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Introduction

Natural gas, as a clean energy source, has attracted more and more attention over the recent years and efficient transportation and storage methods are critical to the utilization of natural gas.¹

Grafting of nano-Ag particles on -SO₃⁻-coated nanopolymers for promoting methane hydrate formation⁺

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Sodium dodecyl sulfate (SDS) has been reported to be the most efficient promoter for hydrate-based natural gas storage and transportation, however, foam generation during hydrate dissociation seriously affects its application. Nano-metal particles have also been demonstrated to be efficient promoters, nevertheless their poor stability is a serious problem. In this work, we first fixed $-SO_3^-$ groups (similar to the hydrophilic group of SDS) covalently on polystyrene through soap-free emulsion polymerization to synthesize $-SO_3^-$ -coated nanopolymers, and by tuning their morphology they existed as amorphous polystyrene macromolecules ($-SO_3^-$ @PSMM) or uniform polystyrene nanospheres ($-SO_3^-$ @PSNS). Afterwards, we grafted nano-Ag particles with the size of 2-5 nm on the $-SO_3^-$ -coated nanopolymers through electrostatic adsorption and in situ reduction to prepare $Ag\theta - SO_3^-$ -coated nanopolymers (denoted as Ag&-SO3-@PSMM and Ag&-SO3-@PSNS), which were then used for the first time to promote methane hydrate formation. When 0.5 mmol L^{-1} amorphous Ag θ -SO₃⁻@PSMM was used at an initial pressure of 6 MPa and temperature of 275.15 K, the induction period was 32.2 \pm 7.9–60.8 \pm 14.2 min, the growth period was $108.8 \pm 8.2-177.1 \pm 38.9$ min and the methane storage capacity reached 143.9 \pm 3.7–145.2 \pm 1.2 v/v, whereas when the spherical Ag&-SO₃⁻@PSNS was used at 0.5 mmol L⁻¹, the induction period and growth period were $17.8 \pm 2.8 - 38.5 \pm 8.0$ and $39.6 \pm 2.8 - 42.1$ \pm 0.9 min, respectively; and the storage capacity reached 149.3 \pm 1.2–151.3 \pm 3.0 v/v, indicating that $Agb-SO_{z}^{-}aPSNS$ were much better promoters compared with $Agb-SO_{z}^{-}aPSMM$. Moreover, Ag&-SO3-@PSNS exhibited excellent recycling performance for 10 cycles of methane hydrate formation-dissociation. To sum up, the $Ag\theta$ - SO_3^- -coated nano-promoters developed in this work showed significant potential in achieving the industrial application of hydrate-based natural gas storage and transportation.

Natural gas hydrates are ice-like and non-stoichiometric compounds formed by water and gas molecules under suitable pressure and temperature.² Natural gas hydrates can achieve a theoretical storage capacity of 172 volumes of gas per volume of hydrates (v/v) and can be stored under relatively mild conditions; therefore, natural gas hydrates are of great potential in natural gas storage and transportation and have aroused great attention since the 1990s.^{3,4} However, gas hydrate formation usually goes through a long induction period and then a slow growth period, which seriously affect the application in natural gas storage and transportation.⁵ Therefore, it's highly necessary to achieve rapid hydrate formation together with high gas storage capacity for the utilization of natural gas hydrates.

Over the past two decades, different kinds of materials have been used to promote gas hydrate formation, among which surfactants have attracted the most attention.⁵⁻¹⁴ For example, Zhong and Rogers⁵ reported that SDS above 242 ppm could improve ethane hydrate formation rate more than 700 times. Ganji *et al.*¹² found that with 300–1000 ppm SDS as the promoter methane hydrate formation under initial conditions

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[†] Electronic supplementary information (ESI) available: The schematic diagram of the hydrate formation apparatus, hydrate formation rate with 0.5 mmol L⁻¹ Ag&-SO₃ @PSNS-25% and deionized water under unstirred conditions, hydrate formation rate with 0.5 mmol L⁻¹ Ag&-SO₃ @PSNS-25% and 1 mmol L⁻¹ SDS, pyrene fluorescence spectrum, XRD spectrum, and methane dissociation morphology of hydrates formed with 0.5 mmol L⁻¹ SDS and 0.5 mmol L⁻¹ Ag&-SO₃ @PSNS-25%, TEM photos of Ag&-SO₃ @PSNS-25% after hydrate formation–dissociation. See DOI: 10.1039/c7ta02830j

