Supporting Information for: Engineered nanoparticles for hydrocarbon detection in oil-field rocks

Jacob M. Berlin,[1,#] Jie Yu,[2,3,#] Wei Lu,[1,#] Erin E. Walsh,[1] Lunliang Zhang,[3,4] Ping Zhang,[3] Wei Chen,[4] Amy T. Kan,[3] Michael S. Wong,[1,2]* Mason B. Tomson[3]* and James M. Tour[1,5]*

[1] Department of Chemistry, Rice University

[2] Department of Chemical and Biomolecular Engineering, Rice University

[3] Department of Civil and Environmental Engineering, Rice University, Houston, Texas 77005, USA

[4] College of Environmental Science and Engineering, Nankai University, Tianjin, P. R. China, 300071

[5] Department of Mechanical Engineering and Materials Science, Rice University, Houston, Texas

# These authors contributed equally.

* To whom correspondence should be addressed: mswong@rice.edu, mtomson@rice.edu, tour@rice.edu

General. Unless note otherwise, all chemicals were purchased from Sigma-Aldrich and used without further purification unless otherwise stated. Acetic acid, $CaCl_2 \cdot 2H_2O$, $MgCl_2 \cdot 6H_2O$, NaCl, KCl, $NaHCO_3$, and Na_2SO_4 were purchased from Fisher Scientific (USA). Deionized water was filtered by reverse osmosis followed by a four stage ion exchange water purification system (a Barnstead high capacity cation/anion column, two Barnstead ultra pure ion exchange columns, and a Barnstead organic removal column). Carbon black (Vulcan 9A32) was purchased from Cabot. Dialysis bags (MWCO 5,000) were purchased from CelluSep H1. SWCNTs (HPR 187.4) were purchased from HiPco Laboratory at Rice University. Centrifugation was done using an Adam Analytical Centrifuge. A dolomite core sample from a Kuwait oil well, a Berea sandstone core sample (Missisippian Age, OH) and an Iceland spar calcite sample were used in this study. The dolomite core sample was washed with toluene and methanol to reduce the amount of trapped oil and sieved. The section of ~106 – 250 μm grain range was used in this study. The Berea sandstone and Iceland spar core samples were ground and sieved to be ~106 – 250 μm grain range in the similar manner. The sandstone and calcite particles were washed five times eash with 1 wt% acetic acid and deionized water to remove clays.

Synthesis of HCCs. The HCCs used in this study were from the same batch as was recently reported.[1]

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[1] Berlin J. M.; Leonard A.; Pham T. T.; Daisuke S.; Marcano D. C.; Yan, S.; Fiorentino, S.; Milas, Z. L.; Kosynkin D. V.; Price, B. K.; Lucente-Shultz, R. M.; Wen, X.; Raso, M. G.; Craig, S. L.; Tran, H. T.; Myers J. N.; Tour J. M. “Effective Drug Delivery, *in vitro* and *in vivo*, By Carbon-Based Nanovectors Non-Covalently Loaded With Unmodified Paclitaxel” *ACS Nano*, 2010, **4**, 4621.

Synthesis of PEG-HCCs. The PEG-HCCs used in this study were from the same batch as was recently reported.[1]

Synthesis of PVA-HCCs. DMF (25 mL) was added to HCCs (25 mg) in a 50 mL round-bottom flask equipped with a stir bar. The mixture was sonicated until the HCCs were completely dispersed in DMF. Then *N*,*N'*-dicyclohexylcarbodiimide (206 mg, 0.1 mmol) and 4-dimethylaminopyridine (2 flakes) were added, followed by 2,000 MW polyvinyl alcohol (4.2 g, 2.1 mmol). The reaction mixture was stirred for 16 h, transferred to a dialysis bag and dialyzed in standing DMF for 1 d then in running DI water for 1 week to furnish 30 mL of a PVA-HCC solution.

Synthesis of OCB. A mixture of sulfuric acid (98 %, 180 mL) and phosphoric acid (85.8 %, 20 mL) was added to CB (1 g, 83 mmol) and the mixture was stirred. Potassium permanganate (6 g, 38 mmol) was added in 3 portions over 15 min to the reaction mixture. After 15 min, the mixture was heated to 58 °C and stirred at that temperature for 1 h. The reaction mixture was cooled to room temperature and poured onto ice containing 10 mL of hydrogen peroxide (30%). Sodium hydroxide was slowly added as a fine powder into the acidic reaction mixture until the OCB precipitated out as a black solid. The OCB was collected by centrifuging at 4100 r.p.m. for 90 min. After the solution was decanted, the resulting wet OCB was redispersed in 150 mL of 10% hydrochloric acid and centrifuged again. This process was repeated twice more. Then the wet OCB was dispersed in 50 mL DI water and transferred to a dialysis bag and dialyzed in running DI water for 1 week to remove the residual acid and inorganic salts. The water was removed under reduced pressure and the damp OCB was dried in a vacuum oven at 70°C for 16 h to provide OCB (0.51 g).

