Ultrafast reclamation of fracking effluents using surface-engineered nanosilicon sponges

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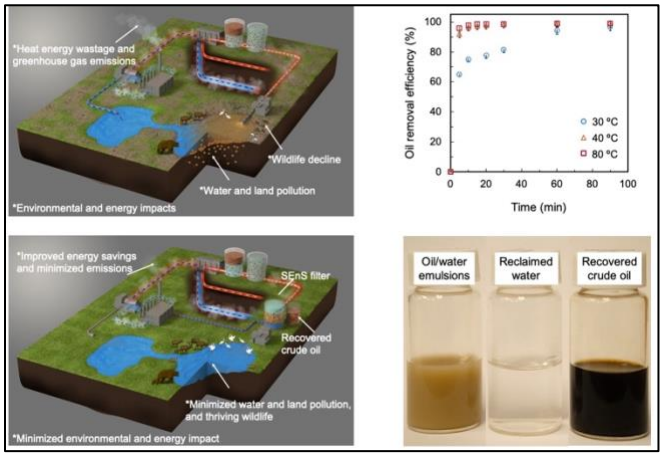
ABSTRACT. Effluents from the fracking process are typically discharged at elevated temperatures and are a major environmental concern. We applied a surface-engineered sponge (SEnS) with thermal stability up to 220 ºC to reclaim emulsified oily wastewater at discharge temperatures between 30-100 ºC. The sponge achieved 92-96% removal efficiency within 5 minutes, where speed increased by 27% by melting waxes. The adsorbed oil from the SEnS was also recovered within 1-2 minutes by diluent wash. These performance metrics suggest that SEnS could emerge as a practical solution to achieve fracking water reclamation processes' Net-Zero goals.



INTRODUCTION

Reclamation of emulsified oily wastewater, a byproduct of steam-based oil extraction processes or fracking, is a global energy and environmental challenge.[1] For example, in Canada, there are currently 1.2 trillion liters of difficult-to-treat emulsified oily wastewater, stored in over 220 km2 of tailing ponds, which has caused a large amounts of greenhouse gas emissions and a 71% decline in local wildlife (**Figure 1a**).[2] Due to lack of thermally stable materials, currently, the fracking effluents are being cooled, stored in tailings ponds, treated to remove emulsified oil using traditional approaches, and reheated from 2 ºC in winter or 25 ºC in summer to ≥80 ºC to extract crude oil.[3] The wastewater heating-cooling-reheating cycles are energy and environmentally intensive, making its reclamation expensive. Moreover, at lower temperatures, the precipitated heavier organic compounds, known as waxes, increase crude oil's viscosity making traditional wastewater reclamation methods slow. Affordable materials that can reclaim oily wastewater and recover residual crude oil at their high discharge temperatures, or above wax crystallization temperature (Tc), can enable direct reuse of fracking wastewater and are urgently required to achieve the Net-Zero goals in the oil industry.

Recently, surface-engineered sponges (SEnS) fabricated by coating porous polymeric substrates with functionalized nanomaterials, have emerged as a new class of sorbents for oil/water separation.[4–7] Although, SEnS have been utilized at elevated temperatures, for example in in-situ heating and collecting viscous crude oil from a water surface, their structure and properties for high-temperature oil/water emulsions separation has not been fully investigated.[8,9] The polymeric substrates used in SEnS fabrication can be thermoplastics or thermosets. As a result of their three-

dimensional crosslink structures, the thermosets exhibit excellent thermomechanical stability, chemical resistance, and ease of surface modification, making them ideal candidates high-temperature adsorbents.[10–12] Furthermore, the adsorbed crude oil from the SEnS can be collected by simply rinsing with safe, crude oil miscible diluents, such as heptane, hexane, and toluene.[13,14] Thus, thermoset-based SEnS can emerge as a techno-economic-environmentally feasible solution for ultrafast fracking water reclamation as well as residual oil recovery to improve environmental sustainability at a critical time for the oil industry (**Figure 1b**).

