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Supporting Information

Self-Decontaminating Nanofibrous Filters for Efficient Particulate Matter Removal and Airborne Bacteria Inactivation

Zan Zhu,[†] *Yu Zhang,* [†] *Liang Bao,*[‡] *Jianping Chen,*[†] *Shun Duan,* [†,‖] *Sheng-Chieh Chen,* [†] *Ping Xu,* [‡] *and Wei-Ning Wang* [*, †]

[†] Department of Mechanical and Nuclear Engineering, Virginia Commonwealth University, Richmond, Virginia 23219, USA.

[‡] Philips Institute for Oral Health Research, Virginia Commonwealth University, Richmond, Virginia, 23298, USA.

[‖] State Key Laboratory of Chemical Resource Engineering, Key Lab of Biomedical Materials of Natural Macromolecules, Ministry of Education, Beijing Laboratory of Biomedical Materials, Beijing University of Chemical Technology, Beijing 100029, China

* Corresponding Author

E-mail: wnwang@vcu.edu

Tel: 1-804-827-4306, 7030 (fax)

CONTENTS

S1. Material Synthesis of UiO-66-NH_2, UiO-BIBB, and UiO-PQDMAEMA

S1.1 Reagents

N, N, N', N'', N''-pentamethyl diethylenetriamine (PMDETA, 99%), 2-(dimethylamino)ethyl methacrylate (DMAEMA, 98%), copper (I) bromide (CuBr, 98%), copper (Ⅱ) bromide ($CuBr_2$, 99%), 2-bromoisobutyryl bromide (BIBB, 98%), 1-bromodecane (98%), isopropyl ether (99%), acetonitrile (99.5%), triethylamine (TEA, 99%), 2-amino-1,4-dicarboxylic acid (BDC-NH_2, 99%), zirconium chloride ($ZrCl_4$, 99.5%), acetic acid (99%), silver nitrate ($AgNO_3$, 99.9%), copper nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$, 99%), sodium sulfide nonahydrate ($Na_2S \cdot 9H_2O$) and polyacrylonitrile (PAN, MW = 150,000) were purchased from Sigma Aldrich. Anhydrous tetrahydrofuran (THF, 99.8%) was obtained from Alfa Aesar. Methanol (99.8%) and N, N-dimethylformamide (DMF, 99%) were purchased from VWR Corporation. All chemicals were used as received without further purification.

S1.2 Preparation of UiO-66-NH_2

UiO-66-NH_2 was prepared based on a previous work with some modifications.[1] Typically, a mixture of 0.2332g $ZrCl_4$, 0.1812g BDC-NH_2, and 6 ml acetic acid were dissolved in 50 ml DMF by ultrasonication for 5 minutes. Subsequently, the above mixture was transferred into a 100 ml Teflon-lined stainless-steel autoclave, which was kept at 120 °C for 24 hours. The obtained precipitates were washed thoroughly by DMF and methanol several times. The activation was conducted by immersing the above particles in 50 ml methanol for 72 hours. Finally, the pale-yellow particles were dried at 100 °C under vacuum for 12 hours.

S1.3 Preparation of UiO-66-BIBB

The UiO-66-BIBB was obtained by functionalizing UiO-66-NH_2 under the protection of nitrogen in a 50 ml flask.[2] In a typical procedure, 0.3 g UiO-66-NH_2 was suspended in 20 ml anhydrous THF by sonication. 418 μL TEA and 124 μL BiBB were dissolved in 10 ml THF separately. The TEA solution was injected into the UiO-66-NH_2 suspension under stirring. Then the BIBB solution was dropwise added into the mixture in 30 minutes with ice water cooling and strong stirring. The reactants were subsequently sealed and stirred at 50 °C for 24 hours. Finally, the particles were washed with THF and methanol and dried under vacuum at 40 °C. The obtained products were named UiO-66-BIBB.

