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# Applications of silver nanoparticles stabilized and/or immobilized by polymer matrixes

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**Abstract:**
Nanomaterials frequently possess unique and noticeably changed physical, chemical and biological properties compared to their macro scaled corresponding item. Utilization of nanoparticles habitually requires the construction of integrated chemical systems. Most popular of these are polymer-supported nanoparticles. In this review, we provide the reader with the last developments and breakthrough technologies concerning silver nanoparticles (AgNPs), one of the most comprehensively studied nanomaterials, considering the polymer types and processes used for the nanocomposite membranes preparation.

**Keywords:** silver, nanoparticle, biofouling

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## 1 Nanotechnology

In today's world, nanoparticles (NPs) and nanotechnology have attracted the attention of the scientific community globally and have emerged as a fast developing and fascinating area of research. In December 1959, Nobel Laureate – Prof. Richard Feynman – gave an infamous lecture entitled "*There's plenty of room at the bottom*" at the California Institute of Technology during a meeting with the American Physical Society. During this meeting, Prof. Feynman for the first time mentioned a process which could potentially manipulate individual atoms and molecules and hence advance the field of synthetic chemistry. He was one of the first to recognize the potential of nanoscale materials for industrial society. In 1974, in order to describe the process of moving or manipulating atoms at the nanoscale (1–100 nm), this type of technology was officially termed as "nanotechnology" [1], and since that year, it has been defined as follows [2]:

> Nanotechnology is the design, characterization, production and application of structures, devices and systems by controlling shape and size at nanometer scale.

NPs, the building blocks for nanotechnology, are engineered materials with at least one dimension less than 100 nm. They may have one (e. g.nanolayers), two (nanowires and nanotubes) or three dimensions on the nanoscale (quantum dots, NPs and metal NPs). NPs may provide solutions to technological and environmental challenges in the areas of solar energy conversion, catalysis, medicine, biotechnology, biological labeling, environmental, water treatment, photography, photonics, optoelectronics and surface-enhanced Raman scattering (SERS) detection [3–5]. Moreover, functionalized, biocompatible and inert nanomaterials have potential applications in cancer diagnosis and therapy [6]. A recent survey found that more than 247 nanomaterial-based medical products have been approved by the USA Food and Drug Administration (FDA) and are currently in various stages of clinical study. Their intended uses range from the treatment of clinically unrespectable cancers to the preparation of antibacterial hand gels to the regeneration of heart tissue. At the same time, common themes emerge when discussing nanomaterials in medicine. Indeed, one of the biggest issues is how to translate nanomaterials from the laboratory to the clinic effectively [7]. This increasing demand must be accompanied by "green" synthesis methods. In the global efforts to reduce generated hazardous waste, "green" chemistry and chemical processes are progressively integrating with modern developments in science and industry. Implementation of these sustainable processes should adopt the 12 fundamental principles of green chemistry:

**1/Prevention** – It is better to prevent waste than to treat or clean up waste after it has been created.

**2/Atom Economy** – Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

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**3/Less Hazardous Chemical Syntheses** – Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

**4/Designing Safer Chemicals** – Chemical products should be designed to affect their desired function while minimizing their toxicity.

**5/Safer Solvents and Auxiliaries** – The use of auxiliary substances (e. g. solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.

**6/Design for Energy Efficiency** – Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.

**7/Use of Renewable Feedstocks** – A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

**8/Reduce Derivatives** – Unnecessary derivatization (use of blocking groups, protection/deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.

**9/Catalysis** – Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

**10/Design for Degradation** – Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.

**11/Real-time analysis for Pollution Prevention** – Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

**12/Inherently Safer Chemistry for Accident Prevention** – Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions and fires.

These principles were first articulated in 1998 as a set of tools to help the design scientist to anticipate downstream issues at the earliest stage of a Research & Development effort [8]. They were geared to guide in minimizing the use of unsafe products and maximizing the efficiency of chemical processes. Hence, any synthetic route or chemical process should address these principles by using environmentally benign solvents and nontoxic chemicals [9, 10]. Conventionally, nanomaterials are synthesized using either chemical or physical methods which include sol process, micelle, chemical precipitation, hydrothermal method, electrochemical techniques, pyrolysis and chemical vapor deposition. Some of these methods are easy and make available control over crystallite size by restoring the reaction environment. But problem still exists with the general stability of the product and in achieving monodisperse nanosize using these methods. Investigations have shown that the size, morphology, stability and chemical and physical properties of the metal NPs are strongly influenced by the experimental conditions, the kinetics of interaction of metal ions with reducing agents and adsorption processes of stabilizing agent with metal NPs. Therefore, the design of a synthesis method in which the size, morphology, stability and properties are controlled has become a major field of interest [11, 12].

Nanomaterials often show unique and considerably changed physical, chemical and biological properties compared to their macroscaled counterparts [13]. Utilization of NPs often requires the construction of integrated chemical systems. Most popular of these are polymer-supported NPs. In this chapter, we provide the reader with the last developments and breakthrough technologies concerning silver nanoparticles (AgNPs) applications in antifouling properties for water and wastewater treatment; SERS enhancement; catalysis and medicine. According to literature and patent reports, AgNPs represent one of the most comprehensively studied nanomaterials [14].

## 2 Silver nanoparticles

Silver, known in metallic form since antiquity, has very early been recognized by mankind for its antimicrobial properties, a phenomenon observed, for example, in the context of drinking water (a silver coin in a well), food (silver cutlery, water storage recipients) and medicine (silver skull plates, teeth). Silver compounds were also shown to be useful. For example, dilute solutions of silver nitrate served long, and still do in some countries, as antimicrobial ointment to be instilled into newborn babies' eyes to prevent contraction of gonorrhea from the mother. Used frequently until the middle of the twentieth century, silver and its compounds were then replaced by the newly discovered antibiotics and nearly forgotten for almost 50 years [11, 15]. Moreover, in the recent past, AgNPs have received enormous attention of the researchers due to their extraordinary defense against wide range of microorganisms and due to the appearance of drug resistance against commonly used antibiotics. AgNPs are used just about everywhere, including in cosmetics, socks, food containers, detergents, sprays and a wide range of other products to stop the spread of germs.

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## 2.1 Polymeric composite membranes containing silver nanoparticles for antifouling properties during water and wastewater treatment

Membrane applications in water and wastewater treatment have increased steadily over the past few years due to improved membrane design, smaller footprint and reliable effluent quality. Microfiltration membranes, in particular, have shown promise as a cost-effective alternative to conventional water treatment, as pretreatment for nanofiltration (NF) and reverse osmosis (RO) and as key components in membrane bioreactors. Despite this potential, organic fouling and biological fouling remain problematic for membranes. Fouling increases operating and replacement costs and compromises membrane performance. The abundance of natural organic matter (NOM) in natural waters makes organic fouling of membrane processes in water treatment inevitable; biofouling is considered more problematic since bacteria can reproduce at the membrane surface, create biofilms and cause additional fouling.

