Electronic Supplementary Material (ESI) for CrystEngComm.

On the complex role of ammonia in the electroless deposition of curved silver patches on silica nanospheres

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Electronic Supplementary Information

EDX (Energy Dispersion X-Ray Analysis) data normalization

In order to compare EDX data from different samples, we normalized the obtained values. First of all, we integrated the Ag count signal generated by silver patches of different morphologies for silica spheres of 140, 290 and 530 nm in diameter. Subsequently, with the help of SEM images we determined the area of interaction of the electron beam with each sample as well as the number of patchy particles generating the signal. As the count signal is inversely proportional to the first and directly proportional to the latter parameter, we performed a normalization step by multiplying the signal by the interaction area and dividing by the number of patchy particles. This procedure was applied to all given sample series, e.g. cup/dendritic-like patches on 140/290/530 nm silica spheres on at least 10 particles per type, in order to have a statistic. In this way we obtained the number of counts generated by a single cup or dendritic-like patch for every silica particle size. Finally, for each set of data we normalized the two corresponding values to their maximum. This procedure allowed us to figure out the ratio of silver contained in patches of different morphologies for a given silica particle size.

Table S1. Amounts and concentrations of reagents used to produce samples shown in Figures 1 and S1

Amine type	Amine final concentration (mM)	Water (µL)	Silica diameter (nm)	Silica (µl of 10 mg/ml dispersion)	1 mM $AgNO_3$ (µL)	CH_2O 37% (µL)	Amine stock Concentration (M)	Amine volume added (µL)
NH3	17	4775	140	15	150	30	2.83	30
MA	17	4775	140	15	150	30	2.83	30
DMA	17	4775	140	15	150	30	2.83	30
TMAH	17	4775	140	15	150	30	2.83	30
TEAH	17	4775	140	15	150	30	2.83	30

Table S2. Amounts and concentrations of reagents used to produce samples shown in Figure 2, Figure 6 (2nd row) and Figure S2

NH_3 final concentration (mM)	Water (µL)	Silica diameter (nm)	Silica (µl of 10 mg/ml dispersion)	1 mM $AgNO_3$ (µL)	CH_2O 37% (µL)	NH_3 stock Concentration (M)	NH_3 volume added (µL)
17	4775	140	15	150	30	2.83	30
10	4775	140	15	150	30	1.67	30
7.5	4775	140	15	150	30	1.25	30
5	4775	140	15	150	30	0.84	30
2.5	4775	140	15	150	30	0.42	30
1	4775	140	15	150	30	0.17	30

Table S3. Amounts and concentrations of reagents used to produce samples shown in Figure S3

NH_3 final concentration (mM)	Water (µL)	Silica diameter (nm)	Silica (µL of 10 mg/ml dispersion)	CH_2O 37% (µL)	Preparation of $[Ag(NH_3)_2]NO_3$ stock			Volume of $[Ag(NH_3)_2]NO_3$ stock added to reaction (µL)
					1 mM $AgNO_3$ (mL)	NH_3 stock Concentration (M)	NH_3 volume (µL)	
17	4805	140	15	30	1.5	17	50	150
10	4805	140	15	30	1.5	10	50	150
7.5	4805	140	15	30	1.5	7.5	50	150
5	4805	140	15	30	1.5	5	50	150
2.5	4805	140	15	30	1.5	2.5	50	150
1	4805	140	15	30	1.5	1	50	150

Table S4. Amounts and concentrations of reagents used to produce samples shown in Figure 3

Salt additive concen tration (mM)	Water (µL)	Silica diam-eter (nm)	Silica (µL of 10 mg/ml dispersion)	CH_2O 37% (µL)	1 mM $AgNO_3$ (µL)	10 mM salt solution (µL)	2.83M NH_3 (µL)
0.01	4770	140	15	30	150	5	30
0.1	4725	140	15	30	150	50	30
1	4275	140	15	30	150	500	30

Table S5. Amounts and concentrations of reagents used to produce samples shown in Figure 6 and Figures S7-S10. For data concerning silver patch growth on 140 nm diameter spheres see Table S2. *Amount of silica to add adjusted to provide roughly equivalent silica surface areas in all cases. [§]Due to an oversight in initial particle size determination, determination of the volume of silica dispersion to add was achieved using particle sizes of 70[§a], 250[§b], 400[§c] and 860[§d] nm. The correct particle sizes are shown in the table. We observed that this error effected the yield and size of the patches, but not the morphology, of primary concern in this work.

Silica di-ameter (nm)	NH_3 final con-centration (mM)	Water (µL)	Silica (µl of 10 mg/ml disper-sion)*	1 mM $AgNO_3$ (µL)	CH_2O 37% (µL)	NH_3 stock Con-centration (M)	NH_3 vol-ume add-ed (µL)
60[§a]	**17**	4775	15	150	30	2.83	30
60[§a]	**10**	4775	15	150	30	1.67	30
60[§a]	**7.5**	4775	15	150	30	1.25	30
60[§a]	**5**	4775	15	150	30	0.84	30
60[§a]	**2.5**	4775	15	150	30	0.42	30
60[§a]	**1**	4775	15	150	30	0.17	30
290[§b]	**17**	4763	27	150	30	2.83	30
290[§b]	**10**	4763	27	150	30	1.67	30
290[§b]	**7.5**	4763	27	150	30	1.25	30
290[§b]	**5**	4763	27	150	30	0.84	30
290[§b]	**2.5**	4763	27	150	30	0.42	30
290[§b]	**1**	4763	27	150	30	0.17	30
530[§c]	**17**	4748	42	150	30	2.83	30
530[§c]	**10**	4748	42	150	30	1.67	30
530[§c]	**7.5**	4748	42	150	30	1.25	30
530[§c]	**5**	4748	42	150	30	0.84	30
530[§c]	**2.5**	4748	42	150	30	0.42	30
530[§c]	**1**	4748	42	150	30	0.17	30
900[§d]	**17**	4698	92	150	30	2.83	30
900[§d]	**10**	4698	92	150	30	1.67	30
900[§d]	**7.5**	4698	92	150	30	1.25	30
900[§d]	**5**	4698	92	150	30	0.84	30
900[§d]	**2.5**	4698	92	150	30	0.42	30
900[§d]	**1**	4698	92	150	30	0.17	30