S1.4 Preparation of UiO-PQDMAEMA

The typical ATRP process was conducted based on a previous work but with some modifications.[3] Poly [2(dimethyl decyl ammonium) ethyl methacrylate] (PQDMAEMA) brushes were prepared by ATRP of QDMAEMA from UiO-66-BIBB. To prepare QDMAEMA, 2.68 ml DMAEMA and 3.9 ml of 1-bromodecane were added into 10 ml acetonitrile in a 50 ml flask and reacted for 24 hours at 40 °C. After cooling to room temperature, the solution was slowly dripped into 200 ml isopropyl ether, and the white precipitates were collected by centrifugation. The precipitate was dissolved in acetonitrile and then carried on the precipitation centrifugation process for another two times. For ATRP, 0.8g QDMAEMA and 200 μL PMDETA were added into a 10 ml mixture of deionized water and methanol (volume ratio = 1:1) in a 50 ml flask. Under the protection of nitrogen, 20 mg $CuBr_2$ and 0.2 g UiO-66-BiBB were added to the mixture. After nitrogen bubbling for 20 minutes, 64.8 mg CuBr was added into the flask, which was then tightly sealed. After stirring for 36 hours at 30 °C, the PQDMAEMA-modified UiO-66-BIBB was prepared (denoted as UiO-PQDMAEMA). The samples were separated by centrifugation and washed by deionized water and methanol for 3 times. Finally, the obtained particles were naturally dried in the air.

S2. Correction of Size-fractionated Particle Filtration Efficiency

To correct the size-fractionated particle filtration efficiency ($PFE(d_x)$) due to the particle diffusion loss, the correlation ratio test was performed.[4] The same particle generator as used for generating challenge aerosols for the test was turned on, but without a test filter medium in the holder. The upstream and downstream samples were measured for the same sampling time internals as used in the tests. The general formula for the correlation ratio, $R(d_x)$, can be calculated as:

$$R(d_x) = \frac{C(d_x)_{downstream,0}}{C(d_x)_{upstream,0}} \#(S1)$$

where $C(d_x)_{downstream,0}$ is the particle concentration with particle size d_x measured at the downstream sampling location without a filter medium; $C(d_x)_{upstream,0}$ is the particle concentration with the particle size d_x measured at the upstream sampling location without a filter medium. The finally corrected $PFE^{'}(d_x)$ takes the following form:

$$PFE^{'}(d_x) = 1 - \frac{P(d_x)}{R(d_x)} \#(S2)$$

S3. Determination of Weight Percentage of Grafted Polymer PQDMAEMA

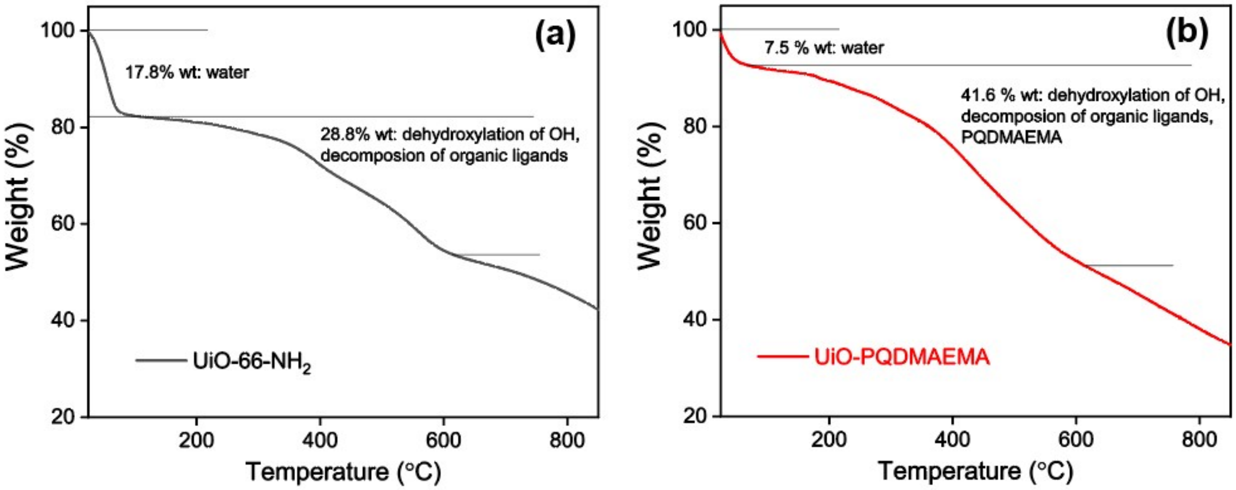

Figure S1. TGA curves of (a) UiO-66-NH_2 and (b) UiO-PQDMAEMA.

