SUPPORTING INFORMATION

Photoelectrocatalytic oxidation of 3-pyridinemethanol to 3-pyridinemethanal and vitamin B_3 by TiO_2 nanotubes

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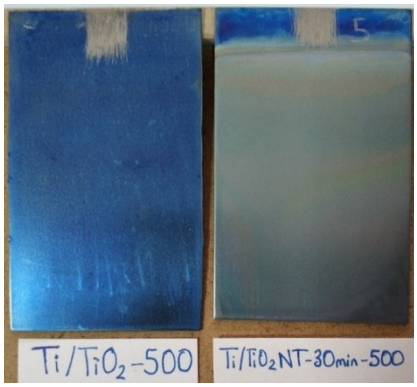


Fig. S1. The photos of Ti/TiO_2-500 and Ti/TiO_2NT-30min-500 photoanodes.

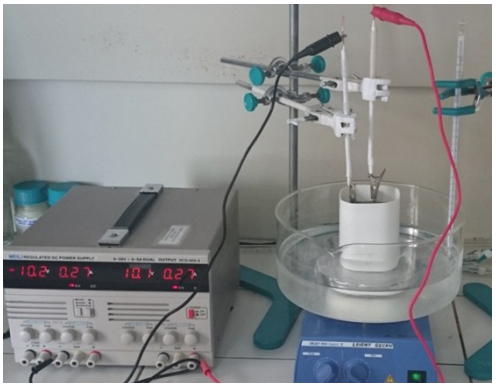


Fig. S2. Experimental setup of two electrode system used for anodic oxidation of photoanodes.

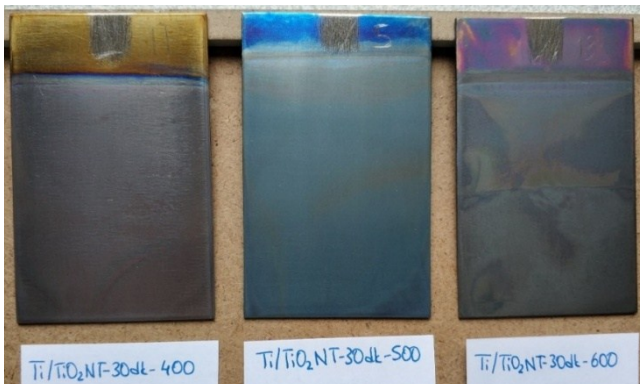
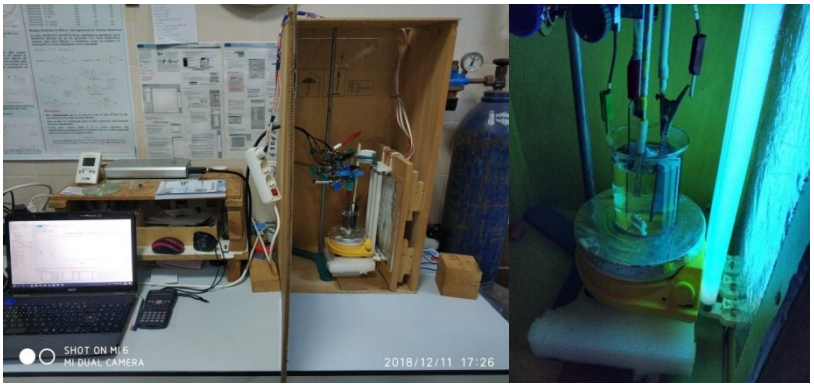


Fig. S3. The photos of Ti/TiO_2NT-30min-400, Ti/TiO_2NT-30min-500 and Ti/TiO_2NT-30min-600 photoanodes, respectively.



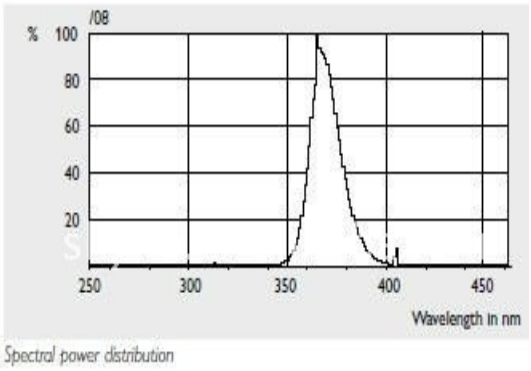


Fig. S4. PC, EC and PEC experiment system (up) and the spectra of the used UV fluorescent lamp (below).