To solve the membrane biofouling problems, a variety of reactive functional materials, such as hydrophilic, charged, photocatalytic or biocidal materials, have been introduced into the ultra- and microfiltration membranes. These materials can reduce membrane biofouling by adhesion inhibition (hydrophilic, charged matters) of hydrophobic foulants or decomposition (biocidal, photocatalytic, positively charged matters) of microbial foulants. Although these material's properties endow good antifouling properties to the water treatment membrane, a number of limitations have been associated with these materials, including stability (autoxidation), pH dependence (losing their charge by deprotonation) and membrane degradation [16]. Exceptionally, among the biocidal materials, AgNPs display strong inhibitory and biocidal properties against a variety of microorganism types with long time periods. Significant efforts have been devoted to introducing AgNPs into polymeric membrane substrates to form AgNPs/membrane nanocomposite. Both *in situ* and *ex situ* methods have been developed to incorporating AgNPs into the membrane surface.

### 2.1.1 *In situ* methods

Under the *in situ* approach, with the aid of reducing agents, the synthesis of AgNPs occurred on the membrane surface sequestering silver ions [17]. For example, the negatively charged carboxylic groups sequestered $Ag^+$ on the polyamide surface of RO membrane, and the silver ions were reduced by sodium borohydride ($NaBH_4$) to form AgNPs [18]. However, the Ag loading amount was very low, and the formed AgNPs were loosely bound on the surface and were easily washed out. Mussel-inspired dopamine chemistry has opened a new route to modify all types of inorganic and organic substrates with controllable film thickness and durable stability [19]. Polydopamine (PDA) has stimulated extensive research in the membrane surface functionalization for antifouling purpose [20, 21]. Interestingly, PDA has been found to reduce $Ag^+$ ions to Ag and to synthesize AgNPs *in situ* on different substrates without any other reducing agent [22]. Furthermore, Lee and co-authors [19] demonstrated that the O- and N-sites of PDA can serve as anchors for the AgNPs to enhance the durability of AgNPs on the surfaces via metal coordination. Consequently, PDA chemistry may pave a simple, yet universal way to immobilize AgNPs on various membrane surfaces for antibiofouling purpose.

Recently, Tang et al. [23] reported that the surface modifications with PDA and AgNPs formed *in situ* can reduce the propensity of polysulfone membranes for bacterial adhesion and growth. Under these studies, the surface of a polysulfone membrane was modified with a bioinspired PDA film followed by the *in situ* formation of AgNPs to mitigate membrane biofouling. According to the authors, the PDA modification enhanced the membrane's bacterial anti-adhesive properties by increasing the surface hydrophilicity, while AgNPs imparted strong antimicrobial properties to the membrane. The authors demonstrated that the AgNPs could be generated on the membrane surface by simply exposing the membrane to $AgNO_3$ solutions. Indeed, the $Ag^+$ ions were reduced by the catechol groups in PDA; the AgNP mass loading increased with exposure time, and the AgNPs were firmly immobilized on the membrane through metal coordination. Generated results shown that during leaching tests, the concentrations of $Ag^+$ ions released were 2–3 orders of magnitude lower than the established contaminant limit for drinking water, thereby providing a safe antimicrobial technology.

Huang et al. [24] have also *in situ* immobilized AgNPs on polysulfone ultrafiltration membrane via PDA deposition. The authors have used a silver ammonia aqueous solution ($Ag(NH_3)_2OH$) for AgNPs) *in situ* reduction and demonstrated that the adhesive and reductive PDA layer existing on the membrane surface induced the reduction of $Ag^+$ on the site of surface without surface pore blockage, and also favored to the firm attachment and uniform distribution of AgNPs onto the membrane. Under this study, the prepared AgNPs-PDA/PSf membranes were characterized by mean of: X-ray photoelectron spectroscopy (XPS), scanning election microscope (SEM), atomic force microscopy (AFM), water contact angle measurement and thermogravimetric analysis (TGA). Obtained results indicated that AgNPs were immobilized on the surface as well as the top layer cross-section of the membranes. The authors reported that the increase of $Ag^+$ ion concentration led to an in-

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crease in the size and density of AgNPs anchored onto the membrane. Moreover, the authors reported that compared with PSf membrane, AgNPs-PDA/PSf membrane showed higher water flux, slower flux decline rate during BSA solution filtration and higher flux recovery ratio after simple water flushing. In mean that prepared AgNPs-PDA/PSf membrane possessed excellent stability with little release of silver during the filtrate operation or static immersion in water for 12 days. Besides, published results clearly demonstrated that the AgNPs-PDA/PSf membrane displayed excellent antibacterial and antibiofouling properties against *Escherichia coli* and *Bacillus subtilis*.

Just a while ago, a simple and facile approach was developed by Liu and Hu [25] to *in situ* generate AgNPs on the thin-film composite forward osmosis (TFC FO) membrane. The authors also have applied a Mussel-inspired dopamine chemistry to grow PDA coating on both surfaces of polysulfone support membranes, followed by the generation of AgNPs upon a simple dip coating in silver nitrate aqueous solution, as illustrated in Figure 1.

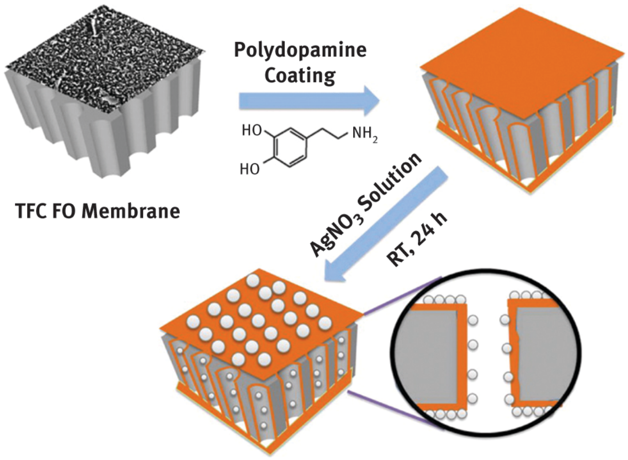

**Figure 1.** *In situ* synthesis procedure of silver nanoparticles on both sides of TFC FO membrane. Reprinted with permission from [25]. Copyright (2016) American Chemical Society.

