The toolbox of porous anodic aluminum oxide–based nanocomposites: from preparation to application

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Abstract

Anodic aluminum oxide (AAO) templates have been intensively investigated during the past decades and have meanwhile been widely applied through both sacrificial and non-sacrificial pathways. In numerous non-sacrificial applications, the AAO membrane is maintained as part of the obtained composite materials; hence, the template structure and topography determine to a great extent the potential applications. Through-hole isotropic AAO features nanochannels that promote transfer of matter, while anisotropic AAO with barrier layer exhibits nanocavities suitable as independent and homogenous containers. By combining the two kinds of AAO membranes with diverse organic and inorganic materials through physical interactions or chemical bonds, AAO composites are designed and applied in versatile fields such as catalysis, drug release platform, separation membrane, optical appliances, sensors, cell culture, energy, and electronic devices. Therefore, within this review, a perspective on exhilarating prospect for complementary advancement on AAO composites both in preparation and application is provided.

Keywords Anodic aluminum oxide · Non-sacrificial · Isotropic · Anisotropic · Nanocomposites

Introduction

Combinations of different materials are often applied to design composites with particular use that is not inconceivable by the individual parts. Nanocomposites involved with nanoscale dimensions or bearing nanometer-scale structures found wide applications in science and technology [1–3]. Porous templates, such as ion track etched membranes, anodic metal oxides, porous silicon, and block copolymer templates, can not only be used for sacrificial nano-patterning but also capable to be fabricated into nanocomposites for applications such as efficient nano-filtration, separation, storage, etc [4–6]. Among these templates, porous anodic aluminum oxide (AAO) stands out because it is characterized with self-organized cylindrical alumina pores obtained from electrochemical oxidation and is recognized as cost effective fundamental substance for constructing functional nanocomposites [7]. The fabrication of AAOs is comprehensively studied and reviewed during the past decades [8–10], to which we aid the readers’ attention.

Literature survey reveals that AAO templates represent high flexibility in template thickness (i.e., pore length), pore diameter and interpore distance, which in turn enables the fabrication of nanomaterials with various dimensions. For instance, the range for pore diameter of AAOs can be attained from 6 to 400 nm, while pore densities reach up to $10^{11}$ cm$^{-2}$, and additionally, the pore length as long as 100 μm is obtainable [11–13]. Moreover, the pores are distributed in a strict well-arranged manner that guarantees well-ordered structures of obtained nanomaterials. AAO membranes have excellent thermal stability and outstanding resistance toward organic chemicals that allow them to be applied as patterning templates for materials of both organic and inorganic nature [14–20]. In addition, high pore density and aspect ratio endow AAO membranes with a large surface-to-volume ratio. The pore walls are accessible for further functionalization that enabled AAO membranes as fundamental materials for preparing diverse nanocomposites [21, 22]. On the other hand, nanocomposites are commonly characterized by anisotropic structure, and clustering of dispersed filler may significantly affect their properties.
Therefore, the modification involves manipulating of AAO membrane surface, pore chemistry, topography, surface roughness, surface charge, surface energy, and wettability and is of particular importance to meet the demand of preparing AAO-based nanocomposites that present novel chemical and physical properties as well as morphological and interfacial characteristics for manifold applications.

Herein, we review the recent research progress on preparation techniques applicable for fabrication of AAO-based nanocomposites. Additionally, grounded on two major types of AAO membranes, isotropic through-hole and anisotropic single open-end AAO nanocomposite implemented in disparate fields are further discussed. Finally, we conclude with a perspective outlook of AAO nanocomposites over preparation to application in nanotechnologies.

Methods for preparation of AAO nanocomposites

AAO membranes provide the opportunities for functionalizing via numerous modification approaches to result in well-designed architectures for practical usages. To date, in order to harness the distinctive properties of AAO templates, AAO-based nanocomposites have been successfully prepared by combining AAO with various materials including small molecules, organic crystals, polymers, and inorganic nanostructures, by means of self-assembly, polymer grafting, coating, and template wetting strategies. Combinations of modification methodologies adjust the materials with enhanced final functionalities of obtained AAO composites. The methods mentioned under this specific subchapter are depicted in Table 1.

### Table 1: Some methods for the preparation of AAO-based composites

| Strategy               | Detailed methodology | Materials                          | Remarks                                      | Refs.               |
|------------------------|----------------------|------------------------------------|----------------------------------------------|---------------------|
| Wetting                | Melt wetting         | Polymer/polymer blends             | Melt wetting with precursor film             | [24]                |
|                        | Solution wetting     | Polymer solution                   | Type of solvent and concentration of solution vary shape morphology | [25]                |
| Polymer grafting       | Grafting from        | Monomers and reactants             | Polymerization initiated from substrate; SI-ATRP, SI-RAFT, SI-ROMP | [26–30]             |
|                        | Grafting to          | Functional polymer                 | Coupled with pre-synthesized polymer         | [31, 32, 33, 34, 35]|
| Self-assembly          | Layer-by-layer deposition | Charged polymers                   | Multi-layer build-up via multiple attractive forces | [33, 36, 37]         |
|                        | Self-assembled monolayer | Organosilanes                  | Covalent -Si-O-Si- bond                       | [38–41]             |
| Coating                | Plasma-enhanced deposition | Reactants/precursor             | Plasma-enhanced reaction deposition          | [42–45]             |
|                        | Atomic layer deposition | Reactants/precursor             | Atomic layer control                        | [46, 47]             |
|                        | Chemical vapor deposition | Reactants/precursor             | Vacuum deposition                            | [48]                |
|                        | Electrochemical deposition | Conductive materials             | Simplex and complex deposition                | [49–51]             |