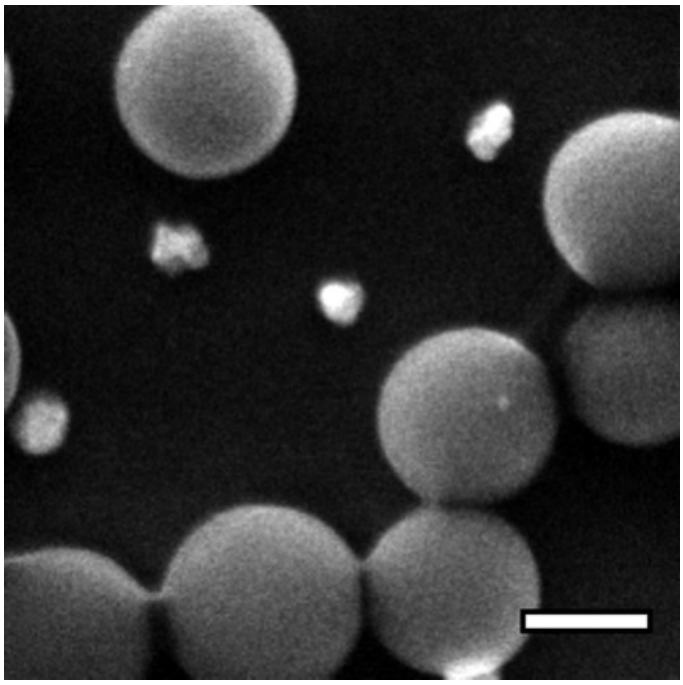

Figure S1. SEM micrographs of the products of attempt to produce silver patches on 140 nm diameter silica spheres using the standard procedure with tetraethylammonium hydroxide (TEAH) as base (concentration of 17 mM). Scale bar corresponds to 100 nm.