The authors demonstrated that the AgNPs have a controllable effect on the membrane performances including the water flux and reverse salt flux in the FO test mode. The water flux and salt permeability of the membranes were tested using a custom laboratory-scale cross-flow FO test system in layer faces the draw solution (AL-DS) membrane orientation. The authors reported that the water flux decreased from 17.49 ± 0.42 to 14.56 ± 0.75 L $m^{-2}$ $h^{-1}$ and 13.31 ± 0.95 L $m^{-2}$ $h^{-1}$, and the reverse salt flux decreased from 34.64 ± 2.6 to 28.24 ± 3.61 g $m^{-2}$ $h^{-1}$ and 22.39 ± 0.54 g $m^{-2}$ $h^{-1}$, for pristine, PDA coated, and AgNP generated membranes, respectively. The obtained results confirmed that the PDA coating decreased the water flux and the reverse salt flux by 16.75 % and 18.48 %, and the AgNP generation decreased the water flux and the reverse salt flux further by 8.58 % and 20.71 %. Therefore, the authors concluded that the PDA coatings have stronger effect on decreasing the water flux than the AgNP generation, whereas the AgNP generation has more benefits on suppressing the reverse salt flux than the PDA coatings. The authors demonstrated the water flux and reverse salt flux could be tailored via controlling the formation of PDA coating by adjusting the immersion time of membranes in 3,4-dihydroxyphenylalanine (DOPA) solution. The published results suggest that the water flux and the reverse salt flux of the TFC FO membranes can be further optimized to achieve controllable effect through optimizing the thickness of the PDA film and the growth of AgNPs. Without any doubts, the presented results shed new light on the development of a simple, universal and applicable approach for constructing long-lasting biofouling-resistant membrane surfaces.

Application of *in situ* method for the formation of AgNPs in a TFC FO membrane structure has also been explored by Soroush and co-workers [26]. The authors have modified a surface of TFC FO membranes by AgNPs in the presence and absence of graphene oxide (GO) nanosheets to impart biocidal properties to the membranes, as it shown in Figure 2.

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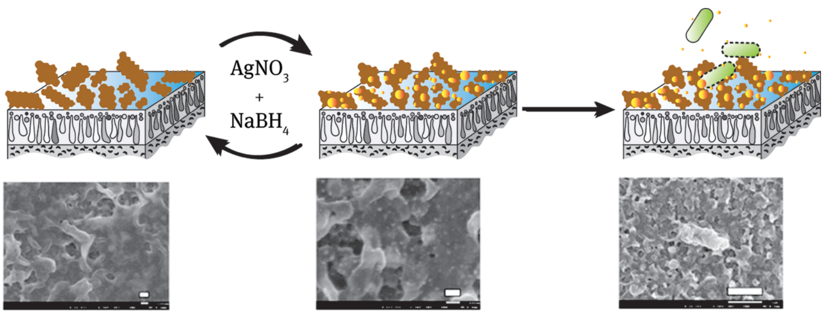

**Figure 2.** Modification of TFC FO membranes surface. Reprinted with permission from [26]. Copyright (2016) American Chemical Society.

The generated results showed that the abundance of oxygen-containing functional groups in GO makes it suitable for anchoring Ag$^+$ ions and governing the size, shape and distribution of AgNPs. Instead, the presence of GO resulted in the formation of smaller and uniformly distributed AgNPs as well as increased silver loading, higher stability and enhanced ion release control. The authors reported that the membranes modified by both GO and Ag exhibited improved (98 %) bacterial inactivation when compared to that of only Ag-modified (80 %) or GO-modified membranes (50 %). Moreover, the investigators reported that after release of Ag ion from GO-Ag-modified membranes for 7 days, AgNP regeneration was conducted in a manner identical to the *in situ* Ag formation procedure. Furthermore, after regeneration, the membrane regained nearly all of its antibacterial properties and 75 % of its initial silver loading.

Madhavan and co-workers [27] incorporated AgNPs into isoporous membranes manufactured by a phase inversion method using a polystyrene-*b*-poly(4-vinylpyridine) (PS-*b*-P4VP) block copolymer. Under this investigation, the AgNPs were obtained by promoting pyridine–silver ion interactions, followed by reaction with a reducing agent.

As shown in Figure 3, the AgNP deposited on the membrane at pH 9 with 1.0 mM AgNO$_3$ solution show well-distributed membrane morphology. Moreover, antibacterial tests performed by the authors show that the NPs have strong biocidal activity and they might be a suitable candidate for practical application. Indeed, flow cytometry measurements, used in this study, demonstrated that, after 72 h of incubation of the membrane systems with *P. aeruginosa*, the proportion of viable cells compared to the control (in absence of AgNPs) was around 20 %.

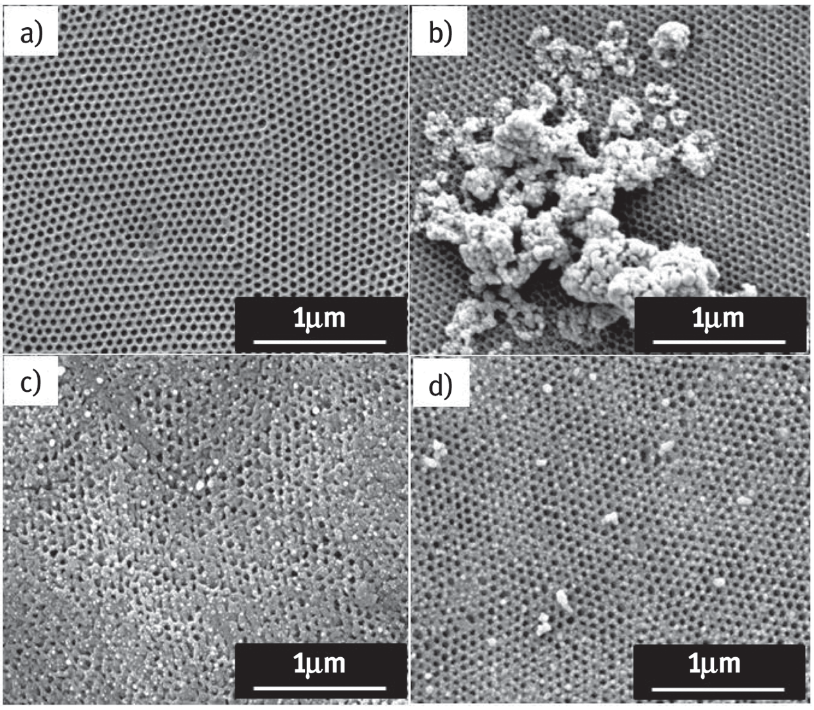

**Figure 3.** SEM images of a (a) plain PS-*b*-P4VP membrane and membranes with Ag nanoparticles prepared at (b) pH 2.1, (c) pH 7 and (d) pH 9 with 1.0 mM AgNO$_3$ solution. Reprinted with permission from [27]. Copyright (2014) American Chemical Society.

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Mishra et al. [28] disclosed an *in situ* synthesis method for preparing silver nanoclusters (AgNCs) embedded in chitosan–polyethylene glycol (CS–PEG) membranes. Under this investigation, the synthesis of AgNCs in CS–PEG matrix was accomplished by the mild *in situ* reduction of silver ions created upon refluxing $AgNO_3$ in the mixed CS–PEG aqueous solution at 90 °C for 6 h, confirmed by a clear golden yellow color of the resulting colloidal system. The authors observed that in the absence of PEG, reduction was very slow and no substantial color change was noted while varying pH from 3 to 7 at 90 °C up to 8 h; however, in the presence of PEG, reduction was faster and at pH 7.0 ± 0.3, CS–PEG matrix color changed to golden yellow within 6 h.

