

Appendix A. Supplementary data

Solar-driven photoelectrocatalytic degradation of anticancer drugs using TiO₂ nanotubes decorated of SnS quantum dots

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Table S1. Elemental composition (in atomic %) in the surface layer of SnS-modified TiO₂ NTs, evaluated by XPS analysis.

Sample label	Elemental composition (atomic %.)							O/Ti	Sn/S	(Sn+S)/(Ti+O)	S*/Ti	(SnS/TiO ₂)**
	Ti	O	Sn	S	C	N	Cl					
IIISnS-Ti/TiO ₂	20.38	59.57	3.99	2.60	12.57	0.77	0.12	2.92	1.53	0.082	0.106	0.071
IIISnS-Ti/TiO ₂	21.16	59.03	3.28	1.83	13.37	1.14	0.19	2.79	1.79	0.064	0.068	0.045
IVSnS-Ti/TiO ₂	17.40	54.01	8.42	6.66	12.70	0.70	0.11	3.10	1.26	0.211	0.360	0.240
VISnS-Ti/TiO ₂	14.08	49.79	13.54	12.22	9.71	0.50	0.16	3.54	1.11	0.403	0.832	0.555
XSnS-Ti/TiO ₂	7.83	38.41	18.28	17.86	17.23	0.39	<0.05	4.91	1.02	0.782	2.231	1.487
Ti/TiO ₂	22.81	59.01	-	0	18.18	0	0	2.59	-	-	-	-

S* - SnS fraction of sulfur (see SnS fraction of S 2p_{3/2} in Table S2)

**assuming atomic ratio Sn:S = 1:1 for SnS and Ti:O = 1:2 for TiO₂ we can roughly estimate SnS/TiO₂ to be 2S*/3Ti

Table S2. Chemical character of Sn and S components in the surface layer of SnS-Ti/TiO₂ nanocomposites, evaluated through deconvolution of Sn 3d and S 2p high resolution XPS spectra.

Sample label	Sn 3d _{5/2} fraction (atomic %)		S 2p _{3/2} fraction (atomic %)	
	SnS, SnO	SnSO ₄ , SnO ₂	SnS	SnSO ₄
	485.0- 485.6 eV	486.4-486.8 eV	160.8-161.5 eV	168.4-169.4 eV
IISnS-Ti/TiO ₂	11.4	88.6	83.3	16.7
IIISnS-Ti/TiO ₂	14.2	85.8	79.2	20.8
IVSnS-Ti/TiO ₂	19.6	80.4	94.0	6.0
VISnS-Ti/TiO ₂	30.1	69.9	95.9	4.1
XSnS-Ti/TiO ₂	20.6	79.4	97.8	2.2

Table S3. The first rate constant k for anticancer drugs photoelectrocatalytic (PEC), photocatalytic (PC) and electrochemical (E) decomposition, total organic carbon removal (Δ TOC), mineralization current efficiency (MEC) and consumed electrical energy (E_{EO})

Photoelectrode	Compound	Process	k (min $^{-1}$)	R^2	Δ TOC (%)	MCE (%)	E_{EO} (kWh m $^{-3}$ order $^{-1}$)
Ti/TiO ₂	IF	PEC	0.0072	0.9827	37 ± 1.5	89	13.7
IISnS-Ti/TiO ₂	IF	PEC	0.0149	0.9846	27 ± 2.1	62	5.44
IIISnS-Ti/TiO ₂	IF	PEC	0.0153	0.9449	27 ± 3.0	62	5.63
IVSnS-Ti/TiO ₂	IF	PEC	0.017	0.9822	27 ± 1.8	62	5.73
VISnS-Ti/TiO ₂	IF	PEC	0.0178	0.9827	56 ± 4.5	129	6.63
XSnS-Ti/TiO ₂	IF	PEC	0.0139	0.9815	1 ± 0.3	2.3	7.84
VISnS-Ti/TiO ₂	IF	PC	0.0085	0.9825	6.5 ± 0.5	12	12.1
VISnS-Ti/TiO ₂	IF	E	-	-	0	-	-
Ti/TiO ₂	5-FU	PEC	0.0104	0.9959	14 ± 0.4	14.5	9.58
VISnS-Ti/TiO ₂	5-FU	PEC	0.0169	0.9982	46 ± 3.6	47.1	6.34
VISnS-Ti/TiO ₂	5-FU	PC	0.0063	0.9849	0	-	13.3
VISnS-Ti/TiO ₂	5-FU	E	-	-	0	-	-
Ti/TiO ₂	IMB	PEC	0.0084	0.9779	3 ± 0.2	1.2	9.54
VISnS-Ti/TiO ₂	IMB	PEC	0.0149	0.9885	15 ± 1.5	47.5	6.66
VISnS-Ti/TiO ₂	IMB	PC	0.0066	0.9957	0	-	16.7
VISnS-Ti/TiO ₂	IMB	E	-	-	0	-	-
VISnS-Ti/TiO ₂	IF	PEC (0.5 V)	0.0123	0.9787	15 ± 1.1	36	8.17
VISnS-Ti/TiO ₂	IF	PEC (1.5 V)	0.0107	0.9777	0	-	9.42

