SI

Design of Experiments

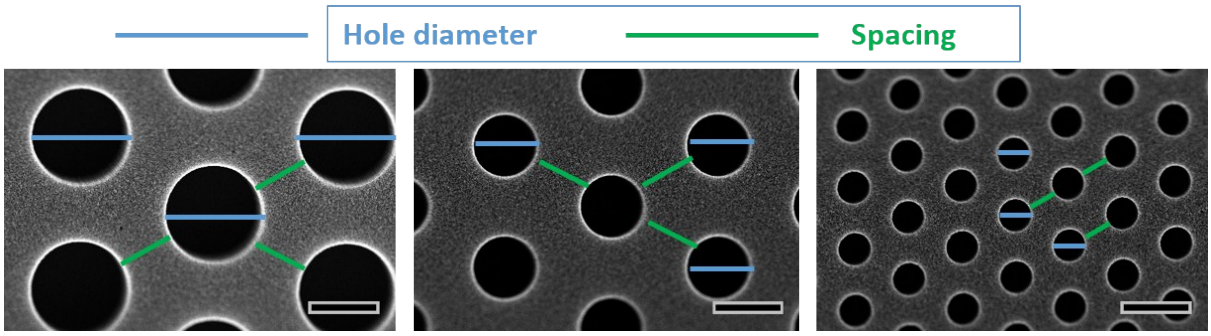


Figure S1. Definition of the hole diameters and spacings used in figure 2. Scale bars are 10 µm.

Factorial Regression: Height versus Diameter, Spacing, Growth time

Stepwise Selection of Terms

α to enter = 0.1, α to remove = 0.1

Analysis of Variance

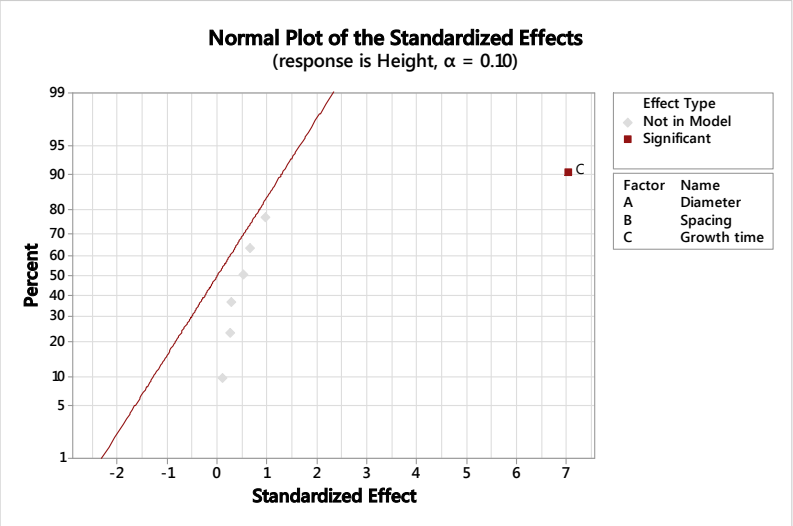
Source	DF	Seq SS	Contribution	Adj SS	Adj MS	F-Value	P-Value
Model	1	4588.8	77.83%	4588.8	4588.84	49.14	0.000
Linear	1	4588.8	77.83%	4588.8	4588.84	49.14	0.000
Growth time	1	4588.8	77.83%	4588.8	4588.84	49.14	0.000
Error	14	1307.3	22.17%	1307.3	93.38		
Lack-of-Fit	6	161.0	2.73%	161.0	26.83	0.19	0.972
Pure Error	8	1146.3	19.44%	1146.3	143.29		
Total	15	5896.1	100.00%				

Model Summary

S	R-sq	R-sq(adj)	PRESS	R-sq(pred)
9.66311	77.83%	76.24%	1707.44	71.04%

Regression Equation in Uncoded Units

Height = -2.83 + 8.47 Growth time



Factorial Regression: Wall thickness versus Diameter, Spacing, Growth time

Stepwise Selection of Terms

α to enter = 0.1, α to remove = 0.1

The stepwise procedure added terms during the procedure in order to maintain a hierarchical model at each step.

