]。必须强调的是, 新的石油泄漏会导致大量饱和和以及有反应活性的芳烃出现在溶解相和油相中[36]。

2.2. 对海洋环境的影响

在直接接触时, 不同浓度的化学物质会对生命产生影响。油乳状液由于其油和水含量以及乳状液密度对环境具有严重影响。毫无疑问, 石油和石油乳状液主要是人为生产的, 对全球经济具有重要作用[37]。油乳状液或受碳氢化合物污染的油水不受控制地释放到外部环境中, 成为对海洋生物和陆地生态系统(如河口、沿海和深海系统)的威胁[38]。在海上, 除非原油被化学物质有效地渗透到整个水体中, 否则损害仅限于表面环境[32,34,39]。由于溶解的有毒成分会严重污染水生环境, 原油和碳氢化合物污染的废水会对沿海草地造成严重损害(图2)。

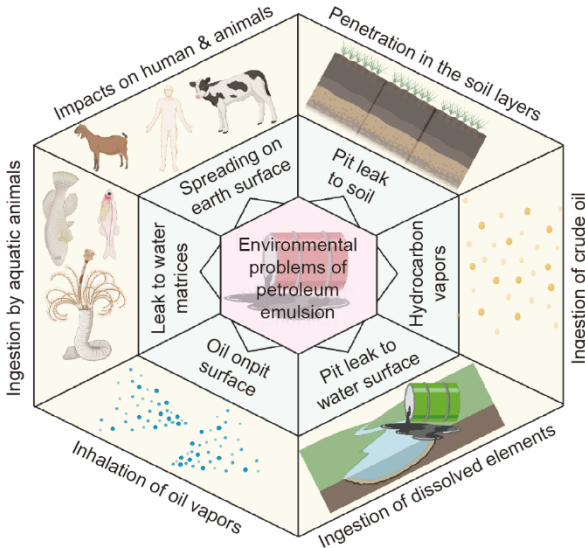


图2. 原油乳状液的环境影响。使用BioRender (<https://biorender.com/>)模板创建并根据高级订阅条款导出。

3. 乳状液分离的背景

3.1. 液态空气润湿性

油包水乳状液的分离是一种润湿行为, 是通过将液体涂覆在固体表面上而发生的。润湿性是固体表面的固有特性, 通常以液滴的接触角(CA)为特征。在光滑理想表面上的空气中, 液体平衡CA(θ)使用杨氏方程[式(1)][40]计算:

$$\cos\theta = (\gamma_{SV} - \gamma_{SL})/\gamma_{LV} \quad (1)$$

式中, γ_{SL} 、 γ_{SV} 和 γ_{LV} 分别代表固-液、固-气和液-气界面的界面张力[图3(a)]。当表面随着时间变得粗糙时, 会通过均质或异质状态发生润湿。通常, 液体在均质状态润湿的情况下会覆盖表面上的所有空隙[图3(b)], 并且可以使用Wenzel方程计算CA(θ_w) [41]:

$$\cos\theta_w = r\cos\theta \quad (2)$$

式中, r 表示表面粗糙度因子, 即实际表面积与其水平投影面积的比值。 r 的值总是大于1。因此, 表面粗糙度的增加直接放大了固体表面的润湿性, 使亲液和疏液表面变得更加疏液和亲液。如果 $r \gg 1$, 则润湿性高, 即 $\theta_w > 150^\circ$ 对应于超疏液表面, $\theta_w \approx 0^\circ$ 对应于超亲液表面。固体/空气异质界面通常由液滴下方的滞留空气形成[图3(c)], 在这种情况下, 使用Cassie-Baxter方程计算CA(θ_{CB}) [42]:

$$\theta_{CB} = f_{SL}\cos\theta + (1 - f_{SL})\cos\pi = f_{SL}\cos\theta + f_{SL} - 1 \quad (3)$$

式中, f_{SL} 是固/液界面的比例。根据Cassie状态, 当空气层被困在液滴下方时, CA会很高, 这可用于制造超疏液表面[43-44]。

3.2. 水下油润湿性

油润湿主要发生在水中的固体表面, 与油水乳状液的分离有关[25]。在光滑的表面上, 油滴形成三相界面, 即油-水-油[图3(d)], 相应的表观油接触角(OCA)(θ_{OW})满足杨氏水下方程:

$$\cos\theta_{OW} = (\gamma_{SW} - \gamma_{SO})/\gamma_{OW} \quad (4)$$

式中, γ_{SO} 、 γ_{SW} 和 γ_{OW} 分别是固-油、固-水和油-水界面的界面张力。空气中的杨氏润湿状态对非常光滑的表面上的油滴[45]和水滴[40]也有效, 空气中相应的水接触角(WCA, θ_{WA})和OCA(θ_{OA})可用杨氏油方程描述:

$$\cos\theta_{OA} = (\gamma_{SA} - \gamma_{SO})/\gamma_{OA} \quad (5)$$

$$\cos\theta_{WA} = (\gamma_{SA} - \gamma_{SW})/\gamma_{WA} \quad (6)$$

式中, γ_{OA} 、 γ_{SO} 、 γ_{SA} 和 γ_{WA} 分别是油-气、固-油、固-气和气-水界面的界面张力。因此 $\gamma_{SO} = \gamma_{SA} - \gamma_{OA}\cos\theta_O$ 和 $\gamma_{SW} = \gamma_{SA} - \gamma_{WA}\cos\theta_W$ 是从式(5)和式(6)进行数学转换而来的。因此, 通过代入 γ_{SW} 和 γ_{SO} 的值, 式(4)可以进一步改写为式(7):

$$\cos\theta_{OW} = (\gamma_{OA}\cos\theta_O - \gamma_{WA}\cos\theta_W)/\gamma_{OW} \quad (7)$$

