Published in "Particle & Particle Systems Characterization 31(6): 645–651, 2014"
which should be cited to refer to this work.

Supporting Information

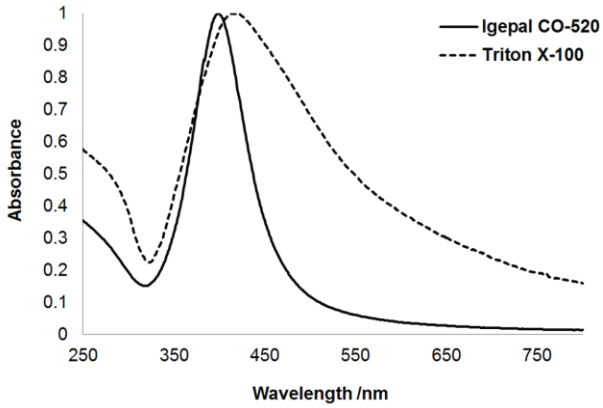
One-pot synthesis and catalytic properties of encapsulated silver nanoparticles in silica nanocontainers

*Magdalena Priebe, and Katharina M. Fromm**

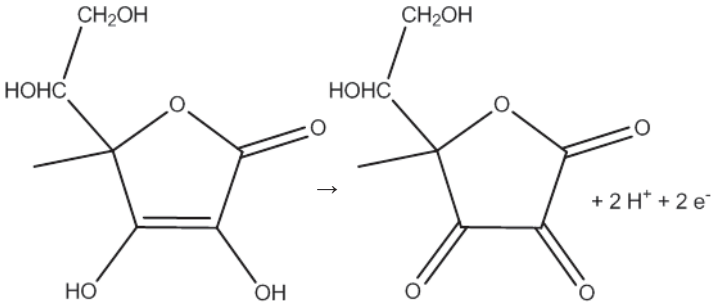
SI 1. Influence of surfactant on formation and coating of AgNPs with silica shell.

4 mL of surfactant was added under vigorous stirring into 10 mL of cyclohexane at room temperature. When the solution was transparent, 325 µL of 0.01 M $AgNO_3$ were added dropwise. When Triton X-100 was used as surfactant no change in color was observed, however in case of Igepal CO-520, the color changed into yellow indicating formation of silver nanoparticles. The system was left for equilibration (80 minutes) and then 50 µL of 9 M hydrazine were added dropwise. The flask containing Igepal CO-520 remained yellow, whereas the one containing Triton X-100 turned black. After 10 minutes 16 µL of aqueous ammonia (28-30%) were added and then 50 µL of TEOS-cyclohexane (volume ratio 1:1). After 24 h reaction, the microemulsion was destabilized with 20 mL of EtOH, centrifuged (15'000 rpm, 30 min, rt), washed twice with EtOH (25 mL) and twice with ultra-pure water (25 mL).

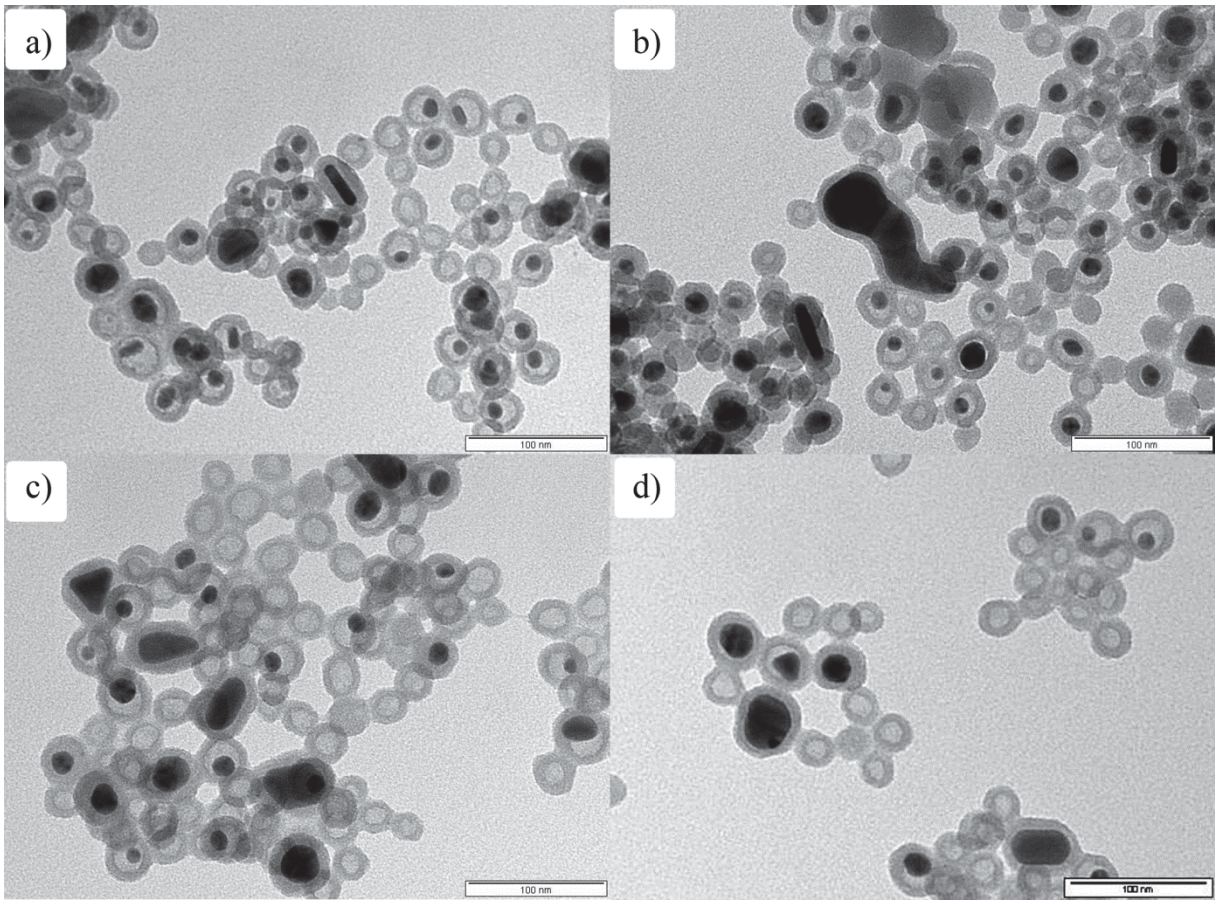
SI 2. UV-vis spectra of the samples prepared by use of Igepal CO-520 and Triton X-100. The spectra were normalized up to an absorbance = 1.



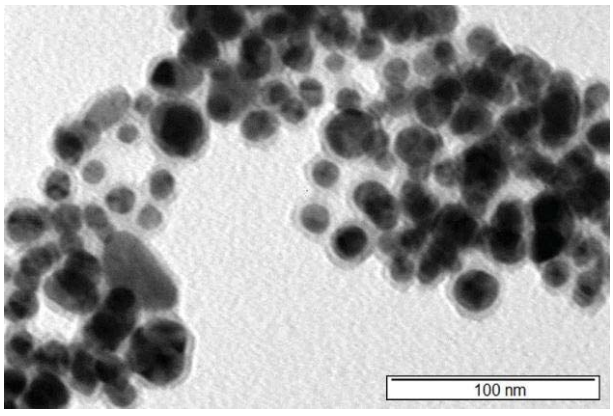
SI 3. Redox potentials of reducing agents.

