Supplementary Information

Fine Tuning and Orientation Control of Surface Cu Complexes on TiO$_2$(110) Premodified with Mercaptobenzoate Molecules: Effect of Different Mercapto Group Positions

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Supplementary information contains the following figures and tables.

Figure S1. Spectroscopic ellipsometry measurements of a typical mercaptobenzoic acid (MBA) layer on TiO$_2$(110) (o-MBA/TiO$_2$(110)) and the o-MBA/TiO$_2$(110) sample after annealing at 200 °C for 1 h in UHV.

Figure S2. Cu K-edge XANES and EXAFS spectra of Cu/o-MBA/TiO$_2$(110) after exposure to air or after annealing at 200 °C for 1 h in UHV.

Figure S3~S5. Side and top views of the model structures for Cu/o-, m- and p-MBA/TiO$_2$(110), respectively. And their selected atomic coordinates used for theoretical calculation of the EXAFS oscillations are also shown in **Table S1~Table S3**.
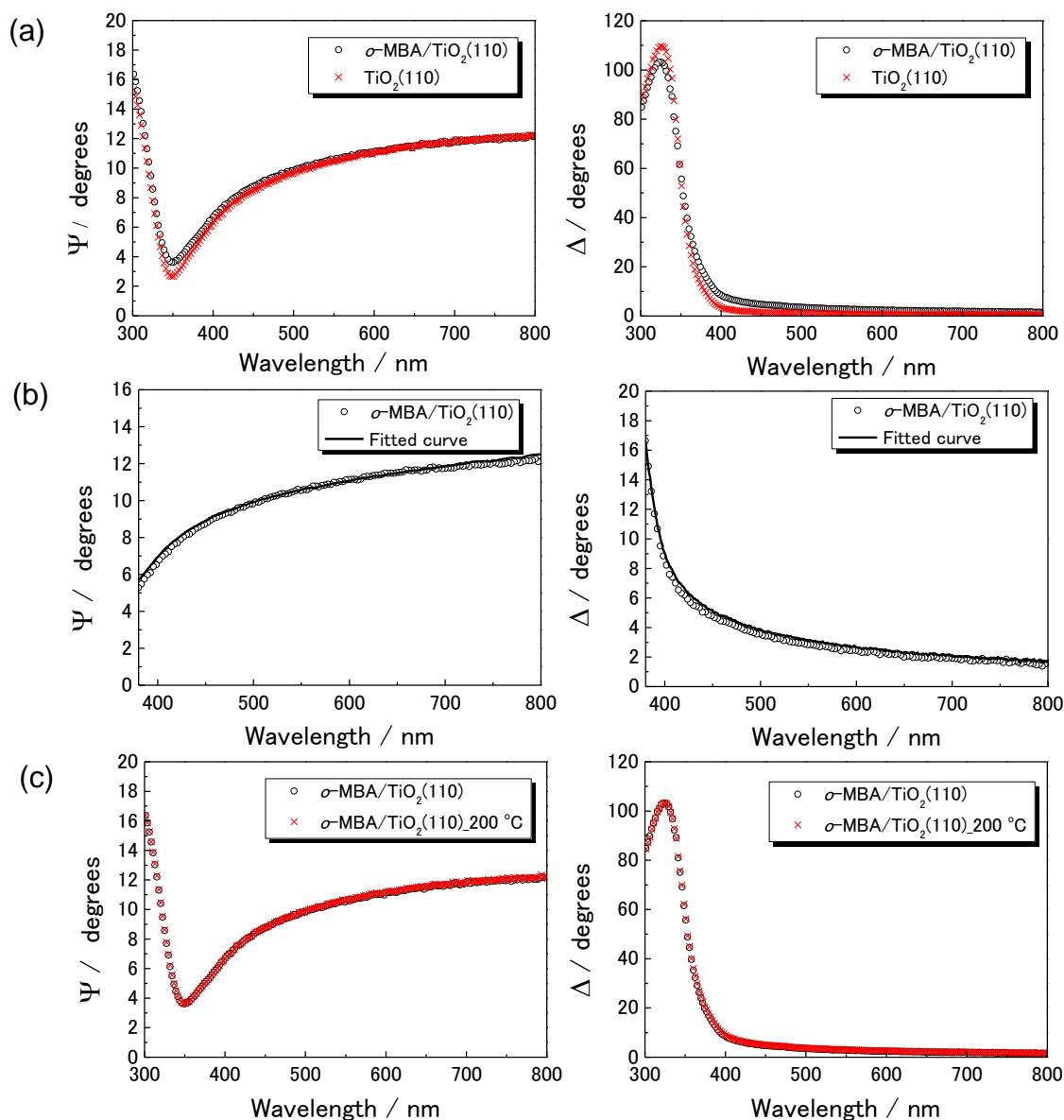
Figure S1. Spectroscopic ellipsometry measurements (GES5E, Semilab) of a typical mercaptobenzoic acid (MBA) layer on $TiO_2(110)$ (o-MBA/$TiO_2(110)$) and its thermal stability. (a) Ellipsometric angles Ψ and Δ for the o-MBA/$TiO_2(110)$ (○) and the $TiO_2(110)$ substrate (×) collected at the incident light angle of 75º from the surface normal. (b) Thickness (d) determination of the o-MBA layer on $TiO_2(110)$ by curve fitting using an optical model consisting of air/MBA layer/$TiO_2(110)$ substrate. The refractive index (n) and the extinction coefficient (k) of the MBA layer were modeled using the Cauchy expression ($n(\lambda)= A+B/\lambda^2+C/\lambda^4$, $k(\lambda) = 0$). We confirmed k was small enough in the wavelength range of 380-800 nm by UV-Vis absorption measurement of the MBA in ethanol solution. We fixed C=0 since its contribution was negligibly small, and the best-fitted result (solid line) was obtained when A=1.50, B=0.05 μm^2, and d=0.85 nm which is in good agreement with the expected monolayer thickness shown in Figure 1 (~0.8 nm). Four measurements were taken at different locations on the sample surface and the obtained d values were reproducible within 0.15 nm. (c) Ellipsometric angles Ψ and Δ for the o-MBA/$TiO_2(110)$ before (○) and after (×) heating at 200ºC for 1 h in UHV. No difference was observed before and after the heating, suggesting the MBA layer was thermally stable.
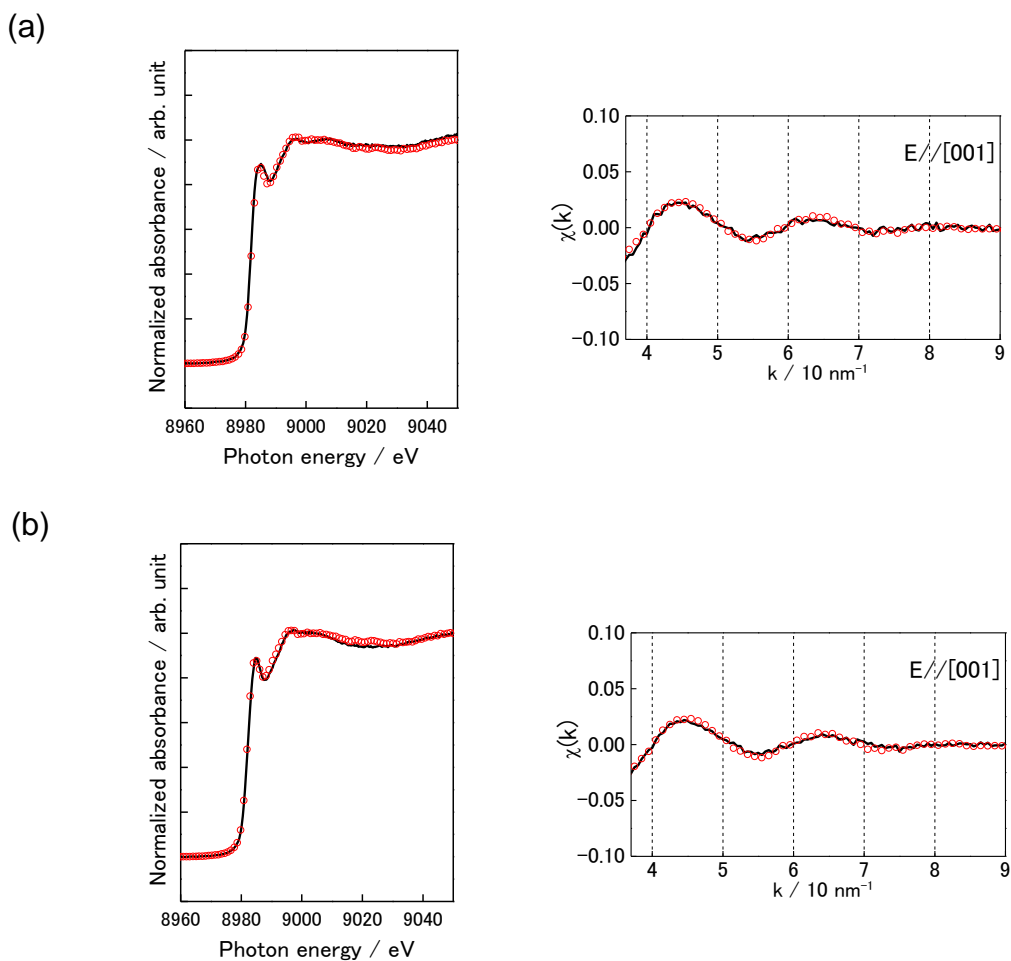
(a)

