Chapter 5
Soft and Hard Surface Manipulation of Nanoporous Anodic Aluminum Oxide (AAO)

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Abstract Nanoporous materials with straight channels have attracted considerable interest due to their unique physical properties and many potential applications such as separation, sensing, biomedical and electronics. For the last few decades, nanoporous alumina or anodic aluminium oxide (AAO) membrane is gaining attention due to its broad applicability in various applications. The unique properties of AAO membrane coupled with tunable surface modification and properties is playing an increasingly important platform in a diverse range of applications such as separation, energy storage, drug delivery and template synthesis, as well as biosensing, tissue engineering and catalytic studies. This chapter aims to introduce the recent advances and challenges for surface manipulation of AAO following the 'soft' and 'hard' modification strategies. The functions of these modified nanostructures materials and latest important applications are evaluated with respect to improved performance and possible implications of those strategies for the future trends of surface engineering are discussed.

5.1 Introduction

AAO surfaces are insulating and suffer from chemical instability in the acidic environment [1]. This limitation can be overcome by changing the surface properties and by adding new surface functionalities. The rich content of hydroxyl groups on the AAO surface allows them to be easily modified via modification with organic molecules with the desired functionality. The motivation for surface

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manipulation of AAO membrane is twofold. First, soft technique approaches include self-assembly processes (thiol, silanes), polymer modifications (polymer grafting and layer-by-layer). Subsequent modifications of the thus introduced functionality with biomolecules or nanoparticles can be carried out. Second, hard surface modification techniques relevant to AAO include thermal vapour chemical and electrochemical deposition, electroless, chemical vapour deposition (CVD) and atomic layer deposition (ALD). Lesser consideration is given to sol-gel derived and template synthesis on AAO since they lie beyond the scope of this chapter and have been previously reviewed elsewhere [2, 3]. With surface manipulation in mind, this chapter will present the fundamentals, important elements and current work on the surface manipulation of AAO using different strategies mentioned above. Such modified AAO offers an attractive feature and open up the new application to which unmodified membranes cannot be applied.

5.1.1   Soft Techniques

5.1.1.1   Self Assembly Monolayers

Self-assembly monolayer (SAMs) is an organic formation that formed spontaneously by adsorption, rearrangement and chemical reaction of molecules species from the liquid or gas phase onto solid surfaces. SAM's preparation is straightforward, and they provide a convenient, uniform, flexible and simple system which displays high chemical and thermal stability. The early work sought to chemically modify the surface using organic acids, thiolates, organosilanes, alkanethiolates, alcohols, amines and carboxylic acids assemblies on AAO-gold-coated surface with the goal of introducing functional groups for specific orientation, functionalities and selectivity. Considerable work has been done involving SAMs focusing on octadecyltrichlorosilane (OTS) that resulted in a rapidly growing body of research [4]. Formation of SAMs from organic acids i.e. carboxylic acid, α-hydroxy-carboxylic acid, alkyne, alkene, phosphonic acid, on AAO possessed a good thermal stability because of their ability to spontaneously adsorb via physical adsorption or chemisorption [5]. In general, unique approaches that combine gold-coating and SAMs on AAO surfaces may play an active role, used solely as immobilization matrix for the biological recognition entity.

For instance, Wu et al. [6] showed that a biosensor to detect the A-beta (1–42) peptide in predicting Alzheimer disease could be fabricated in which SAM (11-mercaptoundecanoic acid) modified gold coated AAO was used as sensing platform. In this configuration, before SAM was done, a thin gold film was sputtered onto the AAO substrate to serve as an electrode for metal deposition. Subsequently, the 11-mercaptoundecanoic acid (MUA) modified surface was further functionalised with EDC/NHS. The uniform distribution of gold nanoparticles on the surface of AAO has increased the number of MUA molecules hence increasing the binding of EDC/NHS and monoclonal antibody IgG molecules on

the AAO membrane that lead to lower limit of detection. Such phenomena have also been observed when densely packed SAMs (MUA-gold-AAO) were attached with another type of bio-receptors. For example, Kumeria et al. [7] investigated the mechanism of antibody-antigen interactions at SAMs (MUA-gold-AAO) electrode using reflectometric interference spectroscopy (RIfS). The mechanism of the system is shown in Fig. 5.1. This AAO biosensor specifically binds to circulating tumor cell, and offered direct and label-free detection of tumor cell with the limit of detection as low as (1000–100,000 cells/mL), hence allowing analysis to be done with little amount of sample (<50 µL). Recently, Tung et al. [8] have described MUA-gold-AAO based biosensor for the impedimetric detection of dengue virus. In this event, IgG-like sensing probes was found to conform the binding event between the dengue virus and the bioreceptor (CLEC5A). Recently, the use of gold-nanoparticle-labeled antibodies to enhance the sensitivity of the localized surface plasmon resonance (LSPR) biosensor was demonstrated by Yeom et al. [9]. The system incorporated MUA-gold-AAO as the immobilising matrix for the antibody (C-reactive protein-CRP), detection and the immunosensor showed high sensitivity over a wide concentration range and enabled a selective immunoassay to be performed. See [10] for more detailed discussion on preparative issues of AAO for chemo and biosensing applications. As the chemistry of AAO surfaces continues to advance, it is expected that additional methods for the preparation of stable monolayers will be realized, contributing further to the technological development of AAO and to a complete understanding of its fundamental and properties.

5.1.1.2 Thiol Surface Chemistry

Most of common method attaching thiol group on AAO membranes are prepared on gold-coated surfaces. This is due to high affinity of the gold surface towards thiol group that binds strongly on its surface without any further side reactions. Generally, thiol functionalization on gold coated AAO membranes is achieved via
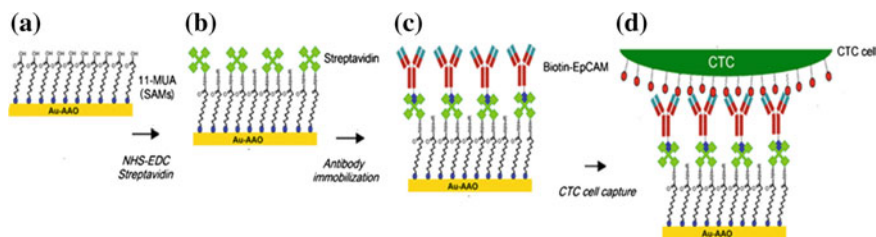

Fig. 5.1 Schematic representation of the surface functionalization steps of gold modified AAO used for RIfS biosensing. The system begins with **a** the formation of self-assembled monolayers (SAMs) of carboxyl-containing thiol followed by **b** covalent attachment of streptavidin on activated SAMs after activation with coupling (NHS/EDC) agents and finally **c** immobilization of biotinylated Anti-EpCAM antibodies; **d** scheme of binding of CTC cell on anti-EpCAM antibodies. Adapted with permission from [7]

immersion of freshly prepared membrane into dilute alkylthiol in an ethanoic solution for 12–24 h at room temperature. A series of experiments were carried out by Le et al. [11] for separation studies using five different kinds of thiol-modified gold coated AAO membranes. These studies suggested that highly polar carboxylic group increases the hydrophilicity while non-polar alkyl group increases the hydrophobicity of the golad-coated AAO membrane. Likely, the hydrophobicity increased with longer alkyl chain thiol modified gold coated AAO membranes. Smuleac et al. [12] demonstrated that the interaction of 3-glycidoxypropyl tri-methoxysilane modified AAO surface with certain ligands (e.g., polyglutamic acid) could cause a conformational transition of the chain to create a polythiol containing 240 repeat units on AAO surface. Such phenomena have also been observed with an ingenious connection to create a polythiol containing 240 repeat units on AAO surface. Building up the concept of gold coated AAO surfaces, Steinem group [13–15] showed that the suspended lipid bilayers could be done on alkanethiols coated AAO supports with the ability to mimic biological membrane and monitor ion channel activities (Fig. 5.2). Their fabrication approach consists of gold coating on AAO followed by formation of alkanethiols with a negatively charged head group. Fusion of lipid vesicle featuring positively charged lipid head groups leads to a suspended bilayer that prevents vesicle fusion inside the pore. In a similar configuration, purple membranes can be adsorbed on freestanding lipid bilayers, termed nano-black lipid membranes (nano-BLMs) for photocurrents measurements [16]. A recent review of suspended bilayers on alkanethiols coated AAO surface has been described in [17].

