Characterisation and photoelectrochemical properties of titania nanotubes

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Overview of presentation

Background to the study

Aims and Objectives

Experimental

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Summary

Photoelectrochemistry

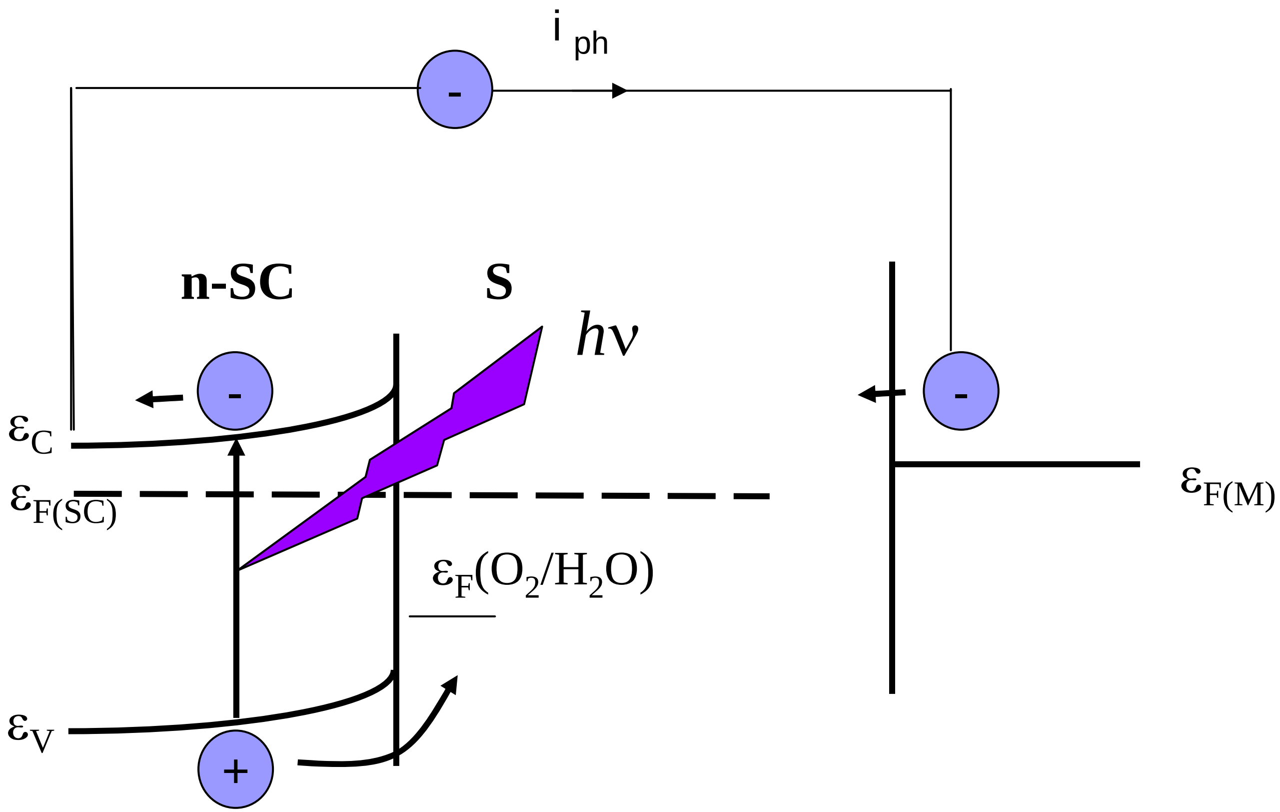


Diagram adopted from Sato (1998)

Titanium Dioxide

- **Fujishima & Honda (1972)** reported photo-splitting of water using n-type single crystal rutile under UV irradiation.

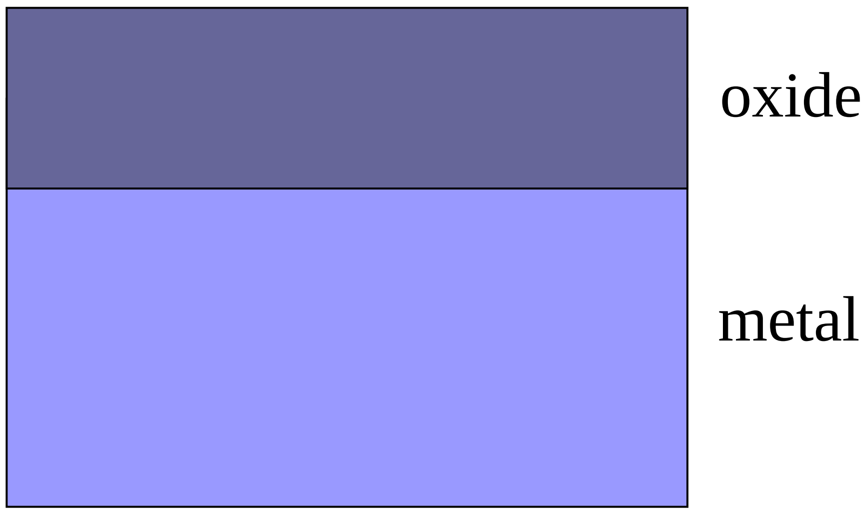
- Titanium dioxide is reported to be a good photocatalyst, it is photostable, chemically stable, insoluble in water, readily available and non-toxic. The wide bandgap energy gives a large potential window for redox reactions, however, it means UV activation.

- **Zwilling et al(1999)** first reported the formation of self organised titania nano-stuctures following anodisation of Ti in F containing electrolyte.

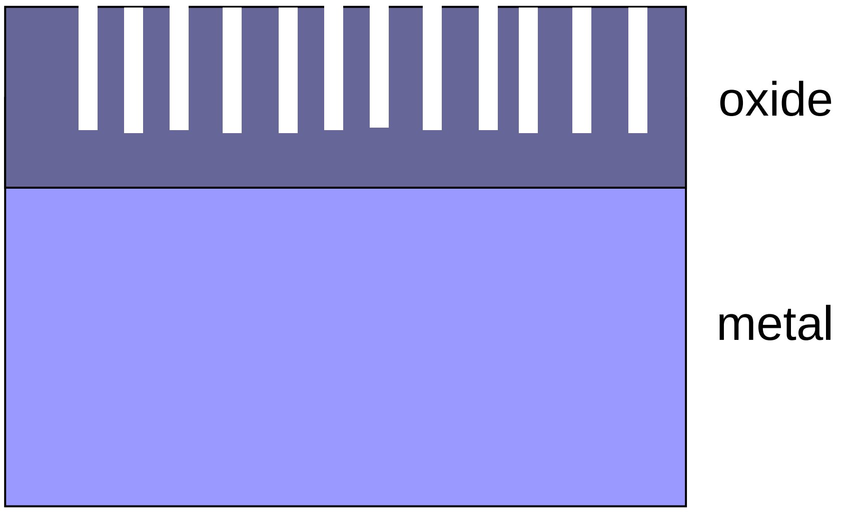
Fujishima, Honda. Nature 1972, 238, 37.

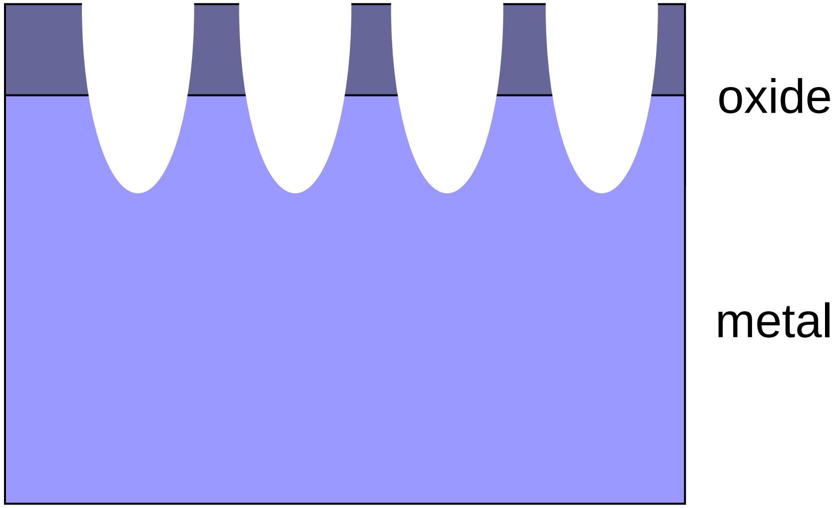
Zwilling, Aucouturier, Darque-Ceretti, Electrochimica Acta 45 (1999) 921–929

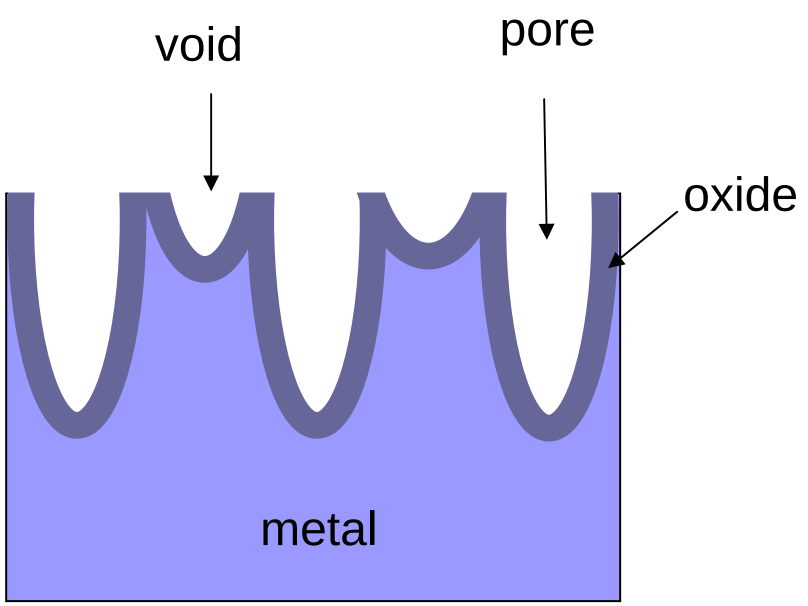
Proposed growth mechanism

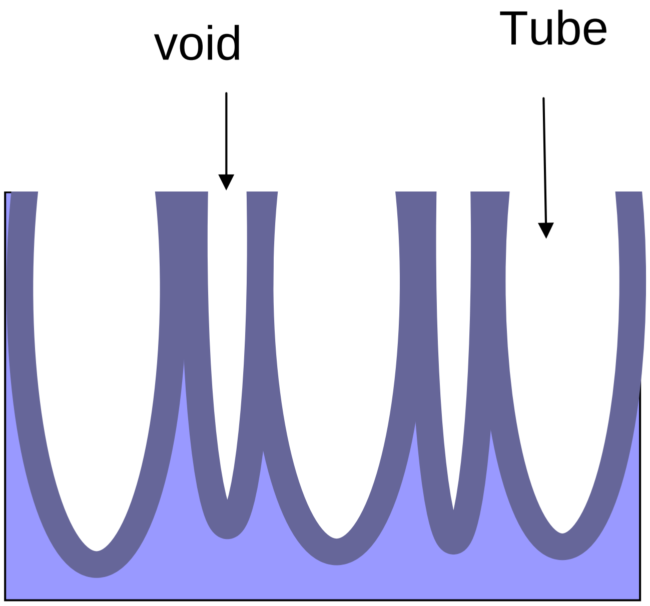


Adapted from: *J. Zhao et al, Solid State Communications 134 (2005) 705–710*


oxide
metal


oxide
metal


void
pore
oxide
metal


void
Tube

Aim of this work

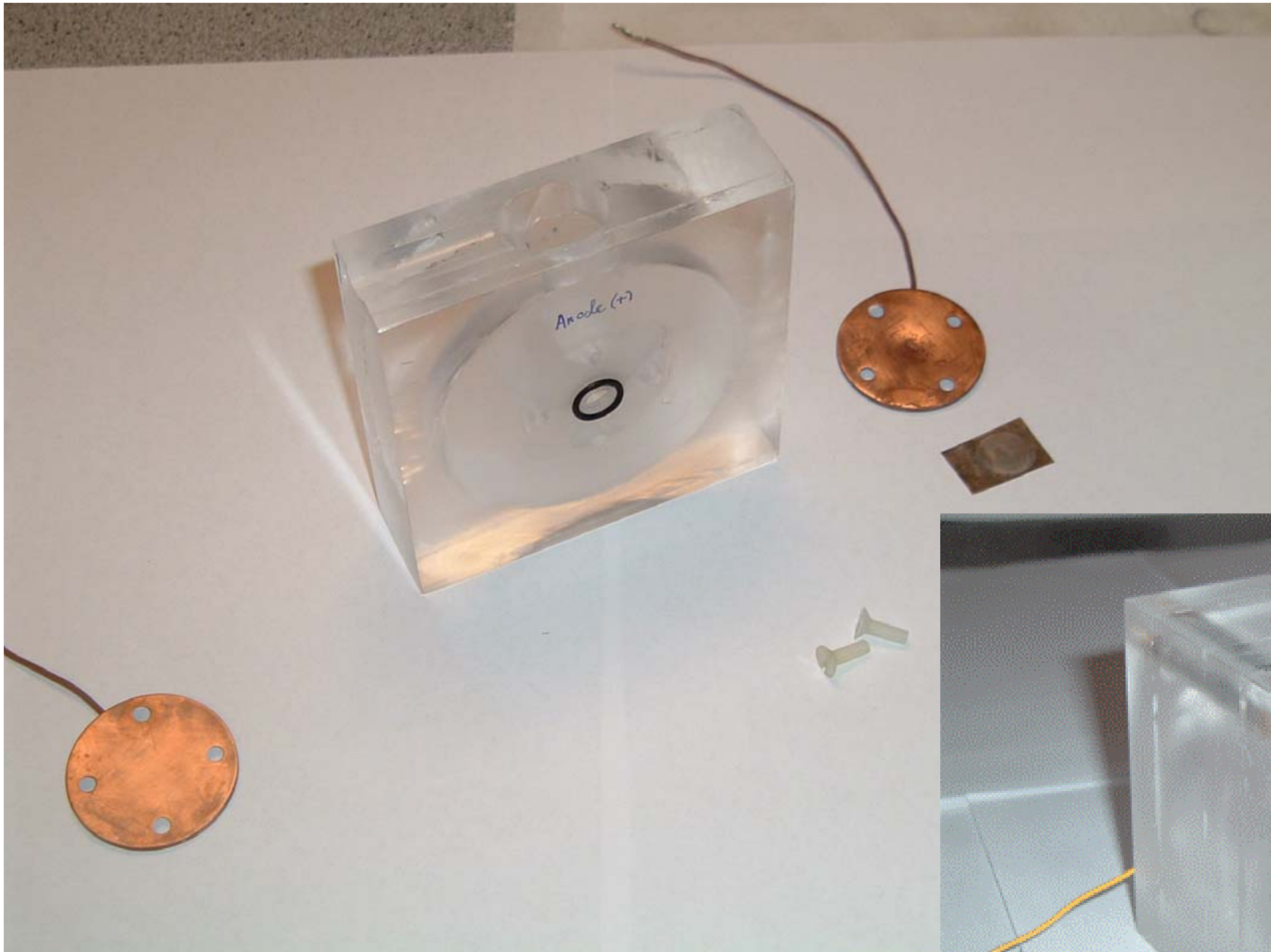
To examine the growth of titania nanotubes by the anodisation of Ti metal in the presence of fluoride and to determine the current-potential response under illumination and the photocatalytic properties.

