Facile colloidal coating of polystyrene nanospheres with tunable gold dendritic patches

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ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Supplementary experimental details:

Synthesis of anionic polystyrene nanospheres

The anionic polystyrene particles used for attempts to coated with gold (see Fig. S7) were synthesized by batch emulsion and polymerization of styrene as previously reported.[*] A mixture of sodium dodecyl sulfate (0.07g) and sodium bicarbonate (0.12g) in 136mL water was filled into a 250mL round bottom flask with nitrogen flow, and another mixture of styrene (20 wt%) and hexadecane (3.5 wt%) was added to the reactor under stirring. The content was deoxygenated with nitrogen flow for 1 hour. After the temperature was increased to 75 °C, potassium persulfate (0.21g) was added to start the polymerization process. After a reaction time of 6 hours, the mixture was cooled down and the particles were separated from the mother solution and washed with water by centrifugation and re-dispersion using ultrasonic agitation. The final suspension has a concentration of 16wt% with the mean particle diameter approximately 380nm.

Preparation of 3-aminopropyltrimethoxysilane (APTMS) functionalized silica particles

The functionalization of silica particles were carried out by the following procedure, 70 μL of APTMS was added to 20 mL silica suspension by dispersing silica particles into pure ethanol at the concentration of 20 mg/mL, the mixture was heated and kept boiling for 4 hours. After that silica particles were separated by centrifugation and washed first with ethanol and water. The final concentration was 20 mg/mL. The zeta potential of particles in 10mM potassium chloride reversed from negative to positive, indicating the binding of APTMS to silica surface.

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[*] N. Joumaa, M. Lansalot, A. Théretz, A. Elaissari, A. Sukhanova, M. Artemyev, I. Nabiev and J. H. M. Cohen, *Langmuir,* 2006, **22**, 1810.

Table S1 Experimental parameters used for the synthesis of all samples (on homemade PS) in figures in the main text

Figure	Ascorbic acid		Chloroauric acid		Molar ratio of AA : Au	PS	Temp	pH	
	C (mM)	V (mL)	C (mM)	V (μL)		V (μL)	°C	Value	adjustment
1	Influence of ascorbic acid concentration (ascorbic acid added last)								
(a)	500	0.05	0.15	5000	33.33	20	RT	-	pH not adjusted
(b)	500	0.005	0.15	5000	3.33	20	RT	-	
(c)	100	0.0125	0.15	5000	1.67	20	RT	-	
(d)	100	0.006	0.15	5000	0.83	20	RT	-	
2/3/4	Influence of ascorbic acid concentration (chloroauric acid added last)								
	100	5	25	30	666.67	20	RT	2.36	pH not adjusted
	10	5	25	30	66.67	20	RT	2.92	
	5	5	25	30	33.33	20	RT	3.11	
	2.5	5	25	30	16.67	20	RT	3.28	
	1	5	25	30	6.67	20	RT	3.49	
	0.5	5	25	30	3.33	20	RT	3.75	
	0.25	5	25	30	1.67	20	RT	4.04	
	0.1	5	25	30	0.67	20	RT	4.45	
	0.05	5	25	30	0.33	20	RT	8.40	
5	Influence of reaction temperature (high ascorbic acid concentration)								
	100	5	25	30	666.67	20	30°C	-	pH not adjusted
	100	5	25	30	666.67	20	40°C	-	
	100	5	25	30	666.67	20	50°C	-	
	100	5	25	30	666.67	20	60°C	-	
6	Comparison with simulation – conditions correspond to Figures 2 and 5								
7	Influence of pH								
	100	5	25	30	666.67	20	RT	2.36	Not adjusted
	100	5	25	30	666.67	20	RT	5.32	NaOH
	100	5	25	30	666.67	20	RT	10.27	NaOH
	1	5	25	30	6.67	20	RT	2.37	HCl
	1	5	25	30	6.67	20	RT	5.08	NaOH
	1	5	25	30	6.67	20	RT	10.43	NaOH
	0.5	5	25	30	3.33	20	RT	2.41	HCl
	0.5	5	25	30	3.33	20	RT	5.30	NaOH
	0.5	5	25	30	3.33	20	RT	10.27	NaOH

Table S2 Experimental parameters used for the synthesis of samples (on homemade PS) in figures in the ESI

Figure	Ascorbic acid		Chloroauric acid		Molar ratio of AA : Au	PS	Temp	pH	
	C (mM)	V (mL)	C (mM)	V (μL)		V (μL)	°C	Value	adjustment
S1	Influence of reducing agent								
	Formaldehyde								
(a)	37%	0.05	0.15	5	-	20	RT	-	pH not adjusted
	Sodium borohydride								
(b)	100	0.01	0.15	5	-	20	RT	-	pH not adjusted
	Hydroxylamine chloride								
(c)	40	0.5	0.15	5	-	20	RT	-	pH not adjusted
	Sodium citrate								pH not adjusted
(d)	100	5	25	30	-	20	RT	-	
(e)	50	5	25	30	-	20	RT	-	
(f)	10	5	25	30	-	20	RT	-	
S2	Influence of ascorbic acid concentration (chloroauric acid added last) – See Figure 2								
S3	PS amount								
(a)	0.5	5	25	30	3.33	5	RT	-	pH not adjusted
(b)	0.5	5	25	30	3.33	10	RT	-	
(c)	0.5	5	25	30	3.33	15	RT	-	
(d)	0.5	5	25	30	3.33	20	RT	-	
S4	Influence of reaction temperature (low ascorbic acid concentration)								
(a)	0.5	5	25	30	3.33	20	RT	-	pH not adjusted
(b)	0.5	5	25	30	3.33	20	50	-	
S5	Variation of patch coverage								
(a)	2.5	5	250	30	3.33	20	RT	-	pH not adjusted
(b)	100	5	25	50	400	10	RT	-	
S7	Use of anionic PS nanospheres as core particles								
(a)	100	5	25	30	666.67	20	RT	-	pH not adjusted
(b)	100	5	25	30	666.67	15	RT	-	
(c)	100	5	25	30	666.67	10	RT	-	