Self-assembly

Self-assembly technique is a commonly employed method for constructing well-defined supramolecular nanostructures [52]. Generally, self-assembly strategy consists of self-assembled monolayer (SAM) and layer-by-layer assemblies which refers to topographic functionalization. During a typical SAM formation, organic molecules assemble spontaneously by adsorbing on a surface [10]. On this account, SAMs are the most forthcoming approach for AAO membrane surface functionalization. AAO membranes offer potential for surface functionalization through reacting with surface hydroxyl groups as immobilization points for arrangement of monolayers [53]. Among the existing methods, silanization is the simplest and most effective SAM method to adjust membrane surface properties. Indeed, organosilanes of RSiX3-type (X=Cl, OCH3) can rapidly form covalent linkages between the membrane surface and the X-groups, which usually stabilizes the monolayer and allows further chemical modifications. During a conventional silanization process the RSiX3-type silanes are either first hydrolyzed into hydroxy silanes that are capable to be adsorbed onto the AAO surface, or the surface hydroxy groups directly react with the silanes forming a stable covalent bond. Further, comprehensive lateral arrangements are taking place resulting in stable surface-cross-linked monolayers that are covalently attached on the AAO surface [54]. For instance, Szczepanski et al. had demonstrated the stability of silanes on alumina porous membrane via typical SAM processing [55]. Additionally, self-assembly silanization can also be processed during template fabrication for constructing complicated hierarchical membranes. Jani et al. [56] had described a facile method to prepare AAO membranes with
a varying surface chemistry as illustrated in Fig. 1. In detail, after the first anodization step, part of the oxidized layer was removed and the remaining barrier layer was then functionalized with 3-aminopropyltriethoxysilane as the first silane layer. Starting from this first silanized layer, a second anodization step was further accomplished and the freshly generated AAO pore surface was then covered with pentafluorophenyldimethyl chlorosilane derivative. Consequently, an AAO membrane that is displaying sharp a contrast in wettability within each pore was obtained. Notably, according to this strategy more surface variations could be achieved in one template via further continuous anodization and silanization steps, in which three kinds of silanes were sequentially deposited inside the AAO membrane, enhancing the surface characteristics of AAO by making the membrane chemically robust [57]. Besides silanes, also phosphonates [58], carboxylates [59], catechols [60], and alkenes/alkynes [61], are widely utilized to modify AAO membranes by forming covalently attached and densely packed organic monolayers on the pore walls.

Layer-by-layer assembly of polymer materials within the cylindrical pores of AAO membrane is also a commonly used method for membrane functionalization. The formation principle underneath is based on multiple intermolecular interactions, such as electrostatic contacts, hydrogen bonding and hydrophobic interactions [62]. For example, AAO functionalization could be achieved by choosing appropriate polyelectrolytes, such as poly(ethyleneimine) (PEI), poly(allylamine) (PAH), poly(diallyldimethylammonium chloride) (PDADMAC), poly(styrenesulfonate) (PSS), poly(vinylsulfate) (PVS), and poly(acrylic acid) (PAA), forming electrostatic layer-by-layer assembly [63]. As an illustration, Li and colleagues [64] have synthesized nanotubes in AAO by alternatively pressurized injection of negatively charged poly(sulfonated styrene) (PSS) polyelectrolyte and positively charged poly(allylamine hydrochloride) (PAH) polyelectrolyte solution into membrane nanopores. Upon electrostatic adsorption, layer-by-layer deposition was accomplished, and multilayers of polyelectrolytes were formed on the inner walls of the membrane. The electrostatic interactions between layers also allow entrapping of biomolecules and/or nanoparticles into assembled nanotubes, and enable the obtained AAO composites to be applied as biosensors and catalytic membranes [59].

Polymer grafting

Grafting of synthetic polymers could endow AAO membranes with a variety of functionalities and surface topographies that are strongly correlated to potential applications. Furthermore, the grafted polymers lead to membrane kaleidoscopic properties by altering parameters such as degree of polymerization, dispersity, grafting density, and distributions along the membrane pores [65]. Generally, polymer grafting methods can be categorized as “grafting to” and “grafting from” strategies. The “grafting to” polymerization relies on an anchor point on the surface of an AAO membrane that is coupled with functional groups from pre-synthesized polymers, either form reactive end-groups or reactive side-groups. Kim et al. had employed a one-step “grafting to” approach to enable an AAO membrane functionalization with polymers [31]. Correspondingly, poly(N-isopropylamime) (PNIPAm) was synthesized through typical reversible addition-fragmentation transfer (RAFT) polymerization and then a catechol moiety was coupled with polymer chain end-group resulting in a catechol terminated PNIPAm chain. Through high binding affinity of catechol groups to aluminum oxide, catechol modified PNIPAm brushes were tethered to the surface of AAO, as shown in Fig. 2.

