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NANO SILVER-COATED POLYPROPYLENE WATER FILTER: I. MANUFACTURE BY ELECTRON BEAM GUN USING A MODIFIED BALZERS 760 MACHINE

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As adequate freshwater supplies decrease steadily, novel technologies are required for water purification. Nanotechnology, a new scientific frontier, promises to revolutionize innovation in many industries. Advancements in nanotechnology are being applied in the water-purification industry to keep harmful bacteria out of drinking water. Due to its bactericidal properties, nano silver is used in many products as an antibacterial. This study aimed to produce a nano silver-coated water-treatment polypropylene filter via the physical vapor deposition method using the Balzers 760 machine equipped with an electron beam gun ESQ 110. The Balzers machine was modified in order to enable coating of the cylindrical filters in a homogenous manner. The nano silver particles were made by electron beam bombardment of the silver metal, which were subsequently deposited on the polypropylene filter evenly. The thickness of the nano layer coated on the filter was about 55.0nm in average, as revealed by the microprocessor unit of the Balzers machine during the coating process. The thickness of the nano layer and the chemical composition of the produced filters were studied by scanning electron microscopy, atomic force microscopy and the X-ray diffraction technique. The filter system produced in this work has the potential to be used as an efficient and cost-effective water treatment method. The inductively coupled plasma/mass spectrometry (ICP/MS) studies revealed that there was no nano silver particle present in the filtered water sample. Hence, there is no risk of contamination of drinking water with the silver nano particles upon application of the manufactured filters. This is the first report on the manufacture of nano silver-coated cylindrical polypropylene filter using the electron beam gun technique.

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Keywords: Nano silver, Electron beam gun, Balzers machine, Polypropylene filter, XRD, SEM, AFM.

1. Introduction

Nanotechnology is emerging as a rapidly growing scientific field for the purpose of manufacturing new materials, with novel properties, at the nanoscale level [1]. Nanomaterials often show unique and considerably different physical, chemical and biological characteristics compared to their macro-scaled counterparts [2]. It is known that the decrease of the size of metal particles to 100 nm and below significantly affects their physico-chemical properties, including catalytic effects [3–6]. The metallic nanoparticles also show good bactericidal properties due to their large surface area to volume ratio. They are very promising antibacterials especially considering the growing microbial resistance against antibiotics and the development of resistant

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strains [7]. The goal of this study was manufacturing a nano silver water filter by physical vapor deposition and electron beam gun (PVDEB). This filter has the potential to kill the pathogenic bacteria in the water purification process. One advantage of the PVDEB method is that the deposition rate can be varied from as low as 1nm/s to as high as few micrometers/s [8-13]. Another advantage of the PVDEB method is that the thickness of the coated layer can be measured, monitored and controlled during the coating process. Therefore, by using this method the accuracy of coating is much more than the other techniques such as chemical vapor deposition method. The coating process was performed using the Balzers 760 machine modified in order to enable coating of the cylindrical filters in a homogenous manner. Scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray diffraction (XRD) techniques were employed to characterize the nano silver layers coated on the polypropylene filters. The inductively coupled plasma/mass spectrometry (ICP/MS) was used to detect the presence of silver nano particles in the treated water sample.

2. Experimental

2.1 Materials

The silver metal used in this study was of high grade (purity: 99.99%) and was supplied by Merck (Germany). The cylindrical polypropylene filters constructed using multi-layers of the polymer were purchased from Omran Mahab Co. (Tehran, Iran) with an average pore-size of 9.86μm. The pore size of the filters was confirmed through scanning electron microscopy examinations as explained below. The polypropylene filter possess high filtering efficiency and can remove dirt, rust, dust, silt, algae and some other particles but not certain microorganisms and bacteria such as coli bacillus. Therefore, it can not be used to remove the water pathogens.