Table S3 Experimental parameters used for the synthesis of the samples with PS-NH$_2$ and Silica-NH$_2$ core particles in Figure S10 in the ESI

Figure	Ascorbic acid		Chloroauric acid		Molar ratio of AA : Au	PS		Temp	pH	
	C (mM)	V (mL)	C (mM)	V (µL)		C (mg/mL)	V (µL)	°C	Value	adjustment
S10	PS-NH2 (500 nm in diameter)									
(a)	100	5	25	30	666.67	50	5	RT	-	Not adjusted
	SiO_2-NH_2 (450 nm in diameter)									
(b)	0.5	5	25	30	3.33	20	15	RT	-	Not adjusted

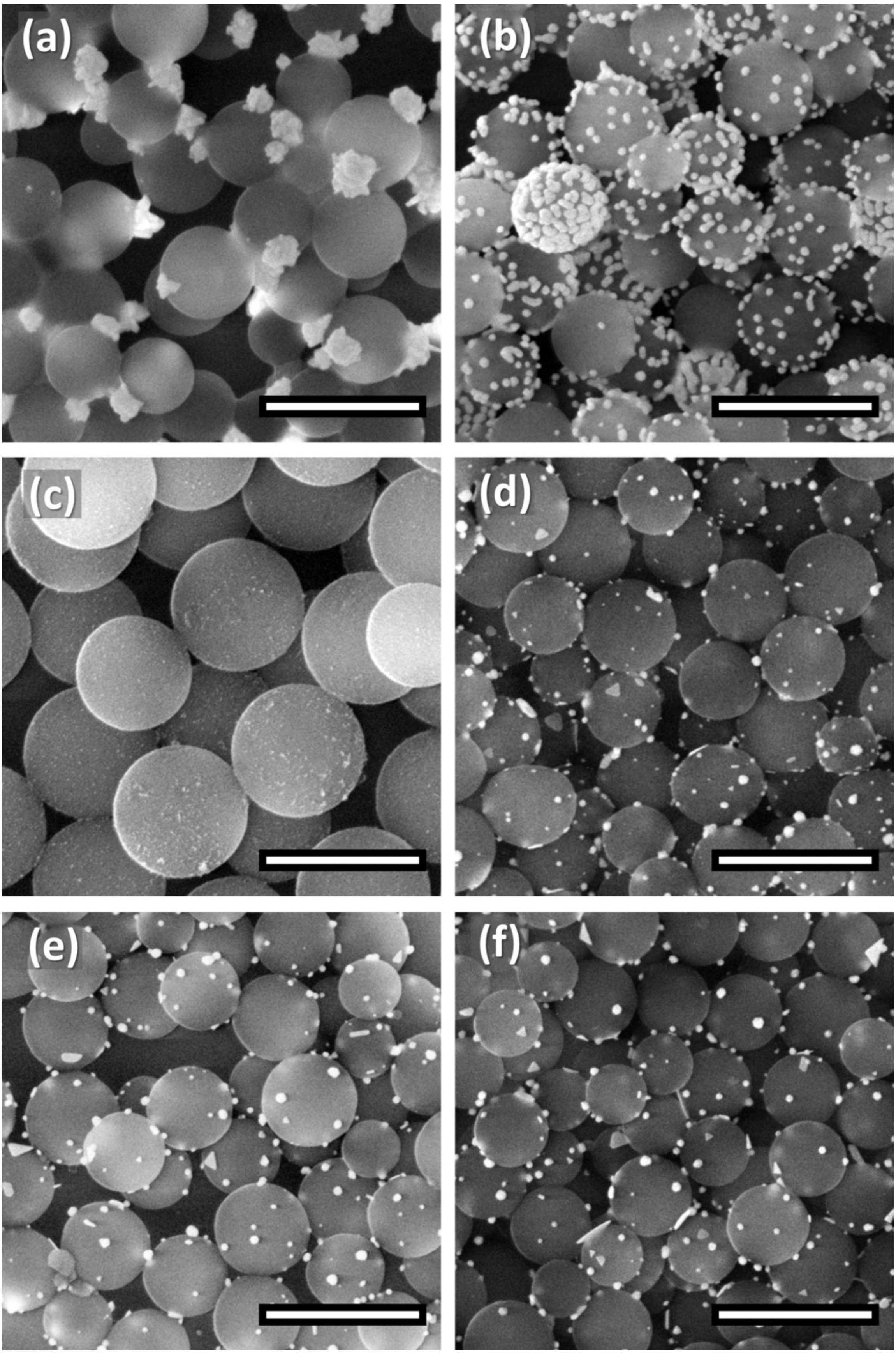

Fig. S1 SEM images of the result of mixing cationic PS nanospheres suspension with chloroauric acid and adding various reducing agents: (a) formaldehyde, (b) hydroxylamine, (c) sodium borohydride, (d) 0.1M, (e) 0.05M and (f) 0.01M sodium citrate. Scalebars correspond to 500 nm.

