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Fabrication and verification of a glass-silicon-glass micro-/nanofluidic model for investigating multiphase flow in shale-like unconventional dualporosity tight porous media

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Unconventional shale or tight oil/gas reservoirs that have micro-/nano-sized dual-scale matrix pore throats with micro-fractures may result in different fluid flow mechanisms compared with conventional oil/gas reservoirs. Microfluidic models, as a potential powerful tool, have been used for decades for investigating fluid flow at the pore-scale in the energy field. However, almost all microfluidic models were fabricated by using etching methods and very few had dual-scale micro-/nanofluidic channels. Herein, we developed a lab-based, guick-processing and cost-effective fabrication method using a lift-off process combined with the anodic bonding method, which avoids the use of any etching methods. A dual-porosity matrix/microfracture pattern, which can mimic the topology of shale with random irregular grain shapes, was designed with the Voronoi algorithm. The pore channel width range is 3 µm to 10 µm for matrices and 100-200 µm for micro-fractures. Silicon is used as the material evaporated and deposited onto a glass wafer and then bonded with another glass wafer. The channel depth is the same (250 nm) as the deposited silicon thickness. By using an advanced confocal laser scanning microscopy (CLSM) system, we directly visualized the pore level flow within micro/nano dual-scale channels with fluorescent-dyed water and oil phases. We found a serious fingering phenomenon when water displaced oil in the conduits even if water has higher viscosity and the residual oil was distributed as different forms in the matrices, micro-fractures and conduits. We demonstrated that different matrix/micro-fracture/macro-fracture geometries would cause different flow patterns that affect the oil recovery consequently. Taking advantage of such a micro/nano dual-scale 'shale-like' microfluidic model fabricated by a much simpler and lower-cost method, studies on complex fluid flow behavior within shale or other tight heterogeneous porous media would be significantly beneficial

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1. Introduction

Unconventional reservoirs, including shale and other types of tight formations, which intrinsically have much lower permeability than conventional reservoirs with micro-/ nanoscale dual-porosity features, can exhibit highly varying properties within microscopic confinement. Therefore, a microfluidic model, as a powerful pore-scale level tool, is needed to better understand the flow behavior and mechanism within the heterogeneous porous media of shalelike tight oil/gas reservoirs. According to the average porethroat diameter size of unconventional shale and other tight oil/gas reservoirs, the ratio of the pore surface area to the pore volume, which can be 50×10^4 cm⁻¹ (approximately 700 if represented by the ratio of the channel width to depth in a microfluidic model), is much larger than that of conventional porous media, which can be 1.8×10^{-4} cm⁻¹ (approximately 16 if represented by the ratio of the channel width to depth in a microfluidic model).^{1,2} Hence, the hypothesized surface/ interfacial phenomenon dominated fluid flow makes the liquid and gas transportation through shale still uncertain.³ Although some microfluidic devices possessing dual-scale matrix/fracture network features have been built by using different fabricating methods,4-7 the channels are all at the microscale for any dimensions and do not have a large width-

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to-depth ratio (2–26), which cannot represent fluid pathways of shale or tight dual-scale reservoirs. Until recently, though the first micro/nano PDMS-glass and quartz-glass dual-scale microfluidic models were developed to represent dual-scale shale,⁸ the width-to-depth ratio (1–25) still remained small. Besides, the fabrication method cannot guarantee oil flow on a PDMS-glass model and high-pressure experiments on a glass-glass model due to bonding issues.

