Silver nanoparticles attached to porous carbon substrates: robust materials for chemical-free water disinfection

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A B S T R A C T

The antibacterial properties of silver are well known, and their potency can strongly depend on the available surface area. Nanoparticles provide the advantage of high surface area per volume, but their use is limited because, once deployed in the environment, they are difficult to retrieve and may become pollutants with potential adverse effects. This issue can be addressed if silver nanoparticles (AgNP) are attached to or encased in larger structures. This research focuses on attachment of AgNP on robust lightweight and tailorable structures of carbon that are easy to handle, yet offer high surface area thereby providing the nanomaterial advantage without the risk of agglomeration, loss, and environmental contamination. Silver nanoparticles were deposited on carbon foams via chemical reduction of silver nitrate in the presence of reducing and capping agents. Scanning electron microscope pictures show AgNP distribution throughout the porous structure. The antibacterial capacity of the prepared structure was tested against influent water contaminated with Gram negative Escherichia coli (E. Coli, JM109) strain of bacteria. The effectiveness of these materials has been demonstrated in two different water flow configurations, rotation in storage containers and incorporation in active or passive filters. These results clearly indicate that incorporation of AgNP onto porous carbon structures is a promising approach to fluid disinfection. There is ample scope for future refinement of these materials through modification of silver concentration, surface areas, flow rates, and/or electric fields.

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1. Introduction and background

The demand for clean water is increasing rapidly and expected to get more acute in the coming years. This will require society to recycle water more effectively, and advanced technologies to remove chemical [1] and biological [2] contaminates from water. Common treatment methods for removing harmful biological species from water involve ozone, or strong oxidants containing halogens, peroxides, or related compounds [3]. However dispersion of chemicals in water leave undesirable chemical byproducts that can be harmful in many ways.

In recent years, silver (Ag) based purification devices have been fabricated and tested [4,5] and it is expected that its effectiveness as biocide will be greatly influenced by the available Ag surface area. This has led to the development of silver nanoparticles (AgNP) that have high specific surface area. Silver nanoparticles are seen to provide long term antibacterial effect even at ultralow doses, without adverse chemical byproducts. However use of isolated AgNP, as is most commonly studied, has the potential issues of aggregation during storage, difficult recovery once dispersed in the environment, and potential toxicity problems related to over-accumulation in the bodies of humans, animals, and plants [6].

Such health and environmental hazards of nanoparticles can be greatly reduced if they can be either enclosed in, or strongly attached to bigger structures. Attachment of any nano-particle (NP) on a new substrate requires focused investigation of the NP-substrate system. Few such devices have been fabricated and include AgNP on ceramic foams [7], polyurethane foam [8], cellulose papers [9], and other low cost filter materials [10]. However it is unclear how durable these earlier structures are and in some cases, AgNP may be loosely attached and observed to leach out [9].

Our interest is to create robust devices utilizing silver nanoparticles attached on porous lightweight substrates that can be integrated into electrically or thermally controlled liquid disinfection devices in the future. Antibacterial properties of silver can be controlled with electric fields [11], and some applications may also require controlled operating temperatures. For such applications, carbon-based porous...
solids such as foams are ideal candidates because of their low density, high porosity, chemical inertness, and structural robustness combined with high thermal and electrical conductivity.

Another consideration is that porous carbon substrates are known to allow unique opportunities for future surface tailoring such as controlled attachment of carbon nanotubes [12] for surface area increase, and catalyst nanoparticles for added functionality [13]. Development of such devices will require high temperature processing not possible in polymeric porous structures such as latex and polyurethane. Porous ceramics may allow that, but they tend to have lower strength and poorer electrical conductivity. Metals tend to be very heavy and prone to corrosion issues. These considerations created the need for robust carbon-based porous supports for silver nanoparticles. However, despite the large number of papers discussing AgNP on isolated carbon nanotubes and activated carbon [14,15], there are none focused on attaching AgNP on larger carbon solids, to the best of our knowledge. It must also be pointed out that in addition to antibacterial applications, AgNP on carbon substrates have potential use in many other electronic devices such as electrodes for fuel cells, high conductivity composites, plasmonic sensors, and hybrid thermal management structures [16].

This paper discusses characterization of AgNP formed on porous carbon foam (AgNP-foam) using Field Emission Scanning Electron Microscope (FESEM) and Energy Dispersive X-ray Electron Spectroscopy (EDS). Their physical durability was tested by detailed characterization before and after water flow tests, and antibacterial properties were examined against gram negative Escherichia coli (E. Coli, K12 derivative). Testing has been performed in two types of potential water flow geometries: one suitable for use in treatment of stored water, another for incorporation into active or passive filtration devices.

