

Supporting Information for

Bi-Functional Random Copolymers for Robust Superamphiphobic Particulate Coatings

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Hydrolyzation and thermogravimetric Analysis of coated filter paper.

Filter paper in coated filter paper was hydrolyzed using cellulase¹, and the resultant sample was accurately quantified and analyzed by TGA to determine the composition of coating on the filter paper. In a typical run, 0.1325g of coated filter paper was smashed to small pieces with a mortar before added into 2.5 g of 1-butyl-3-methylimidazolium chloride ([BMIM]Cl).¹ After the resulting solution was stirred for 1h at 80 °C, 5mL of deionized water was added to generate suspend dispersion. Then, the suspend dispersion was settled by centrifugation at 10000 g for 10 min. After discarding the supernatant, the precipitate was re-dispersed in 10 mL of deionized water before settled again by centrifugation. This rinsing process was repeated five times. The resultant precipitate was dispersed into 10 mL of critic buffer (pH4.8, 0.05mol/L).¹ Then, 5 mg of cellulose (from *Trichoderma reesei*) was

added and the mixture was stirred for 24 h at 50 °C. The precipitate from resulting dispersion which was settled with centrifugation was rinsed with deionized water. The process for enzymatic hydrolysis and rinsing was repeated thrice. 0.0203g of the resultant sample was obtained after dried under vacuum.

No residue was observed for the uncoated filter paper after hydrolyzed under identical condition, suggesting that the filter paper could be completely hydrolyzed using the enzymatic method. Sol-gelled P4 and silica also suffer from hydrolysis process under identical condition. We observed that no weight changed before and after the enzymatic hydrolysis procedure. These controlled experiments ensure the veracity for evaluating of the composition of coating on the filter paper using TGA method.

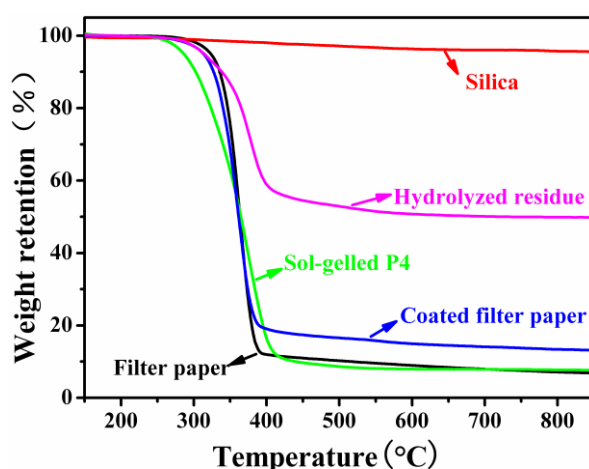


Figure S1. Comparison of TGA curves of silica, sol-gelled P4, filter paper, coated filter paper and hydrolyzed residue of coated filter paper.

Figure S1 compares TGA traces of silica, sol-gelled P4, filter paper, coated filter paper, and hydrolyzed residue of coated filter paper. When the samples were heated from 150 °C to 850 °C, the percentile mass residue R_s for silica at 850 °C was 95.5%. This suggested the thermal stability of silica. Over the same temperature interval,

the mass residue of sol-gelled P4, filter paper, coated filter paper, and hydrolyzed residue of coated filter paper, corresponding to R_{PO} , R_{PA} , R_C , R_{PS} , are 7.60%, 6.83%, 13.05%, 49.76%.

Because filter paper can be easily hydrolyzed in H_2SO_4 solution, we can presume the residue are silica and sol-gelled P4. If we assume that P4 existed in coated filter paper and the sol-gelled P4 had the same TGA characteristics and that the polymer weight fraction in hydrolyzed residue of coated filter paper was x , the following equation applied:

$$R_S(1-x) + R_{PO}x = R_{PS} \quad (S1)$$

Then the x was calculated to be 52.04%.

20.3mg of residue was obtained from 132.5mg coated filter paper, so the silica and sol-gelled P4 were calculated to be 9.7mg and 10.6mg. According to the coating standard condition, the utilizing efficiency of silica and P4 are 97% and 81%. This value showed there are some lose of polymer when coating the filter under the standard conditions. Maybe some of the copolymer had formed sol-gel particles not crosslinking with silica or filter paper and was removed during washing steps.

From the hydrolyzed residue of coated filter paper and the TGA analysis, the mass fraction of silica, sol-gelled P4 and filter paper in coated filter paper are 7.3%, 8.0% and 84.7%. Applied the following equation:

$$R_S \times 7.3\% + R_{PO} \times 8.0\% + R_{PA} \times 84.7\% = R_C \quad (S2)$$

Then the theoretic R_C was calculated to be 13.4%, which is closed to the TGA analysis result of 13.05%.

