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AOT $BaSO_4$

* *

(, , , 100871)

: γ- $K_2S_2O_8$ $BaCl_2$ (2-) (AOT) , $S_2O_8^{2-}$ SO_4^{2-} , $BaSO_4$, . , ( ) (e_{aq}^-) , $S_2O_8^{2-}$ SO_4^{2-} , $BaSO_4$: , e_{aq}^- , SO_4^{2-} , $BaSO_4$; $Ba(NO_3)_2$, NO_3^- e_{aq}^- $S_2O_8^{2-}$, $BaSO_4$; (e_{oil}^-), e_{aq}^- , $BaSO_4$. : e_{aq}^- $BaSO_4$.

: $BaSO_4$; γ- ; ; ;
: O644

Synthesis of $BaSO_4$ Nanofibers Controlled by the Yield of Hydrated Electrons in AOT-Based Microemulsions

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Abstract: Single-crystal $BaSO_4$ nanofibers and multi-architecture bundles were successfully synthesized in sodium bis(2-ethylhexyl) sulfosuccinate (AOT)-based microemulsions containing $K_2S_2O_8$ and $BaCl_2$, in which the controlled release of SO_4^{2-} ions was realized *in situ* by the radiolytic reduction of $S_2O_8^{2-}$ ions. The molar ratio of water to surfactant (values), the counterions of Ba^{2+}, and the addition of aromatic compounds into the oil phase of the microemulsions were used to adjust the yield of hydrated electrons (e_{aq}^-). This allowed for controlling the reduction of $S_2O_8^{2-}$ ions and the release of SO_4^{2-} ions, leading to the shape manipulation of $BaSO_4$ nanoparticle. With an increase in values or dose rate, the yield of e_{aq}^- increased, which led to a quicker release of SO_4^{2-} ions, and this did not favor the formation of $BaSO_4$ nanofibers. When $BaCl_2$ was replaced with $Ba(NO_3)_2$ the formation of nanofilaments became possible at a higher dose rate and a higher value, because NO_3^- effectively decreased the yield of e_{aq}^- and the rate of $S_2O_8^{2-}$ ion reduction. When toluene was added into the oil phase of the microemulsions, the excess electrons were effectively scavenged in the oil phase, and the concentration of e_{aq}^- in the water pool decreased. This favored the formation of nanofibers at higher dose rates. These results showed that the mechanism about morphology

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1

,
.[1] ,
( )
.[1−5] ,
,
(ω) (
)
.[1,6−12]
,
.[13−15]
,
.[15] ,
(e_{aq}^-)
, ;
.[15] ,
, e_{aq}^- :[16−18]
,
(e_{oil}^-) . , e_{aq}^- .[16−19]
ω , e_{aq}^- .[16−19]
, e_{oil}^- ;
, e_{aq}^-
,
e_{aq}^- .[15,20] e_{aq}^- (
: NO_3^-), e_{aq}^- .[15,20] ,
.[15]
, ,
( ) ω
e_{aq}^- ,
Cu^{2+} ,[20] Cu_2O
,[21] , 8V

2.2 $BaSO_4$

0.1 mol·L^{-1} AOT
0.04 mol·L^{-1} Ba^{2+} ($BaCl_2$ $Ba(NO_3)_2$)
0.04 mol·L^{-1} $K_2S_2O_8$ (
ME($BaCl_2$) ME($Ba(NO_3)_2$)), .
ω 5
8 12 20 . ,
20 min ,
(
), 10 kGy.
.

