[**Supporting Information** to accompany Manuscript]

Mussel-Inspired Immobilization of Silver Nanoparticles toward Antimicrobial Cellulose Paper

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Number of pages: 11 (S1 to S11)

Number of figures: 10

Number of tables: 1

Qualitative Tests with Bromocresol Green Indicator. We performed a quick and simple test to get some indications of our surface modification using bromocresol green (BCG) indicator. Bromocresol green shows green color at pH 3.8 – 5.5, yellow at pH below 3.8 and blue at pH above 5.5. Like other acid-base indicator the color change of the BCG is due to the protonation and deprotonation of the molecule that depends on the nature of the pH of the solution, in our case the capability of the surface to protonate or deprotonate the indicator. We washed several times the cellulose paper samples obtained at each steps and dipped the sample in the BCG indicator solution. We then let the paper air dry and monitored the color of the paper. The colors of the paper samples before and after BCG treatment are shown in Figure S1.

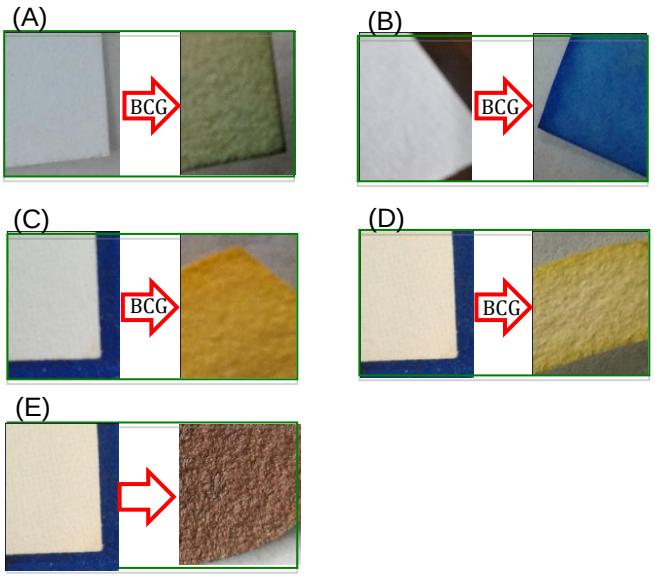

Figure S1. Optical images of the cellulose papers at the different stages of the synthesis before (left side) and after (right side) treatment with bromocresol green (BCG) indicator. (A) regular CP, (B) alkalinated CP, (C) SA-CP, and (D) Dopa-CP. Bromocresol turned the CP green resembling the neutral or slightly acidic nature of the paper surface. When treated with NaOH solution and washed several times the CP gave blue color surface in contact with bromocresol green. After succinylation of the CP the increased carboxylic acid groups on the surface made the SA-CP acidic and deprotonated the bromocresol green to give deep yellow color. Finally, light yellow color was observed for the Dopa-CP when treated with the indicator demonstrating

that the carboxylic acid groups got occupied by dopamine. (E) Optical images of the Dopa-CP (left) and Ag-Dopa-CP (right).

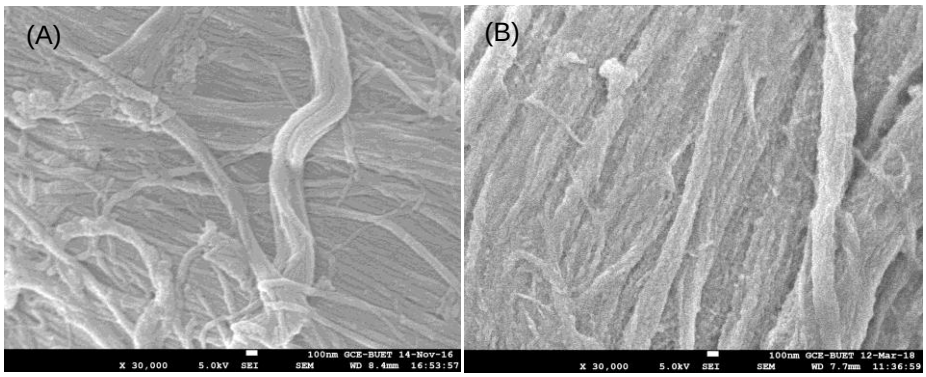

Figure S2. FESEM images of silver nanoparticles decorated (A) cellulose paper, and (B) carboxyl groups functionalized cellulose paper. No significant amount of AgNPs deposited on the surface suggests the need of the dopamine modification of SA-CP in our strategy.

