Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

Electronic Supporting Information

Peptide-directed crystal growth modification in the formation of ZnO

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ESI 1: Atomic percentage of C 1s, Zn 2p3/2, and O 1s peaks obtained from XPS and the relative ratio of Zn/O.

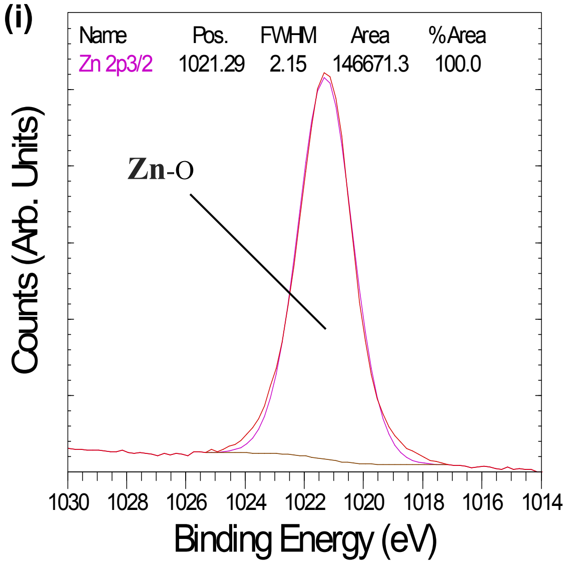
Traces of contamination can be detected by XPS from the ubiquitous carbonaceous contamination (C 1s peak) – the so called adventitious carbon - present even on the cleanest and purest of samples. Practical detection limits for most elements are of the order of 0.5-1.0 at%. Hence, a sample of purchased ZnO 99.999% was analysed by XPS in order to show that the C 1s peak detected in the 48-hour precipitate was not just from trace contamination during the analysis but was also from LBZs in the sample (Table 2). The relative ratio of Zn/O in the samples was calculated, showing a decrease when LBZs was present in the samples (Table 2).

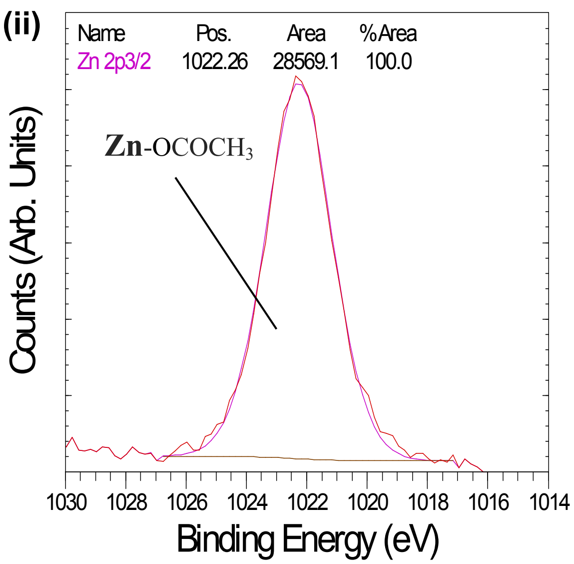
Sample Description	*At % C 1s*	*At % Zn $2p_{3/2}$*	*At % O 1s*	*Rel Zn/O*
Starting material (ZnAc2)	43.9	17.7	38.4	0.5
1-hour precipitate	21.7	32.0	46.3	0.7
48-hour precipitate	18.9	41.0	47.6	0.9
ZnO 99.9% Sigma-Aldrich	13.0	44.5	42.4	1.0

ESI 2: XPS data of Zn, O and C elements on the surface for the precipitate generated in the presence of 0.2 mM of EM-12 collected at 24 hours of reaction together with assignment of the BE values.

