Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.


# Graft of Nano-Ag Particles on -$SO_3^-$-coated Nanopolymers for Promoting Methane Hydrate Formation

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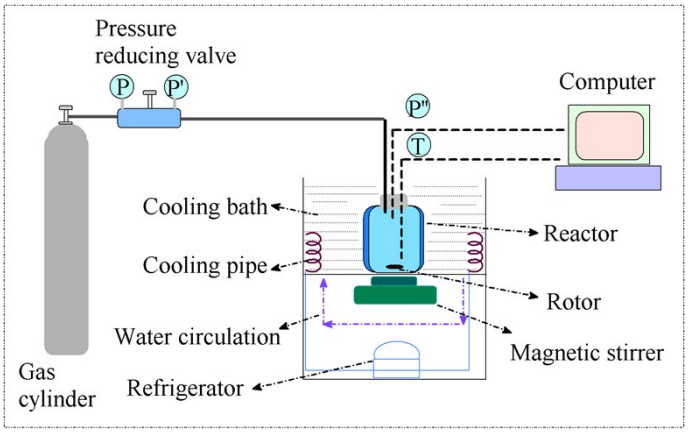


**Fig. S1** Schematic diagram of the methane hydrate formation apparatus

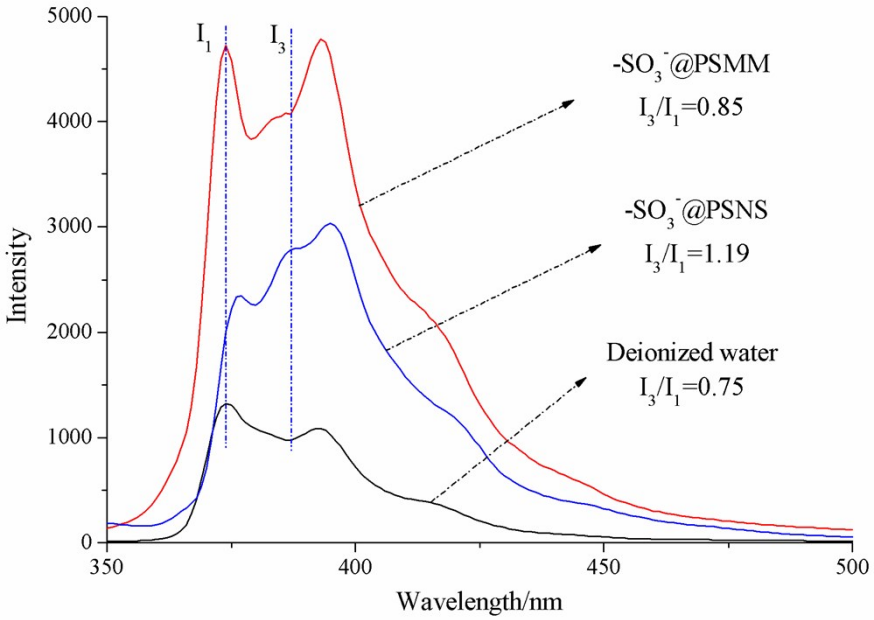


**Fig. S2** Pyrene fluorescence spectra of deionized water, -$SO_3^-$@PSMM emulsion of 0.5 mmol/L and -$SO_3^-$@PSNS emulsion of 0.5 mmol/L

