Green synthesis of polymeric membranes: recent advances and future prospects

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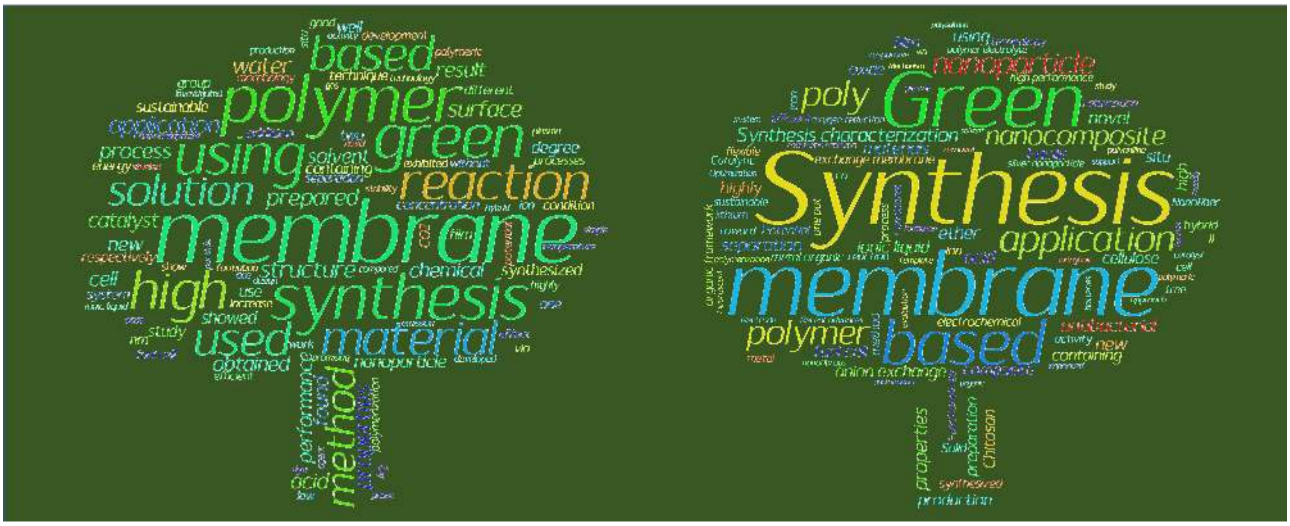
Abstract

Polymeric membranes are widely used in gas separations, liquid separations, and other processes such as fuel cells. However, methods and processes for manufacturing these membranes are usually harmful to the environment and/or human health. Although many new materials and synthesis methods are reported every year, green synthesis only makes up a small proportion. Therefore, more efforts are necessary to raise researchers' awareness to green synthesis of membranes. One popular strategy to greenly synthesize membranes is to avoid toxic organic solvents or use water to replace organic solvents completely. However, many reported green methods could only realize green synthesis partly. The ultimate goal is to synthesize membranes in a completely eco-friendly way, where raw materials, membrane preparation, post-treatment, and other involved procedures are all "green".

Graphical Abstract



Keywords: green synthesis; sustainable synthesis; polymeric membrane; membrane preparation; ion exchange membrane

Introduction

As its name implies, polymeric membranes are made using polymers as the matrix. The vast variety of polymers and synthesis methods contribute to an abundance of polymeric membranes with different properties and applications. Polymeric membranes are widely used in gas separation, liquid separation (e.g., water purification), energy production, and so on [1–4]. Pressure-driven membranes are an important branch of polymeric membranes, and they are usually classified into microfiltration (MF), ultrafiltration (UF), nanofiltration (MF) and reverse osmosis (RO) based on pore size [5,6]. Ion exchange membranes (IEMs) are electrically driven membranes and have been widely used in a lot of applications [7,8]. Other membrane processes include, but are not limited to, forward osmosis (FO), pervaporation (PV), and membrane distillation (MD) [9–11]. Common polymers used for membrane preparation include polystyrene (PS) [12], polypropylene (PP) [13], polyethersulfone (PES) [14], polyvinylidene fluoride (PVDF) [15], polybenzimidazole (PBI) [16], polyvinyl alcohol (PVA) [17], polytetrafluoroethylene (PTFE) [18], polyethylene (PE) [19], polyamide (PA) [20], and polyimide (PI) [21]. Recently, many new types of polymers are emerging which show promising future for membrane synthesis and applications. An example is polymers with intrinsic microporosity (PIMs), which are ideal candidates for gas separation membranes [22–24].