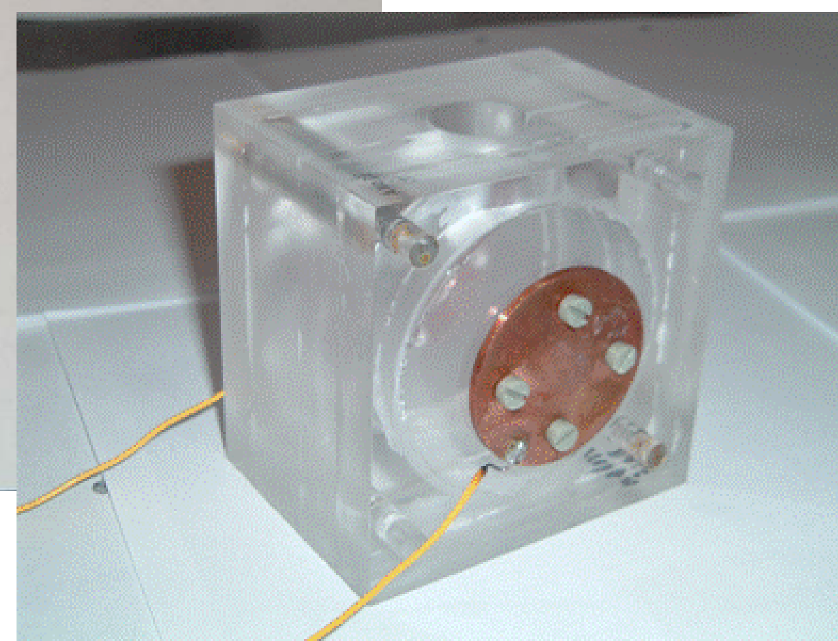
Objectives

- Anodise Ti metal in the presence and absence of fluoride
- Characterise using surface analytical methods
- Determine the current-potential response of the electrodes under illumination
- Determine the photocatalytic properties of the material

Experimental

Electrochemical cell for anodisation





Compact oxide layer

Electrolyte: 1 M H_2SO_4

Anode: Titanium foil diameter of 10 mm (0.785 cm^2)

Cathode: Pt foil diameter 20 mm

Potential applied: constant 20 V dc

Time: 30 min

Current: starts around 18 mA and drops to approx 6 mA

Anneal: 450^oC in air for 1 h (ramp 5^oC min^{-1} up and down)

Titania nanotubes

Electrolyte: 1 M Na_2SO_4 + 0.13 M NaF

Anode: Titanium foil diameter of 10 mm (0.785 cm^2)

Cathode: Platinum foil diameter 20 mm

Potential applied: Constant 20 V dc

Time: 4 h

Current: starts at 20 mA and drops to steady 1 mA

Anneal temp: Range temperatures 350^0C – 750^0C
in air for 1 h (ramp 5^0C min^{-1} up and down)

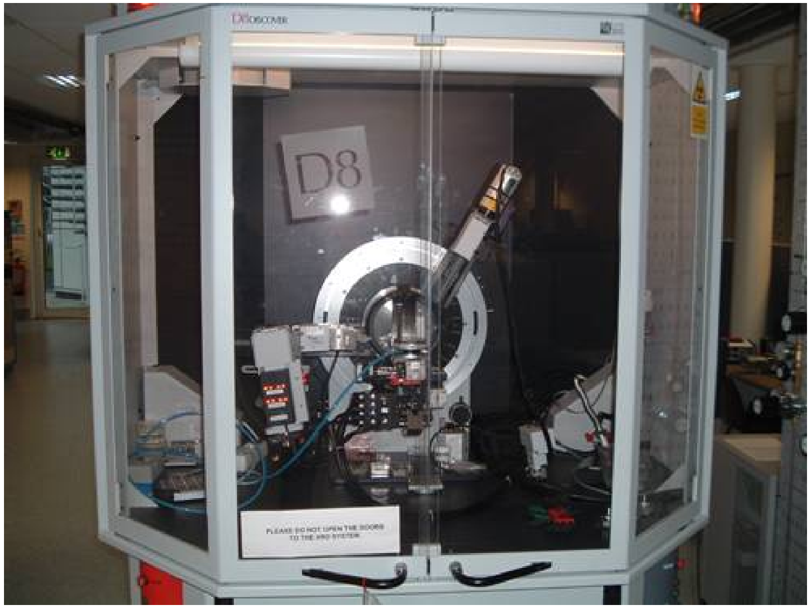
Macak, J; Sirotna, K; Schumki, P. Electrochemica Actu, (2005) , v 50, 18, pp 3679 – 3684

SEM

FEI Quanta 200: tungsten filament electron source, accelerating voltage 20 kV, 42 pA current, spot size 2.5, chamber pressure 1.6 x 10^{-6} Torr.

XRD

Glazing incidence X-ray diffraction was used to determine the crystalline phase of the TiO_2 both before and after annealing using glazing incidence XRD (Bruker D8 Discover X-ray Diffractometer, source fixed at 0.75 degree).



Photoelectrochemistry

One compartment cell with quartz window

Pt paddle CE and SCE RE

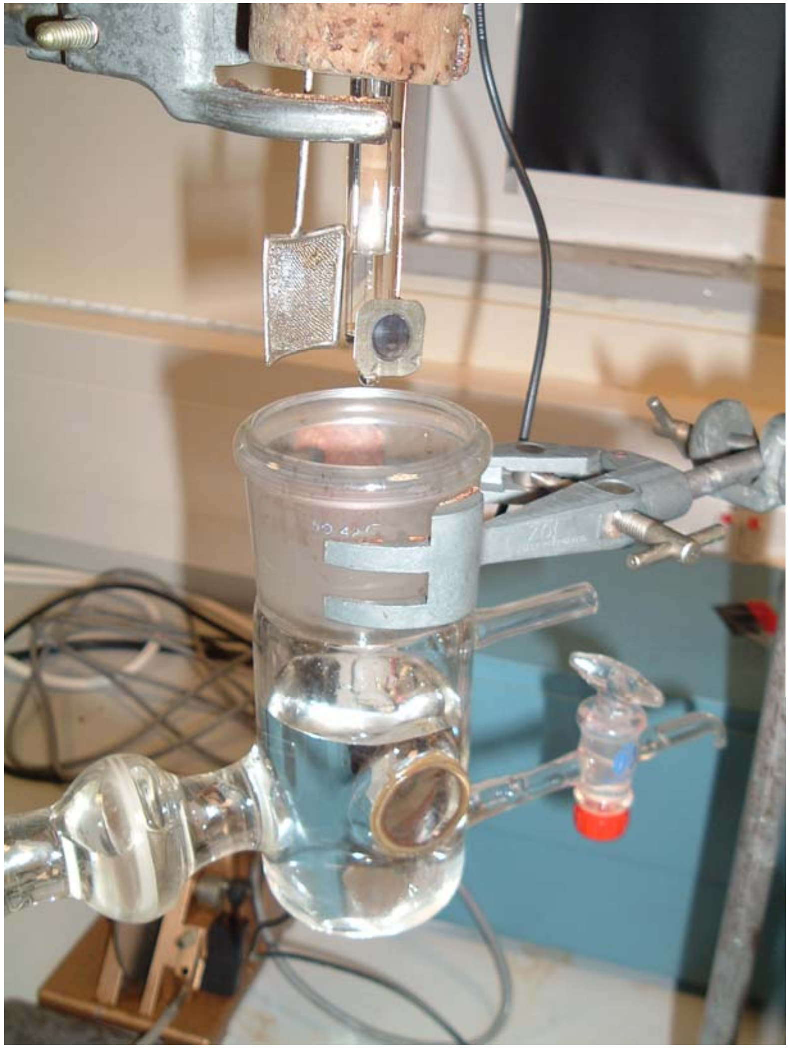
Electrolyte: 0.1 M $NaClO_4$ (air sparged, pH 4.5)

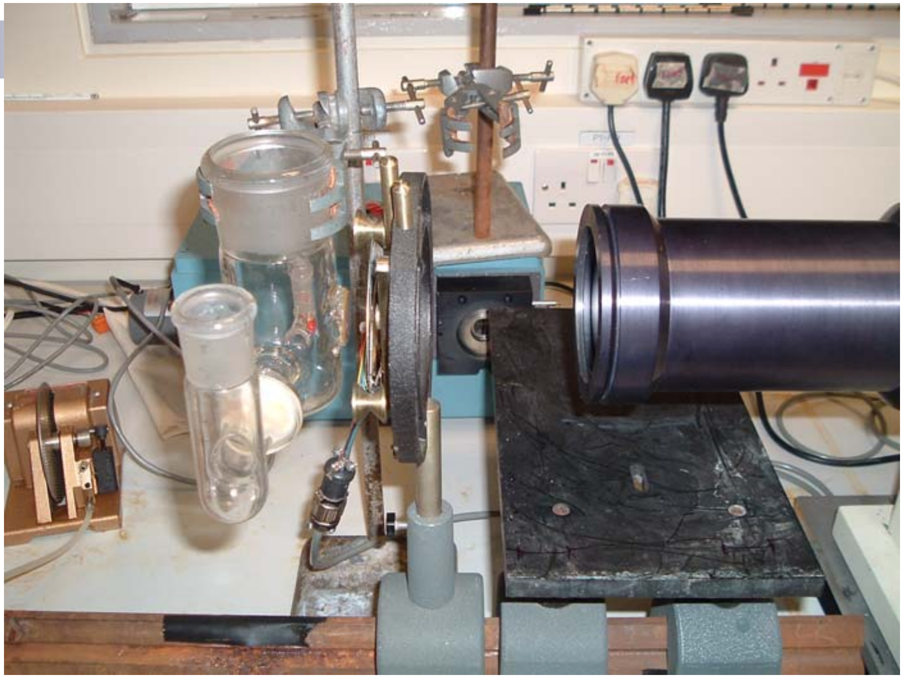
Illumination source 1 kW Xe with AM1.0 filter for solar simulation

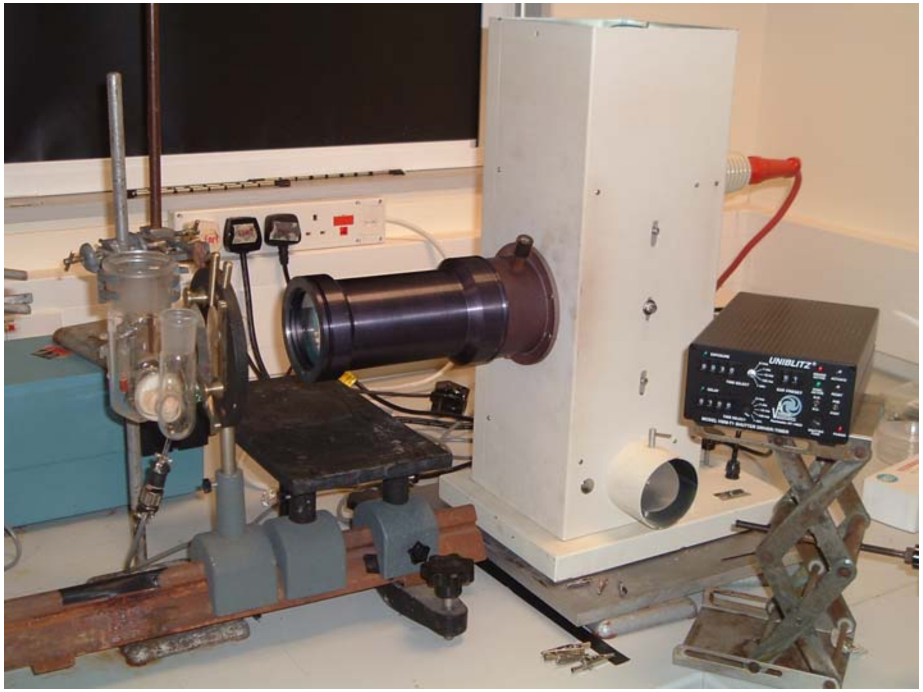
Light intensity measured using Jobin Yvvon spectral radiometer

Potentiostatic control using PG30 Autolab

Photo-cell set-up







Photocatalytic properties

Model pollutants were formic acid and phenol

Illumination was provided by 1 kW xenon with AM1.0 filter

Cell volume was 10 cm^{-3}

Experiments were undertaken at open circuit and with applied bias.

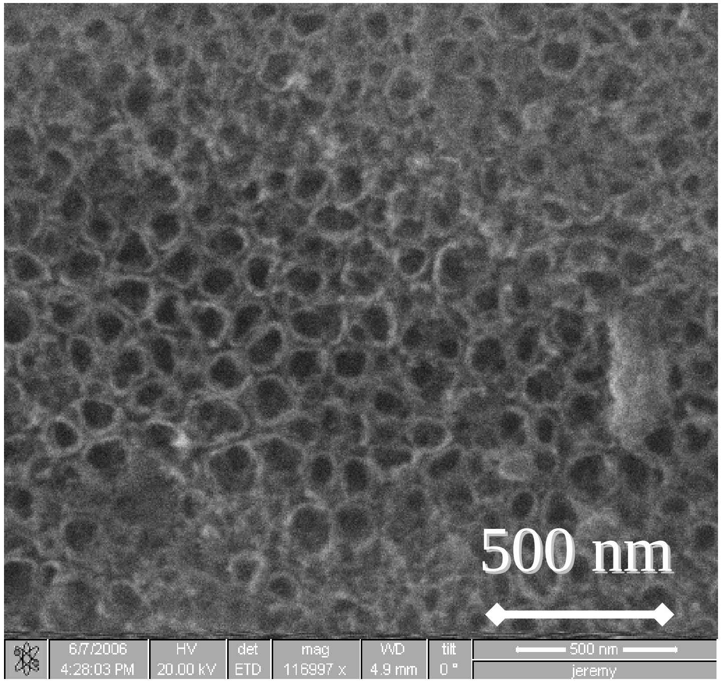
Concentration of formic acid was determined by ion exclusion HPLC

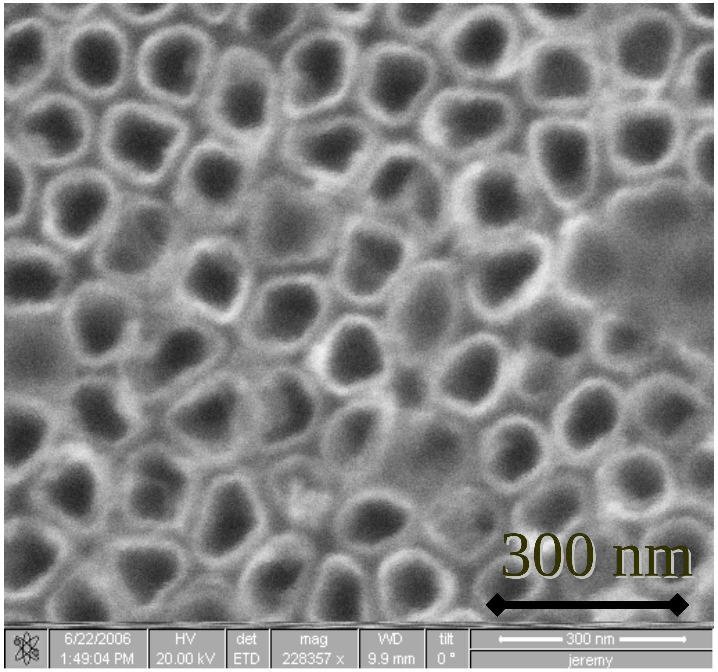
Concentration of phenol was determined by reverse phase HPLC

Photocatalytic Setup.

