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Supplementary Information

Enhancing superhydrophobicity of paper via gas-phase silylation using hexadecyltrimethoxysilane and titanium(IV) isopropoxide

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Abstract

The shift toward paper-based packaging is driven by concerns over the non-biodegradability and environmental impact of plastics. Although paper is biodegradable, its poor water resistance limits broader applications. This study aimed to improve the water resistance of paper through chemical vapor deposition (CVD) silylation using different volumes of hexadecyltrimethoxysilane (HDTMS) in the gas phase, which enables deeper penetration into the paper structure than conventional surface coatings. Titanium (IV) isopropoxide (TTIP) was applied as a catalytic primer via spray coating at various concentrations. The results showed that HDTMS alone, at 28 mL·m^{-2}, produced a hydrophobic surface with a water contact angle of 115° on both sides of the paper. Incorporating 10% v/v TTIP and applying a 30 min vapor deposition generated a superhydrophobic surface, increasing water contact angle from 0° (untreated) to 151° and reducing the Cobb value from 435 g·m^{-2} to 17 g·m^{-2} on both sides of the paper. Meanwhile, the treated paper maintained water vapor and oxygen permeability comparable to the untreated sample. FT-IR, XRF, AFM, and SEM analyses confirmed successful silylation. Overall, the gas-phase silylation approach effectively enhanced water resistance while maintaining vapor permeability, showing promise for developing breathable waterproof paper for medical, healthcare, and fresh-produce packaging applications.

Video S1. Water droplet roll-off test on the superhydrophobic paper surface (click below link).



Video S1. Water droplet roll-off test on the superhydrophobic paper surface.

https://youtu.be/_d9NGZCs0GA

Video S2. Water droplet rolling test on the treated paper (click below link).



https://youtube.com/shorts/js-I_uW9u8g?feature=share

Table S1. Effect of treatment temperature on water contact angle and treatment time.

Temperature (°C)	Treatment time (h)	Water contact angle (°) at different reagent volumes (mL)		
		0.1	**0.5**	**1**
65	24	n/a	n/a	103 ± 4
80	3	n/a	n/a	118 ± 4
100	1	n/a	n/a	130 ± 2
	2	n/a	n/a	129 ± 1
	3	n/a	n/a	130 ± 2
150	1	142 ± 1	143 ± 2	142 ± 2
	2	n/a	n/a	143 ± 1
	3	n/a	n/a	143 ± 2
200	1	n/a	n/a	135 ± 2* Paper browning*

Table S2. Comparison between liquid-phase silane coating and gas-phase silylation.

Author/reference	Coating/modification method	Silane amount and processing time	Substrate and surface topography	Contact angle
Ardakkyzy et al. [1]	**Sol–gel dip coating**	0.2 g HDTMS or triethoxy(octyl)silane in 20 mL ethanol; 15 h immersion + 30 min drying at 80 °C	Cellulose filter paper; **HDTMS: uniform, complete nanoparticle coverage**	**139.2–147.7°**
Peng et al. [2]	Knife wet film coating	0.5 M methyltrichlorosilane (MTS) and octadecyltrichlorosilane (OTS) in toluene; 10 min reaction + 10 min drying at 40°C	carboxymethyl cellulose /PVA/chitosan-coated paper; **MTS: uniform surface; OTS: uneven/warped surface**	MTS: **96.16°**; OTS: **100.32°**; MTS/OTS: **119.38**
Pacaphol et al. [3]	Roll-coating	0.2 wt% to 1.5 wt% HDTMS or POTS; 3 h reaction + 18 h aging + 1 h curing at 120°C	White-back duplex paperboard; **300 µm wet film**	**140.8 ± 1.6°**
Rafieian et al. [4]	CVD	3 mL HDTMS; CVD at 155 °C for 1 h + vacuum drying	Cellulose nanofiber (CNF) aerogel **Porous CNF network retained; slightly denser after CVD**	121.1–138.9°
This work (gas-phase silylation)	CVD	0.1 mL HDTMS; 30 min at 150°C	Blotting paper; no continuous coating film, with the porous fibrous structure retained	151° and SA 4.9°

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