Engineered nanoparticles for hydrocarbon detection in oil-field rocks†

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Received 7th July 2010, Accepted 4th November 2010
DOI: 10.1039/c0ee00237b

Polyvinyl alcohol functionalized oxidized carbon black efficiently carries a hydrophobic compound through a variety of oil-field rock types and releases the compound when the rock contains hydrocarbons.

The transport of small hydrophobic organic molecules through porous media has been studied for many years. In isolation, these hydrophobic molecules sorb very strongly to nearly all types of soil. However, it has been observed that these hydrophobic chemicals disperse more broadly in the environment than would be expected based on their strong affinity for binding to soil.[1] One possible explanation for this behavior is that organic macromolecules, which possess amphiphilic characteristics, may sequester the hydrophobic small molecules and facilitate their transport by carrying them within the macromolecule.[2,3] Laboratory scale experiments have demonstrated this effect, with some cases, such as the use of β-cyclodextrin, showing highly efficient transport of a variety of hydrophobic aromatic molecules through soil.[4,5] However, selective release of the transported cargo has not been reported and β-cyclodextrin only forms 1 : 1 inclusion complexes with its hydrophobic cargo.

Recently, a new class of compounds, nanomaterials, has been investigated for transport through porous media. Nanomaterials are defined as having at least one dimension of less than 100 nm, and they possess a much larger surface area relative to traditional polymers used for the transport of hydrophobic cargo. Nanomaterials are expected to have significantly different transport behavior in porous media as a result of their larger size and more rigid shape as compared to polymers, and the design of nanoparticles (NPs) with efficient subsurface transport is an ongoing challenge. Nanomaterials prepared from a variety of precursors, including carbon, iron and silica, have varying abilities to flow through porous media. Water-dispersible aggregates of [C60]fullerenes can flow through sand samples and glass beads, although the breakthrough of the fullerenes is very low at early pore volumes and gradually increases over time.[6,7] The use of a water-soluble fullerene derivative, as opposed to the water-dispersible aggregates, showed improved breakthrough for a column of glass beads.[8] Single-walled carbon nanotubes (SWCNTs), which are also prone to aggregation, show limited breakthrough in porous media.[9] Reducing the SWCNTs ability to aggregate by wrapping them with a surfactant or binding humic acid to them improves their mobility in porous media.[10] Similar behavior has been observed for silica and iron, as functionalization of the particles with a hydrophilic polymer, either polyethylene glycol (PEG) or carboxymethyl cellulose, reduces their affinity for aggregation and improves their transport through porous media.[11–14]

We have recently developed NPs with rigid cores of less than 40 nm in length and 1 nm wide consisting of PEG-functionalized hydrophilic carbon clusters (collectively, PEG-HCCs). HCCs are prepared from SWCNTs through a harsh oxidation procedure wherein they become highly oxidized, yet they retain some hydrophobic domains.[15,16] Covalently attaching PEG by coupling polymer chains to many of the carboxylic acids on the surface of the HCCs renders the particles soluble in aqueous

Broader context

Worldwide energy demand continues to increase at a rapid pace. In time, it is desirable to find alternative energy sources to meet this demand, but in the near-term there is a pressing need for improved downhole oil identification. Tracers have long been used to map entry/exit well correlations in the oil-field, but they do not provide any information about the environment between the entry and exit locations. Here we show that nanoparticles can be engineered to detect hydrocarbons in oil-field rocks. These nanoparticles could be used as second generation tracers that not only provide entry/exit correlations but also indicate whether or not it is worth attempting to recover oil from that area. This is of overarching significance and could have enormous economic impact as oil-fields become more mature and the easily extracted oil is no longer available. Improved methods of assessment of the nano-sized domains within oil-field environments and between drill-holes in particular could have a profound impact in recovery processes. In addition, this detection ability could also be used in contaminated areas.