**Fig. 1** Schematic stepwise diagram for the preparation of layered silanes in AAO membrane. Reprinted with permission from ref. [57]. Copyright 2010 Wiley

**Fig. 2** Schematic illustration of catechol-PNIPAm grafted AAO composite. Reprinted with permission from ref. [31]. Copyright 2012 Royal Society of Chemistry
Besides, two-step “grafting to” modification methods have been proposed and extensively utilized. Generally, functional anchor groups were firstly grafted onto membrane walls that allow for further stabilized immobilization of pre-synthesized polymer chains. For instance, 3-glycidoxypropyl trimethoxysilane was introduced onto AAO surface to endow the membrane with reactive epoxy groups, which have been employed as reactive sites to graft polymers via a nucleophilic ring-opening reaction of the epoxides [66]. For example, PAA brushes could be grafted onto an AAO membrane through conjugation between epoxy groups and carboxyl groups, which resulted in PAA modified AAO that exhibits rapid and reversible response to external pH variations [32]. In addition, the group of Lu [33] had reported a “grafting to” method via quaternization reaction of the pyridine nitrogen atoms of poly(styrene)-block-poly(4-vinylpyridine) polymers with the bromide group from pre-modified AAO membrane as schematically illustrated in Fig. 3. Owing to the pH responsive characteristic of poly(4-vinylpyridine) block, the wettability of modified membrane could be changed via protonation and de-protonation of 4-vinylpyridine groups upon pH stimulation, which resulted in membrane reversible affinity towards oil and water, respectively. Such a smart membrane has potential to be utilized for oil/water emulsion separation and sewage purification.

Next, in a “grafting from” approach, polymer chains are grown from an initiating site on the AAO membrane surface. Generally, immobilization of initiating site onto AAO membranes is the first crucial step for a successful polymer “grafting from” methodology. Owing to the variation of synthetic approaches, a variety of “grafting from” synthesis strategies for the preparation of AAO nanocomposites have been carried out [67]. In’s group had illustrated a typical surface-initiated atom transfer radical polymerization (SI-ATRP) for the preparation of PNIPAm grafted AAO membrane composites [68]. Amine functionalities were first introduced to AAO membrane via self-assembly of 3-aminopropytriethoxysilane, following the initiator, 2-bromoisobutyryl bromide, was immobilized through amination reaction. Subsequently, polymerization of NIPAm was conducted on AAO membrane, resulting in grafting of PNIPAm brushes on the membrane pore walls [69]. In addition, Chu et al. had also employed SI-ATRP to achieve poly(3-(N-2-methacryloyloxyethyl-N,N-dimethyl)ammonatopropanesulfonate) (PMAPS) grafted AAO composite. The linear relationship of isolated yield and molecular weight between grafted PMAPS and corresponding unbound PMAPS polymer chain via free ATRP initiator has been demonstrated, which further shed light on controlling the polymerization on AAO membranes [14].

Despite the silane sol-gel chemistry to immobilize an ATRP initiator on AAO, initiation from a poly(dopamine) layer which had been pre-adsorbed on the AAO surface, could also be applied for facilitating the introduction of functional initiators. For instance, Wang et al. had first proposed using catechol groups of poly(dopamine) to immobilize an ATRP initiator for further initiating of polymer brushes. The simple approach for covalent immobilization of an ATRP initiator and the inherent versatility of SI-ATRP paved the way for the preparation of diverse polymer functionalized AAO membrane [70].

Although SI-ATRP has been widely used for the preparation of polymer grafted AAO composites, rigorous de-oxygenated atmosphere and indispensable addition of a transition metal catalyst constitutes harsh polymerization conditions that restrict possible use of the preparation method. Some of these limitations have been addressed by Song et al. via employing a surface-initiated RAFT (SI-RAFT) polymerization for growing polymer chains on AAO membrane [26]. In detail, a surface chain transfer agent (CTA) featuring silane end-groups was prepared and covalently bonded onto AAO membrane, subsequently RAFT polymerization was carried out from the immobilized surface CTA, thus accomplish grafting of poly(3-(methacrylamidomethyl)-pyridine) chains (Fig. 4) on AAO. The obtained AAO nanocomposites with grafted polyelectrolyte brushes could be utilized as ion-exchange membranes for protein adsorption and elution.

In addition, diversiform polymerization strategies could be processed in the same AAO membrane via a half-cell reactor for constructing asymmetric nanocomposites. As illustrated in Fig. 5, simultaneous chemical polymerization, such as ATRP, dopamine self-polymerization (DOP-SP) and ring-opening metathesis polymerization (ROMP), were carried out on the respective sides of an AAO membrane to achieve asymmetric...
polymer functionalization [27]. The respectively grafted polymers differed in hydrophilicities or responsive properties, thus endow AAO composites with asymmetric characteristics which are promising in the separation of organic charged molecules, oil/water mixtures, and asymmetric organic catalytic reactions.

