

超亲水-超疏油无机膜材料的制备及在油水分离中的应用

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摘要: 超亲水-超疏油无机膜材料具有抗污染能力强、环境耐受性好等优点, 因而在含油废水处理领域具有较好的应用前景。介绍空气中超亲水-超疏油及超亲水-水下超疏油无机膜材料的制备理论基础, 从选择膜改性材料角度出发, 系统总结归纳空气中超亲水-超疏油和超亲水-水下超疏油 2 种无机膜材料的制备方法。制备空气中的超亲水-超疏油无机膜材料主要采用含氟材料, 并构造亲水性粗糙表面, 通过添加含氟材料降低膜表面能中的色散分量。构造亲水性粗糙表面的方法大多引入亲水性纳米颗粒, 以增加膜表面能中的极性分量, 从而获得亲水特性。制备超亲水-水下超疏油无机膜材料主要通过构造亲水性粗糙表面获得相应性能。材料的选取通常以亲水性聚合物和亲水性纳米颗粒为主。超亲水-超疏油无机膜材料大多应用于以含油废水处理与废油净化为主的环保领域, 相较于“除水过油”处理方式, 它具有耐油污性能好、通量高等优点。最后提出了目前该领域研究中存在的一些问题和不足之处, 展望了该领域未来的发展方向。

关键词: 无机膜; 超亲水-超疏油; 超亲水-水下超疏油; 含油废水; 含氟材料; 油水分离

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Preparation and Application of Superhydrophilic-superoleophobic Inorganic Membrane Materials in Oil-water Separation

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ABSTRACT: Oily wastewater has the characteristics of large amount of water, difficulty in separation, and will cause harm to the environment. Membrane separation is widely used in the treatment of oily wastewater due to its advantages of low energy consumption and simple operation. However, in a variety of oil-water separation membranes, the superhydrophilic-superoleophobic inorganic membrane materials have stronger pollution resistance and environmental tolerance, showing a better application prospect in oil-water separation.

The work aims to introduce the theoretical basis for the preparation of superhydrophilic-superhydrophobic inorganic

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membrane materials in air and superhydrophilic-underwater superoleophobic inorganic membrane materials. Based on the selection of membrane materials, the preparation methods of superhydrophilic-superhydrophobic inorganic membrane materials in air and superhydrophilic-underwater superoleophobic inorganic membrane materials are systematically summarized. During the preparation of superhydrophilic-superhydrophobic inorganic membrane materials in air, fluorine-containing materials are mainly used and hydrophilic rough surface is constructed. Fluorine-containing materials reduce the dispersion component of the membrane surface energy to provide its hydrophobic properties, while most of the methods for constructing hydrophilic rough surface are to introduce hydrophilic nanoparticles to increase the polar component of the membrane surface energy to provide its hydrophilic properties. The hydrophilic nanoparticles are represented by TiO_2 , SiO_2 and kaolin. The preparation of superhydrophilic-underwater superoleophobic inorganic membrane materials is mainly achieved through the construction of hydrophilic rough surface, and the material selection is usually based on hydrophilic polymers and hydrophilic nanoparticles. In the water environment, the modified membrane will absorb a large amount of water to the rough surface, thus reducing the contact area with the oil, lowering the adhesion of the oil, and achieving the effect of superhydrophilic-underwater superoleophobic.

Superhydrophilic-superoleophobic inorganic membranes are mostly used in the environmental protection field of oily wastewater treatment and waste oil purification. In the past, in the separation of oil and water, most of the superoleophilic-superhydrophobic membranes were used. However, the treatment method of "oil-removing through water" adopted by superhydrophilic-superoleophobic in air and superhydrophilic-underwater superoleophobic inorganic membrane has the advantages of good oil resistance and high flux, so it will be better applied in the separation of oil and water. If a photocatalytic material such as titanium dioxide is added to the membrane, the intercepted oil droplets can also be purified.

