

## ELECTRONIC SUPPLEMENTARY INFORMATION

### Anodization of large area Ti: versatile material for caffeine photodegradation and hydrogen production

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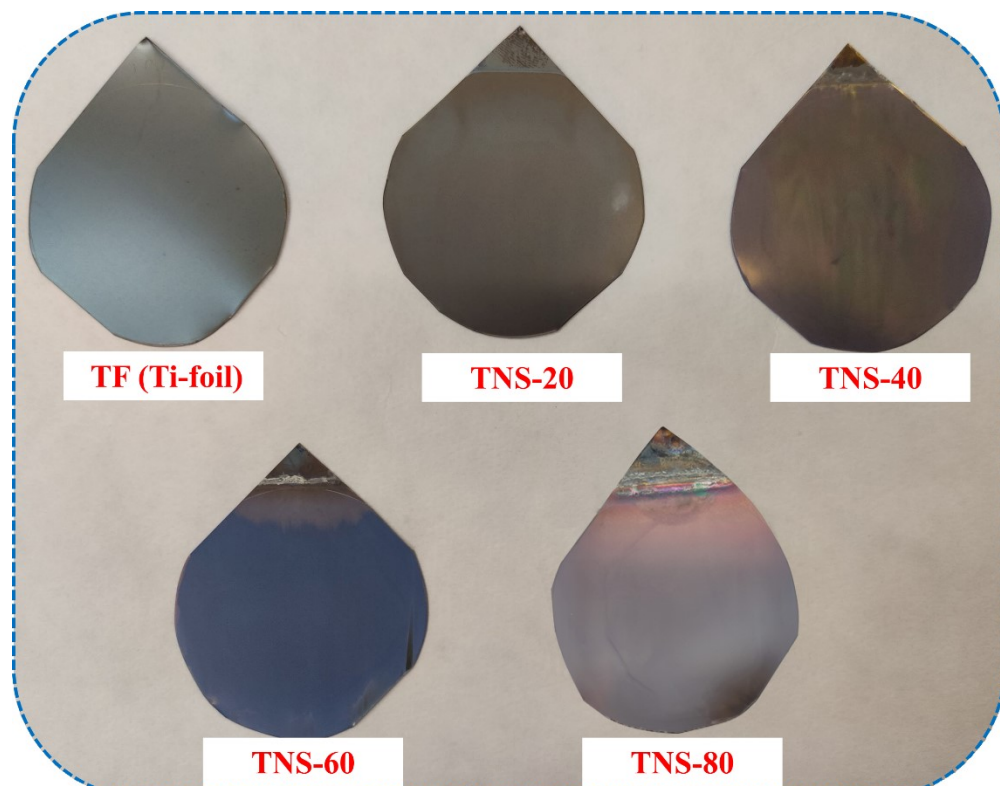
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# Equal contribution

#### Text S1. Photoelectrochemical Measurements

Photoelectrochemical measurements were performed using a photoelectric spectrometer with a 150W Xe lamp used as an irradiation source equipped with a P-IF 1.6 potentiostat (Instytut Fotonowy, Poland). A three-electrode photoelectrochemical cell consisting of TNSs samples (working electrode), saturated Ag/AgCl electrode (reference electrode), and Pt electrode (counter electrode), respectively were immersed in 0.2 M KNO<sub>3</sub> electrolyte solution. The photocurrent transients were recorded under 300 to 420 nm wavelength light irradiation.