2.2 Methods

In this study, a 55.0 nm layer of silver was coated on the polypropylene water filter by the evaporation rate of 2nm/s via the PVDEB method. For this, a modified Balzers 760 machine was employed in order to enable coating of the cylindrical filters evenly. The rate of evaporation of the silver vapor and the thickness of the nano silver coat were constantly monitored by the microprocessor unit of the Balzers machine. The electron beam evaporation source ESQ110 consists of two main components: (1) the electron beam gun, comprising the cathode, Wehnelt shutter and anode, and (2) the water-cooled evaporation molybdenum crucible. The melting and boiling points of silver are 961.78˚C and 2162˚C respectively; while the melting and boiling points of molybdenum are 2623˚C and 4639˚C. Therefore, molybdenum is considered an appropriate crucible for solid silver. Initially, an approximate amount of 3 grams of the silver metal was placed in the molybdenum crucible pot (inner diameter: 15mm, depth: 10mm) and located in the chamber of the Balzers machine within a distance of 50mm from the electron beam source. The polypropylene filter was then fitted on the shaft inside the chamber. This remote-controlled shaft is able to rotate up to 100 rounds per minute (rpm). In the present study, the rotation of the shaft was adjusted to 20rpm. The Balzers machine was equipped with an electrical heater and the temperature of the chamber was adjusted to 30˚C. The chamber was vacuumed at 10^{-7} torr using a rotary and high powerful diffusion pump. The electrons from the D.C. heated cathode (K), extracted through the electrical field, pass the anode (A), and are deflected through approximately 270˚ by the magnetic field produced by the coil (S) and the pole shoes (M) and enter the Molybdenum pot (Fig. 1).

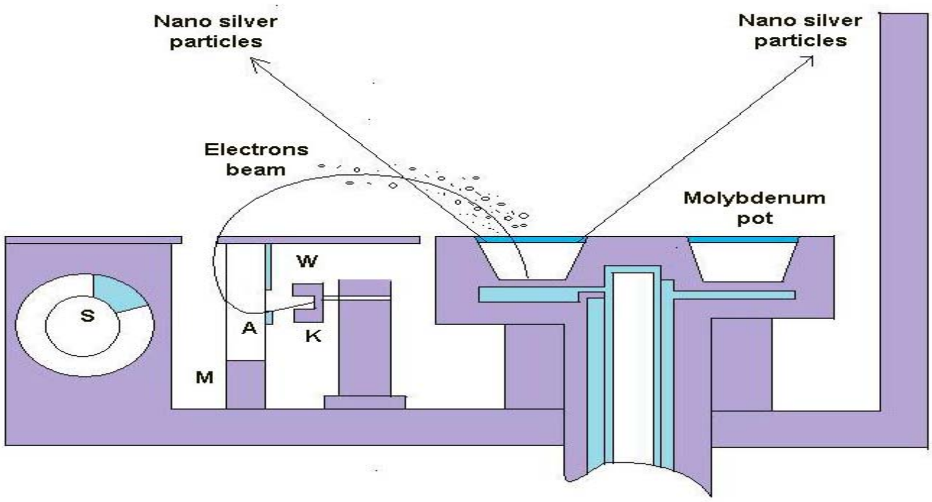

Fig. 1. Schematic representation of the electron beam gun ESQ 110 used in this study. A: anode; K: cathode; M: the pole shoes; S: coil; and W: Wehnelt shutter (see text for details).

The beam area is adjusted by the high voltage connected to the Wehnelt shutter and is focused on the crucible electrostatically. The vapor atoms leaving the crucible are partially ionized by the electron beam. The electrons released by these vapor atoms travel at a much higher speed than the vapor ions, which have a speed distribution approximately equal to the speed of neutral vapor atoms. Hence, high ion densities occur in the electron beam area, with a positive space charge capable of compensating for the negative space charge of the electrons. In fact, resulting from the vapor ions, a positive potential channel forms along the beam axis, which has the focusing effect on the beam electrons. Thus, with a 10kV acceleration voltage, a density effect of the electron beam of approximately 40 kW/cm^2 is produced at the crucible surface. The nano silver film thickness was monitored by the microprocessor using the QSG 301 quartz crystal. The thickness of the film deposited on the quartz crystal was used to measure the evaporation rate of the coating process (displayed in nm/s), as well as the thickness of the silver layer covered the filters. It is possible to control the rate of evaporation and thickness of the coated layer using the microprocessor. The frequency changes of the QSG 301 crystal are transmitted as a square wave signal to the rate meter input in the microprocessor unit. The mathematical equations used for the measurement of the rate of evaporation of the silver metal as well as the nano silver layer thickness are explained in the next section. These changes are a measure of the thickness of the film evaporated or sputtered simultaneously onto the water filter and the quartz crystal used in the machine as a sensor to monitor the film thickness. The deposition rate is proportional to the frequency change and thus the increase in film thickness per unit of time. Frequencies between 0.000 and 30.000Hz can be measured by the microprocessor unit. The rate is calculated from these frequencies in the unit of time and displayed on the rate meter gauge in nm/s. By focusing the high energy electrons beam onto the silver inside the crucible, silver is melted and then evaporated at a rate of 2nm/s and deposited on the water filter. By subtracting the total weight of silver and crucible before and after coating, the weight of the evaporated silver is obtained. For the 45.0nm Ag layer coated on each filter, 2.15 g silver was used in this study. Figure 2 shows the cylindrical water filters before and after the coating.