Results and Discussion

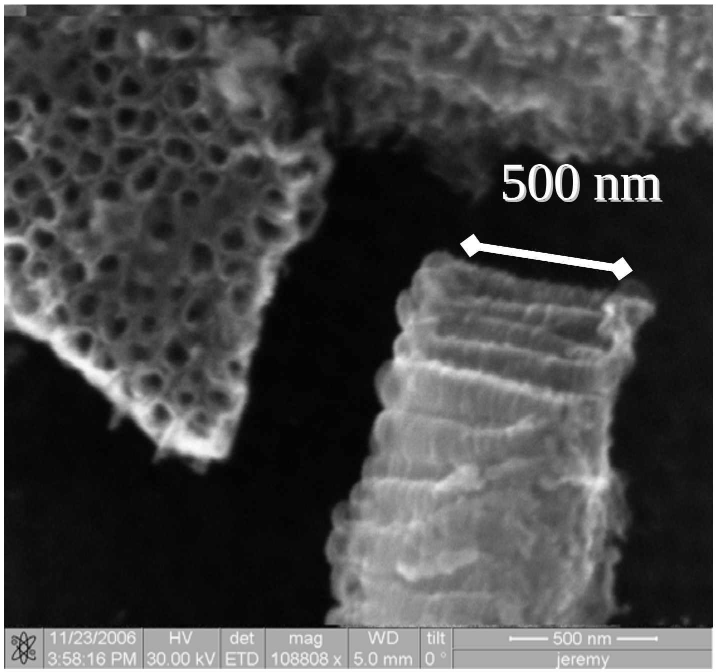
SEM of self –organised titania nanotubes (Top View)

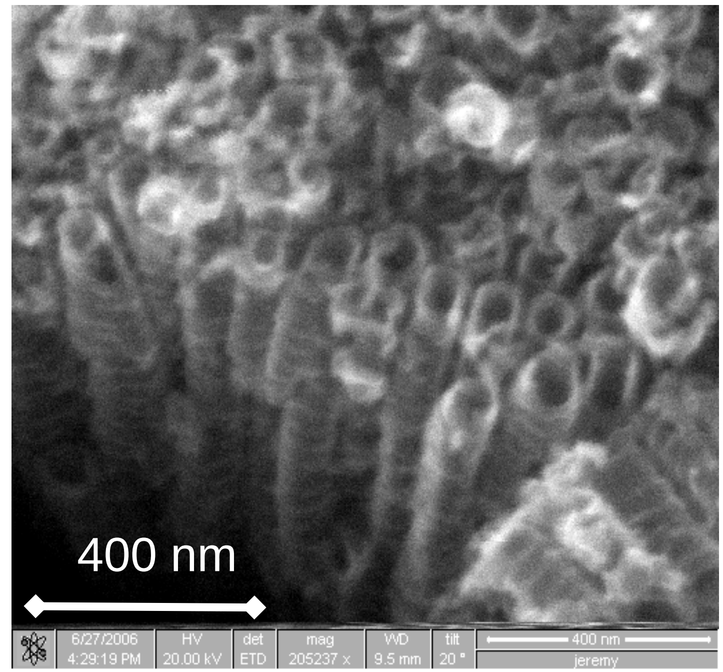




Uniform growth of aligned titania nanotubes
Circular structures with mean internal diameter ca. 90 nm and wall thickness ca. 10 nm

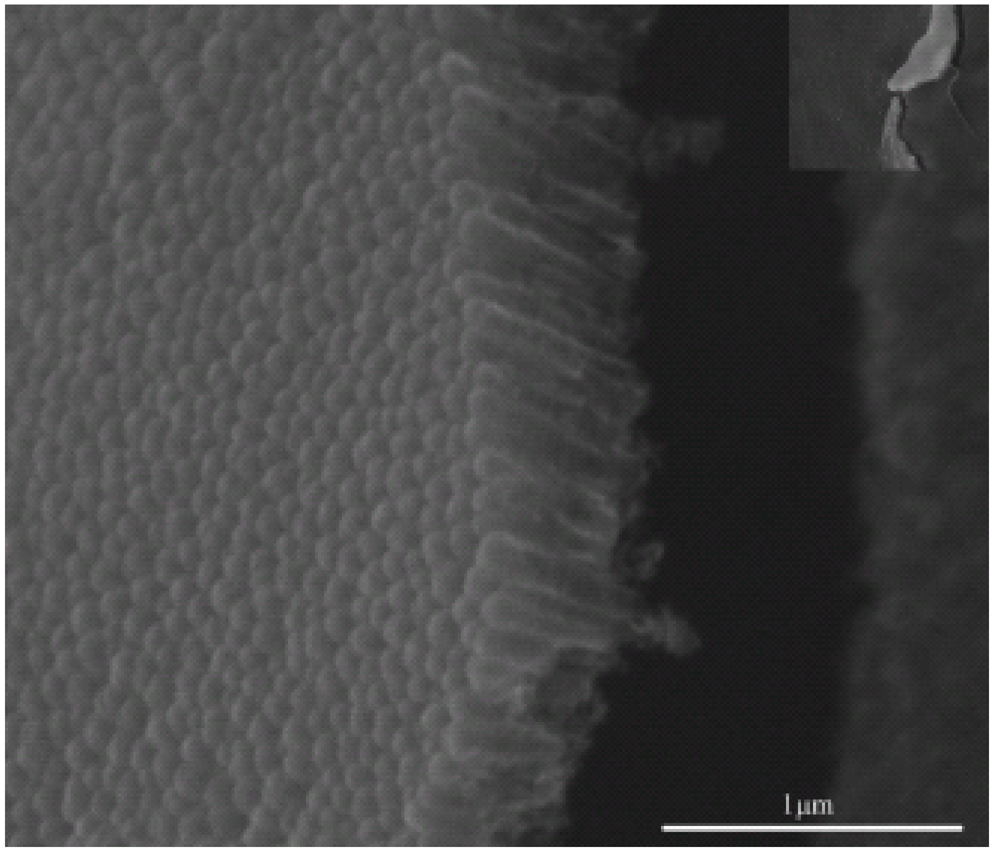
SEM of nanotubes mechanically cracked from support (Side View)





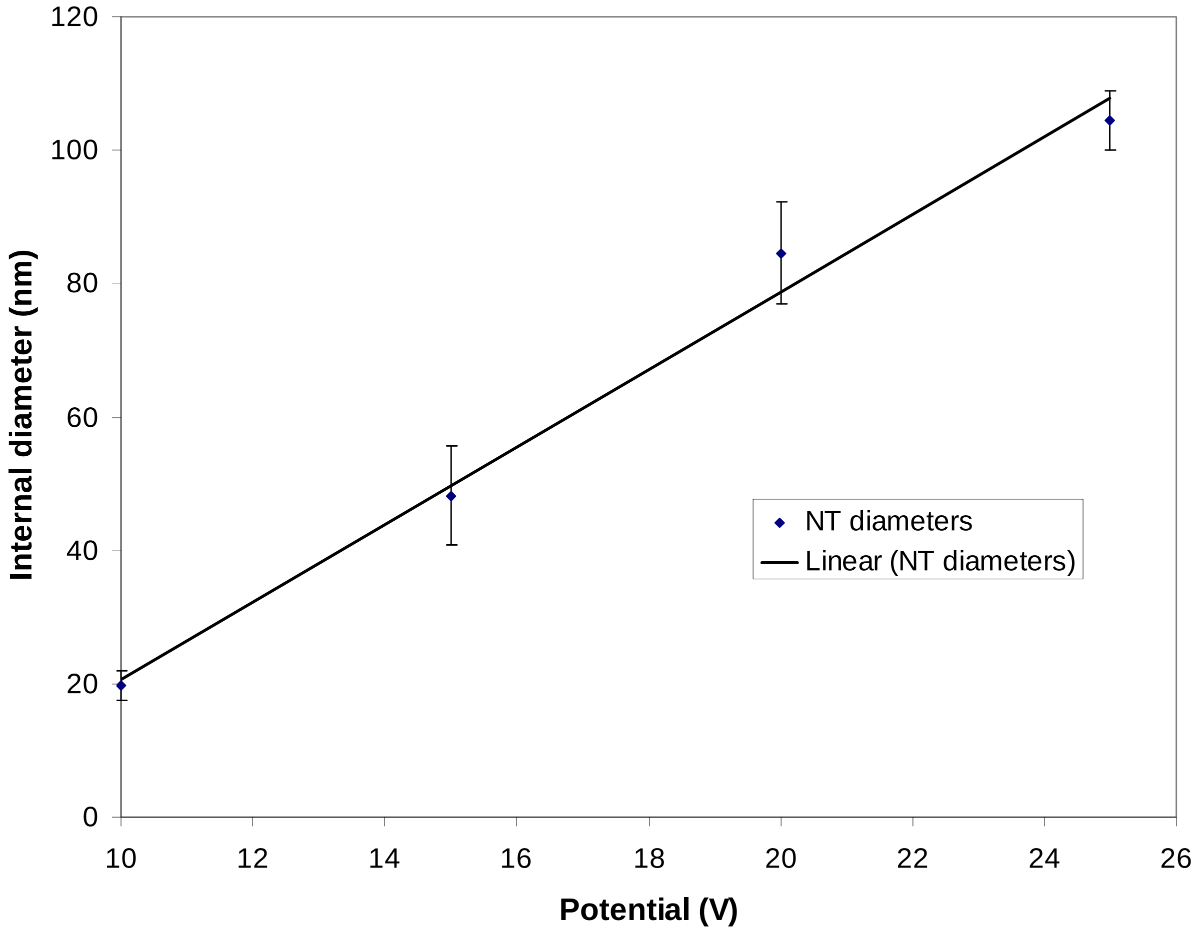
Mechanically cracked sample reveals length ca. 550 nm
Note periodic ring structure along length

SEM of nanotubes mechanically cracked from support (Bottom View)

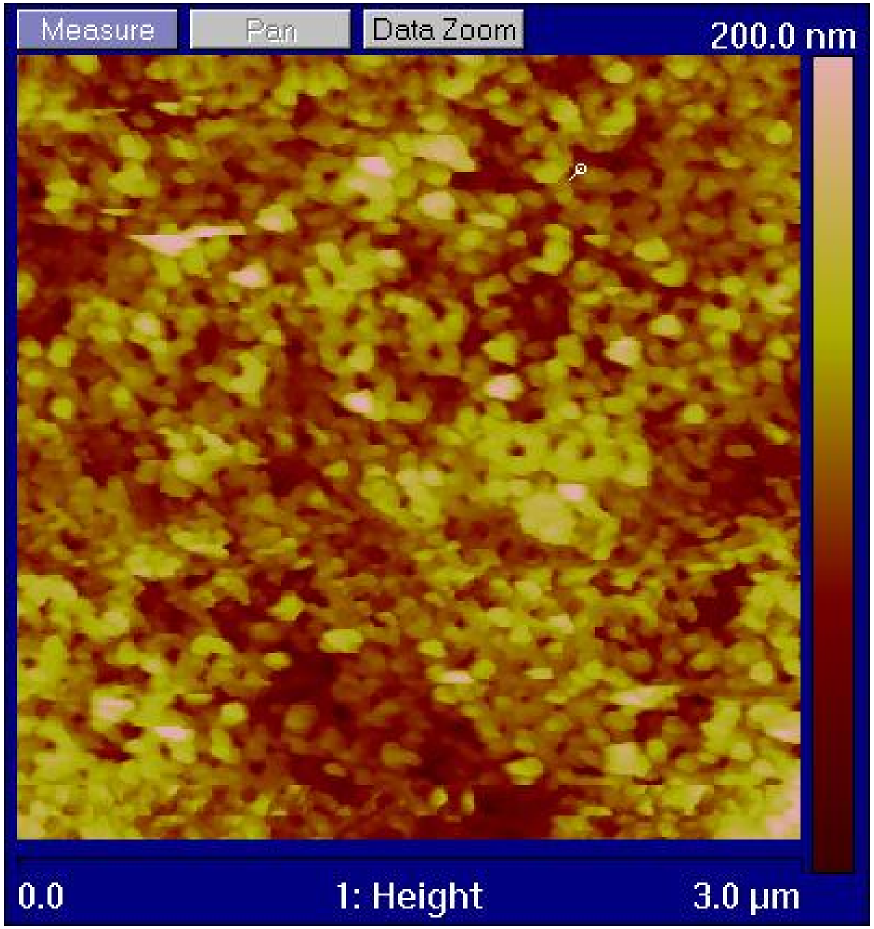


Bottom view of mechanically cracked sample reveals tubes are capped by compact oxide layer which appears as the negative image of pore shape

