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

Supporting Information.

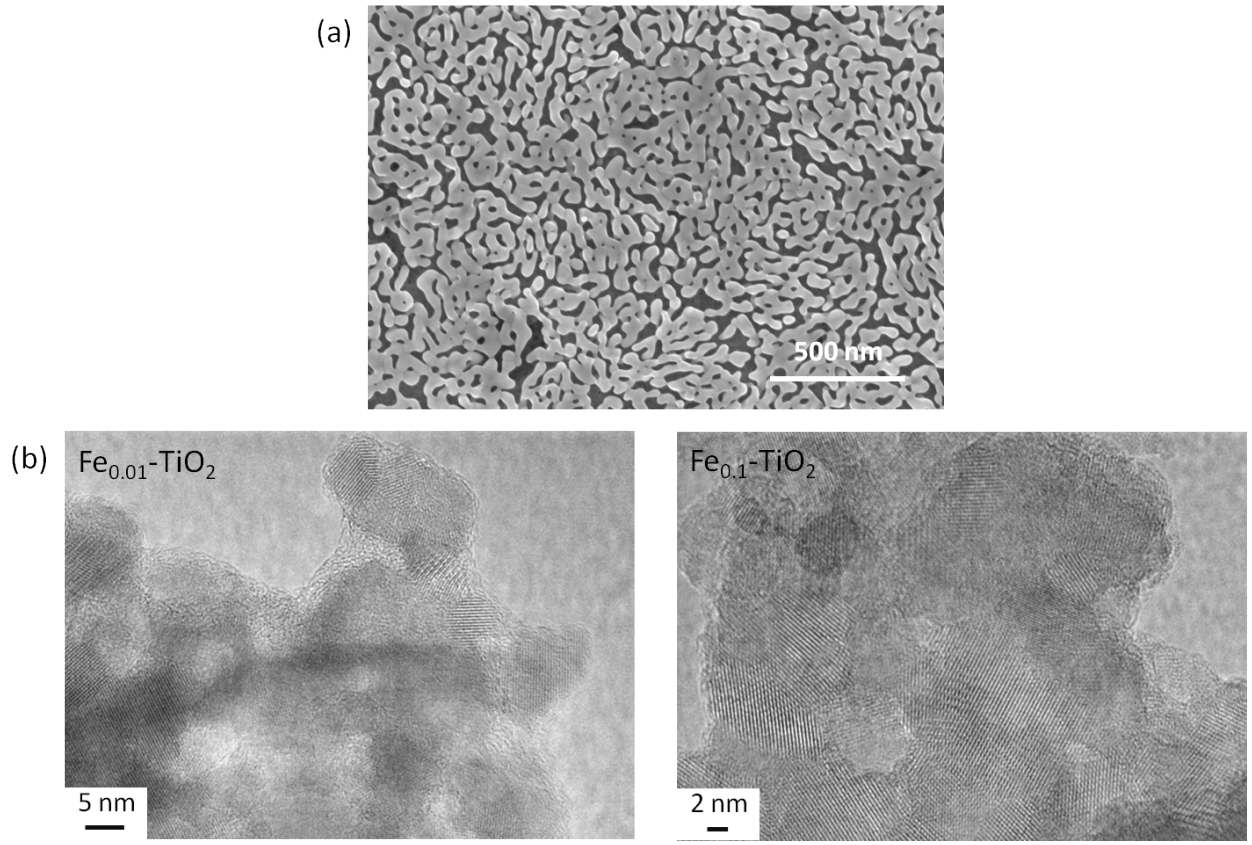

Figure S1. a. FE−SEM of $Fe_{0.2}$−TiO_2 films heated at 600°C under air for 15 min. b. HR−TEM of $Fe_{0.01}$−TiO_2 and $Fe_{0.1}$−TiO_2 mesoporous films heated at 500°C under air for 15 min.

