Design of a Waste Paper-Derived Chemically 'Reactive' and Durable Functional Material with Tailorable Mechanical Property Following an Ambient and Sustainable Chemical Approach

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Abstract: Controlled tailoring of mechanical property and wettability is important for designing various functional materials. The integration of these characteristics with waste materials is immensely challenging to achieve, however, it can provide sustainable solutions to combat relevant environmental pollutions and other relevant challenges. Here, the strategic conversion of discarded and valueless waste paper into functional products has been introduced following a catalyst-free chemical approach to tailor both the mechanical property and water wettability at ambient conditions for sustainable waste management and controlling the relevant environmental pollution. In the current design, the controlled and appropriate silanization of waste paper allowed to modulate both the a) porosity and b) compressive modulus of the paper-derived sponges. Further, the association of 1,4conjugate addition reaction between amine and acrylate groups allowed to obtain an unconventional waste paper-

Introduction

In the past, mechanically durable materials have been fabricated extensively for various prospective energy and health related applications.^[1–3] The strategic integration of carbon nanotubes,^[4,5] graphene derivatives,^[6–8] cellulose nanocrystals,^[9] etc. impart the required mechanical durability for practical applications. Li *et al.*, developed ultralight, compressible covalent organic framework aerogel reinforced with reduced

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	Supporting information for this article is available on the WWW https://doi.org/10.1002/asia.202100475

derived chemically 'reactive' sponge. The appropriate covalent modification of the residual reactive acrylate groups with selected alkylamines at ambient conditions provided a facile basis to tailor the water wettability from moderate hydrophobicity, adhesive superhydrophobicity to non-adhesive superhydrophobicity. The embedded superhydrophobicity in the waste paper-derived sponge was capable of sustaining large physical deformations, severe physical abrasions, prolonged exposure to harsh aqueous conditions, etc. Further, the waste paper-derived, extremely water-repellent sponges and membranes were successfully extended for proof-ofconcept demonstration of a practically relevant outdoor application, where the repetitive remediation of oil spillages has been demonstrated following both selective absorption (25 times) of oils and gravity-driven filtration-based (50 times) separation of oils from oil/water mixtures at different harsh aqueous scenarios.

graphene oxide which exhibits excellent absorption and electrochemical properties.^[7] Wang et al., fabricated highly compressible boron nitride nanotubes aerogel reinforced with reduced graphene oxide with superior mechanical property which was impossible to attain without the reinforcement.^[8] Apart from the commonly used nanomaterials,^[10-12] different other approaches^[13-19] – including association of elastomers, MXenes, electrodeposited nano-alloys etc. have been introduced to develop mechanically durable materials embedded with extreme liquid wettability. However, such approaches are inadequate to tailor the chemical functionality and water wettability - due to the lack of any residual chemical reactivity. In the past, chemically reactive interfaces have been designed adopting click chemistry,^[20,21] azlactone ring opening reaction,^[22] Schiff base reactions^[23] etc. for modulating the chemical functionality, however, such reported materials are inappropriate for tuning the mechanical property. Nevertheless, the demonstration of consecutive tailoring of mechanical property and chemical functionality in the same material is rare in the relevant literature.

In the past, discarded plant bio-mass was transformed into functional material to combat potential environmental pollutions.^[24,25] In that context, here, waste paper that generally poses major concerns including deforestation, water consumption and pollution, landfills, air pollution etc.^[26,27] has been extended to transform into a functional material with tailorable mechanical property and chemical functionalities – following a

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facile and scalable chemical reaction at ambient conditions. In the past, some approaches were adopted to develop paper based functional materials – including rewritable and functional chromogenic interfcaes,^[28] electrochemical devices for on-site bio-sensing,^[29] energy storage devices,^[30] combating electromagnetic pollution^[31] and so on.

Recently, a few water-repellent papers have been successfully developed through the strategic association of bio-inspired wettability for demonstrating controlled droplet manipulation, microbial resistance, self-cleaning performances etc.^[18,32-37] The direct transformation of waste paper into durable and functional materials following a facile and scalable synthesis process is yet to be introduced in the literature.[32-37] For example, Li et al. oxidized office paper with sodium chlorite followed by carbonization at 1000°C under inert atmosphere to develop a compressible carbon aerogel, on which the water droplet beaded with advancing contact angle ~ 150°.^[34] Further, Li et al. utilized Fe₃O₄ modified office paper adopting oxidation and pyrolysis method (200-1000 °C) for fabrication of highly salt resistant, electrically conductive carbon aerogel.[36] In another report, Yue et al. developed a banana peel/waste paper derived hydrophobic, compressible hybrid aerogel with water contact angle ~149° by adopting the pyrolysis approach (900°C).[37] Furthermore, the previously reported approaches lacked the ability to tailor the compressive modulus of the synthesized materials, which could prove beneficial for obtaining the ideal substrate for repetitive and prolonged oil/water separation performance of the paper derived materials. Furthermore, some compressible spongy materials with porous network have already been demonstrated for prospective applications as thermal insulators.^[38-40] In general, the existing approaches for deriving functional superhydrophobic materials from waste paper primarily depends on the high temperature pyrolysis process,^[32-35,39-42] which is an energy consuming, sophisticated approach that leads to secondary pollution. Hence, a facile, economic design for converting waste paper into a chemically 'reactive' sponges with the scope to tailor both the mechanical property and chemistry would provide an avenue for a) develloping eco-friendly/economic thermal insulators, b) prospective use in efficient remediation of oil spillages and c) controlled droplet manipulation.

In this current design, different types of waste papers (i.e. tissue paper, office paper, newspaper, cardboard paper) were reconstructed into lightweight, porous, highly compressible, covalently cross-linked, chemically 'reactive' sponges with tailorable mechanical property and chemical functionality. The strategic condensation of the cellulosic hydroxyl groups (of waste paper) with the hydroxyl groups of an amine functionalized binder i.e. 3-(2-aminoethylamino)-propyltrimethoxysilane (AEPTMS) during the sponge fabrication process, provided a facile basis for the catalyst-free 1,4-conjugate cross-linking of the amine functionalized cellulose with dipentaerythritol pentaacrylate (5Acl). This simple cross-linking process induced the desired chemical 'reactivity' in the waste paper derived sponge. After the association of covalent cross-linking process, the residual acrylate groups in the waste paper derived sponge provided a simple basis to tailor the water wettability from hydrophobic, adhesive superhydrophobic to non-adhesive superhydrophobic (~ 25° to 161°) through association of the desired post covalent modification of the chemically 'reactive' sponge with the appropriate alkylamines following the same 1,4-conjugate addition reaction at ambient conditions. The embedded superhydrophobicity in the waste-paper derived spongy material could sustain various harsh physical abrasions including sand paper abrasion, sand drop test and repetitive manual compression (1000 times) with 60% strain. Moreover, the long term (30 days) exposure to UV radiation and chemically contaminated aqueous phases including extremes of pH (1 and 12), surfactant contaminated water, river and sea water failed to deter the embedded superhydrophobicity of the waste paper derived functional material. Such a durable and highly compressible superhydrophobic sponge was extended to examine its performance or suitability towards practically relevant challenging settings. As a proof of concept of demonstration, selective absorption based repetitive (25 times) cleaning of a wide range of oil/oily contaminants at chemically harsh aqueous settings with high absorption capacities (upto 4000 wt%) has been successfully demonstrated. The analogous waste paper derived membranes were also extended for repetitive (50 times) gravity-driven filtration-based separation of oils from oil/water mixtures even at chemically contaminated aqueous environments without compromising the associated anti-wetting property. Thus, such strategic association of facile and robust chemistries with the valueless waste paper at ambient conditions could be further useful for developing smart bio-interfaces, thermal insulators, open-microfluidic devices etc.