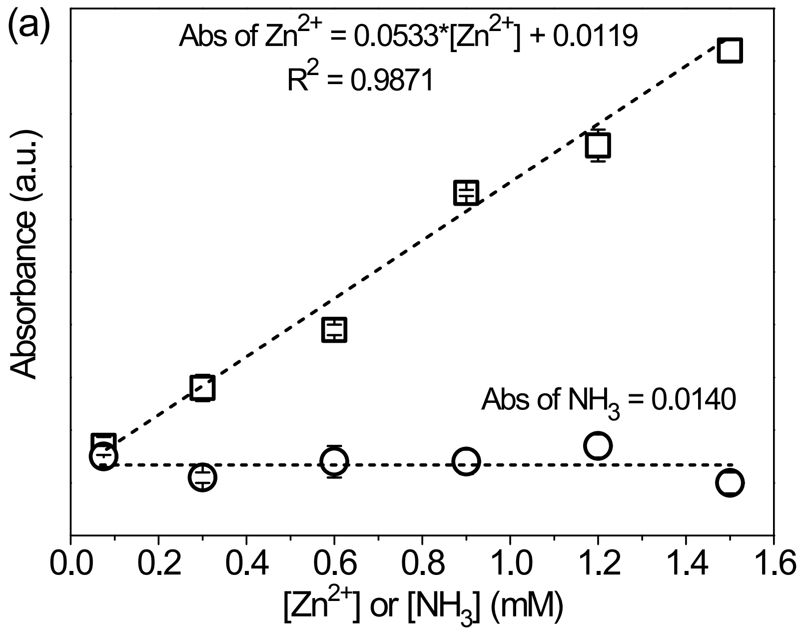
	BE (eV)	**FWHM**	**Assigned**
Zn $2p_{3/2}$			
	1019.3	2.8	LBZs with general formula of $[(Zn^{octa})_3(Zn^{tetra})_2(OH)_8]^{2+} \cdot 2(A^-) \cdot nH_2O$[1]
	1021.5	2.4	Zinc in crystalline ZnO[2, 4]
	1022.2	2.8	Acetate zinc groups ($Zn\text{-}OCOCH_3$)[3, 4]
O1s			
	529.9	2.2	Condensed zincoxane ($-(ZnO)_x-$)[3] and/or oxygen in crystalline ZnO[1]
	531.7	2.1	Hydroxylated oxide surface (Zn-OH)[3, 5]
	532.9	2.5	Carboxyl groups (COO^-)[4, 6]
C1s			
	285.0	2.3	Methyl groups ($-CH_3$)[7, 8]
	288.9	2.5	Carboxyl groups (COO^-)[7, 8]

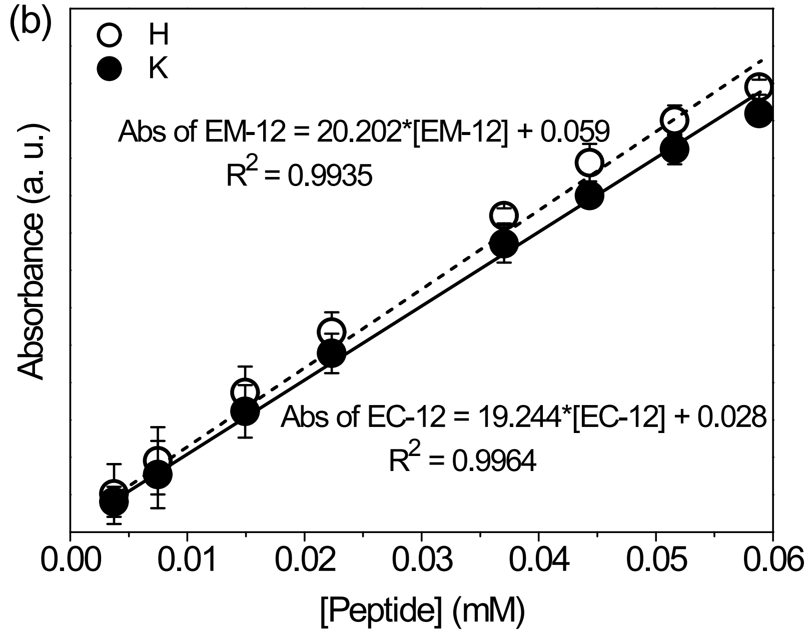
The assignment of Zn in crystalline ZnO and/or LBZA was further supported by the study of the Zn $2p_{3/2}$ region of purchased (i) ZnO (99.999%) and (ii) $ZnAc_2$ (99.99%).



