PEC sensing of glucose using one dimensional TiO_2 nanostructure modified by two dimensional material

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Dr N. Naseri

Outline

- Introduction
- TNAs (TiO_2 Nanotube Arrays) Preparation
- TNAs Characterization
- PEC Performances & Glucose Detection
- Modification by 2D Material
- Mechanism of Sensing Process
- TNW (Branched TiO_2 Nanowire) Preparation
- TNW Characterization
- PEC Performances & Glucose Detection
- Conclusion

Concerns about Diabetes

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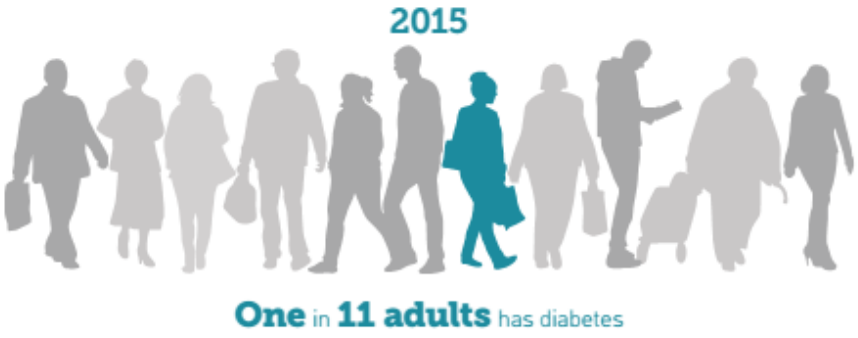
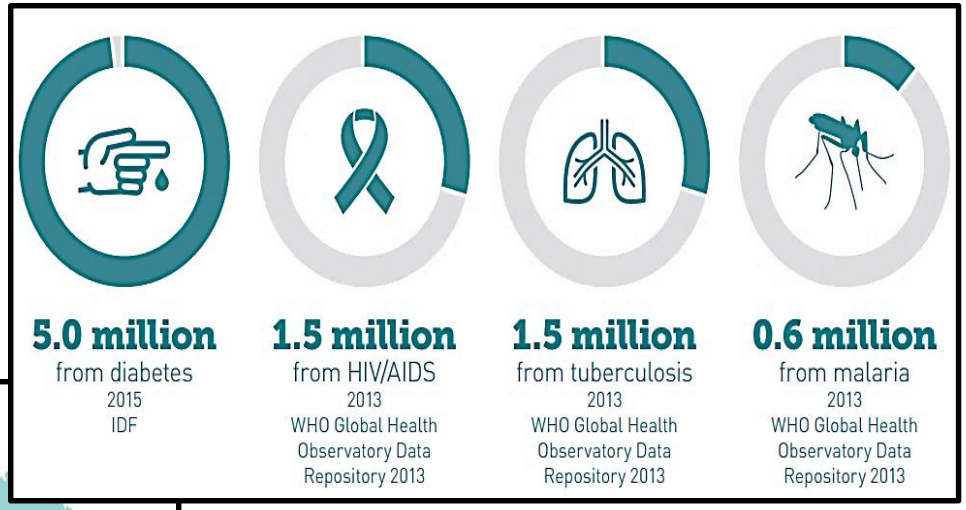
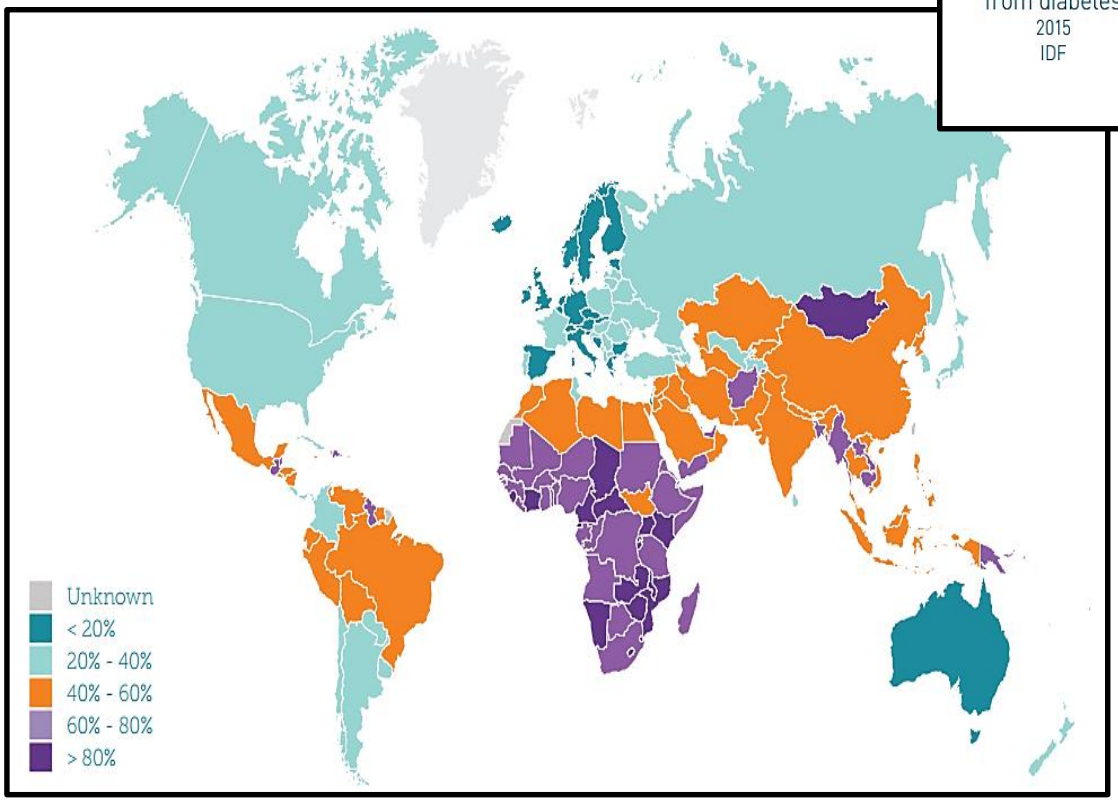
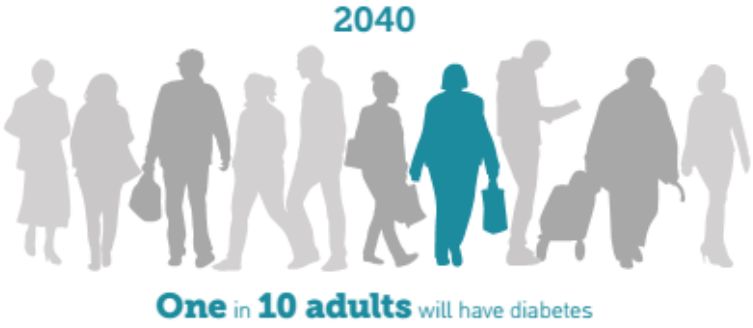




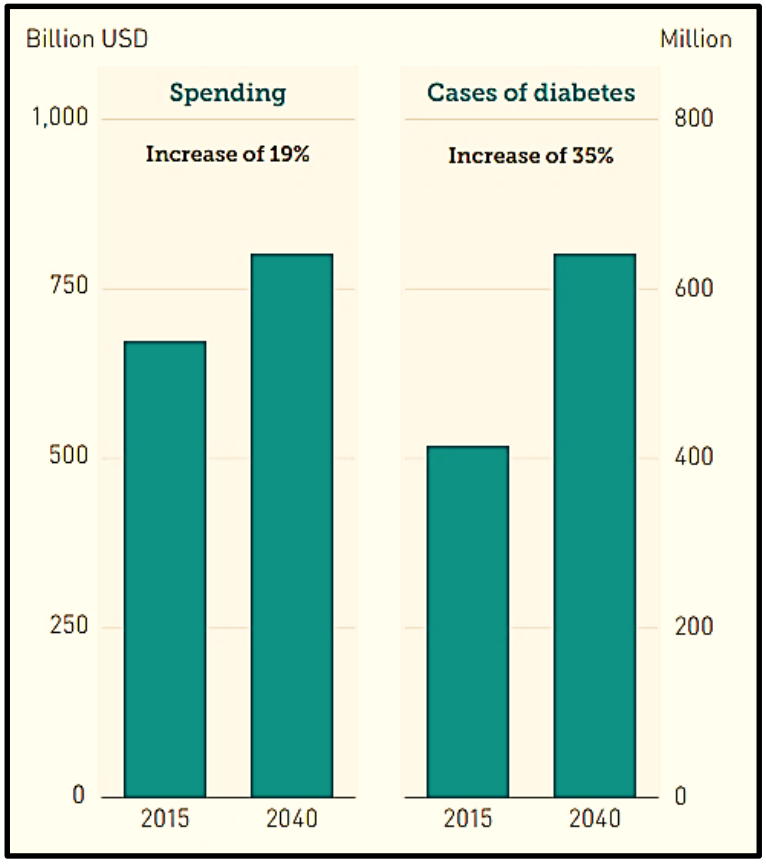


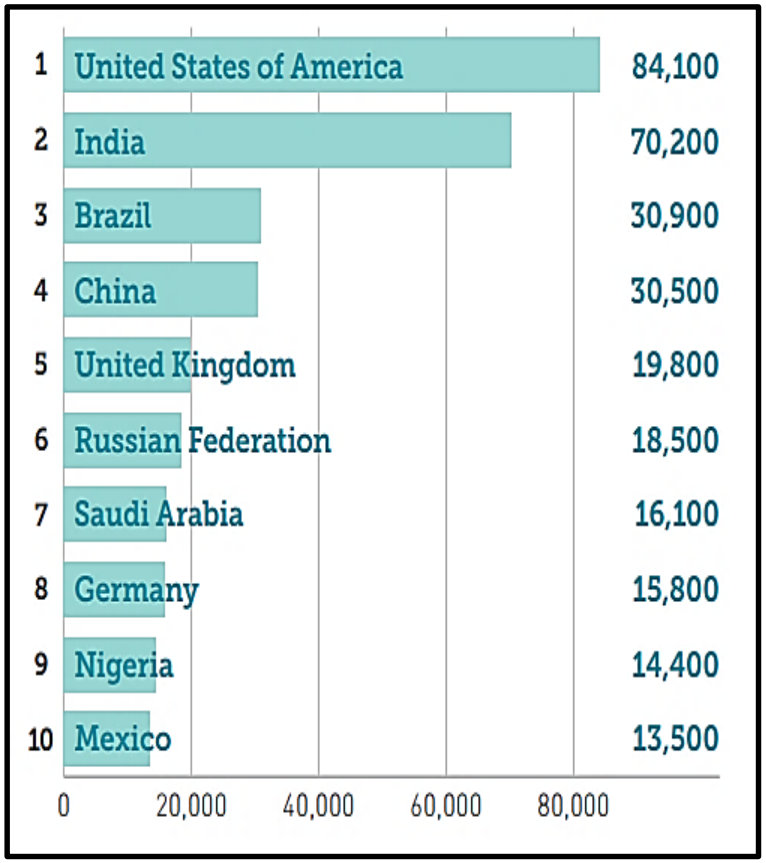


World Health Organization (WHO)

Concerns about Diabetes

Financial Cost





Diabetes in Children

World Health Organization (WHO)
International Diabetes Federation (IDF)

Action on Diabetes

Department of Physics

Prevention → **Management** → **Control** → **Treatment**

www.heart.org
www.stickergenius.com
www.betavib.com
www.idmouse.com
www. stocklogos.com

Glucose Sensing

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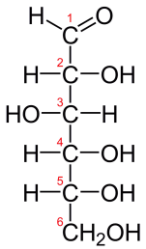
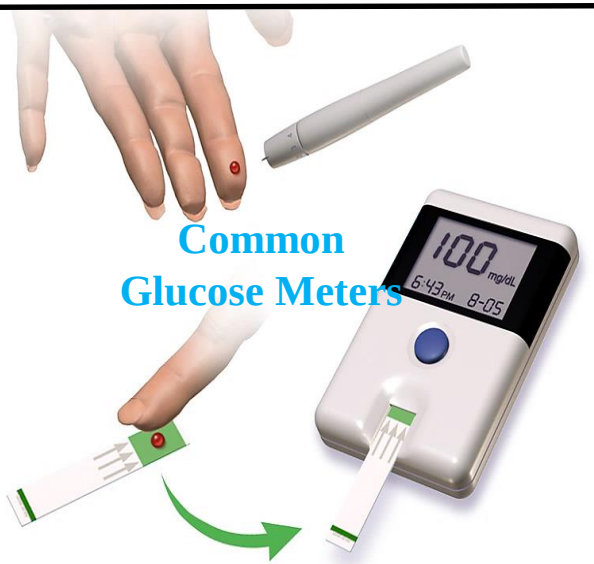
History



Glucose

First Prepared by Lyon and Clark in 1962

$$Glucose + Oxygen \xrightarrow{GOx} Gluconic\ Acid + Hydrogen\ Peroxide$$



https://en.wikipedia.org/wiki/Glucose_meter

Date	*Event*
1962	First glucose enzyme electrode
1973	Glucose enzyme electrode based on peroxide detection
1975	Launch of the first commercial glucose sensor system
1982	Demonstration of in vivo glucose monitoring
1984	Development of ferrocene mediators
1987	Launch of the first personal glucose meter
1987	Electrical wiring of enzymes
1999	Launch of a commercial in vivo glucose sensor
2000	Introduction of a wearable noninvasive glucose monitor

J. Wang, Electroanalysis, 2001

Glucose Sensing:

not only for diabetes but

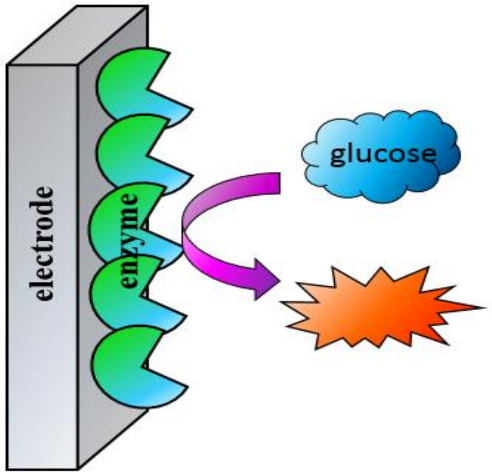
also for food industry

and researches

Glucose Sensing

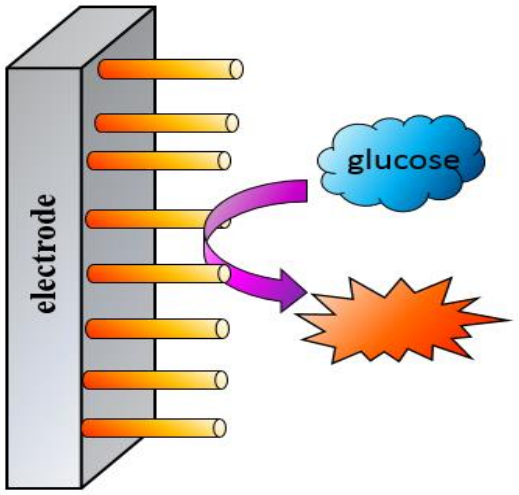
Enzymatic Sensors

- Using Enzyme as Catalysis
- Acceptable Selectivity & Sensitivity
  - Depending on Temperature, pH, Humidity, …
  - Low Stability
  - Low Reproducibility



Non Enzymatic Sensors

- Using Nanostructured Materials
- Good Sensitivity
- High Stability & Reproducibility
- Low Detection Limit
  - Low Selectivity



glucose sensing

Non Enzymatic Sensors

Optical Sensors

- Using light
- High Signal to noise
- High Sensitivity

- Depending on Temperature, ...
- Interfered by other Samples
- Low Selectivity

Electrochemical Sensors

- Using Interaction with Glucose
- Low Detection Limit

- Non-biocompatible
- High Cost
- Low Selectivity

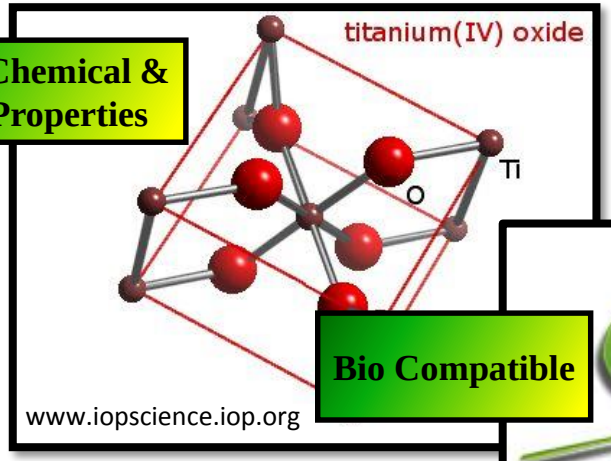
PEC Sensors

- Using Light & Interaction
- Low Cost
- Simple Method
- High Sensitivity

- Low Selectivity

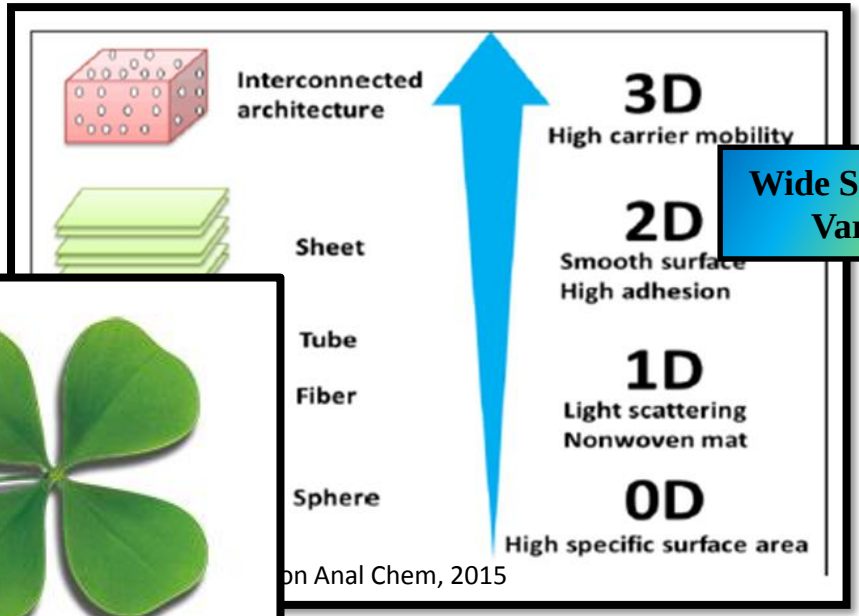
Why TiO_2 material for Sensing?