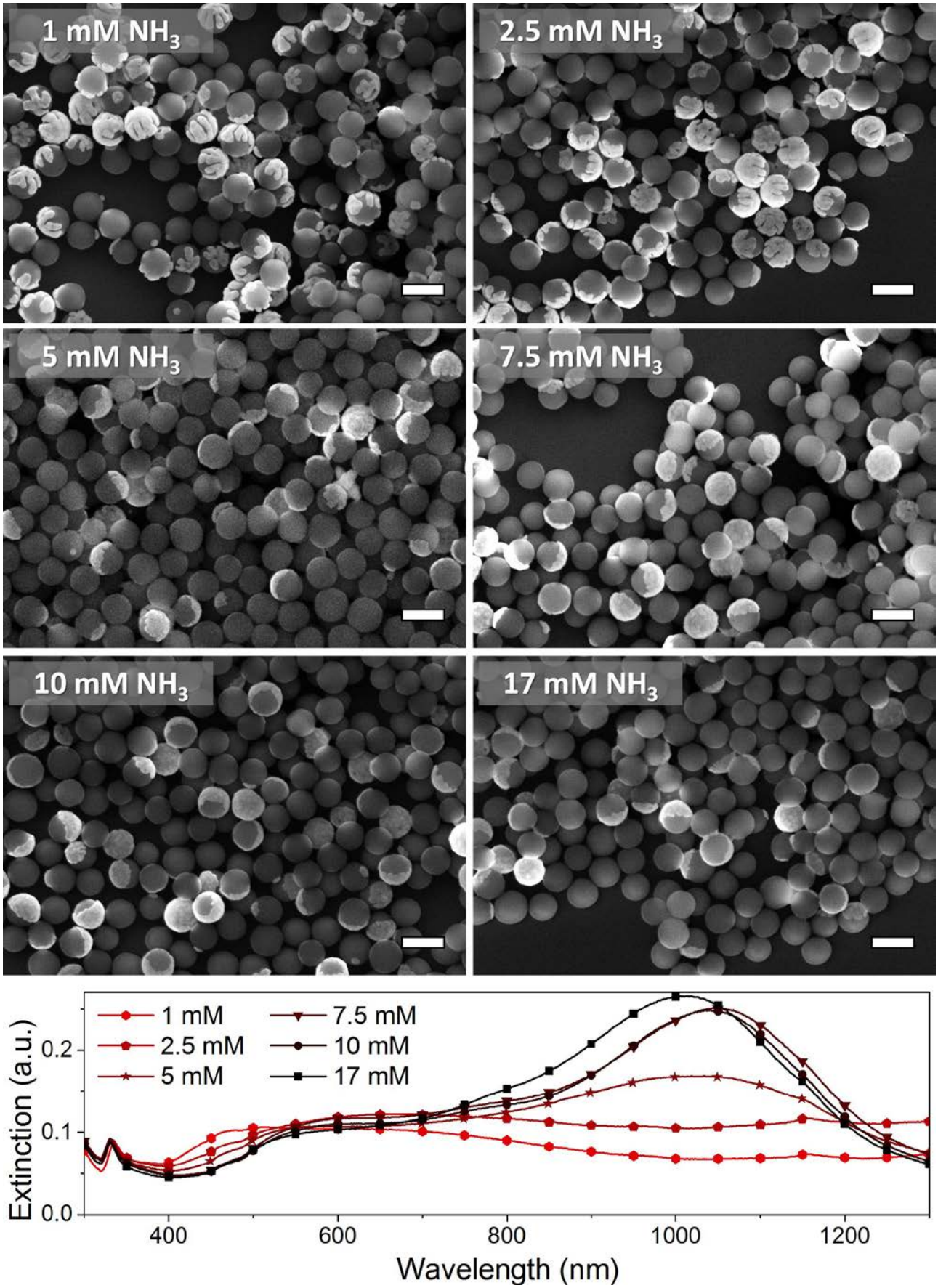

Figure S2. SEM micrographs (top) and extinction spectra (bottom) of silver patches produced on 140 nm diameter silica spheres according to the standard procedure using various concentrations of ammonia. Scale bars correspond to 200 nm.

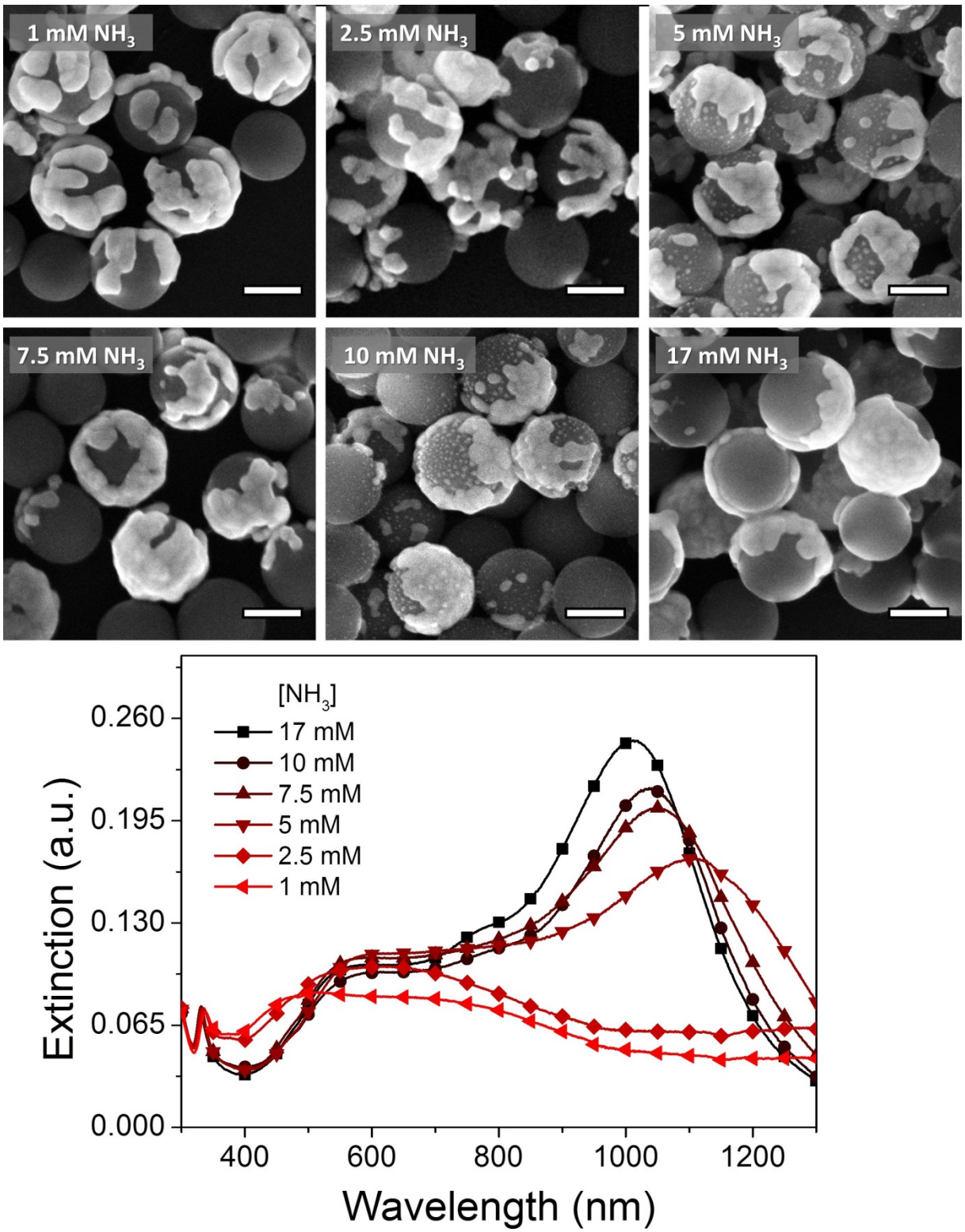

Figure S3 SEM micrographs (top) and extinction spectra (bottom) of silver patches produced on 140 nm diameter silica spheres according to the modified procedure whereby ammoniacal silver nitrate solution was added to a suspension of silica and formaldehyde. Scale bars correspond to 100 nm. Note that the appearance of holes and small (<10 nm) silver nanoparticles in the samples is a result of aging effects due to storage of the SEM samples in a humid environment prior to observation.

