

Supplementary Materials

Visible Light Reductive Photocatalysis of Azo-Dyes with n-n Junctions Based on Chemically Deposited CdS

Michele Mazzanti, Martina Milani, Vito Cristino, Rita Boaretto, Alessandra Molinari * and Stefano Caramori *

Dipartimento di Scienze Chimiche, Farmaceutiche ed Agrarie, Università di Ferrara, Via Luigi Borsari 46, 44121 Ferrara, Italy; michele.mazzanti@unife.it (M.M.); martina.milani@unife.it (M.M.); vito.cristino@unife.it (V.C.); rita.boaretto@unife.it (R.B.)
* Correspondence: alessandra.molinari@unife.it (A.M.); stefano.caramori@unife.it (S.C.)

Table of Contents

Figure S1. Profilometry

Figure S2. AFM 3D map, top view and size analysis of FTO/ZrO₂/CdS and FTO/TiO₂/CdS

Figure S3. XRD patterns of FTO/CdS, FTO/ZrO₂/CdS and FTO/TiO₂/CdS

Figure S4. Tauc Plots of FTO/ZrO₂ /CdS and FTO/TiO₂/CdS

Figure S5. Emission spectrum of FTO/CdS, FTO/ZrO₂/CdS and FTO/TiO₂/CdS

Figure S6. Emission decays of FTO/ZrO₂/CdS

Figure S7. Emission decays of FTO/TiO₂/CdS

Figure S8. Dark Cyclic voltammetry of the FTO/CdS

Figure S9. Dark Cyclic voltammetry of the FTO/TiO₂/CdS

Figure S10. Dark Cyclic voltammetry of the FTO/ZrO₂/CdS

Figure S11. Open circuit chronopotentiometry

Figure S12. Cyclic voltammetry of MO, AO7 and EDS

Figure S13. ESI-MS spectra of MO and EDS after irradiation with FTO/TiO₂/CdS

Figure S14. C/C₀ vs irradiation time of azo-dyes with FTO/ZrO₂/CdS and ESI-MS spectrum of EDS after irradiation

Table S1. Kinetic constant and half time values determined by dyes concentration decrease under visible light irradiation with FTO/MO₂/CdS systems.

