Electronic Supplementary Information

Low temperature sintering of binder-containing TiO_2/metal peroxide pastes for dye-sensitized solar cells

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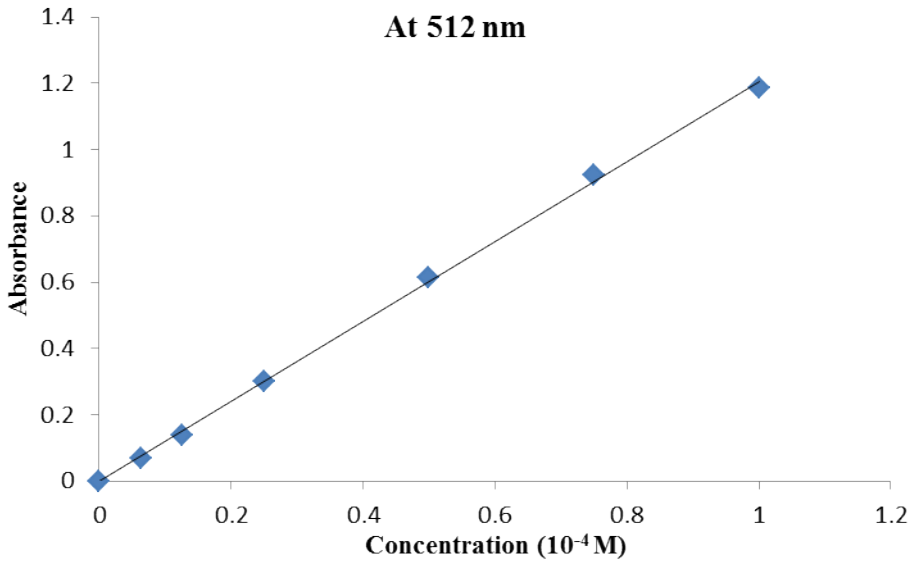
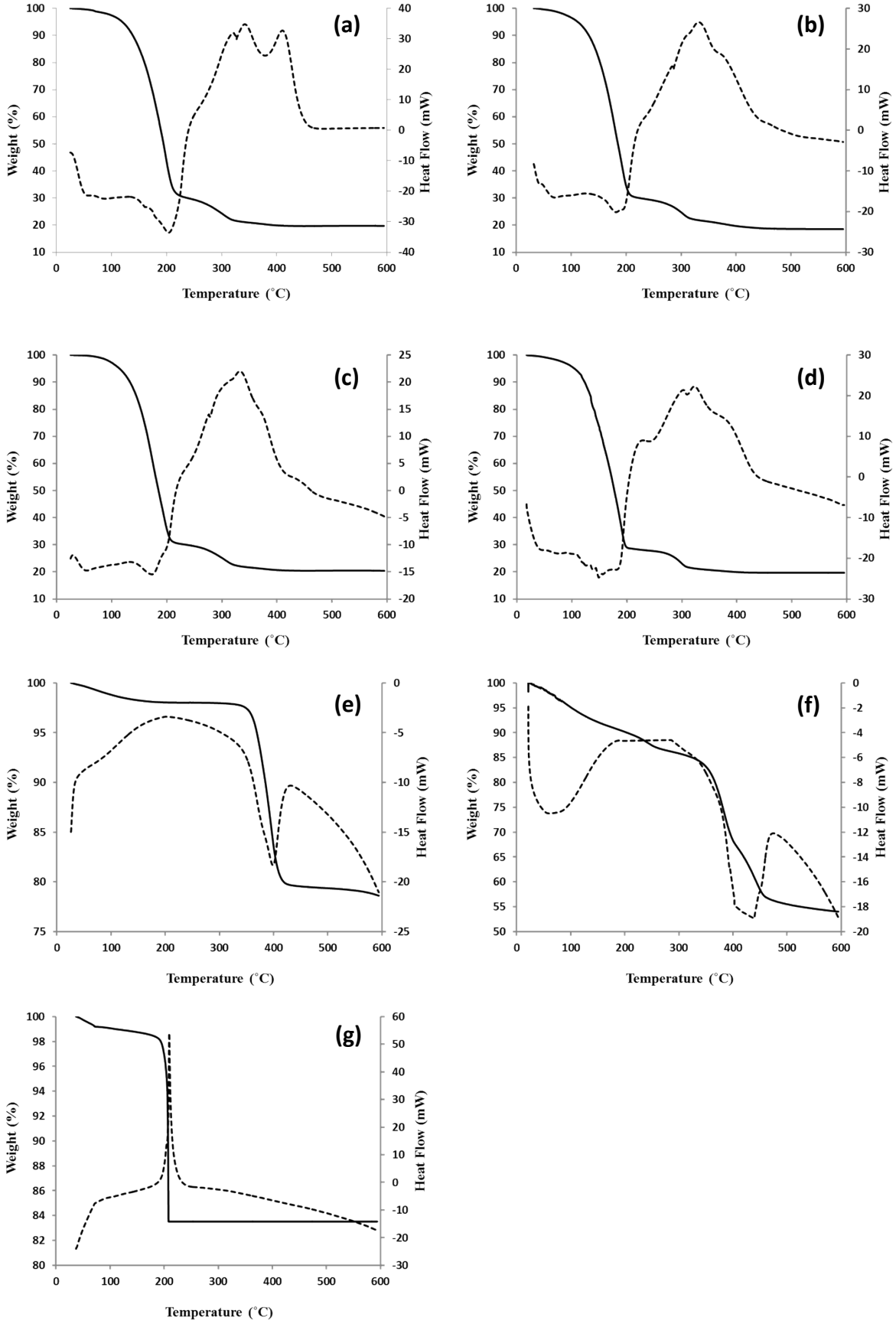
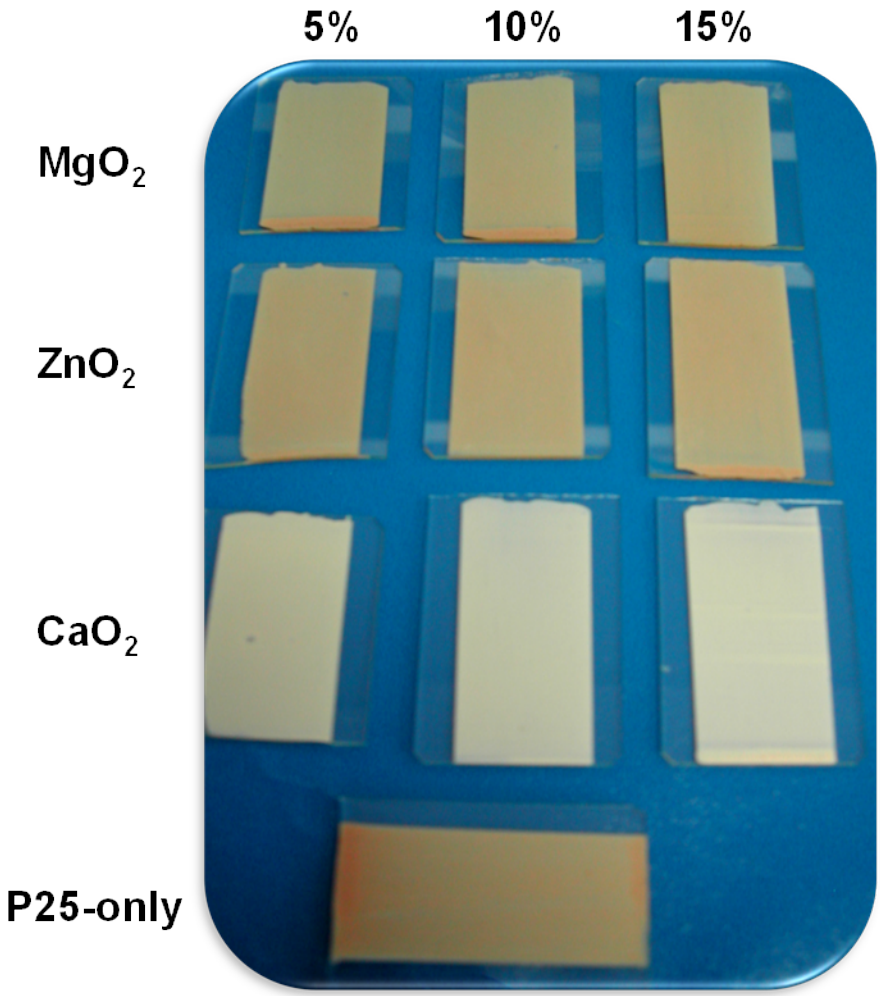
This paper describes the addition of metal peroxide powders (CaO_2, MgO_2 or ZnO_2) to binder-containing P25 doctor-blading pastes for the low temperature sintering of metal oxide films for use in dye-sensitized solar cell (DSC) devices. This ESI contains TGA/DSC data for P25/peroxide films as well as data for the metal peroxides themselves. It also includes XRD data for both P25/peroxide films and the individual sintered metal peroxides as well as SEM/EDX data for a P25/ZnO_2 film. The ESI also includes dye sorption data for N719 onto P25 and P25/ZnO_2.



