Nanostructured Membranes for Water Purification

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6.1 Introduction

Nanoscale materials can be used to achieve wastewater purification, desalination, and inactivation of pathogenic bacteria and viruses, as well as for the adsorption and/or degradation of contaminants [1–16]. The development and sustainability of water treatment technologies have been mostly driven by three primary factors: the discovery of new rare contaminants, the promulgation of new water quality standards, and cost [17–23]. Most sources of water used for public drinking water supplies are not of suitable quality for consumption without some form of treatment [24–30].

The US EPA has ruled that all surface waters must be filtered and disinfected before consumption unless the purveyor can justify avoidance of filtration. Membrane-based water filtration (MWF) processes are currently among the most important and versatile technologies for conventional drinking water production, wastewater treatment, desalination, and water reuse. MWF processes offer unique advantages, such as continuous chemical-free operation, low-energy consumption, easy scale-up and hybridization with other processes, and highly automated process control. Commercially available membrane processes for water purification

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include electrodialysis, electrodeionization, reverse osmosis (RO), ultrafiltration (UF), and microfiltration. However, conventional membrane purification technologies are limited by membrane resistance to flow, imperfections, and fouling [31,32].

Moreover, due to the large pore sizes, conventional membrane filters cannot be used to filter submicron particles or engineered nanoparticles (ENPs). However, in their 1997 work on microporous polypropylene filters with surface charge modification, Kang and Shah demonstrated the use of filtration of ENPs with sizes between 60 and 200 nm [33]. These microporous filters did not work well in this case. The ENPs were captured on filter by adsorption based on surface charge. By using four layers of filters, the capture efficiency was boosted up to 95%. Research carried out by Liang et al. used carbonaceous nanofiber membranes for filtration of gold, silver, and silica ENPs [34]. These membranes were made of carbon nanofibers and had little interaction with the filtered ENPs. Although in the report, the pore size of membranes was not discussed, successful filtrations of ENPs with a wide range (5−150 nm) were demonstrated [34].

Recent work carried out by Krieg et al. showed the ability to trap particles with various sizes bigger than 5 nm using a 12-μm-thick nanoporous membrane [35]. By increasing the thickness to 45 μm, they discovered that the membrane could separate smaller particles (CdTe quantum dots (QDs) of 2−4 nm in size) and act as size-selective chromatography [35]. Several commercial membranes for UF may also be employed for the filtration of ENPs. Most materials that are used in UF are polymeric and naturally hydrophobic. Examples include polysulfone, polyethersulfone, polypropylene, or polyvinylidenefluoride. For example, the DOW™ UF double-walled hollow fiber membrane has uniform pore size of about 30 nm with high removal efficiency for bacteria and viruses. Another application recently reported was inorganic aluminum oxide membrane [36,37]. This membrane has a precise, nondeformable honeycomb pore structure with uniform pore size and an extraordinarily high pore density. Whatman Ltd/GE Healthcare has commercial membrane products named Anodisc™ available at three nominal pore sizes: 20, 100, and 200 nm. These aluminum oxide membranes can be used in micrometer and nanometer filtration [38].

Although these filters have been used for the isolation and separation of ENPs, their inconsistent range in pore size leads to inadequate filtration efficiency. Some extremely small ENPs could still penetrate the pores. Most importantly, these filters cannot be used for both separation and detection (Figure 6.1). Therefore, membrane filters with a broad range of pore sizes are needed for the isolation of diverse classes of ENPs, particularly with respect to size. Nanostructured materials that are specifically designed to purify difficult-to-treat feed water can effectively prevent constituents, which often pose problems to the conventional RO process. The ability to functionalize poly(amic acid) (PAA) membranes with natural polymers or biological building blocks to control the size, shape, and stability at the nanoscale level could potentially address the constraints of conventional MWF technologies.

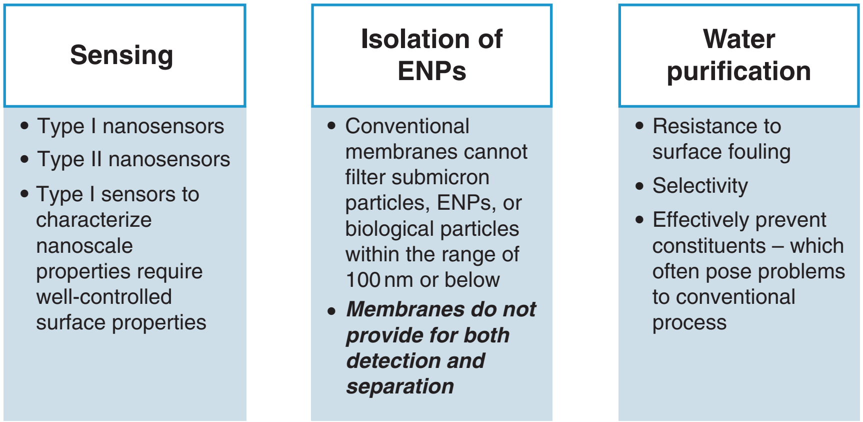

FIGURE 6.1

Research needs in the development of nanostructured materials for environmental applications.