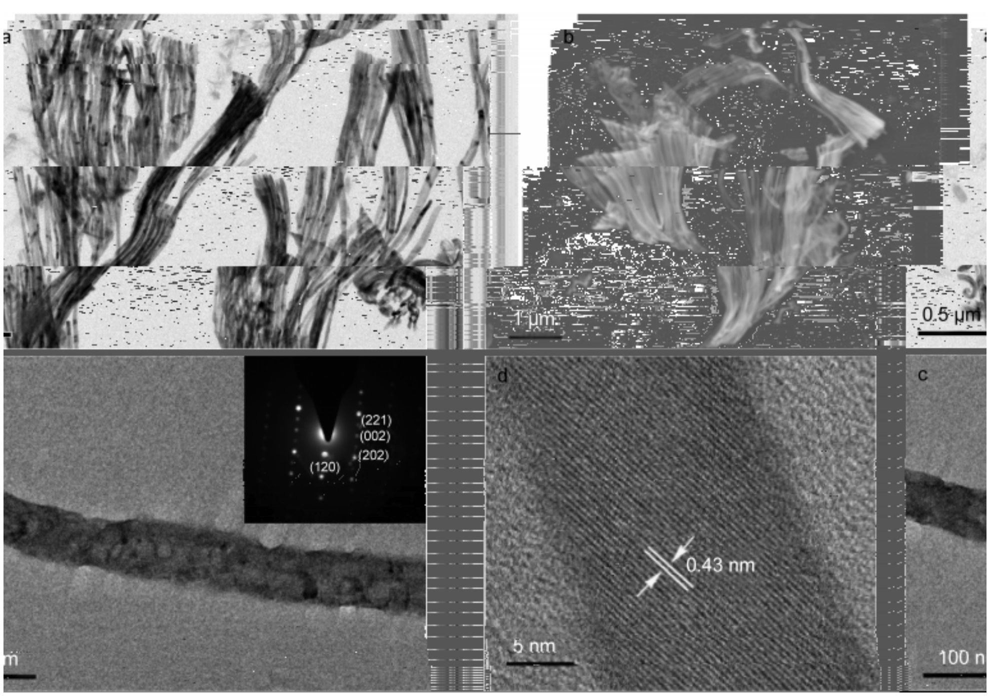
2.3

, 12000 r·
min^{-1} 10 min , ,
,
. ,
, FEI Tecnai G2
T20 (TEM) Nova Nano SEM 430
(SEM) , 200 5
kV, (SAED)
(HRTEM) . Oxford
INCA X-sight (EDS) .
, X ,
D/MAX-PC2500 X (Cu K_α)
(λ=0.154056 nm).

3

3.1 $BaSO_4$

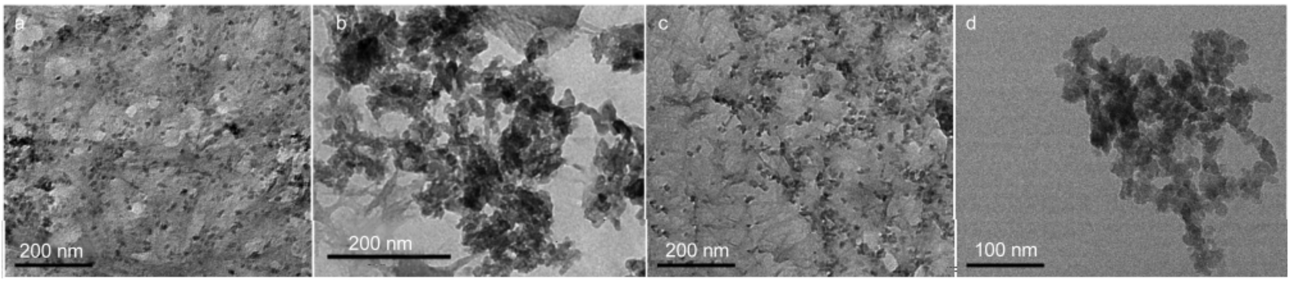
1 10 Gy·min^{-1} , ME($BaCl_2$)
(ω=8) . 1(a, b)
, ,
, ,
, ,
. ,
,
. , ,
5 μm, 20−30 nm .
XRD (2a) $BaSO_4$
(JCPDS card No. 24-1035) ,
$BaSO_4$. 2b EDS ,
Ba S O ,
$BaSO_4$. , Na C



ω

via

: AOT



. ***via***
(a, c) ω=8; (b, d) ω=12. The barium source is $BaCl_2$ and the dose rates are 60 Gy·min^{-1} (a, b) and 120 Gy·min^{-1} (c, d), respectively.

(3). SAED (, 3c) $BaSO_4$ (122) (211) (020) (120) , $BaSO_4$. e_{aq}^- ω ,[16–19] SO_4^{2-} . ω 20 , Ba^{2+} , . , ω , : ω=5 , 9–15 nm , ω=8 20–30 nm ; ω=12 , , 30–50 nm. ω .