Coating

Coating strategies, such as electrochemical deposition, electroless deposition, chemical vapor deposition, and atomic layer deposition, facilitate plating of a wide variety of materials onto AAO membrane for the preparation of corresponding nanocomposites [71]. Among the different deposition methods, electrochemical deposition features an advantage because the growth rate of deposited materials could be easily adjusted. However, electrochemical deposition is limited to fabrication of conductive materials only. During electrochemical deposition, through-hole isotropic AAO membranes were utilized and deposited with conductive materials. For this, an AAO template fixed on conductive substrate is attached to the cathode and brought into contact with the deposition solution. When the electric field is applied, cations diffuse towards the cathode at which they are reduced leading to the actual electrodeposition. As a consequence, nanorods or nanotubes attached to the conductive substrate are obtained inside the template pores [72]. For example, through electrochemical deposition, Cu-CuAl2O4 hybrids were deposited onto AAO membrane [73]. The composite membrane was utilized as a selective solar absorber. Owing to the incorporation of AAO substrate, the solar absorber was found to have optimized optical performance and a high anti-corrosion property when exposed to high temperatures up to 300 °C. Additionally, conductive polymers are also qualified to decorate AAO membrane via electrochemical polymerization. Zhang et al. had deposited polypyrrole inside the AAO by via electrochemical polymerization. The obtained nanocomposite featured an asymmetric component distribution and displayed a pH- and light-modulated ion transport functionality that could be further used for creating smart nanochannel systems [74]. Similarly, the group of Lee had prepared polyaniline, polypyrrole, and poly(3,4-ethylenedioxythiphene) (PEDOT) nanostructures via electrochemical deposition in an AAO membrane [75]. Despite a single material, polymer-metal hybrid materials [76], segmented or core-shell nanostructures [77] could also be fabricated through electrochemical deposition process in AAO membrane through sequentially controlled deposition. As reported, the obtained nanomaterials are showing great potential for energy applications [78].

On the contrary, electroless deposition is a non-galvanic plating method for surface functionalization with conductive layer. However, reducing or oxidizing agents are required
when coating metals and compounds through electroless deposition [79]. Under the effect upon surface catalyzed oxidation of reducing agent, metal ions are reduced into corresponding metal, and deposition of metal, such as copper, palladium, nickel, etc., on AAO was then achieved [75, 80]. Reddy et al. had deposited Cu and Zn onto AAO membrane via electroless deposition, and the obtained Cu-Zn/AAO composites were used for steam reforming of methanol [81].

Chemical vapor deposition (CVD) uses vapor phases for deposition, and subsequently to synthesize organic films directly onto the desired substrates, i.e., AAO. CVD is suitable for diverse materials especially to enhance productivity for those that possess limited solubility and are infusible on membrane surface [82]. For instance, Zhao et al. had prepared carbon and silicon covered AAO membrane via CVD approach. As shown in Fig. 6, carbon nanotubes (CNT) was first deposited onto AAO under atmosphere of ethylene at 800 °C; further cleaned by inductively coupled plasma etching (ICPE) process, and silane was subsequently deposited on formed CNT layer; afterwards further ICPE and CNT deposition process were carried out and resulted in coaxial carbon-silicon-carbon nanotube (CNT/SiNT/CNT) arrays implanted AAO membrane. Owing to the coaxial tubular structure, the AAO composite exhibited high area capacity of approximately 6 mAh cm⁻², which is greater than commercial graphite when used as anodes for lithium-ion batteries [83].

Additionally, the approach by applying a vapor phase that contains reactive monomer and initiator to form chemical deposition on AAO membrane is classified as initiated CVD (iCVD) [84]. During iCVD process, monomers are preferentially adsorbed on the membrane surface, and simultaneously, initiators are decomposed under thermal or plasma excitation and formed reactive radicals. As soon as monomer and initiator radicals mix, radical initiated polymerization on the surface was triggered. iCVD yields conformal coatings with high aspect ratio and ultrathin polymer layers [85–87]. For instance, Losic et al. had utilized plasma iCVD for growing of n-heptyamine polymer onto AAO surface. This methodology is used to control the membrane pore size by adjusting the deposited thickness of the polymer [88]. In addition, thin layer of pH-sensitive poly(methylacrylic acid-co-ethylene glycol dimethacrylate) was deposited onto AAO membrane via thermally initiated iCVD. Owning to the pH responsive character of the grafted polymer, the pore size of the modified AAO membrane could be tuned by swelling and de-swelling of grafted polymer upon changing pH. Hence, the change in pore size facilitated size dependent separation of molecules with diverse sizes. Additionally, protonation and de-protonation of polymer brushes will also alter the surface charge of the membrane. As a result, charge interactions between membrane and permeates will also affect the membrane permeability. As a consequence, the functional membrane was also used for pH stimuli-responsive protein separation [89].

Differing from CVD approach, atomic layer deposition (ALD) could meet the demand for atomic layer control and conformal deposition along the thickness control at Angstrom or monolayer level [90]. Velleman et al. had coated an AAO membrane with silica via ALD using tris(tert-butoxy)silanol and trimethylaluminium as precursors. By adjusting the number of ALD deposition cycles, the coating of silicon on AAO was systematically controlled which further determined the membrane pore diameters [91].

**Template wetting**

Solution-based template wetting is an effective method for the fabrication of numerous composites. In this regard, template wetting methodology that utilizes wetting phenomena to create a uniform coating of a low surface energy material, such as a polymer solution or melts, on a porous AAO template with

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**Fig. 6** Schematic diagram for the preparation of CNT/SiNT/CNT/AAO composites by successive CVD. Reprinted with permission from ref. [83]. Copyright 2012 Royal Society of Chemistry
high surface energy has been widely addressed [25, 92]. Kim et al. had prepared organic nanotubes from bis-acylurea in AAO membrane via solution wetting [93]. In addition, Cannon et al. had prepared poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene vinylene) and poly(3-hexylthiophene) covered AAO membranes via the template wetting method. The desired monomer or polymer was dissolved in suitable solvent and drop casted onto the AAO membrane. Due to surface tension effects, the applied polymer was entrapped into membrane nanopores. After evaporation of the solvent, the residual polymer layer was formed and resulted in polymer covered AAO composites [94].

