Nanostructured $SrTiO_3/WO_3$ Heterojunction Thin Films for Efficient Photoelectrochemical Water Splitting for Hydrogen Generation

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Outline

- **Introduction**
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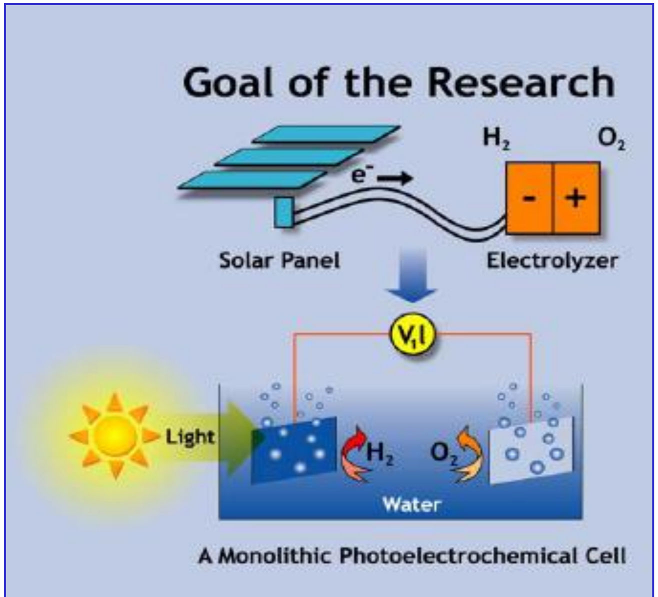


Introduction

Bilayered Photoelectrodes possess:

- **Better absorption in the visible region.**
- **Effective separation of charge carriers.**
- **Inbuilt electric field at the interface, reduces recombination of charge carriers.**
- **Applied external bias promotes transfer and separation of photogenerated charge carriers.**

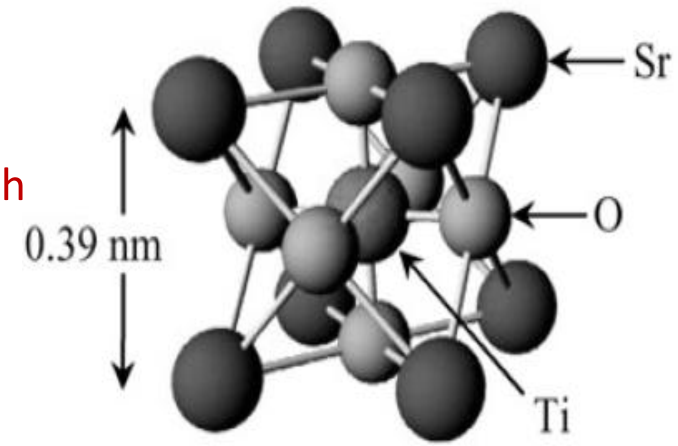
Why $SrTiO_3$ and WO_3 ?

Strontium Titanate ($SrTiO_3$) [Eg :- ~ 3.5 eV]

Advantages:

- Remarkable stability in strong acidic/alkaline solutions.
- Large negative flatband potential (V_{fb}= -0.2V), due to which electrolysis of water is possible without any applied bias.
- Properly aligned band edges with the redox level of water

Problem: **Low photoconversion efficiency due to large band gap and high resistivity.**

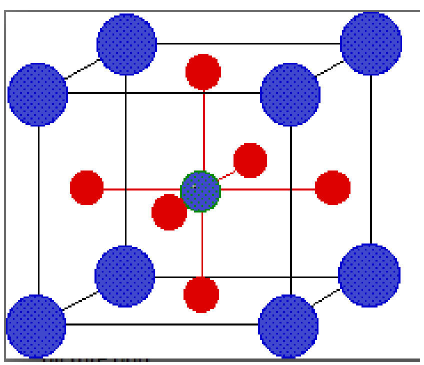


Tungsten Oxide (WO_3) [Eg :- ~ 2.7 eV]

Advantages:

- Basically n-type in nature due to presence of oxygen vacancies within the material.
- Favorable transport properties
- Chemically inert and Photostable

Problem: **Non optimal band-edge alignment of conduction band with redox potential of water.**