Fig. 2. Un-coated (left) and nano silver-coated polypropylene water filters (right).

2.2.1 Scanning Electron Microscopy (SEM)

The structural analysis of the nano silver layer coated on the water filter was carried out by Hitachi S-3400N scanning electron microscope (SEM, Japan). For this, a square-shaped sample with the size of approximately 1cm by 1cm was cut from the filter surface and visualized by the SEM. The pore sizes of the filters, before and after nano silver coating, were also measured using SEM. For this a number of 20-30 pores were randomly selected on 25 images of each sample analysed and the average pore sizes measured by SEM.

2.2.2 Atomic Force Microscopy (AFM)

Topographical analysis of the nano silver layer coated on the water filter was performed under a dry nitrogen atmosphere, in contact mode, using an atomic force microscope (AFM, Quesant Instrument Corporation, USA). For this, a square-shaped sample with the size of approximately 1cm by 1cm was cut from the filter surface and analyzed by the AFM.

2.2.3 X-ray Diffraction Analysis (XRD)

The structure of the prepared nano silver particles was studied using a powder X-ray diffraction (Philips, X'pert Cu K_{α}, Netherlands) in the angle range of $30^{\circ}<2\theta<90^{\circ}$.

2.2.4 Inductively coupled plasma mass spectrometry (ICP/MS)

The inductively coupled plasma/mass spectrometry (ICP/MS) was used to determine any amount of nano silver particles in the water sample at the end of a 5h filtration process. The nano silver-coated filter was put in the housing and distilled water was circulated through the filter for 5 hours. An Optima 7300Dv instrument (Perkin Elmer Corporation, Norwalk, CT, USA) was used according to the reported procedure [14-16] to analyse 100ml samples of the filtered water.

3. Theory and calculations

The changes in the inherent frequency of the crystal were measured during the coating process using the microprocessor unit, as explained above. The mass of the quartz crystal increases as it is coated by the nano silver layer. The inherent frequency of the quartz crystal is calculated using equation 1.

Equation 1:

$$\frac{\Delta f}{f} = -\frac{\Delta d}{d} = -\frac{\Delta m}{\rho q.F.d}$$

Where:
f = inherent frequency of the quartz crystal;
d = crystal thickness;
ρq = crystal density;
F = surface area of crystal;
Δm = mass of the nano silver film covering the crystal.

If Δm/F= φ is the mass of the coating and f.d=N is the frequency constant, equation 2 results for the frequency change.

Equation 2:

$$\Delta f = -\frac{f.\varphi}{d.\rho q} = -\frac{f^2}{N.\rho q}.\varphi$$

The afore-mentioned two equations were used for the measurement of the frequency and finally the rate of evaporation of the silver metal and the nano silver layer thickness.

4. Results and discussion

Silver nanoparticles possess unique electronic and optical properties. Hence, they have been used in a broad range of scientific and technical fields, including catalysis, biological labeling, photonics and surface-enhanced Raman scattering (SERS) [17–22]. In addition, due to its bactericidal properties, nano silver is used in many products as an antibacterial. In the present study, a nano silver-coated water filter was prepared by physical vapor deposition and electron beam gun (PVDEB) using a modified Balzers 760 machine. An advantage of the PVDEB method is that the thickness of the silver layer can be measured and controlled during the coating process. Therefore, by using this method the accuracy of coating is much more than the other available methods such as the sputtering [23] and chemical vapor deposition [24] techniques. The Balzers machine does not allow coating all surfaces of objects in any single run. Therefore, it was modified to enable coating all surfaces of the cylindrical filters in a single run. The microprocessor unit of the Balzers 760 machine continuously monitored the nano silver layer thickness during the coating process. The Ag nano particles were characterized by AFM, SEM and XRD techniques. The AFM technique was employed to confirm the thickness of the coated silver nanolayer on the water filter. Figure 3 shows a representative AFM image of the deposited silver layer. The average thickness of the nano silver layer obtained by the AFM technique is 55.05nm, which is in accordance with the 55.0nm value reported by the microprocessor during the coating.