Reducing agent	Redox reaction	E^0 [V]	Reference
Sodium borohydride	$BH_4^- + 8\ OH^- \rightarrow B(OH)_4^- + 4\ H_2O + 8\ e^-$	1.24	44
Hydrazine	$N_2H_2 + 4\ OH^- \rightarrow N_2 + 4\ H_2O + 4\ e^-$	1.15	45
Ascorbic acid		-0.058	46

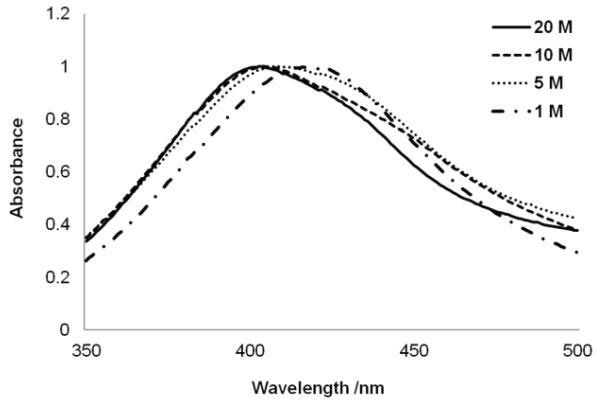
SI 4. TEM images of $Ag@SiO_2$ prepared with 0.1 M $AgNO_3$. Shape variation. Scale bar: 100 nm.



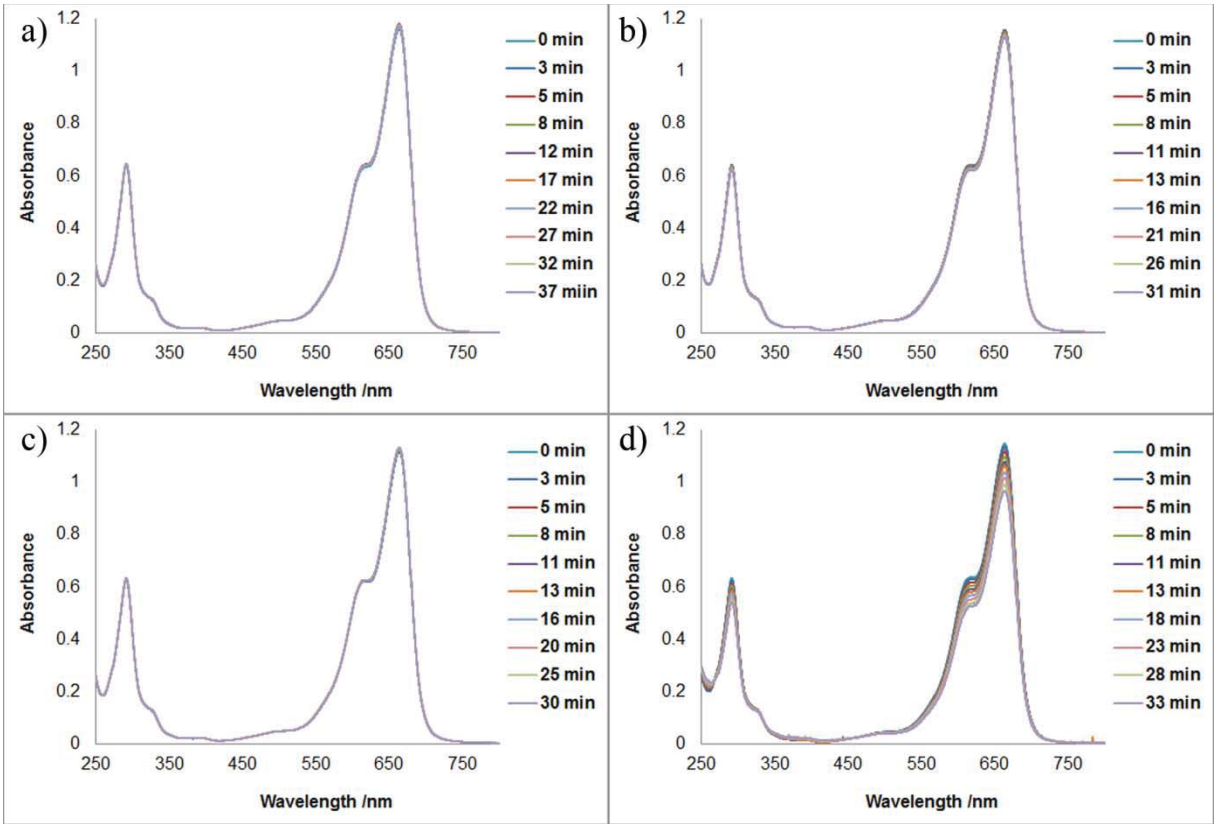
SI 5. TEM images of $Ag@SiO_2$ prepared with 1 M $AgNO_3$ and 250 µL hydrazine. Scale bar: 100 nm.



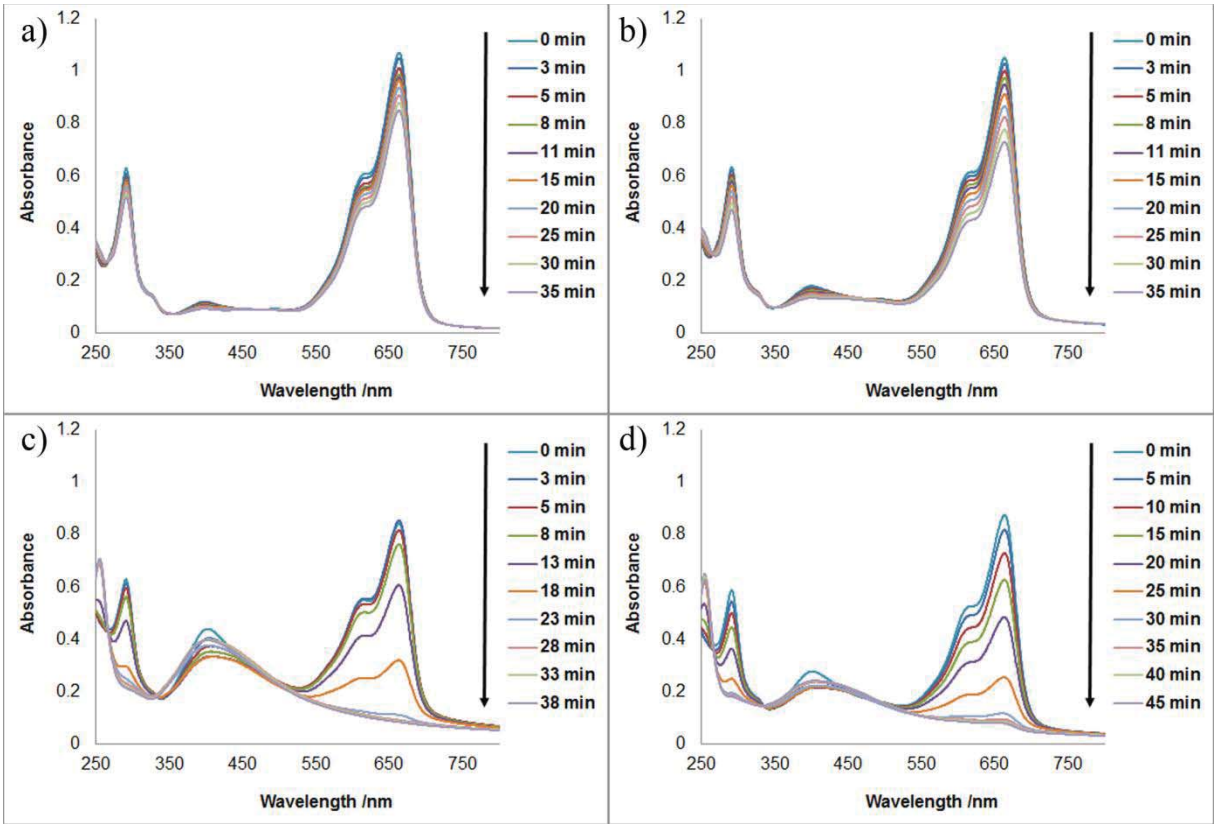
SI 6. UV-vis spectra of $Ag@SiO_2$, prepared using 0.1 M $AgNO_3$ and 20 M, 10 M, 5 M, 1 M hydrazine. The spectra were normalized up to an absorbance = 1.



