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# Highly porous CO<sub>2</sub> hydrate generation aided by silica nanoparticles for potential secure storage of CO<sub>2</sub> and desalination<sup>†</sup>

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We report a new way of storing  $CO_2$  in a highly porous hydrate structure, stabilized by silica nanoparticles (NPs). Such a porous  $CO_2$  hydrate structure was generated either by cooling down NP-stabilized  $CO_2$ -in-seawater foams, or by gently mixing  $CO_2$  and seawater that contains silica NPs under  $CO_2$  hydrate-generating conditions. With the highly porous structure, enhanced desalination was also achievable when the partial meltdown of  $CO_2$  hydrate was allowed.

In situ generation of CO<sub>2</sub> hydrate at deep seabeds has been studied extensively as an economic way of sequestering anthropogenic  $CO_{2}$ ,<sup>1-3</sup> since at the deep sea's near-freezing temperature and high hydrostatic pressure conditions, CO<sub>2</sub> hydrate can be naturally formed from a mixture of CO<sub>2</sub> and seawater.4,5 Being solid with its density slightly higher than that of seawater, the CO<sub>2</sub> hydrate can potentially stay at the deep seabed indefinitely.<sup>6,7</sup> This highly attractive concept, however, has two shortcomings: first, the hydrate formation is known to occur at the interface between CO2 and water and, once a hydrate layer is formed at the CO<sub>2</sub>/water interface,<sup>8</sup> the layer serves as a barrier to further contact between CO<sub>2</sub> and water. Consequently, subsequent hydrate generation is considerably slowed down. Therefore, a vigorous mixing of CO<sub>2</sub> and water, thus a significant input of mechanical energy, is needed not only to generate as much CO<sub>2</sub>/water interfacial area as possible by eliminating heat and mass transfer resistance,<sup>9</sup> but also to disperse the locally trapped salt that was rejected from the hydrate.<sup>10</sup> Second, CO<sub>2</sub> hydrate generally consists of 5.8-7.8 molecules of water per CO2 molecule,11 which means that in order to store a meaningful volume of CO<sub>2</sub> in hydrate form, an inordinate amount of water also has to be processed.

Our finding, here, is that a highly porous  $CO_2$  hydrate structure can be generated by employing high internal-volume  $CO_2$ -in-water foam that is stabilized with hydrophilic silica

nanoparticles (NPs). The concept was derived from two groups of composite materials that are based on NP-stabilized dispersions with a high internal-phase volume fraction. The first is CO<sub>2</sub>-in-water foams that can be employed as an almost waterless fracturing fluid for oil and gas production;12 the other is polymeric foams with high internal void spaces (polyHIPE), which are used as ultralight-weight, high-strength materials for a variety of chemical and biomedical applications.13,14 The generation of both "water-less" CO2 foam and polyHIPE requires the use of NPs or colloidal particles to stabilize the high internal-phase volume fraction dispersion, which has its continuous external phase in the form of very thin lamellae. In order to maintain the stability of such thin films, polymer or viscoelastic surfactant is generally needed in addition to NPs.15 In our case, the CO<sub>2</sub> hydrate particulates generated next to NPs (that straddle the CO<sub>2</sub>/water interface; see Fig. 1) appear to provide certain structural rigidity for the lamella's integrity. This is in a sense similar to polyHIPE in which, once dispersion is formed, thin lamellae polymerize and solidify, thereby generating a high-porosity, low-permeability, sturdy structure. Earlier studies<sup>16-18</sup> found that, when a water-in-CO<sub>2</sub> dispersion



Fig. 1 The presence of hydrophilic nanoparticles at the  $CO_2$ -water interface increases the length of the three-phase contact line, improving  $CO_2$  hydrate nucleation.

