

Transparent TiO₂ nanotubes supporting silver sulfide for photoelectrochemical water splitting

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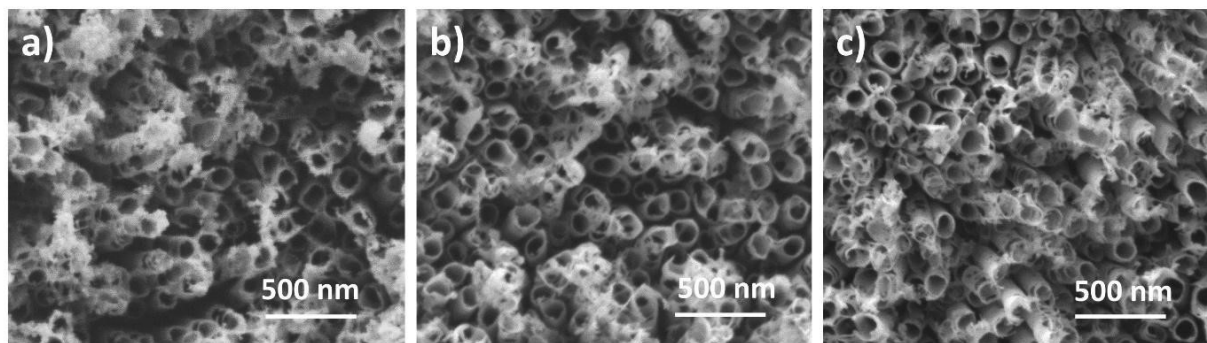


Figure S1 SEM images of a) 5-Ag₂S/fTiNT, b) 25-Ag₂S/fTiNT, c) 45-Ag₂S/fTiNT.

Table S1 The calculated values for electric equivalent circuit elements for nanotubes formed on the foil (fTiNT) and glass substrate (gTiNT).

parameter	unit	fTiNT	gTiNT
Re	$\Omega \text{ cm}^2$	1.2	214
R1	$\Omega \text{ cm}^2$	3143	41
Q1	F cm^{-2}	3×10^{-5}	1×10^{-4}
n1		0.86	0.54
R2	$\Omega \text{ cm}^2$	7.1	15074
Q2	$\Omega \text{ cm}^2$	3×10^{-5}	8×10^{-5}
n2	F cm^{-2}	0.62	0.66
Wor1	-	7×10^{-3}	4×10^{-6}
Woc1	$\Omega \text{ cm}^2 \text{s}^{-1/2}$	4.3×10^{-8}	3.9×10^{-9}

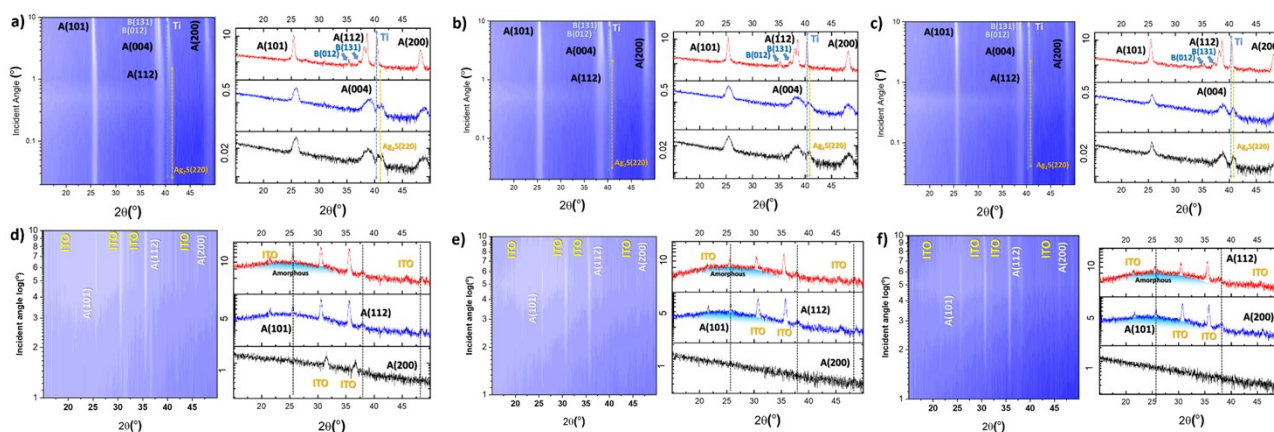


Figure S2. a) 5-Ag₂S/fTiNT, b) 25-Ag₂S/fTiNT, c) 45-Ag₂S/fTiNT, d) 5-Ag₂S/gTiNT, e) 25-Ag₂S/gTiNT, f) 45-Ag₂S/gTiNT.

