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Fluoride-free synthesis of anodic TiO_2 nanotube layers: a promising environmentally friendly method for efficient photocatalyst

Muhammad Bilal Hanif,[a] Guru Karthikeyan Thirunavukkarasu,[a] Viktoriia Liapun,[a] Hryhorii Makarov,[b] Maros Gregor,[b] Tomas Roch,[b] Tomas Plecenik,[b] Karol Hensel,[c] Marcel Sihor,[d] Olivier Monfort,[a] and Martin Motola[a,*]

[a.] *Department of Inorganic Chemistry, Faculty of Natural Sciences, Comenius University Bratislava, Ilkovicova 6, 842 15 Bratislava, Slovakia*

[b.] *Department of Experimental Physics, Faculty of Mathematics, Physics, and Informatics, Comenius University Bratislava, 842 48 Bratislava, Slovakia*

[c.] *Division of Environmental Physics, Faculty of Mathematics, Physics, and Informatics, Comenius University Bratislava, 842 48 Bratislava, Slovakia*

[d.] *Institute of Environmental Technology, CEET, VSB-Technical University of Ostrava, 17. listopadu 15/2172, Ostrava-Poruba, Czech Republic*

** Corresponding author: Martin Motola (✉ martin.motola@uniba.sk; ☎ + 421 2 9014 9374)*

Table S1 Summary of different parameters for TNT layers synthesis via anodization, i.e., electrolyte composition, applied potential, anodized area, counter electrode type, anodization time, temperature, current, and result if the nanotubes were formed or not. The abbreviation of the samples is given in red colour. Blue colour are parameters that led to the most promising TNT layers.

Electrolyte	Potential	Anodized area (cm^2)	Counter Electrode	Time (min)	Temp	Current	Nanotubes Formed
0.5 wt% $AgNO_3$; $AgNO_3$: 1 g; DIW: 100 mL; Ethylene glycol: 100 mL (Ag-NT-1)	20 V	4	Titanium	10	**Start:** 20°C **End:** 20°C	**Start:** 0.014 A **End:** 0.001 A	**Yes (on few places)**
0.5 wt% $AgNO_3$; $AgNO_3$: 1 g; DIW: 100 mL; Ethylene glycol:: 100 mL (Ag-NT-2)	30 V	4	Titanium	10	**Start:** 20°C **End:** 20°C	**Start:** 0.035 A **End:** 0.022 A	**Yes (on few places)**
0.5 wt% $AgNO_3$; $AgNO_3$: 1 g DIW: 200 mL (Ag-NT-3)	30 V	4	Graphite	5	**Start:** 20°C **End:** 20°C	**Start:** 0.146 A **End:** 0.163 A	**Yes (on few places)**
0.5 wt% $AgNO_3$; $AgNO_3$: 1 g; DIW: 200 mL (Ag-NT-4)	30 V	4	Graphite	10	**Start:** 20°C **End:** 20°C	**Start:** 0.2 A **End:** 0.2 A	**Yes (on few places)**
0.5 wt% $AgNO_3$; $AgNO_3$: 1 g; DIW: 200 mL (Ag-NT)	60 V; 1A	4	Graphite	1	**Start:** 20°C **End:** 20°C	**Start:** 1 A **End:** 1 A	**Yes (everywhere)**
0.5 wt% $SrNO_3$; $Sr(NO_3)_2$: 1 g; DIW: 100 mL; Ethylene glycol:: 100 mL (Sr-NT-1)	30 V	4	Titanium	10	**Start:** 20°C **End:** 20°C	**Start:** 0.035 A **End:** 0.014 A	**Yes (on few places)**