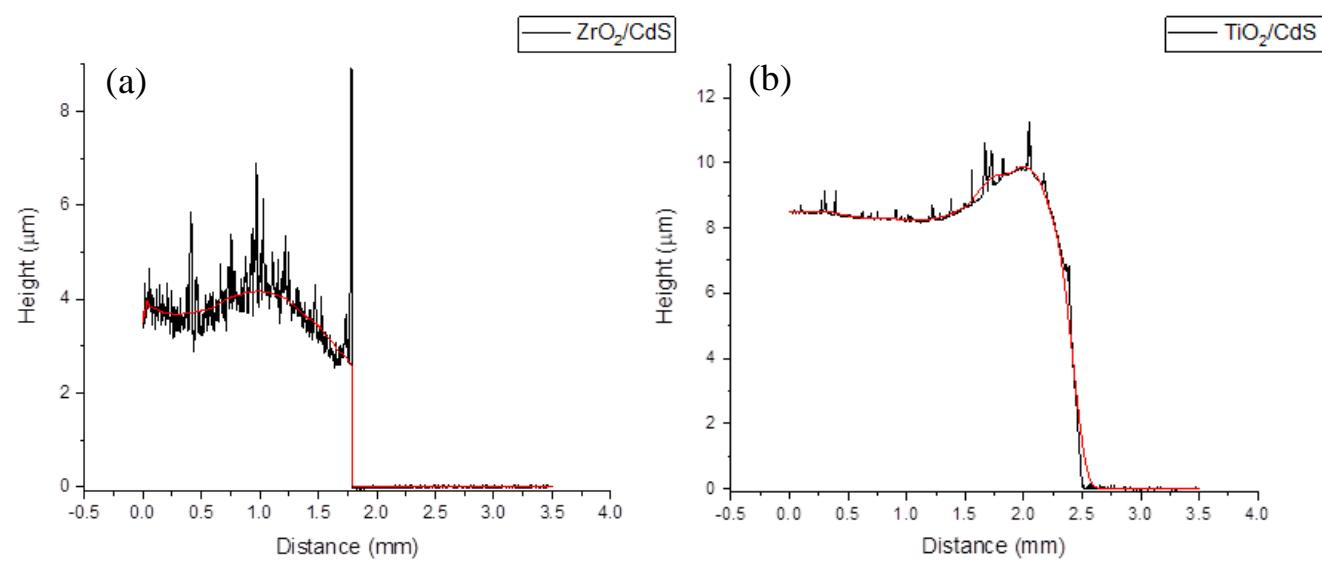


Figure S1. Thickness measurements of (a) FTO/ZrO₂/CdS and (b) FTO/TiO₂/CdS

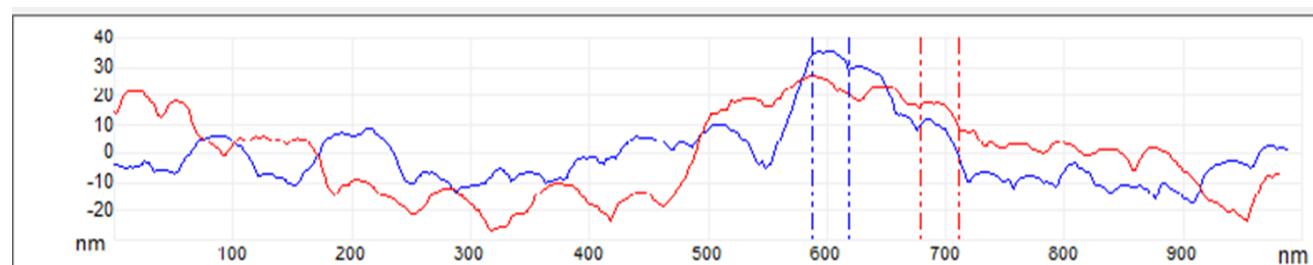
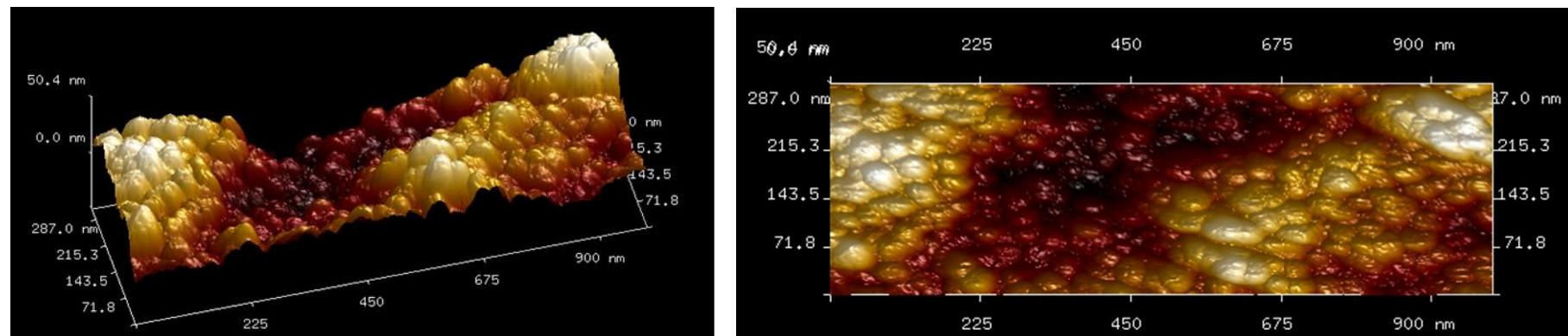