5.1.1.3 Silanization

Silanization has been demonstrated an effective and flexible method for changing the wetting and adsorption properties of AAO membranes. The versatility of this method resides in its straightforwardness, fast and stable as it can be carried out at
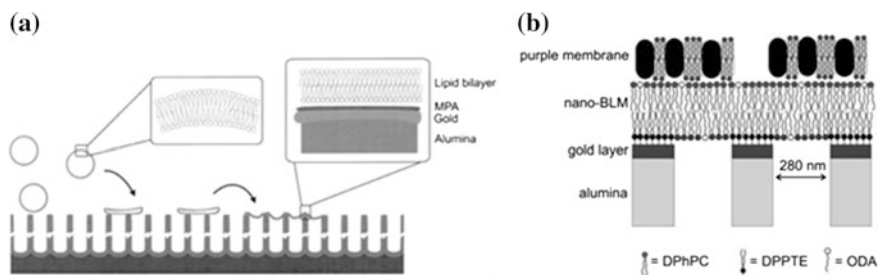

Fig. 5.2 a Schematic representation of pore suspending bilayers made by fusion of large unilamellar vesicles on 3-mercaptopropionic acid monolayer functionalized Au-coated AAO substrates. **b** A schematic illustration of adsorbed purple membranes on nano-BLMs. Adapted with permission from [15, 16]

moderate temperatures, and no particular conditions or expensive equipment are required. This characteristic result in the essential ability of this technique to be applicable to any materials and a wide range of application. The uniformity and stability of this technique are extremely sensitive and depends on the details of the organosilane chemistry and the functionalization conditions. For the attachment of silanes on the surface, the principle involves activation of silane molecules to promote condensation reaction between the silanol group of silane and hydroxysil groups of the surface (in this case the AAO). This reaction will form a stable bond on the surface and releases free alcohols as a side product [18]. Wide varieties of substituted organosilanes are commercially available, and the presences of these silanes significantly change the local environment and properties of the AAO membranes. The main properties of surface modification include hydrophobicity, hydrophilicity, absorption, orientation, charge conduction.

For instance, AAO membranes were rendered hydrophobic by functionalization with octadecyltrimethoxysilane (ODS) has been reported by few studies. ODS modification was accomplished by immersing the membrane into a solution containing ODS with 15 mL of absolute alcohol and 50 mM of sodium acetate buffer [4]. Likewise, a different chain of alkyltricholrosilanes with tail length from C1–C8 can be functionalized on the AAO nanopores [19]. Modification of membrane consists of silane with fluoro tails, i.e., perfluorodecydimethylchlorosilane has changed the wettability of the membrane from 20 to 160° [20, 21]. Other approach employed PEG-silane that is formed by reacting PEG-silicon tetrachloride in the presence of triethylamine as a catalyst. This combination was then reacted on the hydroxylated surfaces of AAO to form a network of Si–O–Si bonds resulting immobilization of PEG on the surface. This study investigated the biocompatibility aspects of PEG coated AAO surfaces for possible use to prevent membrane fouling and immunoisolation [22, 23]. In addition, Steinle et al. [24] derivatized AAO membranes with a silane that terminated with carboxylic acids. This was achieved by incubating the APTES terminated AAO membrane with diacids chloride and diisopropylethylamine. In more advanced work, an interesting development of multi-layered silanes with different types of functionalities and wettability was demonstrated by Jani et al. [25] on AAO nanochannels. This process was based on combination series of anodisations and silanization during fabrication and allowed to further tune the transport properties on the nanochannels (Fig. 5.3) [26].

Silane modifier typically acts as the coupling agent or chemical linker to help attach other molecules or compounds in preparing customized product (Fig. 5.4). Indeed many works have been successfully attached enzyme [27], antibody [28], urease [29], DNA molecules [30], biotin [31], lipid bilayers [32, 33], polymers, cells [34] and nanoparticles [26, 35] to AAO surfaces via silanization. For example, Zhang and co-workers utilized an elegant approach to biosensor development that involved covalent attachment of glucose oxidase (GOD) to the 3-glycidoxypropyl-trimethoxysilane (GPTMS) modified AAO nanochannels. From this, a novel enzyme reactor system that enables a controlled catalysing rate was developed [27]. Shi et al. [36] also utilized GPMTS modified AAO surfaces as the separation and purification sites for haemoglobin from the red cell. This was achieved by reacting
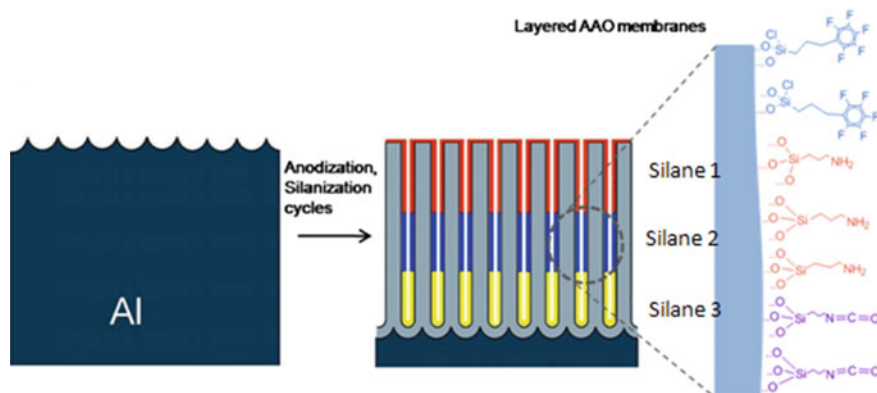
Fig. 5.3 Schematic illustration of anodization and silanization cycles to produce an AAO membrane with multiple silane layers. Adapted with permission from [26]
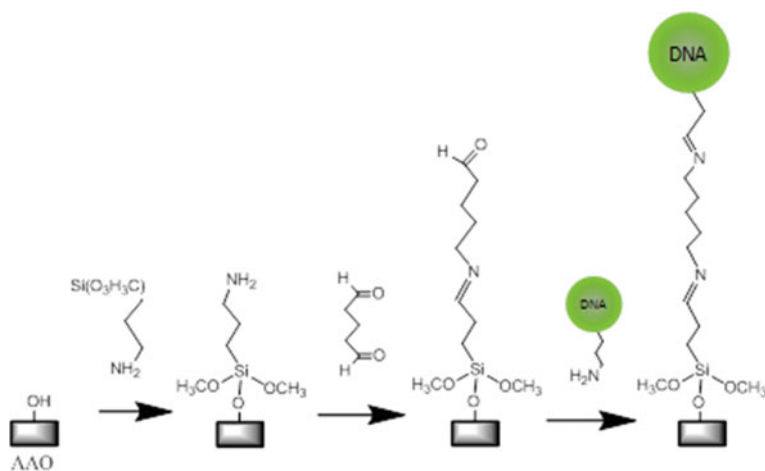

Fig. 5.4 Silanization of hydroxylated AAO surface with isocyanatopropyl triethoxysilane and subsequent immobilization of amino-terminated DNA. Adapted with permission from [45]

