

Cu-TiO₂ Nanoparticles Exhibiting Tuneable Photochromic Behaviour

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Supporting Information

Figures and Captions

Supporting Information

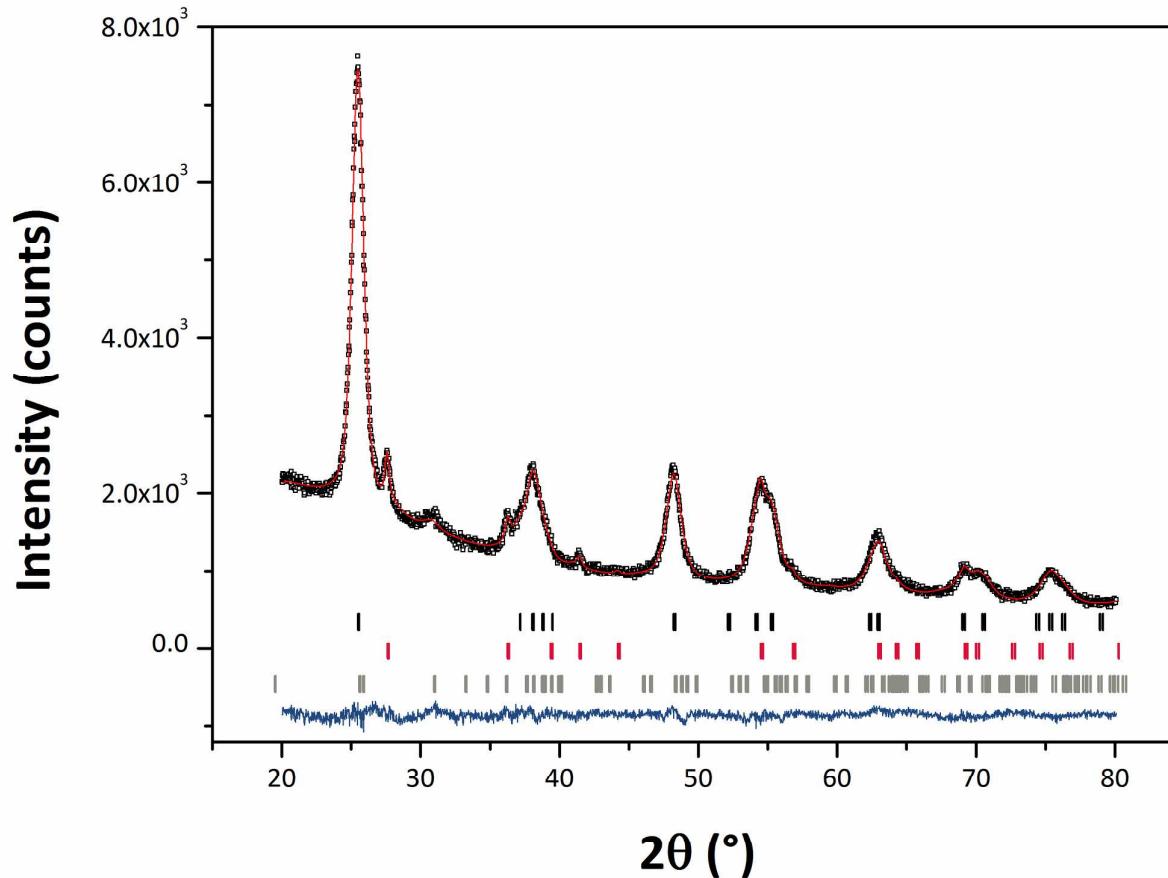


Fig. S1 – Rietveld refinement of the **5Cu-Ti450** specimen. The red line represents the calculated pattern, the black open squares the observed pattern, and the difference curve between observed and calculated profiles is plotted below. The position of reflections is indicated by the small vertical bars (top to bottom: black – anatase; red – rutile; light grey – brookite).