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† Electronic supplementary information (ESI) available: Experimental details; characterization of nanoparticles; breakthrough curves for controls and other materials. See DOI: 10.1039/c0ee00237b

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solutions.[17] Hydrophobic compounds introduced into an aqueous solution of PEG-HCCs are sequestered on the hydrophobic domains of the HCC core. This technique was used to load the PEG-HCCs with the hydrophobic chemotherapy drug paclitaxel and deliver it in vivo.[18]

Here we show that this basic design of sequestering a hydrophobic compound in a NP composed of an oxidized carbon core and a polymer shell can be extended to efficiently transport hydrophobic compounds through oil-field rocks and selectively release them when the rock contains oil. In particular, using oxidized carbon black (OCB) as the core and polyvinyl alcohol (PVA) as the shell, efficient transport and selective release of 2,2′,5,5′-tetrachlorobiphenyl (PCB) is demonstrated. This NP, PVA-OCB, can be produced on large scale and is expected to be environmentally benign though their environmental fate has not yet been assessed. PVA is biodegradable,[19] and carbon black is naturally abundant in the environment.[20] These readily-prepared NPs bearing cargo could be injected into the subsurface and then recovered and analyzed for the presence of the cargo; release of the cargo would indicate the presence of oil. When used in this manner, the NPs can be described as nanoreporters (Fig. 1).

The study was initiated by analyzing the breakthrough of PEG-HCCs in different oil-field rock types. Most previous NP breakthrough studies were done in negatively charged model porous media, such as glass beads and sand. In this paper, we selected two natural rocks for initial study: Berea sandstone and dolomite from an oil-field in Kuwait, in order to evaluate our NPs in a more realistic and more challenging environment. Sandstone is predominantly silica mineral that is negatively charged at neutral pH, but dolomite is a carbonaceous rock, rich in calcium and magnesium, with a net positive charge.[21] Both rock types are common in oil-rich environments. The materials used in this work were obtained from actual field samples. In order to test the flow properties of PEG-HCCs through these materials, the two rock types were separately ground and sieved to provide ~106–250 μm particles that were packed into a glass column. When each packed column was prepared, the volume of liquid contained in the fully saturated column (the pore volume) was determined. The efficiency of nanomaterial breakthrough was determined by measuring the concentration of nanomaterial in the effluent relative to the concentration in the influent as a function of the amount of solution passed through the column, measured in pore volumes. All of the NPs were injected at a concentration of 20 ppm. A synthetic brine solution designed to be equivalent to seawater was chosen as the aqueous carrier solution for the PEG-HCCs, as seawater is the most commonly used aqueous solution for oil-field work. PEG-HCCs in a seawater solution were able to breakthrough in both rock types (Fig. 2). While the breakthrough in sandstone quickly reached greater than 80%, the breakthrough in dolomite initially reached only 60% and then very slowly increased to complete breakthrough. Performing the dolomite experiment using deionized (DI) water instead of seawater as the aqueous carrier for the PEG-HCCs resulted in rapid breakthrough to an extent >80%. The gradual increase in breakthrough over time when seawater is used and the improved breakthrough in DI water suggests that a significant factor for the retarded breakthrough in dolomite is surface interactions between the PEG-HCCs, the salts in solution and the dolomite surface. The zeta potential of the PEG-HCCs was −35 mV, consistent with carboxylic acids remaining on the surface of the HCC cores. These may be forming the bridging interactions.

In order to improve the breakthrough of the NPs, the polymer shell was changed from PEG to PVA (eqn (1), note only one of each functional group on the HCC core is shown). Fewer carboxylic acids should be left on the HCC core after coupling to PVA as compared to PEG, as for similar levels of polymer coverage, the PVA has many more hydroxyl groups available for coupling. Indeed, the zeta potential of PVA-HCCs was found to

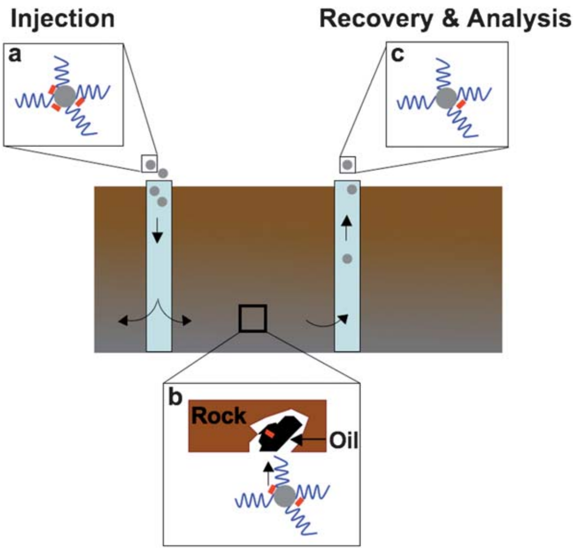


Fig. 1 Schematic of oil detection by nanoreporters. (a) PVA-OCB NPs (grey circle with blue lines radiating) carrying hydrophobic cargo (red rectangles) are injected into the subsurface. (b) While flowing through the subsurface, the nanoreporters encounter oil and release their hydrophobic cargo into the oil. (c) The nanoreporters are recovered and analyzed for the presence of the cargo; the extent of the cargo's absence in the PVA-OCB indicates the extent of subsurface oil.

