A novel point-of-use water treatment method by antimicrobial nanosilver textile material

Hongjun Liu, Xiaosheng Tang and Qishan Liu

ABSTRACT

Pathogenic bacteria are one of the main reasons for worldwide water-borne disease causing a big threat to public health, hence there is an urgent need to develop cost-effective water treatment technologies. Nano-materials in point-of-use systems have recently attracted considerable research and commercial interests as they can overcome the drawbacks of traditional water treatment techniques. We have developed a new point-of-use water disinfection kit with nanosilver textile material. The silver nanoparticles were *in-situ* generated and immobilized onto cotton textile, followed by fixing to a plastic tube to make a water disinfection kit. By soaking and stirring the kit in water, pathogenic bacteria have been killed within minutes. The silver leaching from the kit was insignificant, with values <100 ppb – the current US EPA and WHO limit for silver level in drinking water. Herein, the nanosilver textile water disinfection kit could be a new, efficient and cost-effective point-of-use water treatment method for rural areas and emergency preparedness.

Key words | disinfection, nanosilver textile, silver nanoparticle, water treatment

Hongjun Liu (corresponding author)
Key Laboratory of Natural Medicine and Immuno-Engineering of Henan Province,
Henan University,
Kaifeng,
Henan 475004,
China
E-mail: *hjliu@henu.edu.cn*

Hongjun Liu
Xiaosheng Tang
AGplus Technologies Pte Ltd,
10 Jalan Besar #10-06 Sim Lim Tower,
Singapore 208787

Qishan Liu
School of Architecture and the Built Environment,
Singapore Polytechnic,
500 Dover Road,
Singapore 139651

INTRODUCTION

It was reported by the World Health Organization (WHO & UNICEF 2010) that 884 million people do not have access to safe drinking water, and 2.2 million deaths (mainly children) are attributed to diarrhea, which is transmitted through contaminated water, inadequate sanitation or hygiene (WHO 2002, 2010; Brocklehurst 2004; WHO & UNICEF 2010). One of the biggest threat to public health is caused by bacterial pathogen in drinking water sources, which leads to the outbreaks of diseases such as giardiasis, gastroenteritis, cholera, cryptosporidiosis, etc. Having access to safe drinking water is essential to health, a basic human right and a component of effective policy for health protection (WHO 2011). The traditional method for water disinfection is by chemical agents, such as chlorine and related compounds, due to their effectiveness and simplicity. However, it has many drawbacks, including: (1) long treatment time to get rid of bacterial pathogens; (2) consumption of a significant amount of chemical agents; and (3) side-effects from the formation of harmful disinfection byproducts, e.g., carcinogenic trihalomethanes (WEF 1996; Braghetta 1997; Krasner *et al*. 2006). Recently, nanotechnology for water purification, which potentially overcomes some of the aforementioned problems, has become of considerable interest (Li *et al*. 2008). In particular, nanotechnology can be used for efficient and cost-effective point-of-use systems. It should be strongly promoted because of its low cost, easy-to-use and low energy input, which is very useful in developing countries and in emergency preparedness.

Silver, which has been used for centuries for water storage in containers, has recently been developed into a nano form to provide a larger surface area for contact with microorganisms, enhancing its performance as an antibacterial agent (Davies & Etris 1997; EPA 2010). Nanosilver materials have been mainly used to prevent bacterial fouling of membranes in water purification applications (Chou *et al*. 2005; Yoon *et al*. 2008; Zodrow *et al*. 2009). Recent advances have been made on the application of silver nanoparticles in point-of-use water purification systems, such as in polyurethane foams (Jain & Pradeep 2005) and ceramic filters (Oyanedel-Craver & Smith 2008; Kallman *et al*. 2011;

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Casanova *et al.* 2012). Gray's group has reported an interesting bactericidal paper which was impregnated with silver nanoparticles for point-of-use water treatment (Dankovich & Gray 2011). This silver nanoparticles embedded paper can effectively deactivate pathogenic bacteria by percolation. Similar filtration approaches with silver nanomaterials have also been developed by others. For instance, Tata Swach® with silver nanoparticle-coated rice husks are now commercially available (Vousvouras 2010); silver nanoparticles (AgNPs)-alginate composite beads have also been demonstrated as good simultaneous filtration-disinfection filler materials for portable columns (Lin *et al.* 2013).