GPMTS with chitosan, and the chitosan–AAO composite membrane was successfully used for affinity protein separation specifically for haemoglobin from the haemoglobin-phosphate solution and hemolysate. An alternative approach to covalent immobilization involves antibodies recognition sites. This approach introduced by Joung and co-workers utilized hyaluronic acid that enable ring opening reaction of GPMTS modified AAO surface to be carried out. The hyaluronic acid then functioned as coupling sites with sulfo-NHS esters for antibodies immobilization purpose. This novel label-free immunosensor system demonstrated a remarkable capacity for detecting pathogenic E. coli bacteria [28]. Evidence for

incorporating DNA molecules on silane functionalised AAO surface has been demonstrated by Valssiouk et al. [30, 37]. These have resulted in covalent attachment of DNA oligomer that helps hybridization process inside AAO nanopores [38, 39]. Silane coated surfaces also have been used to suspend lipid bilayers in AAO membranes. The suspended bilayers termed polymer-cushioned lipid bilayers were first achieved by activated the surfaces with aminopropyl-dimethylethoxysilane (ADMS) and the second step consists of grafting the N-hydroxy-succinimidyl carbonate (NHS-PEG) to amino coated surfaces. It was suggested that grafted PEG chains triggered the vesicle fusion and maintained the fluidity of the bilayers [33]. A recent example of silane-glutaraldehyde AAO surfaces is the covalent immobilization of glucose-6-phosphate dehydrogenase (G6PD) was demonstrated. In a similar approach, silanized membranes were incubated with N,N-dimethyl-formamide (DMF) containing 25 mg of N-succinimidyl-3-meleimidoproprionate. The maleimide-grafted membranes were then immobilized with human CYP2E1 by cross-flow filtration at different times [40]. Similarly, a detailed investigation of cellular adhesive peptide (RGDC) dependence of osteoblasts (bone forming cells) on maleimide-grafted AAO membrane was subsequently demonstrated by Leary Swan et al. [34]. APTES coated AAO surface also has been used as the surface attached initiator for grafting polymer brushes on membrane surfaces. For example grafting of poly(γ-benzyl-Lglutame) PBLG [41] and PNIPAM (poly(N-isopropylacrylamide) [42] via surface initiated polymerization. This work determines that, the density of the polymers can be controlled by controlling the density of initiator. This work was later refined by Bruening and co-workers by a method in which the initial step of activating the membrane surface with silane can be excluded by employing synthesized trichlorosilanes initiator (11-[42]undecyltricholorsilane) to grafted PHEMA (poly(2-hydroxyethyl methacrylates) brushes on AAO surfaces [43]. Silanized AAO surfaces also have been used to as a template for fabricating various nanotubes. For example, Sehayek et al. [44] used APTES functionalized AAO membrane to form solid, porous, nanoparticle-based nanotubes. The nanotubes are prepared by passing a citrate-stabilized metal (Au, Ag) colloid solution through the pores of an aminosilane-modified AAO membrane. As a result, mechanically stable and electrically conducting gold or silver naotubes were fabricated.

An interesting derivative of silanisation work on AAO surfaces is a process in which silanization was carried out on gold-coated AAO surface. This work involved depositing a thin layer of gold on AAO using either electrodeposition, electroless or sputtering technique. The ability of depositing tethered lipid bilayer on silanized gold coated surface was investigated by Largueze et al. [46]. In this approach, the bottom part of AAO membrane was coated with gold and prior to lipid deposition the gold layer was functionalized with silanes, undecanethiol and the last step being a PEG-triggered fusion of the surface-attached liposomes. By means of CV, the alterations of lipid membranes can be observed by inducing it with detergent.

5.1.1.4 Polymer Functionalization

Polymeric coatings on AAO membranes offer a high potential in respective areas of applications and have been examined by several research groups. This surface modification technique allows a fine control of surface chemistry, functionality, density and thickness of the coating on the AAO membrane. Polymer layers can be either attached to the top of the pores or inside the pores. Polymer-modified AAO membranes have shown improved binding capacity, selectivity, biocompatibility, stability and lubricant properties in comparison to non-modified AAO membranes. The most common approaches for a polymer functionalization on AAO are polymer grafting, plasma polymerization and polyelectrolytes multilayers.

The modification of AAO membranes with polymer brushes rely on the principle of grafting approaches that can be achieved via non-covalent and covalent interactions between the polymer chains and the membrane. Qi et al. [47] investigated the use of poly(2-methoxy-5-(2′-ethyl-hexyloxy)-p-phenylenevinylene (MEHPPV) or poly(2,3,-diphenyl)phenylenevinylene) DP-PPV polymer brushes into the pores of AAO membranes via physisorption. However, the adsorbed polymer brushes appeared to be suffering from poor stability. Covalent grafting generally occurs through either grafting to or grafting form approaches via atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain transfer polymerization (RAFT), plasma-induced graft polymerization, ring-opening metathesis polymerization (ROMP), and the self-polymerization of dopamine (DOP-SP) methods [48, 49]. The resulting polymer brushes contain multiple binding sites that give rise to high binding capacities. Moreover, the polymers can be asymmetrically modified within the nanochannels of the AAO that exhibit specific biological recognition and provide high selectivity. Nagale et al. [50] reported the grafting of amino-terminated poly(tert-butl acrylate PTBA) to the top layer of AAO surfaces functionalized with of carboxylic acid terminated thiol. In this work, the pores channel is free from a polymer, thereby providing high-flux composite membranes. Sun et al. [51] have developed the ATRP approach to modify the AAO membranes utilizing poly (2-hydroxyethyl methacrylates) (PHEMA) brushes with nitrilotriacetate-Cu^{2+} (NTA–Cu^{2+}) complexes that yielded membranes with bovine serum albumin (BSA)-binding capacity. Static binding capacities of 150 mg BSA/ml and saturation of the membranes with BSA or myoglobin in less than 15 min were determined. Later on, the same group synthesizing different brushes of (PHEMA)-NTA–Ni^{2+} on AAO pores that allow to bind oligohistidine-tagged ubiquitin for protein purification [48]. Other general attributes related to polymer brushes grafted AAO membranes have been described and illustrated by Bruneing et al. [43] in details.

Thermo-responsive polymer brushes of PNIPAM are widely acknowledged and received considerable attention in the recent years. The switchable properties such as hydrophilic/hydrophobic switching at the lower critical solution temperature (LCST) make this polymer attractive for a variety of applications. Generally, ATRP technology has been used to synthesis PNIPAM grafted on AAO membranes. This was first demonstrated by Fu et al. [52] by utilizing one step approach using an

AAO surface functionalized with the ATRP initiator 1-(trichlorosilyl)-2-[m/p (chloromethyl)phenyl]ethane followed by PNIPAM grafting. This result suggests that the length of the polymer in the porous network can be used to control the size of surface pores, surface roughness and the interfacial energy. Changes in initiators have been described as potentially useful in ATRP applications [42, 53]. For example, Li et al. [42] employed 2-boromoisobutyryl bromide (BIBB) on the membrane surface to graft PNIPAM using ATRP method. Likely, Wang et al. [53] demonstrated the preparation of molecular imprinted polymers (MIPs) using surface-initiated ATRP on an AAO membrane. In one recent example, Ma et al. [54] demonstrated by combining ATRP, ROMP and DOP-SP methods, various asymmetric polymer brushes-stabilized Au-Pd in the AAO channels can be formed. The device consisted of poly(3-sulfopropyl methacrylate potassium salt) (PSPMA) on one side and poly(2-(methacryloyloxy)ethylmethylammonium chloride) (PMETAC) on the other side of the membrane fabricated in the reaction cell (Fig. 5.5). This effect was then exploited so as to produce an asymmetrical catalytic array of Au-PMETAC@PSPMA-Pd by depositing Au and Pd on both sides of the AAO membranes, respectively. This new sandwich membrane effectively demonstrates excellent flow-through catalysis.

Polyelectrolytes (PEs) are polymers with a variety interesting properties and applications. Since l997, a large academic interest in the field of layer-by-layer (LBL) arose from the discovery by Decher [55] that alternate depositing of oppositely charged polyelectrolytes (PEs) polymers forming PE multilayers (PEMs). The LBL assembly is a simple, yet versatile and inexpensive technique. Moreover, the film thickness can be easily controlled at the nanometer scale, and the resulting layers can be further functionalized with biomolecules or nanoparticles [43, 56].