SI 7. Time-resolved UV-vis spectra of methylene blue mixed with a) 8 mM, b) 10 mM, c) 13 mM and d) 80 mM $NaBH_4$ solution (prepared as explained in *Determination of catalytic properties* with the only difference that ultra-pure water was used instead of $Ag@SiO_2$ suspension).



SI 8. Time-resolved UV-vis spectra of methylene blue after addition of $Ag@SiO_2$ (Sample 12, **Figure 3 d**) suspensions at different concentrations of silver a) 0.15 mM, b) 0.21 mM, c) 0.58 mM and reduction by 13 mM $NaBH_4$; d) $Ag@SiO_2$ suspension at of silver 0.29 mM and reduction by 8 mM $NaBH_4$.



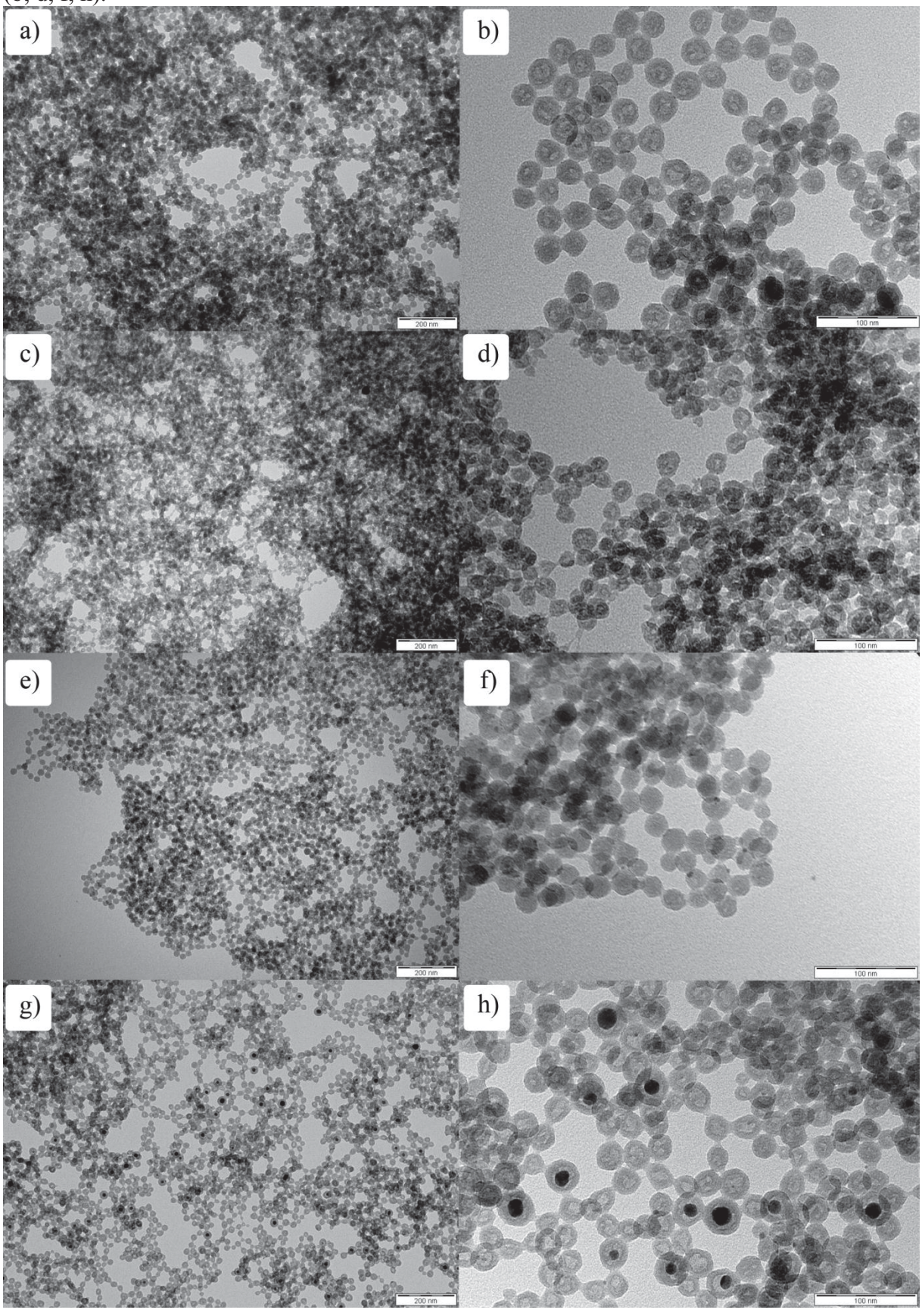
SI 9. Experimental procedure for preparation of $Ag@SiO_2$ nanorattles – variation of the experimental conditions.