Exclusive Chemical & Physical Properties



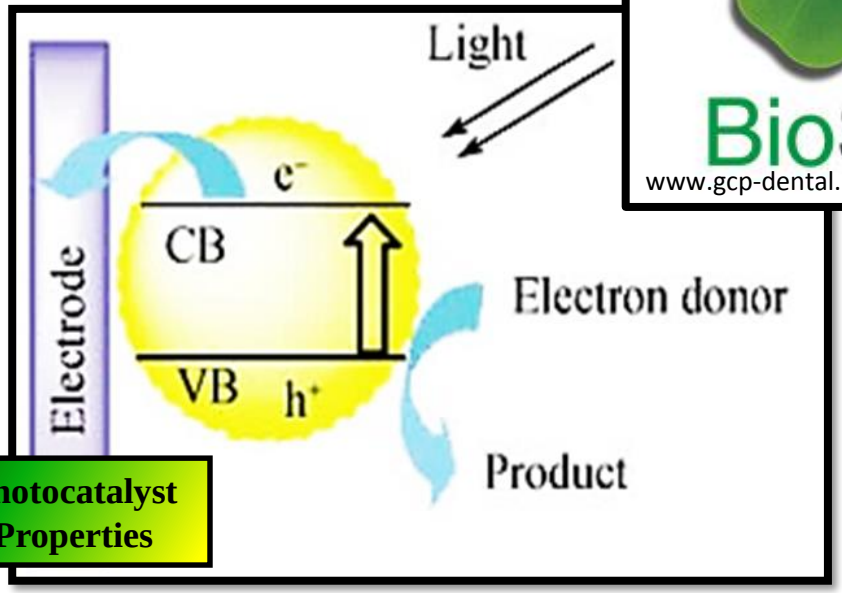
Bio Compatible

Wide Structure Variety



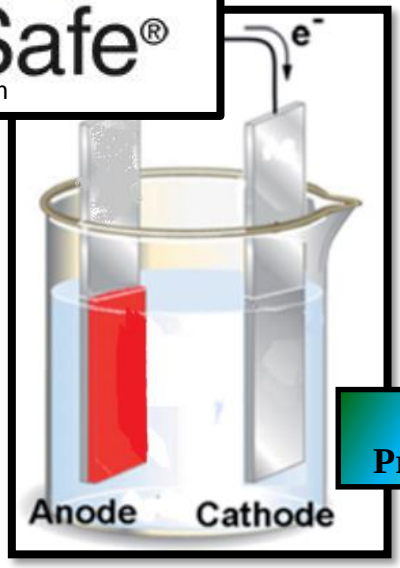
on Anal Chem, 2015

Photocatalyst Properties



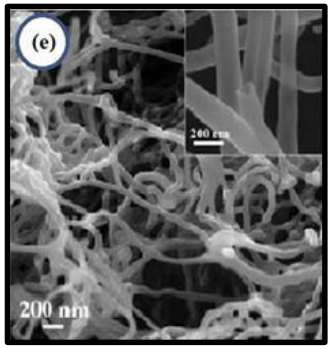
K. Huo et al, RSC Advances, 2014

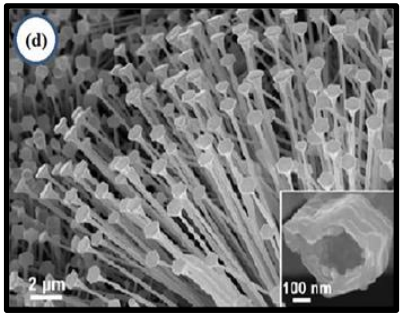
Simple Preparation

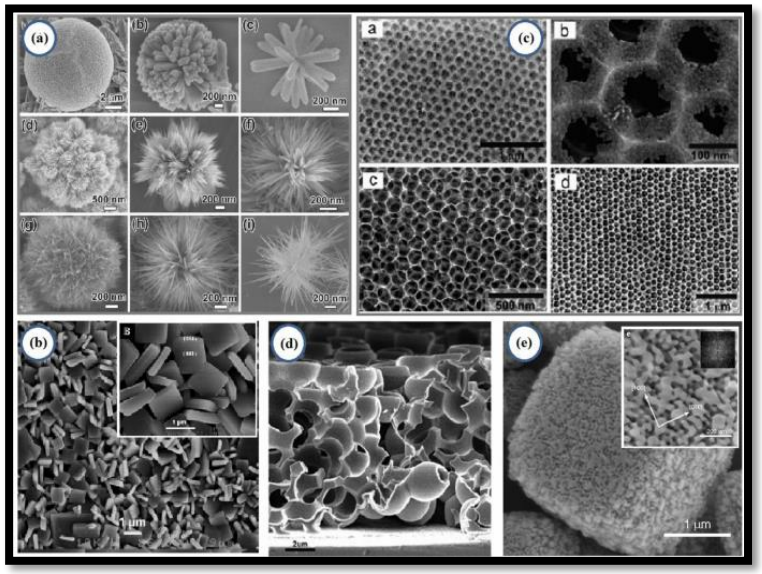


Low Cost

Why TiO_2 Nanostructure for Sensing?

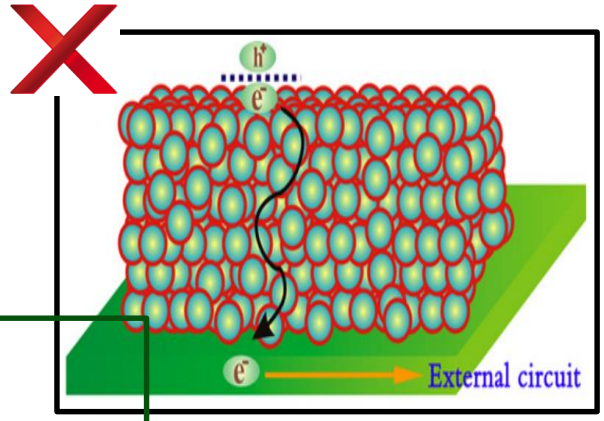


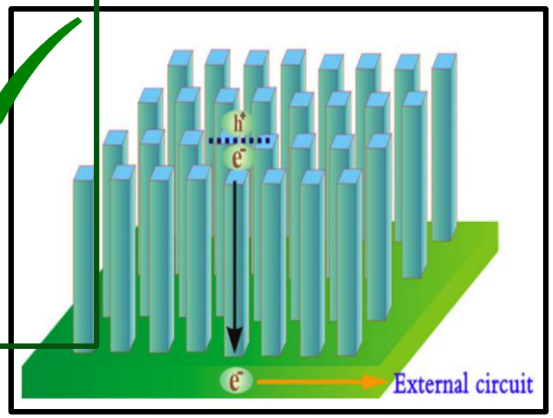




J. Bai et al., Chem. Rev., 2014

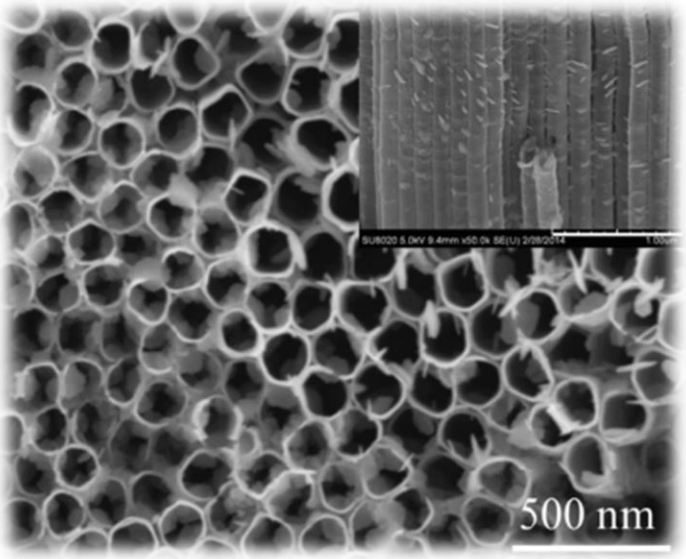
- ✓ Very small size
- ✓ High surface to volume ratio
- ✓ Light trapping
- ✓ Good charge separation
- ✓ Good charge transport





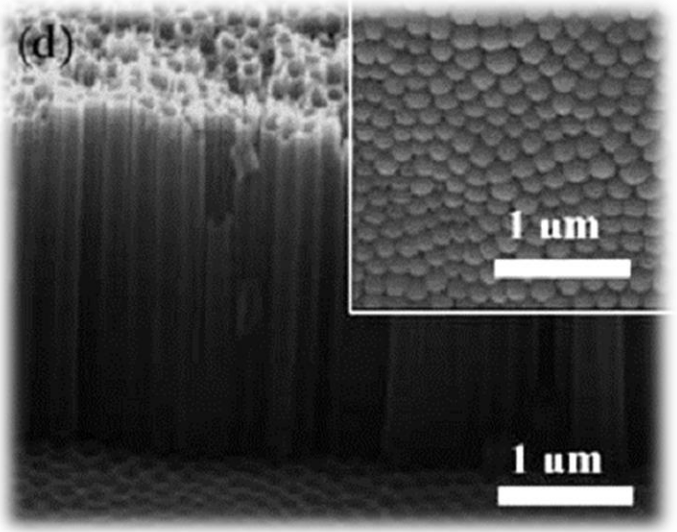
Q. Mua et al, Journal of Hazardous Materials, 2011

Why TiO_2 Nanotube for Sensing?



Y. Pang et al., Dalton Trans., 2015

- ✓ Simple Preparation
- ✓ Adjustable Length, Wall thickness & Diameter
- ✓ Vertically Aligned
- ✓ High Surface Area
- ✓ Open mouth
- ✓ High Stability

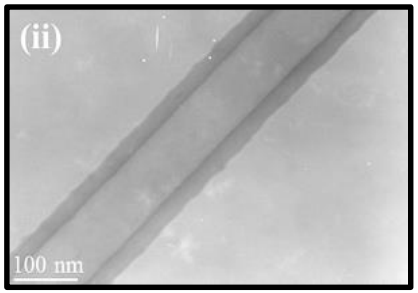


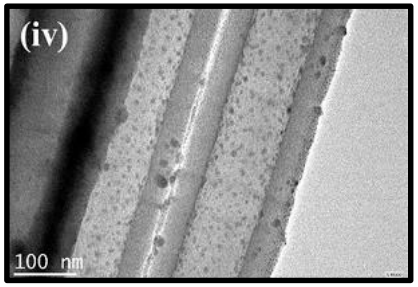
Y. Pang et al., Dalton Trans., 2015

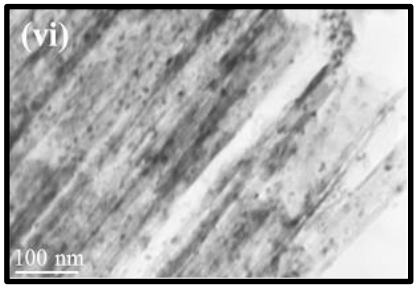
Literature Review

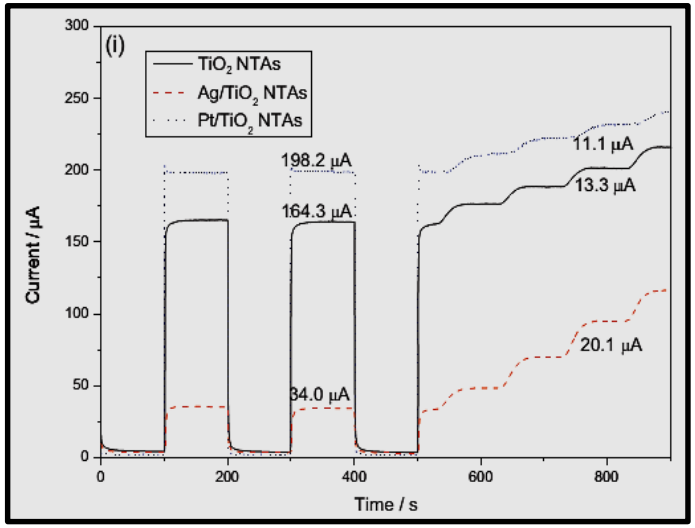
Photoelectrochemical Performances and Potential Applications of TiO_2 Nanotube Arrays Modified with Ag and Pt Nanoparticles

G. Xu et al. Electrochimica Acta. 2014

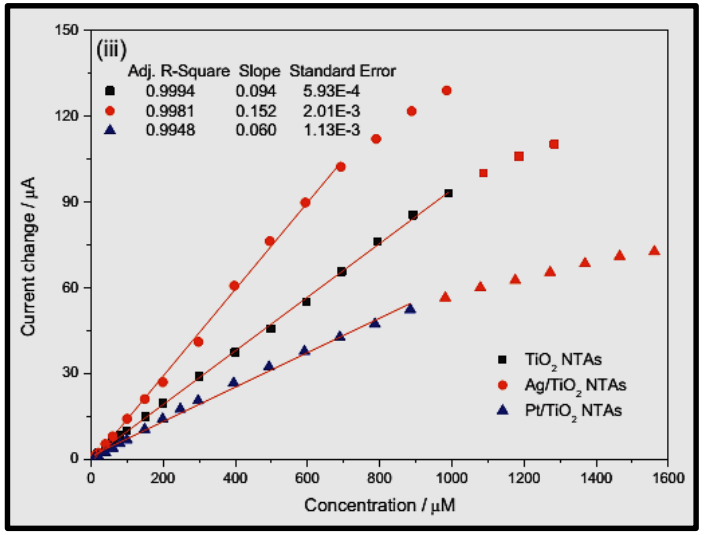








60% Improvement



G. Xu et al. Electrochimica Acta. 2014

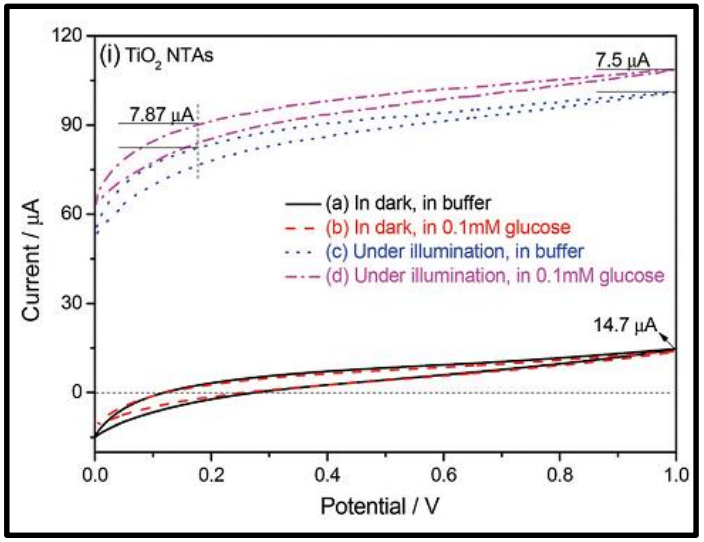
Literature Review

CrossMark click for updates

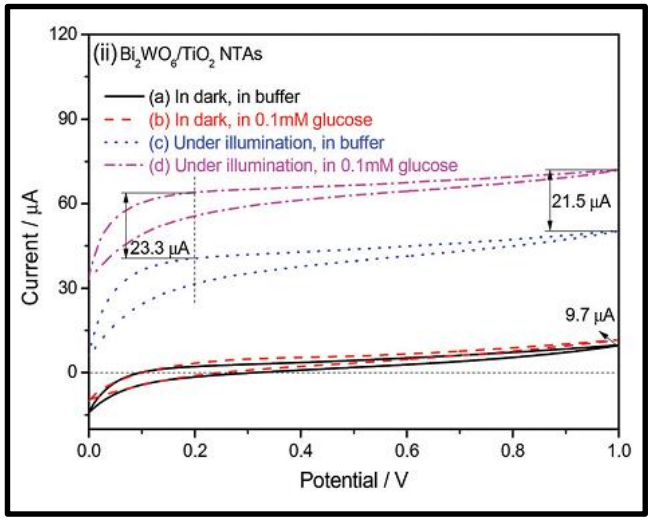
Cite this: *Dalton Trans.*, 2015, **44**, 17784