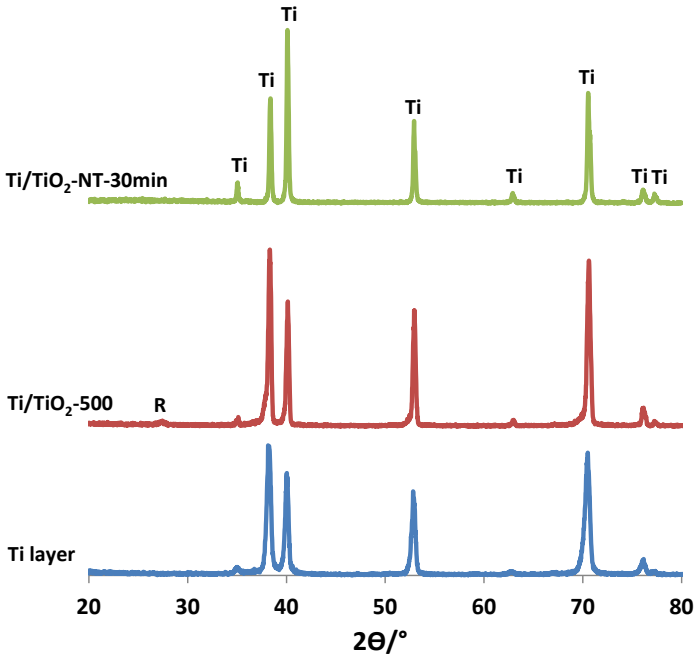


Fig. S5. XRD patterns of Ti/TiO_2-NT-30min (uncalcined), Ti/TiO_2-500, and naked titanium layers.

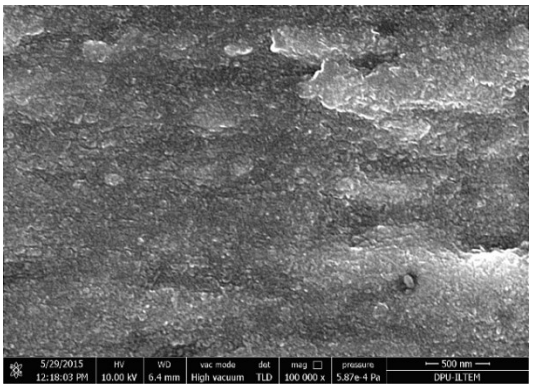
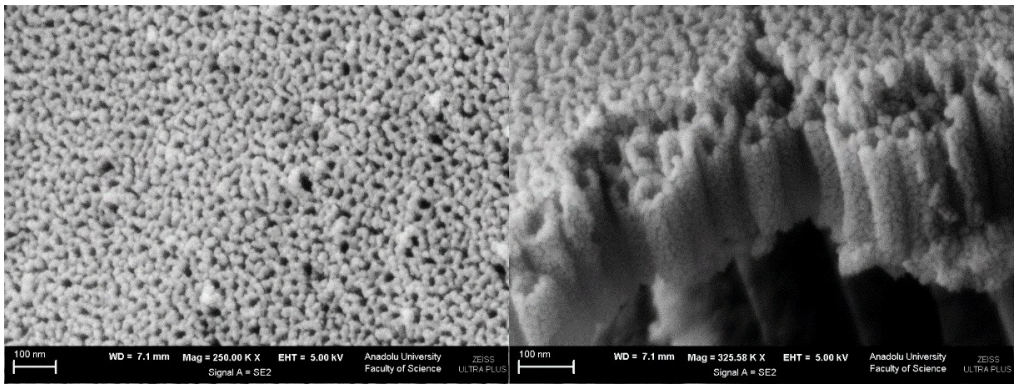
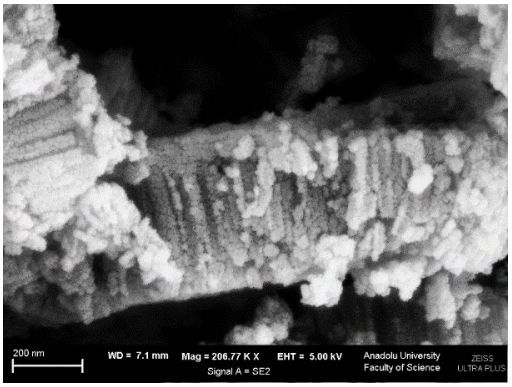


Fig. S6. SEM image of Ti/TiO_2-500 photoanode.

