

Hydrate-based CO₂ capture: kinetic improvement via graphene-carried -SO₃⁻ and Ag nanoparticles

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Experimental section

Materials

Expansile graphite (325 mesh) was provided by Nangjing Jicang Nano Technology Co., Ltd. (Nangjing, China). Potassium permanganate (KMnO₄, A.R.) was purchased from Laiyang Fine Chemical Factory (Laiyang, China). Sodium nitrate (NaNO₃, A.R.), sodium p-amino benzenesulfonate (A.R.), sodium hydroxide (NaOH, A.R.), sulfuric acid (H₂SO₄, 98%), and hydrochloric acid (HCl, 36-38%) were purchase from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Sodium nitrite (NaNO₂, A.R.) was provided by Tianjin Dengke Chemical Reagent Co., Ltd. (Tianjin, Tianjin). Sodium borohydride (NaBH₄, A.R.) was purchased from Chengdu Kelong chemical reagent factory (Chengdu, China). Hydrogen peroxide (H₂O₂, 30%) was purchased from Tianjin Dingshengjin Chemical Reagent Co., Ltd. (Tianjin, China). Hydrazine hydrate (80%) was provided by Tianjin Basifu Chemical Industry (Tianjin, China). Ethyl alcohol (C₂H₅OH, 80%) was purchased from Tainjin Fuyu Refine Chemical Factory (Tianjin, China). Silver nitrate (AgNO₃, A.R.) was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Methane (CH₄, 99.99%) was purchased from Heli Gas Co., Ltd (Qingdao, China). The deionized water (DI water) used in this work was laboratory-made and the conductivity was 1.17±0.1 μs/cm at 298.15 K.

Preparation of graphene oxide (GO)

GO was prepared according to the modified Hummers method. First, 10 g expansible graphite and 5 g NaNO₂ were added into 230 mL H₂SO₄ (98%) respectively at 0-4 °C and under magnetic stirring of 300 rpm. After complete dissolution of the graphite and NaNO₂, 30 g KMnO₄ was added in six time intervals, and continuous stirring of 300 rpm was carried out under 10-15 °C for 2.5 h. Afterwards, a certain amount of deionized water was added into the reaction system, which was kept under 35 °C for 30 min and then at 80-100 °C for 30 min. Then, a certain amount of H₂O₂ (5%) was added and the reaction solution was filtered. The filter residue was firstly washed with HCl solution (5%) until no SO₄²⁻ could be detected, and secondly washed with deionized water, and thirdly dried at 40 °C. GO was finally obtained.

Preparation of sulfonate graphene oxide (SGO)

Step one, the pre-reduced GO was prepared. 15 mL NaBH₄ solution of 40 g/L was added into 75 mL GO solution of 1 g/L and the pH was adjusted to 9-10 with an Na₂CO₃ solution (5%), after which, the reaction solution was stirred under 80 °C for 1 h and the pre-reduced GO was achieved.

Step two, the p-amino benzenesulfonic acid diazonium salt was prepared. Firstly, 5 mL NaOH solution (2%) and 0.5 g p-amino benzenesulfonic acid were added into a flask of 100 mL, respectively. Secondly, 0.2 g NaNO₂ was added into the flask, and then 10 mL ice water and 1 mL of HCl solution (36%) were added, respectively. Afterwards, the above solution was stirred under 0 °C for 15 min, and diazonium salt was obtained.

Step three, the solution of p-amino benzenesulfonic acid diazonium salt was added into the solution of pre-reduced GO drop by drop, after which, the mixed solution was firstly stirred under 0 °C for 2-4 h, and then was centrifuged under 5000 rpm for 10 min. Afterwards, the precipitate was collected and cleaned, and the SGO was obtained.

Preparation of Ag@SGO

Ag@SGO was prepared through electrostatic adsorption and in situ reduction. Firstly, a certain amount of SGO solution was prepared and then AgNO₃ solution of a certain concentration was added under magnetic stirring of 600 rpm with the mass ratio of Ag and SGO as 1:10. Afterwards, the solution was stirred under 600 rpm for 6 h to ensure the Ag⁺ was adequately adsorbed on the nano-sheets of SGO through the electrostatic interaction with -COO⁻ of SGO nano-sheets. Subsequently, superfluous hydrazine hydrate solution was dropped slowly into the SGO solution, which was then stirred under 600 rpm for 2 h to achieve the in situ reduction of Ag⁺ and the fixation of Ag nanoparticles on the SGO nano-sheets.

Characterization

The functional groups on the nano-sheets of SGO and Ag@SGO were determined through an infrared spectrometer (Nicolet iN 10, Thermo Fisher, USA). The original SGO and Ag@SGO solutions were centrifuged at 10000 rpm for 10 min, afterwards, the precipitates were collected and dried at 328.15 K for 24 h, which were then used for the infrared spectroscopy measurement.