Analysis of Variance

Source	DF	Seq SS	Contribution	Adj SS	Adj MS	F-Value	P-Value
Model	7	5.33735	90.11%	5.33735	0.76248	10.42	0.002
Linear	3	3.04330	51.38%	3.04330	1.01443	13.86	0.002
Diameter	1	0.74671	12.61%	0.74671	0.74671	10.20	0.013
Spacing	1	2.29636	38.77%	2.29636	2.29636	31.37	0.001
Growth time	1	0.00023	0.00%	0.00023	0.00023	0.00	0.957
2-Way Interactions	3	0.97471	16.46%	0.97471	0.32490	4.44	0.041
Diameter*Spacing	1	0.27602	4.66%	0.27602	0.27602	3.77	0.088
Diameter*Growth time	1	0.44806	7.56%	0.44806	0.44806	6.12	0.038
Spacing*Growth time	1	0.25063	4.23%	0.25063	0.25063	3.42	0.101
3-Way Interactions	1	1.31934	22.28%	1.31934	1.31934	18.03	0.003

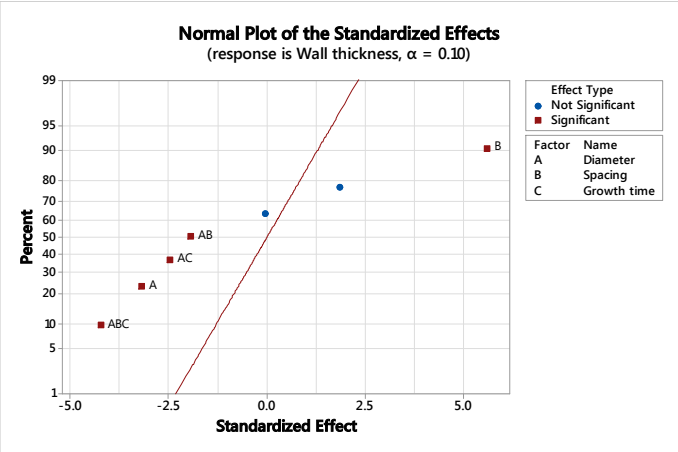
Diameter*Spacing*Growth time	1	1.31934	22.28%	1.31934	1.31934	18.03	0.003
Error	8	0.58555	9.89%	0.58555	0.07319		
Total	15	5.92290	100.00%				

Model Summary

S	R-sq	R-sq(adj)	PRESS	R-sq(pred)
0.270543	90.11%	81.46%	2.34219	60.46%

Regression Equation in Uncoded Units

Wall thickness = 2.552 - 0.1614 Diameter - 0.244 Spacing - 0.768 Growth time + 0.02363 Diameter*Spacing + 0.0463 Diameter*Growth time + 0.1208 Spacing*Growth time - 0.00766 Diameter*Spacing*Growth time



Factorial Regression: Undamaged cells versus Diameter, Spacing, Growth time

Stepwise Selection of Terms

α to enter = 0.1, α to remove = 0.1

The stepwise procedure added terms during the procedure in order to maintain a hierarchical model at each step.

Analysis of Variance

Source	DF	Seq SS	Contribution	Adj SS	Adj MS	F-Value	P-Value
Model	7	1.60997	96.22%	1.60997	0.229995	29.10	0.000
Linear	3	1.05046	62.78%	1.05046	0.350155	44.31	0.000
Diameter	1	0.82358	49.22%	0.82358	0.823583	104.22	0.000
Spacing	1	0.15563	9.30%	0.15563	0.155633	19.69	0.002
Growth time	1	0.07125	4.26%	0.07125	0.071248	9.02	0.017
2-Way Interactions	3	0.38331	22.91%	0.38331	0.127769	16.17	0.001
Diameter*Spacing	1	0.14475	8.65%	0.14475	0.144746	18.32	0.003
Diameter*Growth time	1	0.06693	4.00%	0.06693	0.066930	8.47	0.020
Spacing*Growth time	1	0.17163	10.26%	0.17163	0.171631	21.72	0.002
3-Way Interactions	1	0.17619	10.53%	0.17619	0.176195	22.30	0.001