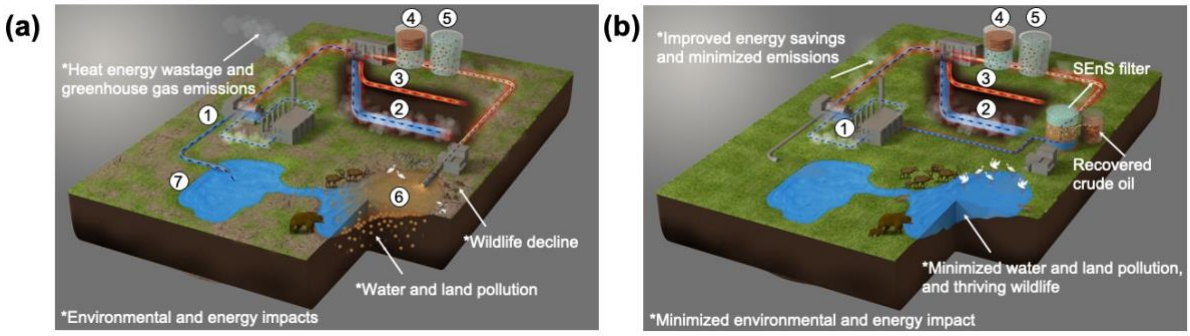


Figure 1. Potential impacts of SEnS-based high-temperature water technology on fracking. a. A simplified fracking wastewater treatment cycle currently used in the oil industry. (1) The cleaned water collected from tailings ponds at 2 ºC in winter or 25 ºC in summer is heated to above 100 ºC using heat exchangers for oil extraction. (2) Steam or hot water enters the oil sands and (3) comes out as the oil and water mixture. (4) The oil-water mixtures are separated using gravity filters. (5) The remaining hot water is difficult to recycle due to presence of emulsified crude oil. (6) Therefore, the oil/water emulsions are stored in tailings ponds, and (7) treated using traditional methods. The cooling-reheating processes from 6 to 1 are energy, environmental, and economically intensive processes. b. However, the SEnS filter could directly reclaim the emulsified oily wastewater at elevated temperatures after (5), eliminating cooling-reheating

processes at (6) to (7), directly recycling the water to generate steam at (1). Also, the adsorbed oil could be collected from the SEnS for recycling to improve the Net-Zero goals in the oil industry.

RESULTS AND DISCUSSION

Previously, we reported SEnS for oil/water emulsions separation across broad pH conditions.[6,13] Here, the suitability of the SEnS were investigated for reclaiming oil/water emulsions at elevated temperatures. **Figure 2a** shows the scanning electron microscopy (SEM) images of the SEnS fabricated by coating a polyester polyurethane (PESPU) thermoset sponge with decyl capped nanosilicon (ncSi-C_{10}) coating using previously reported methods.[6,13,14] Due to crosslinking between polyester and polyurethane, and PESPU-ncSi-C_{10} coating, the SEnS was expected to exhibit surface chemical and thermomechanical stability at desired high temperatures.

To conform with the crude oil's complex organic, acid, and base composition, the SEnS was engineered with organic groups through ncSi-C_{10} coating and the acid and base groups through the PESPU substrate.[6,13] Due to polymer's thermoresponsive stretching, the SEnS surface chemical groups density could vary, changing its selectivity for the oil droplets. Therefore, the integrity of SEnS's surface properties were investigated using inverse gas chromatography (IGC) at 30, 40, and 80 °C (**Figure 2b**). Due to temperature limitation of the instrument, the measurements could not be carried out above this temperature. The acidic composition or Gutmann acid number (K_a) of the SEnS remained constant at 0.13 across tested temperatures. However, the base composition or Gutmann base number (K_b) slightly increased from 0.7 at 30 and 40 °C to 0.78 at 80 °C. The higher K_b suggests amine groups from urethane are more prevalent than the carboxylic groups

from ester. The increase in K_b with temperature could be due to newly exposed amine groups from urethane chains stretching.

According to the Baier curve, surface energies (SE) between 40 and 75 mJ m^{-2} result in good adhesion and between 10 and 20 mJ m^{-2} lead to weak adhesion with the adsorbate.[15,16] The variation in total (γ_S), dispersive (γ_{LV}), and acid-base (γ_{AB}) SE of the SEnS with temperature was measured with IGC (**Figure 2c** to **e**). Due to the polymer chains stretching, the SE of the SEnS at the lower surface coverage increased with increasing temperature but remained within Baier's SE range for γ_{LV} and γ_{AB}. The measured SE suggest that the SEnS could adsorb oil droplets from wastewater by physical forces, such as Lifshitz-van der Waals forces, electrostatic interactions, and hydrogen bonds across tested temperatures. The physisorbed crude oil will be easier to recover from the SEnS to enable oil recovery and SEnS reuse.

