

Supplementary Information

Reduced Graphene Oxide-Coated Microfibers for Oil- Water Separation

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Content

Scanning electron microscopy (SEM) and optical microscopy

A representative portion of each sample was carefully positioned on a metal holder by using sticky carbon paper. Micrographs at different magnifications were taken for each samples at 15kV of accelerating voltage conditions using an Everhart-Thornley detector and an InLens detector. Optical micrographs of the samples were taken through the optical microscope at different magnifications.

Thermal gravimetric analysis (TGA)

Up to 20 mg of each sample were placed in a ceramic crucible (70 μ l) and positioned on the microbalance of the instrument. The samples were measured in air from 25 to 600 °C with a temperature ramp of 10°C/min and a plateau of 10 minutes at 600 °C. The airflow was 50 ml/min.

Raman spectroscopy

Reduced graphene oxide (rGO)-coated microfibers (GCMs) were measured between 200 and 2000 cm^{-1} . Intensities were rescaled for samples showing high fluorescence, in order to achieve a better comparison between the spectra.

Quantitative calibration for oil absorption

For oil concentration calibration, a solution was prepared by mixing 5 ml of 2-propanol and 5 ml of North Sea crude oil to obtain a homogeneous solution. 0.118 ml of the prepared solution was transferred to a 50 ml volumetric flask and diluted up to 50 ml with a 1:1 ratio solution of 2-propanol and Milli-Q water or seawater (24.941 ml of each). A standard stock solution with a concentration of 1.0 g/l of oil was obtained. These standard stock solutions for both Milli-Q and seawater calibration series were then sonicated at 60 °C for 45 min in sealed glass containers. Standard oil samples of 5 ml were prepared with the following concentrations of oil: 0 mg/l (blank), 20 mg/l, 30 mg/l, 40 mg/l, 50 mg/l, 100 mg/l and 150 mg/l. These were obtained by diluting appropriate amounts of the stock solution with a 1:1 ratio mixture of Milli-Q water (or seawater) stock solution and 2-propanol.

The following equation was used for the determination of the volumes and concentrations of the outtake and the diluted sample:

$$C_1V_1 = C_2V_2 \quad (1)$$

Where C_1 is the concentration of the first solution, V_1 is the amount of first solution collected for dilution, C_2 is the diluted concentration and V_2 is the total volume of the diluted samples.

1% (v/v) oil-in-water mixtures were prepared by adding 1 ml of crude oil to 99 ml of Milli-Q water (or seawater) in 100 ml blue cap bottles. The obtained mixture had a concentration of 8.461 g/l, considering the density of crude oil. The mixture was vigorously shaken for several minutes until fine droplets were formed and the mixture assumed a stable yellow-brownish color. Subsequently a 3.0x3.0 cm² sample of MF1 (GCMs prepared with 1 mg/ml graphene oxide (GO) solution) was inserted in a 100 ml blue cap bottle with the oil-water mixture. The bottle was then sealed, shaken and stirred with circular movements for 30 seconds. After this procedure, the MF1 was removed from the bottle and 0.5 ml of the mixture were collected with a micropipette and transferred into a glass vial. The collected sample was subsequently diluted with the 1:1 solution of Milli-Q water and 2-propanol in different proportions. The glass vials were shaken and sonicated until a homogeneous solution was obtained. 2 ml of mixtures after oil absorption were measured under UV-Vis spectrophotometry over the 200-400 nm range. Quartz cuvettes were thoroughly cleaned with Milli-Q water, ethanol and subsequently dried before being used again. Since the concentration of the mixtures before absorption is known (8.461 g/l), this can be used in the calculations to obtain the cleaning efficiency of the tested MF1 samples. The calibration curves and linear fitting equations are shown in Figure S1.

This procedure was repeated up to 5 times for each of the oil-water solutions, each time with a new piece of MF1. After removing the MF1 from the bottle after each absorption, a sample of 2.0 ml of the oil-water mixture was taken and prepared for UV-Vis analysis. All outtakes were subsequently diluted in 50% water and 50% 2-propanol for preparation before UV-Vis.