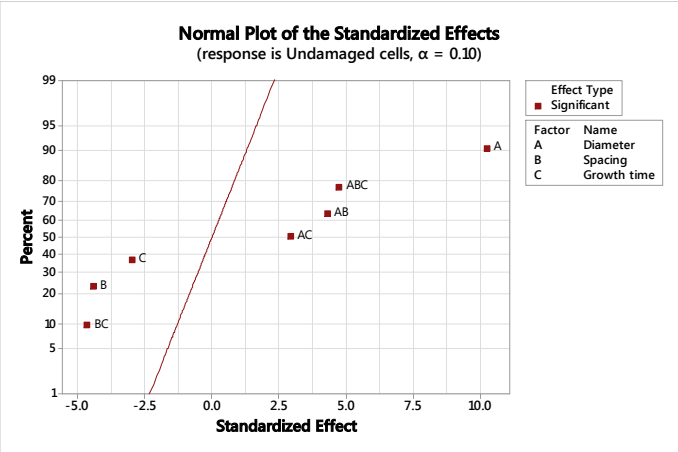
Diameter*Spacing*Growth time	1	0.17619	10.53%	0.17619	0.176195	22.30	0.001
Error	8	0.06322	3.78%	0.06322	0.007903		
Total	15	1.67319	100.00%				

Model Summary

S	R-sq	R-sq(adj)	PRESS	R-sq(pred)
0.0888970	96.22%	92.92%	0.252886	84.89%

Regression Equation in Uncoded Units

Undamaged cells = -0.168 + 0.0589 Diameter + 0.1199 Spacing + 0.3304 Growth time
- 0.00612 Diameter*Spacing - 0.01668 Diameter*Growth time
- 0.05569 Spacing*Growth time
+ 0.002798 Diameter*Spacing*Growth time



Factorial Regression: Cracks over 2 to 5 cells v. Diameter, Spacing, Growth time

Stepwise Selection of Terms

α to enter = 0.1, α to remove = 0.1

The stepwise procedure added terms during the procedure in order to maintain a hierarchical model at each step.

Analysis of Variance

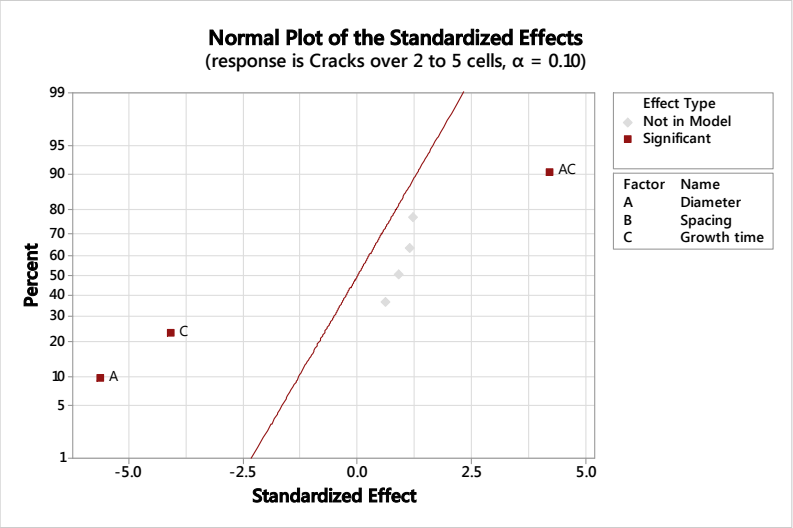
Source	DF	Seq SS	Contribution	Adj SS	Adj MS	F-Value	P-Value
Model	3	0.20193	84.60%	0.20193	0.067309	21.98	0.000
Linear	2	0.14824	62.11%	0.14824	0.074121	24.20	0.000
Diameter	1	0.09696	40.62%	0.09696	0.096963	31.66	0.000
Growth time	1	0.05128	21.48%	0.05128	0.051278	16.74	0.001
2-Way Interactions	1	0.05369	22.49%	0.05369	0.053686	17.53	0.001
Diameter*Growth time	1	0.05369	22.49%	0.05369	0.053686	17.53	0.001
Error	12	0.03675	15.40%	0.03675	0.003063		
Lack-of-Fit	4	0.01192	5.00%	0.01192	0.002981	0.96	0.479
Pure Error	8	0.02483	10.40%	0.02483	0.003104		
Total	15	0.23868	100.00%				