At last, some problems and shortcomings in the current research in this field are put forward, and the current research on the modification of superhydrophilic-superhydrophobic membrane in air and superhydrophilic-underwater superoleophobic membrane mostly focuses on organic materials such as fabric and sponge, while the research on inorganic materials mostly focuses on metal momentum, and the research on inorganic non-metallic membrane such as ceramic membrane is less. At the same time, although modified fluorine-containing materials have a good effect, they are not friendly to the environment, and the price is high. Therefore, they are not suitable for large-scale application. Future research may focus on the use of inorganic non-metallic membranes and green modified materials. In terms of oil-water separation, it is necessary to increase the research on the separation of oil-water emulsion by superhydrophilic-superoleophobic inorganic membrane.

KEY WORDS: inorganic membrane; superhydrophilic-superoleophobic; superhydrophilic-underwater superoleophobic; oily wastewater; fluorine-containing materials; oil-water separation

石油是当今的主要能源,在开采石油过程中产生的含油废水是一类备受关注的污染物^[1]。含油废水具有水量多、水质复杂、难生物降解等特点^[2],会给周边环境带来较大的危害。目前,处理含油废水的常规方法包括物理法、化学法、生物法等。如何更好地实现含油废水处理与废油回收净化是研究者们不断探索的一个方向^[3]。相较于传统处理工艺,膜分离技术具有抗污染能力强、能耗低、操作简单等优点,在含油废水处理中得到了广泛应用^[4-9]。由于无机膜具有稳定的物理化学性质、可重复使用性,因此它在水处理行业受到了越来越多的关注^[10-11]。通过对无机膜进行超亲水-超疏油改性,可以提高过滤膜的耐污染性能,进一步提升对含油废水的处理效能。

超亲水-超疏油不同于普通意义上的亲水疏油,过去很多研究人员通过简单的方法制备了亲水疏油膜材料^[12-13],但它达不到超疏油要求,不适合于油水分离。随着亲水疏油超润湿理论不断完善,制备超亲水-超疏油膜成为可能,继而成为膜研究的一个热

点。采用超亲水-超疏油无机膜材料,可在油水分离过程中做到“除油过水”,相较于“除水过油”分离材料^[14-16],它具有更好的耐油污性能、更高的通量,更适合于处理含油废水。文中主要总结了近几年关于空气中超亲水-超疏油和超亲水-水下超疏油无机膜材料制备的相关工作和进展,概括了其中具有代表性的研究工作,包括超亲水-超疏油理论基础、材料的选择及应用等,最后提出了该领域存在的问题,并展望了未来的发展方向。

1 超亲水-超疏油无机膜材料制备原理及方法

1.1 空气中超亲水-超疏油无机膜材料

水的表面张力比油的表面张力大,因此疏油表面大多是疏水的,这是制造超亲水-超疏油材料的一个难点。随着研究的深入,研究人员发现接触角可细化

为由材料表面色散分量和极性分量决定, 可以用式 (1) 表示。^[17-18]

$$(r_{lv}^d + r_{lv}^p)(1 + \cos \theta) = 2\sqrt{r_{sv}^d r_{lv}^d} + 2\sqrt{r_{sv}^p r_{lv}^p} \quad (1)$$

式中: θ 为接触角; r_{sv}^d 、 r_{sv}^p 为材料表面的色散分量和极性分量; r_{lv}^d 、 r_{lv}^p 为水的色散分量和极性分量。水的表面张力包含极性成分和色散性成分, 由于油通常是非极性的, 所以可以忽略油的极性成分。水与油在材料表面的接触角可以分别用式 (2)~(3) 描述。^[17-18]

$$\cos \theta_w = \frac{2\sqrt{r_{sv}^d r_{lv}^d} + 2\sqrt{r_{sv}^p r_{lv}^p}}{r_{lv}^d + r_{lv}^p} - 1 \quad (2)$$

$$\cos \theta_o = 2\sqrt{\frac{r_{sv}^d}{r_{lv}^d}} - 1 \quad (3)$$

式中: θ_w 为水的接触角; θ_o 为油的接触角; r_{lv}^d 为油的色散分量, 它为定值, 所以对材料表面进行疏油改性需要减小 r_{sv}^d 。因为在确定的条件下, 水的表面张力为定值, 所以水的色散分量和极性分量 r_{lv}^d 、 r_{lv}^p 也为定值。由式 (2) 可知, 对材料表面进行亲水改性需同时增大 r_{sv}^d 、 r_{sv}^p 。结合式 (3) 对材料表面进行亲水疏油改性时, 需减小 r_{sv}^d , 增大 r_{sv}^p 。

