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RESEARCH ARTICLE

Enhanced disinfection of *Escherichia coli* and bacteriophage MS2 in water using a copper and silver loaded titanium dioxide nanowire membrane

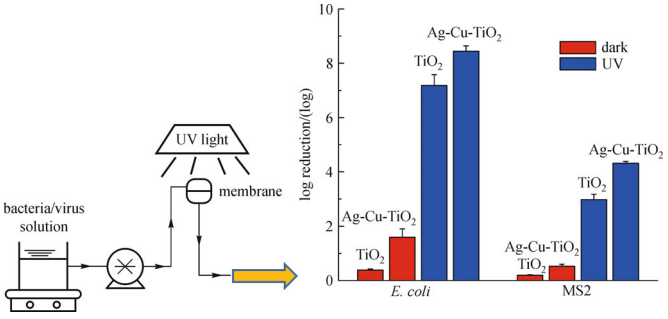
Guiying RAO[1], Kristen S. BRASTAD[2,3], Qianyi ZHANG[2], Rebecca ROBINSON[3], Zhen HE[4], Ying LI (✉)[1]

1 Department of Mechanical Engineering, Texas A&M University, College Station, TX 77843, USA
2 Department of Mechanical Engineering, University of Wisconsin-Milwaukee, Milwaukee, WI 53211, USA
3 A.O. Smith Corporate Technology Center, Milwaukee, WI 53224, USA
4 Department of Civil and Environmental Engineering, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA

HIGHLIGHTS

- A novel photocatalytic Ag-Cu-TiO_2 nanowire membrane was fabricated.
- Bacteria and virus disinfection was improved by co-depositing Ag and Cu onto membrane.
- Synergetic photocatalytic effects and free metal ions of Ag and Cu contribute to disinfection.
- 7.68 log removal of *E. coli* and 4.02 log removal of bacteriophage MS2 were achieved.

GRAPHIC ABSTRACT



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ABSTRACT

Titanium dioxide (TiO_2) is a widely used photocatalyst that has been demonstrated for microorganism disinfection in drinking water. In this study, a new material with a novel structure, silver and copper loaded TiO_2 nanowire membrane (Cu-Ag-TiO_2) was prepared and evaluated for its efficiency to inactivate *E. coli* and bacteriophage MS2. Enhanced photo-activated bactericidal and virucidal activities were obtained by the Cu-Ag-TiO_2 membrane than by the TiO_2, Ag-TiO_2 and Cu-TiO_2 membranes under both dark and UV light illumination. The better performance was attributed to the synergies of enhanced membrane photoactivity by loading silver and copper on the membrane and the synergistic effect between the free silver and copper ions in water. At the end of a 30 min test of dead-end filtration under 254 nm UV irradiation, the Cu-Ag-TiO_2 membrane was able to obtain an *E. coli* removal of 7.68 log and bacteriophage MS2 removal of 4.02 log, which have met the US EPA standard. The free metal ions coming off the membrane have concentrations of less than 10 ppb in the water effluent, far below the US EPA maximum contaminant level for silver and copper ions in drinking water. Therefore, the photo-activated disinfection by the Cu-Ag-TiO_2 membrane is a viable technique for meeting drinking water treatment standards of microbiological water purifiers.

1 Introduction

Microbial contamination of drinking water frequently occurs due to fecal matter from sewage discharges, leaking septic tanks, and runoff from animal feedlots into water bodies. Chlorine and ozone type disinfectants can effectively inactivate microorganisms but disinfection byproducts (DBPs) are detected in water which have potential carcinogenic effects on humans [1,2]. The concern of formation of DBPs leads to considerable interest in alternate disinfection technologies such as the photo-activated processes, which have shown enhanced disinfection capabilities since 1988 [3]. In photo-activated processes, the generation of the highly reactive hydroxyl radicals (e.g., OH·) or reactive oxygen species (ROS) by UV light irradiation can cause oxidative stress damage to

✉ Corresponding author
E-mail: yingli@tamu.edu

cell membranes and effectively inactivate microorganisms [4]. Titanium dioxide (TiO_2) is a most studied photocatalyst because it is inexpensive, abundant, corrosion-resistant and produces no dangerous DBPs [5]. Despite the numerous advantages, TiO_2 suffers from the fast recombination of photo-generated electron-hole pairs [6]. Therefore, loading metal ions such as silver and copper onto photocatalysts was carried out to increase the activity of the photocatalyst by separating the electrons and holes more effectively [7–9]. Silver and copper were also recognized for their antimicrobial effects [8,10] and the antibacterial capabilities of Ag-TiO_2 nanoparticles and Cu-TiO_2 nanoparticles under UV illumination have been studied previously [7,11]. However, the virucidal properties of the metal-ion deposited TiO_2 was seldom examined [12,13], hampering the development of commercially viable applications of photocatalysts such as for drinking water treatment. In addition, the combination of silver and copper together with TiO_2 nanowires remains largely unexplored for its antimicrobial properties, although the combined metal loading of TiO_2 nanoparticles have been recently studied for the removal of organic contaminants from water [14,15].