In this paper, we report a new point-of-use water purification method with nanosilver textile material for the disinfection of pathogenic bacteria, compared to the commonly reported filtration methods. Silver nanoparticles were *in-situ* generated and well distributed onto the cotton textile and displayed as two colors (yellow and gray). The yellowish nanosilver textile has smaller silver particle size comparing to that of the grayish textile. The water disinfection kit was produced by fixing the nanosilver textile material onto the plastic tube. When the kit is soaked and stirred in water, the pathogenic bacteria could be effectively killed. The yellowish textile kit has shown better bacteria disinfection efficiency compared to the grayish textile kit. Silver leaching from the textile material was found to be insignificant, with values less than 100 ppb – the current US EPA and WHO limit for silver level in drinking water. Thus, the nanosilver textile water disinfection kit could be a new, efficient and cost-effective point-of-use water treatment method for rural areas and emergency preparedness.

MATERIALS AND METHODS

Preparation of nanosilver textile water disinfection kit

Chemicals used in the study including silver nitrate, (3-aminopropyl) triethoxysilane (APTES), sodium borohydride ($NaBH_4$), and ethanol were purchased from Sigma-Aldrich. Phenylhydrazine ($PhNHNH_2$) was purchased from Alfa Aesarm, while sodium thiosulfate pentahydrate was purchased from Sinopharm Chemical Reagent Co., Ltd.

The preparation of nanosilver textile followed an *in-situ* reduction technique, a method modified and improved from our previous 'one-pot' synthetic method (Liu *et al.* 2014). White cotton textile (commercially available 'Caressa' brand, USA) was washed with deionized water and dried in oven at 60 °C. Forty-three grams of the washed cotton textile were dipped in a mixture solution of silver nitrate and (3-aminopropyl) APTES in deionized water (2.72 mM of $AgNO_3$) at 60 °C for 10 min. The textile was then removed from the mixture solution and washed sufficiently with deionized water. After that, half of the textile was soaked in a sodium borohydride (5 mM) solution for 10 min at room temperature. The cotton textile was observed to turn a yellow color, indicating the formation of silver nanoparticles. The subsequent washing and drying procedure produced the yellowish nanosilver textile. The other half of the textile was soaked in $PhNHNH_2$ (5 mM) solution. This produces the nanosilver textile in gray color. Both textiles were rinsed with deionized water for 5 min after soaking to remove any excess reactants and unbonded silver nanoparticles. It was then dried at room temperature in a drying cabinet. It was finally cut into small pieces (4.5 cm × 9.0 cm), wrapped and fixed onto a plastic tube 12 mm in diameter and 75 mm in length, to make a nanosilver textile water disinfection kit. Two types of the kits were produced, namely, a yellowish textile kit and grayish textile kit.

Characterization of nanosilver textile

The morphology of nanosilver textile was examined using field emission scanning electron microscopy (SEM, JEOL JSM-5600, Japan).

Bactericidal testing

To evaluate the water disinfection efficiency of the kit in the real world, rain water was collected freshly and transferred into autoclaved glass bottles. Rain water instead of tap water was used in the study because of its easy availability and naturally abundant bacteria, as well as the practical application of the kit. The kit was placed in the bottle and stirred for a specific period of time. The kit was removed from the bottle immediately after stirring and then 1 mL of sodium thiosulfate solution (5.0 wt%), a neutralization agent for Ag +, was added into the bottle. This eliminates the possibility of any antimicrobial effect by the released Ag^{+} from the textile. Water in the bottles was tested for bacteria count by nutrient agar plates (R2A agar). Nutrient broth components for R2A were purchased from NEOGEN Corporation. The plates were incubated overnight at 37 °C for 24 to 48 h, and the number of colonies were counted (A). A series of dilution to the water samples was conducted when needed. Meanwhile, the number of the bacteria in raw water samples (B) was also tested. To calculate the percentage of bacteria reduction or disinfection efficiency, the following equation is used: percentage of bacterial reduction $(\%) = (B - A)/B \times 100$. For *Escherichia coli* disinfection testing, a strain of *E. coli* 8099 was purchased from a local company.