The weight percentage of the grafted PQDMAEMA was determined by the TGA. **Fig. S1** shows the curves of UiO-66-NH_2 and UiO-PQDMAEMA. The first weight loss from 50-150 °C in both UiO-66-NH_2 and UiO-PQDMAEMA can be ascribed to moisture release. The second step of weight loss (28.8%) in UiO-66-NH_2 at 150-600 °C is due to the dihydroxylation of OH^- and decomposition of organic ligands BDC-NH_2.[5, 6] However, a sharp weight percentage decrease (41.6%) is observed in UiO-PQDMAEMA at 150-600 °C is mainly because of the extra decomposition of grafted polymer PQDMAEMA. Therefore, the weight percentage of grafted polymer (Δw) can be calculated as follows:

Absolute percentage of dehydroxylated OH- and BDC-NH_2 ligands in UiO-66-NH_2 ($w1$):

$$w1 = \frac{28.8\%}{1 - 17.8\%\ (water\ loss)} \times 100\% = 35.04\% \tag{S3}$$

Absolute percentage of dehydroxylated OH-, BDC-NH_2 ligands, and PQDMAEMA in UiO-PQDMAEMA (w2):

$$w2 = \frac{41.6\%}{1 - 7.5\%\ (water\ loss)} \times 100\% = 44.97\% \tag{S4}$$

$$\Delta w = w2 - w1 = 9.93\% \tag{S5}$$

S4. Morphologies and Fiber Diameter Distribution of Pure PAN Filters

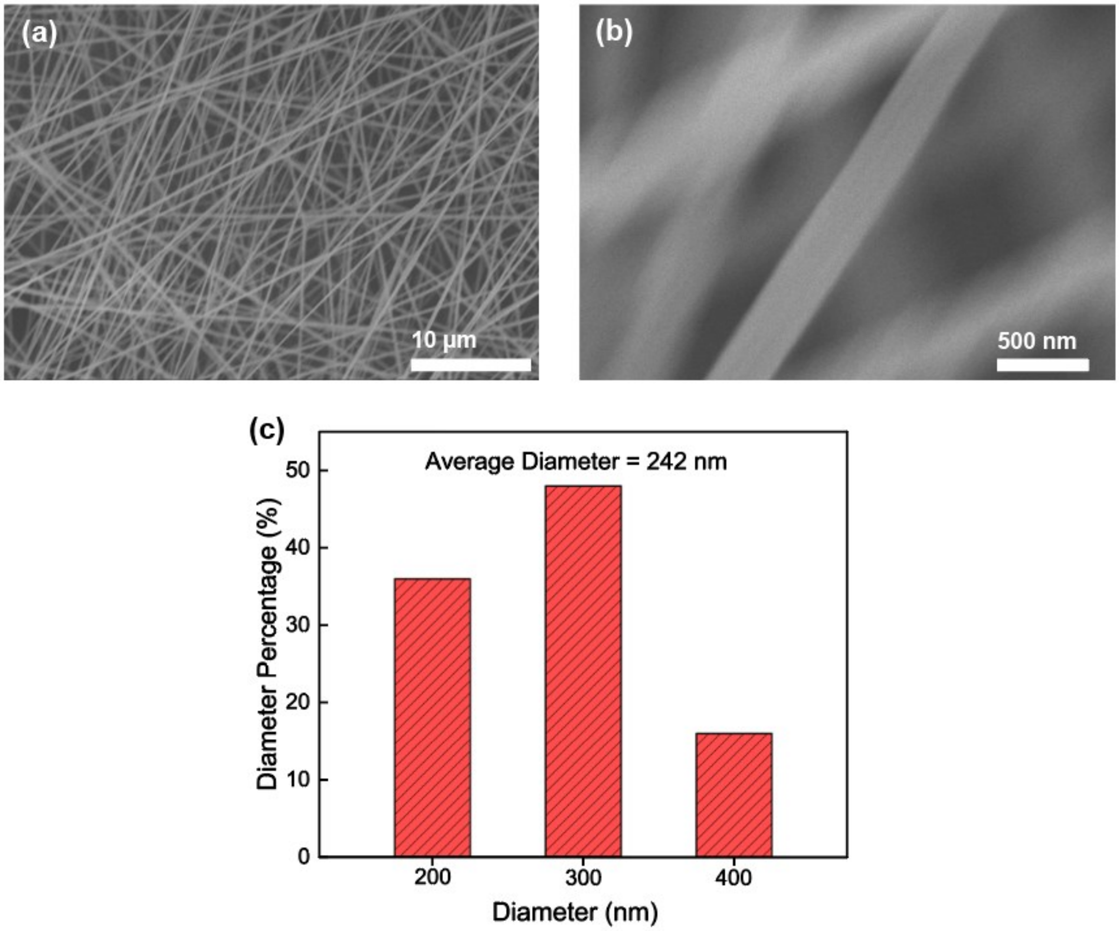

Figure S2. SEM images (a, b) and fiber diameter distribution of the PAN filter synthesized at room temperature with 35% relative humidity (RH).