AAO membrane consisting PEMs was first demonstrated by Balachandra et al. [57] utilizing polyacrylic acid (PAA) partially complexed with Cu^{2+} ions onto a UV/ozone treated AAO membrane followed by immersion in a solution of polyallylamine hydrochloride (PAH). The above procedure was repeated until the desired numbers of bilayers were deposited and conformal and smooth films were formed on the AAO. Subsequent work show AAO pores were not clogged after deposition of 5–7 PEM bilayers thus enabling this system to be employed molecular size selective transport. The number of PEMs layers combined with different compositions of PEMs significantly influenced the flux, transport, rejection rate and selectivity of solutes through these functionalized membranes [43]. For example, Hong et al. [58] showed that PEMs consisting 4.5 bilayers of polystyrene sulfonate/poly(diallyldimethylammonium chloride) (PSS/PDADMAC) on AAO pore gave Fluoride ions rejections more than 70 % with a selectivity factor more than 3 compared to other monovalent anions. They additionally showed that the similar PEMs on AAO revealed 98 % rejection of phosphate ions as compared to the commercial NF90 membrane [59]. More recently, Ouyang et al. [60] investigate the effect of PEMs with five bilayers of PSS/PAH deposited on AAO showing effective rejection of Mg^{2+} and Ca^{2+} cations by 95 %. The selectivity of cations rejection could be enhanced by increasing the charge of the terminated PAH layer by means of increasing ionic strength in the PAH deposition solution. Hong et al.
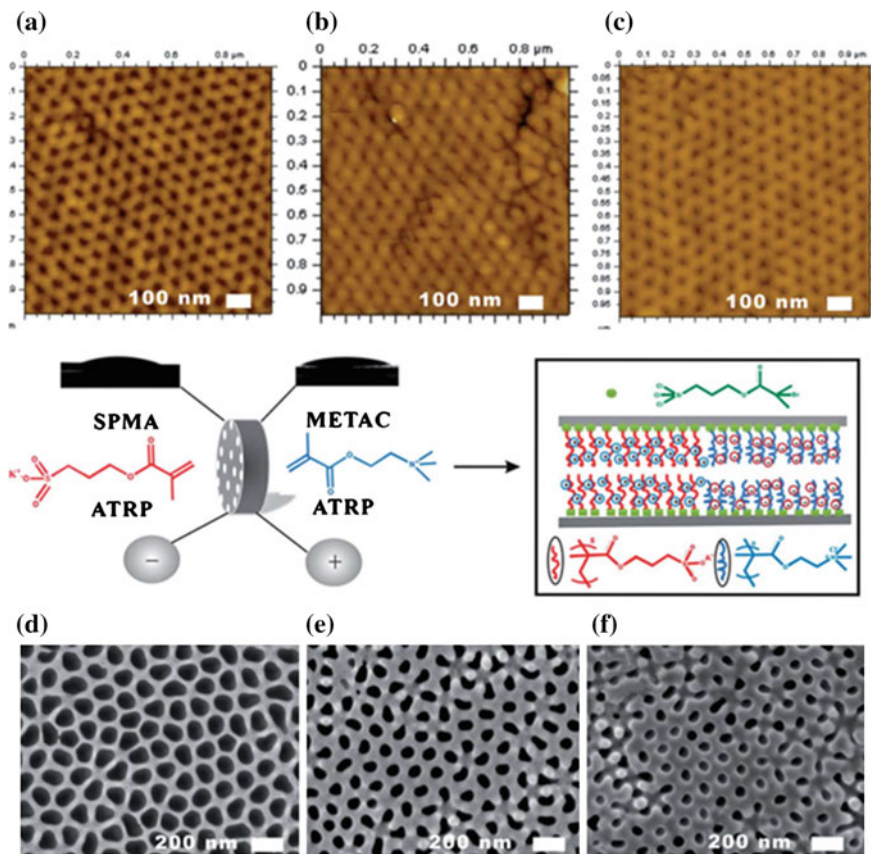
Fig. 5.5 AFM images of AAO membrane (pore size of 30 nm) before (**a**) and after modification with polymer brushes of PMETAC (**b**) and PSPMA (**c**). Schematic illustration of asymmetrical modification with double hydrophilic polymer brushes within AAO channels (*middle*). **d–f** FESEM images of AAO membrane (pore size of 130 nm) before (**d**) and after modification with PMETAC (**e**) and PSPMA (**f**). Adapted with permission from [54]

[61] later showed, seven bilayers of PSS/PAH on AAO yielded a high selectivity of glycine over L-glutamine, whereas 4.5 bilayers of PSS/PAH coated AAO membrane showed a sucrose rejection of about 99 % and increasing the flux of the solution. Both studies demonstrated that the performance of selectivity and rejection are comparable with commercially available membranes.

As noted earlier, biomolecules or nanoparticles could be deposited onto PEMs layer. Dai et al. [62] evaluated the performance of PEMs of PAA/PAH followed by immobilization of antibodies on the carboxylic groups of the PAA layers following the carbodiimide coupling approach. The resulting coating on AAO resisted non-specific protein adsorption. Charged polyelectrolytes on AAO membranes also allowed the immobilization of citrate-stabilized gold nanoparticles on PEMs under

retention of the nanoparticles' catalytic activity as demonstrated by Dotzauer et al. [63, 64]. For a detailed discussion on the synthesis and properties of LbL films, the reader is referred to an excellent review written by Joseph et al. [65].

5.1.2 Hard Modifications

Metal coating by using electrochemical deposition, electroless deposition, thermal vapour deposition, plasma polymerization, atomic layer deposition (ALD) and chemical vapour deposition (CVD) are the examples of hard techniques used to improve the physical, chemical and structural engineering properties of AAO. These innovated modification approaches are utilized to deposit a wide range of materials from metals, metal oxides, semiconductors, ceramics, nitrides, as well as carbon nanotubes onto the AAO membrane [66–69]. It is also highlighted that these developed methods are suitable for the synthesis of diverse nanostructured materials such as nanowires, nanotubes or nanorods with the assistance of that particular AAO as a template. As such, these methods provide a broad scope to engineer AAO-progress in technologies for specific applications by controlling and designing structural growth of AAO with different sizes, arrangements, structures, geometries and pore architectures [45].

5.1.2.1 Electrochemical Deposition

Electrochemical deposition is used extensively to deposit metal or alloy on AAO membrane, mostly owing to its high material transfer efficiency, cost effective and controllable film thickness. In comparison to thermal vapour deposition, ALD or CVD, the electrodeposition route is easy, as well as less skill dependent, and does not require sophisticated instrumentation [70]. The experimental set-up is quite similar to that of anodization, while the AAO serves as the cathode. In most cases, a thin metal layer (commonly Au) is first evaporated on one side of the nanoporous AAO membrane to serve as a working electrode. In particular with regards to electrodeposition method, it is emerged as an accepted versatile approach for AAO template synthesis-pore filling with conducting metals to obtain continuous arrays of nanowires, nanotubes, nanorods or nanoparticles with large aspect ratios [71–75]. See [76] for a more detailed discussion including bottom-up and top down approaches on metal deposition on AAO surface.

For metal nanoparticles deposited on the AAO membrane; Platt et al. [77] used the electrodeposition of Pd nanoparticles at the liquid-liquid interface using AAO template. The resulting nanoparticles were formed at the mouth of the AAO pores, and the locus of their formation is being dictated by the position of the organic-water interface. However, many issues concerning the mechanism of this interfacial deposition process remain to be clarified, and such studies are in progress. Another approach by Lee et al. [78] has developed an alternating current (AC) technique for

dielectrophoretic assembly of Au nanoparticles in the AAO template. This simple preparation mode showed a selectively patterned of Au nanoparticles is successfully fabricated in the pores of AAO, which is expected to lead for exciting sensor applications in various fields. Later it was shown by Masuda group [79] that developed a method to fabricate layered three dimensional (3-D) Au nanoparticles inside an AAO matrix for use as a surface-enhanced Raman scattering (SERS) substrate. The electrodeposition of Au nanoparticles inside the AAO channel is demonstrated by alternating current (AC) electrolysis of AAO. Then, the number of layers of the Au nanoparticle arrays is determined by the number of repetitions of this process, and the gap size between Au nanoparticles is determined by the duration of anodization after the electrochemical anodization of Au.