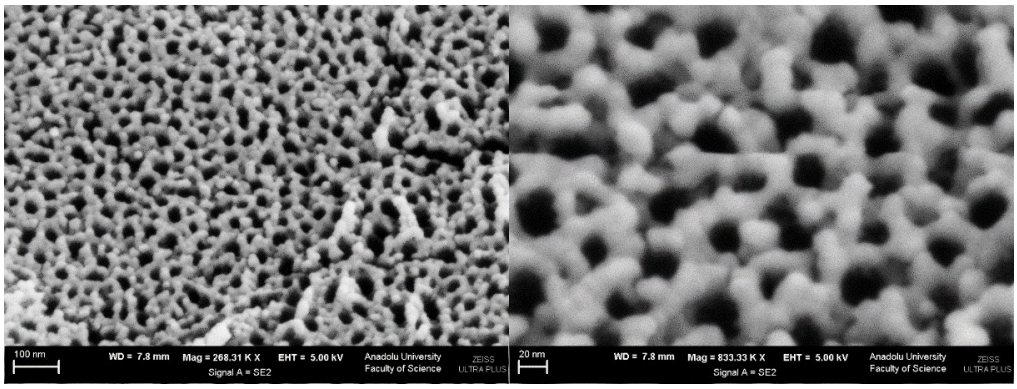


(a) **(b)**



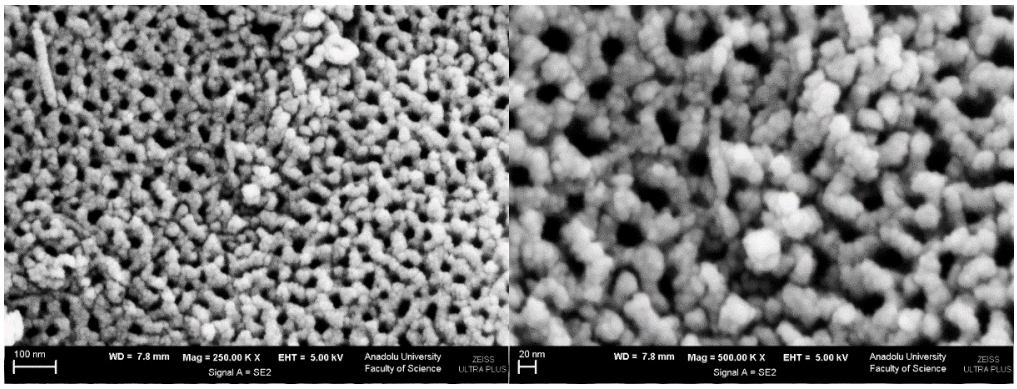
(c)

Fig. S7. Top ((a) and (b)) and cross-section SEM view of Ti/TiO_2NT-10min-500 photoanode.



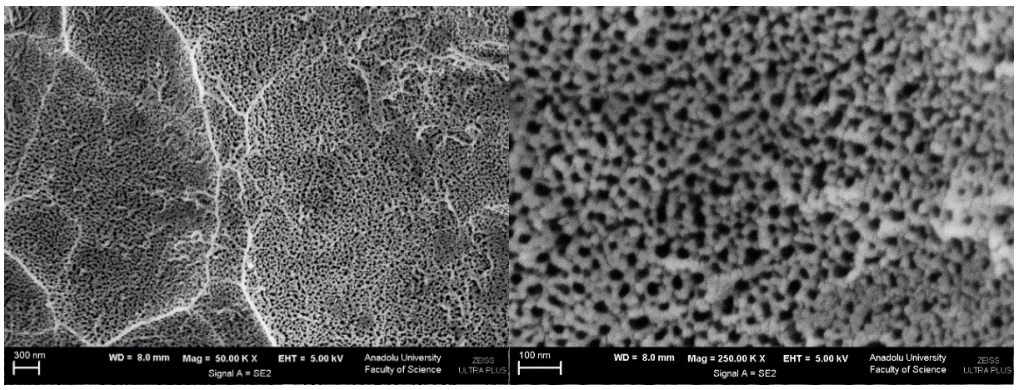
(a) (b)

Fig. S8. SEM images of Ti/TiO_2NT-30min-400 photoanode (a) and (b)).

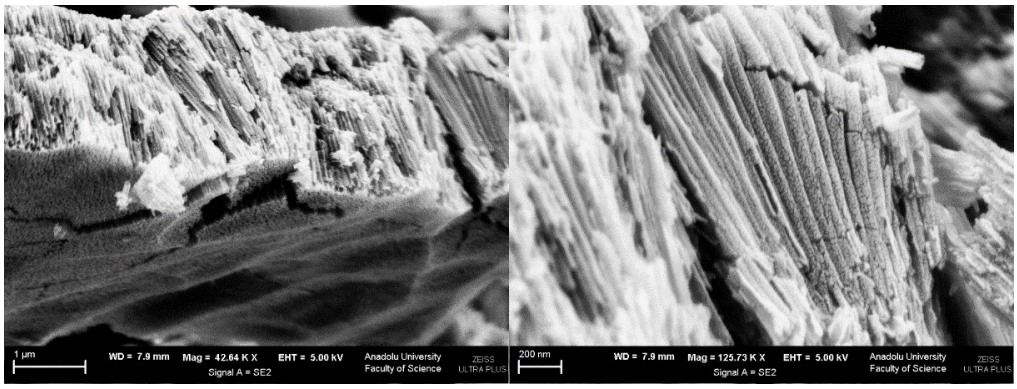


(a) (b)

Fig. S9. SEM images of Ti/TiO_2NT-30min-600 photoanode (a) and (b).