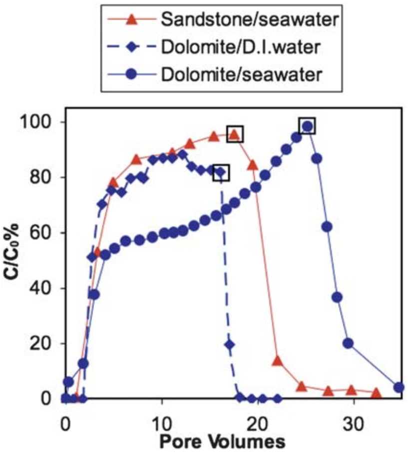
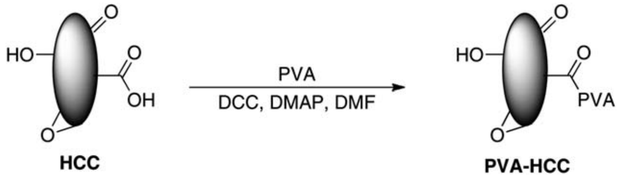


Fig. 2 Breakthrough of PEG-HCCs in sandstone and dolomite. The percentage of PEG-HCCs in the effluent relative to the influent, as determined by UV absorbance. The black boxes indicate when the flow was switched from the PEG-HCC solution to DI water or seawater.

be −20 mV as compared to the −35 mV for PEG-HCCs, suggesting that fewer free carboxylic acids remain.



(1)

If used quickly after being prepared, PVA-HCCs showed comparable breakthrough in sandstone and dramatically improved breakthrough in dolomite relative to PEG-HCCs (Fig. 3). However, if the NPs were stored for 8 d in the seawater solution and then used, the breakthrough in dolomite became significantly retarded.

In an effort to reduce the NPs aggregation, several alternative carbon nanomaterials were evaluated for use as the core of the NPs, including graphene oxide nanoribbons,[22] graphene oxide flakes[23] and oxidized carbon black (OCB). The graphene materials showed significantly reduced breakthrough (See ESI†), but the OCB-containing NPs demonstrated efficient breakthrough, improved stability in seawater and the ability to transport and selectively release a hydrophobic reporter molecule. OCB was prepared by treating carbon black with H_2SO_4, H_3PO_4 and $KMnO_4$, an oxidation procedure we recently developed for the preparation of graphene oxide and graphene oxide nanoribbons (Fig. 4a).[22,23] The OCBs were significantly less oxidized than the HCCs, as the weight loss during thermogravimetric analysis (TGA), which is indicative of the level of oxygen content, was only 17% for OCB while 58% for the HCCs. 2,000 molecular weight (MW) PVA was coupled to the OCB to provide PVA-OCB particles that were 150 nm in diameter in deionized water as determined by dynamic light scattering. PVA-OCB maintains the spherical shape characteristic of carbon black (Fig. 4b). When used immediately after preparation, PVA-OCB demonstrated excellent breakthrough in sandstone and dolomite, and even after being left in a seawater solution for 14 d, they demonstrated good breakthrough in dolomite (Fig. 4c). This is a major improvement over all of the other NPs tested.

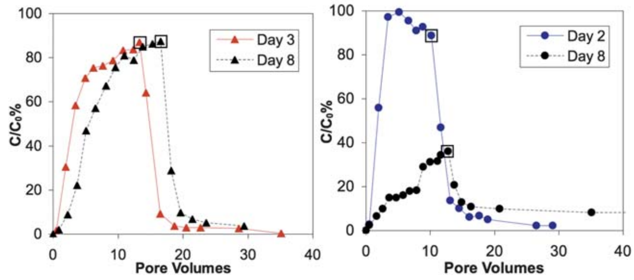


Fig. 3 (a) Measurement of PVA-HCCs flowing through sandstone. (b) Measurement of PVA-HCCs flowing through dolomite. Between the early experiments and those on day 8, the seawater solution of PVA-HCCs was allowed to stand at room temperature. The black boxes indicate that the flow was switched from the PEG-HCC solution to pure synthetic seawater.

