Controlled Size Silver Nanoparticles Synthesis with Water-in-Oil Microemulsion Method: A Topical Review

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Table 1. Various control parameters, characterization tools used and particles size obtained for SNPs (silver nanoparticles) synthesis with microemulsion technique.

Surfactant+ Co-surfactant	Ag precursor	Reducing agent	Continuous Organic Phase	Control parameters studied	ω	Charac-terization	Particle size /avg. dia, nm	Remarks	Ref
AOT	$AgNO_3$	$NaBH_4$	Diethyl ether	---		FT-IR, TEM, XPS,UV, TGA-DTA,EA		Capped by dodacanethiol	22
CTAB, Dh	$AgNO_3$ $HAuCl_4$	$NaBH_4$ and quercetin	n-hexanol	---	12.1	UV NMR	5-6 nm	Single microemulsion scheme is used. Ultrasonication gave more uniform particles. Transferred to aqueous phase.	28
$C_{12}E_5$	$AgNO_3$	$NaBH_4$	Cyclohexane	ω	1.13 2.26 4.5 9 18 36	UV EM	3.3 (ω=1.12) 4.4 (ω=2.25) 8.8 (ω=4.5) 8.8 (ω=9) 6.6 (ω=18) 4.4 (ω=36)	Most uniform particles at ω= 36 i.e. rw=0.8 (8.8 nm).	29
Ag(AOT) Na(AOT)	$AgNO_3$ Ag(AOT)	$NaBH_4$ N_2H_4	Cyclohexane (Ch) Isooctane (Io)	ω, type of RA., type of oil	2 5 7.5 12.5	SAXS, UV TEM, HRTEM, ED	**Ch:** 2.5 (ω=5) 5.5 (ω=7.5) 7 (ω=15) **Io:** 2.7 (ω=5) 3 (ω=7.5) 7 (ω=15)	Smaller particles were favored at low ω. Replacing isooctane by cyclohexane induced a decrease in the intermicellar exchange rate constant.	30
Ag(AOT) Na(AOT)	$AgNO_3$ Ag(AOT)	Na(AOT)/ N_2H_4	Isooctane	ω			2 to 7 nm, on increasing water droplet size	Addition of dodecane thiol and extracted from reverse micelles by SSP method reduced the size.	31
AOT	$AgNO_3$	$NaBH_4$		ω Cm, C_R type of oil, Cs		HRTEM ED, XRD, UV		With increase in AOT concentration, number of SNPs increased, but no significant change in particle size.	32
AOT $C_{12}E_4$	$AgNO_3$	$NaBH_4$	Isooctane	ω p_{CO2}				SNPs recovered by dissolving antisolvent CO_2 and precipitated at suitable pressures. Smaller particles were favored at low ω and high p_{CO2} in recovery process.	33