In addition, by adopting AAO template wetting of photochromic molecules that assemble into crystals, nanocrystallized composites could be achieved. Via template wetting, photomechanical diarylethene nanocrystals were confined in the channels of the AAO membrane resulting in photo-powered composite bending actuators [95]. In fact, the AAO membrane is responsible for structural support and determination of bending direction, while diarylethene component provides photoresponsive ability. Upon directional UV light irritation, as revealed in Fig. 7, only a small part of crystalline nanowires in AAO membrane being directly exposed to UV light underwent photoisomerization while unexposed molecules kept their original state. The energy difference upon UV irradiation along pore orientation results in a bending motion away from the light source. The motion could be cycled multiple times in air or underwater. Besides, via template wetting methodology, Wu et al. prepared one kind lubricant-infused surface (LIS) by simple vacuum impregnation of oil into high aspect ratio AAO nanochannels. The LIS exhibited a better water repellency than the pristine AAO membrane. In addition, the thick porous structure endowed the surface with corrosion resistance, mechanical durability and self-healing properties, which enables LIS for various applications such as antifouling, anti-icing and anti-corrosion [96].

### Applications

As mentioned in the previous section, the most attractive property of AAOs is the strictly self-ordered cylindrical pores with customizable controlled pore size, pore length, and pore structure. Thus, AAO membranes provide unique possibilities in constructing nanocomposites. Utilizing the barrier layer of AAO membrane as demarcation line, AAOs can be divided as isotropic and anisotropic AAO. The isotropic AAO features double-pass cylindrical pores while anisotropic AAO has single open-end and maintains barrier layer. The membrane structure and further functionalization have great impact on the composite application, which will be discussed in this section. Figure 8 summarizes some of the typical applications of isotropic and anisotropic AAO composites ranging from water purification, protein separation, catalysis, drug delivery, smart surfaces, optical to electrical devices.

#### Application of isotropic AAO-based nanocomposites

The most distinguished characteristic of isotropic AAO membranes is the uniform cylindrical channel structure that spans over the entire thickness of the membrane. Therefore, isotropic AAO membranes allow further tuning of transport properties of the nanochannels. Isotropic AAO membranes feature not only high permeability, large surface area, and nanopore structure but are also stiff enough to withstand working under high pressure. Therefore, isotropic AAO membranes with tunable porosity and surface chemistry are widely used as membrane elements for specialized transport processes in the field of protein gating, water purification, photonic device, battery and sensor [91].

#### Protein gating

As reported, nanoporous AAO membranes are widely employed in the construction of protein gating composite membranes in combination with diverse biocompatible
organic and inorganic materials. For example, Chen et al. had adopted sputtering of Au on an AAO membrane for reducing the pore diameter from 27 to 10 nm, followed by modification of the membrane to graft polyhistidine-tagged proteins. This functionalized AAO can act as a biological membrane, which is allowing sequential protein binding and release/pumping cycles. Thus, the fabricated membrane realized the application in bio-pharmaceutical field [97].

Additionally, Lee et al. had prepared double stimuli-responsive gate membranes by grafting PAA and PNIPAm from one side of an isotropic AAO membrane, respectively (Fig. 9). The two distinguishable gates of the membrane can be individually modulated by temperature and pH. For instance, at 40 °C and pH 3, all polymer brushes are dehydrated leaving the gate opened for matter permeance. On the contrary, the gate could be closed by either increasing the temperature above 40 °C or adjusting the pH value above 6, or both, so enable closed state of composite membrane. This autonomous on and off gating membrane reveals controllability in storing and releasing of molecules such as bovine serum albumin (BSA), therefore illustrating potential prospective in mimicking cell membrane [98].

Similarly, Tufani et al. had prepared a Janus AAO membrane composite for protein gating by depositing poly(methylacrylic acid-co-ethylene glycol dimethacrylate), i.e., P(MAA-co-EGDMA), and poly(4-vinylpyridine-co-ethyleneglycol dimethacrylate), i.e., P(4VP-co-EGDMA), on each side of an isotropic AAO template via iCVD. Through the control of pH on each side of the composite, permeation of BSA molecules could be modulated on demand [99]. Further, by anchoring of specific proteins onto the inner pore surface, the membrane composites are capable for selective protein separation. For instance, when grafting lysine onto an AAO membrane, the functionalized composite is suitable for removal of bilirubin owing to the specific selectivity of grafted protein [100]. Besides, a simple deposition of a thin AAO membrane with small pore size (20–30 nm) on top of a silicon substrate enabled a biomolecule separation platform. The composite membrane could be used for electrostatic sieving of biomolecules. For example, when adjusting pH to 4.7, the same as the isoelectric point of BSA, BSA molecules existed in a neutral state, while bovine hemoglobin (BHB) molecules were positively charged owing to their inherent higher isoelectric point. As a consequence, when passing a mixed BSA and BHB protein solution through the membrane, the charged BHB molecules were blocked, while BSA molecules were selectively isolate [101].

**Purification**

AAO membranes bearing functionalized nano-cylindrical pores are utilizable for purification owing to their ability of selectively blocking viruses, small organic molecules, salts as well as other hazardous metal ions. In an exemplary work, Liu et al. had prepared amphiphilic AAO membranes for water “dry condensation” [102]. An amphiphilic AAO membrane was fabricated by modifying one side of the AAO membrane with dodecyltrichlorosilane to increase surface hydrophobicity, while maintaining the hydrophilic character of the other side. The hydrophobic surface prevents the accumulation of water droplets, hence exhibiting a self-cleaning property. The authors showed that this membrane is capable of a “dry condensation” in such way that water droplets are rapidly driven from the hydrophobic surface through the hydrophilic porous channel to the hydrophilic side. Therefore, this material has the potential to be applied in manifold of applications ranging from water-harvesting and phase-change-based desalination to energy generation and transfer.