ESI Fig. 1 Calibration curves of N719 dye in mixture solution of 0.1M $NaOH_{(aq)}$/ ethanol at 1:1 (v/) at different concentrations ($0.0625x10^{-4}$-$1x10^{-4}$) M in 376 and 512 nm.

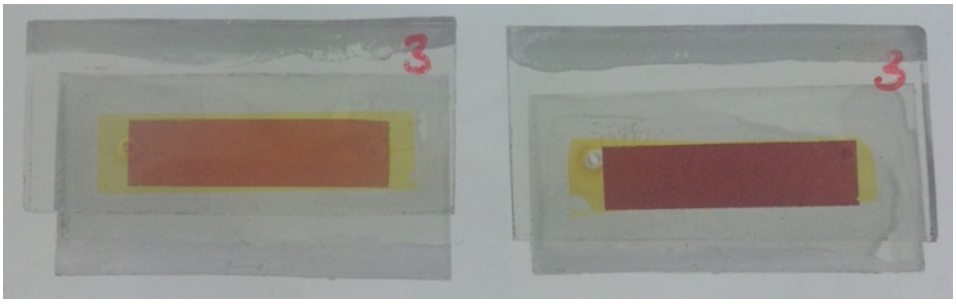


ESI Fig. 2 TGA (solid line) and DSC (dashed line) of (a) P25, (b) P25/CaO_2, (c) P25/MgO_2 and (d) P25/ZnO_2 pastes along with (e) CaO_2, (f) MgO_2 and (g) ZnO_2 powders



ESI Fig. 3 Photograph of films (*ca.* 4x2 cm) prepared from P25 and P25/peroxides (5-15% w/w) binder-containing pastes after sintering for 30 min at 250 ˚C

(a)