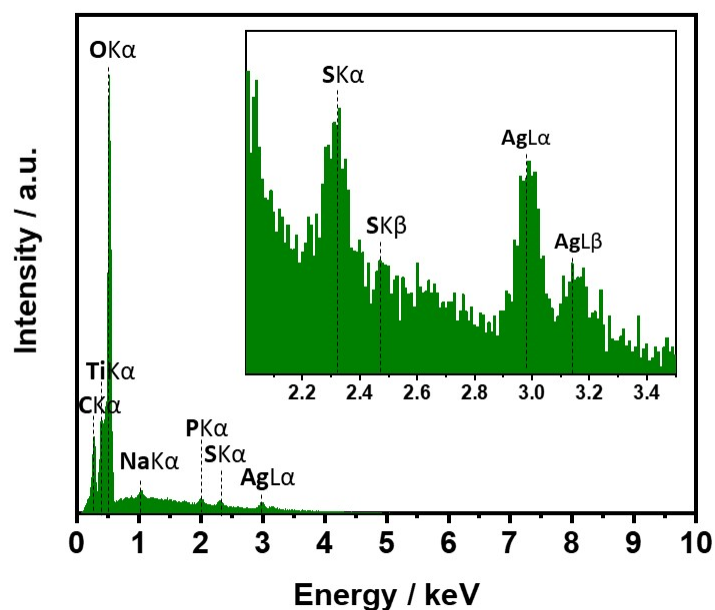


Figure S3 EDX spectrum of sample 45-Ag₂S/gTiNT taken at an acceleration voltage of 5 kV showing the expected elements are present.

Table S2 Tabulated values of the atomic percentages from the EDX spectrum of sample 45-Ag₂S/gTiNT with a ratio of Ag to S of 2.25.

Element	Line	Atom %
C	K	6.36±0.06
O	K	57.06±0.32
Na	K	0.49±0.04
P	K	0.79±0.06
S	K	1.26±0.07
Ti	L	31.20±0.32
Ag	L	2.84±0.12
Total		100.00

Table S3 Percentage contribution (in at.%) and binding energy of core levels (in eV) of gTiNT, fTiNT, 25-Ag₂S/gTiNT, 25-Ag₂S/fTiNT and 45-Ag₂S/gTiNT used for XPS analysis.

Sample	Peak	Component	BE eV	Atomic %	Sample	Peak	Component	BE eV	Atomic %
gTiNT					fTiNT				
	Ti 2p _{3/2}	TiO ₂	458.77	20.70		Ti 2p _{3/2}	TiO ₂	458.52	22.70
	O 1s	TiO ₂	529.97	38.91		O 1s	TiO ₂	529.76	45.65
	O 1s	OH ⁻	531.18	16.78		O 1s	OH ⁻	531.17	6.29