由上述公式可知, 对材料表面进行空气中的超亲水-超疏油改性, 只需减小材料表面的色散分量, 增大材料表面的极性分量。大量研究通过添加含氟材料减小材料表面的色散分量, 使材料表面表现为超疏油特性^[19]。通过添加亲水性纳米颗粒来增大材料表面的极性分量, 同时提高其表面粗糙度, 使材料表现为超亲水特性。改性用亲水性纳米颗粒以 TiO_2 、 SiO_2 为代表, 将它们与含氟材料结合使用, 便可制备出具有超亲水-超疏油性能的无机膜材料。

Li 等^[18,20]提出了一种通过增加表面张力的极性成分来实现材料表面超亲水-超疏油的方法。他们采用全氟辛酸和两性氟表面活性剂 (Capstone FS-50) 来实现疏油, 同时添加 TiO_2 纳米颗粒、 Na^+ , 作为亲水性单元, 通过离子键作用将氟碳链接枝到材料表面, 使得材料具备超亲水-超疏油特性。Xiong 等^[21]通过在 SiO_2 纳米颗粒表面引入亲水基团和疏油基团, 将其制成涂料, 并喷涂在基材上, 使基材具备超亲水-超疏油性能。其中, 亲水性基团由 $-\text{OH}$ 实现, 疏油基团由氟化基团实现。实验首先用碱催化法合成羟基改性 SiO_2 纳米颗粒, 再将壳聚糖季铵盐与 SiO_2 通过氢键结合起来, 最后加入全氟辛酸和壳聚糖季铵盐, 从而形成氟化基团。由此可知, 增加纳米颗粒表面活性位点, 可提高接枝材料的接枝率和改性效率。接枝是在大分子链上通过化学键结合适当的支链或功能性侧基的过程, 接枝共聚反应首先应形成活性接枝点。一般而言, 当活性位点增多, 改性材料与纳米颗粒形成的接枝共聚物越多, 改性效果越好。为了增强 TiO_2 、 SiO_2 等颗粒与基底表面结合的牢固性, 一些研

究者通过添加黏结剂来实现。有研究者用 $\text{Al}(\text{OH})_3$ 与 H_3PO_4 配制出透明且黏稠的 AP 无机黏合剂^[22-24], 采用氟表面活性剂 (Capstone FS-50) 和 SiO_2 为表面修饰材料, 有效增强了超亲水-超疏油涂层与基底的黏附力, 且具有良好的耐酸碱性能。在胶黏剂的选择上, 还应考虑其耐高温和耐碱性, 且使用后不会造成膜孔径堵塞等其他附加问题。

此外, 还有些研究者制备的超亲水-超疏油膜在特定条件下可实现润湿性的转变。Xu 等^[25]使用七氟壬酸改性含有羧酸钛配合物的 TiO_2 , 形成了溶胶混合物, 在溶胶中添加 SiO_2 纳米颗粒, 以提高涂层的粗糙度。通过该方法改性的材料呈现出超疏水-超疏油特性, 在氨的暴露和加热条件下材料表面可在超亲水-超疏油与超疏水-超疏油之间来回转换。由于在润湿性转换过程中膜表面存在疏油效果不断下降的可能^[26], 因此解决疏油效果不佳问题是未来研究的一个难点。空气中亲水-疏油膜典型处理方法如表 1 所示。由表 1 可知, 疏油性体现在含氟材料的添加方面, 含氟材料以全氟辛酸 (PFOA) 和氟表面活性剂 (Capstone FS-50) 为主。改性方法大多为简单的喷涂和浸涂, 此类方法操作简单, 易于工程应用。经改性后无机膜的疏油效果较好, 油水分离效率较高, 油接触角可达 150° 以上, 油水分离效率可达 95% 以上。