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of 8.3 MPa and 276.2 K could be achieved within 2-3 h and the final methane consumption could reach 0.12-0.14 mol gas per mol^{-1} water (119–138 v/v). To date, dozens of surfactants have been applied to promote gas hydrate formation and SDS produced the best results, which has been viewed as the most potential promoter that could industrially achieve hydratebased natural gas storage and transportation.¹⁴ However, the use of surfactants also led to the generation of lot of foam during hydrate dissociation, which not only impacted the application of gas hydrates, but also caused the loss of surfactants.¹⁵⁻¹⁷ Therefore, in our previous work,¹⁸ we fixed -SO₃⁻¹ groups on the surface of polystyrene nanospheres to prepare -SO₃⁻-coated nanopromoters, which at the concentration of 1 mmol L^{-1} could achieve methane hydrate formation within 2 h with the storage capacity reaching 126-142 v/v and without foam generation, however the storage capacity was still far from the theoretical value (172 v/v).

In recent years, nano-metal particles have been employed to accelerate gas hydrate formation, such as nano-Cu, nano-Ag *etc.*, which promoted the reaction efficiently by enhancing the heat and mass transfer.^{19,20} Moreover, mixtures of nano-metals and surfactants have also been adopted to promote gas hydrate formation.^{21–25} For instance, Kakati *et al.*²⁵ used a mixture of SDS and nano-Al₂O₃ to promote methane hydrate formation under the conditions of 6.55 MPa, 282.5 K and magnetic stirring, as a result, the induction and growth period could be shortened to 25 and 55 min, respectively, and the storage capacity could reach 109 v/v. However, the nano-metal particles were usually mechanically dispersed in the liquid phase and therefore had poor stability, which seriously limited the application in gas hydrate formation, and exhibited inferior recycling performance.

In this work, we first fixed $-SO_3^-$ groups covalently on polystyrene through soap-free emulsion polymerization to synthesize $-SO_3^-$ -coated nanopolymers. Afterwards, we grafted nano-Ag particles of 2–5 nm size on the nanopolymers through electrostatic adsorption and *in situ* reduction to prepare Ag&-SO_3^--coated nanopolymers. Therefore, the $-SO_3^-$ groups and nano-Ag particles could exist in the liquid phase stably together with the nanopolymers; moreover, the array on the nanopolymers could enable the $-SO_3^-$ groups and nano-Ag particles to come into contact with the liquid phase more efficiently. Thereafter, the Ag&-SO_3^--coated nanopolymers were applied to promote methane hydrate formation.

Experimental

Materials

Sodium *p*-styrene sulfonate (SS, A.R.) was purchased from Aladdin. Potassium persulfate (KPS, A.R.) was purchased from Shanghai Aibi Chemical Reagent Co., Ltd (Shanghai, China). Acrylic acid (AA, A.R.) was provided by Tianjin Dengke Chemical Reagent Co., Ltd (Tianjin, China). Silver nitrate (A.R.), styrene (St, A.R.) and sodium hydroxide (NaOH, A.R.) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Hydrazine hydrate (A.R.) was supplied by Tianjin Basifu Chemical Reagent Co., Ltd (Tianjin, China). Methane with purity of 99.99% was purchased from Heli Gas Co., Ltd (Qing-dao, China). The deionized water (DI water) used was laboratory-made and the conductivity was $1.17\pm0.1~\mu s~cm^{-1}$ at 298.15 K.

Method design

The grafting of nano-Ag particles on the $-SO_3^-$ -coated nanopolymers was achieved through electrostatic adsorption and *in situ* reduction. To achieve the successful adsorption of Ag⁺ on the $-SO_3^-$ -coated nanopolymers, both $-COO^-$ and $-SO_3^-$ were fixed on the polymers through emulsion co-polymerization of St, SS and AA. The morphology of the nanopolymers was controlled such that the nanopolymers existed as amorphous macromolecules ($-SO_3^-$ @PSMM) or uniform nanospheres ($-SO_3^-$ @PSNS) by varying the percentage of St. Afterwards, Ag⁺ was adsorbed on the surface of the nanopolymers through the electrostatic force between Ag⁺ and $-COO^-$ and then the nano-Ag particles were grafted on the nanopolymers by *in situ* reduction with hydrazine hydrate.