	O 1s	O-C=O	532.59	3.42		O 1s	O-C=O	532.28	2.06
	C 1s	C-C	284.54	14.10		C 1s	C-C	284.61	18.08
	C 1s	C-O-C	286.08	2.82		C 1s	C-O-C	286.21	2.26
	C 1s	O-C=O	288.36	3.27		C 1s	O-C=O	288.61	2.96
25-Ag₂S/gTiNT					25-Ag₂S/fTiNT				
	Ti 2p _{3/2}	TiO ₂	458.51	16.80		Ti 2p _{3/2}	TiO ₂	458.51	16.80
	O 1s	TiO ₂	529.75	44.64		O 1s	TiO ₂	529.79	26.28
	O 1s	OH ⁻	531.15	7.21		O 1s	OH ⁻	530.98	27.56
	O 1s	O-C=O	532.28	2.07		O 1s	O-C=O	532.28	1.50
	C 1s	C-C	284.65	16.58		C 1s	C-C	284.57	18.81
	C 1s	C-O-C	286.1	2.29		C 1s	C-O-C	286.2	1.74
	C 1s	O-C=O	288.36	2.06		C 1s	O-C=O	288.37	1.72
	Ag 3d _{5/2}	Ag ₂ S	367.46	1.54		Ag 3d _{5/2}	Ag ₂ S	367.36	3.07
	S 2p _{3/2}	Ag ₂ S	160.56	0.84		S 2p _{3/2}	Ag ₂ S	160.34	1.23
45-Ag₂S/gTiNT									
	Ti 2p _{3/2}	TiO ₂	458.51	19.48					
	O 1s	TiO ₂	529.76	35.31					
	O 1s	OH ⁻	530.98	16.22					
	O 1s	O-C=O	532.38	1.98					
	C 1s	C-C	284.57	18.44					
	C 1s	C-O-C	286.05	2.08					
	C 1s	O-C=O	288.42	1.82					
	Ag 3d _{5/2}	Ag ₂ S	367.37	2.07					
	S 2p _{3/2}	Ag ₂ S	160.38	1.75					

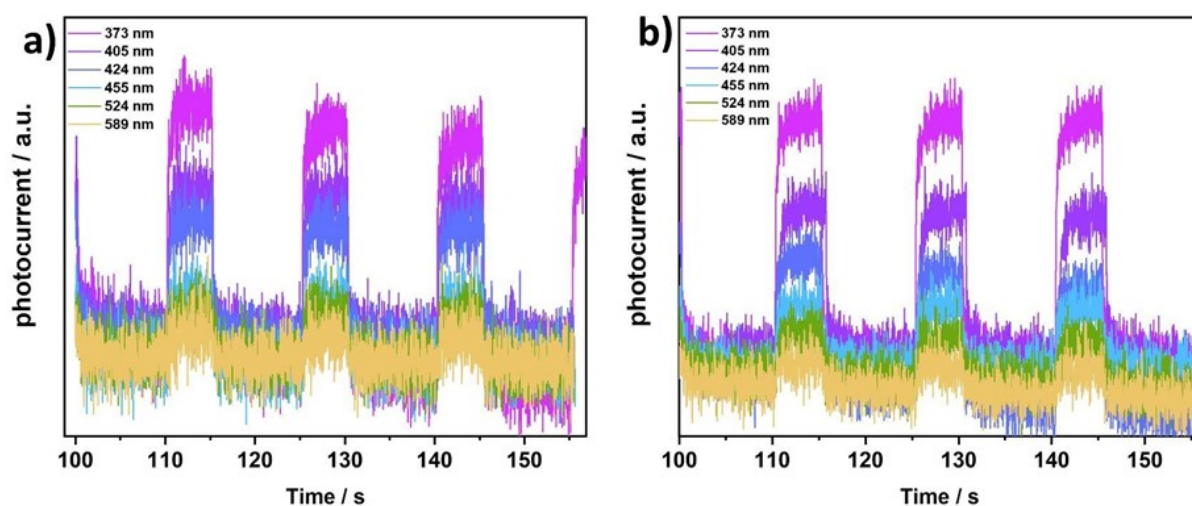


Figure S4 Photocurrent vs. time for different wavelength 25Ag₂S/gTiNT recorded at a) +0.5 V and b) +1 V vs. Ag/AgCl/0.1 M KCl in 0.5 M Na₂SO₄.

Table S4 Location of Raman bands for the 25- and 45-Ag₂S/gTiNT electrode Y stands for yes indicating presence of particular signal on the Raman spectrum.