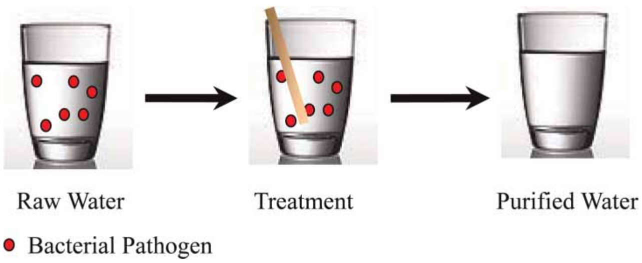

Figure 1 | Schematic description of point-of-use water treatment by nanosilver textile water disinfection kit.

Analysis of silver leaching from textile

To check the amount of silver leaching from the textile material, a water sample was collected from the bottles after the treatment by the kit for silver analysis. It was measured by inductively coupled plasma atomic emission spectrometer (ICP-AES, PerkinElmer, USA).

RESULTS AND DISCUSSION

Nanosilver structure

The concept of the new point-of-use water treatment method with nanosilver textile kit is illustrated in Figure 1. After immersing the kit in the raw water, which may contain bacterial pathogen, it could be disinfected by stirring with the kit for a short period of time. Figure 2 shows the photographs of the textile coated with silver. Figure 2(a) is the control sample of the textile without nanosilver coating, which shows the white color of the natural textile. With *in-situ* preparation, nanosilver particles could be successfully loaded onto the textile material, which displayed two different colors (yellow shown as dark gray in non-color printing for Figure 2(b) and gray shown as light gray in non-color printing for Figure 2(c)) due to the surface plasmon resonance features of the silver nanoparticles at

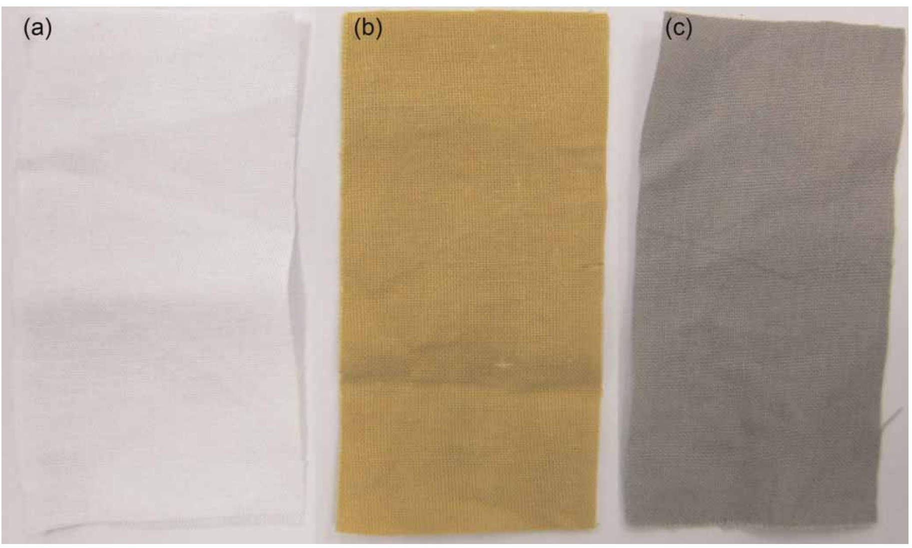

Figure 2 | Photographs of nanosilver textile: (a) natural textile without nanosilver coating; (b) yellowish nanosilver textile; (c) grayish nanosilver textile.