**Fig. S1** Titanium foil (of different voltages) after the anodization and calcination process.



**Fig. S2** Schematic representation of home-made photocatalytic reactor.



**Fig. S3** The batch photoreactor used in the photocatalytic decomposition of methanol.

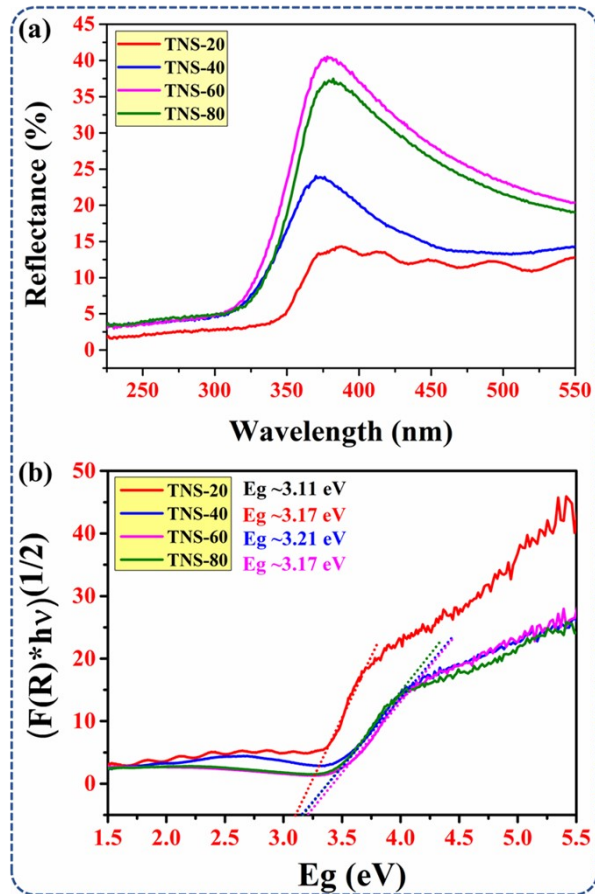


Fig. S4 (a) UV-VIS DRS and (b) Tauc plot with the  $E_g$  of TNS-20, TNS-40, TNS-60, and TNS-80, respectively.

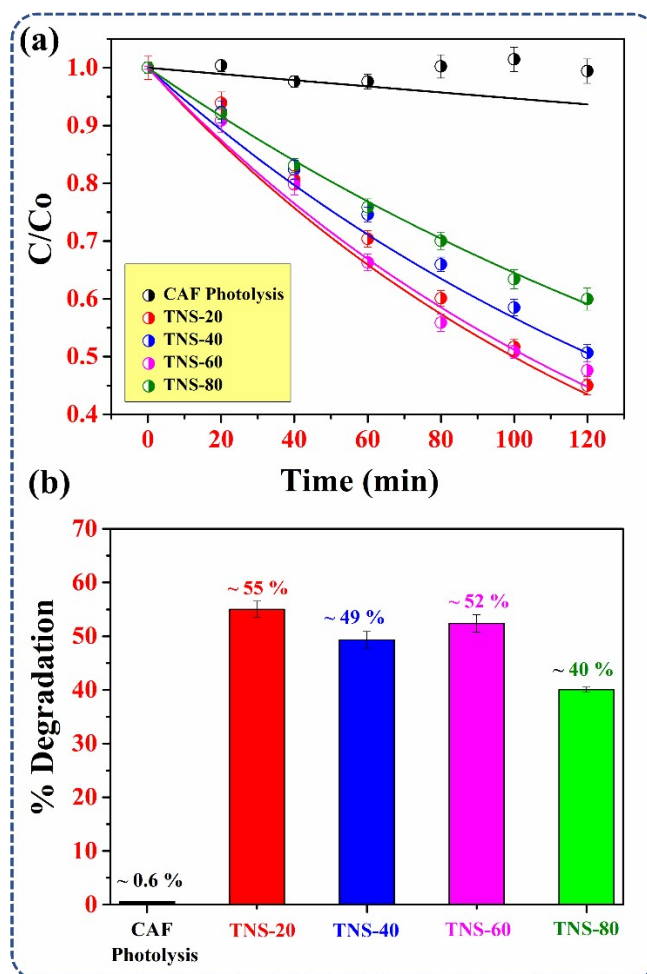


Fig. S5 Photocatalytic degradation of caffeine using TNSs samples (a)  $C/C_0$  curves and (b) degradation % under UV-A irradiation.