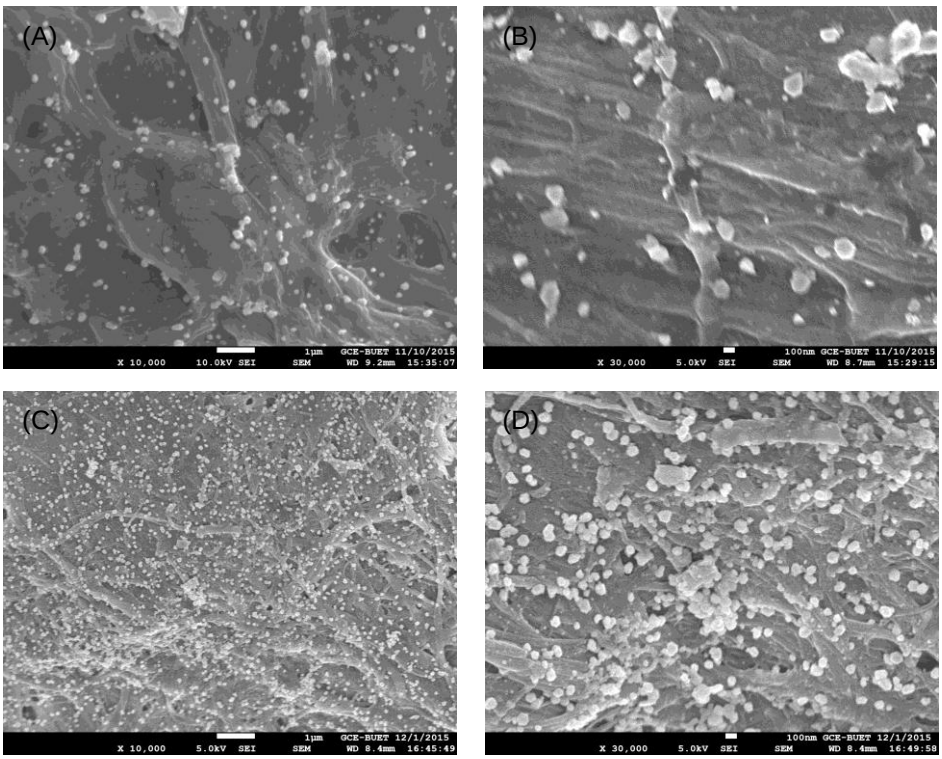

Figure S3. FESEM images of the Ag-Dopa-CP obtained after immersing the Dopa-CP samples in $AgNO_3$ solution (A) 10,000X magnification, and (B) X30,000 magnification; and in ammoniacal $AgNO_3$ solution (C) 10,000X magnification, and (D) 30,000X magnification.

AFM Images of CP and Dopa-CP

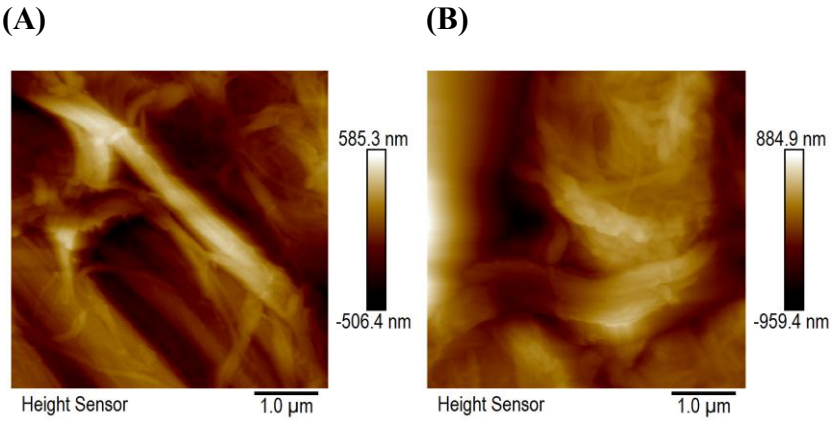

Figure S4. AFM images of the cellulose paper before (left) and after (right) the chemical treatment. The left image is for the fresh CP (A) and the right image is for Dopa-CP (B). The AFM images indicate that the chemical treatment of CP did not change the texture of the paper or the cellulose fibers in the process of the preparation of Dopa-CP.