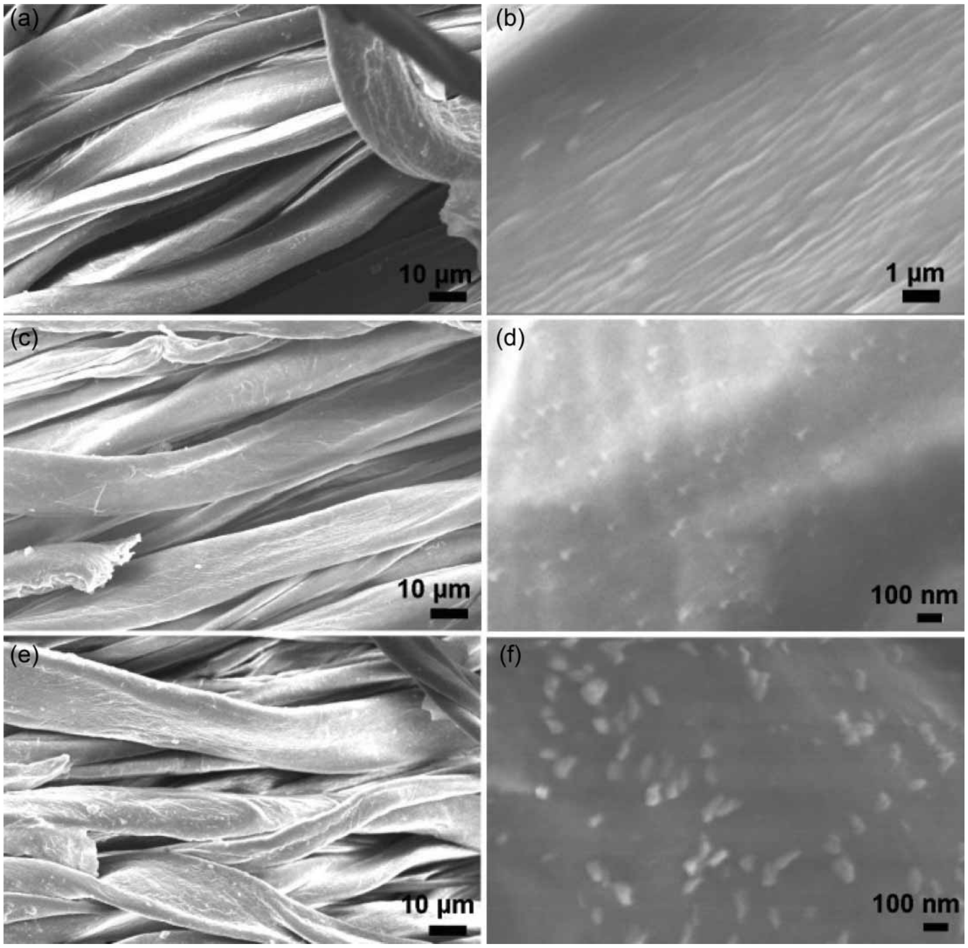

Figure 3 | SEM images of the nanosilver coated textile: (a) and (b) natural textile without nanosilver coating; (c) and (d) yellowish nanosilver textile; (e) and (f) grayish nanosilver textile.

different sizes (González *et al.* 2005; Xia & Halas 2005; Amendola *et al.* 2010).

The morphology of the nanosilver textiles as well as the particle sizes of the nanosilver were revealed by SEM. Figure 3(a) shows the morphology of the textile without nanosilver coating. It could be observed that the surface of the textile was smooth and flat. From the magnified SEM image shown in Figure 3(b), only the fiber could be observed, which was obviously different from Figures 3(d) and 3(f). Comparing Figure 3(a) to Figures 3(c) and 3(e), the surface of the fiber of the latter was much brighter, which is an indication of silver coating. Figure 3(c) shows the SEM image of the yellowish nanosilver textile that is shown in Figure 2(b). Figure 3(d) shows the magnified SEM image of Figure 3(c). It demonstrated that the prepared silver nanoparticles have a particle size of around 30 nm, and were uniformly distributed and attached at the surface of the textile fiber. Figures 3(e) and 3(f) show the SEM images of the grayish textile (photograph in Figure 2(c)). It shows that the size of the nanosilver particles is about 100 nm and they are formed at the surface of the fiber.

Water disinfection by nanosilver textile kit

Water disinfection tests by nanosilver textile kits are shown in Figure 4. For comparison, the yellowish (Figure 4(a)) and grayish (Figure 4(b)) textile kits were each immersed into bottles of 100 mL rain water. By stirring the kit in the water at the same time, the comparative water disinfection results were obtained.

Table 1 shows the results of the bacteria reduction or disinfection efficiency by the two types of kits and the

Figure 4 | Testing of water disinfection by nanosilver textile kits: (a) yellowish textile kit; (b) grayish textile kit.

