## Highly stable carbon nanoparticles designed for downhole hydrocarbon

## detection-electronic supplementary information

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# **Table of Contents**

Figure S1: Dynamic light scattering (DLS) plots, page S2. Materials and methods: page S2-S6.



Figure S1. Dynamic light scattering (DLS) plots for the PVA(50k)-coated fCB NPs before and after the treatment with light or high sulfation. All NPs were dispersed in deionized water and the temperature was controlled from 25  $^{\circ}$ C to 70  $^{\circ}$ C.

### Materials and methods

### Synthesis of functionalized carbon black (fCB)

4,4'-Azobis(4-cyanopentanoic acid) (ACPA) was used for the introduction of carboxyl groups onto the carbon black surface. Typically, carbon black (3.0 g, 0.25 mole) and ACPA (6.0 g, 0.021 mole) were added to THF (120 mL). The solution was stirred at 65 °C under nitrogen for 24 h. The resulting mixture was filtered and the filter cake was washed with excess THF, followed by drying at 100 °C in a vacuum oven overnight to yield carboxyl

group-functionalized carbon black (fCB).

### Synthesis of polyvinyl alcohol grafted fCB (PVA-fCB)

The as-synthesized fCB (15 mg) was dispersed in a 100 mL round bottom flask with anhydrous DMSO (25 mL) by sonication overnight. A separate flask containing polyvinyl alcohol (1.0 g, Mw ~ 50,000) and DMSO (25 mL) was heated to ~70 °C until the PVA was dissolved in the DMSO. When the PVA solution cooled to room temperature, it was transferred to the first round bottom flask containing the fCB in DMSO, and then N,N'-dicyclohexylcarbodiimide (DCC, 140 mg, 0.68 mmol) and 4-dimethylaminopyridine (DMAP, 20 mg, 0.16 mmol) were added. The reaction mixture was stirred at room temperature for 24 h, followed by transfer to a dialysis bag and dialysis in standing DMSO for 3 d then in running DI water for 1 week to furnish PVA-fCB aqueous solution.

### Synthesis of sulfated polyvinyl alcohol grafted fCB (sPVA-fCB)

Similar to the method used to synthesize PVA-fCB, before the second dialysis in running DI water, the resulting PVA-fCB in DMSO was further treated with 1 M ClSO<sub>3</sub>H in CH<sub>3</sub>COOH (3.0 mL) at 60 °C for 30 min to yield lightly sulfated PVA-fCB (LsPVA-fCB), while the highly sulfated PVA-fCB (HsPVA-fCB) was obtained by treating the PVA-fCB in DMSO with 1 M

ClSO<sub>3</sub>H in CH<sub>3</sub>COOH (4.5 mL) at 75 °C for 90 min. After sulfation, the resulting solution was neutralized to ~7.0 with 1 M NaOH(aq) until the pH ~7.0. The LsPVA-fCB or HsPVA-fCB aqueous solution could be obtained after dialysis under running DI water for 1 week.

#### **Preparation of THA/LsPVA-fCB nanoreporter**

Triheptylamine (THA), a highly hydrophobic molecule due to its long alkyl chains, features an odd number of nitrogen atoms, which can be easily determined by mass spectrometry analysis according to the nitrogen rule. Here, we stirred 50 mL of the LsPVA-fCB solution with THA (~5  $\mu$ L) for one day, and then passed the solution through a size exclusive column (PD-10) in order to remove any unbound THA. The remaining THA was physically adsorbed on the LsPVA-fCB hydrophobic domains, so that they would not be filtered out by the PD-10 column.

## **Preparation of API brine**

API brine was prepared by dissolving CaCl<sub>2</sub> (anhydrous, 10 g, 0.09 mole, 2 wt% in final solution) and NaCl (40.0 g, 0.68 mole, 8 wt% in final solution) in deionized water (450 g, 25.0 mole).

### **Transport studies**

### 1. General column preparation

Ground rock grains were slowly packed into the glass column with a length about 6-7 cm

(Omnifit borosilicate glass columns with an adjustable end piece, cross sectional area = 0.34 cm<sup>2</sup>, Bio-Chem Valve Inc., Boonton, NJ). The packed rock materials were retained by 10 µm stainless steel screens (Valco Instruments Inc., Houston, TX) on both ends of the column. A three-way valve was used to connect a 60 mL plastic syringe to the column. PTFE tubing (Omnifit) was used for all tubing connections in the system. The packed columns were flushed with CO<sub>2</sub> (purity > 99%) for 30 min to remove the trapped air bubbles. Then the columns were flushed with API brine at a flow rate of 8 mL/h for 24 h to stabilize the rock grains. Tritiated water, as a non-reactive tracer, was injected into the columns to characterize the porosity and dispersity of the column. The pH of influent solutions in all column experiments was 6.4.

	Flow rate	<b>Dispersion Coefficient</b>	Porosity <sup>a</sup>	$\mathbf{R}^2$
	(m/24h)	(cm <sup>2</sup> /min) <sup>a</sup>		
Sandstone	9.3	0.0245 (0.0026)	0.4795	0.998
			(0.0017)	
Calcite	9.3	0.0416 (0.0032)	0.4500	0.998
			(0.0016)	

Table S1. Column properties

a. Numbers in parentheses are the standard deviations

#### 2. Isooctane-containing column preparation

After flushing the column with API brine for 24 h, the calcite column was then flooded with isooctane (Fisher Scientific, USA) at a flow rate of 6 mL/h until no water was produced in the effluent. Next, API brine was injected into the column at 8 mL/h until no more isooctane was produced in the effluent. The volume of isooctane remaining in the column was calculated by measuring the amount of isooctane produced from the water flood. Residual isooctane saturation is the ratio of the volume of isooctane to the predetermined pore volume.

### 3. Nanomaterial sample breakthrough

The NPs were suspended in the API brine and the mixture was filtered through a 0.45 µm pore size PES filter (Whatman, USA). The NPs suspension was then pumped (New Era Pump System Inc., Wantagh, N.Y.) to the columns at a linear average velocity of 9.3 m/d. The effluent was collected in a 2 mL glass vial. The concentration of nanoparticles was measured by UV-visible spectrophotometer (DR/4000, HACH Company, Loveland, CO) at 232 nm. When the breakthrough reached a plateau, the column was flushed with API brine.