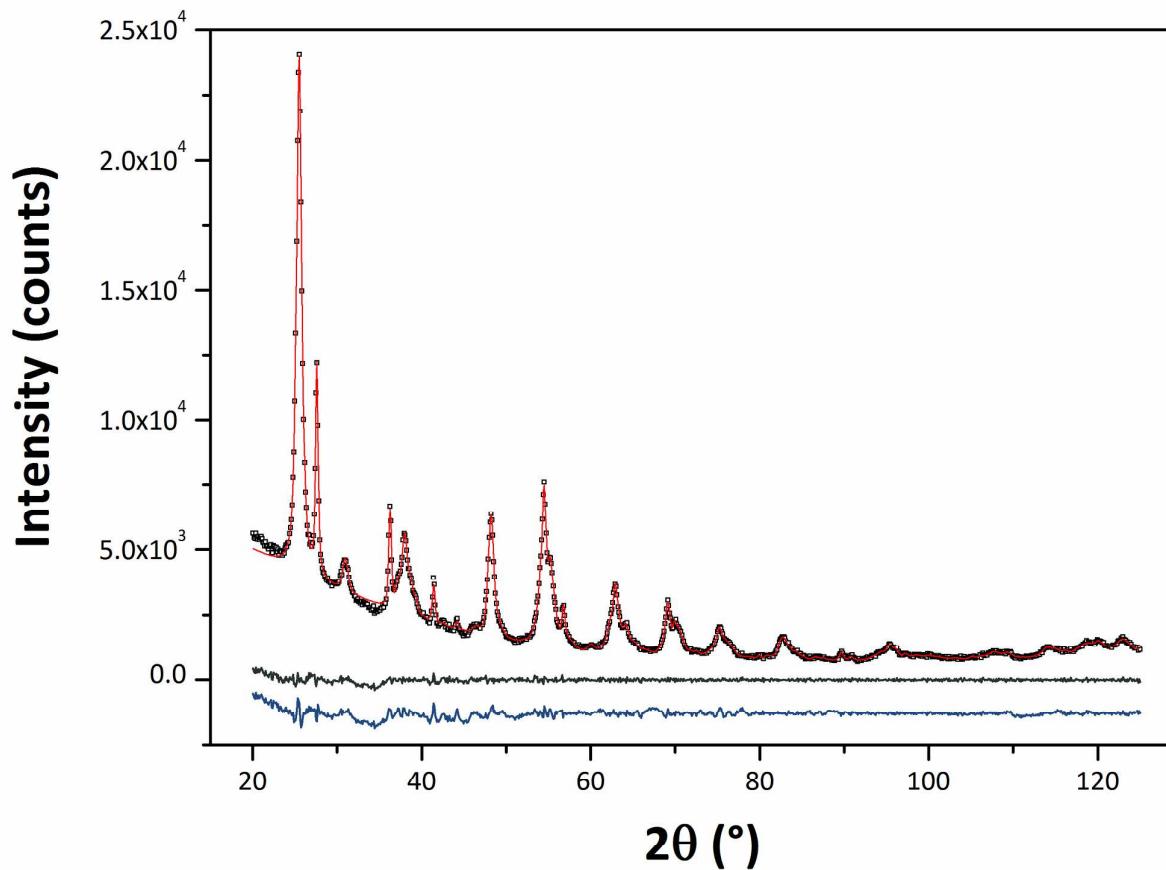


Fig. S2a – WPPM of the **Ti450** specimen. The red line represents the calculated pattern and the black open squares the measured one. The dark grey (upper) and blue (lower) continuous lines at the bottom are the difference curves between observed and calculated profiles, for the proposed bimodal and unimodal size distribution models, respectively.

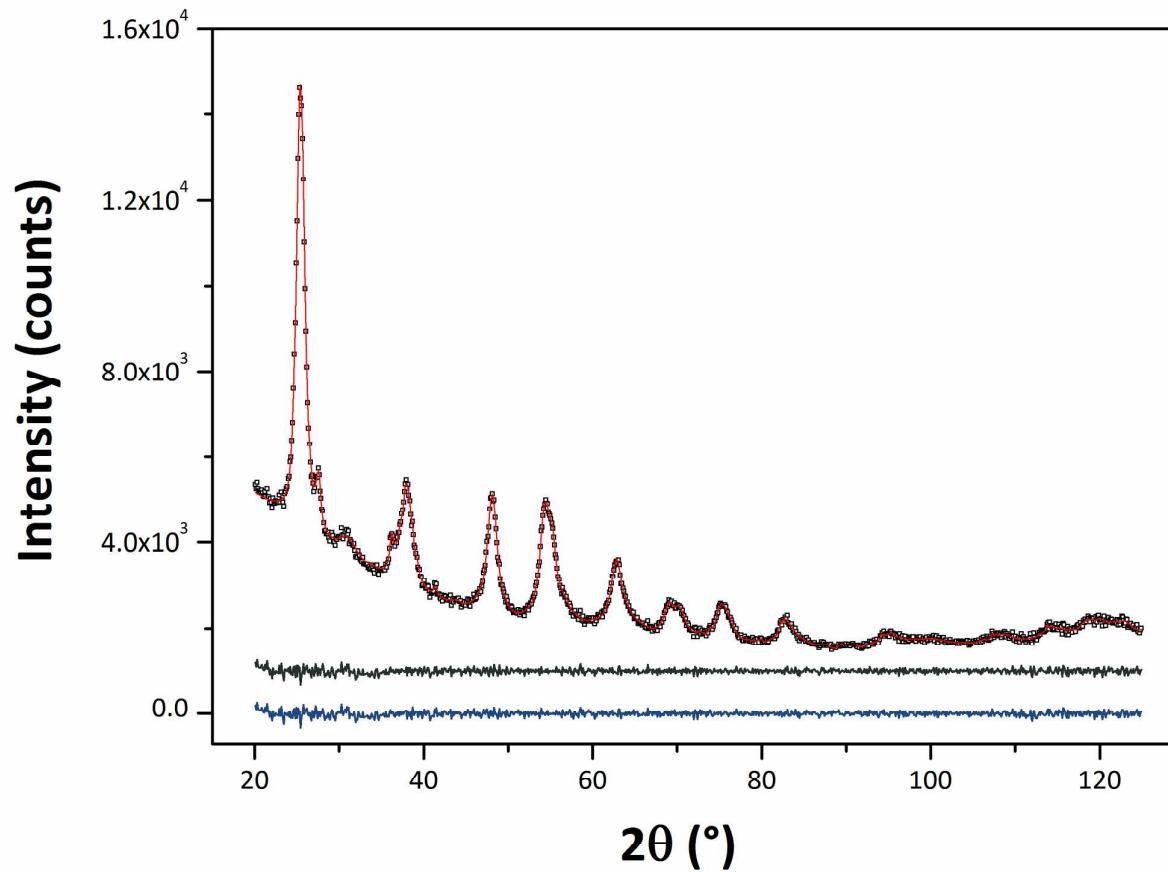


Fig. S2b – WPPM of the **10Cu-Ti450** specimen. The red line represents the calculated pattern and the black open squares the measured one. The dark grey (upper) and blue (lower) continuous lines at the bottom are the difference curves between observed and calculated profiles, for the proposed bimodal and unimodal size distribution models, respectively.