Preparation of -SO₃⁻@PSMM and -SO₃⁻@PSNS

 $-SO_3^-$ @PSMM was prepared through soap-free emulsion copolymerization with St as the hydrophobic monomer, SS and AA as the hydrophilic monomers, and KPS as the initiator, in a 250 mL flask equipped with a stirrer, a nitrogen inlet tube, and a reflux condenser.²⁶ Firstly, 90 g deionized water was added into the flask and stirring was started (300 rpm); secondly, 0.741 g SS, 0.259 g AA and 1 g St were added successively and heating was initiated. After the reaction temperature (343.15 K) was reached, the KPS solution (0.05 g in 5 g deionized water) was added dropwise into the flask through a constant pressure drop funnel (one drop every 3 s); afterwards, the reaction system was kept at 300 rpm and 343.15 K for 5 h until the end of the reaction.

 $-SO_3^-$ @PSNS was prepared through seeded soap-free emulsion copolymerization in the same reaction system and under the same conditions. Firstly, 85 g deionized water, 0.741 g SS, 0.259 g AA and 2 g St were added into the flask successively; afterwards, the initiator solution (0.05 g KPS in 5 g deionized water) was added dropwise into the flask through a constant pressure drop funnel (one drop every 3 s) and the reaction began, which was called as the seeded preparation period. An hour later, 3 g St was added dropwise into the flask through a constant pressure drop funnel (one drop every 5 s). After the addition of St was completed, the initiator solution (0.05 g KPS in 5 g deionized water) was added dropwise and the reaction system was kept at 300 rpm and 343.15 K for 5 h until the end of the reaction. The recipe and conditions of the polymerization are shown in Table 1.

Preparation of Ag&-SO₃⁻@PSMM and Ag&-SO₃⁻@PSNS

The Ag&-SO₃⁻-coated nanopolymers were prepared through electrostatic adsorption and *in situ* reduction. A certain amount of $-SO_3^-$ @PSMM or $-SO_3^-$ @PSNS emulsion was diluted with deionized water; then AgNO₃ solution of a certain concentration was added dropwise into the diluted emulsion under stirring at

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Table 1 Recipe and conditions of the anionic emulsion copolymerization of SS, AA and St

rmerization of SS, AA and St ^a		

Sample	St/g	AA/g	SS/g	KPS/g	DI water ^b /g	T^{c}/K	S ^d /rpm
-SO ₃ ⁻ @PSMM	$\frac{1}{2+3^{e}}$	0.259	0.741	0.05	95	343.15	300
-SO ₃ ⁻ @PSNS		0.259	0.741	0.05 + 0.05	95	343.15	300

^{*a*} The molar ratio between AA and SS was 1 : 1. ^{*b*} "DI water"-deionized water. ^{*c*} "*T*"-temperature. ^{*d*} "*S*"-stirring rate. ^{*e*} "2 + 3"-the St amount during the seed preparation period and normal polymerization period was 2 and 3 g respectively.

1000 rpm and the ratio of Ag⁺ and $-\text{COO}^-$ (n_{Ag^+} : $n_{-\text{COO}^-}$) was controlled at 25% or 50% or 75% to avoid overdose of Ag⁺. Afterwards, the system was stirred at 1000 rpm for 2 h to ensure that the vast majority of the Ag⁺ was adsorbed on the nanopolymers through the electrostatic interaction with $-\text{COO}^-$. Subsequently, superfluous hydrazine hydrate was dropped slowly into the emulsion under stirring to achieve the *in situ* reduction of Ag⁺ and the grafting of Ag to the nanopolymers, which finally resulted in the formation of the Ag&-SO₃⁻-coated nanopolymers, Ag&-SO₃⁻@PSMM and Ag&-SO₃⁻@PSNS.

Characterization

The average particle size and size distribution of the different nanopolymers were measured *via* a Malvern Nano-s90 Laser Particle Size Analyzer made by Malvern, UK.