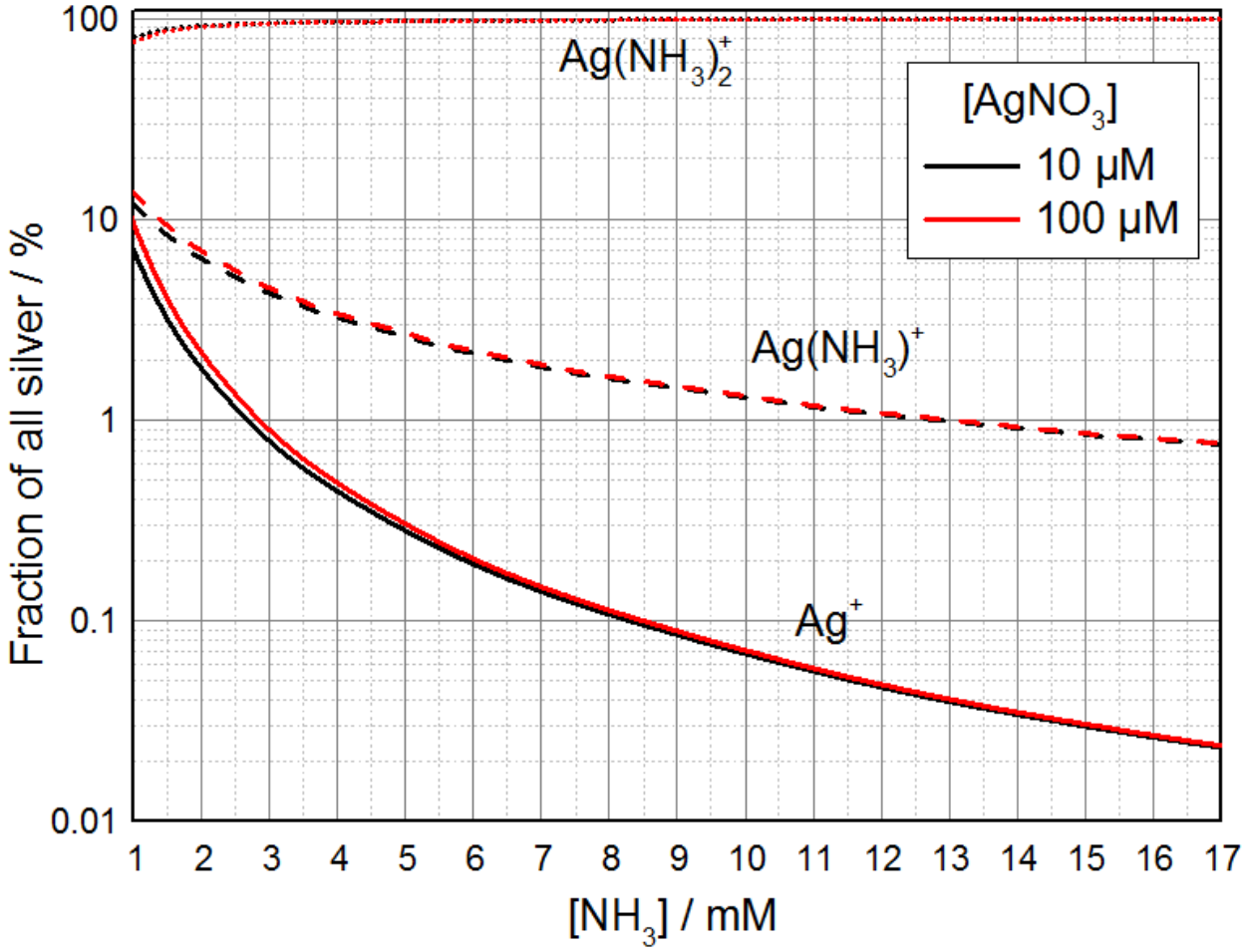

Figure S4 Equilibrium speciation of silver at two different silver nitrate concentrations and for the range of ammonia concentrations used in this work.