Results and Discussion

Fabrication of Waste Paper Fibers derived Mechanically Durable Sponges

In this report, waste paper has been converted into a functional material with the ability to tailor both the 1) mechanical property and 2) chemistry following a catalyst-free, facile chemical approach. In this context, we have introduced a rational and unique strategy for developing waste paper derived chemically 'reactive' deformable sponges following a facile and environment friendly fabrication procedure. The integration of AEPTMS and 5Acl as the binder and covalent cross-linker, respectively, allowed to 1) modulate the mechanical property and 2) induct chemical reactivity in the waste paper derived material as shown in Scheme 1. Further, the appropriate chemical modification of the waste paper derived chemically 'reactive' sponge with the selected alkylamines following the 1,4-conjugate addition reaction allowed to tailor the water wettability. In the recent past, Baidya et al. developed a fluorinated cellulose nanofiber based superhydrophobic coating, where perfluorooctyltriethoxysilane and AEPTMS were covalently integrated with the hydroxyl groups of cellulosic nanofibers.^[18] The polymerization of AEPTMS imparted mechanical stability to the silane modified cellulose nanofibers in





Scheme 1. Schematic illustrating the facile and robust conversion of waste papers into a deformable and chemically 'reactive' sponge. The covalent association of an amine modified silane binder i.e. 3-(2-aminoethylamino)-propyltrimethoxysilane (AEPTMS) with the hydroxyl groups of cellulose (waste paper) during the sponge fabrication process paved an avenue to tailor the mechanical property of the sponge by varying the concentration of the binder used. The catalyst-free 1,4-conjugate addition reaction between the primary amine of the binder with a multi-functional cross-linker provided a facile basis to induce residual chemical 'reactivity' in the waste paper derived sponge. The residual acrylate reactivity was exploited to alter the water wettability of the sponge following the Michael addition reaction between with alkylamines of varying chain lengths.

comparison to the unmodified one. Inspired from this report, in the current study, the association of AEPTMS and chemically 'reactive' cross-linking process with the waste paper allowed to tailor the mechanical property and water wettability respectively, in the waste paper derived sponge denoted as WPDS. Shredded pieces of a model waste paper (i.e. tissue paper) in aqueous media were stirred under room temperature for 6 hours and thereafter, this mixture was poured into cylindrical molds followed by freeze drying to obtain an inherently hydrophilic sponge (beaded water immediately soaked with contact angle of 0°), denoted as $WPS_{control}$ as shown in Figure 1A, B. WPS_{control} underwent permanent deformation on application of an external load (500 g) and failed to regain its original shape as shown in Figure 1C, D. FESEM images of WPS_{control} revealed compact and fibrous domains as shown in Figure 1E, F, the compact network is attributed to the distortion of the skeletal framework of the fragile WPS_{control} while manual handling. However, the strategic in situ association of AEPTMS with this disintegrated waste paper fibers in aqueous media followed by freeze drying yielded a hydrophilic and spongy material that can regain its deformed shape after removal of the external load (500 g) as shown in Figure 1G-J. Thus, the addition of 3.25 wt% AEPTMS w.r.t. 1.96 wt% waste paper denoted as $WPDS_1$ (where 1 denotes the concentration of AEPTMS added, refer to Table S1), resulted in a highly porous interconnected spongy network as shown in Figure 1K, L. Increasing the concentration of AEPTMS further led to change in the morphology and porosity of the as prepared sponges (WPDS₂ and WPDS₃) as shown in Figure S1A–H and Table S1. This change in morphology is attributed to the polymerization of AEPTMS resulting in a polymeric network. The integration of AEPTMS with the waste paper sponge was validated through XPS analysis as shown in Figure 1M, where the additional peaks corresponding to N and Si were exhibited after AEPTMS modification. De-convoluted XPS for C 1s of waste paper sponge (WPS_{control}) is shown in Figure S2B, where the peaks at 284.5, 286.5 and at 287.6 eV corresponds to C--C, C--O and O-C-O respectively. After the association of AEPTMS, the



Figure 1. A–D) Digital image (A) and water contact angle image (B) illustrating the hydrophilic waste paper sponge (WPS_{control}) that was compressed with an external load of 500 g (C) such that WPS_{control} underwent permanent deformation on releasing the load (D). E, F) FESEM images at low (E) and high (F) magnifications revealing the morphology of WPS_{control}. G–L) Digital image (G) and water contact angle image (H) illustrating a waste paper derived sponge that was developed by *in situ* covalent modification of waste paper with an amine modified silane binder (AEPTMS). On compressing the silane modified waste paper derived sponge, (WPDS₁ where 1 denotes the concentration of AEPTMS) with an external load of 500 g (I), WPDS₁ was capable of completely recovering its dimensions on releasing the load (J), thus, validating the role of AEPTMS in imparting mechanical durability to the sponge. K, L) FESEM images at low (K) and high (L) magnification of the silane modified waste paper derived sponge, WPDS₁ revealed the presence of an interconnected fibrous and porous morphology. M) XPS spectra of the AEPTMS modified waste paper sponge, WPDS₁ which reveals the presence of N 2p and Si 2s,2p peaks indicating the association of AEPTMS with waste paper. N) ATR-FTIR analysis of AEPTMS monomer exhibits a peak at 1078 cm⁻¹ corresponding to the Si-O–C bond of the monomer (black) which depleted entirely and a new peak at 1028 cm⁻¹ corresponding to the Si-O–Si bond appeared for the AEPTMS polymer which confirmed the silane polymerization process (red). O) Bar diagram accounting for the varying compressive modulus values of the sponges developed using waste paper doped with different concentrations of the binder.