silver leaching from the textile. In order to determine the optimum disinfection contact time by the kit, three sets of experiments were conducted in parallel at different stirring times (2, 5, and 10 min, respectively). The number of bacteria in untreated raw rain water was 7.32×10^3 colony-forming unit per mL (CFU/mL) and the turbidity was 0.73 nephelometric turbidity unit (NTU). It was observed that the overall disinfection efficiency of the yellowish nanosilver textile kit is better than the grayish textile kit. For instance, the total number of bacteria was reduced to 1.79×10^3 CFU/mL by the yellowish textile kit after 2 min of contact time, i.e., 75.5% removal, while it was reduced to 5.53×10^3 CFU/mL by the grayish textile kit, which achieves only 24.5% removal. By increasing the contact time to 5 min, the disinfection efficiency improved to 88.3% for the yellowish kit, while it was only 52.7% for the grayish kit. Looking at 10 min of contact time, the efficiency was not improved significantly. It is postulated that the higher disinfection efficiency by the yellowish nanosilver textile kit is attributed to the smaller sizes of the nanosilver particles, and subsequently the larger surface area for the disinfection to occur. Other studies have shown similar findings (Xia & Halas 2005; Liu *et al.* 2014). It is clear that the size of the silver nanoparticles on the textile material plays an important role in the water disinfection.

The results of silver leaching showed 26 ppb at 2 min of contact time, but increased to 38 ppb at 5 min, and further increased to 58 ppb at 10 min from the yellowish textile kit. For the grayish textile kit, it was 9, 42, and 51 ppb, respectively, displaying similar increasing trends as compared to the yellowish kit. It can be seen that the silver released from both types of the textiles are comparable, and the amount of silver concentration is much less than the current US EPA and WHO limit in drinking water at 100 ppb. It is also well within the WHO recommended human no observed adverse effect level (NOAEL) of total life oral intake of about 10 g of silver if calculated by a life of 70 years with 3.7 L of daily drinking water intake (WHO 1996; Institute of Medicine 2004). Therefore, the kit can be a novel point-of-use water treatment method which will be very useful for travellers, rural areas, emergency and disaster relief purposes.

Table 1 | Water disinfection efficiency of nanosilver textile kits and silver leaching

	Yellowish textile kit			**Grayish textile kit**		
Contact time (mins)	**Bacteria number (CFU/mL)[a]**	**Disinfection efficiency (%)**	**Silver leaching (ppb)**	**Bacteria number (CFU/mL)**	**Disinfection efficiency (%)**	**Silver leaching (ppb)**
2	1.79×10^3	75.5	26	5.53×10^3	24.5	9
5	8.6×10^2	88.3	38	3.46×10^3	52.7	42
10	7.9×10^2	89.2	58	3.43×10^3	53.1	51

[a]Bacteria number in raw rain water: 7.32×10^3 CFU/mL.

Table 2 | Water disinfection efficiency at multiple usages of nanosilver textile kits with 5 min contact time

	Yellowish textile kit			Grayish textile kit		
Usage (times)	Bacteria number (CFU/mL)[a]	Disinfection efficiency (%)	Silver leaching (ppb)	Bacteria number (CFU/mL)	Disinfection efficiency (%)	Silver leaching (ppb)
1	19	98.0	42	164	82.8	36
2	29	97.0	27	352	63.0	24
3	104	89.1	12	500	47.5	21
4	21	97.8	16	374	60.7	15
5	44	95.4	12	768	19.3	8
6	34	96.4	17	896	5.9	7

[a]Bacteria number in raw rain water: 952 CFU/mL.

For practical application, we believe a 5 min contact time is appropriate considering the disinfection efficiency, silver leaching, and the user experience. We have also investigated the durability of the textile kits for multiple usages. A new batch of rain water was collected for testing. The amount of bacteria in the raw rain water was 9.52×10^2 CFU/mL with a turbidity of 0.64 NTU. As shown in Table 2, the yellowish textile kit performed consistent good disinfection efficiency after six times of usage, and the amount of bacteria was well within the recommended drinking water limit of