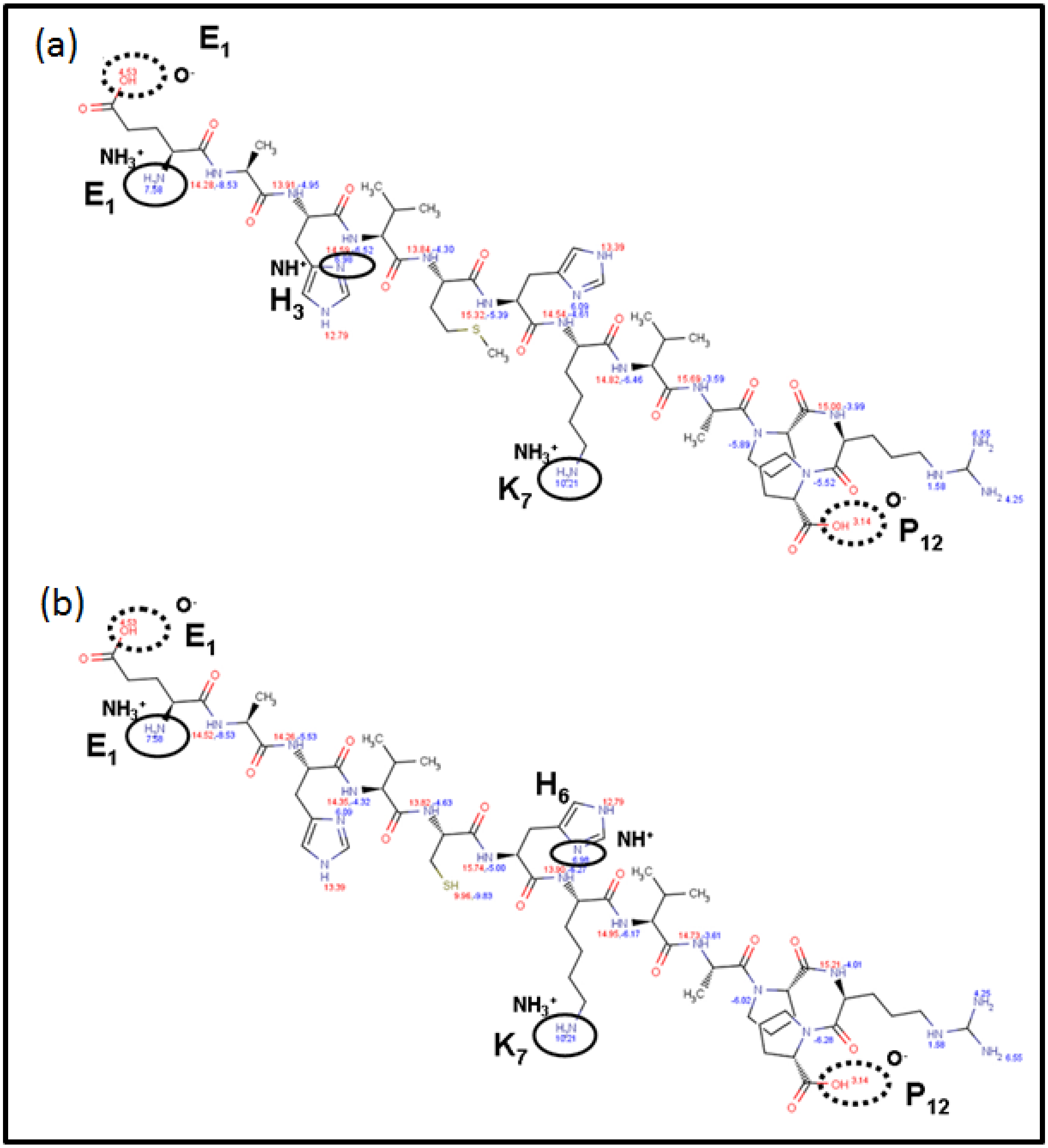


ESI 3: Absorbance calibration curves of (a) $ZnAc_2$ and NH_3, and (b) EM-12 and EC-12, at 214nm using a quartz cuvette and a Unicam UV2 UV-VIS spectrometer.

