Purely visible-light induced photochromism in Ag-TiO_2 nano-heterostructures

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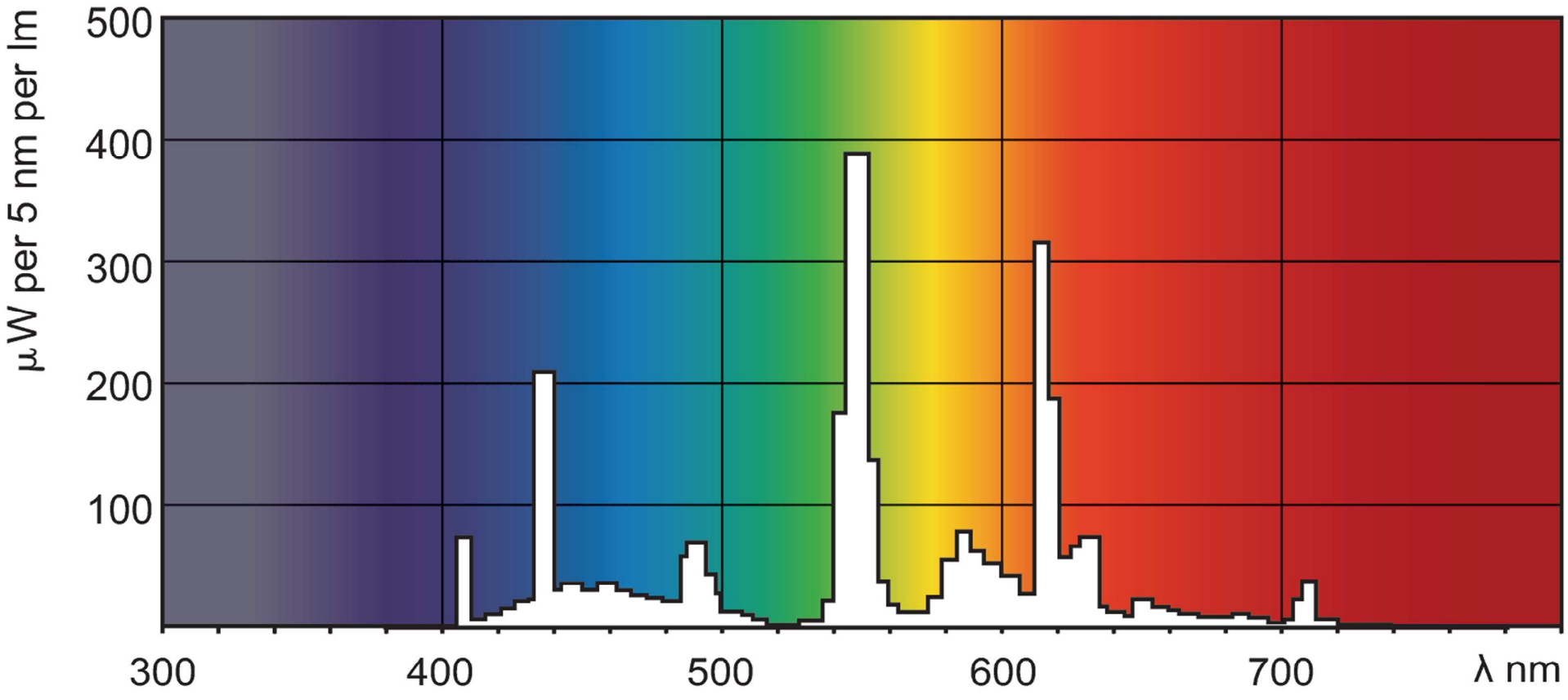

Fig. S1 – Emission spectrum of the visible lamp used in the photochromic experiments, from www.philips.com

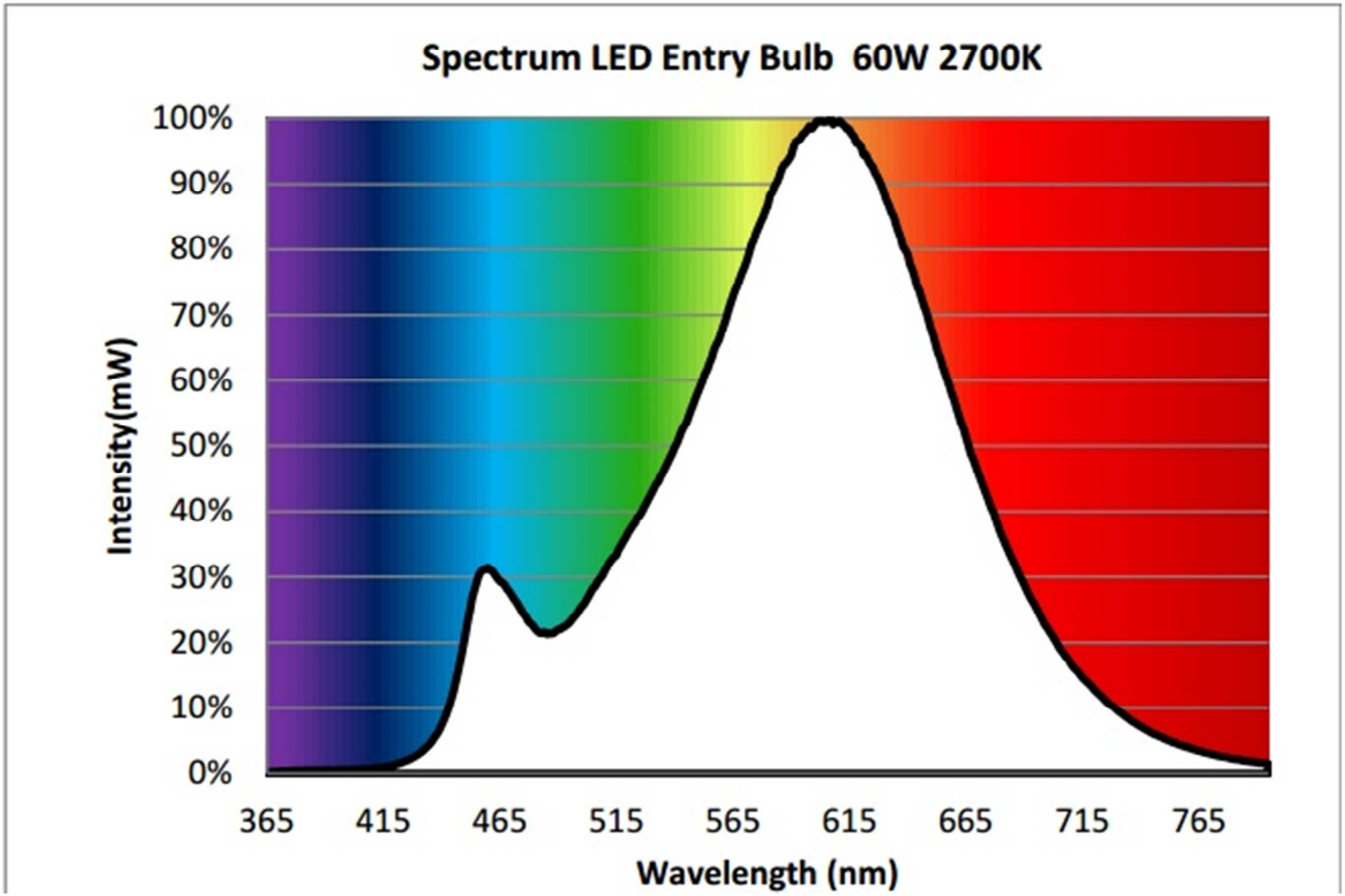

Fig. S2 – Emission spectrum of the white LED lamp used in the photocatalytic experiments, from www.philips.com