Model Summary

S	R-sq	R-sq(adj)	PRESS	R-sq(pred)
0.0553428	84.60%	80.75%	0.0653403	72.62%

Regression Equation in Uncoded Units

Cracks over 2 to 5 cells = 0.5257 - 0.02583 Diameter - 0.0766 Growth time + 0.003862 Diameter*Growth time



Hydrothermal synthesis

Experimental section for Hydrothermal syntheses. Following a published protocol for olive-like bismuth vanadate ($BiVO_4$) nanostructures,[38] solutions of 1 mmol bismuth nitrate pentahydrate ($Bi(NO_3)_3$, Sigma Aldrich) in 30 mL EG and 1 mmol ammonium metavanadate (NH_4VO_3, Sigma Aldrich) in 10 mL DI-water are prepared and stirred for 30 minutes. Then 5 mL of the vanadium precursor and 15 mL of the bismuth precursor are filled into a teflon liner for the microwave reactor. To introduce hydrophilicity and reactive groups, the CNT honeycomb structures on the Si-wafer chips are treated with UV-ozone for 30 minutes and then slowly put into the solution. The liners are put into the microwave and heated to 140 °C for 4 hours. Afterwards the solution is filtered using vacuum filtration and the CNT structure is washed multiple times with DI-water. The filtered particles and the coated structure are dried at 80 °C overnight.

Adapting the first published, hydrothermal protocol for bismuth vanadate ($BiVO_4$),[37] solutions of 1 mmol bismuth nitrate pentahydrate ($Bi(NO_3)_3$, Sigma Aldrich) in 20 mL DI-water and 1 mmol sodium vanadium oxide ($NaVO_3$) are prepared. $NaVO_3$ is prepared by dissolving 39.997 mg NaOH in 20 mL DI-water and adding 9.09 mg vanadium(V)oxide (V_2O_5, Sigma Aldrich). All solutions are stirred for 30 minutes and then mixed together. The pH is adjusted to 7 using NaOH. Then 20 mL of the mixed precursor solution is filled into a Teflon liner for the microwave reactor. To introduce hydrophilicity and reactive groups, the CNT honeycomb structures on the Si-wafer chips are treated with UV-ozone for 30 minutes and then slowly put into the solution. The liners are put into the microwave and heated to 140 °C for 3 hours. Afterwards the solution is filtered using vacuum filtration and the CNT structure is washed multiple times with DI-water. The filtered particles and the coated structure are dried at 80 °C overnight. The concentration is lowered to 1/10 for some experiments.

Following a published protocol for hierarchical bismuth vanadate ($BiVO_4$) nanostructures,[36] a solution of 0.5 mmol bismuth nitrate pentahydrate ($Bi(NO_3)_3$, Sigma Aldrich) and 0.5 mmol ammonium metavanadate (NH_4VO_3, Sigma Aldrich) in 40 mL ethylene glycol (EG, Acros Organics) is prepared and stirred for 10 minutes. Then 20 mL each of the solution are filled into two teflon liners for the microwave reactor. To introduce hydrophilicity and reactive groups, the honeycomb structures on the Si-wafer chips are treated with UV-ozone for 30 minutes and then slowly put into the solution. The liners are put into the microwave and heated to 140 °C for one hour. Afterwards the solution is filtered using vacuum filtration and the CNT structure is washed multiple times with DI-water. The filtered particles and the coated structure are dried at 80 °C overnight.