The morphology of the nanopolymers was investigated using a JEM-1200EX Transmission Electron Microscope (TEM) made by Japan Electronics Co., Ltd.

The XRD spectrum of the nanopolymers was obtained using a D8 Advance X-ray diffractometer made by Bruker, Germany. The original nanopolymer emulsion was frozen and thawed repeatedly until obvious precipitation could be observed. Afterwards, the emulsion was centrifuged at 10 000 rpm for 10 min and the precipitate was collected and dried at 328.15 K for 24 h to obtain the nanopolymers as a solid, which was then used for the X-ray diffraction analysis.

The steady-state fluorescence spectrum of the emulsion was recorded using a Hitachi-4600 Fluorescence Spectrophotometer, with pyrene as the probe, and Ar light at the wavelength of 337 nm as the excitation light source; the concentration of pyrene in the emulsion was 10^{-6} mol L⁻¹.

Methane hydrate formation

Fig. S1 (ESI[†]) shows the schematic diagram of the methane hydrate formation apparatus used in this work. The main part was a reactor made of 316L stainless steel, with a volume of 80 mL and maximum pressure capability of 20 MPa. 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 stirring at 0–1000 rpm was installed under the reactor and a rotor with the size of 4 mm \times 10 mm (diameter \times length) was used for stirring.

First, the reactor was cleaned with deionized water three times, then 10 mL reaction solution was charged into the reactor and the cooling system and stirring were turned on. When the desired temperature was reached, the reactor was purified with methane three times and then pressurized with methane to the experimental pressure. The evolution of temperature and pressure during the methane hydrate formation were recorded using a computer.

The methane consumption at time *t* during the hydrate formation process is defined as n_t and calculated using eqn (1) and (2), which were derived in our previous study:²⁷

$$n_{t} = \frac{\frac{P_{0}V_{0}}{z_{0}RT_{0}} - \frac{P_{t}V_{0}}{z_{t}RT_{t}}}{1 - \frac{P_{t}\Delta Vm}{z_{t}RT_{t}}}$$
(1)

$$z_{t} = 1 + \left[0.083 - 0.422 \times \left(\frac{T_{c}}{T_{t}}\right)^{1.6} \right] \frac{P_{t}T_{c}}{P_{c}T_{t}} + \omega \left[0.139 - 0.172 \times \left(\frac{T_{c}}{T_{t}}\right)^{4.2} \right] \frac{P_{t}T_{c}}{P_{c}T_{t}}$$
(2)

where *P* is the pressure in the reactor; *V* is the volume of the gas phase in the reactor; *T* is the temperature in the reactor; *R* is the universal gas constant; *m* is the hydration number;²⁸ ΔV is the molar volume difference between methane hydrates and water;²⁹ *z* is the compressibility factor; for methane, *T*_c, *P*_c and ω are 190.6 K, 4.599 MPa and 0.012, respectively;³⁰ the subscripts 0 and *t* are the time.

Then the hydrate storage capacity (c_s) at time t can be calculated by:

$$c_{\rm s} = n_t \times \frac{V_{\rm mg} \times V_{\rm mw}}{V_{\rm w} \times (V_{\rm mw} + \Delta V)} \tag{3}$$

where $V_{\rm mg}$ and $V_{\rm mw}$ are the molar volumes of gas and water respectively, and $V_{\rm w}$ is the volume of the initial reaction solution.

Results and discussion

Characterization of Ag&-SO3 @PSMM and Ag&-SO3 @PSNS

Fig. 1 shows the morphology, hydrodynamic particle size and size distribution of Ag&-SO₃⁻@PSMM with different ratios of Ag⁺ and -COO⁻. Without nano-Ag grafting, Ag&-SO₃⁻@PSMM-0% (-SO₃⁻@PSMM) existed as amorphous particles with the average hydrodynamic size of 44.68 nm. The amorphous form of $-SO_3^-$ @PSMM could be evidenced by the I_3/I_1 value of the pyrene fluorescence spectrum, which was 0.8 (Fig. S2, ESI[†]), slightly higher than that of deionized water and therefore confirming that $-SO_3^-$ @PSMM existed as amorphous macromolecules.¹⁸ For Ag&-SO₃⁻@PSMM-25%-50%-75%, it was obvious