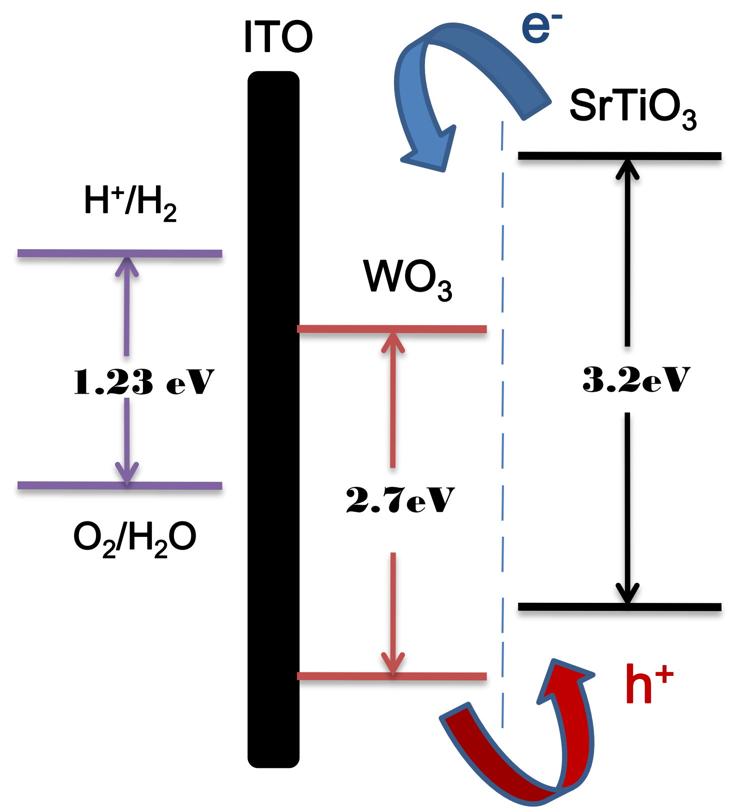
$SrTiO_3/WO_3$ Bilayered films

- Bilayered semiconductors in this study, typically composed of two semiconductors, one with a wide band gap ($SrTiO_3$) and another with a moderate band gap (WO_3).

- WO_3 is responsible for sensitizing $SrTiO_3$ semiconductor through hole injection.

- The energy layers in the $SrTiO_3/WO_3$ semiconductor can cover visible spectrum thereby offering synergistic effect.

- Inbuilt electric field at the $SrTiO_3/WO_3$ heterojunction facilitates charge carrier transfer easily across the interface of the heterojunction.



Energy band diagram of $SrTiO_3/WO_3$ Heterojunction on ITO substrate

Experimental Study

- **Preparation of Bilayered $SrTiO_3/WO_3$ thin film:**
  - Sol-gel spin-coating Technique

- **Characterization Techniques:**
  - ✓ X-ray Diffraction (XRD)
  - ✓ UV-Visible Absorption Spectrophotometery
  - ✓ Scanning Electron Microscopy (SEM)

- **Photoelectrochemical (PEC) Study on Bilayered thin film**

Thin Film Preparation

Precursor solution of WO_3 obtained by sol-gel spin-coating method[1]

↓

Multiple layer of precursor solution was spin coated on two third portion of ITO substrate

↓ Annealed the films at 450^oC for 1 hr

Precursor solution of $SrTiO_3$ obtained by sol-gel spin-coating method[2] , deposited on pre-deposited WO_3 films