Deposition of AgNPs on Papers using $AgNO_3$ as an Ag Source. We compared silver nitrate and ammoniacal silver nitrate solutions as sources of AgNPs to investigate the effects of ammonia in the solution. We immersed the freshly prepared Dopa-CP samples in these two solutions separately and kept shaking at 150 rpm in a shaker. After 8 h of the immersion time both the samples were air dried and analyzed by SEM. The FESEM images are shown in Figure S4. It is clearly seen that the presence of ammonia in the $AgNO_3$ solution played an important role on both the size and population of the particles per unit area. Silver nitrate solution without ammonia gave comparatively larger particles and low particle density, which is consistent with previous observation described elsewhere.[1]

XPS Spectra of C1s Region for SA-CP.

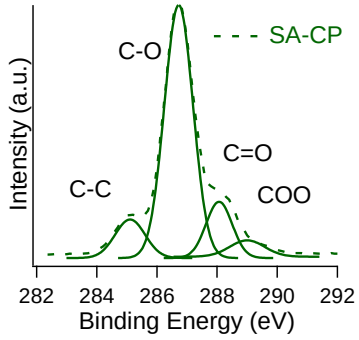

Figure S5. XPS region C 1s of SA-CP. Bond percentage of C-C, C-O, C=O, and COO for SA-CP are calculated as 10.9%, 64.4%, 15.2%, and 9.5%, respectively. The increase of COO bond percentage from that of CP suggests the introduction of COO group via the succinylation of CP. The ratio of the chemical bonds C-O to C=O increased slightly (from 4.2 to 4.6) after the dopamine modification of SA-CP owing to the C-O bonds in the catechol groups on the Dopa-CP surface. This observation also suggests that the catechol groups remain unoxidized during the amidation process and protection of the catechol groups was not required. Had the catechol groups been oxidized we were supposed to observe a decrease in the C-O to C=O ratio for Dopa-CP.

UV–Visible Spectral Analysis. The uv-visible spectral analysis of the ammoniacal silver nitrate solutions after variable immersion time (i.e. 15 m, 4 h, 8 h, 12 h) of Dopa-CP was carried out using a double beam spectrophotometer. The existence of polydopamine moieties in the silver nitrate solution after reaction was particularly studied using this technique. No clear absorption at 285 nm for catecholic groups was observed until we increased the amount of Dopa-CP samples in the silver deposition mixture indicating that the amount of dopamine adsorbed on the cellulose paper surface was very low. After increasing the amount of Dopa-CP seven times compared to the regular amount used for the synthesis keeping the volume and concentration of $AgNO_3$ unchanged we observed significant absorption immediately after 5 m of the reaction. The absorption peak shifted to red and broadened after 4 h. The absorbance became leveled off and no significant increase was further observed suggesting no more adsorbed dopamine or dopamine oligomers on the paper surface left out.

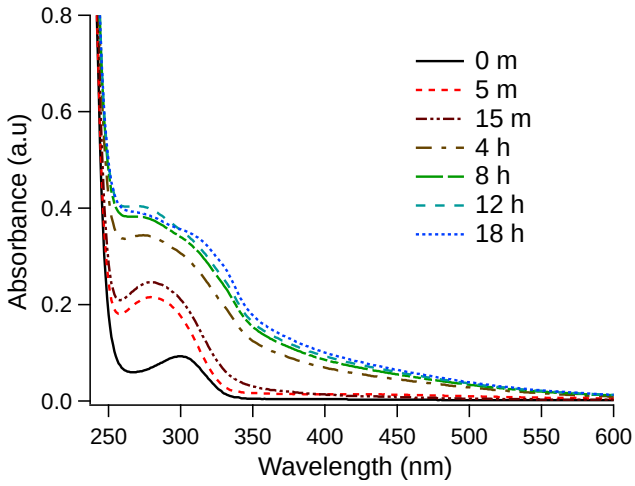

Figure S6. Absorption spectra of the aliquots obtained after immersing the Dopa-CP in ammoniacal silver nitrate solution for variable times.