The SEnS's thermomechanical stability was determined using thermogravimetric analysis (TGA), dynamic scanning calorimetry (DSC), and dynamic mechanical analysis (DMA) techniques. The TGA curve shows thermal degradation of the SEnS as weight loss during heating between 30-600 °C (**Figure 2f**). The first weight loss of approximately 10% occurred at 220 °C, indicating the loss of moisture, plasticizer, and solvents. The second and third weight losses indicate the SEnS has undergone pyrolysis. A weight loss of approximately 28.7% near 320 °C could be attributed to the pyrolysis of polyurethane, and an additional 30.1% near 400 °C could be attributed to polyester. The fourth weight loss of approximately 30% could be from carbon compounds combustion.[17] Approximately 1.2% of the inorganic silica/silicon remained as a residue. The thermogram

suggests that the SEnS is thermally stable up to 220 °C, which is significantly higher than the desired oil/water emulsions separation temperature of 80 °C.

The DSC curve indicates the glass transition temperature of the SEnS was at -32.57 °C (**Figure 2g**). Above this temperature, the SEnS remained in a rubbery state. The DMA curves obtained under shear with a temperature ramp show that the storage modulus (G'') slightly decreased with increasing temperature. The sinusoidal shape of the loss factor (tan δ) indicates that the SEnS mechanical structure remained stable between 30 and 100 °C (**Figure 2h**). Due to the three-dimensional interconnected PESPU network, the SEnS exhibits stable thermomechanical properties, therefore, has the potential to perform oil/water emulsion separation at elevated temperatures.

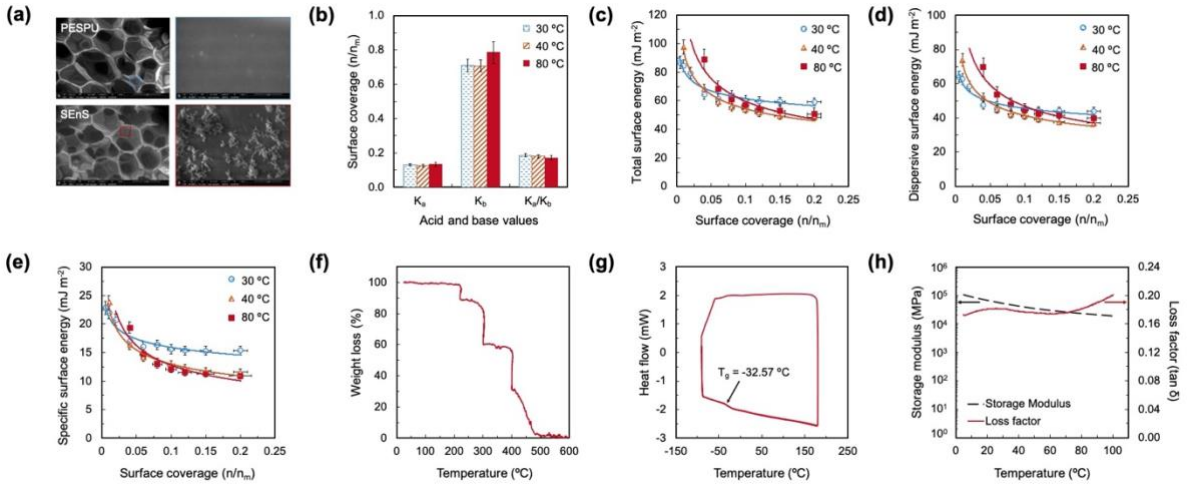


Figure 2. Influence of temperature on the surface and mechanical properties of SEnS. **(a)** scanning electron microscopy images of PESPU (top) and SEnS (bottom). **(b)** Gutmann acid and base number show the acid number remains constant between 30 and 80 °C but the base number increases at 80 °C. **(c)** Total, **(d)** dispersion, and **(e)** acid-base surface energies. The dispersive and

acid-base surface energies are in the range of 40-75 mJ m^{-2} and 10-20 mJ m^{-2}, respectively between 30 and 80 °C. **(f)** SEnS has thermogravimetric stability up to 220 °C. **(g)** The glass transition temperature of the SEnS is -32.57 °C. **(h)** The storable modulus and loss factor of the SEnS are stable between 5 and 100 °C. (a) The data were average of 20 scans and (b)-(e) average of three samples.