When photochromic groups (such as spiropyran [103], diarylethene [104], or azobenzene [105]) are combined with AAO composite, smart optical materials could be fabricated. For instance, a photo-induced separation membrane can be achieved by grafting of azobenzene groups onto a AAO membrane via SAM approach [106]. The immobilized azobenzene groups are capable to undergo a cis-trans isomerization upon UV/vis stimulation, inducing a change of the membrane permeability. The azobenzene-AAO composite membrane is schematically illustrated in Fig. 10. Owing to the rapid

![Fig. 9](image-url)

**Fig. 9** Dual stimuli-responsive AAO composite with temperature-controlled PNIPAm gate and pH-controlled PAA gate. Reprinted with permission from ref. [98]. Copyright 2016 American Chemical Society
isomerization of azobenzene groups on membrane surface, vaporization of water is induced and promotes infiltration of aqueous solution, while the dissolved dyes, salt or protein molecules are rejected from permeation. As a consequence, the azobenzene-AAO composites are qualified for water purification and seawater desalination.

Additionally, Song et al. had prepared AAO composites for hazardous heavy metal ion removal from aqueous solution. In this regard, polyrhodanine was immobilized on AAO membrane via vapor deposition polymerization and the obtained polyrhodanine-AAO composite filtration setup is illustrated in Fig. 11 [107]. Attributing to the strong metal binding sites of polyrhodanine, the polyrhodanine-AAO composite reveals high metal uptake capability towards metal ions such as Hg(II), Ag(II), and Pt(I) [108]. Hence, when an aqueous mixture was passed through polyrhodanine-AAO composite membrane, metal ions were adsorbed by the immobilized polyrhodanine. Additionally, the composite membrane could be recycled and used again for heavy metal removal by further deposition of polyrhodanine.

Inspired by sand filter, nanoparticle-embedded AAO composites were prepared for finer filtration of small molecules in the nanoscale dimension. Phuong et al. had incorporated diverse polystyrene (PS) nanoparticles inside AAO channels by varying the size of entrapped nanoparticle from 24 to 150 nm, as illustrated in Fig. 12, and the permeability of the membrane composite was then modulated. In addition, upon functionalization of embedded nanoparticles with arginine/phenylalainine peptide groups, filtration based on charge selection was achieved for the separation of charged molecules, such as methylene blue from aqueous solution. Consequently, such a nano-sand filter is expected to be applied in water purification [109].

Additionally, Petukhov et al. had prepared an AAO supported graphene oxide composite membrane via spin-coating and demonstrated the usage of the obtained membrane for pressure-assisted filtration of gas de-humidification [110]. On one hand, the graphene oxide layer exhibited high permeability towards water and water soluble gases like CO₂, while acting as a barrier to most gases such as CH₄, N₂, O₂, and C₄H₁₀. On the other hand, AAO acted as a stable support and showed high affinity towards graphene oxide sheets via inherent hydrogen oxide groups; additionally, Al³⁺ cations formed an interlocking between graphene oxide sheets, which ensured the composite to be stable enough for gas de-humidification.

Catalysis

Besides being used as obstacles for unwanted substances, isotropic AAO membranes featuring highly arranged nanochannels are also ideal fundamental materials for promoting flow-through of desired materials, such as in catalysis. The porous structure of AAO membranes facilitates a better assembling of catalysts, and the inherent high thermal and mechanical properties of AAO membrane enable the utilization under harsh working conditions [111]. For example, Liu et al. had grafted poly(methacrylatoethyltrimethylammonium chloride) polymer brushes onto AAO channels via SI-RAFT polymerization, followed by a further in situ reduction of Au nanoparticles inside the nanochannels, thus resulting in the stabilization of Au nanoparticles in the AAO membrane. This AAO composite was applied for Au-mediated catalytic reduction of 4-nitrophenol under flow-through conditions. Channels of this composite membrane act as
nanosized reactors, and the high aspect ratio of the porous membrane and large amount of homogenously restrained Au nanoparticle attributed to a highly catalytic performance [30]. Additionally, Yang et al. had incorporated metal-organic frameworks (MOFs) within an isotropic AAO membrane. The AAO-MOFs composite had increased the compatibility, dispersity and stability of MOFs as catalyst reactor for the Knoevenagel condensation reaction [112]. Compared with metal catalysis, immobilization of enzyme catalysis is relatively more difficult owing to the high retention of protein activity upon chemical modification. In order to solve this problem, Lu et al. had proposed immobilization of enzyme in hierarchically structured AAO membrane. As shown in Fig. 13, enzyme catalysts were entrapped into mesoporous silica that was grown inside an AAO membrane. Further, an additional mesoporous nanoparticle film was covered on both sides of the AAO composite, benefiting the adaptive permeability, strong adhesion and smart integration. The resulting AAO-silica-enzyme composite membrane has demonstrated size-selective permeability of small molecules. When Trypsin was entrapped within the composite membrane, it was observed to promote the bio-catalytic hydrolysis of $\text{N}^\alpha-p$-tosyl-L-arginine methyl ester hydrochloride while keep constant activity even running up to 30 cycles [113].