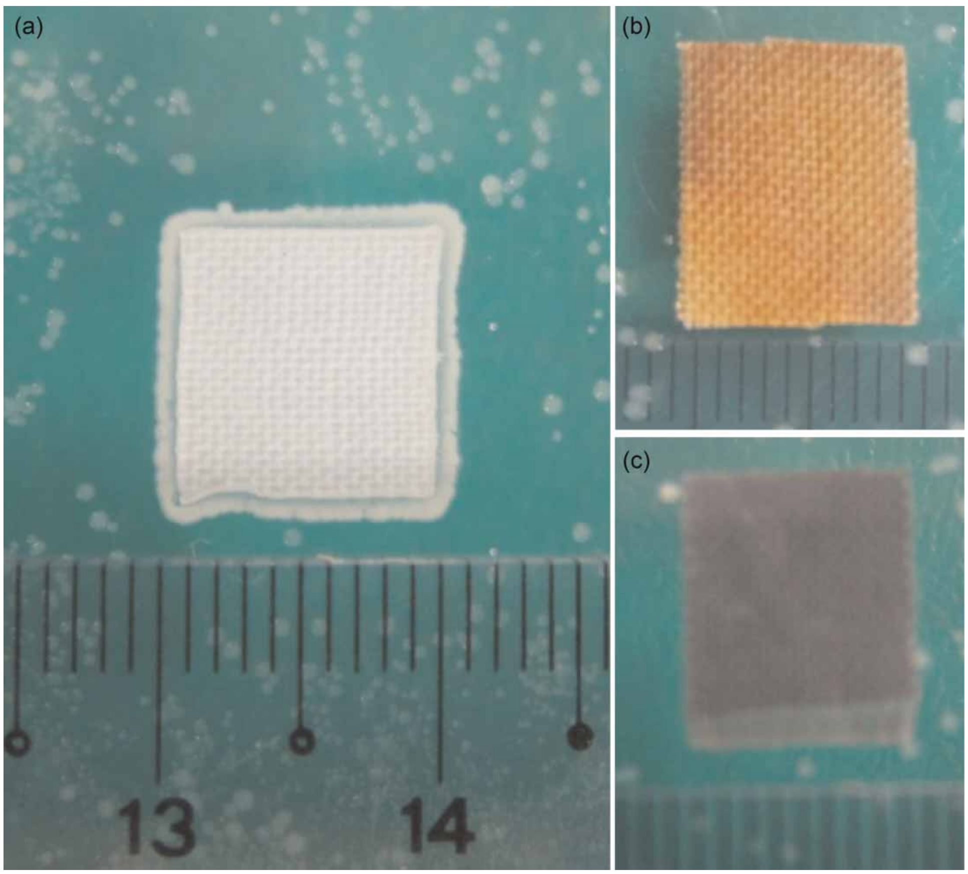

Figure 5 | Photographs of zone inhibition test: (a) natural textile without nanosilver coating; (b) yellowish nanosilver textile; (c) grayish nanosilver textile.

100 CFU/mL by some countries, e.g., Australian Drinking Water Guidelines and China National Drinking Water Standard. In contrast, the disinfection efficiency by the grayish textile kit decreased with the number of usages. After six cycles of usage, almost no disinfection ability was observed for the grayish textile kit, which is only about 5.9%. For both cases, the amount of silver leaching showed a decreasing trend. It is recommended that the yellowish nanosilver textile kit could be a better candidate for further development into a new commercial point-of-use water disinfection product. The yellowish nanosilver textile kit was further tested for *E. coli* disinfection capability. A strain of *E. coli* 8099 was cultivated and placed in the glass bottle for disinfection test. It was found that within 5 min of contact time, 1.9×10^5 CFU/mL of *E. coli* was reduced to 4.2×10^3 CFU/mL, achieving 97.8% removal efficiency.

Antimicrobial testing of nanosilver textile

To further investigate the antimicrobial property of the nanosilver textile material, a modified Kirby-Bauer test was conducted. Raw rain water was used for testing on agar plates for 24 hours with nanosilver textile (1 cm × 1 cm) and with the uncoated natural textile for comparison purposes. The results are displayed in Figure 5. The zone inhibition test clearly showed that the bacteria had grown at the uncoated natural textile (Figure 5(a)), particularly the four edges of the textile, forming a thick colony line. No bacteria growth was observed on the nanosilver coated textile (Figures 5(b) and 5(c)), which demonstrated its antimicrobial property. Moreover, it was also observed that the inhibition zone for the yellowish nanosilver textile is relatively larger than that of the grayish textile.

CONCLUSION

We have developed a novel point-of-use water disinfection method by nanosilver textile kit. The kit is simply fabricated from nanosilver textile material, which was prepared by a unique *in-situ* reduction technique. The yellowish nanosilver textile kit having smaller silver particle size around 30 nm could disinfect water and remove more than 90% of the bacteria in minutes even after six times of usage. Although a detailed investigation in the real-world environment needs to be further conducted with the consideration of several factors such as organic, inorganic, and colloidal containments in the raw water, the reported point-of-use nanosilver textile kit provides the basis for a new, cheap, and easy-to-use water disinfection method.

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