One of the most effective approaches of electrodeposition is to fabricate nano-wires by embedding metal in the AAO matrix. Whitney [80] recently employed electrodeposition approach prepared by nuclear track etching to fabricate Ni and Co nanowires into the AAO template. In addition, high uniformity of metal/alloy deposition has been demonstrated by the group of GÖsele using current-controlled deposition sequences [81–83]. A few years later, this group has successfully pre-pared segmented Ag–Au alloy nanowires inside the AAO membrane via the electrodeposition approach [84]. The Ag component could then be selectively removed using nitric acid. Other critical preparative issue during electrodeposition, which is an unstable electrical current that causes uniform filling of the pores cannot achieve smoothly. Therefore, it is of paramount interest by Kim et al. [85] to fabricate free-standing Pd nanowires via pulsed electrodeposition (PED), in which the electrodeposition of Pd is carried out galvanostatically with a pulse mode. In this work, PED method is more reliable for deposition into high aspect ratio materials and can compensate for the slow diffusion-driven transport in the narrow pores. The prepared Pd nanowire arrays are standing freely on a Ti-coated Si wafer after removing the AAO template. The most recent work was demonstrated by Pecko et al. [86], they synthesized Fe-Pd nanowires by applying both potentiostat and PED regimes. When using potentiostat deposition, only fragmented nanowires are obtained, and the use of PED is shown to be effective for producing solid nanowires. In particular, another work by Wang et al. [87] used supercritical electrodeposition method, an electroplating reaction with the emulsion of carbon dioxide (CO_2), surfactant and electroplating solution to prepare highly ordered of Ni nanowires. The plating in the emulsion is similar to pulse plating, and it is also highlighted that the developed method showed a wide range of variable parameters for obtaining Ni nanowire arrays with uniform characteristics using AAO template.

On the other hand, electrodeposition technique for semiconductor nanowires such as CdS was used after pioneering work by Routkevitch and co-workers [88] in 1996. It also has been reported by Xu et al. [89–91] that single crystal compound semiconductor nanowires of CdS, CdSe and CdTe can be fabricated into the nanoporous AAO template by sequential deposition of cationic and anionic com-ponents of the semiconductor by reverse potential sweeping. Taking CdSe as an example, a small amount of Se is first deposited followed by the deposition of excess Cd and subsequently stripping of the Cd during the reverse potential sweep

[92]. The most recent work by Chen et al. [93] showed transitional metal chalcogenide compound CuS nanowires are successfully fabricated via electrodeposition and sulfurization. Cu nanowires are first synthesized and then sulfurized to form CuS nanowires. Results indicated an appropriate pH value of a deposition solution, a sufficient amount of sulphur powder and temperature during sulfurization is crucial to forming well-crystallized CuS nanowires.

The AAO template method for the synthesis of one dimensional (1-D) nanostructured material such as nanorods or nanotubes is first introduced by Martin and the co-workers [71]. The method is based on the electrochemical deposition of Au within the pores of nanoporous AAO template membranes. The authors showed that the Au/AAO composites can be optically transparent in the visible and also that by changing the aspect ratio of the prepared nanocylinders; the colour of the composite membrane can be varied. In another approach, Burdick et al. [94] demonstrated the high-throughput fabrication of alternate multisegment deposition of Au with short gaps of Ag. Likewise, Hoang et al. [95] demonstrated the growth of multisegmented nanorods comprising Au and sacrificial Ag segments using an electrochemical wet etching approach. In particular, Kim et al. [69] have fabricated striped multimetal nanorods by direct current (DC) electrodepositing three different metals of Au, Ni and Cu sequentially in the pores of AAO templates. The lengths and the sequence of metal segments in a striped rod can be tailored readily by controlling the durations of electrodeposition and the order of electroplating solutions, respectively. Another study by Wang et al. [96], they reported a novel approach for the fabrication of TiO_2 nanotubes arrays by electrodeposition on the nanoporous AAO template from inorganic aqueous containing $TiCl_3$ and Na_2CO_3. The method applied in this work can be used for the preparation of other order 1-D semiconductor nanotubes as well.

Up till now, studies of the growth mechanism of nanotubes have been concerned with the nature of the material and the chemistry of the pore wall. However, the effect of a back electrode on the formation of electrodeposited nanotubes has not been reported. Herein, Atalay et al. [97] studied the electrodeposition of CoNiFe nanotubes on vitreous templates placed on highly ordered nanoporous AAO. It was found that the back electrode placed on AAO template was an important factor in controlling the shapes and properties of the nanostructure. It is remarkable that a nano-engineering strategy for fabricating SnO_2/MnO_2 core/shell nanotube arrays is innovated by Grote et al. [98]. The SnO_2 core inside the nanoporous AAO is fabricated by atomic layer deposition and subsequently a thin MnO_2 shell is coated by electrochemical deposition onto the SnO_2 core. The fabrication process allows precise controlling of the length, spacing, diameter, wall thickness and the selection of open-end or closed-end nature of the prepared nanotubes. Another advancement of nanostructured materials prepared by electrodeposition has been reviewed by Gurappa et al. [99], Bicelli et al. [100] and Hurst et al. [70].

5.1.2.2   Electroless Deposition

Electroless deposition is defined as a deposition of a metal coating either by immersion of a metal in a suitable bath containing a chemical reducing agent. Compared with electrochemical deposition, the advantage of the electroless deposition is that there is no necessity for the surface to be electronically conductive [101] and the deposition starts from the pore walls and growth inwardly [102]. Martin et al. [71] first applied this approach to AAO membranes using Au deposition. The Au nanotube/AAO composite membranes are successfully used for molecular separations showing size, charge and chemistry based selectivity. By varying the electroless deposition time, hollow tubes can be obtained with short deposition time while solid nanorods can be obtained using longer deposition time [70]. Another work by Cheng et al. [103] used the electroless deposition technique to fabricate high performance SERS-active Au nanoparticles arrays with tuneable particle gaps on AAO substrates. They reported that pH and the temperature were the main factors controlling the size, shape and aggregation of Au nanoparticles, as well as the inter-particle distance. As a matter of fact, catalytic and SERS properties of Au nanotubes inside the AAO pores are demonstrated as the results of clustered Au surface inside the nanotubes, as well as the Au nucleation process during chemical deposition. Interestingly, the SERS technique also can be used for mapping the gold layer integrated with 3-mercaptobenzoic acid (mMBA) inside AAO pore channels as investigated by Velleman et al. [104]. In this fashion, the gold layer was deposited by electroless deposition prior to the formation of SAMs of mMBA inside pore channels (Fig. 5.6). Their findings suggested that the developed SERS active surface can be applied for ultrasensitive sensing applications.

Although this method seems convenient and versatile in preparing nanotubes, one problem is that the plating reaction occurs not only on the pore walls but also on the surface of AAO membrane. If the deposition rate is too fast, the pore entrance is
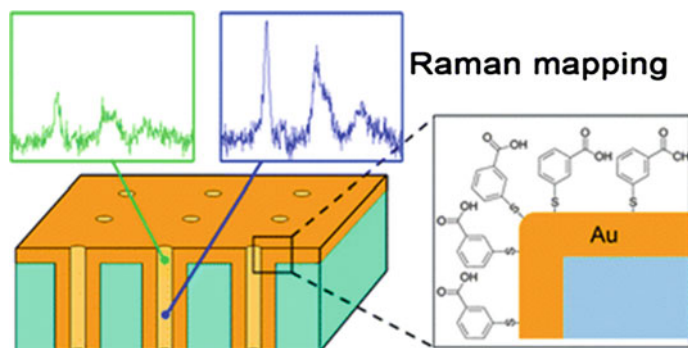

Fig. 5.6 Schematic diagram of AAO membrane coated with gold layer via electroless deposition and subsequent functionalized with 3-mercaptobenzoic acid (mMBA). Surface enhanced Raman scattering (SERS) conformed spatial distribution of mMBA inside the channels. Adapted with permission from [104]

sealed before the reactant can get through the full length of the pore. Therefore, further progress in this area has seen the developed meet of a variety of fabrication approach to design exotic patterns and arrangements of nanotubes inside the AAO membranes. Li et al. [105] showed an elegant approach for preparing Cu nanotube arrays with open-ends by electroless deposition. This is accomplished by a four steps procedure, i.e. pore-wall modification, polishing treatment, sensitization-activation and electroless deposition. Additionally, sensitization-activation is necessary to produce a conformal coating. This nanotube arrays with open-ends have potential application in preparing novel core-shell nanocable metal alloys and other interesting nanomaterials. Another work by Zhang et al. [106], they synthesized Ag nanotubes by electroless deposition in nanoporous AAO templates. The reaction used for the formation Ag nanotubes within AAO is well-known Tollens' test in sugar chemistry. Ag nanotubes with lengths over 10 μm are successfully fabricated inside the AAO membranes. Likewise, Ag nanoparticles with uniform size and smooth surface are deposited inside AAO using this technique [67, 107].