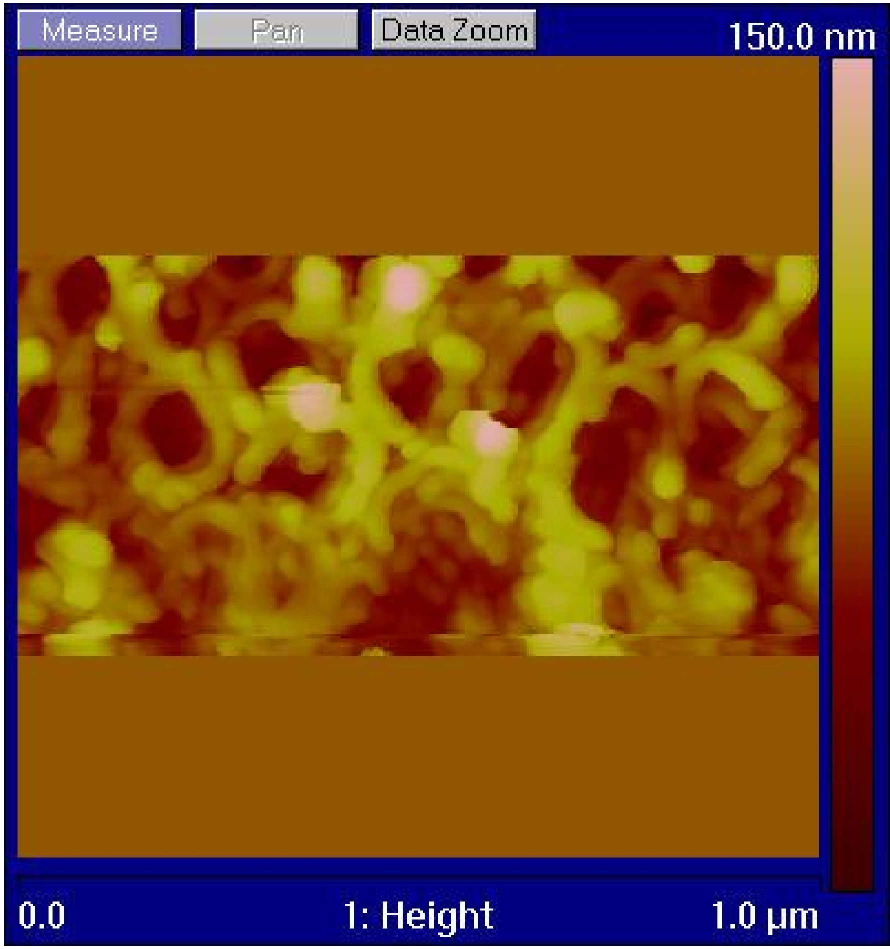
TUBE DIAMETER VS POTENTIAL



AFM



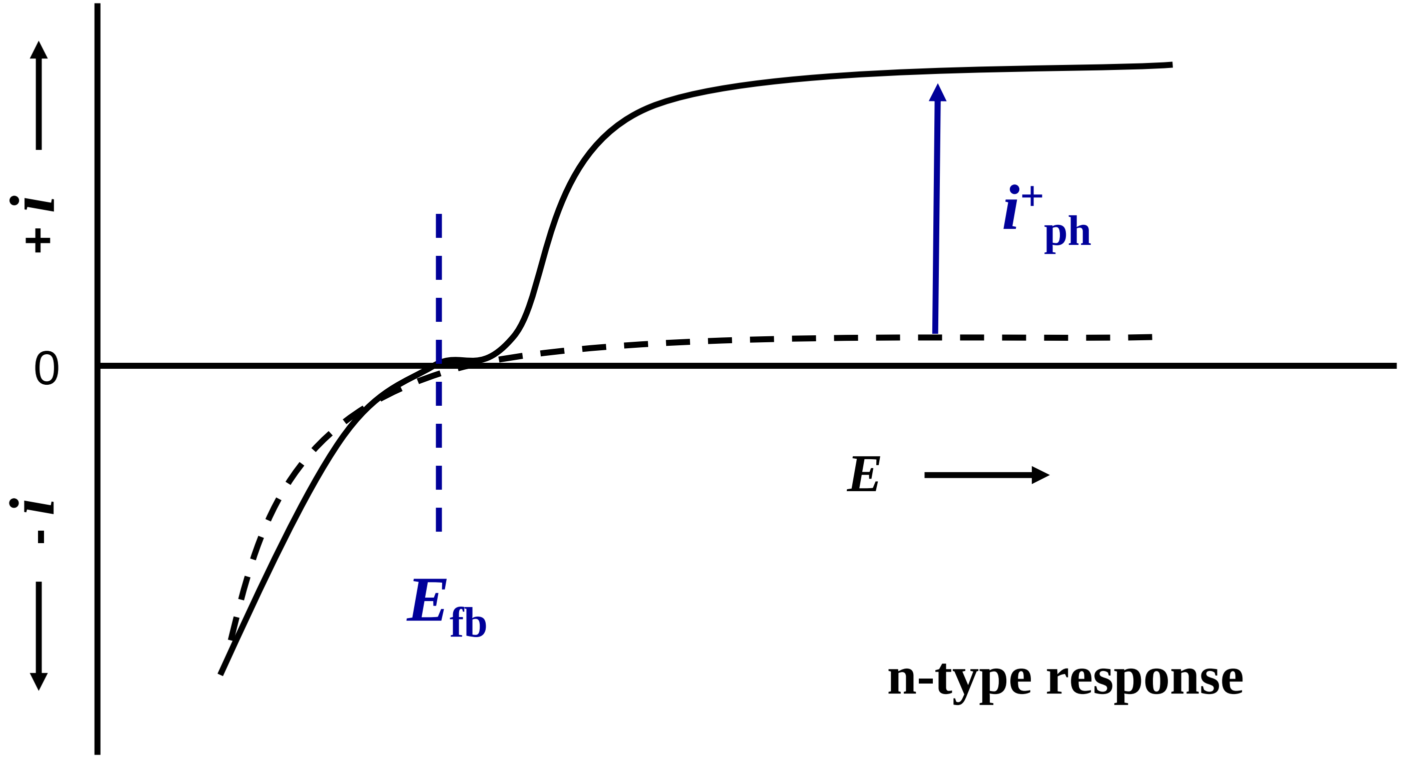
AFM : Tapping mode

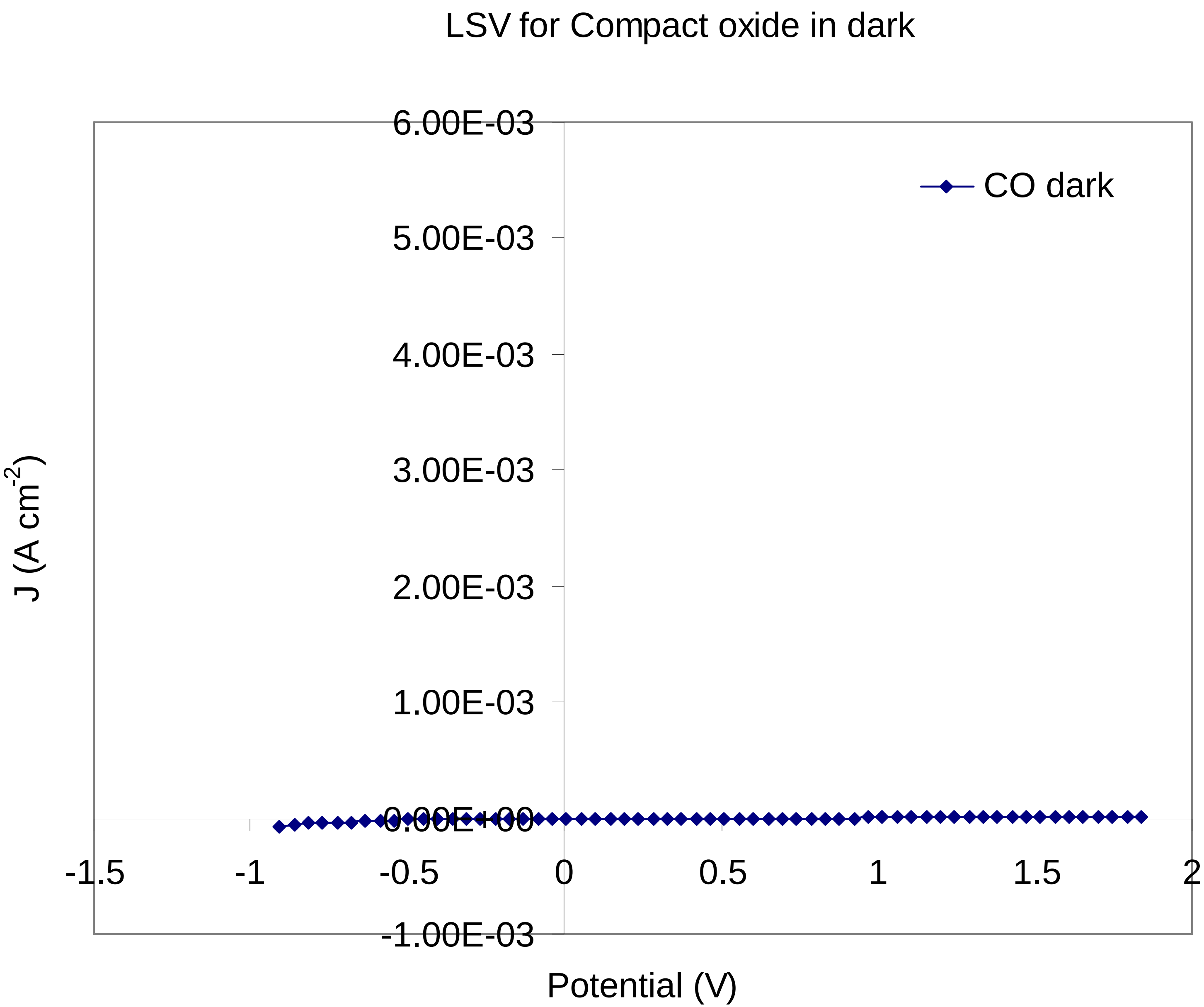


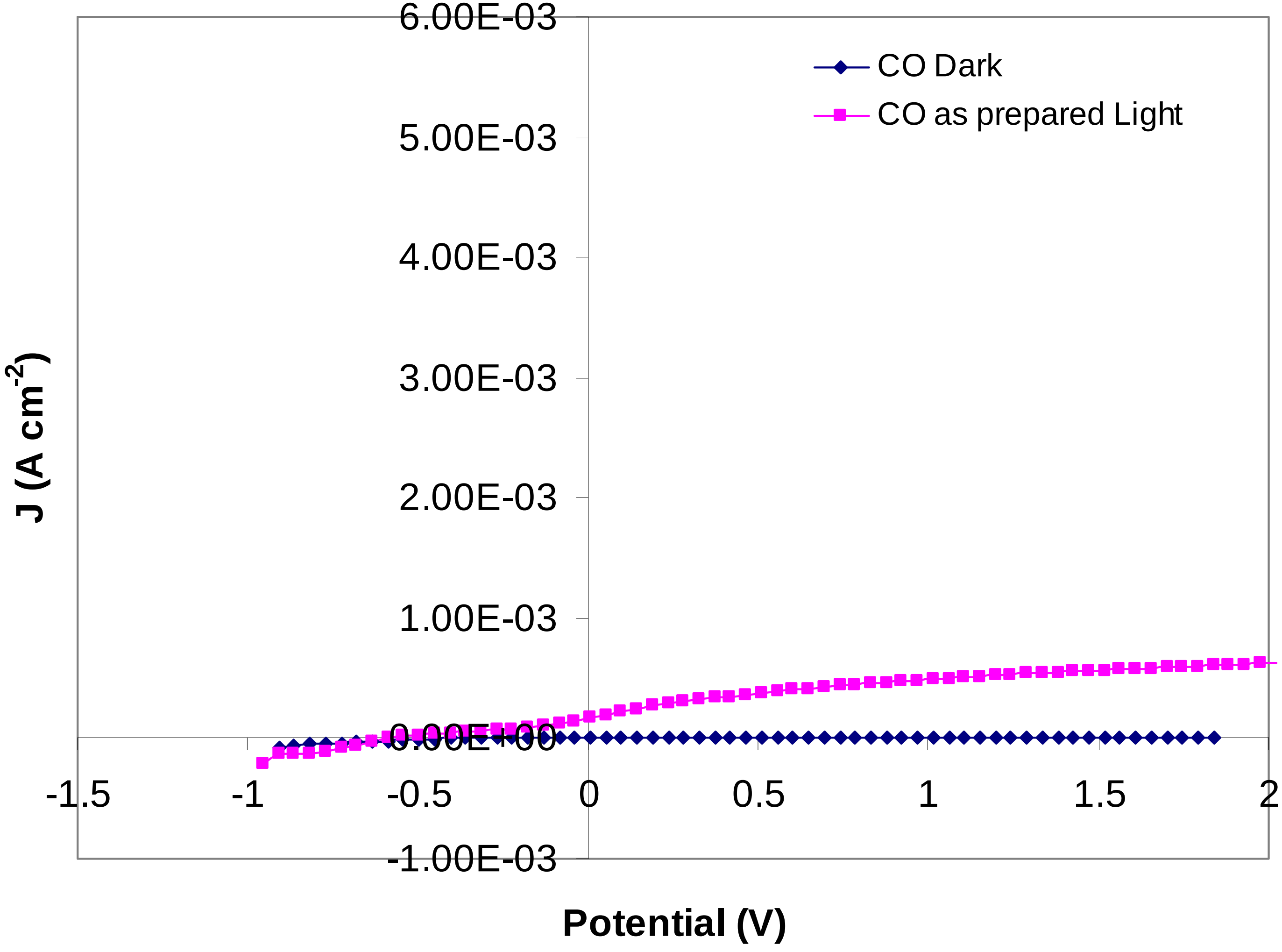
AFM : Tapping mode

Photoelectrochemical Characterisation

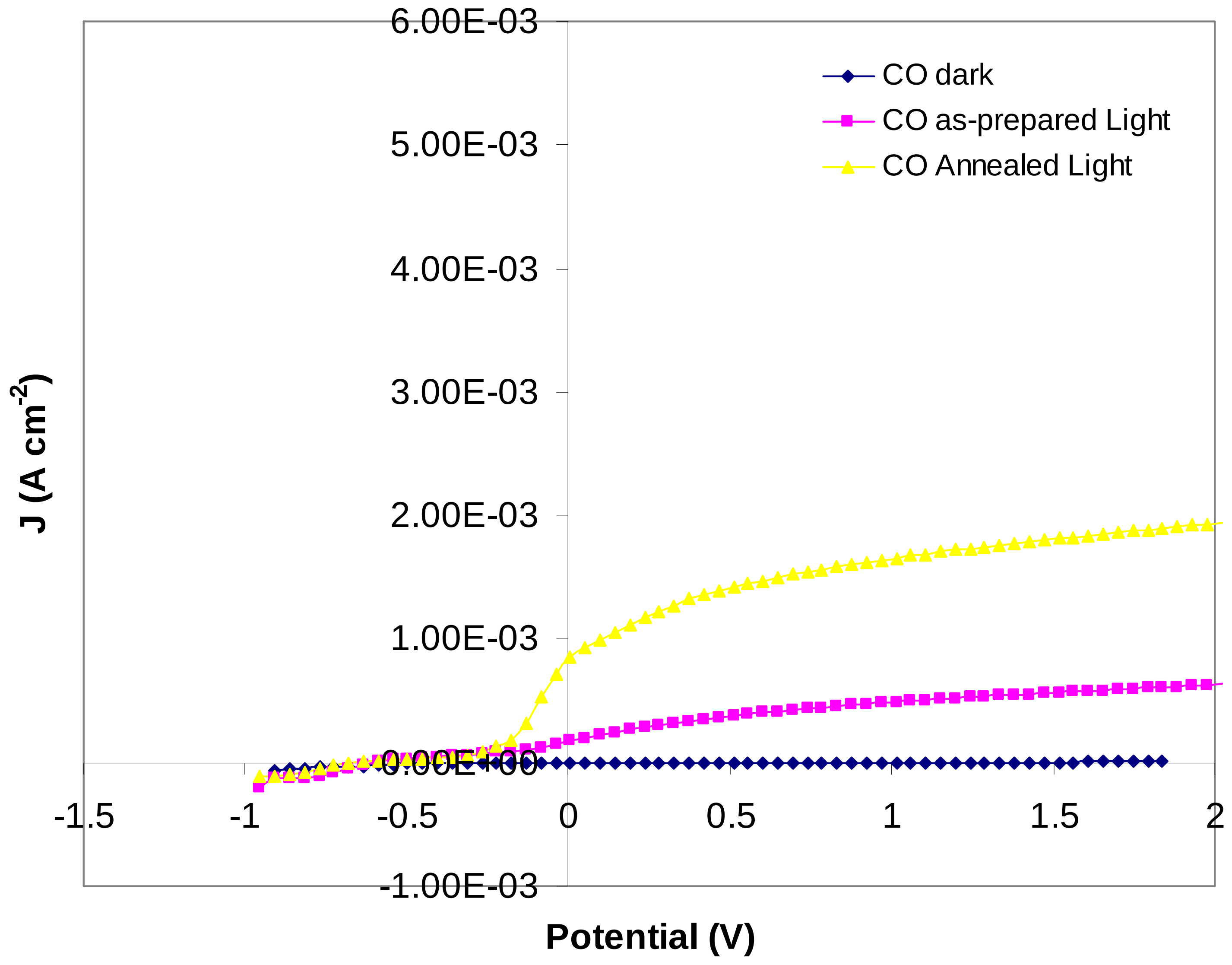
Linear sweep voltammetry provides a fast and effective means of evaluating the photoelectrochemical properties of electrode materials




LSV for Compact oxide in dark
CO dark
6.00E-03
5.00E-03
4.00E-03
3.00E-03
2.00E-03
1.00E-03
0.00E+00
-1.00E-03
J (A cm^{-2})
-1.5
-1
-0.5
0
0.5
1
1.5
2
Potential (V)