Wavenumber / cm ⁻¹	145	225	240-290		295-360		790	970	
			250	276	310	340			
25-Ag₂S/gTiNT									
before	-	Y	Y	Y	-	Y	-	-	
after 3 cycles	-	Y	Y	Y	Y	Y	Y	-	
after 10 cycles	Y	Y	Y	Y	Y	Y	Y	Y	
45-Ag₂S/gTiNT									
before	-	Y	Y	-	-	-	-	-	
after 3 cycles	Y	Y	Y	-	-	Y	-	Y	
after 10 cycles	Y	-	-	Y	Y	Y	Y	-	
	Ag ₂ SO ₃	Ag-S/ Ag-O	Ag-S		Ag-O		O-Ag-O	S-O	

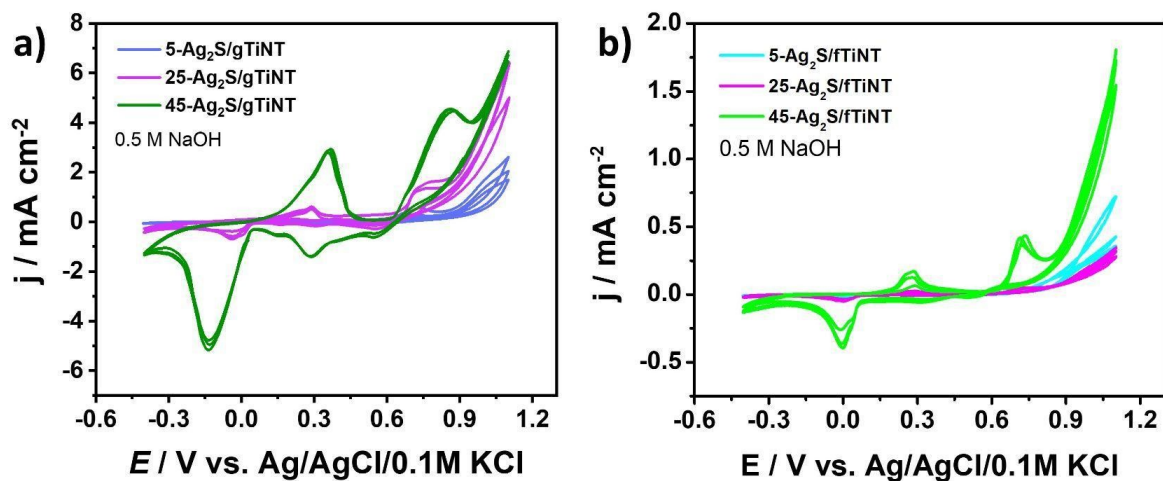


Figure S5 Repeatability test for a) Ag_2S coated gTiNT and b) Ag_2S coated fTiNT (3 cycles, scan rate 50 mV/s).