Igepal CO-520	$AgNO_3$	$N_2H_4{\cdot}H_2O$	Cyclohexane	ω		TEM ED XRD	5 (ω=4) 10 (ω=6) 10.5 (ω=8)	The average size and distribution of the synthesized Ag particles increased slightly from 4 to 8 with increased ω.	34
AOT	$AgNO_3$	$N_2H_4{\cdot}H_2O$	Dodecane	ω Cm, C_R	3, 5	UV TEM	2-5 nm	Size increased with ω.	35
AOT	$AgNO_3$	$N_2H_4{\cdot}H_2O$	Dodecane	ω Cm, (study)		TEM FT-IR UV	ω: 1.52(ω=2.5) 3.39(ω=7.5) 4.98(ω=15) Cm: 3.93 (0.1 M) 2.6 (0.2 M)	TEM study showed that size increased with increase in ω.	36
SDS + isoamylalcohol	$AgNO_3$	$N_2H_4{\cdot}H_2O$	Cyclohexane	ω Cm	ω,t [M]	UV TEM	6.5 (ω=5) 9.4(ω=10) 12.1(ω=20)	Monodisperse particles obtained at low ω. UV study carried over only for Cm variation.	37
TritonX-100	$AgNO_3$	$NaBH_4$	Cyclohexane	ω Cm (0.05, 0.1 M)	1,3, 5,7	DLS TEM		No effect of Cm on size or λ_{max} for Ag; whereas for bimetallic and gold particles, drastic increase in size as well as λ_{max} was observed.	38
AOT	$AgNO_3$	$N_2H_4{\cdot}H_2O$ $NaBH_4$	Cyclohexane	ω Cm		UV		Smaller SNPs obtained on increasing the Cm and on decreasing the ω value.	39
AOT	$AgNO_3$	$N_2H_4{\cdot}H_2O$	Dodecane	C_S	-		3.9 nm (C_S=0.2 M) 1.6 nm (C_S=0.4 M)	Smaller SNPs obtained on increasing the Cm.	40
AOT SDS DTAB NP-5	$AgNO_3$	$NaBH_4$	Cyclohexane heptane decane	type of oil, Additional surfactant		UV TEM		With increased chain length of the oil, intermicellar exchange rate coefficient increased leading to decreased particle size. Particle size decreased considerably on addition of a nonionic surfactant (NP-5), but no change was observed with DTAB and SDS.	41
AOT	$Cd(NO_3)_2$	Na_2S	Isooctane			UV		Used a combined approach of spectroscopy and Monte Carlo simulation and found it to be helpful in elucidating the mechanism of formation	42
AOT	$AgNO_3$	$NaBH_4$	Cyclohexane	ω,type of oil, Addition of cations		TEM		Intermicellar exchange rate varied by type of oil, ω and by addition of benzyl alcohol and cations. Particle size, the polydispersity, and the number of particles formed were dependent on the intermicellar exchange rate and/or the rigidity of the surfactant shell.	43
AOT	$AgNO_3$	$NaBH_4$	Isooctane					Simulation is only performed on experimental work taken from literature. Autocatalysis and ripening, favor the slow growth of the biggest nanoparticles leading to the production of larger particles when the reaction is slower.	44
AOT	-	-	-	-	-	-	-	Effects of additives (*e.g.* alcohols) on the exchange kinetics is studied	45
$C_{12}E_4$/Brij 30 AOT	$AgNO_3$	$C_{12}E_4$	Cyclohexane heptane decane	Cm		UV TEM		Surfactants act both as reducing agent and structure-directing agent. Cm variation did not affect droplet's size and shape noticeably.	46
CTAB, SDOSS, AOT	$AgNO_3$	$NaBH_4$ And quercetin	Isooctane Chloroform	ω, type of RA.	3.62 -7.5		5-15 nm size various RA and solvent combination	Vietnamese chitosan used as stabilizer. Inhibition in 30 min exposure time was as follows: E.coli of 3 ppm, TPC and fungi of 15 ppm, Vibrio Cholerae cells of 0.5 ppm.	47
AOT	$AgNO_3$	Quercetine	Octane Heptane	t, R	1-10	UV, Surface	1-1.5 nm	No change was observed in size with time or reducing agent concentration.	48