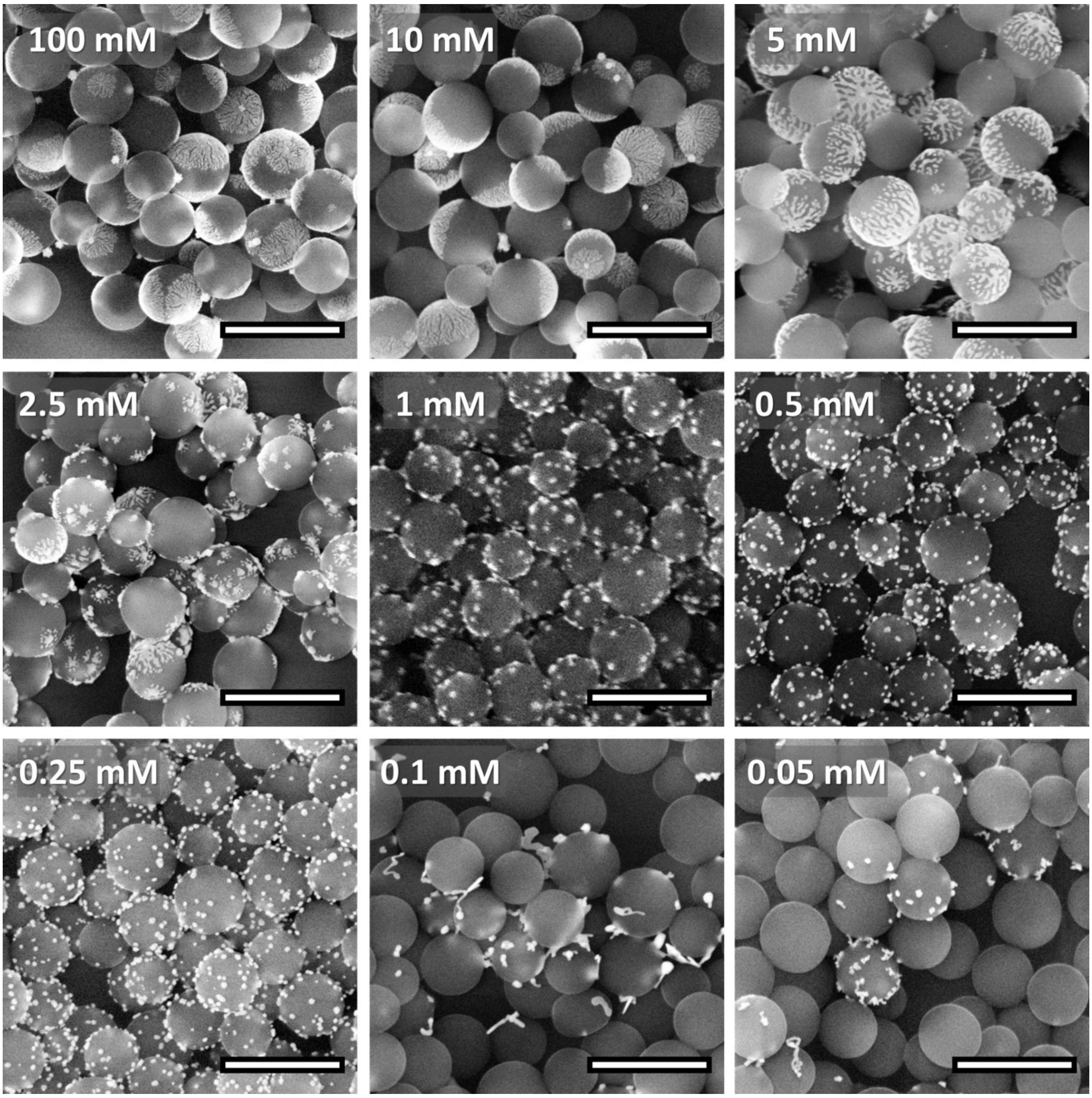

Fig. S2 SEM images of gold nanostructure-decorated cores formed by mixing the same amount of cationic PS nanospheres with different concentrations of ascorbic acid followed by addition of the same amount of chloroauric acid. This figure shows wider areas of the same samples shown in Fig. 2 in the article. Scalebars correspond to 500 nm.