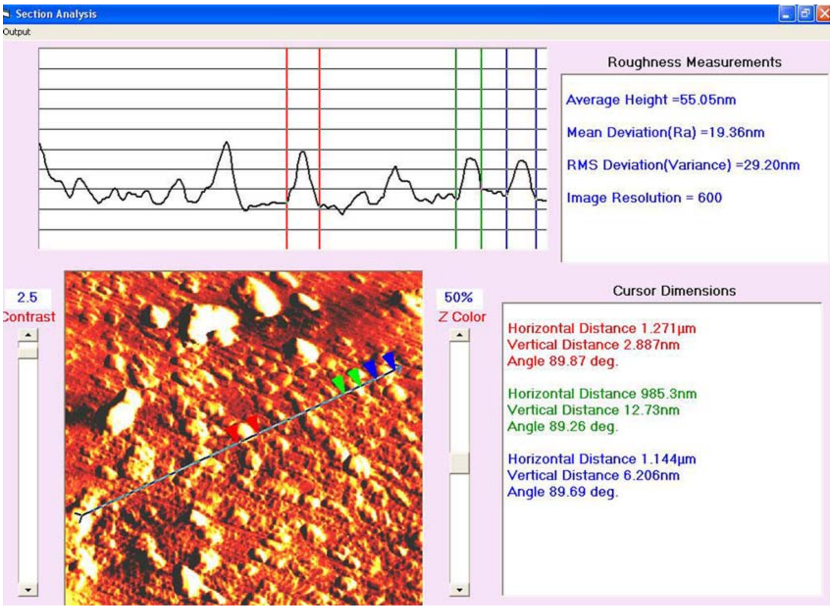

Fig. 3. A representative atomic force microscopy image of a section of the nano silver filter surface. The average thickness of the nano silver layer is 55.05nm.

The structure of the cylindrical polypropylene water filter coated with nano silver layer was studied by scanning electron microscopy. Figure 4 and Table 1 depict SEM analysis of the chemical structure of a section of the filter surface. SEM analyses attest that the covered layer on the surface of the filters was indeed silver. The weight % of silver in the sample was 2.19 and its Atom % was 0.37 (Table 1).

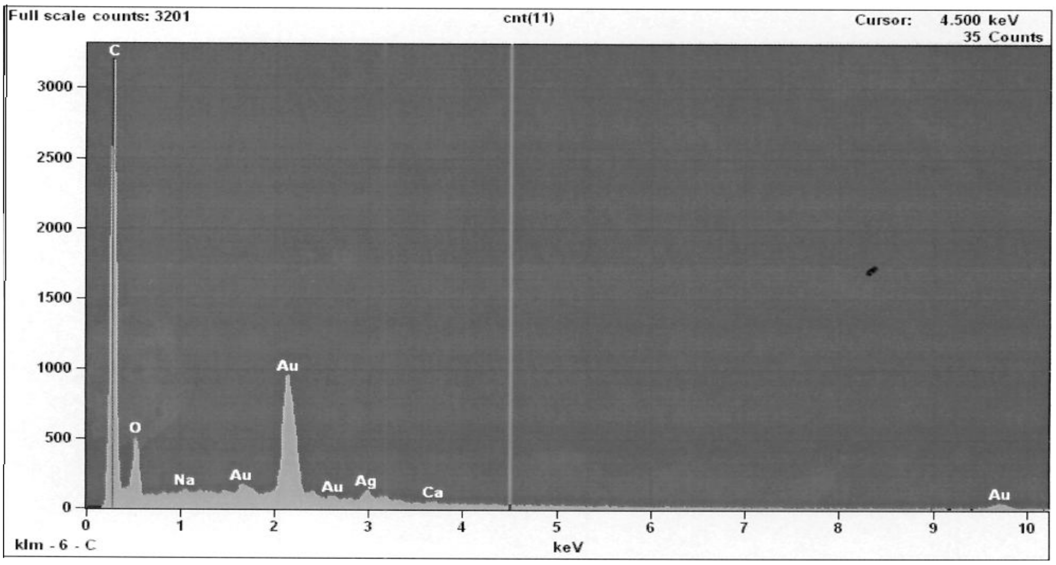

Fig. 4. Scanning electron microscopy analysis of the material structure of the Ag filter.