The morphology of the nano-sheets of SGO and Ag@SGO were observed using a JEM-1200EX Transmission Electron Microscope (TEM) made by Japan Electronics Co., Ltd. The original SGO and Ag@SGO solutions were firstly diluted 200-fold with deionized water and then applied for TEM measurement.

The XRD spectra of the nano-sheets of SGO and Ag@SGO were obtained using a D8 Advance X-ray diffractometer made by Bruker, Germany. The original SGO and Ag@SGO solutions were centrifuged at 10000 rpm for 10 min, afterwards, the precipitates were collected and dried at 328.15 K for 24 h, which were then used for the X-ray diffraction analysis.

CO₂ hydrate formation experiments

CO₂ hydrate formation was carried out in a high-pressure reactor made of 316L stainless steel, with the volume of 80 mL and maximum pressure capability of 20 MPa, of which, the schematic diagram was shown by **Fig. S1**. The reactor was placed in a thermostatic water bath with the temperature range of 253.15 - 323.15 K and equipped with a PT100 temperature transducer with the uncertainty of 0.01 K and a SDD-601 pressure transducer with the uncertainty of 0.01 MPa. Moreover, a magnetic stirring apparatus with the stirring at 0 - 1000 rpm was installed under the reactor and a rotor with the size of 4 mm * 10 mm (diameter * length) was used for stirring.

Firstly, the reactor was cleaned with deionized water three times; then 10 mL reaction solution was charged into the reactor and the cooling and stirring were started. When the desired temperature (275.15 K) was reached, the reactor was purged with CO₂ and then pressurized with CO₂ to the experimental pressure (3.7 MPa). The evolutions of the temperature and pressure during the CO₂ hydrate formation were recorded by the computer.

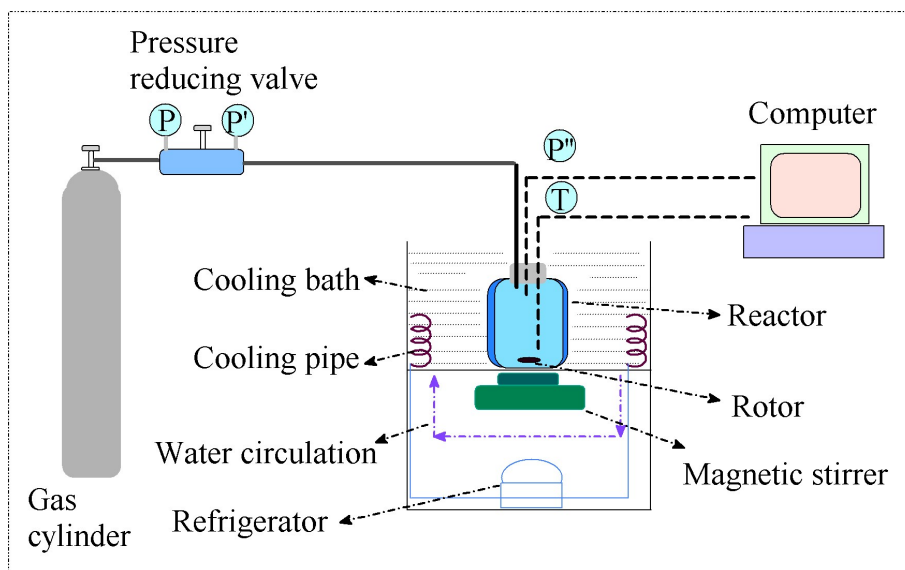


Fig. S1 Schematic diagram of the CO₂ hydrate formation apparatus used in this work

Calculation methods

(1) Gas dissolving period

Fig. S2 shows the pressure evolutions during CO₂ hydrate formation under the initial 3.7 MPa, 275.15 K and 300 rpm. Normally, as shown by curve 1, the whole process consisted of three stages: firstly the CO₂ dissolution period, then the induction period and finally the hydrate formation period. However, for some experiments, as shown by curve 2, no obvious induction period was observed; therefore, to determine the CO₂ dissolution period and hydrate formation period, the calculation of CO₂ solubility was carried out.