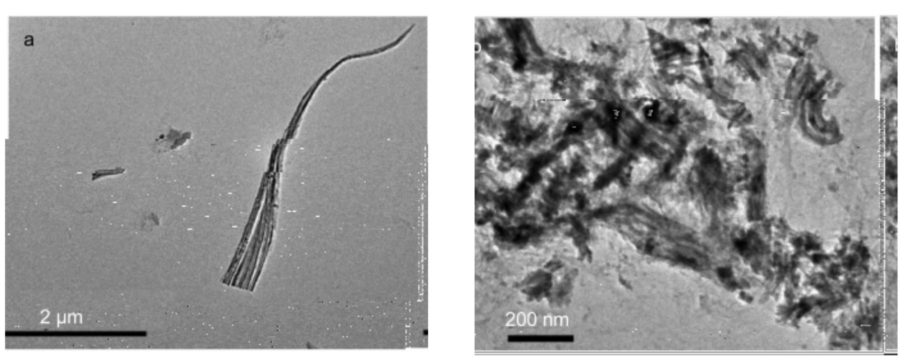
3.2.2

. , 10 Gy·min^{-1} 60 Gy·min^{-1} , ME($BaCl_2$) (ω=8, 12) $BaSO_4$, 10 18 nm (4(a, b)). 120 Gy·min^{-1} , ME($BaCl_2$) (ω=8, 12) $BaSO_4$ (4(c, d)). , e_{aq}^- , SO_4^{2-} , ,[21] .

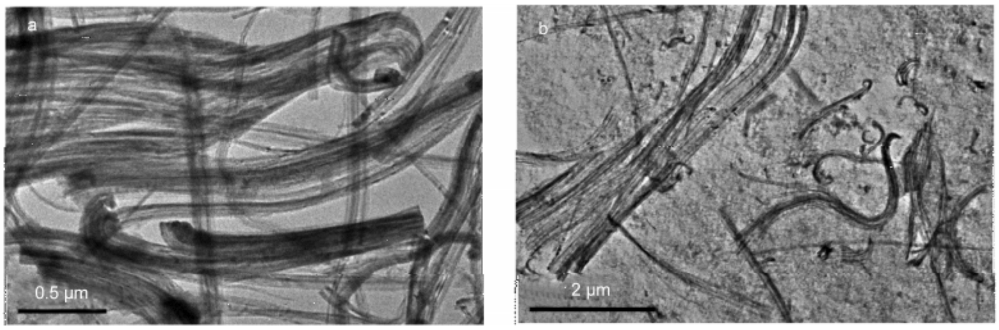
3.2.3

ω $BaSO_4$, $Ba(NO_3)_2$. 60 Gy·min^{-1} , ME($Ba(NO_3)_2$) (ω=8, 12) $BaSO_4$ (5), ME($BaCl_2$) (ω=8, 12) (4(a, b)). ω : ω=8 , $BaSO_4$ 4–5 μm; ω=12 , $BaSO_4$. NO_3^- e_{aq}^- . , e_{aq}^- NO_3^- e_{aq}^- Cl^- (Eqs.(2, 3)),[20,33] NO_3^- e_{aq}^-. ω , NO_3^- e_{aq}^- , $S_2O_8^{2-}$, . , , $Ba(NO_3)_2$ $BaCl_2$, $BaSO_4$, ω .

$$NO_3^- + e_{aq}^- \quad NO_3^{2-} \ (k=9.7\times10^9\ \mathrm{L\cdot mol^{-1}\cdot s^{-1}}) \qquad (2)$$



. ***via*** . ω . .
ME($Ba(NO_3)_2$): 0.1 mol·L^{-1} AOT in isooctane, in water pool, [$Ba(NO_3)_2$]=0.02 mol·L^{-1}, [$K_2S_2O_8$]=0.02 mol·L^{-1}; (a) ω=8; (b) ω=12.
The barium source is $Ba(NO_3)_2$ and the dose rate is 60 Gy·min^{-1}.



ω

. ***via*** ***ω*** .

The barium source is $BaCl_2$ and the dose rates are 60 Gy·min^{-1} (a) and 120 Gy·min^{-1} (b), respectively.

. . . .