This study experimentally established the individual and combined effects of silver and copper loaded TiO_2 nanowire membrane on the inactivation of bacteria and virus. *Escherichia coli* (*E. coli*) was used as the model bacteria that is also frequently used in the literature for bacterial inactivation study [10,11,16]. It is relatively more UV resistant [17] and is a typical biologic indicator of water disinfection quality [18]. Bacteriophage MS2 was used as a model virus because of its simplicity to propagate and enumerate, similarity to many waterborne pathogenic viruses, and more resistance to UV disinfection than other bacteriophages [13]. Bacteriophage MS2 has also been frequently reported as a model virus for viral inactivation studies in the literature [13,19,20]. Unlike the traditional methods of using particulate and colloidal TiO_2 suspensions, which shield the UV light transmission and have difficulties for separation and reuse of the photocatalysts, the TiO_2 membrane is a relatively new form of the catalyst. It allows reuse of the material and combines the photocatalysis mechanism for organic degradation and microbial inactivation with the physical separation of membrane filtration into a single reactor [21].

2 Experimental

2.1 Membrane preparation

The photocatalytic membranes were fabricated in a two-step procedure. First the TiO_2 nanowires were prepared through a hydrothermal process, and then metal species were added through photodeposition for silver and through adsorption for copper. To make the TiO_2 nanowires, 1 g of TiO_2 P25 nanopowders (Sigma-Aldrich, St. Louis, MO, USA), 65 mL of 10 M NaOH (Sigma-Aldrich, St. Louis, MO, USA) and 65 mL of ethanol (Sigma-Aldrich, St. Louis, MO, USA) were mixed together inside a PTFE lined autoclave at 160°C for 12 h. The resulting white gel was then washed with 0.1 M HCl and deionized water alternatively until pH 7. The TiO_2 nanowires were then suspended in deionized water with a total volume of 500 mL. To prepare the TiO_2 membrane, 50 mL of the TiO_2 nanowire suspension was sonicated for 15 min in a sonicator (FB505, Fisher Scientific, Pittsburgh, PA, USA) and then vacuum filtered onto a 47 mm diameter fiberglass substrate. A uniformly distributed layer was observed on the substrate surface. The membrane was air-dried overnight and calcined at 375°C for 12 h.

To photo-deposit silver onto TiO_2 nanowires, 3 M HNO_3 was first added into 50 mL of the TiO_2 nanowire suspension to reach pH 3. Next, $AgNO_3$ (Sigma-Aldrich, St. Louis, MO, USA) was added into the suspension with a silver to TiO_2 atomic ratio of 2%, which is an optimum ratio identified by prior work [22]. Finally, 2 mL of 2.5% $HClO_4$ solution (Sigma-Aldrich, St. Louis, MO, USA) was added to the suspension and the solution was mixed continuously under UV irradiation (λ = 365 nm, UVP LLC, Upland, CA, USA) for 3 h. A dark gray color was observed at the end, suggesting the successful deposition of silver onto the TiO_2 nanowires. The Ag-TiO_2 membrane was prepared via the same vacuum filtration and calcination methods for the TiO_2 membrane preparation.

The adsorption of copper ions onto the TiO_2 and Ag-TiO_2 nanowires was achieved by mixing the TiO_2 suspension and the Ag-TiO_2 suspension (after photodeposition) with $Cu(NO_3)_2$ solution (Sigma-Aldrich, St. Louis, MO, USA). The optimal copper to TiO_2 atomic ratio was selected as 3%, which is the optimum ratio identified by the prior research [23]. The solution was shaken on an orbital shaker (IKA® Works, Inc., NC, USA) for 16 h and the copper loaded membranes were prepared using the same method for the TiO_2 membrane preparation.

2.2 Membrane surface morphology and characterization

The membrane pore size was estimated by analyzing the pore size distribution using a mercury porosimetry method [24]. The membrane surface morphology was evaluated through scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS; Hitachi S570, Tokyo, Japan). The presence of loaded metals and the actual concentrations of metal attached to the TiO_2 nanowires were confirmed by EDS analysis (Oxford Instruments, UK) and atomic elemental analysis via inductively coupled plasma mass spectrometry (ICP-MS; Agilent Technologies, CA, USA), respectively. Briefly, the Ag-TiO_2, Cu-TiO_2, and Cu-Ag-TiO_2 solutions was each vacuum filtered onto a Pall 0.45 μm GN-6 filter paper, which was then placed into a beaker containing 60 mL of

nitric acid solution and was heated to just below boiling. After that, the solution was centrifuged and the supernatant was analyzed using ICP-MS.