Although a PDMS micromodel can now realize sub-100 nm dimensions,^{8,9} it is still not a suitable candidate for conducting experiments involving organic nonpolar fluids,¹⁰ which are ubiquitous in many petroleum and environmental scenarios.11-14 Hence, non-organic material based siliconglass or glass-glass microfluidic models have emerged in response and have widely been used to fabricate micro-/ nanofluidic models capable of handling harsh physical and chemical conditions in the energy field.¹⁵⁻¹⁹ For the siliconglass ones, since silicon is not transparent to visible light, a glass wafer as a transparent cover plate is always anodically bonded over the silicon substrate to make it possible for direct observation under a microscope.²⁰⁻²² To achieve full transparency and superior compatibility with many solvents,^{23,24} high stiffness for handling high pressure fluid flow experiments²⁵⁻²⁷ and ease of surface wettability alteration by different methods,^{28,29} glass itself has long been the preferred microfluidic model substrate. The choice between the two mainly depends on the goals and needs. A silicon substrate would be chosen when one needs more precise channel sizes and straight channel side walls when using a dry etching method.³⁰ Although glass substrates can also be dry-etched,^{31,32} its low etching rate, low etching selectivity and high facility cost make wet etching a more popular method, which makes use of buffered hydrofluoric acid or mixtures of acids as the etchant solutions to etch channels on glass substrates.^{33–35} The main drawback is that the isotropic wet etching process cannot achieve perfect vertical walls,³³ yet the imperfect trapezoidal shape can be leveraged to generate a 2.5D micromodel by controlling the etching depths of two neighboring pores.³⁶ Other fabrications of semi- or fully transparent microfluidic models for energy and other fields can be found elsewhere in detail.³⁷⁻⁴²

Among all available fabrication methods, thin film deposition, as a fast, low cost and simple process, has been used to produce micro-/nanochannels in several applications.⁴³⁻⁴⁵ However, for energy field microfluidic systems, it is rarely used or used only as an auxiliary method to deposit a protection layer and hard mask for a subsequent wet etching or dry etching process.^{8,46,47} The aforementioned glass-quartz transparent micro-/nanofluidic devices that emulate the dual-scale properties of shale and tight-oil reservoirs also utilized thin film deposition to help make the model.⁸ They used thermal deposition to coat a Cu film onto a lacey carbon support film and reactive ion-etched the quartz substrate based on the mask. Finally, two glass wafers were bonded by continuously flushing demineralized water between the two wafers and combining and allowing them to

stand for more than 3 hours.⁴⁸ However, the reactive ion etching method can produce etching by-products that could clog the thinner channels and 'sagging' of the lacey carbon film is very likely to occur across larger apertures. Besides, it needs a standing time of at least 3 to 4 days for two plates bonded to reach at least 80% strength, which is 61.8 ± 2.6 N cm⁻², to be used for a fluid flow experiment. Although this bonding method can be realized at room temperature to avoid deformation of glasses at high temperature by using fusion bonding, the bonding strength and temperature resistance are questionable.

How to fabricate a 'shale-like' micro-/nanofluidic model that has a large width-to-depth ratio (12-2000) in a timeefficient and cost-effective way while keeping it fully transparent and strongly bonded remains a challenge and is needed these days. In this work, we, for the first time, deliver such a possibility by using the direct lift-off process combined with the anodic bonding process. For glass-based models, both wet etching and dry etching need to deposit a metal layer at the first step and then do the etching at the second step. The lift-off process and the etching process on a glass substrate both require a photolithography pattern and thin film deposition.⁴⁹ Therefore, instead of using any etching methods downwards the substrate, we build the grains upwards and use them directly as the intermediate layer for anodic bonding. By skipping the etching process, one may save more than 5 hours a day for fabricating 20 samples $(2 \text{ cm} \times 2 \text{ cm})$ excluding other preparation times for etching. This simple, time-saving and cost-effective method improves the efficiency of fabricating a micro-/nanofluidic model significantly. The detailed fabrication processes are presented in the following sections. Finally, the functionality and practicability of the micro-/nanofluidic model are demonstrated based on the multiphase fluid flow experimental results.

2. Results and discussion

2.1. Dual-porosity pore network design

To generate a complex heterogeneous porous medium for investigating multiphase flow with a microfluidic model, the Voronoi tessellation algorithm was utilized to mimic real reservoirs with random geometries and labyrinth-like pore networks.50 The Voronoi diagram, also called Voronoi tessellation or Voronoi decomposition, uses a computational geometry algorithm to partition a plane into different sizes of non-overlapping regions based on the closest distances among the randomly preset points on the plane.⁵¹ However, a simple Voronoi tessellation pattern with connected straight channels all sharing the same width cannot represent the real 'convergent-divergent' conditions within the porous media. Herein, we used the improved Voronoi tessellation algorithm in AutoCAD software to design a dual-porosity pattern with two matrices and micro-fractures connected with the matrices with different channel widths. Further, the grains were designed as close as possible to granular shapes