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<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: Detailed microscopic analysis, CO<sub>2</sub> hydrate generation with DI water and dry water, temperature, CO<sub>2</sub> equilibrium curve, and ion removal efficiency data. See DOI: 10.1039/c6ra26366f

is generated by way of "dry water" (water-in-air Pickering dispersion, stabilized with hydrophobic silica NPs<sup>19</sup>) and is subsequently brought to the hydrate-generating condition, hydrate generation kinetics are significantly enhanced. Such enhancement is in line with earlier observations that the presence of silica surface enhances CO<sub>2</sub> hydrate nucleation and growth. Importantly, the enhancement may result not only from the large solid surface area available from silica NPs, but also from the generation of tremendous lengths of three-phase (CO<sub>2</sub>/ water/silica) contact line on the NPs adsorbed at the CO2/water interfaces of the dispersion. Recent molecular dynamics simulations<sup>20</sup> showed that the CO<sub>2</sub>/water/silica contact line zone serves as a highly favourable nucleation site for CO<sub>2</sub> hydrates. Since the hydrophilic NPs stabilizes CO2-in-water dispersions while hydrophobic NPs stabilize water-in-CO<sub>2</sub> dispersion, and since the use of hydrophilic NPs such as zinc oxide<sup>21</sup> and graphite<sup>22</sup> to enhance CO<sub>2</sub> hydrate generation has been reported, we experimentally investigated the effect of the hydrophilic silica NPs on the CO<sub>2</sub> hydrate generation and its structure. In addition to much lower cost of manufacturing, the hydrophilic silica NP can be easily dispersed in the water, without going through somewhat tedious step of "dry water" generation. Two important requirements for the hydrophilic NP's surface property are: (i) the NPs should have long-term dispersion stability in seawater; and (ii) they should have the hydrophilicity to form stable CO<sub>2</sub>-in-water foams when sufficient mechanical energy input is applied. These requirements were verified for the NPs we used, based on our earlier studies.23,24

#### CO<sub>2</sub> hydrate formation experiments

 $CO_2$  hydrate was generated in two different ways: (i) *via* prior generation of  $CO_2$ -in-seawater foam and (ii) by gentle mixing of  $CO_2$  and seawater. Similar tests were conducted with DI water, also,  $CO_2$  hydrate was generated *via* "dry water" (hydrophobic nanoparticle-stabilized water dispersion in air) as a supplementary study (details in ESI<sup>†</sup>).

The synthetic seawater (ASTM D 1141, Ricca Chemical Company®, USA) and the liquid  $CO_2$  (Praxair, USA) were employed to generate  $CO_2$  hydrate in the 12.5 mL sapphire cell (Separex, France). For nanoparticles, the nominal 5 nm-spherical hydrophilic silica nanoparticles coated with polyethylene glycol (3M, USA) were used.

For the  $CO_2$  hydrate *via*  $CO_2$ -in-seawater foams, the nanoparticle-stabilized  $CO_2$  foam generating system in previous study<sup>25</sup> was utilized as shown in Fig. 2(A). The  $CO_2$  and seawater with 1 wt% hydrophilic nanoparticles were co-injected into a sandpack (filled with 350 µm Ottawa sand) by HPLC pump (1500 HPLC, Supercritical Fluid Technologies, Inc., USA) and high pressure syringe pump (500D, Teledyne ISCO, Inc., USA), generating  $CO_2$ -in-seawater foams through the effluent line at the ambient temperature. The total flow rate was controlled at 10 mL min<sup>-1</sup> with a constant volume fraction of  $CO_2$  at 0.75. At the flow condition, the interstitial velocity, shear rate, and residence time were 3.39 cm s<sup>-1</sup>, 10 600 s<sup>-1</sup>, and 9 s, respectively. The entire system pressure was maintained at 11.7 MPa



Fig. 2 Experimental system to generate  $CO_2$  hydrate *via* (A)  $CO_2$ -inseawater foam and (B) gentle mixing of  $CO_2$  and seawater.

by the back pressure regulator (Core Laboratories, USA). The pressure was also monitored by the pressure gauge (Swagelok, USA) connected to the sapphire cell. When the  $CO_2$ -in-seawater foam fully filled the sapphire cell, it was then kept at 4 °C in a stationary condition for 24 h (Fig S3†).