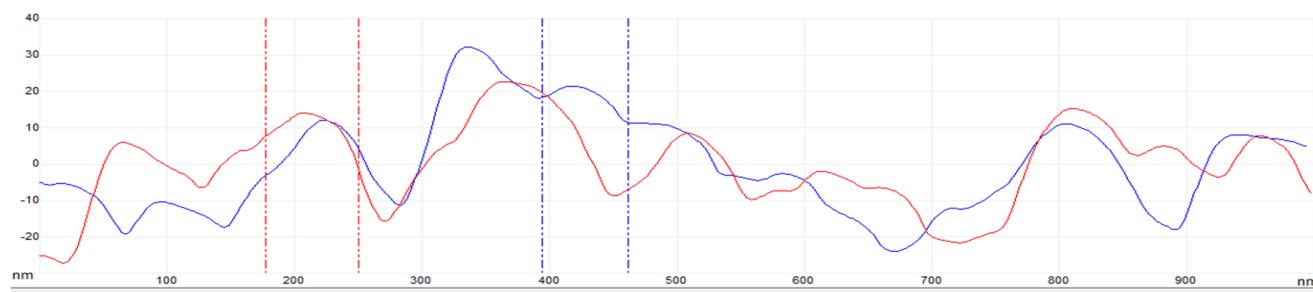
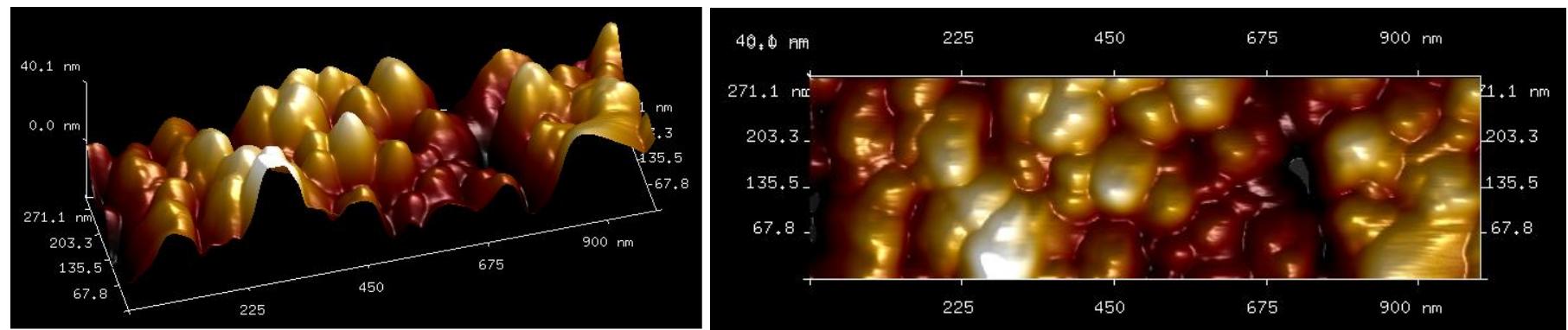
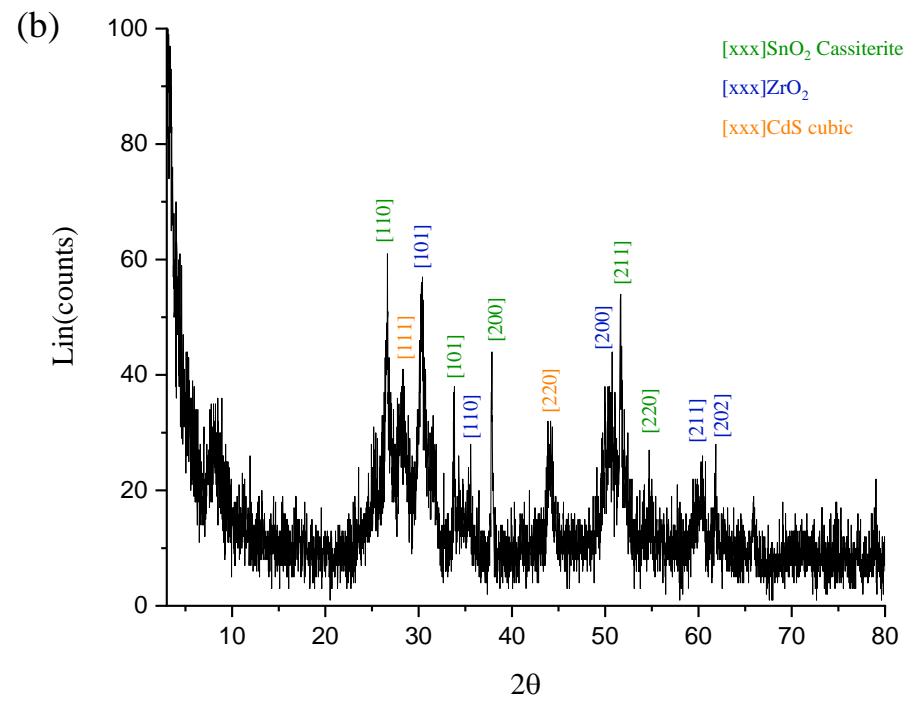
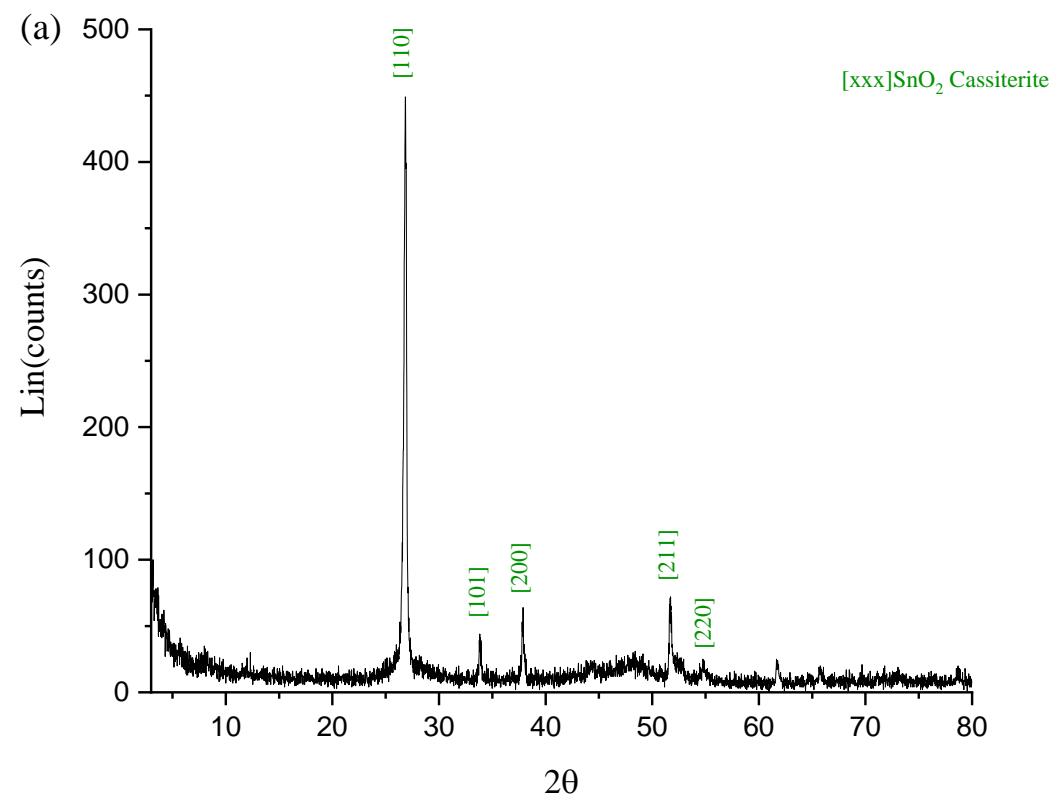