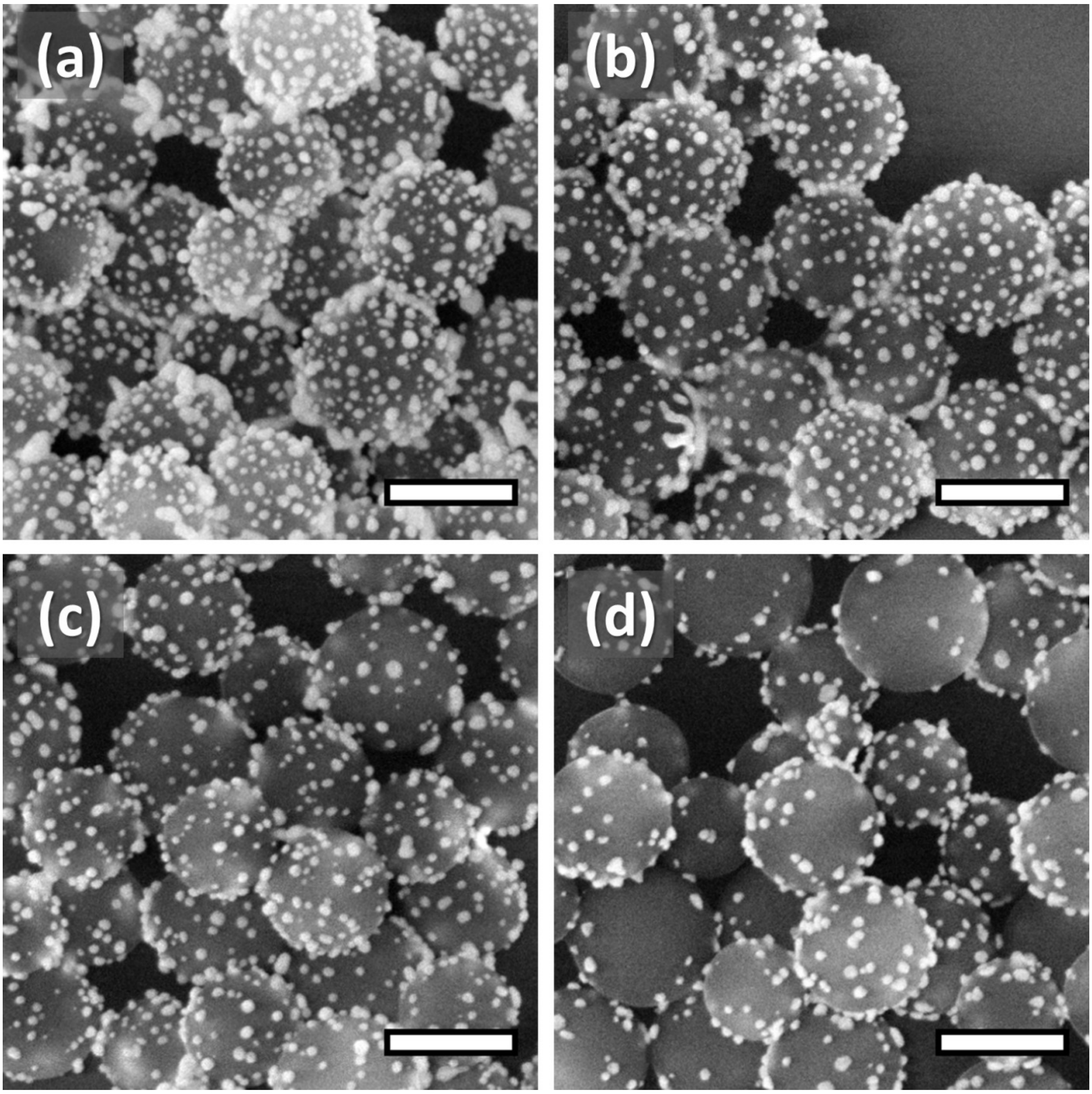

Fig. S3 SEM image of the result of mixing (a) 5 μL, (b) 10 μL, (c) 15 μL and (d) 20 μL of cationic PS nanospheres suspension with ascorbic acid solution and adding chloroauric acid. Scalebars correspond to 250 nm.

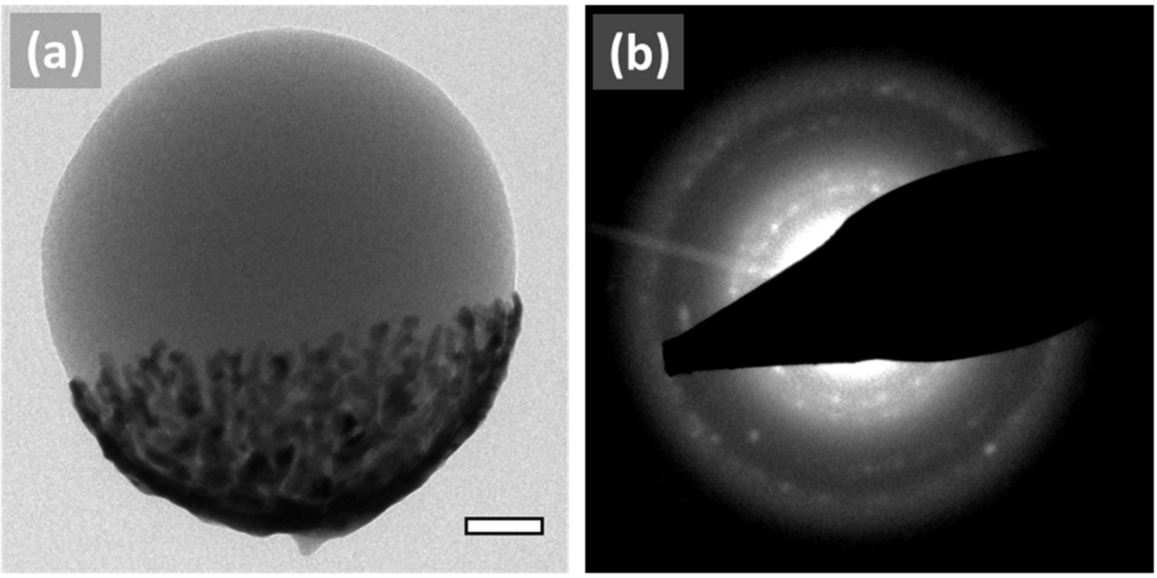

Fig. S4 (a) TEM image of a PS spheres with a dendritic gold patch and (b) its corresponding electron diffraction pattern which indicates the polycrystallinity of the gold patch.