空气中的亲水表面和部分空气中的疏水表面表现出完全的水下疏油性。随着粗糙度和异质界面(即固体/水异质界面)的引入, 可以实现水下Wenzel[图3(e)]和Cassie[图3(f)]状态。Wenzel[式(8)]和Cassie[式(9)]状态可以用水中相应的可能OCA、 θ_w^* 和 θ_{CB}^* 来描述:

$$\cos\theta_w^* = r\cos\theta_{OW} \quad (8)$$

$\cos\theta_{CB}^* = f_{SO}\cos\theta_{OW} + (1 - f_{SO})\cos\pi = f_{SO}\cos\theta_{OW} + f_{SO} - 1$ (9)
 式中, f_{SO} 是固体/油界面局部区域的函数。与空气情况类似, 由于油滴下方的水层(拒油), Cassie水下润湿状态允许制造具有低油黏附性的水下疏油表面。

4. 高分子材料的制备及油水分离技术的应用

可用于分离油水混合物的杂化材料种类丰富。然而, 这些材料在用于油水分离或用于去除废水中的碳氢化合物污染时, 大多面临着不相容和吸收效率低等问题。因此, 一些很有前景的智能表面材料, 如磁性材料[13–15,46]、纤维素基材料[47]、石墨烯或氧化石墨烯[48]、金属和金属氧化物网格[49]、高分子材料[50], 已经被开发出来, 并且其具有优良的润湿性。特别是具有疏水性、亲水性或两亲性的智能表面材料可能具有更高效的油水分离性能[29,51]。此外, 一些树脂基氢化物材料在吸油、阻油和可重复使用方面具有良好的特性[52]。

4.1. 用于油水分离的膜基材料

化学结构和表面形态都影响了制备的混合材料, 如膜和纤维基材料的分离效率。纤维基膜是最重要的分离膜。近年来, 各种具有不同化学结构和形态的膜, 如棉纤维[51]、纤维素纤维、金属丝[53]、碳纤维[54]、静电纺丝制备的纤维基材料[55]、碳纳米管[56]和金属氧化物(二氧化锰)线材[57], 已被开发出来, 并且其具有优良的油水分离性。许多交联纤维具有相互连接的孔隙结构, 可用于设计和构建不同的膜。油水混合物的有效分离取决于孔隙大小, 可根据具体要求进行调整。尤其是, 大孔隙能有效提高流速, 使油水完全分离。孔隙尺寸可根据油水混合物分离的具体要求进行调整。为了提高分离效率和流速, 具

有大孔隙的膜更加可取。木材的分层结构包含了很多层, 是构建多层膜的一个很好的例子。Song等[58]使用了一种逐层组装的方法, 在浆液中一个独特的通道构建了木质层。该浆液通过将无机矿物聚合物微粒(GP)掺杂到海藻酸钠(SA)基质中制备而成。然后, 利用壳聚糖(CS)将韧皮部层转化为一种复杂且致密的形式。所制备的多层仿生膜存在于独特明确的工程结构中, 并在去除油水混合物中的碳氢化合物和其他污染物方面表现优异[58]。图4中描述了将GP掺杂到仿生异质多层膜(GHMM)的构建过程, 以及GP和GP-SA浆液的制备[58]。

通过三甲氧(十八烷基)硅烷和羟基的单步溶胶-凝胶反应, 将聚乙烯醇(PVA)和硅酸钠(Na_2SiO_3)放入水溶液中制备大孔材料[59]。为完全分离油水, 将表面能低的物质接枝到大孔材料上用来制备具有超疏水性的三维大孔膜。这里, Na_2SiO_3 是一种环保、低成本且易于生产的交联剂。此外, 依据溶胶-凝胶反应, 用表面能低的物质通过强硅-氧键来制备材料, 制备好的多孔材料(PVA/ Na_2SiO_3)显示出良好的油水分离性能[59]。通过在非常恶劣的条件下对聚乙烯(PE)粉末进行挤压、刮擦和刺破, 制备了聚乙烯网, 该网也显示出良好的油水分离性能。所制备的聚乙烯网还表现出超低水黏合性、超疏水性和超疏油性, 它能够允许油通过网的同时留住水, 使油水乳化剂变得不稳定。该操作经过多个周期依然有效, 即使浸泡在强酸性或碱性溶液中, 网片也仍然保持有效[60]。此外, 还开发了一种新型的水辅助和热冲击方法, 用来设计和制备一种具有显著油水分离性能的无表层超疏水聚乳酸(PLA)泡沫材料。在不同的水含量下制备了微纳米结构可控的PLA泡沫塑料。为了进一步提高材料表面的疏水性, 提出了一种新型环保的剥离技术来去除泡沫的光滑表