rather than polygonal shapes to represent the real rock grains in reservoirs, which make the pore networks have the 'convergent-divergent' profiles. As shown in Fig. 1, the porous medium including two matrices and micro-fractures is sandwiched between two flow conduits, which can be regarded as macro-fractures. The lengths of the two flow conduits and the porous medium are 1.3 cm and 0.8 cm and the widths are 0.05 cm and 0.2 cm, respectively. Connected to the flow conduits that have side lengths of 0.1 cm are the inlet and outlet for flow injection and recovery. The outer squares with a 0.3 cm side length are the pre-saturation zone to decrease the probability of blocking when injecting and recovering the fluids. The intergranular channels within the matrices are the narrowest ones with widths from 3 µm to 10 µm and 100-200 µm for the micro-fractures. Several vugs were also yielded by eliminating a number of grains at the left and right sides of the porous medium. The porous medium, excluding the flow conduits, consists of 192 grains with a total porosity of 28%, which could be smaller if the vugs are not counted. The porosity for the two matrices is approximately 5% and 23% for combined micro-fractures and vugs.

2.2. Micromodel fabrication

The micromodel was fabricated in the laboratory and the successive fabrication steps of the micromodel are presented in Fig. 2(a-f). A glass substrate was first spin-coated with an S1813 positive photoresist and then the pattern was developed under UV exposure using an MF321 developer. The substrate was then loaded into a vacuum chamber and coated with an amorphous silicon layer using e-beam evaporation at an average rate of 1.6 Å s⁻¹ at temperatures of 16–50 degrees Celsius. Finally, the lift-off process removed the photoresist in the channels using Remover-PG (a proprietary solvent stripper designed for efficient and



Fig. 2 Schematic workflow of the micro-/nanofluidic model fabrication process: (a) spin-coating of photoresist on the glass substrate; (b) UV exposure to change the chemical properties of uncovered photoresist; (c) developer application to wash away exposed photoresist; (d) e-beam evaporation used to deposit a thin silicon layer onto the glass substrate; (e) removal of residual photoresist in the channels using Remover-PG; (f) anodic bonding with another glass wafer on top; (g) and (h) comparative illustrations of deposition with poor and good step coverage; (i) and (j) positive and negative photoresist undercut profile comparison when coated on the substrate.

complete removal of photoresists). The glass substrate was anodically bonded with another glass wafer after two holes were punched as the inlet and outlet using a UV laser. In contrast to the high cost and long fabrication workflow with a wet or dry etching process for a glass-based micromodel with complex porous medium patterns, this simple, fast and cost-effective fabricating method may produce a number of micro-/nanofluidic models in a short time period (average of twenty samples per day). Details of each fabrication process are discussed in the following sections.

2.2.1. Materials. For fabricating one complete glasssilicon-glass micromodel, two glass wafers were used as both the substrate and the cover plate. The Schott Borofloat 33 glass wafers were square and double side polished (University Wafer), with a side length of 5 cm and a thickness of $500 \pm$ 20 µm. Silicon pellets (R.D. Mathis) were used as the evaporation material to be coated onto the glass substrate to enable an easy anodic bonding process with glass since they have similar thermal coefficients of expansion (for silicon, 2.6 × 10⁻⁶ K⁻¹ and for Borofloat 33 glass, 3.25×10^{-6} K⁻¹ at 20 °C).

2.2.2. Photolithography. First, the glass substrate was rinsed with acetone and methanol two times to remove dust and oil, and then blow-dried completely using dry air. The Microposit S1813 positive photoresist was spin coated uniformly onto the glass substrate at 4000 rpm for 40 s with a thickness of 1.3 microns. Then, the substrate was soft baked on a hot plate at 115 degrees Celsius for one minute to eliminate the moisture on the substrate. Later, the substrate was brought into soft contact with the printed polymeric mask and exposed to UV400 ultraviolet (UV) light using a Karl Suss MA6 aligner. The UV exposure time depends on the photoresist type. We used S1813 which requires 150 mJ cm⁻². The exposure power of our mask aligner is about 11 mW cm⁻² so the exposure time is 10-15 s for our samples. Lastly, the exposed photoresist was removed by soaking the substrate in the MF321 developer for 50 s until the pattern can be seen clearly and then rinsed using deionized (DI) water for thirty seconds. One substrate contains two patterns to save space.