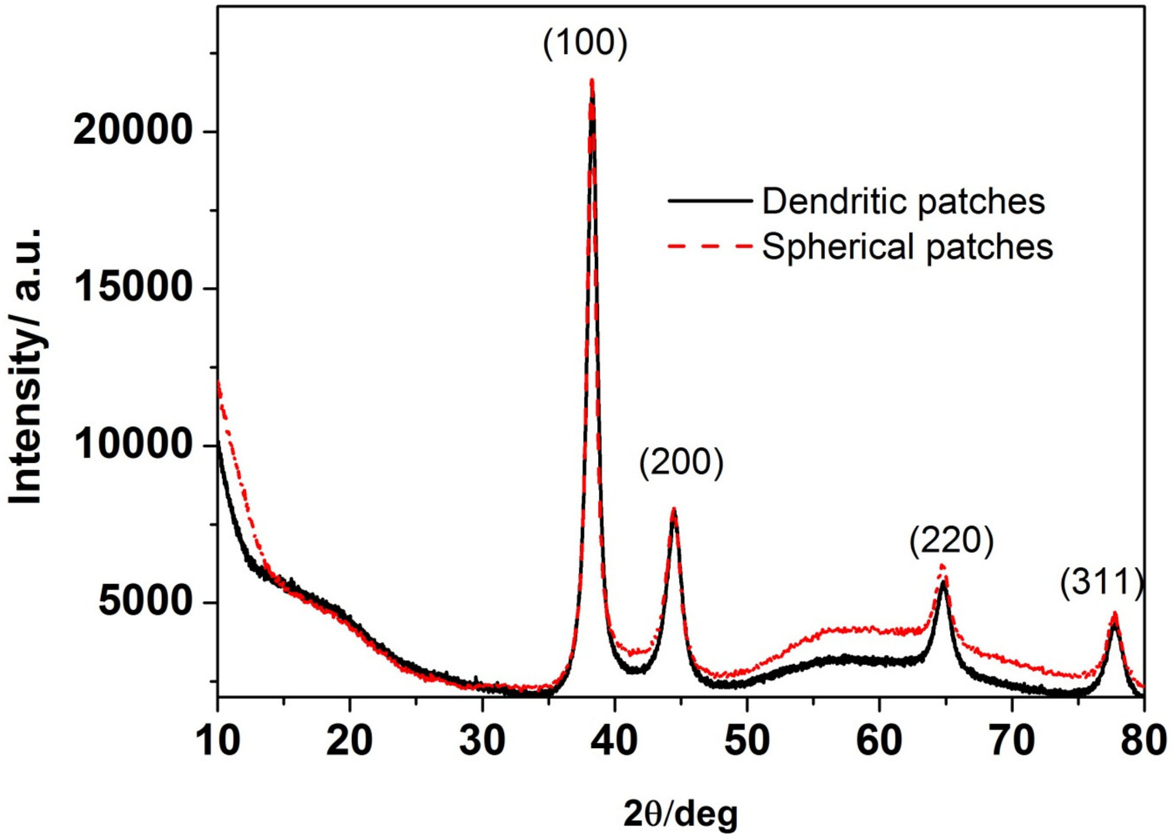

Fig. S5 Indexed XRD pattern of gold patches formed by addition the equal amount of chloroauric acid to the mixture of cationic PS nanospheres and ascorbic acid with the concentration of 100 mM (dendritric patches) and 0.5 mM (spheroidal patches). The features at around 20° and 60° are due to the amorphous background of polystyrene.

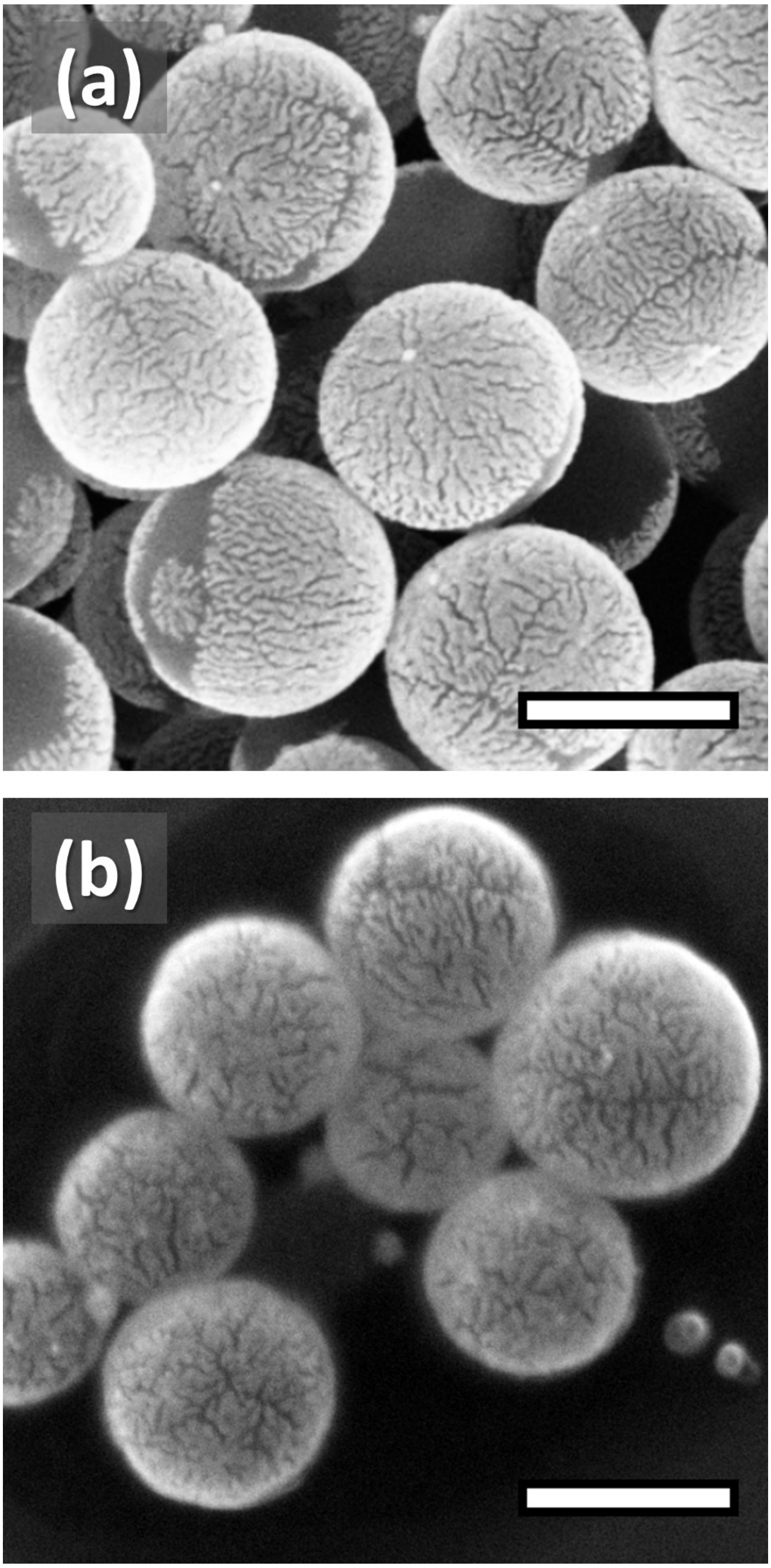

Fig. S6 SEM images of gold patchy particles with almost complete patch coverages formed by (a) increasing the amount of gold added, and (b) reducing the amount of core particles added. Scalebars correspond to 250 nm. SEM images of gold nanostructure-decorated cores formed by mixing the same amount of cationic PS nanospheres in 0.5 mM ascorbic acid followed by addition of the same amount of chloroauric acid. This reaction was carried out at the different temperatures shown. Scalebars correspond to 200 nm.