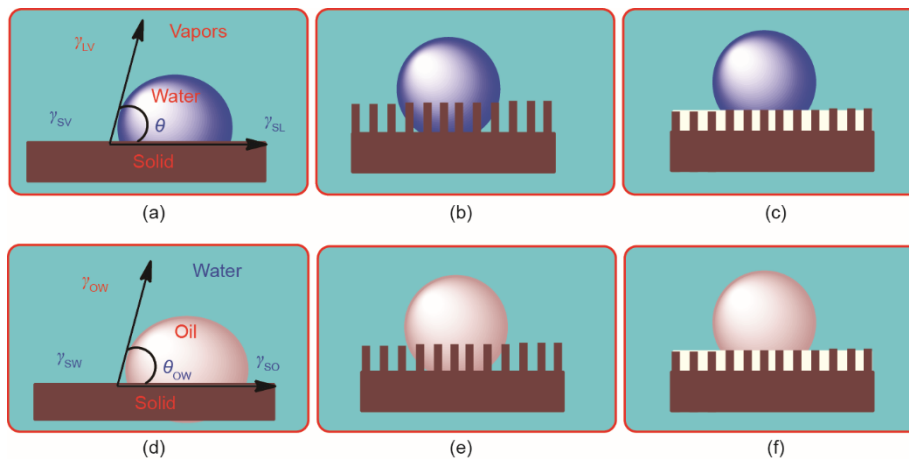


图3. 空气(蒸汽)中不同粗糙度的固体表面液滴润湿状态: (a) Young, (b) Wenzel, (c) Cassie状态; 各种水下固体表面上油滴的润湿状态: (d) 水下Young, (e) 水下Wenzel, (f) 水下Cassie状态。

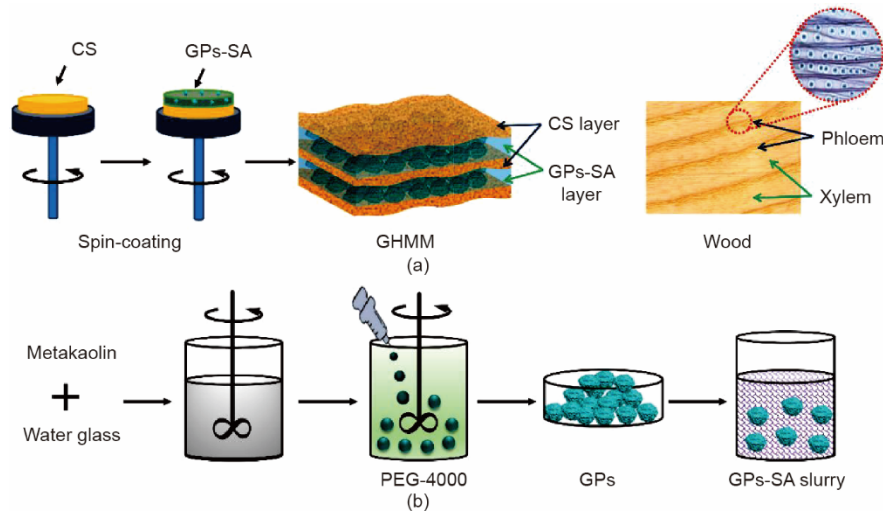


图4. 图中描述了GHMM的构建 (a) 和GP和GP-SA浆液的制备 (b)。这个主题灵感来自于木材的层次结构。经美国化学学会许可，转载自参考文献[58]，©2020。PEG: 聚乙二醇。

层，从而获得良好的油水分离性能[61]。

4.2. 用于油水分离的聚合杂化材料

具有智能表面的聚合材料由于其简便的制造工艺，以及表面润湿的可切换性和刺激响应特性，是控制油水分离的合适候选材料。特别是，其具有刺激响应特性这一优点，允许与表面能或链构象相关的化学成分根据要求进行

切换，例如，在设计直接调整成高活性的多孔材料（即吸收性材料或纤维过滤膜）的共聚物时。根据具体应用，设计、合成和测试了许多具有智能表面、刺激响应特性和高润湿性的高分子材料，以实现油水乳状液的可控和高效分离。表1总结了聚合物基复合材料的最新进展，这些材料由不同尺寸、形状和表面形态的聚合物或聚合物/无机混合物制成，用于油水分离[60–114]。

表1 用于油水分离的高分子混合纳米材料的制造技术研究进展

Material type	Components	Wettability	Fabrication technique	Emulsion type	Separation (%)	Reference
Membrane hybrid material	Poly(dodecylmethacrylate-3-trimethoxysilyl propyl-methacrylate-2-dimethyl amino ethyl methacrylate) (PDMA-PTMSPMA-PDMAEMA)/SiO ₂	Superhydrophilic/superhydrophobic	<i>In situ</i> and <i>ex situ</i> treatment	gasoline/water	98	[62]
	Polytetrafluoroethylene	Superhydrophobic/superoleophilic	Self-assembly coating/sintering process	Decane/water, gasoline/water	98	[63]
	Poly(sulfobetaine methacrylate) (PSBMA)	Superhydrophilic/underwater superoleophobic	Coating/surface-initiated atom transfer radical polymerization (SI-ATRP)	Hexadecane/water	–	[64]
	Poly(dimethylamino)ethyl methacrylate-4-vinyl benzyl chloride (P(DMAEMA-VBC))	Superhydrophilic in air/superoleophobic	Vapor phase via initiated chemical vapor deposition (iCVD)	–	99.8	[65]
	Poly(acrylamide-co-acrylic acid)/chitosan/methacryloxy propyl trimethoxyl silane modified SiO ₂ (P(AA)/CS/MPS-SiO ₂)	Underwater superoleophobic	Free-radical polymerization	<i>n</i> -Hexane/water	99.5	[66]
Meshes hybrid material	Silica nanoparticles and decanoic acid-modified TiO ₂	Superhydrophobic	Coating	<i>n</i> -Hexane/water	99	[67]
	Fibrous, isotropically bonded elastic reconstructed (FIBER) aerogels/SiO ₂	Superhydrophobic/superoleophilic	Electrospun nanofibers and freeze-shaping	–	–	[68]
	Styrene-acrylonitrile (SAN) nonwoven/NaOH	Superhydrophilic/superoleophobic	Controlled electro spinning/thermal treatment	Light oil/water	99.99	[69]