relative peak intensity corresponding to C-O depleted and slightly shifted (to 286.1 eV) as shown in Figure S2E, which was attributed to the covalent bonding between Si of (AEPTMS) with the hydroxyl groups of cellulose.^[18] Further, the polymerization of AEPTMS in aqueous media was confirmed through the standard FTIR analysis. The AEPTMS monomer exhibited the characteristic Si-O-C stretching peak at 1078 cm⁻¹. On polymerization of AEPTMS, the peak at 1078 cm⁻¹ diminished and a new peak at 1020 cm⁻¹ appeared which corresponds to the Si-O-Si stretching as shown in Figure 1N. Moreover, Energy Dispersive X-ray (EDX) analysis of the sponges confirmed the doping of AEPTMS into the sponges, where the peaks corresponding to N and Si elements were exhibited in addition to the C and O peaks of cellulose as shown in Figure S3A-D. The uniform and varying distribution of C, O, N, Si was confirmed with elemental mapping for all the AEPTMS associated sponges as shown in Figure S4A-T. Hence, EDX analysis confirmed the homogenous integration of AEPTMS with the waste paper mixture, providing a uniform skeletal network of AEPTMS all throughout the sponges. The compressive stress-strain analysis further revealed that AEPTMS modification played the major role in tailoring the compressive modulus of the sponges that were modified with different wt% AEPTMS. The compressive modulus values decrease in the order as $WPDS_3\!>\!WPDS_2\!>\!WPDS_1\!>\!WPDS_{0.5}\!>\!WPS_{control}$ as shown in Figure 10. In-plane compression test was further performed to evaluate the shape recovery of the AEPTMS associated sponge after application of different percentage of external strain. The physically deformed WPDS₁, which was subjected to 20%, 40% and 60% compressive strain, recovered its original shape, once the applied load was released as evident from the hysteresis curve as shown in Figure S5B. Moreover, the cyclic compressive study of WPDS_{0.5}, WPDS₁, WPDS₂ and WPDS₃ revealed that the as fabricated sponges exhibited satisfactory recovery even after 1000 cycles of compression (Figure S6B–E), except the WPS_{control}. A permanent physical deformation was observed for WPS_{control} after the 1st cycle of compression as shown in Figure S6A. Thus, the controlled association of AEPTMS with waste paper allowed to adopt a route for tailorable and durable mechanical property.

Induction of Chemical 'Reactivity' in the Waste Paper Derived Highly Compressible Sponges

The waste paper derived functional substrates developed till date for a wide range of applications are reported in Table 1. However, the reported materials lack the covalent cross-linking network and none of the reported approaches provides an avenue to associate diverse and desired chemical functionalities (Table 1). In this work, the simple and catalyst-free 1,4conjugate addition reaction between amine and acrylate has been adopted to associate both i) covalent cross-linkage in the sponge and ii) readily 'reactive' residual acrylate groups for post covalent modification with different nucleophiles at ambient conditions.^[45,46] The XPS analysis of the deconvoluted N 2p peak (at ~400 eV, Figure 2A) of WPDS₁ revealed the presence of primary amine moiety in the paper sponge after addition of binder. The induction of chemical reactivity in the paper sponge was achieved through the reaction of the primary amine groups of the binder with a multifunctional acrylate cross-linker(5Acl) following the catalyst-free 1,4-conjugate addition reaction between amine and acrylate groups at ambient conditions (Scheme 1). The presence of 'reactive' acrylate groups in the waste paper sponge rendered it highly reactive at ambient conditions towards some specific nucleophiles (Figure 2B). The post covalent modification (Figure 2C) of the chemically 'reactive' waste paper sponge with amine containing small molecule, octadecylamine (ODA) transformed the hydrophilic sponge into a superhydrophobic sponge with water contact angle (WCA) ~160° as shown in Figure 2D, E. The successful modification of residual acrylate groups in the amine functionalized waste paper derived sponge was further confirmed through standard FTIR analysis.^[43,44] The appearance of the peak at 1408 cm⁻¹ and 1730 cm^{-1} corresponding to the C–H stretching of β carbon of the vinyl group and the carbonyl stretching respectively confirmed the presence of the multifunctional acrylate crosslinker, i.e. 5Acl. (Figure 2F, red). These FTIR signatures were not observed in the WPDS₁ prior to treatment with 5Acl as shown in Figure 2F (green). Interestingly, after post modification of the chemically 'reactive' waste paper derived sponge with ODA the FTIR peak intensity at 1408 cm⁻¹ decreases with respect to the normalized carbonyl peak at 1730 cm⁻¹ (which serves as the internal standard) as shown in Figure 2F (black). Hence, the FTIR analysis confirms the successful post modification of the paper sponge with ODA. As shown in Figure S7E, F, 3.25 wt% AEPTMS w.r.t. 1.96 wt% of waste paper (denoted as waste paper derived superhydrophobic sponge, WPDSHS₁) is the minimum concentration of AEPTMS required to display superhydrophobicity. However, the waste paper derived chemically 'reactive' sponge with 1.65 wt% AEPTMS (denoted as WPDSHS_{0.5}) after post modification displayed only hydrophobicity with water contact angle 144° as shown in Figure S7A, B. The sponges developed with concentrations above 3.25 wt% of AEPTMS (denoted as WPDSHS₂ and WPDSHS₃) successfully displayed the extreme anti-wetting property with advancing water contact angles above 150° and contact angle hysteresis below 10° as shown in Figure S7I, J, M, N and Table S2. Moreover, the presence of residual chemical reactivity provided a facile basis to tune the wettability from 25° to 161° following the 1,4-conjugate addition reaction of residual acrylates with amine containing lower analogues of ODA as shown in Figure 2G and Figure S8A-V. After the modification of chemically 'reactive' sponge with ODA, non-adhesive superhydrophobicity was noted, where a stream of water readily bounced off from the surface of WPDSHS₁ as shown in Figure 2H and Movie 1. Moreover, on submerging WPDSHS₁ underwater, a shiny interface was observed which confirms the presence of a metastable trapped air layer that is responsible for the existence of heterogeneous wettability as shown in Figure 2I. The waste paper derived superhydrophobic sponge displayed contrasting water and oil wettability, wherein the oil droplet was soaked immediately with oil contact angle 0° as shown in Figure 2J, K. Such contrast in liquid wettability is beneficial for remediation of oil spillages following both selective absorption and filtration processes. Moreover, the post treatment with 5Acl and ODA did not alter the mechanical durability as confirmed from the compressive modulus of the sponge before and after post chemical modification as shown in Figure S9A (black line), thus, reassuring that AEPTMS is responsible for the enhanced mechanical durability of the sponges. Moreover, the porosity remained unaltered after post covalent modification as shown in Figure S9A (red line).