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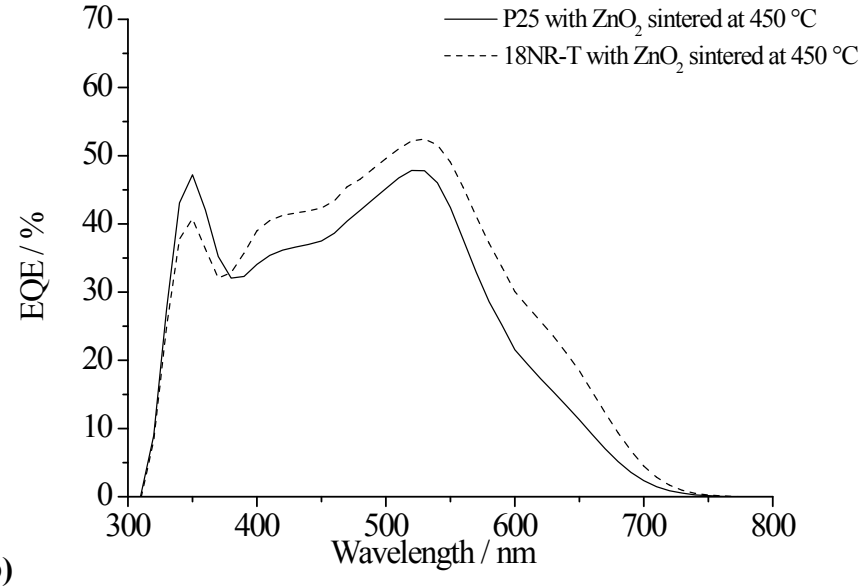
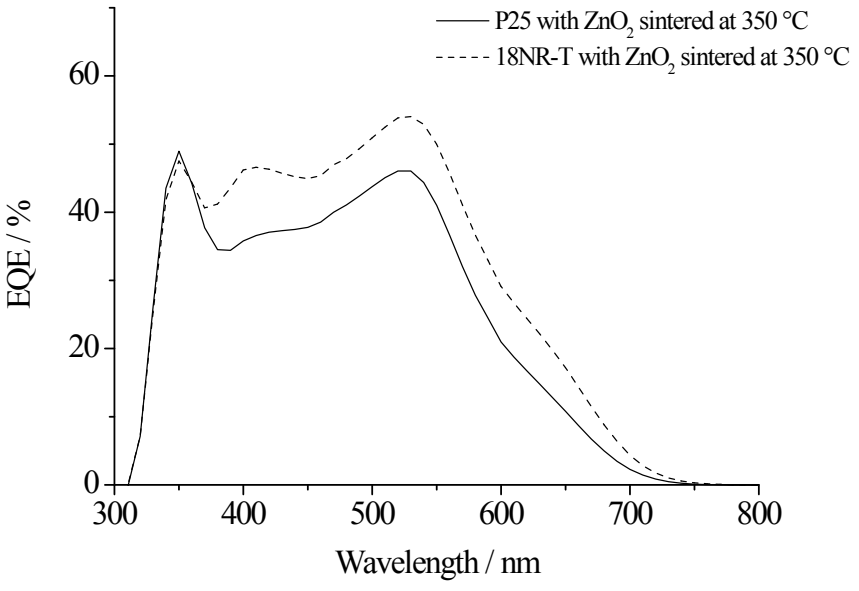


(c)



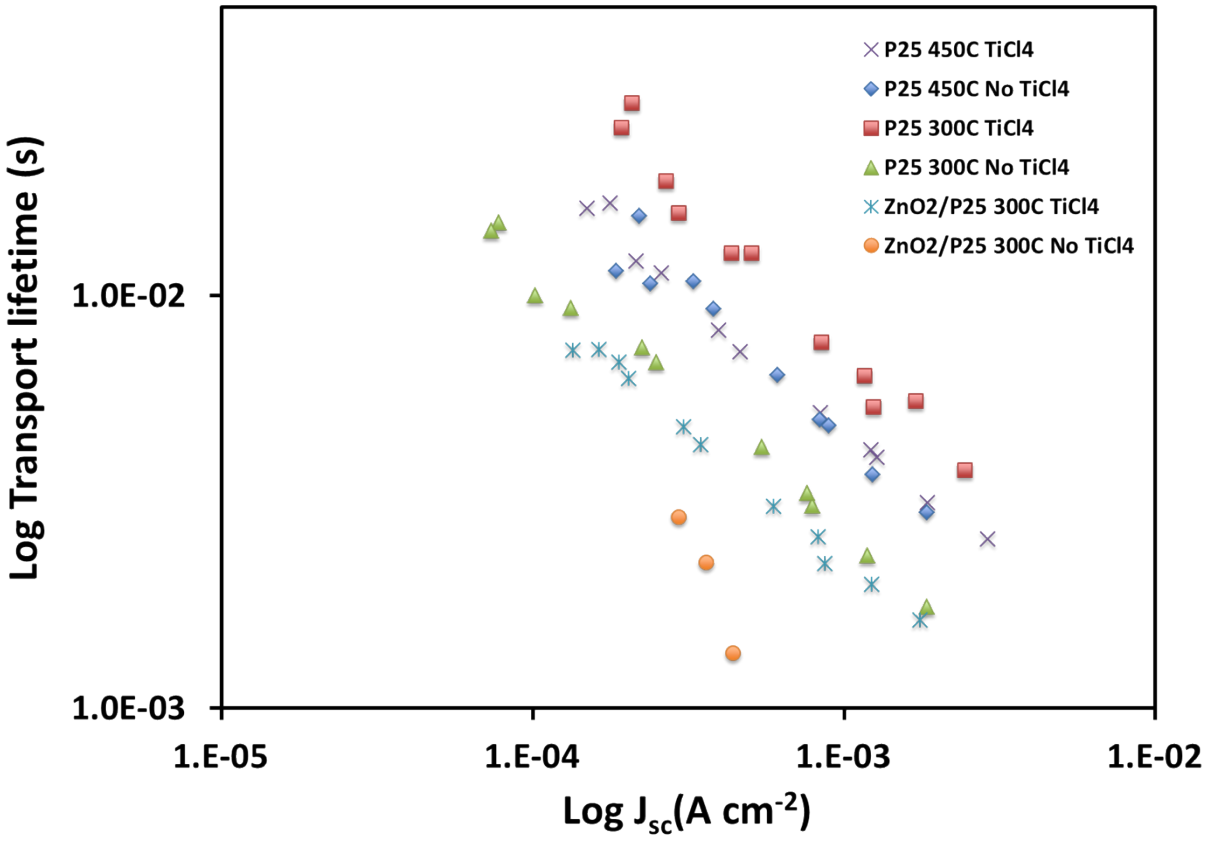
ESI Fig. 4 (a) Photographs of N719-dyed devices for P25 paste (left) and higher dye loading on DSL18NR-T device (right) and EQE of devices sintered at (b) 450 °C or (c) 350 °C

ESI Table 1 I-V data for N179 DSC devices made using P25 films with 5%, 15% or 25% ZnO_2, sintered at 300 ˚C and $TiCl_4$ treated