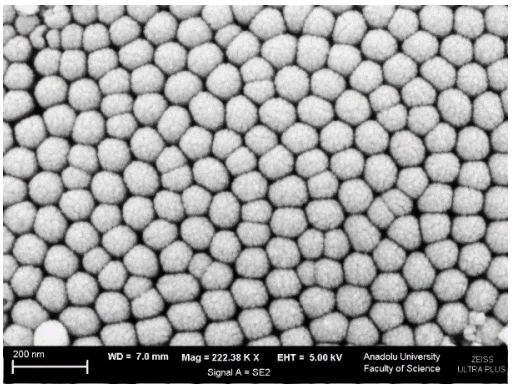


(a) (b)



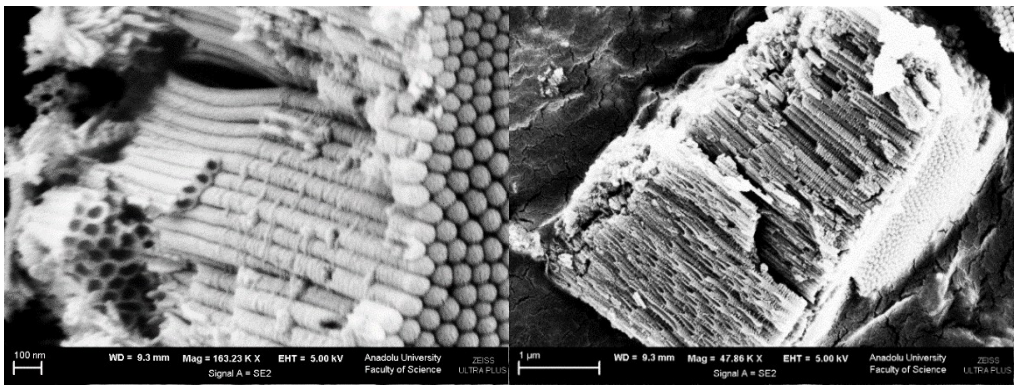
(c) (d)

Fig. S10. SEM images of Ti/TiO_2NT-1h-500 photoanode at top (a and b) and at cross-section (c and d).



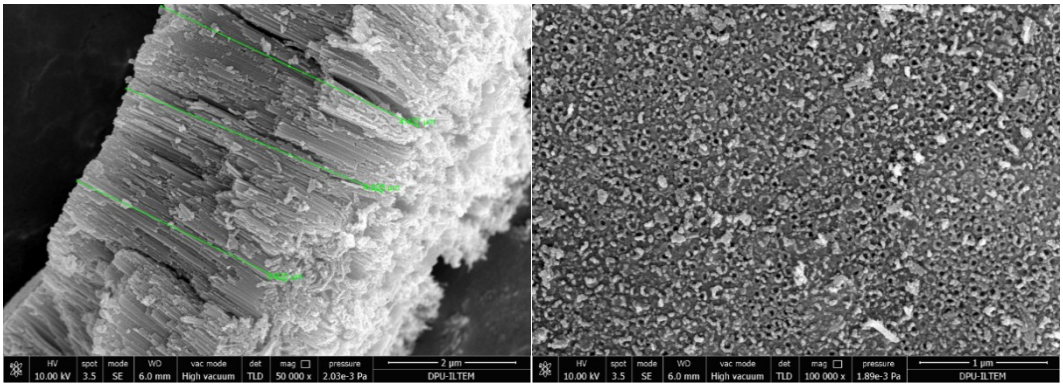
(a)

Fig. S11. SEM images of Ti/TiO_2NT-2h-500 photoanode at bottom.



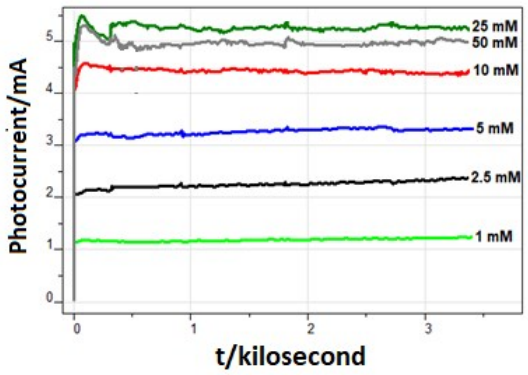
(a) (b)

Fig. S12. Cross-section SEM images of Ti/TiO_2NT-3h-500 photoanode.