Green synthesis is becoming more and more important in membrane synthesis. Generally, green synthesis can be partly achieved by replacing conventional toxic organic solvents with water or non-toxic organic solvents. A completely green synthesis should avoid using any chemicals, reactions, and processes that are dangerous to humans and/or the environment. Meanwhile, the raw materials used for synthesis should also be fabricated greenly. In other words, life cycle assessment (LCA) technique should be used when designing green synthesis routes.

Nevertheless, although there are various synthesis methods for polymeric membranes, only a small portion of these methods can be classified as green synthesis methods. Usually, organic solvents are inevitable in membrane synthesis. Common organic solvents used for synthesis include acetone [25], methanol [26], dimethylformamide (DMF) [27], dimethylacetamide (DMAc) [28], toluene [29], N-methyl-2-pyrrolidone (NMP) [30], dimethyl sulfoxide (DMSO) [31], and tetrahydrofuran (THF) [32]. Among these solvents, many are toxic to human health and hazardous to the environment. Besides, many membrane synthesis processes involve dangerous reactants or produce a lot of hazardous waste.

Although many reviews on synthesizing different types of polymeric membranes are available, there are few reviews on green synthesis of polymeric membranes. This paper briefly discusses recent advances and limitations of green synthesis of polymeric membranes and provides future directions for green synthesis.

Green synthesis of polymeric membranes: recent advances and limitations

Generally, polymeric membranes are synthesized via two routes, where one involves chemical reactions while the other one does not involve chemical reactions. The chemical-reaction route usually involves polymerization and/or functionalization. For the non-chemical-reaction route, polymers are usually dissolved in organic solvents, followed by solution casting and phase inversion/solvent evaporation process.

Green synthesis of IEMs

Typically, there are two successive steps for synthesizing anion exchange membranes (AEMs), including chloromethylation followed by quaternization to introduce quaternary ammonium groups (Figure 1a) [33,34]. However, toxic and/or carcinogenic chemicals are usually unavoidable in this method [35,36]. For example, chloromethyl methyl ether (CMME) is often used for chloromethylation [25,33,37]. According to the International Agency for Research on Cancer (IARC), CMME is carcinogenic to human beings. Also, organic solvents are often used in this method [38]. In some studies, CMME is replaced by other chemicals (e.g., paraformaldehyde and chlorotrimethylsilane [39]). However, even if these chemicals are not as dangerous as CMME, they are only relatively safer than CMME. Therefore, researchers have developed various methods to skip the chloromethylation process and to directly quaternize polymers that contain nitrogen groups. For example, Hou et al. [40] reported a green route to prepare AEMs by quaternizing PBI using bromoethane. This route is very simple and no dangerous chloromethylation reagents are used. From this aspect, it could be classified as green synthesis. However, on the other hand, a lot of DMAc is used to dissolve PBI. According to IARC, DMAc is possibly carcinogenic to humans. Qaisrani et al. [41] synthesized a new kind of AEMs through thermal treatment of benzoxazine monomer on PTFE support. Similarly, no chloromethylation is needed in this route. However, formaldehyde is used for benzoxazine synthesis. According to IARC, formaldehyde is a human carcinogen. Besides, as a solvent, 1,4-dioxane is used for both benzoxazine synthesis and the following membrane preparation. According to IARC, 1,4-dioxane is a probable human carcinogen. Also, other hazardous chemicals, though not classified as carcinogenic due to lack of evidence, are used in the above routes. Therefore, strictly speaking, the routes developed by Hou et al. and Qaisrani et al. only realize green synthesis partly compared to traditional methods. Examples of other studies which can also be classified as "partly green" are the synthesis of materials for 4-nitrophenol removal, where DMF and 1,2-dichloroethane are used as the solvents [42], and the synthesis of radiation-grafted AEMs, where conventional organic chemical propan-2-ol is replaced by water [43]. According to IARC, 1,2-dichloroethane is possibly carcinogenic to humans. Hu et al. [44] developed a more environment-friendly route to prepare AEMs via plasma grafting, polymerization of (ar-vinylbenzyl)trimethylammonium chloride (VBTAC) which contains functional quaternary ammonium groups, and solution casting technique. Neither chloromethylation nor quaternization is needed for this route, which is its main advantage over other synthesis routes. The main drawback is that organic solvent DMF is still needed due to the use of solution casting. However, this study opens up new doors for preparing AEMs in a "greener" way, which is to directly use monomers containing functional groups (Figure 1b). It should be pointed out, though, that when using this methodology, other strategies (e.g., plasma grafting, crosslinking reagents) have to be applied at the same time to make the polymers (in salt form) insoluble in water and more resistant to membrane swelling.