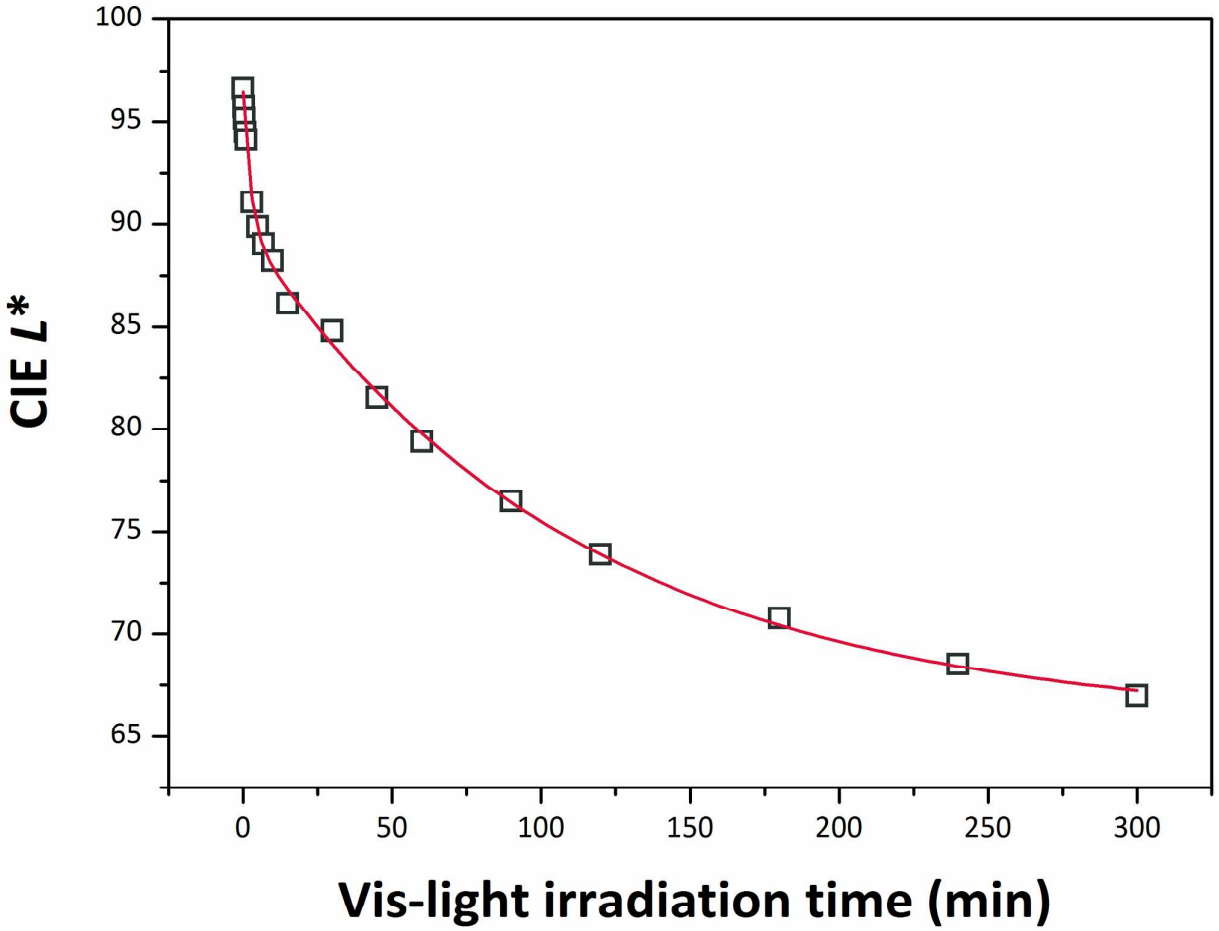

Fig. S3a – Evolution of the CIE *L** value with the increase in visible-light irradiation time, specimen **Ag-Ti450**.

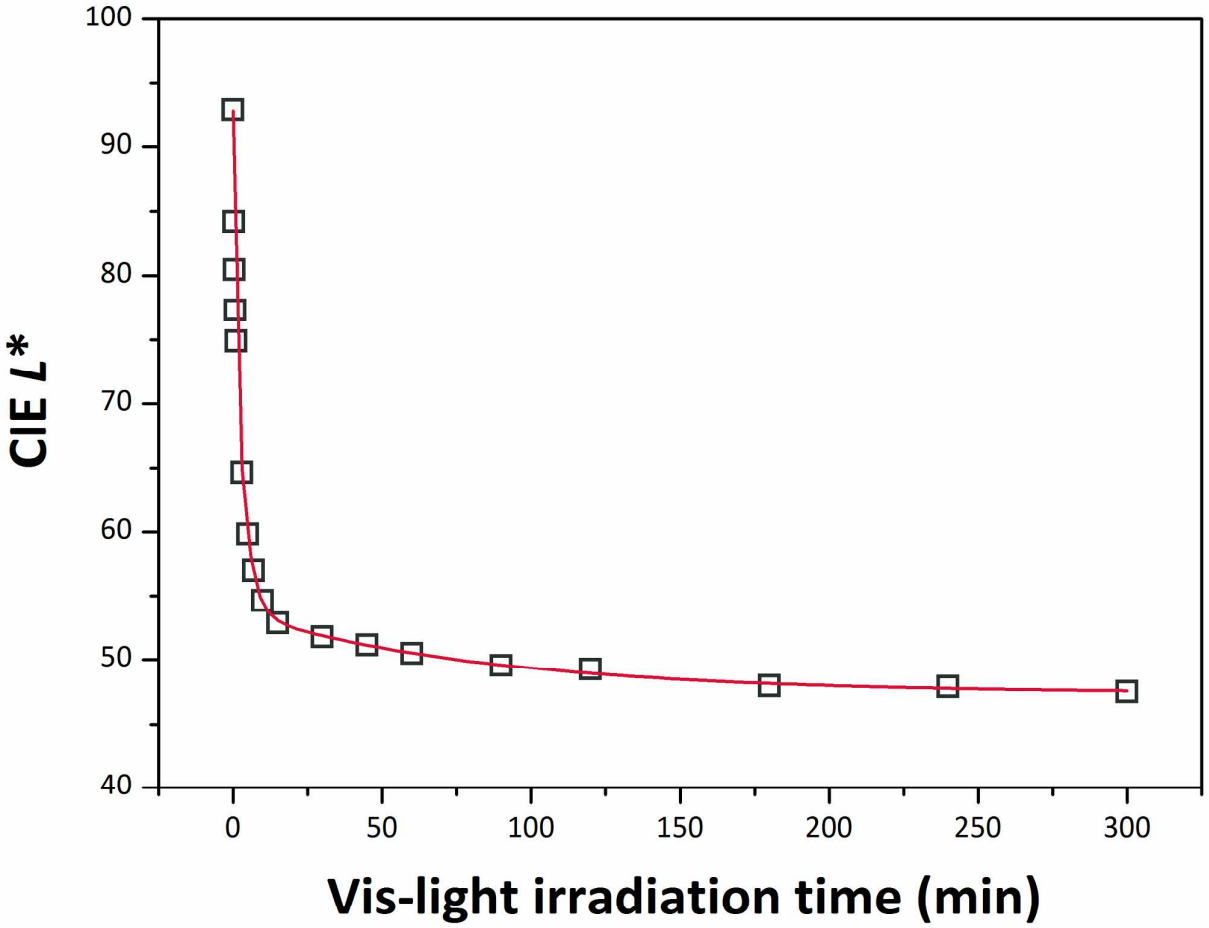

Fig. S3b – Evolution of the CIE *L** value with the increase in visible-light irradiation time, specimen **2Ag-Ti450**.

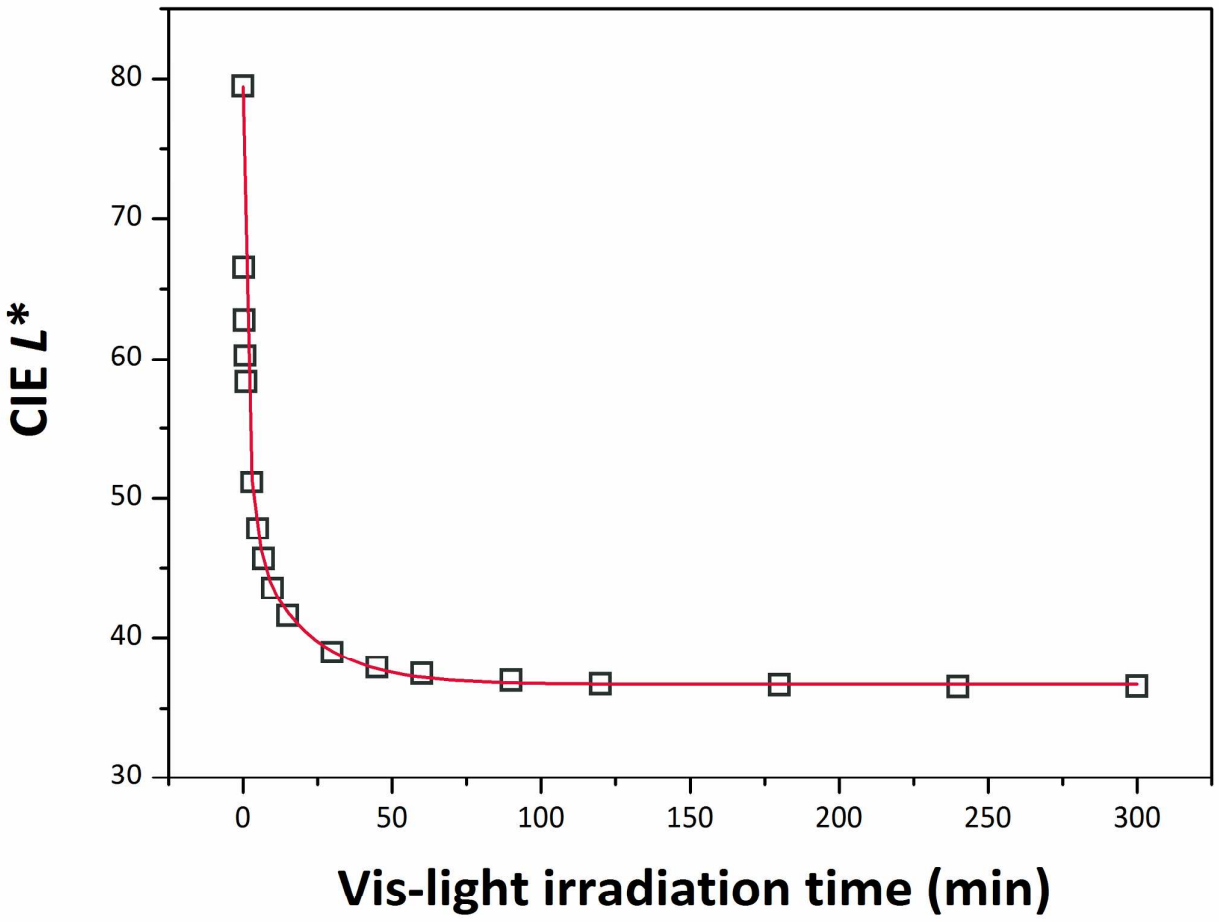

Fig. S3c – Evolution of the CIE *L** value with the increase in visible-light irradiation time, specimen **5Ag-Ti450**.