Supporting Information

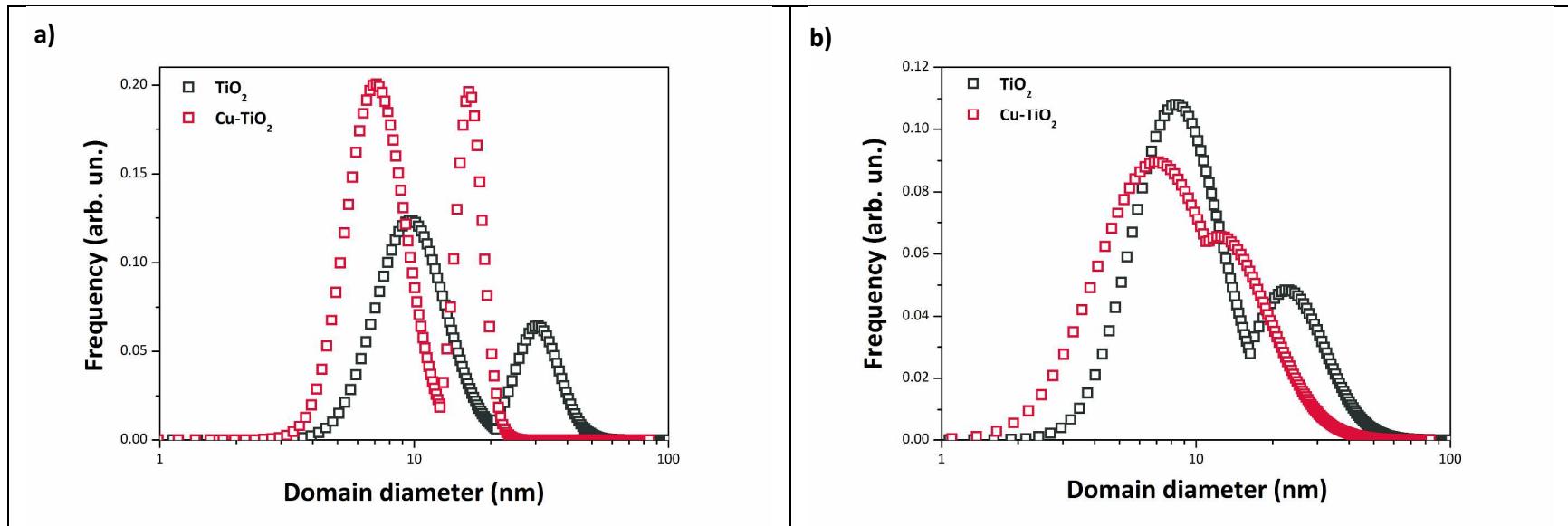


Fig. S3 – Bimodal size distribution for a) anatase, and b) rutile (size reported in log-scale in both figures), as obtained from the WPPM analysis in selected samples.

Supporting Information

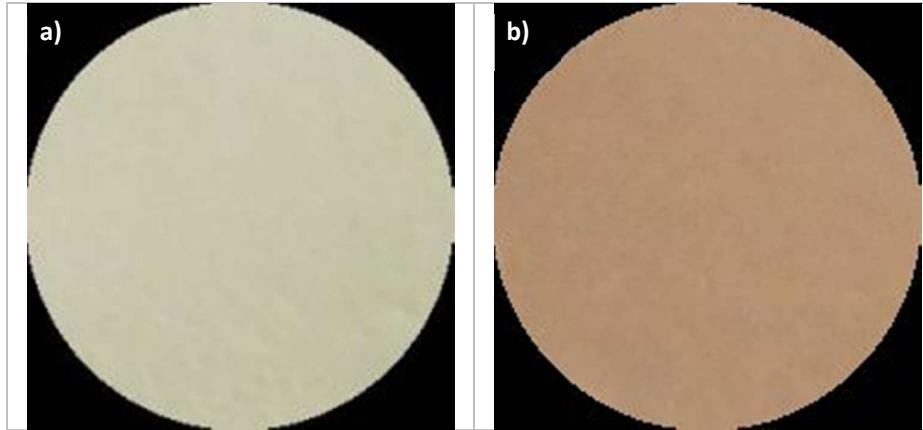


Fig. S4 – Digital photographs of sample **2Cu-Ti450**: (a) prior UVA-light irradiation; after 90 min UVA-light exposure.