Synthesis of PVA-OCB. DMF (25 mL) was added to OCB (25 mg) in a 50 mL round-bottom flask equipped with a stir bar. The mixture was sonicated until the OCB was completely dispersed in DMF. Then *N*,*N'*-dicyclohexylcarbodiimide (206 mg, 0.1 mmol) and 4-dimethylaminopyridine (2 flakes) were added, followed by 2,000 MW polyvinyl alcohol (4.2 g, 2.1 mmol). The reaction mixture was stirred for 16 h, transferred to a dialysis bag and dialyzed in standing DMF for 1 d then in running DI water for 1 week to furnish 30 mL of a PVA-OCB solution with a concentration of 250 ppm, as determined by UV.

Preparation of Seawater. Salts were added to deionized water to prepare a solution with the following concentrations: $CaCl_2$ (0.386 g/L), $MgCl_2$ (0.523 g/L), KCl (1.478 g/L), NaCl (28.311 g/L), Na_2SO_4 (0.072 g/L), $NaHCO_3$ (0.181 g/L).

Preparation of PCB*/PVA-OCB. PVA-OCB (2 mL) was diluted in seawater (47 mL) and PCB* (40 μL) was added. The mixture was stirred at rt for 3 d in the dark and then kept at 4 °C for 14 d without stirring. The mixture was then passed through a PD-10 column (GE Healthcare) to remove free PCB*. The final concentration of PCB* in the mixture was 4 ppb as determined by a scintillation measurement.

Characterization.

Instrument and Sample Preparation Information.

SEM imaging was performed on a high resolution field emission scanning electron microscope (FEI Quanta 400). The dry powders (CB, OCB and PVA-OCB) were mounted onto the conductive tape for imaging. The hydrodynamic diameter of each nanomaterial was characterized through dynamic light scattering (Brookhaven, ZetaPALS with BI-9000AT digital autocorrelator, λ = 656 nm). The electrophoretic mobility of these aggregates was measured by phase analysis light scattering (PALS) using the ZetaPALS setup. A dip-in (Uzgiris type) electrode system with 4 mL polystyrene cuvettes was used, and measurements were taken at 20 °C. TGA was obtained on Q50 TA Instrument, using argon from room temperature to 950 °C at 10°C/min rate. UV data were collected from a Shidmadzu UV-3101 PC and samples contained in 1 mL quartz cuvettes. Samples were dispersed in deionized water upon sonication. Raman spectra were obtained on a Renishaw Raman scope using a 514 nm HeNe laser. XPS experiments were performed on a PHI Quantera SXM scanning X-ray microprobe with 26.00 eV passing energy, 45° take-off angle and a 100 μm beam size.

Determination of Extinction Coefficient at 280 nm.

For each nanomaterial, an aqueous solution was prepared with a known concentration of the nanomaterial. A series of diluted samples were then prepared, and the absorbance of each diluted suspension was measured at λ_{max} 280 nm. The slope of the linear absorbance vs. concentration curve was used to calculate the extinction coefficient of carbon materials at λ_{max} 280 nm according to Beer’s law. The calculated extinction coefficient was 0.0509 L/mg for PEG-HCCs, PVA-HCCs, and PVA-OCBs. A typical calibration curve of PVA-OCBs is shown in Fig. S1.