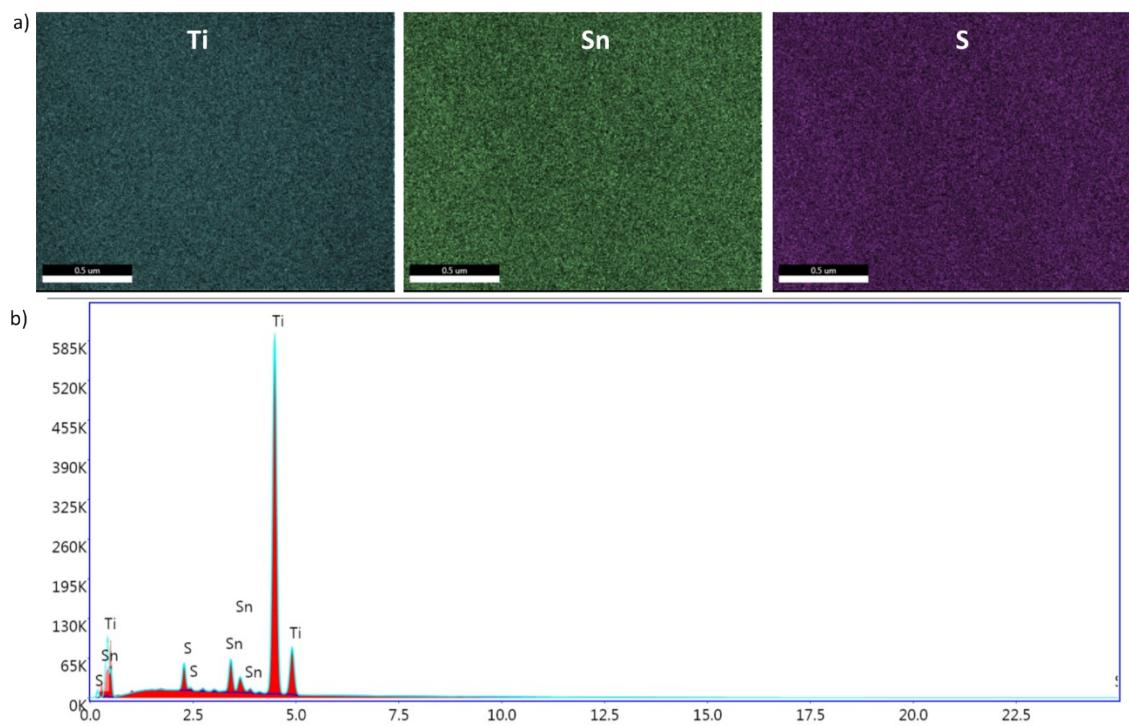


Fig. S1. The EDS (a) mapping and (b) spectrum of V_xSn_yS-Ti/TiO₂ photoelectrodes.