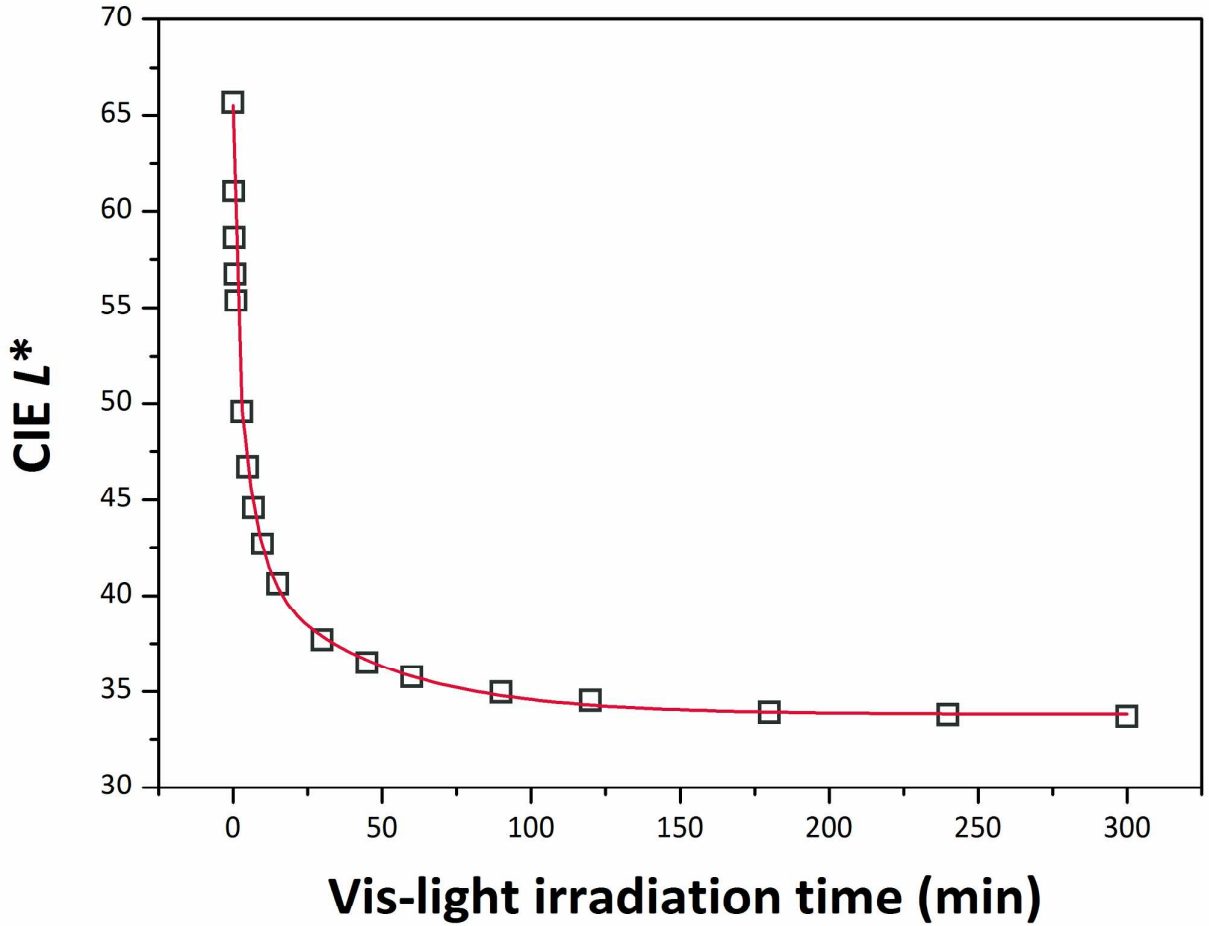

Fig. S3d – Evolution of the CIE *L** value with the increase in visible-light irradiation time, specimen **10Ag-Ti450**.

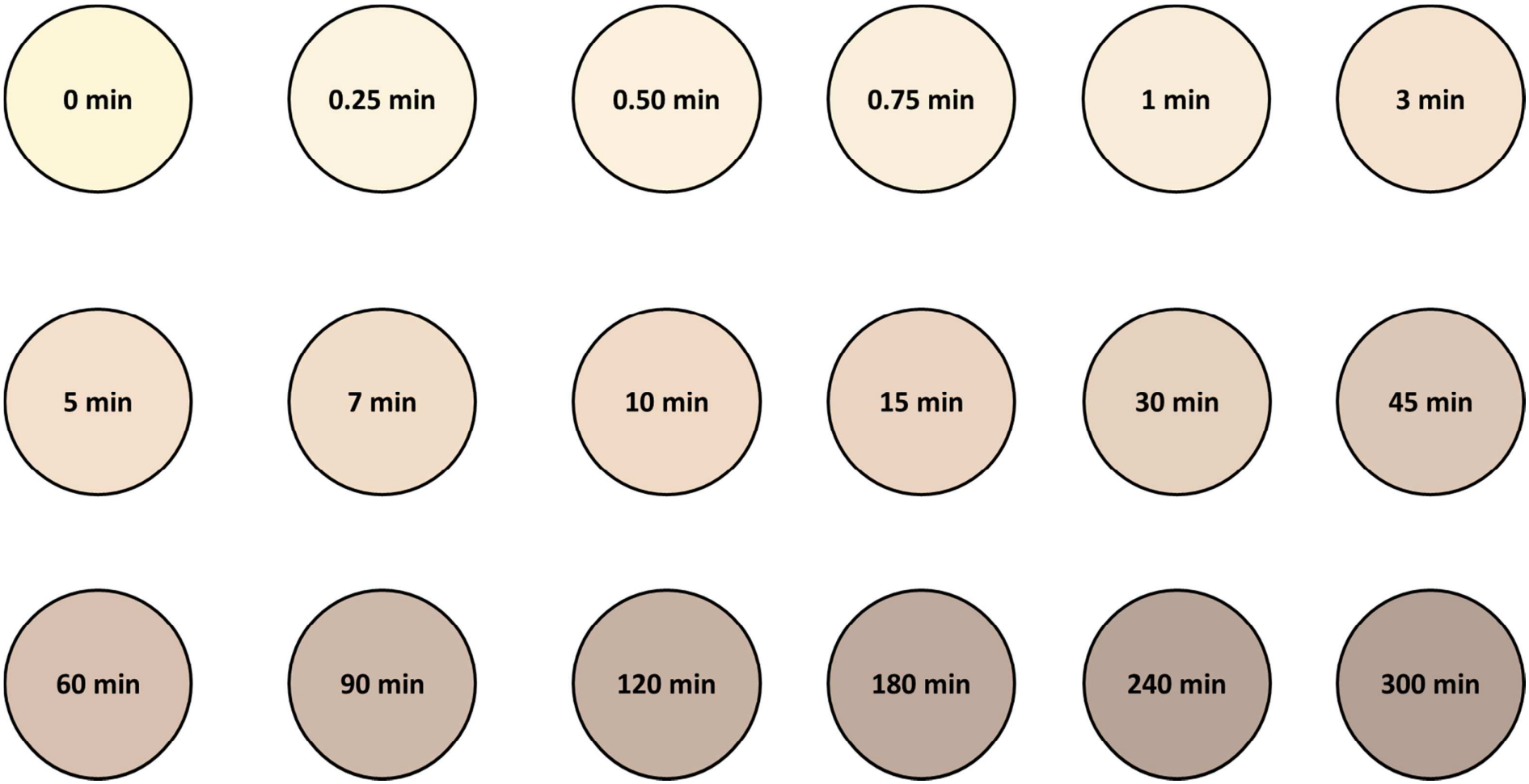

Fig. S4a – Visual RGB colour rendering of **Ag-Ti450** specimens after the different visible-light exposure time.