For the hydrate formation by gentle mixing of  $CO_2$  and seawater, the entire set-up was placed in the 4 °C cold room overnight prior to the test. The sapphire cell was filled with 6 mL of seawater with or without 1 wt% hydrophilic nanoparticles, followed by the pressurization with  $CO_2$  up to 3.8 MPa.  $CO_2$  was stored in a pressure vessel which was held at 3.8 MPa at 4 °C and connected to the sapphire cell to pressurize it. Once the cell was pressurized, the initial test pressure was confirmed by the pressure gauge (Kodiak Controls Inc., USA) attached to the cell. Then, the sapphire cell was placed in a tumbler which rotated at 7 rpm for 2 h. The rotating speed of the tumbler was selected to keep the  $CO_2$  hydrate generation in a gentle mixing condition.

Overall, the following improvements in experimental procedure over the earlier reported<sup>16–18</sup> were made. First, the entire generation process was carried out in a 4 °C cold room to ensure a constant temperature condition. The cold room was designed to keep 4 °C constantly with a real-time temperature monitoring panel. Second, sapphire cells with pressure control were employed to directly observe the progress of hydrate generation process. After the visual observation that the hydrate generation was established, the cell was depressurized, the generated hydrate was drained of any excess water and was immediately taken in an ice bath to the cold-stage scanning electron microscopy (SEM) to obtain microscopic structural images (details in ESI†).

Note that water used in our main experiments reported here was synthetic seawater. Although the water that forms hydrate

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cage does not include any salts, seawater with high salt content can still be included in between hydrate aggregates during the process of the rapid  $CO_2$  hydrate generation.<sup>26</sup> Therefore, the Na<sup>+</sup>, Mg<sup>2+</sup>, and Ca<sup>2+</sup> ion concentrations of the hydrate samples taken from the depressurized cell were measured by ion chromatography (Dionex ICS-1100, Thermo Scientific, USA) equipped with cation exchange column (IonPac CS12A, Thermo Scientific, USA) to quantify their change from the pre-hydrate concentrations, in order to approximately estimate the extent of seawater trapping. To further analyze the effect of  $CO_2$ hydrate melting on the trapped ion concentrations, a part of  $CO_2$  hydrate taken out of the sapphire cell was sampled for the ion concentration analysis before melting, and the rest of the hydrate was placed on a disposable wiper (Kimwipes, Kimberly-Clark, USA) to drain the trapped seawater for 10 min at 4 °C and

# was sampled at 5 and 10 min, respectively, which was allowed to melt completely for the ion chromatography analysis. SEM observations of different hydrate

ambient pressure condition, as the hydrate partially melted slowly. During the partial melting process,<sup>27</sup> the  $CO_2$  hydrate

Fig. 3(A) shows the hydrate generated from the pre-formed  $CO_2$ in-seawater foam stabilized with hydrophilic silica NPs. As described above, the lamella's stability was maintained by the NPs adsorbed on its two interfaces, and the newly generated hydrates attached to the NPs appear to provide additional rigidity to the lamellae. With the sapphire cell depressurization, the CO<sub>2</sub> bubbles would have expanded and burst the lamellae; however, unlike the conventional foam lamellae which, when destabilized, would immediately contract and disappear, the CO2 hydrate-covered lamellae still left a considerable degree of "skeletal boundaries", similar to the polymerized polyHIPE structure. This suggests that, as discussed above with the molecular dynamics simulations,<sup>20</sup> the CO<sub>2</sub> hydrate generation from CO<sub>2</sub> foam occurred at three-phase contact line throughout the lamellae, forming a highly porous NP-stabilized CO2 hydrate structure even after depressurization.