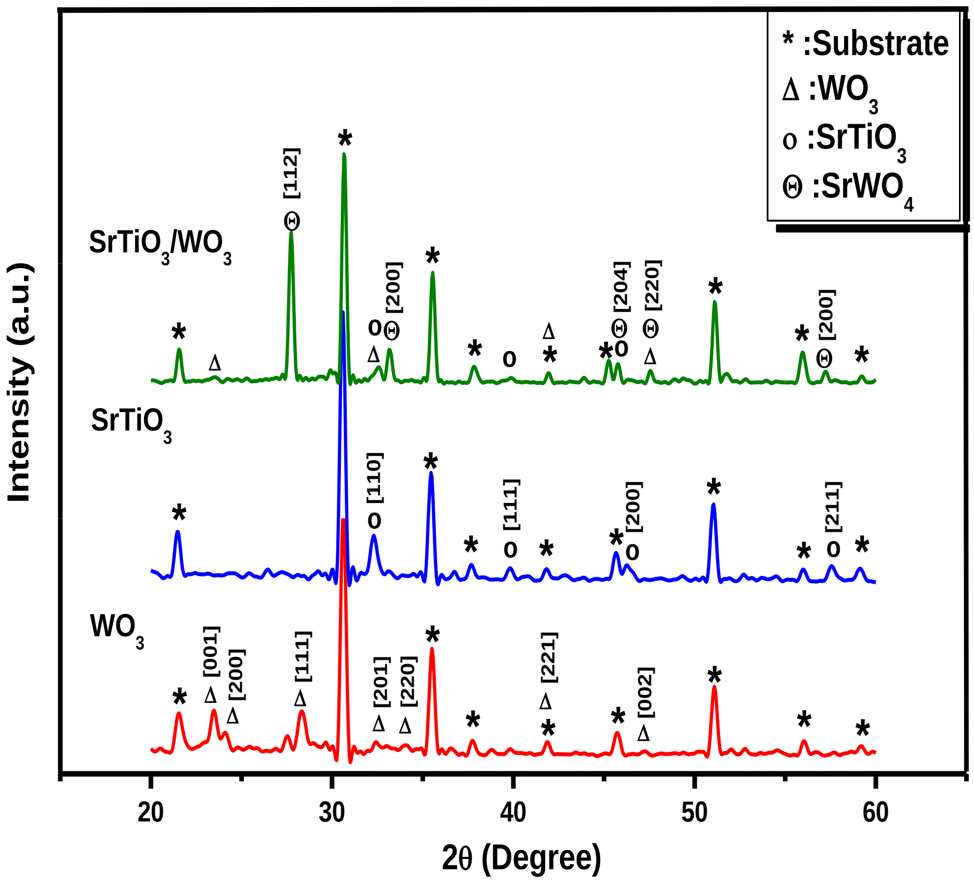
↓ Annealed the films at 600^oC for 1 hr

Bilayered thin films of $SrTiO_3/WO_3$

Optimizing Parameters of the Study:
No. of layers of the two materials or Thickness

1. Luo et al, J. Phys. D: Appl. Phys. 40 (2007) 1091–1096.
2. Solanki et al, Int. J of Hydrogen Energy 36 (2011) 5236-5245.

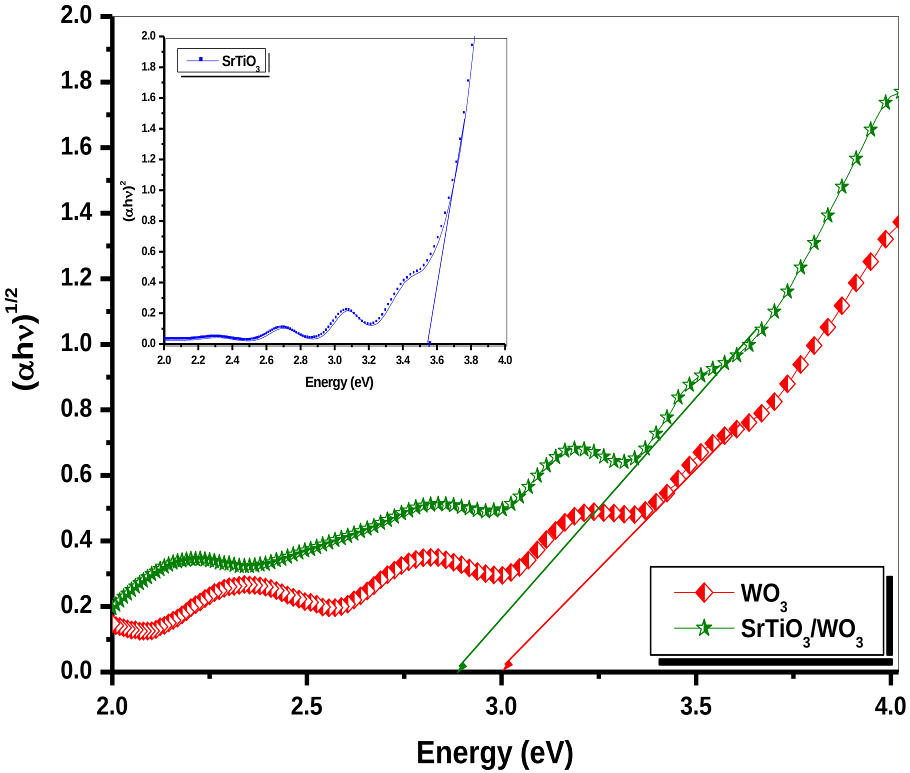
XRD Study



XRD pattern of Tungsten Oxide, Strontium Titanate and Bilayered ($SrTiO_3/WO_3$) thin films

