SUPPORTING INFORMATION

Formation of Hollow Silica Nanospheres by Reverse Microemulsion

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List of Methods, Figures and Tables

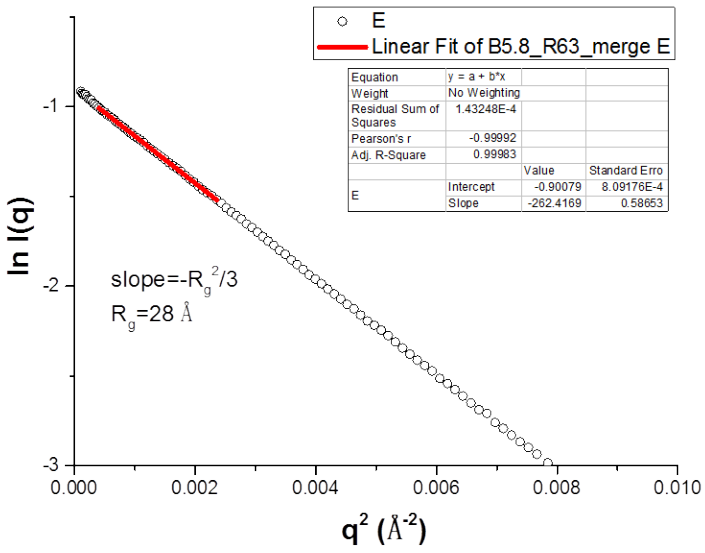
Materials: Cyclohexane, *n*-hexane, *n*-octane, *n*-decane, *n*-dodecane, *n*-hexanol (98%), ammonium hydroxide (NH_4OH, 28-30 wt %), tetraethylorthosilicate (TEOS, 98%), 3-aminopropyltrimethoxysilane (APTS, 95%), polyoxyethylene (10) isooctylphenylether (Triton X-100) were purchased from Acros. Polyoxyethylene (5) isooctylphenyl ether (Igepal CA-520) was purchased from Sigma Aldrich. Ultrapure deionized (D.I.) water was generated using a Millipore Milli-Q plus system. All reagents were used without additional purification.

Data Analysis for SAXS measurements:

The radii of gyration Rg of nanoparticles are evaluated using the Guinier approximation assuming that at very small angles ($q < 1.3 \times Rg$), the intensity is represented as

$I(q) \approx I_0 \exp(-q^2 R_g^2/3)$

For monodisperse solutions, I(q) can be related to Rg of the nanoparticles by the Guinier equation, which is represented by the Guinier plot.



The gyration radii of the nanospheres derived from Guinier approximation are evaluated using Primus program of ATSAS software package.[1] Data analysis is using unimodal or bimodal size distributions (Schulz size distributions) provided by the NCNR[2] based on the IGOR Pro software.

References:

1. P. V. Konarev, V. V. Volkov, A. V. Sokolova, M. H. J. Koch and D. I. Svergun, *J. Appl. Crystallogr.*, 2003, **36**, 1277-1282.
2. S. R. Kline, *J. Appl. Crystallogr.*, 2006, **39**, 895-900.