Results:

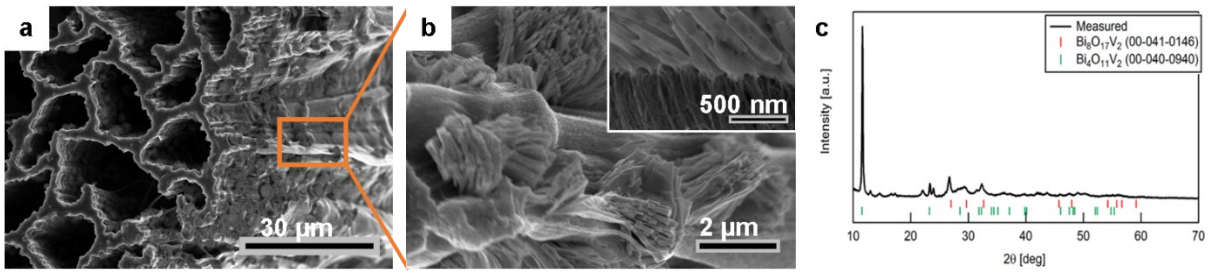


Figure S2. A microwave-assisted, hydrothermal synthesis following a protocol by Shang et al.[36] is used to synthesize particles on the CNT surface, SEM images are shown in a and b

with some nucleation but no uniform coating, and XRD measurements (c) confirm a different composition of bismuth vanadium oxide (c), not the desired $BiVO_4$.

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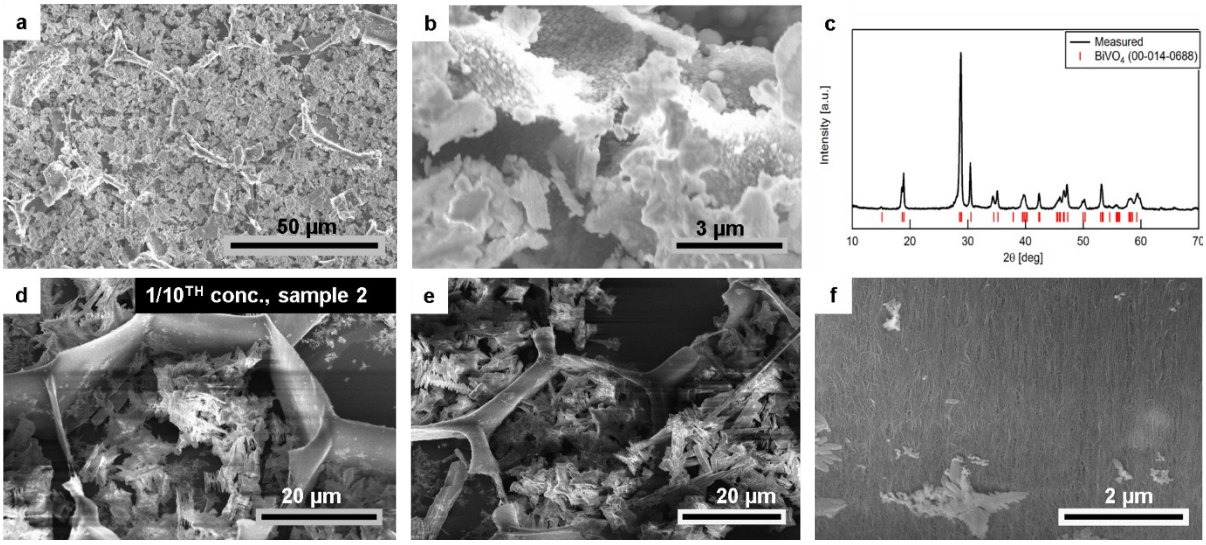

Figure S3. The hydrothermal, microwave-assisted protocol by Liu et al.[37] shows a large amount of nanoparticles that cover the CNT honeycomb structure (a), coat the sidewalls (b) and are of the desired composition, monoclinic $BiVO_4$ (c). A decrease in concentration leaves the CNT honeycombs intact (d, e), but doesn't lead to much nucleation and thus no uniform coating on the sidewalls (f).