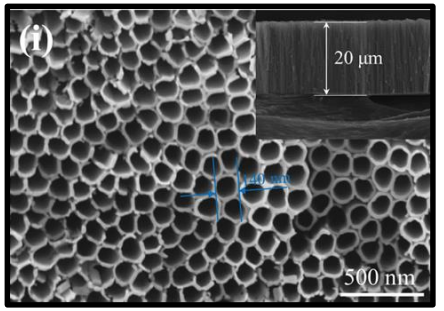
Photoelectrochemical properties and the detection mechanism of Bi_2WO_6 nanosheet modified TiO_2 nanotube arrays

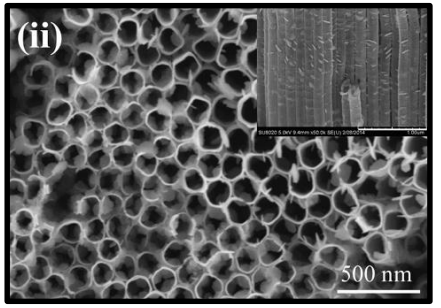
Y. Pang et al. Dalton Trans., 2015



40% Improvement







Y. Pang et al. Dalton Trans., 2015

Our Work

Department of Physics

Step 1 **Optimizing**

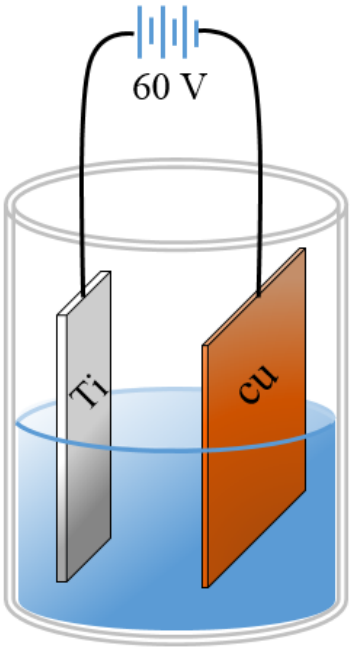
The Length and Annealing Ambient of TNAs toward Glucose Sensing

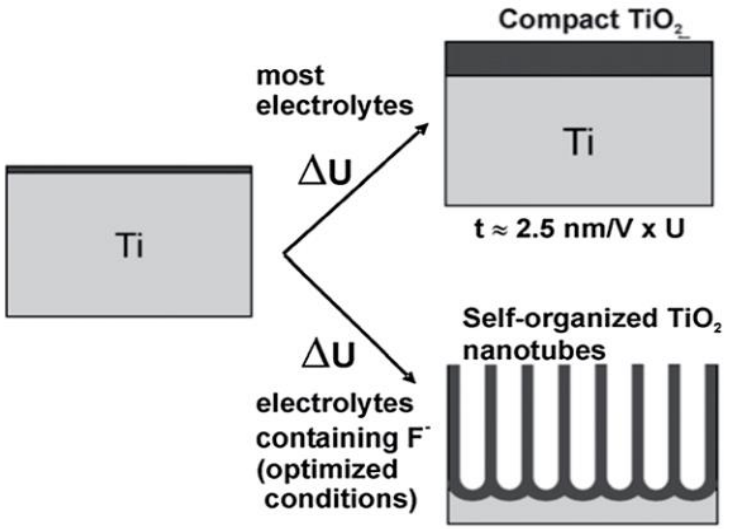
Step 2 **Modifying**

Optimum TNAs by 2D Material to Improve Glucose Sensing

TNT Preparation

- ✓ **Electrolyte:** → Water, EG, NH_4F
- ✓ **Anodization Time:** → 30, 60, 120 and 240 min
- ✓ **Removing Top Layer:** → 30s Sonicating in Water
- ✓ **Heating:** → 520 °C for 6 h in Air & 400 °C in Ar/H_2