Sample	H_2O [µL]	$AgNO_3$ [µL]	$AgNO_3$ [M]	Reducer	Reducer [µL]	Reducer [M]	TEOS [µL]	Sequence	Color	λ_{max} of UV-vis	Comments
1	700	700	0.01	CA	50	1	200	1	t	n	Almost no hollow structures of SiO_2, tiny AgNPs
2	700	700	0.01	AA	50	1	200	1	sy	n	Hollow structure of SiO_2 hardly visible, tiny AgNPs
3	700	700	0.01	SB	50	1	200	1	y	n	Mainly full SiO_2, tiny AgNPs
4	700	700	0.01	H	50	1	200	1	dy	n	Nanorattle $Ag@SiO_2$, small spherical AgNPs, incomplete loading
5	0	1400	0.1	H	50	20	200	2	bl	403	Nanorattle $Ag@SiO_2$, AgNPs of various sizes
6	0	1400	0.1	H	50	10	200	2	bl	404	
7	0	1400	0.1	H	50	5	200	2	bl	408	
8	0	1400	0.1	H	50	1	200	2	bl-br	422	Empty solid SiO_2 of smaller size AgNPs much larger then SiO_2, tight coating
9	1400	0	0	-	-	-	200	2	t	n	Hollow SiO_2
10	0	1400	0.01	H	50	20	200	2	o	403	$Ag@SiO_2$ (Conc. of $AgNO_3$↑, size of AgNP and loading ↑)
11	0	1400	0.05	H	50	20	200	2	br	400	
12	0	1400	0.1	H	50	20	200	2	bl	401	
13	0	1400	0.2	H	50	20	200	2	bl	405	
14	0	1400	0.3	H	50	20	200	2	bl	410	$Ag@SiO_2$ – disappearing nanorattle pattern
15	0	1400	0.5	H	50	20	200	2	bl	410	$Ag@SiO_2$ – no nanorattle pattern
16	0	1400	1	H	50	20	200	2	bl	404	No $Ag@SiO_2$ pattern
17	0	1400	1	H	250	20	200	2	bl	422	$Ag@SiO_2$ – no nanorattle pattern
18	0	1400	0.2	H	50	20	100	2	bl	409	$Ag@SiO_2$ (Conc. of TEOS↑, silica wall thickness ↑)
19	0	1400	0.2	H	50	20	200	2	bl	406	
20	0	1400	0.2	H	50	20	300	2	bl	407	
21	0	1400	0.2	H	50	20	400	2	bl	404	

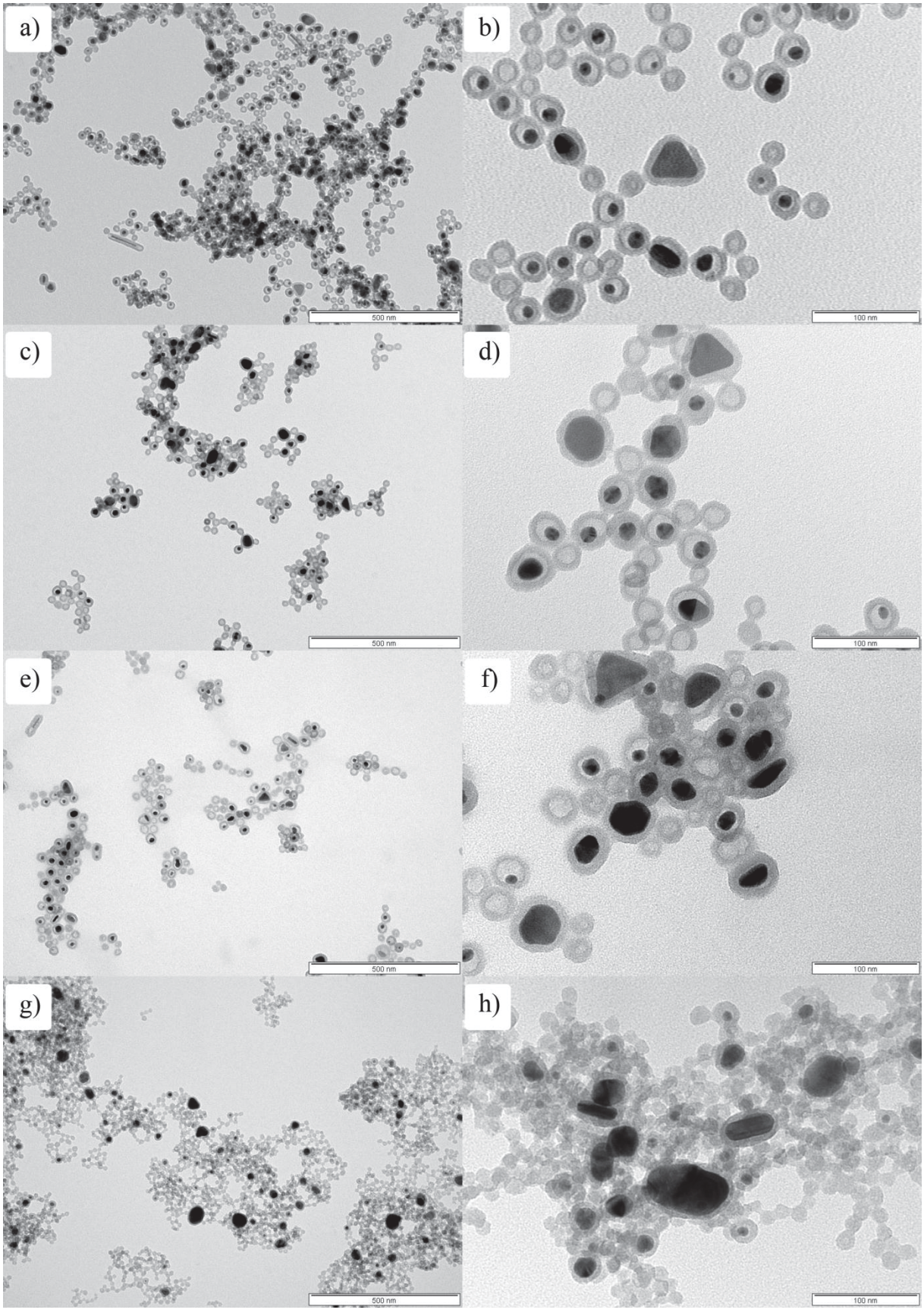
[Sequence 1] cyclohexane + Igepal CO-520 + H_2O → TEOS/APTS → $AgNO_3$ → reducing agent → NH_4OH; [Sequence 2] cyclohexane + Igepal CO-520 → $AgNO_3$ → reducing agent → TEOS/APTS → NH_4OH; [t] transparent, colorless; [y] yellow; [sy] slightly yellow; [dy] dark yellow; [o] orange; [br] brown, [bl] black; [n] not measured or no AgNPs; [CA] citric acid; [AA] ascorbic acid; [SB] sodium borohydrate; [H] hydrazine.

TEM images of the samples are shown in **SI 10-15**, whereas UV-vis spectra in **SI 16-20**.