0.5 wt% $SrNO_3$; $Sr(NO_3)_2$: 1 g; DIW: 100 mL; Ethylene glycol:: 100 mL (Sr-NT-2)	30 V	4	Titanium	30	**Start:** 20°C **End:** 20°C	**Start:** 0.034 A **End:** 0.011 A	**Yes (on few places)**
0.5 wt% $SrNO_3$; $Sr(NO_3)_2$: 1 g DIW: 200 mL (Sr-NT-3; CS-2)	60 V; 1 A	4	Graphite	2	**Start:** 20°C **End:** 20°C	**Start:** 1 A **End:** 1 A	**Yes (on few places)**
0.5 wt% $Sr(NO_3)_2$; $SrNO_3$: 1 g DIW: 200 mL (Sr-NT-4; CS-3)	60 V; 1 A	4	Graphite	2	**Start:** 20°C **End:** 20°C	**Start:** 1 A **End:** 1 A	**Yes (on few places)**
0.5 wt% $Sr(NO_3)_2$; $SrNO_3$: 1 g; DIW: 200 mL (Ag-NT)	30 V; 1 A	4	Graphite	5	**Start:** 20°C **End:** 20°C	**Start:** 1 A **End:** 1 A	**Yes (everywhere)**
0.5 wt% KNO_3; KNO_3: 1 g; DIW: 200 mL (K-NT-1)	30 V	4	Titanium	2	**Start:** 20°C **End:** 20°C	**Start:** 0.279 A **End:** 0.181 A	**Yes (on few places)**
0.5 wt% KNO_3; KNO_3: 1 g; DIW: 200 mL (K-NT-2)	35 V	4	Titanium	2	**Start:** 20°C **End:** 20°C	**Start:** 0.3 A **End:** 0.3 A	**Yes (on few places)**
0.5 wt% KNO_3; KNO_3: 1 g; DIW: 200 mL (K-NT-3; K5)	30 V; 1 A	4	Graphite	2	**Start:** 20°C **End:** 20°C	**Start:** 1 A **End:** 1 A	**Yes (on few places)**
0.5 wt% KNO_3; KNO_3: 1 g; DIW: 200 mL (K-NT-4; K6)	30 V; 0.8 A	4	Graphite	2	**Start:** 20°C **End:** 20°C	**Start:** 0.8 A **End:** 0.8 A	**Yes (on few places)**
0.5 wt% KNO_3; KNO_3: 1 g; DIW: 200 mL (K-NT)	60 V; 1 A	4	Graphite	2	**Start:** 20°C **End:** 20°C	**Start:** 1 A **End:** 1 A	**Yes (everywhere)**
0.5 wt% $NaNO_3$; $NaNO_3$: 1 g; DIW: 200 mL (Na-NT-1)	60 V	4	Titanium	1	**Start:** 20°C **End:** 20°C	**Start:** 1 A **End:** 1 A	**Yes (on few places)**
0.5 wt% $NaNO_3$; $NaNO_3$: 1 g; DIW: 200 mL (Na-NT-2)	30 V	4	Titanium	2	**Start:** 20°C **End:** 20°C	**Start:** 1 A **End:** 1 A	**Yes (on few places)**
0.5 wt% $NaNO_3$; $NaNO_3$: 1 g; DIW: 200 mL (Na-NT-3; N-6)	30 V; 1 A	4	Graphite	2	**Start:** 20°C **End:** 20°C	**Start:** 1 A **End:** 1 A	**Yes (on few places)**
0.5 wt% $NaNO_3$; $NaNO_3$: 1 g; DIW: 200 mL (Na-NT-4)	30 V; 1 A	4	Titanium	2	**Start:** 20°C **End:** 20°C	**Start:** 1 A **End:** 1 A	**Yes (on few places)**
0.5 wt% $NaNO_3$; $NaNO_3$: 1 g; DIW: 200 mL (Na-NT; N-7)	30 V; 0.8A	4	Graphite	2	**Start:** 20°C **End:** 20°C	**Start:** 0.8 A **End:** 0.8 A	**Yes (everywhere)**