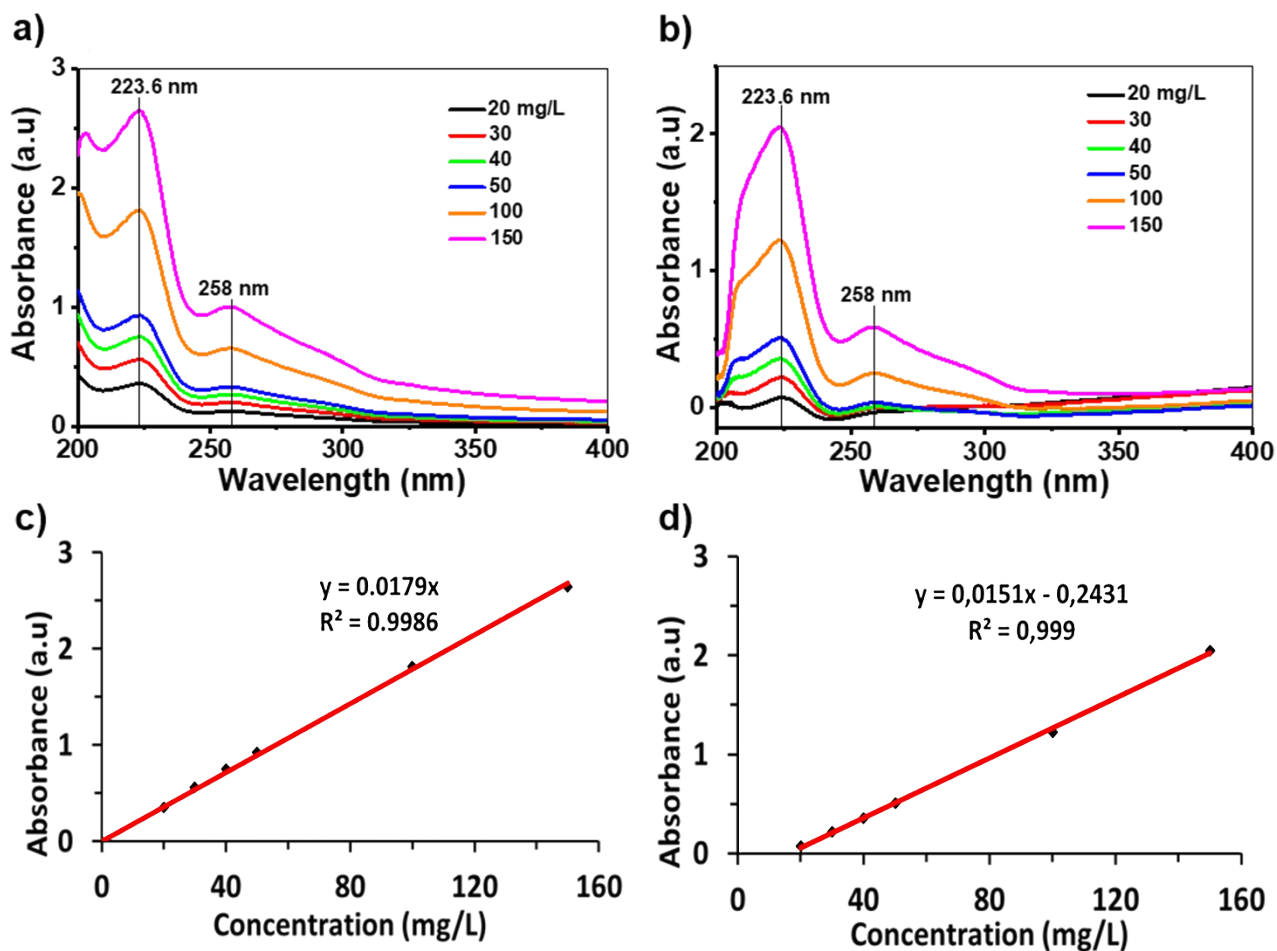


Figure S1. UV-Vis Calibration curves of oil-water mixtures with standard oil concentrations: (a) Milli-Q water and (b) seawater. (c) and (d) show the linear equations used to calculate the concentration of the oil in Milli-Q water and seawater respectively.

Calibration for rGO residue in water

An experiment was performed to analyze the residue rGO from released by GCMs into the solution. The calibration curve of released rGO in water was measured using UV-Vis analysis. A 0.02 mg/ml GO dispersion was reduced with 25 μ l of 5% hydrazine solution and 40 μ l of 25% ammonia solution. The mixture was kept under constant stirring for 1 hour at 95 $^{\circ}$ C using a condenser to avoid

evaporation of the liquids. The obtained rGO dispersion was sonicated for 1 hour to avoid agglomerates and then dilution series were performed in order to obtain a calibration curve.