The thermoresponsive chemical structure and rheological properties of the crude oil can also influence its adsorption and recovery from SEnS. In this work, a natural wax containing crude oil with $T_c \approx 38$ °C was used in the model emulsions. The elongated bee structures in the mass spectroscopy images confirm the presence of crystallized waxes on the oil surface below $T_c \approx 30$ °C (**Figure 3a**). The saturated aliphatic ions at m/z 71 ($C_5H_{11}^+$), 83 ($C_6H_{11}^+$), and 97 ($C_7H_{13}^+$) show reduced signal intensity inside the bee structures. The high m/z aromatic fragments 221 ($C_{16}H_{15}N^+$), 239 ($C_{17}H_7N_2^+$), and 281 ($C_{19}H_8NO_2^+$), also display inhomogeneous distribution, which was not overlapped with the saturated aliphatic pattern. These segregated or bee structures are consistent with natural waxes in crude oil reported elsewhere.[18–21] Above T_c, the crystallized wax can melt and dissolve into the crude oil. The phase change of waxes, observed under polarized microscopy, showed they were present at 30 °C but completely dissolved at 40 and 80 °C (**Figure 3b**). Also, crude oil's density was reduced by only 0.9% from 30 to 40 °C and 1.1% from 40 to 80 °C (**Figure 3c**). In contrast, the viscosity of crude oil was reduced by 37.8% from 30 to 40 °C and 68.8% from 40 to 80 °C (**Figure 3d**). The negligible influence of temperature on density, but dramatic decline in viscosity is a typical indicator of waxes phase change.[22] Below 38 °C, the waxes hinder crude oil's flowability making the oil/water emulsions separation slow.

Alternatively, above 38 °C, the dissolved waxes increase the crude oil's flowability, thus the separation of oil/water emulsions above this temperature is expected to be faster.