2.2.3. E-Beam vapor evaporation. Choosing a suitable evaporation method for depositing a thin silicon film on the glass substrate is of great importance throughout the whole work. Different from the chemical vapor deposition (CVD) method that takes place at high temperatures, e-beam evaporation allows deposition at a relatively low substrate temperature of around 16-50 degrees Celsius while yielding a high deposition rate (1.6 Å s^{-1} at temperatures of 16–50 degrees Celsius) and has been used for micro-electromechanical systems (MEMS) for a long time.^{31,52,53} The low deposition temperature prevents the deformation of the glass wafers at high temperatures of around 550 degrees Celsius. Thermal evaporation, as another type of physical evaporation, may as well heat up the substrate to over 250-300 degrees Celsius during the deposition process.54 Besides, chemical vapor deposition may generate gaseous or liquid by-products which may lead to impurities on the substrate. Except for these two reasons, the deposition temperature and contaminants, the most important reason for choosing e-beam physical evaporation is the consideration of the poor step coverage of the deposited film as shown in Fig. 2(g) and (h). Although chemical deposition and physical sputtering both have better step coverage than isotropic deposition, this will lead to the full coverage of the surface of the substrate. The deposition would happen not only on the top of the photoresists in the channels but also on the sides, which prevents the photoresist from being washed away through the open sides. On the other hand, by leveraging the directional deposition of e-beam deposition with poor step coverage, the silicon will only be deposited onto the top of the photoresist, leaving the sides open to air. Therefore, the photoresist can be washed away easily through the open sides. To ensure the thorough removal of the photoresist, it is better if the silicon layer coating is less than one fourth of the photoresist layer thickness, which is 1.3 µm, to give more height difference between the photoresist layer and the silicon layer on the substrate. Thus, we chose to deposit a 250 nm silicon layer. The photoresist patterned substrate was loaded into the e-beam evaporation chamber, which was pumped down to 2×10^{-6} Torr base pressure. The e-beam deposition is performed at an average rate of 1.6 Å s^{-1} at temperatures of 16-50 degrees Celsius; thus it only takes no more than thirty minutes to reach ~250 nm for all loaded samples (20 samples per load with sample dimensions of 2 $cm \times 2 cm$).

2.2.4. Lift-off process. The lift-off process after thin film deposition has been used for decades in semiconductor and integrated circuit (IC) areas as a simple and quick method for patterning thin metal material films.⁵⁵⁻⁵⁷ However, it has rarely been used in the microfluidic model fabrication field. We herein utilized a direct lift-off process after the e-beam evaporation process to wash away the remaining photoresists in the channels. The substrate was first soaked in the Remover-PG solution and left to stand for 10 min. Then, an ultrasonic cleaner with deionized water was used to clear out most of the photoresist preliminarily. Later, the substrate was cleaned intensively by immersing it in piranha solution $(3:1 H_2SO_4:H_2O_2)$ for 20 min to remove the photoresist residues and other contaminants. Finally, the substrate was rinsed with deionized water and blow-dried thoroughly. The lift-off process would peel off the photoresist with top-coated silicon layers from the substrate completely, leaving the channels clean to give space for fluid flow. However, in some situations due to improper and incomplete dissolution of the photoresist, retention problems would occur. The top-coated silicon would adhere to the bottom silicon grains that should remain. To handle this problem, we conducted several lift-off processes with deposited silicon layers of different thicknesses from 100 nm to 500 nm with intervals of 50 nm. It was not surprising that the thicker the deposited silicon layers are, the more possible the retention problem becomes, which causes more difficulties in washing away the