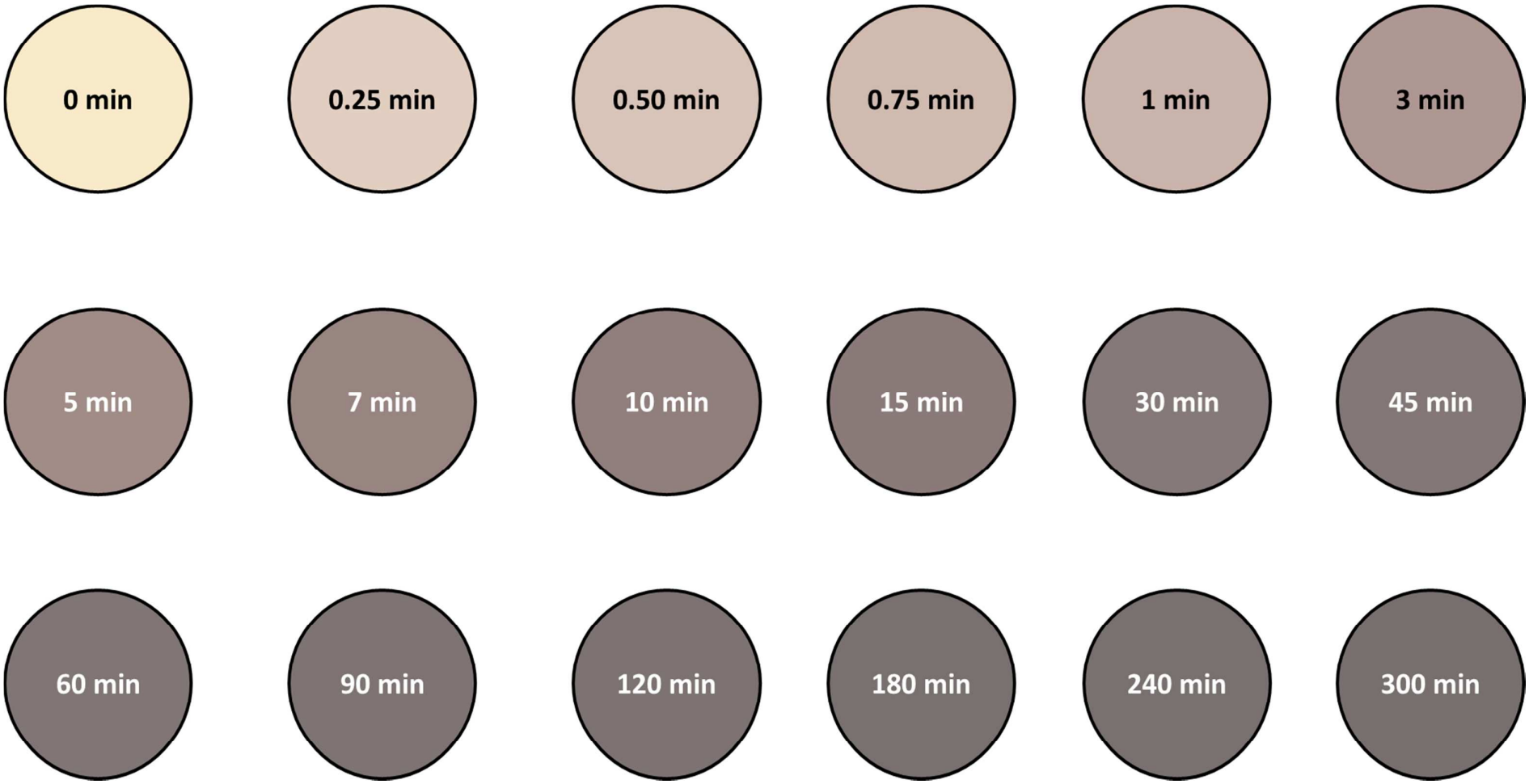

Fig. S4b – Visual RGB colour rendering of **2Ag-Ti450** specimens after the different visible-light exposure time.

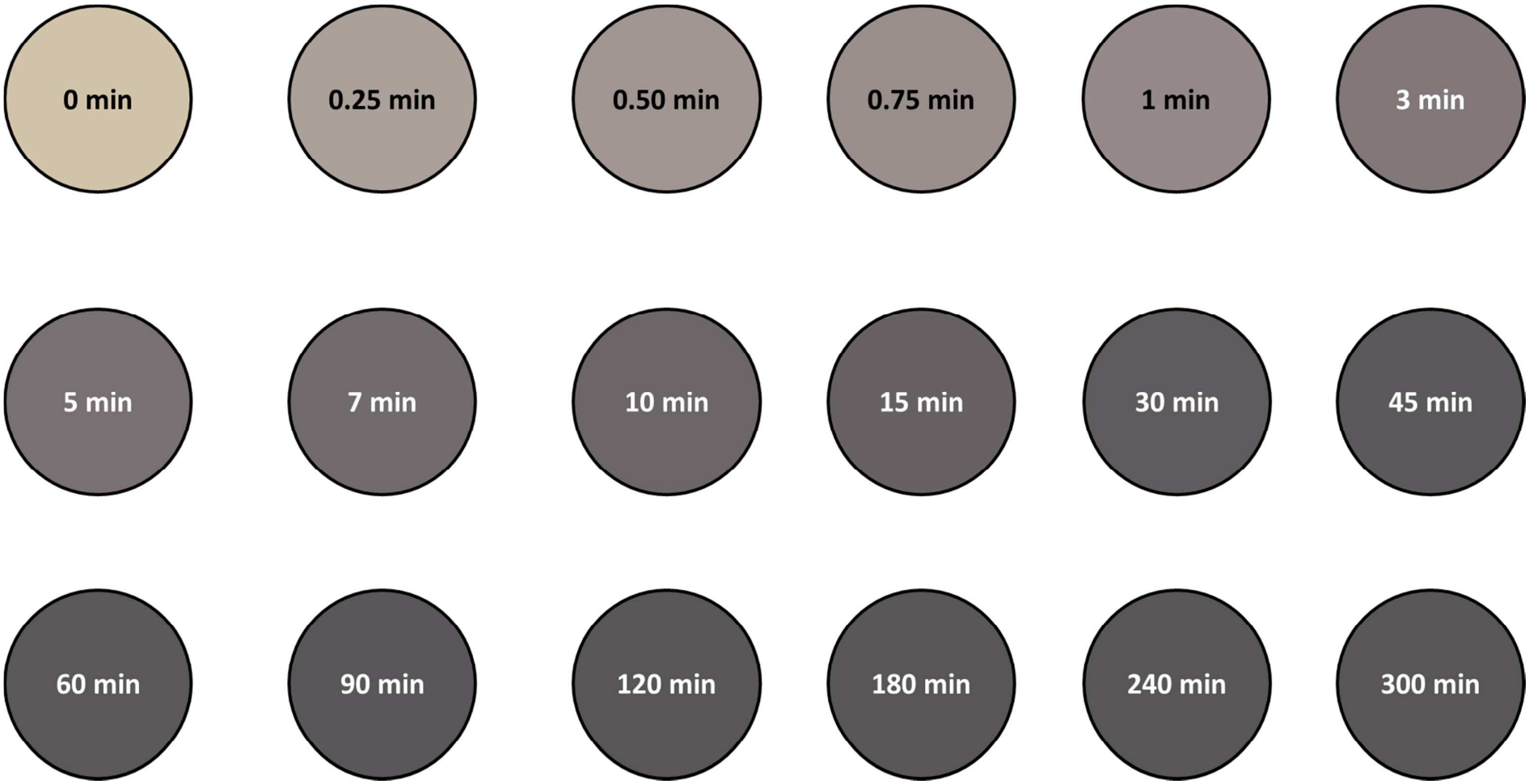

Fig. S4c – Visual RGB colour rendering of **5Ag-Ti450** specimens after the different visible-light exposure time.