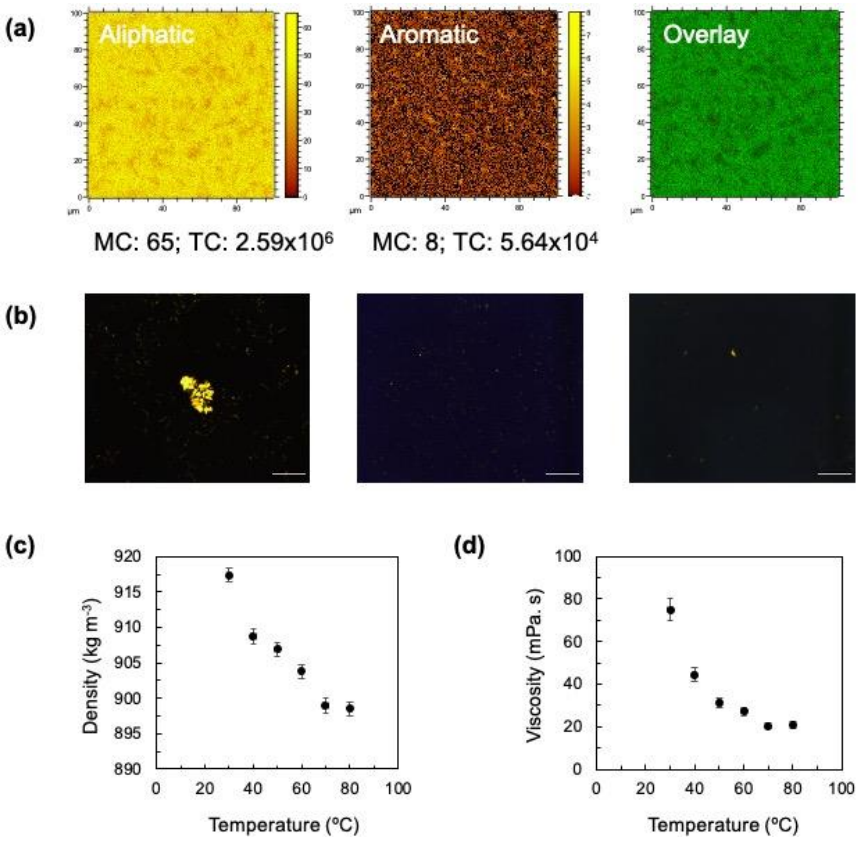


Figure 3. Influence of temperature on crude oil structure and properties. **(a)** Crude oil microstructure at 30 °C: aliphatic structures at ($C_5H_{11}^+$), 83 ($C_6H_{11}^+$), and 97 ($C_7H_{13}^+$) show segregated structures (left); aromatic structures at m/z 221 ($C_{16}H_{15}N^+$), 239 ($C_{17}H_7N_2^+$), and 281 ($C_{19}H_8NO_2^+$) (middle); overlaid aliphatic and aromatic structures show segregated structures (right). MC: maximum count and TC: total count. **(b)** Polarized microscopy images show presence of wax crystallites in the crude oil at 30 °C but crystallites were dissolved at 40 °C and 80 °C. Scale bar 20 µm. **(c)** The density of crude oil reduced slightly with increasing temperature, but a small yet noticeable decline occurred between 30 and 40 °C. **(d)** The viscosity of the crude oil decreased with an increase in temperature, where a noticeable decline of approximately 40%

occurred between 30 and 40 °C. In (b) and (c), the data reported was an average of between three to five measurements.

Previously, we reported PESPU and SEnS performance to remove oil droplets from saline and freshwater at variable pH levels.[6,13,14,23] In this work, the SEnS was evaluated for oil/water emulsions separation at high temperatures (30-100 °C) and pressure (40 psi). As shown in **Figure 4a**, the SEnS demonstrated oil uptakes between 1155 and 1236 mg g^{-1} for tested temperatures, but the speed of removal varied (**Figure 4b**). In the initial 5 minutes, the SEnS adsorbed approximately 65% of the crude oil at 30 °C, 92% at 40 °C, and 96% at 80 °C. Between 30-40 °C, with only an increase of 10 °C, the speed of oil removal was improved by 27% with a reduction in viscosity of 38%. In contrast, between 40-80 °C, with an increase of 40 °C, the speed of oil removal was improved by 4% only despite a larger viscosity reduction of 69%. The speed of removal did not improve even at higher temperature (100 °C) and pressure (40 psi) (**Figure 4c**). This indicates wax crystallization but not the viscosity is the limiting factor in the oil adsorption kinetics. Therefore, SEnS that can withstand temperatures above T_c, could be sufficient for ultrafast oil/water emulsions separation for remediating fracking effluents at their discharge point and in the tailing ponds.

The adsorption kinetics of the oil droplets onto the SEnS were described using the pseudo-second-order model (**Figure 4d**) and experimental data correlated well with an R^2 value between 0.996-0.999 (**Table 1**).[24] The second order model predicted an oil uptake capacity of 1250 mg g^{-1}, matching with the experimental oil uptake of 1236 mg g^{-1}. The rate constants calculated over 180

min suggested that the speed of oil removal increased by approximately 8 and 3 times between 30-40 °C and 40-80 °C, respectively. In addition to reclaiming the wastewater at elevated temperatures, the SEnS offers the advantage of recovering the adsorbed crude oil and being reused. Based on crude oil's solubility, heptol (60% heptane and 40% toluene mixture) was used to clean the sponge and collect the adsorbed crude oil within 1-2 minutes. The cleaned SEnS also removed over 99% of oil droplets from wastewater at 80 °C without experiencing degradation across ten cycles (**Figure 4e**). The recovered crude oil (**Figure 4f**) and solvent also can be separated by distillation for reuse.