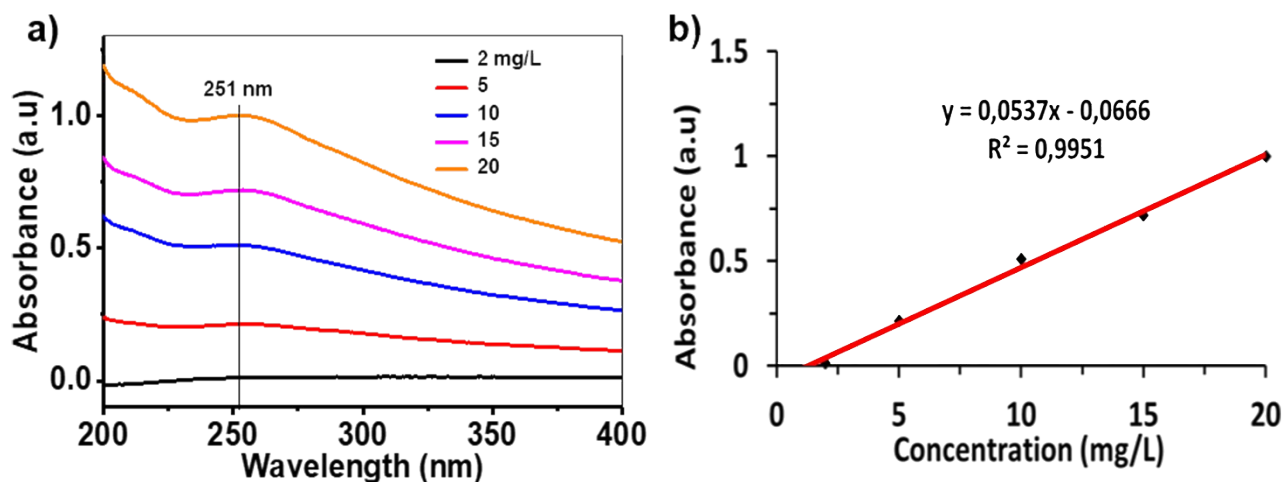


Figure S2. (a) UV-Vis Calibration curves of rGO in Milli-Q water at different concentrations and (b) linear equation used to calculate the concentration of rGO in water.

From the calibration curves and Lambert-Beer's law, a linear correlation for the concentration of rGO in water and the absorbance, was acquired. We calculated the concentration of rGO in water samples, which is convenient in order to discover how much of the coating might be released from the GCMs when used. A 3.0x3.0 cm² piece of MF1 was inserted in a blue cap bottle with 100 ml of Milli-Q water. The piece of MF1 was vigorously stirred or mildly stirred with a magnetic stirrer and 2 ml of water were collected after 10, 20 and 30 minutes. The concentration of rGO was measured using UV-Vis spectrophotometry. The same procedure was used with sonication instead of stirring.

Trials with other types of microfibers and textiles

Other types of commercial microfibers such as kitchen cloth (KC) (Colored Long-Lasting Cleaning Cloth 194450, Tork, Sweden) and absorbing paper (AP) (Cleaning Cloth 510104, Tork, Sweden) have been used to produce GCMs using the same synthetic route. The former is composed of viscose

and polyester while the latter is polyester, polypropylene and cellulose as stated by the supplier. The various materials were coated using 1 or 4 mg/ml GO dispersions (e.g. KC1 and KC4 respectively) and subsequently reduced following the synthesis reported in our work. All samples were highly hydrophobic and the oil uptake capacities between the different microfibers were comparable, indicating the effectiveness of this synthesis method to coat various substrates with rGO. The differences in reusability are attributed to the different mechanical properties of the original fabrics. The samples coated with 4 mg/ml GO showed slightly lower performance in oil uptake capacity, higher consumption of GO and non-uniform coatings with presence of rGO agglomerates. Therefore, they have not been used for additional experiments.