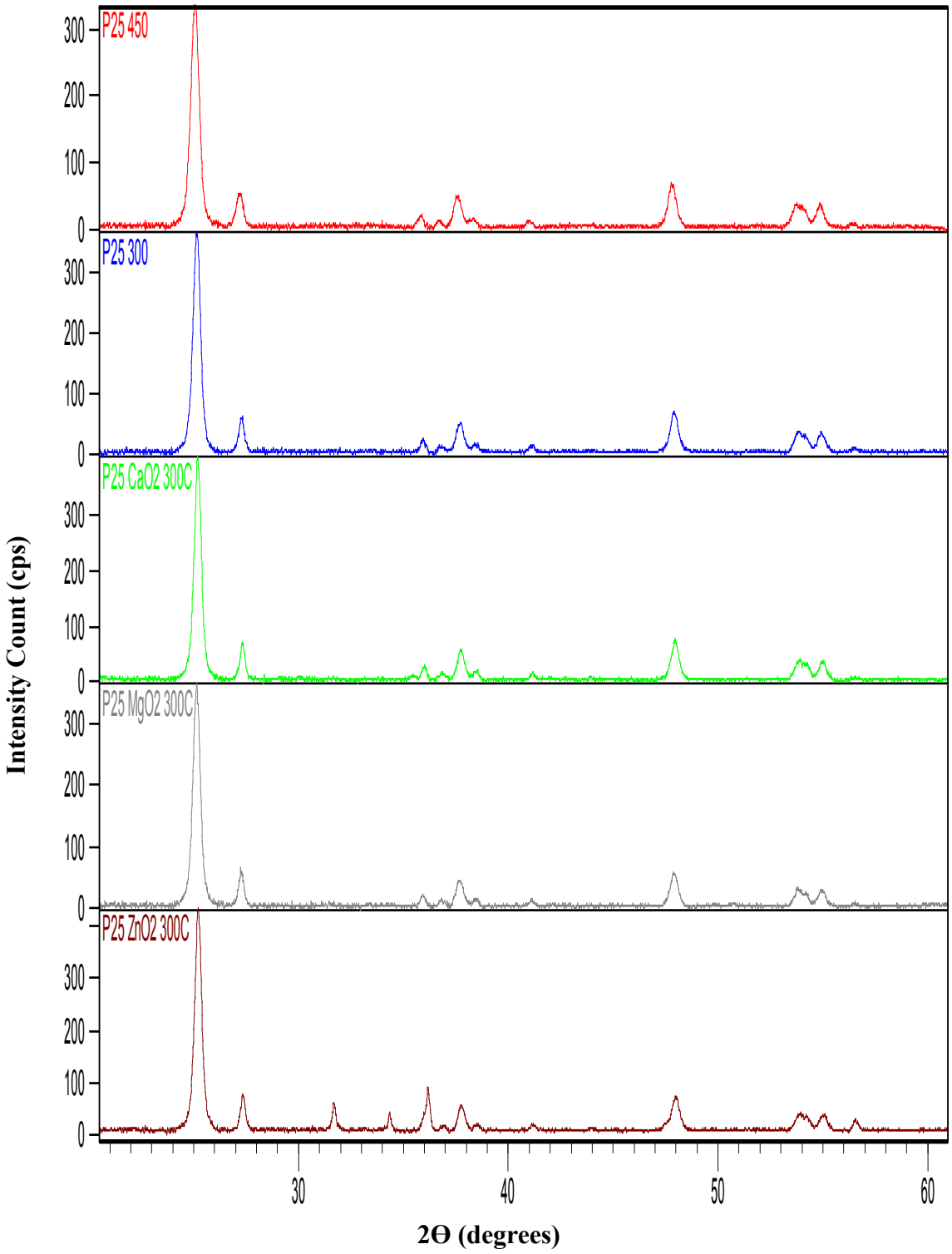
Ratio of ZnO_2 in P25 paste	**η (%)**	**FF**	**V_{oc} (V)**	**J_{sc} (mA cm^{-2})**
5%	3.9	0.60	0.79	8.38
15%	3.3	0.60	0.74	7.58
25%	3.1	0.60	0.72	7.14

ESI Table 2 I-V data for N719 DSC devices made using P25/ZnO_2 films with $TiCl_4$ treatment, sintered at 300˚C for 30, 60 or 120 min.

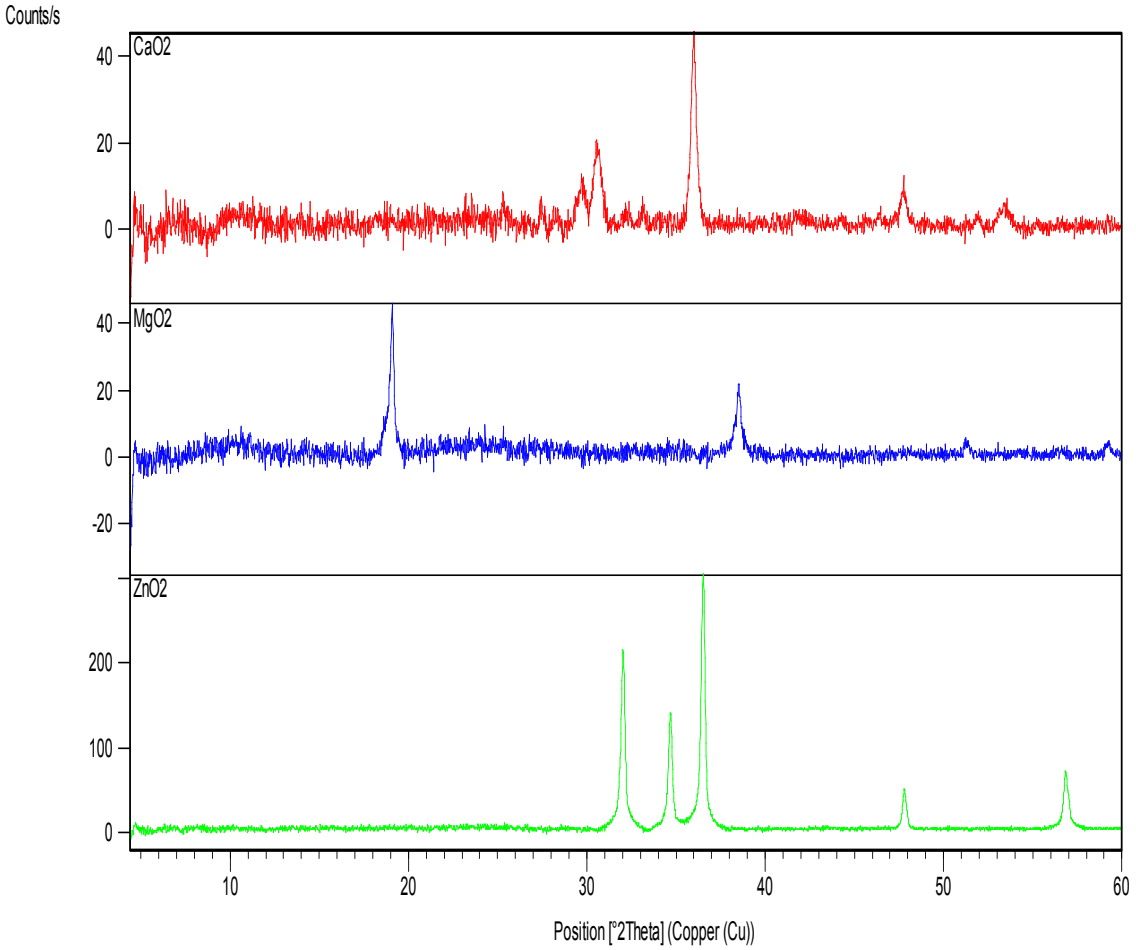
Sintering time (min)	**η (%)**	**FF**	**V_{oc} (V)**	**J_{sc} (mA cm^{-2})**
30	3.9	0.62	0.79	8.31
60	3.7	0.62	0.75	8.0
120	3.6	0.62	0.74	7.93