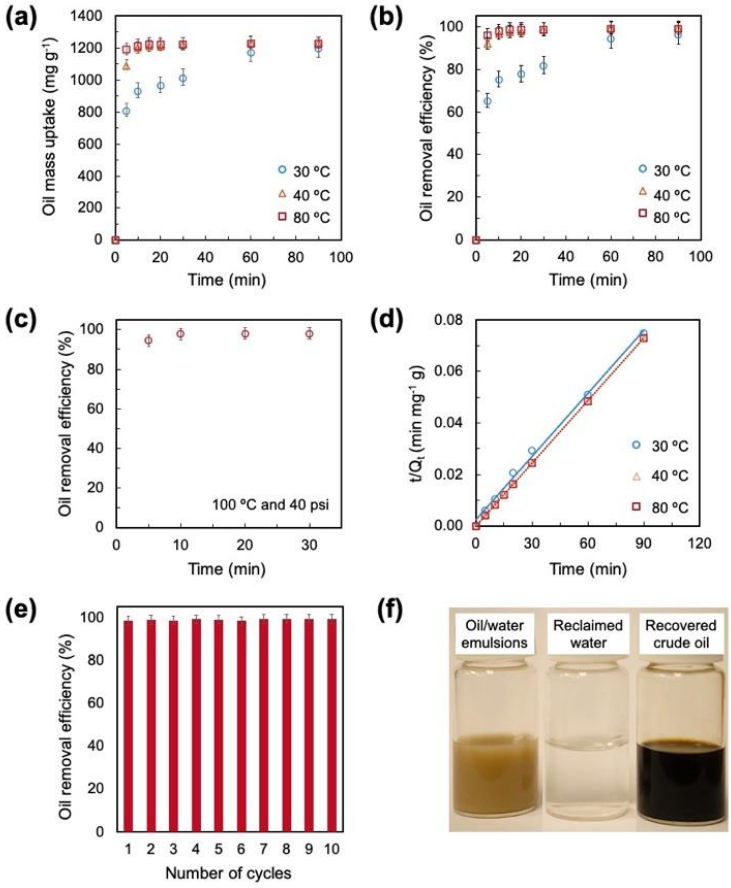


Figure 4. Emulsified oily wastewater reclamation with SEnS. (**a**). Crude oil mass uptake, (**b**) crude oil removal efficiency, and (**c**) crude oil removal efficiency at 100 °C and 40 psi. (**d**). adsorption

kinetics between 30 and 80 °C. (**e**). SEnS reuse for 10 cycles at 80 °C. (**f**). Oil/water emulsions before separation (left), reclaimed water (middle), and adsorbed crude oil recovered from SEnS by rinsing with heptol (right). The data was average of three to five measurements.

Table 1. Kinetic model fitting parameters

Temperature (ºC)	Experimental uptake (mg g^{-1})	Theoretical uptake (mg g^{-1})	Rate constant k^2 (mg g^{-1} min)	R^2
30	1155	1250	2.65 x 10^{-4}	0.9960
40	1236	1250	2.13 x 10^{-3}	0.9999
80	1234	1250	7.11 x 10^{-3}	0.9999

CONCLUSIONS

In conclusion, the impressive thermal stability up to 220 °C of the thermoset-based, nanosilicon functionalized SEnS enables the removal of emulsified crude oil from wastewater between 40-100 °C with 92-96% efficiency in as little as 5 minutes. A straightforward heptol wash ensures the adsorbed crude oil can be recovered from the SEnS within 1-2 minutes. The reused SEnS showed consistent and reproducible oil removal efficiency for tested ten cycles. The oil removal efficiency increases by 27% between 30-40 °C (T_c) and by 4% between 40-100 °C. Although viscosity of the crude oil continued to decrease at higher temperatures, there was no noticeable increase in oil removal efficiency after the waxes were melted. These insights indicate that the SEnS could enable ultrafast separation of oil/water emulsions at high discharge temperatures of fracking enabling

water reuse. Consequently, the redundant cooling-reheating cycles could be eliminated from the traditional fracking effluent treatment processes, reducing energy wastage, carbon emissions, and conservation of water. In addition, recovered residual crude oil from the SEnS could make wastewater reclamation economically viable from otherwise toxic waste, and reduce demand for fossil fuel extraction. Finally, the knowledge accrued from this work indicate that excessive wastewater in tailings ponds could be treated above T_c to speed up the ecosystem restoration efforts, such as releasing the water back into the rivers, wildlife protection, and forestation. The potential environmental, energy, and economic benefits of SEnS-based high-temperature water technologies could revolutionize fracking operations at a much-needed time for the oil industry. In the future, we will investigate the structure-property-functionality of SEnS with aging to determine its service life for fracking water reclamation and resource recovery.

