Toward Reservoir-on-a-Chip: Fabricating Reservoir Micromodels by \textit{in Situ} Growing Calcium Carbonate Nanocrystals in Microfluidic Channels

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\section*{ABSTRACT:} We introduce a novel and simple method to fabricate calcium carbonate (CaCO$_3$) micromodels by \textit{in situ} growing a thin layer of CaCO$_3$ nanocrystals with a thickness of 1–2 $\mu$m in microfluidic channels. This approach enables us to fabricate synthetic CaCO$_3$ reservoir micromodels having surfaces fully covered with calcite, while the dimensions and geometries of the micromodels are controllable on the basis of the original microfluidic channels. We have tuned the wettability of the CaCO$_3$-coated microchannels at simulated oil reservoir conditions without introducing any chemical additives to the system; thus the resulting oil-wet surface makes the micromodel more faithfully resemble a natural carbonate reservoir rock. With the advantage of its excellent optical transparency, the micromodel allows us to directly visualize the complex multiphase flows and geochemical fluid–calcite interactions by spectroscopic and microscopic imaging techniques. The CaCO$_3$-coated microfluidic channels provide new capabilities as a micromodel system to mimic real carbonate reservoir properties, which would allow us to perform a water–oil displacement experiment in small-volume samples for the rapid screening of candidate fluids for enhanced oil recovery (EOR). The immiscible fluid displacement process within carbonate micromodels has been demonstrated showing the water–oil–carbonate interactions at pore-scale in real time by fluorescence microscopic imaging.

\section*{KEYWORDS:} calcite micromodel, calcium carbonate nanocrystal, microfluidic channel, reservoir-on-a-chip, optical imaging

\section*{INTRODUCTION}

In oil reservoirs, when extracting oil by natural pressure differences is no longer possible, waterflooding, i.e., injection of waters without or with surfactants, is usually applied to recover the residual oil phase in the reservoir rock. Traditional lab-scale flooding experiments have used a cylindrical core from a sample reservoir rock collected during drilling to estimate the oil recovery data, through what is known as a core-flooding experiment. However, the fluid transport processes in a reservoir rock occur at a pore-scale on the order of nano- to micrometers,\textsuperscript{1−4} and the conventional core-flooding tests are not able to provide structural information at such a scale. In order to develop efficient methods for oil recovery, we need to understand the underlying physical processes which occur at the pore scale. For example, in the Ghawar Arab-D reservoir in Saudi Arabia, the largest collection of carbonate reservoirs in the world, the microporosity (pore throats and channels <10 $\mu$m) constitutes up to 50% of the total porosity in the carbonate rock.\textsuperscript{5,6,7} A significant proportion of the world's oil reserves are found in carbonate reservoirs. For example, it is estimated that around 70% of oil and 90% of gas reserves are held in carbonate reservoirs in the Middle East. Thus, micromodels for a carbonate reservoir are highly desired.

Micromodels are artificial porous apparatus to mimic microstructures of reservoir rocks. Micromodels are usually fabricated as two-dimensional (2D) with transparent windows, which offer a direct visualization of a complex flow environment at the pore scale.\textsuperscript{6−14} Micromodels have been widely used to understand oil–water–rock-phase interactions and behaviors in underground oil reservoirs.\textsuperscript{7,8,10,11,14} A variety of methods have been developed to fabricate synthetic micromodels with designed geometries and morphologies through both top-down and bottom-up approaches, and some common micromodel devices such as glass microfluidic chips are also commercially available. However, these micromodels have mostly been made of glass,\textsuperscript{9,15} silicon,\textsuperscript{8,16} and polymeric materials\textsuperscript{6,10,12,13,17−21} instead of real rock,\textsuperscript{22,23} and thus they have limitations for studying the interactions between geochemical fluids and reservoir rocks such as calcium carbonate (CaCO$_3$) in simulated enhanced oil recovery (EOR) experiments. For example, Mitra et al.\textsuperscript{8} have designed a microfluidic chip, termed as "reservoir-on-a-chip", to represent the pore structure of a naturally occurring oil-bearing reservoir rock. In their fabrication process, the pore network has been etched in a silicon substrate and bonded with a glass covering layer to make a complete microfluidic chip. However, this chip still has limits in representing the structure of the carbonate reservoir because the fluids are still in contact with the glass surface. More recently, Doyle et al.\textsuperscript{11} have reported a bottom-up approach for achieving quasi-two-dimensional porous CaCO$_3$ micromodels. CaCO$_3$ nanoparticles/polymer composite microstructures were fabricated by a photolithographic technique and a subsequent