Additionally, Hussain et al. had prepared embedded ruthenium (Ru) in an AAO by reduction of ruthenium precursor via a sonochemical method, and the obtained Ru@AAO was able to catalyze the oxidation reaction of 1-naphthalenemethanol with higher catalytic activity owing to the porous structure and surface area of AAO [114].

**Photonic- and electrical-related devices**

Other key applications of isotropic AAO membranes include combination with conductive materials for the constructing of optical, electrical or photoelectrical devices. Via vapor deposition, Zhou et al. had prepared an AAO-based plasmonic absorber that can absorb light in a wide wavelength range [115]. During the process, gold nanoparticles are finely deposited on top surface and inner walls of the AAO membrane in a hierarchical distribution along the pore walls. The assembled gold nanoparticles are larger and sparser on the top surface, whereas smaller and more density packed nanoparticles...
were observed inside the membrane channel. The heterogeneous distribution of gold nanoparticles and isotropic porous structure enabled AAO composites with efficient and broadband plasmonic absorption, which can be further used for solar steam generation.

Furthermore, Kwon et al. had fabricated micro-solid oxide fuel cells from isotropic AAO templates. In their study AAO membranes acted as substrates of the fuel cells. Unlike traditional foil substrates, the porous structure of AAO membranes provides gas-channels that improve the thermo-mechanical stability of the device further [116]. In addition, porous AAO membranes have been used as separators for lithium batteries. The porous structure of AAO membranes minimizes ionic resistance and shortens diffusion path of ions, which in turn enhance the discharge capacity of the battery. Additionally, the AAO separator has a high affinity to electrolytes, and good ionic conductivity. As a result, compared with commercial separators, porous AAO membranes are found to have better mechanical stability, and also showed better performances on electrolyte infiltration and retention [117].

Nanoporous isotropic AAO membranes are also widely used in sensing applications [118]. In comparison with flat sensor materials, porous AAO membranes are protruding because of their large surface area [54]. AAO-based sensors are widely utilized for pressure, humidity, chemical or bio-related sensing. For instance, a porous AAO membrane was incorporated into a pressure sensor device for isolating conductive wrinkled graphene layers which prevent excessive energy consumption from nonworking condition. The introduction of isolating AAO layer not only avoids energy combustion in the “off” state but also improves the sensitivity of the pressure sensor by taking advantage of AAO porous structure [119]. Besides, Ma et al. had constructed an AAO membrane as air filter in an optical gas sensor. With the introduction of the AAO membrane, the system can prevent particle contamination above 70 nm. By varying the incorporated pore size of AAO, the sensitivity of sensor system to particle contamination could be fine-tuned [120]. Additionally, Tabrizi et al. had designed a biosensor based on AAO via immobilized with DNAzyme. The obtained biosensor is able to detect lead(II) ions with different concentrations ranging from 50 to 3200 nM [121].

As a versatile substrate, AAO membranes could also be used to prepare nanofluidic devices for osmotic energy conversion. Xin et al. had deposited silk nanofibril (SNF) on to variable-channel AAO membrane for constructing a composite membrane for osmotic energy harvesting within a reverse electrodialysis device. The SNF dominated the ion transportation owing to its surface negativity, while AAO provide tunable pores with amphoteric groups enable the establishing of asymmetric nanofluidic system [122].

### Application of anisotropic AAO-based nanocomposites

The major application of anisotropic AAO membranes is patterning of uniform nanostructures, and in these processes AAO membranes are used as sacrificial templates. However, AAO membranes can also be maintained as substrates after nano-patterning for preparing nanostructured surfaces that are applied as antifouling and adhesive composite materials. Additionally, the large number of nanocavities are facilitating to load different materials, e.g. dye molecules, drug molecules, nanoparticles, and thus the filled AAO composites could be further used for storage and delivery of corresponding molecules. In this section, applications of nanocomposites that are established from anisotropic AAO membrane are discussed.

#### Smart surfaces

AAO membranes offer the opportunity to fabricate highly aligned nanostructured films, which could be used as structured functional surfaces with superior wettability for potential industrial application. Kim et al. had prepared a AAO/polydimethylsiloxane (PMDS) hybrid mold, where the AAO template was attached to PDMS plate which is flexible and can be used for roll-to-roll nanoimprinting [123]. However, for the fabrication of high-performance films only unitary nanostructures are woefully inadequate, hence, structural features such as pillar size, aspect ratio, tip shape, tilting angle, and hierarchical structures should also be considered [124–128]. Zhang et al. had incorporated anionic and zwitter-ionic polymers into AAO membranes and consequently smart gel surfaces with antifouling properties could be obtained. The surfaces showed underwater superoleophobicity with ultralow oil adhesion, which are usually observed for prohibited algae adhesion. This kind of gel surface is promising for usage in bio-adhesion industry or as antifouling coatings [129]. In addition, complex topography could also be built on AAO membrane by adopting the same strategy. Du et al. had fabricated underwater a micro/nano-brush dual structural surface on the substrate of AAO template from modulating template channels. The surface consisted of numerous poly(acrylic acid) gel pillars. The rough surface could entrap large amount of water to form underwater “lotus” state and exhibited underwater superoleophobic with low adhesion to oil droplets. Additionally, ATRP initiator was trapped in PAA gel microbrushes, and subsequently, the micro-brush could be further modified with stimuli-responsive polymer nano-brushes via SI-ATRP. Therefore, the surface was endowed with smart properties. For instance, by modifying with thermo-responsive PNIPAm brushes, the surface exhibited a low oil adhesion at 20 °C, and the adhesion increased when the...
temperature raised to 60 °C. Further, polyelectrolyte, poly(3-sulfopropyl methacrylate potassium salt), modified surfaces revealed an increased oil adhesion with the addition of salt and featured exceptional performance against algal attachment, which paved the way towards potential application for the design of antifouling materials in marine industry [130].