Figure S2. AFM 3D map, top view and cross sectional size analysis of **(a)** FTO/TiO₂/CdS and **(b)** FTO/ZrO₂/CdS



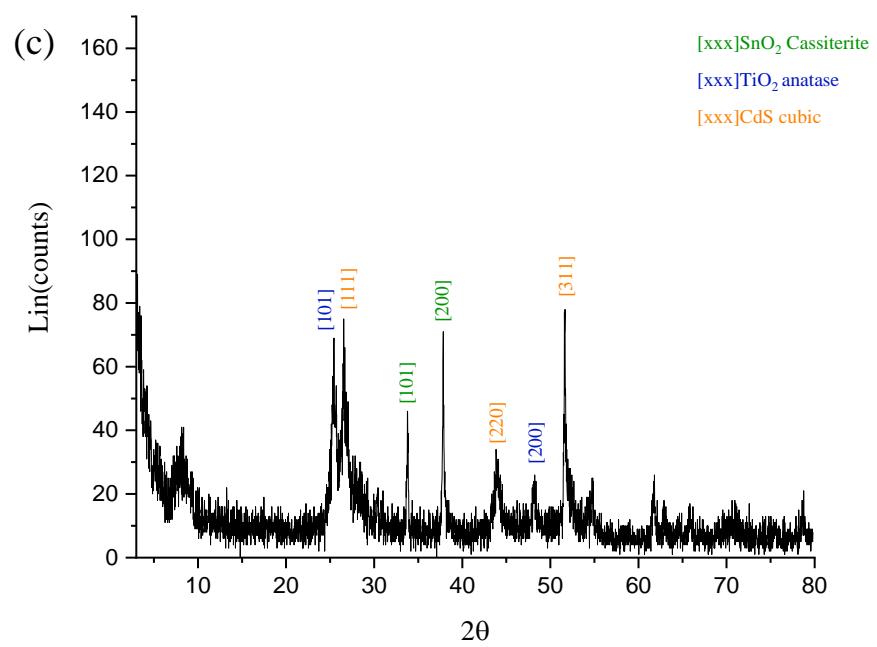


Figure S3. XRD patterns of (a) FTO/CdS, (b) FTO/ZrO₂/CdS (c) FTO/TiO₂/CdS

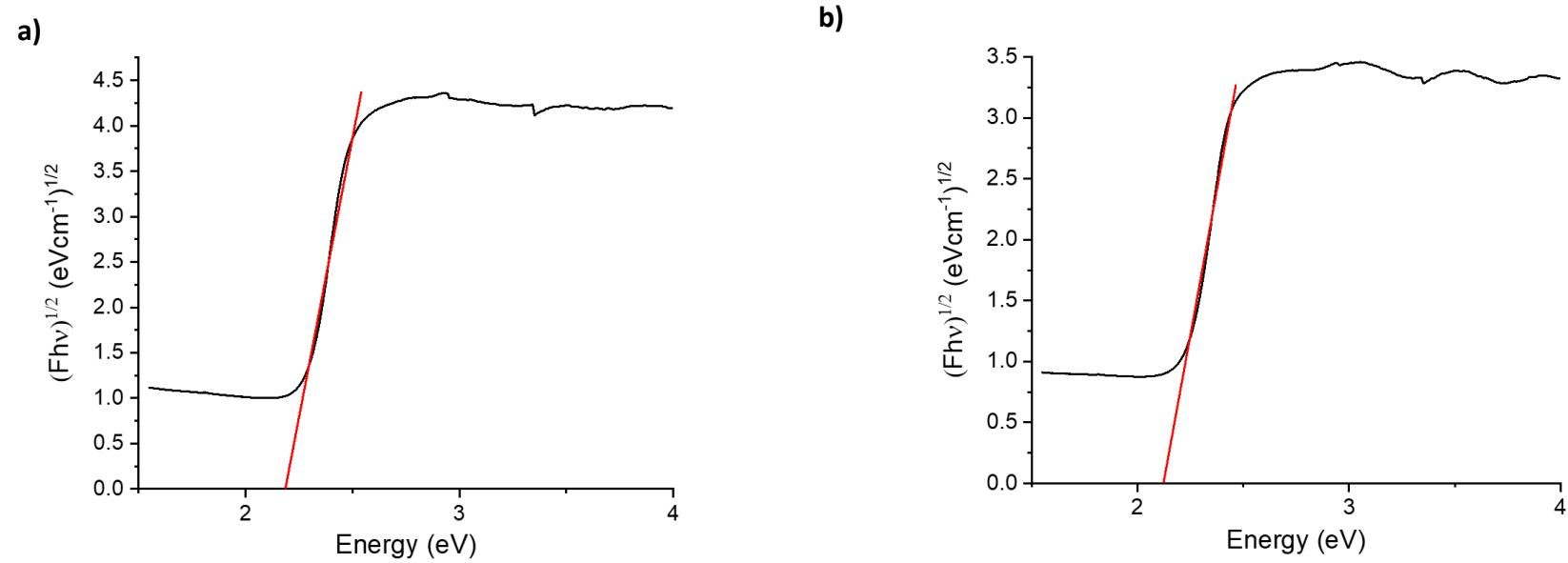


Figure S4. Tauc Plots of (a) FTO/ZrO₂/CdS and (b) FTO/TiO₂/CdS

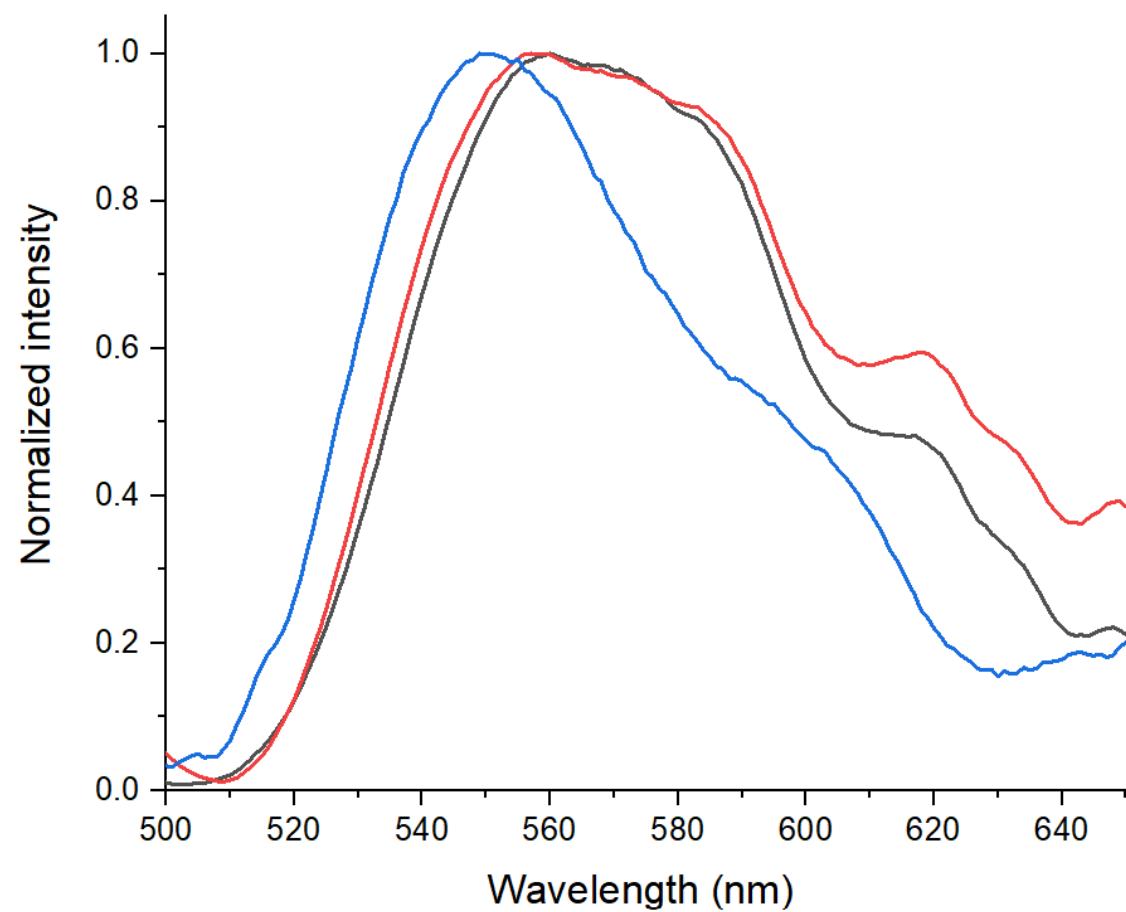
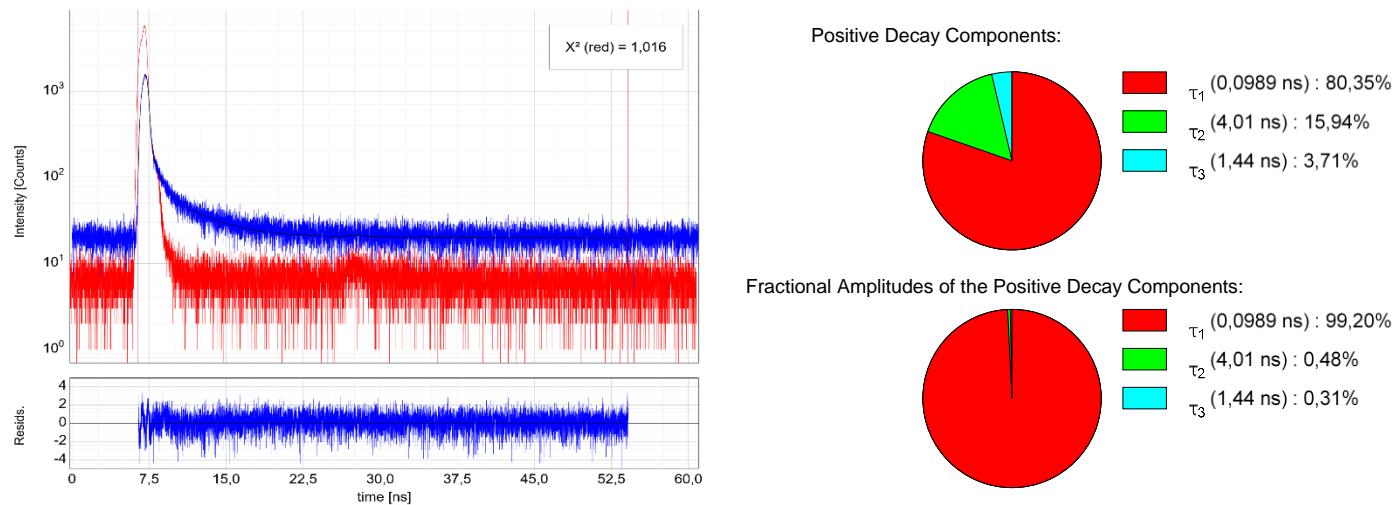
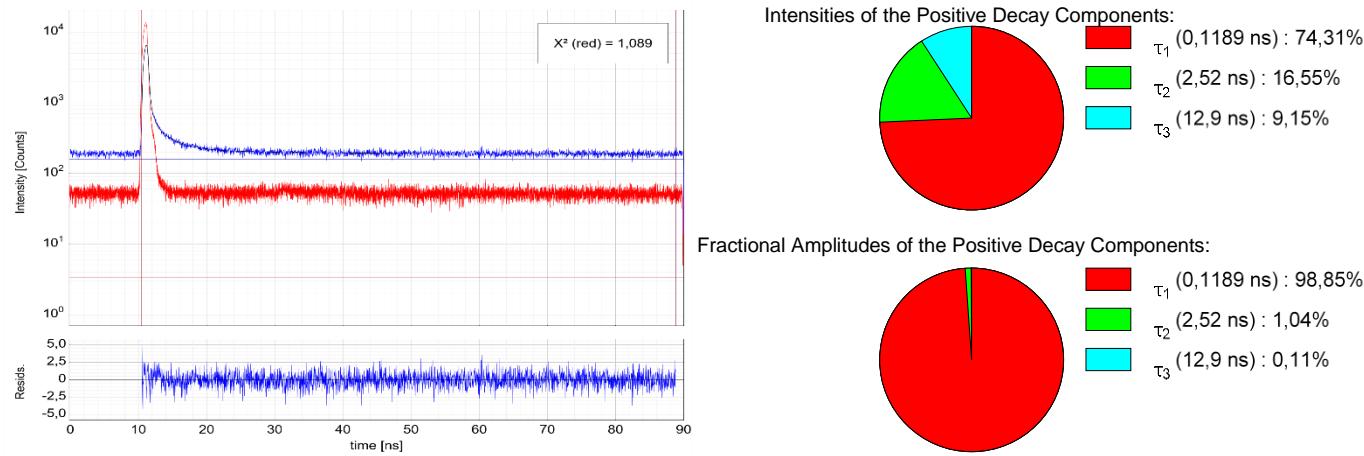