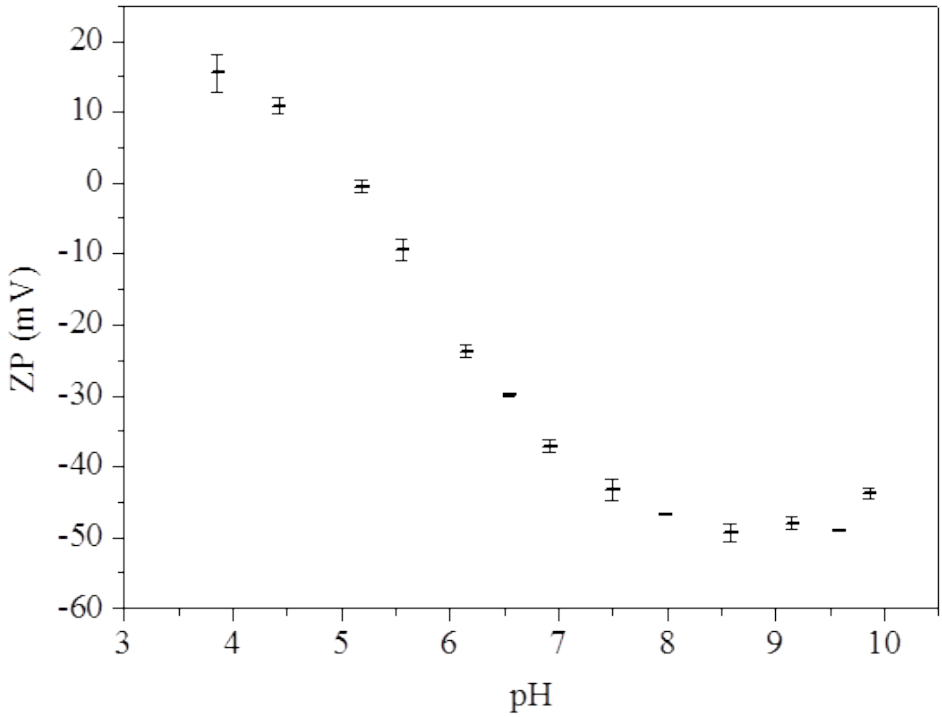


Figure S1. The zeta potential for HSN titration measurements at different pH varying from 3 to 10.

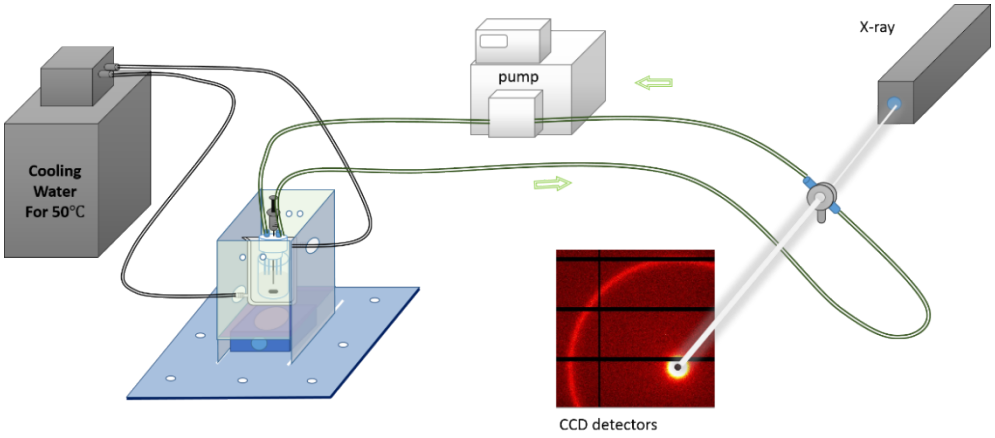


Figure S2. Schematic design diagram for *in situ* SAXS measurements at BL23A SWAXS end station in National Synchrotron Radiation Research Center (NSRRC, Taiwan).

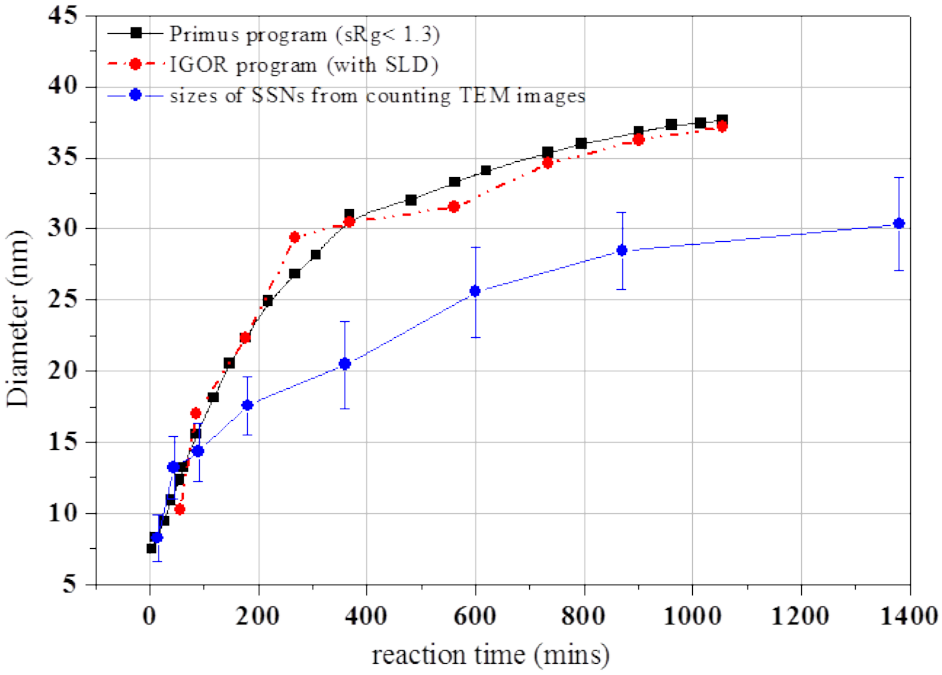


Figure S3. The comparisons between the SSN diameters from SAXS fitting results (Primus and IGOR) and statistic measurements from time-resolved TEM images.