The synthesis of cation exchange membranes (CEMs) generally involves sulfonation to introduce functional sulfonic groups (Figure 1c) [45]. Dangerous acids such as concentrated sulfuric acid or chlorosulfonic acid are typically used in sulfonation. The acid waste is also hazardous to the environment and additional efforts are needed to handle the waste properly. Another common method to synthesize CEMs is to disperse cation exchange resins into polymer solution, followed by solution casting and solvent removal (e.g., phase inversion, solvent evaporation by heating) to get the membrane [46]. However, organic solvents are inevitable in this route. In order to solve these problems, Hao et al. [47] developed a green route to synthesize PVA-based CEMs (Figure 1d). Since PVA is soluble in water, all the preparation is carried out in aqueous media. Therefore, no organic solvent is used. Also, no sulfonation is needed.

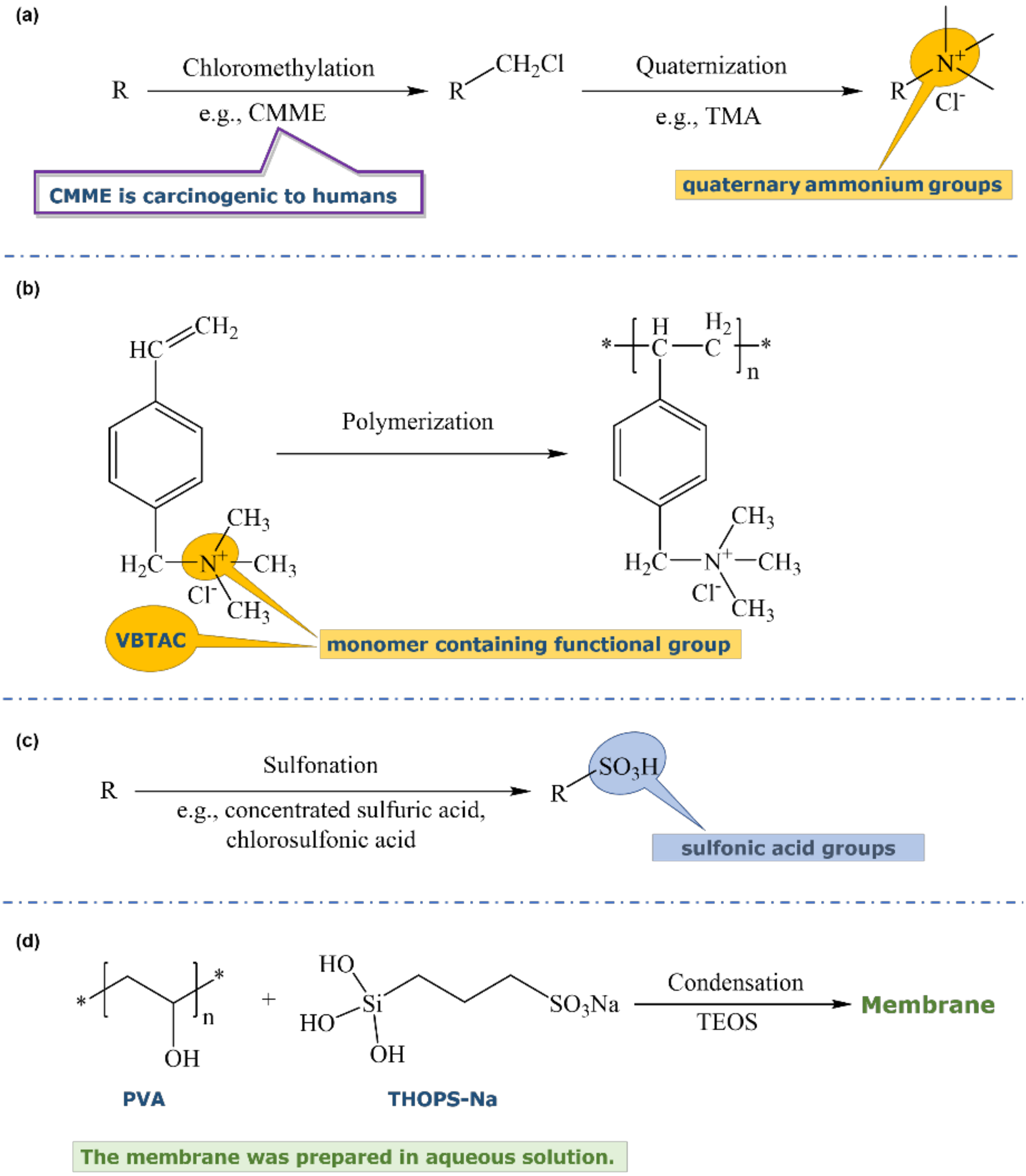


Figure 1. Conventional routes and green routes for synthesizing IEMs. (a) Conventional route for synthesizing AEMs. (b) An example of green synthesis of AEMs. (c) Conventional route for synthesizing CEMs. (d) An example of green synthesis of CEMs. TMA: Trimethylamine; THOPS: 3-trihydroxysilyl-1-propanesulfonic acid; TEOS: Tetraethyl orthosilicate.

Green synthesis of other polymeric membranes

In fact, not limited to IEMs, many polymeric membranes are “greenly” synthesized in aqueous media [48]. For example, Baatout et al. [49] synthesized cyclodextrin membranes as humidity sensors in aqueous media. Li et al. [50] prepared different kinds of polydimethylsiloxane (PDMS)-PVDF composite membranes via traditional route using toxic n-hexane and green route using water coupled with surfactant. The authors found that membranes prepared using green route demonstrated better PV performance than membranes prepared using conventional routes. Using water as the solvent, Peng et al. [51] developed a green method to synthesize β-MnOOH nanofibers. Unfortunately, toxic organic solvent, i.e., toluene, is also used during memrbane prepration. Bibi et al. [52] prepared green nanocomposite membranes using water as the major media (Figure 2). Using this green method, they carried out a series of studies [53–55]. There are several green strategies involved in their synthesis that are worth discussing. First and foremost, most of the chemicals used for synthesis are water-soluble, including polymers. Therefore, no toxic organic solvents are needed since water can be used as the substitute. Secondly, polymers are used for membrane preparation. Therefore, no polymerization is needed. In other words, no dangerous monomers are needed. Thirdly, if a chemical has to be used but cannot be dissolved in water, then other green strategies can be applied. For example, sonication can be used to disperse carbon nanotubes (CNTs) into aqueous solution. Finally, if organic solvent has to be used, then low toxic ones are chosen, such as ethanol. More details derived from the last strategy are discussed below.

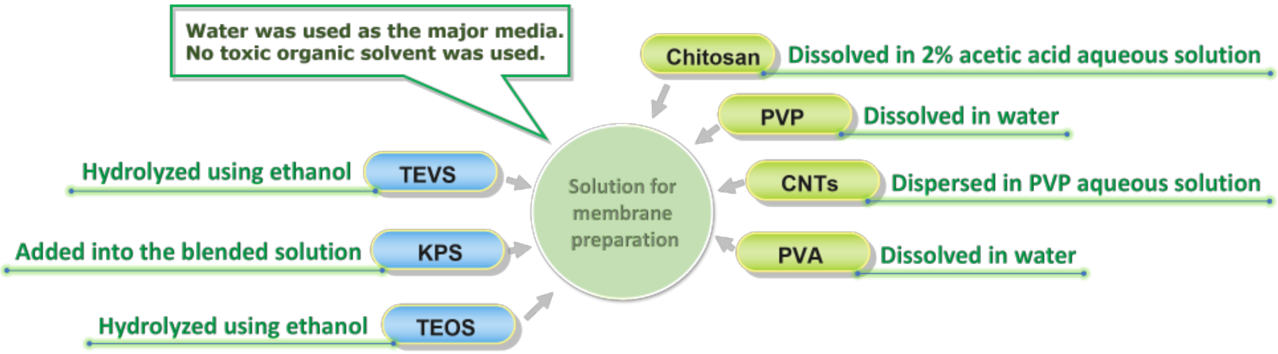


Figure 2. An example of green synthesis of nanocomposite membranes. PVP: Polyvinylpyrrolidone; TEVS: Triethoxyvinylsilane; KPS: Potassium persulfate.