photoresist. Either the side windows were too small to let Remover-PG flush out the photoresist completely or the silicon grains were peeled off together with the photoresist. The deposited material layer should not be thicker than two thirds of the photoresist to ensure complete separation.⁵⁸ However, we found that it began to become difficult when the deposited silicon layer thickness is above 300 nm, which is about one fourth of the photoresist thickness (1.3 µm). It is also the nature of the positive photoresist that limits the height of the deposition layer. As shown in Fig. 2(i) and (j), the undercut profiles are different between the positive and negative photoresists with silicon deposited on the top. They both have trapezoidal shapes after exposure. However, the undercut profile of the positive resist is less advantageous than that of the negative photoresist whose inverted profile leads to much more exposure to the Remover-PG solution. Although negative resists have been used mostly in lift-off processes in the microelectronics field, the higher cost and the difficult removal process still need to be considered. A diffuser which diverts UV light can be utilized to change the positive photoresist undercut profile to the re-entrant profile to facilitate the lift-off process.⁵⁹ For our experiment, we did not use any other auxiliary method to ease the lift-off process

since we seriously controlled the deposited silicon layer thickness below one fourth of the positive photoresist thickness to achieve a complete lift-off process.

2.2.5. Surface and channel characteristics. After the lift-off process, the surface and the channel characteristics were analyzed. The thickness of the deposited silicon was measured using a Sloan Dektak 3030 surface profiler measuring system. The probe went 300 µm across two random grains and measured the channel depth between them. Inside the test area, the channel width is approximately 20 µm and the depth is about 277.7 nm. The surface is of good flatness, except for a few sharp peaks caused possibly by the dust on the substrate surface. To demonstrate the profile of channel side walls, scanning electron microscopy (SEM) images of the model at a tilt angle of 45 degrees were taken using a Hitachi S-4700 FESEM microscope as shown in Fig. 3. Fig. 3(a) shows the top view of one part of the matrix and adjacent micro-fractures generated using the Voronoi tessellation algorithm, which shows the matrix parts with a smaller pore size and the micro-fractures with a larger pore size. Although the channel may have some degree of roughness due to the lift-off process, as shown in Fig. 3(b) and (c), the channel side walls



Fig. 3 SEM image of (a) the matrix and micro-fractures; (b) matrix channel with a width of 8 μm; (c) sidewall roughness; (d) straight channel wall profile with a depth of 277 nm.

are shown to be vertical to the substrate as shown in Fig. 3(d), which have a better profile than those from wet etching.

2.2.6. Anodic bonding. Anodic bonding can deliver strong bonding strength while keeping the substrate at low temperature.⁶⁰ Glass to glass anodic bonding can be realized by using silicon or other metal films as the intermediate layers and anodic bonding at no more than 400 degrees Celsius and 700 volts makes it possible for optical detection with fluorescence microscopy in biological and biomedical fields, where microfluidic systems with transparent walls were required.^{32,61-63} We used our self-assembled anodic bonding device to conduct the final anodic bonding process to seal the glass substrate with a silicon layer and a plain glass cover hermetically. As shown in Fig. 4, our selfassembled anodic bonding device includes an HP Keysight 6515A high voltage DC power supply (0-1600 V, 5 mA), a hot plate covered with aluminum-foil paper, an ammeter and a probe stand with a fixed metal probe. The aluminum-foil paper was wrapped over the hot plate surface tightly as the conducting layer. The substrate with the silicon layer was placed first onto the aluminum as layer 1, followed by the placement of the cover glass onto the substrate as layer 2. Before placing, the substrate and the cover glass were already rinsed together in piranha solution $(3:1 H_2SO_4:H_2O_2)$ for 20 min after the lift-off process to avoid bonding issues because of the residual contaminants. The SEM images also show that there are no visible additive residues in the channels. In the meantime, they were both changed to have strong hydrophilicity. The conductive probe was adjusted vertically to press onto the cover glass to initially apply a force for prebonding. By connecting the anode to the aluminum-foil paper and the cathode to the probe through the ammeter, the preparation for bonding was finished. We then switched

