15 Membrane Techniques for the Preparation of Nanomaterials

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Abstract

Nanomaterials are always in demand owing to its wide variety of applications in various fields of science. Various methods are available for the synthesis of nanomaterials, but membrane techniques proved to be efficient in the preparation of nanoparticles. The present chapter reviews the membrane techniques reported in the fabrication of various types of nanomaterials such as nanowires, nanorods, nanospheres, and others.

Keywords

Membrane · Techniques · Nanomaterials · Template

1 Introduction

Nowadays terms like "nanoscience" and "nanotechnology" are not only limited to the research field but also used in day to day life. The applied science involves the technology at nanoscale, which is about 1–100 nanometers. Nanomaterials are used in wide array of science including electronics (Kamyshny and Magdassi 2019), optics (Shen et al. 2000), composite materials (Sahay et al. 2014), energy storage (Liu et al. 2017), electrochemistry (Li et al. 2009), food science (Singh et al. 2017), and health science (Chen et al. 2013). Nanomaterials are nanotech product designed to be very small with unique physical and chemical characteristics that prevails at nanoscale. The physical and chemical properties at nanoscale are largely varied than their large-scale version, which can prove to be beneficial. For instance, nanoscale particles are reported to cross the complex blood-brain barrier, which can further host for targeted health benefits (Saraiva et al. 2016; Thomsen et al. 2015). Thus, since the discovery of nanomaterials, a deep interest has been developed for these nano-objects, and extensive research has been done. These nano-objects with their large surface area show trenchant thermal, mechanical, optical, electronic, and chemical properties as compared to its bulk counterpart. This unique characteristic is developed due to the quantum size of the material (Roduner 2006). The nanomaterials can be clas-

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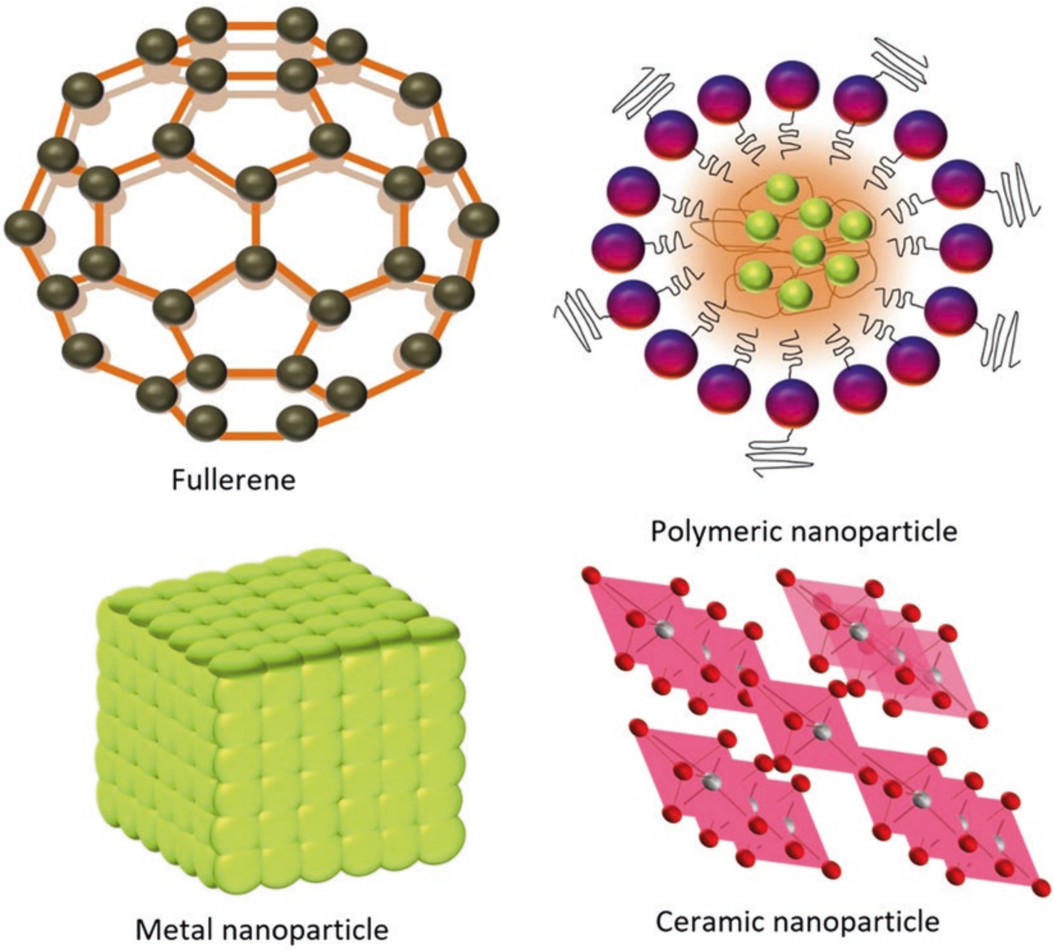