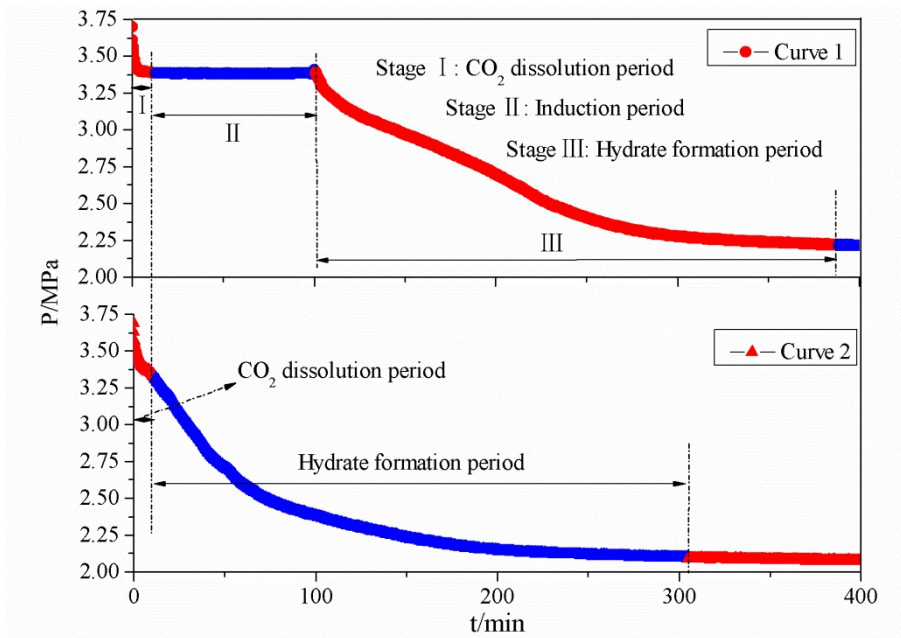


Fig. S2 Pressure evolutions during CO₂ hydrate formation process (the initial pressure was 3.7 MPa, the temperature was 275.15 K and the stirring was 300 rpm).

For the calculation of CO₂ solubility, the amount of CO₂ dissolved in water (n_s) is calculated by equation (1),

$$n_s = \frac{x_{CO_2}}{(1 - x_{CO_2})} n_w \quad (1)$$

where, x_{CO_2} is the molar fraction of CO₂ in the liquid phase and n_w is the water

amount.

x_{CO_2} is calculated by equation (2),¹

$$x_{CO_2} = \frac{y_{CO_2} P \varphi_{CO_2}^V}{H_{CO_2}^* \exp\left[\frac{v_{CO_2}^\infty}{RT} (P - P_{H_2O}^{sat})\right]} \quad (2)$$

where, P is the pressure, $\varphi_{CO_2}^V$ is the fugacity coefficient of CO_2 , $H_{CO_2}^*$ is the Henry's constant, $v_{CO_2}^\infty$ is the partial molar volume of CO_2 in pure water at infinite dilution and the arithmetic average value gives as $3.32 \times 10^{-5} \text{ m}^3/\text{mol}$, $P_{H_2O}^{sat}$ is the vapor pressure of water.

y is calculated by equation (3),²

$$y = 1 - (0.1256T - 0.0212) \times 10^{-3} - P(0.065T + 1.121) \times 10^{-5} \quad (3)$$

$\varphi_{CO_2}^V$ is expressed by using the PR-EOS and mixing rules,

$$\ln(\phi_{CO_2}^V) = (Z - 1) - \ln(Z - B) - \frac{A}{2\sqrt{2}B} \times \ln\left(\frac{Z + (1 + \sqrt{2})B}{Z - (1 - \sqrt{2})B}\right) \quad (4)$$

$H_{CO_2}^*$ is calculated by equation (5),¹

$$H_{CO_2}^* = \exp\left(13.99194 - \frac{2650.11724}{T}\right) \quad (5)$$

$P_{H_2O}^{sat}$ is calculated by equation (6),¹

$$P_{H_2O}^{sat} = \left[73.649 - \frac{7258.2}{T} - 7.3037 \ln(T) + 4.17 \times 10^{-6} T^2\right] \quad (6)$$

To evaluate the accuracy of the CO_2 solubility calculation, the experimental determination of CO_2 dissolution was conducted, in which, unstirred condition was carried out to avoid hydrate formation. During the CO_2 dissolution period, the gas consumption (n_i) is equal to the CO_2 dissolution amount, which can be calculated by equation (7),

$$n_t = \frac{P_0 V_0}{z_0 R T_0} - \frac{P_t V_t}{z_t R T_t} \quad (7)$$

where, P is the pressure in the reactor, T is the temperature in the reactor, V is the volume of gas phase in the reactor and V_t is viewed as equal to V_0 considering that the dissolution of CO_2 does not change volume of the liquid phase, z is the compressibility factor and calculated by equation (8),³

$$z_t = 1 + [0.083 - 0.422 \times \left(\frac{T_c}{T_t}\right)^{1.6}] \frac{P_t T_c}{P_c T_t} + \omega [0.139 - 0.172 \times \left(\frac{T_c}{T_t}\right)^{4.2}] \frac{P_t T_c}{P_c T_t} \quad (8)$$

where, T_c , P_c and ω are 304.2 K, 7.338 MPa and 0.224, respectively.