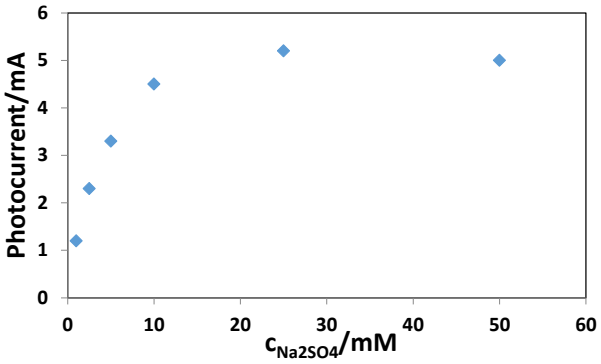


(a) (b)

Fig. S13. Cross-section (a) and top (b) view of SEM images of Ti/TiO_2NT-6h-500 photoanode.



(a)



(b)

Fig. S14. The photocurrent profiles of Ti/TiO_2NT-30min-500 anode for different Na_2SO_4 concentrations in the presence of 0.5 mM 3-pyridinemethanol. Applied potential: 0.5 V *vs* Ag/AgCl (3 M KCl).

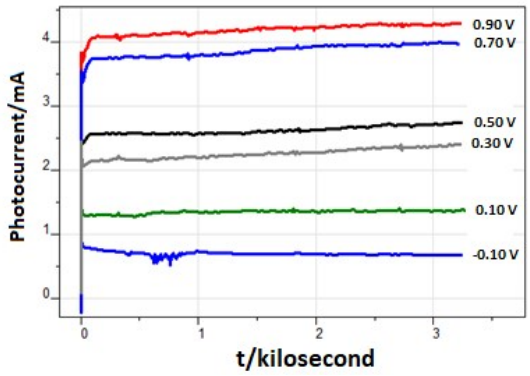


Fig. S15. The photocurrent profiles obtained the PEC experiments performed with Ti/TiO_2NT-30min-500 photoanode in the presence of different applied potential values. Reference electrode: Ag/AgCl (3 M KCl).

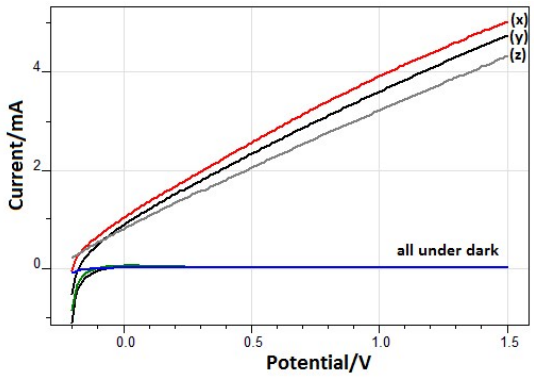
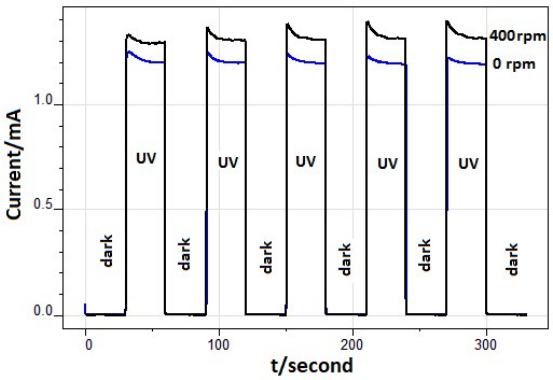
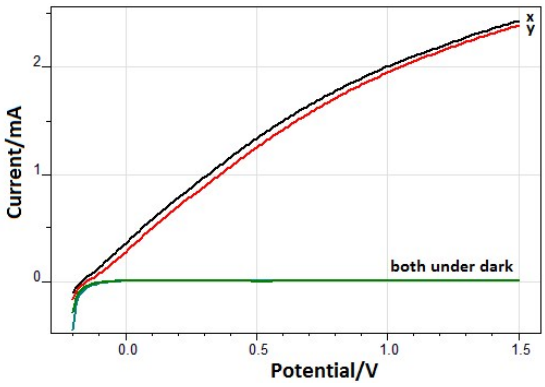


Fig. S16. The (photo)current-potential profiles of Ti/TiO_2NT-30min-500 (x), Ti/TiO_2NT-30min-400 (y) and Ti/TiO_2NT-30min-600 (z) anodes under UV and dark conditions. [Na_2SO_4] = 5 mM. Stirring speed: 400 rpm. pH~ 7. Scan rate: 10 mV s^{-1}. Reference electrode: Ag/AgCl (3 M KCl).