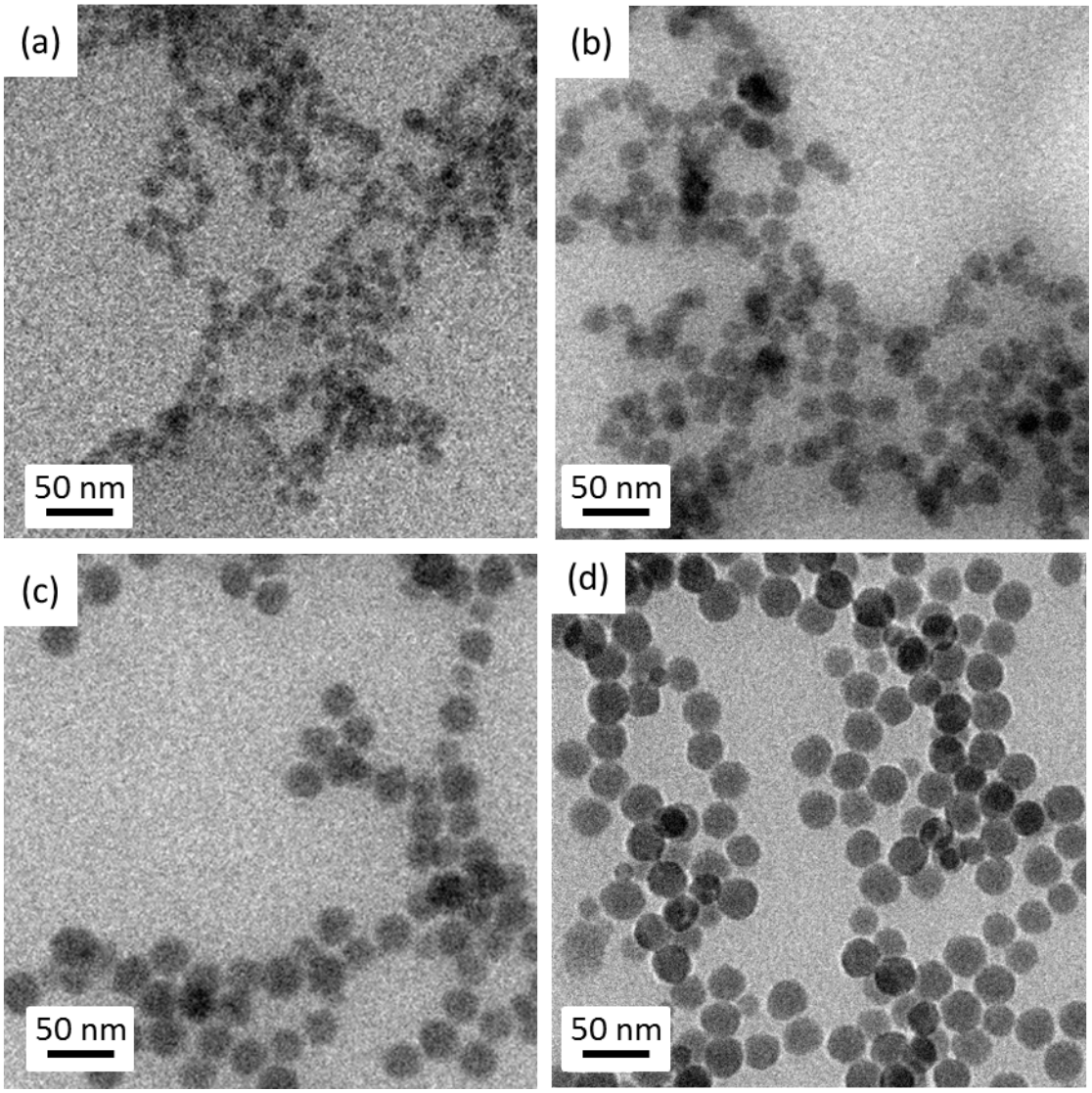


Figure S4. Representative TEM images of as-synthesized solid silica nanoparticles (SSNs) taken at (a) 45 min, (b) 180 min, (c) 10 h, and (d) 24 h after reaction. The growing nanoparticles also have uncertain boundaries due to excess organic residue (CA-520) that was not completed removed prior to TEM specimen preparation.