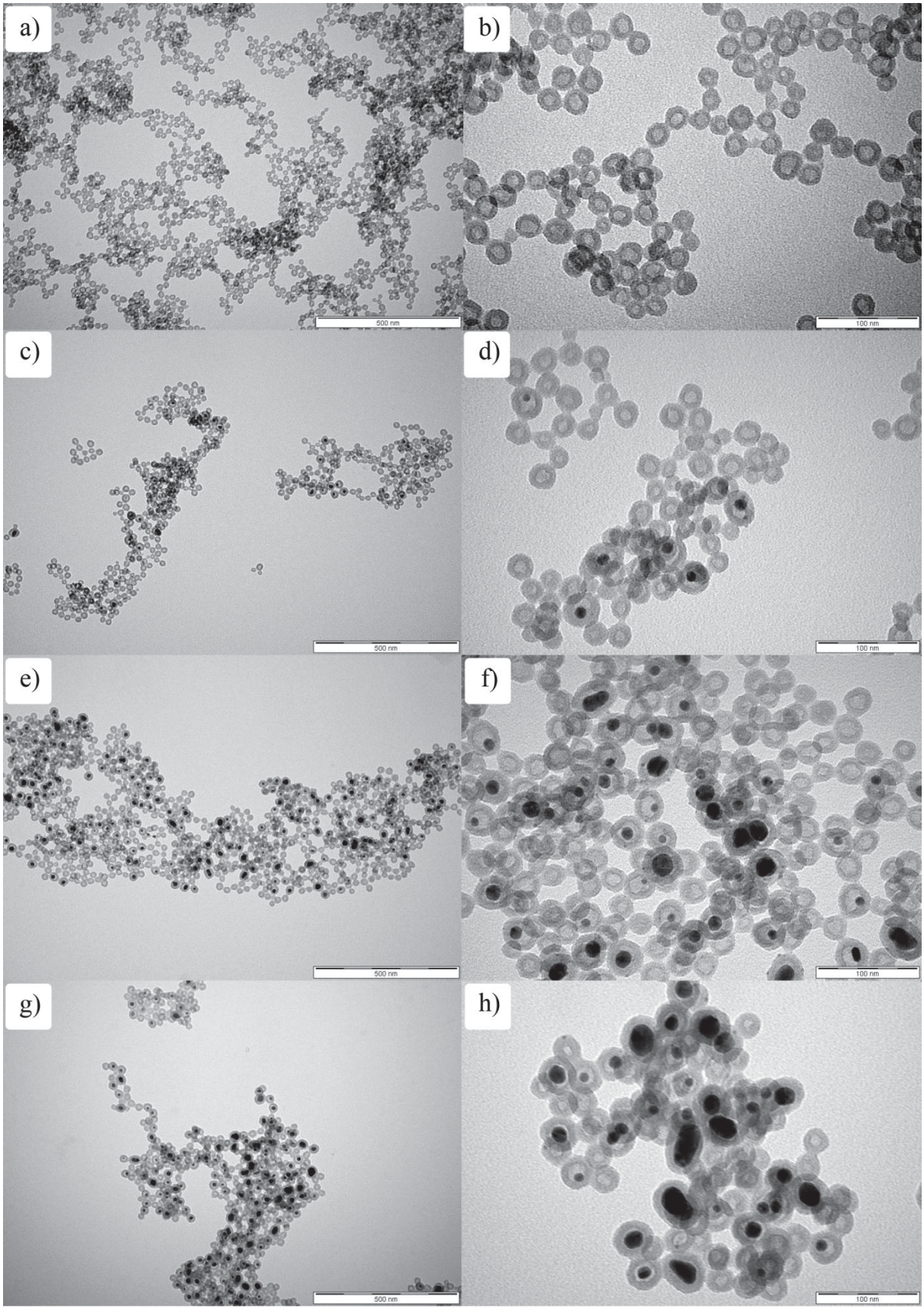
SI 10. TEM images of samples prepared with 700 µL of H_2O, with 700 µL 0.01 M $AgNO_3$, and 50 µL of: a, b) citric acid (Sample 1); c, d) ascorbic acid (Sample 2); e, f) sodium borohydrate (Sample 3); g, h) hydrazine (Sample 4). Scale bar 200 nm (a, c, e, g) and 100 nm (b, d, f, h).



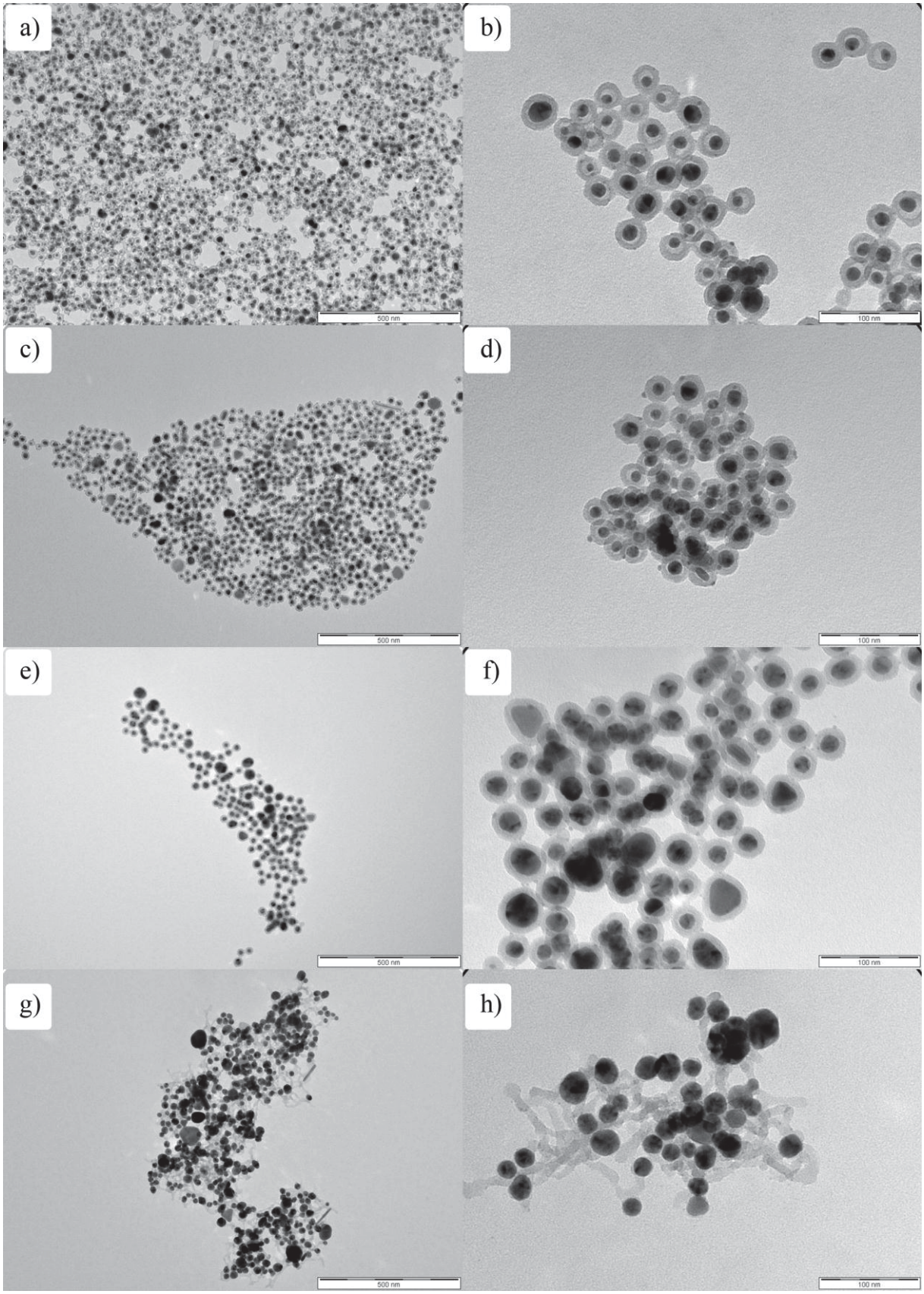
SI 11. TEM images of samples prepared with 1400 µL of 0.1 M $AgNO_3$ and 50 µL of: a, b) 20 M (Sample 5); c, d) 10 M (Sample 6); e, f) 5 M (Sample 7); g, h) 1 M hydrazine (Sample 8). Scale bar 500 nm (a, c, e, g) and 100 nm (b, d, f, h).