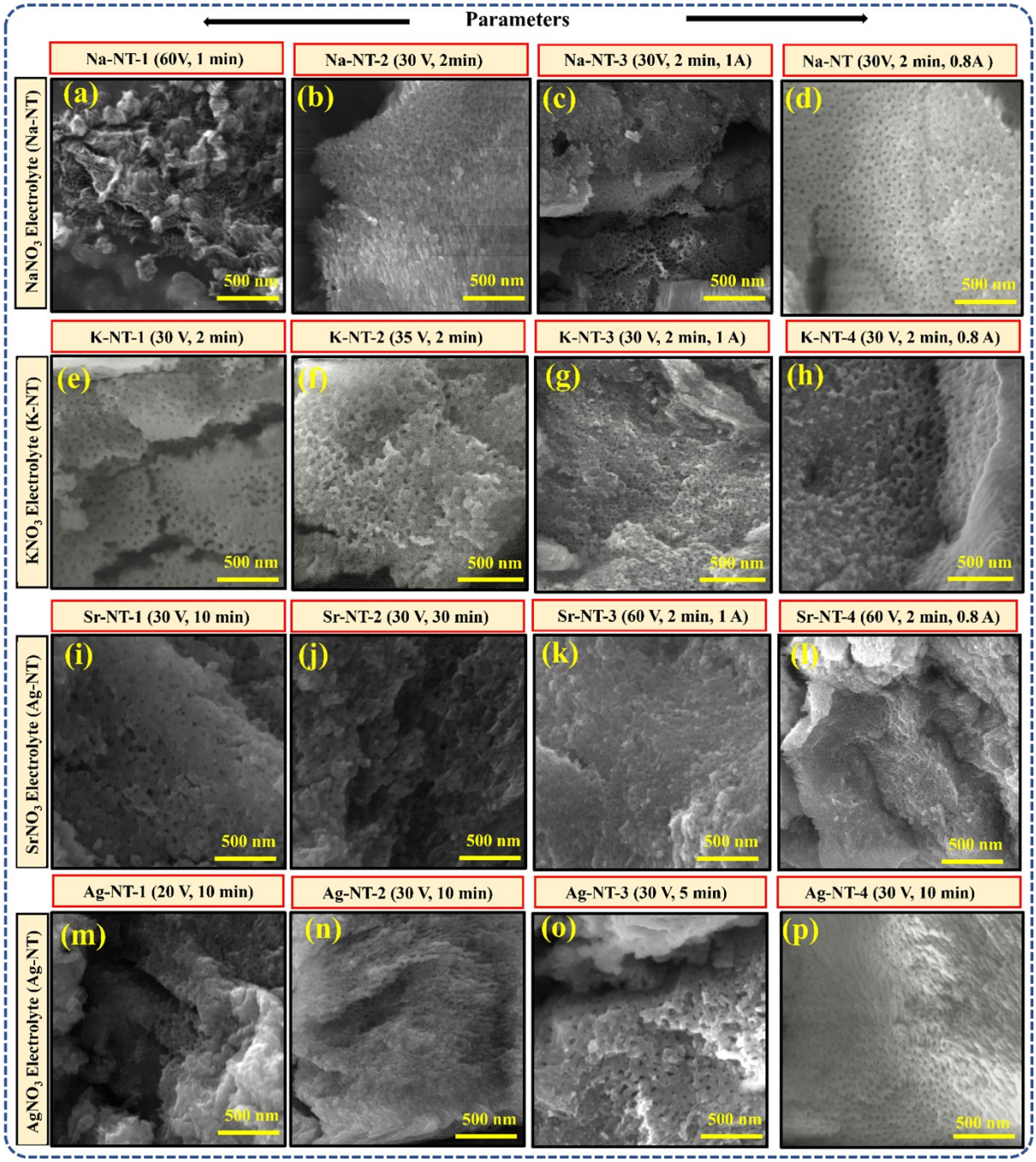

Figure S1: Representative SEM images of TNT layers prepared in **(a-d)** $NaNO_3$ (Na-NT), **(e-h)** KNO_3 (K-NT), **(i-l)** $Sr(NO_3)_2$ (Sr-NT), and **(m-p)** $AgNO_3$ (Ag-NT) using different parameters, based on **Table S1**.