2.3 Preparation of the microbial challenge solutions

To prepare the *E. coli* challenge water, 8.0 g lysogeny broth (LB Broth) was added into 400 mL of Type III deionized water in an autoclavable bottle and was gently heated until boiling. The solution was then autoclaved at 121°C for 60 min to obtain the sterilized broth solution. After cooling to room temperature, a loop of freeze-dried *E. coli* (ATCC® 11303™) was inoculated into the solution, which was then shaken at 130 $r \cdot min^{-1}$ on an incubated shaker at 35°C for 18 h. Next, the solution was centrifuged at 6000 × g for 5 min and the supernatant was poured off and replaced with 50 mL of Type III deionized water.

The bacteriophage MS2 that has a similar activity of enteric viruses was prepared in the following manner. First, 5-8 mL of the sterilized broth solution was poured into a sterile test tube and inoculated with a loopful of freeze-dried bacteriophage MS2 (ATCC® 15597-B1™), which (1 mL) was then pipetted into a sterile test tube with 5–8 mL of an agar solution. The agar solution was prepared by mixing 4.0 g tryptone, 3.2 g sea salt, 0.4 g yeast extract, and 3.2 g agar with 400 mL of Type III deionized water in an autoclavable bottle and heated to a boiling followed by autoclaved at 121°C for 60 min. The mixture inside the test tube was then poured onto a solidified layer surface in a plate. The solidified layer was prepared by pouring 5–8 mL of the agar solution in an autoclavable bottle and was autoclaved at 121°C for 60 min. After the entire solidification, the plate was inverted and stored in an incubator at 35°C for 18 h. Next 8 mL of sterile 10% phosphate buffer saline (PBS) solution, the stock solution of which was prepared by dissolving 80 g NaCl, 2 g KH_2PO_4, 29 g $Na_2HPO_4 \cdot 12H_2O$ and 2 g KCl in Type III deionized water to a final volume of 1 L and autoclaved at 121°C for 60 min, was pipetted onto the plate that contains the bacteriophage MS2. The plate was then placed back into the incubator at 35°C. After 20 min, the PBS solution was centrifuged at 6000 × g for 5 min and the supernatant was passed through a 0.45 μm syringe filter. The filtered liquid was labeled as the MS2 stock solution and was placed in a refrigerator at 4°C for storage.

2.4 Photo-activated disinfection test setup

The bench-scale photo-activated disinfection apparatus is shown in Fig. 1. The challenge solution containing microorganisms was continuously pumped into an acrylic membrane holder by a peristaltic pump (Masterflex L/S 7523-80, Vernon Hills, IL, USA) with a flow rate of 5 $mL \cdot min^{-1}$, corresponding to a membrane flux of 173 $L \cdot m^{-2} \cdot h^{-1}$. Each experiment lasted for 30 min and samples were taken every 10 min to estimate the rejection of microorganism. The TiO_2 membrane, Ag-TiO_2 membrane, Cu-TiO_2 membrane, and Cu-Ag-TiO_2 membranes were tested under both UV light irradiation (λ = 254 nm, 11 W, Phillips, NJ, USA) and dark conditions, each test being repeated in triplicate. The challenge solution contained 10^7 $CFU \cdot mL^{-1}$ of *E. coli* or 10^5 $PFU \cdot mL^{-1}$ of bacteriophage MS2. The amount of bacteria in water was determined by the heterotrophic plate counts with a pour plate method using USEPA Method 9215. The amount of virus was determined by a double-layer pour plate method. The final log removal of each filter was determined by dividing the concentration of bacteria or viruses in treated