Barium source	Dose rate (Gy·min^{-1})	Additive	Morphology			
			ω=5	*ω*=8	*ω*=12	*ω*=20
$BaCl_2$	10	–	nanofilament bundles	nanofilament bundles	nanofilament bundles	quasi-spherical anoparticles
	60	–	–	quasi-spherical anoparticles	quasi-spherical nanoparticles	–
		toluene	–	nanofilament bundles	–	–
	120	–	–	quasi-spherical nanoparticles	quasi-spherical nanoparticles	–
		toluene	–	nanofilament bundles	–	–
$Ba(NO_3)_2$	60	–	–	nanofilament bundles	short nanofibers	–

$Cl^- + e^-_{aq}$ products (k<1.0×10^6 L·mol^{-1}·s^{-1}) (3) .

3.2.4

ω

$BaSO_4$, ME($BaCl_2$) (0.36 mol·L^{-1}). 60 120 Gy·min^{-1} , *ω* 8 $BaSO_4$ (6).

e^-_{aq} (e^-_{oil}) . e^-_{oil} , (Eq.(4))[35] (: e^-_{oil} ,), e^-_{oil} , e^-_{aq} , SO_4^{2-} , Ba^{2+} , .

$$CH_3C_6H_5 + e_{oil} \xrightarrow{\text{cyclohexane}} CH_3C_6H_5^{-\bullet}$$

(k=4.0×10^9 L·mol^{-1}·s^{-1}) (4)

1 . , , *ω* e^-_{aq} $BaSO_4$, e^-_{aq} $BaSO_4$

4

γ- $K_2S_2O_8$ $BaCl_2$ AOT , SO_4^{2-} , SO_4^{2-} $BaSO_4$, . , *ω* $BaSO_4$: *ω* , e^-_{aq} , SO_4^{2-} , $BaSO_4$; NO_3^- e^-_{aq} $S_2O_8^{2-}$, *ω* $Ba(NO_3)_2$ $BaSO_4$; , e^-_{oil} , e^-_{aq} , $BaSO_4$. , e^-_{aq} . , e^-_{aq} $BaSO_4$. , . , ,

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(1) Burda, C.; Chen, X. B.; Narayanan, R.; El-Sayed, M. A. *Chem. Rev.* *105*, 1025. doi: 10.1021/cr030063a

(2) Eastoe, J.; Hollamby, M. J.; Hudson, L. *dv. Colloid Interface Sci.* *128–130*, 5. doi:10.1016/j.cis.2006.11.009

(3) Destrée, C.; B.Nagy, J. *dv. Colloid Interface Sci.* *123–126*, 353. doi:10.1016/j.cis.2006.05.022

(4) Cao, Y. L.; Ding, X. L.; Li, H. C.; Yi, Z. G.; Wang, X. F.; Zhu, J. J.; Kan, C. X. *cta Phys. -Chim. Sin.* *27*, 1273. [, , , , , , . , *27*, 1273.] doi: 10.3866/PKU.WHXB20110604

(5) He, P.; Shen, X. H.; Gao, H. C. *cta Phys. -Chim. Sin.* *20*, 1200. [, , . , *20*, 1200.] doi: 10.3866/PKU.WHXB20041007

(6) Qi, L. M.; Ma, J. M.; Cheng, H. M.; Zhao, Z. G. *J. Phys. Chem. B* *101*, 3460. doi: 10.1021/jp970419k

(7) Qi, L. M.; Ma, J. M.; Cheng, H. M.; Zhao, Z. G. *Colloid Surf. -Physicochem. Eng. sp.* *108*, 117. doi: 10.1016/0927-7757(95)03317-3

(8) Hopwood, J. D.; Mann, S. *Chem. Mater.* *9*, 1819. doi: 10.1021/cm970113q

(9) Bagwe, R. P.; Khilar, K. C. *Langmuir* *13*, 6432. doi: 10.1021/la9700681

(10) Modes, S.; Lianos, P. *J. Phys. Chem.* *93*, 5854. doi: 10.1021/j100352a040

(11) Han, Y.; Zhu, L.; Shen, M.; Li, H. H. *cta Phys. -Chim. Sin.* *29*, 131. [, , , . , *29*, 131.] doi: 10.3866/PKU.WHXB201210082

(12) Zhu, W. Q.; Xu, L.; Ma, J.; Ren, J. M.; Chen, Y. S. *cta Phys. -Chim. Sin.* *26*, 1284. [, , , , . , *26*, 1284.] doi: 10.3866/PKU.WHXB20100333