S5. Characterization of UiO-PQDMAEMA@PAN Filter

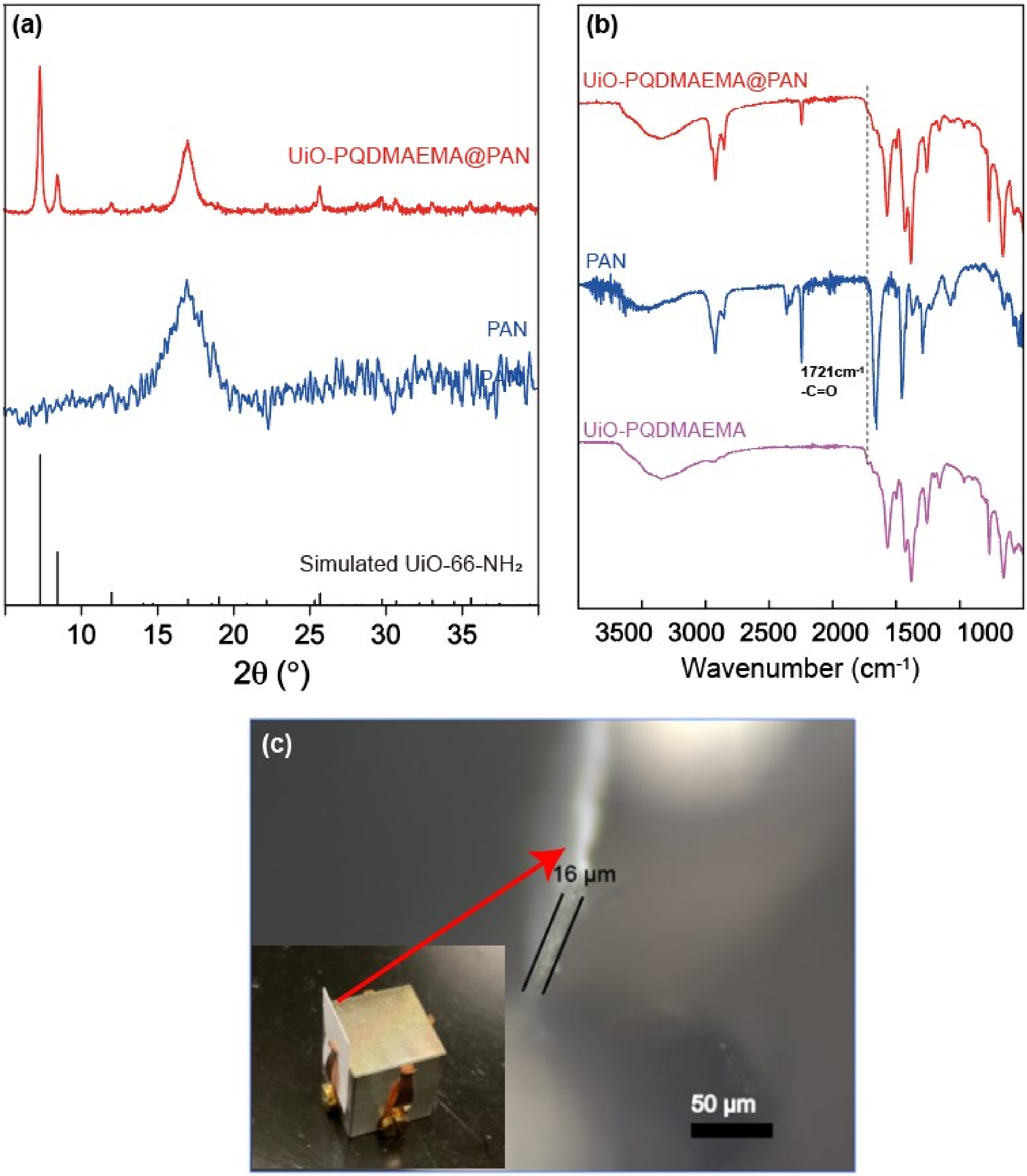

Figure S3. (a) XRD patterns of pure PAN and UiO-PQDMAEMA@PAN filters; (b) FT-IR spectra of UiO-PQDMAEMA, pure PAN filter, and UiO-PQDMAEMA@PAN filter; (c) Cross-sectional optical image of UiO-PQDMAEMA@PAN filter.