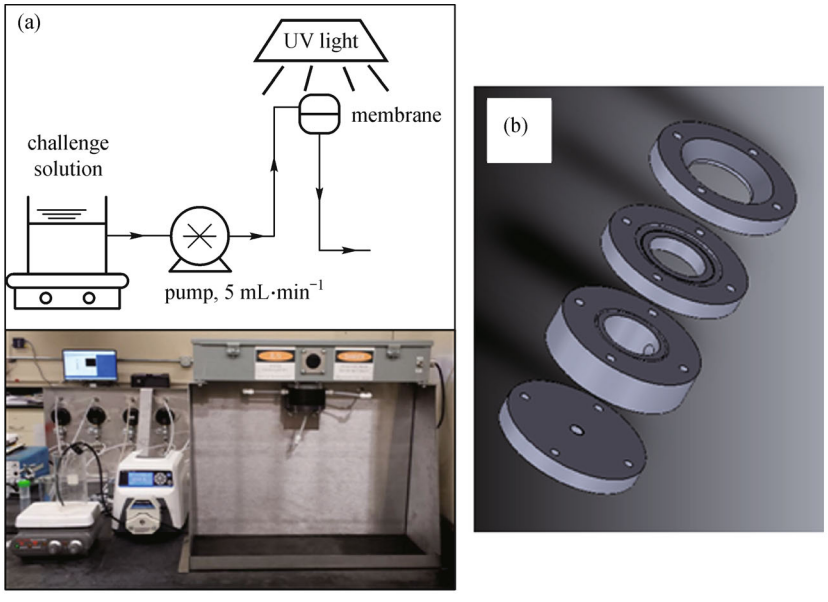

Fig. 1 Schematic of the test setup (a) and the exploded diagram of the membrane holder (b)

water (N_{out}) by the concentration in the feed water (N_{in}):

$$\log_{removal} = -\log_{10}\left(\frac{N_{out}}{N_{in}}\right), \quad (1)$$

The concentrations of free metal ions released from membranes to water under the dark condition were also analyzed using ICP-MS. To check if the releasing of loaded metal ions into water would deleteriously affect the metal weight ratios in the membrane, the amount of free ions coming off the Cu-Ag-TiO_2 membrane was analyzed over a 10 h period. Water samples were collected every 20 min and analyzed through ICP-MS.

3 Results and discussion

3.1 Membrane surface morphology and characterization

The surface morphology of the nanowire membranes were analyzed by SEM and a uniform distribution of the TiO_2 nanowires (length of around 5 μm and diameter of tens of nanometers) with random orientation was observed on each membrane (Fig. 2). The nanowires were identified as anatase TiO_2 (JCPDS No. 21-1272 [25]; Fig. S1, please see it in Supplementary material). The XRD analysis of the Cu-Ag-TiO_2 composite was also performed but no peak of Ag or Cu was found, likely because of the low metal concentration and well dispersion of metals onto TiO_2 surface [15]. The lack of high temperature treatment (photo-deposition of Ag and adsorption of Cu, followed by air calcination at 375°C) in the materials synthesis process makes it unlikely that Ag and Cu be incorporated into the TiO_2 lattice (consistent with the literature [15,26]) and the metal particle surfaces may form silver oxides and copper oxides. Unfortunately, ICP-MS could not differentiate metal oxides from metals, and XPS or XRD could not give accurate information on the composition, crystal structure and chemical states of Ag or Cu because of their very low concentrations. Because the metal ion loaded membranes have a surface morphology similar to that of the TiO_2 membrane (Figs. 2a–2b), only the SEM images of the TiO_2 and the Cu-Ag-TiO_2 membranes were given here. Although silver and copper on the membrane were not observed under SEM, the EDS analysis verified their presence (Figs. 2c–2e). Subsequent digestion of the silver and copper off the TiO_2 nanowires with the ensuing analysis by ICP-MS confirmed the concentration was 2% for silver and 3% for copper. The membrane cross-section image (with glassfiber substrate removed) is displayed in Fig. 2f. The membrane has a uniform thickness of 35±2 μm, thick enough to block the UV as the literature reported that the depth of UV penetration through TiO_2 is only a few micrometers [27,28]. The light intensities across the membrane (without glassfiber substrate) were then measured using the ILT950 Spectroradiometer (International Light Technologies, Inc., MA, USA) and were found to be fully shielded by the membrane; therefore, the photoreaction only occurred on membrane surface.

Membrane pore size distribution was characterized using the mercury porosimetry method. Results are displayed in Fig. 3 where the *y*-axis, d*V*/dlog*D*, is the specific mercury intrusion volume (V) versus the logarithm of pore diameter (D). As can be seen, all membranes have pore sizes peaked in the range of 4 to 8 μm. The Cu-Ag-TiO_2 membrane has relatively smaller pore volume (smaller *y*-axis value) over the entire pore size range thus less porous than other membranes. The pore suppression for the Cu-Ag-TiO_2 membrane may be due to the loading of both copper and silver metals. Because the membrane pore sizes are much greater than the typical sizes of *E. coli* (0.25-1 μm in diameter and 2 μm in length [29]) and bacteriophage MS2 (275 Å [30]), the microorganism rejection by each membrane via membrane filtration alone may not cause much difference. However, the large membrane pore size is beneficial to achieve a high pollutant (e.g., microorganisms, natural organic matters) removal at a low transmembrane pressure (<300 kPa) when deposited with photocatalysts [31].