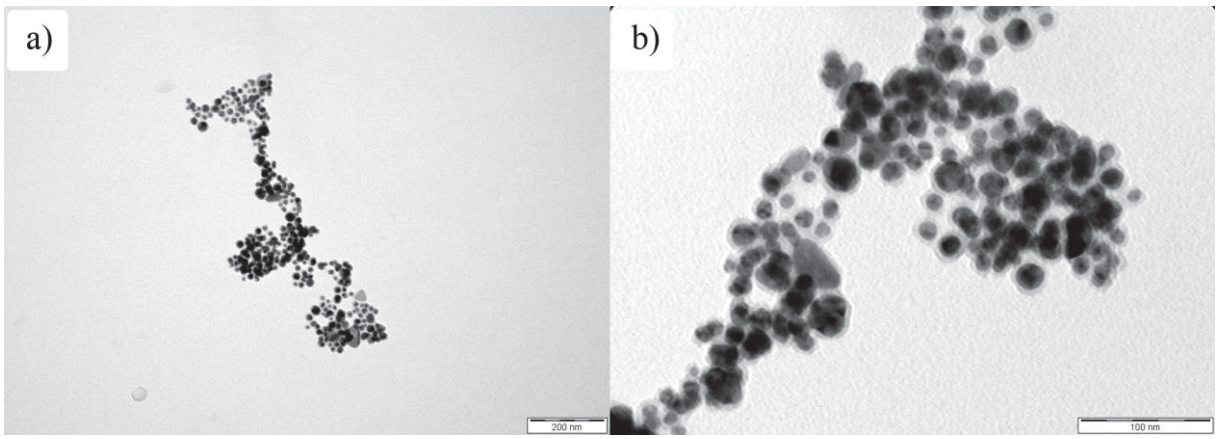
SI 12. TEM images of samples prepared with 1400 μL of: a, b) H_2O (Sample 9); c, d) 0.01 M $AgNO_3$ (Sample 10); e, f) 0.05 M $AgNO_3$ (Sample 11); g, h) 0.1 M $AgNO_3$ (Sample 12). Scale bar 500 nm (a, c, e, g) and 100 nm (b, d, f, h).



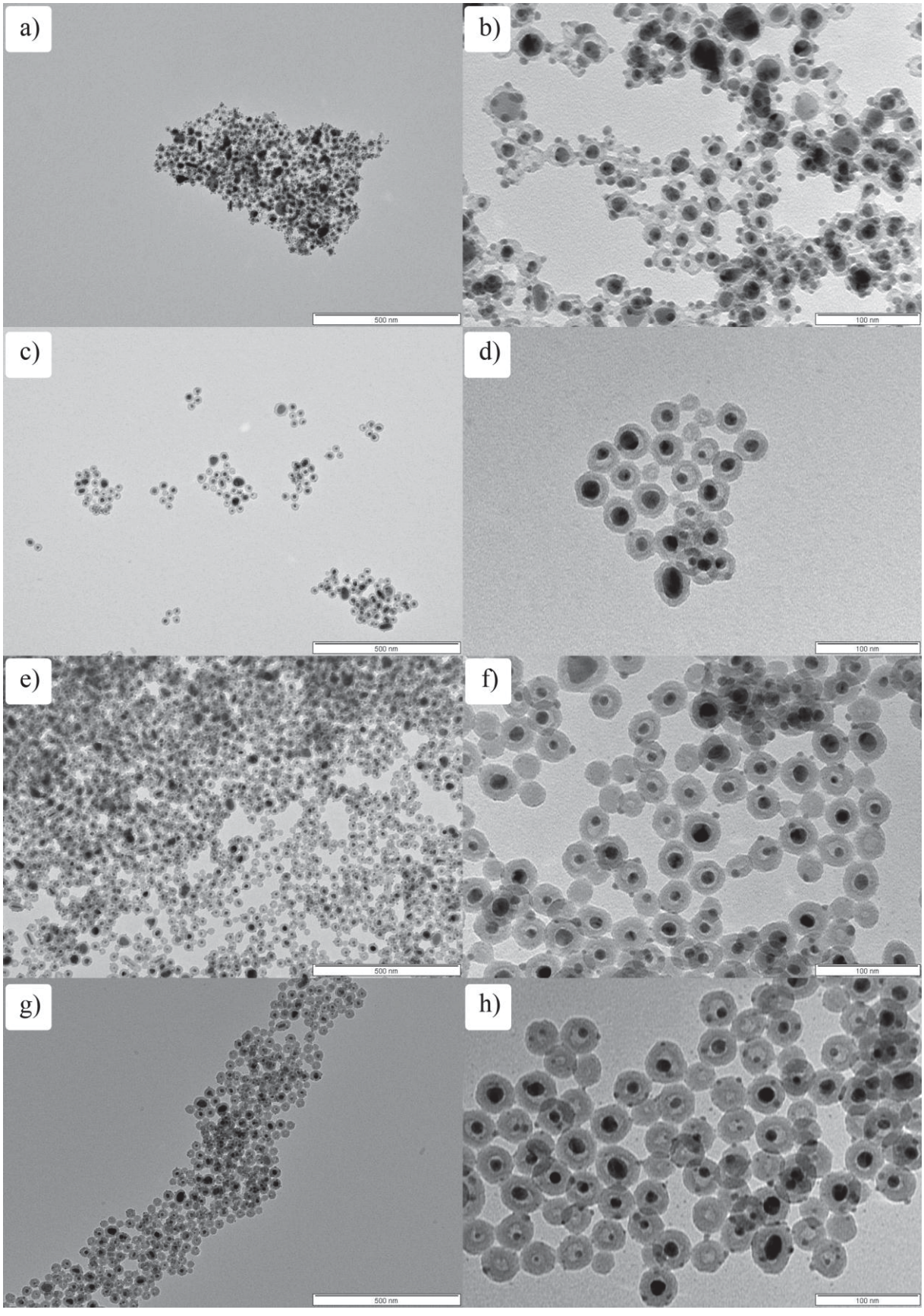
SI 13. TEM images of samples prepared with 1400 µL of: a, b) 0.2 M (Sample 13); c, d) 0.3 M (Sample 14); e, f) 0.5 M (Sample 15); g, h) 1 M $AgNO_3$ (Sample 16). Scale bar 500 nm (a, c, e, g) and 100 nm (b, d, f, h).



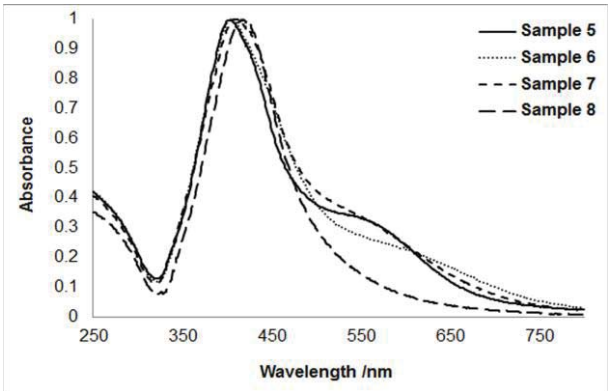
SI 14. TEM images of sample 17 prepared with 1400 µL of 1 M $AgNO_3$ and 250 µL of hydrazine. Scale bar 200 nm (a) and 100 nm (b).