We hereby present the use of nanostructured conducting phase-inverted poly(amic acid) (nPAA) membranes as novel filters for isolation and identification of ENPs especially in complex matrices (Figure 6.1).

6.2 Conducting PAA membranes

In general, nanosensors can be divided into two broad groups, namely nanotechnology-enabled sensors and nanoproperty-quantifiable sensors [39,40]. The former entails all sensors that are nano sized or have nanosized components in them, while the latter includes sensors that are used to measure nanoproperties. Since the dimensions of most biomolecules are on the same scale as nanomaterials, type I sensors have been greatly used to construct enzyme sensors, immunosensors, and genosensors, achieve direct wiring of enzymes and promote spectroelectrochemical reaction, impose barcodes for biomaterials and amplify signal of biorecognition events [41,42]. In addition, a number of research papers and reviews reporting on the use of nanomaterials for chemical and bioassays have been published [43]. The motivation behind this study was to incorporate novel materials that can serve as filters while providing intrinsic signals for quantitative analysis of the nanoscale materials itself. In that respect, there have been only a few sensors that are currently available to measure nanoscale properties especially in complex environmental matrixes. Type II sensors should be able to detect and accurately quantify nanomaterials in complex environmental samples. Recently, our laboratory showed that if beta-cyclodextrins (beta-CDs) are immobilized on an appropriate transducer such as a piezoelectric crystal, nanosized organics could be isolated and detected based on the ability of the CDs to complex the organics according to size exclusion mechanism [44]. The central idea is to utilize the ability of the CDs to complex a comparable sized fullerene (e.g., C_{60}), exclude it from the mixture of other fullerenes like C_{70}, hence measure the mass changes on a quartz crystal microbalance (QCM) according to the Sauebrey equation.

We have explored the feasibility of designing advanced conducting polymeric materials for sensing and remediation applications [46–68]. Examples include polyphenols, PAA nanomembranes, polyoxydianilines, and sequestered metal nanoparticles within electroconducting polypyrrole. However, the extreme hydrophobicity and insolubility of the polypyrrole matrix triggers protein adsorption and makes it less than ideal material for practical sensing applications. Alternative polymeric materials are needed that should possess a hydrophilic surface for low unspecific binding. Moreover, these materials should either possess the necessary functional groups needed for the attachment of biomolecules or can be easily functionalized. Hence we are focusing on creating advanced functional materials, which should be compatible with patterning of cells, neurons, and proteins as well as with modern electronics packaging.

PAA is a conducting electroactive polymer and its properties can be tuned by manipulating the delocalized π electron system for chemical and electrocatalytic applications. Its molecular structure and synthetic approach are shown in Figure 6.2. PAA provides a means of generating nanocomposites containing monodispersed metal particles while retaining its physical and chemical properties. It is versatile in both organic and inorganic solvents due to its chemical resistance. The carbonyl and amide functionalities in PAAs act as anchors that have

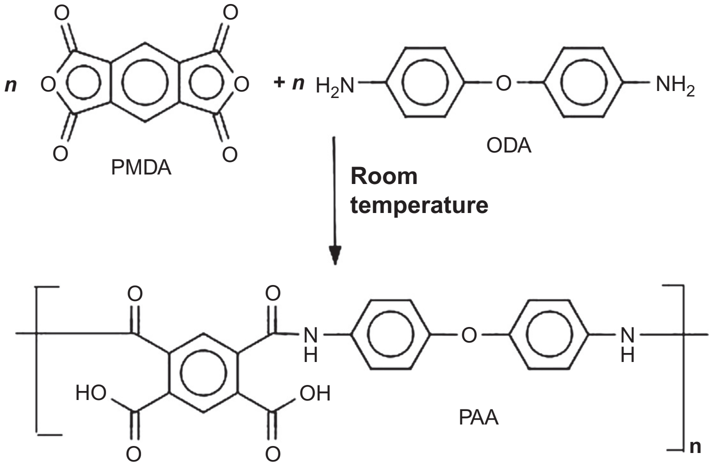

FIGURE 6.2

Synthesis and molecular structure of PAA. PMDA: Pyromelletic dianhydrate; ODA: 4,4’-oxydianiline.

been previously employed in the fabrication of flexible nanostructured PAA-silica (PSG) films [69,70].