3.2 Membrane performance for *E. coli* inactivation

The removal of bacteria, *E. coli*, by the photocatalytic membranes under both dark and UV light conditions are shown in Fig. 4. Under the dark condition (Fig. 4a), removal of *E. coli* was mainly achieved via membrane retention. A decrease of bacteria inactivation was observed over time for all the membranes except the Cu-Ag-TiO_2 membrane. The Cu-Ag-TiO_2 membrane also shows the highest *E. coli* inactivation in most situations among all the membranes. Because the smaller membrane pore size (Fig. 2) may not be significant enough to cause such higher inactivation, the free silver and copper ions (released from the membrane) in the solution surrounding the membrane may be the reason [13], as metal ions on membrane photocatalyst are typically not bioavailable to kill bacteria [32]. In addition, a synergistic effect between silver and copper ions is likely present because only photo-depositing silver (the Ag-TiO_2 membrane) did not lead to better membrane performance and only loading copper (the Cu-TiO_2 membranes) led to worse performance comparing to the TiO_2 membrane (Fig. 4a). The very high inactivation of *E. coli* at the beginning of the test using the Ag-TiO_2 membrane (consistent with [13]) is likely because of the high concentration of silver ions coming off the membrane (Fig. 5). This phenomenon together with the fact of an inconsistent trend between *E. coli* inactivation (Fig. 4a) and concentrations of free silver ions in water (Fig. 5) suggests the bactericidal property of silver ions may be most effective at the beginning of the test when the water surrounding the membrane has relatively high silver

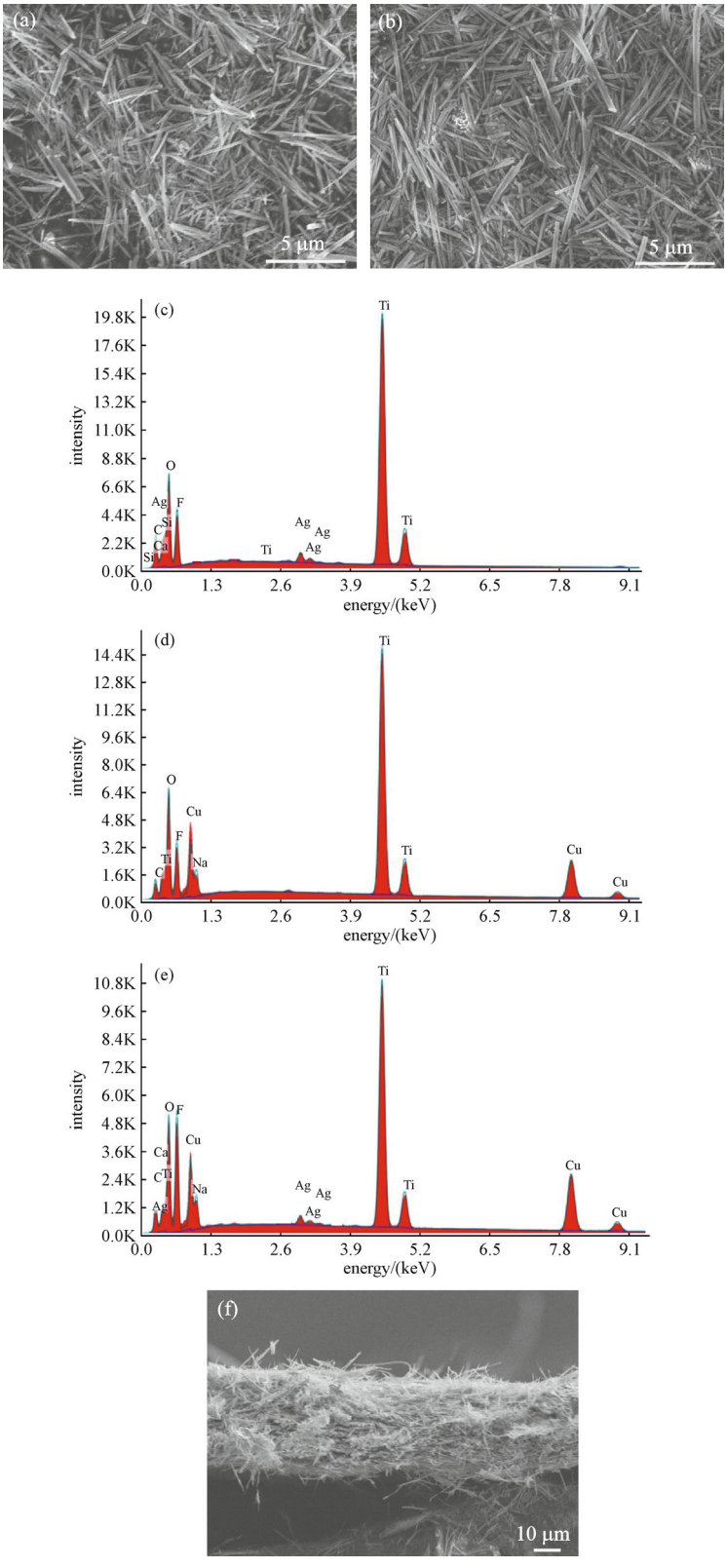

Fig. 2 SEM images of the TiO_2 membrane (a) and the Cu-Ag-TiO_2 membrane (b); EDS analysis results of the Ag-TiO_2 membrane (c), the Cu-TiO_2 membrane (d) and the Cu-Ag-TiO_2 membrane (e); and membrane cross-section (f)