1.2 超亲水-水下超疏油无机膜材料

超亲水-水下超疏油膜在水下的油接触角可达 150° , 并具有超亲水效果^[32]。一般来说, 这种膜性能来源于分级微/纳米结构和亲水接枝材料的协同效应。在水环境中, 改性膜将大量的水吸收到粗糙表面, 从而减少了与油的接触面积, 降低了油的附着力^[33], 达到了超亲水-水下超疏油的效果。制备空气中超亲水-超疏油无机膜的亲水性原理也同样适用于超亲水-水下超疏油膜。

采用在膜上引入或生长亲水性纳米颗粒的方法来提高亲水性和表面粗糙度, 是制备超亲水-水下超疏油无机膜常见的方法^[34]。Zhang 等^[35]通过简单的磁控溅射和水热氧化在 Al_2O_3 多孔陶瓷膜表面制备了 TiO_2 纳米棒阵列。其中, TiO_2 纳米棒阵列层的生长可以降低陶瓷膜的孔径, 进而提高膜的过滤性能, 经表面改性后陶瓷膜提高了过水通量和防油污能力。Wang 等^[36]以废弃凹凸棒土和 $\alpha\text{-Al}_2\text{O}_3$ 为原料制备陶瓷膜, 通过在膜上引入 TiO_2 种子层, 生长出 TiO_2 纳米阵列, 进而对陶瓷膜进行超亲水-水下超疏油改性。Wang 等^[31]以高岭土颗粒 ($\text{Al}_2\text{Si}_2\text{O}_5\text{H}_4$)、3-氨基丙基三乙氧基硅烷、十二烷基硫酸钠和二乙氧基二甲基硅烷为主要材料, 制备了高岭土悬浮液, 通过浸渍方法获得了超亲水-水下超疏油不锈钢网。该改性钢网表面形成了独特的微粗糙度和孔隙结构, 各种有机溶剂和油与其接触角均大于 150° 。通常, 采用直接引入亲水性纳米颗粒制成悬浮液, 再喷涂或浸渍, 使其附着于

表 1 空气中亲水-疏油膜典型处理方法
Tab.1 Typical treatment methods of hydrophilic-oleophobic membrane in air

Base material	Principal raw material	Method of coating	Oil contact angle/(°)	Oil-water separation efficiency/%	References
Glass lens, fabric, cotton	Fluorine surfactant (Capstone FS-50), ethyl alcohol, TiO ₂ NPs, PFOA, NaOH, TEOS	Repeated spraying	>150		[18, 20]
Glass lens, nickel foam, stainless steel wire, ceramic, zinc plate	H ₃ PO ₄ , Al(OH) ₃ , SiO ₂ NPs, fluorine surfactant (Capstone FS-50)	N ₂ spraying	>150	99	[22]
Glass lens, aluminum, iron, cotton	PFOA, MCC, NaOH, 1H, 1H, 2H, 2H, perfluoro-decyl trichlorosilane	Spraying	>150	96.8	[27]
Polyester filter cloth	PASP, PAA, PVA, SiO ₂ NPs, 1H, 1H, 2H, 2H perfluorooctane triethoxy silane	Dip coating	99.8	98	[13]
Glass lens	Perfluorinated polyethers	Dip coating	93.2		[12, 28]
Glass lens	Kaolin particles, Stearic acid, DEDMS, MSDS, PFOA, Trichloro (1H, 1H, 2H, 2HP perfluorooctane) silanes	Simple coating	>150		[29]
Glass lens, filter paper, sponge, fabric, cotton, copper screen	Shell, PFOA, APTES, BTMEPA	Spraying	>150	99	[30]
Stainless steel wire	Kaolin particles, APTES, SDS, DEDMS	Dip coating	>150	99	[31]
Stainless steel wire	SiO ₂ NPs, PFOA, HACC, Silane coupling agent KH550	Spraying	>150	99.2	[21]

膜材料表面的方法,可能会产生膜层与基材结合不牢固等问题,而直接生长亲水性纳米颗粒虽解决了牢固性问题,但会使实验操作变得相对复杂。与空气中超亲水-超疏油无机膜的制备一样,引入胶黏剂也是一种提高膜材料牢固性的方法。Zhou 等^[37]以偏硅酸锂为胶黏剂,将微晶纤维素颗粒黏附在不锈钢网上,使其具备超亲水-水下超疏油性能。通过砂纸磨损试验和手指按压试验测试证明,该网膜具有较好的牢固性和耐久性。