MATERIALS AND METHODS

Materials. A thermosetting polyester polyurethane (PESPU) sponge was purchased from a local vendor. The crude oil containing natural waxes was purchased from Texas Raw Crude. Plasma synthesized silicon nanocrystals, with average particle size of approximately 100 nm at 99% purity, were purchased from Alfa Aesar. All the chemicals, including hydrofluoric acid (HF, 48 wt% in H_2O), 1-decene, ethanol, toluene, and heptane were purchased from Sigma-Aldrich.

SEnS fabrication. Detailed protocols on the nanocoating synthesis and SEnS fabrication are reported elsewhere[13,14,25]. Briefly, a commercial PESPU thermosetting porous sponge was used as the substrate. Prior to experiments, the samples were rinsed with ethanol and deionized water, and

dried at 80 ºC. The nanocoating was synthesized by capping the decyl group onto the silicon particles by thermal hydrosilylation reaction. First, 20 mL of hydrofluoric acid (HF, 48 wt% in H_2O, 20 mL) was added to approximately 10 mL of ethanol containing 0.2 g of nanosilicon (ncSi). The mixture was stirred for 1.5 hrs to convert ncSi into ncSi:H (hydride-terminated ncSi). Hydrofluoric acid is a hazardous material, and the personnel must be well-trained to handle without accidents. Next, the 1-decene (abbreviated as C10) as ligands were bonded onto the ncSi-H via a thermal hydrosilylation reaction at 170 °C under a nitrogen environment for 20 hrs. The resulting C10 capped ncSi was referred to as the ncSi-C10 or simply nanocoating. Then, the dispersion was transferred to falcon tubes and centrifuged for 20 minutes to collect the ncSi-C10 particles. Then the ncSi-C10 was redispersed in hexanes (mixture of isomers) as the suspension for the final dip coating (0.4-0.5 mg mL^{-1}) process. Then, approximately 0.85 g of the PESPU sponge was dipped into 30 mL of the nanosuspension, dried overnight in the vacuum, and annealed at 170 ºC for 1.5 hrs. The annealed SEnS were used for subsequent characterization and adsorption experiments.

SEnS characterization

Chemical structure characterization. The acid-base surface properties and surface energies of the SEnS were measured using IGC from Surface Measurement Systems, Alperton, UK (Model IGC-SEA). Approximately 50 mg of the SEnS sample was packed into a silanized glass column (300 mm long, 4 mm diameter). Helium was used to precondition the samples at 30 ºC for 120 minutes and methane was used for dead volume correction. The dispersive surface energy was measured using n-alkane (octane, nonane, decane) probe molecules according to the Dorris and Gray method. The acid-base surface energy was measured with polar probe molecules (chloroform, dichloromethane, ethyl acetate, ethanol, and toluene) according to the van Oss-Good-Chaudhury

model. The data were analyzed using SEA Analysis software. Due to instrument limitations, the surface energy could not be measured above 80 °C.

Thermomechanical properties characterization. The TGA was carried out with a TA Instruments Q50 apparatus under nitrogen flow of 40 mL min^{-1}. An approximately 3 mg sample was heated from 30 to 600 °C at a rate of 10 °C min^{-1}. The glass transition temperature of the SEnS was determined using DSC Q2000 from TA Instruments. An approximately 4 mg sample was heated from -90 to 180 °C at a rate of 10 °C min^{-1}. The data sets were analyzed using TA Instruments Universal software. The DMA measurements were carried out in shear mode using Anton Paar Modular Compact Rheometer. The cylindrical SEnS specimens of approximately 8 mm diameter and 5 mm thickness were tested under shear mode between 5 and 100 °C.