Fig. 3(B) shows a SEM image of the hydrate generated from gentle mixing of CO<sub>2</sub> and hydrophilic silica NP-containing seawater in a tumbler. At ambient conditions, such a gentle mixing cannot produce stable CO2-in-water foam, because the adsorption of NPs to the CO2/water interface requires to overcome a certain energy barrier.28 Brought to the hydrategenerating condition, however, it appears that the CO2-inseawater foam generation was possible even with only moderate energy input, from synergy between the newly generated hydrate at the CO<sub>2</sub>/water interface and the NPs that were attached to the hydrates and thus more easily brought to the CO<sub>2</sub>/water interface. The adsorbed NPs, in turn, would enhance further hydrate generation at three-phase contact lines. The image suggests that the lamellae did not have as much rigidity as the case of pre-generated foam (Fig. 3(A)), with fewer "skeletal boundaries" remaining after the depressurization. This is probably because not as many NPs were able to be



**Fig. 3** SEM images of  $CO_2$  hydrate *via* (A) nanoparticle-stabilized  $CO_2$ in-seawater foams, (B) gentle mixing of  $CO_2$  and seawater with nanoparticles, and (C) gentle mixing of  $CO_2$  and seawater without nanoparticles.

adsorbed at the bubble interface, due to insufficient mixing energy input. Also the larger pore size suggests larger  $CO_2$ bubbles. Nevertheless, it seems that the NP-stabilized  $CO_2$ hydrate structure, even generated with gentle mixing only, could hold a substantial volume of  $CO_2$  throughout the numerous lamellae. The NPs added to water thus appear to contribute to formation of a highly porous  $CO_2$  hydrate structure by way of generation of  $CO_2$  foams with highly stable, NPstabilized lamellae.

structures

Fig. 3(C) shows the CO<sub>2</sub> hydrate generated from gentle mixing of CO<sub>2</sub> and seawater, but without NPs. The planar surface indicates that there was little possibility to form stable CO<sub>2</sub> bubbles without the NPs. As a result, the CO<sub>2</sub>/seawater interface as a large plane served as the CO<sub>2</sub> hydrate generation sites, leading to a planar growth in the entire cell. This type of surface structure was also found with the CO<sub>2</sub> hydrate generated by gentle mixing of CO<sub>2</sub> and DI water (Fig. S1(A)†). This also suggests that the stability of the CO<sub>2</sub> hydrate-induced CO<sub>2</sub>/ seawater dispersion in the absence of NPs is rather tenuous, and the ability of such hydrate structure to hold CO<sub>2</sub> is quite uncertain.

Fig. 4 shows a nanoscale SEM image of CO<sub>2</sub> hydrate generated by gentle mixing of CO2 and seawater with NPs (see Fig. 3(B)). The skeletal structure, which is the vestige of the CO<sub>2</sub> foam lamellae, was clearly captured, displaying its thickness around 200-500 nm. The swollen three-way junction appears to represent a plateau border with the formerly continuous aqueous phase.<sup>29</sup> This SEM image suggests simultaneous CO<sub>2</sub> foam generation and hydrate generation. Although the threshold shear rate is required to overcome the adsorption energy barrier<sup>24</sup> for CO<sub>2</sub> foam generation, little has been studied for the CO<sub>2</sub> foam generation at such a low temperature. The CO<sub>2</sub> foam stability was known to increase as temperature decreases. Also, the increased CO<sub>2</sub> density at such a low temperature would require less mechanical mixing for CO<sub>2</sub> foam generation.<sup>23</sup> In addition, the nucleation and the growth of CO<sub>2</sub> hydrate in the CO<sub>2</sub>/seawater mixture might provide additional shear to the fluid as small solid CO<sub>2</sub> hydrate particles or aggregates rotate in it.