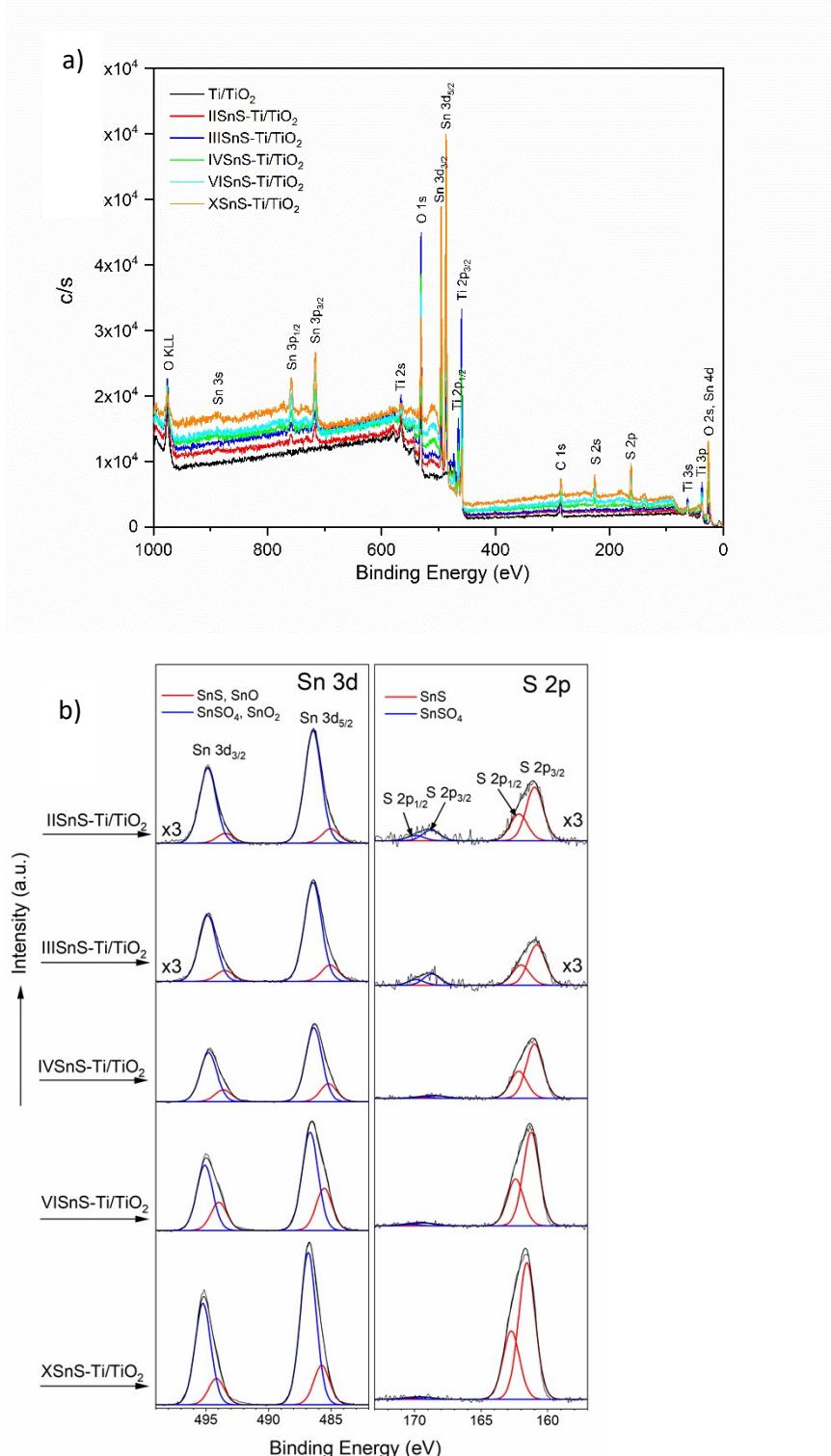


Fig. S2. The survey spectra a) and high resolution Sn3d and S2p XPS spectra b) recorded on SnS-Ti/TiO₂ nanocomposites prepared using 2, 3, 4, 6 and 10 SILAR cycles.