Fig. S3 shows the evolutions of pressure and gas consumption during CO_2 dissolution process in deionized water under initial 3.7 MPa, 275.15 K and unstirred condition. The pressure dropped rapidly from 3.7 MPa and gradually achieved balance at about 3.26 MPa at 21 min; correspondingly, the gas consumption stabilized at about 2.01 mmol/mL water. As no hydrate formation was observed, we assumed that the gas consumption was caused by CO_2 dissolution. While according to equation (1)-(6), the solubility of CO_2 in water at 275.15 K and 3.26 MPa was calculated as 2.07 mmol/mL, very close to the experimental data and confirming the excellent accuracy of CO_2 solubility calculation.

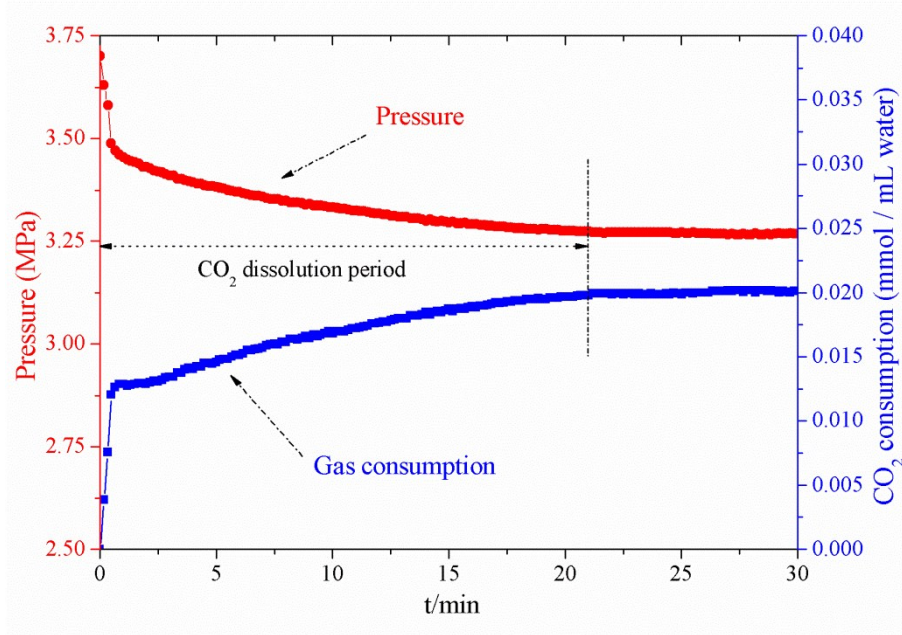


Fig. S3 Evolutions of the pressure and gas consumption during CO₂ dissolution process in deionized water under the initial 3.7 MPa, 275.15 K and unstirred condition.

(2) Gas hydrate formation period

During the hydrate formation period, both the CO₂ dissolved in liquid phase and the CO₂ in gas phase would be enclathrated into the hydrate cages. Moreover, with the formation of hydrate phase, both the pressure in gas phase and the volume of liquid phase changed due to the consumption of gas and water, causing the continuous variation of the CO₂ dissolution amount.

In this work, the CO₂ amount during hydrate formation period can be expressed as follows:

$$n_0 = n_g + n_s + n_h \quad (9)$$

where, n_0 is the total CO₂ in the reactor, n_g is the CO₂ in the gas phase, n_s is the dissolved CO₂, n_h is the CO₂ encaged in hydrates and n_0 , n_g , n_s are calculated by equation (10)-(12), respectively.

$$n_0 = \frac{P_0 V_0}{z_0 R T_0} \quad (10)$$

$$n_t = \frac{P_t V_t}{z_t R T_t} \quad (11)$$

$$n_s = \frac{x_{CO_2}}{(1 - x_{CO_2})} n_w \quad (12)$$

where, x_{CO_2} is molar fraction of CO₂ in the liquid phase and n_w is the amount of water at time t.

It should be noted that with the formation of hydrates, V_t changed due to the different densities of water and hydrates, which therefore can be calculated as follows:⁴

$$V_t = V_0 - mn_h \Delta V \quad (13)$$

where, m is the hydration number,⁵ ΔV is the molar volume difference between methane hydrates and water.⁶

n_w is calculated by,

$$n_w = n_{w0} - n_h m \quad (14)$$

where, n_{w0} is the initial water amount in the reactor.

Therefore, equation (9) can be compressed as follows:

$$\frac{P_0 V_0}{z_0 R T_0} = \frac{P_t (V_0 - mn_h \Delta V)}{z_t R T_t} + \frac{x_{CO_2}}{(1 - x_{CO_2})} (n_{w0} - n_h m) + n_h \quad (15)$$

As a result, the CO₂ consumption by hydrate formation (n_h) is calculated as follows:

$$n_h = \frac{\frac{P_0 V_0}{z_0 R T_0} - \frac{P_t V_0}{z_t R T_t} - \frac{x_{CO_2}}{(1 - x_{CO_2})} n_{w0}}{1 - \frac{x_{CO_2}}{(1 - x_{CO_2})} m - \frac{P_t m \Delta V}{z_t R T_t}} \quad (16)$$

References

1. M. Ricaurte, J. P. Torr , A. Asbai et al. Experimental data, modeling, and

correlation of carbon dioxide solubility in aqueous solutions containing low concentrations of clathrate hydrate promoters: application to CO₂-CH₄ gas mixtures. *Ind. Eng. Chem. Res.*, 2012, **51**, 3157-3169.