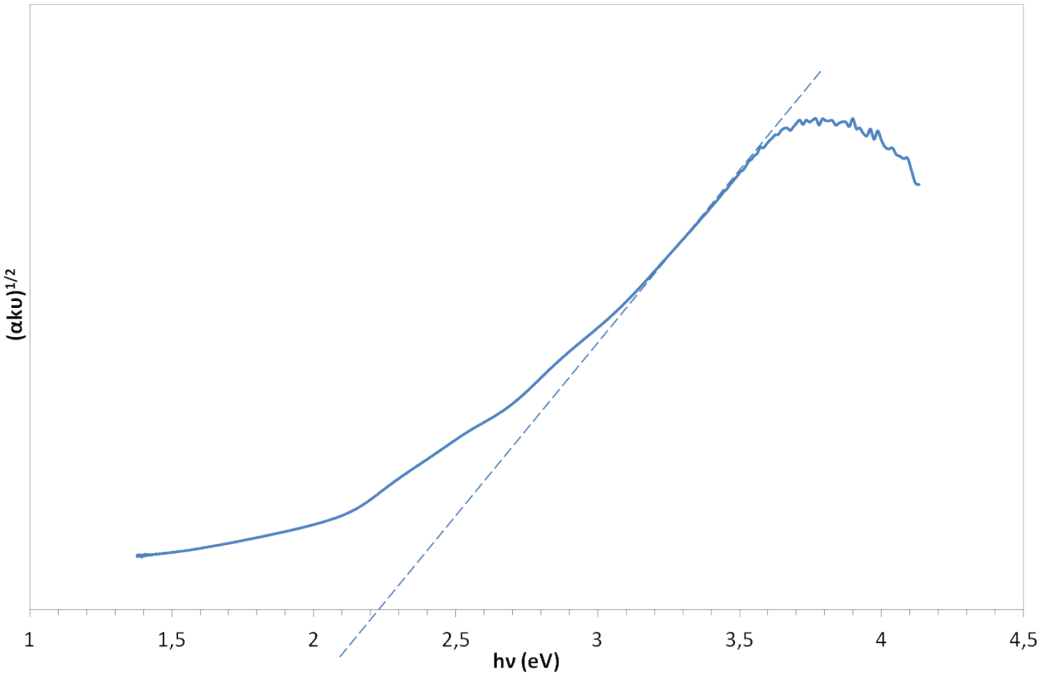

Figure S2. Determination of bandgap: variation of $(\alpha k\upsilon)^{1/2}$ as function of hν.

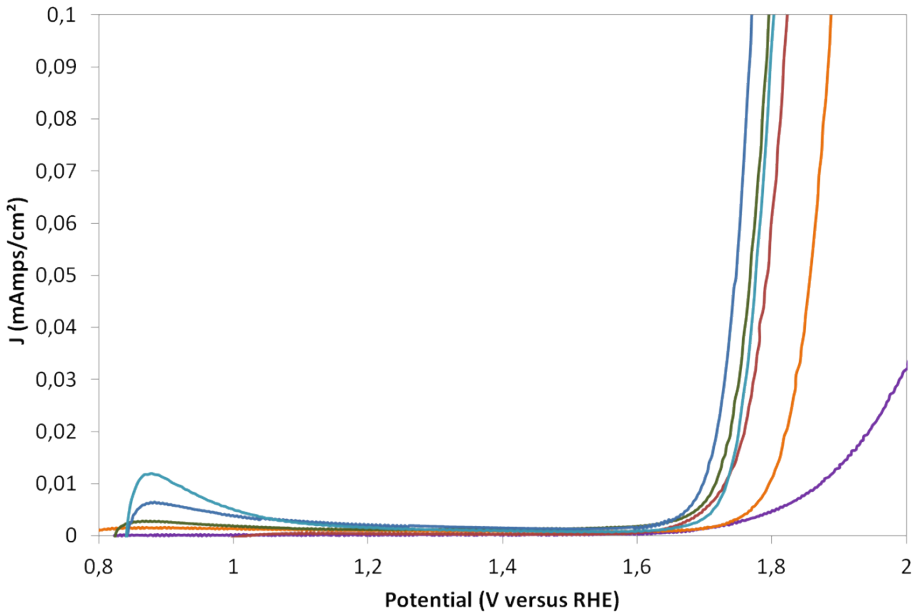

Figure S3. Current density *vs* applied potential (J−V) plots for the Fe_x−TiO_2 electrodes as function of the iron content: TiO_2 (purple); $Fe_{0.01}$−TiO_2 (orange); $Fe_{0.05}$−TiO_2 (green); $Fe_{0.1}$−TiO_2 (dark red); $Fe_{0.2}$−TiO_2 (dark blue); $Fe_{0.3}$−TiO_2 (light blue).