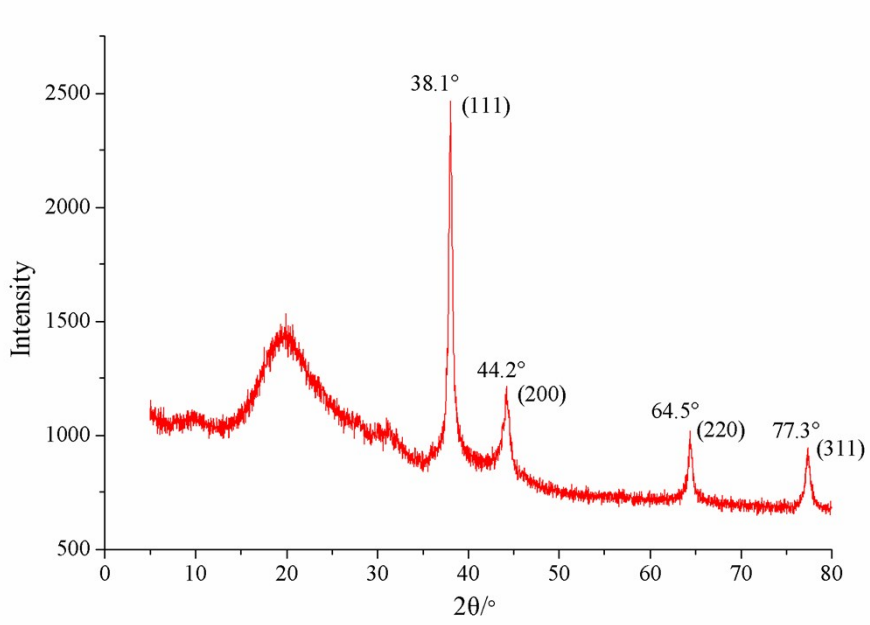


**Fig. S3** XRD spectrum of the precipitate of Ag&-$SO_3^-$@PSMM-25%

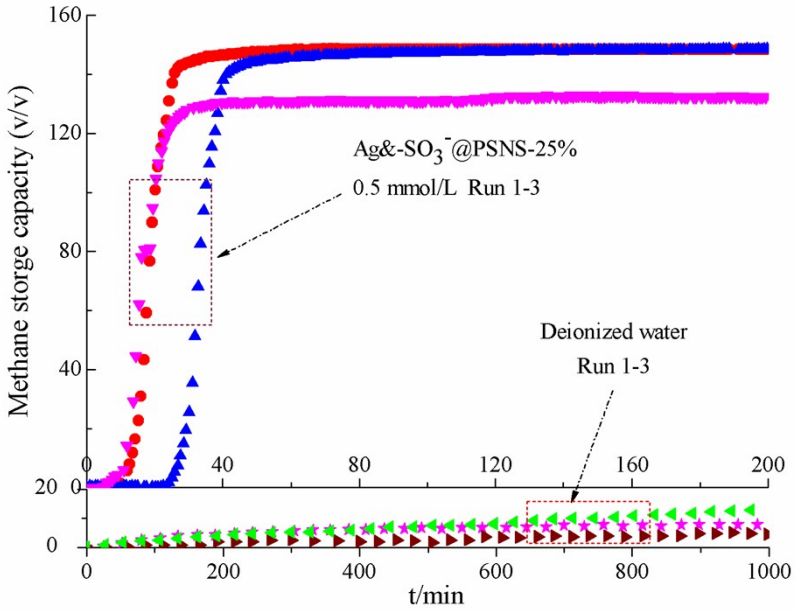


**Fig. S4** Evolution of methane storage capacity during methane hydrate formation with Ag&-$SO_3^-$@PSNS-25% of 0.5 mmol/L and deionized water at unstirred condition (the initial pressure was 6 MPa, the temperature was 275.15 K)

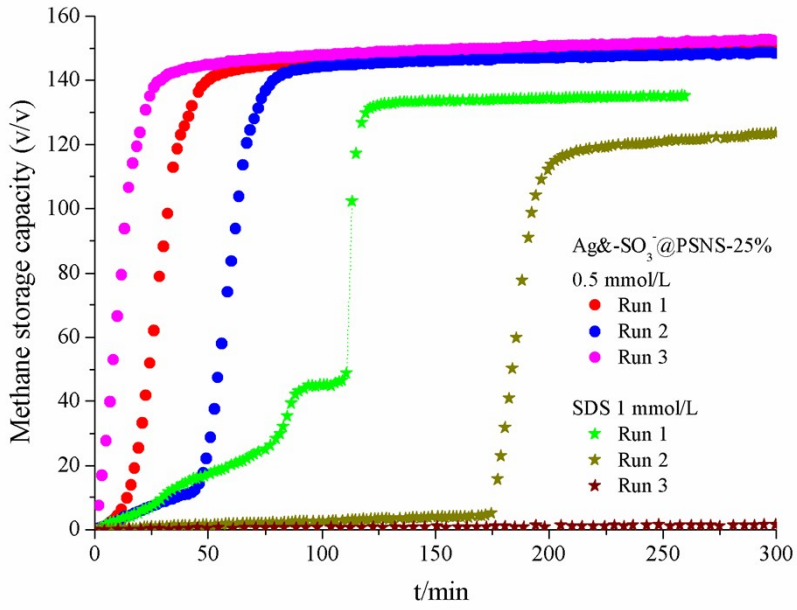


**Fig. S5** Evolutions of methane storage capacity during methane hydrate formation with Ag&-$SO_3^-$@PSNS-25% of 0.5 mmol/L and SDS of 1 mmol/L (the initial pressure was 6 MPa, the temperature was 275.15 K, the stirring was 300 rpm)

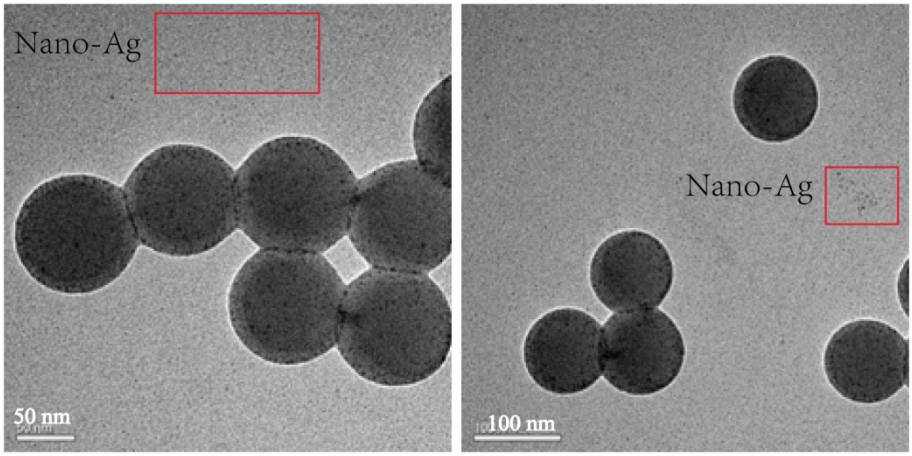


**Fig. S6** TEM photos of Ag&-$SO_3^-$@PSNS-25% after hydrate formation-dissociation

**Table S1** Induction time, growth period, growth rate and methane storage capacity of methane hydrate formation with Ag&-$SO_3^-$@PSMM of different Ag amounts (the initial pressure was 6 MPa, the temperature was 275.15 K, the stirring was 300 rpm)