此外,有些研究者通过蚀刻或氧化方法来增加膜表面的粗糙度。Wang 等^[38]使用激光机蚀刻不锈钢网,形成了粗糙表面,然后采用化学沉积法和浸涂法将 WO₃ 和 TiO₂ 附着在不锈钢网表面,WO₃/TiO₂ 微纳米双结构使得膜具有良好的超亲水性和水下超疏油性。耐摩擦实验证明,即使在 20 kPa 下用粗糙的砂纸(800 目)摩擦后,该网膜仍具有水下超疏油性。Agano 等^[39]先对高纯铜网膜进行阳极氧化,形成混合相氧化铜(Cu_xO)层,然后在氩气与氧气的混合等离子体中,通过反应溅射方法沉积生长了 TiO₂ 薄膜,从而制备出超亲水-水下超疏油 Cu_xO/TiO₂ 网膜。Pi 等^[40]采用电化学阳极氧化方法,以铜网为材料,制备出超亲水-水下超疏油且具有独特卷曲板状结构的新型 Cu₂S 涂层网膜。采用蚀刻增加膜表面粗糙度的方法大多只适用于金属网膜材料,对于无机非金属材料,尤其是陶瓷膜的蚀刻来说相对较困难,其蚀刻条件较苛刻、不

易实现。通过电化学沉积法来提高膜材料表面亲水性粗糙度也是一种较好的改性方法。喻溪亭等^[41]运用电化学沉积法,将金属镍镀在不锈钢网基底上,使其表面形成了一种钟乳石状的微纳米粗糙结构,使得改性网膜具备超亲水-水下超疏油性能。张容容^[42]将铜网浸泡在氢氧化钠与过硫酸钾的混合溶液中,使铜网表面生成了微米结构的氢氧化铜,铜网表面亲水性粗糙度增加,表现出超亲水-水下超疏油性,水下油接触角达到 150°。

除使用单一亲水无机材料外,有些研究者将聚合物材料与无机亲水纳米颗粒相结合,进一步提高了材料粗糙表面的亲水性^[33]。Li 等^[43]以 ZnO 纳米颗粒和水性聚氨酯(PU)为主要材料,制备出超亲水-水下超疏油网膜。加入 ZnO 纳米颗粒增大了膜的表面粗糙度,而 ZnO 和 PU 表面成分中含有的大量亲水基团的协同作用使得膜具备了超亲水-水下超疏油性能。Qing 等^[44]通过静电纺丝技术制备聚乙烯醇(PVA)纳米纤维,然后在其表面原位生长 SiO₂ 纳米粒子,制备出超亲水-水下超疏油膜。Lu 等^[45]首先制备了聚合物硅丙乳液,再将其与纳米 SiO₂ 颗粒机械混合,2 种物质含有的大量羟基之间会发生缩聚作用,使二氧化硅颗粒和聚合物乳液生成了交联结构,将其喷涂在基材表面,成功制备了超亲水-水下超疏油无机网膜,它具有较好的耐酸碱性能。壳聚糖作为一种绿色材料,通常被研究者们用于改性高分子材料^[46]。You

等^[47]以壳聚糖、TiO₂、PVA 为主要材料, 将其涂覆于铜网表面, 以戊二醛为交联剂, 制备出超亲水-水下超疏油网膜, 并用于油水分离。Wang 等^[48]将多巴胺颗粒原位沉积在基体表面, 通过吸附作用将亲水性壳聚糖吸附在基体表面, 提高了基体的超亲水-水下超疏油性能。在改性方法与聚合物材料的选择上, 应考虑环境友好问题, 宜选用绿色材料。超亲水-水下超疏油膜典型处理方法及相应的实验数据

如表 2 所示。从表 2 可以看出, 超亲水-水下超疏油膜的改性材料大多为亲水性的纳米颗粒, 同时添加了一些亲水性聚合物; 改性方法较简单, 喷涂、浸涂等方法占多数, 其中也包含原位生长改性方法。值得注意的是, 通过原位生长方法改性的膜层相对于喷涂、浸涂 2 种方法改性的膜层更加牢固, 研究表明其膜层水下油接触角在 150°以上, 油水分离效率在 98%以上。