Material type	Components	Wettability	Fabrication technique	Emulsion type	Separation (%)	Reference
	Polydopamine (PDA)/stainless steel	Hydrophobic	Coating/mussel-inspired/ Michael addition reaction	Diesel/water	99.95	[70]
	PDA and polyethylene polyamine/copper (Cu) mesh	Superhydrophobic	–	Octane/water	99.8	[71]
	1,8-triethylene glycoldiyl-3,3'-divinylimidazolium dibromide ([DVIIm-(EG) ₃]Br ₂)	Hydrophilicity/ oleophobic	One-step photopolymerization	Diesel/water, crude oil/water	99.9	[72]
	Dimethylamino ethyl methacrylate (DMAEMA)/stainless steel	Superhydrophilic/ underwater oleophobic	Photoinitiated free radical polymerization	Gasoline/water		[73]
	Calcium alginate-coated (Ca-Alg) mesh	Superhydrophilic/ underwater oleophobic	Fabrication	Hexane/water, toluene/water	99.6	[74]
	Ag-coated stainless steel mesh	Superhydrophobic/ superoleophilic	Fabrication/coating	kerosene/water, hexane/water, heptane/water	98	[75]
	Magnesium stearate (M-S)	Superhydrophobic	Fabrication/substrates + adhesive + coating method	<i>n</i> -Hexane/water, toluene/water	96	[76]
	Polyvinyl butyral (PVB)/stainless steel	Hydrophobic/oleophilic	Electrospinning approach	Layered oil/water	99.7	[77]
	Stainless steel mesh	Superhydrophobic	Fabrication	Hexadecane/water	96	[78]
	ZnO nanowire (NW) coated stainless steel mesh	Hydrophilic/ underwater oleophobic	Chemical vapor deposition/coating	Diesel/water, Hexane/water	99.5	[79]
Sponge	Polypyrrole (PPy) coated polyurethane sponges	Superhydrophobic	Fabrication	Motor oil/water	–	[80]
hybrid material	Poly(2-vinylpyridine- <i>b</i> -dimethylsiloxane) (P ₂ VP-PDMS), melamine sponge/dopamine, Melamine, Span 80 (C ₂₄ H ₄₄ O ₆), diacrylate ester	Superoleophilic/ superoleophobic	Oxidative self-polymerization	–	99	[81]
	Polyurethane (PU)	Superhydrophobic	Fabrication/coating	Water/isooctane	99.98	[82]
	Melamine, polydimethylsiloxane (PDMS)/silicone	Superhydrophobic/ oleophilic	Fabrication/interfacial polymerization	Diesel oil/water	–	[83]
	Melamine, isocyanate-terminated poly(dimethylsiloxane) (iPD)	Superhydrophobic	UV-assisted thiol-ene click reactions	Chloroform/water	–	[84]
	Melamine, isocyanate-terminated poly(dimethylsiloxane) (iPD)	Superhydrophobic	Fabrication	Hexane/water, hexadecane/water, toluene/water	85.1–98.7	[85]
	Poly(vinylidene fluoride), poly(vinylidene fluoride-trifluoro ethylene-terchloro trifluoroethylene), polystyrene/polyurethane/fluoroalkylsilane modified SiO ₂	Superhydrophobic	Drop-coating method	Peanut oil/water	–	[86]
	Poly(<i>N</i> -isopropyl acrylamide) (PNIPAAm)	Superhydrophilic/ superhydrophobic	Interface-initiated atom transfer radical polymerization	Gasoline/water, hexadecane/water	70	[87]
	PU sponge	Superhydrophobic/ superoleophilic	Fabrication	Chloroform/water	75	[88]
	Clay dust/polydimethylsiloxane (PDMS)	Superhydrophobic/ superoleophilic		Kerosene/water	98	[89]