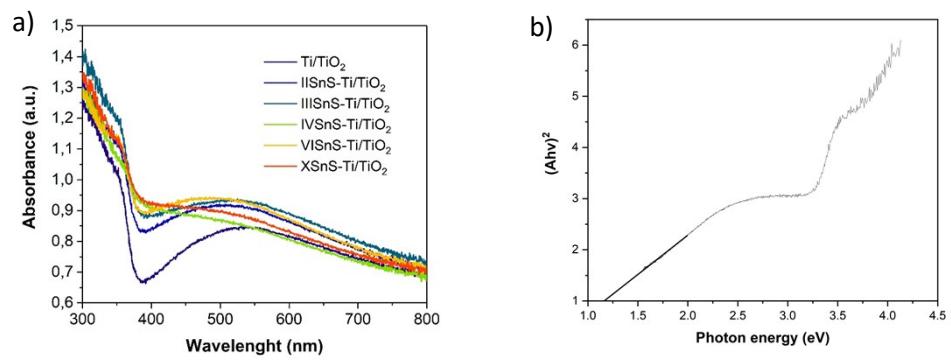


Fig. S3. UV-Vis spectra of the Ti/TiO₂ and SnS-Ti/TiO₂ photoelectrodes (a) and Tauc plot of VISnS-Ti/TiO₂ photoelectrode (b).

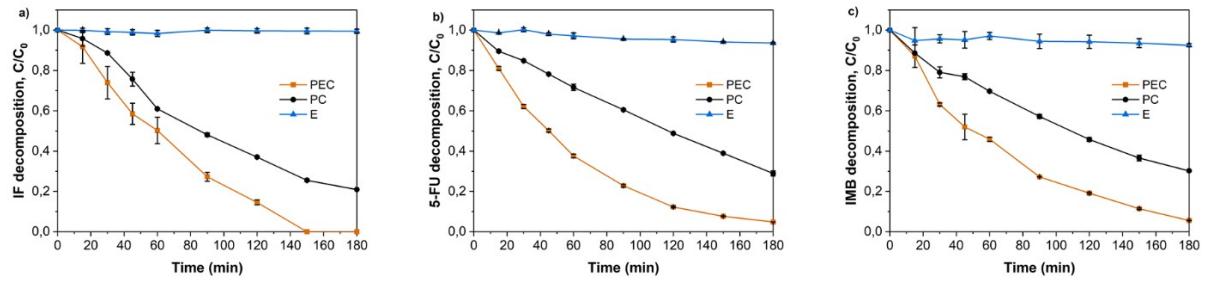


Fig. S4. Photoelectrocatalytic (PEC), photocatalytic (PC) and electrochemical (E) decomposition of IF a), 5-FU b) and IMB c).

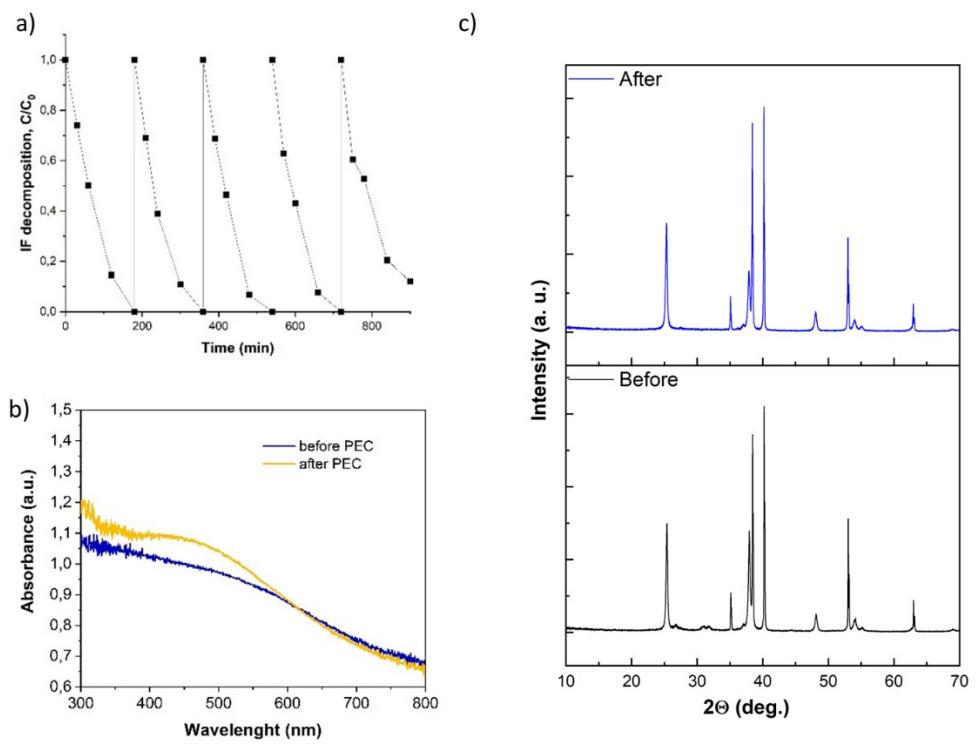


Fig. S5. The recycled PEC degradation of IF for VI_xSnS/Ti/TiO₂ (a) and DRS UV-Vis (b) and XRD (c) analysis of photoelectrode SnS-Ti/TiO₂ before and after stability test