Figure S5. Emission spectra ($\lambda_{\text{exc}} = 450 \text{ nm}$) of FTO/CdS, FTO/ZrO₂/CdS, FTO/TiO₂/CdS thin films at room temperature.



Parameter	Value	Conf. Lower	Conf. Upper	Conf. Estimation
A ₁ [Cnts]	2312	-50	+50	Fitting
τ ₁ [ns]	0,0989	-0,0021	+0,0021	Fitting
A ₂ [Cnts]	11,30	-0,96	+0,96	Fitting
τ ₂ [ns]	4,01	-0,31	+0,31	Fitting
A ₃ [Cnts]	7,3	-2,3	+2,3	Fitting
τ ₃ [ns]	1,44	-0,47	+0,47	Fitting
Bkgr. Dec [Cnts]	-6,83	-0,81	+0,81	Fitting
Bkgr. IRF [Cnts]	-67,3	-2,2	+2,2	Fitting
Shift IRF [ns]	-0,209	-0,010	+0,010	Fitting
A Scat [Cnts]	-57900	-7200	+7200	Fitting
Period Rep [ns]	0,0587	-0,0048	+0,0048	Fitting

Figure S6. Single photon timing emission decay of FTO/ZrO₂/CdS in 1M sodium formate



Parameter	Value	Conf. Lower	Conf. Upper	Conf. Estimation
A ₁ [Cnts]	8150	-190	+190	Fitting
τ_1 [ns]	0,1189	-0,0027	+0,0027	Fitting
A ₂ [Cnts]	85,7	-7,5	+7,5	Fitting
τ_2 [ns]	2,52	-0,20	+0,20	Fitting
A ₃ [Cnts]	9,3	-2,0	+2,0	Fitting
τ_3 [ns]	12,9	-2,9	+2,9	Fitting
Bkgr. Dec [Cnts]	158,9	-2,4	+2,4	Fitting
Bkgr. IRF [Cnts]	3,4	-3,7	+3,7	Fitting
Shift IRF [ns]	-0,1421	-0,0077	+0,0077	Fitting
A Scat [Cnts]	145000	-37000	+37000	Fitting
Period Rep [ns]	-0,00026	-0,0071	+0,0071	Fitting

Figure S7. Single photon timing emission decay of FTO/TiO₂/CdS in 1M sodium formate

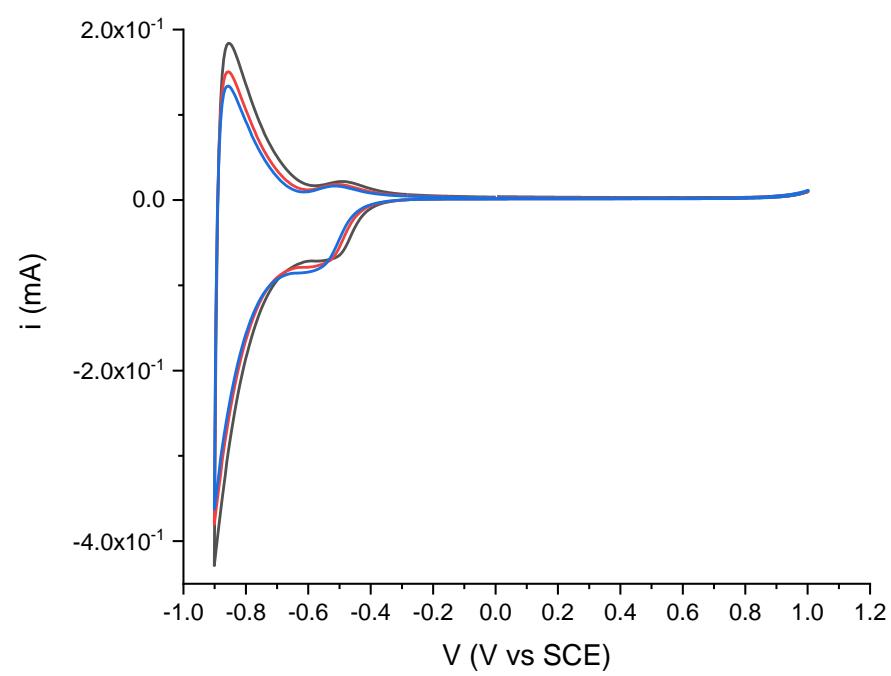


Figure S8. Dark cyclic voltammetry of the FTO/TiO₂/CdS recorded in HCOONa 1M at pH 7 between -1V/1V vs SCE at a scan rate of 50mV/s