Material type	Components	Wettability	Fabrication technique	Emulsion type	Separation (%)	Reference
	PU sponges/ PDMS	Superhydrophilic/ superhydrophobic/ hydrophilic	Fabrication/simple dip- ping-coating method	Hexadecane/ water, decane/ water	99	[90]
Polymer based hybrids materials	DA/glass wool PDMS	Superhydrophobic	Polymerization/fabrica- tion	Toluene, <i>n</i> -hex- ane/water	97	[91]
	Polyethylene	Superhydrophobic	Pressing, scratching, and pricking	<i>n</i> -Hexane/water	99.5	[60]
	Poly(lactic acid)	Superhydrophobic	Template-free water-as- sisted thermally impact- ed phase separation ap- proach with skin peeling	Dioxin/water	98	[61]
	Polystyrene	Amphiphilic	Emulsion polymerization	Chlorobenzene/ water	70	[92]
	Poly cardanol	Amphiphilic	Polymerization	Asphaltene/wa - ter	-	[93]
	Poly(2, 2, 3, 4, 4, 4-hexafluorobutyl meth acrylate)-poly (<i>N</i> -isopropylacrylamide)	Superoleophilic/ hydrophilic	Atom-transfer radical po- lymerization (ATRP)	water/heptane, 98 water/ <i>n</i> -octane, water/petro - leum ether	[94]	
	Vinyl-terminated PDMS copper sulfate (CuSO ₄)/steel	Hydrophobic	Fabrication/electro-less replacement deposition	Hexane/water, 96.8 chloroform/wa - ter	[95]	
	Poly(ether amine) (PEA)-PDA	Superamphiphobic	Fabrication/self-polym- erization	Toluene/water, - octane/water	[96]	
	2-hydroxy-4-methoxy benzophenone (HMB), bisphenol A (BPA), bisphenol AF, 3-(hydroxysilyl)-1-propane sulfonic acid (THSP), and perfluoro-2-methyl-3-oxa- hexanoic acid (RF/COOH) SiO ₂ Talc	Oleophobic/super- hydrophobic	Coating/encapsulation	Span 80/water	-	[97]
	Polysulfone (PSF)	Hydrophobic/su - peroleophilic	Water-in-oil-in-water emulsion solvent evapo- ration	Motor oil/water	[98]	
	Polyhemiaminal (PHA) aerogel	Hydrophobic	One-step precipitation- polymerization	Gasoline/water	90	[99]
	Thiol-acrylate resins, 2-carboxyethyl acrylate, poly(eth- yl glycol) diacrylate/SiO ₂ nanoparticles	Superhydrophilic/ superoleophobic	Thiol-acrylate photo-po- lymerization	Hexadecane/ water	99.9	[100]
	Polyelectrolyte-fluorosurfactant	Oleophobic/hydro- philic	Single-step polymeriza- tion	Hexadecane/ water	98	[101]
	Polyurethane	Superhydrophobic/ underwater oleo- phobic	Fabrication/coating	Hexane/water, - <i>n</i> -hexadecane/ water	[102]	
Fluoropolymers modified Kaolin nanoparticles	Superhydrophilic/ superoleophobic	Fabrication	Glycerol/water, 92 sunflower oil/ water, castor oil/water	[103]		
Cationic polyethyleneimine		Polymerization	Heavy oil/water	[104]		

Material type	Components	Wettability	Fabrication technique	Emulsion type	Separation (%)	Reference
	PU grafted of carbon nanofiber (CNF)	Hydrophobic/superoleophilic	- Dip coating	Hexane/water, heptane/water, octane/water,	97.8, 99.8, 95.0, 96.3	[105]
	Chromium (Cr), a zirconium (IV) metal-organic framework composed of six-metal clusters and terephthalic acid ligands (UiO-66), octadecylamine (OA), metal-organic framework	Superhydrophobic/superoleophilic	-	Toluene/water, hexane/water	99.9	[106]
Natural and wood based hybrids	Wood sheet	Underwater oleophobic	Simple drilling process	Hexadecane/heptane/water	-	[107]
	Wood/epoxy biocomposites	Hydrophobic/oleophilic	Fabrication/coating	Diesel oil/water, hexane/water	-	[108]
	Chitosan-coated mesh	Hydrophilic in air/superoleophobic in water	Coating	Hexane/water, gasoline/water, crude oil/water	99	[109]
	Chitin/halloysite nanotubes	Hydrophobic	Freezing/thawing	Hexane/water, toluene/water	98.7	[110]
Inorganic salt based hybrid materials	-	-	One-step Mannich-like reaction	Crude oil/water	97.8	[111]
	Cu(OH) ₂ nanowires	Hydrophilic/superoleophobic	Fabrication	Diesel/water	98.5	[112]
	Aluminum (Al)/ZnCl ₂ , α -Al ₂ O ₃ /lauric acid (C ₁₁ H ₂₃ COOH)	Hydrophobic/underwater oleophilic	- Coating and electro-chemical deposition	Hexane/water, petroleum ether/water	98	[113]
	Calcium sulfate hemihydrate (CaSO ₄ ·5H ₂ O)	-	-	Water/trans former oil	- 99.85	[114]

Li等[115]设计了一种可测试pH值的聚二甲基硅氧烷(PDMS)嵌块聚(4-乙烯基吡啶)(P4VP)材料, 该材料具有可切换pH值的油/水润湿性, 并通过改变pH值和施加重力驱动力从水/油层中有效分离油或水。由于吡啶基的质子化和去质子化, 含P4VP的嵌段共聚物膜的润湿性随着所接触pH值的变化而明显变化。该嵌块(PDMS)聚合物具有固有的疏水性和水下亲油性, 由于其无毒、灵活性高、热稳定性强, 被强烈推荐用于制造具有特殊润湿性能的表面, 以用于分离油/水混合物[115-118]。

此外, 从水中分离油水混合物和其他污染物也取得了进展[71]。用多乙烯多胺和聚多巴胺(PDA)共沉积膜成功制备了具有不同结构和孔径的基片。在Tris存在的情况下, 多巴胺的自聚合使有机和无机基片的表面形成了良好的黏合膜[119]。富含氨基的聚合物聚乙烯多胺(PEPA)具有高度亲水性, 成本低且很容易获得, 它可以与多巴胺产生席夫碱反应或在胺和儿茶酚之间产生Michael加成反应[120-121]。图5阐述了PDA/PEPA改性材料的制备方案及其在油水乳状液分离、吸附甲基蓝和Cu²⁺中的应用