Fig. 15.1 Various types of nanomaterials

sified into various groups, namely, fullerenes, metal nanoparticles, ceramic nanoparticles, and polymeric nanoparticles (Fig. 15.1).

Significant development has been made in the improvement of methods for the synthesis of nanomaterials. Methods are classified into physical, chemical, biological, and hybrid approaches. Physical approaches can be further classified into mechanical methods, such as high-energy ball milling (Yadav et al. 2012) and melt blending (Bikiaris et al. 2006), and vapor methods, such as physical vapor deposition (Horprathum et al. 2014), laser ablation (Kim et al. 2017), sputter deposition (Galdino et al. 2017), and electric arc (El-Khatib et al. 2018). Chemical approaches can be classified into five major classes, viz., (i) colloidal methods (Kang et al. 2007), (ii) sol-gel processes (Mackenzie and Bescher 2007), (iii) water-in-oil microemulsion methods (Malik et al. 2012), (iv) hydrothermal synthesis (Darr et al. 2017), and (v) polyol method (Fievet et al. 2018). Biological methods involve the use of DNA (Seeman 2010), microorganisms (Sharma et al. 2015), and enzymes (Kolhatkar et al. 2015). Hybrid methods include electrochemical method (Singaravelan and Alwar 2015), chemical vapor deposition (Manawi et al. 2018), and microwave-assisted reverse microemulsion method (Lu et al. 2016).

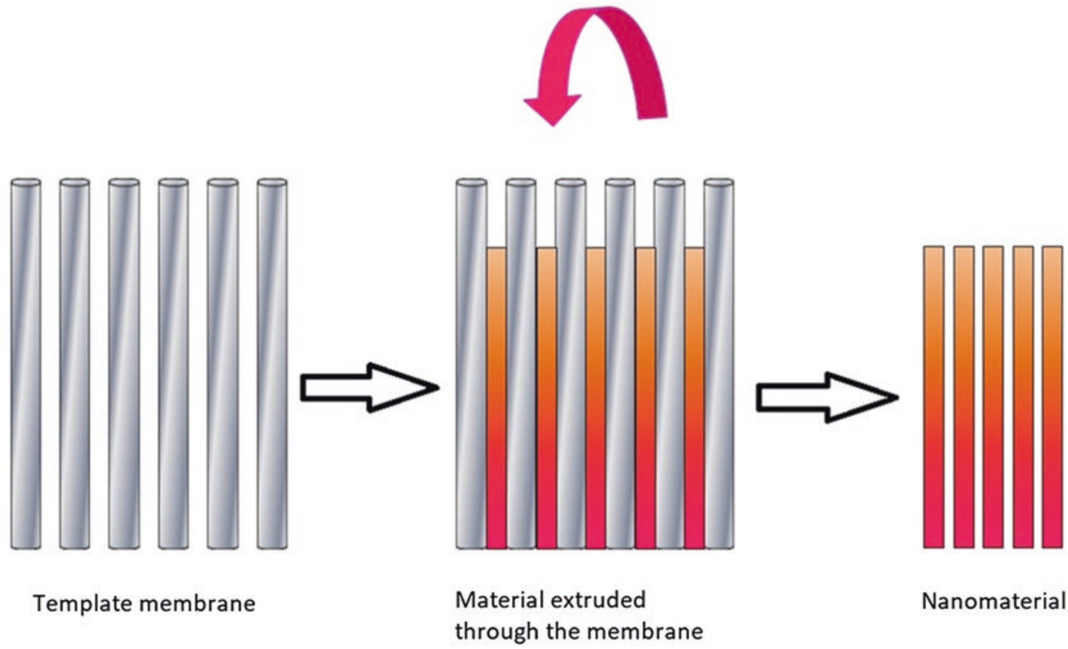

Fig. 15.2 Schematic representation of extrusion of nanomaterial through template membrane