Table 1. Chemical composition of the Ag filter obtained by scanning electron microscopy.

Element	Weight %	Weight % Error	Atom %	Atom % Error
C	53.46	+/-0.37	80.93	+/-0.55
O	13.84	+/-0.32	15.73	+/-0.37
Na	0.14	+/-0.04	0.11	+/-0.03
Ca	0.16	+/-0.04	0.07	+/-0.02
Ca	---	---	---	---
Ag	2.19	+/-0.26	0.37	0.04
Ag	---	---	---	---
Au	30.20	+/-3.27	2.79	+/-0.30
Au	---	---	---	---
Total	100.00		100.00	

The average pore size of the uncoated filter was 9.86μm and nano silver-coated filter contains pore sizes with an average diameter of 0.7μm, as measured by SEM (Figures 5 and 6). These analyses show that the 55.0nm layer of nano silver covering has resulted in a reduction of the pore size of the water filters by more than fourteen folds.

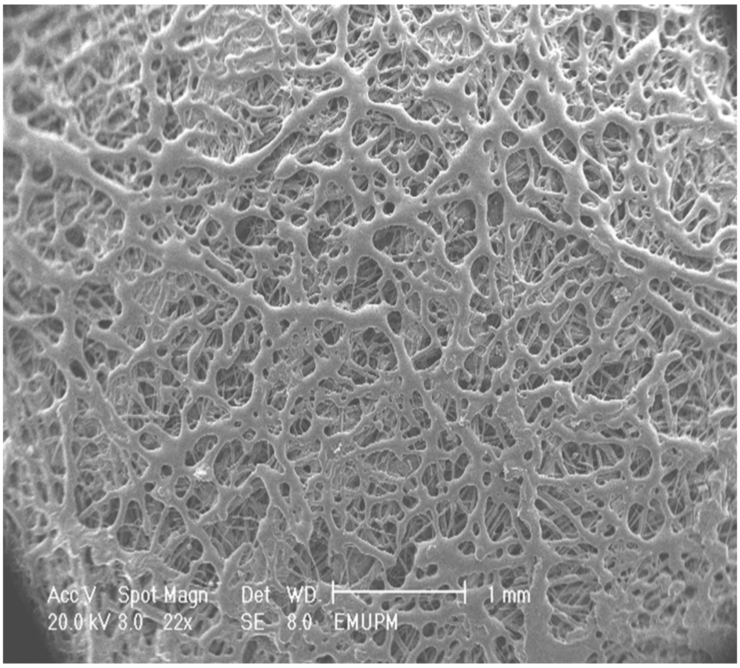

Fig. 5. Representative scanning electron microscopy image of the uncoated polypropylene water filter.

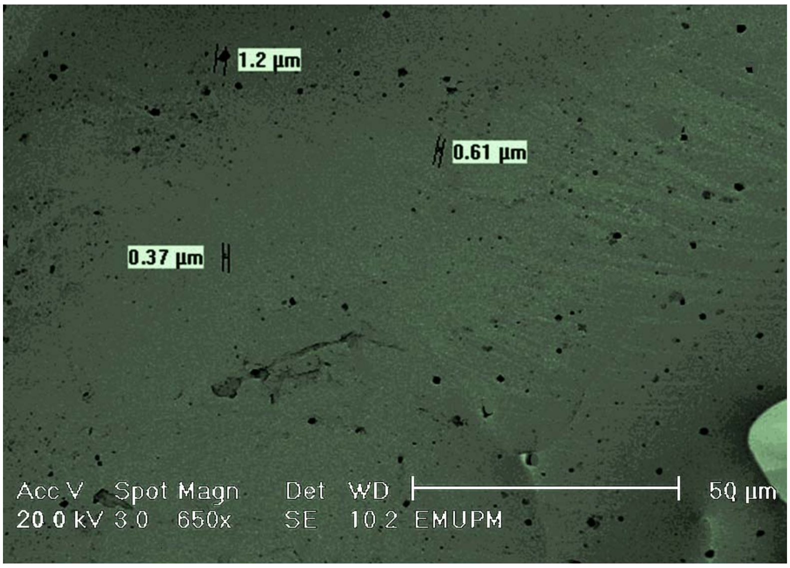

Fig. 6. Representative scanning electron microscopy image of a section of Ag coated polypropylene water filter.