[71]。所生成的杂化材料具有超亲水性和水下超疏油性。利用这些涂层材料仅一步就可以有效分离各种油水乳状液, 包括表面活性剂稳定的乳状液和不混溶的油水乳状液。该材料的分离效率大于99.6%, 对甲基蓝、Cu²⁺等污染物通过率较高, 这些污染物可以通过吸附有效地从水溶液中去。在大规模制备产品时, 可以用该设计方法制备不同的有机和无机基质。

在通过化学气相沉降(iCVD)制备各种气相交联离子聚合物(CIP)的单步合成程序中取得进展是一个转折点。在设计过程中, 将单体2-(二甲基氨基)甲基丙烯酸乙基(DMAEMA)和4-氯乙烯(VBC)在气相中添加到iCVD反应器中, 让它们生成共聚物膜。在沉积过程中, DMAEMA中的三胺和VBC中的苯基氯进行亲核取代反应, 产生离子氯化铵络合物, 形成具有高度交联结构的聚(DMAEMA-co-VBC)离子嵌段共聚物膜。这是第一个关于在气相中设计和制备具有大表面积和可控厚度的CIP膜的研究报告。所设计的方法不需要任何额外的交联剂。新设计的CIP薄膜具有较强的亲水性, 可进一步应用于油水

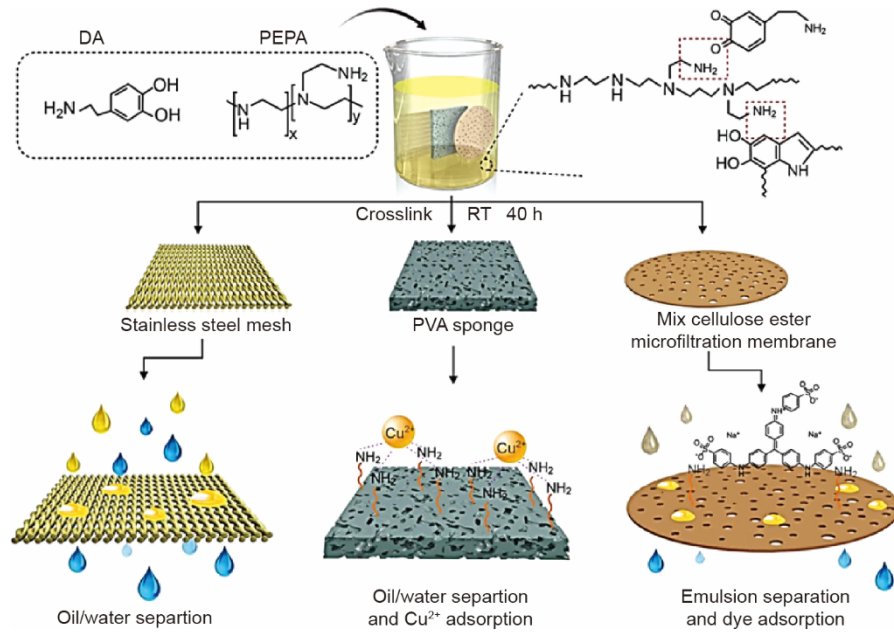


图5. 制备 PDA/PEPA 改性材料的工艺示意图及油水分离和吸附 Cu^{2+} 和甲基蓝的过程。RT: 室温。经美国化学学会许可, 转载自参考文献[71], © 2016。

乳状液的分离[65]。

高达 99.8% [122]。

4.3. 用于油水分离的金属和金属氧化物筛网

能制备一种设计良好的经碱溶液处理的防油无纺布网非常鼓舞人心。通过控制对苯乙烯-丙烯腈 (SAN) 共聚物进行静电纺丝, 然后在碱溶液中进行热处理, 使其获得了可切换 pH 值的润湿性。所制备的灵活且坚固的可切换 pH 值的防油网, 有着良好的设计和三维多孔几何结构, 在空气中具有超亲水性和超疏油性能。由于具有良好的抗油特性, pH 值可切换的表面仅用重力驱动力就可长期分离不混溶的轻油和水乳状液, 并且在重复使用期间不会积累任何有害物质[69]。防油网还显示出可调节的特性, 可从简单乙醇介质中的混合物中去除可溶性污染物。经氢氧化钠处理后的网片在高水流速 ($13\ 700\ \text{L}\cdot\text{s}^{-1}\cdot\text{m}^{-2}$) 的情况下对轻油的去除率 (99.99%) 很高。由于具有独特的多孔无纺布结构以及存在较高的 pH 值响应剂, 该网也表现出良好的回收稳定性。原位热聚合 (ISTP) 方法在一步制造超疏水杂化材料时可能很有用, 即所谓的“一锅”合成方法。具体来说, 制备 *N,N*-二甲基十二烷基 (4-乙烯基苄基) 氯化铵 (DDVAC) 并将其作为离子液体 (IL) 前驱体, 通过 ISTP 分别在空气和氮气中成功制备了两种聚合物 DDVAC-O (在空气环境下制备) 和 DDVAC-N (在氮气环境下制备)。系统地分析了 DDVAC-O 的成功合成机制。用 DDVAC-OCC 制备了一种超疏水不锈钢网 (SSM) (图 6) [122], 通过包裹二氧化硅纳米粒子生成微/纳米分层表面结构, 所制备的 SSM 在油水分离中效率