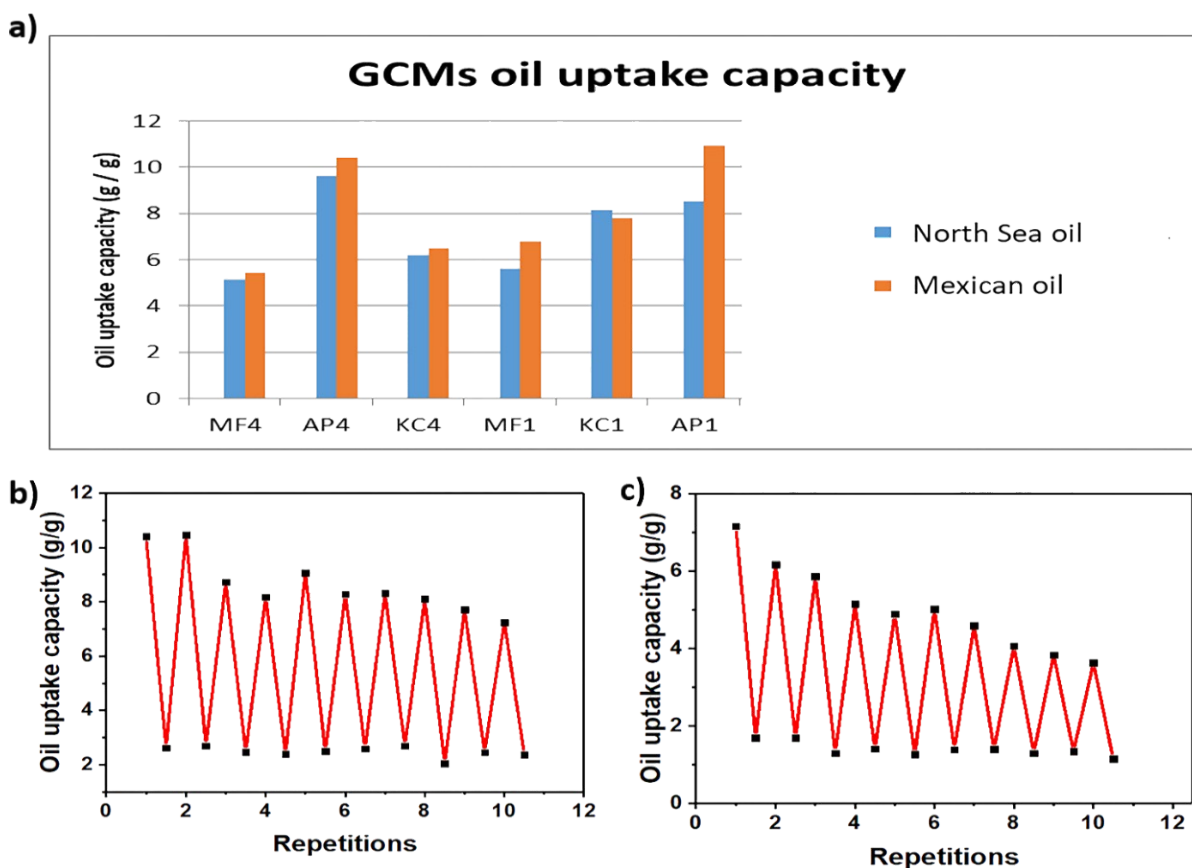


Figure S3. (a) Oil uptake capacity of each GCMs using different crude oils. (b) Reusability test of AP1. (c) Reusability test of KC1.