Unfortunately, in many situations, water cannot take the role of conventional toxic organic solvents. In these cases, non-toxic or less toxic solvents can be used. Examples of green or less toxic organic solvents are methyl lactate, ethyl lactate, supercritical carbon dioxide (sCO_2), ionic liquids, DMSO and triethylphosphate (TEP) [56]. For example, PIMs are commonly synthesized using toxic organic solvents, such as DMAc and toluene [57–59]. Ponomarev et al. [60] developed a new method to effectively synthesize PIMs using DMSO as the solvent. Marino et al. [61] synthesized PVDF membranes for MD applications using solution casting method, where TEP is used as the solvent to replace conventional toxic solvents. Barroso et al. [62] synthesized polyacrylonitrile (PAN)-based UF membranes in sCO_2 with improved antifouling performance.

In order to meet the requirements for different applications of polymeric membranes, there is a growing interest to incorporate nanoparticles (NPs) into the polymer matrix to tune membrane properties [63]. Since NPs are part of the membranes, the synthesis of NPs is expected to be green as well. There have been quite a few studies on green synthesis of NPs, many of which are done in aqueous media [64,65]. Sharma et al. [66] conducted a comprehensive review on green synthesis of silver NPs. Smuleac et al. [67] developed a novel green route to prepare membranes for the degradation of chlorinated organic pollutants (Figure 3). Specifically, PVDF membranes were functionalized by in situ polymerization of acrylic acid (AA) in an aqueous phase. Then Fe NPs were synthesized in polyacrylic acid (PAA) functionalized PVDF membranes using green tea extract, instead of the conventional dangerous reducing agent, i.e., sodium borohydride. This green route is exemplary because no organic solvents are used during membrane preparation. Instead, water is used as the solvent. Furthermore, as a substitute for traditional reducing agents, green tea extract is innovatively used for NPs synthesis. Green tea extract is biodegradable, naturally available, and non-toxic. This enlightening study opens up new possibilities for green synthesis, which is to explore green materials from the natural world to replace conventional chemicals.

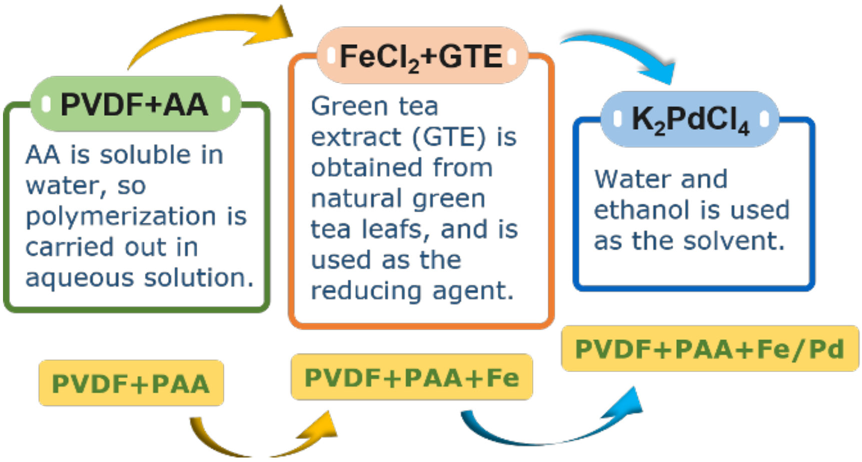


Figure 3. An example of green synthesis of membranes using natural available resources.

As indicated above, researchers have been exploiting natural resources, such as carboxymethyl cellulose (CMC) and natural tree gums (NTGs), as the substitutes for conventional chemicals. As a biodegradable polymer, CMC is derived from nature resources [68]. Unlu et al. [68] synthesized a catalytic membrane for biodiesel production. They used CMC as the polymer. Moreover, the prepration is carried out in aqueous solution at room temperature since CMC is also soluble in water. But unfortunately, chloroacetic acid is usually used in CMC production and it is considered as a hazardous chemical. Gum karaya and gum kondagogu are two examples of NTGs. As the green reducing agents, they are used for synthesis of NPs [69–71].