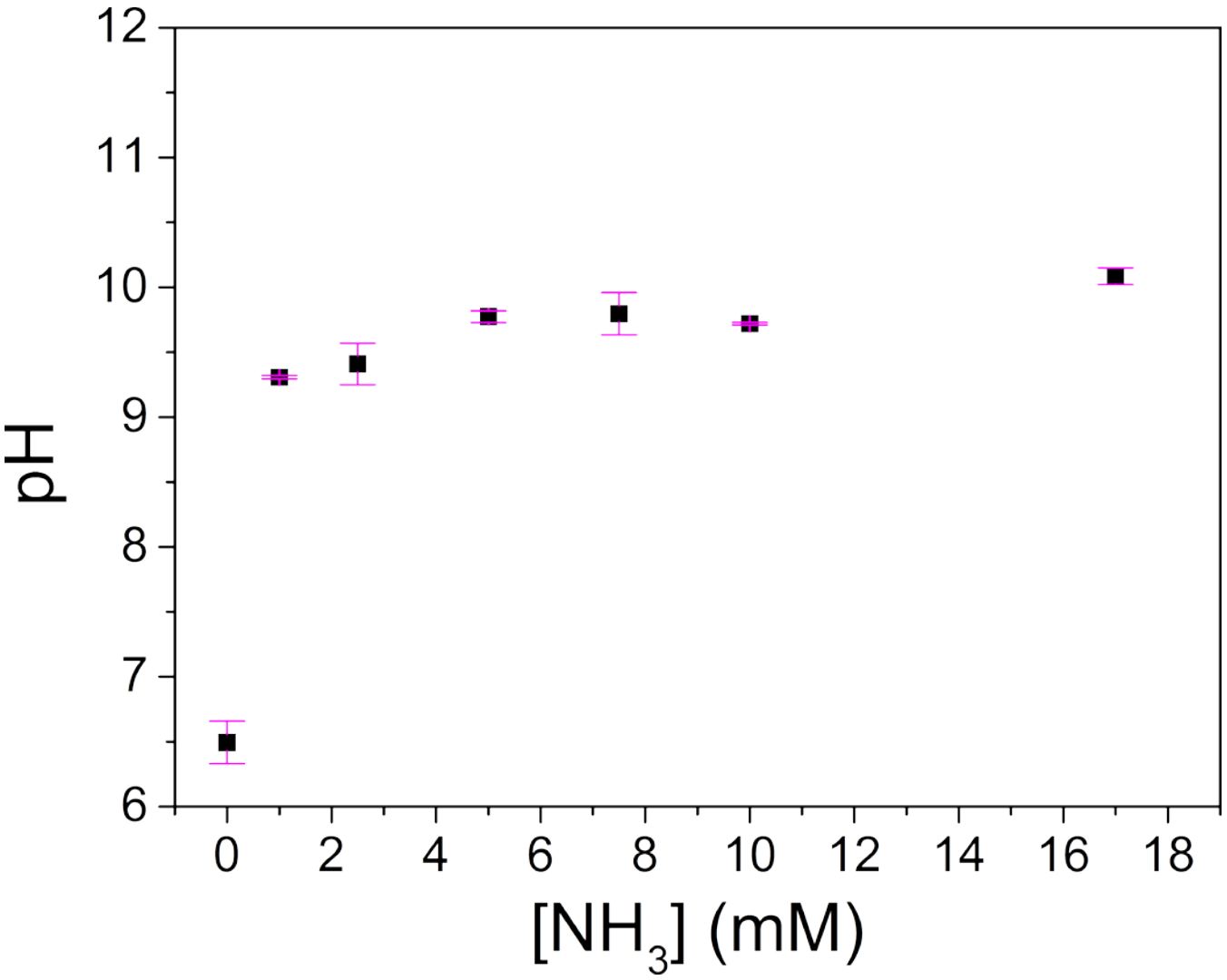

Figure S5 Variation of pH with concentration of ammonia according to the values used in this study.

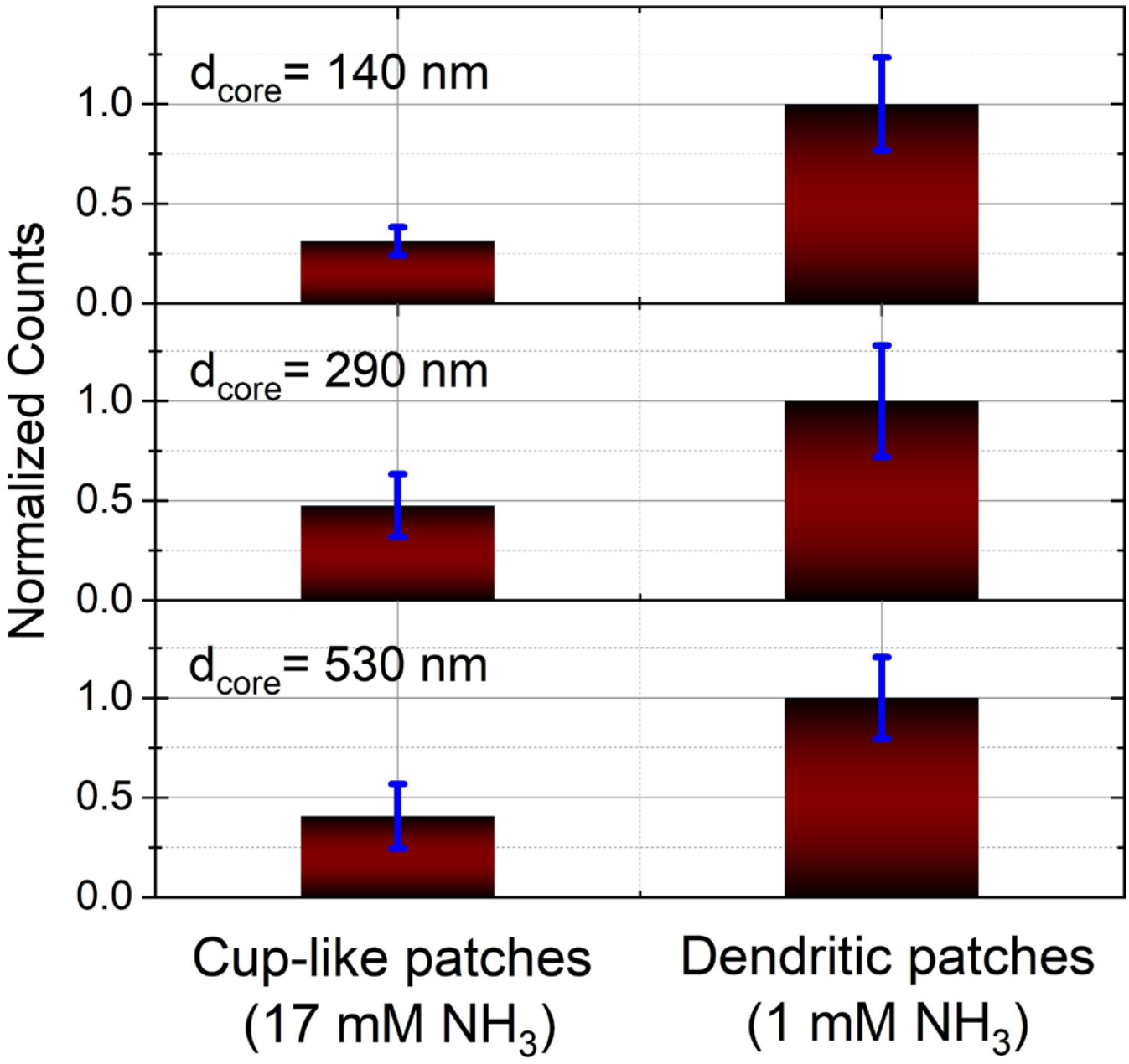

Figure S6 Result of EDX analysis of silver patches on three different sizes of silica sphere produced according to the standard procedure using two ammonia concentrations. See above for details of the analysis procedure.