Supporting Information

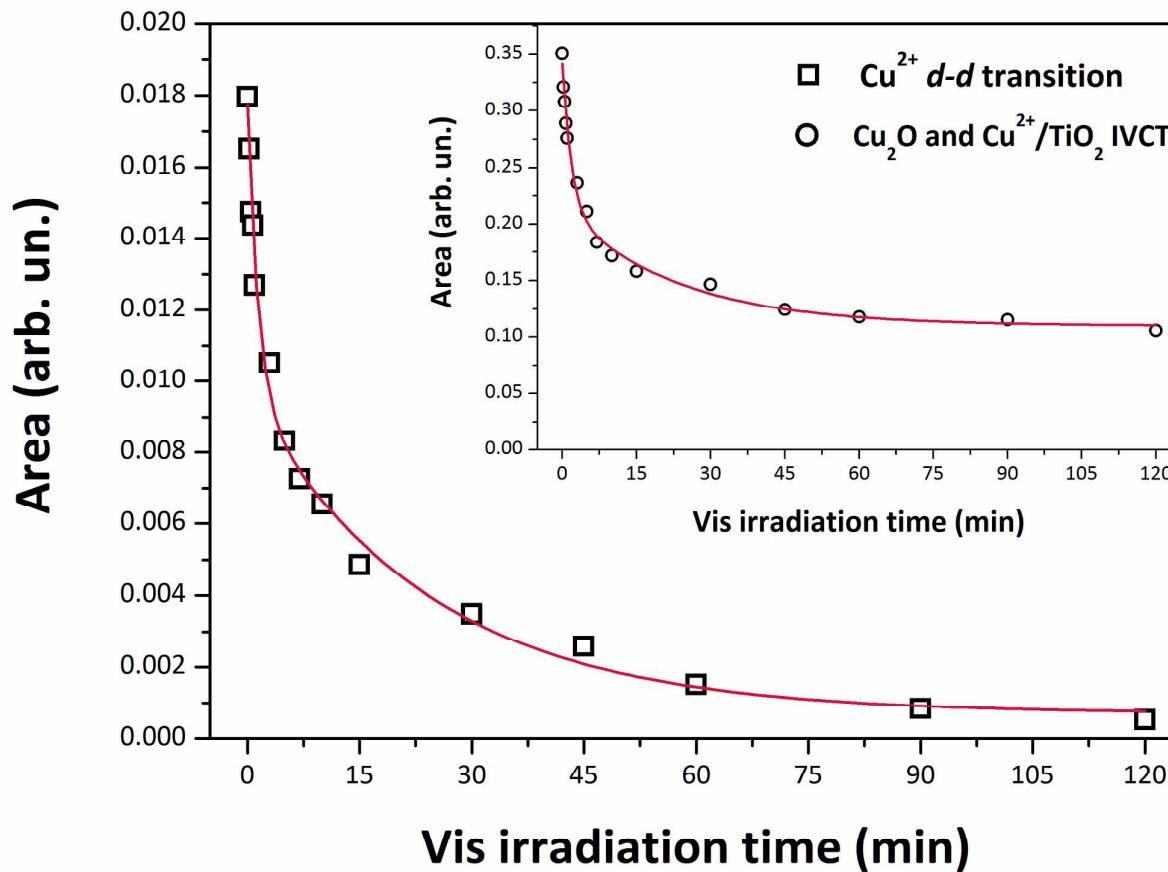


Fig. S5 – Area of the band due to the Cu²⁺ d-d transition in **Cu-Ti450** versus visible-light exposure time (empty squares); the coefficient of determination R^2 of the double exponential decay function adopted for the fitting was 0.993. In the inset is reported area of the bands due to Cu₂O and Cu²⁺/TiO₂ IVCT **Cu-Ti450** versus visible-light exposure time (empty circles), the coefficient of determination R^2 was 0.992.

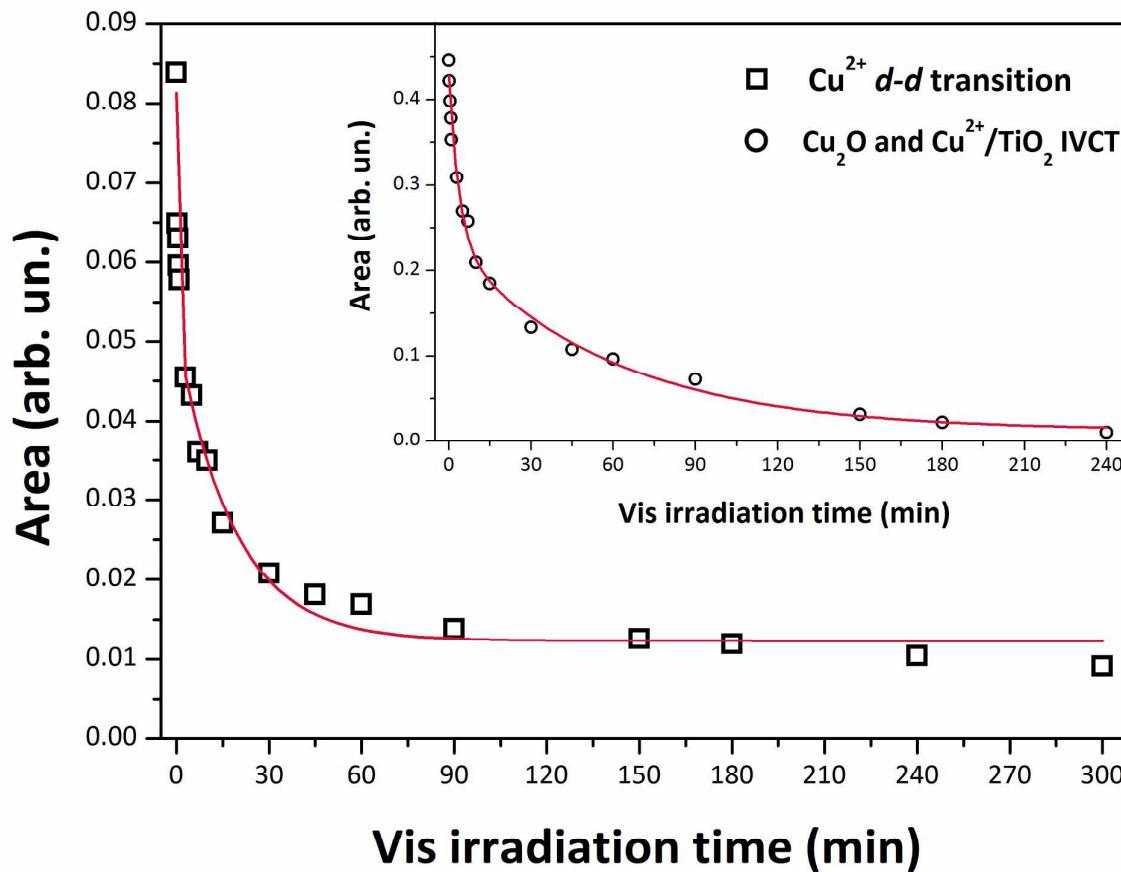


Fig. S6 – Area of the band due to the Cu²⁺ *d-d* transition in **2Cu-Ti450** *versus* visible-light exposure time (empty squares); the coefficient of determination R^2 of the double exponential decay function adopted for the fitting was 0.986. In the inset is reported area of the bands due to Cu₂O and Cu²⁺/TiO₂ IVCT **2Cu-Ti450** *versus* visible-light exposure time (empty circles), the coefficient of determination R^2 was 0.993.