Irrespective of the type of waste paper, this facile fabrication procedure could be further extended for developing compressible superhydrophobic sponges using different types of waste papers, including office paper (A4 paper), newspaper and cardboard paper as shown in Figure 3A, F and Table S3. The water droplets beaded with contact angles above 150° and contact angle hysteresis below 10°. Even the mixture (1:1:1:1 weight ratio) of all the different types of waste papers (tissue paper, cardboard, newspaper and office paper) remained efficient to provide a superhydrophobic spongy material as shown in Figure 3G, H and Table S3. The compressive modulus of the synthesized superhydrophobic sponges varied based on the nature of the waste paper even though the silanization and post-covalent modification process remains unchanged. Interestingly, the compressive modulus was noticed to be maximum (1285 kPa) for the spongy material that was prepared using the mixture of waste papers. Moreover, the porosity of the different sponges decreased in the order as i.e. newspaper > office paper > cardboard paper > mixture of papers. The order of porosity and compressive modulus followed a completely opposite order as shown in Figure 3I since increased porosity reduces the cross-sectional area for stress tolerance. The maximum compressive modulus (1285 kPa) and minimum

Table 1. Illustrating the utilization properties and the associated duration	of waste paper as the major constituent or subs ability of the functional substrates has also been	strate for remoulding into various fu compared in the table.	unctional material following var	ious chemical approaches for different rel	levant applications. The embedc	led physical
Components Used	Chemistries Involved/Reaction Conditions	Major Physical Properties	Physical Durability	Chemical Durability	Applications	Ref.
Filter Paper	Electrochemical device assimilated on paper used as substrate	Electrical Conductivity	Not Performed	Not Performed	Biosensing	[27]]
Newspaper, Office Paper, Cardboard Paper, Glossv Brochure Paper	Metallic resonator pattern drawn using silver ink on the paper substrates	Electromagnetic shielding	Not Performed	Not Performed	Electromagnetic Pollution	[29]
Cellulose Filter Papers	Condensation of hydroxyl condensation of hydroxyl groups with fluorinated silane 0. plasma etching/Heating (50°C–130°C)	Extremes of Liquid Wettability	Not Performed	Not Performed	Microfluidic Devices	[30]
Office Paper	Used as substrate without any modification	Extremes of Liquid Wettability	Not Performed	Performed only at various pH	Oil/Water Separation	[31]
Office Paper, Cardboard Paper, Newspaper	Acidic Oxidation Carbonization (at 1000°C in N, atmosohere)	Extreme Water Wettability	Not Performed	Not Performed	Oil/Water Separation	[32]
Office Paper	Carbonization (at 1000°C in N. atmosphere)	Electrical Conductivity, Extreme Water Wettability	Not Performed	Not Performed	Electrocatalyst Oil/Water Separation	[33]
Office Paper	Carbonization (200–1000 °C n Na atmosphere) O. Plasma	Electrical Conductivity, Magnetic, Janus Water Wettability	Not Performed	Performed only at saline conditions	Heavy metal processors soluble organics and Oil/Water Separation	[34]
Office Paper/Banana Peel	Carbonization (at 900 °C in N2 atmosphere)	Extreme Water Wettability	Not Performed	Performed (24 hours exposure to acidic and basic pH, salt water, river water and organic solvents	Oil/Water Separation	[35]
Office Paper	Heating (50–90°C)	Extremes of Liquid Wettability, Photochromism	Not Performed	Not Performed	Photochromism	[39]
Waste Paper	Carbonization (at 1000°C in N. atmosphere)	Electrical Conductivity Thermal Conductivity	Not Performed	Not Performed	Wearable Device	[40]
Office Paper	Hydrothermal Processing (180 °C) Carbonization (800 °C)	Electrical Conductivity	Not Performed	Not Performed	Ultracapacitor Electrodes	[41]
Office Paper	Draining, Pressing and Drying	Electrical Conductivity	Not Performed	Not Performed	Strain Sensor	[42]
Waste Paper (Tissue Paper, Office Paper, Cardboard paper and Newspaper)	1,4-Conjugate Addition Reaction	Tailorable Water Wettability and Compressive Modulus	Performed (Sand paper abrasion, sand drop test, load compression and manual squeezing)	Performed (30 days exposure to acidic and basic PH, surfactants, sea water, river water, organic solvents and UV radiation)	Oil/Water Separation	Current Work

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Waste Paper Sponge with Tailorable Chemical Reactivity C- NH В С Α R-NH 1,4-Conjugate Addition Reaction Chemically 'Reactive' Waste Paper derived Sponge Waste Paper Sponge With Tailorable Wettability 390 395 400 405 After Post Binding energy (eV) Modification Waste Paper derived Superhydrophobic Sponge Chemically Reactive' Sponge D Е AEPTMS Integrated Sponge θ_{water}~160° 1408cm⁻¹ C-H Stretching 1730cm⁻¹ of β carbon of C=O Stretching G Vinyl group 180 25 800 1000 1200 1400 1600 1800 2000 Static Water Contact Angle (°) 0 160 Wavenumber (cm⁻¹) **Hysteresis** 20 140 Н 120 15 100 Contact Angle Water Oil 80 10 60 Κ 40 5 20 θ_{Oil}~0° 0 0 Decylamine Octadecylamine Butylamine Pentylamine Hexylamine Octylamine

Figure 2. A) De-convulated XPS spectra of N 2p of the waste paper derived sponge that was covalently associated with AEPTMS. The peak at 400 eV indicates the presence of primary amines in the fabricated sponge owing to the presence of AEPTMS. B, C) Schematic illustrating the 1,4-conjugate addition reaction of the chemically 'reactive' waste paper derived sponge with amine containing small molecules that provides an avenue to tailor the water wettability of the sponge. D, E) Digital image (D) and water contact angle image (E) of the beaded water droplet on the waste paper derived sponge, WPDSHS₁ that was post modified with octadecylamine (ODA). F) ATR-FTIR analysis of the chemically 'reactive' waste paper derived sponge (red) revealed the presence of paeks at 1408 cm⁻¹ and 1730 cm⁻¹ which corresponds to the symmetric deformation of the C–H bond of β carbon of the vinyl group and carbonyl stretching frequency respectively. However, the AEPTMS modified waste paper derived sponge (WPDS₁) did not exhibit the mentioned peaks (green). The reduction in the peak intensity at 1408 cm⁻¹ with respect to the normalized carbonyl peak at 1730 cm⁻¹ confirmed the covalent linkage of the residual acrylate functionalities with the amine containing small molecule i.e. octadecylamine (black). G) Bar diagram representing the static water contact angles (black) and contact angle hysteresis (red) of the beaded water droplet on the waste paper derived sponge that was modified with different amine containing small molecules including butylamine, pentylamine, octylamine, decylamine and octadecylamine. H) Digital image demonstrating the bouncing of a stream of water from the surface of the waste paper derived sponge, WPDSH₅. I) The waste paper derived superhydrophobic sponge, WPDSH₅. I) The waste paper derived superhydrophobic sponge, WPDSH₅. J) bigital image (J) and oil contact angle (K) displaying the presence of contrasting oil and water wettability, where the water droplet is extremely repelled by the waste pape

porosity (85%) was observed for the sponge derived from the mixture of different papers as shown in Figure 3I.