on the hotplate and set the goal temperature to around 350 degrees Celsius and waited for the substrate to be pre-heated for 10 minutes. We used an infrared thermometer to measure the surface temperature. After the temperature was stable at around 350 degrees Celsius, we slowly increased the voltage to 1200 V and checked the ammeter at the same time. The ammeter was used as an indicator for whether short circuiting occurred when increasing the voltage. If the current is over 1 mA at any time during voltage increase, the voltage should be decreased to zero and the electrode connections checked. The bonding process using the point cathode electrode contact method can be observed, spreading radially outwards from the probe pinpoint. This radial propagation process also avoids air trapping between the interface of glass and silicon. However, the bonding process cannot be completed by only being in contact with one point due to the large area of the chip surfaces. Therefore, whenever the spreading stopped, we moved the conductive probe to another point to continue the bonding process until all parts were bonded together. This point contact bonding method is much faster than the flat cathode electrode contact method and is also costless.⁶⁴ It is also noteworthy that there were no collapsed channels found after the anodic bonding process. The channel aspect ratio (depth to width) has been demonstrated to be a crucial parameter when conducting a bonding process for either glass-silicon or glass-glass models.⁶⁵ For a glass cover anodically bonded onto a silicon substrate, due to the applied strong electrical force, the top and bottom surfaces would be in contact with each other and seal the channel permanently if the aspect ratio is smaller than 0.004. For a fusion bonding process between two glass wafers, the high temperature would deform the glass material and thus cause the collapse of the channels if the aspect ratio is smaller than 0.0005. For our anodic bonding



Fig. 4 Schematic of the lab-based anodic bonding apparatus. a. High voltage DC power supply (0–1600 V, 5 mA); b. hot plate; c. aluminum paper; d. two glass wafers with an intermediate silicon layer; e. probe stand; f. ammeter.

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process at low temperature, there are also no strong electrical interactions between the top and bottom glass wafers. Therefore, the channels all survived with an aspect ratio even smaller than 0.0005 (*e.g.* conduits and the vugs).

3. Experimental verification for the glass-silicon micromodel

We tested the practicability of the glass-silicon-glass micromodel by conducting a two-phase fluid displacement experiment. Deionized water (DI water) was used as the wetting phase and decane as the non-wetting phase. The fluid flow process was investigated by utilizing confocal laser scanning microscopy (CLSM). To distinguish the two kinds of fluids under different lasers, they were both fluorescent-dyed using Alexa Fluor 594 for the water phase and Nile Red for the oil phase (both from Sigma-Aldrich), respectively. The DI water was red and the decane was green after being separately excited by lasers at 488 nm and 561 nm. The micromodel was firstly saturated with the decane injected by using a syringe pump (Harvard Apparatus, model 88-3015). Then, the decane was displaced by the DI water at a flow rate of 0.02 mL h⁻¹. Because it is a large field micromodel, even if we used a 10× objective lens that has the biggest field of vision among all lenses, we can only observe partial areas. Therefore, the stage was set to move automatically from the left corner inlet to the right corner outlet with 19 horizontal steps and 5 vertical steps. All fields were then stitched together to obtain a whole image which covers all parts of the model. We scanned and recorded the whole injection process using resonant scanning mirrors instead of traditional galvanometer mirrors to acquire high scanning speed. Although the resolution became worse, the scanning speed can be up to 7.7 frames per second and it takes only 40 seconds to scan the whole model. All experiments were conducted at room temperature.

3.1. Oil saturation process

In this research, since our focus is to fabricate the model and verify its usability to conduct a flooding experiment, we did not consider the irreducible water saturation to mimic the real reservoir saturation history as it is negligible for verifying the usability of this model. Therefore, we only did the water flooding imbibition test by directly saturating the model with oil first. Decane (0.92 cP at 20 °C) was injected using 1/16 inch inner diameter tubing into the inlet nanoport (IDEX Health & Science LLC) at a flow rate of 0.02 mL L^{-1} . As shown in Fig. 5, it took about 10 hours to fully saturate the microfluidic model with the decane phase. The flow direction was from the top left corner inlet to the bottom right outlet which was always open to air with no backpressure added. From the time sequence from the top to the bottom with a time interval of 2 hours, we can observe that the intensity of fluorescence increased with the gradual saturation of the oil phase. From T = 4 h, the flow started to flow into the bottom



Fig. 5 Oil saturation process in a time sequence (top to bottom) with the flow direction (left to right).

conduit, mostly from the middle micro-fractures rather than the matrix at the left, which verifies the assumption for the interface conditions governing the coupled flow in a dualporosity medium and its adjacent conduits.⁶⁶ At T = 6 h, the bottom conduit has more fluid flowed than the matrix at the right. Until the end of the injection, except for the left corner of the bottom conduit, all the top and bottom conduits were saturated, together with the two matrices and microfractures. The bonding failure may occur at the edges of the inlet and outlet, as well as some edges at the matrix boundaries as indicated in Fig. 5 (T = 10 h). The partial bonding failure would not affect the general trend of the fluid flow inside the porous medium seriously. We did not observe any leakage from the chip until the injection pressure was higher than 420 psi when the solidified epoxy that fixed the nanoport on the chip started to crack and leak but not for other parts of the model. However, our injection pressure was no more than 200 psi so there was no leakage observed throughout the experiments. The water phase was then ready to be injected until there was no fluorescence intensity increase observed which means that the porous medium was fully saturated with the decane oil phase.

