Surface mapping of photocatalytic activity in heterogeneous TiO_2 films

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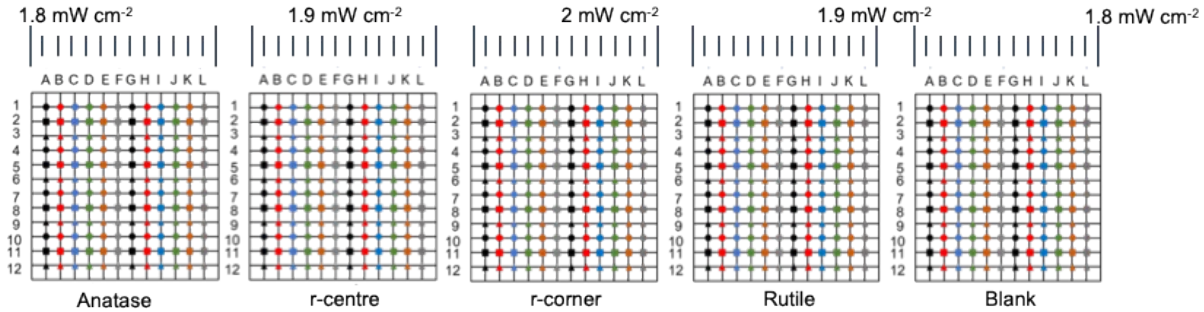
Supplementary Information

Irradiation Conditions

Table S1. Irradiance, *I* (units, mW cm^{-2}) and corresponding quantum flux, *E* (units, mol cm^{-2} s^{-1}) measured across the photoreactor under UVA light (λ= 365 nm). Averaged values were, respectively, 1.93(±0.05) mW cm^{-2} and 5.9(±0.16)×10^{-9} mol cm^{-2} s^{-1}.

		A	B	C	D	E	F	G	H	I	J	K	L
Anatase	***I*** (mW cm^{-2})	1.83	1.84	1.85	1.85	1.86	1.86	1.87	1.87	1.88	1.89	1.89	1.90
	E ×10^{-9} (mol cm^{-2} s^{-1})	5.60	5.61	5.63	5.65	5.67	5.68	5.70	5.72	5.74	5.75	5.77	5.79
r-centre	***I*** (mW cm^{-2})	1.90	1.91	1.91	1.92	1.93	1.93	1.94	1.94	1.95	1.95	1.96	1.97
	E ×10^{-9} (mol cm^{-2} s^{-1})	5.81	5.82	5.84	5.86	5.88	5.89	5.91	5.93	5.95	5.96	5.98	6.00
r-corner	***I*** (mW cm^{-2})	1.97	1.98	1.98	1.99	1.99	2.00	1.99	1.99	1.98	1.98	1.97	1.97
	E ×10^{-9} (mol cm^{-2} s^{-1})	6.02	6.03	6.05	6.07	6.08	6.10	6.08	6.07	6.05	6.03	6.02	6.00



Film characterisation

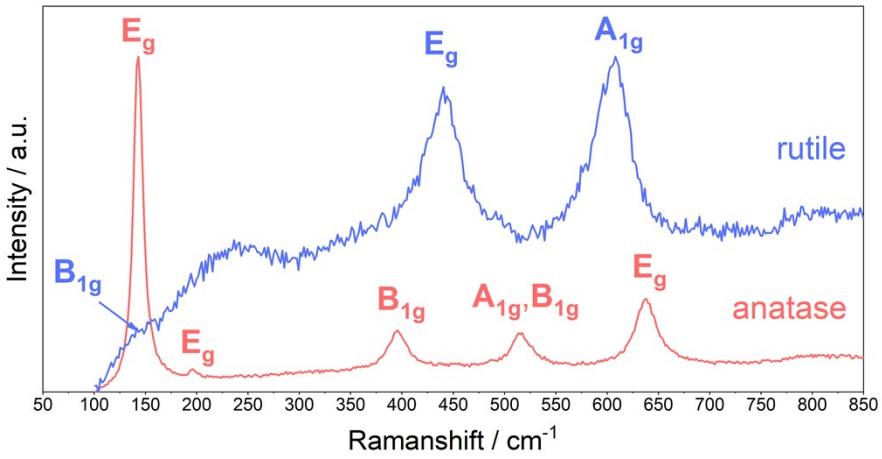


Fig. S1. Raman spectra recorded on the anatase (red line) and rutile (blue line) 'parent' films. The assigned modes confirm the presence of the anatase and rutile phases (*e.g.*, Li Bassi *et al. J. Appl. Phys.* 2005, 98, 074305).