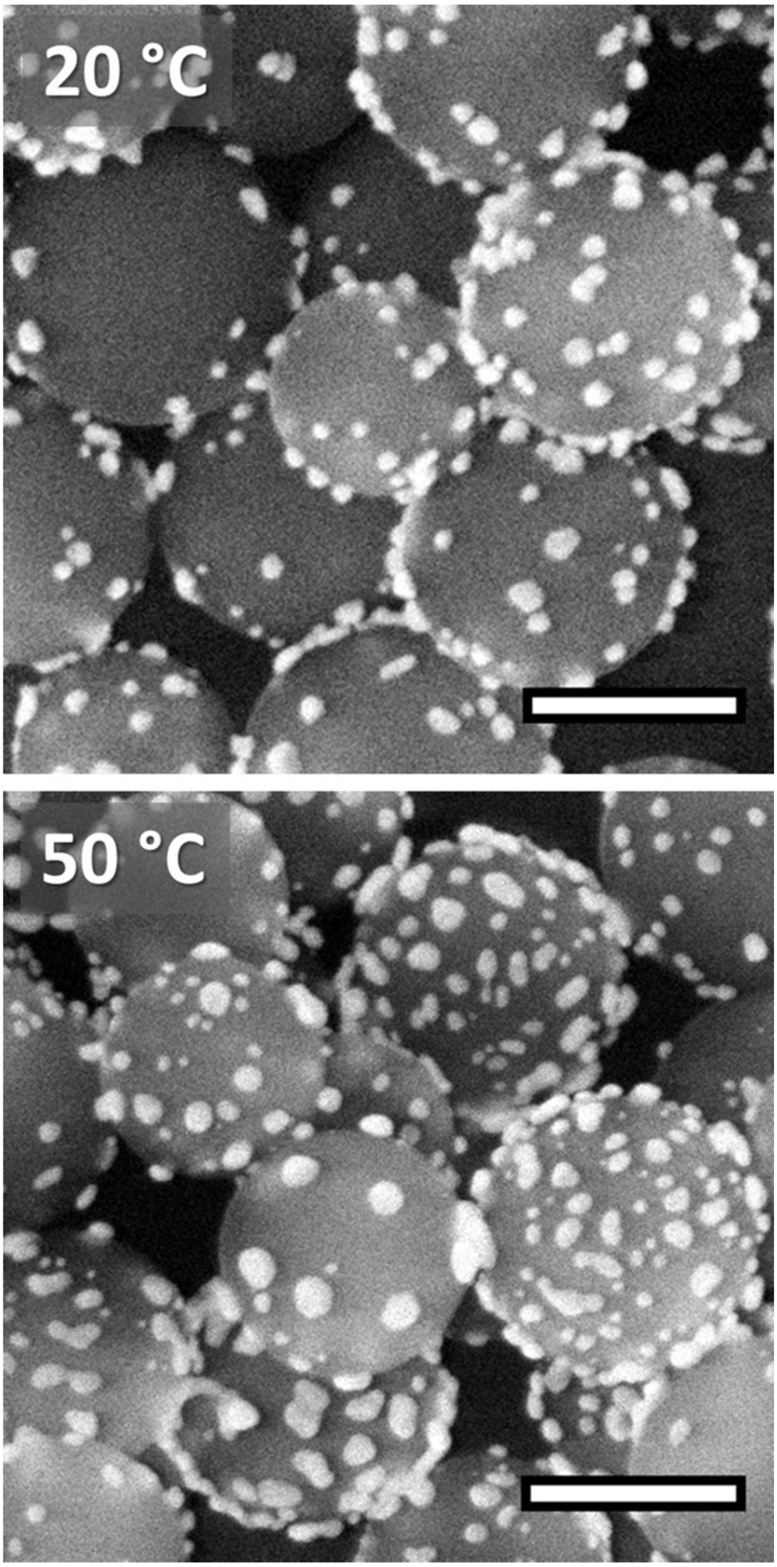

Fig. S7 SEM images of gold nanostructure-decorated cores formed by mixing the same amount of cationic PS nanospheres in 0.5 mM ascorbic acid followed by addition of the same amount of chloroauric acid. This reaction was carried out at the different temperatures shown. Scalebars correspond to 200 nm.