表 2 超亲水-水下超疏油膜典型处理方法
Tab.2 Typical treatment methods of superhydrophilic - underwater superhydrophobic membrane

Base material	Principal raw material	Method	Underwater oil contact angle/(°)	Oil-water separation efficiency/%	References
Fabric	Dopamine hydrochloride, CTS, Trimethylaminomethane hydrochloride	Dip coating	>150	99	[48]
Copper screen	NaOH, Ammonium persulfate	In-situ growth	>150		[49]
Stainless steel wire	Glass dust	Simple coating	>150	99	[50]
Titanium foam	Acetone, Methyl alcohol, HF, HCl	Corrosion	>150	98	[51]
Stainless steel wire	SiO ₂ NPs, BA, MMA, HEA, VTES, TEOS	Spraying	>155	99	[44]
Stainless steel wire	ZnO NPs, WPU, Acetone	Spraying	>150	99	[43]
Copper screen	TiO ₂ NPs, CTS, PVA, Glutaraldehyde	Dip coating	>150	99.7	[47]
Ceramic membrane	TiO ₂ NPs, TBOT, H ₂ O ₂ , Melamine	In-situ growth	>150	99	[36]

2 超亲水-超疏油无机膜材料在油水分离中的应用

超亲水-超疏油膜材料的油水分离机理可以用式 (4) 解释, 液体在材料表面的静压力 Δp 与前进角 θ_c 之间的关系由拉普拉斯方程描述, 见式 (4)。

$$\Delta p = \frac{2r_{lv}}{R} = \frac{Lr_{lv}(\cos\theta_c)}{A} \tag{4}$$

式中: Δp 为液体在材料表面的静压力, 也称突破压力; r_{lv} 为液体的表面张力; R 为弯液面的曲率半径; L 为材料网孔的周长; A 为网孔的面积; θ_c 为液滴前进的接触角。

通过式 (4) 可以看出, 当 $\theta_c > 90^\circ$ 时, $\Delta p > 0$, 材料表面可以支持一定的外部压力, 液体不易渗透; 当 $\theta_c < 90^\circ$ 时, $\Delta p < 0$, 液体易渗透, 所以为超亲水-超疏油膜材料表面, 水容易通过膜孔, 油不易通过, 使得油水分离^[52-53]。在注入压力作用下, 注入水驱动大孔道中的油向前流动, 由油所占据的空间被水替换。

Qu 等^[54]采用 PFOA 改性的高岭土纳米颗粒在空气中和水下都具有较好的超亲水-超疏油效果, 将改性后的高岭土颗粒在色谱柱中紧密填充, 以硅棉为支撑基底, 通过重力驱动分离油/水体积比约为 1:1 的混合物。结果表明, 该材料对葵花籽油/水、十六烷/水、大豆/水和甲苯/水的分离效率分别为 92.8%、92.3%、92.1%、93.2%。此外, 改性高岭土材料还可

直接分离各种稳定的水包油乳液, 对水包十六烷乳液、水包葵花油乳液、水包二氯甲烷乳液和水包甲苯乳液的分离效率均大于 92%。Jiang 等^[51]将在钛泡沫上生成的花状 TiO₂ 纳米结构与表面的氧化钛氟化物共同作用, 制备出具有超亲水-水下超疏油性质的钛泡沫。通过油水分离实验证明, 钛泡沫对煤油乳状液的分离效率高达 99.5%, 对其他油的分离效率高于 96%。Wei 等^[55]通过改性 SiO₂ 和壳聚糖, 制备了具备超亲水-水下超疏油性能的石英砂滤料 (CHQS)。研究表明, CHQS 对机油和水的混合物的分离效率达到 99.99%。在乳化油的分离方面, CHQS 出口的油浓度比原始石英砂过滤器的降低了 24.4%, 且水的渗透系数增加了 19%, 油的渗透系数降低了 6%, 显示出更好的除油性能。Anis 等^[56]制备了孔隙率为 55%、平均孔径为 28 nm 的超亲水-水下超疏油纳米沸石超滤膜, 二氯甲烷在该膜的水下接触角达到 156°。以机油、二甲苯和 600 mg/L 的原油制备了水包油乳液。通过油水分离实验证明, 该膜具有良好的排水能力, 油的渗透浓度 >3 mg/L, 分离效率 ≥ 99.5%。Li 等^[27]使用 2,2,6,6-四甲基-1-哌啶氧基和 PFOA 对粗微晶纤维素颗粒进行了超亲水-超疏油改性, 实验结果表明, 通过该方法改性的棉膜可有效分离高黏度油和水的混合物, 分离效率高于 98%。在油水乳液分离上, 对十六烷、液体石蜡和发动机油乳液的分离效率分别为 97.40%、97.00%、96.80%。Xue 等^[57]采用光引发聚合工艺, 制备出一种超亲水-水下超疏