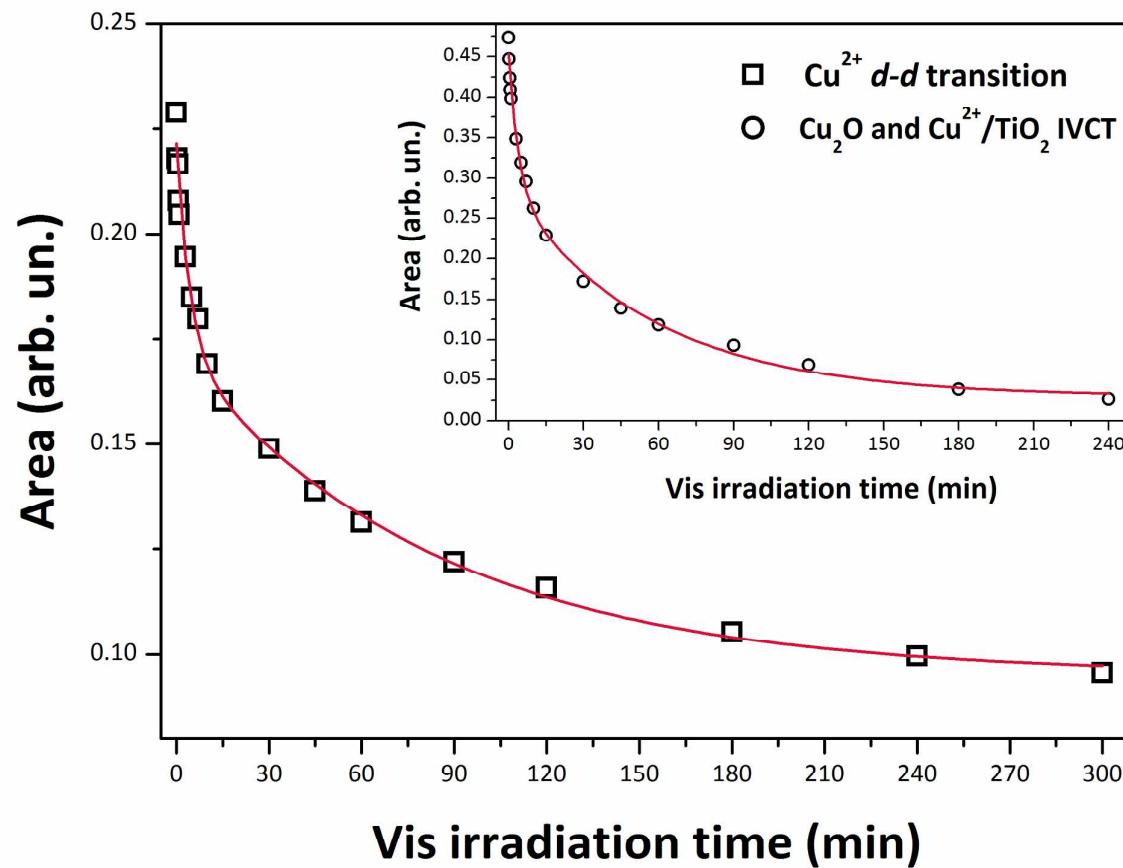


Fig. S7 – Area of the band due to the Cu^{2+} $d-d$ transition in **5Cu-Ti450** *versus* visible-light exposure time (empty squares); the coefficient of determination R^2 of the double exponential decay function adopted for the fitting was 0.994. In the inset is reported area of the bands due to Cu_2O and $\text{Cu}^{2+}/\text{TiO}_2$ IVCT **5Cu-Ti450** *versus* visible-light exposure time (empty circles), the coefficient of determination R^2 was 0.995.