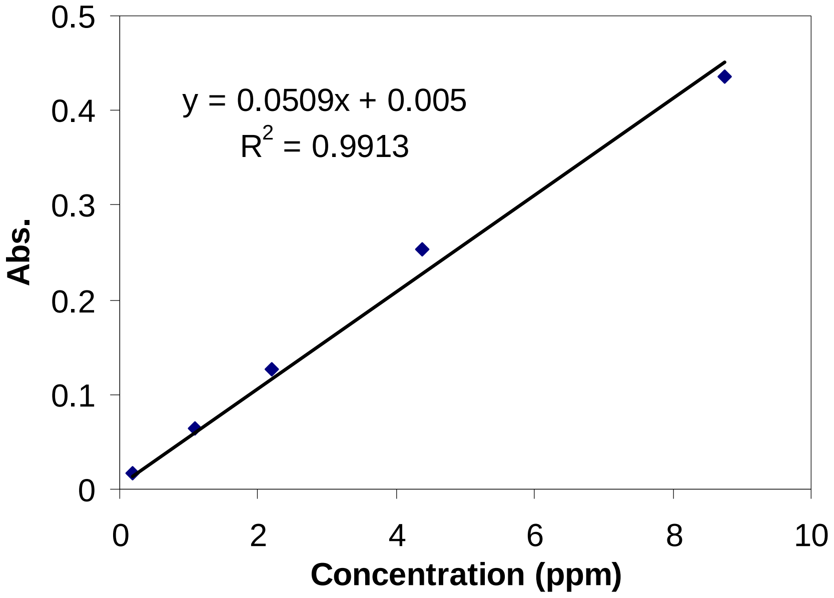


Figure S1. Calibration curve for PVA-OCB absorbance at 280 nm.

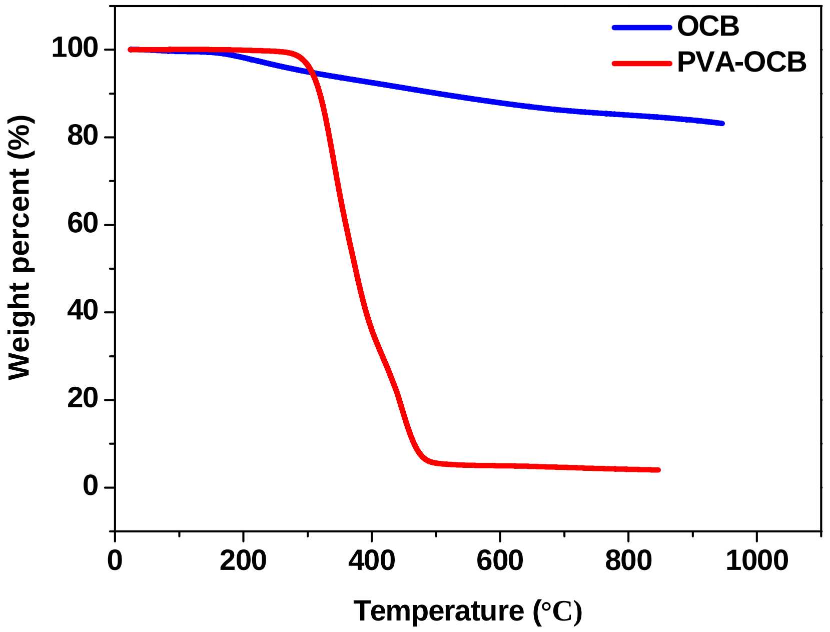


Figure S2. TGA analysis of OCB and PVA-OCB. The weight loss for OCB was 17% and for PVA-OCB it was 96%.

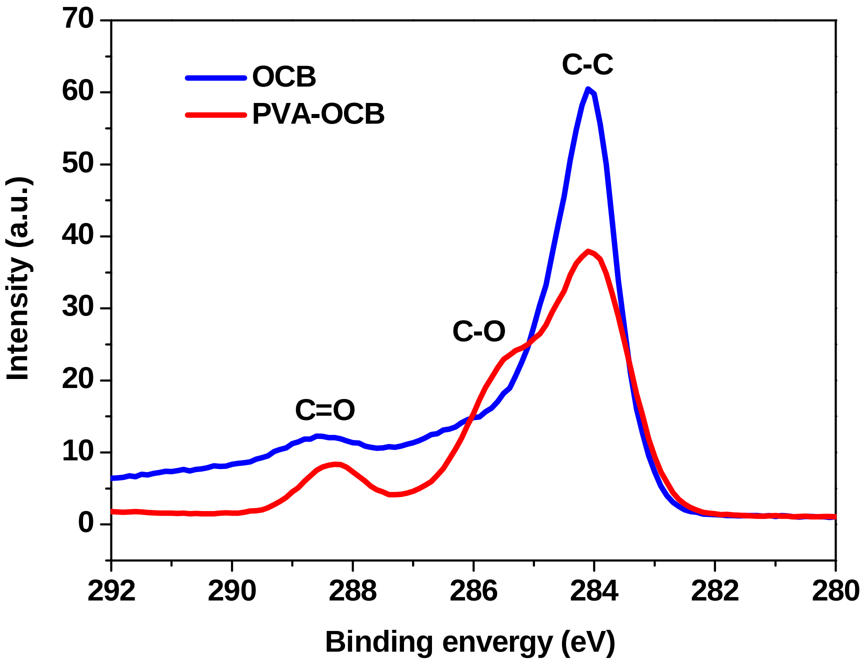


Figure S3. XPS analysis of OCB and PVA-OCB. The oxidation of the OCB is evidenced by the peak at 288.5 eV, indicative of C=O bonds. The PVA functionalization is evidenced by the new peak at 286 eV, indicative of C-O bonds.