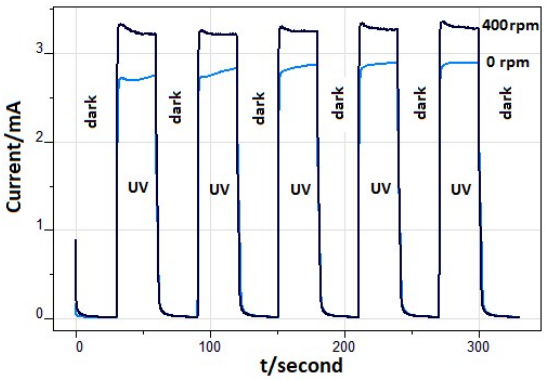


(a)

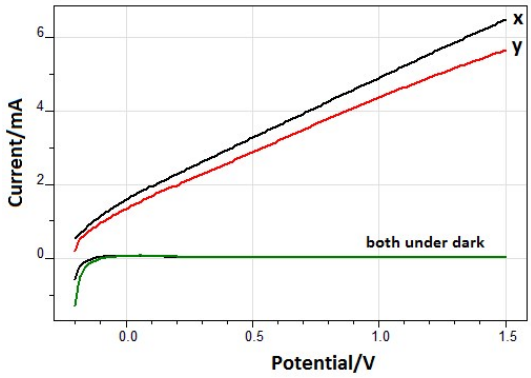


(b)

Fig. S17 a) The (photo)current profiles of Ti/TiO_2-500 photoanode for 400 rpm stirring speed (x) and without stirring (y) in the presence of 0.5 mM 3-pyridinemethanol and 5 mM Na_2SO_4 at 0.5 V. b) The (photo)current-potential values of Ti/TiO_2-500 anode for 400 rpm stirring speed (x) and without stirring (y) in the presence 0.5 mM 3-pyridinemethanol and 5 mM Na_2SO_4. Reference electrode: Ag/AgCl (3 M KCl). Scan rate: 10 mV s^{-1}.



(a)



(b)

Fig. S18 a) The (photo)current profiles of Ti/TiO_2NT-3h-500 photoanode for 400 rpm stirring speed (x) and without stirring (y) in the presence of 0.5 mM 3-pyridinemethanol and 5 mM Na_2SO_4 at 0.5 V. b) The (photo)current-potential values of Ti/TiO_2NT-3h-500 anode for 400 rpm stirring speed (x) and without stirring (y) in the presence 0.5 mM 3-pyridinemethanol and 5 mM Na_2SO_4. Reference electrode: Ag/AgCl (3 M KCl). Scan rate: 10 mV s^{-1}.

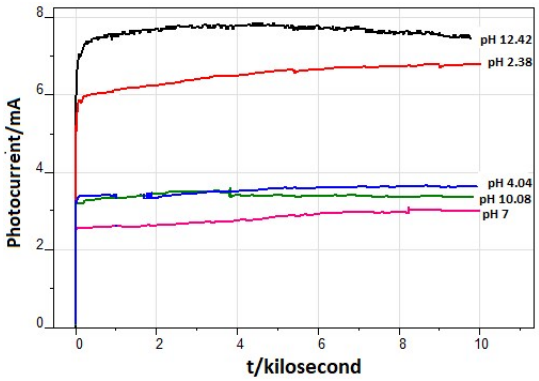


Fig. S19. The photocurrent profiles obtained the PEC experiments performed with Ti/TiO_2NT-3h-500 photoanode for different pH values. Applied potential: 0.5 V *vs* Ag/AgCl (3 M KCl). [Na_2SO_4] = 5 mM.