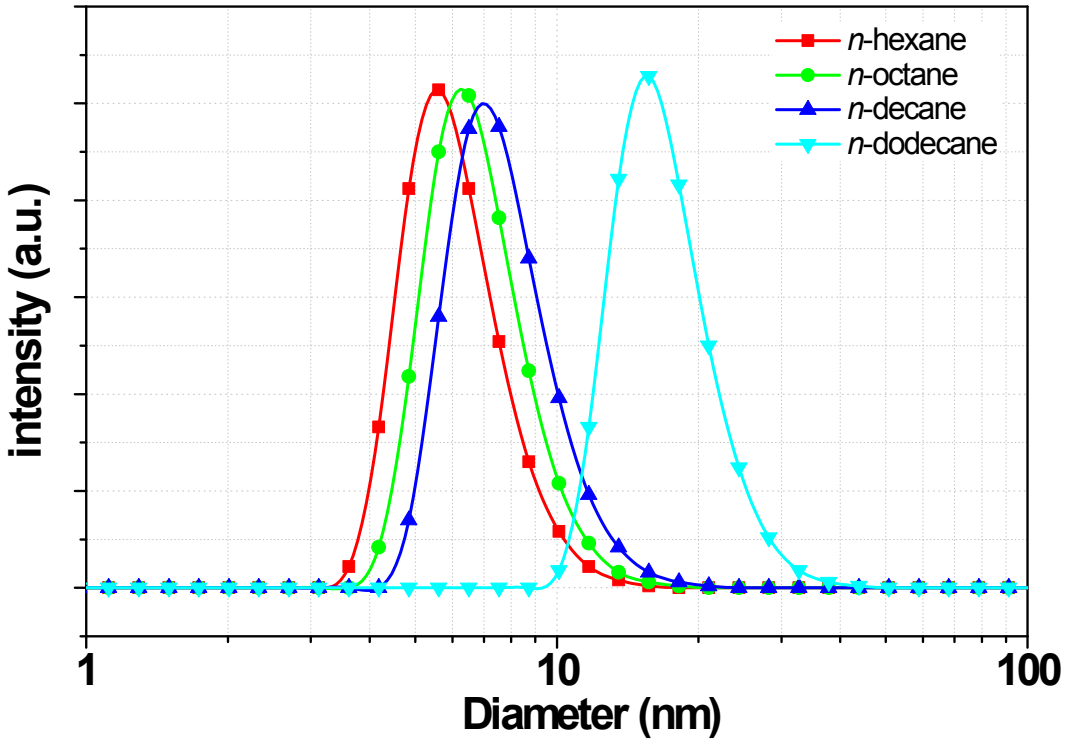


Figure S5. Hydrodynamic diameter distribution of microemulsion with different solvents as oil phase.