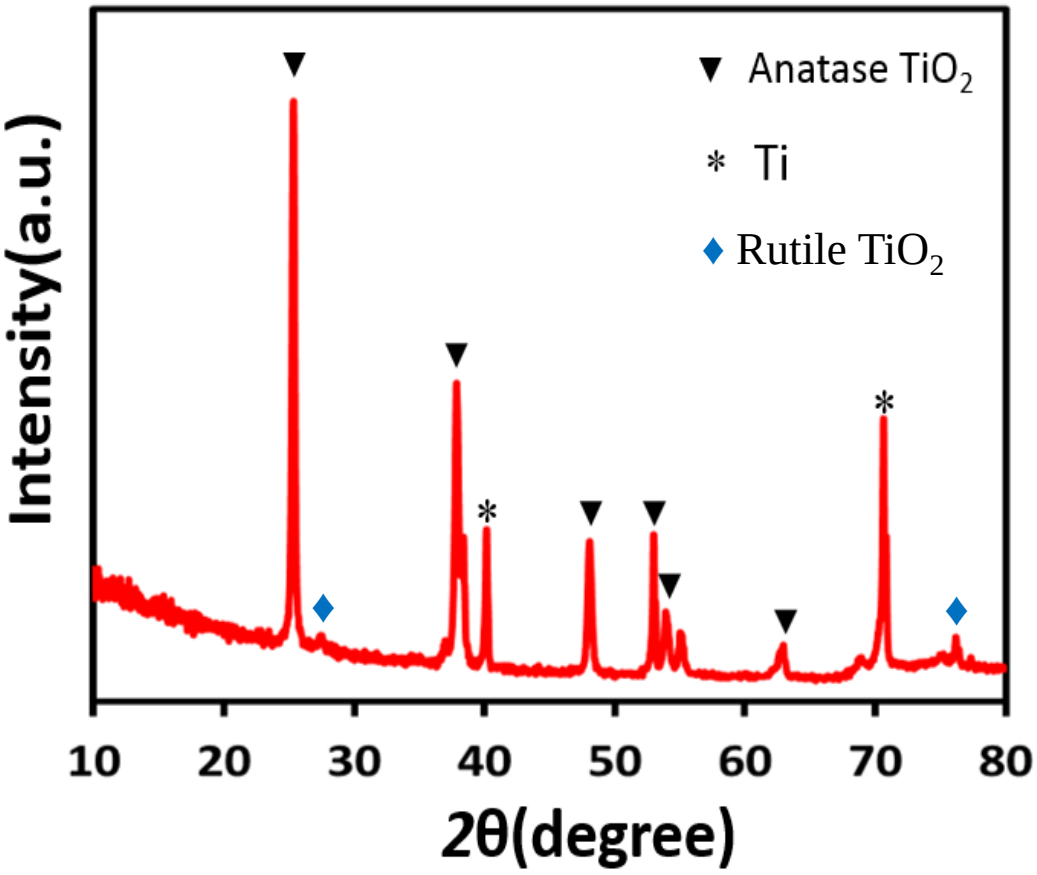




Anodization Method

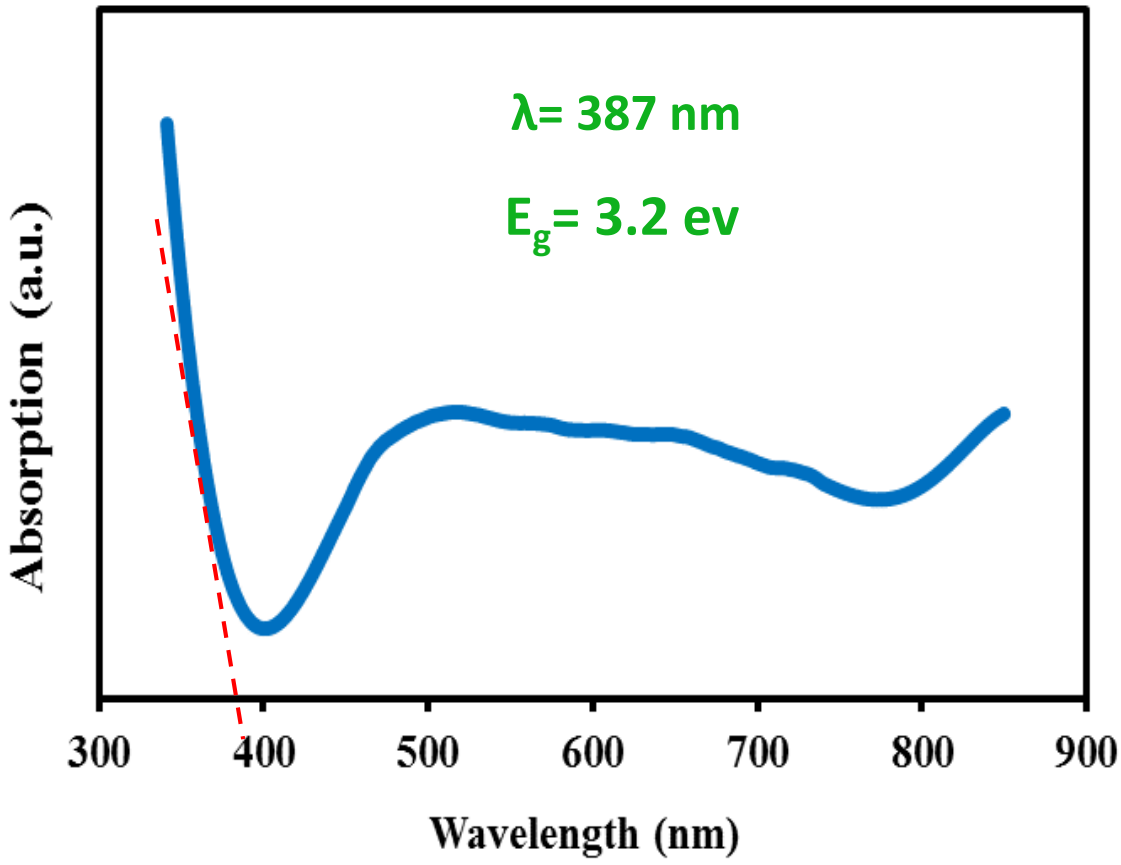
K. Huo et al, RSC Advances, 2014

Crystalline Structure



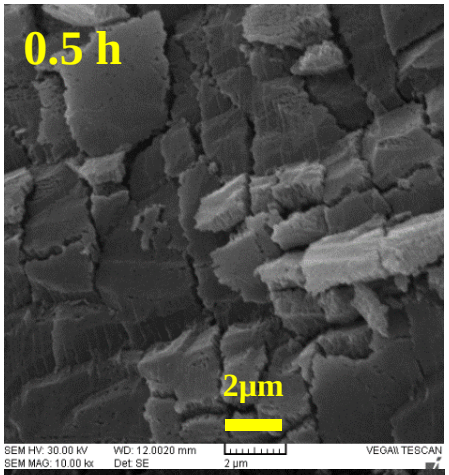
XRD pattern of TNAs grown for 2 h

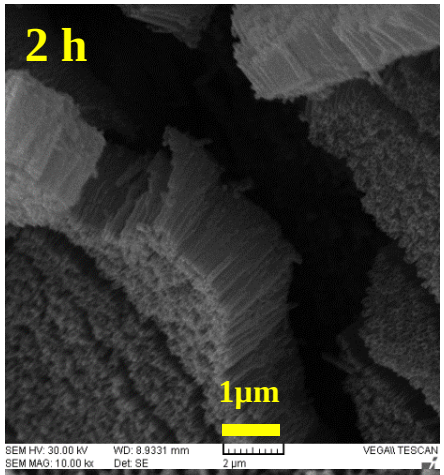
Optical Absorption

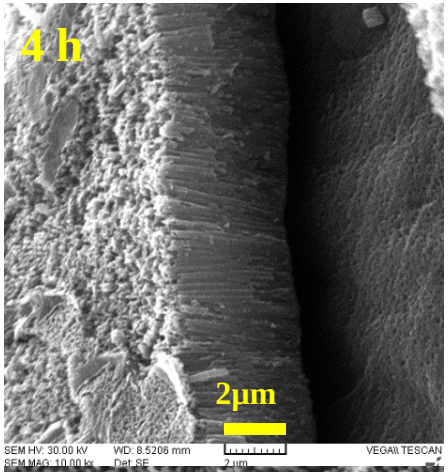


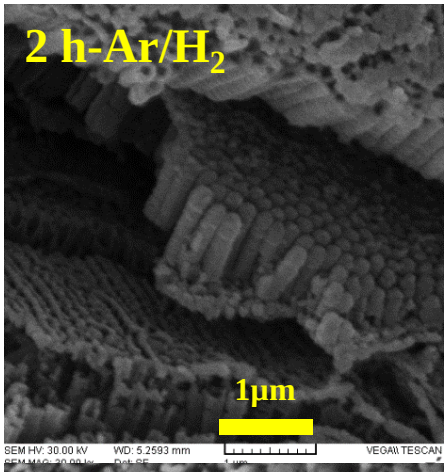
DRS of TNAs grown for 2 h

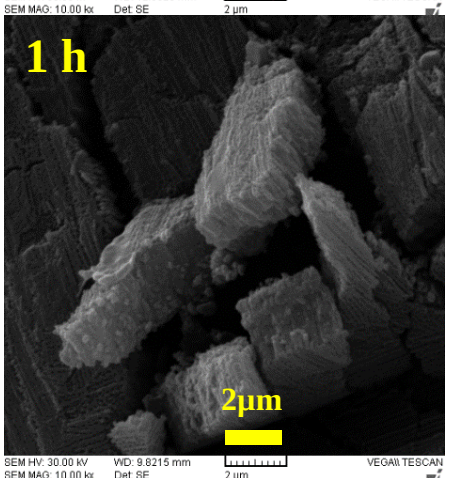
Surface Morphology

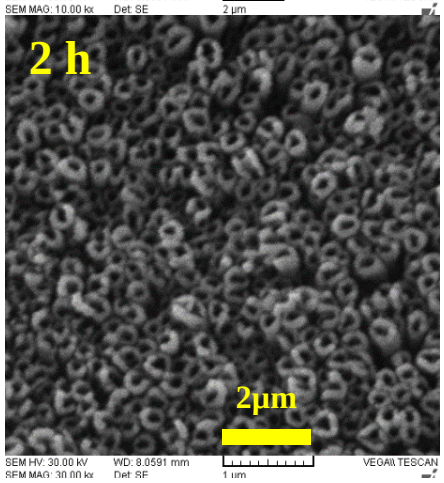


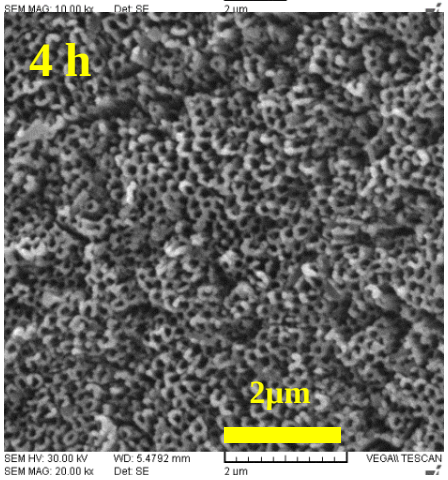


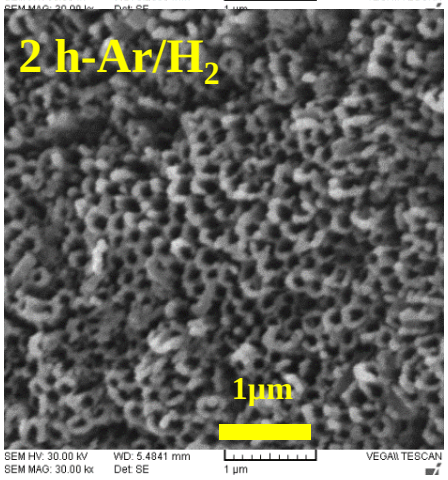












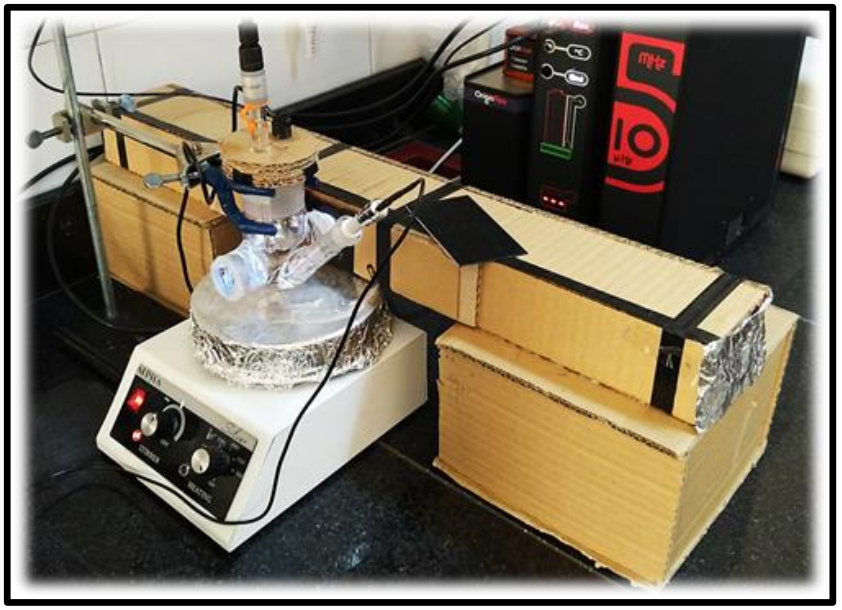
Surface Morphology

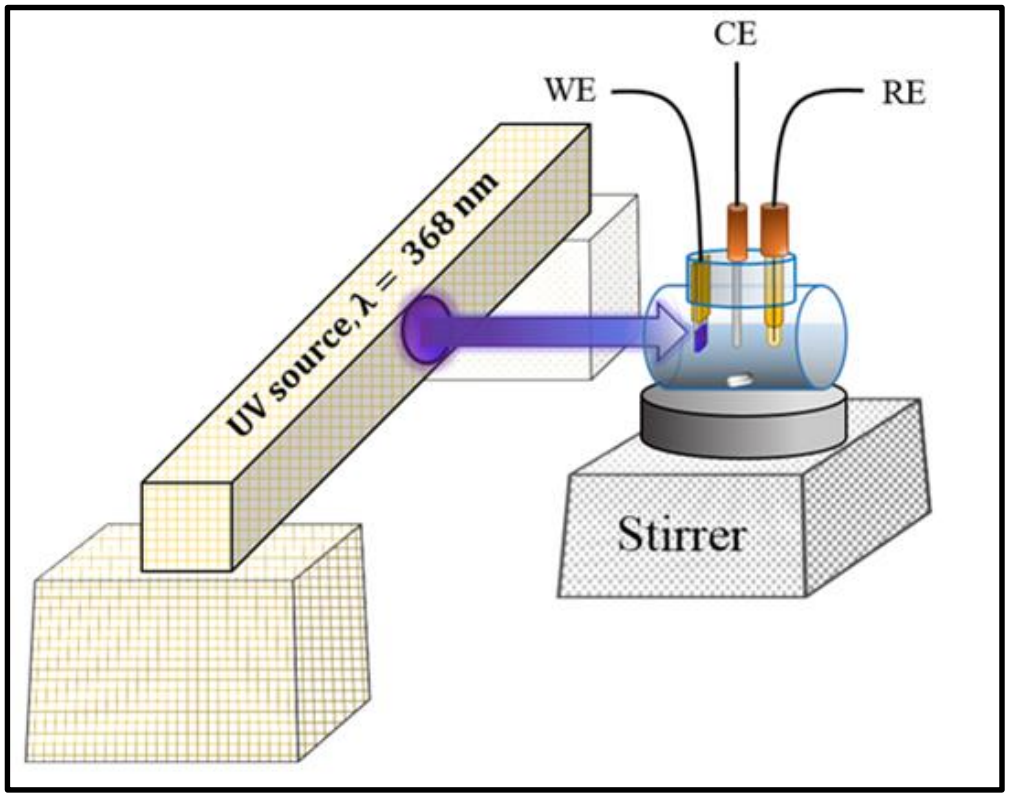
- **Anodization time did not change the surface morphology of tubes**
- **Anodization time change the tube length**

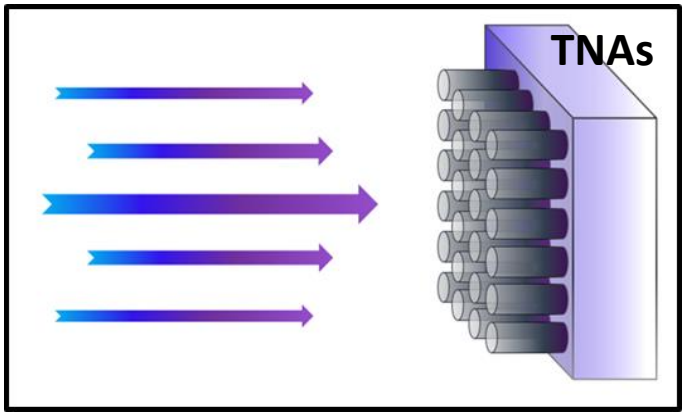
Anodization time (min)	**Length** (μm)	**Wall thickness** (nm)	**Diameter** (nm)
30 ± 1	0.60 ± 0.04	NA	NA
60 ± 1	1.45 ± 0.05	NA	NA
120 ± 1	2.70 ± 0.06	14 ± 2	138 ± 10
240 ± 1	3.96 ± 0.06	15 ± 2	143 ± 13

PEC Measurement

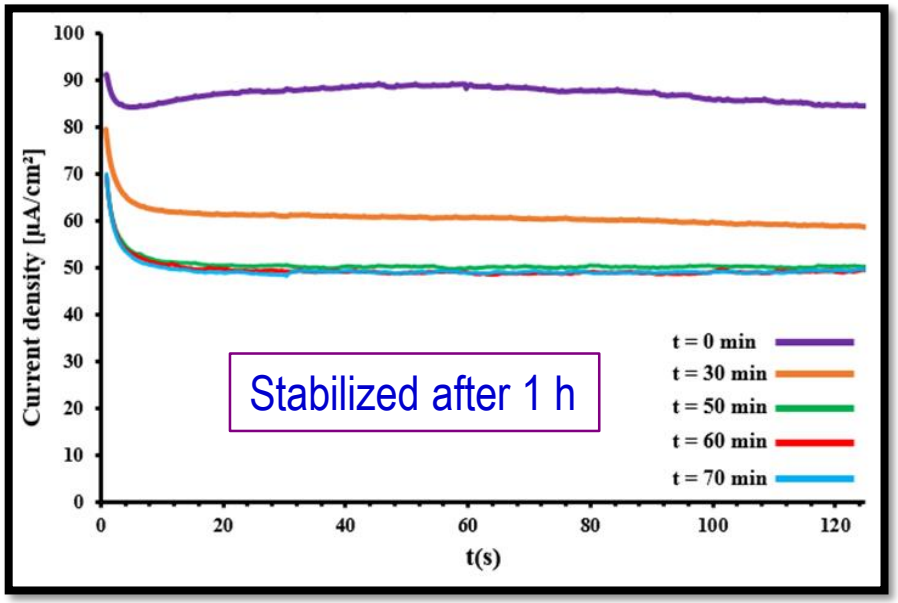
- ✓ **Electrolyte:** 0.1M $NaNO_3$
- ✓ **Light :** UV Lamp, λ=368 nm
- ✓ **Electrodes:** Ag/AgCl & Pt

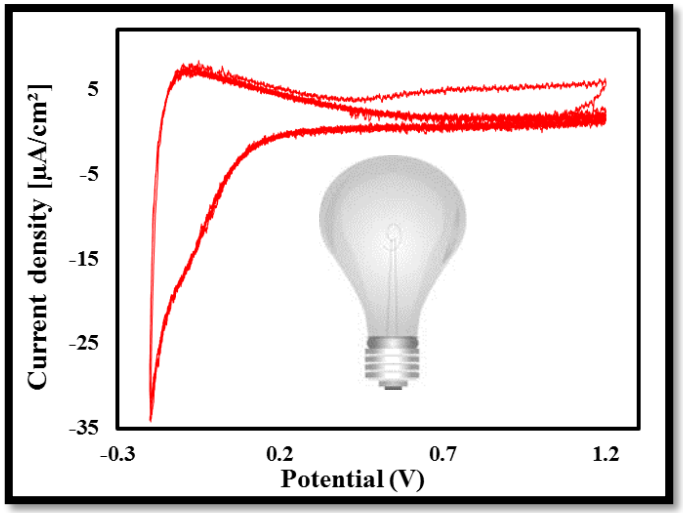


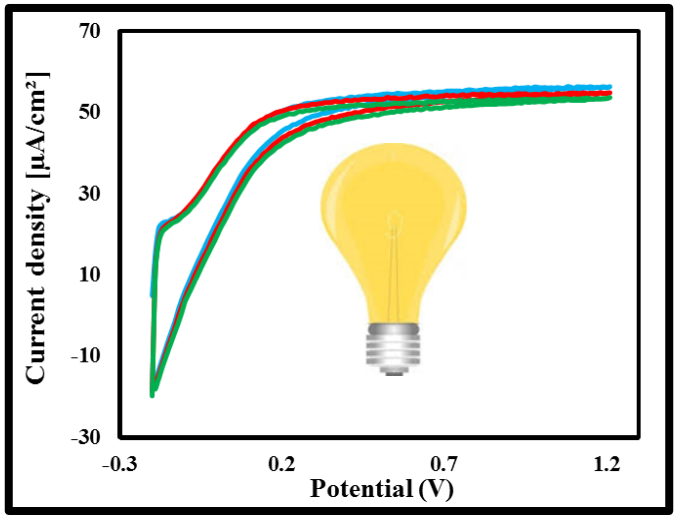




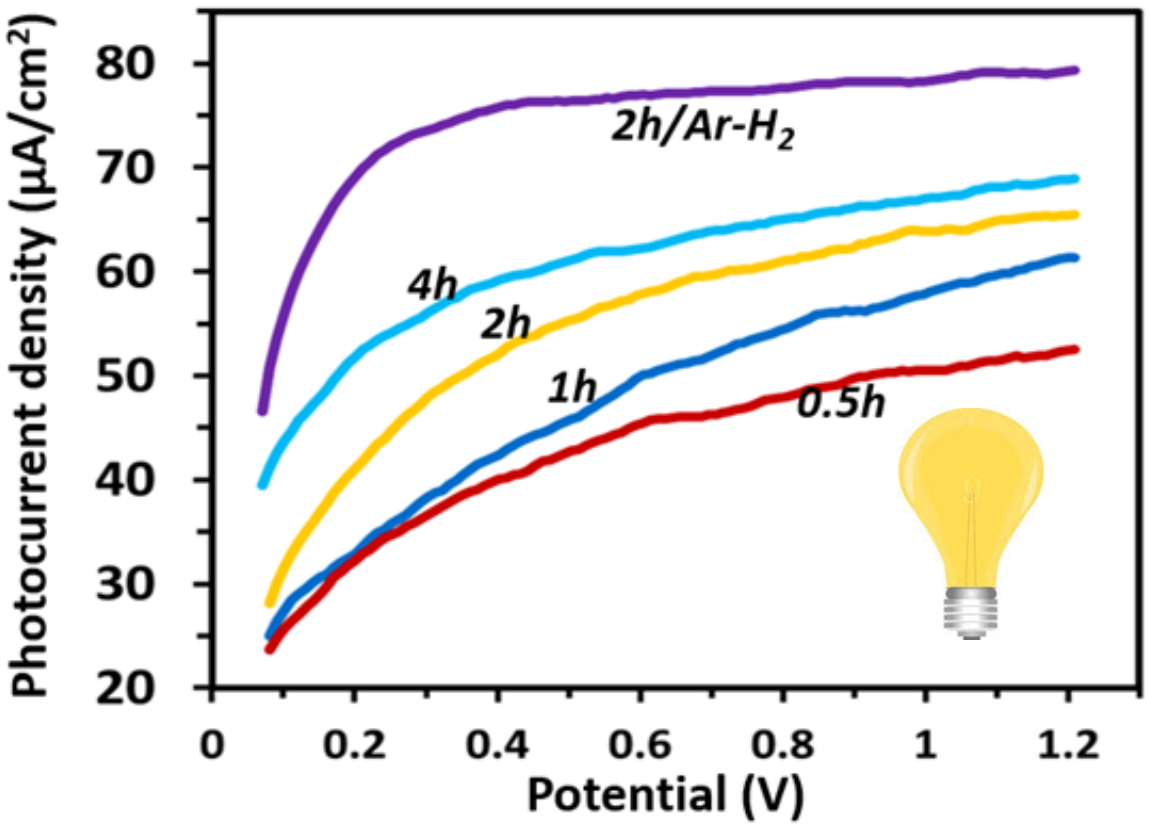
Photoanode Stability







Linear Sweep Voltammetry



Photocurrent Response

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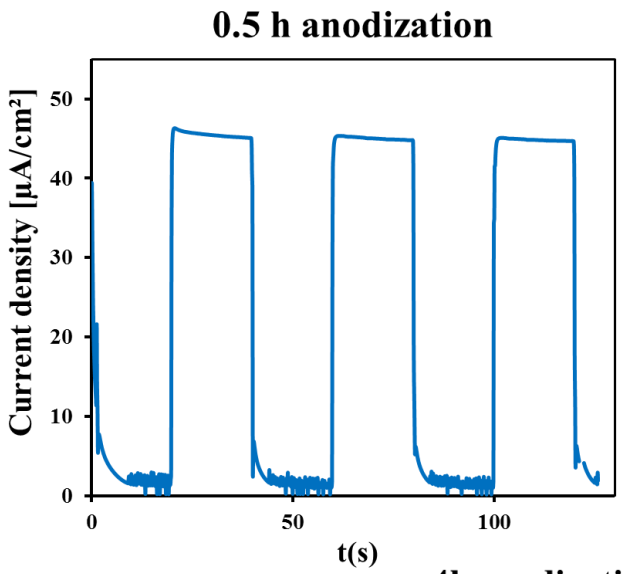