3.2. Forced water imbibition process

We conducted the water imbibition processes in two directions with a constant flow rate of 0.02 mL h^{-1} . One is positive injection from the inlet and the other one is reverse injection from the outlet. The two matrices were adjacent to the bottom conduit when the water was forward injected into

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the micromodel and were adjacent to the top conduit when the water was reversely injected. The decane oil phase and water phase were in true excitation colors of green and red. Both two imbibition processes were successful with no leakage found and stopped at about fifty minutes when no more significant phase changes occurred after water breakthrough within the models.

Because of the strong hydrophilicity of glass and the silicon layer after being rinsed in piranha solution before bonding, and with the very low flow rate, the water tended to be imbibed into the matrices first rather than the microfractures from the top conduit. For the forward injection process as shown in Fig. 6, the water started to invade the top conduit and was imbibed into the first matrix at the same time at around 5 minutes from the imbibition beginning. The water flow then branched into two different directions. One branch continued to flow in the conduit and another branch flowed into the bottom conduit. Although some of the water in the matrix flowed into the middle micro-fractures, faster flow velocity was found at the top and



Fig. 6 Water imbibition process in a time sequence (top to bottom) with the flow direction (left to right).

bottom conduits. Consequently, at T = 8 minutes, the water from the top conduit was imbibed into the second matrix and started to displace the oil into the bottom conduit forced by the backpressure of water behind it. Since the decane oil



Fig. 7 Reverse water imbibition process in a time sequence (top to bottom) with the flow direction (left to right).

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is less viscous than the water, a fingering phenomenon was observed as the oil flow had a finger-like structure as it travelled towards the outlet while remaining connected. Besides, as the pressure built up within the whole model, some of the remaining oil at the upstream conduit also started to be displaced and also became finger-like when it met the water that has already been in the top conduit as shown at T = 10 and 15 minutes. The fingering became more remarkable at T = 30 minutes at both conduits and some of the matrices and micro-fractures were re-saturated by some upstream remaining oil. From T = 30 minutes to T = 50minutes, there were no other significant changes, but some connected finger-like oil was stretched longer or disconnected into dispersed oil droplets by the continuous water flooding. The fingering phenomenon was also found in the reverse injection process. However, it happened mostly only in the bottom conduit and was only rarely found in the top conduit as shown in Fig. 7. At the beginning, the water flowed uniformly into the top conduit with much less remaining oil left at the upstream conduit. The water reached the first matrix on the top at T = 6 to T = 8 minutes and was imbibed into it. Meanwhile, some water was also diverted towards the left-side vug. At T = 9 minutes, the water in the first matrix started to flow into the bottom conduit and continued to flow right to the middle micro-fractures afterwards. As the water in the top conduit continued to reach the second matrix at the top right corner, the water in the micro-fractures firstly flowed into the bottom conduit and converged with water from the second matrix later at T =10 minutes. The fingering occurred in the bottom conduit at

T = 15 minutes as the upstream remaining oil in the bottom conduit was displaced towards the outlet and became the most serious at T = 50 minutes. Although there was also some fingering observed at the boundaries of the top conduit, it was much less significant than that of the scenario in which the water was forward injected. The hypothesized reason is that, when the water was forward injected, the two matrices were much closer to the inlet, which may generate a strong imbibition area for the water at the very beginning of the flooding process. In contrast, the two matrices were adjacent to the top conduit and farther to the inlet. Therefore, the water would not prefer to flow into the micro-fracture at the beginning, but rather flow steadily in the top conduit until reaching the first matrix. Thus, there was much less remaining oil left at the upstream since most of it has already been displaced through the top conduit. As a result, the fingering was not likely to be found in the top conduit for the reverse injection scenario, which in turn leads to a higher oil recovery.