Examining the Physical and Chemical Durability of the Embedded Water Repellence

The sustainability of the waste paper derived superhydrophobic sponges at severe challenging physical and chemical environments is of utmost importance for real life applicability. WPDSHS₁ with a) 3.25 wt% of AEPTMS, which was the minimum concentration required to exhibit superhydrophobic property

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Figure 3. A–H) Digital images (A,C,E,G) and water contact angle images (B,D,F,H) of superhydrophobic sponges that were developed using different types of waste paper i.e. office paper (A, B), newspaper (C,D), cardboard paper (E, F) and a mixture of the mentioned papers (G, H). I) Plot illustrating the compressive modulus (black) and porosity (red) of the different types of waste paper derived superhydrophobic sponges.

and b) the least compressive modulus (and thus, enhanced compressibility) was chosen to investigate the durability of its water repellence behavior. To examine the impact of physical deformation on the embedded water wettability of the waste paper derived sponge, WPDSHS₁ gradually increasing manual compressive strain was applied on the as fabricated superhydrophobic sponge. Exposure to 60% compressive strain followed by release of the strain revealed that the sponge recovered to its original shape without perturbing the embedded extreme water repellence behavior as shown in Figure 4A. Further, imposing repetitive compressive strain using an external load of 500 g for 1000 consecutive cycles failed to perturb the embedded anti-wetting property in the sponge (WPDSHS₁) with advancing contact angles above 150° and contact angle hysteresises below 10° as shown in Figure 4B. Moreover, the anti-wetting property is not just limited to the surface of the sponge but was exhibited by the bulk of the prepared sponge as well as shown in Figure 4C, D, where WPDSHS₁ (inset image) was arbitrarily sliced into pieces to randomly expose the interior of the sponge. The freshly exposed interiors of the waste paper derived superhydrophobic sponge continued to repel the beaded water with contact angles above 155°. Next, a standard and widely accepted abrasive test, i.e., sand paper abrasion was performed on the waste paper derived superhydrophobic material (Figure 4E). An abrasive sand paper was rubbed with an applied load of 500 g in back and forth direction multiple times (Figure 4F) on WPDSHS₁. Although the physical integrity of the sponge was compromised (Figure 4G), the embedded water repellence on the physically abraded interface remained intact with advancing contact angle ~155° and contact angle hysteresis ~8° as shown in Figure 3G, H. Furthermore, 150 g of sand grains were poured onto the surface of WPDSHS₁ (tilted at 45°) from a height of 25 cm. The sand grains exposed interface of WPDSHS₁ displayed extreme water repellence with water contact angle $\sim 157^{\circ}$ and contact angle hysteresis $\sim\!6^\circ$ as shown in Figure S10A–C. In addition to various severe physical abrasions, chemical durability is also vital for practical applications. In that context, WPDSHS₁ was exposed to severe harsh and practically relevant complex aqueous media including acidic water (pH 1), basic water (pH 12), surfactant water (SDS, DTAB), river water and seawater for a prolonged duration (30 days). The anti-wetting property was examined at regular intervals, it was concluded that the embedded bio-inspired water-repellent property remained intact with advancing water contact angle above 150° and contact angle hysteresis below 10° as shown in Figure 4I. Moreover, the prolonged (30 days) exposure to both short (254 nm) and long (365 nm) UV radiation failed to perturb the embedded water repellence, which is evident with advancing contact angle greater than 150° and contact angle hysteresis below 10° as shown in Figure S10D. Furthermore, WPDSHS₁ was exposed to various polar and non-polar organic solvents for 30 days, however, the embedded water repellence remained unaltered as shown in Figure S11. Hence, the abundant and valueless waste paper was successfully reconstructed into a highly compressible superhydrophobic spongy material with extremely durable embedded water repellence property - that would be sustainable for performance at harsh and hostile practical settings.

Absorption based Oil/Water Separation Performance at Challenging Environments

In the past, a few approaches were introduced to convert the valueless and highly abundant waste paper into functional materials for various applications as included in Table 1. However, most of the earlier approaches failed to demonstrate the physical and chemical durability of the waste paper derived functional materials. Some of the waste paper derived bioinspired materials that were prepared following the carbonization process at very high temperatures were successfully extended to demonstrate the oil/water separation, however, tolerance of such materials at harsh physical and chemical settings was not examined as noted in Table 1. In contrast to the earlier reports, the current design allowed to convert waste paper into a durable superhydrophobic spongy material as discussed above. The highly compressible waste paper derived sponge with an interconnected porous network exhibited high porosity (above 95%, Figure S9A) and the presence of contrasting water/oil wettability was exploited to demonstrate the energy efficient and environment friendly separation of oil/oily contaminants from the aqueous phase.[46,47] The embedded superhydrophobicity allowed the selective infiltration of the oil phase, while higher porosity facilitated the absorption and gravity-driven filtration of the oil/oily phases. The oil absorption



Figure 4. A) Plot accounting for the advancing contact angle (black) and contact angle hysteresis (red) of the beaded water droplet on the waste paper derived superhydrophobic sponge, WPDSHS₁ that was subjected to 60% manual compression. The inset images further exhibit that the embedded water repellence behaviour remains intact before (left), during (middle) and after (right) compression. B) Plot representing the advancing contact angle (black) and contact angle hysteresis (red) of the beaded water droplet on the waste paper derived superhydrophobic sponge, WPDSHS₁ that was repetitively deformed for 1000 cycles under 60% manual compression. C, D) Digital image (C) and contact angle image (D) of the waste paper derived superhydrophobic sponge, WPDSHS₁ (inset image) that was arbitrarily sliced into pieces to investigate the presence of bulk superhydrophobic property. E–H) Digital images illustrating the rubbing of a sand paper on the surface of the waste paper derived superhydrophobic sponge, WPDSHS₁ with a 500 g load on top (F). The freshly exposed interior of the superhydrophobic sponge continued to display unperturbed water repellence behaviour (G, H). I) Plot accounting for the advancing contact angle and contact angle hysteresis of the beaded water droplet on the waste paper derived superhydrophobic sponge, WPDSHS₁ that was exposed to chemically contaminated, harsh aqueous phases including pH 1 (black), pH 12 (green), SDS (yellow), DTAB (red), river water (blue), artificial sea water (violet) for 30 days.