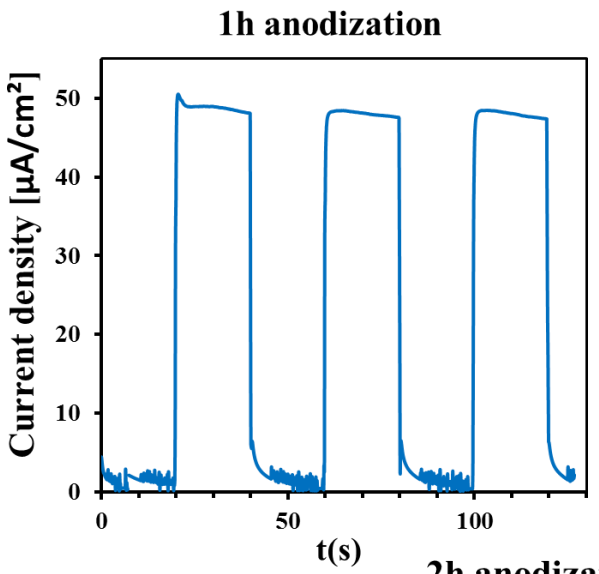

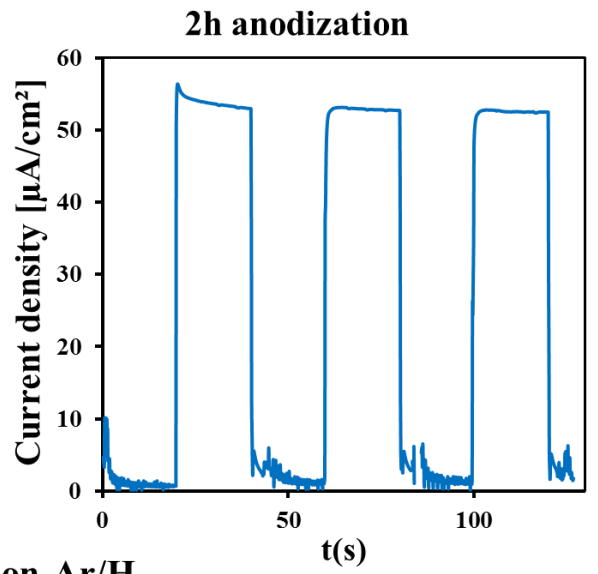

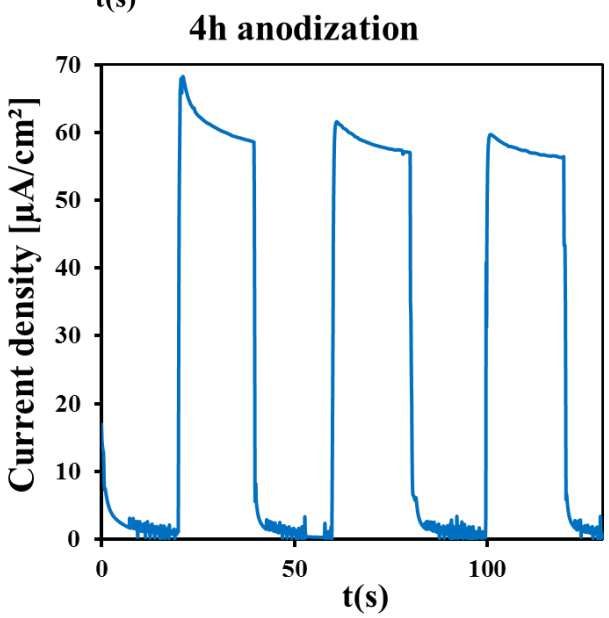

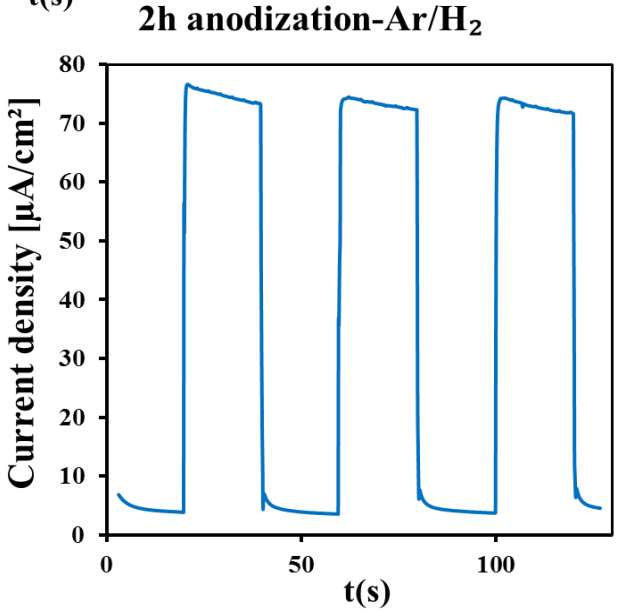

PEC Glucose Detection

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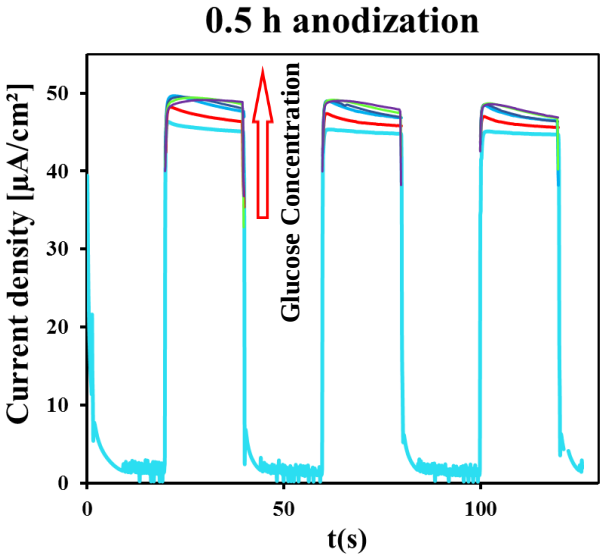
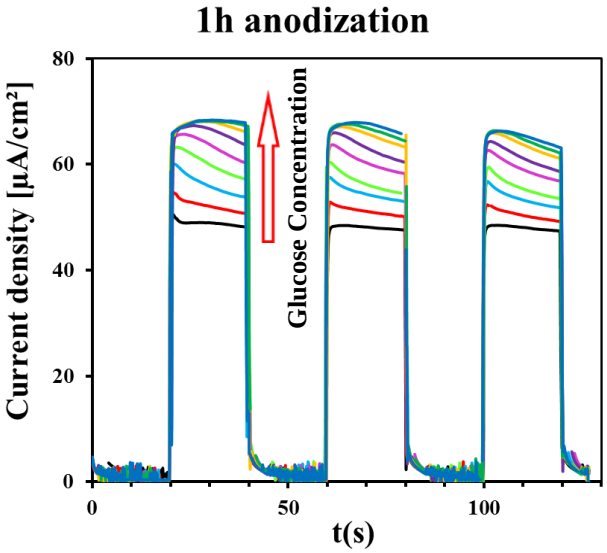
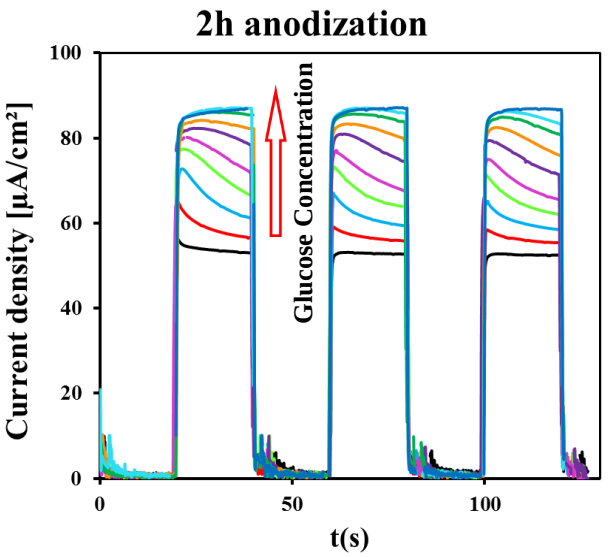
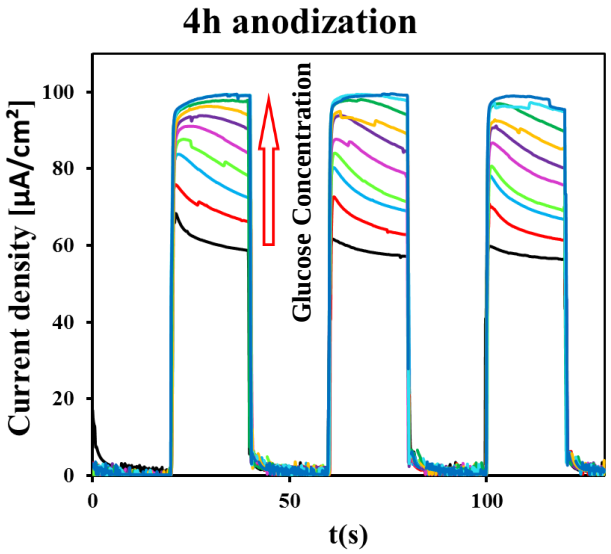
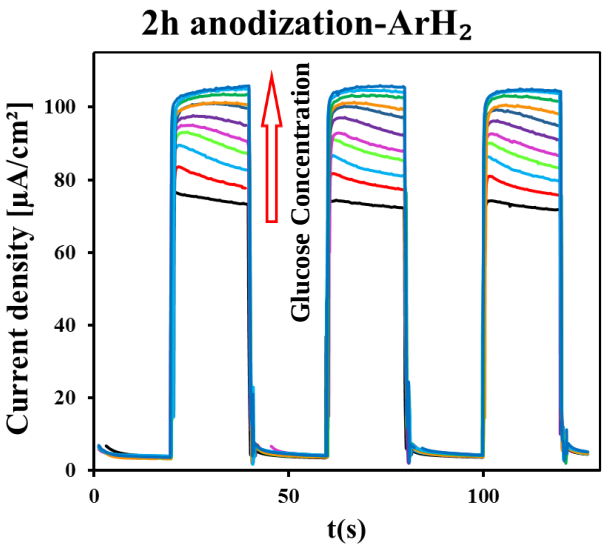


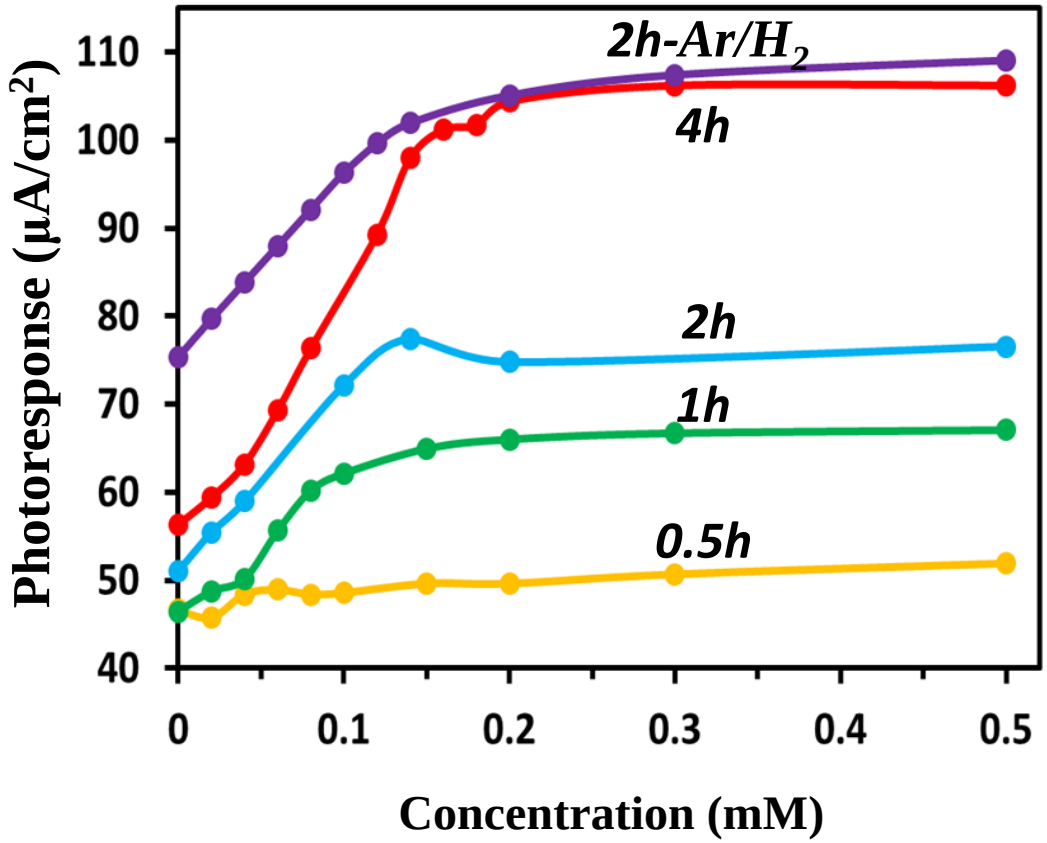








Glucose Sensing Performances



PEC & Sensitivity Characteristics

- ✓ Sensitivity increase with anodization time

- ○ Standard deviation increase with time

t(h)	I_{ph} (μA)	α (μA/mM.cm²)	C_0(mM)
0.5	46.1 ± 0.6	55.0 ± 15.5	0.04 ± 0.00
1	43.5 ± 8.6	145.4 ± 32.8	0.12 ± 0.03
2	53.7 ± 3.7	244.5 ± 48.0	0.14 ± 0.01
4	57.9 ± 1.1	255.5 ± 62.9	0.18 ± 0.01
2h – Ar/H_2	72.9 ± 1.7	188.4 ± 8.7	0.18 ± 0.02

Conclusion

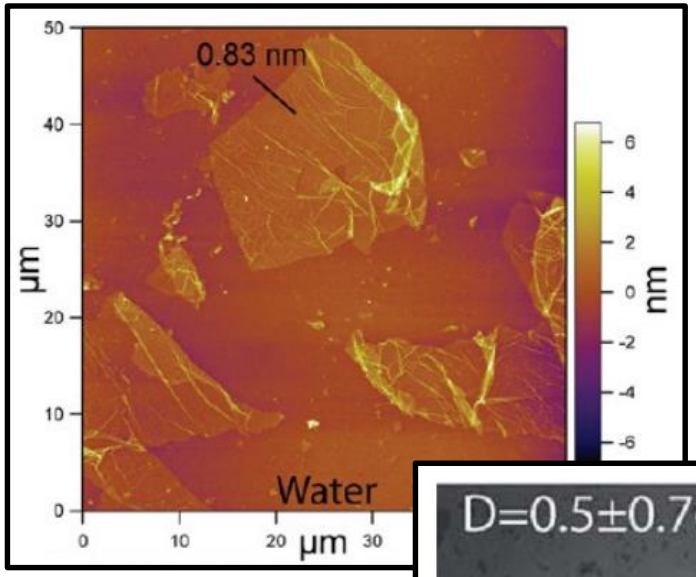
- **Optimum Preparation Condition:** 2h Anodization and Annealing in air
- **Sensitivity Factor of Optimum Sample:** 244.5 ± 48.0 µA/mM.cm^2
- **Upper Performance Limit of Optimum Sample:** 0.14 ± 0.01 mM

Optimum TNAs can act as a promising semiconductor host for future modification

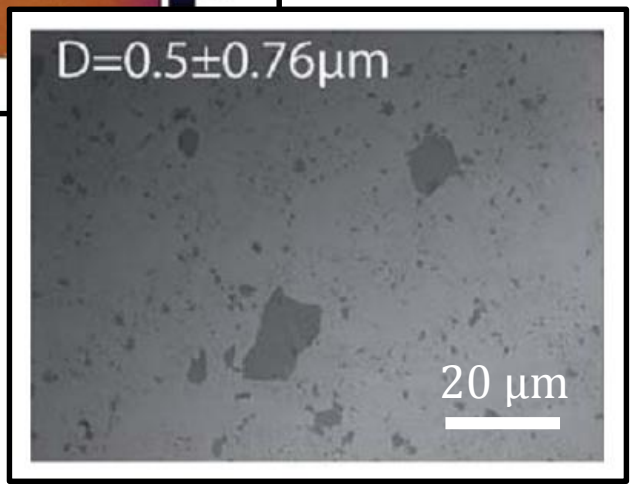
2D Material

2D Material From IPM

Institute for Research in Fundamental Sciences



R. Jalili et al, ACS NANO, 7, 2013



R. Jalili et al, Mater. Horiz., 2014

Preparation Method:

► Exfoliation of Expanded Graphite ◄

Mean Seat Size: 1μm

Mean Lateral Size: 1nm

TNAs Modification

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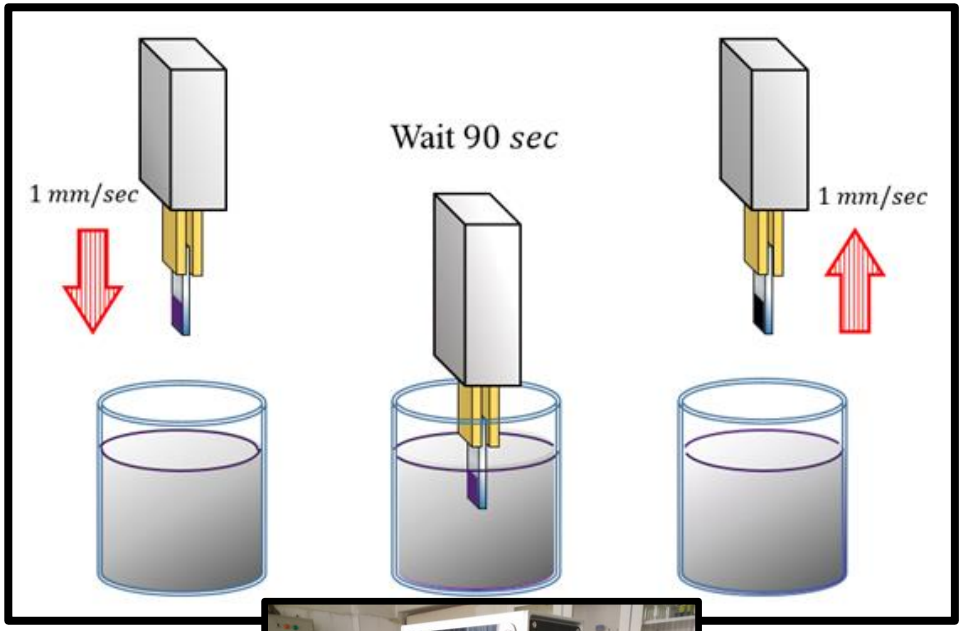
Deep Coating