2 Membrane Approach

Membrane-based approach for the synthesis of nanomaterials is known since the 1990s. The general approach for nanomaterial preparation is "template method" because the pores of the nanoporous membranes are utilized as template in the fabrication of nanomaterials. Figure 15.2 demonstrates the mechanism of process of forming nanomaterials when entered into a membrane. Membranes contain cylindrical pores of definite length and width. Material is extruded through the membrane under pressure resulting into formation of nanomaterials. Template method is utilized to fabricate nanotubes and nanowires. Another method in membrane technique uses membrane contactor to prepare nanomaterials. Figure 15.3 exhibits the working principle of the method in which one phase is introduced in the membrane through the pores and another phase flows tangentially to the membrane surface. Nanomaterials are produced when both phases come into contact with each other. Polymeric nanoparticles, solid lipid nanoparticles, and nanocrystals can be prepared using this technique.

3 Template Method

Over the past few decades, template method has proved to be the most successful method for the fabrication of nanomaterials. The method generally involves formation of desired materials in the nano-range of the pores of the membrane. Depending on the physical characteristics of the nanopore membrane, size, shape, and structure of the fabricated nanomaterial can be managed. Morphology of the nanomaterials can be changed during the process by controlling the nucleation and growth of nuclei. Three basic steps involved in the template method of fabrication of nanomaterials are (i) preparation of template; (ii) application of some synthetic approach like sol-gel, precipitation, etc.; and (iii) template removal. Templates are classified into two groups soft and hard templates based on the structure of the template material.

Removal of template is the last step in the process of nanomaterial fabrication. Method selection is made such that the physical and chemical properties of the nanomaterials remain unaf-

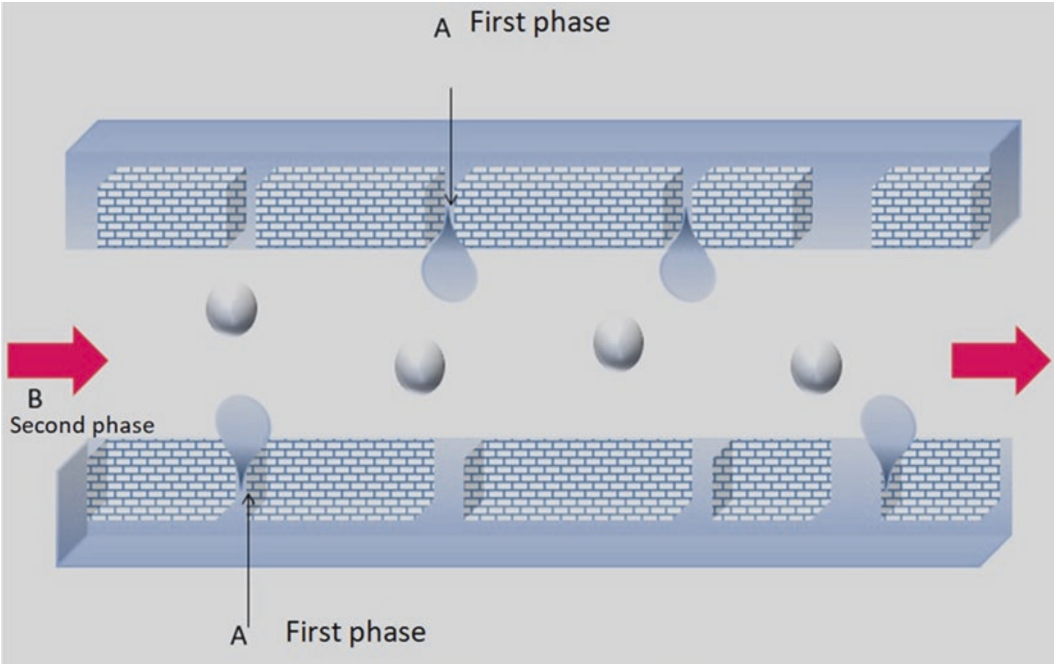

Fig. 15.3 Working principle of the template method

fected. Removal methods are classified as physical (e.g., dissolution) and chemical (e.g., calcination and etching).