2. L. W. Diamond, N. N. Akinfiev. Solubility of CO₂ in water from -1.5 to 100°C and from 0.1 to 100 MPa: evaluation of literature data and thermodynamic modeling. *Fluid Phase Equilib.*, 2003, **208**, 265-290.
3. J. M. Smith, N. H. C. Van, M. M. Abbott. in Introduction to Chemical Engineering Thermodynamics, McGraw-Hill Education, Singapore, 6th edn., **2001**, pp. 96-98.
4. F. Wang, S. J. Luo, S. F. Fu, Z. Z. Jia, M. Dai, C. S. Wang, R. B. Guo. Methane Hydrate Formation with Surfactants Fixed on the Surface of Polystyrene Nanospheres. *J. Mater. Chem. A*, 2015, **3**, 8316-8323.
5. C. Gutt, B. Asmussen, W. Press, M. R. Johnson, Y. P. Handa, J. S. Tse. The Structure of Deuterated Methane-hydrate. *J. Chem. Phys.*, 2000, **113**, 4713.
6. J. L. Wu, X. P. Shen, L. Jiang, K. Wang, K. M. Chen. Solvothermal synthesis and characterization of sandwich-like graphene/ZnO nano-composites. *Appl. Surf. Sci.*, 2010, **256**, 2826-2830.