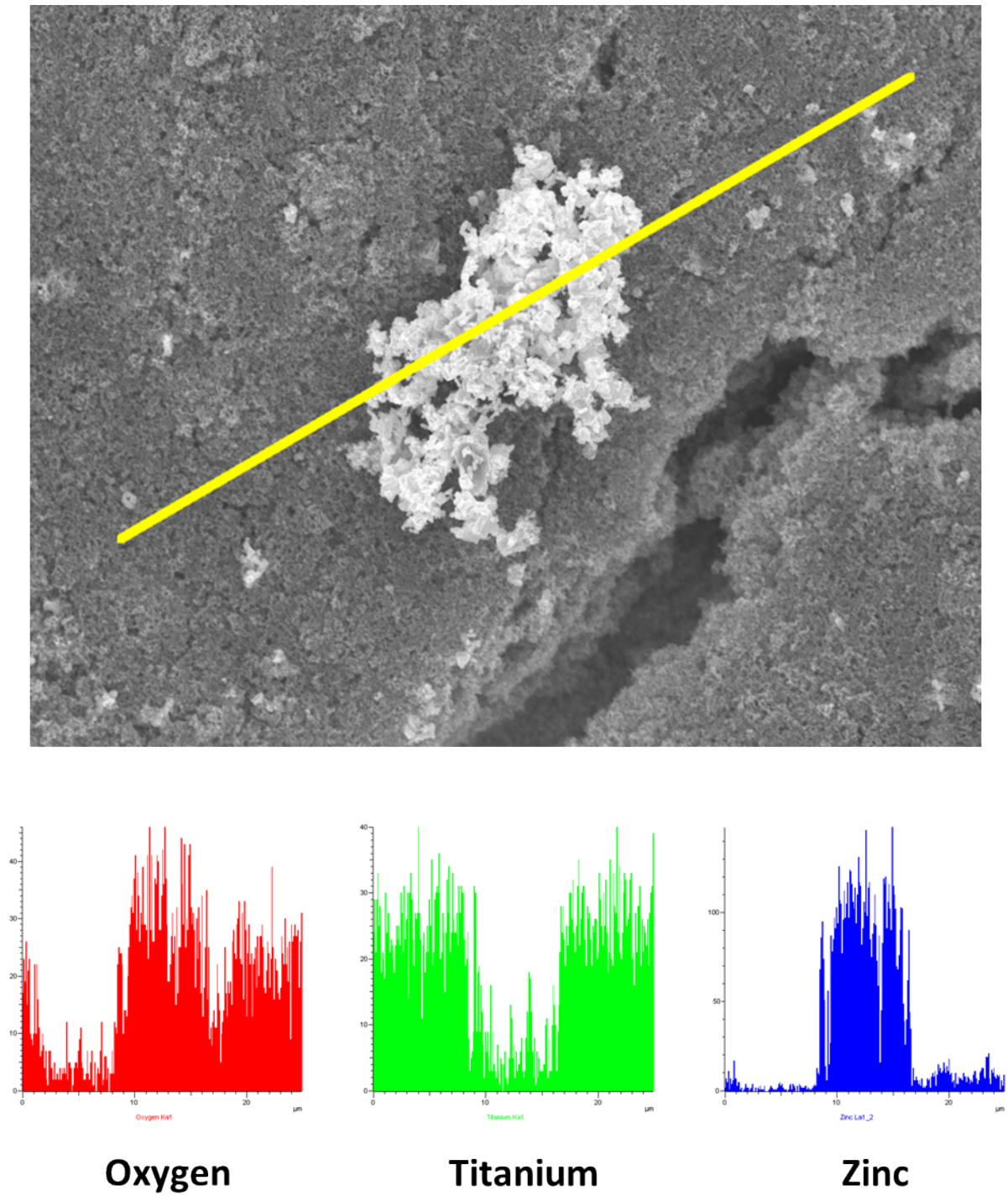
ESI Fig. 5 Log transport time *versus* Log J_{sc} for various devices as shown. Data calculated from transient photo-current measurements