Unlike other polymers such as self-assembled monolayers on mesoporous supports, dendrimers, carbon nanotubes, and metalloporphyrinogens, PAA has the following advantages: it is easily synthesized, soluble in both organic and inorganic solvents, able to retain the orientation of its functional groups, and displays both reduction and chelation properties due to the presence of both carboxylic and amide groups that can reduce and chelate metal ions. PAA has also the ability to generate nanocomposites containing monodispersed metal particles, i.e., in this case it acted as a stabilizer.

Figure 6.3 depicts how metal nanoparticle coordinates aryl ether rings using interconnecting PAA or ester rings perpendicular to the surface. The carbonyl and amide groups in PAA act as molecular anchors that bind the nanoparticle to the surface. Similarly, PAA can chelate Cr(III) using its amide and carbonyl functional groups forming an eight-membered ring making the metal ion less available in the aqueous phase.

The complexing power of PAA is significantly higher than that of the imide form, implying the ability of the carboxylic acid groups in PAA to exhibit polyfunctional behavior. Moreover, the possibility of creating monodispersed, nanoscale particles of noble metals can be used to create a high density of anchor groups for directed immobilization of Cr(VI). We reported the electrodeposited PAA films at low temperature (<100°C) with potentials for sensing biomolecules [71]. Compared to the imide form, the PAA have a significantly higher cation complexing property. This means that salts of noble metals having labile anions can react *in situ* to generate metal–polymeric blends. Thus, a single crosslink

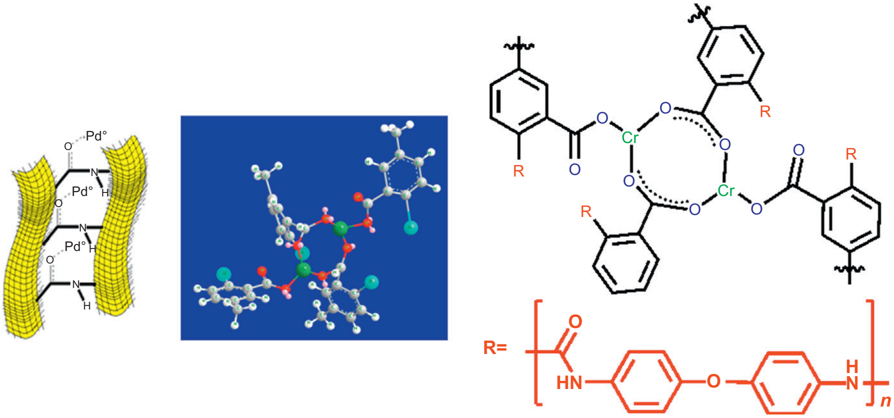

FIGURE 6.3

Model structures for the coordination of PAA with palladium nanoparticles (left) and chromium (III) following *in situ* catalytic reduction of chromium (VI) (right). Green, Cr(III); white, hydrogen; grey, carbon; blue, amide group; and red, carboxylic acid group.

between two molecules of PAA and noble metal composites can result in a stable, high molecular weight network. An average functionality in PAA can vary from 160 to 600 depending upon its molecular weight. Any reactive metal or complexing agents can crosslink the PAA to produce a high molecular weight crosslinked polymeric framework (Figure 6.2). In the following sections, we present the use of PAA membranes as filters for nanoparticles and for absolute removal of bacteria from water.

6.2.1 PAA membranes for nanofiltration of ENPs

We have shown that PAA nanomembranes can be used as nanofilters to isolate and remove silver nanoparticles and titanium dioxide particles in food supplements, aqueous environmental samples, and industrially relevant aerosol nanoparticles [72] with filtration efficiency of over 99%. We successfully synthesized a series of PAA and functionalized PAA membranes. We tested the PAA membranes as nanofilters to isolate and remove silver nanoparticles, QDs, and titanium dioxide particles in environmental samples. Filtration efficiency of over 99.98% was recorded for most contaminants. We observed high rates of particle removal using pressure-driven flow. Aqueous solutions of nanoparticles were filtered using the device illustrated in Figure 6.4A (left). PAA membranes with different porosities were used to target different nanoparticles and the performance of the PAA membranes (filtration efficiency) was compared with those of commercial Anodisc membranes (Table 6.1). The filtration of 20 nm QDs in aqueous solution was achieved using the membrane. The left cuvette contained orange QDs solution before filtration, and this solution turned colorless as shown on the right side after filtration. At the same time, the orange color (of the captured QDs) appeared on the light yellow PAA membrane.