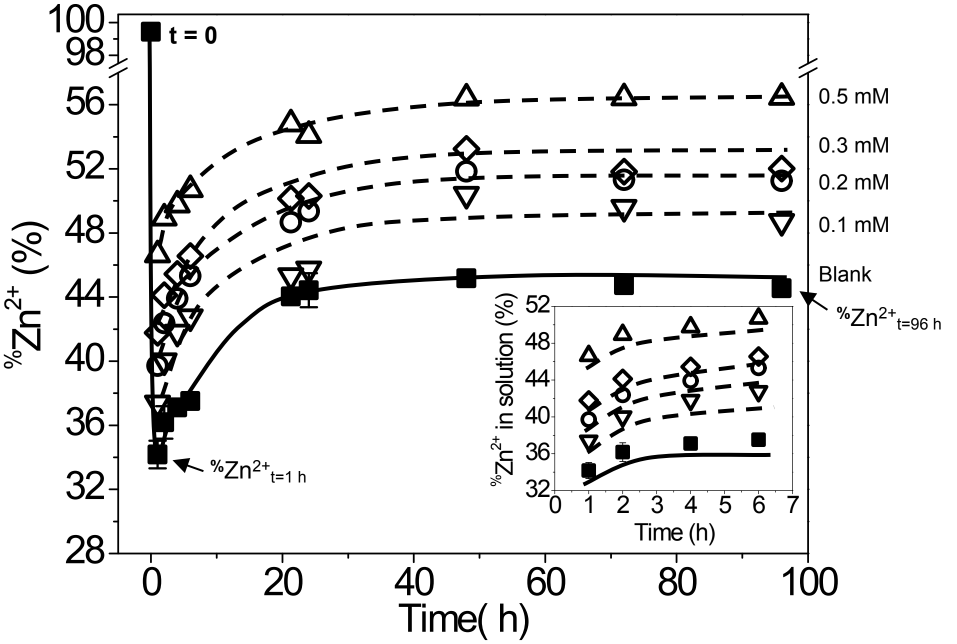




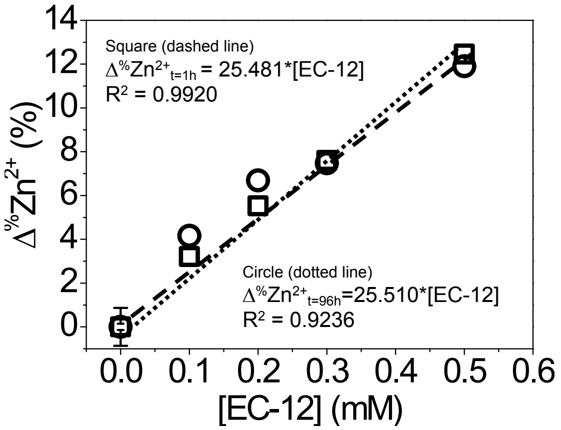
ESI 4: Calculated pK_a data for (a) EM-12 and (b) EC-12 by Marvin Calculator (298 K). Cationic and anionic moieties involving at least 50% of the side chain of a residue are shown. Cationic and anionic moieties are marked with solid-circles and dotted-circles respectively.



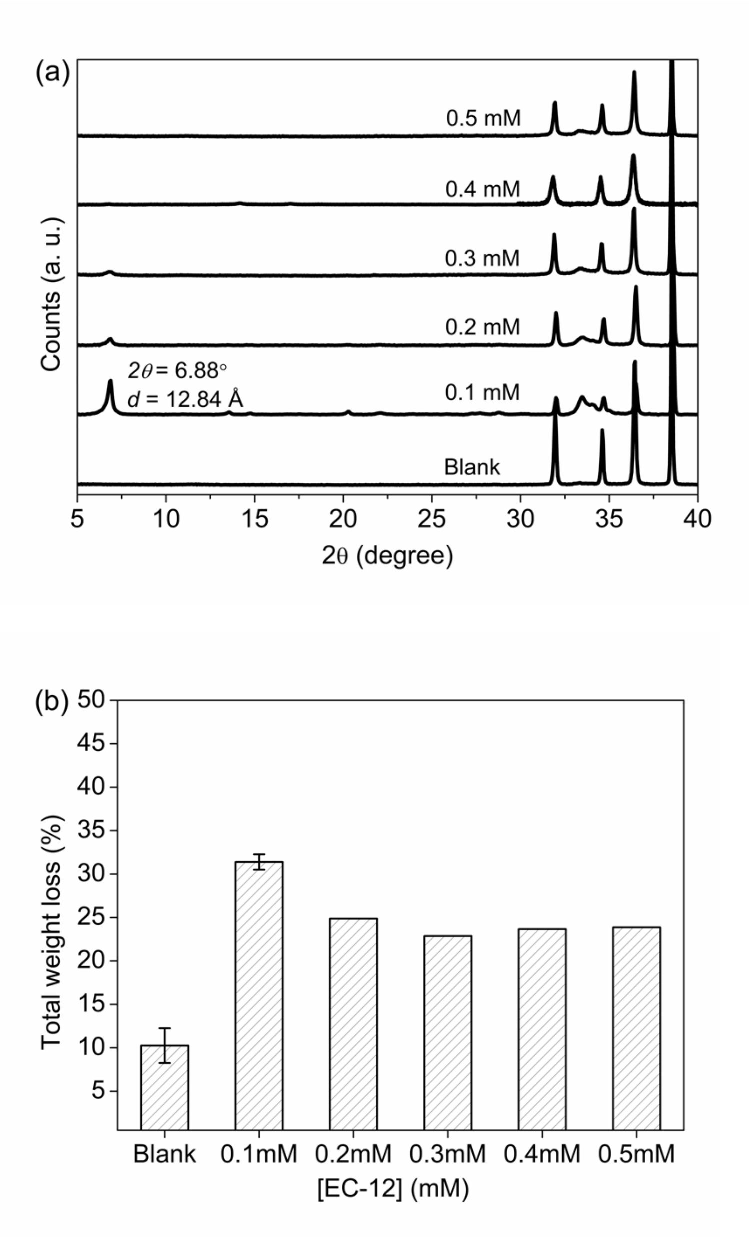
ESI 5: The amount of Zn^{2+} in solution (%) as a function of reaction time for reactions in the presence of EC-12 at different concentrations. $^{\%}Zn^{2+}_{t=1hr}$ and $^{\%}Zn^{2+}_{t=96hr}$ correspond to the percentage of zinc retained in solution at the LBZA formation stage (1 hour) and at equilibrium (96 hours) respectively.