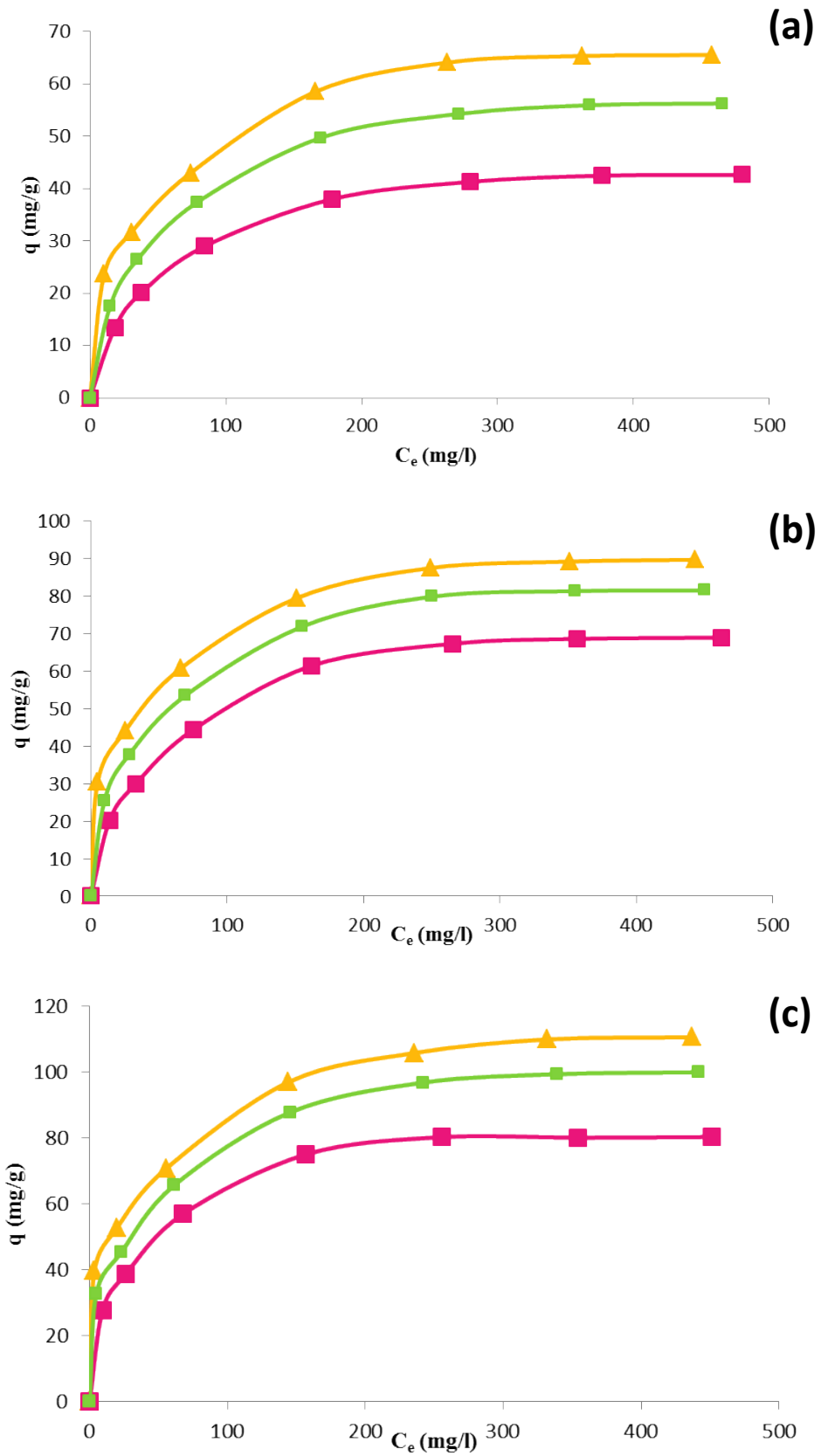
ESI Fig. 6 XRD data for a P25 film sintered at 450 ˚C or at 300 ˚C for 30 min and for P25/CaO_2, P25/MgO_2 and P25/ZnO_2 films after sintering at 300 ˚C for 30 min.



ESI Fig. 7 XRD data for a CaO_2, MgO_2 and ZnO_2 powders sintered at 300˚C for 30 min.



ESI Fig. 8 SEM image of particle on surface of P25 film. Yellow line (25 µm) denotes line of EDX analysis with data for oxygen (red), titanium (green) and zinc (blue) shown underneath.



ESI Fig. 9 Adsorption isotherms for N719 on P25 films sintered at 450˚C (red lines), and also onto P25/ZnO_2 films sintered at either 450 (green lines) or 300˚C (yellow lines). Dyeing temperature was (a) 22, (b) 40 or (c) 50˚C.

ESI Table 3 Adsorption parameters for N719 dye on P25 or P25/ZnO_2 films sintered at 300 or 450 ˚C. Dyeing was at ambient temperature (22˚C).

P25 sintered at 450˚C			**P25/ZnO_2 sintered at 450˚C**			**P25/ZnO_2 sintered at 300˚C**		
C_0 (mg/l)	C_e (mg/l)	q (mg/g)	C_0 (mg/l)	C_e (mg/l)	q (mg/g)	C_0 (mg/l)	C_e (mg/l)	q (mg/g)
26.47	18.43	13.40	25.37	14.87	17.5	24.67	10.61	23.60
49.74	37.72	20.03	50.64	34.80	26.4	49.64	30.63	31.68
101.58	84.21	28.95	101.07	78.67	37.33	99.98	74.18	43.0
200.86	178.08	37.96	199.96	170.12	49.73	200.95	165.85	58.51
304.23	279.46	41.28	303.89	271.33	54.26	301.83	263.37	64.10
401.91	376.44	42.45	401.11	367.55	55.93	401.21	362.01	65.33
505.38	479.81	42.61	498.79	465.04	56.25	497.19	457.88	65.51

ESI Table 4 Adsorption parameters for N719 dye on P25 or P25/ZnO_2 films sintered at 300 or 450 ˚C. Dyeing temperatures were 40 or 50 ˚C.