capacities were calculated for all the waste paper derived superhydrophobic sponges (WPDSHS₁, WPDSHS₂, WPDSHS₃) having different porosities using the formula given below,

$$Q = \frac{M_2 - M_1}{M_1}$$

where, M_1 and M_2 is the weight of the sponge before and after oil absorption. Irrespective of the density and viscosity of the used oil/oily phases, the oil absorption capacity of WPDSHS₁ was found to be maximum (up to 3960 wt%) in comparison to both WPDSHS₂ and WPDSHS₃ as shown in Figure 5A. The gradual increment of AEPTMS amount in the waste paper derived superhydrophobic sponges elevated the density of the prepared sponges as noted in Table S2. The density of WPDSHS₁ was found to be minimum ~0.017 g/cm³, whereas the other superhydrophobic sponges had higher density. The association of high compressibility, which allows easy compressive deformation is appropriate for repetitive absorption/desorption of oil/oily phase without compromising the physical integrity. Compressive modulus and cyclic compressibility analysis revealed that WPDSHS₁ is the most compressible variant with unperturbed embedded water repellence even after 1000 cycles of compression (as shown in Figure 4B). Therefore, the highly porous, durable and compressible WPDSHS₁ proved to be the ideal candidate for repetitive collection of the oil phase



Figure 5. A) Plot accounting for the oil absorption capacities of the different waste paper derived compressible, superhydrophobic sponges i.e. WPDSHS₁, WPDSHS₂, WPDSHS₃ for a wide range of oils with varying densities and viscosities. B–G) Digital images illustrating the absorption based selective oil absorption of light oil i.e. motor oil (B–D) and model heavy oil i.e. dichloromethane (E–G) by the waste paper derived compressible, superhydrophobic sponge, WPDSHS₁ from an oil/water interface, such that the absorbed oil can be re-collected by manually squeezing the sponge (D,G). H) Plot illustrating the selective oil absorption capacity of WPDSHS₁ for both light (red) and heavy (black) oils at practically relevant settings where the water phase was chemically contaminated with acid, base, surfactants, salt etc. I) Plot illustrating the repetitive oil absorption capacity of WPDSHS₁ upto 25 cycles for both light (red) and heavy (black) oils.

selectively from the water phase with a high oil absorption capacity.

First, floating oil i.e. motor oil was placed in a petri-dish filled with water and subsequently, WPDSHS₁ was placed at the oil/water interface such that it rapidly and selectively absorbed only the oil phase while repelling the water phase as shown in Figure 5B-D and Movie 2. The absorbed oil was collected by manual squeezing of the sponge as shown in Figure 5D. Furthermore, the same sponge was extended for selective removal of various other floating oils including silicone oil, petrol, diesel, vegetable oil as shown in Figure S12A-P. Moreover, WPDSHS₁ was also extended for selective collection of model sediment oil i.e. dichloromethane (DCM; dyed pink for visual inspection) as shown in Figure 5E-G and Movie 3. The absorbed oil was collected, and no trace of water was observed even though the sponge was first in contact with the aqueous phase prior to absorption of the model heavy oil phase as shown in Figure 5G. The oil absorption capacity of WPDSHS₁ was further calculated for motor oil and dichloromethane in chemically harsh aqueous environments including acidic water (pH 1), basic water (pH 12), surfactant contaminated water (SDS, DTAB), river water and seawater. Remarkably, the oil absorption capacity remained unperturbed (i.e. ~2500 wt% for motor oil and ~3500 wt% for DCM) even at such extreme environments as shown in Figure 5H. Recyclability of the oil absorbents is an essential factor for real-life practical applications. The repetitive absorption-desorption ability of WPDSHS₁ was examined with motor oil and DCM for 25 cycles and it was observed that the oil absorption capacities remained unaltered as shown in Figure 5I. The extreme water repellence was examined after every 5 cycles of absorption-desorption for both floating and sediment oils and it was found that the anti-wetting property remained intact for both the oils with advancing water contact angle above 150° and contact angle hysteresis below 10° as shown in Figure S13A.

Gravity-driven filtration-based oil/water separation

Furthermore, this design provided a single strategy to fabricate waste paper derived superhydrophobic membranes of varying tensile strengths with analogous compositions to that of the sponges. The waste paper derived superhydrophobic membranes (WPDSHM₁, WPDSHM₂, WPDSHM₃) with varying compositions of AEPTMS displayed bio-mimicked extreme water repellence with advancing contact angle above 150° and contact angle hysteresis below 10° as shown in Figure S14A–F and Table S4. The tensile strength of the membranes revealed

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that the increase in AEPTMS content led to an increase in the tensile modulus in the order WPDSHM₃> WPDSHM₂> WPDSHM₁ as shown in Figure S14G, H. To maximize the utilization of the current design, the waste paper derived superhydrophobic membranes were extended for gravitydriven filtration-based oil/water separation. All three superhydrophobic membranes (WPDSHM₁, WPDSHM₂, WPDSHM₃), were individually tied to the open end of a lab made prototype to demonstrate the gravity driven selective filtration of oil/oily phase from oil/water mixture as shown in Figure 6A. Firstly, model sediment oil i.e. dichloromethane (dyed pink for visual inspection)/water (dyed blue for visual inspection) mixture was poured through the funnel at the opposite end of the tube. The oil phase selectively permeated through the WPDSHM₁ while the water phase remained suspended and restricted by the superhydrophobic membrane as shown in Figure 6A-C and Movie 4. Furthermore, the same approach was extended for separation of floating oil i.e. kerosene/water (dyed red for visual inspection) mixture where the oil phase selectively permeated through the membrane as shown in Figure 6D-F and Movie 5. This energy efficient separation technique was also used for separation of other floating oil/water mixtures including petrol and diesel (Figure S15A–H). The oil separation efficiency of WPDSHM₁ was calculated for a wide range of oils including petrol, diesel, kerosene, dichloromethane and chloroform using the formula given below,

$$\eta = (Vr/Vi) imes 100$$

where, Vr and Vi is the volume of the oil before and after separation. The oil separation efficiency remained above 97% irrespective of the densities of the oils used as shown in Figure 6G. Other membranes (WPDSHM₂ & WPDSHM₃) were also efficient for selective filtration of the oil phase but the flux of the selectively filtrated oil/oily phases was low in comparison to WPDSHM₁ (~25000 Lm⁻²h⁻¹ for dichloromethane and ~13500 Lm⁻²h⁻¹ for kerosene). The porosity of the superhydrophobic membranes which decreased (from ~99% to ~96%) in the order: WPDSHM₁ > WPDSHM₂ > WPDSHM₃ as tabulated in Table S4 affected the rate of flux of the oils. For a given oil/oily phase, the flux for the filtrated oil phase decreased in the similar order as that of porosity i.e. WPDSHM₁ >