油性质的绿色聚丙烯酰胺 (PAM) 水凝胶改性不锈钢网, 使其具有水下超疏油和低黏油性能, 可有效分离原油和水 (体积分数 30%) 的混合物, 且成功分离了汽油、柴油、植物油、己烷和石油醚等多种油/水和有机溶剂/水混合物。另外, 该涂层网易于清洗, 可重复使用。在油水分离应用方面, 应增加对实际含油废水进行分离的实验内容, 更好地展示改性膜的应用效果。

有研究人员使用具有光催化性能的材料对膜进行改性, 在油水分离的同时, 还可对截留废油进行净化。Yuan 等^[58]通过电化学氧化和沉积的方法在铜网上制备出具有光催化性能的超亲水-水下超疏油 TiO_2/CuO 涂层铜网, 该铜网具有较高的分离效率, 水通量大于 $80 \text{ kL}/(\text{h}\cdot\text{m}^2)$ 。同时, 该铜网具有自清洁特性, 在紫外光照射下, 能够分解吸附在分离网表面的有机污染物和污垢物质。Li 等^[20]以 TiO_2 纳米颗粒和氟表面活性剂 (Capstone FS-50) 制备出超亲水-超疏油膜材料, 用十六烷、大豆油和柴油 3 种油制备了稳定的油包水和水包油乳液, 油滴的平均粒径小于 $20 \mu\text{m}$ 。使用该膜分离后的滤液清澈, 且未检测到油

滴。此外, 采用该方法改性的棉膜具有 98.5% 的高油水分离效率, 以及 $600 \text{ L}/(\text{h}\cdot\text{m}^2)$ 以上的通量, 适用于多种油水乳剂的分离。在废油净化实验中以有害油性苏丹红 III 为目标污染物, 在 UV 照射下膜层在 45 min 内逐渐失去超疏油性, 污染物被降解, 纯化的油渗入涂层网, 并被收集。在废油净化方面, 膜经 UV 照射后大多会失去疏油性能, 因此制备出一种油水分离与净化为一体的膜, 且经多次使用后不会损失其分离净化性能, 这是研究人员需关注的问题。此外, Lu 等^[30]设计的超亲水-超疏油贝壳粉改性铜网对极性低的油具有较强的驱避性, 对极性高的油具有较强的亲和力, 可对极性相差较大的不同油进行分离。他们使用改性铜网对发动机机油和甲酰胺混合物进行分离过滤, 实验结果表明, 高极性甲酰胺渗入过滤器, 而低极性发动机机油保留在过滤器表面上方, 实现了不同极性油的分离。超亲水-水下超疏油膜在水中的疏油性如图 1a 所示, 超亲水-超疏油膜油水分离示意图如图 1b 所示。具有光催化功能的超亲水-超疏油膜油水分离及净化示意图如图 1c~d 所示, 其中图 1c 示意分离阶段, 图 1d 示意净化阶段。