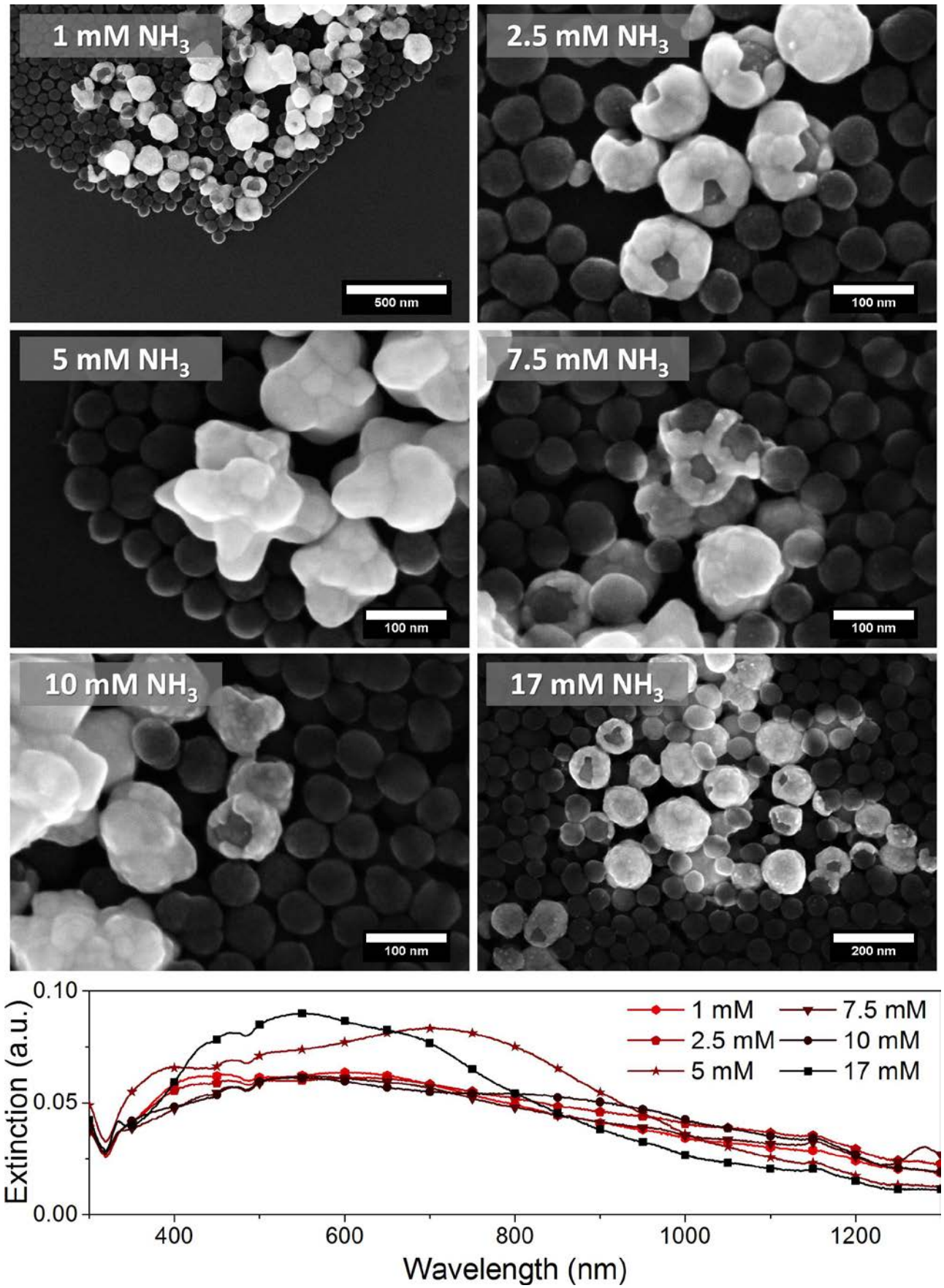

Figure S7. SEM micrographs (top) and extinction spectra (bottom) of silver patches produced on 60 nm diameter silica spheres according to the standard procedure using various concentrations of ammonia.