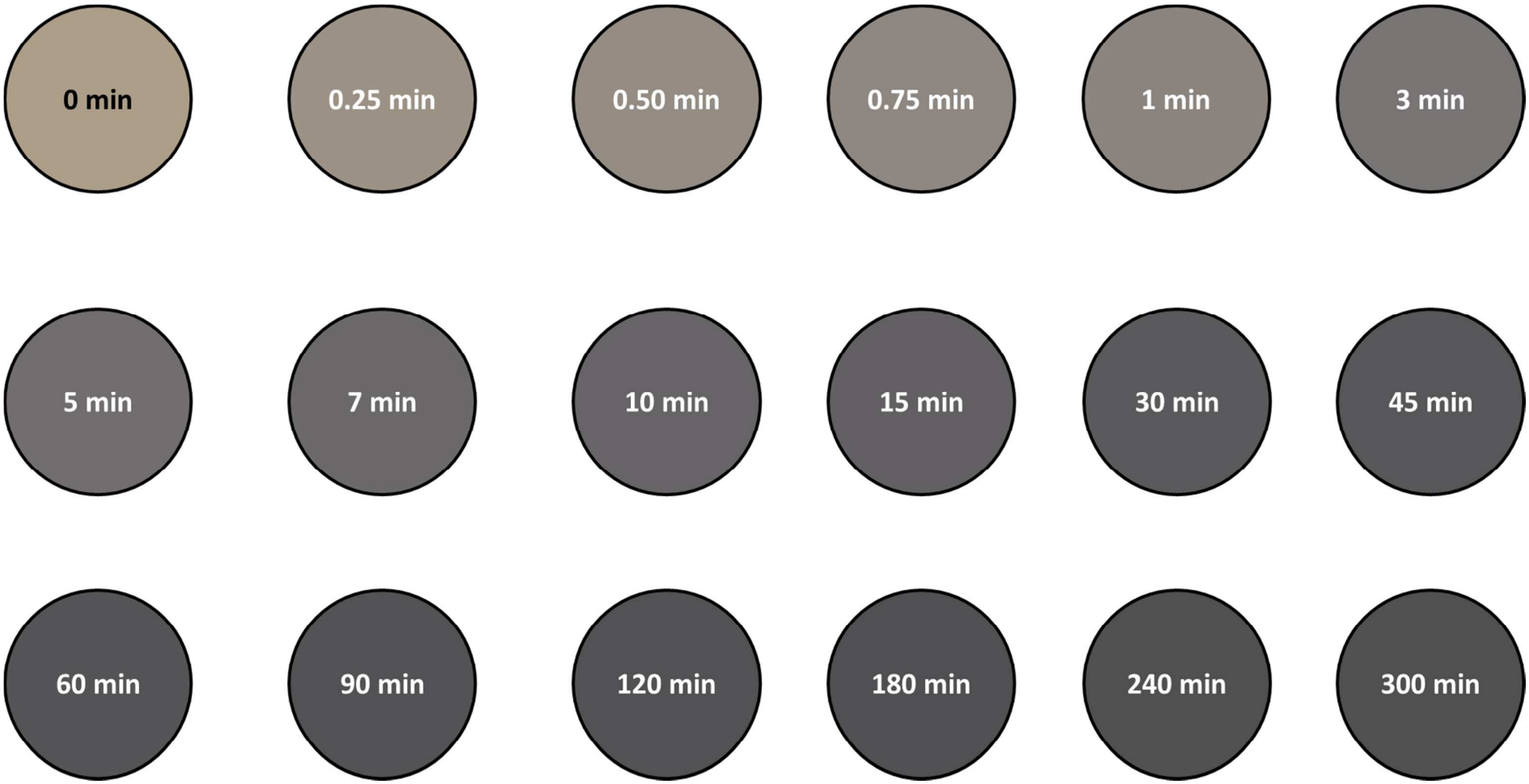

Fig. S4d – Visual RGB colour rendering of **10Ag-Ti450** specimens after the different visible-light exposure time.

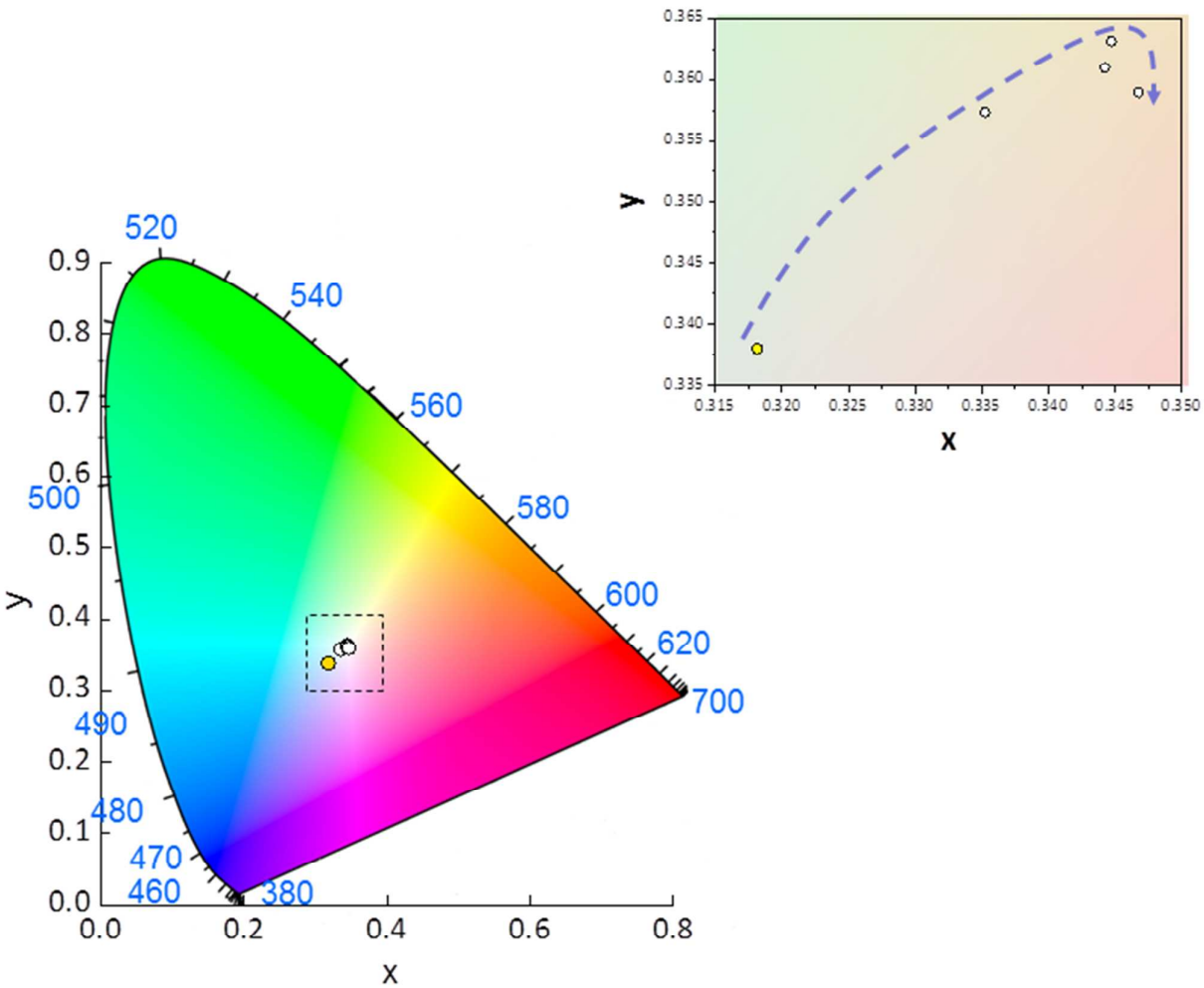

Fig. S5a – Chromaticity diagrams of unmodified and Ag-modified TiO_2 prior to exposure to visible-light. The inset shows a magnification of the region in the square, in which the yellow dot is the unmodified TiO_2, while the dashed arrow is a guide for the eye showing the increase with Ag mol%.