#### Salinities in different hydrate structures

In principle,  $CO_2$  hydrate generation can be a good desalination method because hydrate molecular cage contains water with zero salinity. However, when  $CO_2$  hydrate is generated from seawater, the seawater inclusion among  $CO_2$  hydrate aggregates is inevitable, leaving a certain level of salinity. Since the highly porous  $CO_2$  hydrate would trap less seawater due to their more internally connected structure, it was desirable to measure the salinity from the  $CO_2$  hydrate samples. Because it is difficult to distinguish the hydrate from the trapped seawater based on the SEM images of the skeletal structure, the following indirect way



Fig. 4 Nanoscale SEM image of  $CO_2$  hydrate formed by gentle mixing of  $CO_2$  and seawater with nanoparticles: focusing on (A) a rod and (B) a three-way junction.

of estimating the respective mass fractions of major salt ions was attempted. After the  $CO_2$  hydrate samples were taken out from the depressurized sapphire cell and excess seawater was drained off, three different samples were prepared; one taken immediately after the seawater drainage; and two taken after 5 and 10 minutes of the partial melting of  $CO_2$  hydrate sample at 4 °C for the further drainage and removal of the trapped seawater. Then, the concentration of three major cations (Na<sup>+</sup>, Mg<sup>2+</sup>, and Ca<sup>2+</sup> ion initially 1.13%, 0.06%, and 0.13%, respectively) in seawater was measured from these three different samples. Fig. 5 shows the overall removal efficiency (measured concentration over original seawater concentration) of the salt ions. Without partial melting, the removal efficiency was 6.68– 9.24% higher with NPs than without NPs. When the samples were taken after the partial melting was allowed for 10 min, the



Fig. 5 Effect of nanoparticles on removal efficiency of major cations in seawater via  $CO_2$  hydrate followed by a partial melting: (A)  $Na^+$ , (B)  $Mg^{2+}$ , and (C)  $Ca^{2+}$ .

removal efficiency was increased up to 65.30% (without NPs) and 86.26% (with NPs), supporting the greater drainage rate of the trapped seawater with NPs, specifically, with the highly porous structure. The ESI data regarding the removal efficiency is included in Table S1.<sup>†</sup> The qualitatively similar removal trend was obtained over the series of tests although some fluctuations in the measurements were also observed because the identical CO<sub>2</sub> hydrate surface area was difficult to obtain. Therefore, the constant test condition with a detailed control protocol should be maintained to minimize the fluctuations in the removal efficiency. Considering the similar trend in removal pattern among the major ions tested here, other minor salts are expected to show such removal pattern as well. In fact, for the hydrate-based desalination process,<sup>30</sup> the salt trapping turned out to be a major hindrance for its practical development. The facts that the NP-aided CO<sub>2</sub> hydrate structure contained much less trapped salt, and that the drainage of trapped seawater was achievable by simple partial melting of CO<sub>2</sub> hydrate, offer an intriguing possibility that NP-aided CO<sub>2</sub> hydrate-based desalination process may provide an economic way of producing lowsalinity water, e.g., for the recently developed low-salinity enhanced oil recovery process for offshore oilfields.31

### Conclusions

Based on the  $CO_2$  hydrate formation mechanism, it is expected that the diffusion of water to liquid  $CO_2$  would occur along with the hydrophilic silica NP surface located at the  $CO_2$ /water interface, offering numerous sites for  $CO_2$  hydrate nucleation. In addition, the conversion of  $CO_2$ -in-seawater foams to  $CO_2$ hydrate shown in this study demonstrates the  $CO_2$  hydrate could be pre-shaped in a lamellar structure resulting in a highly porous  $CO_2$  hydrate.

The generation of such highly porous  $CO_2$  hydrate structure, *in situ* either in geological formations or at subsea, has a couple of potential applications. First, such porous hydrate structures containing  $CO_2$  could be securely sequestered in quantity in the shallow subsurface of deep-sea sediments, which are abundantly available worldwide. Second, as described above, an economic desalination process could be developed *via* natural formation of NP-stabilized  $CO_2$  hydrate, at subsea, to obtain low-salinity water for injection for enhanced oil recovery from offshore oil reservoirs. The currently available desalination options are either too costly or difficult to implement on platforms. Such utilization of  $CO_2$  in hydrate form will improve the overall economics of  $CO_2$  sequestration as well as offshore oilfield operation, so that  $CO_2$  can be sequestered in truly meaningful quantities.

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