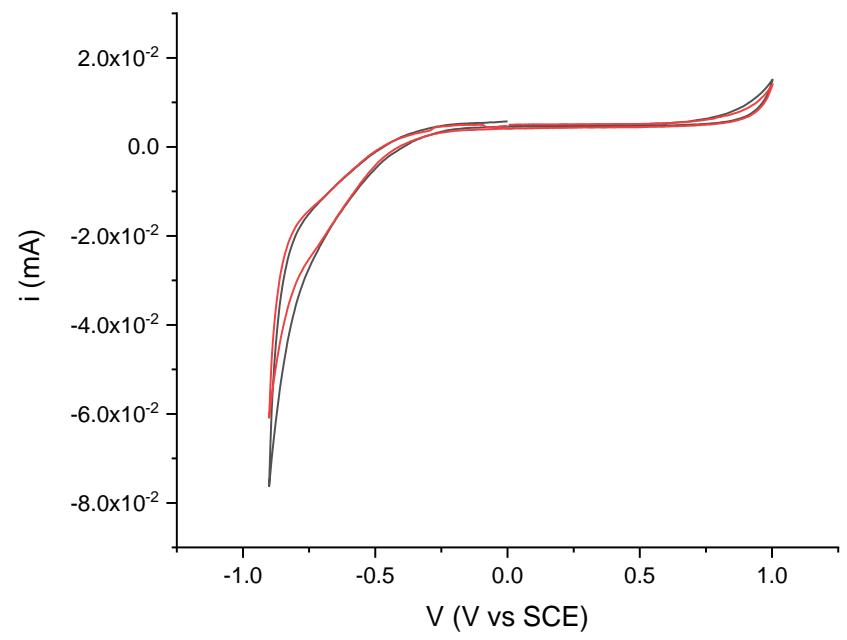


Figure S9. Dark cyclic voltammetry of the FTO/CdS recorded in HCOONa 1M at pH 7 between -1V/1V vs SCE at a scan rate of 50mV/s

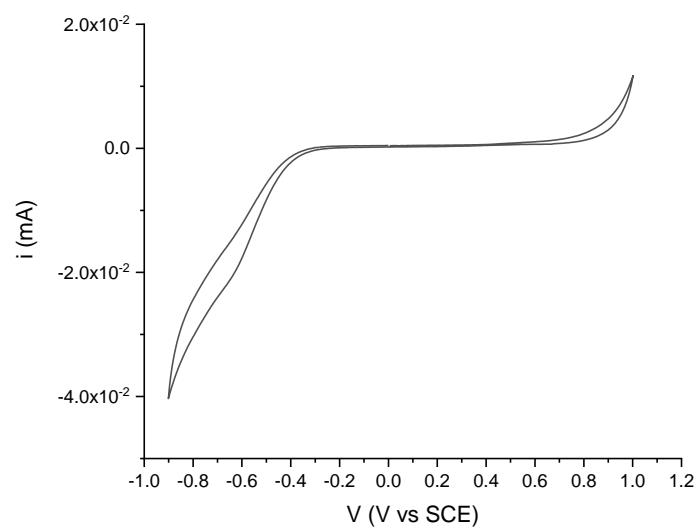


Figure S10. Dark cyclic voltammetry of the FTO/ZrO₂/CdS recorded in HCOONa 1M at pH 7 between -1V/1V vs SCE at a scan rate of 50mV/s

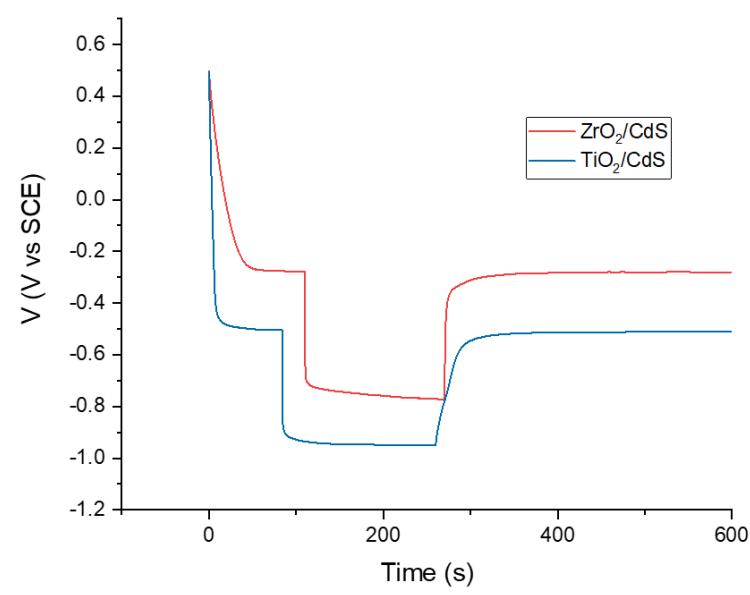


Figure S11. Open circuit chronopotentiometry of FTO/ ZrO_2/CdS (red) and FTO/ TiO_2/CdS (blue) in the presence of 1 M HCOONa at pH 7.