FESEM Image Processing. We employed MIPAR image processing software to extract the particle size distributions. The size distributions are shown along with the respective FESEM images in Figure S7.

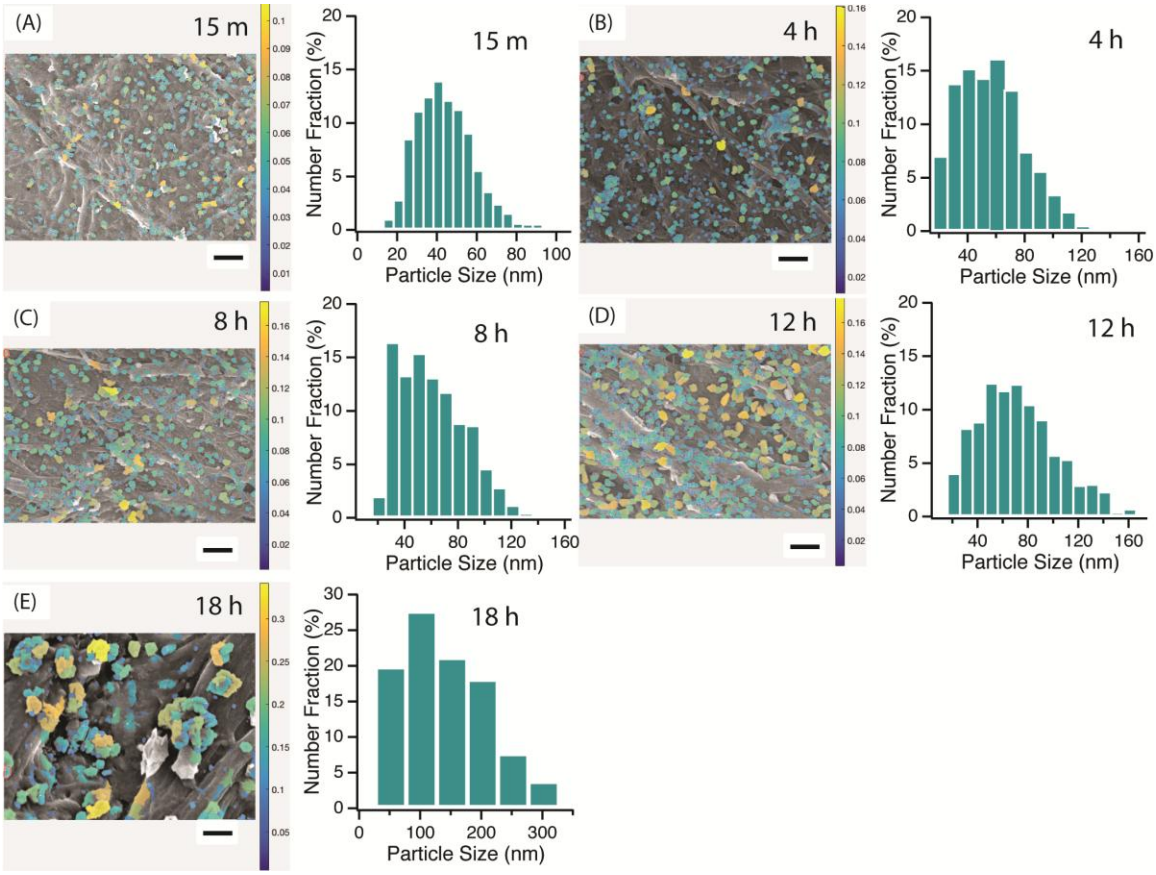

Figure S7. Processed FESEM images and respective size distribution of the AgNPs decorated cellulose papers after processing with MIPAR image analysis software. Image and size distribution of Ag-Dopa-CP after variable immersion time in ammoniacal $AgNO_3$ solution, (A) 15 m, (B) 4 h, (C) 8 h, (D) 12 h, (E) 18 h.