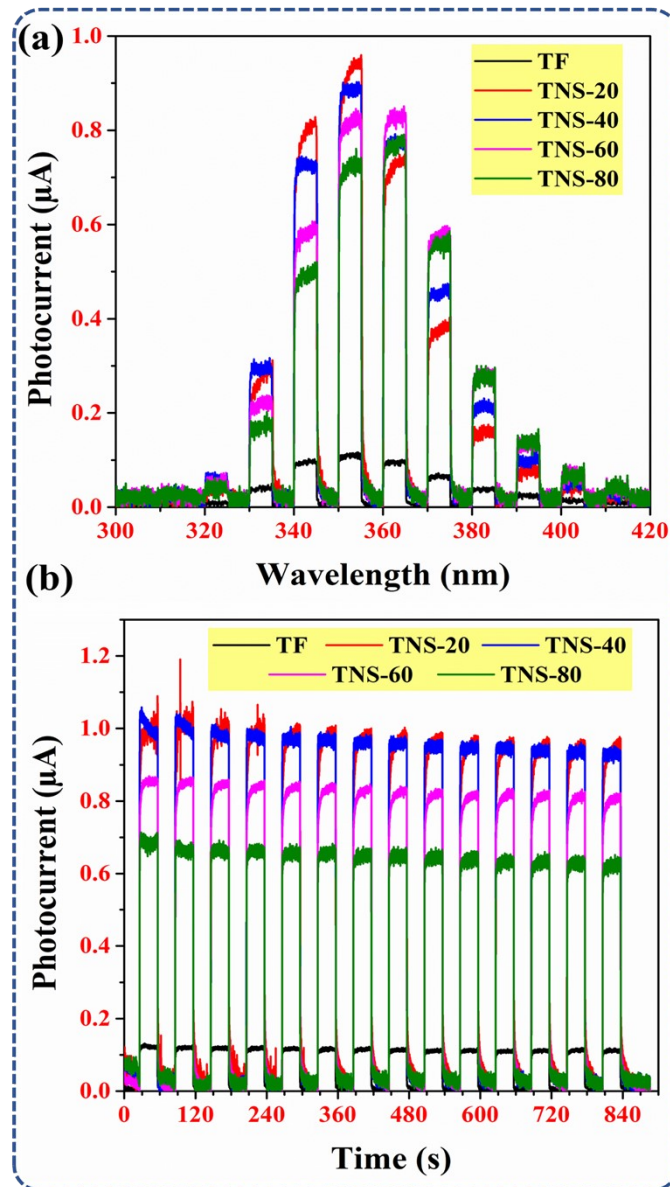


Fig. S6 (a) Photocurrent densities of TNSs samples with (b) corresponding transient currents from 300 to 420 nm.

Table S1: The electrochemical anodization parameters during the synthesis of TNS samples.

Sample	Voltage (V)	Time (min)	Current Density (A) Starting	Current Density (A) Ending
TF	-	-	-	-
TNS-20	20	100	0.305	0.040

<b>TNS-40</b>	40	100	0.370	0.035
<b>TNS-60</b>	60	100	0.320	0.035
<b>TNS-80</b>	80	100	0.361	0.039

**Table S2:** The Average Roughness ( $S_a$ ), Root Mean Square ( $S_q$ ), and Surface Skewness ( $S_{sk}$ ), and Coefficient of Kurtosis ( $S_{ka}$ ) values obtained from atomic force microscopy.

<b>Sample</b>	<b>Average Roughness <math>S_a</math> (nm)</b>	<b>Root Mean Square <math>S_q</math> (nm)</b>	<b>Surface Skewness <math>S_{sk}</math></b>	<b>Coefficient of kurtosis <math>S_{ka}</math></b>
<b>TF</b>	43.625	55.858	0.110	0.191
<b>TNS-20</b>	74.039	92.373	0.423	-0.097
<b>TNS-40</b>	61.691	78.719	0.212	0.516
<b>TNS-60</b>	81.298	102.138	0.359	0.063
<b>TNS-80</b>	122.047	150.843	0.187	-0.352

**Table S3:** A summary of different areas of  $TiO_2$  photocatalysts under UV light irradiation. Wherever was possible, the area, parameters, target pollutant with its concentration, rate constants, time duration, and  $H_2$  production were supplemented from the given references.