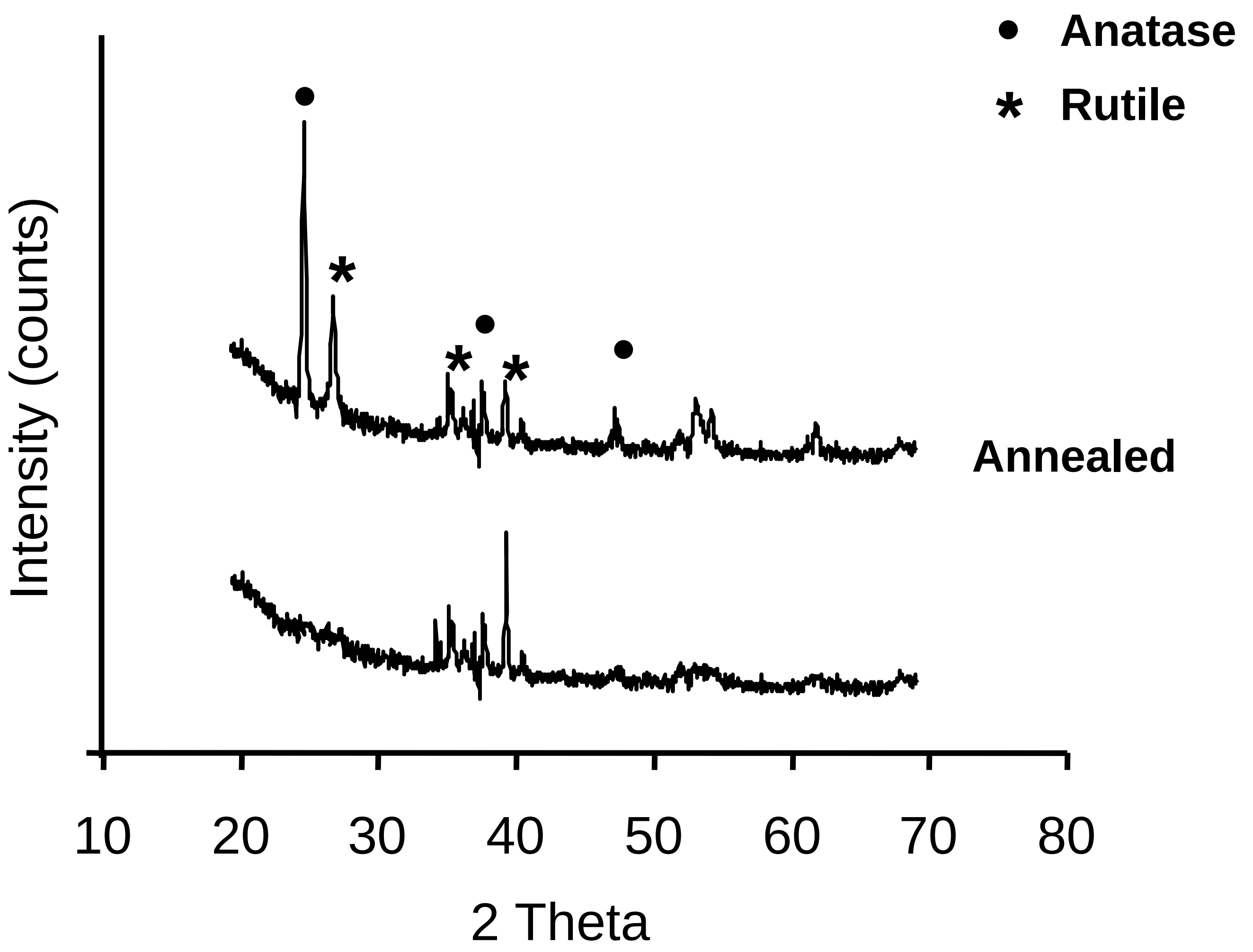


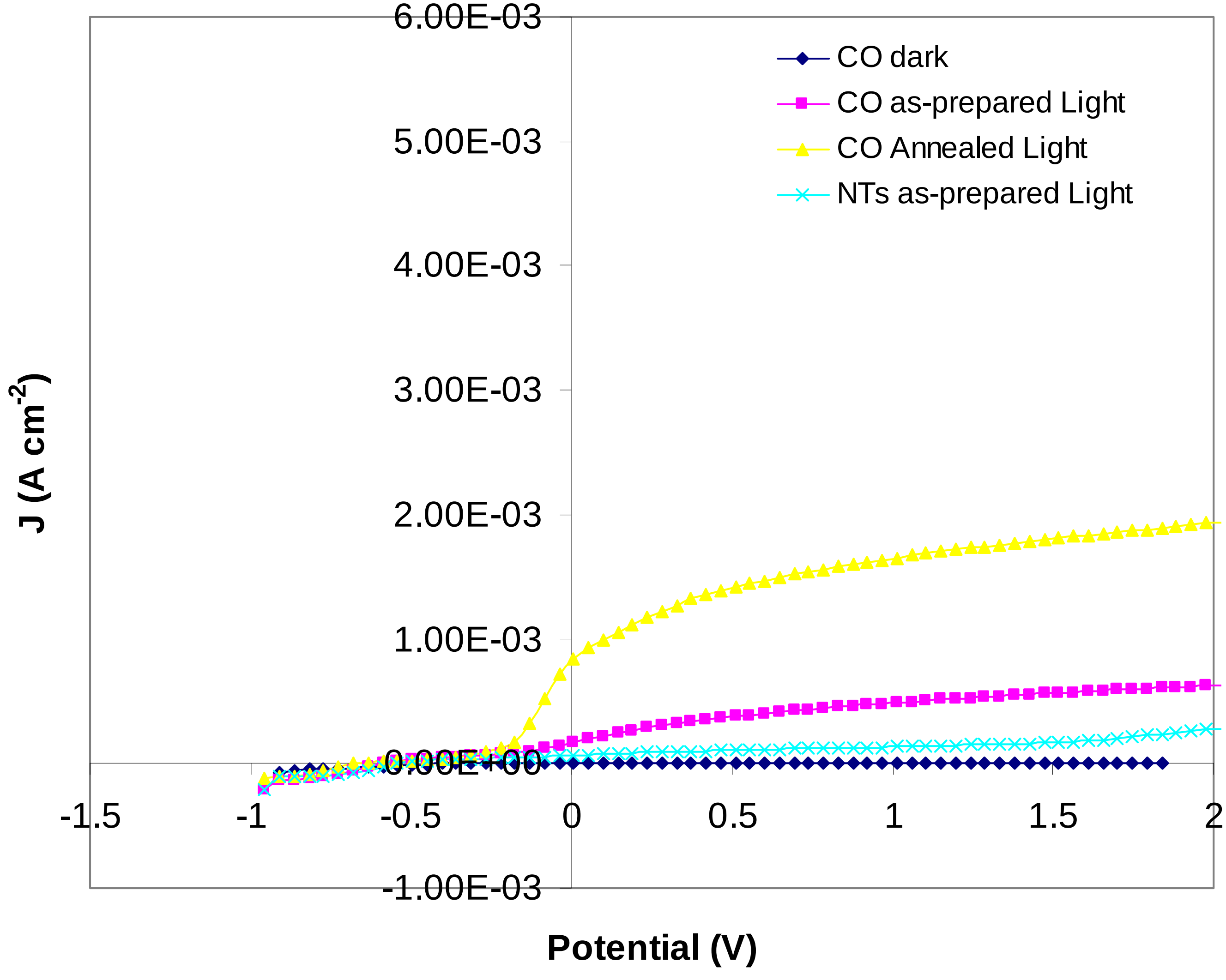
6.00E-03
5.00E-03
4.00E-03
3.00E-03
2.00E-03
1.00E-03
0.00E+00
-1.00E-03
-1.5
-1
-0.5
0
0.5
1
1.5
2
J (A cm-2)
Potential (V)
CO Dark
CO as prepared Light



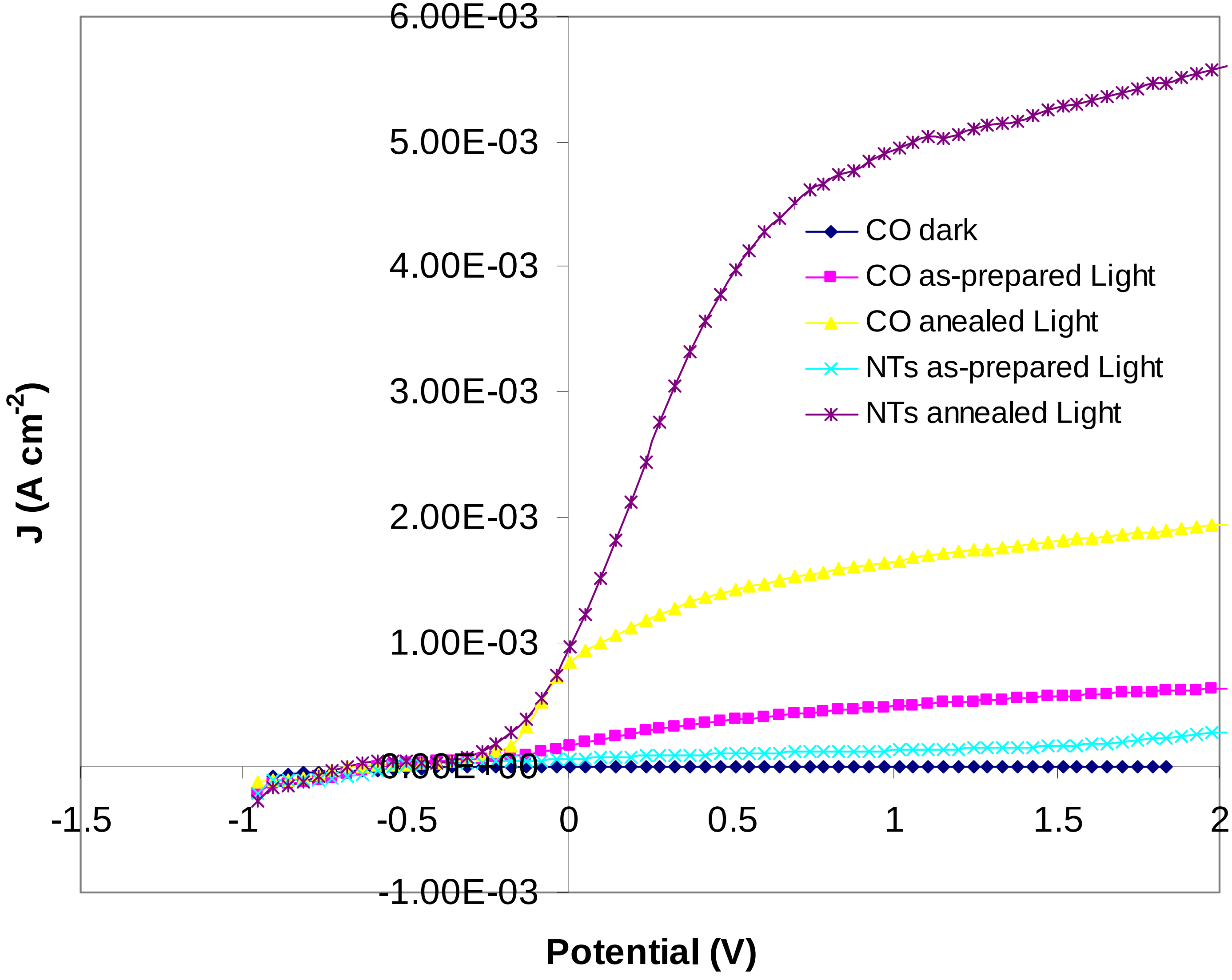
CO dark
CO as-prepared Light
CO Annealed Light
6.00E-03
5.00E-03
4.00E-03
3.00E-03
2.00E-03
1.00E-03
0.00E+00
-1.00E-03
-1.5
-1
-0.5
0
0.5
1
1.5
2
J (A cm-2)
Potential (V)

XRD analysis of compact oxide film pre- and post- anneal

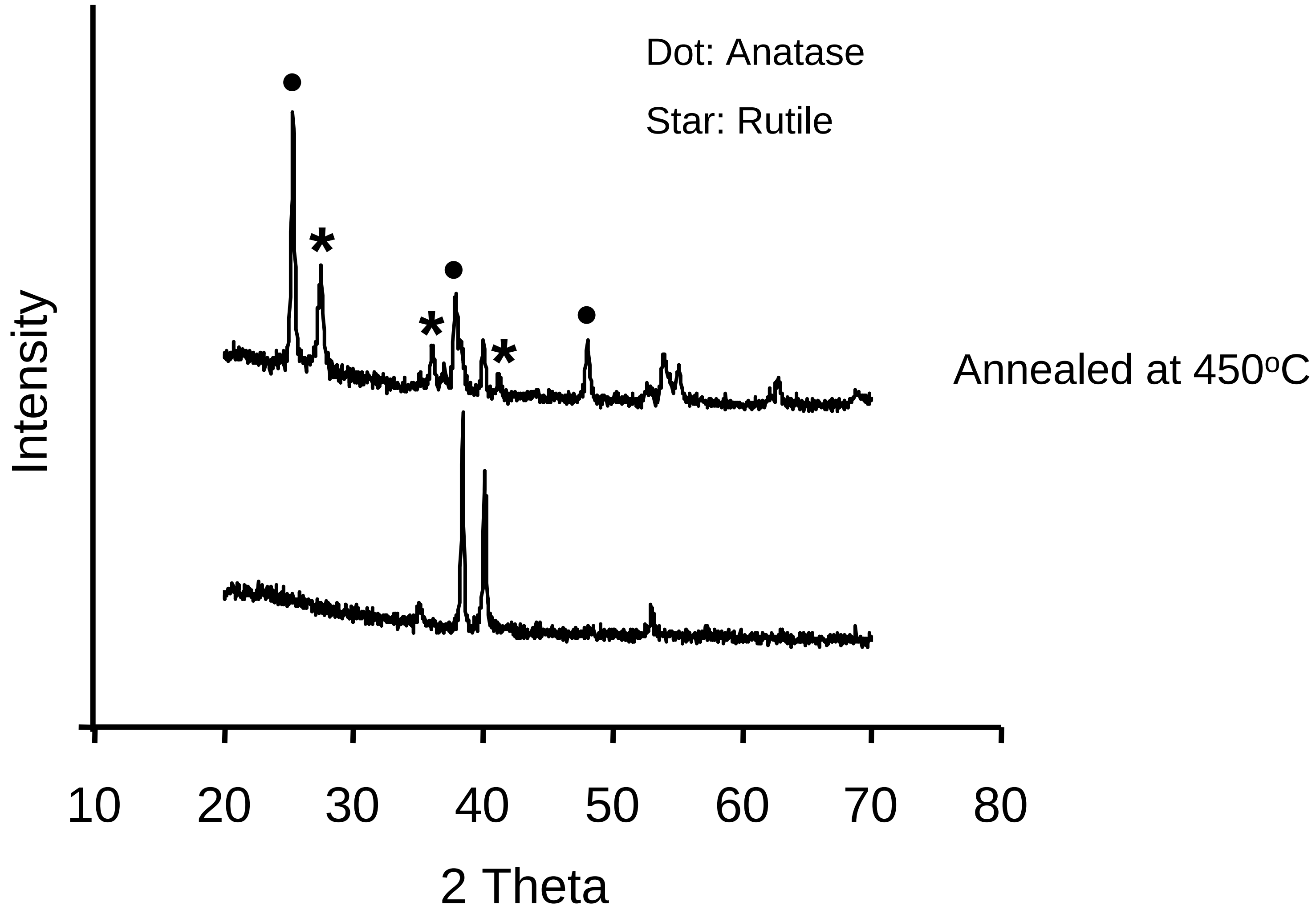


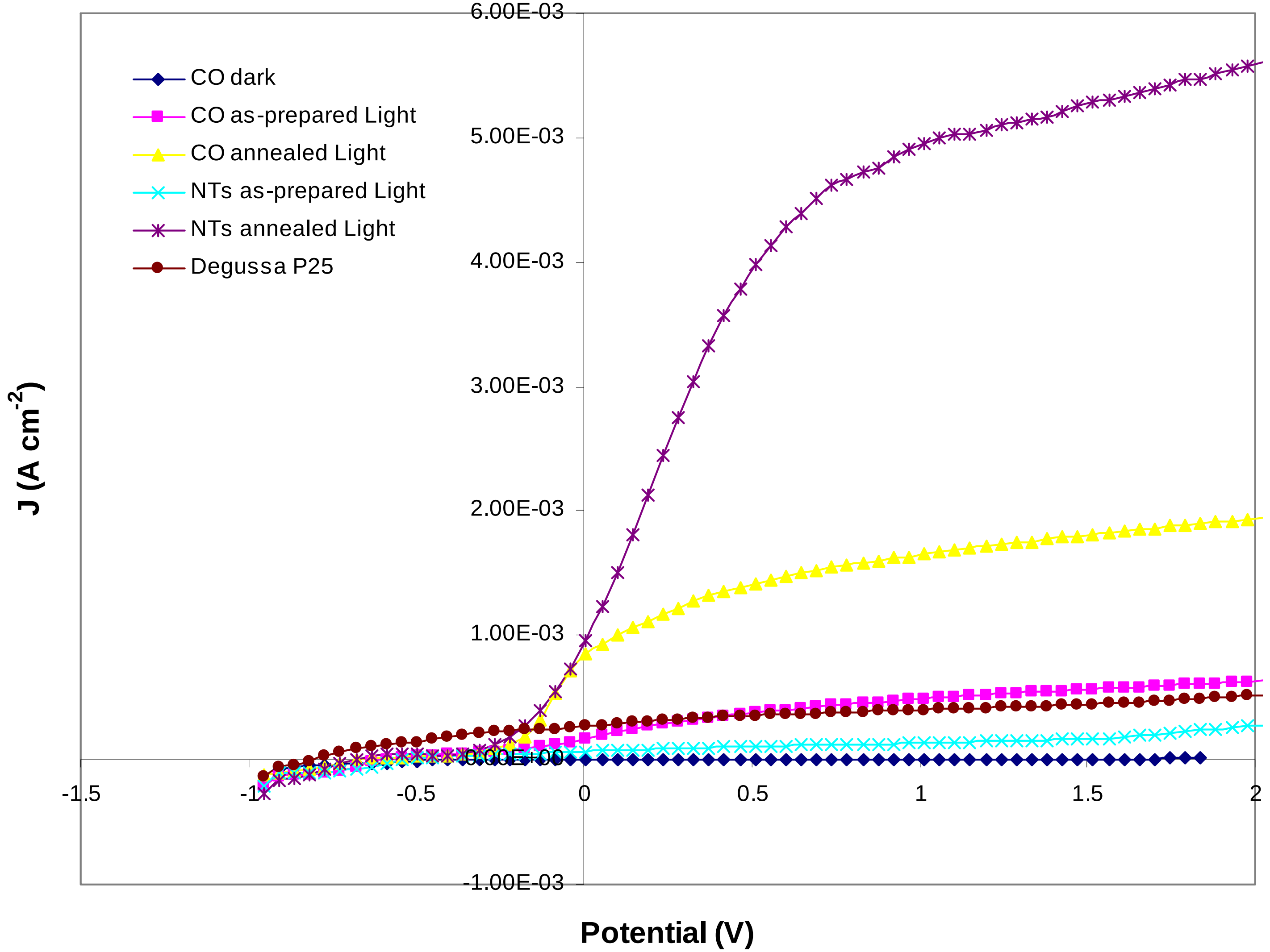


CO dark
CO as-prepared Light
CO Annealed Light
NTs as-prepared Light
6.00E-03
5.00E-03
4.00E-03
3.00E-03
2.00E-03
1.00E-03
0.00E+00
-1.00E-03
-1.5
-1
-0.5
0
0.5
1
1.5
2
J (A cm-2)
Potential (V)