Supporting Information

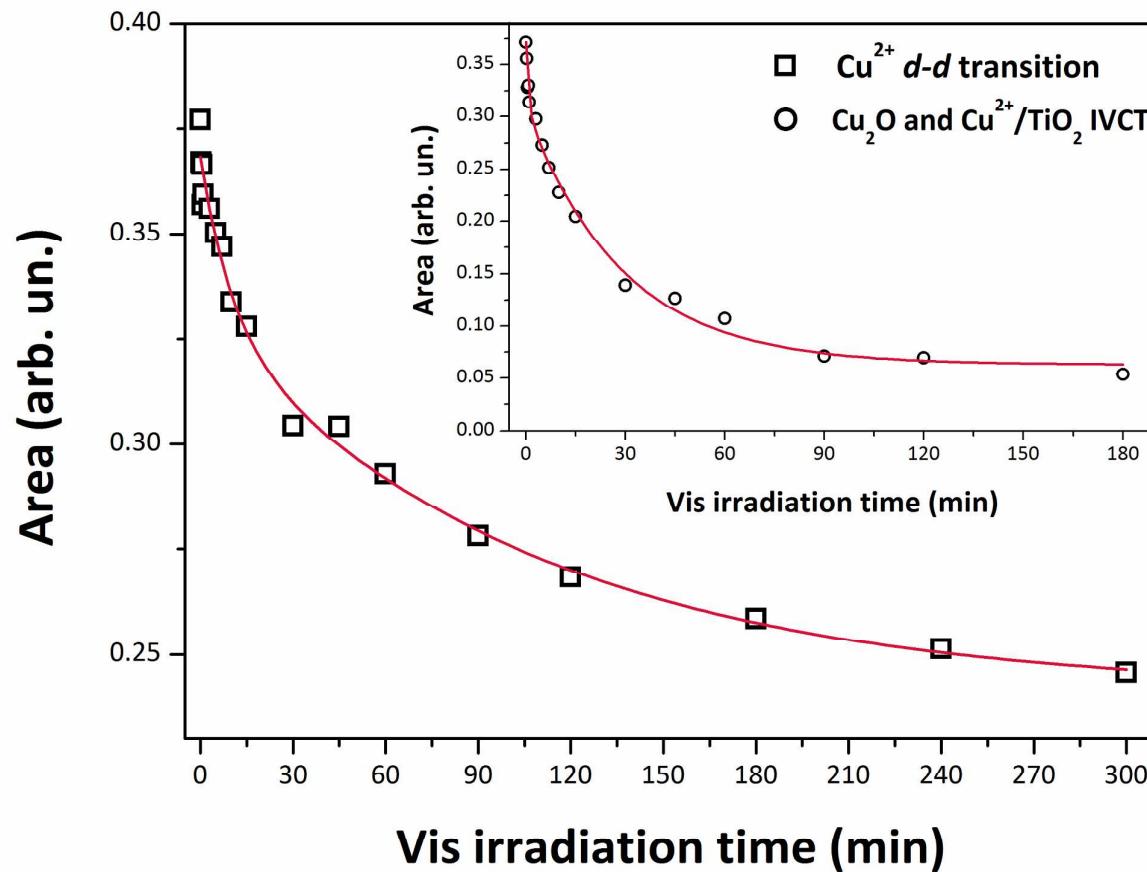


Fig. S8 – Area of the band due to the Cu²⁺ *d-d* transition in **10Cu-Ti450** *versus* visible-light exposure time (empty squares); the coefficient of determination R^2 of the double exponential decay function adopted for the fitting was 0.991. In the inset is reported area of the bands due to Cu₂O and Cu²⁺/TiO₂ IVCT **10Cu-Ti450** *versus* visible-light exposure time (empty circles), the coefficient of determination R^2 was 0.993.

Tables

Table S1 – Energy (centroid), band splitting (FWHM), and intensity (area) of the Cu²⁺ *d–d* transition and Cu₂O & Cu²⁺/TiO₂ IVCT transitions in **2Cu-Ti450** after UVA-light irradiation time. The coefficient of determination R^2 was ≥ 0.958 for all the fitting of the *d–d* transition; for the fit > 7 min $R^2 \geq 0.862$. For the IVCT, R^2 was ≥ 0.912 for all the data.

UVA-light exposure time (min)	Cu ²⁺ <i>d–d</i> transition			Cu ₂ O and Cu ²⁺ /TiO ₂ IVCT		
	Centroid (eV)	FWHM (eV)	Area (arb. units)	Centroid (eV)	FWHM (eV)	Area (arb. units)
0	1.5226(5)	0.5932(11)	0.0701(2)	2.7544(10)	1.0025(35)	0.6543(29)
0.25	1.5373(8)	0.5217(22)	0.0386(3)	2.6871(5)	1.0558(20)	0.4521(12)
0.50	1.5463(9)	0.4779(32)	0.0259(3)	2.6544(8)	1.0433(33)	0.3531(16)
0.75	1.5687(7)	0.4088(26)	0.0172(2)	2.6210(6)	1.0309(28)	0.2895(11)
1	1.5620(9)	0.3964(32)	0.0146(2)	2.6259(5)	1.0796(22)	0.2736(8)
3	1.5886(7)	0.4226(84)	0.0100(4)	2.5787(5)	1.0595(24)	0.1547(5)
5	1.6084(7)	0.3257(79)	0.0042(2)	2.5358(6)	1.0215(29)	0.1036(5)
7	1.6301(8)	0.2427(68)	0.0017(1)	1.6223(46)	0.6738(111)	0.0367(7)
10	1.6578(12)	0.1952(95)	0.0008(1)	1.6260(49)	0.6302(115)	0.0214(5)
15	1.5274(29)	0.0717(45)	0.0003(1)	2.2785(10)	0.7075(51)	0.0135(1)
30	–	–	–	3.0038(113)	1.1393(142)	0.0076(6)
45	–	–	–	1.7328(313)	3.2833(164)	0.0074(4)

Supporting Information

Table S2 – Energy (centroid), band splitting (FWHM), and intensity (area) of the Cu²⁺ *d–d* transition and Cu₂O & Cu²⁺/TiO₂ IVCT transitions in **5Cu-Ti450** after UVA-light irradiation time. The coefficient of determination R^2 was ≥ 0.998 for all the fitting of the *d–d* transition. For the IVCT, R^2 was ≥ 0.922 for all data. For 90 min, and 120 min irradiation time the fitting did not give any reliable data.

UVA-light exposure time (min)	Cu ²⁺ <i>d–d</i> transition			Cu ₂ O and Cu ²⁺ /TiO ₂ IVCT		
	Centroid (eV)	FWHM (eV)	Area (arb. units)	Centroid (eV)	FWHM (eV)	Area (arb. units)
0	1.5511(3)	0.6244(10)	0.2385(6)	2.7030(4)	1.0385(14)	0.8514(16)
0.25	1.5536(3)	0.5962(10)	0.2022(5)	2.6733(4)	1.0438(16)	0.7009(15)
0.50	1.5549(4)	0.5787(13)	0.1828(6)	2.6533(3)	1.0449(12)	0.6202(10)
0.75	1.5587(3)	0.5602(10)	0.1636(5)	2.6451(4)	1.0440(20)	0.5611(15)
1	1.5591(3)	0.5573(11)	0.1583(5)	2.6225(4)	1.0270(16)	0.5026(11)
3	1.5639(3)	0.5148(11)	0.1206(4)	2.5983(4)	1.0110(18)	0.3717(9)
5	1.5680(3)	0.4936(10)	0.1054(3)	2.5797(4)	1.0079(18)	0.3053(8)
7	1.5682(3)	0.4800(11)	0.0951(3)	2.5731(4)	1.0271(21)	0.2660(8)
10	1.5709(3)	0.4608(12)	0.0844(3)	2.5444(6)	0.9998(28)	0.2130(9)
15	1.5749(3)	0.4437(11)	0.0740(3)	2.5194(4)	0.9817(22)	0.1586(5)
30	1.5815(3)	0.4008(12)	0.0523(2)	2.4678(11)	0.9216(55)	0.0609(6)
45	1.5849(3)	0.3744(14)	0.0440(2)	2.2813(17)	0.9504(140)	0.0241(6)
60	1.5868(3)	0.3765(16)	0.0404(3)	2.2757(14)	0.6044(52)	0.0088(1)
90	1.5881(4)	0.3649(17)	0.0365(3)	–	–	–
120	1.5873(3)	0.3672(16)	0.0375(3)	–	–	–

Supporting Information

Table S3 – Energy (centroid), band splitting (FWHM), and intensity (area) of the Cu²⁺ *d–d* transition and Cu₂O & Cu²⁺/TiO₂ IVCT transitions in **10Cu-Ti450** after UVA-light irradiation time. The coefficient of determination R^2 was ≥ 0.998 for all the fitting of the *d–d* transition. For the IVCT, R^2 was ≥ 0.964 for all data except those at 120 and 180 min, where it was equal to 0.839 and 0.875, respectively.