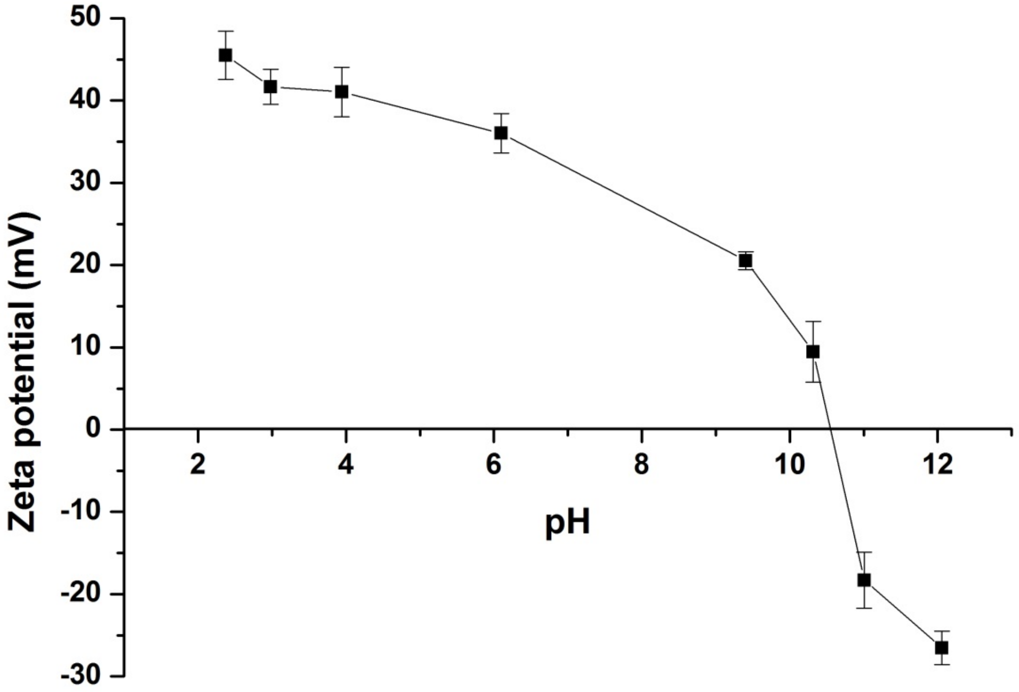

Fig. S8 Zeta potential versus pH for the cationic PS nanospheres used in this work. The pH was adjusted by additions of hydrochloric acid or sodium hydroxide solution.

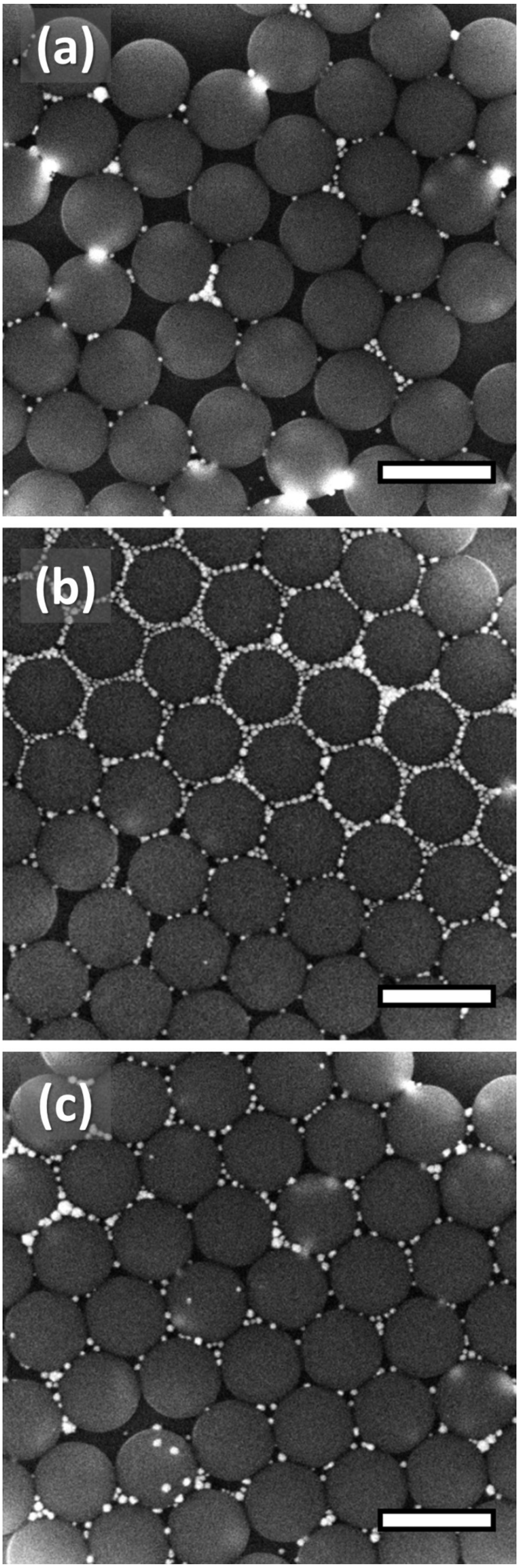

Fig. S9 SEM image of the result of mixing (a) 20 μL, (b) 15 μL and (c) 10 μL of anionic PS nanospheres suspension (see text at the start of the ESI for method of preparation) with ascorbic acid and adding chloroauric acid. Scalebars correspond to 500 nm.