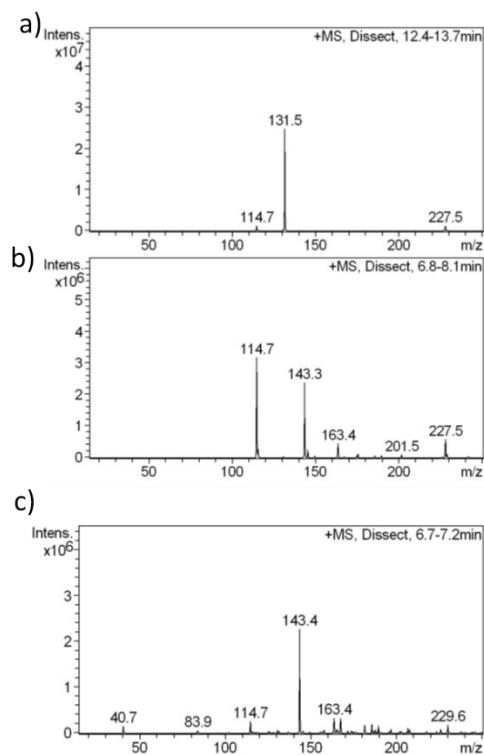


Fig. S6. MS spectra of 5-FU (a) and degradation products with $[M+H]^+=163$ (b) and $[M+H]^+=143$ (c).

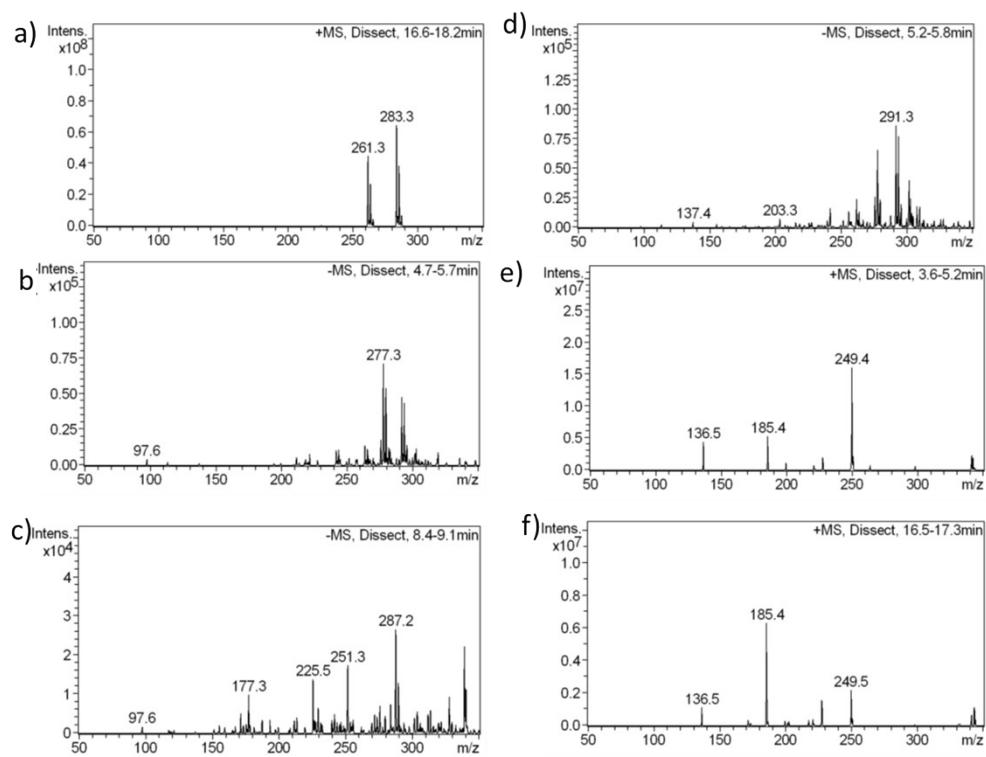


Fig. S7. MS spectra of IF (a) and degradation products with $[M-H]^- = 277$ (b), $[M-H]^- = 287$ (c), $[M-H]^- = 291$ (d), $[M+H]^+ = 249$ (e) and $[M+H]^+ = 185$ (f).