S6. Bacterial Fluorescent Staining Assays

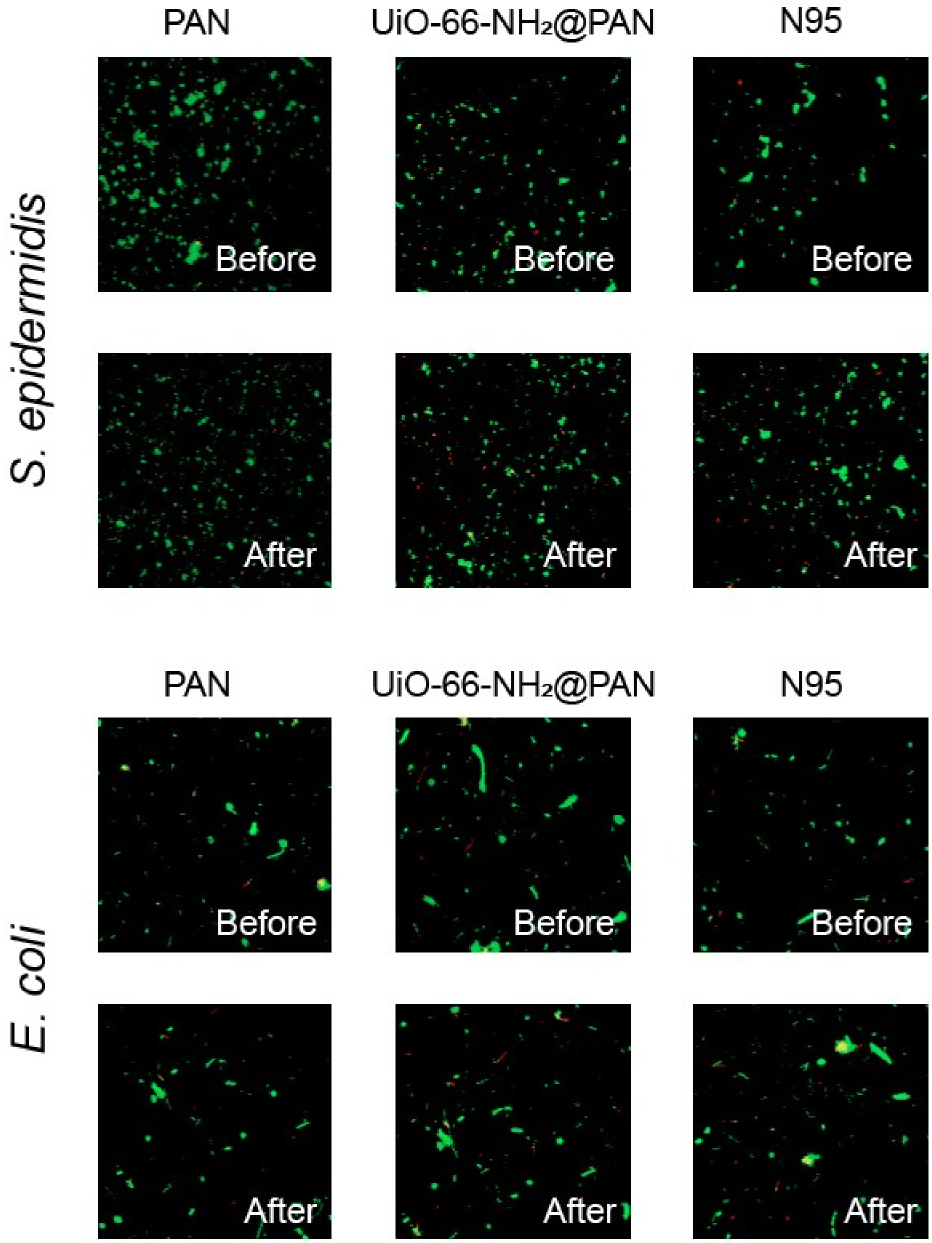

Figure S4. Fluorescence images of pure PAN filter, UiO-66-NH_2@PAN filter, and commercial N95 face mask before and after contacting the *S. epidermidis* and *E. coli*.

S7. The Time Course of Bacteria Inactivation

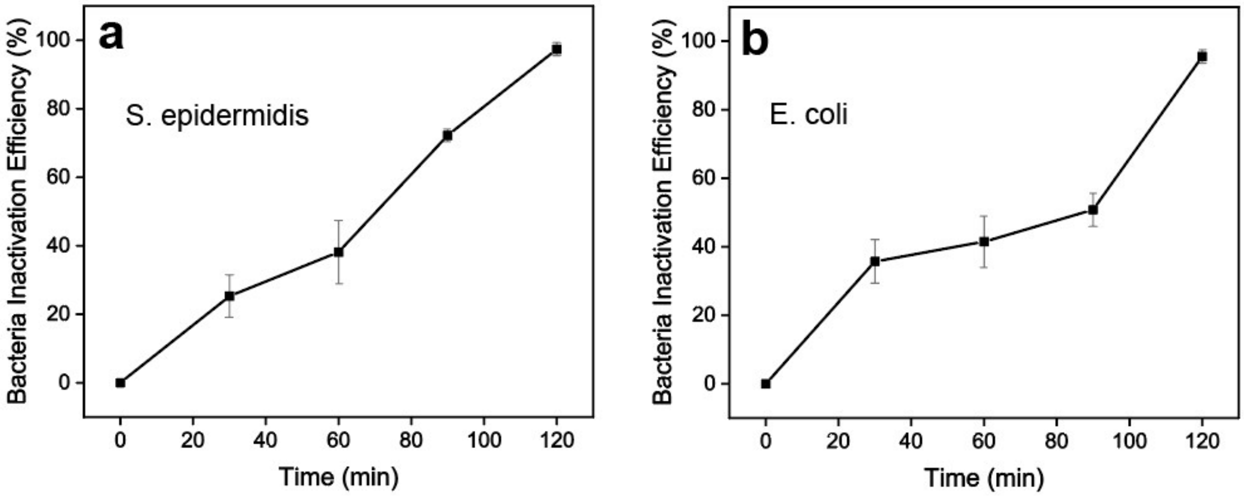

Figure S5. The time course of *S. epidermidis* (a) and *E. coli* (b) inactivation by the UiO-PQDMAEMA@PAN filter.

S8. Estimation of Charge Density on UiO-PQDMAEMA

To estimate the charge density (CD) on the UiO-PQDMAEMA, several assumptions were made as follow:

1. Each UiO-66-NH_2 crystal is the same as the one in **Fig. S6**.
2. The PQDMAEMA was evenly grafted and distributed on each UiO-66-NH_2 crystal.
3. Each monomer QDMAEMA has one N^+.
4. The surface area of UiO-PQDMAEMA equals to that of unmodified UiO-66-NH_2.