6.00E-03
5.00E-03
4.00E-03
3.00E-03
2.00E-03
1.00E-03
0.00E+00
-1.00E-03
J (A cm-2)
-1.5
-1
-0.5
0
0.5
1
1.5
2
Potential (V)
CO dark
CO as-prepared Light
CO anealed Light
NTs as-prepared Light
NTs annealed Light

XRD analysis of nanotubes pre- and post- anneal

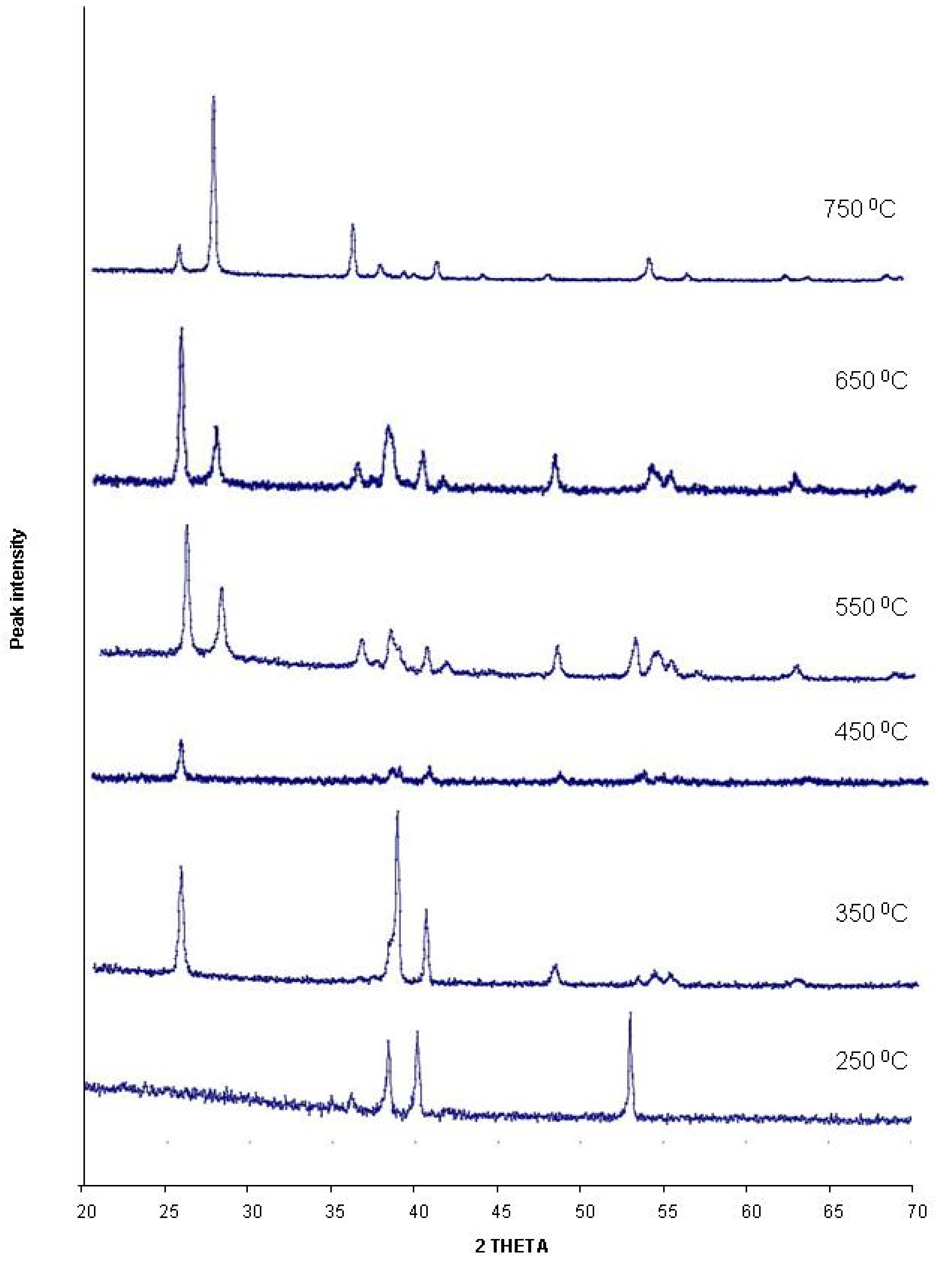


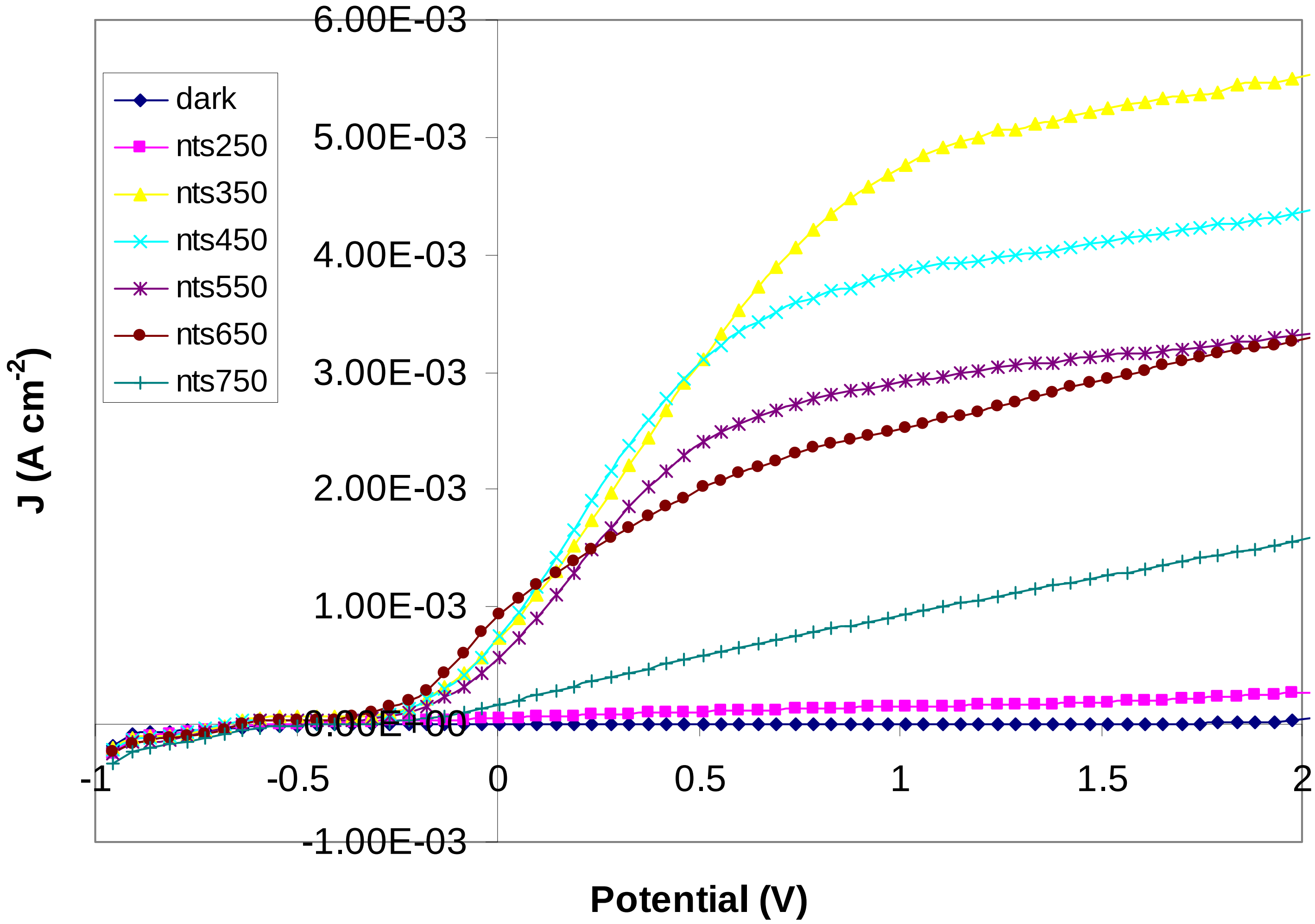


CO dark
CO as-prepared Light
CO annealed Light
NTs as-prepared Light
NTs annealed Light
Degussa P25
6.00E-03
5.00E-03
4.00E-03
3.00E-03
2.00E-03
1.00E-03
0.00E+00
-1.00E-03
-1.5
-1
-0.5
0
0.5
1
1.5
2
J (A cm-2)
Potential (V)

XRD DATA VS ANNEAL TEMP

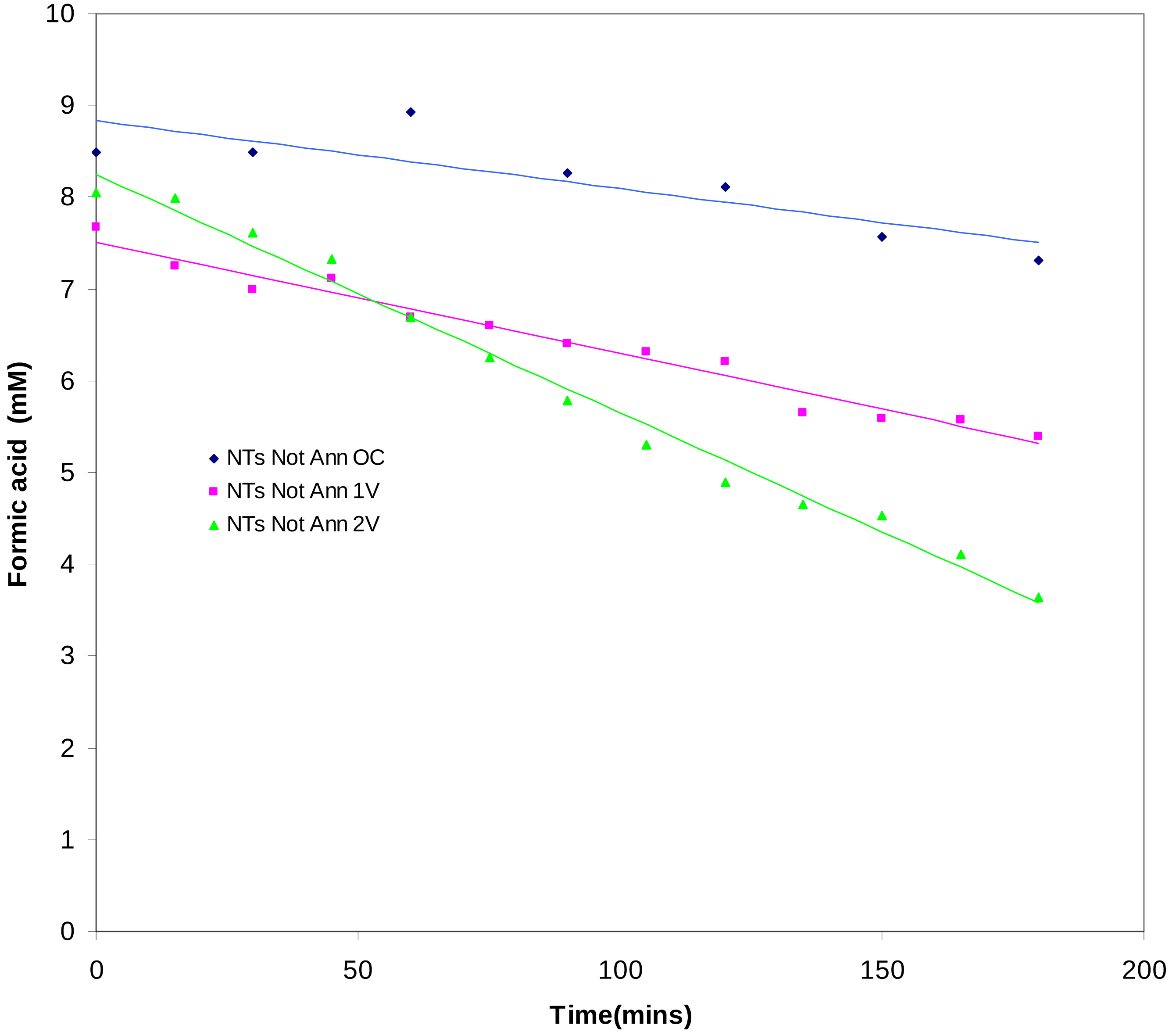
	Ratio Anatase / Rutile	
Annealing Temperature (^0C)	Anatase	Rutile
250	0	0
350	1	0
450	1	0
550	0.63	0.37
650	0.56	0.43
750	0.17	0.83