Figure 6. A–F) Digital images illustrating the gravity-driven filtration based selective passage of model sediment oil phase i.e. dichloromethane (A–C) and light oil i.e. kerosene (D–F) from an oil/water mixture through the waste paper derived superhydrophobic membrane, WPDSHM₁ (inset image in A). The water phase remained restricted by the extreme water-repellent membrane. G) Plot illustrating the oil separation efficiency of WPDSHM₁ for a wide range of oils with varying densities. H) Plot depicting the oil separation efficiency of WPDSHM₁ for both light (red) and heavy (black) oils at practically relevant settings where the water phase was chemically contaminated with acid, base, surfactants, salt etc. I) Plot illustrating the repetitive oil separation efficiency of WPDSHM₁ upto 50 cycles for both light (red) and heavy (black) oils.

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WPDSHM₂ > WPDSHM₃ as shown in Figure S16A. Thus, WPDSHM₁ emerged as the best candidate for gravity-driven filtration of oil/oily phase from an oil/water mixture. Moreover, the separation efficiency was calculated at extremes of harsh aqueous media including acidic water (pH 1), basic water (pH 12), surfactant contaminated water (SDS, DTAB), river water and seawater for oil/water mixtures using both heavy (i.e. dichloromethane) and light (i.e. kerosene) oils as shown in Figure 6H, Figure S17A-L, Figure S18A-L. The oil/water separation performance remained merely perturbed even at severe settings (Figure 6H). The recycling ability of the membrane was also examined for 50 cycles of separation for both sediment (dichloromethane) and floating (kerosene) oils and the oil separation efficiency remained above 95% for 50 consecutive cycles as shown in Figure 6I. Moreover, the embedded water repellence of the membrane was examined after every 5 cycles of separation for both dichloromethane and kerosene and the anti-wetting property remained intact with advancing contact angle above 150° and contact angle hysteresis below 10° as shown in Figure S19A. Thus, such a robust and highly durable substrate involves facile fabrication and impeccable recyclability can be applied extensively for applications at practical context.

Conclusion

Here, we have reported the unconventional restructuring of discarded and valueless waste paper into a highly porous, compressible and chemically 'reactive' sponge embedded with extreme water repellence behavior. The varying concentration of the covalently integrated amine functionalized silane binder with the waste paper provided a basis to tailor the mechanical property. Further, the catalyst-free 1,4-conjugate addition reaction at ambient conditions between the labile amines of the selected binder and a multi-functional acrylate cross-linker allowed to induce chemical 'reactivity' in the waste paper derived sponge. The strategic post covalent modification of the residual acrylate functionalities in the waste paper derived sponge was extended to tailor the water wettability from hydrophobic to 3D-superhydrophobic. The as developed waste paper based superhydrophobic sponges could sustain repetitive compression (60% compressive strain) for 1000 cycles, severe physical abrasions including sand paper abrasion, sand drop test, prolonged (30 days) exposure to harsh chemical aqueous conditions including extremes of pH (1, 12), surfactant contamination (SDS, DTAB), river water, seawater and UV irradiation for 30 days without compromising the embedded anti-wetting property. These highly compressible, physically and chemically durable waste paper derived sponges were successfully extended for repetitive (25 times) absorption-based separation of viscous oils from the aqueous phase without compromising the embedded water repellence and physical integrity even at chemically harsh aqueous settings. Furthermore, the waste paper derived membranes were utilized for repetitive (50 times) gravity-driven filtration-based oil/water remediation at chemically harsh aqueous settings without compromising the embedded lotus-leaf inspired anti-wetting property. Such an

approach of converting waste paper into functional materials could be further useful for developing various other functional interfaces.

Experimental Section

Materials: Dipentaerythritol penta-acrylate (5Acl, MW~524.21 g/ mol), silicone oil (CAS No. 63148-58-3), methylene blue (CAS No. 122965-43-9), rhodamine 6G (CAS No. 989-38-8), Nile red (CAS No. 7385-67-3), octadecylamine, decylamine, octylamine, hexylamine, pentylamine, butylamine, 3-(2-aminoethylamino)-propyltrimethoxysilane (CAS No. 1760-24-3), sodium dodecyl sulfate (SDS), dodecyl trimethyl ammonium chloride (DTAB) were obtained from Sigma-Aldrich (Bangalore, India). Chloroform, tetrahydrofuran, dichloromethane was procured from FINAR. Ethyl acetate was procured from RANKEM (Maharashtra, India). Sodium chloride, magnesium chloride, calcium chloride, magnesium sulphate, and sodium hydroxide were purchased from Merck Specialties Private Limited. Hydrochloric acid was purchased from Fischer Scientific (Hyderabad, India). Ethanol was purchased from Changshu Hongsheng Fine Chemical Co. Ltd. Adhesive tape, calibration weights, vegetable oil, tissue paper, sand paper were purchased from Amazon, India. Motor Oil (Castrol GTX 20 W-50), kerosene oil, petrol and diesel were purchased from Indian Oil petrol pump. Newspaper, cardboard paper, office paper was purchased from a local store in IIT Guwahati. Sand grains were collected from a construction site at IIT Guwahati and rinsed with water, dried prior to use. River water was procured from Brahmaputra River, Guwahati (Assam, India).

General Considerations: All the glass wares were washed with acetone prior to use. Contact angle measurements were carried out using a KRUSS Drop Shape Analyzer-DSA25 with an automatic liquid dispenser at ambient conditions. The contact angles were measured using 5 μ l water droplet at three different locations for each sample. Labconco Freezone Freeze Dryer was used for lyophilization of the sponges. Scanning electron microscope images were acquired using the Sigma Carl Zeiss scanning electron microscope. The samples were sputtered with gold prior to imaging. ATR-FTIR spectra was recorded using the Perkin Elmer instrument at ambient conditions. To identify the chemical oxidation states of the elements, XPS was performed by using an ESCA probe TPD spectrometer, Omicron Nanotechnology with a polychromatic Al K α (hv = 1486.6 eV) X-ray source with a step size of 0.1 eV per second. The binding energy (B.E) of all the elements was calibrated with respect to C1s (284.8 eV). Compressive and tensile measurements were carried out using a 5 kN electromechanical Universal Testing Machine. Digital images were acquired using a Canon Power shot SX420 IS digital camera. Milli-Q grade water was used for all experiments.