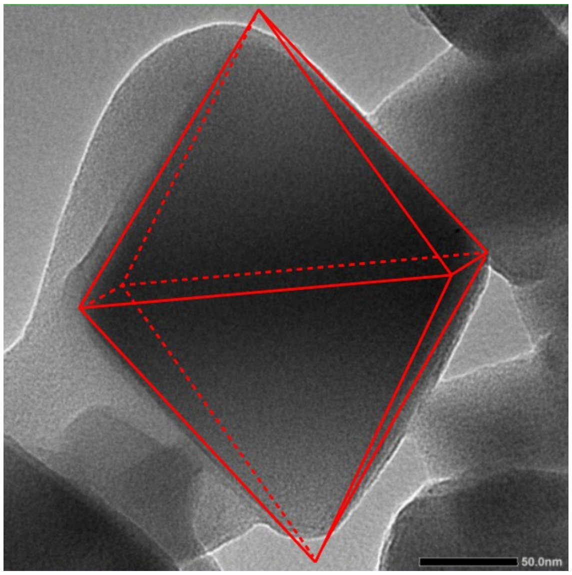

Figure S6. TEM image of a UiO-PQDMAEMA crystal. The red contour is the outline of UiO-66-NH_2 crystal.

UiO-66-NH_2 is an octahedron crystal.[7] As shown in **Fig. S6**, the side length (a) of UiO-66-NH_2 (red contour) is ~200 nm (2×10^{-5} cm). The surface area A can be calculated by:

$$A = 2\sqrt{3}a^2 = 1.38 \times 10^{-9}\, cm^2 \#(S6)$$

The volume of UiO-66-NH$_2$ ($V_{UiO-66-NH_2}$) can be calculated based on the equation:

$$V_{UiO-66-NH_2} = \frac{\sqrt{2}a^3}{3} = 3.77 \times 10^{-15} cm^3 \#(S7)$$

The mass of this UiO-66-NH$_2$ crystal ($m_{UiO-66-NH_2}$) can then be calculated by:

$$m_{UiO-66-NH_2} = \rho_{UiO-66-NH_2} \times V_{UiO-66-NH_2} = 4.8 \times 10^{-15}\ g \#(S8)$$

where $\rho_{UiO-66-NH_2}$ (1.26 g/cm^3) is the crystal density of UiO-66-NH$_2$.[8]

According to the TGA analysis (**Fig. S1**), the average weight percentage of the grafted PQDMAEMA in UiO-PQDMAEMA is 9.93%. Therefore, the mass of grafted PQDMAEMA ($m_{PQDMAEMA}$) is calculated to be $5.3 \times 10^{-16}\ g$. The number of QDMAEMA or the number of N$^+$ (n) can then be estimated by:

$$n = \frac{m_{PQDMAEMA}}{M_{QDMAEMA}} \times N_A = 8.4 \times 10^5 \#(S9)$$

where $M_{QDMAEMA}$ is the molecular weight of monomer QDMAEMA (406 g/mol) and N_A is the Avogadro number (6.02×10^{23}).

The quaternization degree (QD) of UiO-PQDMAEMA can be estimated by:[9]

$$QD = \frac{s_{N^+}}{s_{N^0}} = 48\ \% \#(S10)$$

where s_{N^+} and s_{N^0} are the peak areas of N$^+$ and N^0 in the XPS spectrum in **Fig. S7**, respectively.

The cationic CD of UiO-PQDMAEMA was calculated using the equation:

$$CD = \frac{Q}{A} = \frac{n \times QD \times 1\ N^+}{A} = 3 \times 10^{14} \frac{N^+}{cm^2} \#(S11)$$

where Q is the surface charge and A the surface area.