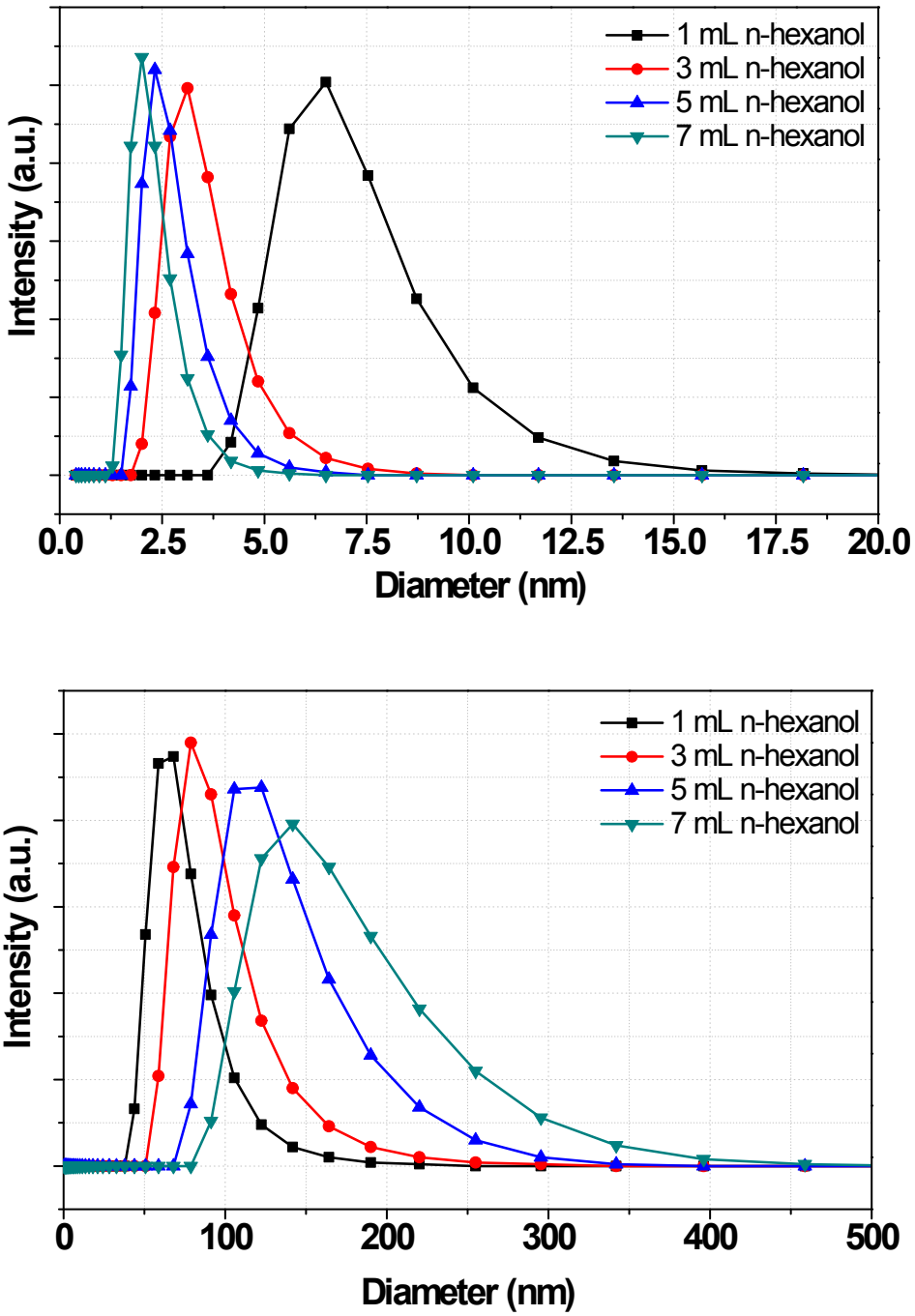


Figure S6 Hydrodynamic diameter distribution of (a) as-prepared w/o microemulsion formed with different volume of *n*-hexanol in the system and (b) hollow silica nanospheres synthesized with different volume of n-hexanol.