Figure 4shows the possible mechanism of AgNC synthesis in CS–PEG solution. The pH of the mixed solution was adjusted to 7.0 ± 0.3 by adding of $CH_3COOH$ and NaOH. The $Ag^+$ ions initially coordinated with the nonprotonated electron donor amine groups of CS are subsequently stabilized as AgNCs during reduction process that occurs on heating. A multiple array of characterization techniques, employed by the investigators, confirmed the formation of fluorescent AgNCs with sizes of ~3 nm uniformly distributed in CS–PEG matrix. Moreover, exhausted characterization confirmed that the AgNCs play an active role in determining the fraction and interconnectivity of the microporous membranes. Furthermore, reported results showed that the presence and increasing contents of AgNCs enhanced the mechanical stability of membranes and decreased their susceptibility to degradation in the presence of lysozyme and $H_2O_2$. Moreover, the presence and increasing concentrations of AgNCs hindered biofilm formation against *Escherichia coli* (Gram negative) and *Staphylococcus aureus* (Gram positive) and enabled a sustainable release of an anti-inflammatory drug naproxen *in vitro* until 24 h. The overall results gathered and reported in this work make the AgNC-impregnated CS–PEG membranes highly promising multifunctional devices combining efficient antibacterial activity in antifauling studies and biocompatibility with active local drug delivery.

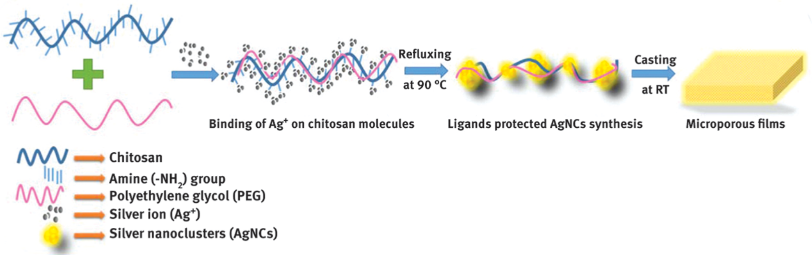

**Figure 4.** Formation mechanism of AgNCs in CS-PEG solution. Reprinted with permission from [28]. Copyright (2016) American Chemical Society.

Investigations carried out by Diagne et al. [29] were addressed to reduce both organic and biological fouling by modifying the surface of commercially available poly(ether sulfone) (PES) membranes using the polyelectrolyte multilayer modification method with poly(styrenesulfonate) (PSS), poly(diallyldimethylammonium chloride) (PDADMAC), and AgNPs (nanoAg) integrated onto the surface as stable, thin films. The authors reported that the PSS increases the hydrophilicity of the membrane and increases the negative surface charge, while integration of nanoAg into the top PSS layer imparts biocidal characteristics to the modified surface.

AgNPs have also been coated directly onto polymer membrane substrates to form AgNP/membrane nanocomposite. Nisola et al. [30] have coated polyether-*block*-polyamide copolymer (PEBA) dense film containing AgNPs onto ultrafiltration polysulfone membranes; however, the practical utility of these methods has been limited by the low efficiency of AgNP deposition onto the membrane surfaces. The authors demonstrated that the immobilized AgNPs can be easily released (or leached) from the membranes owing to the lack of interaction between AgNPs and membrane.

Meagan and coworkers [31] described the preparation of AgNP/membrane nanocomposites in which the AgNPs were electrostatically assembled on the membrane, as shown in Figure 5.

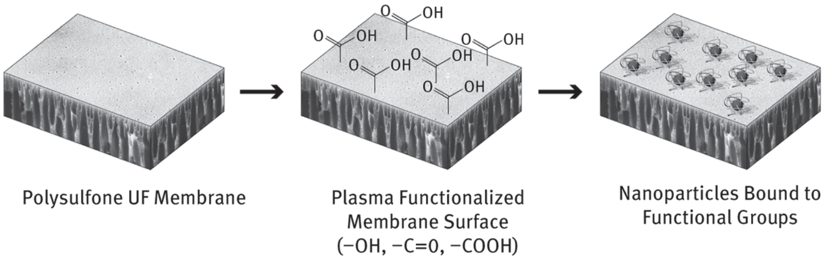

**Figure 5.** Scheme of polysulfone membrane fictionalization with encapsulated AgNPs. Reprinted with permission from [31]. Copyright (2011) American Chemical Society.

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The membrane was prepared by means of the assembly between the AgNPs encapsulated with the positively charged polyethyleneimine (PEI) and the polysulfone membrane functionalized with the negative charged carboxylic acid. Electrostatic interactions were useful for depositing the AgNPs on the membrane substrate; however, the AgNPs were eventually released from the membrane due to the weakness of the electrostatic attraction between the AgNPs and the membrane. Stable and robust bonds between the AgNPs and the membrane are important for ensuring the preparation of safe, ecofriendly, stable, antibiofouling and high-efficiency membranes.

Nanosilver has been incorporated into cellulose acetate [32] and polyimide [33] membranes; however, the long-term effectiveness of the incorporated nanosilver in preventing biofouling during continuous filtration has not been addressed.

### 2.1.2 *Ex situ* methods

This silver loss resulted in a significant loss of antibacterial and antiviral activity. Thus, successful fabrication of nanoAg-impregnated membranes needs to allow for the release of sufficient silver ions for microbial control while preventing a rapid depletion of silver. The unwanted loss of the AgNPs from the membrane brings about the deterioration in the desired properties such as an antibiofouling property and a membrane lifetime. Most problematic of all, the AgNPs released from the membrane can penetrate easily into the human body and can produce cell damage and cancer.

The *ex situ* method generally involves two steps including the synthesis of AgNPs first and their immobilization on the membrane surface, requiring either AgNPs or membrane surface being functionalized to promote their strong bonding. Conventionally, AgNPs have been synthesized using either chemical or physical methods which include sol process, micelle, chemical precipitation, hydrothermal method, electrochemical techniques, pyrolysis and chemical vapor deposition. Some of these methods are easy and make available control over crystallite size by restoring the reaction environment. But problem still exists with the general stability of the product and in achieving monodisperse nanosize using these methods. Investigations have shown that the size, morphology, stability and properties (chemical and physical) of the metal NPs are strongly influenced by the experimental conditions, the kinetics of interaction of metal ions with reducing agents and adsorption processes of stabilizing agent with metal NPs. Therefore, the design of a synthesis method in which the size, morphology, stability and properties are controlled has become a major field of interest [11, 12].