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in situ growth of CaCO₃. Although this approach allows the quick creation of CaCO₃ microfluidic test beds with tunable topographies and geochemical properties, it only converted the silica surface partially to CaCO₃ in the controlled area, which did not generate a complete CaCO₃ surface.

In this study, we have developed a novel and simple method to coat a CaCO₃ nanocrystal layer with controlled thickness onto glass microfluidic channels and fully convert the inner surface of the microfluidic channels from silica to CaCO₃. Because of its excellent optical transparency, complex multiphase flows and geochemical fluid–CaCO₃ interactions can be in situ observed and monitored in the microfluidic channels by advanced spectroscopic and imaging techniques. To our knowledge, this is the first successfully fabricated carbonate micromodel having surfaces fully covered with CaCO₃ toward the "reservoir-on-a-chip".

■ EXPERIMENTAL SECTION

Fabrication of CaCO₃ Micromodels. Borosilicate glass microfluidic chips (Micronit Microtechnologies) were first cleaned with base piranha solution (3:1 ammonium hydroxide to hydrogen peroxide), and then, 1 M sodium hydroxide aqueous solution was pumped through the microfluidic channels at 0.1 mL/min for 30 min, followed by rinsing with deionized (DI) water. For functionalization of the surface of the glass, 2 mL of silane coupling agent, N-(trimethoxysilylpropyl)ethylenediaminetriacetate trisodium salt (TES-PEDTA, Gelest, 35% in water), was mixed with 20 mL of chloroform–water (volume ratio 1:1) under magnetic stirring, and then, the pH value of the mixture was adjusted to ~1.5 by hydrochloric acid to transfer the silane molecules into the chloroform phase. The chloroform phase containing silane was pumped through the microchannels at 0.1 mL/min for 5 min, and then, the solution was allowed to stay in the microchannel for 15 min before blowing by air flow. This process was repeated for 3–5 times, and then, the microchannels were rinsed with ethanol and 0.05 M CaCl₂ solution and dried at 60 °C overnight.

For CaCO₃ growing, first, a 0.05 M CaCl₂ solution was pumped through the channels at 0.1 mL/min for 2 min, then allowed to stay for 10 min and removed by flow of air; second, a 0.05 M Na₂CO₃ solution was pumped through the channels at 0.1 mL/min for 2 min, then allowed to stay for 10 min and removed by flow of air. The above process was repeated for 5–20 times depending on the need for different thicknesses of the CaCO₃ layer, and finally the channels were rinsed by water and dried at 60 °C in air.

To tune the wettability of the carbonate surfaces, the CaCO₃-coated microchannels were rinsed by water and ethanol and finally dried at 60 °C in air. The crude oil used in this research is composed of 33.1% saturates, 47.3% aromatics, 8.7% resins (polars I), and 10.9% asphaltenes (polars II) according to SARA (saturate, aromatic, resin, and asphaltene) analysis.

As reference, parallel experiments at similar conditions for the CaCO₃ coating and aging in crude oil were also performed with flat borosilicate glass slides.

Characterization. The micromodels were imaged by scanning electron microscopy (SEM, JEOL, JSM-7100F field emission) at 5 kV, and energy dispersive X-ray spectroscopy (EDS) analysis was taken at 20 kV; no additional coating was applied onto the sample surface.

Raman spectra and images were recorded in a confocal Raman microspectroscopy system (Horiba LabRam HR). Selected areas of samples were scanned with a continuous 532 nm laser beam with lateral and depth resolutions of 250 and 500 nm, respectively.