Fig. 1 TEM photo, hydrodynamic particle size and size distribution of Ag&-SO₃⁻@PSMM with different ratios of Ag⁺ and -COO⁻.

that nano-particles with the size of 2-5 nm were grafted on the polymers. Fig. S3 (ESI[†]) shows the XRD spectrum of the precipitate of Ag&-SO₃ (a)PSMM-25% and the four peaks at 2θ angles of 38.1° , 44.2° , 64.5° and 77.3° correspond to the reflections of (111), (200), (220) and (311) crystalline planes of the face-centered cubic structure of Ag (JCPDS no. 04-0783), confirming that the nano-particles were Ag.³¹ However, as shown in Fig. 1E the particle sizes of Ag&-SO3⁻@PSMM-25%-50%-75% were 27.98, 39.39 and 42.11 nm respectively, indicating that the grafting of nano-Ag caused the reduction of the hydrodynamic particle size of -SO3⁻@PSMM. This was because the arrangement of nano-Ag would reduce the hydrophilicity of -SO₃⁻@PSMM, as a result, the macromolecules of -SO₃⁻@PSMM would aggregate to remain stable. Moreover, Fig. 1E also shows that the increase in Ag⁺ resulted in the increase of the particle size of Ag&-SO₃⁻@PSMM. On one hand, more nano-Ag grafting on the polymer particles would increase the particle size; on the other hand, the increase of nano-Ag would cause the aggregation of the polymer particles.

Fig. 2 shows the morphology, hydrodynamic particle size and size distribution of Ag&-SO₃ @PSNS with different ratios of Ag⁺ and -COO⁻. Without nano-Ag grafting, Ag&-SO₃⁻@PSNS-0% (-SO₃ @PSNS) existed as uniform nanospheres with the average hydrodynamic size of 108.76 nm. As shown in Fig. S2 (ESI[†]), the I_3/I_1 value of 0.5 mmol L⁻¹ –SO₃⁻@PSNS was 1.19, indicating the existence of nonpolar microdomains in the -SO₃⁻@PSNS emulsion, consistent with the form of existence of -SO3⁻@PSNS in solution.¹⁸ For Ag&-SO3⁻@PSNS-25%-50%-75%, nano-Ag particles with the size of 2-5 nm were successfully arranged on the surface of -SO3⁻@PSNS and a higher ratio of Ag⁺ and -COO⁻ resulted in more nano-Ag particles on the surface of -SO₃ @PSNS and higher hydrodynamic particle size. Different from -SO₃ @PSMM, the grafting of nano-Ag did not cause reduction of the hydrodynamic particle size of -SO3-@PSNS, which was because -SO3-@PSNS existed as

uniform nanospheres and the grafting of nano-Ag particles did not change the morphology of $-SO_3^-$ @PSNS in solution.

Above all, we confirmed the successful grafting of nano-Ag particles on the nanopolymers of $-SO_3^-$ @PSMM and $-SO_3^-$ @PSNS. For Ag&-SO_3^-@PSMM, both nano-Ag particles and $-SO_3^-$ groups existed irregularly together with the macromolecules of $-SO_3^-$ @PSMM; for Ag&-SO_3^-@PSNS, nano-Ag particles and $-SO_3^-$ groups were arranged uniformly on the surface of the nanospheres of $-SO_3^-$ @PSNS, as shown in Fig. 3A.