						plasmon spectra			
SFAE	$AgNO_3$	N_2H_5OH	Isooctane			TEM		The resultant silver colloid could be preserved for at least 1 month without precipitation.	49
NP-5, NP-9, NP-1+pentanol	$AgNO_3$	$NaBH_4$	Cyclohexane	Type of surf.	35	UV TEM	18.6 (NP-5) 6.25 (NP-9) 15.2 (NP-ll)	NP-5 and NP-11 gave larger SNPs than NP-9 due to their lamellae like Structure.	50
AOT	$AgNO_3$	N_2H_4	Cyclohexane		4-10 25-30	UV TEM, SANS	Spherical cylindrical	Size and shape were found to be composition dependent.	51
Rhamnolipid	$AgNO_3$	$NaBH_4$	n- heptane	t		UV TEM, AFM	2-8 nm (TEM) 6-11 nm (AFM)	Green biosurfactant, small aggregation, Spherical, Intrinsic enlarging effect of pin point in AFM.	52
18-3(OH)-18 (gemini surfactant)	AgNO3	$NaBH_4$	n- heptane	-	-	TEM, AFM UV–vis XRD XPS	silica-coated SNPs	Visible luminescence at 448 nm.	53
Ag(AOT) Na(AOT	$AgNO_3$ Ag(AOT)	N_2H_4	Isooctane	-	40	UV TEM SAXS	3.4 3.5 (after extraction) 4.1 (after SPP)	More smaller and less polydispersity after extraction and fractionation.	54
AOT	$AgNO_3$	NaH_2PO_2	Isooctane	-	6	UV, Flourescens, STM	2D- 3.2 nm nanodiscs, 3D-1.5 nm nanostructures	Cluster formation 1st stage– 2D 2nd stage–3D	56
SDS + isoamylalcohol	$AgNO_3$	$N_2H_4{\cdot}H_2O$	Cyclohexane		5	TEM	6.5	Flake-like powders on centrifugation (self assembled).	57
Igepal CO-520	$AgNO_3$-$Pd(NO_3)_2$	NH_4OH	Cyclohexane isooctane			TEM-EDS		On increasing ω, the Ag–Pd particles distribution of the core-shell composite particles was influenced and the distribution of Ag–Pd particles was broadened. On increase in $AgNO_3$ solution, sizes of both the types of nanoparticles linearly increased	58
AOT+ SDS	$AgNO_3$	NaH_2PO_2	Toluene			XRD AAS HRTEM		Yields obtained were much higher than typical yields.	59
AOT+ SDS	$AgNO_3$	$NaBH_4$	Toluene	C_R Dosing time		XRD AAS TEM	3 nm	At higher and medium C_R values, formation of only worm-like structures promoted; but at low values, mixture of Ag nanoparticles (≈ 3 nm) and worm-like structures promoted. Yields obtained were much higher than typical yields.	60
Oleylamine	AgNO3	Ascorbic acid	Toluene			FE-SEM	Silica-coated SNPs		61
1-dodecanethiol	$AgNO_3$	$NaBH_4$	Toluene	Cm. t_{rea}		TEM, UV XRD FT-IR	t_{rea} = 24 h: 35 (Cm=0.03M) 30(Cm=0.01M) t_{rea}=6 h: 21,Cm=0.03M)	DTAB is used as phase transfer agent. Self assembled to give 0-D quanta-dot arrays. Single microemulsion scheme is used.	62
AOT+ Arlacel-20	$AgNO_3$		n- heptane Decane Dodecane	ω	5 10	UV		G (Growth rate) increases. Slow with Ghept>Gdecane>Gdodecane	63

18-3(OH)-18: 2-hydroxy-1, 3-bis(octadecyldimethylammonium) propane dibromide (a gemini surfactant)
AAS: Atomic absorption spectroscopy
AFM: Atomic force microscopy
AOT: Sodium bis-(2-ethylhexyl) sulfosuccinate
$C_{12}E_4$/Brij 30: Tetraethylene glycol dodecyl ether
$C_{12}E_5$: Pentaethylene glycol monododecyl ether

Cm :	metal (Ag) ion concentration
C_R :	concentration of reducing agent
Cs :	surfactant concentration
CTAB:	Cetyltrimethylammonium bromide
Dh:	Dodecyl-heptaethyleneglycol-ether ($C_{12}H_{25}$-O-(CH_2-CH_2-O-)$_6$ CH_2-CH_2-OH)
DLS:	Dynamic light scattering
DTAB:	n-Dodecyl trimethylammonium bromide
EA:	elemental analyses
ED:	Electron diffraction
FT-IR:	Fourier transform infra red spectroscopy
HRTEM:	High-resolution transmission electron microscopy
Igepal CO-520:	Poly (oxyethylene) nonylphenyl ether
$N_2H_4 \cdot H_2O$:	Hydrazine hydrate
N_2H_5OH :	Hydrazinium hydroxide
$NaBH_4$:	Sodium borohydrate
p_{CO2} :	Antisolvent CO_2 pressure
RA:	Reducing agent
SANS:	small-angle neutron scattering
SAXS:	Small-angle X-ray scattering
SDOSS:	Sodium dioctyl sulfosuccinate
SDS:	Sodium dodecyl sulfate
SFAE:	Sucrose fatty acid esters
STM:	Scanning tunneling microscopy
TEM:	Transmission electron microscopy
TEM-EDS:	Transmission Electron Microscopy-Energy- Dispersion Spectrum
TEOS:	Tetraethyl orthosilicate
TPC:	Total aerobic bacteria
UV:	UV–vis absorption spectroscopy
XPS:	X-ray photoelectron spectroscopy
XRD:	X-ray diffraction
ω:	Water to surfactant mole ratio

Ref 63: Shah, D. O.; Bagwe, R. P.; Parmer, B. S. The effect of interfacial viscosity on the kinetics of formation of silver nanoparticles using water-in-oil microemulsions as nanoreactors. *Mat. Res. Soc. Symp. Proc*. **2002,** *704 (Nanoparticle Materials),* 327.