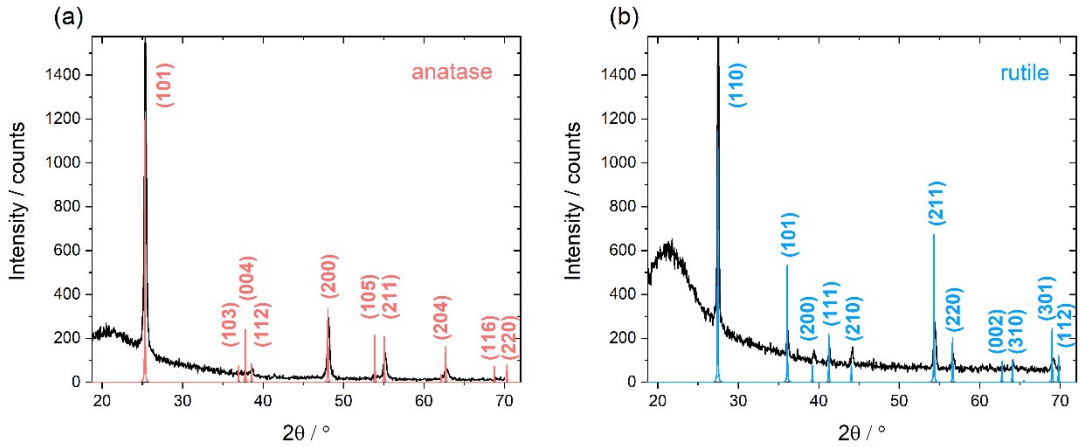


Fig. S2. XRD spectra recorded on the (a) anatase and (b) rutile 'parent' films. The peaks are in agreement with reference patterns recorded on pure phase powders.

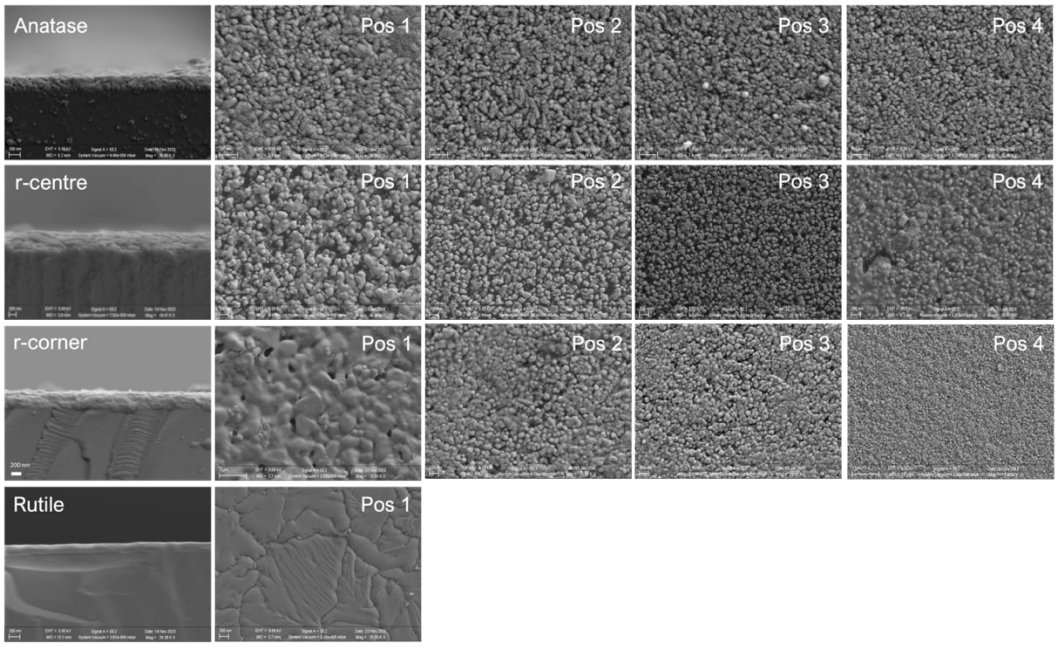


Fig. S3. Side-on and top-down SEM images of pure and mixed-phase TiO_2 samples (positions as in Fig. 1).