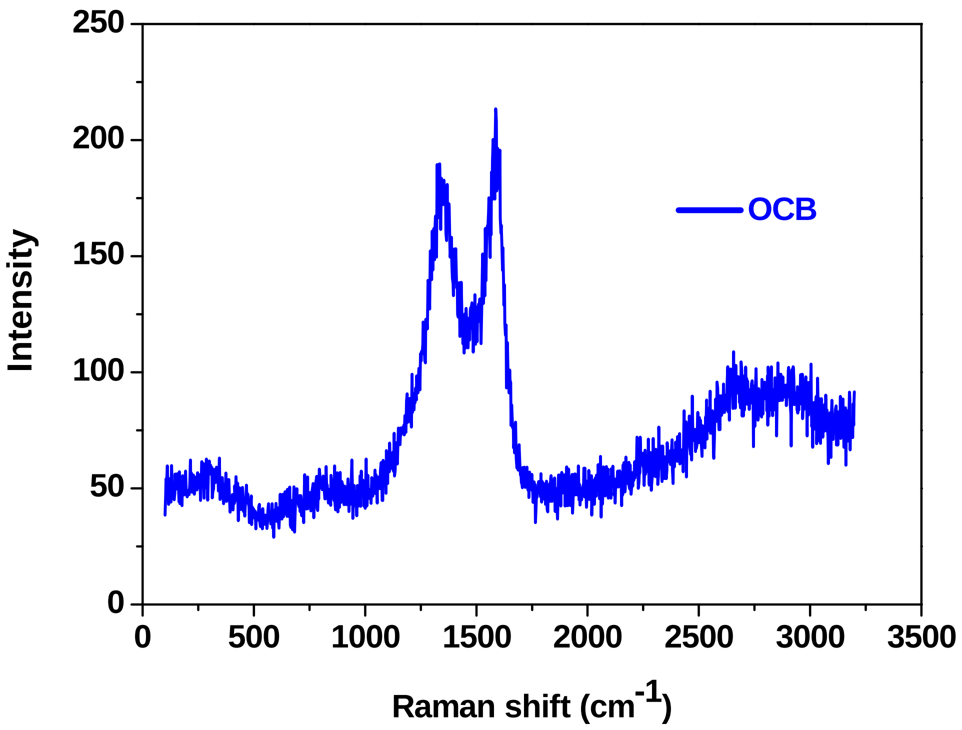


Figure S4. Raman spectrum for OCB. No Raman spectrum could be obtained for the PVA-OCB.