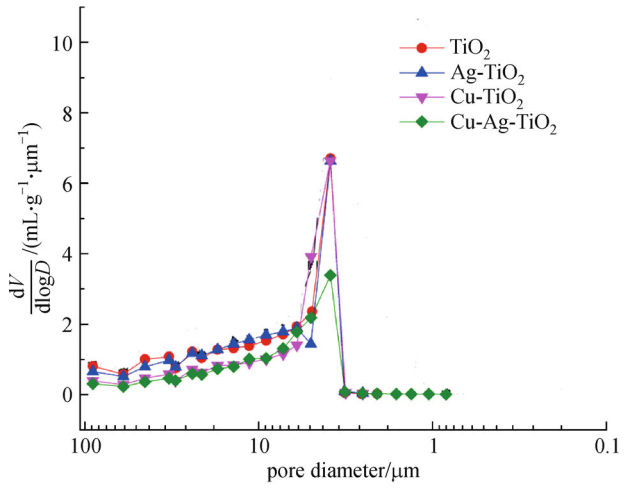

Fig. 3 Pore size distributions of the prepared membranes

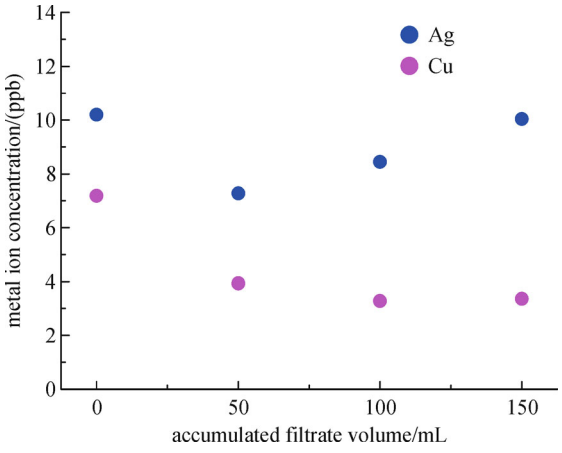

Fig. 5 Concentrations of free silver ions in water effluent for the Ag-TiO_2 membrane and copper ions for the Cu-TiO_2 membrane under the dark condition

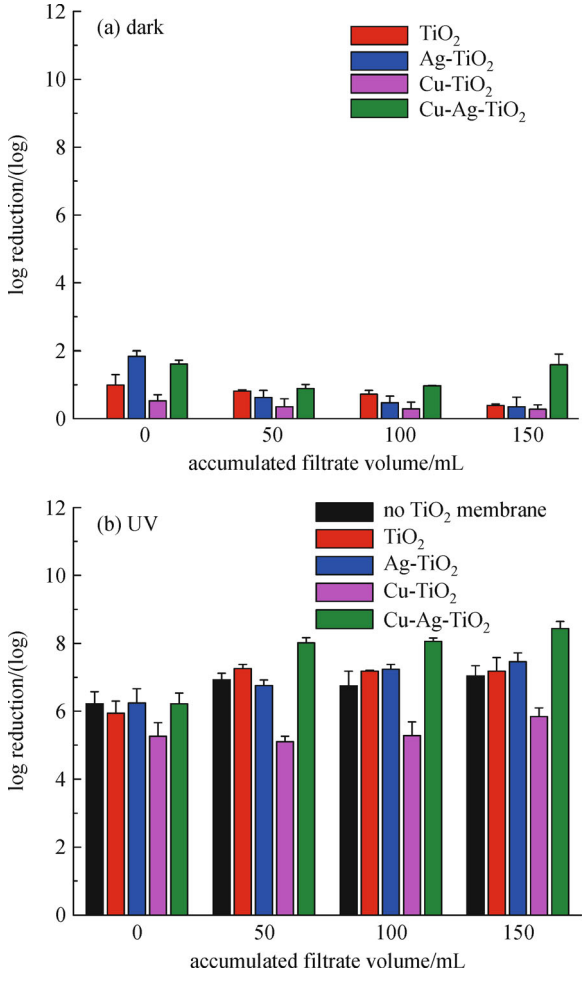

Fig. 4 Inactivation of *E. coli* by the TiO_2, Ag-TiO_2, Cu-TiO_2, and Cu-Ag-TiO_2 membranes under dark (a) and UV (b) conditions.