In addition, Figure 6.4 shows the SEM data demonstrating that PAA membranes can be used to capture a broad range of ENPs including QDs, TiO_2, and silver nanoparticles. Following the capture of the nanoparticles, the simultaneous detection was achieved using differential pulse voltammetry. The metal particles were thoroughly oxidized to metal ions using the applied electrical potential. Results show that there was no electrochemical signal recorded either for the blank electrode or for the neat PAA membranes. However, upon coating the membranes with the nanoparticles, the redox peak was observed at $\sim$100 mV and was linearly dependent on the concentration of the silver nanoparticles.

6.2.2 Application of PAA membranes for absolute disinfection of drinking water

We have integrated biological building blocks, such as glutaraldehyde and chitosan, with PAA to detect, disinfect, and completely remove pathogens in water. We described the synthesis of PAA and chitosan-modified PAA (PAA-CS) [73]. The resulting membrane was used for an absolute decontamination of bacteria in

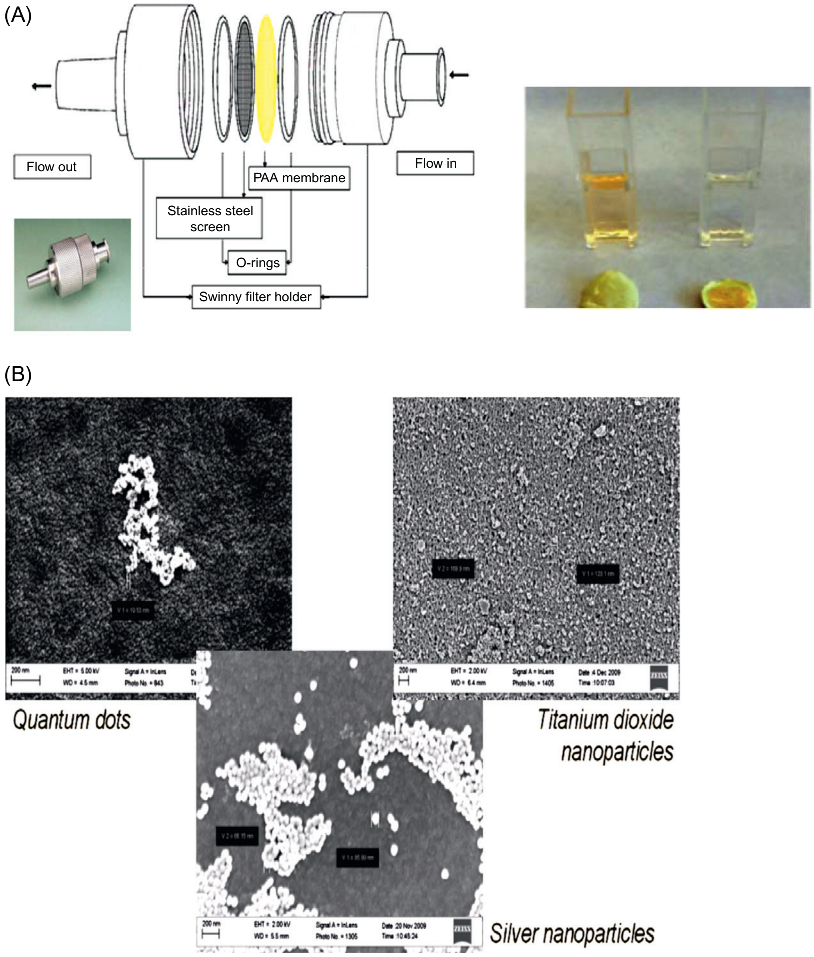

FIGURE 6.4

(A) Swinny filter holder and device setup. (Right) Images of 20 nm QDs in aqueous solutions before and after filtration using PAA membranes. (B) SEM micrographs of PAA membranes after being used to capture QDs (left), TiO_2 (right), and silver nanoparticles (bottom).

drinking water. The characterization data from Nuclear Magnetic Resonance (NMR), Fourier Transformation Infrared Spectroscopy (FT-IR), Scanning Electron Microscopy (SEM), and cyclic voltammetry confirmed the successful formation of electroactive, bifunctional, glutaraldehyde-linked PAA membranes. After the morphological, toxicological, and mechanical testing of the membranes using SEM and 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) assays, the results showed the successful formation of nontoxic, porous, free-standing, and