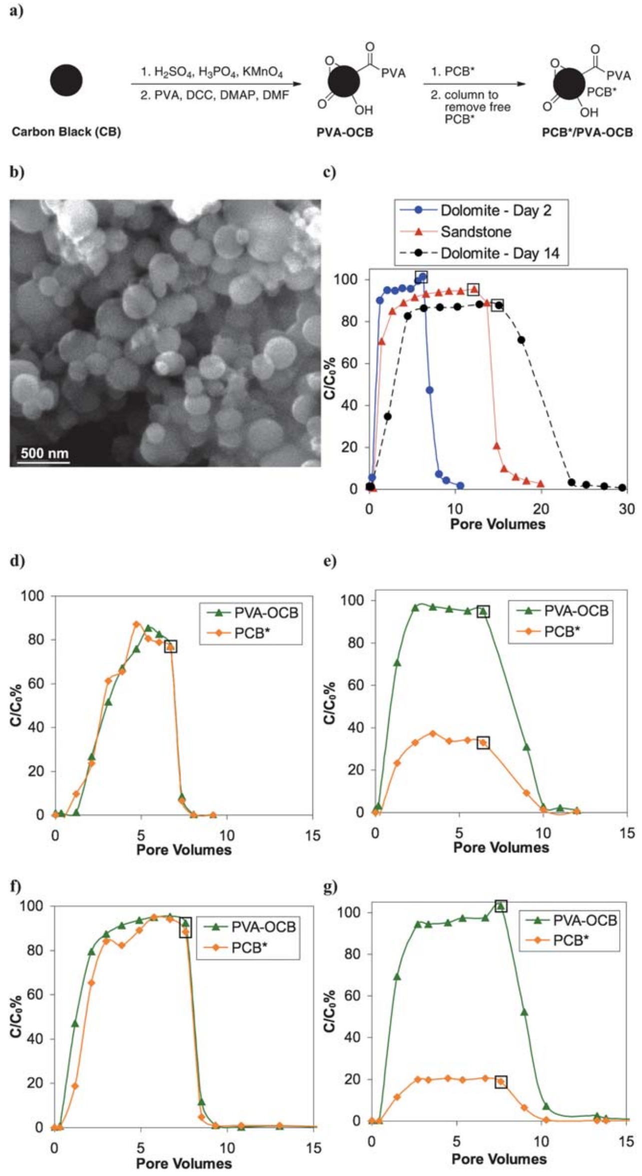


Fig. 4 (a) Synthesis of PVA-OCB and sequestration of PCB*. (b) SEM of PVA-OCB. (c) Breakthrough of PVA-OCBs in sandstone and dolomite immediately after preparation and after 14 d. Breakthrough for both components of PCB*/PVA-OCBs in (d) sandstone, (e) isooctane-containing sandstone, (f) calcite and (g) oil-containing dolomite. The black boxes indicate that the flow was switched from the PEG-HCC solution to pure synthetic seawater.

The granular filler in the columns had a size from 106 to 250 μm and the porosity was 0.52 for the sandstone column and 0.67 for the dolomite column, suggesting that the pore sizes were tens of microns. Since all of the NPs are significantly smaller than that and were filtered through a 0.45 μm filter prior to introduction to the columns, it is unlikely that straining of individual NPs is responsible for the different breakthrough properties of the PEG-HCCs, PVA-HCCs and PVA-OCBs in sandstone and dolomite. Instead, NP aggregation plays a large role as this is an equilibrium phenomenon, so even after filtration, larger aggregates can be reformed. Breakthrough is likely reduced by NP aggregates being strained by the columns.[24,25] The retention of

NP aggregates blocks smaller pores in the columns resulting in the increased breakthrough seen over time for many conditions. The presence of salt ions promotes aggregation for oxidized carbon nanomaterials, explaining the improved breakthrough when DI water is used instead of seawater. The tendency of these carbon-based NPs to aggregate in the presence of salt ions is a materials property that can be controlled by judicious choice of the polymer coating. The aggregates are also generally retained more by the dolomite than the sandstone, as the dolomite is carbonaceous and can form bridging interactions with the salt ions that are part of the aggregates.