The crystallographic microstructure of the thin silver film deposited on the surface of polypropylene filters was investigated by the XRD technique (Fig. 7). The conventional XRD was carried out in a range of 30º to 90º. According to powder XRD standards (PXRD, Ref. No. 01-087-0718), the PXRD peaks at 2θ of 38.2º, 44.3º and 64.5º, 77.6º, and 83.3º can be attributed to the (111), (200) and (220), (311), and (331) crystallographic planes of face-centered cubic (fcc) silver crystals, respectively [25]. From the XRD results it was found that the preferred growth orientation of thin silver film is fixed at (111) direction, and possess a crystallographic plane of face-centered cubic (fcc) structure in the deposition process [26]. The PXRD peak broadenings of silver nano particles are mostly because of presence of the nano-sized particles [27]. These results prove that the water filters were successfully covered by polygonal plane of face-centered cubic (fcc) nano silver particles.

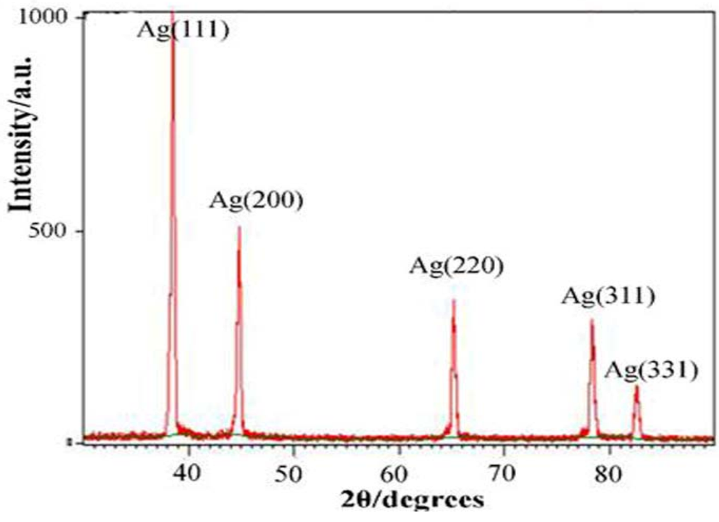

Fig. 7. XRD pattern of the nanosilver particles. The overwhelmingly intensive peak located at 2θ = 38.02° corresponds to the diffraction of (111) lattice plane of face-centered (fcc) structure. This indicates that (111) planes of Ag nanoparticles were highly oriented parallel to the supporting substrate.

The inductively coupled plasma/mass spectrometry (ICP/MS) was used to determine any amount of silver nano particles in the water sample after 5h filtration. The output count of nano silver particles in the filtered water sample was nil, indicating the stability of the manufactured filters and their ability to retain the silver nanoparticles on their surface. According to the literature, the average abundance of silver in the U.S. drinking waters is 0.23μg/L [28]. Consequently, the nano silver-coated filter technology can offer a completely efficient and safe solution for the treatment of drinking water.

5. Conclusions

In this work, the ultra-dispersed silver powders were coated on cylindrical polypropylene water filters by electron beam gun ESQ 110 employing a modified Balzers 760 machine. Using the modified Balzers machine it was possible to coat all surfaces of the cylindrical filters in a single run. The structure and thickness of thin silver film were investigated by SEM, XRD and AFM. AFM images confirmed the accuracy of the values obtained by the microprocessor for the thickness of the coated nano silver layers. The SEM and XRD techniques were employed to confirm that the material that covered the surface of water filters was silver. Coating the water filters by the nano silver layers resulted in more than fourteen fold reduction of the pore size of the filters. The inductively coupled plasma/mass spectrometry examination revealed that there was no nano silver particle in the filtered water sample. The filter system manufactured in this study has the potential to be used as an efficient and cost-effective water treatment technique.

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