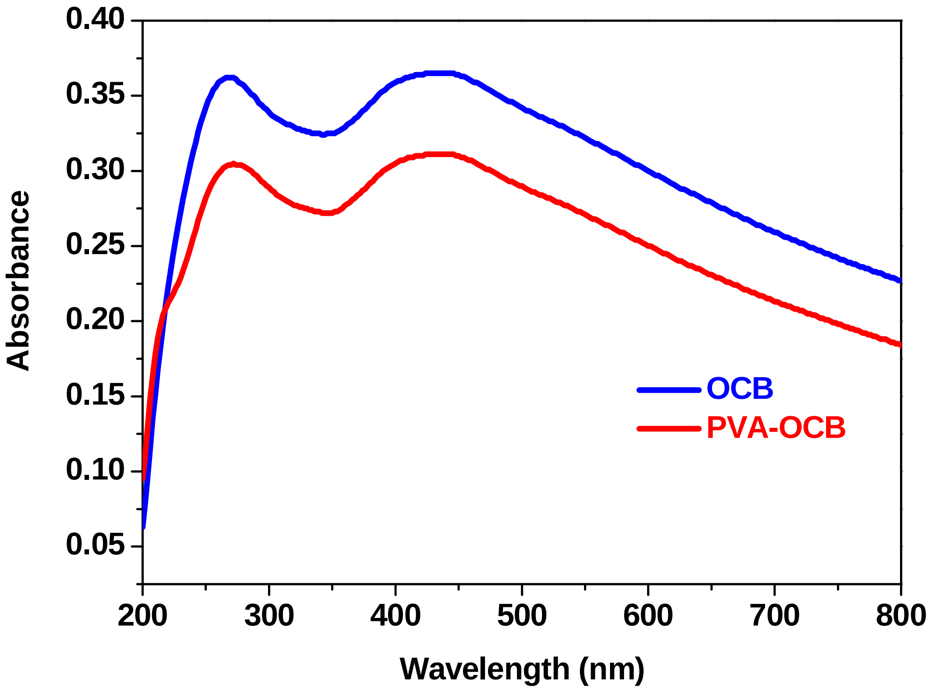


Figure S5. UV spectroscopy for OCB and PVA-OCB. The two peaks are 270 and 425 nm.

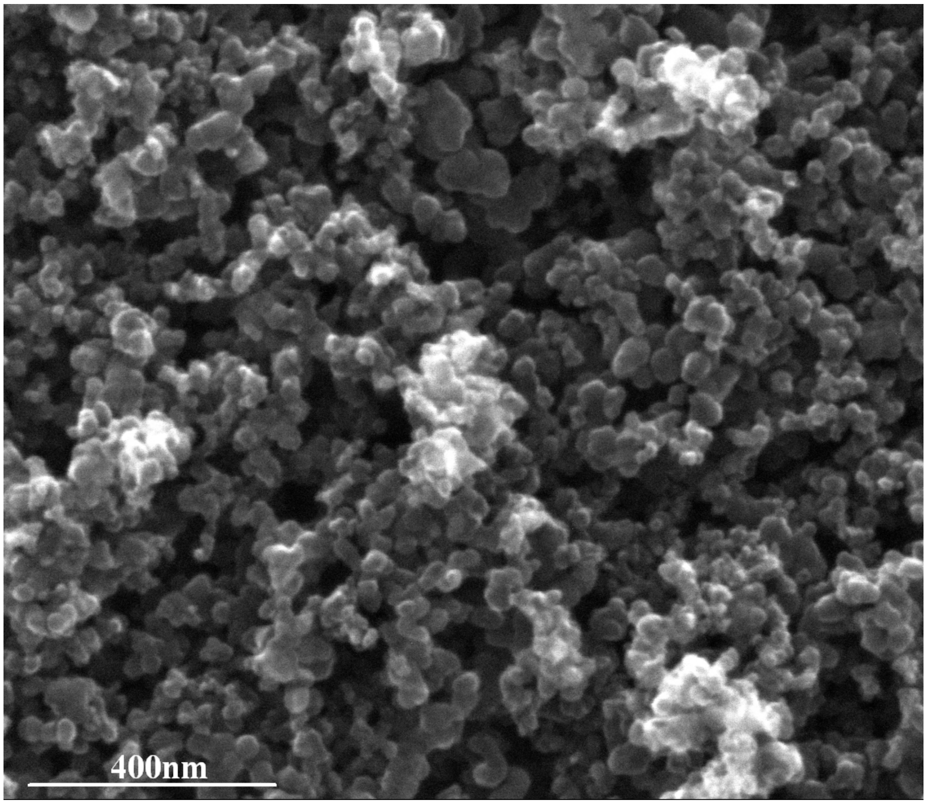


Figure S6. SEM imaging of carbon black.