PVA-OCBs can be used as nanoreporters by loading them with hydrophobic cargo and selectively releasing the cargo when the oil-field rock contains hydrocarbons. ^{14}C-labeled 2,2′,5,5′-tetrachlorobiphenyl (PCB*) was selected as a model compound because it is extremely hydrophobic, and we have extensive experience monitoring its interaction with porous media. The PCB* was adsorbed onto the PVA-OCBs by mixing them together in synthetic seawater, allowing the solution to equilibrate at 4 °C and then passing it through a PD-10 desalting column to remove any unbound PCB* (Fig. 4a, adsorbed formulation PCB*/PVA-OCB). The PCB*/PVA-OCBs were flowed through a sandstone column, and the two components of the nanoreporter were independently monitored; the PCB* in the effluent was measured by its radioactivity while the PVA-OCB was measured by its UV absorbance at 280 nm (Fig. 4d). Almost none of the PCB was lost from the PVA-OCBs, as the two measurements of concentration were equal throughout the experiment. Control experiments using just a solution of PCB* or PCB* mixed with PVA showed very low levels of PCB* transport through the sandstone (See ESI†), indicating that the OCB core of the NPs is required for the efficient transport of PCB*. In order to demonstrate the principle of selective release, a sandstone column was prepared impregnated with 12 wt% of isooctane. When the PCB/PVA-OCBs were flowed through this column, a significant amount of the PCB* was released (Fig. 4e). In this model system, the PVA-OCBs efficiently transported the hydrophobic reporter molecule through the bare rock and released the reporter molecule when the rock contained oil. A more realistic system with a much reduced amount of hydrophobic organic content was also studied. PCB*/PVA-OCBs were flowed through Iceland spar calcite, a representative carbonaceous material with no bound organic material, and again very little of the PCB* was released (Fig. 4f). The PCB*/PVA-OCBs were then passed through dolomite from an actual oil reservoir in Kuwait that had been washed with toluene and contained only 0.8 wt% oil, and 80% of the PCB* was released (Fig. 4g). Thus, hydrocarbons in oil-field rocks can be detected by measuring the amount of hydrophobic cargo our NPs transport through the rocks.

The exact process for PCB* partitioning from PVA-OCBs to the oil phase is ambiguous at this stage. While the adsorption of PCB* onto PVA-OCBs is very strong, there will always be an equilibrium with a small amount of the PCB* desorbed into the surrounding environment. We have previously observed this adsorption/desorption phenomenon for naphthalene with fullerene NP.[26,27] It is likely that the presence of organic matter (isooctane or crude oil in this study) causes the small amount of desorbed PCB* to partition into the organic phase. This dramatically shifts the equilibrium and results in the unloading of most of the PCB* from the PVA-OCB into the organic phase. This is supported by the fact that for the dolomite column containing crude oil, the total organic content in the column was less than the amount of PVA-OCBs added, but most of PCB* partitioned away from the NPs. Since the PVA-OCBs are soluble in aqueous solutions, but nearly insoluble in organic media, such as isooctane or crude oil, it is likely that when they are at the oil–water interface, they remain in the water. This allows for the efficient recovery observed for the NPs.

The ability to efficiently transport a hydrophobic molecule through oil-field rock and selectively release it when a hydrocarbon is encountered has potential applications in oil detection down hole. Clearly, PCB* was used only as a proof-of-principle cargo, and much of the benefit of the technique will be realized by selecting appropriate cargo to be transported and released. Oil could be detected by passing reporter-loaded NPs through an area of interest and then recovering the NPs and analyzing them for the amount of reporter retained. This cargo-carrying methodology could also potentially be applied to contaminated subsurface areas where remediation could occur by transporting an agent to assist in the decomposition or removal of hydrophobic pollutants.

Acknowledgements

We are grateful to the Advanced Energy Consortium (Baker Hughes, Halliburton, Conoco Phillips, bp, OXY, Marathon, Shell, Total, Petrobras, Schlumberger) for financial support.