4 Hard Template

The name itself suggests the property of hard template, which is made up of rigid and stable material like polymers, silica, and carbon. Hard template is also known as exotemplate method and determines the size and morphology of the mesoporous structure. The process is analogous to casting method in metallurgy, where the template acts as casting molds. Thus, it is referred as nanocasting, where the casting process is at nano-level. Various types of hard templates are available, such as mesoporous silica, porous anodic aluminum oxide (AAO), and carbon.

Mesoporous silica is explored as hard template due to its well organized structure and pores, high surface area, high thermal stability, low toxicity, and high compatibility with wide variety of materials (Deng et al. 2017). Upon removal of the template mold, the metal precursors will take the shape of the mesoporous silica hard template. Mesoporous silica such as SBA-15 is commonly used for the fabrication of mesoporous nanostructures. For example, silica templates with cylindrical channels will yield nanowires (Lu and Schuth 2005), template with spherical pores will give nanospheres (Lu and Schuth 2006), and template with bicontinuous pores will produce bicontinuous mesostructures (Yang and Zhao 2005). SBA-15 has distinct characteristics such as uniform hexagonal pores with narrow pore size distribution ranging between 5 nm and 15 nm, wall thickness of about 3.1 to 6.4 nm, and internal surface area of about 400–900 m^2/g (Thielemann et al. 2011). Takai and co-workers synthesized nanowires of noble metals (Pt, Ag, and Au) by using SBA-15 powder as template through vapor-infiltration process employing dimethylamine borane as reducing agent (Takai et al. 2010). Seo and co-workers reported synthesis of carbon nanomaterials using mesoporous silica as template. SBA-15, SBA-16, and KIT-6 mesoporous silica templates were employed for the synthesis. Further the templates were impregnated with mineral acids such as

Table 15.1 Various mesoporous silica used as hard template

Mesoporous silica type	Material synthesized	Precursor	References
SBA-15	CdS nanowire	Cadmium xanthate	Yuan et al. (2009)
SBA-15	Mesoporous carbon	Polyacrylonitrile	Kruk et al. (2005)
SBA-15 and B56-E-20	Mesoporous PAF-45HX	Biphenyl	Li et al. (2018)
SBA-15 and KIT-6	Co_3O_4 nanostructures	Cobalt oxide	Rumplecker et al. (2007)
KIT-6	Mesoporous carbon	Sucrose	Dai et al. (2010)
MCM-48	Osmium and platinum 3D nanonetworks	Organometallic	Lee et al. (2006)
MCF	Mesostructured graphitic carbon nitride materials	Carbon tetrachloride and ethylenediamine	Xu et al. (2013)
HMS aluminosilicate	Mesoporous carbon	Phenol and formaldehyde	Lee et al. (2000)
MSUF	Mesocellular carbon foam	Sulfur	Jeong et al. (2017)
SBA-15	Mesoporous NiO	Nickel	Wahab and Darain (2014)
SBA-15 and KIT-6	Mesoporous and nanowire SnO_2 anode	SnO_2	Kim and Cho (2008)
SBA-15	Mesoporous $NiCo_2O_4$ nanowires	$Ni(NO_3)_2{\cdot}6H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$	Wang et al. (2018a, b)
SBA-15	Mesoporous $CoFe_2O_4$ and $CoLa_{0.12}Fe_{1.88}O_4$	$Co(NO_3)_3{\cdot}6H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$	Shang et al. (2018)
KIT-6	Mesoporous Fe-In_2O_3	Indium and ferric nitrate salts	Zhao et al. (2014)
KIT-6	Mesoporous structures of In_2O_3-decorated NiO	Nickel nitrate	Dong and Liu (2018)
MCM-48	Mesoporous CeO_2	Cerium nitrate	Ji et al. (2008)
KIT-6	Mesoporous Fe_3O_4/CeO_2	CeO_2 and $Fe(NO_3)_3{\cdot}9H_2O$	Li et al. (2017)
KIT-6	Mesoporous WO_3	Phosphotungstic acid hydrate	Villa et al. (2015)
KIT-6	Mesoporous Fe_2O_3–TiO_2	$Ti(OCH_2CH_3)_4$	Park et al. (2017)
KIT-6	Mesoporous Fe_3O_4	$Fe(NO_3)_3.9H_2O$	Zhu et al. (2017)
SBA-15	Mesoporous MnO_2	$Mn(NO_3)_2.6H_2O$	Zhi et al. (2014)
KIT-6	Mesoporous MnO2	$Mn(NO_3)_2.4H_2O$	Bai et al. (2016)
SBA-15	Mesoporous transition metal sulfide@N-doped carbon composites	MClx (metal chlorides) and methionine	Zhu et al. (2019)
SBA-15	SnO_2 nanowires	$SnCl_2$ $\cdot 2H_2O$	Zhang et al. (2011)