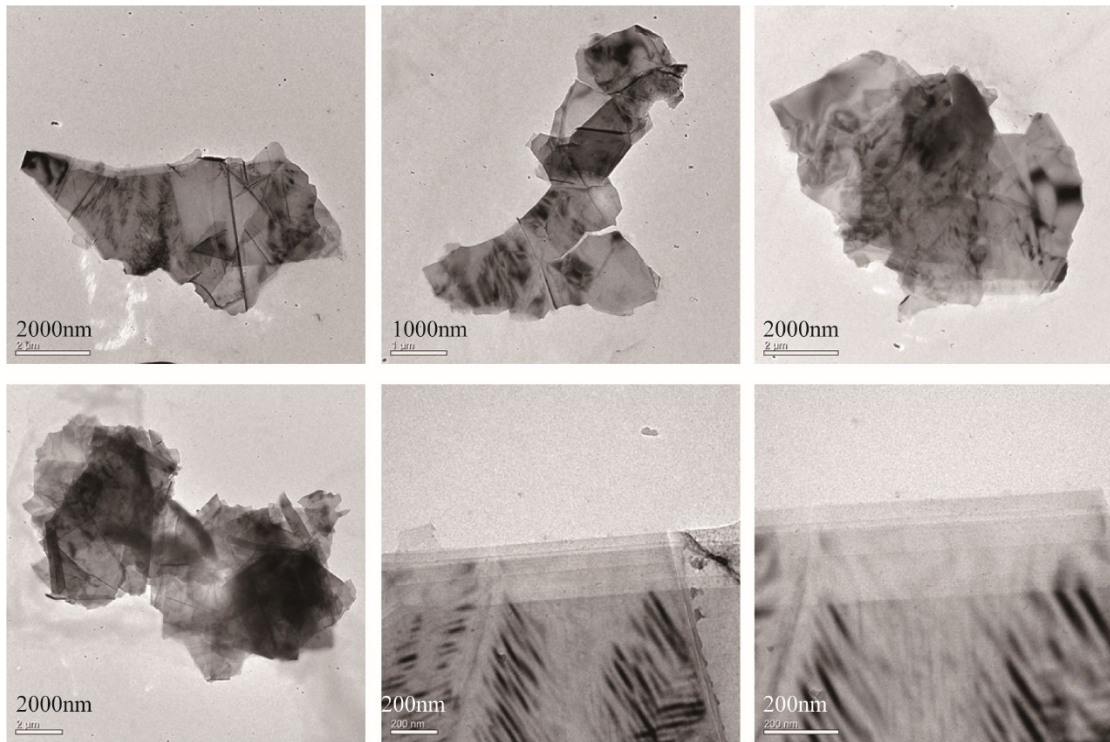


Fig. S4 TEM photos of graphite particles

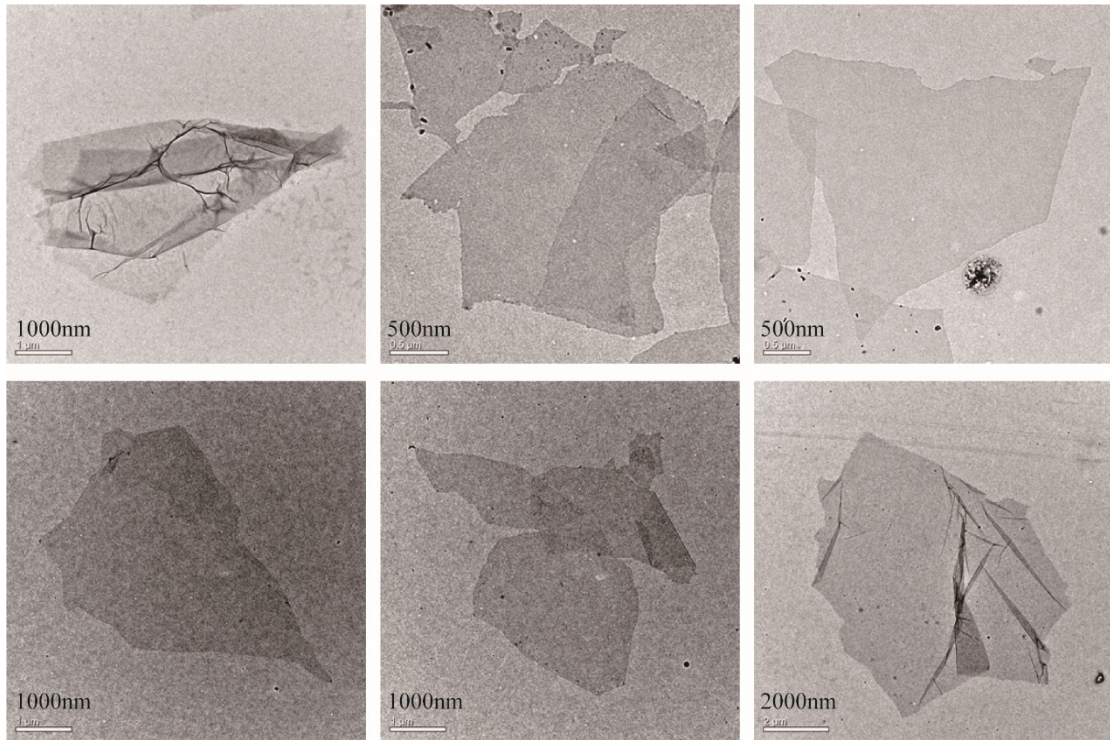


Fig. S5 TEM photos of GO

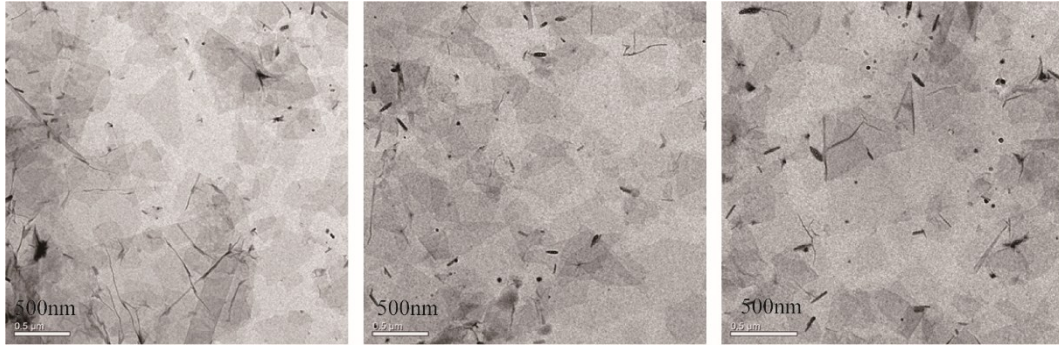


Fig. S6 TEM photos of SGO

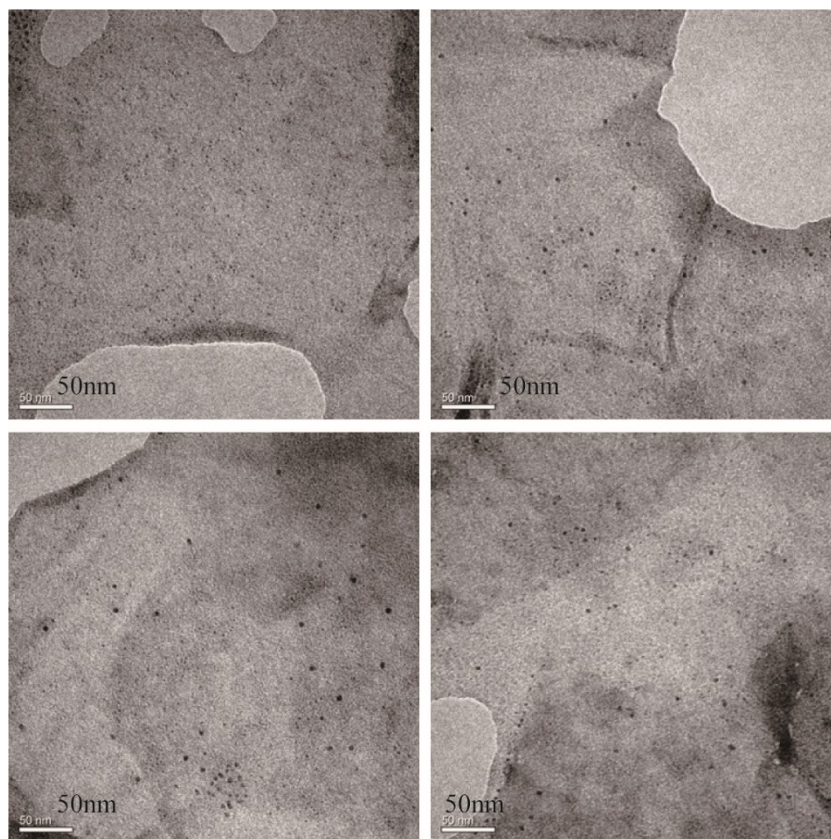


Fig. S7 TEM photos of Ag@SGO