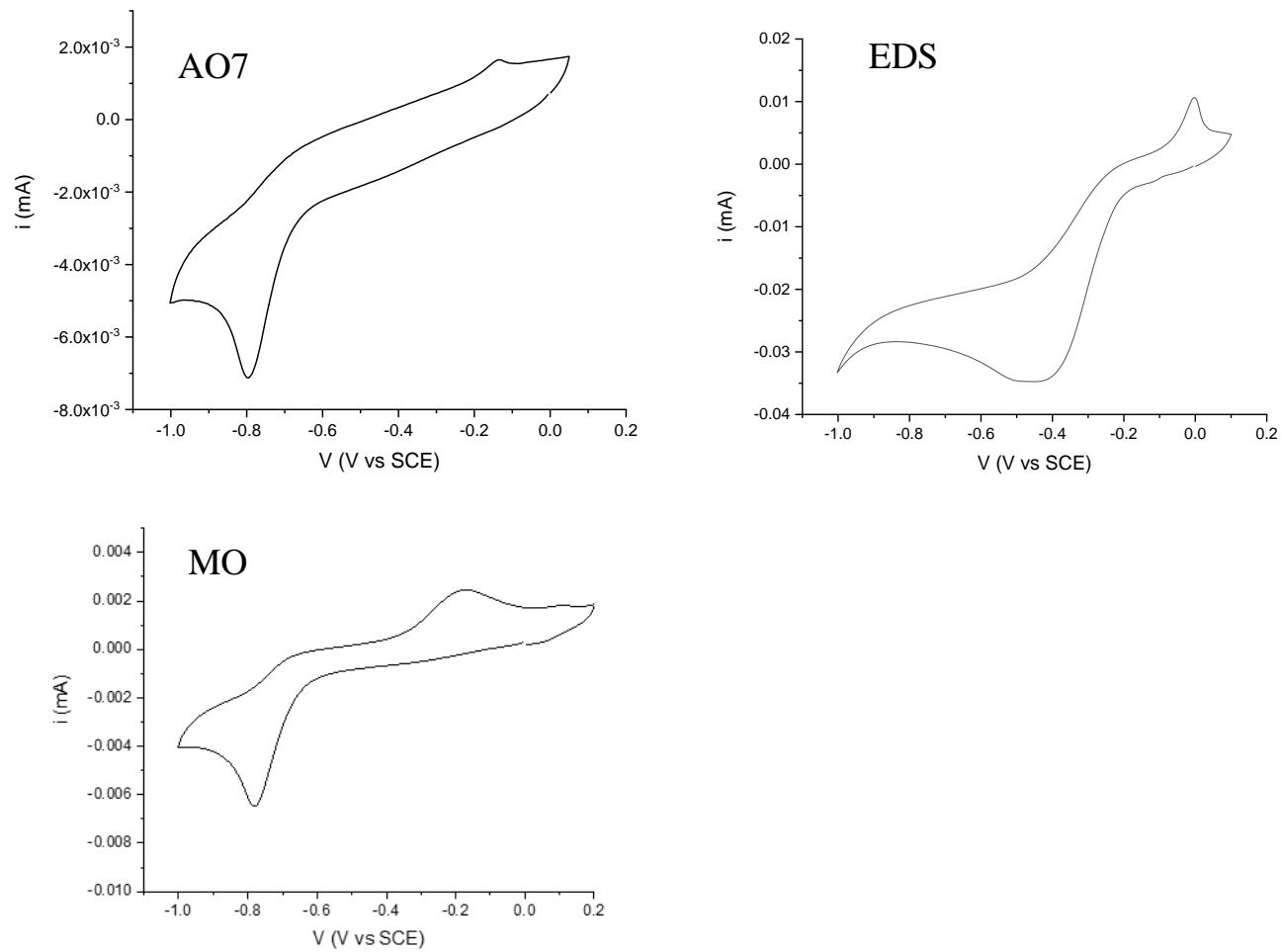


Figure S12. Cyclic voltammetry of the MO, AO7 and EDS dyes (20 mV/s) recorded in the presence of 0.1 M LiClO₄ at a glassy carbon electrode.