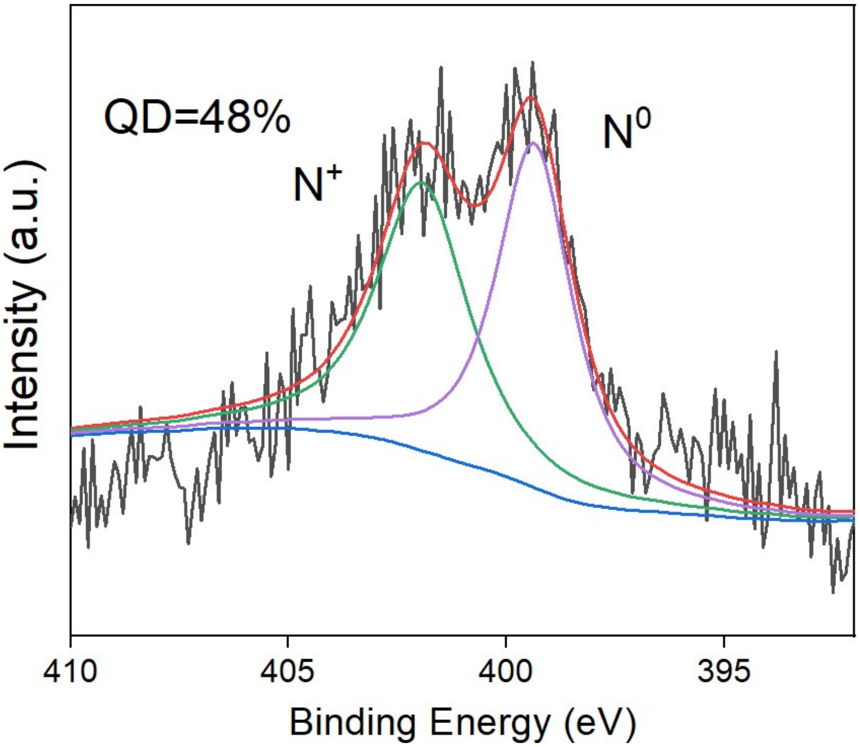

Figure S7. High-resolution N 1s XPS spectrum of UiO-PQDMAEMA.

S9. Leakage Evaluation

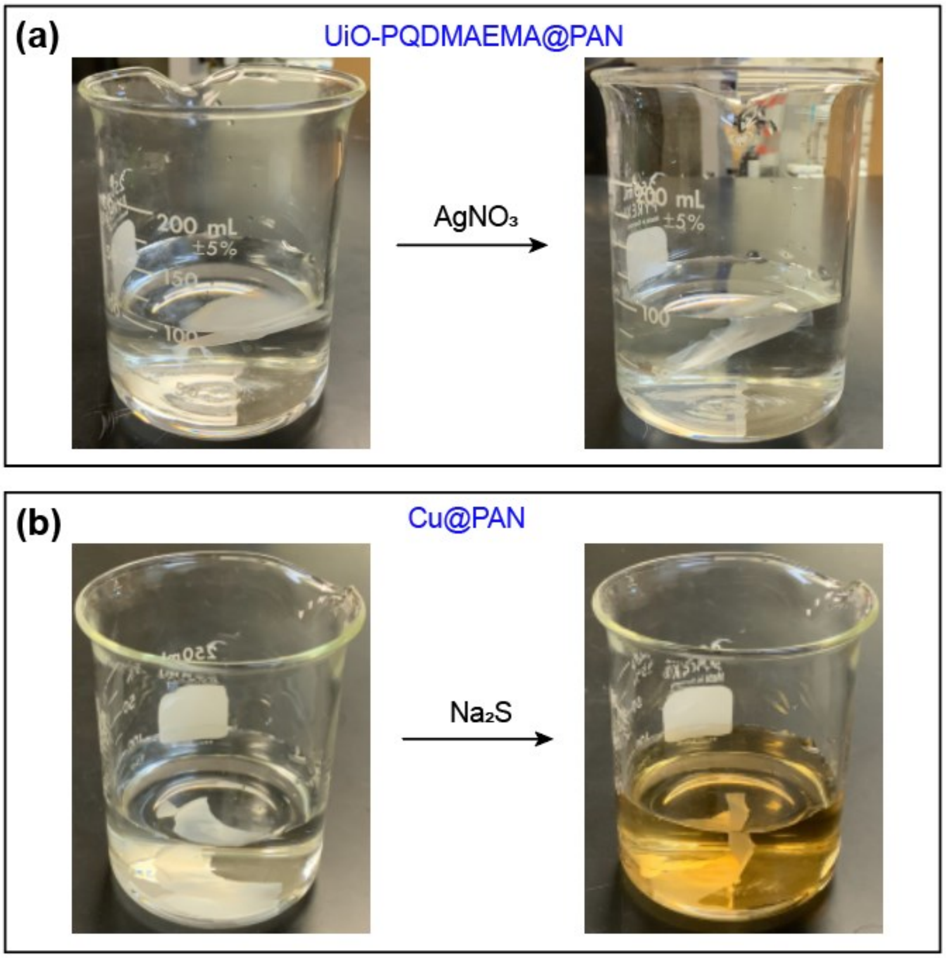

Figure S8. Leakage tests of UiO-PQDMAEMA@PAN (a) and Cu@PAN (b) filters in DI water.

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