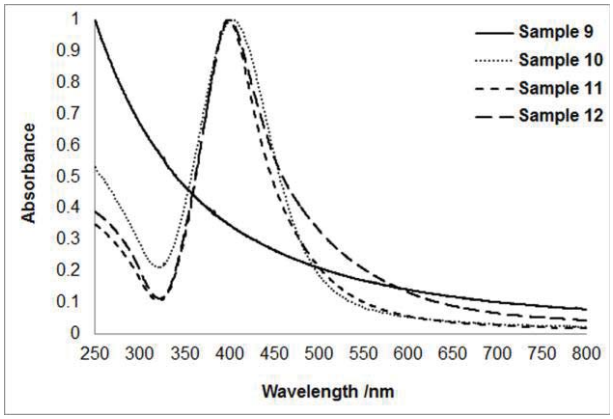
SI 15. TEM images of samples prepared with a, b) 100 µL (Sample 18); c, d) 200 µL (Sample 19); e, f) 300 µL (Sample 20); g, h) 400 µL (Sample 21) of TEOS. Scale bar 500 nm (a, c, e, g) and 100 nm (b, d, f, h).



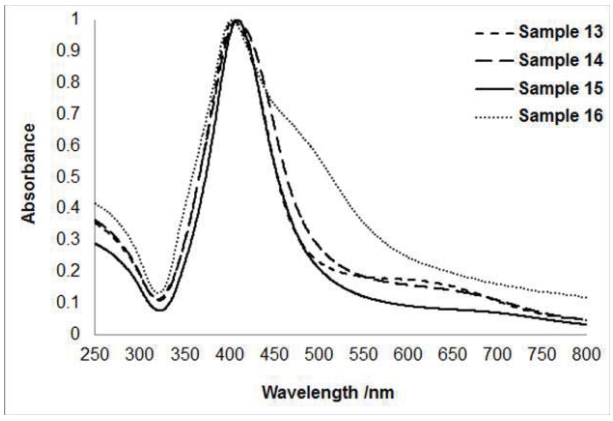
SI 16. UV-vis spectra of samples prepared with 1400 µL of 0.1 M $AgNO_3$ and 50 µL of 20 M (Sample 5), 10 M (Sample 6), 5 M (Sample 7), 1 M hydrazine (Sample 8). The spectra were normalized up to an absorbance = 1.



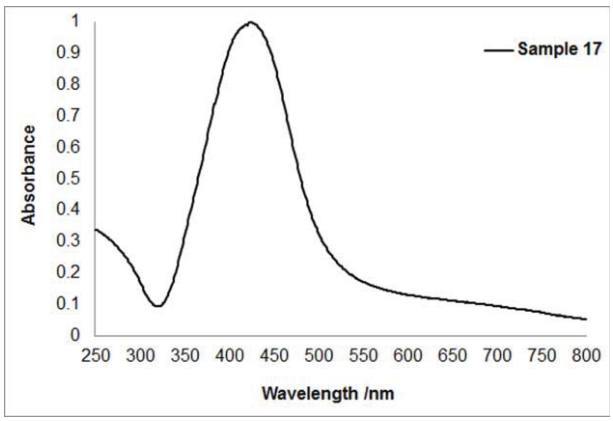
SI 17. UV-vis spectra of samples prepared with 1400 µL of H_2O (Sample 9), 0.01 M $AgNO_3$ (Sample 10), 0.05 M $AgNO_3$ (Sample 11), 0.1 M $AgNO_3$ (Sample 12). The spectra were normalized up to an absorbance = 1.



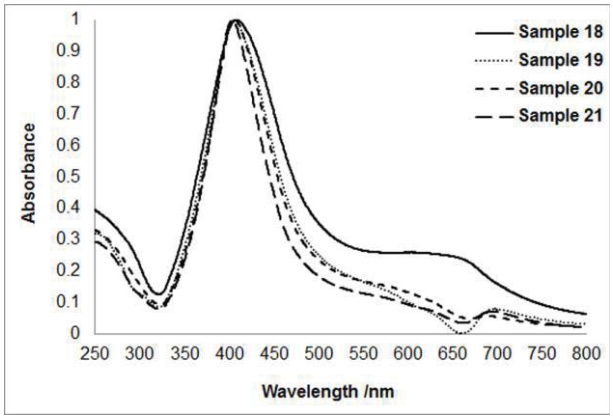
SI 18. UV-vis spectra of samples prepared with 1400 µL of 0.2 M $AgNO_3$ (Sample 13), 0.3 M $AgNO_3$ (Sample 14), 0.5 M $AgNO_3$ (Sample 15) and 1 M $AgNO_3$ (Sample 15). The spectra were normalized up to an absorbance = 1.



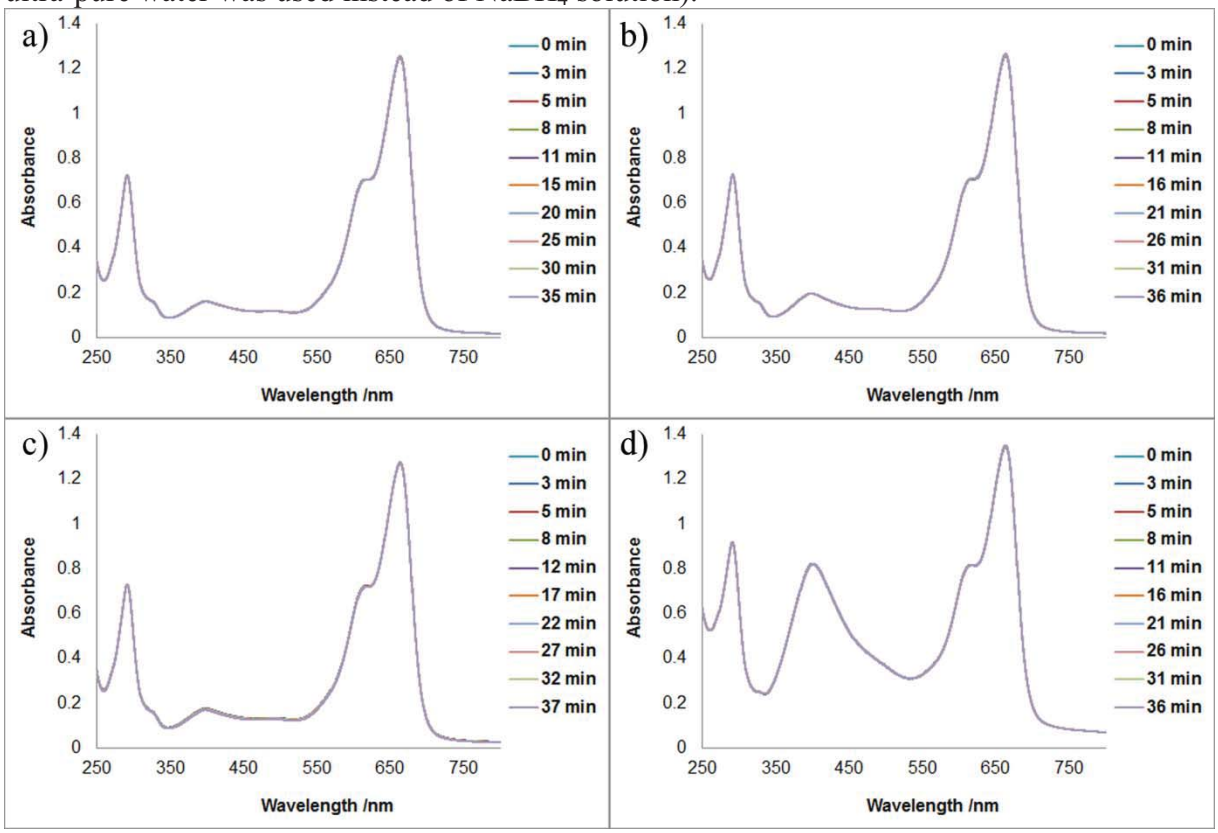
SI 19. UV-vis spectrum of Sample 17 prepared with 1400 µL of 1 M $AgNO_3$ and 250 µL hydrazine. The spectrum was normalized up to an absorbance = 1.