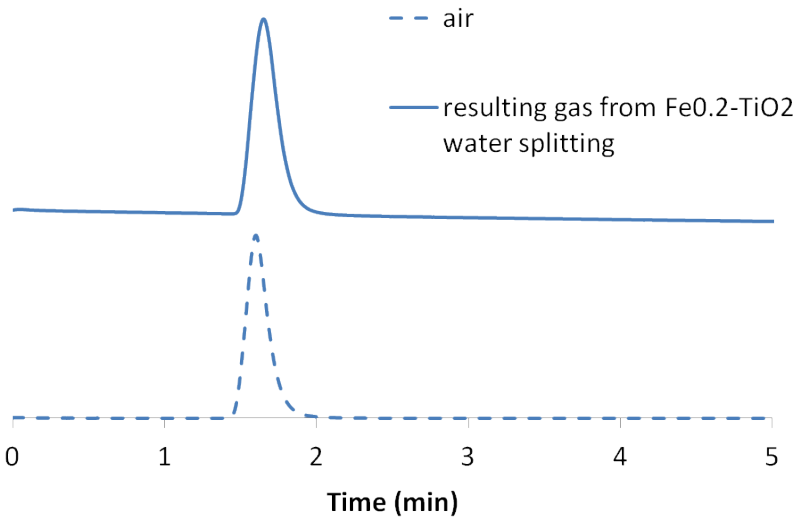

Figure S4. Gas chromatogram of the resulting gas from water splitting with the $Fe_{0.2}$-TiO_2 photoanode during 6 hours and of air.