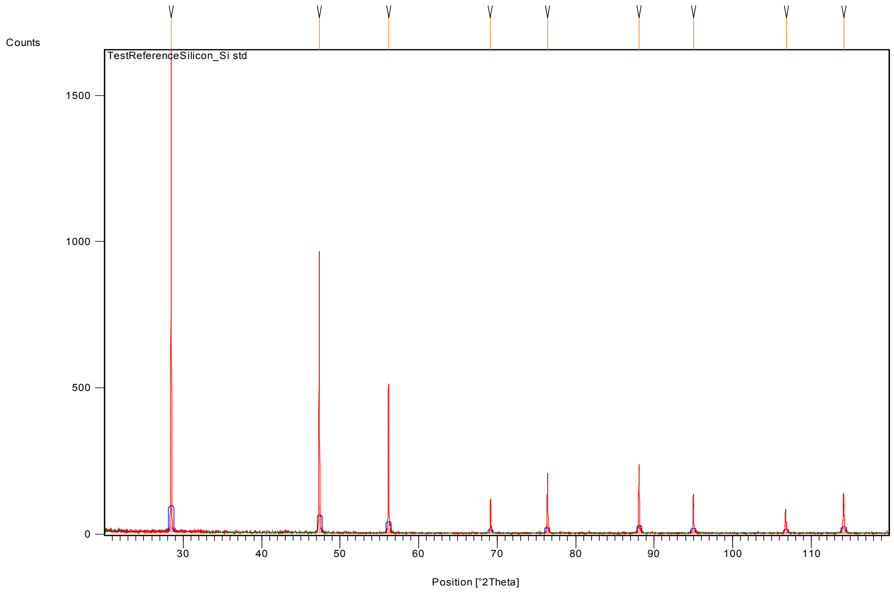
The increase of $^{\%}Zn^{2+}$ with respect to the Blank at LBZA formation stage (square, dashed line), $\Delta^{\%}Zn^{2+}_{t=1h} = {}^{\%}Zn^{2+}_{t=1h/Sample} - {}^{\%}Zn^{2+}_{t=1h/Blank}$, and at equilibrium (circle, dotted line), $\Delta^{\%}Zn^{2+}_{t=96h} = {}^{\%}Zn^{2+}_{t=96h/Sample} - {}^{\%}Zn^{2+}_{t=96h/Blank}$.



ESI 6: Characterization of 24 hour-precipitates formed in the presence of EC-12 at different concentrations using (a) XRD and (b) TGA techniques. The position of a diffraction peak from the aluminum sample holder is marked with an asterisk in (a), and *d* denotes the interlayer spacing of LBZA.