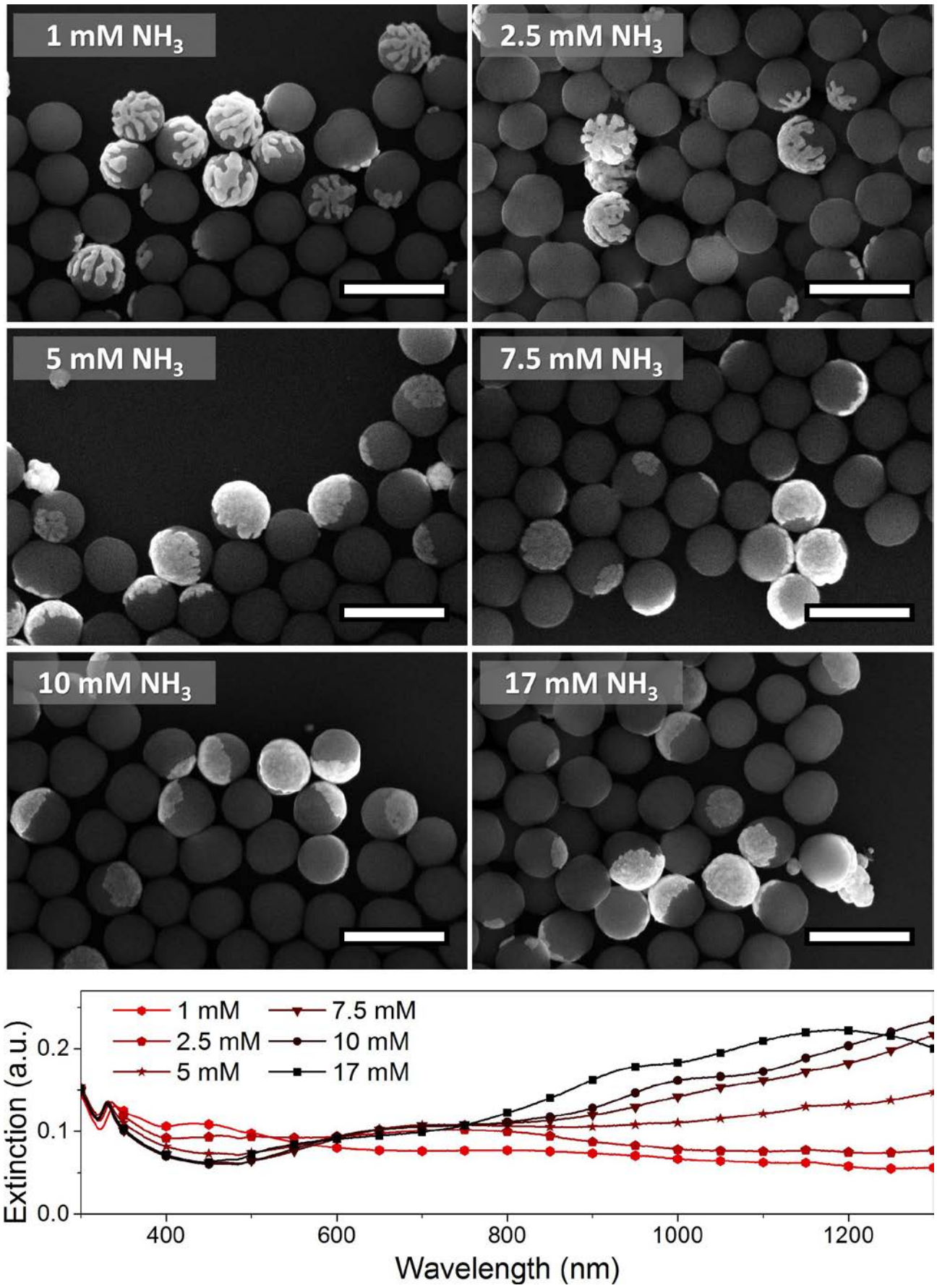

Figure S8. SEM micrographs (top) and extinction spectra (bottom) of silver patches produced on 290 nm diameter silica spheres according to the standard procedure using various concentrations of ammonia. Scale bars correspond to 500 nm.