Similarly, by slight adjustment, a PAA-AAO composite is capable to be used as adhesive. For this, PAA hydrogel-pillars were fabricated via free radical polymerization inside the pores of an anisotropic AAO membrane. The hydrogel-pillars provided simultaneous friction on both side of the membrane. Moreover, attributing to the pH stimuli-responsive property of PAA brushes, the membrane composites showed in situ, stable, fast, and durable friction switch between low and high states under high load of 40 N. The membrane composites were used for mimicking a gecko’s feet, particularly, the reversible attachment and detachment. Intriguingly, the strategy mentioned within this work facilitated the design of multi-stimuli-responsive interface-actuated devices for the potential application as underwater robots, sensors and other bionic devices [131].

Drug delivery

The nanopores of anisotropic AAO membrane are applicable as cavities for drug storage. For instance, Kwak and colleagues had used paclitaxel for investigation of drug loading and releasing from an AAO membrane. They revealed that the amount of released drug decreased upon increasing the pore depth from 0.5 μm to 4 μm, while the pore diameter had not substantial impact on the drug release [132]. In addition, SI-ATRP of PNIPAm was employed by the group of Zapotoczny to transform an anisotropic AAO membrane into a pulsatile releasing platform as revealed in Fig. 14. Since PNIPAm could undergo conformational changes upon temperature changes below or above its lower critical solution temperature (LCST), the grafted PNIPAm brushes served as thermally responsive valves that displayed an autonomous gate control on the membrane pores, and thus endowed the controlled pulse release of entrapped dye molecules. At high temperature, PNIPAm brushes were dehydrated and collapsed, thus resulting in open pores and pre-entrapped calcein molecules could be released. On the contrary, upon decreasing temperature, PNIPAm brushes underwent rehydrating into stretched chains that blocked the membrane pores. As a result, calcein molecules were blocked from being released from the template. By further adjusting the temperature, reversible control of releasing could be achieved. The loading capacity and releasing rate could be also easily controlled via regulating of pore diameter and length of AAO membrane, and hence the modified membrane showed potential for application as nano/microfluidic systems [133].

Compositive nanodevices

By taking advantage of moderated transparency and a low absorption coefficient, anisotropic AAO membranes could also be build-up as optical- and energy-related devices. And indeed, AAO membranes were incorporated for the fabrication of liquid crystal display (LCD) panels [134]. As reported, liquid crystal molecules were filled into the nanocavities of an AAO membrane and due to capillary forces the liquid crystals were accurately aligned inside the pores. Hence, the AAO acted as an alignment layer with the LCD exhibiting excellent electro-optical performance.

In another example, a low temperature (32–230 °C) thermochemical heat storage (THS) system was built based on AAO membranes by impregnating various salts into the AAO nanocavities under vacuum. In a THS system, upon discharging humid air passed through cylindrical pores of AAO, adsorption of water vapor occurred; on the contrary, upon charging hot dry air is passed through the same pores and vaporize adsorbed water. The desorption enabled heat storage while adsorption heat recovering. Owing to the adjustability of the AAO structure, the storage capacity is controllable, which in turn provided insight for the development of advanced energy storage materials [135]. Additionally, anisotropic AAO nanocomposites have been explored as colorimetric sensors [136], self-lubricated membranes [35], and bio-sensing chips [137].

Fig. 14 Molecule loading and releasing from PNIPAm grafted AAO nanovalves. Reprinted with permission from ref. [133]. Copyright 2013 American chemical Society
Conclusion and outlook

To conclude, taking advantage of uniform nanostructure, controllable geometries, excellent biocompatibility, thermal, mechanical, and organic chemical resistance as well as the low fabrication costs, AAO templates have attracted plenty of interest in the field of nanotechnology, specifically for the fabrication of nanocomposites for the development of functional devices [138–140]. In this review, we summarized advanced methodologies for constructing AAO-based composites. In addition, relevant applications depending on isotropic and anisotropic type AAO were further discussed. Innovative methodologies on designing and fabricating AAO nanocomposite are application driven. Indeed, the significant number of publications in this field now exceeds the size of one hundred per year. Hence the perspective on future AAO nanocomposite will be specific on enhancing of properties when devoted of AAO membrane into different field, for instance, raise the storage capacity of electronic device, enhance entrap and release efficiency of drug storage template, increase filtration efficiency of filters, faster sensing reaction of sensors, or explore complex pore structures for preparing hierarchical smart pillar-array-surfaces. AAO nanocomposites bearing a fruitful variability are highly promising to be applied in future areas such as energy, bio-pharmaceutical and food industry. Depending on the unpredictable needs, AAO membranes are capable to fulfill the demand due to their high variability in dimensions. However, from laboratory work to commercial products, numerous challenges are required to be solved. In fact, we could postulate that more efforts in the field of basic research should be devoted to develop substantially better electrochemical oxidation of aluminum and of forming a specific porous structure of oxide layers. In addition, it is essential to improve the existing functionalization methods in order to fabricate AAO composite materials with enhanced stability and durability.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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