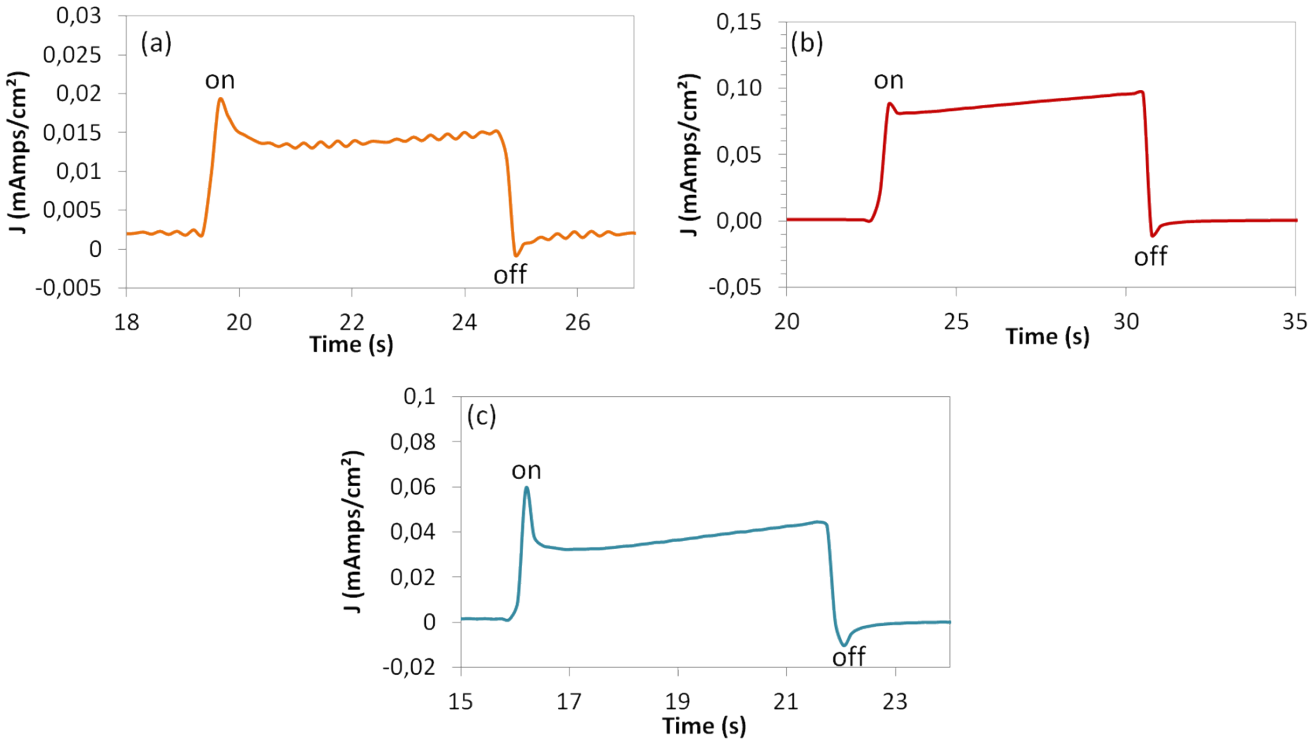

Figure S5. Chopped light photocurrent response of the (a) $Fe_{0.01}$–TiO_2, (b) $Fe_{0.1}$–TiO_2, (c) $Fe_{0.3}$–TiO_2 thin film electrode

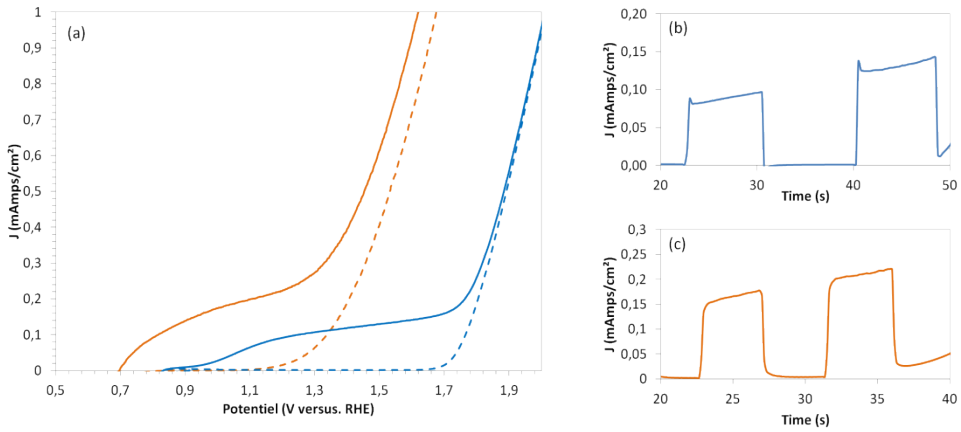

Figure S6. a. Current density *vs* applied potential (J−V) plots for the $Fe_{0.1}$- TiO_2 electrodes: dotted line (dark current); plain line (under illumination) in NaOH electrolyte (blue) and in NaOH (1M) + H_2O_2 (0.5 M) electrolyte (orange). b. Chopped light photocurrent response in NaOH (1 M) electrolyte, c. Chopped light photocurrent response in NaOH (1 M) + H_2O_2 (0.5 M) electrolyte.

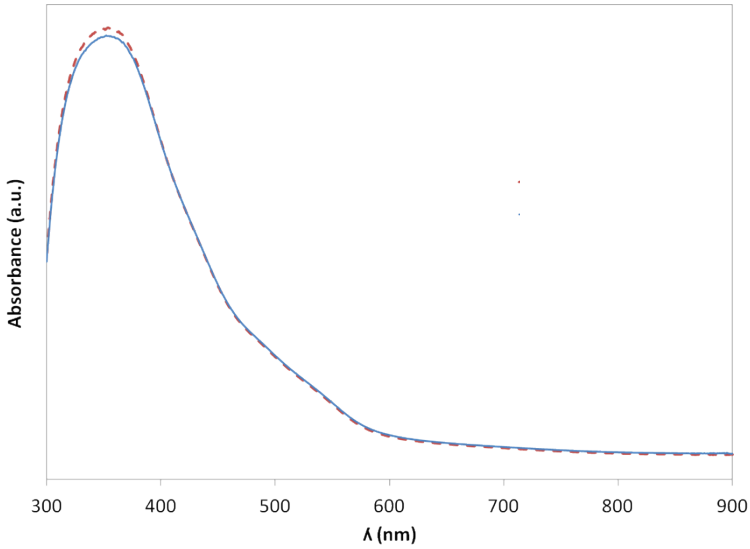

Figure S7. Absorbance for the $Fe_{0.2}$−TiO_2 films before (red dotted line) and after Co deposition (plain blue line)