References

1 J. E. Baker, P. D. Capel and S. J. Eisenreich, *Environ. Sci. Technol.*, 1986, **20**, 1136.
2 J. F. McCarthy and J. M. Zachara, *Environ. Sci. Technol.*, 1989, **23**, 496.
3 C. G. Enfield and G. Bengtsson, *Ground Water*, 1988, **26**, 64.
4 M. L. Brussea, X. Wang and Q. Hu, *Environ. Sci. Technol.*, 1994, **28**, 952.
5 B. R. Magee, L. W. Lion and A. T. Lemley, *Environ. Sci. Technol.*, 1991, **25**, 323–331.
6 Y. Wang, Y. Li, J. D. Fortner, J. B. Hughes, L. M. Abriola and K. D. Pennell, *Environ. Sci. Technol.*, 2008, **42**, 3588.
7 Y. Li, Y. Wang, K. D. Pennell and L. M. Abriola, *Environ. Sci. Technol.*, 2008, **42**, 7174.
8 H. F. Lecoanet, J.-Y. Bottero and M. R. Wiesner, *Environ. Sci. Technol.*, 2004, **38**, 5164.
9 D. P. Jaisi and M. Elimelech, *Environ. Sci. Technol.*, 2009, **43**, 9161.
10 P. Wang, Q. Shi, H. Liang, D. W. Steuerman, G. D. Stucky and A. A. Keller, *Small*, 2008, **4**, 2166.
11 J. J. Lenhart and J. E. Saiers, *Environ. Sci. Technol.*, 2002, **36**, 769.
12 E. Rodriguez, M. R. Roberts, H. Yu, C. Huh and S. L. Bryant, *SPE Annual Technical Conference*, 2009, SPE 124418.
13 F. He, M. Zhang, T. Qian and D. Zhao, *J. Colloid Interface Sci.*, 2009, **334**, 96.
14 N. Saleh, K. Sirk, Y. Liu, T. Phenrat, B. Dufour, K. Matyjaszewski, R. D. Tilton and G. V. Lowry, *Environ. Eng. Sci.*, 2007, **24**, 45.
15 Z. Chen, K. Kobashi, U. Rauwald, R. Booker, H. Fan, W.-F. Hwang and J. M. Tour, *J. Am. Chem. Soc.*, 2006, **128**, 10568.
16 B. K. Price, J. R. Lomeda and J. M. Tour, *Chem. Mater.*, 2009, **21**, 3917.
17 J. J. Stephenson, J. L. Hudson, A. D. Leonard, B. P. Price and J. M. Tour, *Chem. Mater.*, 2007, **19**, 3491.
18 J. M. Berlin, A. D. Leonard, T. T. Pham, S. Daisuke, D. C. Marcano, S. Yan, S. Fiorentino, Z. L. Milas, D. V. Kosynkin, B. K. Price, R. M. Lucente-Shultz, X. Wen, M. G. Raso, S. L. Craig, H. T. Tran, J. N. Myers and J. M. Tour, *ACS Nano*, 2010, **4**, 4621.
19 E. Chiellini, A. Corti, S. D'Antone and R. Solaro, *Prog. Polym. Sci.*, 2003, **28**, 963.

20 B. T. Nguyen, J. Lehmann, J. Kinyangi, R. Smernik, S. J. Riha and M. H. Engelhard, *Biogeochemistry*, 2009, **92**, 163.

21 A. T. Kan, L. Yan, P. B. Bedient, J. E. Oddo and M. B. Tomson, *SPE*, 1991, 747, SPE 21714.

22 A. L. Higginbotham, D. V. Kosynkin, A. Sinitskii, Z. Sun and J. M. Tour, *ACS Nano*, 2010, **4**, 2059.

23 D. M. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, L. B. Alemany, W. Lu and J. M. Tour, *ACS Nano*, 2010, **4**, 4806.

24 D. P. Jaisi and M. Elimelech, *Environ. Sci. Technol.*, 2009, **43**, 9161.

25 M. Elimelech, J. Gregory, X. Jia and R. A. Williams, *Particle Deposition and Aggregation – Measurement, Modelling and Simulation*. Elsevier: 1995.

26 X. K. Cheng, A. T. Kan and M. B. Tomson, *J. Chem. Eng. Data*, 2004, **49**, 675.

27 X. K. Cheng, A. T. Kan and M. B. Tomson, *J. Mater. Res.*, 2005, **20**, 3244.