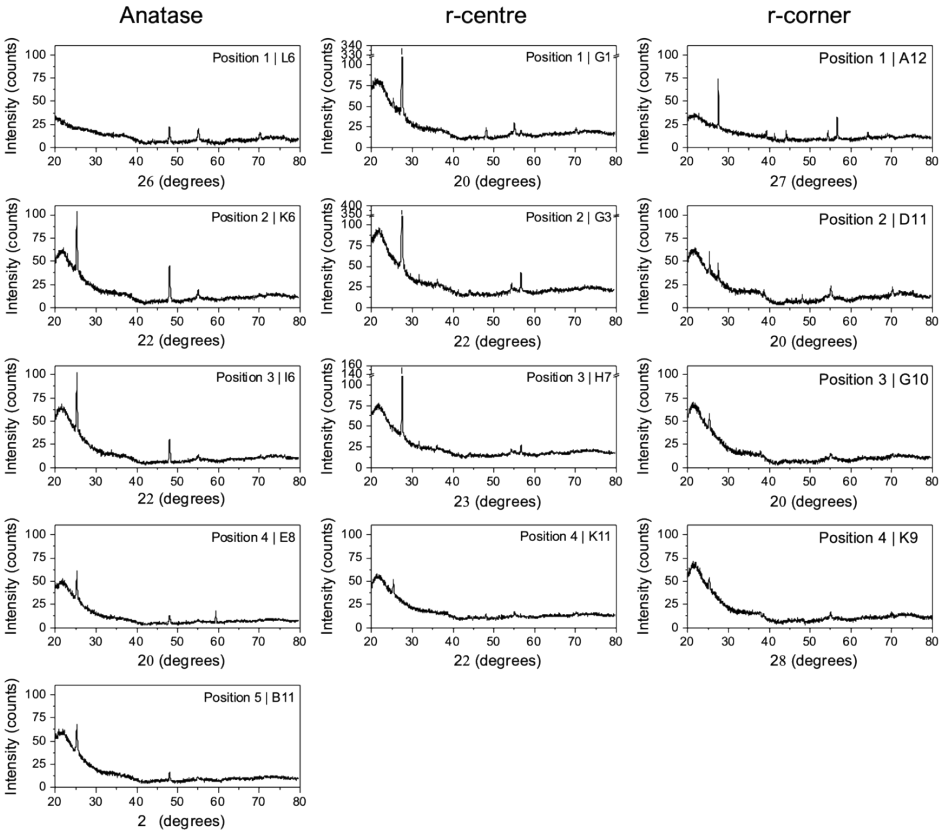


Fig. S4. X-ray diffraction patterns at selected positions (Fig. 1) on anatase, r-centre and r-corner samples.

Table S2. Surface phase composition determined via VB XPS mapping across a 12×12 grid on r-centre and r-corner samples. The values are given in % anatase phase.

r-centre

	A	B	C	D	E	F	G	H	I	J	K	L
1	80	100	91	100	100	84	100	100	100	94	99	100
2	100	95	96	97	96	100	94	100	100	100	97	97
3	96	100	97	100	100	100	96	100	100	100	100	100
4	100	100	97	100	100	98	92	100	100	100	100	100
5	100	94	100	96	62	58	86	98	100	100	100	100
6	93	100	100	74	36	23	58	82	100	100	100	100
7	98	100	95	65	25	28	36	69	98	100	96	100
8	100	97	98	70	42	24	32	48	90	100	92	100
9	100	100	100	95	54	33	39	63	100	100	100	99
10	100	95	98	98	99	98	98	100	100	100	100	96
11	100	100	100	100	100	100	100	100	100	100	98	100
12	85	100	100	100	100	100	99	100	100	100	100	100

r-corner

	A	B	C	D	E	F	G	H	I	J	K	L
1	90	96	98	97	95	98	100	100	100	99	100	100
2	100	93	100	100	97	97	96	97	100	94	99	100
3	100	98	95	98	98	100	100	96	100	100	98	100
4	100	97	100	100	94	100	100	100	94	100	95	99
5	97	97	99	97	99	100	100	100	100	98	98	100
6	100	100	97	100	96	100	100	100	96	97	99	100
7	100	100	100	100	100	100	100	100	98	100	100	97
8	100	100	97	100	100	98	100	100	95	100	100	100
9	2	100	100	100	100	94	100	100	97	100	100	94
10	2	0	100	100	100	100	100	100	95	100	96	93
11	5	4	3	100	93	100	97	100	98	100	100	97
12	68	17	1	100	100	98	98	95	96	100	98	94

Photocatalytic mapping

The full photocatalytic mapping across the surfaces followed changes in normalised red component R_t of resazurin dye (**Fig. S5**). The corresponding *ttb(90)* values are listed in **Table S3**.