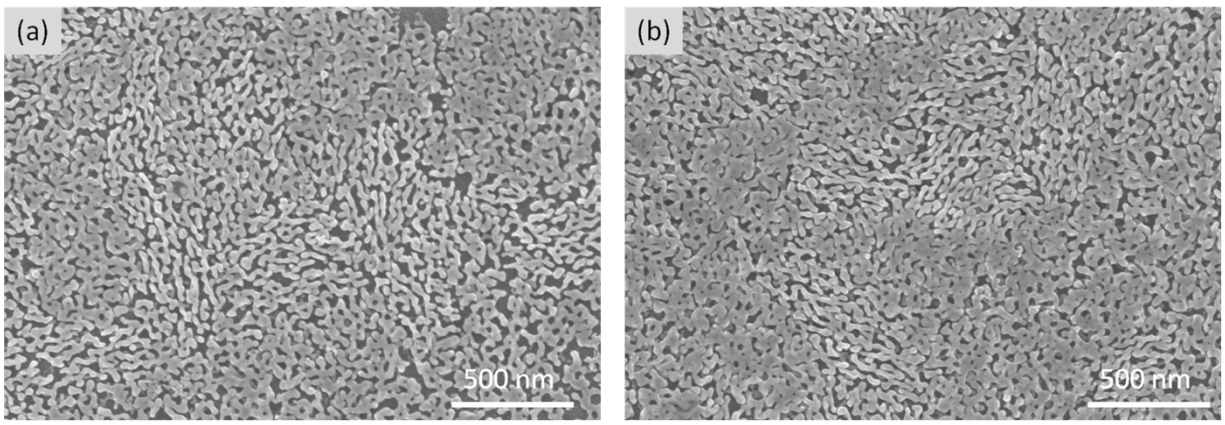

Figure S8. FE−SEM of $Fe_{0.2}$-TiO_2 after annealing the film in 5%H_2/Ar 30 min at 200 (a) and 300°C (b).

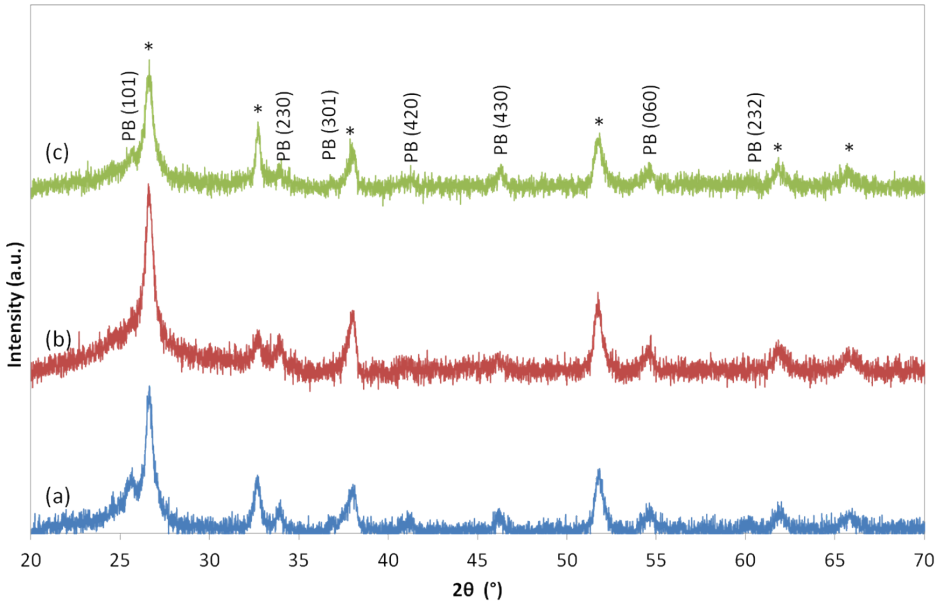

Figure S9. X−ray diffraction spectra of $Fe_{0.2}$−TiO_2 after annealing the film in 5%H_2/Ar for 30 min at 200°C (b) and 300°C (c). As comparison purpose, X−ray diffraction spectra of $Fe_{0.2}$−TiO_2 heated at 500°C for 15 min in air; *: FTO.