3.3. Residual oil distribution comparison

The residual oil is the oil that cannot be recovered by a simple conventional water flooding method. We repeated the experiments in two other models built with the same method and still found that when the two matrices were adjacent to the top conduit the residual oil was much less than that of the case in which the two matrices were adjacent to the bottom conduit. For both cases, the residual oil would exist in different forms within the matrices as shown in



Fig. 8 Residual oil distribution condition comparisons in the matrices and micro-fractures of two different geometries: (a) and (c) top conduit with adjacent matrices; (b) and (d) bottom conduit with adjacent matrices; (e) bottom conduit.

Fig. 8(a) and (b) and the micro-fractures as shown in Fig. 8(c) and (d). Some of them adhered to the rough surface and cannot be displaced by the water while most of them were left in the middle of the channel in different shapes. Besides, snap-off was also observed at very thin matrix channels, resulting in slugs of oil droplets trapped in the pore throats with the water phase trapped among them. It was also found that the re-saturated oil can be hardly driven off by the following water flooding process when the two matrices were adjacent to the bottom conduit, which causes much more residual oil as shown in Fig. 8(b) and (d) than the reverse injection case as shown in Fig. 8(a) and (c). However, the residual oil was distributed similarly in the bottom conduit for both cases, as the finger-structured oil plumes were destroyed by constant water flooding and randomly dispersed to the direction pointing to the outlet.

4. Conclusion and future work

We successfully used e-beam physical evaporation-deposition, a lift-off process and the anodic bonding method to fabricate a fully transparent, shale-like dual-porosity glass-siliconglass micro-/nanofluidic model in a simple, fast and low-cost way. The fabrication process gets rid of the time-consuming and complicated etching method while still generating a complex porous medium network with uniform channels in a much shorter time. To verify the functionality and practicability of the model, two phase fluid flow displacement experiments with two injection modes were conducted separately and visualized using confocal laser scanning microscopy. Owing to the large width-to-depth ratio range (12-2000) of the model, especially for the two conduits at the top and bottom, the fingering phenomenon that may happen in a Hele-Shaw cell was observed. Moreover, we observed that it is possible that the fingering problem could exist when the displacing phase viscosity is higher than that of the displaced phase due to the geometry of the porous medium. Besides, the residual oil was distributed as different forms in the matrices, micro-fractures and conduits. Snapped-off oil droplets trapped in thin channel pore throats, oil chains left in the wider matrix channels, boundary-adhered oil films due to the surface roughness, and dispersed oil droplets in the conduits were found, respectively. By changing the flow pattern by shifting the two matrices to be adjacent to the bottom and then to the top conduits, we demonstrated that different matrix/microfracture/macro-fracture interlacing geometries may affect flow patterns, which would affect the oil recovery seriously for dual-porosity heterogeneous shale porous media.

Although this micro-/nanofluidic model provides a quick and simple platform for directly visualizing the fluid flow dynamically in a dual-scale porous medium, there are still further expectations for future work. The micro-/nanofluidic model can be improved by designing more different patterns that represent more complicated reservoir conditions. The limitation of the depth-to-width aspect ratio by using the glass–glass anodic bonding method still needs to be further investigated, which would provide the possibility of fabricating a micromodel at even the sub-10 nm scale. The residual oil distribution, flow velocity, pressure difference and fingering problem still need to be further studied quantitatively and systematically to obtain a comprehensive understanding of the fluid flow within dual-scale micro-/nano channels at the pore level.

Author contributions

Y. Zhang designed and fabricated the microfluidic chips, implemented the experiments, and prepared the original manuscript. C. Zhou offered the use of photolithography equipment and materials, and gave guidance and suggestions on the lift-off process. C. Qu offered the use of the e-beam evaporator and deposition materials, and gave guidance and suggestions on the e-beam evaporation deposition process. B. Bai is the principal supervisor and advisor of this research. M. Wei and X. He are the co-supervisors and co-advisors of this research. All supervisors proposed the conceptualization of this research and provided the funding support. All authors had discussions about the results and contributed to the manuscript correction and proofreading.

Conflicts of interest

The authors declare no conflicts of interest.

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