2. Materials and procedures

Preparation of support structures: Carbon foam used in this research was supplied by Koppers Inc. (Grade L1a) and has open porosity of approximately 80% and pore radius of 300 µm.

Synthesis of AgNP on support structures: There are several established methods to synthesize AgNP. Among them, the most suitable and cost effective in this case is the chemical reduction of silver salts in the presence of suitable reducing and stabilizing agents. In this research, we used chemical reduction of silver nitrate (AgNO₃) in the presence of dimethyl sulfoxide (DMSO) and Tri sodium citrate [17]. This involved a two-step process: deposition of AgNO₃ on support structures followed by in-situ chemical reduction in DMSO-citrate solution.

3. Testing the efficiency of filter system

Bacteria culture and influent water preparation: E. coli strain of bacteria was selected to test the antimicrobial property of the materials, based on its role as an indicator for total fecal contamination in water systems as well as its prevalence in antimicrobial testing. E. coli strains were cultured aerobically in Luria–Bertani (LB) broth (growing medium) at 37 °C for about 20 h. From Optical density measurement via UV–vis Spectrophotometer, It was calculated that the approximate number of colony forming units (CFU) per ml is 10⁶ and this was further diluted to 10² CFU/ml in pure water. This was used as model contaminated (influent) water for antibacterial tests.

Testing for antibacterial effectiveness: The antibacterial property of the AgNP-foam was tested via two methods; rotation and filtration. In both cases, disc shaped sample having thickness of 2.5 mm and diameter of 11.5 mm were used.

In rotation method, 500 ml influent water was filled in a glass jar containing AgNP-foam specimen. A control experiment was also performed using bare, as received foam without AgNP. The sealed glass jars were then tumbled at a speed of 60 rpm for 40 min. 50 µl aliquots of the water sample was acquired at 0, 5, 10, 20 and 40 min and plated onto LB agar plates in order to measure the surviving bacteria concentration.

In filtration method, influent water was kept in a storage container and pumped at a fixed rate of 100 ml/min into the filtration cartridge that consists of a foam specimen fitted inside an acrylic casing. The schematic of the set-up is shown in Fig. 1A and the cartridge shown as inset (Fig. 1B). Influent water was filtered through AgNP-foam sample and 50 µl aliquots of the water sample were acquired at the start and the end of each filtration step and plated on agar plates. This step was repeated three times.

![Fig. 1. Schematic representation of filtration set up (A), acrylic casing used to house AgNP-foam in inset (B).](image-url)
in order to measure the progressive change of bacteria counts with each pass through the specimen.

In order to increase the validation of our data and to reduce sampling error, multiple aliquots were plated in each case. The surviving bacteria (collected on agar plates) were cultured in an incubator at 37°C for 20 h and bacteria colonies were counted optically. Results are reported as % bacteria survival (bacteria colonies formed from the water sampled after the treatment expressed as percentage of that from water before treatment). For the rotation test, % survival is plotted as a function of rotation time, and for the filtration test, this is plotted as a function of number of percolations.

These flowing water tests are expected to put significant mechanical stresses on the silver nanoparticles. In order to test their durability, microstructure images and EDS analyses were performed before and after such tests to monitor any changes in Ag content.

4. Results and discussion

Silver nanoparticles on porous carbon supports: Formation of AgNP was confirmed by series of microstructures (Fig. 2A–D) taken at ligament, pore walls, and inner pores (Fig. 2B–D). Repeated microstructure analysis on multiple samples showed that exterior as well as interior pores were deposited with AgNP. Some non-uniformity of nanoparticle density is expected in these uneven porous substrates due to local variations of surface curvatures, precursor wettability, and graphitic alignment. It was seen that external ligaments and outer pores of the foam have higher nanoparticle density, averaging at about 92/μm² and 72/μm² respectively, compared to about 18/μm² in the deeper pores. However, particle size distribution across various pore levels that could be imaged by FESEM was observed to be uniform. Most AgNP ranged in diameter from 2–25 nm with the median particle size at about 5 nm. Few particles coalesced into clusters larger than 25 nm. The particle size distribution seen here is wider than those reported earlier [17,18], but that may be attributed to the fact that these substrates are uneven and complex compared to earlier studies.

From EDS quantitative analysis, it was observed that the averaged silver concentration in these samples are in the 1.5–2.5 wt% range (Table 1). X-Ray diffraction (XRD) showed absence of AgNO₃ diffraction peaks and presence of peaks that correspond to face-centered cubic (fcc) silver indicating complete reduction of the precursor salt into metallic AgNP.