Graphene
(0.675 mg/ml)

Graphene Oxide
(0.338 mg/ml)

S-GO
(0.675 mg/ml)

TNAs/Graphene

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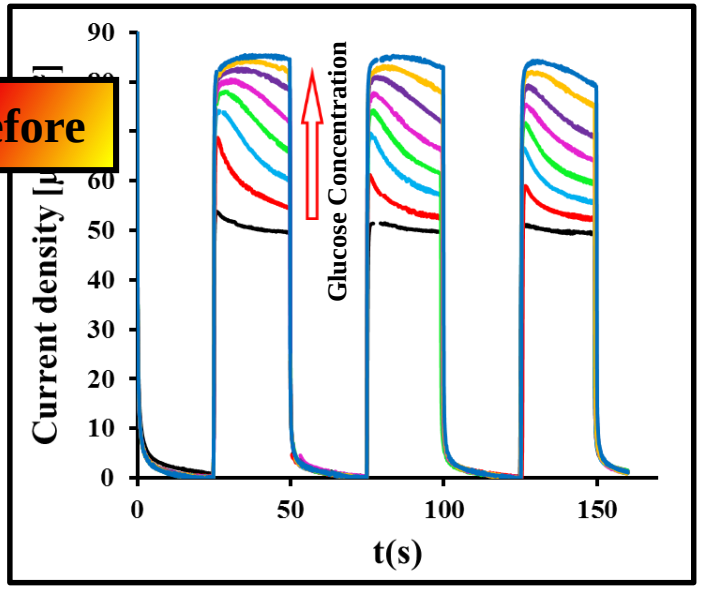
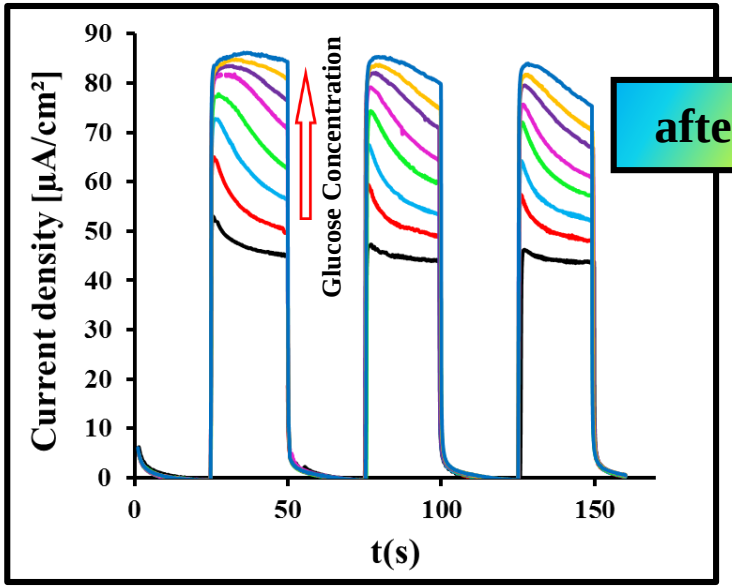
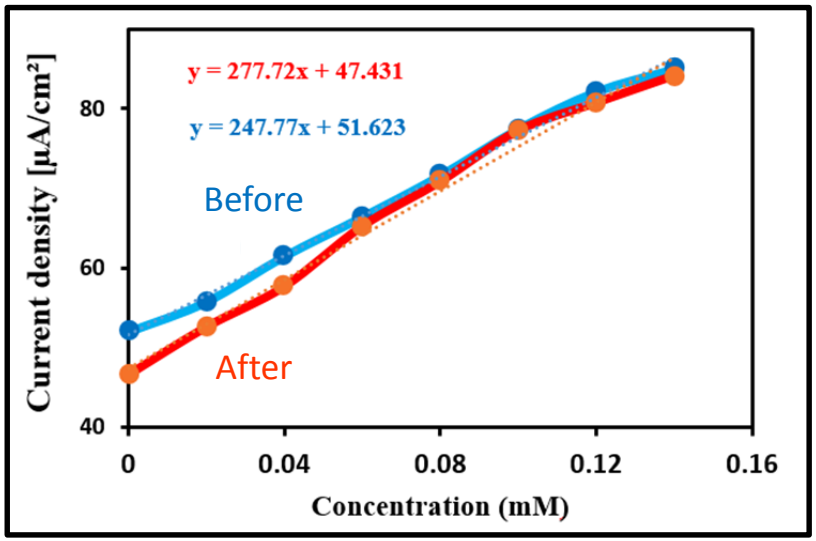
before