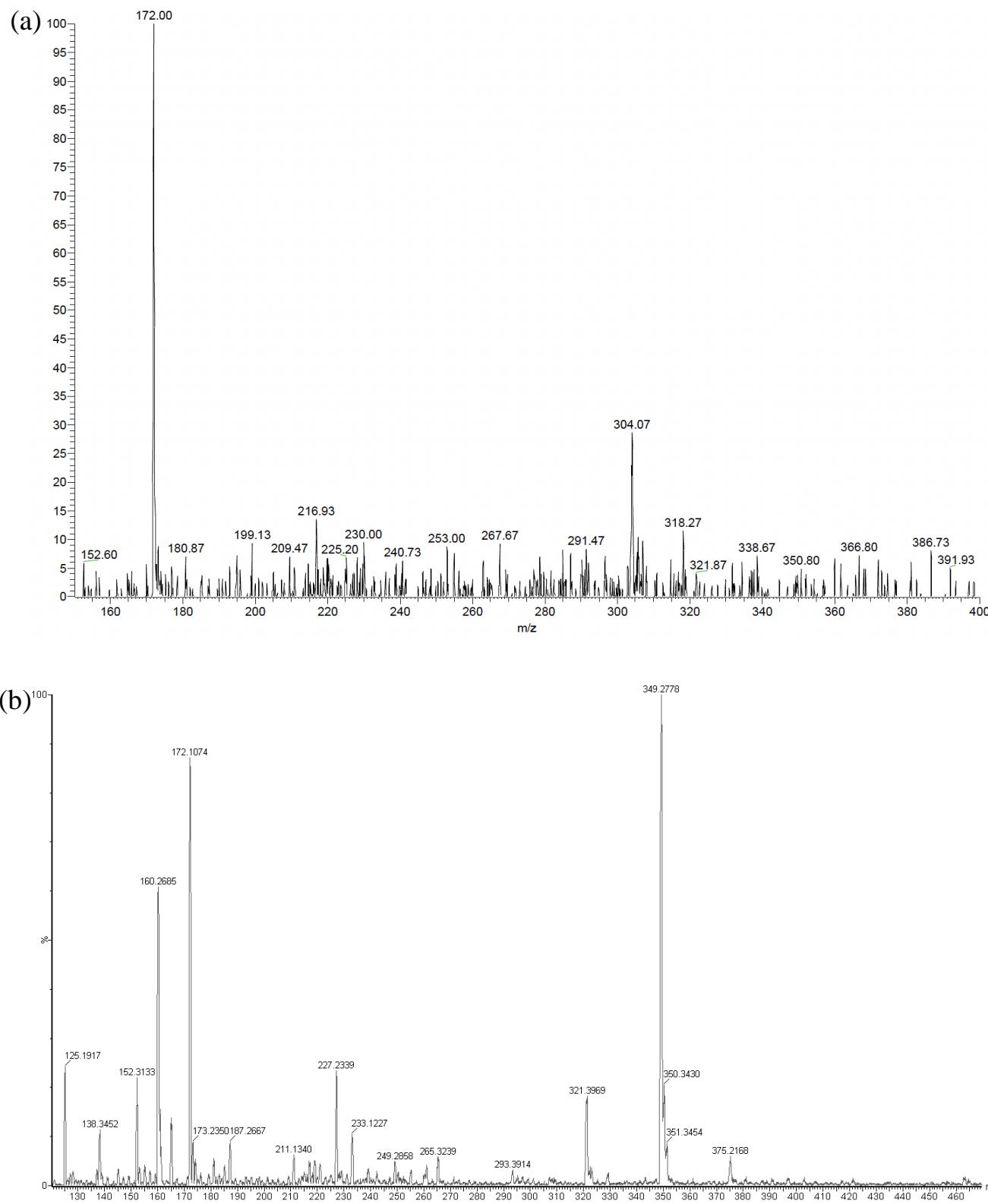


Figure S13. (a): ESI-MS spectrum of the deaerated aqueous solution containing MO (10 ppm) and ethanol (10% v/v) after irradiation ($\lambda \geq 420$ nm) in the presence of FTO/TiO₂/CdS system. (b) the same as part a but with EDS (10 ppm). Ethanol is used here in place of formate as a nonionic hole scavenger.

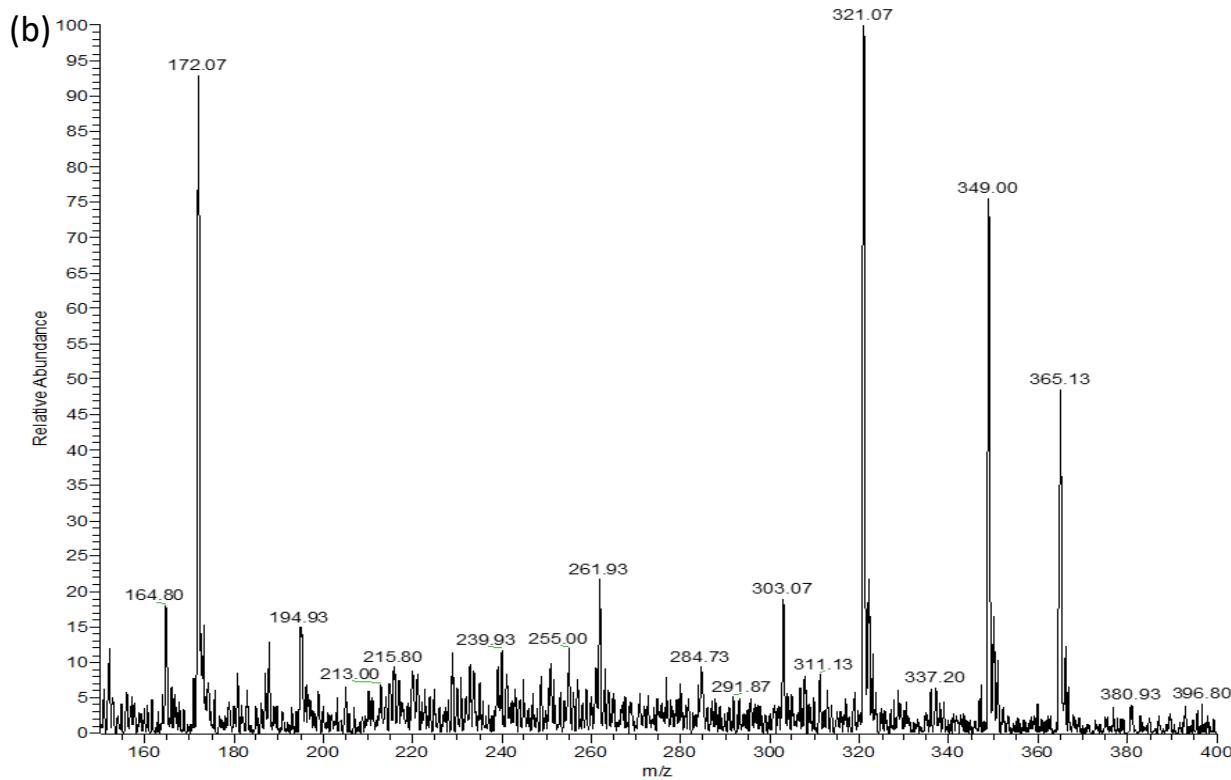
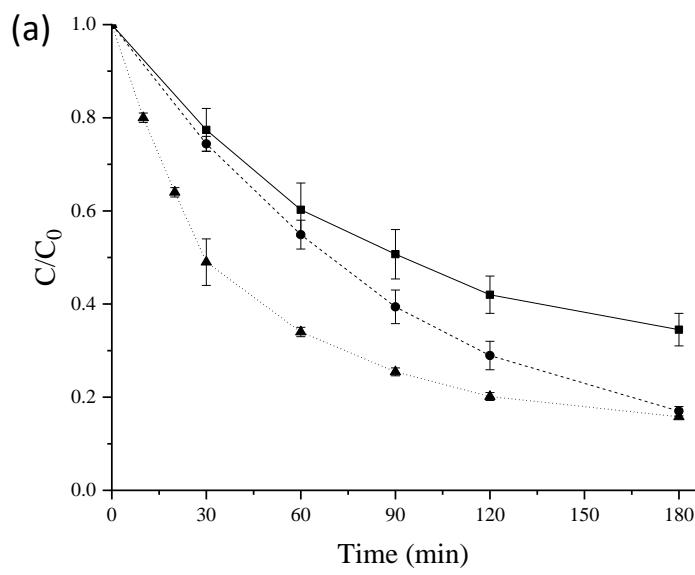


Figure S14. (a) C/C₀ ratio vs. time profiles obtained upon irradiation ($\lambda \geq 420$ nm) of FTO/ZrO₂/CdS film immersed in deaerated aqueous solutions containing HCOONa (1 M) and MO (circle), or AO7 (triangle), or EDS (square). C₀ = 10 ppm. Reported data are the mean of three repeated experiments. (b) ESI-MS spectrum of deaerated aqueous solution containing EDS (10 ppm) and ethanol (10% v/v) after irradiation ($\lambda > 420$ nm) in the presence of FTO/ZrO₂/CdS system

Table S1. Kinetic constants and half-time values determined by dyes concentration decrease under visible light irradiation with FTO/MO₂/CdS systems.

	Dye	k (min ⁻¹)	t _{1/2}	R ²
FTO/TiO ₂ /CdS	MO	0.0125	55	0.9977
	AO7	0.0283	24	0.9726
	EDS	0.0123	56	0.9004
FTO/ZrO ₂ /CdS	MO	0.0104	66	0.9933
	AO7	0.0178	39	0.9407
	EDS	0.0072	96	0.9711