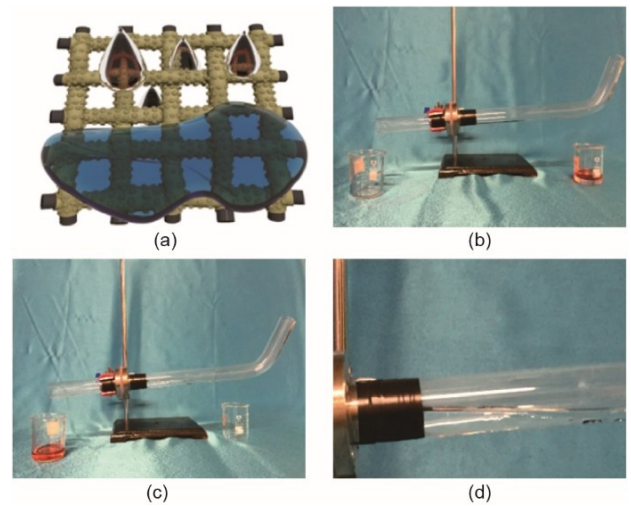


图6. 所获得的 SSM-O 油水分离过程。(a) 示意图说明; (b) 分离前将网固定在两个不锈钢凸缘之间; (c) 正辛烷 (红油染色) 和水的混合物倒入上玻璃管, 分离后正辛烷通过网; (d) 放大的图片显示分离后上部玻璃中仍有水而没有油。经美国化学学会许可, 转载自参考文献[122], ©2017。

采用连续光原子转移自由基聚合法合成了热响应性嵌段共聚物——聚 (2,2,3,4,4,4-甲基丙烯酸丁酯) 嵌段聚 (*N*-异丙基丙烯酰胺) (PHFBMA-PNIPAAm)。下一步, 将制备的共聚物直接涂在 SSM 的表面, 用于可控温度下的油水分离[94]。由于表面温度、化学成分、粗糙度和官能团的取向的综合作用, 所制备的网的表面可以在疏水性和亲水性之间切换。在最后一步, 为了了解分离机制, 我

们设计了一种坚固的材料来破乳化油水乳状液,结果显示在高渗透通量(正己烷 $2.78\text{ L}\cdot\text{s}^{-1}\cdot\text{m}^{-2}$ 和水 $2.50\text{ L}\cdot\text{s}^{-1}\cdot\text{m}^{-2}$)下正己烷与水的分离效率为98%。由于不同污染物对环境来说都危害严重,因此制备双功能材料如聚(乙胺)(PEA)-PDA修饰的双功能过滤材料很重要,用以分离油水乳状液和吸附污染物,如阴离子偶氮染料[96]。PEA和PDA通过Michael加成反应在聚氨酯海绵底物上进行聚合。PEA具有较强的亲水性,被用作吸附染料理想聚合物[123]。聚氨酯海绵因成本低廉且具有多孔三维结构被选作底物,其可增强聚合物涂层的润湿性[124]。所制备的杂化材料具有超亲水性和水下超疏油性能。吸附后,材料被压缩在玻璃容器中,制备的材料可在高通量的各种油水乳状液进行有效油水分离。此外,经PEA-PDA修饰的双功能过滤材料能有效地吸附大量有害的偶氮染料。简单和可扩展的策略已被报道用于制造表现出空气超疏油性和超亲水性的润湿性表面。利用硫酯丙烯酸树脂的喷射沉积和光聚合反应来制备具有疏油性和亲水性化学部分的纳米颗粒[100]。利用二氧化硅纳米颗粒、2-羧基丙烯酸乙酯和聚(乙二醇)二丙烯酸酯,有效地构建了界面上的亲水性来源。同时,经1*H*,1*H*-全氟-*n*-十烷基修饰的多功能硫醇成功地用于赋予界面疏油性能[100],随后制备了各种多孔底物并用于扰乱油水乳状液。0.45 μm 的尼龙膜支架同时具有超亲水性和超疏油性能,达到 $699\text{ L}\cdot\text{s}^{-1}\cdot\text{m}^{-2}$ 渗透量和99.9%分离效率[100]。

通过将分子自组装和界面聚合相结合,发现了一种具有超疏水性的聚氨酯海绵,它在分离柴油和水的乳状液中非常有用。聚氨酯海绵在空气中具有超亲脂性、超润湿性,在油和空气中均具有超疏水性,可有效、选择性地分离不同种类的油,所分离的重量能达到其自身重量的29.9倍左右[83]。选择乙氧基化的聚乙烯亚胺(PEI)作为水相单体,油相单体为1,3,5-苯三甲酰氯(1,3,5-benzenetricarbonyl trichloride)。根据界面聚合所形成的厚膜, Al_2O_3 纳米颗粒迅速沉积在聚氨酯海绵骨架上,形成荷叶状层次结构[26]。与此同时,PEI为棕榈酸的自组装提供了一个平台,其通过脱水剂[*N,N'*-二环己基碳二亚胺(*N,N'*-dicyclohexyl carbodiimide)]和酰胺催化剂[4-二甲氨基吡啶(4-dimethyl aminopyridine)]的介导反应进行。由于1,3,5-苯三甲酰氯可以与原聚氨酯海绵的仲胺和所制备的薄膜快速反应,反应得到的膜能通过共价键牢固地支撑在海绵表面,这提高了材料的持久性和稳定性[125]。与其他发表的实验相比,所制备的聚氨酯海绵在分离油水乳状液中表现出良好的吸油性和的可重复使用性(>500次循环),而不失去其弹性和超疏水性[126-127]。