In particular, Wang et al. [101] synthesized a wide range of metals nanotube arrays in AAO templates including Co, Ni and Cu arrays via electroless deposition on APTES-functionalized AAO membranes. The inner diameter of the nanotubes can be tailored by adjusting the deposition times while the length of the nanotubes is determined by the thickness of the AAO template. Remarkably, a novel approach is obtained during fabrication of end-closed NiFeCo-B nanotube arrays via electroless deposition by Azizi et al. [102]. This work is different from previous efforts as the formation of end-closed nanotubes is successfully fabricated for the first time. A different approach has been applied by Kang et al. [108]; superhydrophilic/ superhydrophobic Ni micro-arrays structure and a substrate with strong mechanical strength are fabricated by combining a simple electroless deposition and self-assembly silanization process. These Ni nanoparticles are deposited on an etched AAO membrane template by electroless deposition without activation and sensitization. Recently, boron-doping Ni@Au hybrid magnetic nanotubes are deposited rapidly on AAO membrane via electroless method [109]. This peculiar work differs from previous efforts because of the more rapid and facile synthesis of Ni@Au nanotubes. Moreover, this study is the first to explore the in vitro cytotoxicity of Ni@Au nanotubes on Molt-4-cells, which makes them potentially applicable for biomedicine. Another comprehensive review on electroless deposition method can be found by Ali et al. [110] and Stojan et al. [111].

5.1.2.3 Thermal Vapour Deposition

Thermal vapour deposition is one of the simplest and most popular approaches for fabricating various types of nanostructures with certain characteristics. The basic process of this method is sublimating source material(s) in powder form at high temperature, and a subsequent deposition of the vapour in a certain temperature region to form desired nanostructures. The aim of this modification is not only typical to improve conductivity and chemical stability of the AAO material, but also

to introduce some intriguing properties such as catalytic, electrochemical, magnetic, optical and transport [66, 112]. Lei et al. [66] has reviewed the AAO coated with metal such as Ni or Co which improved magnetic properties whereas catalytic properties have been introduced by coating with Au, Pd, Pt, Ti/TiO$_2$. In addition, metal coating also served as the basis for a further chemical modification approach to help in binding AAO with various chemical and biological species for optical sensing and molecular separation applications. Arguably, the main disadvantage of this technique is that only the top part of the nanopores can be modified and the deposition of internal pore surface is limited. Therefore, this will provide a glimpse of opportunities to many researchers for the metal deposition approaches on the AAO to be explored.

Toh et al. [113] has successfully prepared Pt-coated AAO membranes for selective transport and separations of charged proteins by sputtering the AAO membranes with Pt. During separation experiment of charged proteins, electrical potential is applied to create a high electric field. In fact, further size selective separation is achieved by increasing the thickness of sputtered Pt layer. Another approach by Qiu et al. [114] has fabricated a highly ordered hemispherical Ag nanocap arrays template on AAO membrane by using a direct current magnetron sputtering system. The surface structure can be tuned further to optimize the enhancement factor according to optional AAO fabrication and Ag deposition parameters. The design of Ag nanocap array with uniform and highly reproducible SERS-active properties may provide a breakthrough for the fabrication of robust, cost-effective, exceptionally sensitive and large-area SERS-based sensors. Besides, Yin et al. [115] reported a facile method for the synthesis of silica nanotubes by thermal decomposition of polydimethylsiloxane (PDMS) rubbers. At elevated temperature, PDMS rubbers could be first decomposed into volatile cyclic oligomers while under inert conditions. When the oligomers are oxidized in air, vapour phase silica is formed, which nucleated and grew heterogeneously on the walls of AAO templates. The diameter and length of the silica nanotubes are mainly determined by the pore size of the AAO template while the wall thickness of the nanotubes could be controlled by the initial amount of PDMS rubbers.

For the synthesis of metal and metal oxide nanotube arrays, Whitesides et al. [116] reported the synthesis of Au and ITO nanotube arrays with a thin backing using shadow evaporation. In the synthesis, the AAO membranes are tilted with respect to the column of evaporating materials, controlling the geometry of the tubes. Meanwhile, rotation of the membrane during evaporation ensured the uniformity of the resultant materials. In another approach, Pereira et al. [117] reported on a simple process for the formation of a functionally modified AAO channel by using pulsed laser deposition (PLD) method to deposit a metal (i.e. Au, Pt) or a mixture of metal (i.e. Pt–Ru) on the AAO membrane. PLD method is a versatile and powerful tool for the growth of high purity thin films and nanostructured materials. This work has achieved an optimizing kinetic energy of the deposited metal in contact with the AAO substrate. Particularly, Wang et al. [118] combined physical vapour deposition, gating ion milling and thermal annealing techniques for the fabrication of metal nanodot arrays on AAO. This new approach is based on the
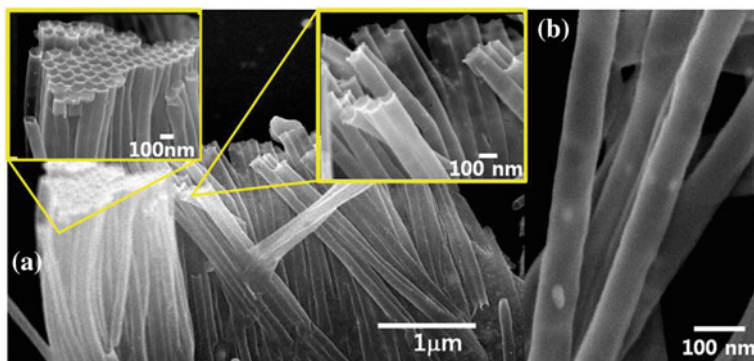
Fig. 5.7 Scanning electron microscope (SEM) images of Au-CNT-AAO prepared at 973 K. Inset images in **a** are magnified images of indicated areas, **b** is magnified SEM image of another part in the same sample. Adapted with permission from [119]

fabrication of ring and half-moon shaped nanostructured arrays and a further annealing process. Such approach will probably broaden the potential applications of template based nanostructures. More recently, Lee and co-workers [119] have demonstrated a facile and efficient method for preparation of bamboo-like Au-carbon nanotubes by thermal decomposition of sucrose in an Au-AAO template (Fig. 5.7). The crystalline Au nanoparticles attached on the bamboo-like conducting carbon nanotubes obviously improved the electrochemical response of the nanotubes.