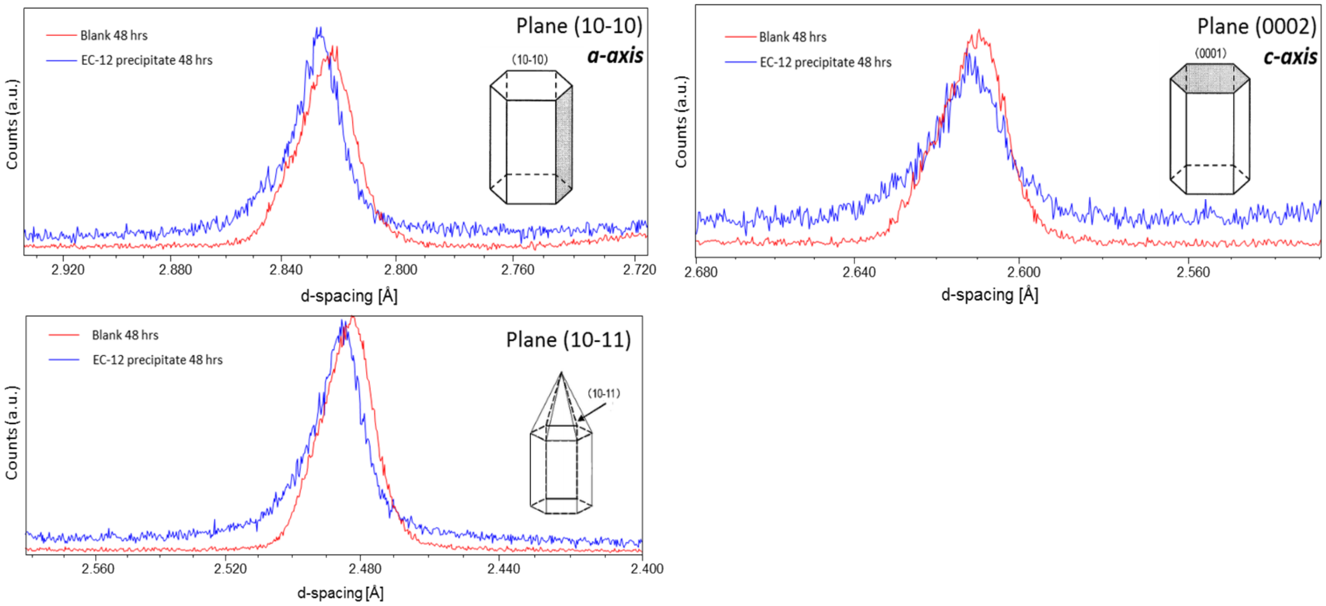
ESI 7: The lattice strain of ZnO along the a-axis was calculated following Brif and co-workers studies[9] in which a high-resolution powder diffraction was used. Our study; however, due to the facilities available, has been carried out using a X-ray diffractometer as described in section of Materials and Methods. Therefore, the wavelength of the X-ray diffractometer was calculated prior the analysis to ensure accurate d-spacing values. The wavelength of the instrument is calculated by analysis of a reference Silicon standard:



(hkl)	*Rel.Int %*	*2Θ*	*Θ*	*Θ(rad)*	*sinΘ*	*n*	*d-spacing*	*λ=d*sinθ*
(111)	100.00	28.473	14.236	0.248	0.246	1	3.132	0.770
(220)	67.60	47.362	23.681	0.413	0.402	2	1.919	0.771
(311)	42.26	56.196	28.098	0.490	0.471	3	1.636	0.770
(400)	13.52	69.155	34.578	0.603	0.568	4	1.357	0.770
(331)	21.08	76.387	38.194	0.667	0.618	5	1.245	0.770
(422)	29.84	88.101	44.050	0.769	0.695	6	1.108	0.770
(333)	16.81	95.010	47.505	0.829	0.737	7	1.045	0.770

XRD diffraction peaks of ZnO crystals for the Blank and in the presence of 0.2 mM of EC-12 were studied.

XRD diffraction peak of ZnO crystals for the Blank and in the presence of 0.2 mM of EC-12.