Kwak and co-workers have studied metal–polymer (cellulose [34] or poly(vinylidene fluoride) [35]) fabrics nanocomposite, in which AgNPs have been covalently assembled onto a thiolated polymer fabric. The author reported that the thiol group in the thiolated cellulose formed a robust covalent bond with the Ag atoms on the surface of the metal NPs, thereby significantly reducing the number of metal NPs released from the fabric during washing [34]. Furthermore, the same authors showed [35] that the AgNP–poly(vinylidene fluoride) (Ag–PVDF) membrane nanocomposites have a sustainable antibiofouling property through the covalent assembly of the AgNPs onto the PVDF membrane surface via a thiol end-functionalized amphiphilic block copolymeric linker, as illustrated in Figure 6. To this end, the thiol end-functionalized amphiphilic block copolymer as a covalent linker between the AgNPs and the membrane was physically anchored onto the membrane via hydrophilic–hydrophobic phase recognition of the amphiphilic linkers during the membrane fabrication process, resulting in the thiolated PVDF membrane. AgNPs then covalently bound to the thiolated PVDF membrane via a simple impregnation process. Surprisingly, the resulting Ag–PVDF membrane nanocomposite did not release detectable amounts of AgNPs from the membrane, and the membrane displayed excellent antibiofouling property. This makes them tremendously attractive in applications ranging from high-efficiency membrane to ecofriendly water purification systems.

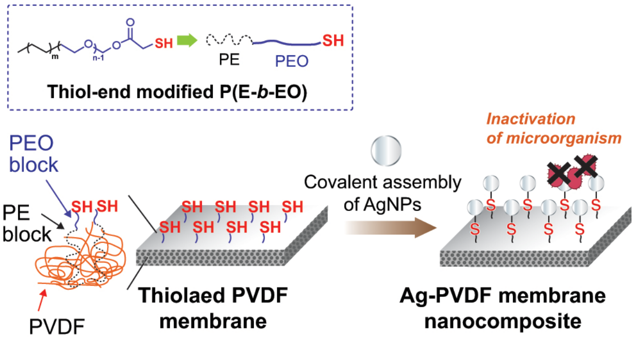

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**Figure 6.** Sustainable anti-biofouling ultrafiltration membrane nanocomposites by covalently immobilizing silver nanoparticles (AgNPs) onto poly(vinylidene fluoride) (PVDF) membrane mediated by a thiol-end functional amphiphilic block copolymer linker. Reprinted with permission from [31]. Copyright (2011) American Chemical Society.

The same concept of silver–composite membrane formation via the Ag–S chemical bonding has also been carried out by Yin et al. [36]. The authors reported that the AgNPs with approximately 15 nm in diameter were effectively attached to the surface of polyamide TFC membrane via covalent bonding, with cysteamine as a bridging agent. Gusseme et al. [37] immobilized the silver nanopraticles in polyvinylidene fluoride membranes and investigated the disinfection capacity toward virus in water. However, the researchers were mainly focused on application of antibiofouling performance of AgNPs in membrane fabrication, but the hydrophilicity of membrane surface provided by AgNPs has rarely been reported. Li et al. [38] immobilized AgNPs on the surface of poly(vinylidene fluoride)-g-poly(acrylic acid) (PVDF-g-PAA) membranes obtaining composite membranes with excellent surface hydrophilicity and outstanding antifouling performance. Under this investigation, the authors first prepared the PVDF membranes by a classical method-immersion precipitation inversion process. Then by using a physisorbed free radical grafting technique, they grafted a PAA brush on PVDF membrane surface. Next, they decorated the membrane with Ag ions by immersion of the grafted membrane in a silver nitrate solution. After this step, the silver ions were coordinately bonded with the carboxyl group of PAA. In order to get the Ag-PVDF-g-PAA membranes, the silver ions were further reduced with $NaBH_4$, as illustrated in Figure 7.

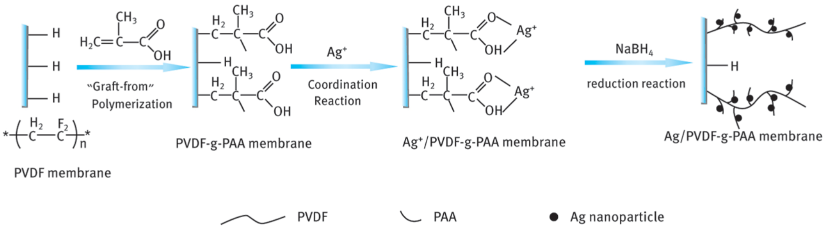

**Figure 7.** Silver modification of PVDF membrane.

Unfortunately, the approaches that have been performed by Kwak and co-workers [34, 35], as well as by Yin and co-workers [39] or Li and co-workers [38], require the membrane surface having certain functionalities to immobilize AgNPs, and they are not applicable to most of other different membranes.

## 2.2 Polymeric stabilized silver nanoparticles for SERS properties

Raman spectroscopy arises from the inelastic light scattering by molecular vibrations, which could provide "fingerprint" information for molecular diagnostics [40]. However, the inherently low scattering intensity of conventional Raman spectroscopy limits its widespread applicability. Over the last few decades, surface-enhanced Raman spectroscopy (SERS) has received intense attention because of its great potential for ultrasensitive detection down to the single-molecular level that are often found in art materials that exhibit a highly fluorescent background occurring when the studied materials are excited in the visible and near infrared (NIR) in spontaneous Raman scattering measurements [41–43]. It is well-known that the extremely large electromagnetic SERS enhancement (proportional to field enhancement to the fourth power) up to $10^{10}$ has been theoretically predicted and experimentally demonstrated for small areas called as "hot spots" [44–46]. Because SERS "hot spots" usually reside in the interstitial voids of metal NPs and metal structures with intersections, bifurcations and high radius of curvatures, exquisite preparation of metal NPs with controlled size and morphology and delicate manipulation of the NP assemblies are required in order to maximize the sensitivity of the prepared SERS platforms. To this objective, various designs of SERS-active substrates have been reported, such as roughened metal substrates, metal NP assemblies, porous or holey substrates and even semiconductor-based substrates. However, SERS substrates must be reproducible, highly sensitive and facile for fabrication and have site-independent "hot spots," while most of the above-mentioned candidates require relatively complicated and expensive manipulations [24]. The polymer engineering opens a new path for NP assembling and their successive application in SERS technologies. Illustrative examples include the synthesis of Ag/poly(butyl acrylate) composites using microemulsions [47], the preparation of poly(methyl methacrylate) durable plastic films using an Ag/PVP colloid [48], incorporation of AgNPs in soft polymers to produce active SERS substrates [49] and the preparation of Ag/bionanocomposites using cellulose [50], chitosan [51] or sporopollenin [52]. It is important to underline that most of the polymer–AgNP matrix preparations are based on *in situ* methods. Some of the most exciting examples are described below.

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Recently, Yan et al. [53] reported a facile synthesis of homogeneous AgNPs fully covering the polyaniline (PANI) membrane surface simply by introducing organic acid in the $AgNO_3$ reaction solution, as an improved technique to fabricate well-defined Ag nanostructures on PANI substrates through a direct chemical deposition method described in [54]. The authors found that the chemical nature of the acid is crucial to create a homogeneous nucleation environment for Ag growth, where, in this case, homogeneous AgNPs that are assembled by Ag nanosheets are produced with the assistance of succinic acid and lactic acid, but only scattered AgNPs with camphorsulfonic acid. According to the authors, improved surface wettability of PANI membranes after acid doping may also account for the higher surface coverage of Ag nanostructures. The authors reported that the Ag nanostructures fully covering the PANI surface, and they are extremely sensitive in the detection of a target analyte, 4-mercaptobenzoic acid (4-MBA), using SERS, with a detection limit of $10^{-12}$ M. The authors believe the facilely fabricated SERS-active substrates based on conducting polymer-mediated growth of Ag nanostructures can be promising in the trace detection of chemical and biological molecules.