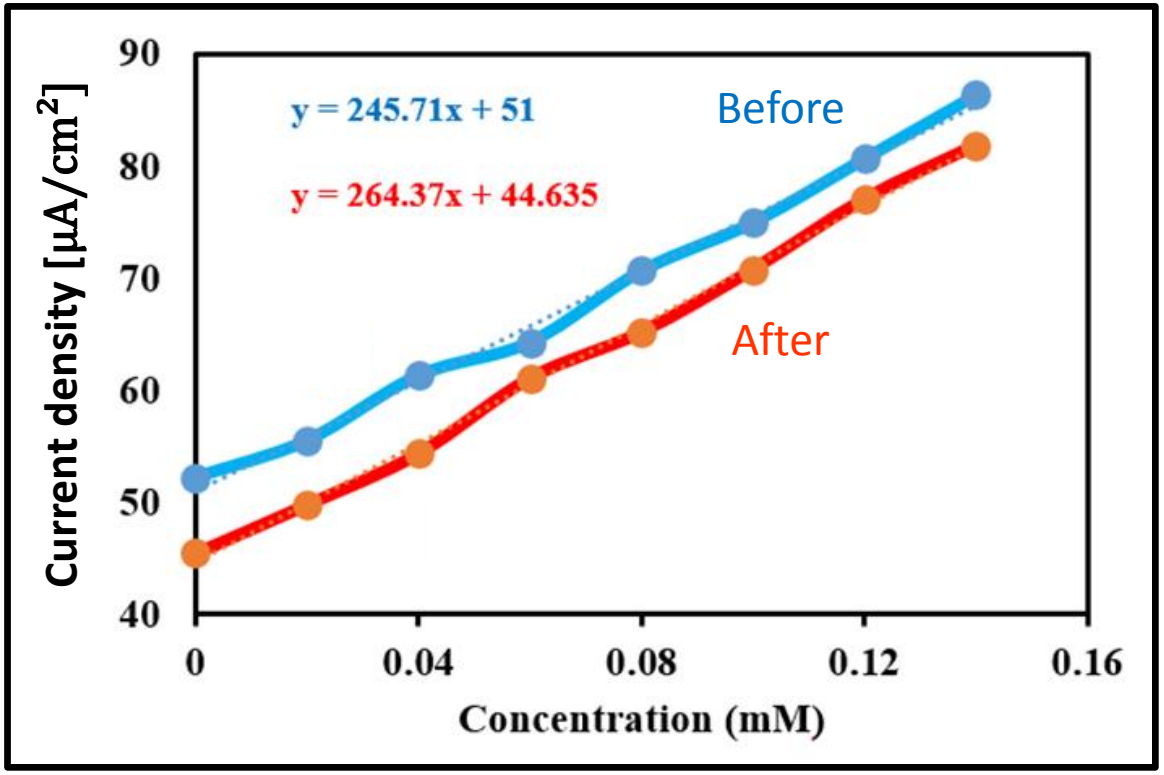
after





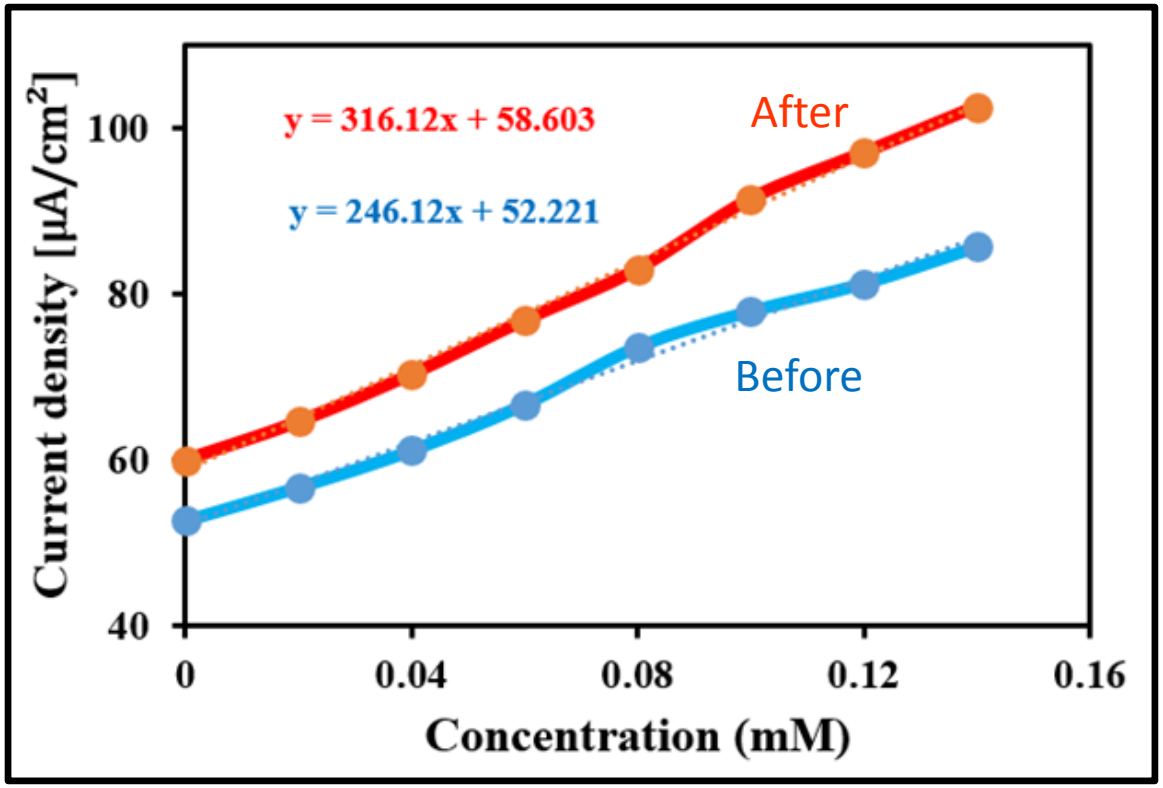
12% Improvement

TNAs/Graphene Oxide



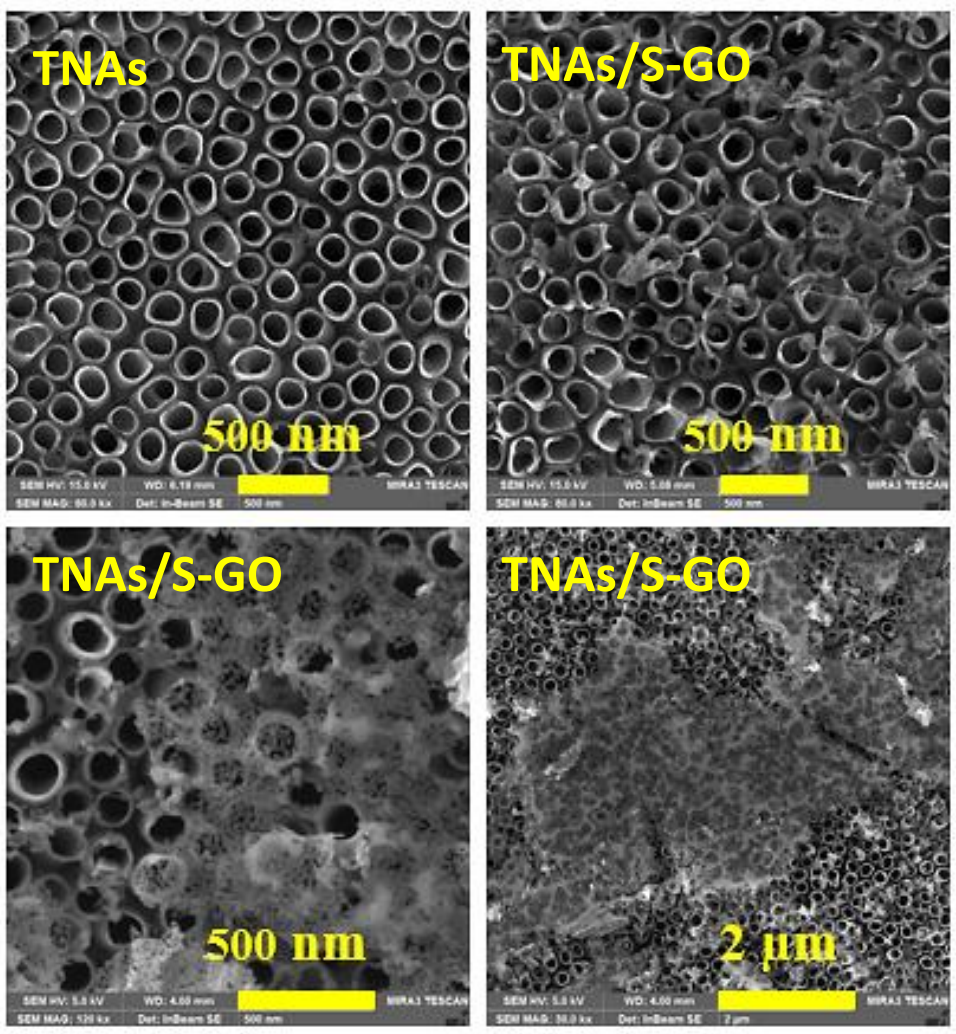
7.6% Improvement

TNAs/S-GO

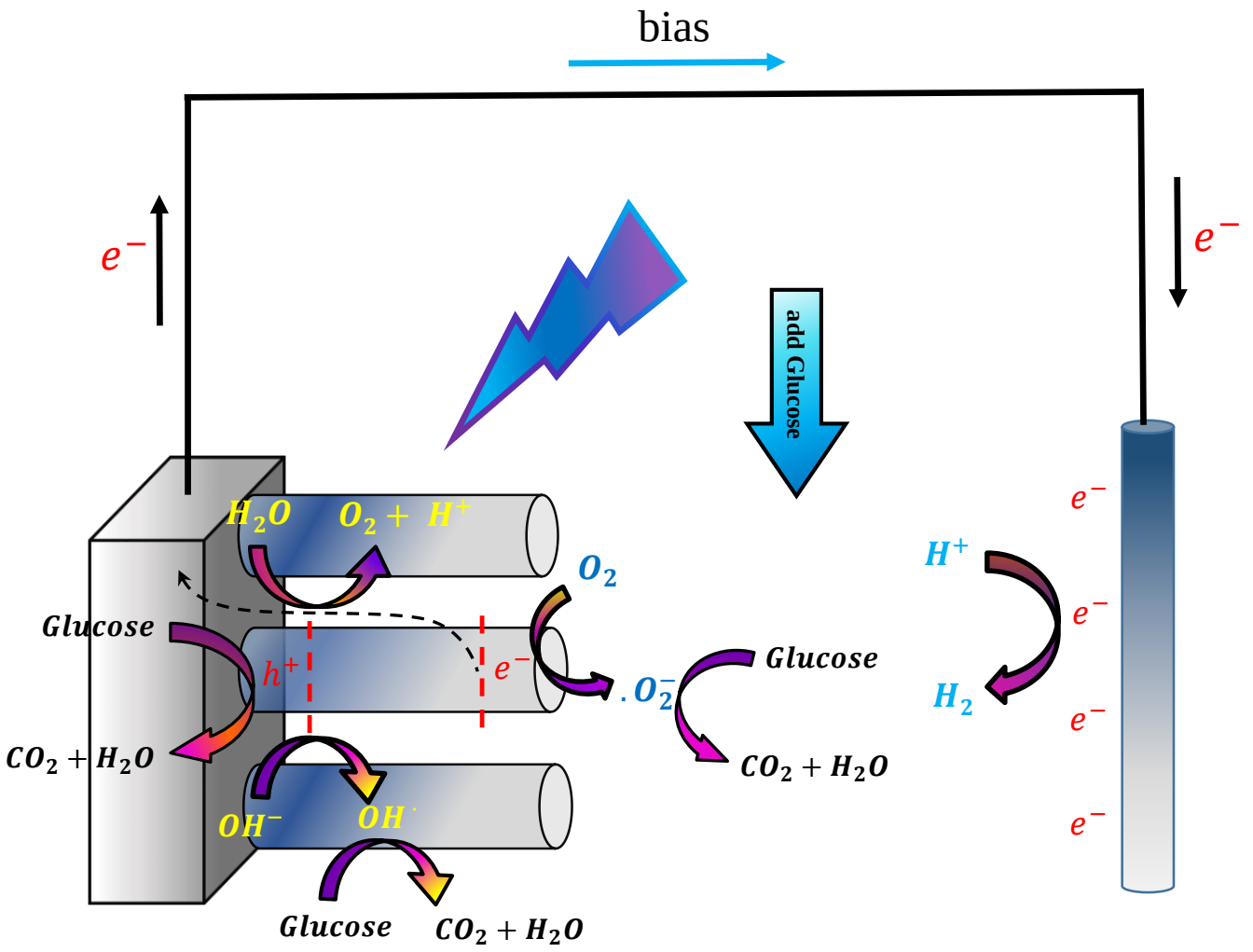


28.5% Improvement

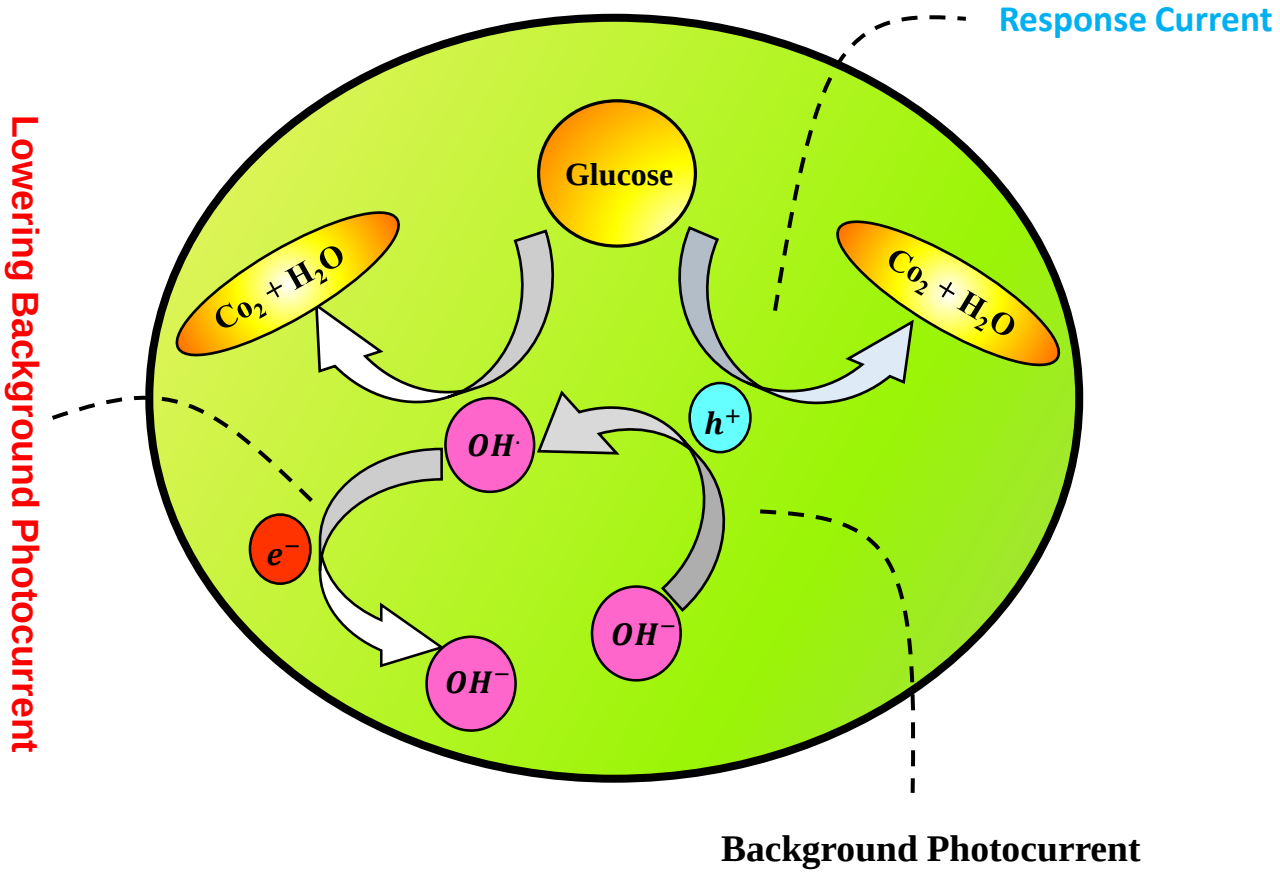
Surface Morphology



Glucose Sensing on TNAs

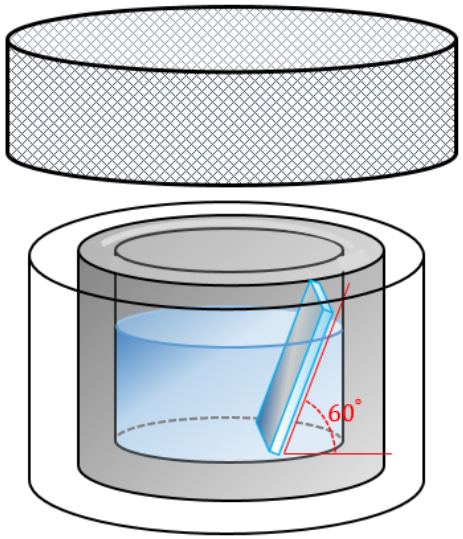


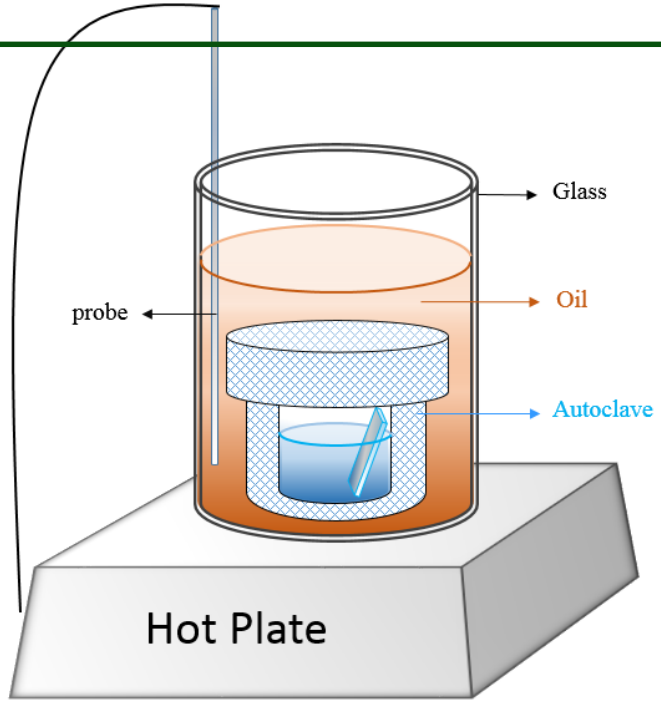
Effect of 2D Material



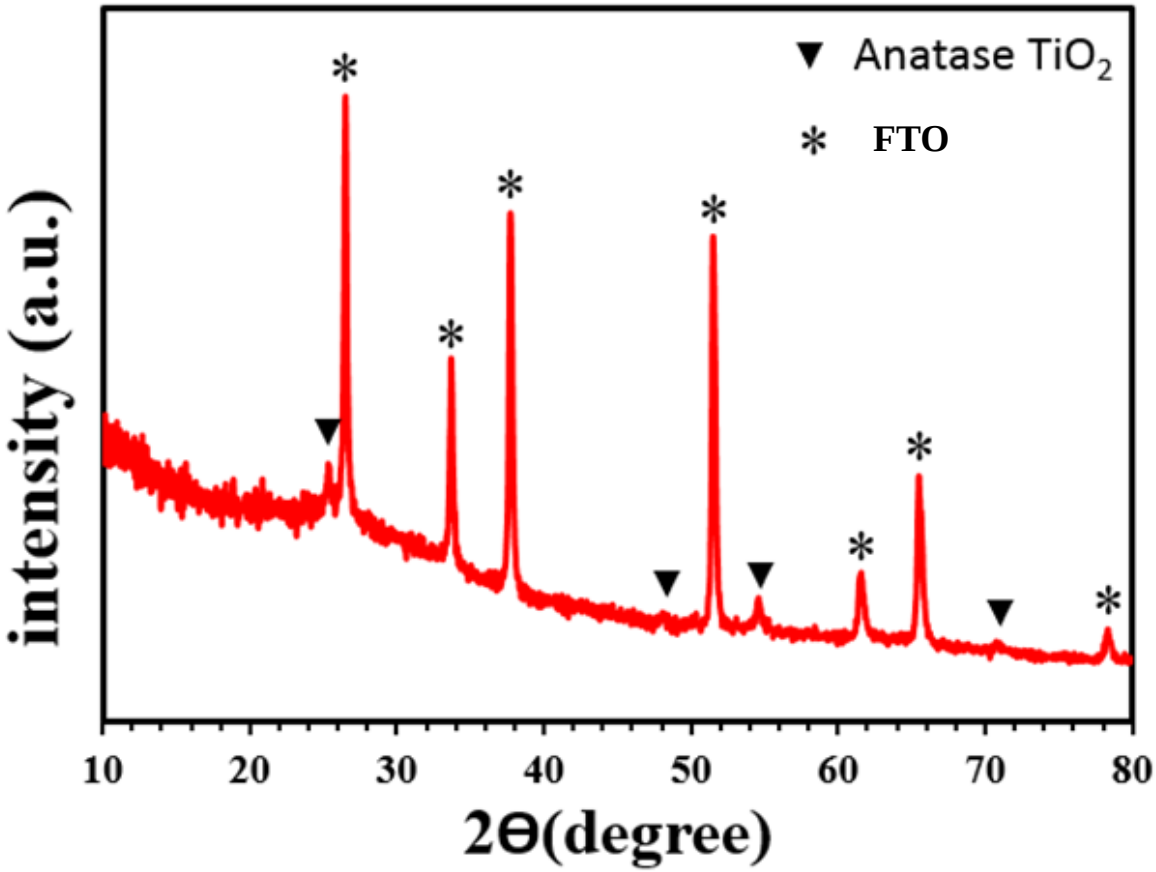
TNW Preparation

- ✓ **Solution:** DEG, Water and PTO
- ✓ **Hydrothermal Temperature:** 200 °C
- ✓ **Hydrothermal Time:** 6h and 11h
- ✓ **Heating:** 500 °C for 1 h