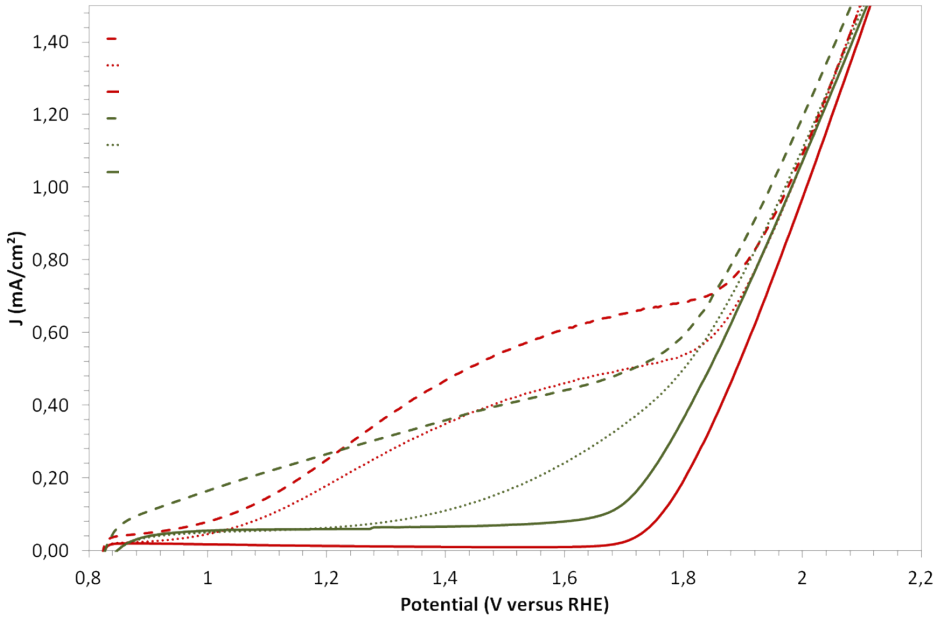

Figure S10. Current density *vs* applied potential (J−V) plots for the $Fe_{0.2}$-TiO_2 electrodes as function of the number of cycles (cycle 1 : dash line; cycle 2: small dashed line) for films heat-treated at 200°C under 5%H_2/Ar (red) and at 300°C under 5%H_2/Ar (green). The dark current is reported for comparison purpose (plain line).

Table S1 : Grain size of the different phases in the films calcined at 500°C, depending on the Fe concentration.

	Anatase	**Pseudobrookite**	**Hematite**
$Fe_{0.01}$-TiO_2	18 ± 1 nm	-	-
$Fe_{0.05}$-TiO_2	14 ± 1 nm	12 ± 1 nm	-
$Fe_{0.1}$-TiO_2	8 ± 1 nm	21 ± 1 nm	-
$Fe_{0.2}$-TiO_2	6 ± 1 nm	25 ± 1 nm	19 ± 1 nm
$Fe_{0.3}$-TiO_2	-	23 ± 1 nm	19 ± 1 nm

Table S2: Room temperature ^{57}Fe Mössbauer parameters of the studied samples.

Sample	B (T)	Δ/ε (mm/s)	δ (mm/s)	Area (mm/s)	Site
$Fe_{0.3}$-TiO_2	52,0(2)	-0,16(4)	0,40(2)	20(4)	Hematite
	-	0,90(2)	0,40(1)	38(4)	Fe_2TiO_5 – site 4c
	-	0,53(2)	0,40(1)	42(4)	Fe_2TiO_5 – site 8f
$Fe_{0.1}$-TiO_2	51,9(3)	-0,22(6)	0,38(4)	16(4)	Hematite
	-	0,90(2)	0,38(1)	43(4)	Fe_2TiO_5 – site 4c
	-	0,59(3)	0,39(1)	41(4)	Fe_2TiO_5 – site 8f
$Fe_{0.01}$-TiO_2	-	1,0(1)	0,36(5)	100	Fe(III)