- ❖ Films are crystalline in nature.
- ❖ XRD pattern for $SrTiO_3$ and WO_3 confirmed the cubic and orthorhombic phase respectively.
- ❖ Average particle size of $SrTiO_3$ and WO_3 was 45 nm and 39 nm respectively.
- ❖ $SrWO_4$ in Bilayered films: due to the diffusion of Ti^{4+} (0.605 Å) and W^{6+} (0.60 Å) ions at the interface. Similar ionic radii making easy substitution of ions at the interface.

Optical Characterization



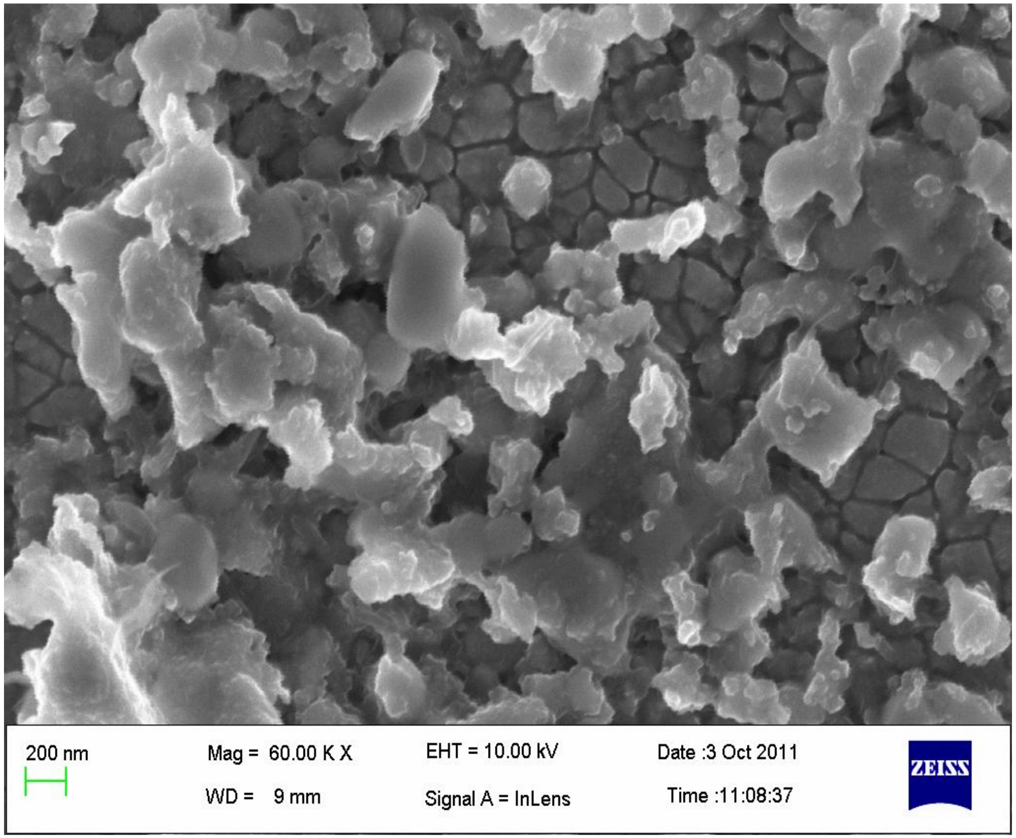
Tauc plot of Tungsten Oxide and Bilayered ($SrTiO_3/WO_3$) thin films. Inset shows Tauc plot for Strontium Titanate.