| Sample | Run 1 | Run 2 | Run 3 | av [a] | sd [b] |
|---|---|---|---|---|---|
| | Induction time (min) [c] | | | | |
| Ag&-$SO_3^-$@PSMM-25% | 59.9 | 43.9 | 78.7 | 60.8 | 14.2 |
| Ag&-$SO_3^-$@PSMM-50% | 44.9 | 54.0 | 59.3 | 52.7 | 5.9 |
| Ag&-$SO_3^-$@PSMM-75% | 43.3 | 25.1 | 28.2 | 32.2 | 7.9 |
| | Growth rate (mmol gas·mL water$^{-1}$·min$^{-1}$) | | | | |
| Ag&-$SO_3^-$@PSMM-25% | 0.069 | 0.082 | 0.075 | 0.075 | 0.006 |
| Ag&-$SO_3^-$@PSMM-50% | 0.061 | 0.094 | 0.062 | 0.072 | 0.015 |
| Ag&-$SO_3^-$@PSMM-75% | 0.066 | 0.043 | 0.036 | 0.048 | 0.013 |
| | Growth period (min) [d] | | | | |
| Ag&-$SO_3^-$@PSMM-25% | 118.1 | 98.1 | 110.3 | 108.8 | 8.2 |
| Ag&-$SO_3^-$@PSMM-50% | 133.2 | 88.2 | 125.7 | 115.7 | 19.7 |
| Ag&-$SO_3^-$@PSMM-75% | 127.8 | 180.5 | 223.0 | 177.1 | 38.9 |
| | Storage capacity (v/v) [e] | | | | |
| Ag&-$SO_3^-$@PSMM-25% | 144.6 | 144.1 | 146.8 | 145.2 | 1.2 |
| Ag&-$SO_3^-$@PSMM-50% | 144.7 | 148.0 | 139.0 | 143.9 | 3.7 |
| Ag&-$SO_3^-$@PSMM-75% | 149.9 | 140.0 | 142.4 | 144.1 | 4.2 |

[a] av - average value; [b] sd - standard deviation; [c] induction time was calculated as the time from charging methane into the reactor to obvious pressure decrease was observed; [d] growth period was viewed as the time from the end of induction period to new pressure balance was reached; [e] methane storage capacity was calculated as the storage capacity at 200 min during hydrate growth period.

**Table S2** Induction time, growth period, growth rate and methane storage capacity of methane hydrate formation with Ag&-$SO_3^-$@PSNS of different Ag amounts (the initial pressure was 6 MPa, the temperature was 275.15 K, the stirring was 300 rpm)

| Sample | Run 1 | Run 2 | Run 3 | av | sd |
|---|---|---|---|---|---|
| | Induction time (min) | | | | |
| Ag&-$SO_3^-$@PSNS-25% | 12.6 | 45.3 | 0.4 | 19.4 | 19.0 |
| Ag&-$SO_3^-$@PSNS-50% | 28.5 | 38.8 | 48.2 | 38.5 | 8.0 |
| Ag&-$SO_3^-$@PSNS-75% | 21.2 | 17.7 | 14.4 | 17.8 | 2.8 |
| | Growth rate (mmol gas·mL water$^{-1}$·min$^{-1}$) | | | | |
| Ag&-$SO_3^-$@PSNS-25% | 0.20 | 0.21 | 0.23 | 0.21 | 0.02 |
| Ag&-$SO_3^-$@PSNS-50% | 0.20 | 0.21 | 0.20 | 0.20 | 0.01 |
| Ag&-$SO_3^-$@PSNS-75% | 0.20 | 0.19 | 0.23 | 0.21 | 0.02 |
| | Growth period (min) | | | | |
| Ag&-$SO_3^-$@PSNS-25% | 42.8 | 39.9 | 36 | 39.6 | 2.8 |
| Ag&-$SO_3^-$@PSNS-50% | 43.3 | 41.2 | 41.8 | 42.1 | 0.9 |
| Ag&-$SO_3^-$@PSNS-75% | 41.4 | 43.1 | 38.8 | 41.1 | 1.8 |
| | Storage capacity (v/v) | | | | |
| Ag&-$SO_3^-$@PSNS-25% | 149.4 | 147.9 | 150.8 | 149.3 | 1.2 |
| Ag&-$SO_3^-$@PSNS-50% | 153.3 | 153.5 | 147.1 | 151.3 | 3.0 |
| Ag&-$SO_3^-$@PSNS-75% | 146.5 | 146.7 | 156.9 | 150.0 | 4.9 |