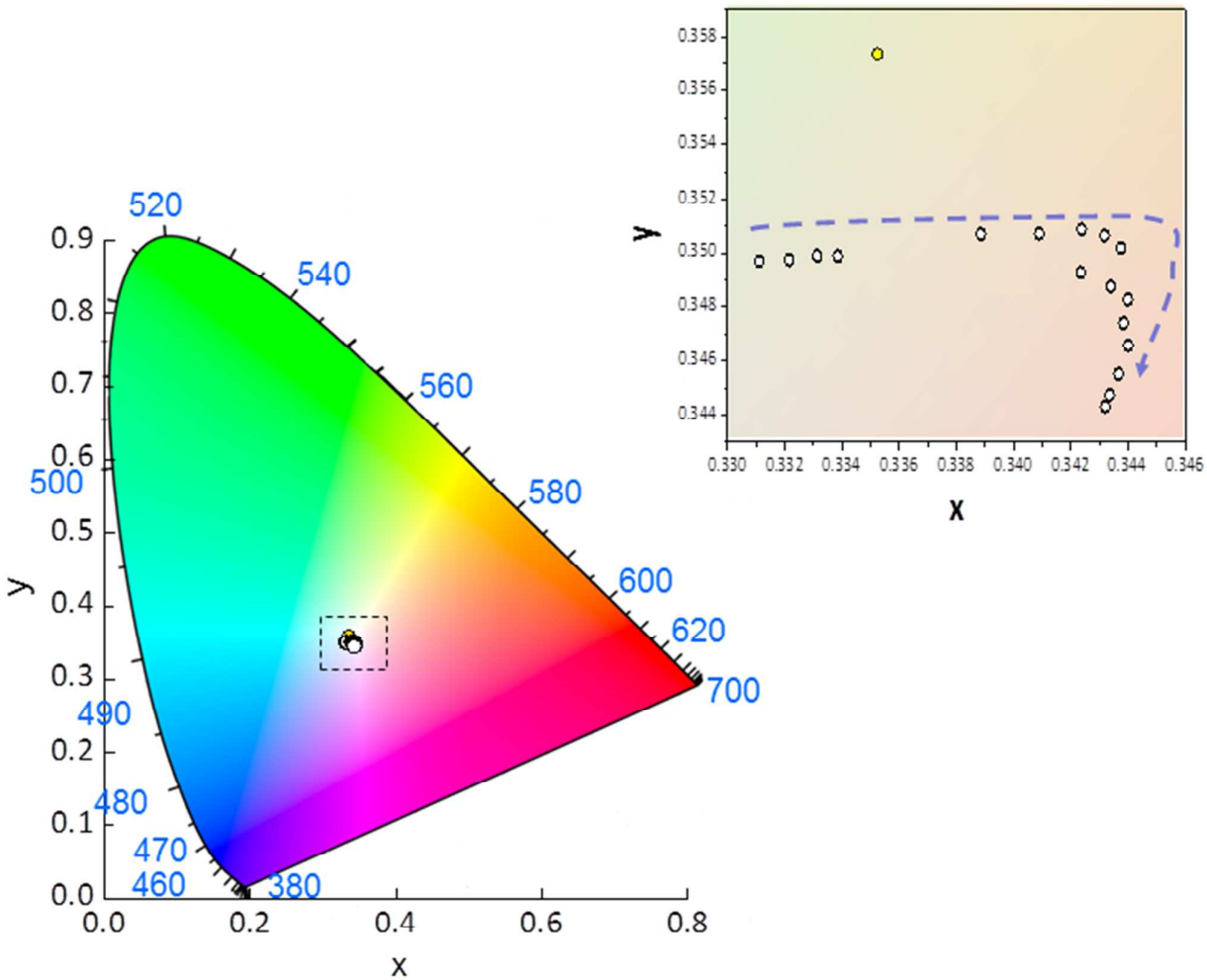

Fig.S5b – Chromaticity diagrams of **Ag-Ti450** after visible-light exposure; the inset shows a magnification of the region in the square, in which the dashed arrow is just a guide for the eye, indicating the evolution of the x, y chromaticity coordinates with the increase in visible-light exposure time. The yellow dot represents the x and y chromaticity coordinates of the specimen **BEFORE** irradiation with the visible lamp.

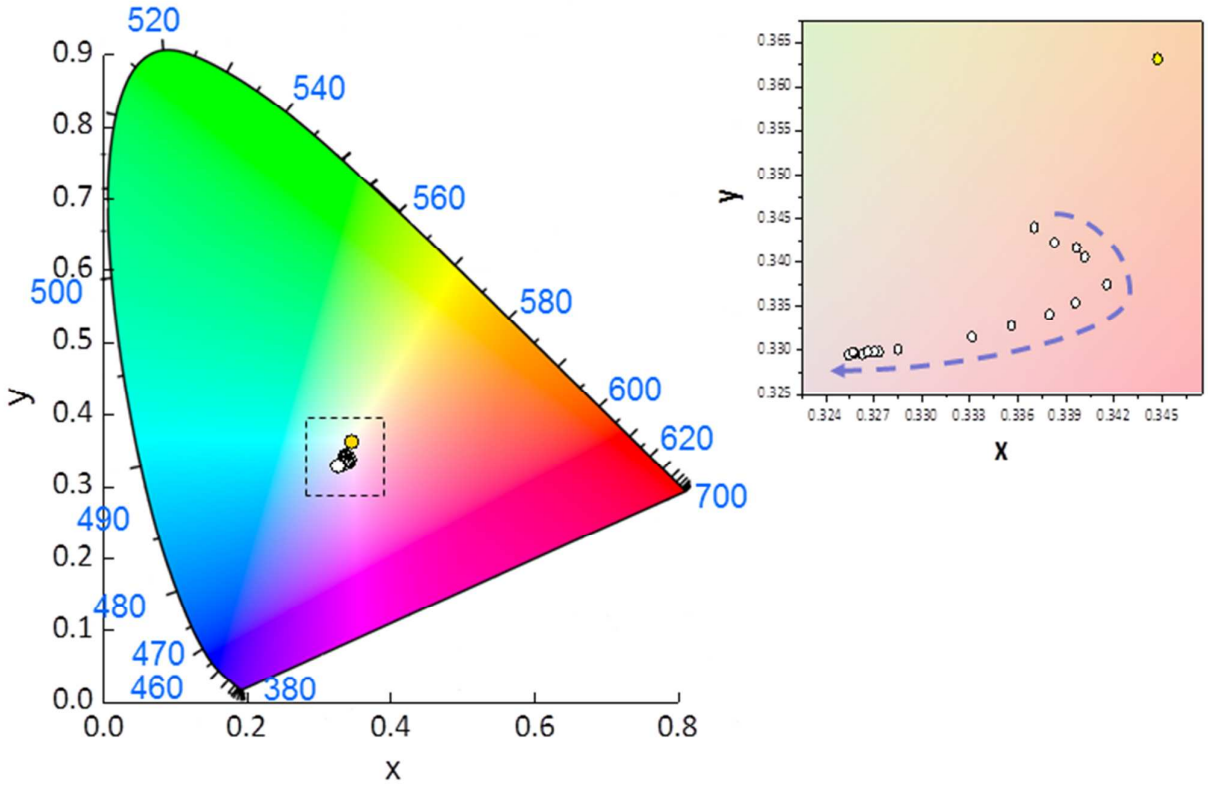

Fig.S5c – Chromaticity diagrams of **2Ag-Ti450** after visible-light exposure; the inset shows a magnification of the region in the square, in which the dashed arrow is just a guide for the eye, indicating the evolution of the x, y chromaticity coordinates with the increase in visible-light exposure time. The yellow dot represents the x and y chromaticity coordinates of the specimen **BEFORE** irradiation with the visible lamp.

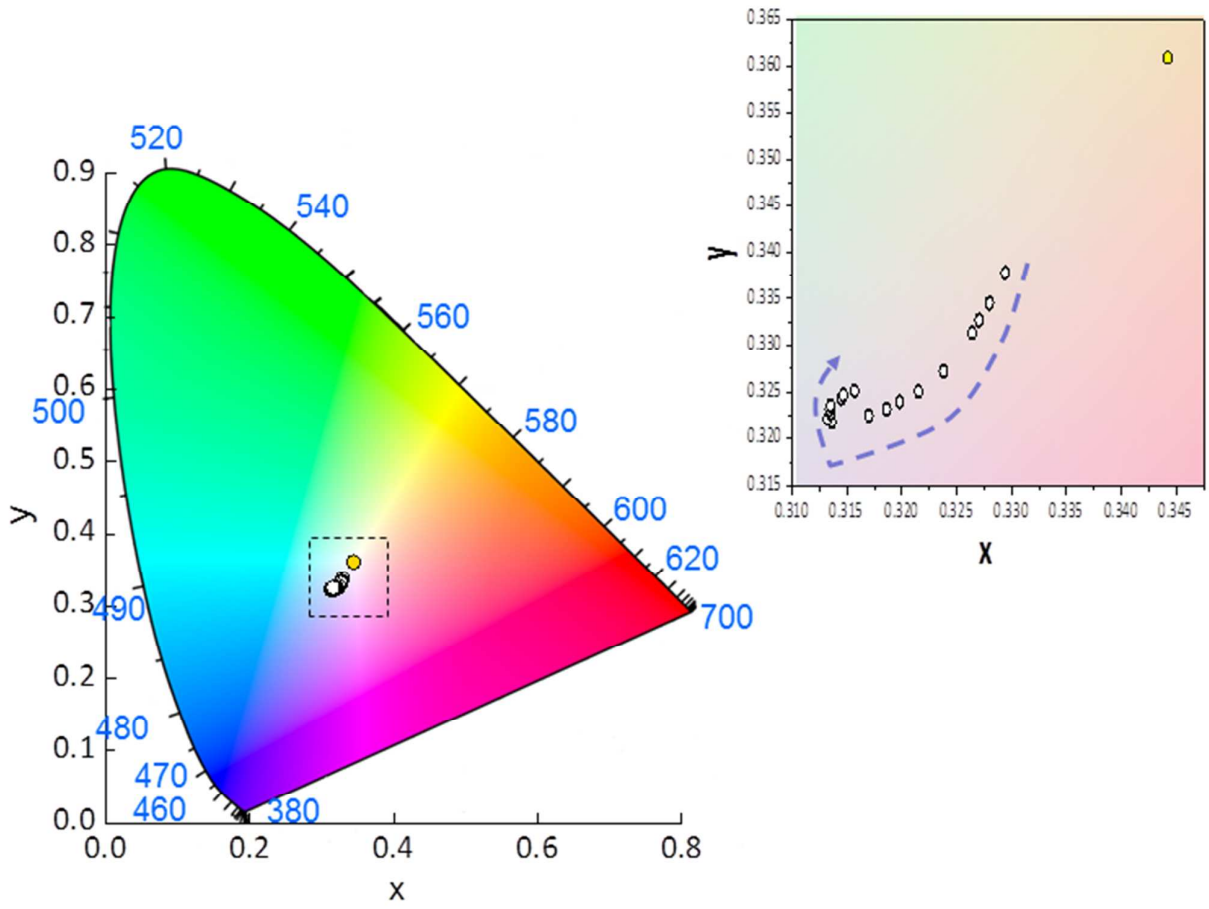

Fig.S5d – Chromaticity diagrams of **5Ag-Ti450** after visible-light exposure; the inset shows a magnification of the region in the square, in which the dashed arrow is just a guide for the eye, indicating the evolution of the x, y chromaticity coordinates with the increase in visible-light exposure time. The yellow dot represents the x and y chromaticity coordinates of the specimen **BEFORE** irradiation with the visible lamp.