Li and co-workers have focused their investigation on the development of sensitive detection methods for environmental antibiotics monitoring due to the increasing pollution of aquatic environments by antibiotics. Recently, the authors published very interesting results concerning a preparation of AgNPs and carbon nanotube-intercalated graphene oxide laminar membranes (AgNPs/CNT-GO membranes) (Figure 8) for enrichment and SERS detection of antibiotics [55].

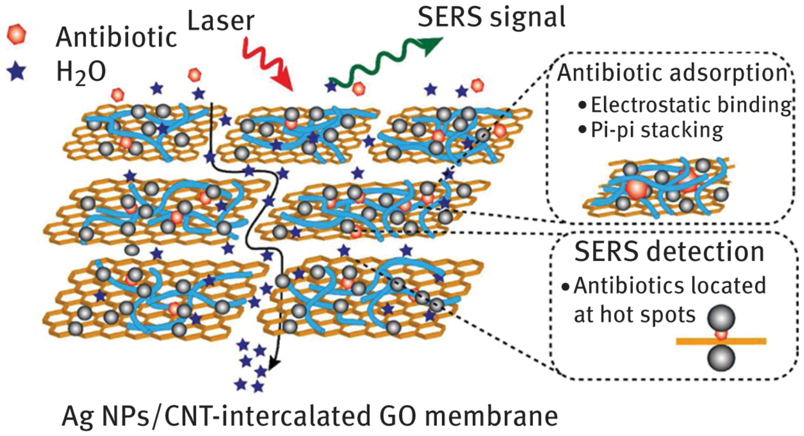

**Figure 8.** Scheme of AgNPs/CNT-GO membranes for SERS detection of antibiotics. Reprinted with permission from [54]. Copyright (2016) American Chemical Society.

The achieved results show that the prepared Ag NPs/CNT-GO membranes exhibit a high enrichment ability because of the $\pi$–$\pi$ stacking and electrostatic interactions of GO toward antibiotic molecules, which enhance the sensitivity of SERS measurements and enable the antibiotics to be determined at sub-nM concentrations. In addition, the nanochannels created by the intercalation of CNTs into GO layers result in an eightfold enhancement in the water permeance of Ag NPs/CNT-GO membranes compared to that of pure GO membranes. More importantly, the obtained Ag NPs/CNT-GO membranes exhibit high reproducibility and long-term stability. The presented results show that the spot-to-spot variation in SERS intensity was less than 15 %, and the SERS performance can be maintained for at least 70 days. The Ag NPs/CNT-GO membranes were also used for SERS detection of antibiotics in real samples. The results showed that the characteristic peaks of antibiotics were obviously recognizable. Thus, the authors expect that the reported ultrasensitive SERS detection of antibiotics can improve practical applications of Ag NPs/CNT-GO in environmental analysis.

Mondal et al. [56] have decorated PANI fibers with AgNPs by using a solution-dipping technique. Then, the authors evolved the fibers as sensitive materials for the detection of trace amounts of 4-mercaptobenzoic acid and rhodamine 6 G as an analyte of SERS. The investigators reported that the developed decorated fibers possess a down detection limit to nanomolar concentrations with excellent recyclability. Furthermore, the authors demonstrated that synthesized fiber composites can be apply simultaneously as an active SERS substrate and a superior catalyst for reduction of 4-nitrothiophenol. Figure 9shows an SEM micrograph of Ag/PANI fiber and SERS enhancements.

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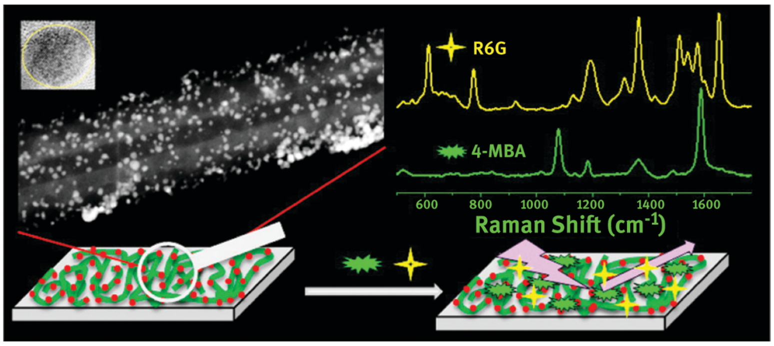

**Figure 9.** SEM micrograph of Ag /polyaniline fiber and SERS enhancements. Reprinted with permission from [56]. Copyright (2015) American Chemical Society.

Polymers whose behavior is sensitive to external stimuli are attracting great interest as they might add complementary functionalities to the composite of the SERS active metal. Accordingly, Au/Ag nanorods in thermoresponsive hydrogel networks [57] or mechanical responsive Ag-loaded agarose gels [58] have been reported as substrates that show a SERS behavior dependent on "hot spots" induced by the synergistic action of the plasmonic metal nanostructures and the external stimuli responsive polymer. Trindade and co-workers have focused their investigation on the development of κ-carrageenan-based nanocapsules containing nanometals and SERS platforms. The authors have shown that κ-carrageenan can incorporate diverse types of inorganic NPs via encapsulation in the biopolymer structures [59–61]. Recently, the investigators reported that blended nanocomposites of Ag have been prepared in order to obtain new analytical SERS platforms [62]. According to the authors, because of κ-carrageenan tunable colloidal behavior between the sol–gel state, carrageenans are foreseen as interesting matrices to develop thermosensitive SERS substrates provided that there is the ability to create dynamic hot spots by varying the gelation conditions. The authors demonstrated that the rheological behavior of Ag-containing hydrogels influences their performance as SERS platforms. The published results provided new insights into SERS associated with changes on the rheological behavior of chemical environments comprising active metal surfaces such as AgNPs. Furthermore, the authors provided a possible mechanism that correlates the gel strength of the biopolymer matrix with the SERS signal, as consequence of the formation of metal nanojuntions caused by the closer proximity of AgNPs as the biopolymer chains interaction. The authors believe that reported results can motivate research on the design of thermosensitive polymers that use rheological parameters for controlling the analytical sensitivity when used as SERS substrates.