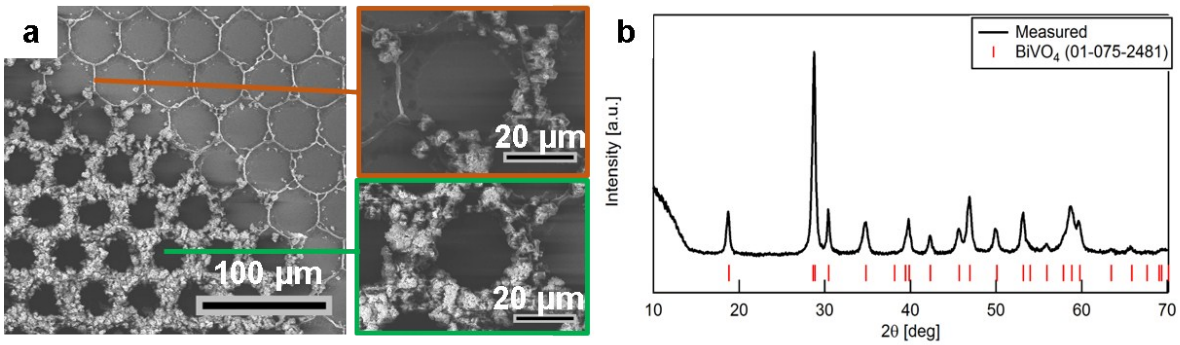

Figure S4. After the microwave-assisted, hydrothermal synthesis adapted from Ma et al.[38] half of the structure is nicely coated, whereas other parts are not coated at all (a). The composition of the particles from this reaction is monoclinic $BiVO_4$ (b).

Hot-casting

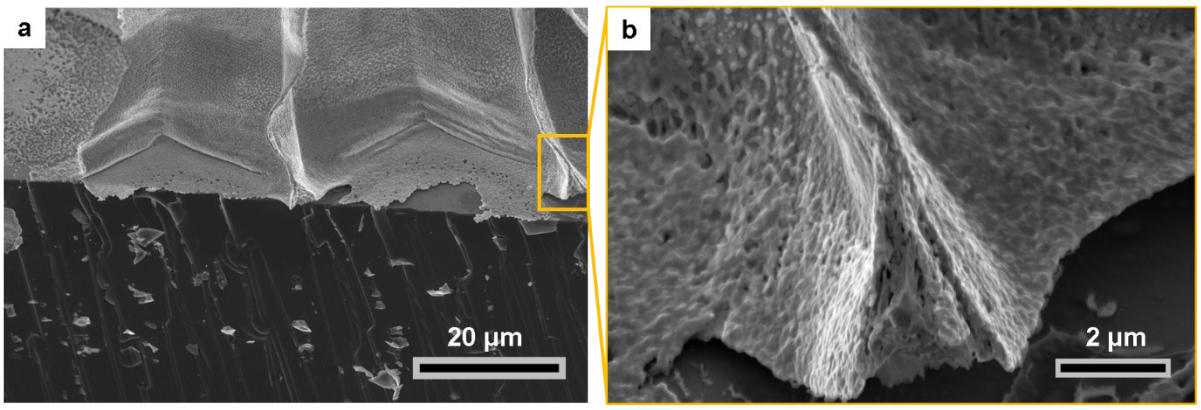

Figure S5. A chipped substrate wafer that shows the coating is also on the inside of the CNT walls.

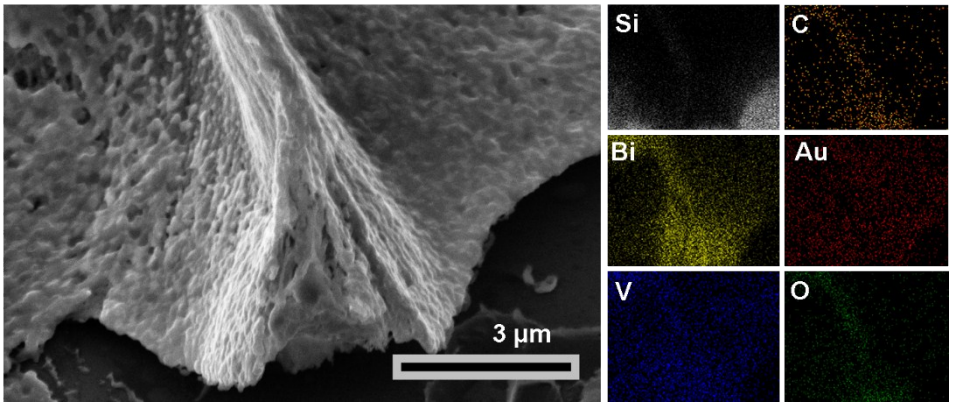

Figure S6. An EDX measurement of the chipped substrate wafer to determine the location of specific elements.