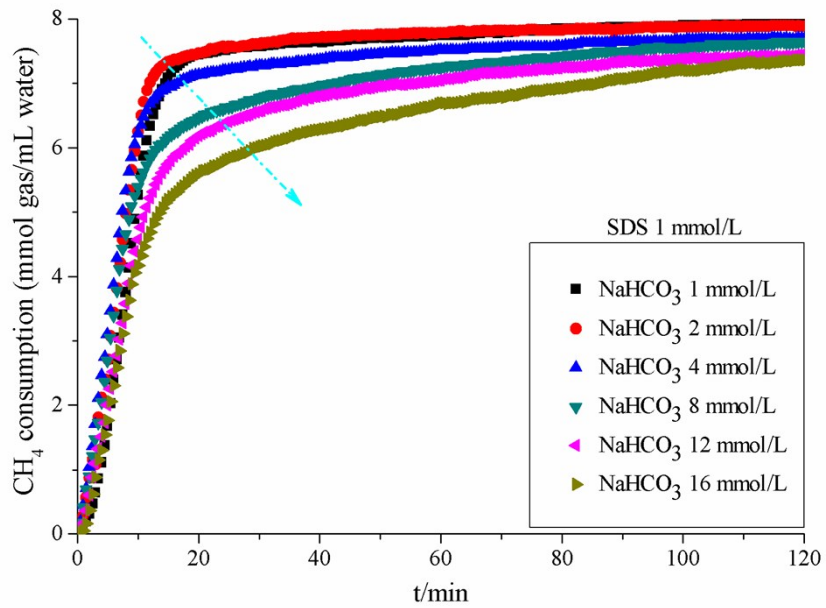


Fig. S8 Evolutions of gas consumption during methane hydrate formation with SDS of 1 mmol/L and NaHCO₃ of different concentrations. (The initial pressure was 6 MPa, the temperature was 275.15 K and the stirring was 300 rpm)