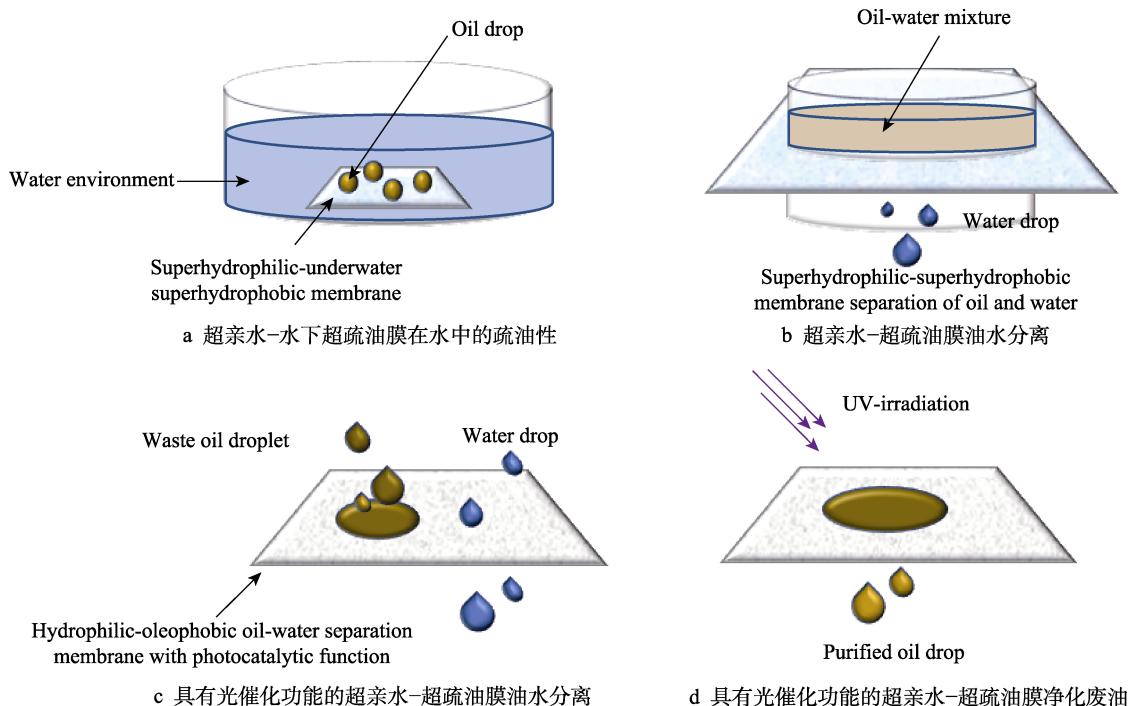


图 1 超亲水-超疏油膜油水分离及废油净化示意图

Fig.1 Diagram of oil-water separation and waste oil purification of superhydrophilic-superhydrophobic membrane: a) oleophobicity of the superhydrophilic-underwater superoleophobic membrane in water; b) superhydrophilic-superoleophobic membrane oil-water separation; c) oil-water separation of the superhydrophilic-superoleophobic membrane with photocatalytic function; d) superhydrophilic-superoleophobic membrane with photocatalytic function to purify waste oil

3 结语

超亲水-超疏油膜材料在油水分离领域具有较好的应用前景, 得到了研究者的广泛关注。超亲水-超

疏油可分为空气中超亲水-超疏油和超亲水-水下超疏油, 制备空气中超亲水-超疏油无机膜材料主要采用含氟材料, 并构造亲水性粗糙表面, 构造亲水性粗糙表面大多会引入以 TiO_2 、 SiO_2 、高岭土为代表的纳米颗粒。制备超亲水-水下超疏油无机膜材料主要通

过构造亲水性粗糙表面达到目的, 通常将亲水性聚合物与亲水性纳米颗粒相结合, 实现最大的亲水效果。在改性剂选用方面, 虽然含氟材料在超疏油改性方面具有很好的效果, 但其环境不够友好, 且价格偏高, 不易大规模应用。另外, 在使用纳米粒子进行亲水改性研究时, 纳米粒子的附着强度及膜的耐酸碱性能也是值得关注的方向。由于无机膜超亲水-超疏油改性大多集中于金属网膜, 未来研究可聚焦于无机非金属膜与绿色改性材料的使用。油水分离方面, 在保证油水分离效果的同时应更多关注膜的改性成本、使用寿命及重复利用率等方面。此外, 还需加大超亲水-超疏油无机膜材料在分离油水乳液方面的研究力度。

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