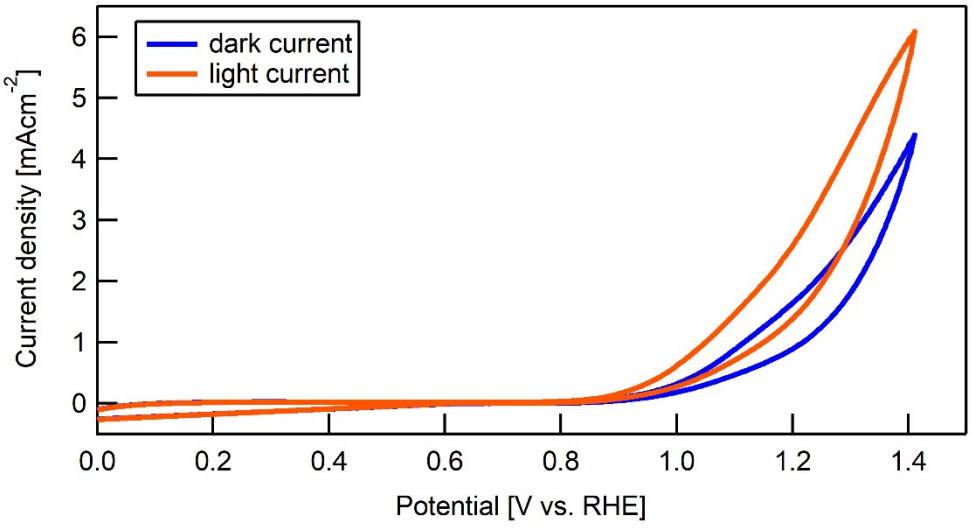

Figure S7. CV measurement (100 mV/s) in the dark and under irradiation, for an additional sample with exceptionally good performance. Current ranges in the samples shown in the manuscript are more representative for the performances we measured in most samples.

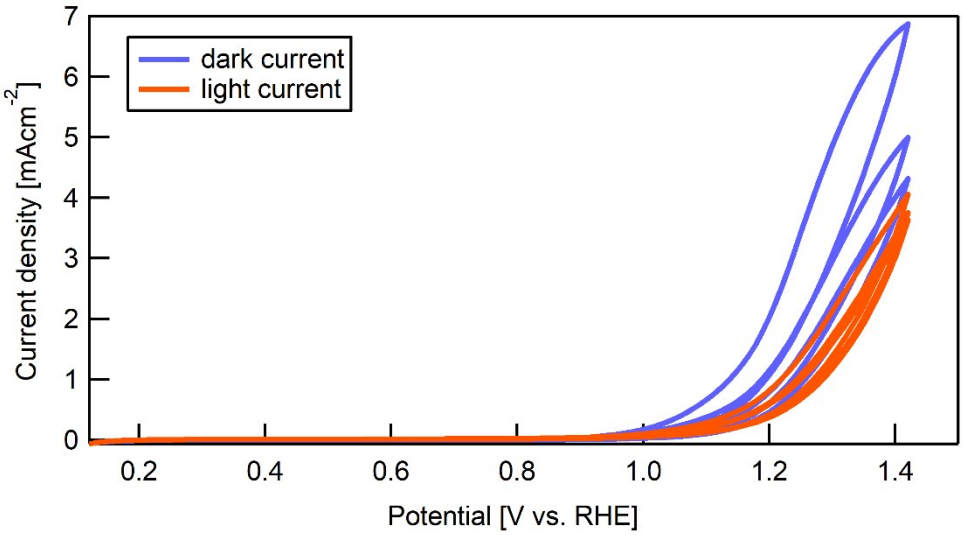

Figure S8. CV measurement (100 mV/s) in the dark and under irradiation, for another sample where delamination of the CNTs is observed, causing progressively worse performance. Remaining activity is attributed to the Au layer, which shows no photoresponse.