concentrations (~10 ppb; Fig. 5). The unexpectedly poor performance of the Cu-TiO_2 membrane is likely because of copper ions in water facilitating the growth of *E. coli,* leading to a poor *E. coli* rejection. It was reported that copper was an essential trace element vital to the growth of microorganisms because of its ability to be incorporated into a variety of essential metabolic proteins and metalloenzymes, stimulating the immune system to fight infections, repair injured tissues, and promote healing [33,34]. The reason that copper benefits *E. coli* rather than poisoning it here may be due to its very low concentration ($<$ 10 ppb by ICP-MS; Fig. 5). For comparison, copper (II) concentrations of 3.18 to 127 ppm were studied for its toxicity to *E. coli* [10] and the inactivation was found to increase with higher copper content [16]. However, a high copper content may suppress the membrane photocatalytic activity if exposed to UV irradiation because it may form recombination centers of photo-induced charges [15]; therefore, there exists an optimal ratio of copper adsorbed onto the membrane.

The effectiveness of *E. coli* inactivation under UV irradiation was also studied and a significant higher inactivation was observed (Fig. 4b) than that under the dark condition (Fig. 4a). The TiO_2 membrane showed slightly higher disinfection performances than that without TiO_2 membrane (black column in Fig. 4b, UV only), and the Cu-Ag-TiO_2 membrane showed much greater disinfection capability than that without membrane. The reason that UV disinfection is slightly higher than the TiO_2 membrane (red column in Fig. 4b) at the beginning of the test is likely due to the membrane light shielding effect. The improved TiO_2 membrane disinfection after 10 min (accumulated filtrate volume of 50 mL) suggests a short ($\leqslant$10 min) activation time is needed for TiO_2 to initiate photocatalytic disinfection. The Ag-TiO_2 membrane shows comparable or higher inactivation of *E. coli* in most cases than the TiO_2 membrane; thus the improved membrane photocatalytic disinfection by photo-depositing silver may be demonstrated [15]. Similar to the dark

condition, a poor performance of the Cu-TiO_2 membrane was observed, thus it is unclear if loading copper has increased the membrane photocatalytic activity (thus disinfection). Still, the Cu-Ag-TiO_2 membrane shows the highest *E. coli* inactivation among all the membranes, although loading silver or copper alone did not significantly improve the inactivation. The possible reasons are: (1) the synergistic effect between free silver and copper ions in water for *E. coli* inactivation (as observed under the dark condition in Fig. 4a) and (2) the enhanced photocatalytic activity of TiO_2 because of co-loading Ag and Cu on the membrane. An increase in photocatalytic activity due to combining silver and copper was also recently reported by Behnajady et al. for the removal of C. I. Acid Orange 7 as compared to Ag-TiO_2 nanoparticles and Cu-TiO_2 nanoparticles [15]. It should be noted that the bacteria removal of 7.68±0.99 logs by the Cu-Ag-TiO_2 membrane has largely exceeded the US EPA standard for bacteria inactivation, which requires a 6 log removal of bacteria certified under the National Sanitation Foundation (NSF)/American National Standards Institute (ANSI) standard P231. Also, the free silver and copper ions in water (Fig. 5) have concentrations that are far below the US EPA maximum contaminant level of 100 ppb for silver and 1300 ppb for copper ions in drinking water [35].

3.3 Membrane performance for bacteriophage MS2 inactivation

For the virus experiments performed under the dark condition, removal of bacteriophage MS2 was achieved mainly via membrane retention and very little viruscidal inactivation was observed (Fig. 6a). Compared to the TiO_2 membrane, the Cu-TiO_2 membrane shows a comparable performance for bacteriophage MS2 inactivation and the free copper ions in water has insignificant effect on membrane viruscidal activity. Therefore, the virus, bacteriophage MS2, may be less susceptible to copper ions in water than *E. coli* is at the current investigated concentration level. It can also be seen from Fig. 6a that the Ag-TiO_2 membrane always has higher inactivation than the TiO_2 membrane, which is likely attributed to the free silver ions in water, thus bacteriophage MS2 is more susceptible to silver ions than *E. coli* is. Similar to the test for *E. coli* inactivation (Fig. 4a), a much higher bacteriophage MS2 inactivation was observed by the Cu-Ag-TiO_2 membrane. Hence, a similar synergistic effect between copper and silver ions in the water filtration system as previously discussed for *E. coli* inactivation may have taken place for bacteriophage MS2 inactivation.