Methane hydrate formation with Ag&-SO₃⁻@PSMM

Fig. 4 shows the evolution of methane storage capacity during methane hydrate formation with Ag&-SO₃ @PSMM-25%. In our previous study,18 when the amorphous -SO3--coated nanopolymer ($-SO_3^{-}$ @PSNS-1) was used at 1 mmol L⁻¹, the methane storage capacity reached about 70 v/v at 1000 min. However, in this work, when nano-Ag particles were grafted on the -SO₃⁻-coated nanopolymer (Ag&-SO₃⁻@PSMM-25%), much better methane hydrate formation was achieved at a lower dosage. As shown in Fig. 4, even at 0.25 mmol L^{-1} Ag&-SO₃ @PSMM-25% methane hydrate formation could be achieved within 400-800 min with the methane storage capacity reaching 140-150 v/v, and two steps appeared when Ag&-SO3-@PSMM-25% of 0.25 mmol L^{-1} was used, which might be due to that the rotor in the reactor was stuck by the formed hydrates. What's more, when Ag&-SO₃⁻@PSMM-25% was used at 0.5 mmol L^{-1} , all the three methane hydrate formation processes were complete within 200 min and the methane storage capacity could reach almost 150 v/v, indicating that the array of nano-Ag on the amorphous nanopolymer significantly improved methane hydrate formation. This was because the nano-Ag particles arranged on the polymers could conduct the heat released from hydrate nucleation rapidly and therefore serve as more efficient hydrate nucleation sites compared with the $-SO_3^-$ groups. As a result, hydrates might nucleate initially with the nano-Ag as



Fig. 2 TEM photo, hydrodynamic particle size and size distribution of $Ag\theta - SO_3^-$ @PSNS with different ratios of Ag^+ and $-COO^-$.



Fig. 3 (A) Schematic diagram of the structures of $Agb-SO_3^-$ @PSMM and $Agb-SO_3^-$ @PSNS; (B) schematic diagram of hydrate nucleation with $Agb-SO_3^-$ @PSMM and $Agb-SO_3^-$ @PSNS as the promoters.

nucleation sites through the reaction between the methane molecules dissolved in the spaces of the macromolecules²⁷ and the water molecules associated by the $-SO_3^-$ groups,⁵ as shown in Fig. 4B, which led to more efficient promotion of the reaction compared with the $-SO_3^-$ -coated promoters reported in our previous study.¹⁸

Fig. 5 shows the evolution of methane storage capacity during the methane hydrate growth period with 0.5 mmol L⁻¹ Ag&-SO₃⁻@PSMM and different Ag amounts (25%, 50%, 75%); the induction time, growth period, growth rate and storage capacity are shown in Table S1 (ESI†). The induction times of Ag&-SO₃⁻@PSMM-25%-50%-75% were 60.8 ± 14.2 , 52.7 ± 5.9 and 32.2 ± 7.9 min respectively, indicating that a higher amount of Ag in Ag&-SO₃⁻@PSMM led to an obviously shorter induction period. This was because more nano-Ag grafting on



Fig. 4 Evolution of methane storage capacity during methane hydrate formation with $Ag\theta-SO_3^-$ @PSMM-25% (the initial pressure was 6 MPa, the temperature was 275.15 K, the stirring rate was 300 rpm, the concentration was calculated as the concentration of $-SO_3^-$ in the solution; the ratio of Ag^+ and $-COO^-$ was 25%).

the polymer particles indicated better thermal conductivity, which could better promote hydrate nucleation and therefore result in a shorter induction period. However, increase in the Ag amount of Ag&–SO₃[–]@PSMM also resulted in a slower hydrate growth rate and longer growth period (especially when the ratio of Ag⁺ and –COO[–] was 75%), which were 0.075 ± 0.006 , 0.072 ± 0.015 , 0.048 ± 0.013 mmol gas mL per water per min and 108.8 ± 8.2 , 115.7 ± 19.7 , 177.1 ± 38.9 min for Ag&–SO₃[–]@PSMM-25%-50%-75%. The possible reason was that a large amount of Ag would cause the agglomeration and even precipitation of the polymer particles and this would reduce the number of effective polymer particles in the liquid phase and therefore lead to a slow hydrate growth rate. Moreover, it should also be noted that the polymer particles with different nano-Ag amounts resulted in similar methane storage capacities, which were

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Fig. 5 Evolution of methane storage capacity during methane hydrate growth with $Ag\vartheta-SO_3^-$ @PSMM of different Ag amounts (the initial pressure was 6 MPa, the temperature was 275.15 K, the stirring speed was 300 rpm, the concentration was calculated as the concentration of $-SO_3^-$ in the solution).

145.2 \pm 1.2, 143.9 \pm 3.7, 144.1 \pm 4.2 v/v for Ag&–SO $_3^-$ @PSMM-25%-50%-75%.