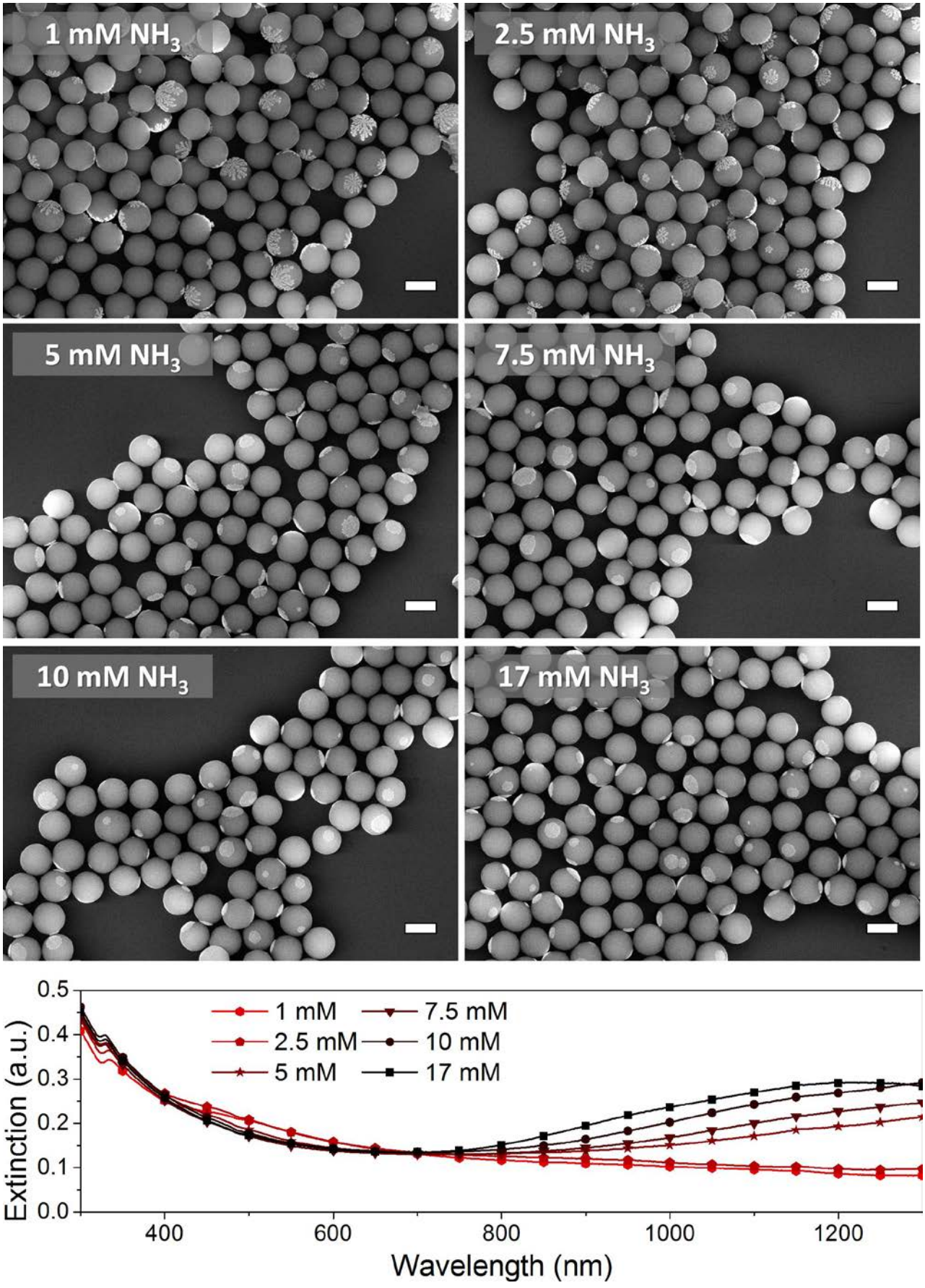

Figure S9. SEM micrographs (top) and extinction spectra (bottom) of silver patches produced on 530 nm diameter silica spheres according to the standard procedure using various concentrations of ammonia. Scale bars correspond to 500 nm.

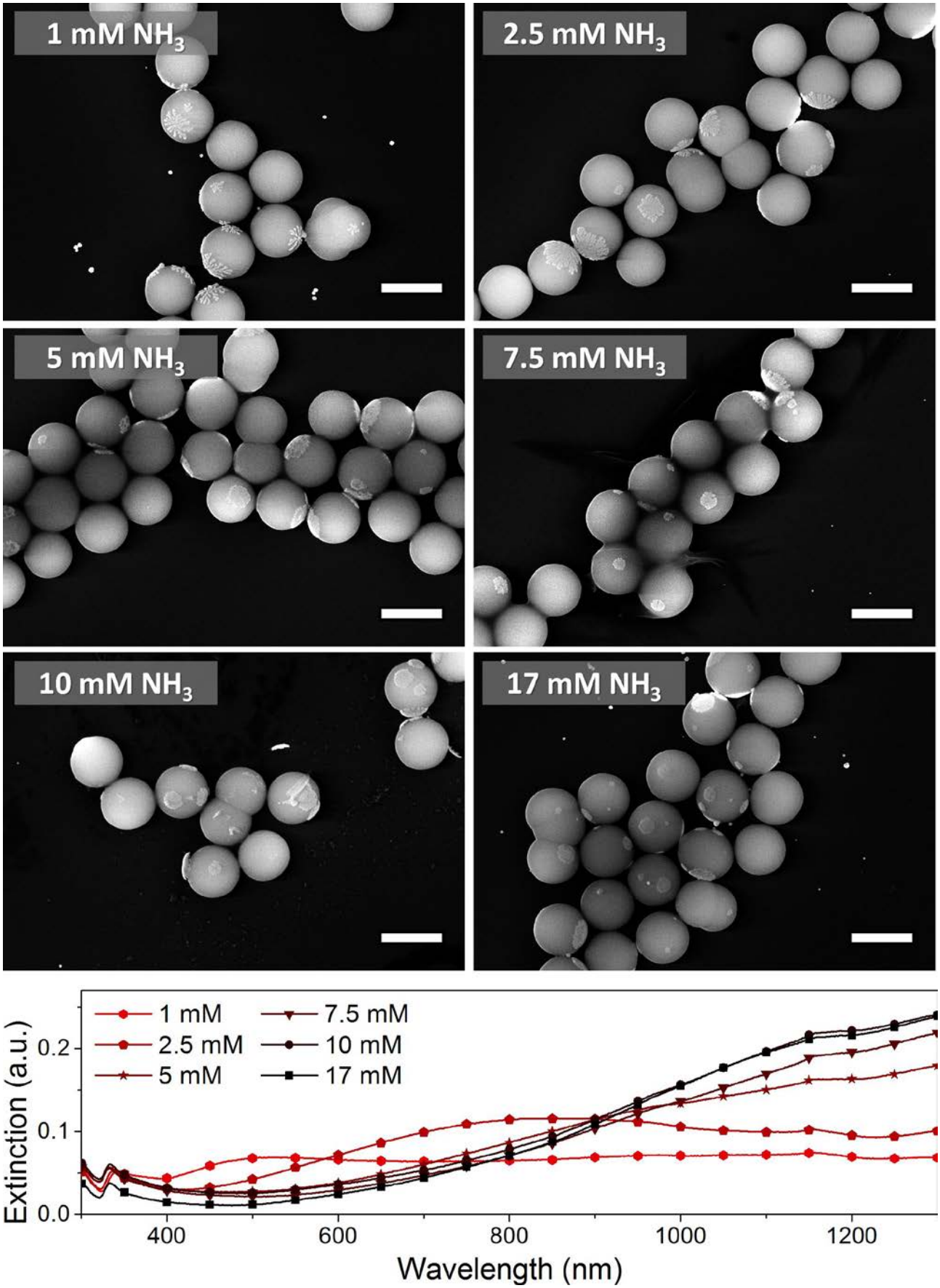

Figure S10. SEM micrographs (top) and extinction spectra (bottom) of silver patches produced on 900 nm diameter silica spheres according to the standard procedure using various concentrations of ammonia. Scale bars correspond to 1000 nm.