## 2.3 Polymeric stabilized silver nanoparticles as catalyst

As mentioned in the beginning of this chapter in recent years, the synthesis of metal nanostructures using noble metals has gathered notable attention. Especially, polymer-embedded metal NPs seem to have special advantages that, in addition to providing stabilizing and protecting effects to metal NPs, polymers also offer unique possibilities for enhancing access of reactants to catalytic sites by way of a preconcentration effect, thereby exerting synergism in catalytic activities. An efficient and widespread way of synthesis of aromatic amines is the reduction of nitroaromatics using catalysts. Metal NPs have been used widely for the catalytic reduction of nitroaromatics in the presence of $NaBH_4$ [63].Various mono- and bi-metal NPs such as Ag, Pt, Au, Au–Ag, Pt/C and Ni–Pt have been used for the catalytic conversion of nitroaromatics into their corresponding amino compounds. Generally, Pt, Pd, Au and its bi-metal NPs are expensive and are considered to have better catalytic activity than AgNPs. However, Ag is the cheapest metal available among them. Hence, the preparation of catalytically more active AgNPs over other noble metal NPs through a simple procedure is of significance in this field of research. Viswanathan and Ramaraj [64] developed a simple protocol for silver ion reducing by using dopamine in the presence of the polyelectrolyte poly[acrylamide-*co*-(diallyldimethylammonium chloride)] (PADA) and amine-functionalized silane. The authors have used the polymer-stabilized AgNPs as catalyst for the reduction of 4-nitrophenol (4-NP). Reported results demonstrated that interestingly dopamine-reduced AgNPs show better catalytic activity ($k$=10.99×$10^{-3}$ $s^{-1}$) than those reduced using the conventional reducing agent $NaBH_4$ ($k$=4.16×$10^{-3}$ $s^{-1}$) toward the reduction of 4-NP.

Jayabal and Ramaraj have also developed a simple method for the preparation of bimetallic gold/silver nanorods embedded in amine functionalized silicate sol–gel matrix (Au/Ag–TPDTNRs) in the aqueous medium [63]. The authors have used $N^1$-[3-trimethoxysilyl)propyl]diethylene triamine (TPDT) as a reducing as well as stabilizing agent to prepare the Au/Ag–TPDTNRs. Furthermore, the authors have investigated the Au/Ag–TPDTNR application for a catalytic reduction of nitrobenzene. The catalytic activity of the Au/Ag–TPDTNRs was evaluated by studying the catalytic reduction of nitrobenzene to aniline upon the addition of

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$NaBH_4$ in an aqueous solution. The Au/Ag–TPDTNRs was found to be a good catalyst when compared to the Au–TPDTNRs and AuNRs for the reduction of nitrobenzene to aniline at room temperature. According to the authors, the enhanced catalytic activity of Au/Ag–TPDTNRs is due to the synergistic effect of Au and Ag present in the bimetallic Au/Ag–TPDNRs. The reaction rate constants ($k$) are estimated to be 0.4050, 0.2515 and 0.1235 $min^{-1}$ for Au/Ag–TPDTNRs, Au–TPDTNRs and AuNRs, respectively. The electrocatalytic reduction of nitrobenzene at pH 7 using the Au/Ag–TPDTNRs modified electrode was also investigated by the authors and compared with the Au–TPDTNRs. The generated results showed that the higher electrocatalytic activity of Au/Ag–TPDTNRs is due to the synergistic effect of Au and Ag present in the bimetallic Au/Ag–TPDTNRs. The results of the reported study demonstrated that the Au/Ag–TPDNRs are efficient catalysts for the catalytic reduction of nitrobenzene.

The use of smart polymer microgels as microreactors for the synthesis of AgNPs and for stabilizing them is increasing due to the unique combination of tunable optical and catalytic properties of AgNPs and responsive behavior of the microgels. *N*-isopropylacrylamide (NIPAM)-based microgels are generally used for *in situ* fabrication of AgNPs [65]. AgNPs fabricated with microgels have been widely used as catalysts for various organic reactions due to their easy synthesis, control over size and shape of NPs, open network of microgels for diffusion of reactants toward the surface of NPs, long-term stability, good reusability, non-toxicity, low cost, easy availability, quasi-homogeneous catalytic nature and tunable catalytic activity [66]. Liu et al. [67] synthesized AgNPs inside poly(NIPAM) microgels by *in situ* reduction method and used this hybrid system for catalytic reduction of 4-NP in aqueous medium. The authors reported that the catalytic activity of AgNPs can be tuned by swelling and de-swelling of the hybrid microgels. Dong et al. [68] fabricated AgNPs in poly(*N*-isopropylacrylamide-*co*-acrylic acid) microgels and explained the stability of AgNPs inside the network on the basis of the electron donor–acceptor concept. Khan et al. [69] used poly(*N*-isopropylacrylamide-*co*-methacrylic acid) microgels as microreactors for the fabrication of AgNPs for catalytic applications. The amide groups in NIPAM and acrylamide units of P(NIPAM-*co*-AAm) microgels may act as ligand to stabilize the AgNPs inside the network, and the hybrid system can be used as a catalyst for various reactions in aqueous medium. The copolymerization of NIPAM with acrylamide can not only increase the volume phase transition temperature of the microgels to increase their catalytic temperature range but it may also increase the diffusion of hydrophilic reactants from outside to inside the network. These ideas stimulated Begum and co-workers [70] to fabricate AgNPs in P(NIPAM-*co*-AAm) microgels for catalytic application. Under this investigation, the uniformly loaded AgNPs were found to be stable for a long time due to donor–acceptor interaction between amide groups of polymer network and AgNPs. The hybrid microgels were successfully used by the authors as a catalyst for rapid reduction of 4-Nitrophenol (4-NP) into 4-aminophenol (4-AP) in aqueous medium. They reported that the apparent rate constant increased with increasing concentration of catalyst and $NaBH_4$. The hybrid system reported in the publication has a potential to be used as a catalyst for many other organic reactions. According to the authors, provided results could inspire others researchers to fabricate NPs of other metals like Pt, Pd, Ru, etc., inside P(NIPAM-*co*-AAm) microgels, and these hybrid systems may be used in future as catalysts for reduction of nitroarenes and other systems. According to the investigators, developed hybrid microgels can also be used for applications other than catalysis.

## 2.4 Silver polymer-based material in medical applications

Implant associated and joint replacement bacterial infections are high at 1.0–4.0 % and are one of the most serious complications in orthopedic surgery because they are extremely difficult to treat and result in increased morbidity and significantly worse outcomes [71–73]. Bone infection, also called osteomyelitis, can result when bacteria invade a bone. Treatment of osteomyelitis usually requires surgical debridement and prolonged antimicrobial therapy. The rising incidence of infection with multidrug-resistant bacteria, in particular methicillin-resistant *S. aureus* (MRSA), however, limits the antimicrobial treatment options available [74]. Therefore, AgNPs have been incorporated into plain poly(methyl methacrylate) bone cement, used for the secure attachment of joint prostheses hip and knee replacement surgery, as a way to reduce bacterial resistance [72, 75]. Soo and co-workers have investigated incorporating AgNPs into poly(lactic-co-glycolic acid) (PLGA) grafts as a potential for implant and fixation material in orthopedic and orthodontic surgery [76, 77]. The authors demonstrated that metallic nanosilver particles (with a size of 20–40 nm)–(PLGA) composite grafts have strong antibacterial properties [76]. In addition, nanosilver particle–PLGA composite grafts did not inhibit adherence, proliferation, alkaline phosphatase activity or mineralization of on growth MC3T3-E1 pre-osteoblasts compared to PLGA controls. Furthermore, the authors reported that the nanosilver particles did not affect the osteoinductivity of bone morphogenetic protein 2 (BMP-2). Infected femoral defects implanted with BMP-2 coupled 2.0 % nanosilver particle–PLGA composite grafts healed in 12 weeks without evidence of residual bacteria. In contrast, BMP-2-coupled PLGA control grafts failed to heal in the presence of continued bacterial colonies. The obtained results indicated that nanosilver of defined particle size is bactericidal without discernible *in vitro*