(b)

Figure S2. Cu K-edge XANES and EXAFS spectra of Cu/*o*-MBA/TiO$_2$(110) (a) after exposure to air for 10 min and then transfer back to the UHV chamber (*E*//[001]) or (b) after heating at 200 ºC for 1 h in UHV (*E*//[001]). The red circles (○) show the XANES and EXAFS spectra before each treatment (the same spectra with those shown in Figure 2 (a) (XANES at *E*//[001]) and Figure 3 (a) (EXAFS at *E*//[001])). No significant difference was recognized before and after each treatment and Cu-S (0.219 nm) and Cu-O (0.185 nm) bonds were detected in the EXAFS spectra, suggesting the Cu species was stable after air exposure and heating at 200 ºC in UHV.
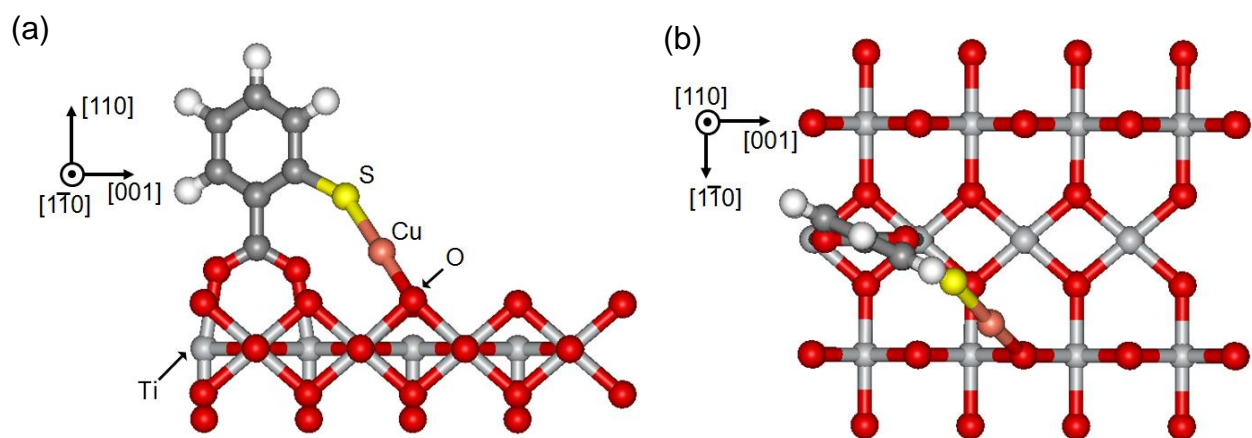
Figure S3. (a) Side and (b) top views of the proposed model structure for Cu/*o*-MBA/TiO$_2$(110).
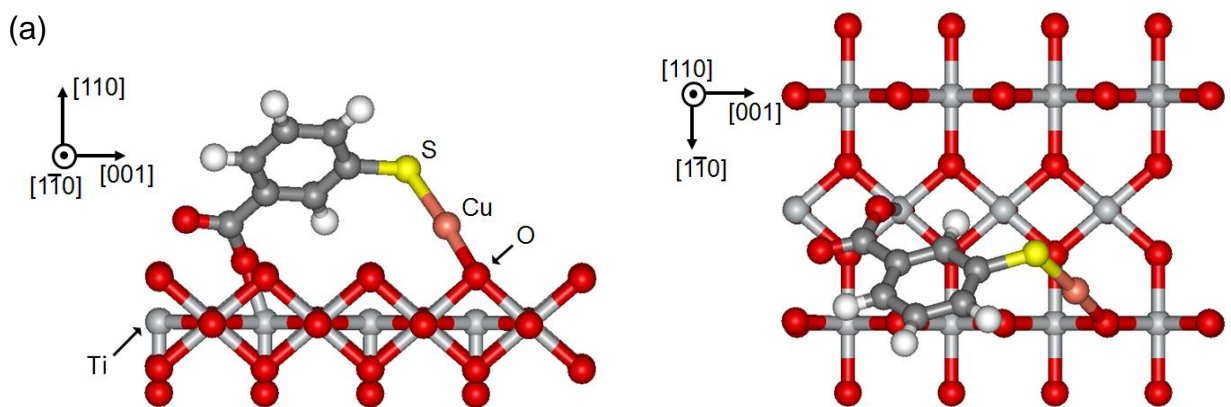