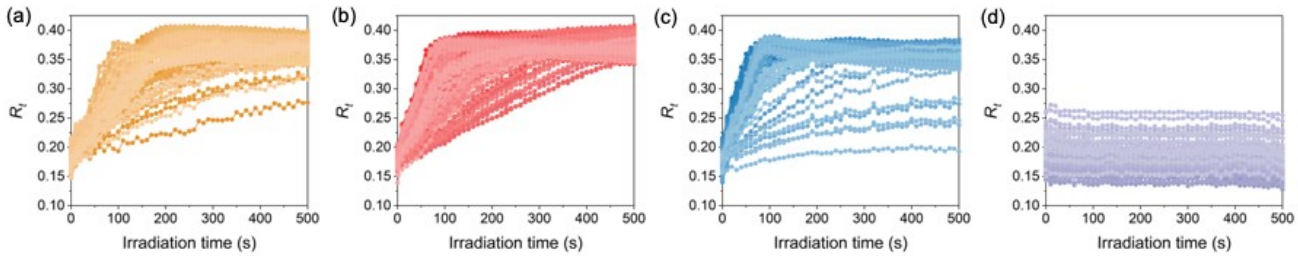


Fig. S5. Normalised red component R_t curves as a function of irradiation time on (a) anatase; (b) r-centre; (c) r-corner; and (d) rutile samples.

Table S3. Time to bleach 90% of the red component of the ink, ttb(90), across a 12×12 grid on anatase, r-centre and r-corner samples. Positions highlighted in grey were inactive and did not reach a plateau.

Anatase

	A	B	C	D	E	F	G	H	I	J	K	L
1		416	231	215	221	222	238	313	308	294	292	448
2		190	168	189	198	169	138	159	143	107	91	250
3		181	162	177	188	170	164	164	145	106	94	173
4		179	164	173	177	178	169	160	141	101	92	170
5		177	168	170	173	188	185	159	137	106	84	161
6		175	167	166	168	169	182	171	141	99	81	163
7		169	163	160	155	176	181	171	121	91	77	133
8		170	162	157	160	172	175	161	118	98	85	175
9		186	164	156	166	170	160	151	132	101	87	172
10		204	160	155	159	157	152	142	134	112	88	240
11		212	169	160	155	158	144	136	131	124	107	363
12			420	344	326	322	308	307	349	343	349	

r-centre

	A	B	C	D	E	F	G	H	I	J	K	L
1	322	220	157	139	160	173	160	155	159	156	230	370
2	313	158	90	87	90	83	75	72	66	64	75	307
3	317	120	99	110	119	132	130	115	89	69	76	331
4	309	118	125	166	329	333	327	256	168	91	80	282
5	279	112	129	321	498	479	417	329	258	130	99	259
6	203	89	125	370	517	582	471	345	241	165	104	231
7	133	79	116	315	535	629	651	489	300	209	100	155
8	123	85	103	250	434	552	560	490	336	209	90	140
9	117	73	78	145	278	399	428	356	262	130	75	166
10	136	62	67	98	159	247	279	237	131	94	72	147
11	149	55	62	79	98	115	122	119	104	82	79	150
12	216	90	87	101	107	118	124	126	116	116	178	363

r-corner

	A	B	C	D	E	F	G	H	I	J	K	L
1	87	70	72	78	101	104	87	78	78	77	91	124
2	62	53	56	53	56	56	56	59	63	55	47	63
3	78	56	52	55	63	67	67	72	74	72	66	80
4	96	57	57	60	67	75	78	75	75	75	84	115
5	140	104	72	72	76	83	85	80	76	74	88	134
6	182	100	77	77	87	90	87	84	76	76	83	135
7		102	80	80	91	91	91	88	80	78	82	122
8		112	95	77	85	87	87	83	80	78	80	125
9		128	101	72	72	79	83	81	74	74	77	120
10			84	71	68	68	70	79	74	70	67	126
11				77	75	75	77	81	78	71	67	144
12					153	135	132	158	153	121	110	