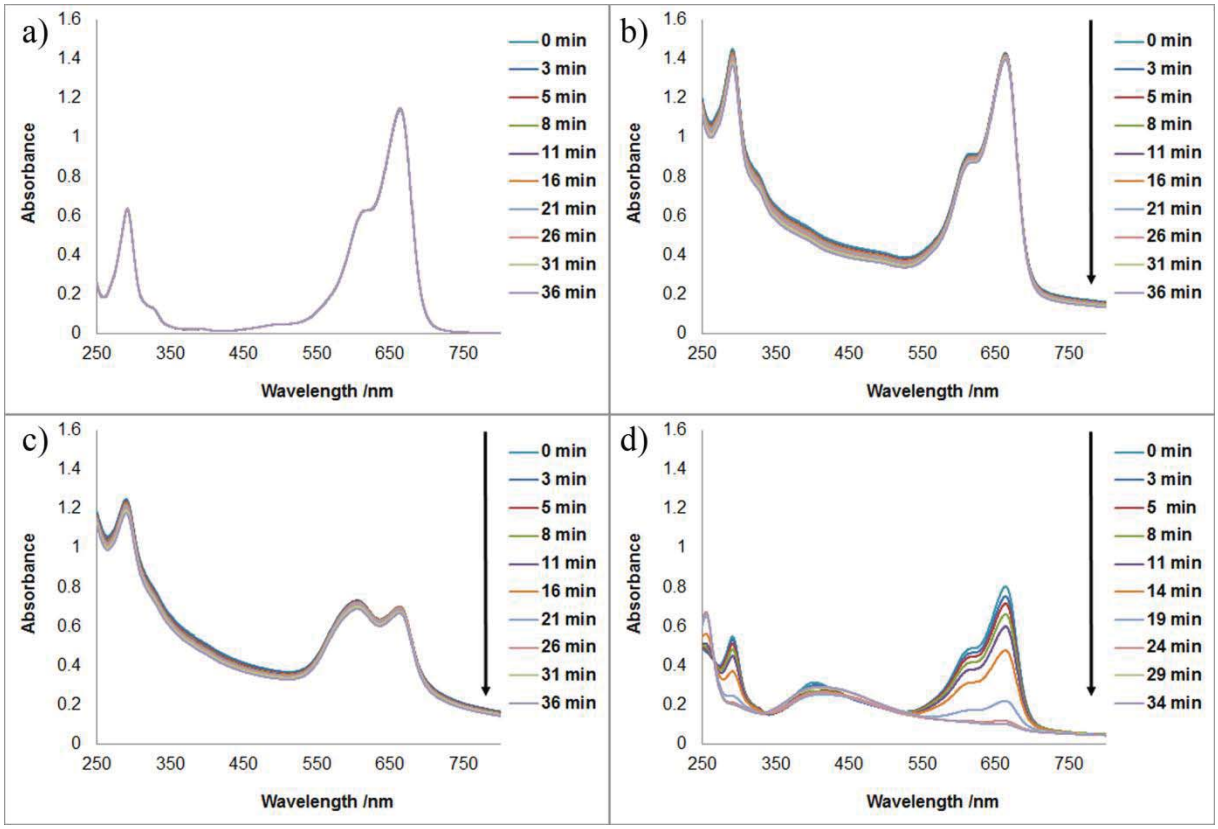
SI 20. UV-vis spectra of samples prepared with 100 µL (Sample 18), 200 µL (Sample 19), 300 µL (Sample 20) and 400 µL (Sample 21) of TEOS. The spectra were normalized up to an absorbance = 1.



SI 21. Time-resolved UV-vis spectra of methylene blue mixed with $Ag@SiO_2$ suspension (Sample 12) at concentration of silver a) 0.15 mM, b) 0.20 mM, c) 0.24 mM and d) 0.93 mM (prepared as explained in *Determination of catalytic properties* with the only difference that ultra-pure water was used instead of $NaBH_4$ solution).



SI 22. Time-resolved UV-vis spectra of 2 mL of methylene blue mixed with a) 200 µL of 9 mM $NaBH_4$ and 200 µL of ultra-pure water, b) 200 µL of 69 mM SiO_2 suspension (Sample 9, **Figure 3 a**) and 200 µL of ultra-pure water (no waiting for sedimentation of particles), c) 200 µL of 69 mM SiO_2 suspension (Sample 9, **Figure 3 a**) and 200 µL of 9 mM $NaBH_4$ (no waiting for sedimentation of particles), d) 200 µL of 9 mM $NaBH_4$ and 200 µL of Ag@SiO_2 suspension (after waiting for sedimentation of particles, Sample 12, **Figure 3 d**).
As shown in (**b**) and (**c**), addition of relatively concentrated SiO_2 hollow spheres shifts overall spectrum of methylene blue which adapts partially shape of SiO_2 alone (compare **SI 17, sample 9** for UV-vis spectrum of SiO_2 hollow spheres). In addition, during the measurement, all spectra are shifted downwards, probably due to agglomeration and sedimentation of NPs. Interestingly, a band with maximum of absorbance at λ_{max} = 663 nm in (**c**) decreases significantly compared to (**b**). However, a characteristic band of oxidized form of methylene blue, at λ_{max} = 255 nm, well visible in (**d**), does not occur neither in (**b**) nor in (**c**).



SI 23. X-ray diffractograms (XRPD) of a) SiO_2 (Sample 9) and $Ag@SiO_2$ prepared with b) 0.01 M (Sample 10), c) 0.05 M (Sample 11) and d) 0.1 M (Sample 12) $AgNO_3$. Insets: corresponding UV-vis spectra normalized to 1 (From **SI 17**).

Note that: SiO_2 nanocontainers are amorphous (**a**). At low concentration of AgNPs, their presence can be confirmed only by UV-vis spectrum. In XRPD they are invisible due to large background of silica (**b**).