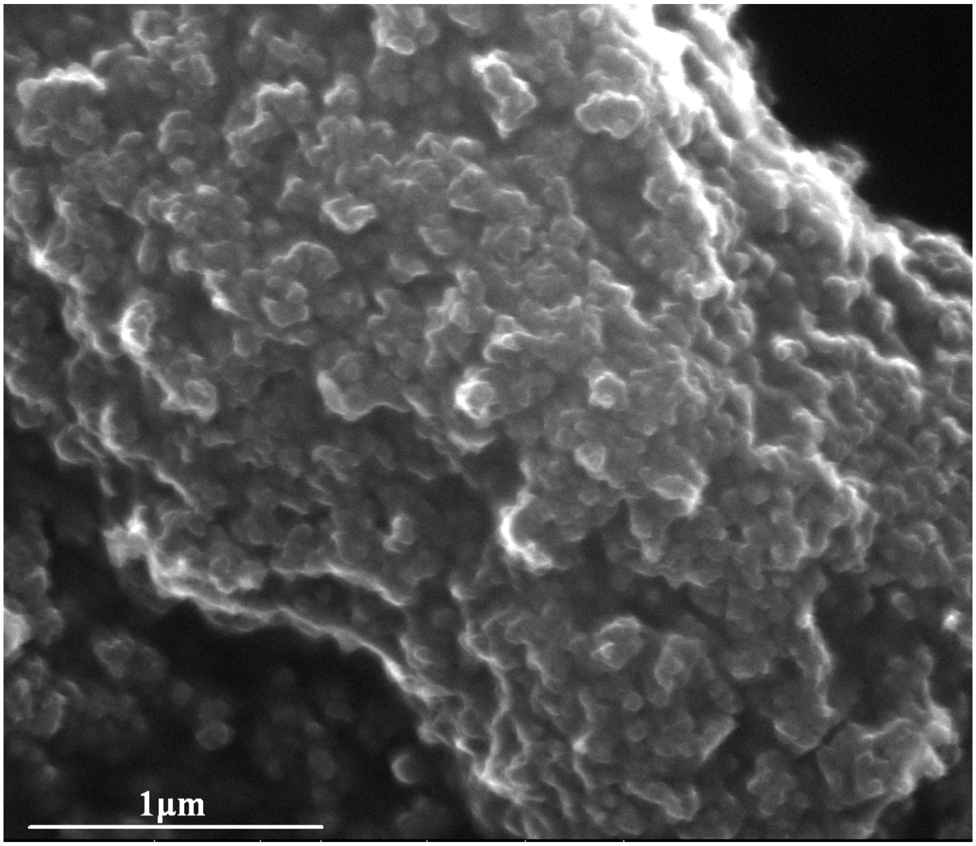


Figure S7. SEM imaging of OCB.

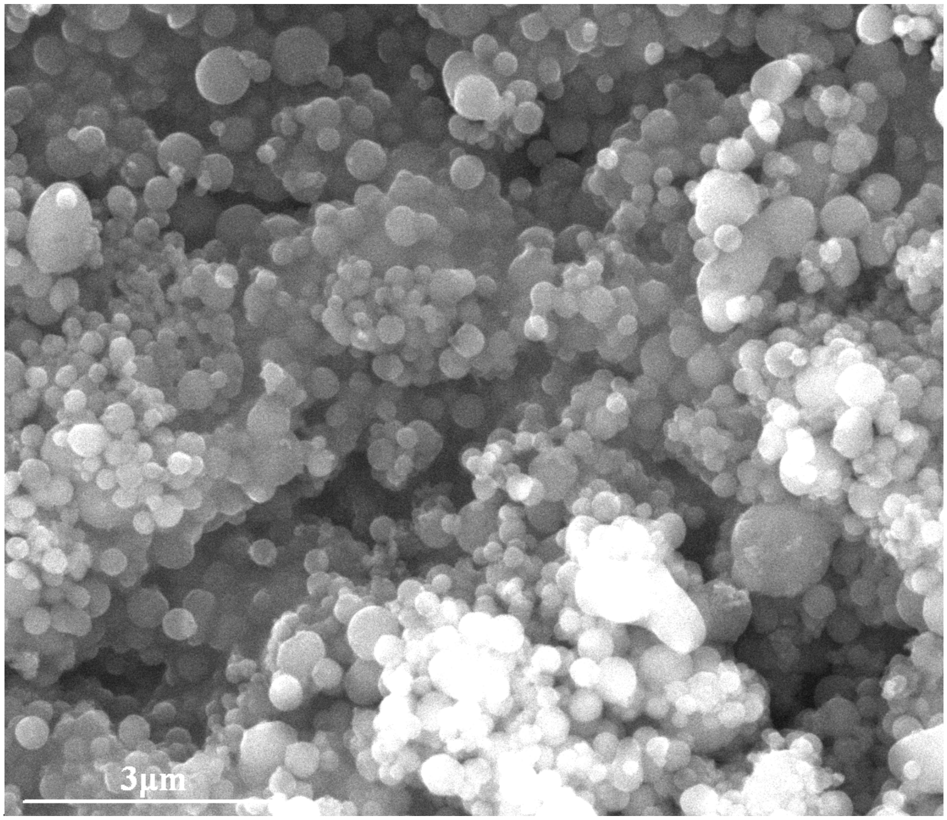


Figure S8. SEM image of PVA-OCB

Transport studies.