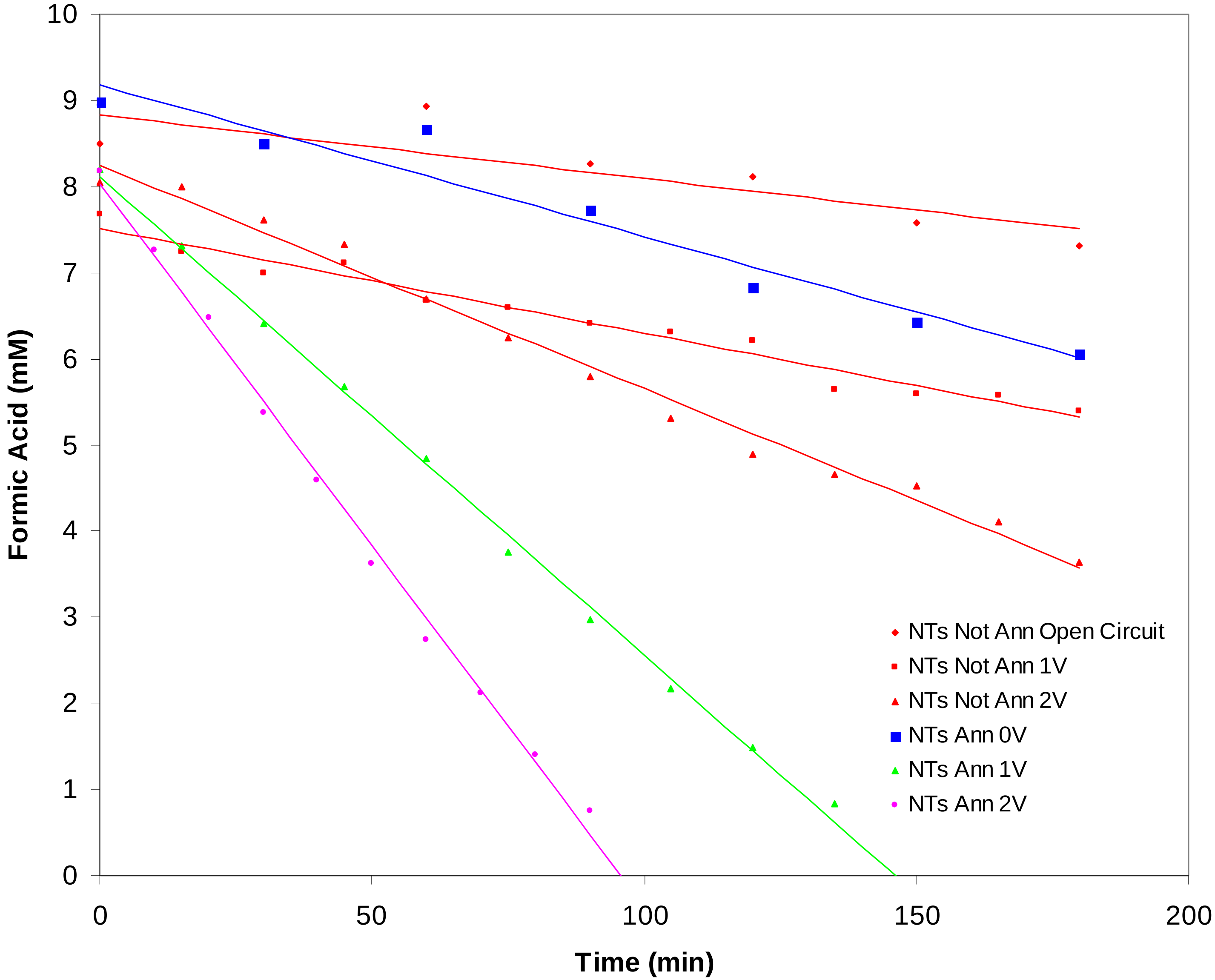


6.00E-03
5.00E-03
4.00E-03
3.00E-03
2.00E-03
1.00E-03
0.00E+00
-1.00E-03
-1
-0.5
0
0.5
1
1.5
2
J (A cm-2)
Potential (V)
dark
nts250
nts350
nts450
nts550
nts650
nts750

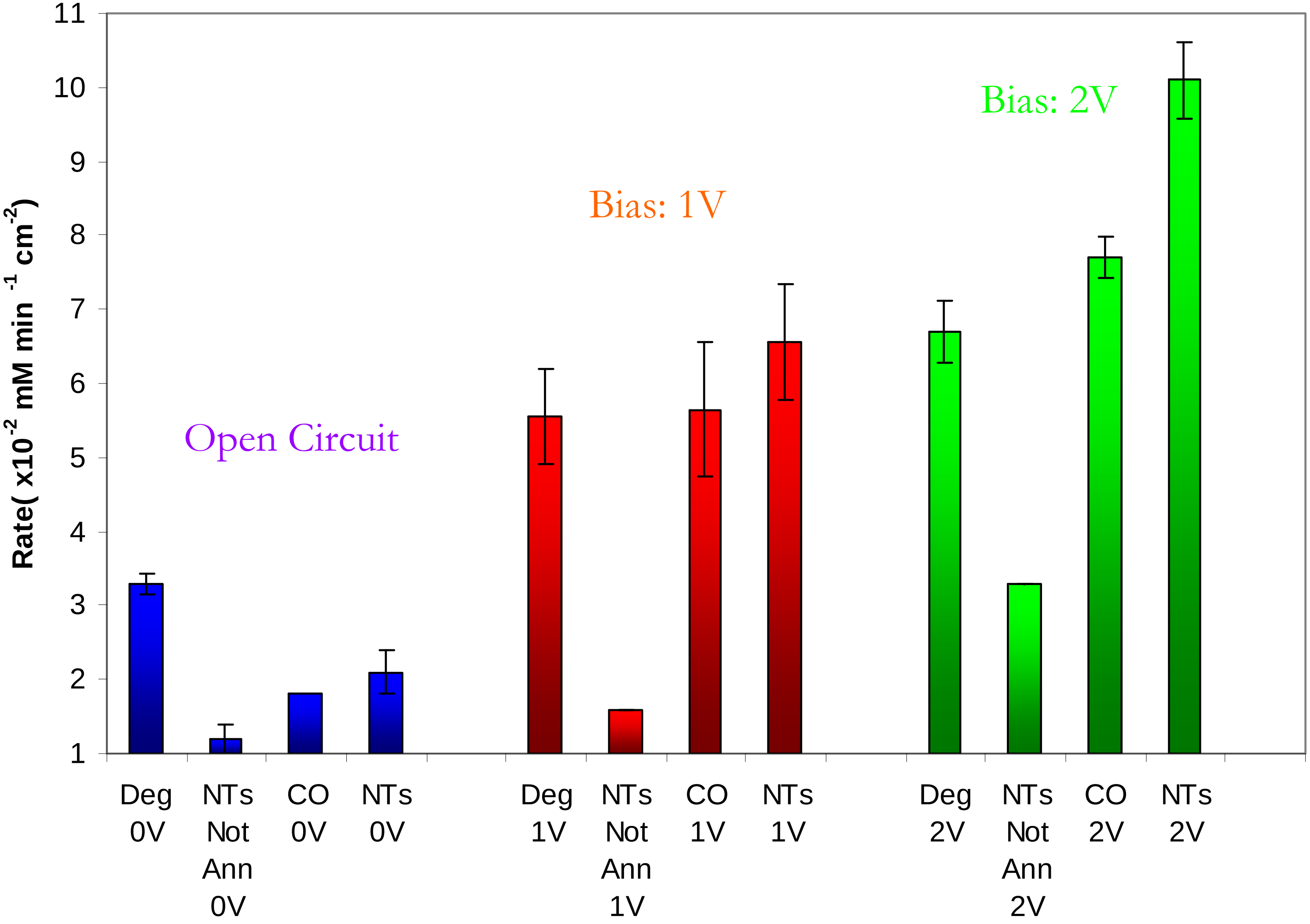
Photocatalytic degradation of pollutants (Formic Acid + Phenol)



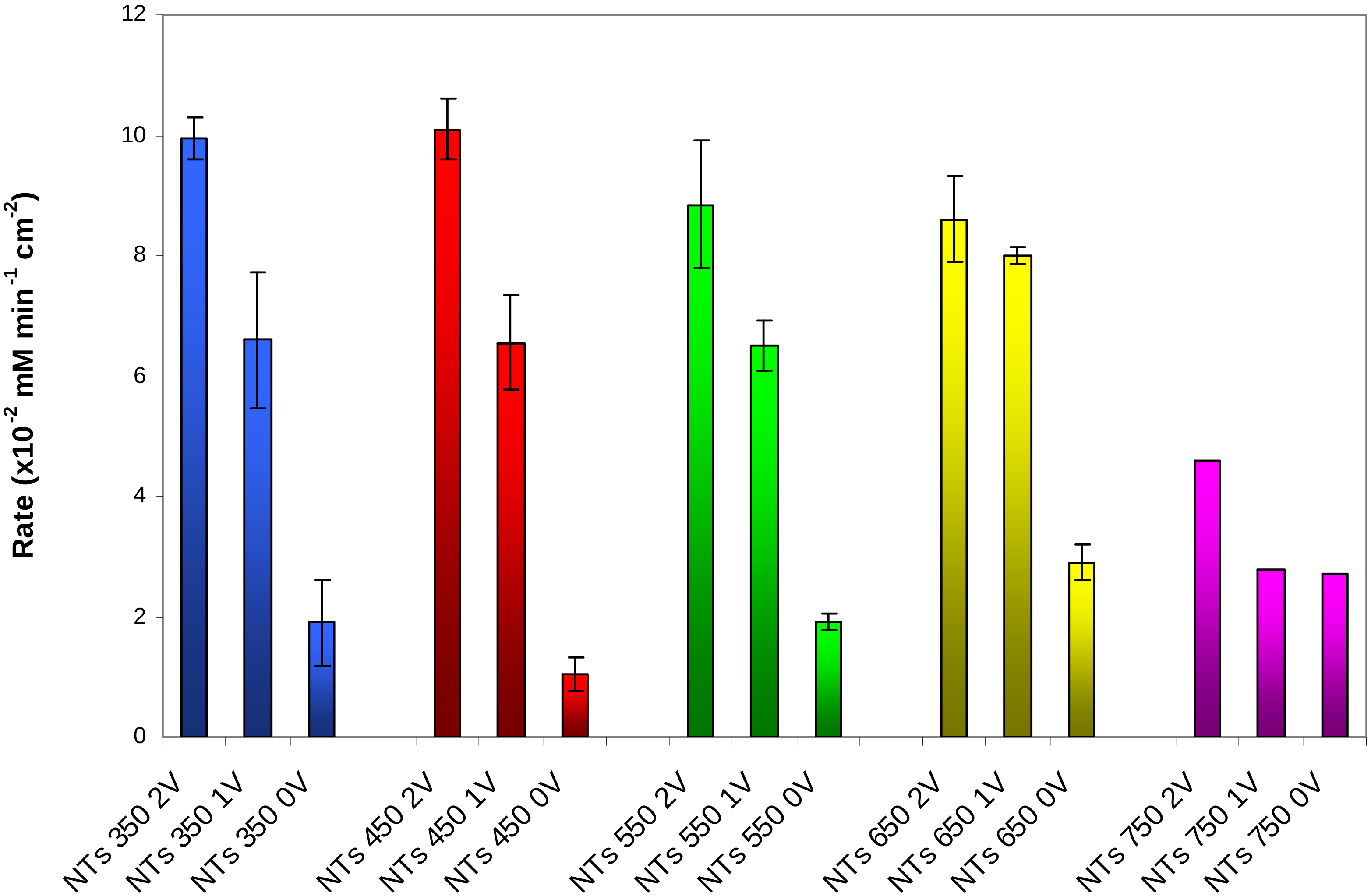
10
9
8
7
6
5
4
3
2
1
0
0
50
100
150
200
Formic acid (mM)
Time(mins)
NTs Not Ann OC
NTs Not Ann 1V
NTs Not Ann 2V



Formic Acid (mM)
Time (min)
0
1
2
3
4
5
6
7
8
9
10
0
50
100
150
200
NTs Not Ann Open Circuit
NTs Not Ann 1V
NTs Not Ann 2V
NTs Ann 0V
NTs Ann 1V
NTs Ann 2V