Conclusions and future prospects

With the continuous improvement of our society, in combination with the growing concern of global environmental pollution, green and sustainable synthesis is the only way forward. Unfortunately, for polymeric membrane preparation, green synthesis studies only account for a small portion of the total studies. Moreover, most of the current green strategies can only realize green synthesis partly. Therefore, there is still a long way to go. Before reaching the ultimate goal of green synthesis, there are several stages to go (Figure 4).

Increase the proportion of green synthesis to total synthesis (Stage 1)

In this stage, more researchers are considering green synthesis strategies when designing their experiments. One typical route is, toxic solvents are gradually replaced by less toxic or non-toxic solvents which are commercially available. Another typical route is, chemicals which “only” dissolves in toxic solvents are gradually replaced by more environment-friendly chemicals. The two routes are not mutually exclusive. If fact, they can be proceeded simultaneously. An example is to use existing water-soluble polymers to replace water-insoluble polymers, therefore water can be used to dissolve the polymers.

Increase the proportion of “near-complete green synthesis” to total green synthesis (Stage 2)

In this stage, more synthesis methods are developed to realize “near-complete green synthesis”, which means that no toxic solvents are used, no toxic reactants are used, and no dangerous or unsustainable processes/procedures are used. For example, in these green routes, there is no need to use a lot of solvents to wash the membranes to remove unreacted chemicals, and there is no hazardous waste produced during synthesis.

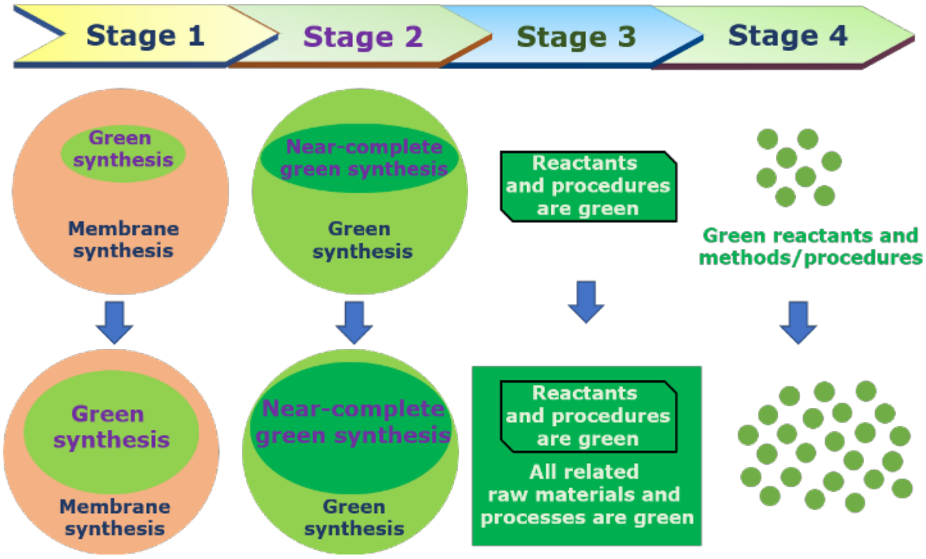


Figure 4. Four stages of green synthesis of polymeric membranes.

Apply the "LCA methodology" to realize green synthesis completely (Stage 3)

In this stage, when designing a synthesis route, the origin of the chemicals used for synthesis, as well as other materials involved in the synthesis procedure, should also be considered as green. In other words, not only should a chemical itself be safe/non-toxic, but the sources and procedures used to produce this chemical should be green as well. One route is to use natural resources to extract chemicals that are harmless to humans and the environment. It should be addressed that, the extraction process should be green as well.

Continuously develop more green chemicals and synthesis methods (Stage 4)

In this stage, it is very hard to find membranes synthesized via environment-unfriendly ways because there are plenty of green methods available, there are a vast variety of green chemicals which are commercially available, and more chemicals are being developed or discovered in green and sustainable ways. At this stage, the ultimate goal of green synthesis is fully achieved.

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