(13) Belloni, J. *Catal. Today* *113*, 141. doi: 10.1016/j.cattod.2005.11.082

(14) Abedini, A.; Daud, A. R.; Hamid, M. A. A.; Othman, N. K.; Saion, E. *Nanoscale Res. Lett.* *8*, 1. doi: 10.1186/1556-276X-8-1

(15) Chen, Q. D.; Shen, X. H.; Gao, H. C. *dv. Colloid Interface Sci.* *159*, 32. doi: 10.1016/j.cis.2010.05.002

(16) Wong, M.; Grätzel, M.; Thomas, J. K. *Chem. Phys. Lett.* *30*, 329. doi: 10.1016/0009-2614(75)80134-5

(17) Adhikari, S.; Joshi, R.; Gopinathan, C. *Int. J. Chem. Kinet.* *30*, 699. doi: 10.1002/(SICI)1097-4601(1998)

(18) Gebicki, J. L.; Gebicka, L.; Kroh, J. *J. Chem. Soc.-Faraday Trans.* *90*, 3411. doi: 10.1039/ft9949003411

(19) Pileni, M. P.; Hickel, B.; Ferradini, C.; Pucheault, J. *Chem. Phys. Lett.* *92*, 308. doi: 10.1016/0009-2614(82)80282-0

(20) Chen, Q. D.; Shen, X. H.; Gao, H. C. *J. Colloid Interface Sci.* *308*, 491. doi: 10.1016/j.jcis.2006.12.021

(21) He, P.; Shen, X. H.; Gao, H. C. *J. Colloid Interface Sci.* *28* , 510. doi: 10.1016/j.jcis.2004.10.060

(22) Chen, Q. D.; Shen, X. H.; Gao, H. C. *J. Colloid Interface Sci.* *312*, 272. doi: 10.1016/j.jcis.2007.03.036

(23) Romero-Ibarra, I. C.; Rodriguez-Gattorno, G.; Garcia-Sanchez, M. F.; Sanchez-Solis, A.; Manero, O. *Langmuir* *26*, 6954. doi: 10.1021/la904197k

(24) Niemann, B.; Veit, P.; Sundmacher, K. *Langmuir* *2* , 4320. doi: 10.1021/la703566v

(25) Nagaraja, B. M.; Abimanyu, H.; Jung, K. D.; Yoo, K. S. *J. Colloid Interface Sci.* *316*, 645. doi: 10.1016/j.jcis.2007.09.004

(26) Jones, F.; Richmond, W. R.; Rohl, A. L. *J. Phys. Chem. B* *110*, 7414. doi: 10.1021/jp054916+

(27) Coveney, P. V.; Davey, R.; Griffin, J. L.; He, Y.; Hamlin, J. D.; Stackhouse, S.; Whiting, A. *J. m. Chem. Soc.* *122*, 11557. doi: 10.1021/ja990885i

(28) Lutter, S.; Koetz, J.; Tiersch, B.; Kosmella, S. *J. Disper. Sci. Technol.* *30*, 745. doi: 10.1080/01932690802643113

(29) Iida, S.; Shoji, T.; Obatake, N.; Sato, H.; Ohgaki, K. *J. Chem. Eng. Jpn.* *38*, 357. doi: 10.1252/jcej.38.357

(30) Li, M.; Mann, S. *Langmuir* *16*, 7088. doi: 10.1021/la0000668

(31) Chen, Q. D.; Bao, H. Y.; Shen, X. H. *Radiat. Phys. Chem.* *77*, 974. doi: 10.1016/j.radphyschem.2008.02.001

(32) Chen, Q. D.; Shen, X. H. *Cryst. Growth Des.* *10*, 3838. doi: 10.1021/cg100307r

(33) Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* *17*, 513. doi: 10.1063/1.555805

(34) Zhou, J.; Zhao, H. K.; Shi, J. F.; Chen, Q. D.; Shen, X. H. *Radiat. Phys. Chem.* *97*, 366. doi: 10.1016/j.radphyschem.2013.07.027

(35) Tupikov, V. I. *Organic Radiation Chemistry Handbook*; Milinchuk, V. K., Tupikov, V. I. Eds.; Ellis Horwood Ltd.: Chichester, 1989; p 46.