High Magnification Image of Ag-Dopa-CP after 18 h of Deposition

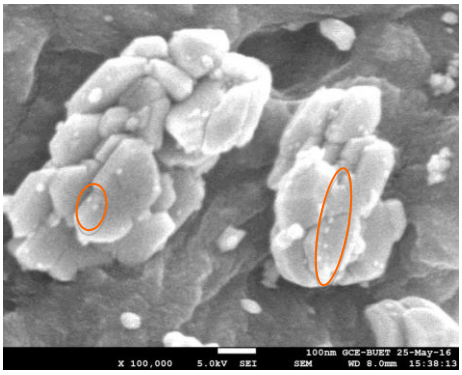

Figure S8. 100,000X magnification image of Ag-Dopa-CP after 18 h immersion in ammoniacal silver nitrate solution. The ellipse indicates the coagulation of very small AgNPs (diameter is ~2 nm), which probably led to the bigger clusters.

Phytotoxic effects on Barley leaf and wheat seeds. The germination of wheat seeds was carried out putting the sterilized (autoclaved and dried) AgNP-Dopa-CP discs aseptically in the culture media setting 95% humidity at 28 ºC and applying light for 16 h and dark for 6 h. No toxic effects by the Ag-Dopa-CP were observed on the germination of the seeds. Besides, the sterilized Ag-Dopa-CP discs were placed on a fresh barley leaf using sterile forceps under the same conditions and examined for the possible appearance of dark circle around the Ag-Dopa-CP disc even after 7 days indicating no phytotoxic effects on the leaf by the synthesized antibacterial papers.

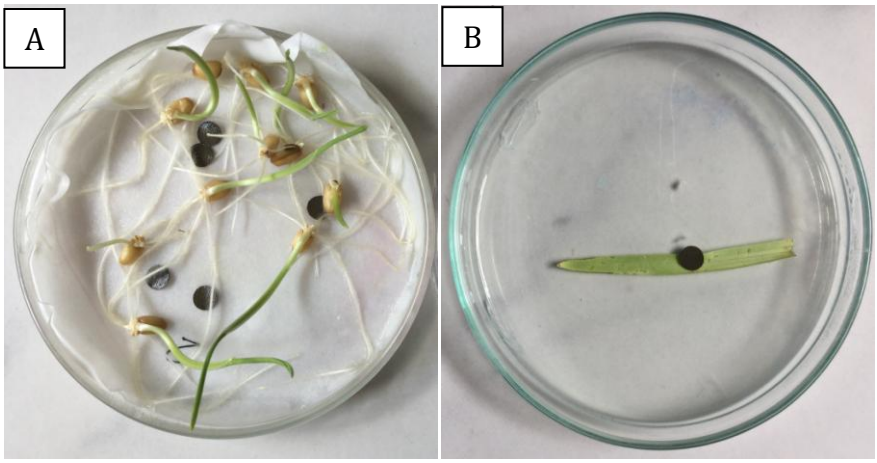

Figure S9. (A) No phytotoxic effect by Ag-Dopa-CP on germination of wheat seeds. The germinations of wheat seeds at 28 ºC in presence of sterilized (autoclaved and dried) Ag-Dopa-CP discs maintaining 95% humidity after applying light for 16 h and dark for 6 h indicate no phytotoxic effects. (B) No phytotoxic effect by Ag-Dopa-CP on barley leaf. The sterilized Ag-Dopa-CP discs were placed on the barley leaf using sterile forceps under the same conditions and no appearance of any dark circle around the paper disc was observed after 7 days.