UVA-light exposure time (min)	Cu ²⁺ <i>d–d</i> transition			Cu ₂ O and Cu ²⁺ /TiO ₂ IVCT		
	Centroid (eV)	FWHM (eV)	Area (arb. units)	Centroid (eV)	FWHM (eV)	Area (arb. units)
0	1.5585(4)	0.6183(14)	0.3868(14)	2.6096(4)	1.0105(18)	0.7297(19)
0.25	1.5631(5)	0.5926(15)	0.3477(14)	2.5726(4)	0.9794(16)	0.6064(15)
0.50	1.5605(4)	0.5939(14)	0.3393(12)	2.5613(5)	0.9783(23)	0.5590(19)
0.75	1.5632(6)	0.5707(18)	0.3089(15)	2.5521(4)	0.9696(19)	0.5112(15)
1	1.5636(5)	0.5696(16)	0.3007(13)	2.5460(5)	0.9634(24)	0.4736(17)
3	1.5665(5)	0.5481(17)	0.2683(12)	2.4927(4)	0.9121(20)	0.3479(11)
5	1.5664(4)	0.5434(15)	0.2519(11)	2.5033(6)	0.9384(29)	0.3145(15)
7	1.5676(4)	0.5396(14)	0.2437(10)	2.4772(7)	0.8975(32)	0.2594(14)
10	1.5683(4)	0.5263(14)	0.2252(9)	2.4695(6)	0.9008(30)	0.2269(11)
15	1.5703(5)	0.5145(16)	0.2089(10)	2.4418(7)	0.8752(33)	0.1778(10)
30	1.5715(5)	0.4960(16)	0.1864(9)	2.3653(6)	0.7863(27)	0.1081(5)
45	1.5717(6)	0.4902(19)	0.1731(11)	2.3647(5)	0.7575(24)	0.0749(3)
60	1.5763(4)	0.4764(15)	0.1594(8)	2.2806(5)	0.6009(20)	0.0371(2)
90	1.5764(4)	0.4644(15)	0.1474(7)	2.2422(10)	0.5484(36)	0.0207(2)
120	1.5758(4)	0.4772(16)	0.1500(8)	2.2084(22)	0.5477(76)	0.0123(2)
180	1.5728(4)	0.4791(18)	0.1483(9)	2.2468(19)	0.5127(63)	0.0054(1)
240	1.5740(4)	0.4699(16)	0.1417(7)	–	–	–

Supporting Information

Table S4 – Energy (centroid), band splitting (FWHM), and intensity (area) of the Cu²⁺ *d–d* transition and Cu₂O & Cu²⁺/TiO₂ IVCT transitions in **2Cu-Ti450** after visible-light irradiation time. The coefficient of determination R^2 was ≥ 0.992 for all the fitting of the *d–d* transition. For the IVCT, R^2 was ≥ 0.906 for all data.

Visible-light exposure time (min)	Cu ²⁺ <i>d–d</i> transition			Cu ₂ O and Cu ²⁺ /TiO ₂ IVCT		
	Centroid (eV)	FWHM (eV)	Area (arb. units)	Centroid (eV)	FWHM (eV)	Area (arb. units)
0	1.5204(3)	0.6006(8)	0.0839(2)	2.7271(11)	0.9767(38)	0.4460(22)
0.25	1.5289(4)	0.5707(9)	0.0649(2)	2.7435(8)	0.9991(30)	0.4127(17)
0.50	1.5294(4)	0.5675(11)	0.0630(2)	2.7393(6)	1.0350(23)	0.3984(12)
0.75	1.5287(4)	0.5598(11)	0.0596(2)	2.7317(7)	1.0281(25)	0.3782(12)
1	1.5316(5)	0.5543(12)	0.0578(2)	2.7116(9)	1.0050(32)	0.3531(15)
3	1.5385(4)	0.5127(12)	0.0455(2)	2.7076(7)	1.0420(26)	0.3093(10)
5	1.5399(5)	0.5067(15)	0.0432(2)	2.6765(7)	1.0381(27)	0.2692(10)
7	1.5425(5)	0.4835(15)	0.0360(2)	2.6999(5)	1.0668(21)	0.2578(7)
10	1.5430(6)	0.4782(19)	0.0350(2)	2.6424(10)	1.0234(41)	0.2094(12)
15	1.5500(6)	0.4431(18)	0.0271(2)	2.6558(10)	1.0403(41)	0.1847(10)
30	1.5547(6)	0.4112(21)	0.0208(2)	2.6306(8)	1.0675(35)	0.1337(7)
45	1.5560(7)	0.3946(24)	0.0181(2)	2.6126(7)	1.0881(31)	0.1075(5)
60	1.5592(7)	0.3965(25)	0.0169(2)	2.6344(6)	1.1131(28)	0.0963(4)
90	1.5609(7)	0.3764(27)	0.0139(2)	2.6406(6)	1.1050(28)	0.0723(3)
150	1.5676(6)	0.3782(30)	0.0126(2)	2.4795(12)	1.2167(103)	0.0320(5)
180	1.5685(6)	0.3760(32)	0.0120(2)	2.4994(13)	1.0605(73)	0.0223(3)
240	1.5709(6)	0.3640(32)	0.0104(2)	2.3931(22)	1.0795(192)	0.0107(4)
300	1.5700(7)	0.3592(40)	0.0091(2)	–	–	–

Supporting Information

Table S5 – Energy (centroid), band splitting (FWHM), and intensity (area) of the Cu²⁺ *d–d* transition and Cu₂O & Cu²⁺/TiO₂ IVCT transitions in **5Cu-Ti450** after visible-light irradiation time. The coefficient of determination R^2 was ≥ 0.998 for all the fitting of the *d–d* transition. For the IVCT, R^2 was ≥ 0.904 for all data, except that at time 180 min, those R^2 being equal to 0.813.