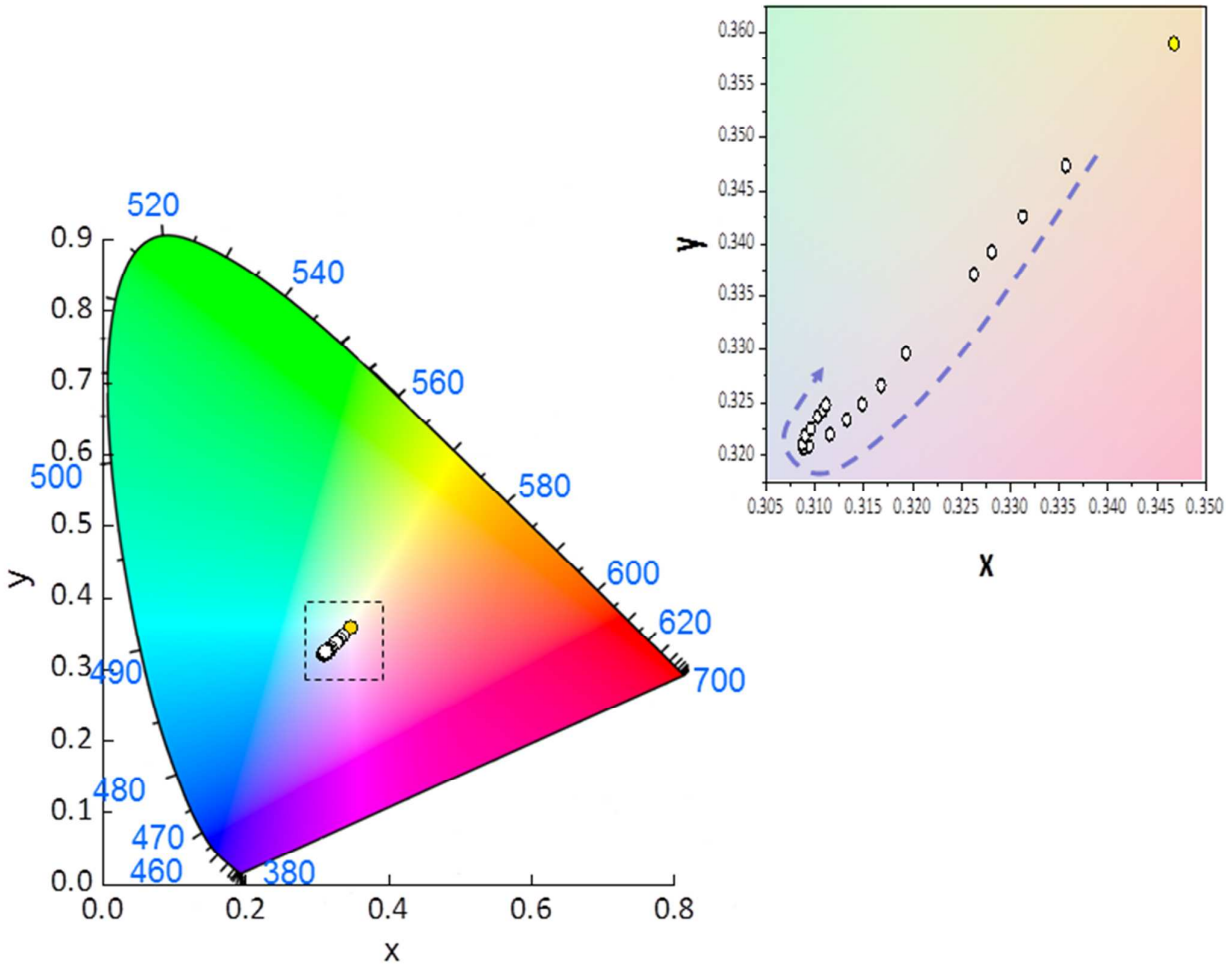

Fig.S5e – Chromaticity diagrams of **10Ag-Ti450** after visible-light exposure; the inset shows a magnification of the region in the square, in which the dashed arrow is just a guide for the eye, indicating the evolution of the x, y chromaticity coordinates with the increase in visible-light exposure time. The yellow dot represents the x and y chromaticity coordinates of the specimen **BEFORE** irradiation with the visible lamp.

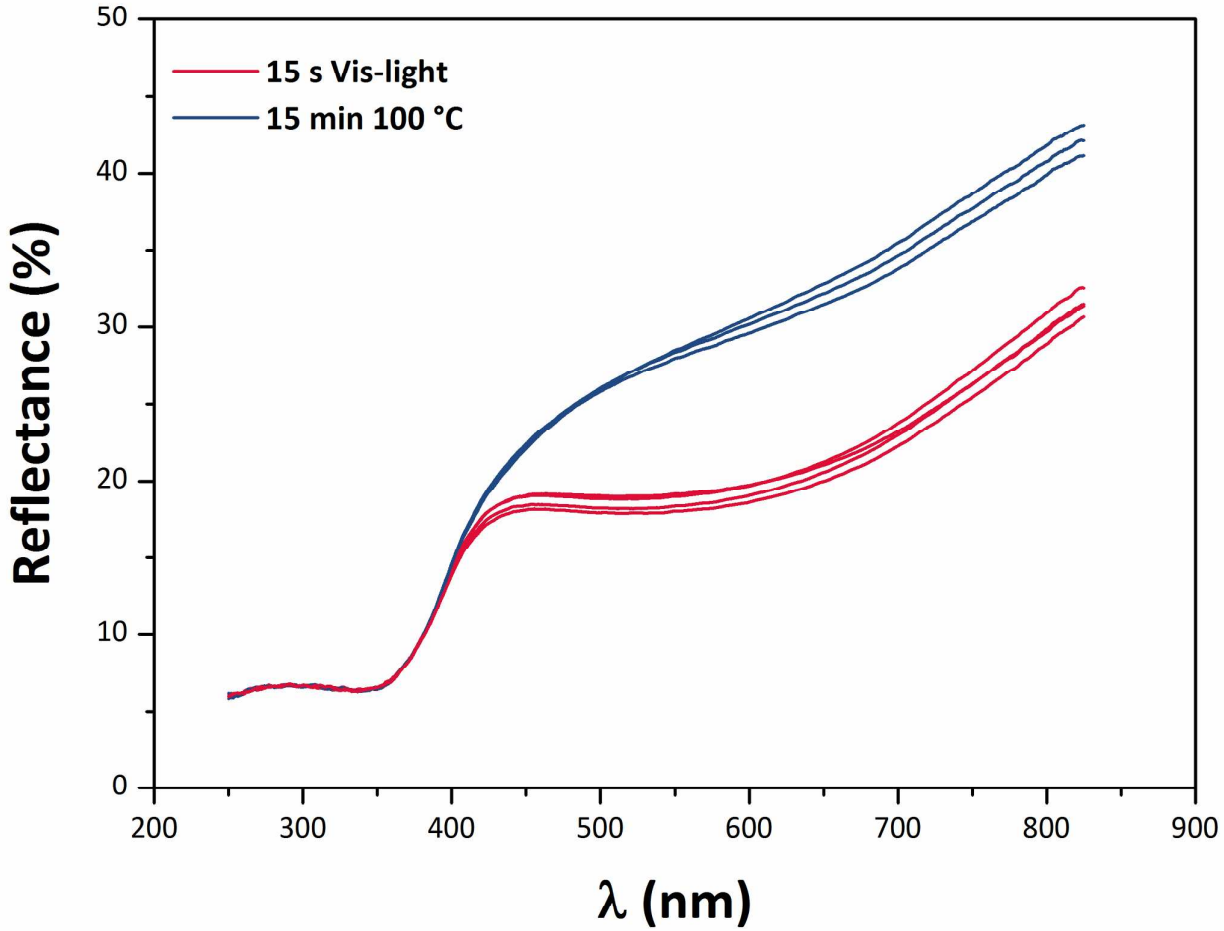

Fig. S6 – Reflectance spectra of specimen **5Ag-Ti450** showing the photochromic recovery with repeated visible-light (red line) / dark @ 100 °C (blue line) cycles.