❖ **Mode of transition for : -**

- **$SrTiO_3$ - Direct nature ($(\alpha h\upsilon)^2$ versus $h\upsilon$ is linear)**
- **WO_3 & Bilayered films - Indirect nature ($(\alpha h\upsilon)^{1/2}$ versus $h\upsilon$ is linear)**

Sample ID	Band Gap (eV)
$SrTiO_3$	3.52
WO_3	2.98
$SrTiO_3$ / WO_3	2.87

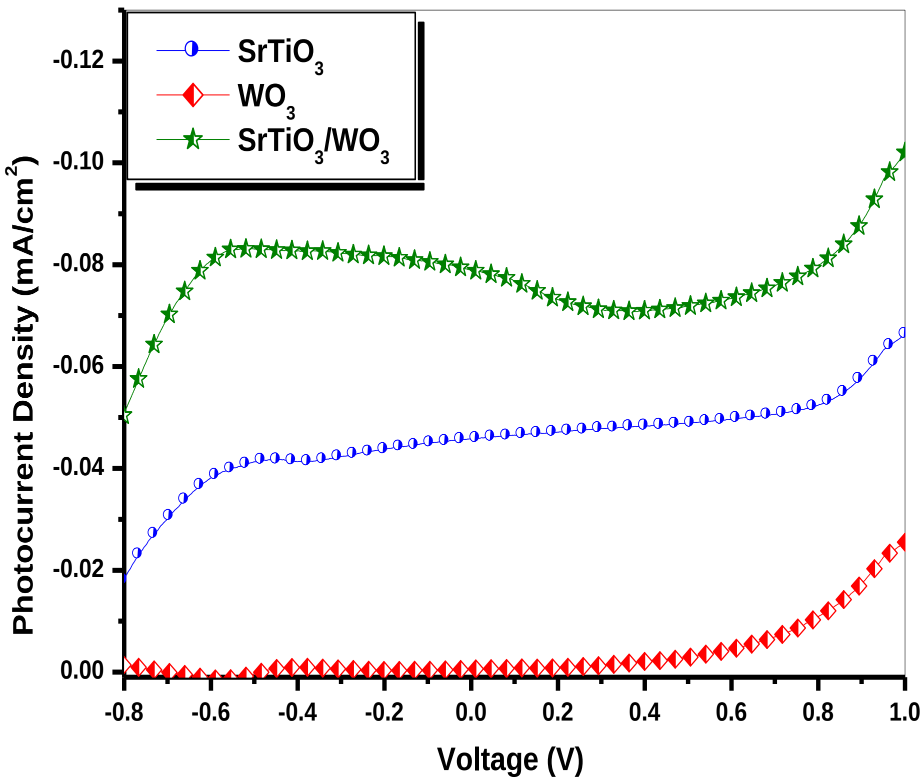
Surface Morphology



FE-SEM image of $SrTiO_3/WO_3$

- Homogeneous WO_3 film deposited on ITO substrate.
- Good film-to-substrate adhesion of WO_3 film was observed.
- Rough surface with aggregation of grains is shown in upper $SrTiO_3$ film.
- $SrTiO_3$ layer shows porous structure that may be beneficial for the diffusion of electrolytes and the effective scattering of incident light.

I-V Characteristics



Sample ID	Photocurrent Density ($mAcm^{-2}$)	
	0 V/SCE	0.9 V/SCE
$SrTiO_3$	0.046	0.059
WO_3	0.002	0.018
$SrTiO_3/WO_3$	0.079	0.088

Photocurrent density versus applied potential curve for Strontium titanate, Tungsten oxide and Bilayered thin film.

Conclusion

- Maximum Photocurrent density of $SrTiO_3/WO_3$ Bilayered films = 0.079 mA/cm^2 at 0 V/SCE, which is approx. two times higher than that of $SrTiO_3$ (0.046 mA/cm^2) and much higher than that of WO_3 (0.002 mA/cm^2) at zero bias.

- Increase in absorbance of WO_3 towards visible region or red shift from 420 nm to 432 nm was observed.

- The nanostructured porous morphology of upper most $SrTiO_3$ layer provided more surface area for interaction with electrolyte (increased liquid-semiconductor contact area).

- The increase in photocurrent of $SrTiO_3/WO_3$ is attributed to increased absorption and improved charge separation across the interface of two oxide layers leading toward the reduced combination of photogenerated charge carriers.

Thank You