Visible-light exposure time (min)	Cu ²⁺ <i>d–d</i> transition			Cu ₂ O and Cu ²⁺ /TiO ₂ IVCT		
	Centroid (eV)	FWHM (eV)	Area (arb. units)	Centroid (eV)	FWHM (eV)	Area (arb. units)
0	1.5472(4)	0.6289(12)	0.6289(12)	2.7193(8)	0.9763(29)	0.4734(18)
0.25	1.5461(4)	0.6214(12)	0.2181(7)	2.7207(6)	0.9924(23)	0.4473(14)
0.50	1.5478(4)	0.6179(12)	0.2167(7)	2.7025(8)	0.9832(31)	0.4240(18)
0.75	1.5463(5)	0.6116(14)	0.2079(7)	2.7054(8)	0.9800(28)	0.4091(16)
1	1.5468(5)	0.6074(13)	0.2047(7)	2.7020(8)	0.9830(29)	0.3985(16)
3	1.5502(4)	0.5973(13)	0.1945(7)	2.6832(7)	0.9879(29)	0.3483(14)
5	1.5487(4)	0.5908(13)	0.1850(6)	2.6809(6)	0.9930(24)	0.3195(11)
7	1.5483(5)	0.5870(14)	0.1798(7)	2.6718(18)	0.9938(29)	0.2956(12)
10	1.5524(4)	0.5733(13)	0.1691(6)	2.6605(8)	0.9856(33)	0.2624(12)
15	1.5529(4)	0.5649(12)	0.1603(5)	2.6515(7)	0.9975(29)	0.2292(9)
30	1.5512(4)	0.5570(13)	0.1489(6)	2.6086(15)	1.0006(65)	0.1724(16)
45	1.5519(4)	0.5475(13)	0.1387(5)	2.6289(11)	1.0053(45)	0.1388(9)
60	1.5534(4)	0.5386(14)	0.1313(5)	2.6322(13)	1.0142(53)	0.1184(9)
90	1.5544(5)	0.5246(16)	0.1220(6)	2.6273(23)	1.0186(99)	0.0931(13)
120	1.5571(4)	0.5168(15)	0.1158(5)	2.6264(27)	1.0054(114)	0.0689(11)
180	1.5583(5)	0.5016(15)	0.1054(5)	2.6499(40)	1.0488(176)	0.0382(9)
240	1.5609(4)	0.4870(14)	0.0996(4)	2.6935(27)	1.1997(123)	0.0266(4)
300	1.5611(4)	0.4835(14)	0.0957(4)	–	–	–

Supporting Information

Table S6 – Energy (centroid), band splitting (FWHM), and intensity (area) of the Cu²⁺ *d–d* transition and Cu₂O & Cu²⁺/TiO₂ IVCT transitions in **10Cu-Ti450** after visible-light irradiation time. The coefficient of determination R^2 was ≥ 0.998 for all the fitting of the *d–d* transition. For the IVCT, R^2 was ≥ 0.969 for all the data.

Visible-light exposure time (min)	Cu ²⁺ <i>d–d</i> transition			Cu ₂ O and Cu ²⁺ /TiO ₂ IVCT		
	Centroid (eV)	FWHM (eV)	Area (arb. units)	Centroid (eV)	FWHM (eV)	Area (arb. units)
0	1.5617(3)	0.6172(10)	0.3771(10)	2.6724(4)	0.9705(16)	0.3713(8)
0.25	1.5617(3)	0.6117(10)	0.3672(9)	2.6746(6)	0.9723(23)	0.3558(11)
0.50	1.5620(3)	0.6101(10)	0.3666(10)	2.6466(5)	0.9399(18)	0.3279(8)
0.75	1.5619(3)	0.6053(10)	0.3570(9)	2.6662(5)	0.9645(18)	0.3301(8)
1	1.5618(3)	0.6044(10)	0.3594(9)	2.6411(5)	0.9428(19)	0.3140(9)
3	1.5608(3)	0.6039(11)	0.3561(10)	2.6384(5)	0.9588(18)	0.2976(7)
5	1.5604(4)	0.5996(12)	0.3503(11)	2.6155(4)	0.9472(17)	0.2728(7)
7	1.5607(3)	0.5993(10)	0.3470(9)	2.6093(5)	0.9428(20)	0.2519(7)
10	1.5629(3)	0.5892(11)	0.3339(10)	2.5963(6)	0.9356(22)	0.2280(8)
15	1.5620(3)	0.5885(10)	0.3280(9)	2.5924(5)	0.9259(21)	0.2046(6)
30	1.5644(3)	0.5730(11)	0.3045(9)	2.5421(5)	0.8824(19)	0.1389(4)
45	1.5615(3)	0.5781(10)	0.3043(8)	2.5565(6)	0.9220(21)	0.1268(4)
60	1.5626(3)	0.5690(11)	0.2928(9)	2.5465(14)	0.9404(60)	0.1072(10)
90	1.5658(3)	0.5584(10)	0.2781(8)	2.5051(7)	0.8402(29)	0.0710(3)
120	1.5667(3)	0.5502(10)	0.2684(8)	2.5356(3)	0.9387(17)	0.0697(2)
180	1.5663(3)	0.5466(10)	0.2585(7)	2.6332(18)	1.0510(74)	0.0534(5)
240	1.5670(3)	0.5425(11)	0.2513(8)	2.4433(9)	0.8259(78)	0.0153(3)
300	1.5663(3)	0.5410(11)	0.2457(8)	–	–	–