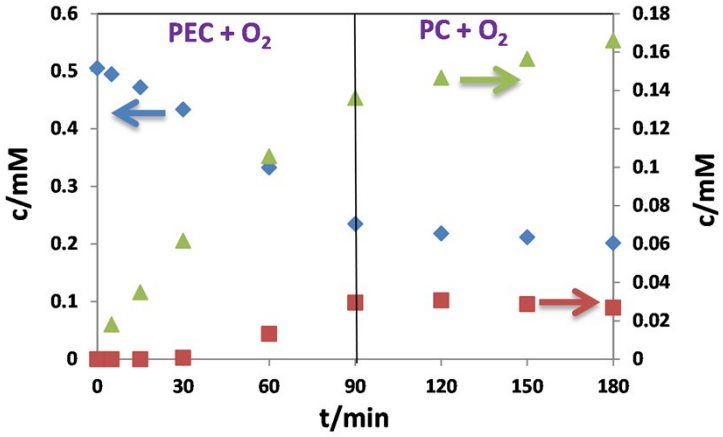


Fig. S20. Results of PEC (the first 90 min) and PC (the second 90 min) oxidation of 3-pyridinemethanal (♦) to 3-pyridinemethanol (■) (its reduction product) and vitamin B_3 (▲) (its oxidation product) *vs* time by using Ti/TiO_2NT-3h-500 anode under UV irradiation and in presence of air from atmosphere. [Na_2SO_4] = 5 mM, stirring speed: 400 rpm, pH~ 7. Applied potential for PEC experiment: 0.5 V *vs* Ag/AgCl (3 M KCl).

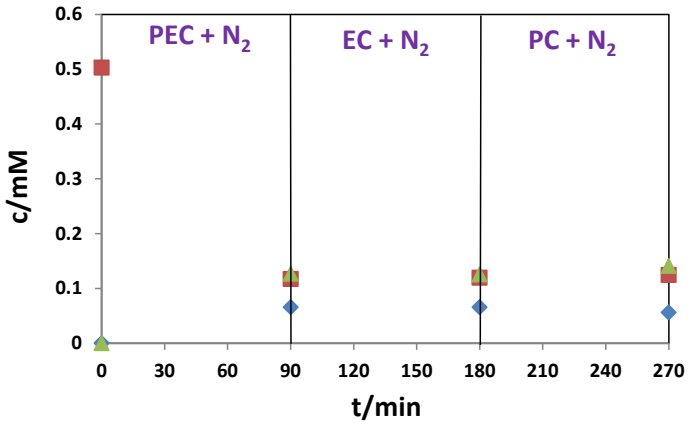


Fig. S21. Results of PEC (the first 90 min), EC (the second 90 min) and PC (the third 90 min) oxidation of 3-pyridinemethanal (■) to 3-pyridinemethanol (♦) (its reduction product) and vitamin B_3 (▲) (its oxidation product) *vs* time by using Ti/TiO_2NT-3h-500 anode under UV irradiation (for PEC and PC) and in presence of N_2. [Na_2SO_4] = 5 mM, stirring speed: 400 rpm, pH~ 7. Applied potential for PEC and EC experiment: 0.5 V *vs* Ag/AgCl (3 M KCl).

Table S1. Results of PEC 3-pyridinemethanol (0.5 mM) oxidation under UV irradiation by using Ti/TiO_2NT-30min-Y photoanodes calcined at different temperatures. [Na_2SO_4] = 5 mM. Stirring speed: 200 rpm. pH~ 7. Applied potential: 0.5 V *vs* Ag/AgCl (3 M KCl).

Electrode	$-r_0 \times 10^3$ (mM h^{-1})	$k \times 10^3$ (h^{-1})	$t_{1/2}$ (h)	$^aS_{3\text{-Pyridinemethanal}}$ $X_{0.15}$ (%)	$^bS_{\text{Vitamin B3}}$ $X_{0.15}$ (%)	$^cS_{[CO2]}/6$ X_{3h}, (%)	X_{1h} (%)	X_{3h} (%)	pH X_{3h}
Ti/TiO_2NT-30min	-	-						<1	
Ti/TiO_2NT-30min-400	83.2	171	4.05	32	37	20	17	40	5.40
Ti/TiO_2NT-30min-500	125	217	3.19	39	30		20	52	5.59
Ti/TiO_2NT-30min-600	88.3	157	4.41	46	29	14	16	37	5.80

$-r_0$: initial reaction rate, k: first order rate constant, and $t_{1/2}$: half life time.
$^aS_{3\text{-Pyridinemethanal}}$ and $^bS_{\text{Vitamin B3}}$: 3-pyridinemethanal and vitamin B_3 selectivities after 15% ($X_{0.15}$) conversion.
X_{1h} and X_{3h}: the conversion values after 1h and 3h of reaction times.
$^cCO_2$ selectivities were considered after 3h of reaction time (X_{3h}).

Table S2. Results of PEC 3-pyridinemethanol (0.5 mM) oxidation under UV irradiation by using Ti/TiO_2NT-30min-500 photoanode for different Na_2SO_4 concentrations. Stirring speed: 200 rpm. pH~ 7. Applied potential: 0.5 V *vs* Ag/AgCl (3 M KCl).