5. 乳状液的破乳、生态毒性,并升级到工业水平

目前有多种破乳技术,包括化学法、电法、热法和膜过滤法,本文对这些技术进行了简要的综述。在化学方法中,各种化学物质(化学混合物)具有不同的润湿特性,如脂肪酸、酸、碱、醇、丙酮、胺和丙烯的共聚物和环氧乙烷[29,128]。具有不同润湿性的化学物质,即超疏水性、超亲水性或可切换润湿性,可以移动到油或水界面,并将亲水和疏水部分分别朝向水和油[129]。影响化学破乳剂性能的因素包括乳状液稳定性、温度、破乳剂结构、水相的pH值和含盐量以及搅拌速度。一些影响破乳剂性能的重要考量因素是:①破乳剂的结构;②在大部分乳状液中分散的能力;③搅拌速度;④在界面相之间的分区特性;⑤环境温度;⑥乳状液的稳定性;⑦水相的pH值和含盐量[29,130]。另一个重要因素是化学破乳剂的浓度,即高临界胶束浓度(CMC)可能会降低破乳剂的效率,而浓度不足可能不利于破乳[115]。

在乳状液的热处理过程中,所施加的热量降低了界面膜的机械强度,促进了水滴的聚结。目前,微波和传统加热系统都在使用中,微波比传统加热要好得多,因为后者需要更多的时间和人工[131]。此外,在微波加热中,微波加热仪器可以优化所想要的加热过程,并可以根据具体要求进行修改,这有助于尽量减少电力消耗,减少环境污染[132]。在电破乳中,使用不同的电流,即直流电和交流电;脉冲或连续电流。交流电法是一种常见的、最古老的乳状液分离方法,因为它是一种比脉冲法更简单、更经济的方法。而后者应用于高含水量的乳状液中并以较高的液滴聚结效率为特点。直流电主要用于处理低含水量的乳状液,通过液滴的电泳运动改善了液滴聚合。然而,在交流电场中,通过发生在场中的电泳运动也可以促进液滴聚合;因此,这种类型的电场更适合进行破乳[133]。

对原油乳状液和碳氢化合物污染的废水进行适当的风险评估,能够对环境的预测损害及其修复进行量化。基于上述的讨论可以清楚地看出,环境并不只对单一物种敏感。此外,选择适当的生物标志物和生物指标可能会更准确地对环境影响进行评估。因此,为了估计明确的生态风险,必须对这些数据进行推断,以便在人口和社区层面上正视这些影响。已开发的大多数模型能解释乳化问题,但它们却很少能调查以稳定乳状液形式存在的新油泄漏对环境的影响。例如,泄漏影响模型应用包(SIMAP)公布了对新油暴露的成功评估以及新油的泄漏、缓解措施、急性毒性和对资源的间接影响等方面所造成的冲击。对资源的间接影响包括,受影响的栖息地/人口在死亡率、食物

资源和伤亡方面所受冲击而造成的损失。然而，该模型不能对环境系统结构中的亚致死量和慢性影响或变化，以及增强的繁殖压力及对生存和生长的影响进行评估[134]。因此，未来的研究应该明确收集以稳定乳状液形式存在的新油泄漏信息及其在群落水平上对单个物种可能产生的反应，包括亚致死效应。这将有助于开发工具并将其纳入石油和碳氢化合物污染的环境和生物评估中成为可能。

具有智能表面和可切换润湿性的聚合物材料在油水分离方面表现良好，需要进行工业规模的生产。此外，还应探索安全措施、认证标准和有效、准确的操作过程。研究主要应关注这些智能聚合物材料在有效和可持续分离油水乳状液方面的应用。更新颖的策略将有助于开发新的替代技术，为大规模应用设计稳健的功能材料。

6. 结论和未来展望

如上述例子所言，乳状液或碳氢化合物污染的废水会对环境产生严重的影响。石油污染水体的乳化和净化是当今最重要的研究课题之一。因此，开发具有多功能和刺激响应性能的材料，即开发具有可切换润湿性和抗微生物特性的材料，是分离油水乳状液所必需的。石油污染的水体既是一个严重的环境问题，也是一个严重的健康问题，当需要分离高度稳定和浓稠的乳状液时，这将变得更加具有挑战性。为了更好地解决这个问题，我们需要制造多孔材料来提高材料的水下疏油性。这些材料对水具有高亲和力、低表面能和空气超疏油性。具有可切换润湿性的界面活性材料可能会为解决石油乳状液和碳氢化合物污染废水造成的环境问题提供了一种可能的解决方法。本文综述的数据表明，界面和润湿现象的研究已经成熟，可以成为解决油水乳状液导致的环境问题的一种简单解决方案。

此外，开发具有高机械强度的聚合物材料或聚合物/无机复合材料可能是一种用来防止外部源造成损害的解决方案，这些外部源包括液体流动、机械应力和高压等。此外，现有的合成程序是大规模生产的基础，这造成了另一个严重的环境问题。因此，开发具有成本效益且简单的方法是重要和紧迫的。然而，挑战仍然存在，这可以激发当前研究范式的变化，从而带来丰硕的成果。例如，开发具有超智能表面、可调化学性和微观结构的材料，有助于更精确地设计材料的表面性能。

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Compliance with ethics guidelines

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