General Column preparation

In a typical set-up, ground rock grains were slowly packed into the glass column with a length about 6 - 7 cm (Borosilicate glass columns with an adjustable end piece, cross sectional area=0.3421 cm^2, Omnifit, Bio-Chem Valve Inc., Boonton, NJ). The dry column was flushed with deionized water for several days to remove the trapped air bubbles. Porosity of columns was gravimetrically determined. A three-way valve (Omnifit) was used to connect a 60-mL plastic syringe (BD, Franklin Lakes, NJ, USA) and the column. The whole system was connected by PTFE tubing (Omnifit). A non-reactive tracer, tritiated water, was loaded into the syringe and flowed through the column. The breakthrough of tritiated water was measured to characterize the porosity and dispersity of the column. Prior to sample injection, each column was washed with sample-free solution (deionized water or synthetic seawater) for 16 h.

The characteristic parameters for each type of columns and the flow parameters are given in Table S1.

Table S1. Column properties.

	Flow rate (mL/min)	Retardation factor (R)	Dispersion coefficient (D) (cm^2/min)	Porosity (%)
Sandstone	0.13	1.21	0.03	0.52
Calcite	0.13	1.09	0.05	0.65
Dolomite	0.13	1.01	0.03	0.67

Nanomaterial Sample Preparation and Breakthrough

Before loading, the nanomaterial suspension was sonicated using an ultrasonic processor (VCW-500W, 22% output, Sonics & Materials Inc., Newtown, CT) with a titanium alloy tapered microtip (Ti-6Al-4V) and was filtered through a PES filter of 0.45 μm pore size (Whatman, USA). For nanomaterial breakthrough, a nanomaterial suspension was loaded into the syringe and was pumped (New Era Pump System Inc., Wantagh, N.Y.) to the column at a linear average pore velocity of ~0.67 cm/min. For each pore volume, the effluent from the column was collected in a 2 mL glass vial. The concentration of the nanomaterial in the effluent was determined by absorbance at 280 nm on UV-visible spectrophotometer (DR/4000, HACH Company, Loveland, CO). When the breakthrough reached a plateau or the total breakthrough was 100%, the column was flushed with the sample-free background solution.

In addition to the materials described in the main body of the manuscript, we also evaluated the breakthrough of PEGylated graphene oxide nanoribbons (PEG-GONR) and PEGylated graphene oxide (PEG-GO), but they performed poorly.

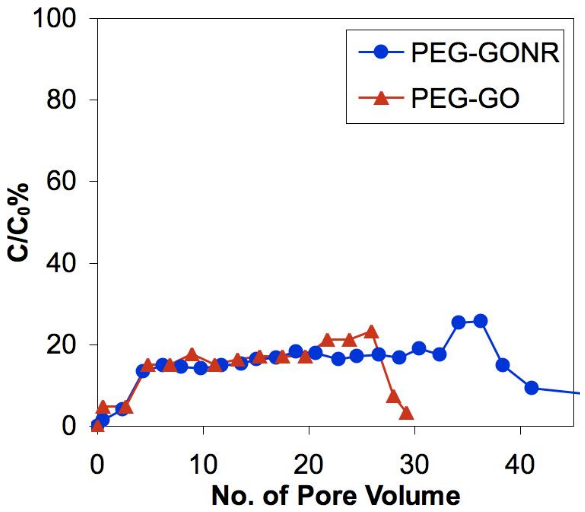
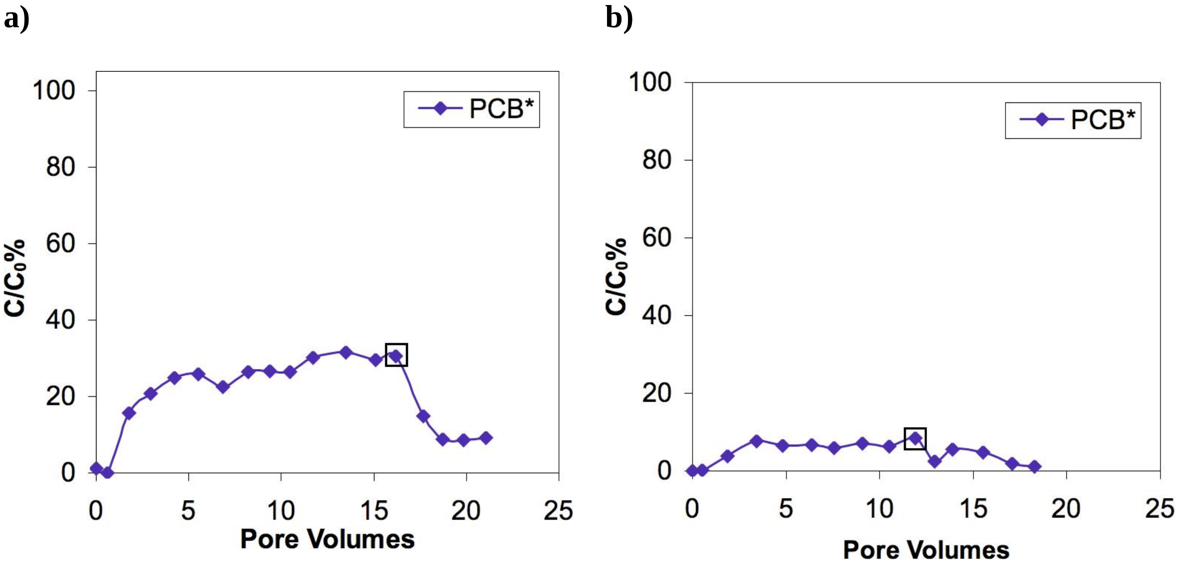