phosphoric acid and sulfuric acid which formed as ester with the surface silanol and thereby prevented external carbon deposition (Seo et al. 2015a, b). Different mesoporous silica exploited for the synthesis of various nanomaterials are demonstrated in Table 15.1.

Porous anodic aluminum oxide (AAO) is widely exploited in the preparation of nanomaterials because of its flexibility and quantum-level pore size. Generally, the template is prepared from alumina sheet using electrochemical methods. Porous alumina is a self-organized structure resembling to honeycomb formed by high-density arrangement of ordered and parallel pores with diameter of 100–500 nm, pore density ranging from 10^7 to 10^{11} pore/cm^2, and diameter of 1–300 μm (Chen et al. 2012, Ide et al. 2017). Porous anodic alumina is reported in the preparation of a wide variety of nanomaterials, viz., nanowires, nanotubes, and nanodots. In one study, researchers had synthesized biological active surface-modified nanowires of anticancer drug (paclitaxel) by solvent annealing method using AAO templates. The surface was modified using n-octadecyltrichlorosilane, which thereby prevented agglomeration of nanowires (Abumaree et al. 2011). Copper nanowires were synthesized using a galvanic displacement process in combination with AAO templates. AAO template was prepared by anodizing alumina with oxalic acid. Nanowires were fabricated to use as an electrode for electrochemical denitrification (Ganapathi et al. 2019). Gold nanodot arrays were fabricated using AAO template with controlled size between 20 and 80 nm using nanoimprint method (Kwon et al. 2011). In another study, Mn-doped K0.5Na0.5NbO3 nanodots were synthesized on an Nb-doped $SrTiO_3$substrate by means of AAO template. Resulting nanodots had a diameter of 50 nm and thickness of 34 nm (Ahn and Son 2016). Carbon nanotubes are reported to be fabricated by AAO template method using impregnation method (Peng Xiang et al. 2012), microwave plasma chemical vapor deposition method (Zuidema et al. 2013), and catalytic chemical vapor deposition method (Hekmat et al. 2017) and employing microwave radiation (Dadras and Faraji 2018).

Carbon is one of the abundant elements found in nature. It can be present in different structures with various physical and chemical properties. Carbon is being exploited as template for synthesis of a wide variety of nanomaterials due to its thermal and chemical stability (Zhu et al. 2012). It has uniform pore distribution and has diameter less than 50 nm and high specific area (Zhang et al. 2016). Hollow metal oxide fibers (TiO_2 and Fe_2O_3) have been synthesized using activated carbon fibers as the templates employing impregnation and heat treatment (Yuan et al. 2006). In another study, metal oxide nanowall structures of α-Fe_2O_3 were fabricated using carbon nanowalls as template by plasma-enhanced chemical vapor deposition technique (Akikubo et al. 2019). Metal oxide hollow spheres of Cr_2O_3, α-Fe_2O_3, Co_3O_4, NiO, and ZnO have been fabricated employing glucose derived-carbonaceous spheres as sacrificial templates. Respective metal oxides were used as precursors (Abdelaal and Harbrecht 2014). Researchers demonstrated the use of carbon nanofibers as template in the fabrication of porous metal oxide nanowires of Fe_2O_3, Co_3O_4, NiO, and CuO. These nanowires were further studied for their photocatalytic performance in which porous Fe_2O_3 showed the best results (Fan et al. 2015).