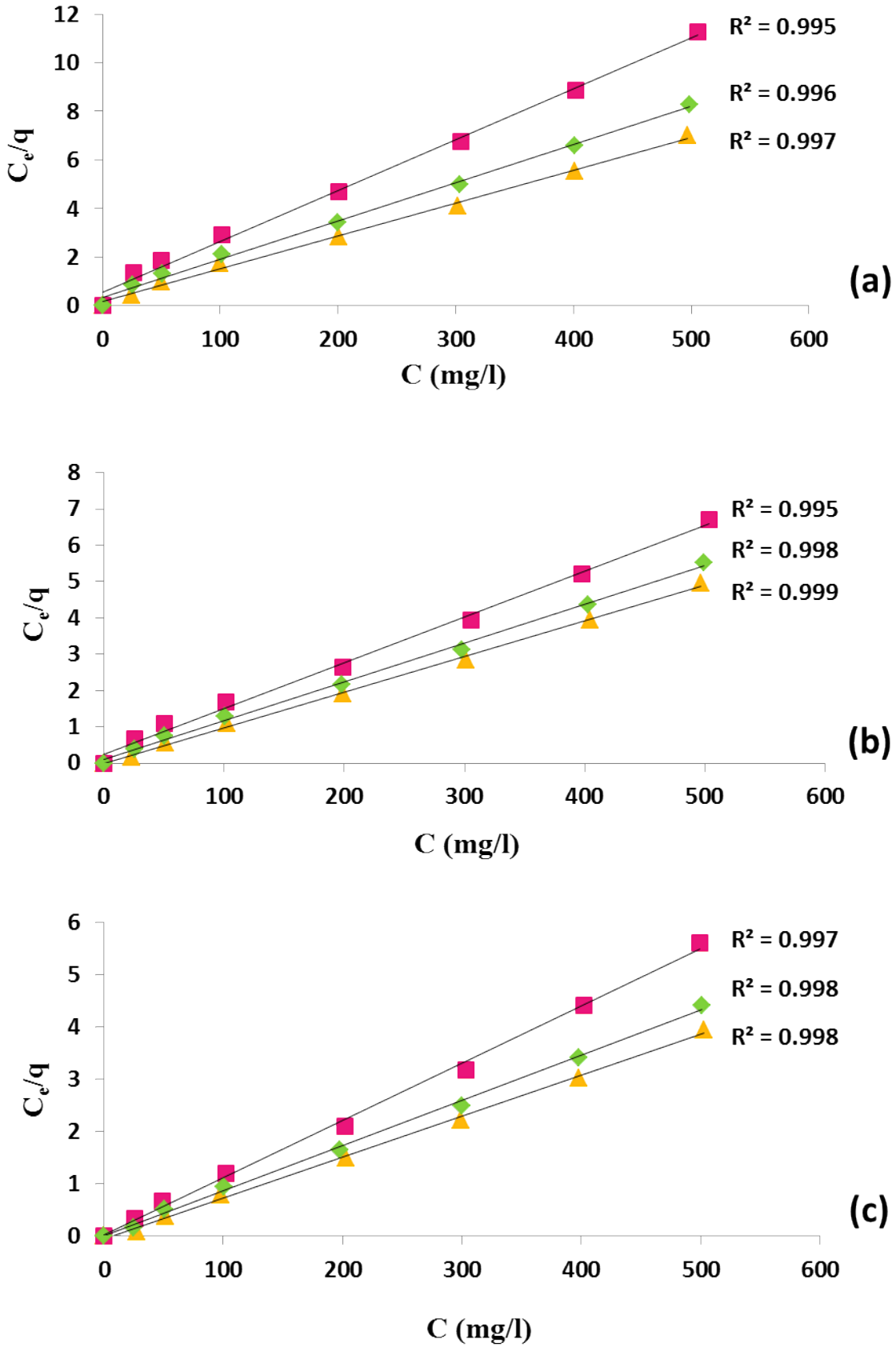
Dyeing temperature of 40˚C								
P25 sintered at 450 ˚C			**P25/ZnO_2 sintered at 450 ˚C**			**P25/ZnO_2 sintered at 300 ˚C**		
C_0 (mg/l)	C_e (mg/l)	q (mg/g)	C_0 (mg/l)	C_e (mg/l)	q (mg/g)	C_0 (mg/l)	C_e (mg/l)	q (mg/g)
25.87	13.72	20.25	25.27	9.94	25.55	23.272	4.99	30.47
50.54	32.63	29.85	50.64	28.0	37.73	51.43	25.02	44.02
101.98	75.32	44.43	101.08	69.05	53.38	102.57	66.12	60.75
198.56	161.74	61.37	198.06	164.98	71.80	198.96	151.29	79.45
305.33	265.0	57.22	298.04	250.17	79.78	301.32	248.89	87.38
397.32	356.21	68.52	403.21	354.47	81.23	404.31	350.86	89.08
503.19	461.87	68.87	498.99	450.12	81.45	496.79	443.04	89.58
Dyeing temperature of 50 ˚C								
P25 sintered at 450 ˚C			**P25/ZnO_2 sintered at 450 ˚C**			**P25/ZnO_2 sintered at 300 ˚C**		
C_0 (mg/l)	C_e (mg/l)	q (mg/g)	C_0 (mg/l)	C_e (mg/l)	q (mg/g)	C_0 (mg/l)	C_e (mg/l)	q (mg/g)
25.97	9.37	27.66	24.57	4.91	32.76	27.27	3.51	39.6
49.34	26.11	38.71	50.64	23.31	45.55	51.43	19.79	52.73
101.98	67.78	57.00	100.88	61.44	65.73	98.28	55.76	70.86
202.05	156.98	75.12	198.06	145.35	87.85	202.65	144.41	97.06
303.53	255.32	80.35	300.03	241.88	96.91	298.93	235.40	105.88
402.31	354.21	80.16	398.51	338.84	99.45	398.01	332.0	110.01
499.70	451.47	80.38	501.39	441.36	100.05	503.38	436.97	110.68

ESI Table 5 Parameters derived from Langmuir isotherms for N719 dyed at 22, 40 or 50 ˚C onto P25 sintered at 450 ˚C or onto P25/ZnO_2 films sintered at 300 or 450 ˚C