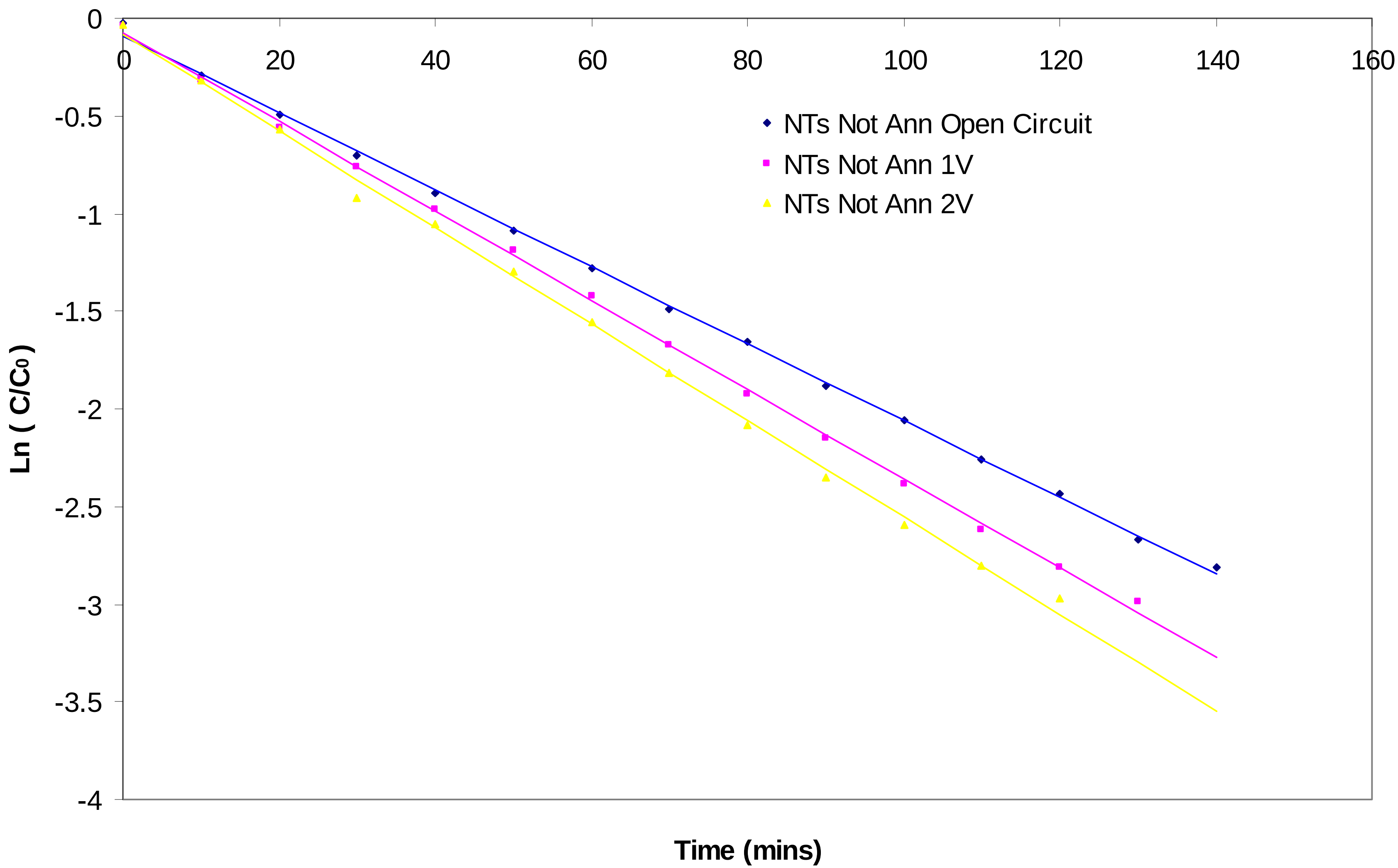


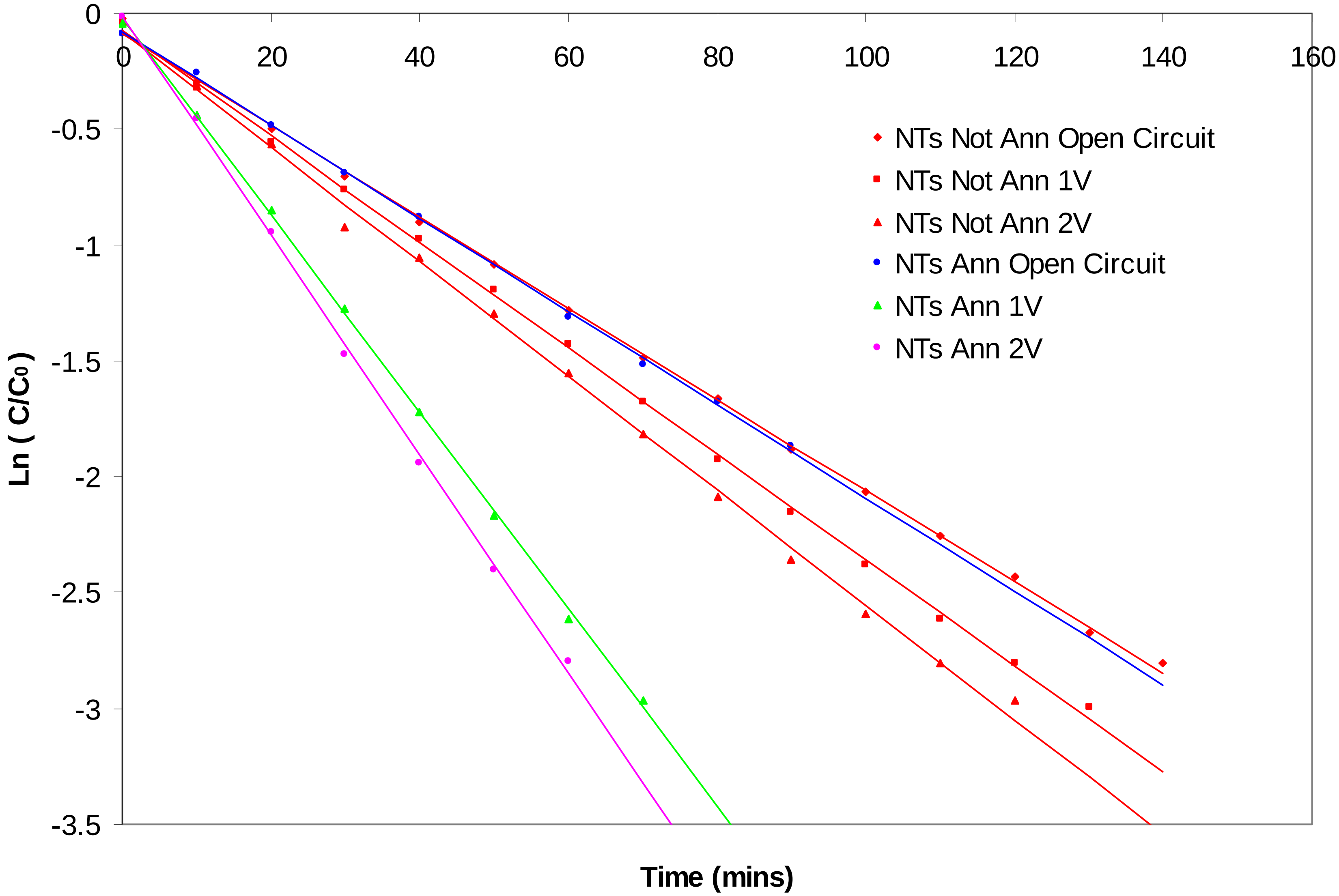
Rate(x10-2 mM min -1 cm-2)
11
10
9
8
7
6
5
4
3
2
1
Open Circuit
Bias: 1V
Bias: 2V
Deg 0V
NTs Not Ann 0V
CO 0V
NTs 0V
Deg 1V
NTs Not Ann 1V
CO 1V
NTs 1V
Deg 2V
NTs Not Ann 2V
CO 2V
NTs 2V



Rate (x10^{-2} mM min^{-1} cm^{-2})
0
2
4
6
8
10
12
NTs 350 2V
NTs 350 1V
NTs 350 0V
NTs 450 2V
NTs 450 1V
NTs 450 0V
NTs 550 2V
NTs 550 1V
NTs 550 0V
NTs 650 2V
NTs 650 1V
NTs 650 0V
NTs 750 2V
NTs 750 1V
NTs 750 0V

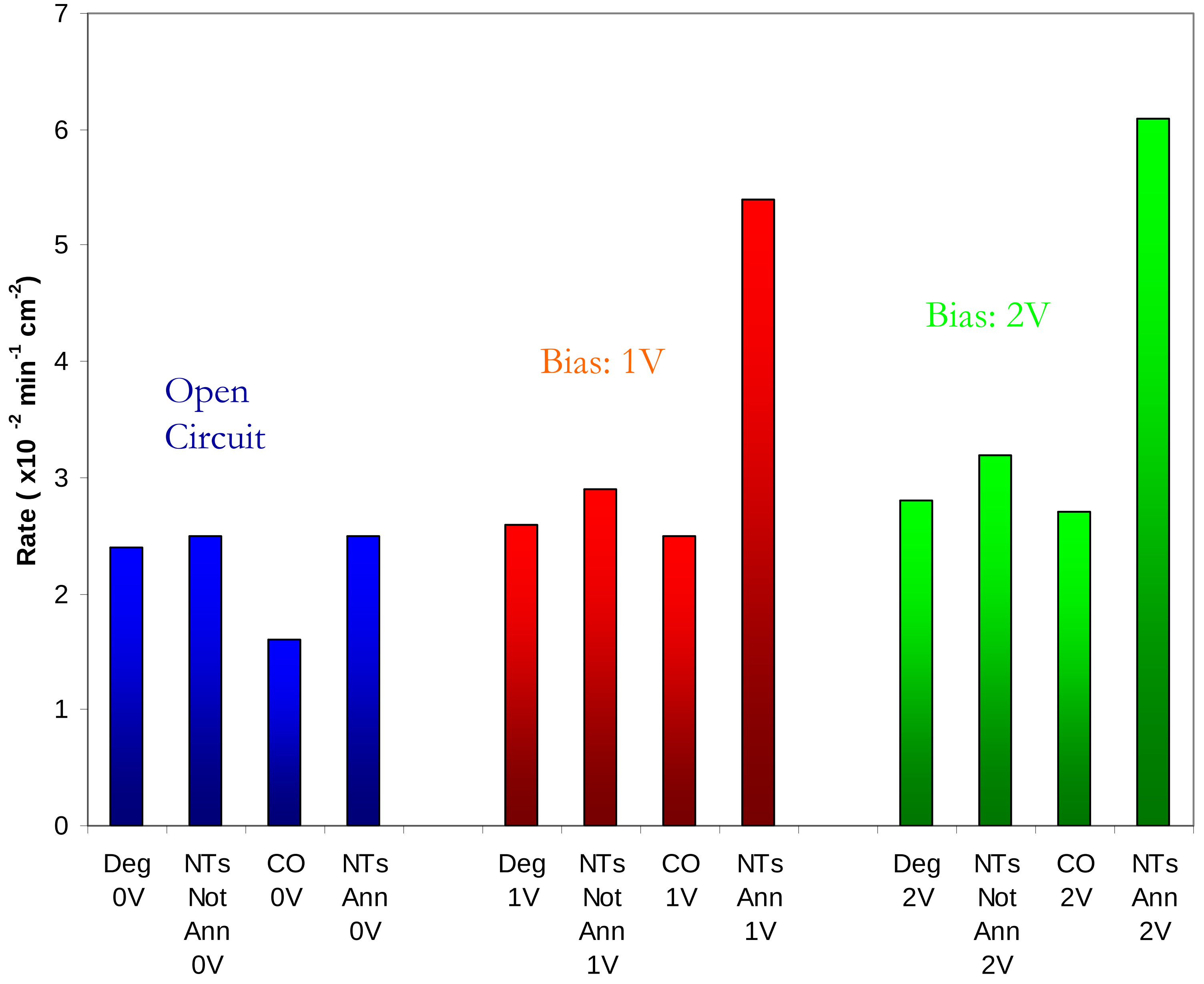
Photocatalytic degradation of phenol



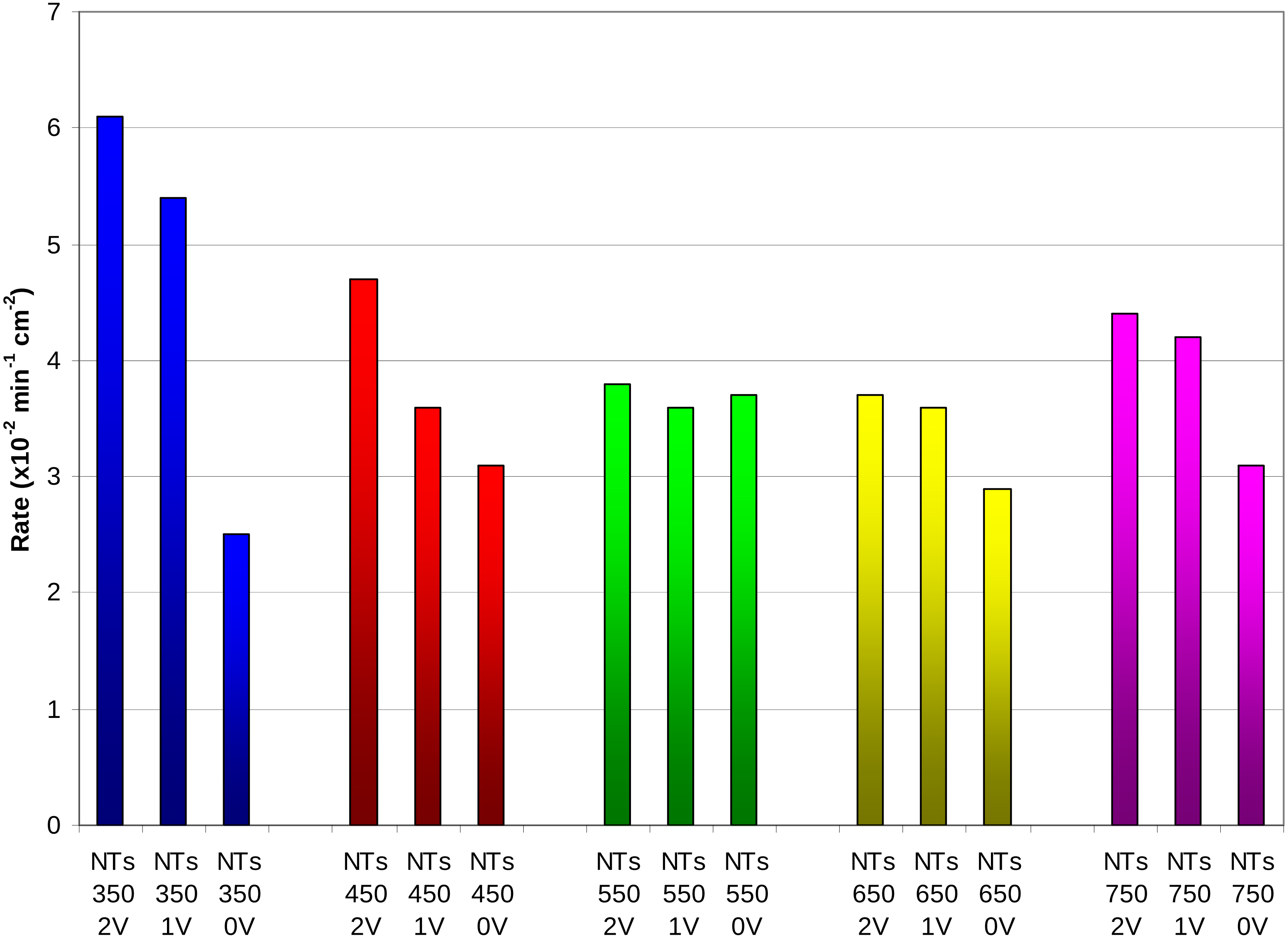


0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
0
20
40
60
80
100
120
140
160
NTs Not Ann Open Circuit
NTs Not Ann 1V
NTs Not Ann 2V
NTs Ann Open Circuit
NTs Ann 1V
NTs Ann 2V
Ln (C/C0)
Time (mins)

Phenol



Rate (x10 -2 min-1 cm-2)
0
1
2
3
4
5
6
7
Open Circuit
Bias: 1V
Bias: 2V
Deg 0V
NTs Not Ann 0V
CO 0V
NTs Ann 0V
Deg 1V
NTs Not Ann 1V
CO 1V
NTs Ann 1V
Deg 2V
NTs Not Ann 2V
CO 2V
NTs Ann 2V



Rate (x10^{-2} min^{-1} cm^{-2})
0
1
2
3
4
5
6
7
NTs 350 2V
NTs 350 1V
NTs 350 0V
NTs 450 2V
NTs 450 1V
NTs 450 0V
NTs 550 2V
NTs 550 1V
NTs 550 0V
NTs 650 2V
NTs 650 1V
NTs 650 0V
NTs 750 2V
NTs 750 1V
NTs 750 0V

Electron Transport

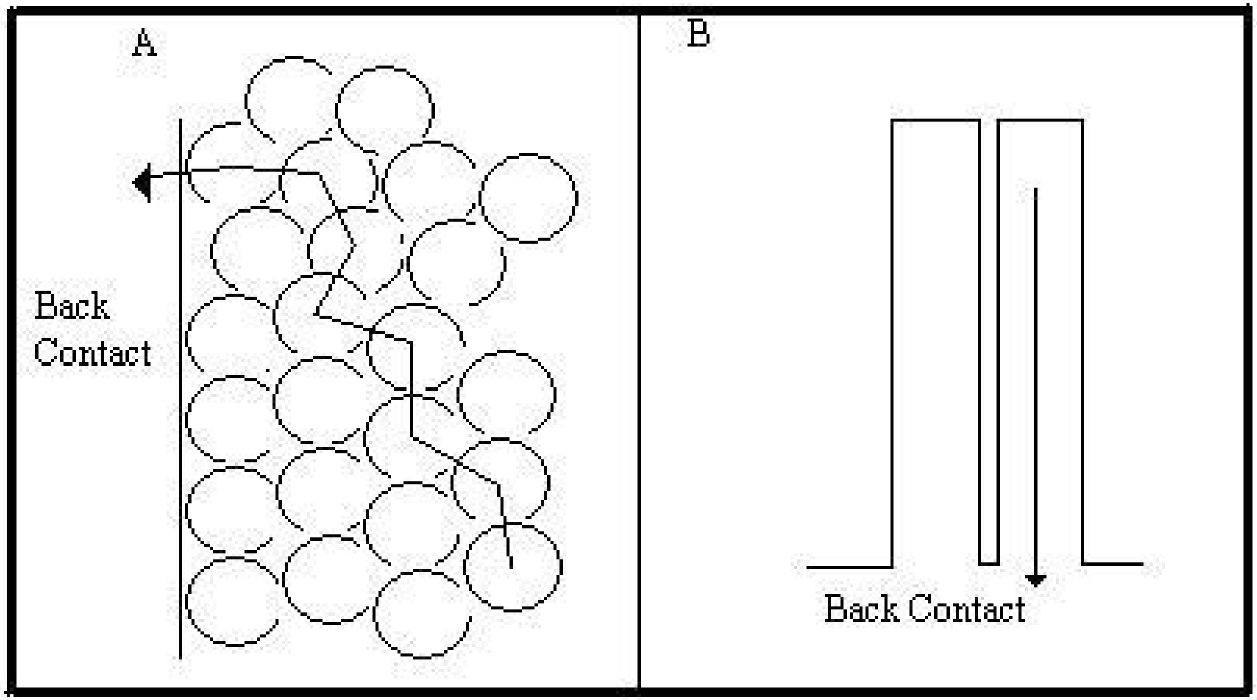


Figure: Visual representation of electron transport in (a) degussa P25 film and (b) nanotubes

De Jongh & Vanmaekelbergh, Physical review letters, v77 , 1996 , 3427 - 3430

Summary

Self-organised titania nanotube arrays can be produced by anodising Ti metal in the presence of fluoride.

The as-prepared NTs are amorphous and have a relatively poor photoelectrochemical response

Annealing the NTs results in a dramatically improved photocurrent response

Annealed NTs show better photocatalytic efficiency when compared to P25 films under applied bias

Acknowledgements

Dept of Employment and Learning Northern Ireland

Technical staff of SE, University of Ulster

Degussa for supplying free sample of P25