Methane hydrate formation with Ag&-SO₃⁻@PSNS

Fig. 6 shows the evolution of methane storage capacity during the methane hydrate growth period with 0.5 mmol L⁻¹ Ag&-SO₃⁻@PSNS and different Ag amounts (25%, 50%, 75%); the values of induction time, growth period, growth rate and storage capacity are shown in Table S2 (ESI†). For Ag&-SO₃⁻@PSNS-25%-50%-75%, the induction time was 19.4 ± 19.0, 38.5 ± 8.0, and 17.8 ± 2.8 min respectively; the hydrate growth rate was 0.21 ± 0.02, 0.20 ± 0.01 and 0.21 ± 0.02 mmol gas mL per water per min respectively; the hydrate growth period was 39.6 ± 2.8, 42.1 ± 0.9 and 41.1 ± 1.8 min respectively; the methane storage capacity was 149.3 ± 1.2, 151.3 ± 3.0 and 150.0 ± 4.9 respectively. On one hand, Ag&-SO₃⁻@PSNS promoted the reaction better (shorter



Fig. 6 Evolution of methane storage capacity during methane hydrate growth with $Ag\theta$ - SO_3^- (aPSNS of different Ag amounts (the concentration was calculated as the concentration of $-SO_3^-$ in the solution; the initial pressure was 6 MPa, the temperature was 275.15 K, the stirring rate was 300 rpm).

induction period, more rapid hydrate growth, shorter growth period and higher methane storage capacity) than Ag&–SO₃⁻@PSMM, which was because the nano-Ag particles and $-SO_3^-$ groups fixed on the surface of nanospheres could exist more stably and come into contact with the water and methane molecules more efficiently compared with those fixed on amorphous macromolecules. On the other hand, the Ag&–SO₃⁻-coated nanospheres in this work promoted the reaction in a much better way at lower dosage compared with the $-SO_3^-$ -coated nanospheres without the nano-Ag array in our previous study,¹⁸ which at 1 mmol L⁻¹ resulted in methane hydrate formation within 1–2 h with storage capacity reaching 126–142 v/v, confirming that the grafting of nano-Ag particles on the nanopromoters could obviously improve the methane hydrate formation.

Moreover, as shown in Fig. S4 (ESI[†]), even without stirring 0.5 mmol L^{-1} Ag&-SO₃⁻@PSNS-25% resulted in methane hydrate formation within 1 h with the storage capacity reaching 142.7 \pm 7.5 v/v, much more efficiently than -SO₃⁻@PSNS under static conditions in our previous study,¹⁸ which at 1 mmol L^{-1} resulted in methane hydrate formation within 3–4 h with the methane storage capacity reaching 117 v/v, once again confirming the significant improvement of the promotion efficiency caused by the grafting of nano-Ag particles on the -SO₃⁻ coated nanopromoters.

Fig. S5[†] shows the comparison between the methane hydrate formation rate with Ag&-SO3 @PSNS-25% and with SDS, which has been demonstrated to be the most efficient surfactant for promotion of gas hydrate formation. It's obvious that Ag&-SO3⁻@PSNS-25% promoted methane hydrate formation more efficiently than SDS, with respect to hydrate formation rate as well as storage capacity. Moreover, Ag&-SO₃-@PSNS-25% also promoted the reaction more efficiently than the mixtures of SDS and nano-metal particles, which have been employed by many researchers to enhance gas hydrate formation. For instance, as reported in ref. 25, a mixture of SDS and nano-Al₂O₃ under conditions of 6.55 MPa, 282.5 K and magnetic stirring resulted in the induction time, growth period and methane hydrate storage capacity of 25 min, 55 min and 109 v/v, respectively. Even the induction time and hydrate growth period were similar to the results obtained for Ag&-SO3⁻@PSNS-25% in this work, but the hydrate storage capacity was much lower. Moreover, the dosages of -SO₃⁻ and nano-Ag used in Ag&-SO₃⁻@PSNS-25% in this work were merely 0.5 mmol L^{-1} and 0.22 g L^{-1} , much lower than the dosages of SDS and nano-Al2O3 used in ref. 25, which were 1.04 mmol L^{-1} and 1 g L^{-1} . According to ref. 32, when a mixture of SDS (1.2 mmol L^{-1}) and nano-CuO (0.5 g L^{-1}) was used under the conditions of 5 MPa, 276.45 K and 500 rpm, the induction time and growth period were 19 and 38 min, indicating very efficient promotion of gas hydrate formation, however the hydrate storage capacity was only 59.5 v/v, much lower than that achieved when Ag&-SO3⁻@PSNS-25% was used in this work.