<b>Material</b>	<b>Area</b>	<b>Anodization conditions</b>	<b>Target pollutant and concentration</b>	<b>Pollutant Degradation rate (<math>k</math>)/ Percentage (%)</b>	<b>Time (min)</b>	<b><math>H_2</math> production</b>	<b>Ref</b>
<b>TNT-10um</b>	(10×50× 0.1 mm)	3-vol% $H_2O$ + 0.5-wt% $NH_4F$ in EG electrolyte (60V for 2-20 min)	Acid orange (25 $\mu M$ )	0.019 $min^{-1}$	150	---	1
<b><math>TiO_2</math>-NTs</b>	146.09 $mm^2$	95 : 5 wt% ethylene glycol/water containing 0.15M $NH_4F$ (40 V for 20 min)	---	---	---	---	2
<b>TNT- <math>TiO_2</math></b>	5×10 $cm^2$	176 mM $NH_4F$ + 1.5 vol% DI- $H_2O$ (60 V for 4 h)	---	---	---	---	3
<b>TNTs+2c <math>MoS_2</math></b>	2.25 $cm^2$	Prepared by atomic layer deposition	Methylene blue ( $1 \times 10^{-5}$ M)	0.0190 $min^{-1}$	120	---	4
<b><math>TiO_2</math></b>	12.5 $cm^2$	0.3 wt.% $NH_4F$ and 2 vol.% $H_2O$ in -EG electrolyte	---	---	---	---	5

<b>TiO<sub>2</sub>-SG</b>	5×10 cm <sup>2</sup>	(60 V for 72 h) 0.5 wt% -EG electrolyte + NH <sub>4</sub> F and 0.2 wt% DI-H <sub>2</sub> O (40V for 4 h)	Methylene blue (3×10 <sup>-5</sup> M)	0.003 s <sup>-1</sup>	---	---	6
<b>TiO<sub>2</sub></b>	50 cm <sup>2</sup>	0.3 wt.% of NH <sub>4</sub> F +2 vol.% of DI-H <sub>2</sub> O in an ethylene glycol electrolyte (60 V for 6 h)	Caffeine (50 mM.)	44%	180	---	7
<b>Pine-cone TiO<sub>2</sub></b>	30 mm × 40 mm	0.6 wt % NH <sub>4</sub> F -10 vol % H <sub>2</sub> O-EG electrolyte (60 V for 2 h)	Methylene orange (20.0 mM)	85%	120	---	8
<b>TiO<sub>2</sub>NTs@ Fe<sub>3</sub>O<sub>4</sub></b>	2.25 cm <sup>2</sup>	0.15 M NH <sub>4</sub> F + 10% DI- H <sub>2</sub> O in glycol-based electrolyte (100 V for 4 h)	Methylene blue (1×10 <sup>-5</sup> M)	0.38 h <sup>-1</sup>	120	---	9
<b>TiO<sub>2</sub></b>	10 mm x 15 mm	0.5 wt.% NH <sub>4</sub> F+10% DI-H <sub>2</sub> O + 90 vol.% EG (30 V for 1 h)	Methylene orange	0.00040 min <sup>-1</sup>	240	---	10
<b>TiO<sub>2</sub> film</b>	25 × 25 × 1 mm	NH <sub>4</sub> F (0.3 wt %) and H <sub>2</sub> O (2 vol%) in EG (60V for 3h)	Caffeine (10 mg.L <sup>-1</sup> )	1.882 mmol.L <sup>-1</sup> h <sup>-1</sup>	---	---	11
<b>TiO<sub>2</sub> nanotube films</b>	98.5 mm diamter	NH <sub>4</sub> F (0.3 wt %) and H <sub>2</sub> O (2 vol%) in EG (60V for 6 h)	Caffeine (50 mg.L <sup>-1</sup> )	60%/ 0.014 × 10 <sup>-6</sup> mol.L <sup>-1</sup>	180	---	12
<b>TiO<sub>2</sub> NTs</b>	---	NH <sub>4</sub> F (0.3 wt %) and H <sub>2</sub> O (2 vol%) in EG (60V for 3 h)	Caffeine 10 ppm	1.65 × 10 <sup>-2</sup> min <sup>-1</sup>	180	---	13
<b>V-TNT</b>	~0.79 cm <sup>2</sup>	1.3 g NH <sub>4</sub> F + 197 mL EG + 3 mL H <sub>2</sub> O (60 V for 4 h)	Caffeine (20 ppm)	3.25 × 10 <sup>-3</sup> min <sup>-1</sup>	120	---	14
<b>TNS-20</b>	~20 cm <sup>2</sup>	<b>2g NH<sub>4</sub>F +100 ml DI- H<sub>2</sub>O in glycerol-based electrolyte (20 V for 100 min)</b>	<b>Caffeine (20 ppm)</b>	<b>0.0069 min<sup>-1</sup></b>	<b>120</b>	<b>~6200 ppm</b>	<b>This Study</b>

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