Thermogravimetric Analysis of coated cotton fabric. The sol-gelled P4 and silica on cotton fabric were also investigated by TGA analysis. Figure S2 compares TGA traces of S2 silica particles, a sol-gelled P4 sample, an uncoated cotton fabric sample, and a coated cotton fabric sample. When the samples were heated from 150 °C to 850 °C, the mass residue of cotton fabric and coated cotton fabric, corresponding to R_{CF} , R_{CCF} , are 5.90%, 13.29%.

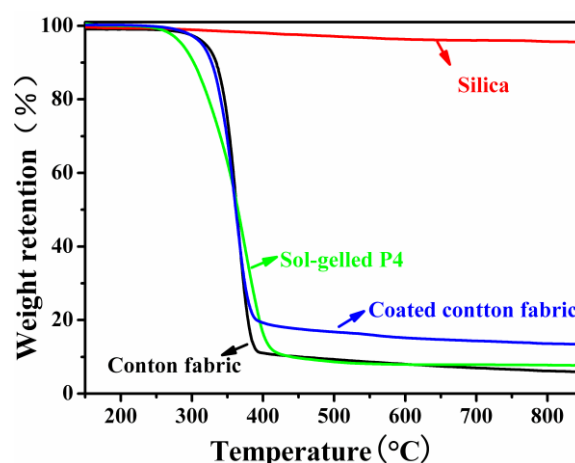


Figure S2. Comparison of TGA curves of S2 silica particles, sol-gelled P4, uncoated cotton fabric, and coated cotton fabric.

There are 49.3mg cotton fabric in 60.2mg coated cotton fabric, which mass fraction should be 81.9%. If we assume that the silica weight fraction was x , and P4 existed in coated cotton fabric had the same TGA characteristics with the sol-gelled P4 and that the polymer weight fraction in coated cotton fabric was y , and the following equation applied:

$$81.9\% + x + y = 1 \quad (\text{S3})$$

$$R_{CF} \times 81.9\% + R_S \times x + R_{PO} \times y = R_{CCF} \quad (S4)$$

Then the x and y was calculated to be 8.06% and 10.04%, respectively. So the silica and sol-gelled P4 were calculated to be 4.8mg and 6.0mg in coated cotton fabric. According to the standard coating conditions, the utilizing efficiency of silica and P4 are 96% and 89%.

Thermogravimetric Analysis of coated glass plate. Three glass plates were coated at the same conditions for weight analysis. The total mass of silica and polymer deposited on one glass plate should be 7.5 mg. The coatings was separated from the glass plates for TGA analysis.

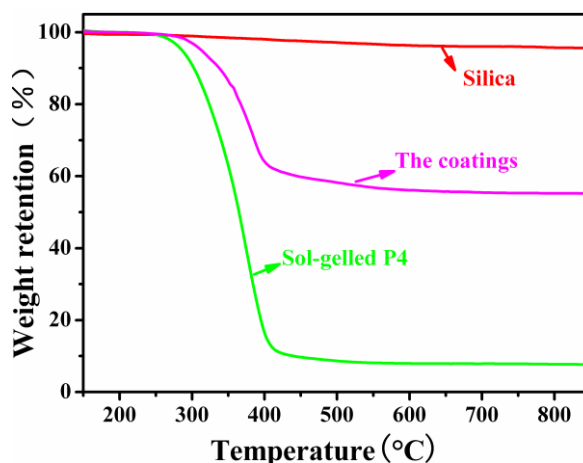


Figure S3. Comparison of TGA curves of silica, sol-gelled P4, and the coatings on glass plates.

Figure S3 compares TGA traces of silica, sol-gelled P4, and the coatings. When the samples were heated from 150 °C to 850 °C, the percentile mass residue of silica, sol-gelled P4, and the coatings, corresponding to R_S , R_{PO} , R_{PS} , are 95.5%, 7.60%, 55.13%. If we assume that the silica weight fraction was x , and P4 existed in the

coatings had the same TGA characteristics with the sol-gelled P4 and that the polymer weight fraction in the coatings was y , and the following equation applied:

$$x + y = 1 \quad (\text{S5})$$

$$R_s \times x + R_{\text{PO}} \times y = R_{\text{PS}} \quad (\text{S6})$$

Then the x and y was calculated to be 54.1% and 45.9%, respectively. So the silica and sol-gelled P4 were calculated to be 4.1mg and 3.4mg in coated glass plate. According to the standard coating conditions, the utilizing efficiency of silica and P4 are 82% and 51%.

References

1. W. Xiao, W. Yin, S. Xia and P. Ma, *Carbohydrate Polymers*, 2012, **87**, 2019-2023.