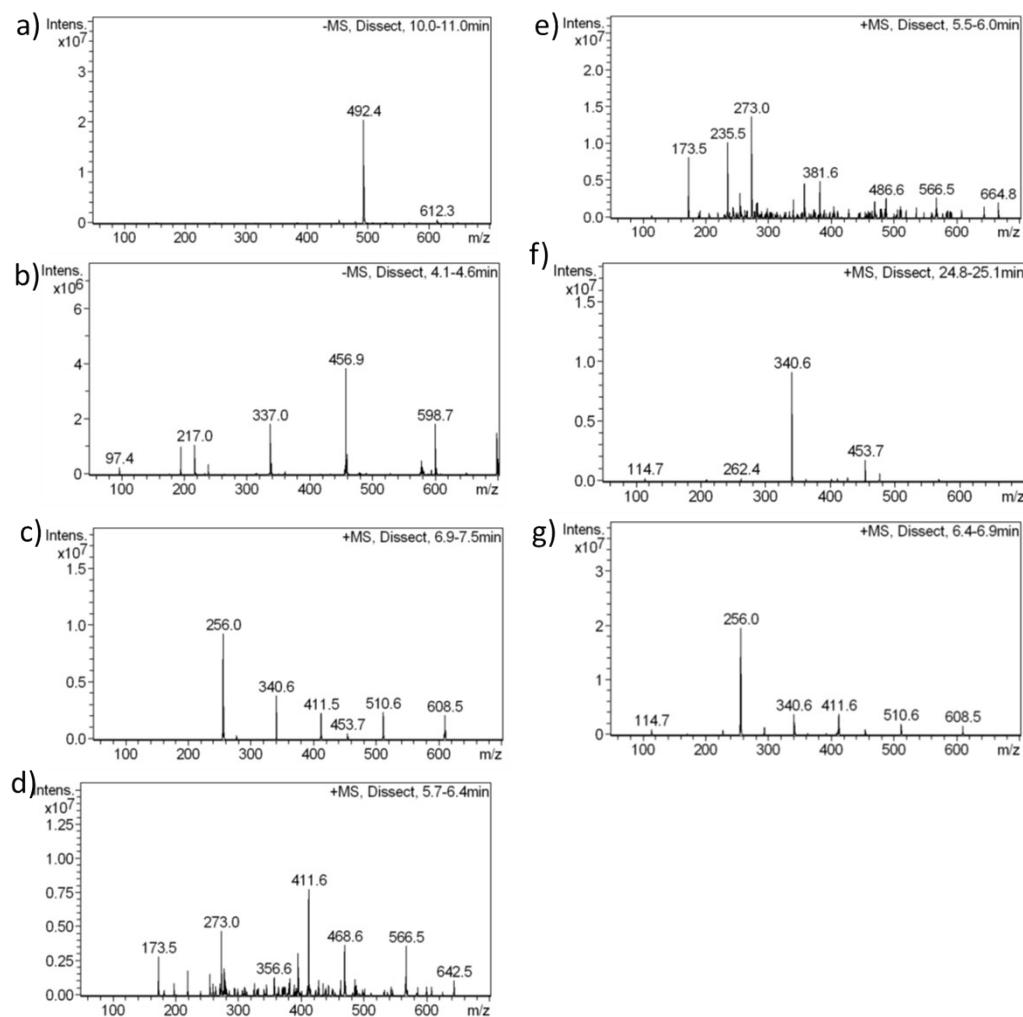


Fig. S8. MS spectra of IMB (a) and degradation products with $[M-H]^- = 337$ (b), $[M+H]^+ = 510$ (c), $[M+H]^+ = 411$ (d), $[M+H]^+ = 273$ (e), $[M+H]^+ = 262$ (f) and $[M+H]^+ = 256$ (g).