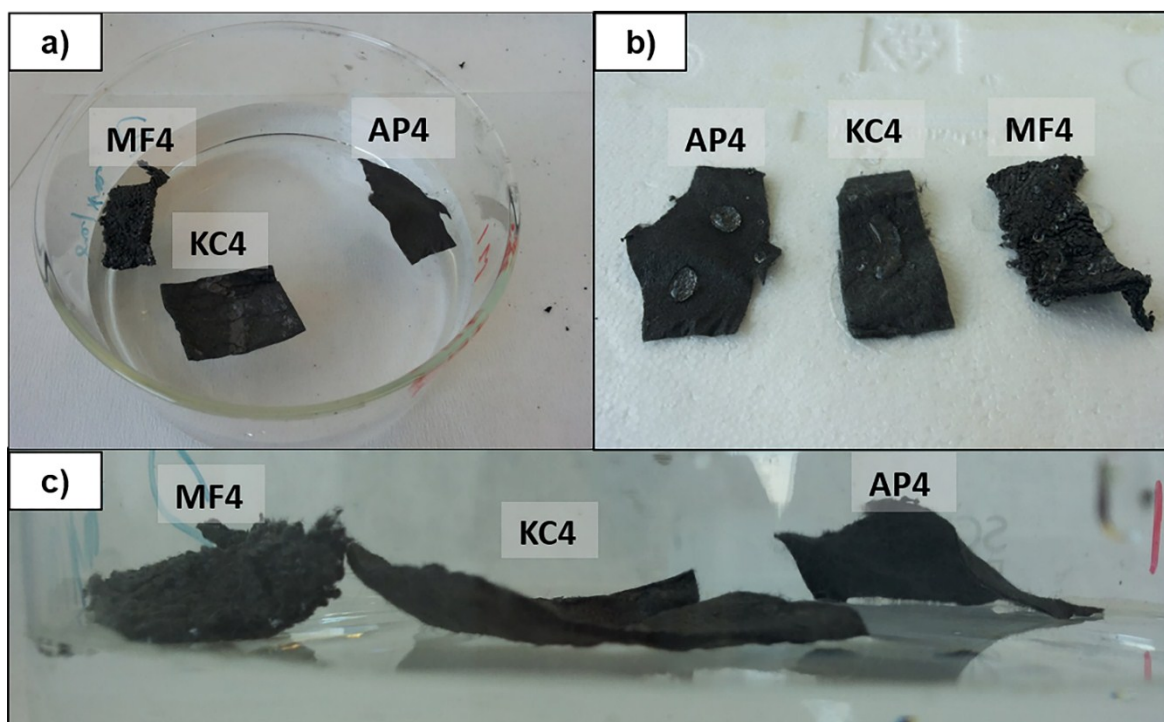


Figure S4. (a) Different GCMs floating in water. (b, c) Hydrophobic behavior of GCMs.

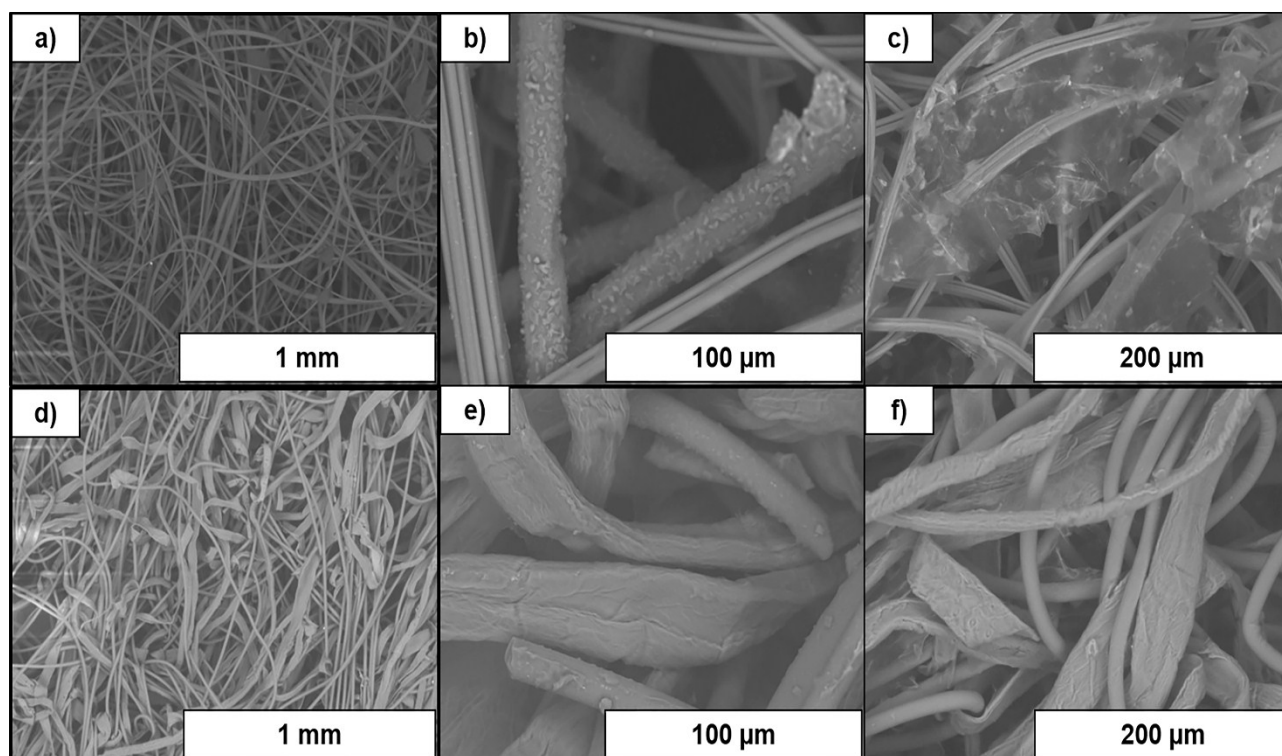


Figure S5: (a) uncoated KC, (b) rGO-coated KC1, (c) rGO-coated KC4 with large rGO agglomerates. (d) uncoated AP, (e) rGO-coated AP1, rGO-coated AP4 with few rGO agglomerates.