Figure S9. Breakthrough in a sandstone column of PEG-GONR and PEG-GO in seawater.

Control Studies on PCB transport

PCB*: A control PCB*/seawater sample was prepared by diluting a methanol solution (20 μL) of PCB* (23 ppm) into 50 mL of synthetic seawater at room temperature through a glass syringe equipped with a stainless steel needle. The PCB*/seawater mixture was stirred at rt for 3 d in the dark and then kept at 4 °C for 14 d without stirring. For the column experiment, the PCB*/seawater solution was loaded into a 100 mL glass syringe (Hamilton, Nevada, USA). Due to the adsorption of PCB* to glass and PTFE, the actual PCB* concentrations in the inlet and outlet flows were determined by scintillation measurement. The concentration of inlet PCB was calculated to be 8 ppb.

PCB*/PVA: In order to evaluate if PVA alone could transport PCB*, a highly concentrated aqueous solution of PVA was added to a PCB*/seawater mixture to furnish a final sample containing 8 ppb PCB* and 20 ppm PVA. The sample was then loaded into a 100 mL glass syringe (Hamilton, Nevada, USA) and pumped into a sandstone column.



c)

d)

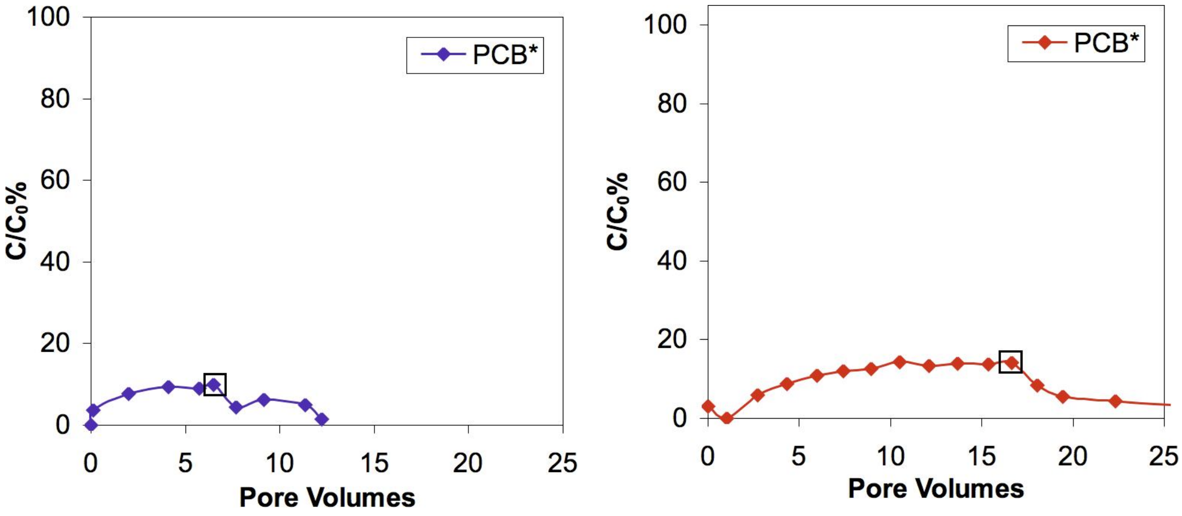


Figure S8. Breakthrough of PCB* without a nanoparticle carrier. a) Breakthrough for calcite; b) breakthrough for dolomite; c) breakthrough for sandstone; d) breakthrough when mixed with PVA for sandstone. The black boxes indicate when the flow was switched from the PEG-HCC solution to seawater.