5.1.2.4 Plasma Polymer Deposition

Plasma polymer deposition (or plasma polymerization) is defined as the formation of polymeric materials under the influence of plasma condition [120]. In the plasma polymerization process, a monomer gas is pumped into a vacuum chamber where it is polymerized by plasma to form a thin, clear coating. This technique is particularly efficient and convenient because the ultrathin polymer films of various functionalities can be deposited on any surfaces without the need of surface pre-modification [121]. It is well-established by the first report of plasma treatment on AAO membrane from Brevnov et al. [122], who prepared Janus-type membranes with a hydrophilic and hydrophobic side. This approach reported that a super-hydrophobic surface is obtained on AAO membranes using inductively coupled plasma polymerization of fluorocarbon (C_4F_8) monomer, with a water contact angle (WCA) of 150°. The other side of the membrane is left unmodified and showed a WCA less than 5°. In comparison with other methods used for the surface modification of AAO membrane, the advantages of plasma polymerization are that it is a one-step, fast and low-temperature deposition process with a sterile and solvent free technique [123]. Considering the important of the above backdrop,
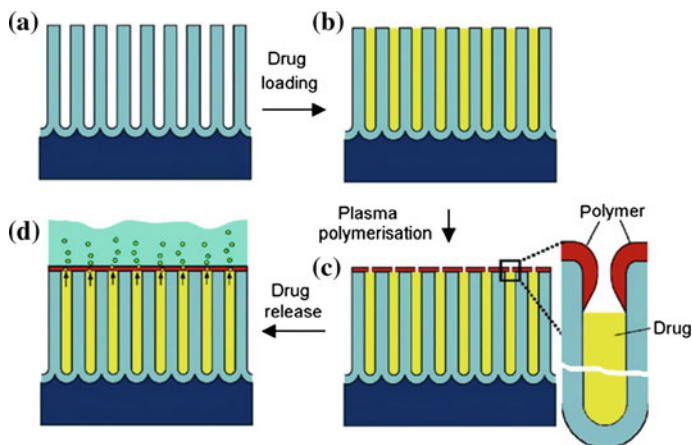
Fig. 5.8 Schematic illustration of Plasma modification of AAO membrane for controlled drug release. **a** AAO porous layer fabricated by electrochemical anodization, **b** drug loading (vancomycin) inside of pores, **c** the deposition of the plasma polymer layer (allylamine) on the top of the pores and finally **d** the release of drug from the pores into solution. Adapted with permission from [124]

hence Losic et al. [123] aim to investigate the potential of plasma polymerization of *n*-heptylamine in order to create *n*-heptylamine layers with surface amine groups on AAO membrane. The modified AAO membranes with active amino groups are a promising platform for the development of novel functional and smart membranes for advanced controlled drug release (Fig. 5.8) [124].

5.1.2.5 Chemical Vapor Deposition

Chemical vapor deposition (CVD) involves the dissociation of gaseous molecules in an activated (heat, light, plasma) environment followed by the formation of stable and conformal films on a substrate [125]. CVD has the capability of producing highly dense and pure materials, offers an excellent control over coating thickness and coverage as well as sustains fast growth rates as compared to other deposition processes [126]. The CVD method is widely used to modify AAO membrane for the fabrication of carbon nanotubes (CNTs) [127–129]. An aligned multi walled CNTs can be further applied as catalyst support [130], drug delivery [131] and field emitters [132]. Fabrication of CNTs by CVD can be catalyst-assisted or without the use of a catalyst.

Rana et al. [128] produced aligned and dense CNT forests over AAO and AAO/Si substrates with the use of ethanol based precursor. These hybrid structures can potentially be applied in the electronics industry as structures for building light emitting diodes, solar cells and super capacitors [132]. Meanwhile, Fang et al. [133] studied the fabrication of nanoporous alumina–carbon nanohybrid by plasma CVD.

The process starts from the electrochemical fabrication of free-standing AAO membranes (Fig. 5.9). The membrane is then coated with a thin gold layer followed by the growth of carbon nanowall in the presence of methane and argon gas mixture. The presence of thin layer gold is reported to govern the density and size of the carbon nanowall.

Fabrication of well-aligned, open-ended CNTs inside the pores of AAO template without using any metallic catalyst was reported by Sarno et al. [134]. An effective volume conductivity of CNT/AO composite was obtained from a few up to 10 kS/m, which is in line with the literature [135]. Recently, Altalhi et al. [136] introduced the well-organized CNT membranes with tunable molecular transport properties using a plastic bag as the carbon source by catalyst/solvent free CVD approach (Fig. 5.10). In this study, a small piece of the plastic bag was put into the pyrolysis zone while AAO membrane was placed in the deposition zone of the CVD reactor. The optimal deposition achieved were 850 °C and 30 min with further deposition time, resulted in an increased of CNTs wall thickness. The fabricated CNTs-AAO membrane demonstrates the ability to selectively tune molecular transport as a function of the interaction between molecules and the inner surface of CNTs. Later it was shown by Segura's group [137], who reported the synthesizing of gold nanoparticles and carbon nanotubes (Au-CNT) hybrid structures inside the pores of AAO by the non-catalytic decomposition of acetylene. The CNT-AAO
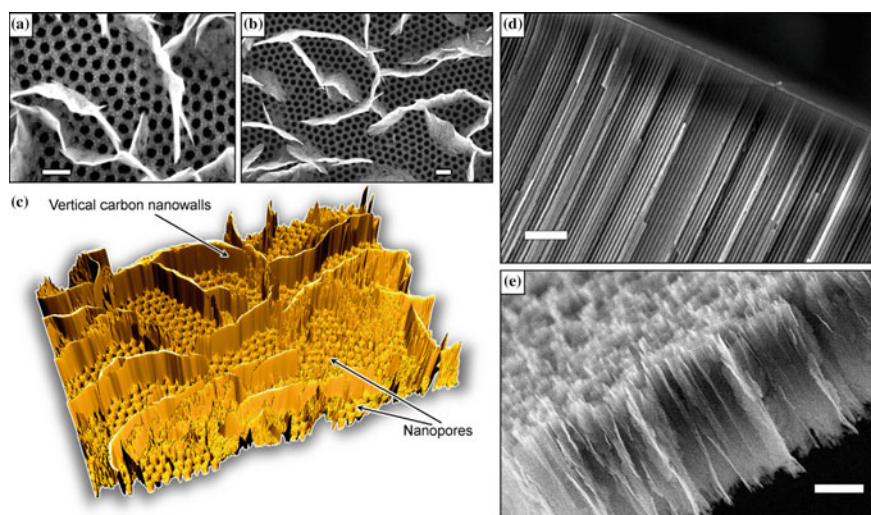

Fig. 5.9 Carbon nanowalls are grown on AAO templates at the methane flow rate of 10 sccm for 10 min. **a** and **b** High-resolution SEM images of the nanowall patterns on gold-covered and bare membranes with the pore sizes of 60 nm. **c** 3D reconstruction of the pattern shown in (**b**). **d** Side view of the AAO template, straight channels are clearly visible. **e** Side view of the carbon nanowalls with the height of about 2 lm, grown on the gold-covered membrane with the pore sizes of 60 nm. Scale bars are 200 nm (**a** and **b**) and 1000 nm (**d** and **e**). Adapted with permission from [133]
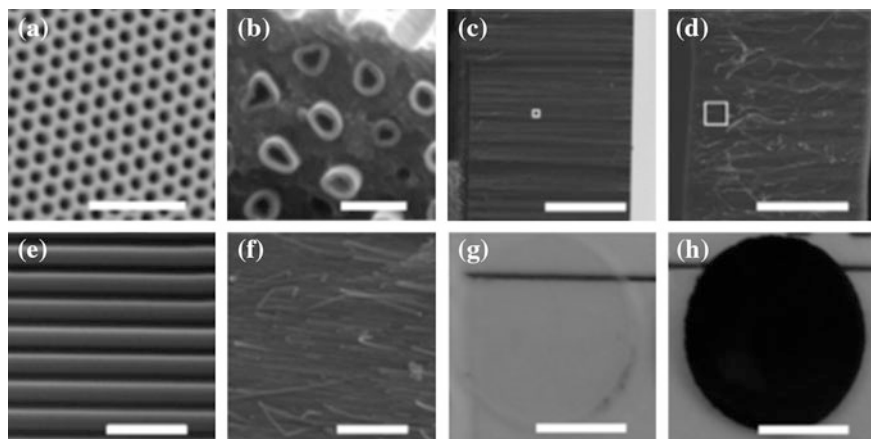
Fig. 5.10 Set of SEM images of as-produced NAAMs and CNTs–NAAMs fabricated by CVD synthesis from commercially available non-degradable plastic bags. **a** NAAM template *top view* (scale bar = 500 nm). **b** Detail of CNTs embedded in a NAAM template (scale bar = 100 nm). **c** NAAM template cross-section view (scale bar = 25 μm). **d** CNTs–NAAM cross-section view (scale bar = 25 μm). **e** and **f** Magnified views of *white squares* shown in (**c**) and (**d**), respectively (scale bars = 250 nm and 2 μm, respectively). **g** and **h** Digital photographs of a NAAM before and after CVD of CNTs, respectively (scale bar = 0.5 cm). Adapted with permission from [136]

composite membranes were impregnated with a HAuCl4/2-propanol solution by dip-coating or drop-casting. The AAO template was then removed with NaOH solution to produce an Au-CNT hybrid. This Au-CNT hybrid is supported on interdigitated microelectrodes (IME) chips to be applied as a sensor for the detection of hydrocarbon gas as acetylene.