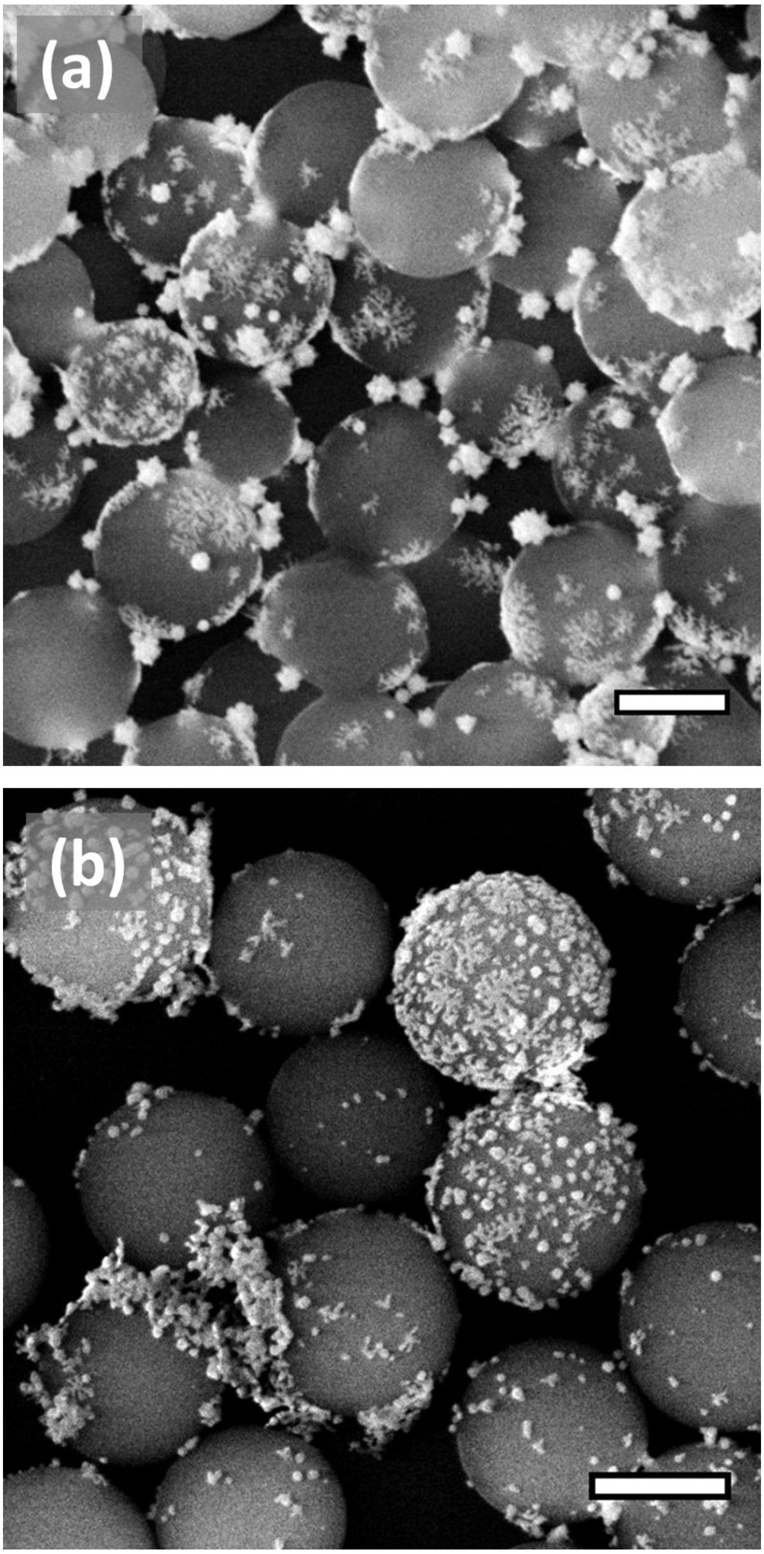

Fig. S10 SEM images of the result of mixing cationic amine functionalized (a) PS, and (b) silica nanospheres with ascorbic acid followed by and addition of chloroauric acid. See Table S3 for further synthetic details. Scale bars correspond to 300 nm.

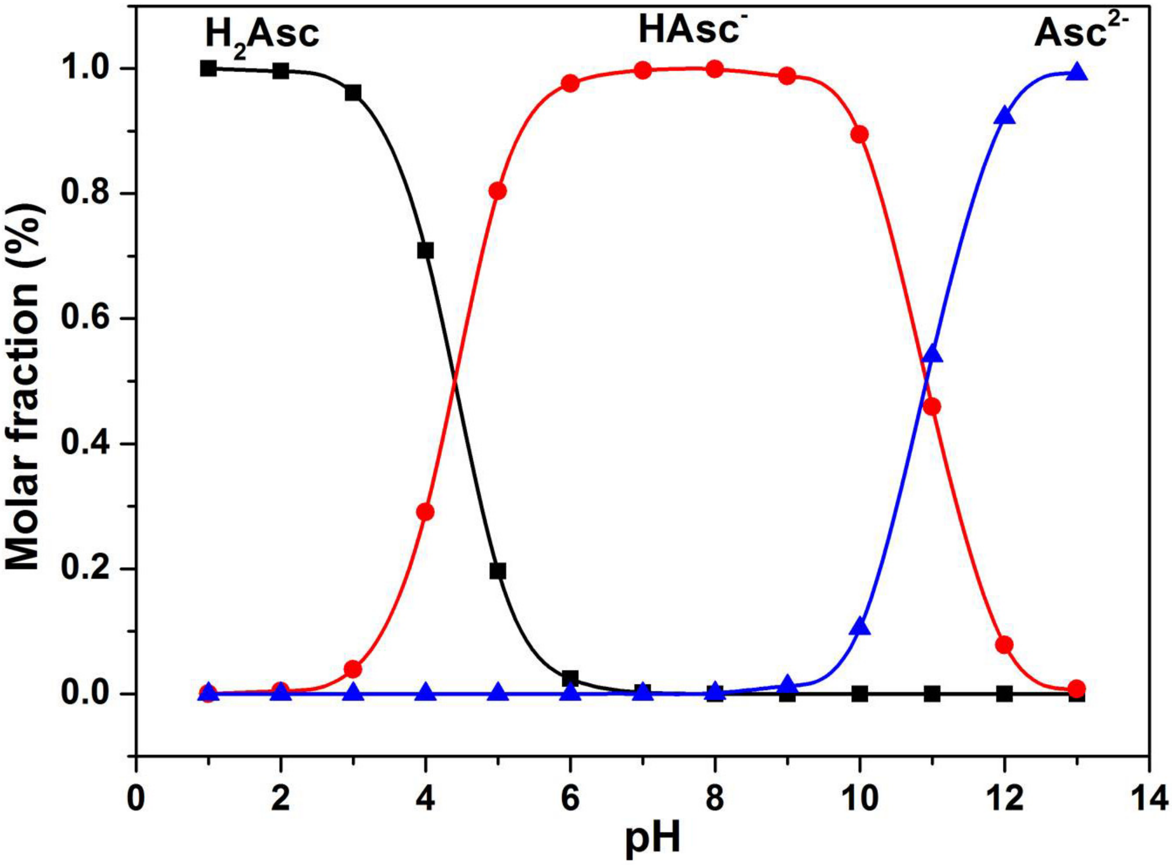

Fig. S11 Plot showing the coexistence of ascorbic acid and dissociation products at different pH values. These curves were determined using the widely tabulated dissociation constants of L-ascorbic acid: $pK_{a,1} = 4.17$ and $pK_{a,2} = 11.58$.