Contact angles of fluids on the solid surface were measured with a goniometer (ramé-hart).

Optical microscope images were collected using a widefield optical fluorescence microscope (Zeiss LSM 780) with a 10× microscope objective. For differentiation between oil and aqueous phase, 1 × 10⁻⁴ M fluorescein in water was used to produce fluorescence and crude oil was used as-is.

■ RESULTS AND DISCUSSION

Surface Functionalization. Calcium carbonate is one of the standard model systems and has been extensively used to study the biomineralization processes in bulk crystallization experiments. One of the methods to grow 2D thin films of CaCO₃ is to crystallize the CaCO₃ under Langmuir monolayers of many different lipids, especially stearic acid (SA).²⁴⁻²⁹ It has been demonstrated that the carboxylate polar heads of surfactants played a crucial role in the growth of thin films of CaCO₃ beneath Langmuir monolayers of stearic acid, and it has been inferred that a crystallization process was induced by a precursor phase with a thin, filmlike structure.²⁷⁻²⁹ Therefore, for the growth of CaCO₃ onto a silica surface, the most crucial part is to functionalize the surface of silica to enhance its affinity to CaCO₃. As known from our previous studies,³⁰⁻³² silane compounds with carboxylate groups can be chemically grafted as a monolayer onto the silica surface through a hydrolysis reaction. In this research, we treat the surface of the glass microchannel with a silane agent, TMS-PEDTA to graft multiple COO⁻ groups on the internal surface of the microchannel, as illustrated in Figure 1.
Growth of CaCO₃ Nanocrystal Layers. In the presence of Ca²⁺ in solution, the carboxylate groups bind with Ca²⁺ ions to form a thin film-like precursor layer, and with the supply of more Ca²⁺ and CO₃²⁻ ions, the calcium carbonate nanocrystals will form in the precursor layers and eventually form a thin layer of nanocrystals (Figure 1).

Most bottom-up fabrication methods involve both homogeneous and heterogeneous nucleation, and growth processes in solutions and on templates, which result in the inevitable problems of undesirable mineralization on channel walls and blocking of the channels. In our procedure, by the alternative flow of Ca²⁺ and CO₃²⁻ solutions through the microchannels, the chemical reaction was confined on and near the surface of the channels, which reduces the nucleation and formation of CaCO₃ nanocrystals in bulk solution. Thus, CaCO₃ nanocrystals were more likely grown around the CaCO₃ seeds and eventually formed thin layers of nanocrystals.

In addition to the surface functionalization of glass, another key development to create a highly uniform CaCO₃ coating is mixing Ca²⁺ and CO₃²⁻ ions in a controlled manner by alternatively replacing and supplying fresh solutions with Ca²⁺ and CO₃²⁻ at certain concentrations with proper time intervals, providing selective uniform CaCO₃ formation only on and near the surface of microchannels. Spontaneous precipitation occurs when solutions are not replaced frequently, which leads to unwanted precipitation of CaCO₃ in the microchannel which may aggregate and block the microchannel.

A photograph of a typical microfluidic chip is shown in Figure 2a, and an SEM image of a cross section of the microfluidic chip shows the dimension of the channel in 50 μm × 1,000 μm (Figure 2b). A uniform thin layer of CaCO₃ particles can be clearly seen on walls of the microchannel (Figure 2c,d). Images with higher resolution in Figure 2e–h reveal that these coated particles are well-crystallized and that the thickness of the crystal layers on the wall of microchannel is about a couple of micrometers. For this thickness, the thin film was formed by a coating process with 8 cycles of alternatively supplying the Ca²⁺ and CO₃²⁻ ions in reaction. The thickness of coated CaCO₃ layers could be adjusted by more or fewer cycles of the reaction during the coating process. In the images from Figure 2e–h, it can be noticed that the coated CaCO₃ includes multiple layers of particles with different sizes. The microcrystals, ~1–2 μm in size, form the major part of the coating layers, and there is another compact layer composed of smaller particles in submicron and nanometer sizes underneath the microcrystals. It is clear that these nano- and sub-micro-sized particles are directly formed on the surface of glass and that the microrized crystals are further grown from them, which confirms the seed-growing mechanism used in the synthesis. These coatings generate a fully covered surface of microchannels by CaCO₃.