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and *in vivo* cytotoxicity or negative effects on BMP-2 osteoinductivity, making it an ideal antimicrobial for bone regeneration in infected wounds. Moreover, the same research group has evaluated AgNP/PLGA-coated stainless steel alloy (SNPSA) as a potential antimicrobial implant material [77]. The authors reported that SNPSA exhibited strong antibacterial activity *in vitro* and *ex vivo* and promoted MC3T3-E1 pre-osteoblast proliferation and maturation in vitro. Furthermore, SNPSA implants induced osteogenesis while suppressing bacterial survival in contaminated rat femoral canals. The generated results pointed out that SNPSA has simultaneous antimicrobial and osteoinductive properties that make it a promising therapeutic material in orthopedic surgery.

Catheters used in the hospital setting have a high propensity for infection, which can lead to unwanted complications. Thus, AgNPs have been investigated as a method of reducing biofilm growth on catheters. Recently, polyurethane catheters have been modified with a coat of AgNPs to create effective antibacterial catheters [78]. Silver-coated catheters prepared by Roe et al. [79] showed significant *in vitro* antimicrobial activity and prevented biofilm formation using *Escherichia coli, Enterococcus, Staphylococcus aureus*, coagulase-negative *staphylococci, Pseudomonas aeruginosa* and *Candida albicans*. Approximately 15 % of the coated silver eluted from the catheters in 10 days *in vivo*, with predominant excretion in faces (8 %), accumulation at the implantation site (3 %) and no organ accumulation (≤0.1 %). Moreover, multiple studies have reported that AgNP-coated catheters can effectively reduce bacteria for up to 72 h in animal models [78, 80]. A clinical pilot study performed by Lacknerand co-workers was focused on investigating the prevention of catheter-associated ventriculitis (CAV) with AgNPs. The authors did not find any incidence of CAV, and all cerebrospinal fluid cultures were negative in the 19 patients that received a AgNP-coated catheter [81]. On the contrary, in the control group of 20 patients by using the catheter without AgNPs, five were positive for CAV [81].

AgNPs have also been applied to dental medicine. The oral environment is considered to be an asperous environment for restored tooth structure. Recurrent dental caries is a common cause of failure of tooth-colored restorations. Bacterial acids, microleakage and cyclic stresses can lead to deterioration of the polymeric resin–tooth bonded interface. Research on the incorporation of cutting-edge anticaries agents for the design of new, long-lasting, bioactive resin-based dental materials is a demanding and provoking work. Released antibacterial agents such as AgNPs, nonreleased antibacterial macromolecules (DMAHDM, dimethylaminohexadecyl methacrylate) and released acid neutralizer amorphous calcium phosphate nanoparticles (NACP) have shown potential as individual and dual anticaries approaches. Melo and co-workers [82] performed an exhausted investigations on AgNP synthesis, and their future incorporated into all the dental materials required to perform a composite restoration: dental primer, adhesive and composite (Figure 10).

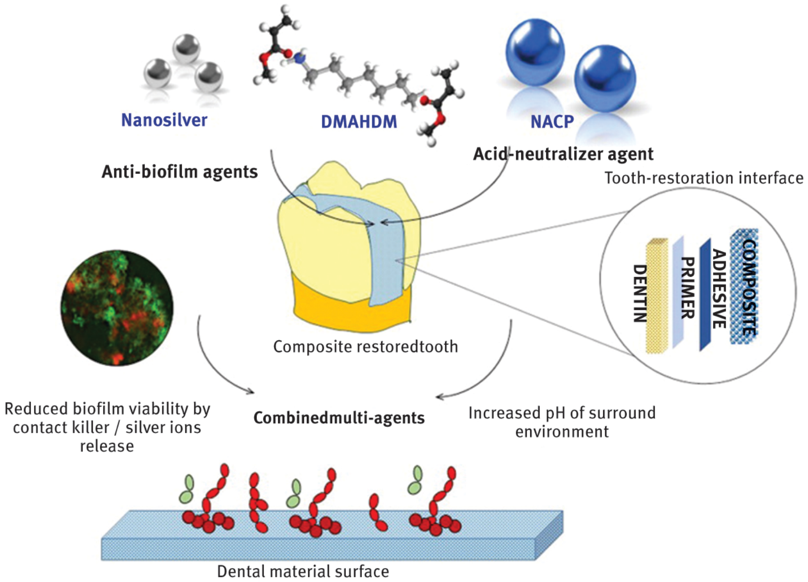

**Figure 10.** Incorporation of AgNPs into dental structure. Reprinted with permission from [82]. Copyright (2016) American Chemical Society.

The authors focused on combining different dental materials loaded with multiagents to improve the durability of the complex dental bonding interface. A combined effect of bacterial acid attack and fatigue on the bonding interface simulated the harsh oral environment. Human saliva-derived oral biofilm was grown on each sample prior to the cyclic loading. The oral biofilm viability during the fatigue performance was monitored by the live–dead assay. Damage of the samples that developed during the test was quantified from the fatigue life distributions. Results achieved by the authors indicate that the resultant multiagent dental composite materials were able to reduce the acidic impact of the oral biofilm, thereby improving the strength and resistance

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to fatigue failure of the dentin–resin bonded interface. Besides, studies performed by Melo et al. [82] showed that dental restorative materials containing multiple therapeutic agents of different chemical characteristics can be beneficial toward improving resistance to mechanical and acidic challenges in oral environments. Akhavan et al. [83] reported that incorporation of AgNPs into orthodontic adhesives could increase or maintain the shear bond strength of an orthodontic adhesive while simultaneously increasing its resistance to bacteria. A recent study carried out by researchers Zmudzkin and co-workers [84] demonstrated that integration of AgNPs into dental composites could reduce the microbial colonization of lining materials, enhancing the antifungal efficiency. Similarly, AgNP amalgamation into endodontic fillings displays an increased antibacterial effect against *Streptococcus milleri, Staphylococcus aureus* and *Enterococcus faecalis* [85]. Degrazia et al. [86] investigated an effect of AgNPs on the physicochemical and antimicrobial properties of an orthodontic adhesive. The authors found that the addition of AgNP solutions to Transbond™ XT adhesive primer inhibited *Streptococcus mutans* growth without compromising the chemical and physical properties of the adhesive.

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