The porosity measurements were calculated using the widely adapted standard formula,

Porosity (%) =
$$\left(1 - \frac{\rho}{\rho s}\right) \times 100$$

Where, ρ and ρ_s is the volumetric mass density of the porous sponge and solid sponge respectively.^{[49,50]}

Fabrication of chemically 'reactive' waste paper derived sponges followed by post covalent chemical modification: To fabricate the waste-paper derived sponges, 1.96 wt% of waste paper was shredded into pieces and dispersed in 30 mL of water under constant stirring for 1 hour followed by addition of 3-(2-amino-

ethylamino)-propyltrimethoxysilane (AEPTMS) in desired amounts (1.65 wt%, 3.25 wt%, 4.79 wt%, 6.29 wt%) which are denoted as WPDS_{0.5}, WPDS₁, WPDS₂, WPDS₃ respectively. Here, tissue paper was selected as the model waste paper for performing all the experiments. The AEPTMS added waste paper mixture was kept under continuous stirring at room temperature for 6 hours to ensure uniform mixing. Thereafter, the mixture was poured into cylindrical molds and glass petri-dish for fabricating the sponges and membranes respectively. The molds were frozen in liquid N₂ and subsequently, lyophilized at -101 °C for 36 hours. Afterwards, the dried sponges/membranes were further treated with an ethanolic solution of dipentaerythritol penta-acrylate (1.325 g 5Acl in 10 mL ethanol) for 3 hours followed by thorough washing in ethanol for 15 mins and THF each. Thereafter, the sponges were subjected to post covalent modification with amine containing small molecules i.e. butylamine (30 mg/mL), pentylamine (30 mg/mL), hexylamine (30 mg/mL), octylamine (30 mg/mL), decylamine (30 mg/mL) and octadecylamine (5 mg/mL) for 12 hours. Then, the samples were thoroughly washed with THF and subsequently dried at ambient conditions.

Physical and Chemical Durability Tests: To examine the durability of the embedded anti-wetting property of the waste paper derived superhydrophobic sponges, various harsh physical and chemical challenges were imposed as described in detail below.

Sand Paper Abrasion: In this test, the waste paper derived compressible, superhydrophobic sponge, WPDSHS₁ (length ~5 cm) was rubbed manually with a sand paper for 20 times back and forth with a 500 g load on top to inflict severe damage to the sponge. Thereafter, the embedded anti-wetting property on the freshly exposed interior of the sponge was examined through contact angle measurements and digital images.

Bulk Superhydrophobicity: The presence of three-dimensional water wettability in the waste paper derived sponge (WPDSHS₁) was examined by arbitrarily slicing the sponge into pieces to expose the interiors. Subsequently, the anti-wetting property was examined using contact angle measurements.

Sand Drop Test: In this test, 150 g of sand grains were poured from a height of 25 cm on the waste paper derived superhydrophobic sponge, WPDSHS₁ (length ~4 cm) which was pre-tilted at 45°. Thereafter, the embedded anti-wetting property was examined on the abraded surface of the sponge using contact angle measurements and digital images.

UV Irradiation: The waste paper derived compressible superhydrophobic sponge, $WPDSHS_1$ was subjected to both short (254 nm) and long (365 nm) UV irradiation for 30 days. The embedded water-repellent property was examined at regular intervals through contact angle measurements and digital images.

Chemical Durability: The waste paper derived superhydrophobic sponge, WPDSHS₁ was exposed to various harsh chemically complex aqueous phases including acidic water (pH 1), basic water (pH 12), surfactant contaminated water (SDS, 1 mM and DTAB, 1 mM), river water (Brahmaputra River, Assam, India) and artificial seawater. Artificial seawater was prepared by mixing MgCl₂ (0.226 g), MgSO₄ (0.325 g), NaCl (2.673 g) and CaCl₂ (0.112 g) in 100 mL of de-ionized water in a volumetric flask. Similarly, the waste paper derived superhydrophobic sponge, WPDSHS₁ was exposed to various polar and non-polar organic solvents including methanol, ethanol, tetrahydrofuran, dimethyl sulfoxide, acetone, chloroform, hexane, dichloromethane for 30 days and subsequently, the embedded water repellence was examined at regular intervals through contact angle measurements.

Absorption Based Oil/Water Separation: The waste paper derived compressible superhydrophobic sponges were exploited successfully for absorption-based collection of oils of varying densities and viscosities from an oil/water interface. Briefly, 1 mL of the oil (dyed with Nile red for petrol, diesel, silicone and vegetable oil for visual inspection) was placed in a petri-dish filled with water. Then, the waste paper derived superhydrophobic sponge was placed at the oil/water interface such that it selectively absorbed only the oil phase. The absorbed oil was recovered by manually squeezing the sponge. Furthermore, this absorption-based selective separation was extended for model heavy oil i.e. dichloromethane, DCM (dyed with Nile red). Briefly, 5 mL of DCM was poured in a beaker filled with 15 mL of water followed by immersion of the superhydrophobic sponge into the oil/water mixture such that sediment oil phase was selectively absorbed. The absorbed oil was recovered by manual squeezing of the sponge.

Gravity-Driven Filtration based Oil/Water Separation: The waste paper derived superhydrophobic membranes were further extended for gravity-driven selective filtration of various light and heavy oils from an oil/water mixture. A lab made proto-type was developed using a 50 mL falcon tube where one end of the tube was tied with the waste paper derived superhydrophobic membrane and a hole was made at the closed end of the tube to pour the oil/water mixture with the help of a funnel. Water was dyed with methylene blue and rhodamine 6G as required and dichloromethane (model heavy oil) was dyed with Nile red. To demonstrate the gravity-driven filtration-based oil/water separation, an equal amount of oil and water (20 mL each) was poured through the funnel at the closed end such that the oil phase selectively permeated through the superhydrophobic membrane, while the water phase remained restricted by the water-repellent membrane.

Acknowledgements

We acknowledge the financial support from Science and Engineering Research Board (CVD/2020/000018), Government of India. We thank CIF and Department of Chemistry, Indian Institute of Technology-Guwahati, for their generous assistance in executing various experiments and for the infrastructure. Ms. Arpita Shome and Mr. Adil Majeed Rather thanks IIT Guwahati for their PhD fellowship. Angana Borbora thanks MoE and Council of Scientific & Industrial Research (CSIR, India) for the PhD scholarship. Pillalamarri Srikrishnarka and Avijit Baidya thanks IIT Madras for their PhD fellowship.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Waste paper · mechanically tailorable · chemically reactive · facile chemistry · tunable water wettability

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Manuscript received: May 4, 2021 Revised manuscript received: June 1, 2021 Accepted manuscript online: June 1, 2021

Version of record online: June 22, 2021