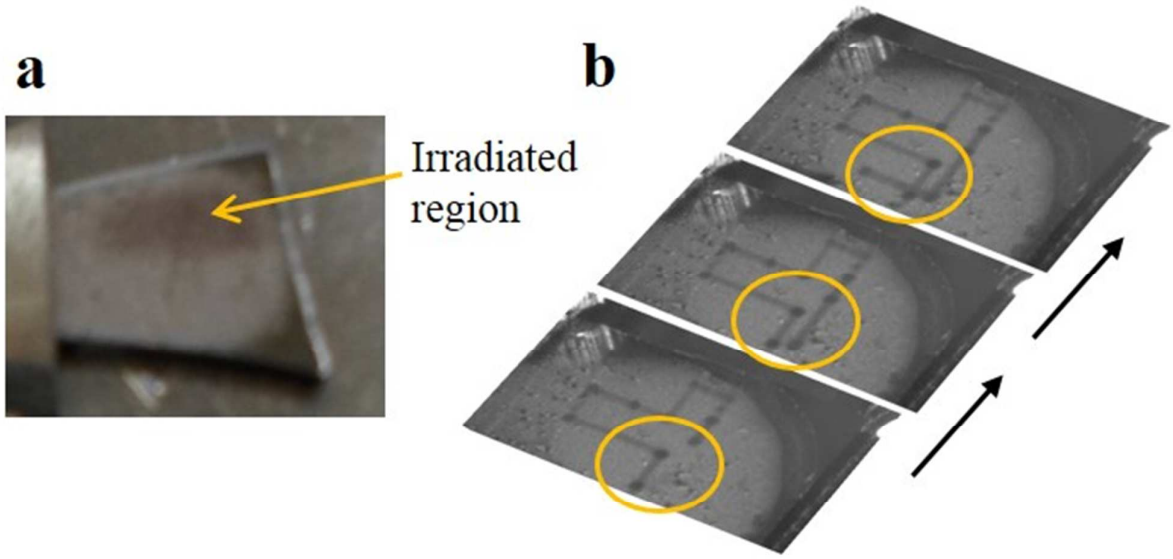

Fig. S7 – Digital photographs of the change produced on the samples by XPS (a), and a focussed electron beam (b).

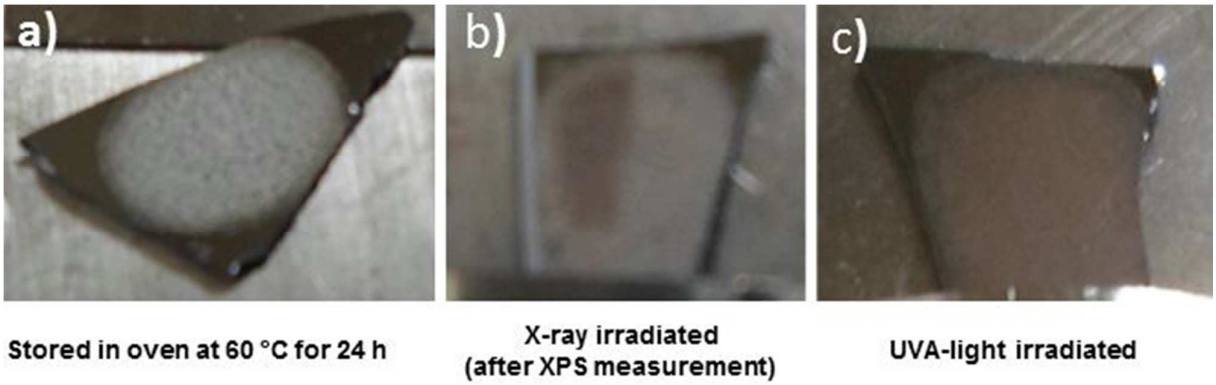

Fig. S8 – Digital photographs of specimen **2Ag-Ti450**: a) stored in a dark oven at 60 °C for 24 h prior to assessing the XPS analysis; b) after XPS analysis (the dark-region was that irradiated with X-ray); c) fresh specimen as in figure S7a, but irradiated with a UVA-lamp, as visual comparison.

Table S1 – Rietveld agreement factors and crystalline phase composition of the unmodified and Ag-modified TiO_2.[†]

Sample	No. of variables	Agreement factors				Phase composition (wt%)		
		$R(_F^2)$ (%)	R_{wp} (%)	χ^2		anatase	rutile	brookite
Ti450	20	3.54	4.03	1.74		56.5±0.1	19.8±0.2	23.6±0.6
Ag-Ti450	21	4.14	3.28	1.75		85.5±0.1	5.2±0.2	8.3±0.5
2Ag-Ti450	21	4.36	3.10	1.70		86.8±0.1	5.4±0.3	7.9±0.5
5Ag-Ti450	20	5.12	3.06	1.85		83.3±0.1	7.8±0.4	8.8±0.6
10Ag-Ti450	22	6.95	3.01	1.82		84.4±0.2	7.4±0.4	8.2±0.8

Note: there were 2285 observations for every refinement; the number of anatase, rutile and brookite reflections was 32, 31 and 106, respectively.

[†] *From reference [40].*

Table S2 – CIE*L***a***b** change of coordinates of **Ag-Ti450** after incremental visible-light exposure time.

Visible-light irradiation time, min	***L****	***a****	***b****
0	96.61	–1.71	13.79
0.25	95.73	–0.22	10.11
0.50	95.17	0.26	10.28
0.75	94.48	0.66	10.45
1	94.12	1.01	10.55
3	91.07	2.92	11.47
5	89.86	3.80	11.72
7	89.03	4.36	11.96
10	88.23	4.78	11.93
15	86.12	5.13	11.64
30	84.80	4.84	10.94
45	81.53	5.34	10.59
60	79.38	5.65	10.31
90	76.50	5.76	9.71
120	73.87	5.97	9.21
180	70.78	6.03	8.54
240	68.51	6.04	8.05
300	66.98	6.02	7.77

Table S3 – CIE*L***a***b** change of coordinates of **2Ag-Ti450** after incremental visible-light exposure time.

Visible-light irradiation time, min	***L****	***a****	***b****
0	92.94	0.18	17.20
0.25	84.18	4.74	8.21
0.50	80.46	5.81	7.55
0.75	77.29	6.42	7.33
1	74.89	6.87	6.89
3	64.62	7.64	5.48
5	59.80	7.24	4.37
7	56.94	6.87	3.67
10	54.63	6.32	2.97
15	52.84	5.80	2.31
30	51.76	4.75	1.43
45	51.13	4.44	1.22
60	50.46	4.30	1.18
90	49.51	4.10	1.02
120	49.23	4.10	1.11
180	47.92	3.79	0.89
240	47.87	3.81	0.98
300	47.49	3.74	0.98

Table S4 – CIE*L***a***b** change of coordinates of **5Ag-Ti450** after incremental visible-light exposure time.

Visible-light irradiation time, min	***L****	***a****	***b****
0	79.48	0.80	14.31
0.25	66.51	3.38	3.98
0.50	62.71	3.82	2.76
0.75	60.23	3.98	2.08
1	58.35	4.11	1.63
3	51.15	4.16	0.23
5	47.82	3.90	–0.48
7	45.65	3.60	–0.87
10	43.56	3.37	–1.12
15	41.58	3.00	–1.36
30	38.95	2.20	–1.74
45	37.90	1.96	–1.67
60	37.45	1.87	–1.53
90	36.96	1.73	–1.44
120	36.70	1.65	–1.35
180	36.63	1.70	–1.13
240	36.51	1.67	–1.05
300	36.53	1.82	–0.89

Table S5 – CIE*L***a***b** change of coordinates of **10Ag-Ti450** after incremental visible-light exposure time.

Visible-light irradiation time, min	***L****	***a****	***b****
0	65.67	2.21	12.08
0.25	61.03	2.11	7.00
0.50	58.63	2.12	5.03
0.75	56.72	2.09	3.71
1	55.34	2.11	2.91
3	49.59	2.03	0.28
5	46.70	2.04	–0.62
7	44.57	1.91	–1.16
10	42.68	1.82	–1.57
15	40.60	1.64	–1.94
30	37.69	1.31	–2.24
45	36.49	1.16	–2.26
60	35.76	1.04	–2.17
90	34.96	0.92	–1.98
120	34.54	0.89	–1.80
180	33.94	0.79	–1.52
240	33.81	0.78	–1.37
300	33.73	0.73	–1.25