Durability of AgNP attached carbon surfaces: Microstructure and elemental composition of AgNP-foam were monitored before and after all water flow tests using SEM and EDS. No microstructural changes were apparent, and EDS results are tabulated in Table 1. It can be seen that initial Ag concentration remained unchanged after both types of test. It must also be noted that durability studies of AgNP grown by this method on various carbon substrates have been conducted in the past [18]. Some tests performed under harsher test conditions involving high power ultrasonic agitation had shown no change in AgNP densities or particle size distributions. Therefore, it is not surprising that these particles remain attached within the range of tests performed here. Long term field testing involving more forceful water flow or years of operation may be needed before detectable degradation occurs in these samples.

Bactericidal effectiveness of the AgNP-foam: The antibacterial properties of AgNP-foam were tested as explained earlier. From rotation test (Fig. 3A), it was observed that the % bacteria survival gradually decreased with time and more than 99% of initial bacteria were degraded in 40 min. On the other hand, less than 10% bacteria were degraded when treated with as-received foams. Examples of agar plates containing E. Coli colonies before and after 40 min treatment are shown in Fig. 3B and C respectively.

From filtration test (Fig. 3D), it was observed that, almost 90% degradation in bacteria loading was achieved within two percolations of 5 min each, and complete degradation achieved by three filtrations.
Incubated agar plates at the start and after three filtrations are shown in Fig. 3E and F respectively. However, it should be noted here that control sample also showed detectable bacteria loss with each subsequent filtration. This effect was clearly not seen during rotation test. This may be attributed to bacteria trapping at the pores of the foam, when the entire volume water is forced through them. Longer tests and additional imaging of the foams with fluorescence microscopy will be performed in future to confirm if trapped bacteria is indeed present. What is clearly evident from these studies is that the presence of AgNP aids strongly in bacteria degradation from water. Treatment via filtration appears to be a very efficient approach where two passes totaling 10 min of flow may be all that is needed to achieve over 90% degradation of bacteria. Relatively lower degradation rate is seen in treatment via rotation method, which may be due to the poor water infiltration into the pores of carbon foam, resulting in less efficient contact with AgNP [19].

In case of filtration, the influent is forced through the foams and makes contact with all surface AgNPs, hence wettability is less of an issue. Future surface modifications to improve the wettability of the porous substrate are expected to increase the rate of bacteria degradation in the rotation mode.

The antibacterial mechanism of silver is still debated in the literature, and two possible mechanisms appear most prevalent: bactericidal effect and bacteriostatic effect [20]. In both cases, the antibacterial efficacy of AgNP comes from availability of Ag⁺ ions. This effect is expected to improve as AgNP becomes smaller resulting in increase of surface chemical activity. It is clear that the AgNP-foam hybrid structures developed in this study are effective against E. Coli bacteria. The potency of these structures may be easily increased by increasing the concentration of AgNP, changing porosity of the support, application of electric field, or enhancing water percolation through increase of surface wettability.

### Table 1

<table>
<thead>
<tr>
<th>Ag NP coated foam (wt%)</th>
<th>After rotation test (wt%)</th>
<th>After percolation test (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CK 95 ± 0.5</td>
<td>94.3 ± 0.6</td>
<td>95.1 ± 0.6</td>
</tr>
<tr>
<td>OK 3.2 ± 0.5</td>
<td>3.8 ± 0.8</td>
<td>3.1 ± 0.4</td>
</tr>
<tr>
<td>AgL 1.8 ± 0.3</td>
<td>1.9 ± 0.3</td>
<td>1.8 ± 0.6</td>
</tr>
</tbody>
</table>

5. **Summary**

In this research, AgNP were attached on carbon substrates by infiltration of AgNO₃ followed by reduction in controlled temperature in presence of reducing and capping agents. The AgNP was seen to grow at various levels of pores. Diameters range from 2–25 nm with median diameter at about 5 nm. The nanoparticles remained attached after prolonged testing in flowing water. The antibacterial properties of the prepared structures were tested against *Gram negative* E. Coli. Influent water was tested in rotation and filtration modes and bacteria degradation of more than 99% was observed in both cases, confirming the potency of these hybrid materials. The antibacterial effectiveness can be enhanced in future by increasing specific surface area of support structures, silver loading, enhanced wettability with water, and application of...
electric fields. The prepared structures have additional potential in other applications such as porous electrodes, sensors, thermal management composites, and other electronic devices.

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