Crude oil characterization. The surface microstructure of the crude oil at 30 ºC was imaged using time-of-flight secondary ion mass spectroscopy (TOF-SIMS, IONTOF GmbH) following the method reported elsewhere.[14,18,26] Briefly, approximately 1 mL of crude oil was deposited on a UV/ozone cleaned silicon wafer using a glass pipette. The mass and ion spectra were collected by probing approximately 100 nm depth and an area of 500 x 500 μm^2 in the static mode of the instrument. The data sets were analyzed using Surface Lab v5, IONTOF GmbH. The density of the crude oil at desired temperatures was measured with a 10 mL pycnometer. The viscosity of the crude oil was measured with an Anton Paar Rheometer MCR 302 equipped with Peltier cooling and 40 mm serrated plate. The gap of 0.6 mm was maintained between the parallel plates to control temperature and minimize the shrinkage effect. The samples were heated at 2 ºC min^{-1}. Due to instrument limitations, the viscosity measurements were performed to a maximum temperature of

80 °C. The variation in wax crystallites state with crude oil temperature were observed under an inverted Nikon High Content widefield microscope equipped with LED or laser illumination, a polarized filter, and Nikon JOBS acquisition software. Prior to imaging, the samples were preheated to 30, 40, and 80 °C. The images were post processed using image analysis software, imageJ.

Adsorption experiments. The wastewater samples with crude oil droplets of size ≤10 μm were prepared following the procedure reported elsewhere.[6] Briefly, approximately 100 mL of emulsion samples were prepared by mixing 1 vol% of crude oil with deionized water in a blender at 22,000 rpm for 30 minutes. The adsorption experiments were carried out with a stationary SEnS of 0.85 g and by mixing emulsions at 500 rpm at 30, 40 or 80 °C. The experiments were performed in a sealed beaker to prevent vapors entering the atmosphere. The experiments at 100 °C and 40 psi were performed using a CEM microwave reactor. In the reactor experiments, approximately 25 mL of emulsion samples were cleaned with 0.2 g of SEnS. In both experiments, at predefined time intervals, 1 mL of emulsion samples were collected and analyzed using total organic carbon analyzer (Shimadzu, TOC-VCPN). The oil mass uptake by the SEnS was calculated using,

$$Q_e = \frac{(C_o - C_e)V}{m} \quad (1)$$

where C_o and C_e represent the initial and instantaneous oil concentrations in mg L^{-1}, V is the volume of the emulsion in L, and m is the mass of the SEnS in g. The oil removal efficiency was evaluated using,

$$\eta\% = \frac{(C_o - C_e)}{C_o} X\ 100 \quad (2)$$

SEnS regeneration and oil recovery. Based on the variable water and crude oil wetting properties, the SEnS was regenerated within 1-2 minutes, using mechanical compression and a solvent wash[2,3]. The hydrophobicity of the SEnS enabled the entrapped water inside the pores to be removed by simple mechanical compression. Due to oleophilicity and the low surface energies of the SEnS, the adsorbed crude oil droplets were strongly adhered to the SEnS. Based on linear and aromatic composition of the selected crude oil, heptol (60% heptane and 40% toluene mixture) was used to displace the crude oil from the SEnS surface and collected using gravity. Due to its high miscibility with oil, the heptol could displace the crude oil spontaneously from the SEnS. The heptol also acts as a diluent in reducing the viscosity of collected crude oil for subsequent transportation. After a final distillation process, the heptol solvents were also collected from crude oil to reuse for SEnS regeneration. The cleaned sponge was dried in the vacuum oven at 60 ºC to remove residual solvents and reused for oil adsorption experiments at 80 ºC using the adsorption experimental protocol. Due to cleaned water, crude oil recovery, SEnS reuse and heptol reuse, the regeneration process described here can be closed loop with minimal process waste.

ASSOCIATED CONTENT

Supporting Information.

Table S1. Kinetic model fitting parameters

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Author Contributions

P.C. conceptualized and designed the research. P.C. and W.S. performed the experiments. P.C. analyzed the data and drafted the manuscript. A.M.B. revised the manuscript. All authors critically reviewed the manuscript. D.R.W., G.A.O., and A.M.B. supervised surface science, nanoscience, and water treatment aspects of the project.

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Notes

The data sets required are required to assess the findings in the paper are included in the paper and/or Supplementary Information.

Competing financial interests

The authors declare no competing financial interests.

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