5 Soft Template

Soft templates are not fixed, rigid structures but are formed during the process of fabrication of nanoparticles. Because of some intermolecular or intramolecular force of interaction, the aggregate is formed with specific structure. The inorganic materials deposit on the surface or interface of these templates by means of some methods, namely, electrochemical deposition, chemical deposition, and/or other deposition techniques. This process of deposition leads to the formation of particles of definite shape and size. Soft templates show wide variety of application in the fabrication of nanomaterials due its versatile characteristics, easy method of preparation, non-toxicity, and repeatability. It is also known as endotemplate method in which structure-directing agents like surfactants arrange to self-assemblies (micelles) leading to mesopores (2–30 nm). The assemblies are governed by weak forces like non-covalent bonds, van der Waals force, and electrostatic attraction (Zhang et al. 2019).

Mainly soft templates include cationic, anionic, nonionic, and mixed surfactant systems to synthesize self-assembled porous structures. Mixed anionic surfactants such as sodium dodecyl benzene sulfonate and sodium dodecyl sulfate were used as template in the synthesis of mesoporous silica nanoparticles. The co-structure-directing agent employed was 3-aminopropyltrimethoxysilane (Gai et al. 2016). In another study, mesoporous hollow silica nanoparticles were synthesized using dual soft template system. Cationic surfactant cetyltrimethylammonium bromide along with triblock copolymer poly(styrene-b-2-vinyl pyridine-b-ethylene oxide) with a center void of about 17 nm was used to fabricate the nanoparticles. The ion interaction between cationic surfactant and silica leads to formation of mesostructures (Li et al. 2015). Shen and co-workers fabricated three-dimensional dendritic biodegradable mesoporous silica nanospheres using cationic cetyltrimethylammonium chloride as soft template and triethanolamine as catalyst (Shen et al. 2014).

Polymers possessing properties like large molecular weight, stability, and diverse molecular structure are used as soft template for the synthesis of nanomaterials. Block copolymers are generally utilized for the synthesis of nanomaterials by soft template method. Linear arrangement of blocks of monomers leads to more than one characteristic and thereby becomes helpful in the nanomaterial's fabrication. Choma and co-workers synthesized mesoporous carbon containing silver nanoparticles using soft template method. Triblock copolymer $EO_{101}PO_{56}EO_{101}$ was used as soft template, while resorcinol and formaldehyde were employed as carbon precursors (Choma et al. 2011). Nanostructured titania materials were fabricated using randomly methylated beta-cyclodextrin and block copolymer P123 as soft template. Controlled amount of cyclodextrin promoted sphericity of particles (Lannoy et al. 2014).

Many researchers employed a combination of hard and soft template techniques to exploit each templating characteristics in the preparation of nanomaterials. A combination of hard and soft template methods were employed in the preparation of silica hollow microcoils with nanostructred walls. Acid group (-COOH)-functionalized carbon microcoils were used as hard template, whereas hexadecyltrimethylammonium bromide (a surfactant) or perylenebis(dicarboximide) (amphiphilic dye aggregates) was used as soft templates (Rodriguez-Abreu et al. 2011). In another research, Zhang and co-workers fabricated hollow mesoporous silica nanoparticles via a facile soft-hard template route. Carbon nanosphere was used as hard template, and cetyltrimethylammonium bromide was utilized as soft template (Zhang et al. 2015).