Apparent photonic efficiency

The apparent absorbance of the red component of the dye, *A(sR)* was estimated from **Eq. s1**, using the linear red component, *sR* for each position within the 12×12 grid:

$$A(sR) = \log \frac{sR_0}{sR_{Rz}} \qquad \text{(s1)}$$

Where $^{sR}{}_0$ and $^{sR}{}_{Rz}$ are the *intensity* values of the red component of the digital image in the absence and presence of resazurin, respectively. The value for $^{sR}{}_0$ was taken as equivalent to 255. The application of this equation requires conversion of *non-linear* (*gamma*) parameters, *sR'*, used for digital imaging treatment, into *linear sR* counterparts. The mathematical expression to obtain *sR* values depends whether *sR'* is below, equal to or above 0.0405, according to **Eq. s2** (Yusufu and Mills, *Sens Actuators B Chem* 273, 2018, 1187–1194):

$$sR = 12.92 \cdot sR' \qquad for\ sR'\ values \leq 0.0405$$
$$sR = \left(\frac{sR' + 0.055}{1.055}\right)^{2.4} \qquad for\ sR'\ values > 0.0405 \qquad \text{(s2)}$$

Where sR and sR' are given in their fractional form (*i.e.* values between 0–1). *A(sR)* curves from pure anatase, r-centre and r-corner films are shown in **Fig S6**.

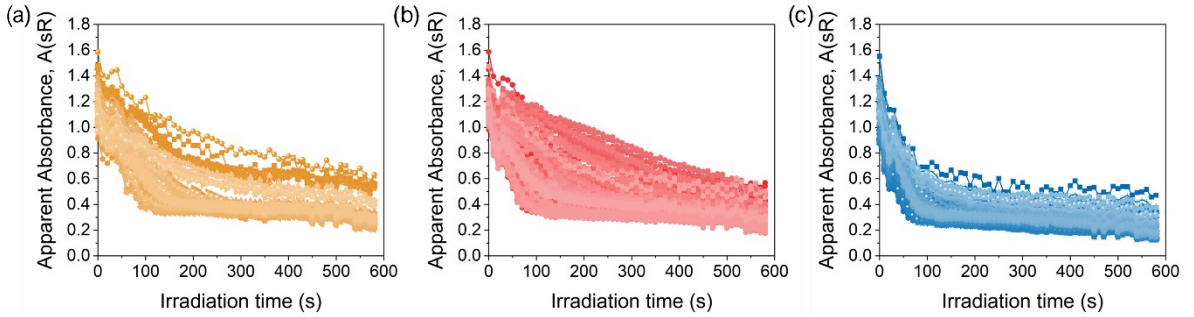


Fig. S6. Red component of apparent absorbance, *A(sR)* for (a) pure anatase, (b) r-centre and (c) r-corner samples.

The rate of R_z reduction, *r* (Eq. 4) is based on the change in absorbance, d|*A(sR)*|/*dt* as obtained from linear regression of the initial (zero-order) section (**Fig. S7**). This evaluation excluded *A(sR)* curves showing an exponential decay. The *r* values are listed in **Table S4**.

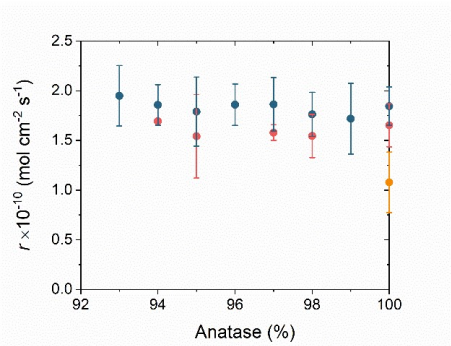


Fig. S7. Rate of R_z reduction, r (units, mol cm^{-2} s^{-1}) as a function of surface anatase content (>90%).

Table S4. Rate of dye reduction, r ($\times 10^{-10}$) (units, mol cm^{-2} s^{-1}) as estimated from Eq. 4, using linear regression of selected *A(sR)* curves.

Anatase

	A	B	C	D	E	F	G	H	I	J	K	L
1												
2										1.21	1.36	
3									0.97	1.24	1.42	
4									1.06	1.39	1.52	
5					0.78				1.13	1.45	1.74	
6			0.70		0.86	0.95	0.94	0.97		1.57	1.70	
7				0.81	0.94	0.94	0.97	1.01		1.69	1.73	
8				0.82	0.90	0.91	0.95	1.04	1.34	1.53E	1.48	
9				0.77	0.78	0.83	0.92	0.98	1.15	1.39	1.48	
10				0.73	0.75	0.77	0.83	0.91	1.01	1.19	1.39	
11				0.67	0.71	0.71	0.77	0.82	0.88	0.98	1.09	
12												