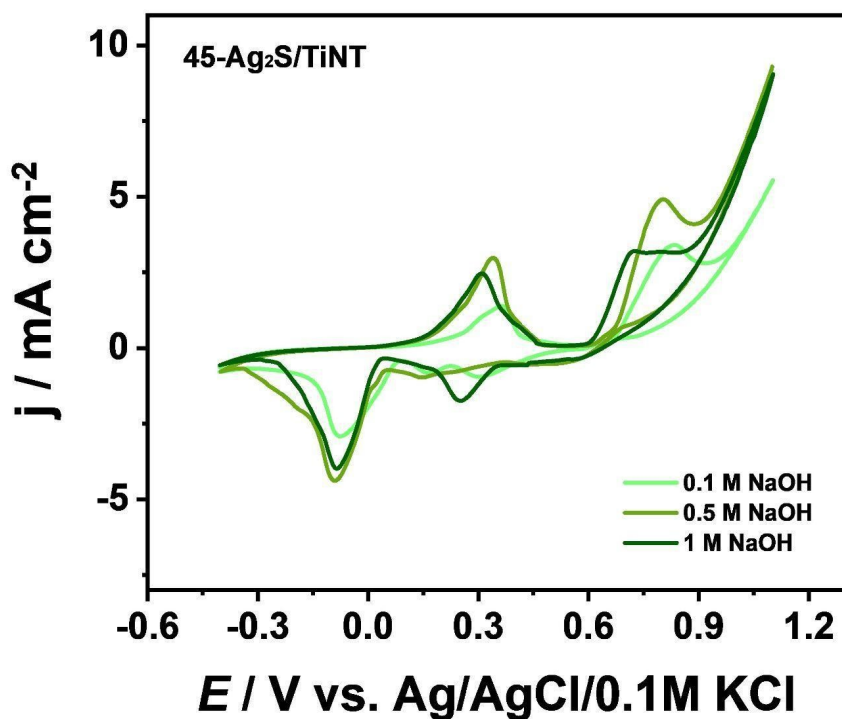


Figure S6 Cyclic voltammetry curves for $45\text{-Ag}_2\text{S/TiNT}$ in 0.1 M , 0.5 M and 1 M NaOH electrolyte (scan rate 50 mV/s).

Table S5 Location of Raman bands for the 25- and 45- $\text{Ag}_2\text{S/gTiNT}$ electrode
 Y stands for yes indicating presence of particular signal on the Raman spectrum.

Wavenumber / cm^{-1}	145	225	240-290			295-360		790	980	1077
			255	270	280	300	330			
25-$\text{Ag}_2\text{S/gTiNT}$										
before	-	Y	Y	-	Y	-	Y	-	-	-
after 3 cycles	-	Y	Y	-	Y	-	Y	-	-	-
after 10 cycles	Y	-	-	Y	-	Y	Y	Y	-	Y
45-$\text{Ag}_2\text{S/gTiNT}$										
before	-	Y	Y			-	-	-	-	-
after 3 cycles	Y	Y	Y			-	-	-	-	-
after 10 cycles	Y	-	-			Y	Y	Y	Y	Y
	T Ag-S	Ag-S/ Ag-O	Ag-S			Ag-O		O-Ag-O	S-O	Ag-O

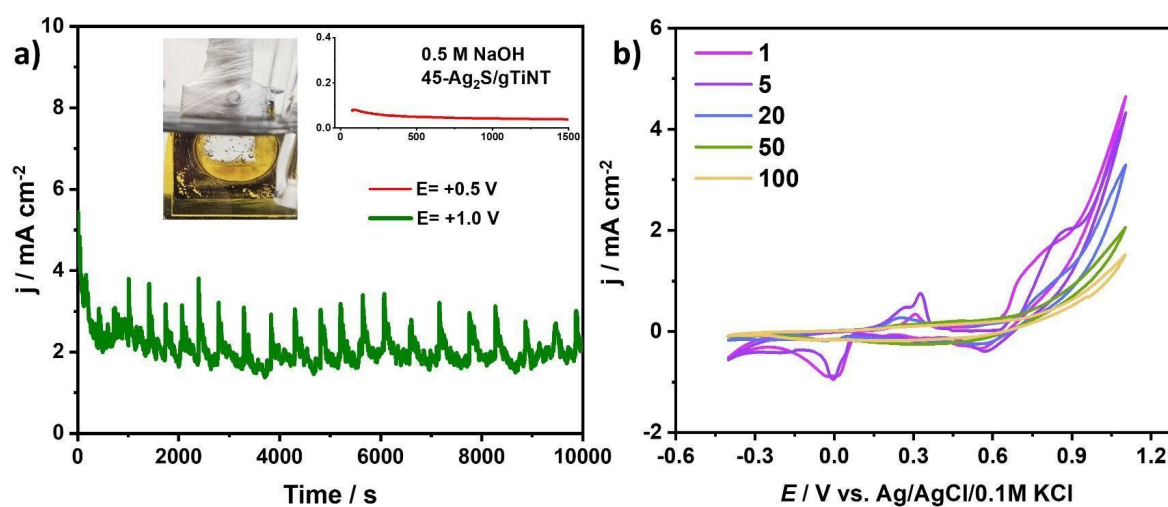


Figure S7 a) Chronoamperometry curves for the 45- $\text{Ag}_2\text{S/gTiNT}$ registered at +1.0 V in 0.5 M NaOH. The inset shows a reference measurement registered at +0.5 V, b) Cyclic voltamperometry curves for the 45- $\text{Ag}_2\text{S/gTiNT}$ in 0.5 M NaOH recorded at 50 mV/s.