Thermal stability is a concern with hydrocarbon-based polymer templates undergoing thermal treatment. However, carbonization of polymer templates helps to improve thermal stability but is limited to a certain extent. Also carbonized polymer template can undergo oxidation resulting into breakdown of the porous structure. Another method is to couple inorganic elements with polymer templates where inorganic nanoparticles serve as hard template and polymers as soft template. Thus, advantages of both hard and soft template methods can be achieved, and this combination is known as colloidal template method. Kang and co-workers demonstrated colloidal template method for the synthesis of $C@MoS_2$ nanoadsorbents. Colloidal microporous organic network nanotemplates were prepared through the networking of organic building blocks in the presence of poly(vinylpyrrolidone). MoS_2precursors were incorporated into the nanotemplates, and heat treatment led to surface-engineered core-shell nanoadsorbents. $C@MoS_2$ nanoparticles with a diameter of 80 nm, a negative zeta potential (−39.5 mV), a high surface area (508 $m^2 g^{-1}$), and excellent adsorption performance toward cationic dyes were successfully prepared using colloidal template method (Kang et al. 2019).

6 Membrane Contactor

In membrane contactor technique, one phase is introduced into another phase through the membrane pores. The other phase is flowing perpendicular to the membrane surface. Pore droplets are formed at the pore outlets and are solidified in the second phase flowing tangentially to the membrane surface (Fig. 15.4). The process has similarity to membrane emulsification technique (Fig. 15.5) in which oil in water, water in oil, or multiemulsions are prepared. In some process mixing and reaction such as polymerization, precipitation occurs between two phases inside the membrane unit. Polymeric hollow fibers and tubelike inorganic membranes are generally employed in the fabrication of nanomaterials using membrane contactor technique. For instance, nanoparticles of $BaSO_4$ were fabricated employing hollow fiber ultrafiltration membrane using membrane contactor technique (Jia and Liu 2002). In another work, nanoparticles with average size of 360 nm were prepared using ceramic membranes with an active ZrO_2 layer on an Al_2O_3-TiO_2 support (Charcosset and Fessi 2006). Various nanoparticles prepared using membrane contactor technique include polymeric nanoparticles, solid lipid nanoparticles, and inorganic nanoparticles (Table 15.2).

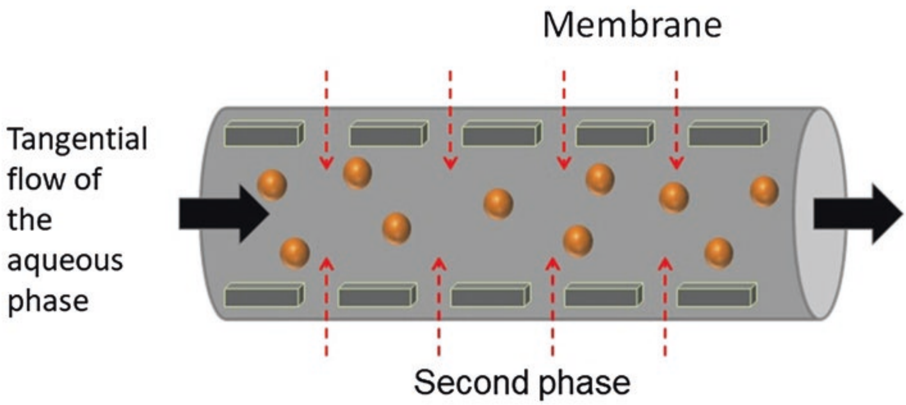

Fig. 15.4 Schematic representation of membrane contactor technique

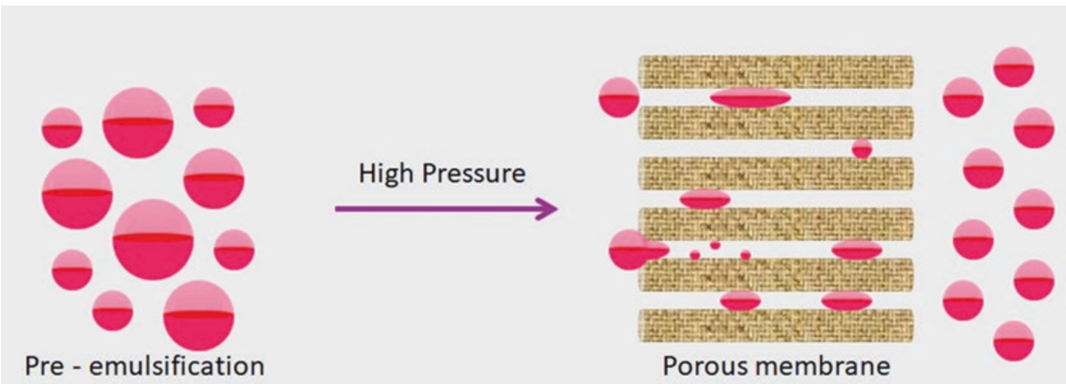

Fig. 15.5 Schematic representation of membrane emulsification method for the preparation of nanomaterials