Element analysis by EDS measurement further confirmed the chemical composition of the coated CaCO₃ crystal layers. Calcium and carbon are clearly dominant elements on the wall of microfluidic channels (Figure 3).

Micro-Raman spectroscopy has been used to study the structure of coated nanocrystal layers. The coated microfluidic channels, the band positions at 1091 cm⁻¹ from symmetric CO₃ stretching, at 716 cm⁻¹ from symmetric CO₃ deformation, and at 281 and 156 cm⁻¹ from the translational lattice mode of Ca–CO precisely match those for reference calcite rock (Figure 4a,b). All the vibrational bands also coincide very well with the values reported for calcite in the literature. In the Raman spectra, there are no characteristic peaks from other phases of CaCO₃, and this suggests that the structure of the coated nanocrystals is pure calcite throughout the microfluidic channel. Raman intensity mapping of the band around 1091 cm⁻¹ exhibits clear profiles of the coated calcite layers on the microchannel (Figure 5). The coated CaCO₃ layer on the microfluidic channels is stable at simulated reservoir conditions, and the Raman spectrum (Figure 4c) has confirmed its integrity after multiple waterflooding experiments. For evaluation of the uniformity of the CaCO₃-coated layers with the method developed in this study, a parallel coating on a flat glass slide was also performed with the same growth conditions. As shown by SEM images at different magnifications in Figure 6, the glass surface was covered by CaCO₃ nanocrystals to nearly 100%, and the general sizes of CaCO₃ nanocrystals are about 0.5–2 μm.

Although we chose a simple straight structured microchannel for easiness to demonstrate the characterization in this report, the dimension and geometries of the micromodels are designable from original microfluidic channels. With the developed CaCO₃ coating procedure, we have also modified surfaces for enhanced oil recovery chips (Figure 9a). The EOR chips fabricated on the basis of a morphological analysis of natural rock, limestone, and its pores and channel connections (~20–50 μm) are generally comparable with real reservoir...
Typical reservoir depths the calcite content is >87 wt % and reservoir rocks in the Arabian Peninsula, studies show that at (XRD) analysis for more than 700 samples of carbonate calcite and dolomite. On the basis of X-ray powder, it is well-known that carbonate rocks are mainly composed of and their comparison at controlled experimental conditions. It enables the performance of unlimited experiments on the microfluidic channels.

Unlike the natural rocks with inhomogeneous morphologies, the accurately reproduced morphology in the EOR chips allows understanding fundamental fluid behaviors and interactions between oil–water–rock phases.

It is known that calcite has inherently water-wet characteristics in the presence of oil and water, while the surface wettability of natural carbonate reservoirs is ~84% oil-wet. There have been significant improvements in post-treatment methods to modify wettability within micromodels to mimic the wettability in reservoir rocks. For example, the surface wettability of CaCO₃ can be modified by chemical functionalization, such as stearic acid coating, to decrease the surface energy of CaCO₃ to make the surface more oil-wet. However, the grafting of organic molecules could alter the surface properties of calcite and thus smear the real observation of water–oil–rock interactions.

In this study, to change the wettability of surfaces of the calcite micromodel, we have treated the microchannels in a simulated reservoir condition. The microchannels were filled with and immersed in crude oil, and then heated in an autoclave. After aging at 150 °C for 12 h, the microchannels were washed by water and ethanol, and then dried at 60 °C in air.

Contact-angle measurements (Figure 7) of a CaCO₃-coated flat glass slide confirmed that the CaCO₃ surface turns dominantly oil-wet after the crude oil aging treatment. In the crude oil aging process, no additional chemical was introduced into the system, and the resulting hydrophobic surface makes the microchannels of a micromodel more faithfully resemble those of a natural carbonate reservoir rock.