Recycling of Ag&–SO₃⁻@PSNS in methane hydrate formation– dissociation

In hydrate-based natural gas storage and transportation, the natural gas is initially encapsulated into hydrates for storage or



Fig. 7 The induction time and hydrate growth rate of 10 cycles of methane hydrate formation with 0.5 mmol L⁻¹ Ag θ -SO₃⁻@PSNS-25% (the initial pressure was 6 MPa, the temperature was 275.15 K, the stirring rate was 300 rpm, the column diagram indicates the induction time).

transportation and then released through hydrate dissociation as required, therefore the desired promoter should not only facilitate sufficient promotion of the reaction but also exhibit excellent recycling performance. Even though SDS has been demonstrated to be the most efficient promoter for gas hydrate formation, lot of foam would be generated during hydrate dissociation, as shown by the dissociation process of methane hydrates formed with 0.5 mmol L^{-1} SDS (Video S1, ESI[†]). This not only affects the gas release process but also causes serious surfactant loss and therefore indicates that SDS cannot exhibit good recycling performance. However, when 0.5 mmol L⁻¹ Ag&-SO₃ @PSNS-25% was used, as shown in Video S2 (ESI⁺), no foam was generated during hydrate dissociation. Afterwards, we carried out 10 cycles of methane hydrate formation with 0.5 mmol L⁻¹ Ag&-SO₃ @PSNS-25% to study the recycling performance of Ag&-SO₃⁻@PSNS and the results are shown in Fig. 7. After each cycle of hydrate formation, the reactor was depressurized to atmospheric pressure and then kept at 298.15 K for 3-4 h to make the hydrates completely dissociated; afterwards, the reactor was cooled to 275.15 K and then pressurized with methane to 6 MPa to start a new cycle of hydrate formation. As shown in Fig. 7, the induction time presented a certain degree of discreteness, varying from 5.5 to 91.9 min (38.9 \pm 29.2), which might be due to that some nano-Ag particles falled off from the surface of the promoters (Fig. S6[†]) and some promoter particles aggregated after several hydrate formation-dissociation cycles. However, given the stochasticity of hydrate nucleation, the discreteness of induction time was acceptable; moreover, all the hydrate growth periods during the 10 cycles of hydrate formation were complete within 1 h with the methane storage capacity reaching 140 v/v. Therefore we concluded that Ag&-SO3 @PSNS exhibited excellent recycling performance in promoting methane hydrate formation.

Conclusion

Nano-Ag particles with the size of 2-5 nm were successfully grafted on $-SO_3^-$ -coated nanopolymers through electrostatic

adsorption and in situ reduction, which were applied for the first time to promote methane hydrate formation. When the amorphous Ag&-SO₃⁻@PSMM was used, the induction period, growth period and growth rate were 32.2 ± 7.9 – 60.8 ± 14.2 min, 108.8 \pm 8.2–177.1 \pm 38.9 min, and 0.048 \pm 0.013–0.075 \pm 0.006 mmol gas mL per water per min, respectively, and the methane storage capacity reached 143.9 \pm 3.7–145.2 \pm 1.2 v/v. When the uniformly spherical Ag&-SO₃ @PSNS was used, the induction period, growth period, growth rate and storage capacity were 17.8 \pm 2.8–38.5 \pm 8.0 min, 39.6 \pm 2.8–42.1 \pm $0.9 \text{ min}, 0.2 \pm 0.01 - 0.21 \pm 0.02 \text{ mmol gas mL per water per min},$ and 149.3 \pm 1.2-151.3 \pm 3.0 v/v, respectively. Moreover, Ag&-SO₃ @PSNS displayed much better promotion of the reaction compared to SDS and the mixtures of SDS and nanometal particles. Ag&-SO₃ @PSNS also exhibited excellent recycling performance in promoting methane hydrate formation. To sum up, the Ag&-SO₃⁻-coated nano-promoters developed in this work showed significant potential in achieving the industrial application of hydrate-based natural gas storage and transportation.

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