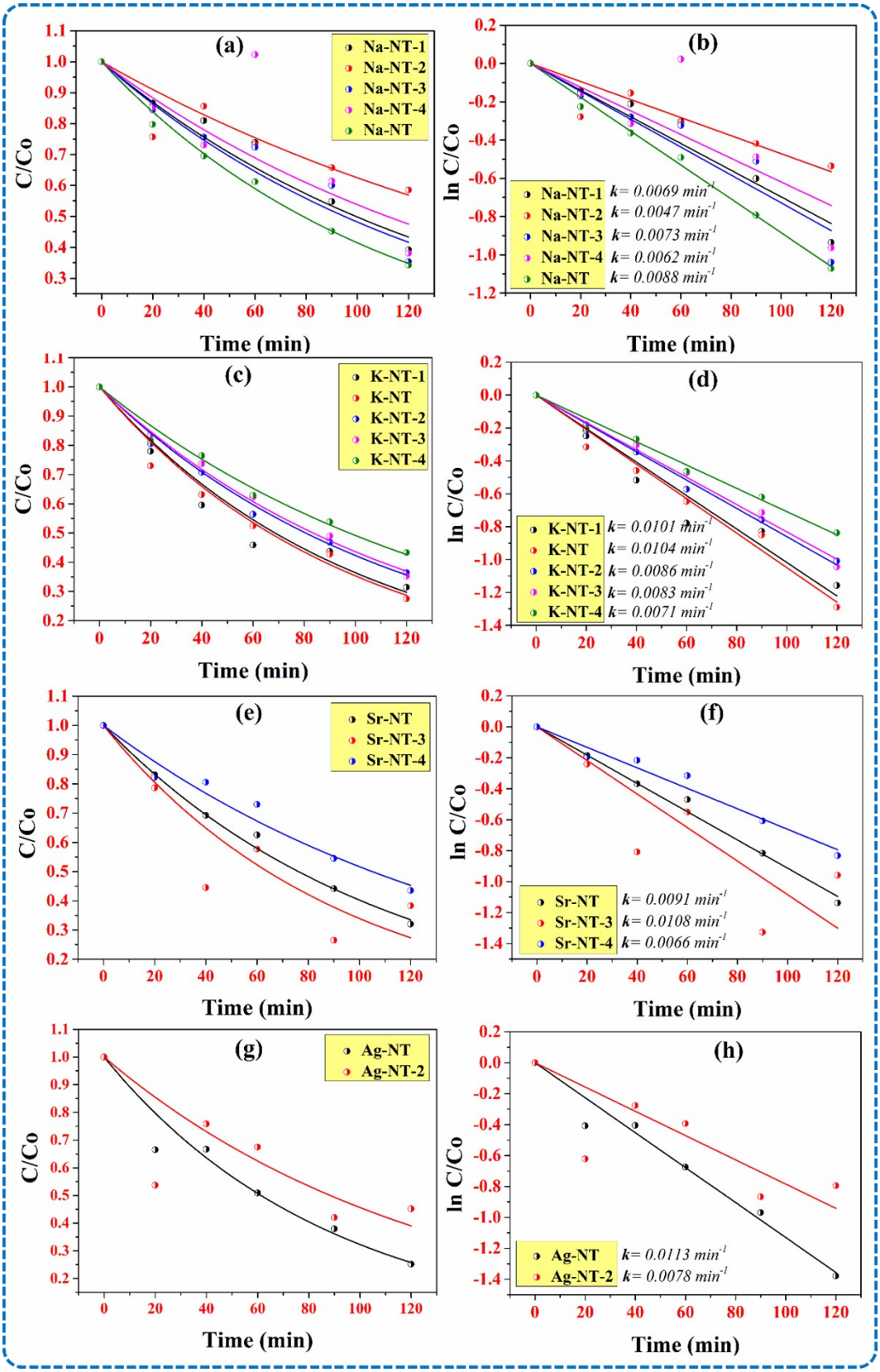

Figure S2: Photocatalytic degradation rate of methylene blue using TNT layers prepared in **(a,b)** $NaNO_3$ (Na-NT), **(c,d)** KNO_3 (K-NT), **(e,f)** $Sr(NO_3)_2$ (Sr-NT), and **(g,h)** $AgNO_3$ (Ag-NT) using different parameters, based on **Table S1.**