**Fluorescence Imaging of Water–Oil Displacement.**

For a study of fluid behavior in carbonate reservoirs, traditional core-scale core-flooding measurements and conventional micromodels fabricated using glass or polymer materials are not able to demonstrate the geochemical fluid–rock interaction because of their optical opaqueness or material property limitations. The advantage for the micromodel developed in this research is that its CaCO₃ surface is still optically transparent. Because of the excellent optical transparency, the fluid behavior in the microchannel and at the calcite–fluid interface can be observed in real time by spectroscopic techniques, such as fluorescence and Raman imaging. Oil–water displacement experiments were conducted by injecting surfactant in seawater into a crude-oil-aged CaCO₃-coated microfluidic channel under a constant flow rate (0.1 mL/min). Crude oil has strong inherent fluorescence in a wide visible spectral range and in Figure 8 is marked as red, while the water phase was labeled by dissolved fluorescein dye molecules and marked as green. Fluid propagation into the porous network of the chip has been imaged by optical fluorescence microscopy.

Figure 8 demonstrates an example of optical fluorescence images of oil–water displacement in a selected microchannel area caught during the waterflooding experiment, and the interfaces between the two immiscible liquids and between liquid and the CaCO₃ wall can be clearly identified.

Advanced
in situ spectroscopic techniques such as Raman spectroscopy can also be used to study chemical species at a molecular level and visualize their adsorption or desorption from the carbonate rocks, which can provide a better understanding of chemical and physical features at oil–rock or water–rock interfaces. With the micromodel described in this research, the fluid behaviors and fluid–rock interactions can be investigated.

**CONCLUSIONS**

We have presented a novel method to convert the surface of microfluidic channels from silica to carbonate through a controlled in situ growth of CaCO₃ nanocrystals, and further tune the wettability of the coated CaCO₃ surface through an aging process at simulated reservoir conditions. The excellent optical transparency of the microfluidic channels facilitates the direct visualization of complex multiphase flows and geochemical fluid–CaCO₃ interactions by spectroscopic and microfluidic techniques, and the effects from different aqueous phases, seawater or surfactant solution, can be quantitatively differentiated on the basis of the image analysis (Figure 9b–d). A detailed study about the surfactant EOR experiments using the CaCO₃-coated EOR chips will be followed by a separate paper. The further investigation with the carbonate micromodel will broaden our understanding of how the fluid properties affect the displacement process for EOR, enabling this micromodel system to be a very useful platform for studies in waterflooding, chemical EOR, foam EOR, CO₂ storage, and CO₂-EOR in carbonate reservoirs.41,42

![Figure 5](image1.png)

**Figure 5.** (a) Optical image with indicated points for Raman signal collection and (b) Raman intensity mapping at 1091 cm⁻¹ of coated CaCO₃ layers at a cross section of a microfluidic channel.

![Figure 6](image2.png)

**Figure 6.** SEM images of a coated CaCO₃ layer on the surface of a glass slide at different scales: (a) 10 and (b) 2 μm.

![Figure 7](image3.png)

**Figure 7.** Photographs of contact angles of (a) an oil and (b) a water droplet on a CaCO₃-coated glass surface. The surface was treated by aging in crude oil at 150 °C for 12 h.

![Figure 8](image4.png)

**Figure 8.** Representative optical microscope images of an oil–water (red–green) displacement experiment in a CaCO₃-coated microfluidic chip using (a) seawater and (b) house-made surfactant in seawater. The water-phase fluids were labeled by fluorescein dye at a concentration of 1 × 10⁻⁴ M.

![Figure 9](image5.png)

**Figure 9** demonstrates fluorescence images obtained during an EOR waterflooding experiment with the CaCO₃-coated EOR microfluidic chips, and representative images of the oil recovery process in the CaCO₃-coated reservoir chip obtained after (b) initial oil saturation, (c) seawater flooding, and (d) surfactant in seawater flooding by a widefield optical fluorescence microscope (oil, red; seawater, green).
microscopic techniques. The CaCO₃-coated microfluidic channels provide new capabilities as a micromodel system to mimic real carbonate reservoir properties, which allows us to perform water–oil displacement experiments for rapid screening of candidate chemicals for EOR.

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