Mechanical Strength of the Antimicrobial Papers. Mechanical properties are critical for the use of paper in packaging materials. It was therefore required to make sure that the cellulose paper after the modification did not lose its mechanical strength. We utilized a Testresources 100 series electromechanical universal test machine equipped with 1.1 kN load to measure the strain-stress curves of the CP, Dopa-CP and Ag-Dopa-CP samples (Figure S7) and extracted their corresponding tensile strength, which is the maximum tensile stress in the stress–strain curve per unit area (width × thickness). The averaged tensile strengths of all three samples were very close to each other. The slight decrease of the tensile strength of Dopa-CP (8.30 ± 0.15 MPa) from CP (9.01 ± 0.07 MPa) was attributed to the somewhat less availability of hydrogen bonds due to the engagement of the surface $–CH_2OH$ groups in succinylation. On the other hand, the averaged tensile strength of the Ag-Dopa-CP (9.67 ± 0.11 MPa) significantly improved by

16.5%, compared with that of Dopa-CP. We hypothesized that this increased stress force was because the bonding of silver nanoparticles with catechol groups on the surface might increase the extent of linking between the cellulose threads. However, the elongation-at-break of regular CP (4.2%) is higher than that of the paper modified with dopamine, Dopa-CP (2.8%) and AgNPs decorated paper, Ag-Dopa-CP (3.3%). This decrease in elongation-at-break after introducing nanoparticles is consistent with what Guo and coworkers observed when they incorporated Fe_3O_4 nanoparticles to the regular paper.[2]

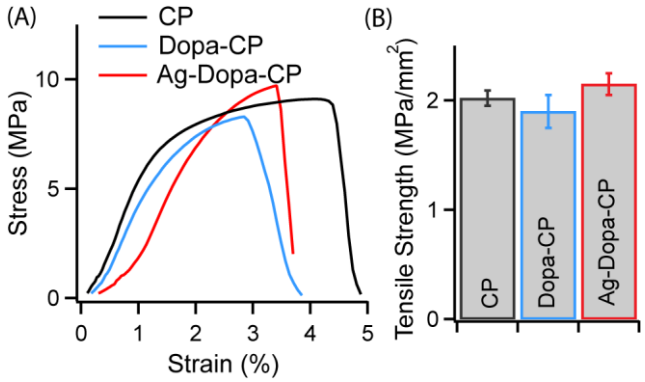

Figure S10. Mechanical properties of the paper samples. (A) stress-strain curves of CP (black line), Dopa-CP (blue line), and Ag-Dopa-CP (red line); (B) tensile strengths of the respective samples.

Table S1. Cost analysis for chemical treatment of 0.5 g (0.023 m^2) Whatman filter paper to obtain antimicrobial paper following a procedure described in the manuscript.

Name of the Chemicals/Solvents	Quantity	Price $/g, $/mL	Cost (in USD)
1. Dopamine hydrochloride	0.0425 g	4.85	0.206
2. Succinic anhydride	2.5 g	0.28	0.70
3. $AgNO_3$	0.25 g	1.5	0.375
4. EDC	0.07 g	7.2	0.506
5. Pyridine	2.2 mL	0.015	0.033
6. Toluene	7.8 mL	0.013	0.10
7. NaOH	1 g	0.014	0.014
8. NH_4OH	5 mL	0.012	0.125

9. Acetone	20 mL	0.011	0.22
10. Absolute ethanol	20 mL	0.014	0.28
11. PBS buffer	20 mL	0.0035	0.070
			Total 2.63

Lab scale cost of the as-synthesized antimicrobial paper is 114 USD/m^2. The cost analysis provided in Table S1 is based on a very small scale synthesis in the laboratory. If we had scaled up the synthesis we could reduce the price significantly. Price of the chemicals and solvents were estimated using the price provided by Sigma-Aldrich, Fisher-Scientific and Merck, India.

REFERENCES

(1) Xie, Y.; Yan, B.; Xu, H.; Chen, J.; Liu, Q.; Deng, Y.; Zeng, H. Highly regenerable mussel-inspired Fe_3O_4@polydopamine-Ag core–shell microspheres as catalyst and adsorbent for methylene blue removal. *ACS Appl. Mater. Interfaces* **2014**, *6*, 8845-8852.

(2) Gu, H.; Guo, J.; Wei, H.; Guo, S.; Liu, J.; Huang, Y.; Khan, M. A.; Wang, X.; Young, D. P.; Wei, S.; Guo, Z. Strengthened Magnetoresistive Epoxy Nanocomposite Papers Derived from Synergistic Nanomagnetite-Carbon Nanofiber Nanohybrids. *Adv. Mater. (Deerfield Beach, Fla.)* **2015**, *27*, 6277-6282.