r-centre

	A	B	C	D	E	F	G	H	I	J	K	L
1												
2							1.69	1.81	1.87	1.91	1.63	
3									1.47	1.69	1.61	
4										1.52	1.61	
5												
6		1.45									1.24	
7		1.66	1.24								1.30	
8		1.52	1.43								1.38	
9		1.83	1.70								1.59	
10		1.84	1.80							1.29	1.56	
11		2.01	1.93								1.41	
12												

r-corner

	A	B	C	D	E	F	G	H	I	J	K	L
1												
2		2.16	2.14	2.32	2.29	2.20	2.08	1.88	1.89	1.99	2.22	
3		1.84	1.94	1.91	1.81	1.74	1.67	1.54	1.46	1.43	1.53	
4		1.71	1.77	1.78	1.74	1.73	1.66	1.67	1.63	1.52	1.28	
5			1.45	1.70	1.73	1.80	1.79	1.81	1.82	1.67	1.34	
6			1.41	1.70	1.80	1.94	1.99	2.03	1.99	1.80	1.47	
7			1.59	1.76	1.91	2.05	2.08	2.07	2.00	1.86	1.63	
8				1.89	1.99	2.02	2.09	2.11	2.06	1.90	1.69	
9				1.90	2.07	2.07	2.05	2.03	1.99	1.88	1.76	
10			1.48	1.81	2.00	2.04	2.01	1.86	1.87	1.96	1.90	
11				1.56	1.73	1.70	1.78	1.66	1.72	1.90	1.83	
12												

An apparent photonic efficiency, ξ' (units, $mol_{Rz}\ mol_{\phi}^{-1}$) is given by the rate of dye reduction, *r* (Table S3) as a function of incident photon flux, ϕ (Table S1), according to Eq. 5. The resulting ξ'values are listed in **Table S5**.

Table S5. Apparent formal quantum efficiency, ξ' (units, $mol_{Rz}\ mol_{\phi}^{-1}$) as estimated from Eq. 5.

Anatase

	A	B	C	D	E	F	G	H	I	J	K	L
1												
2										0.0210	0.0235	
3									0.0168	0.0216	0.0246	
4									0.0184	0.0241	0.0263	
5					0.0137				0.0197	0.0251	0.0302	
6			0.0124		0.0151	0.0168	0.0165	0.0169		0.0273	0.0295	
7				0.0144	0.0166	0.0165	0.0171	0.0177		0.0294	0.0300	
8				0.0145	0.0158	0.0159	0.0168	0.0182	0.0233	0.0266	0.0257	
9				0.0136	0.0137	0.0145	0.0162	0.0171	0.0200	0.0241	0.0256	
10				0.0129	0.0132	0.0135	0.0146	0.0159	0.0176	0.0207	0.0240	
11				0.0118	0.0125	0.0126	0.0135	0.0144	0.0154	0.0171	0.0189	
12												

r-centre

	A	B	C	D	E	F	G	H	I	J	K	L
1												
2							0.0287	0.0305	0.0315	0.0321	0.0273	
3									0.0247	0.0284	0.0270	
4										0.0255	0.0269	
5												
6		0.0249									0.021	
7		0.0285	0.0213								0.022	
8		0.0262	0.0244								0.023	
9		0.0314	0.0291								0.027	
10		0.0316	0.0307							0.0216	0.026	
11		0.0345	0.0330								0.024	
12												

r-corner

	A	B	C	D	E	F	G	H	I	J	K	L
1												
2		0.0359	0.0354	0.0383	0.0376	0.0360	0.0342	0.0310	0.0312	0.0329	0.0369	
3		0.0305	0.0321	0.0316	0.0298	0.0286	0.0274	0.0253	0.0242	0.0237	0.0254	
4		0.0284	0.0292	0.0294	0.0286	0.0283	0.0273	0.0276	0.0270	0.0253	0.0213	
5			0.0240	0.0281	0.0285	0.0294	0.0294	0.0298	0.0301	0.0277	0.0224	
6			0.0232	0.0279	0.0295	0.0318	0.0326	0.0335	0.0328	0.0299	0.0244	
7			0.0263	0.0290	0.0314	0.0335	0.0341	0.0342	0.0331	0.0309	0.0271	
8				0.0312	0.0326	0.0332	0.0343	0.0348	0.0341	0.0315	0.0280	
9				0.0313	0.0341	0.0339	0.0337	0.0335	0.0329	0.0312	0.0293	
10			0.0244	0.0298	0.0329	0.0334	0.0331	0.0306	0.0309	0.0324	0.0315	
11				0.0256	0.0285	0.0279	0.0292	0.0273	0.0284	0.0315	0.0305	
12												