Table 6.1 Filtration Efficiency of Nanoporous PAA Membranes Versus Commercial Filters

	Average Percentage of Silver Nanoparticles Remaining in Filtrate (%)	Average Filtration Efficiency (%)	SD (%)
Whatman filter paper (FP)	98.76	1.24	1.33
Nylon filter membrane (NL)	55.48	44.52	3.15
PAA membrane (PAA)	1.50	98.50	0.10

mechanically strong PAA and PAA-CS membranes. The pore sizes were experimentally controlled from 4 to 35 nm, and the optimized membranes were tested against three of the most common drinking water contaminants, namely *Escherichia coli*, *Citrobacter freundii*, and *Staphylococcus epidermidis*. As a result, we were able to remove 100% of these microbial species through dead-end filtration and tangential flow filtration (Figure 6.5). The results were validated using plate counting and post-filtration SEM imaging.

6.3 Conclusions

We have developed a number of nanostructured materials as candidates for assessing the occurrence of water contamination. We have also reported the application of these materials for the design of nanostructured membrane filters and sensors. These membranes have shown good-to-excellent pathogen recovery efficiencies as well as a reasonable efficacy for sensing contaminants from water. Through this work, we envisage an advancement of innovative technologies for treating drinking water by simultaneously removing and inactivating classes of bacteria contaminants using low-cost, reusable, and sustainable biomembrane technologies. Nanotechnology applications for water treatment are not years away; they are already available and many more are likely to come on the market in the coming years. It is evident that nanotechnology research is being conducted in a broad spectrum of areas relevant to water treatment, including filters, catalysts, magnetic nanoparticles, and sensors. However, the maturity of research and development efforts is uneven across these areas with nanofiltration currently appearing most mature. Interest in the application of nanotechnology for water treatment appears to be driven by several factors including, but not limited to, reduced costs, improved ability to selectively remove contaminants, durability, and size of the device. While the current generation of nanofilters may be relatively simple, many researchers believe that future generations of nanotechnology-based water treatment devices will capitalize on the new properties of nanoscale materials. Advances through nanotechnology, therefore, may prove to be of significant interest to both developed and developing countries.

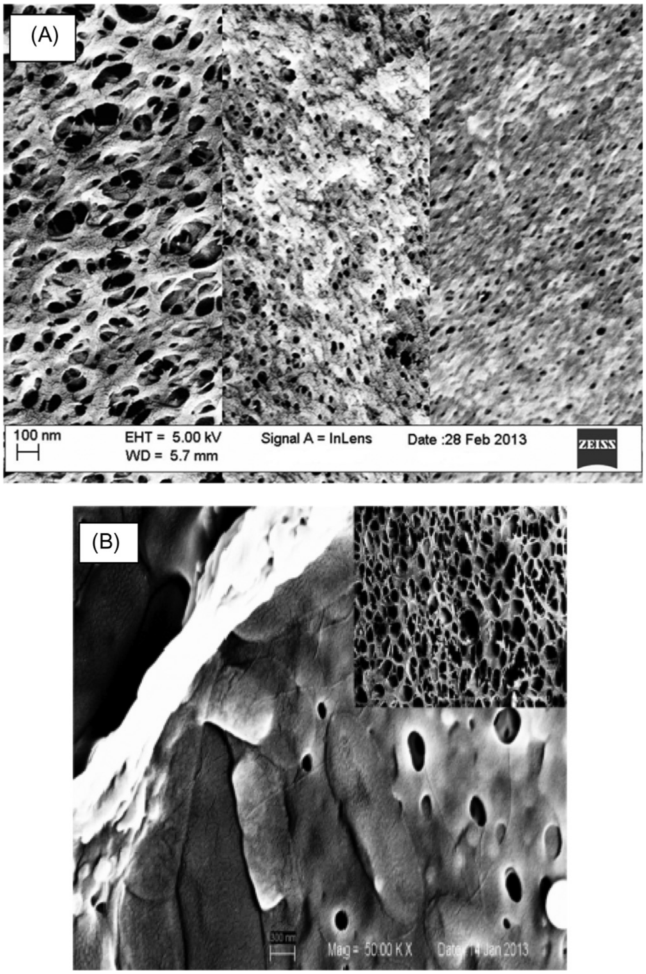

FIGURE 6.5

(A) SEM showing the effect of PAA concentration on pore size-increasing concentration (left to right) decreased pore size. (B) Nanostructured PAA membranes for capture and removal of pathogenic bacteria from drinking water.

Acknowledgments

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