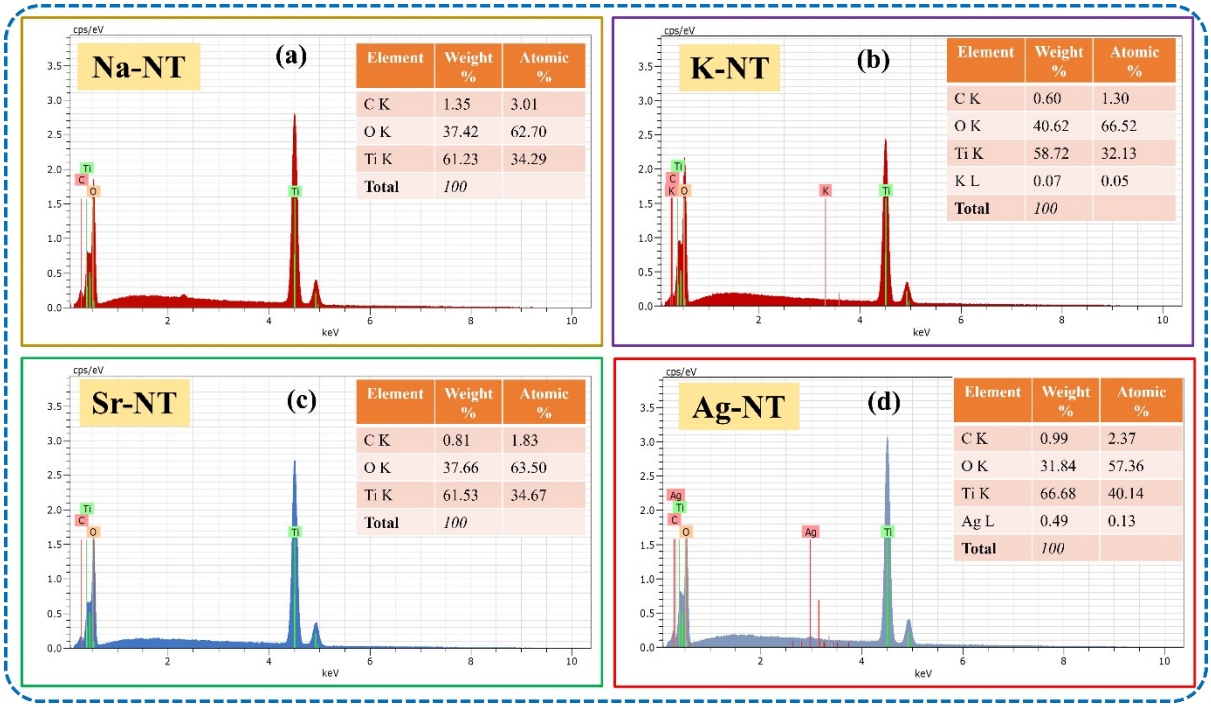

Figure S3: EDS analysis of TNT layers prepared in **(a)** $NaNO_3$ (Na-NT), **(b)** KNO_3 (K-NT), **(c)** $Sr(NO_3)_2$ (Sr-NT), and **(d)** $AgNO_3$ (Ag-NT).

Table S2: Average roughness (S_a), root mean square (S_q), surface skewness (S_{sk}), and coefficient of kurtosis (S_{ka}) values obtained from atomic force microscopy.

Sample	Average roughness (S_a) nm	Root mean square (S_q) nm	Surface skewness (S_{sk})	Coefficient of kurtosis (S_{ka})
Na-NT	45.1907	55.4632	-0.0848	-0.4566
K-NT	63.9377	81.8114	-0.3387	1.1050
Sr-NT	21.8758	27.0157	-0.0969	-0.1676
Ag-NT	4.50594	6.40418	0.2569	2.7457

Table S3: Miller indices and respective 2 theta (deg) of anatase and rutile TiO2 phases and Titanium obtained from XRD diffractogram**.**

Anatase

h k l	2 theta (deg)
1 0 1	25.306
1 0 3	36.954
0 0 4	37.800
2 0 0	48.039
1 0 5	53.894
2 1 1	55.064

Rutile-R

h k l	2 theta (deg)
1 1 0	27.434

Titanium

h k l	2 theta (deg)
1 0 0	35.066
0 0 2	38.405
1 0 1	40.153
1 0 2	53.012

Table S4: Crystallite sizes of Na-NT, K-NT, Sr-NT, and Ag-NT calculated from GI-XRD by Xpert-HighScore software.

Crystallite Size (Xpert-HighScore-GIXRD)

Sample	Crystallite Size (nm)
Na-NT	approx. 35
K-NT	approx. 30
Sr-NT	approx. 30
Ag-NT	approx. 30