Membrane performance under UV light irradiation for bacteriophage MS2 inactivation is displayed in Fig. 6b. Similar to *E. coli*, much higher disinfection of MS2 were observed than in dark condition likely due to the UV disinfection (black column in Fig. 6b) and the photocatalytic disinfection induced by the TiO_2 photocatalyst materials. Still, the UV disinfection showed slightly higher performance than the TiO_2 membrane at the beginning of the test likely due to the membrane light shielding effect. A slightly higher average inactivation by the Ag-TiO_2 membrane than by the TiO_2 membrane was observed over the 30 min period. However, it is not clear whether the improved inactivation was due to the enhanced photocatalytic activity of TiO_2 or due to the free silver ions in water (as demonstrated in the dark condition). The performance of the Cu-TiO_2 membrane did not have significant difference from the TiO_2 membrane. The inactivation by the Cu-Ag-TiO_2 membrane is significantly higher than the other membranes under UV. The synergy effect of free silver and copper ions in water (as demonstrated under the dark condition in Fig. 6a) could not contribute to such a high inactivation. Thus, the enhanced photocatalytic effect of TiO_2 due to co-loading Ag and Cu should have made contribution to the overall high inactivation. It should be noted that the virus removal of 4.06±0.27 log by the Cu-Ag-TiO_2 membrane has

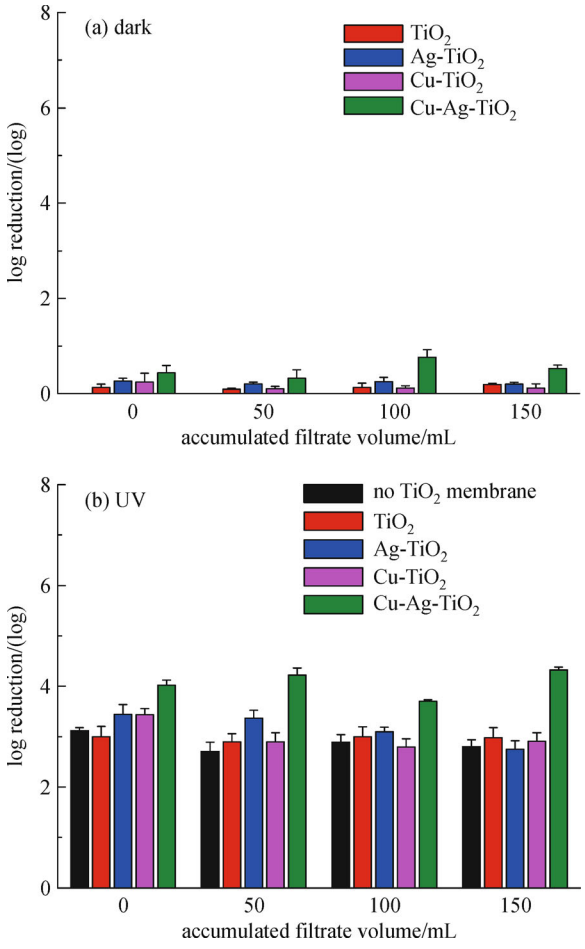

Fig. 6 Inactivation of bacteriophage MS2 for the TiO_2, Ag-TiO_2, Cu-TiO_2, and Cu-Ag-TiO_2 membranes under dark (a) and UV (b) conditions.

almost reached the US EPA standard for virus inactivation, which requires a 4 log removal of virus certified under the National Sanitation Foundation (NSF)/American National Standards Institute (ANSI) standard P231.

3.4 Effect of metal releasing on metal atomic ratio in the membrane

Over a 10 h test, both silver and copper ions were detected in the water effluent, suggesting a continuing releasing of metal ions from membrane into water thus a gradual decrease of the metal atomic ratio on the membrane. At the end of the test, the amount of silver and copper released into water accounted for only 0.16% and 0.02%, respectively, of the original amount loaded on the membrane, indicating the metals are stable on TiO_2 surface. At this release rate, it would take thousands of hours to completely deplete the silver and copper, longer than a typical membrane lifetime. In addition, the minimal change in metal concentration would not cause dramatic change of membrane performances for microorganism inactivation over a long period.

4 Conclusions

This study fabricated a silver and copper loaded TiO_2 nanowire membrane that shows enhanced photo-activated disinfection of bacteria and virus from drinking water. During a 30 min test, the *E. coli* removal by the Cu-Ag-TiO_2 membrane largely exceeded the US EPA standard and the virus removal almost met the standard. Although metals were released from the membrane into the water, the ion concentration in the water effluent are far below the US EPA MCL for silver and copper ions in drinking water. The enhanced photo-activated disinfection by the Cu-Ag-TiO_2 membrane was attributed to the synergistic effect between the free silver and copper ions in water and the synergies of the loaded metal ions on the membrane that have enhanced the membrane photocatalytic activity. Contribution of each effect on the improvement of microorganism disinfection needs to be investigated in future.

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Electronic Supplementary Material Supplementary material is available in the online version of this article at http://dx.doi.org/10.1007/s11783-016-0854-x and is accessible for authorized users.

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