Figure S4. (a) Side and (b) top views of the proposed model structure for Cu/*m*-MBA/TiO$_2$(110).
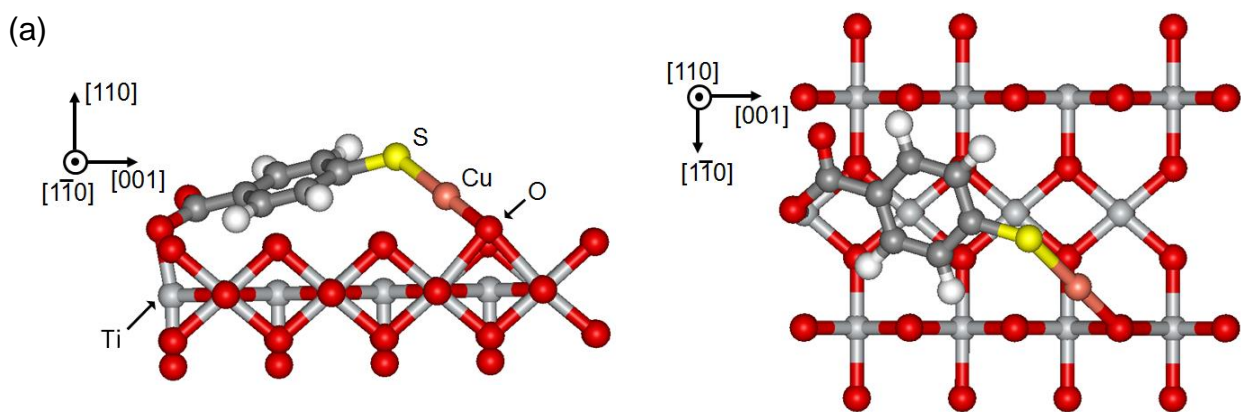

Figure S5. (a) Side and (b) top views of the proposed model structure for Cu/*p*-MBA/TiO$_2$(110).

4

Table S1. Selected atomic coordinates used for theoretical calculation of the EXAFS oscillations for Cu/*o*-MBA/TiO$_2$(110).

Atoms	X / Å	Y / Å	Z / Å
C	1.84	2.81	2.82
C	1.11	3.94	3.38
C	0.01	4.47	2.70
C	1.51	4.48	4.60
C	0.81	5.56	5.14
C	-0.68	5.55	3.24
C	-0.29	6.09	4.46
Cu	-0.33	3.02	-0.83
H	2.37	4.06	5.13
H	1.12	5.99	6.10
H	-1.55	5.97	2.70
H	-0.84	6.95	4.89
O	1.24	1.99	2.01
O	3.08	2.62	3.14
O	-0.13	2.20	-2.47
S	-0.59	3.88	1.18
Ti	4.46	0.99	2.49
Ti	2.04	0.16	1.01
Ti	-0.66	0.72	-3.72
Ti	1.76	1.55	-2.24

Table S2. Selected atomic coordinates used for theoretical calculation of the EXAFS oscillations for Cu/*m*-MBA/TiO$_2$(110).

Atoms	X / Å	Y / Å	Z / Å
C	2.87	3.09	-0.16
C	2.31	2.37	0.90
C	4.19	3.54	-0.08
C	4.95	3.26	1.06
C	3.07	2.09	2.04
C	4.39	2.54	2.11
C	2.48	1.32	3.17
Cu	1.90	1.80	-3.03
H	4.63	4.10	-0.91
H	5.99	3.61	1.12
H	1.27	2.02	0.84
H	5.00	2.32	3.01
O	1.90	0.34	-4.16
O	1.14	0.76	3.04
O	3.13	1.16	4.22
S	1.92	3.43	-1.57
Ti	1.82	-1.14	-2.82
Ti	0.94	-0.67	-5.60
Ti	0.31	-0.71	2.45

Table S3. Selected atomic coordinates used for theoretical calculation of the EXAFS oscillations for Cu/p-MBA/TiO$_2$(110).

Atoms	X / Å	Y / Å	Z / Å
C	1.46	2.64	0.71
C	2.33	1.67	1.23
C	0.52	3.24	1.55
C	0.45	2.88	2.90
C	2.26	1.31	2.57
C	1.32	1.92	3.41
C	1.25	1.54	4.85
Cu	1.90	1.79	-2.74
H	-0.16	4.00	1.15
H	-0.29	3.36	3.56
H	3.07	1.19	0.57
H	2.95	0.55	2.97
O	2.21	0.69	-4.26
O	2.10	0.54	5.50
O	0.36	2.16	5.46
S	1.55	3.08	-0.96
Ti	2.00	-1.11	-2.93
Ti	1.11	-0.64	-5.71
Ti	1.37	-1.15	5.12