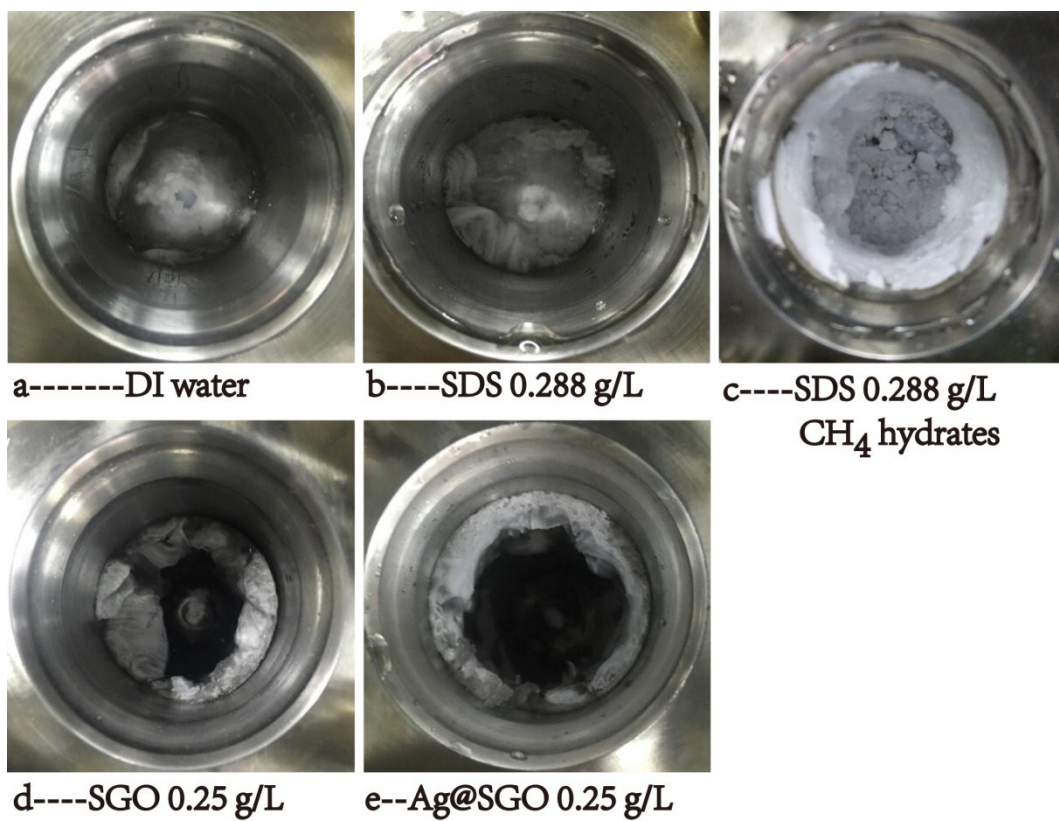


Fig. S9 Morphologies of CO₂ hydrates in the reactor formed with different promoters (CH₄ hydrate formation was carried out at initial 6 MPa and 275.15 K; CO₂ hydrate formation was carried out at initial 3.7 MPa, 275.15 K and 300 rpm)

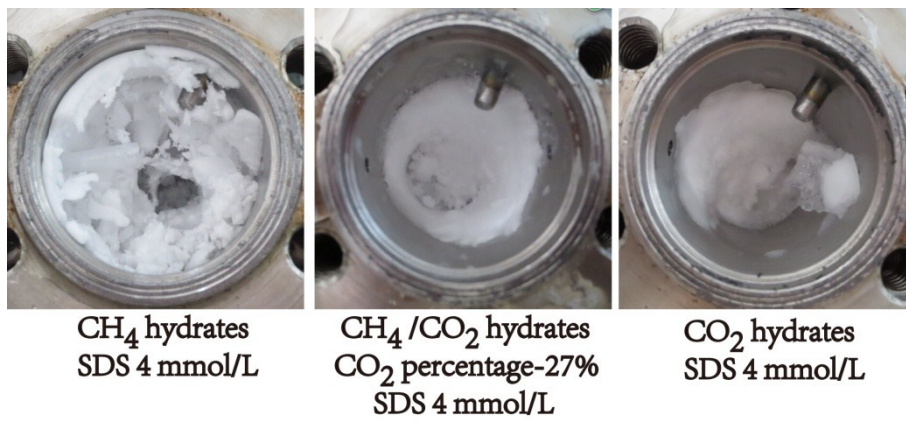


Fig. S10 Morphologies of hydrates formed with different formers. (The initial pressure was 6 MPa and the temperature was 275.15 K)

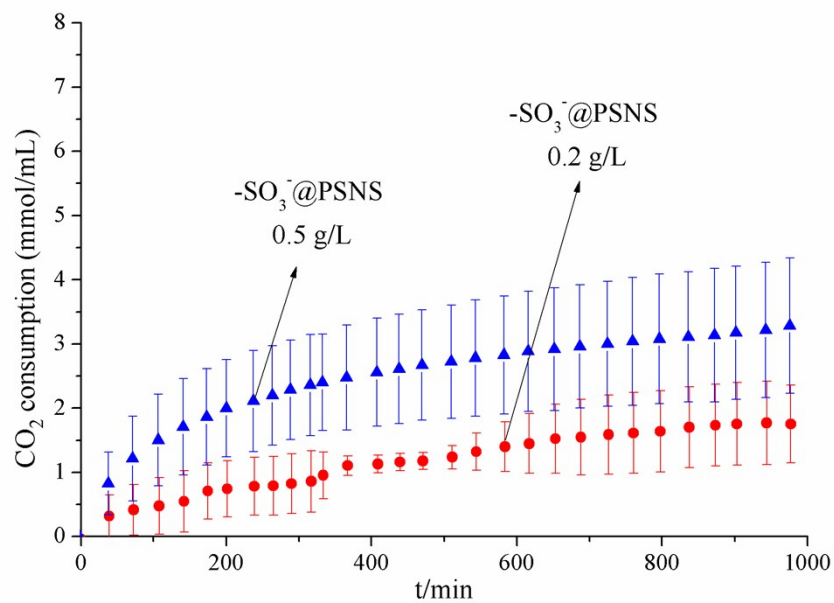


Fig. S11 Evolutions of the gas consumption during CO₂ hydrate formation with -SO₃⁻@PSNS (the initial pressure was 3.7 MPa, the temperature was 275.15 K and the stirring was 300 rpm)