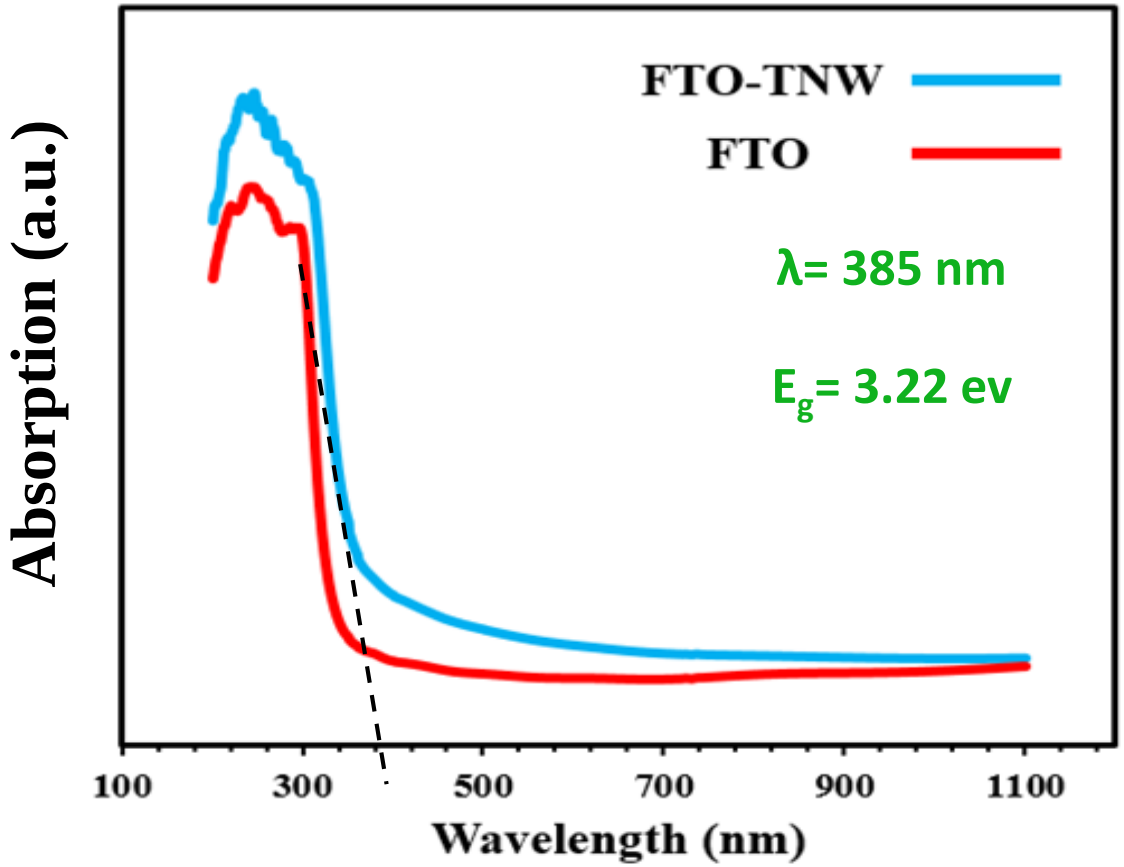


Crystalline Structure



XRD pattern of TNW

Optical Absorption



Surface morphology

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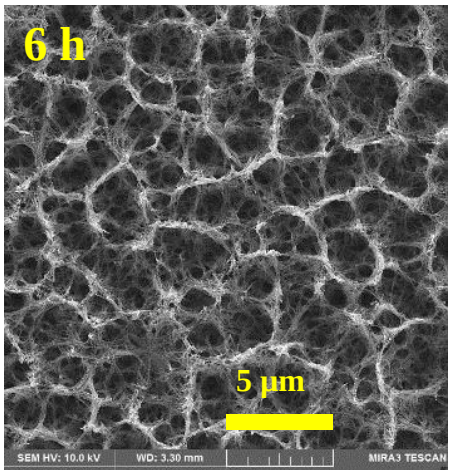
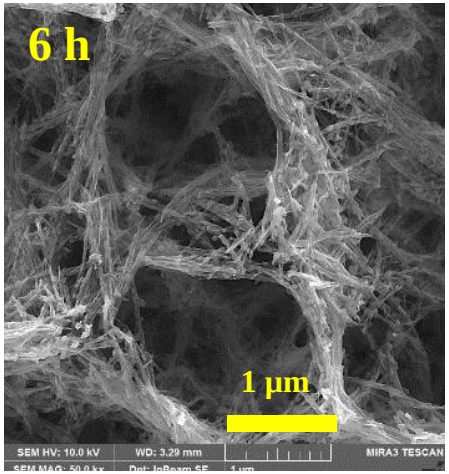
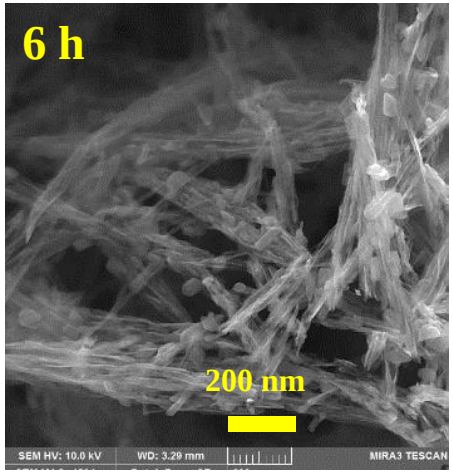
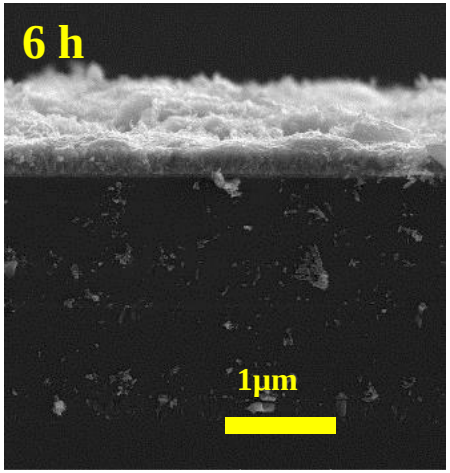
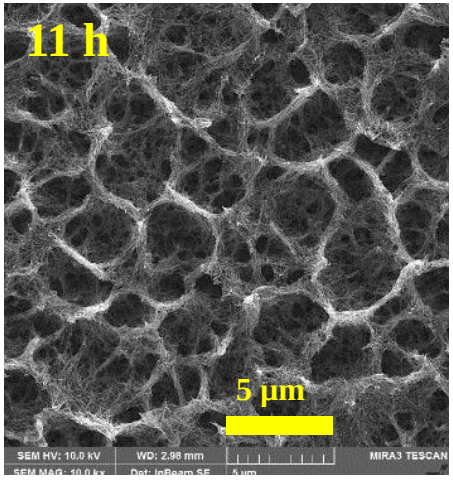
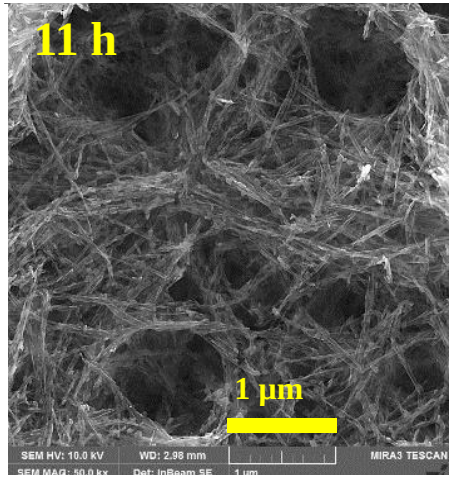


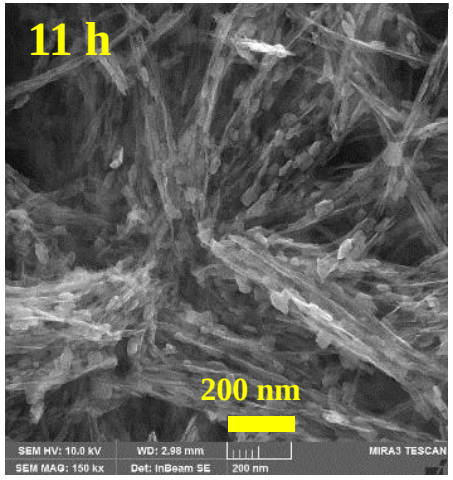


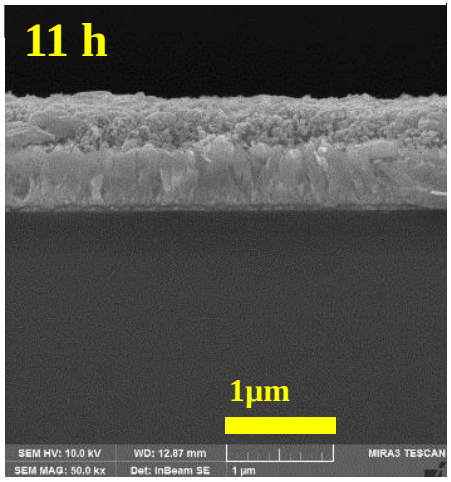








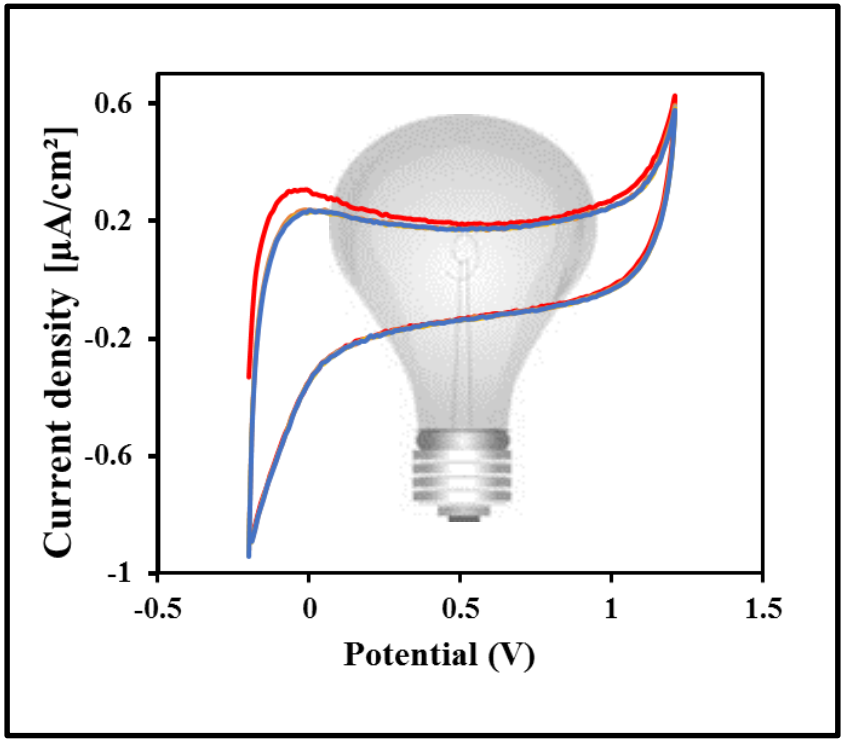


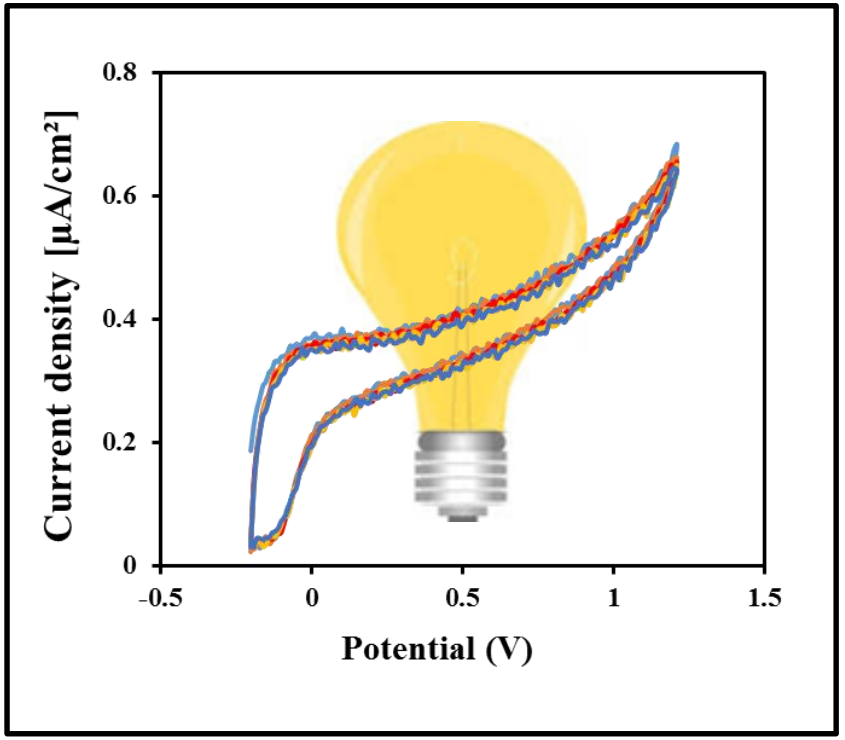


Hydrothermal time did not change the surface morphology of wire

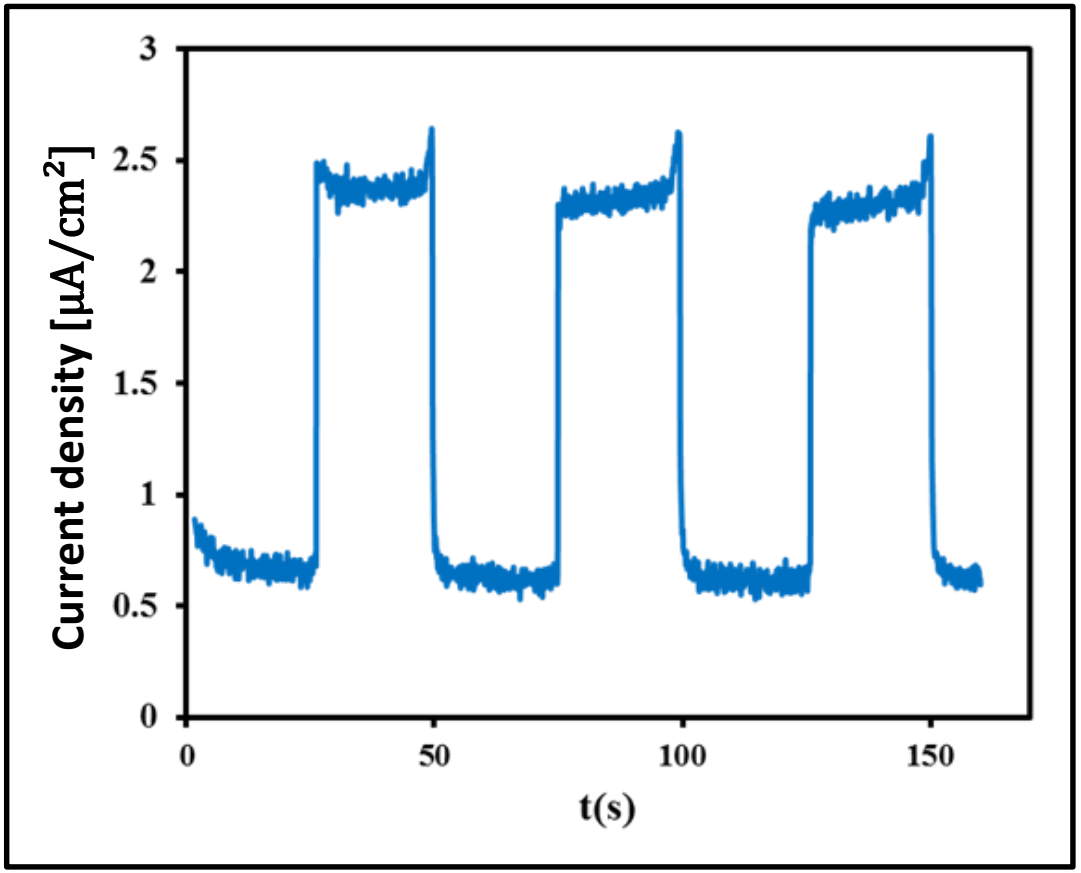
Wire Thickness:	**80 nm**
Bead Size:	**65 nm**

Photoanode Stability





Photocurrent Response



PEC Glucose Detection

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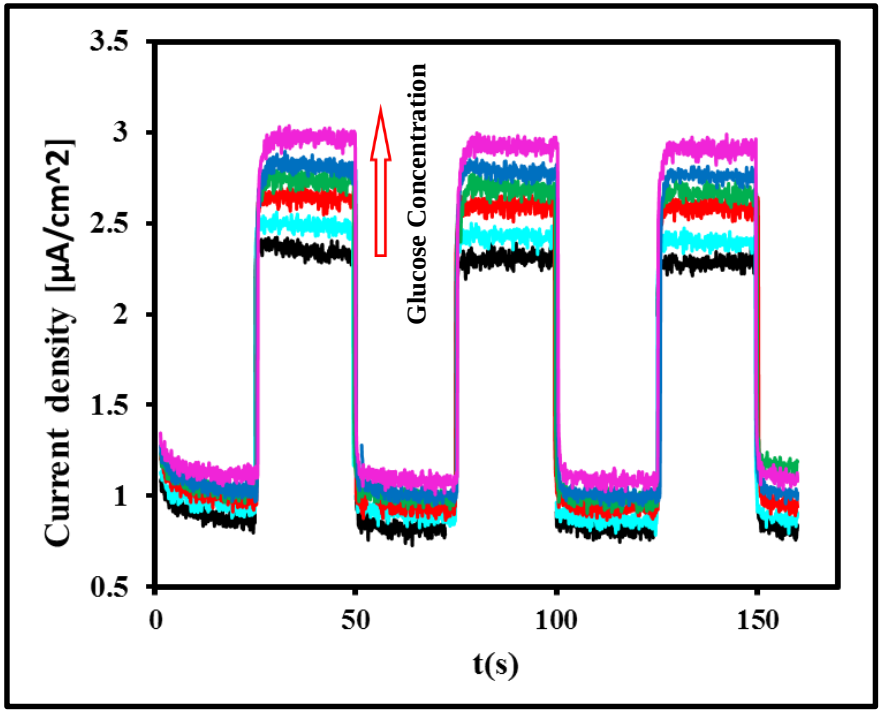
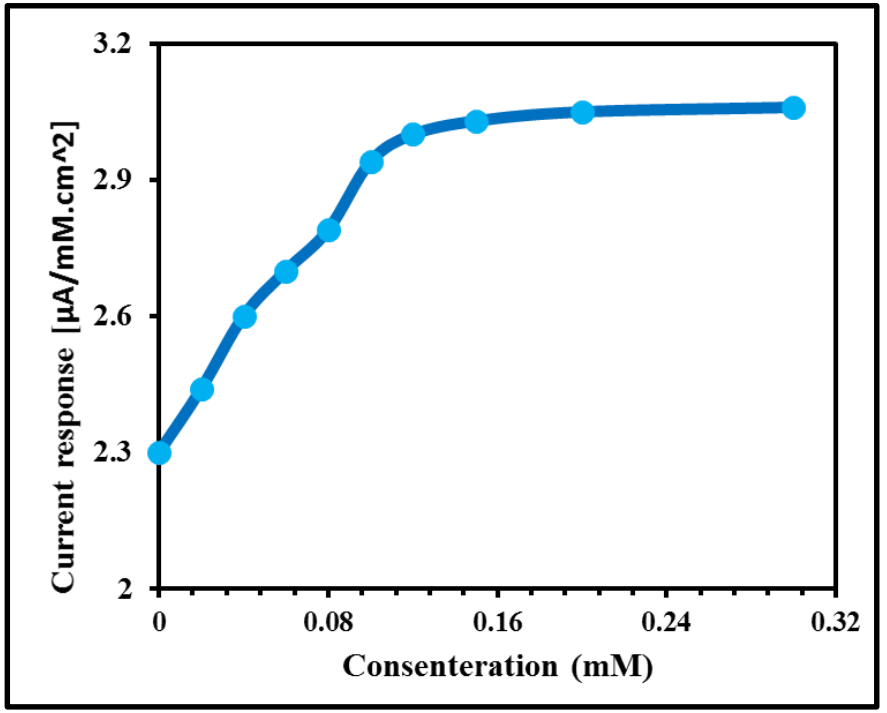


$$\alpha = 6\ \mu A/mMcm^2$$



Conclusion

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TNAs

Optimum TNAs Growth Condition: → 2h Anodization, Annealing in Air

Sensitivity Factor about 245 $\mu A/mMcm^2$ → More than Similar Works

Modification by 2D Material → Improvement of Sensitivity

Low Detection Limit

TNW

- Low PEC Performance
- Low PEC Sensitivity
- Low Stability

Reproducibility

Branched TNW

Outlook

TNAs

Optimizing Diameter and Wall Thickness of Tubes

Modification by Graphene Oxide and Important Electrocatalyst Composition

TNW

Trying other precursors and Substrates

Trying other Preparation Methods

Sensing

Trying other Active Species

Paper

Enhancing PEC Glucose Sensing of TiO_2 Nanotubes by Tuning the Length and Annealing Ambient

A.A. Saadati[1, a)], M.M. Tahmasebi[1, b)] and N. Naseri[1, c)]

Oral Presented by Ali Akbar Saadati

Thank You!

Clean Energy Lab

Sharif university of technology

Department of Physics