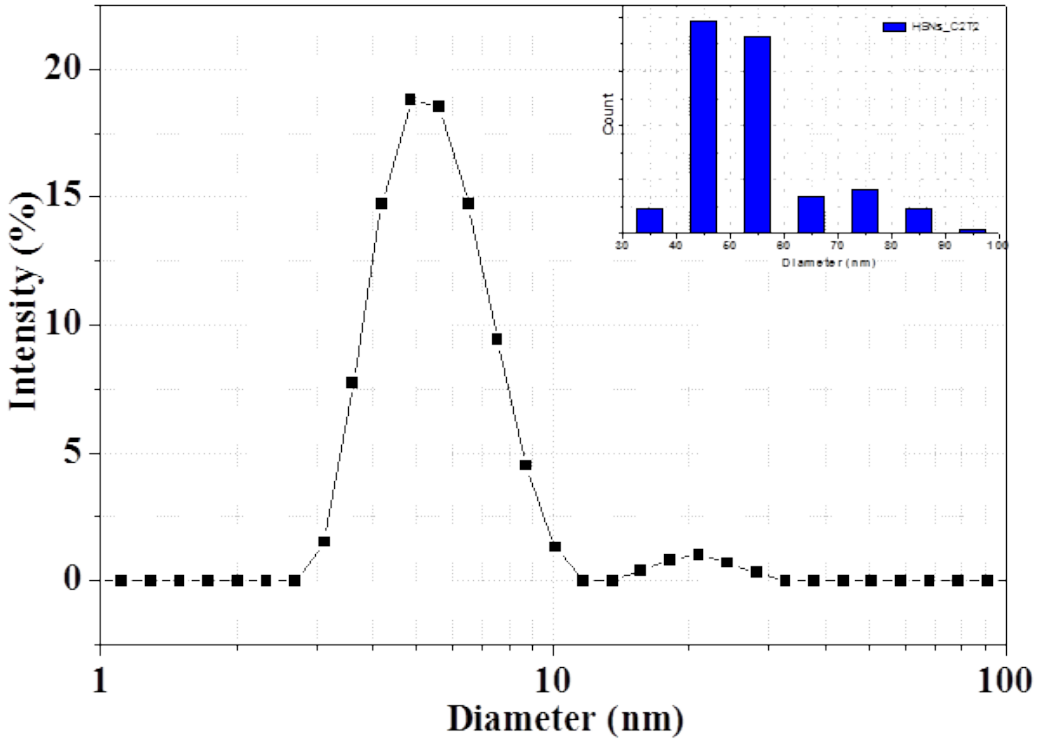


Figure S7. Hydrodynamic diameter distribution of as-prepared w/o microemulsion formed with an equal molar ratio of Triton X-100 to CA-520 (50%:50%). The inset is the hydrodynamic diameter distribution of hollow silica nanospheres synthesized with the same condition.

Table S1 Elemental analysis of solid silica nanospheres, hollow silica nanospheres and dried precipitates from etching solution

	C %	H %	N %	O % (*calculated*)	SiO_2 % (*calculated*)
SSN	3.638	1.895	0.460	12.4	81.6
HSN	4.134	1.927	0.935	12.7	80.3
Precipitates from supernatant	2.569	0.968	0.195	12.9	91.4

Table S2 Calculations of mass transfer of TEOS and APTS from SSN to HSN.

	APS* (mmol/100g)	CA-520 (mmol/100g)	H_2O (mmol/100g)	SiO_2 (TEOS+APTMS) (mmol/100g)
SSN wt. ratios	33	8	615	1338
Mole ratio	1			40.5
	100% APTMS			100% TEOS
HNS wt. ratios	67	6	557	1315
Mole ratio	1			19.6
Portion from SSN	76.1% APTMS			35.8% TEOS
Supernatant precipitates *wt. ratios*	14	7	267	1495
Mole ratio	1			107
Portion from SSN	23.9% APTMS			64.2% TEOS

* APS: 3-aminopropylsilyl group

Table S3. The solid state NMR area percentage of different kinds of silane structure in different treatment stages

Si NMR	Q^4 (%)	Q^3 (%)	Q^2 (%)	T (%)	Summation (%)
	$Si(OSi)_4$	$Si(OSi)_3(OH)_1$	$Si(OSi)_2(OH)_2$		
Before water washing (SSNs)	58.73	29.59	7.41	4.27	100
After water washing (HSNs)	60.47	27.59	5.43	6.51	100

Table S4TEM. The summary of the different approaches to investigate the size of HSNs

	composition of reverse microemulsion				Diameter of HSNs	
	Organic solvent (g)	surfactant CA-520(ml)/ TritonX-100(g)	Co-surfactant n-hexanol(μL)	water (μL)	Diameter (nm)	Standard deviation
Solvent effect	n-hexane(30.29)	3.26/0	2500	700	42.4	3.9
	n-octane(40.24)	3.26/0	2500	700	50.6	5.6
	n-decane(50.1)	3.26/0	2500	700	59.7	5.4
	n-dodecane(60)	3.26/0	2500	700	70.5	7.4
Co-surfactant effect	cyclohexane*	0/5	1000	350	67.2	10.7
	cyclohexane*	0/5	3000	350	93.5	10.1
	cyclohexane*	0/5	5000	350	125	18.6
	cyclohexane*	0/5	7000	350	175	17.9
The different ratio of CA-520 to Triton X-100	cyclohexane*	3.26/0	0	350	22.9	2.2
	cyclohexane*	2.45/1.25	1000	350	38.4	3.9
	cyclohexane*	1.63/2.5	2000	350	53.4	11.7
	cyclohexane*	0.82/3.75	3000	350	87.0	18.6
	cyclohexane*	0/5	4000	350	138.7	18.1

*: Weight of cyclohexane is 14.83 gram