Besides CNTs, the CVD method is also been utilized for fabrication of silicon nanowires (SiNWs). Significant improvement of the electrode capacitance per planar surface area and nanowires length unit are achieved compared to electrodes made from SiNWs grown from gold colloids [138]. While Lefeuvre et al. [139] developed highly organized SiNWs by hot wire assisted chemical vapor deposition (HWCVD) process. Tungsten hot wire is used to prevent the deposition of parasitic amorphous silicon (a-Si) that can clog the pores and thus prevent the SiNWs growth. The obtained SiNWs have a high potential for device realization, like PIN junctions, FETs or electrodes for Li-ion batteries. In the meantime, Zhao et al. [140] reported the fabrication of vertically aligned CrO_2 nanowire arrays via atmospheric-pressure CVD assisted by AAO templates. The CrO_2 nanowire arrays show remarkably enhanced coercivity compared with CrO_2 films or bulk. It was reported that the length of CrO2 nanowire was greatly influenced by the pore diameter of the AAO template used. This highly ordered nanowire arrays have important applications in ultrahigh-density perpendicular magnetic recording devices and the mass production of spintronic nanodevices. Polymeric nanotubes can also be synthesized within the AAO membranes based on initiated chemical

vapor deposition (iCVD) technique. Ince et al. [141] synthesized polymeric nanotubes for biorecognition of immunoglobulin G (IgG). The imprinted polymeric nanotubes possess relatively good monodispersity, high binding capacity and significant specific recognition ability toward target molecules.

5.1.2.6 Atomic Layer Deposition (ALD)

Atomic layer deposition (ALD) is a thin film growth technique which employs a cyclic process of self-limiting chemical reactions between gaseous precursors and a substrate [142]. Suntola and Antson pioneered this technique last few decades by producing highly oriented ZnS thin film from H_2S and $ZnCl_2$ precursors [143, 144]. The ALD technique allows the deposition of various materials such as oxides, nitrides, sulfides and metals with coating with precise thickness and compositional control as well as high conformality [45, 145, 146]. This technique has been exploited for surface modification of AAO membrane [147].

The ALD of silica, titania and alumina on AAO membrane enables a controlled reduction of the AAO pore dimension, hence improve its catalytic, optical and transport properties [148–150]. For a review on specific surface chemistry employing ALD of silica on AAO that improved properties for desirable applications in molecular separation, tissue engineering, biosensing and drug delivery see [151]. Meanwhile, Comstock et al. successfully synthesized activated iridium oxide (IrOx) films by utilizing ALD to deposit a thin conformal Ir film within an AAO membrane [152]. The Ir film is then activated by potential cycling in H_2SO_4 to form an activated IrOx films. The ALD method provides a control of film porosity that results in an enhancement of cathodal charge storage capacities for the application in electrochromic devices, pH sensing, and neural stimulation.

Different ALD strategies have been applied to coat AAO nanopores using single metal oxide (Fe_2O_3, ZnO, TiO), mixtures of metal oxides ($SiO_2/Fe_2O_3/SiO_2$), nitrides (WNx) and composite materials ($TiN–Al_2O_3–TiN$) by using conventional gas or even liquid phase ALD. Bachmann et al. [153] have fabricated ordered magnetic Fe_2O_3 nanotube arrays by means of ALD using AAO membranes as templates for potential application in high-density data storage. Recently, Norek et al. [154] synthesized AAO/ZnO and AAO/ZnO/Ag composite by ALD. An enhancement of luminescence properties by a factor of ~ 2.5 for AAO/ZnO/Ag has been reported upon Ag deposition. Pitzschel et al. [155] used regulated AAO membrane prepared by a combination of HA and MA anodization techniques for fabrication of layered nanotubes composed of $SiO_2/Fe_2O_3/SiO_2$ using ferrocene and APTES as precursors for ALD. Later on, Banerjee et al. [156] prepared alternate layers of metal–insulator–metal (MIM) by depositing $TiN–Al_2O_3–TiN$ multilayers inside AAO nanopores yielding nanotubular capacitors with equivalent planar capacitance up to 100 μF cm^{-2}. AAO as a template for fabrication of multiple-walled coaxial nanotubes of five nested layers using ALD was reported by Gu et al. [157]. This template-guided ALD allows remarkable control of nanotube thickness, diameter and spacing within the atomic resolution. Free-standing
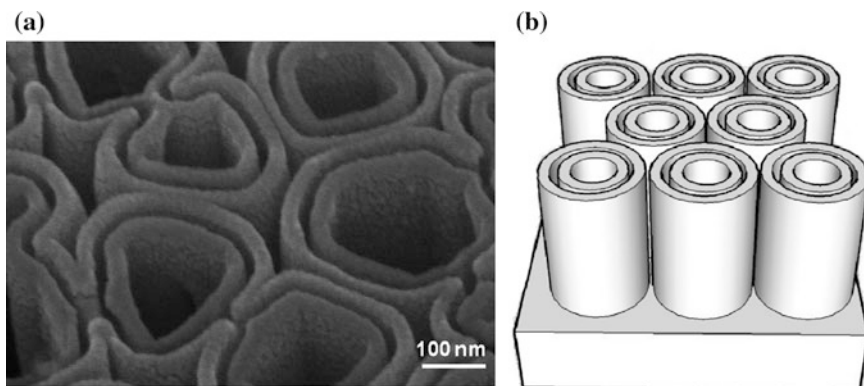
Fig. 5.11 **a** High-magnification tilted SEM *top view* of resultant coaxial HfO$_2$ nanotubes following release from the AAO template and removing the sacrificial spacer Al$_2$O$_3$ layer to expose both the inner and outer surfaces of the nested nanotubes. **b** Schematic model highlighting the design of arrays of free-standing coaxial nested nanotubes. Adapted with permission from [158]

double-walled HfO$_2$ tube-in-tube structure was successfully synthesized with 15 nm HfO$_2$ film and 25 nm sacrificial spacer. The dimension of the spacer gap between two active nanotubes can be engineered with the precise control afforded by ALD. This reported fabrication technique can be extended to produce nanostructures of different materials (metal oxides, semiconductors, and metals) which enable the custom design of broadband sensors and detectors. Recently, Pardon et al. [158] presented the functionalization of AAO membrane by ALD of Pt and Al$_2$O$_3$ for potential development as nanofluidic biosensors (Fig. 5.11). Conformal deposition of Al$_2$O$_3$ layer on Pt film forms a metal-insulator stack inside the AAO nanopore which allows the field effect control of the nanofluidic properties, thus opens novel possibilities for the potential development of nanofluidic biosensors.

5.2 Concluding Remarks

There are numerous ways in which AAO membrane can interact with active compounds. The strategy of manipulating AAO membranes using soft and hard technique has been described in this chapter. These approaches can be used to create a collection of AAO with different surface functionalities. With regards to soft technique, a different approach that gave impact on properties of the resulting materials, as well as applications enabled by these surface modifications has been highlighted. In addition, manipulating the AAO surface by hard technique through metal or metal oxide coating facilitates new synergetic effects which are greatly influenced by the processing conditions. This technique can be easily extended to produce more delicate inverse nanostructures and the diameter, length and degree of orientation of the resultant nanostructures can be manipulated by controlling the

shape of the AAO template. Despite all this progress, the future application of functionalized AAO membranes will depend mainly on the unpredictable needs of the market, however this will be influenced by the developments in device performance and cost. In summary, this field still holds many challenges and opportunities for researchers to explore.

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