[Na_2SO_4] (mM)	$-r_0 \times 10^3$ (mM h^{-1})	$k \times 10^3$ (h^{-1})	$t_{1/2}$ (h)	$^aS_{3\text{-Pyridinemethanal}}$ (%) $X_{0.15}$	$^bS_{\text{Vitamin B3}}$ (%) $X_{0.15}$	X_{1h} (%)	pH X_{1h}
1.0	65.3	118	5.87	45	24	11	7
2.5	91.6	200	3.47	39	30	18	6.32
5.0	125	217	3.19	30	33	20	6.59
10	116	229	3.03	24	32	20	5.95
25	121	253	2.74	21	32	22	5.59
50	109	247	2.81	19	39	20	5.17

$-r_0$: initial reaction rate, k: first order rate constant, and $t_{1/2}$: half life time.
$^aS_{3\text{-Pyridinemethanal}}$ and $^bS_{\text{Vitamin B3}}$: 3-pyridinemethanal and vitamin B_3 selectivities after 15% ($X_{0.15}$) conversion.
X_{1h}: the conversion values after 1h of reaction times.

Table S3. Results of PEC 3-pyridinemethanol (0.5 mM) oxidation under UV irradiation by using Ti/TiO_2NT-30min-500 photoanode for different applied potential values. [Na_2SO_4] = 5 mM. Stirring speed: 200 rpm. pH~ 7. Reference electrode: Ag/AgCl (3 M KCl).

Applied potential, (V)		$-r_0 \times 10^3$ (mM h^{-1})	$k \times 10^3$ (h^{-1})	$t_{1/2}$ (h)	$^aS_{3\text{-Pyridynmethanal}}$ (%) $X_{0.15}$	$^bS_{\text{Vitamin B3}}$ (%) $X_{0.15}$	X_{1h} (%)	pH X_{1h}
-	PC	44.3	91.5	7.58	56	12	9	6.04
-0.1	PEC	72.7	133	5.21	56	25	12	6.67
0.0	PEC	85.1	155	4.47	58	20	14	6.41
0.1	PEC	111	241	2.88	53	27	21	6.20
0.3	PEC	129	241	2.88	38	30	22	6.30
0.5	PEC	125	217	3.19	30	33	20	5.59
0.7	PEC	119	239	2.90	26	33	21	5.81
0.9	PEC	120	248	2.79	24	33	22	6.25

$-r_0$: initial reaction rate, k: first order rate constant, and $t_{1/2}$: half life time.
$^aS_{3\text{-Pyridinemethanal}}$ and $^bS_{\text{Vitamin B3}}$: 3-pyridinemethanal and vitamin B_3 selectivities for 15% ($X_{0.15}$) conversion.
X_{1h}: the conversion values after 1h of reaction time.

Table S4. Results of PC, EC and PEC 3-pyridinemethanol, 3-pyridinemethanal and vitamin B_3 (0.5 mM) oxidation (and/or reduction) under UV irradiation in the presence of O_2 or N_2 by using Ti/TiO_2NT-3h-500 photoanode. Stirring speed: 400 rpm. [Na_2SO_4] = 5 mM. Applied potential for EC and PEC runs: 0.5 V *vs* Ag/AgCl (3 M KCl).

Substrate		**pH**		$^{a}S_{3\text{-Pyridinemethanol}}$ **(%)**	$^{b}S_{3\text{Pyridinemethanal}}$ **(%)**	$^{c}S_{\text{Vitamin B3}}$ **(%)**		$X_{1.5h}$ **(%)**	X_{3h} **(%)**
				$X_{1.5h}$	X_{3h}	$X_{1.5h}$	X_{3h}		
3-pyridinemethanal	PEC	7	N_2	16		32		77	
3-pyridinemethanal	PEC	7	O_2	10		48		54	
3-pyridinemethanal	PC	7	O_2	no reduction product		71		24	
3-pyridinemethanal	PC	7	N_2	no activity					
3-pyridinemethanal	EC	7	N_2	no activity					
vitamin B_3	PEC	7	N_2	no reduction products				16	
vitamin B_3	PEC	4.3	N_2	no reduction products				15	
vitamin B_3	PEC	7	O_2	no reduction products				13	
vitamin B_3	PEC	4.3	O_2	no reduction products				12	
3-pyridinemethanol	PEC	7	N_2		11		45		59
3-pyridinemethanol	PEC	7	O_2		23		37		55

$^{a}S_{3\text{-Pyridinemethanol}}$, $^{b}S_{3\text{-Pyridinemethanal}}$ and $^{c}S_{\text{Vitamin B3}}$: 3-pyridinemethanol, 3-pyridinemethanal and vitamin B_3 selectivities after 1.5h ($X_{1.5h}$) and 3h (X_{3h}) reaction times. $X_{1.5h}$ and X_{3h}: the conversion values after 1.5h and 3h of reaction times.