7 Miscellaneous Methods

Membrane techniques are investigated extensively using various novel materials as membrane for synthesis of nanoparticles. For instance, Wang and co-workers used eggshell as membrane template in fabrication of MnO_2 nanoparticles from potassium permanganate by in situ redox reaction (Wang et al. 2018a, b). In another work, tin oxide nanoparticles were synthesized from tin chloride dihydrate using eggshell as biotemplate (Selvakumari et al. 2018). Nanoparticle size ranged from 13 to 40 nm. Gold nanorods were synthesized by electrochemical template synthesis using track-etched polycarbonate membrane. Chloroauric acid ($HAuCl_4$) was employed as precursor in the preparation of gold nanorods and mercury as cathode for the electrochemical deposition process (Sharma et al. 2012). In another such work, AgCl microstructures and Pt nanowires were fabricated using etched ion track polycarbonate as membrane template employing simple ion exchange mechanism (Kumar and Chakarvarti 2012, Naderi et al. 2012). Shirasu porous glass (SPG) membranes are utilized by various researchers in the preparation of nanoparticles. Itraconazole nanoparticles were fabricated using SPG membrane using antisolvent precipitation method (Seo et al. 2015a, b). In another such work, polymeric nanoparticles (around 300 nm in size) of docetaxel were prepared by SPG membrane emulsification method using poly(lactide)-D-α-tocopheryl polyethylene glycol 1000 succinate polymer (Yu et al. 2013).

Membrane techniques for fabrication of nanomaterials were introduced since the 1980s, and

Table 15.2 Examples of nanoparticles prepared using membrane contactor technique

Product	Membrane type	References
$CaCO_3$ nanoparticles	Polypropylene hollow fiber	Jia et al. (2013)
$CaCO_3$, $SrCO_3$, $Al(OH)_3$, and Al nanoparticles	Polypropylene hollow fiber	Jia et al. (2009)
Albumin nanoparticles	Porous glass	Yedomon et al. (2013)
Solid lipid nanoparticles	Ceramic membranes with an active ZrO_2 layer on an Al_2O_3-TiO_2 support	El-Harati et al. (2006)
Polycaprolactone 10,000 nanoparticles	Ceramic membranes with an active ZrO_2 layer on an Al_2O_3-TiO_2 support	Charcosset and Fessi (2005)
Solid lipid nanoparticles	Ceramic membranes with an active ZrO_2 layer on an Al_2O_3-TiO_2 support	Charcosset et al. (2005)
$CaCO_3$ nanoparticles	Polypropylene hollow fiber	Jia et al. (2010)
Gold nanoparticles, polycaprolactone nanoparticles, biodegradable micelles from poly(ε-caprolactone)/poly(ethylene glycol) diblock copolymers and liposomes	Nickel microengineered membrane	Vladisavljevic (2019)
$BaSO_4$ nanoparticles	Hollow fiber membrane	Jia and Liu (2002)
CeO_2Nanoparticles	Stainless steel microfiltration membrane	Yao et al. (2017)
ZnO nanoparticles	Stainless steel microfiltration membrane	Wang et al. (2010)
Silica nanoparticles	Stainless steel microfiltration membrane	Zhang et al. (2014)
Indium tin oxide nanoparticles	Stainless steel microfiltration membrane	Wang et al. (2016)
ZnO nanoparticles	Stainless steel microfiltration membrane	Huang et al. (2013)
Pseudoboehmite nanoparticles	Stainless steel microfiltration membrane	Wang et al. (2011)

till today various new membranes are investigated and reported for the same. Membrane template methods are widely used among the other methods available for the synthesis of nanoparticles. However, new polymers and materials are exploited for the efficient preparation of nanoparticles.

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