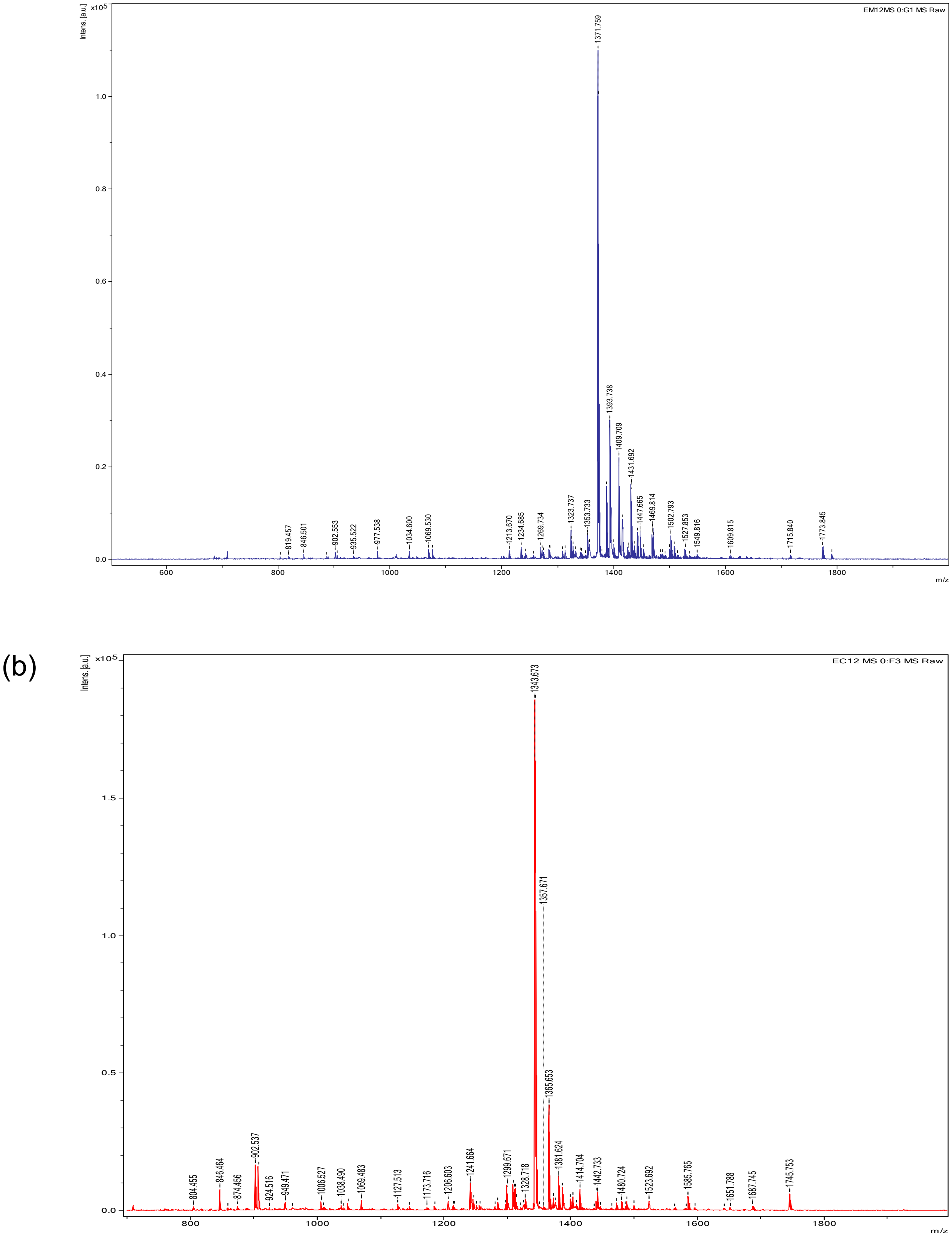
The d-spacing values were calculated using Bragg equation: $d = (n \cdot \lambda)/2 \cdot \sin\theta$, where $n = 1$, λ = average of wavelength calculated and θ = 15.828° and 15.810°; Blank and EC-12/EM-12, respectively.

	(10$\bar{1}$0)		(0002)		(10$\bar{1}$**Error!**1)	
(10$\bar{1}$0)	measured	calculated	measured	calculated	measured	calculated
Blank	2.824	2.823	2.611	2.610	2.482	2.481
EC12	2.827	2.826	2.612	2.611	2.486	2.485

The lattice strain of ZnO along different axis is in the presence of EC-12 was:

	%strain		
	(10$\bar{1}$0)	**(0002)**	**(10$\bar{1}$Error!1)**
EC12	0.108	0.039	0.128

ESI 8: Mass spectra of (a) EM-12and (b) EC-12



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