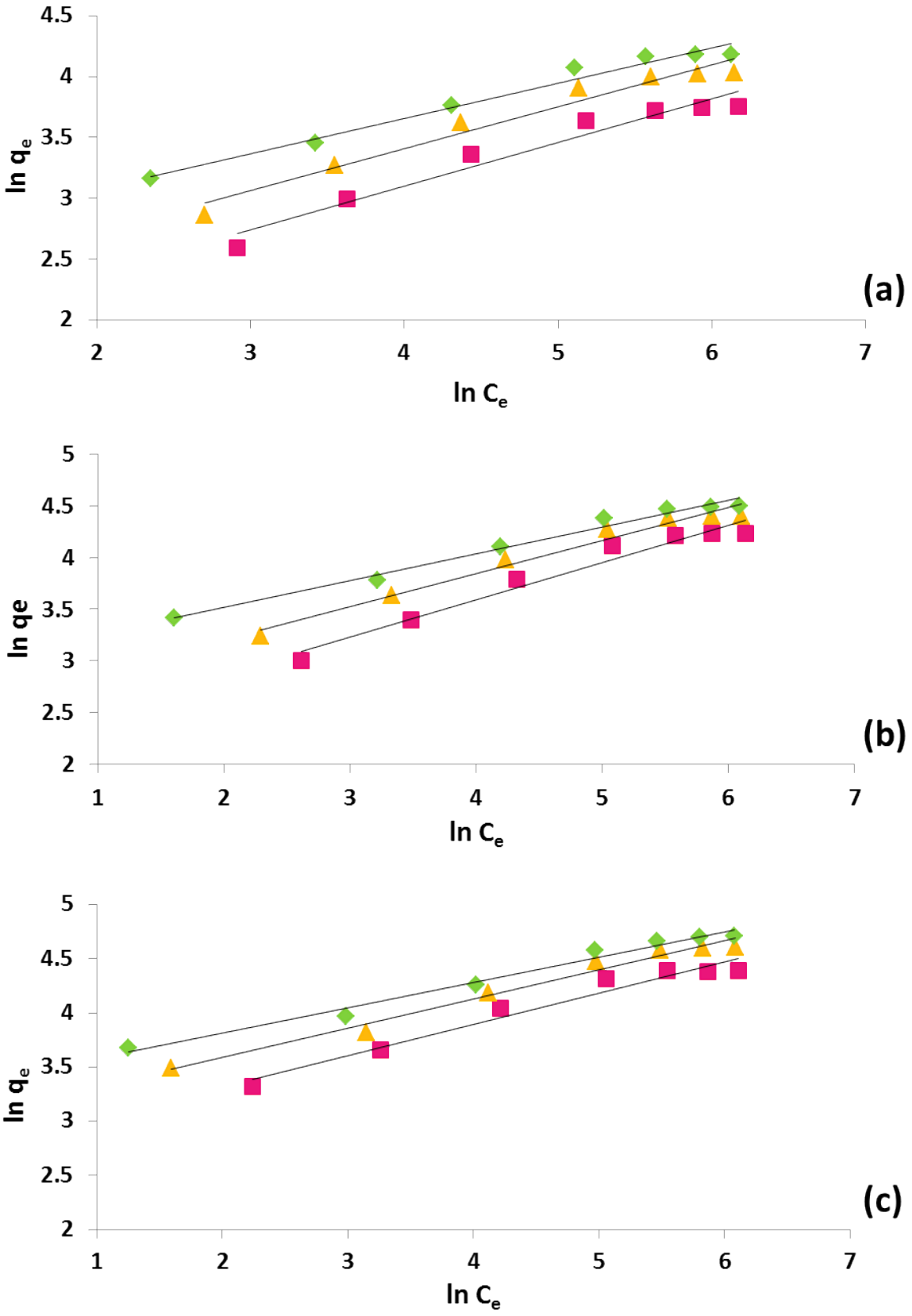
Electrode	**Dyeing temp. (˚C)**	**q_m (mg/g)**	**K_L (l/mg)**	**R^2**	**R_L**
P25 (450C˚)	22	47.53	0.021	0.999	0.088
	40	76.57	0.022	0.998	0.082
	50	85.94	0.030	0.998	0.050
P25/ZnO_2 (450˚C)	22	62.13	0.023	0.999	0.081
	40	88.40	0.029	0.998	0.064
	50	106.25	0.038	0.997	0.050
P25/ZnO_2 (300˚C)	22	70.89	0.029	0.997	0.064
	40	94.82	0.040	0.997	0.048
	50	116.22	0.044	0.997	0.043

ESI Table 6 Parameters derived from Freundlich isotherms for N719 dyed at 22, 40 or 50 ˚C onto P25 sintered at 450 ˚C or onto P25/ZnO_2 films sintered at 300 or 450 ˚C

Electrode	**Dyeing temp. (˚C)**	**K_f (mg/g)**	**n (L/mg)**	**R^2**
P25 (450˚C)	22	5.32	2.80	0.963
	40	8.52	2.76	0.962
	50	15.40	3.45	0.958
P25/ZnO_2 (450˚C)	22	7.59	2.90	0.952
	40	13.14	3.16	0.972
	50	21.12	3.72	0.979
P25/ZnO_2 (300˚C)	22	12.14	3.45	0.979
	40	20.22	3.89	0.983
	50	28.50	4.31	0.982



ESI Fig. 10 Adsorption data fitted to Langmuir isotherms for N719 dye uptake on P25 films sintered at 450 ˚C (red squares) and onto P25/ZnO_2 films sintered either at 450 (green diamonds) or 300 ˚C (yellow triangles). Dyeing temperatures were (a) 22, (b) 40 or (c) 50 ˚C.



ESI Fig. 11 Adsorption data fitted to Freundich isotherms for N719 dye uptake on P25 films sintered at 450˚C (red squares) and onto P25/ZnO_2 films sintered either at 450 (green diamonds) or 300 ˚C (yellow triangles). Dyeing temperatures were (a) 22, (b) 40 or (c) 50 ˚C.