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Design and Development of Semiconductor Nanocomposites for Photoelectrocatalytic Applications

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Abstract

Humanity is currently facing an unprecedented challenge: anthropogenic climate change. This complex phenomenon is driven by a multitude of factors, including scientific, psychological, societal, and social dimensions, among others. the release of greenhouse gases, such as CO_2, CH_4, N_2O, HFCs, and PFCs have increased significantly. Since the industrial revolution, atmospheric CO_2 levels have surged by 50%. Although gases like CO_2 and CH_4 occur naturally and are essential for maintaining the Earth's temperature, their rapid increase is primarily driven by human activities, which are unnatural. This surge has caused substantial harm to humanity, biodiversity, and ecological balance. Major contributors to this increase include the extensive use of fossil fuels for energy and widespread deforestation. In response, scientists worldwide are actively seeking environmentally friendly alternative energy sources. Hydrogen fuel is a promising alternative, with several production methods available, including Steam Methane Reforming (SMR), water electrolysis, Photoelectrochemical (P.E.C.) water splitting, and microbial biomass conversion. Steam Methane Reforming (SMR) is the most cost-effective and commonly used method among these techniques. However, SMR generates significant CO_2 emissions, thus contributing to climate change. Water electrolysis, on the other hand, can produce extremely pure hydrogen and, when powered by renewable energy, is a clean method. Nonetheless, it remains expensive due to the high costs of electricity and electrolyzers. Another promising method that has gained attention is Photoelectrochemical (P.E.C.) water splitting. This article focused on the P.E.C. water splitting method. This article explored the use of this method to generate hydrogen, employing a range of photocatalysts. To achieve this, we developed semiconductor nanocomposites to enhance the efficiency and effectiveness of hydrogen production through P.E.C. water splitting. In this article, various experiments using different photocatalysts and developed semiconductor nanocomposites were conducted to optimize the process. The results of Article have been informative and unique, providing valuable insights into the optimization of P.E.C. water splitting for efficient hydrogen production.

Keywords: Semiconductor nanocomposites, photoelectrochemical water splitting, TiO_2, different concentrations of Ag doped TiO_2, $BiVO_4$

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INTRODUCTION

Background

Photoelectrochemical (P.E.C.) water splitting utilizes sunlight to break water molecules into hydrogen and oxygen. A semiconductor material absorbs photons from sunlight, creating electron-hole pairs. These charge carriers are separated, with the electrons driving the reduction of hydrogen ions to produce hydrogen, while the holes facilitate the oxidation of water to form oxygen. This method is an exciting step toward sustainable hydrogen production, offering a clean, renewable energy

source. and transported to the electrodes, where they facilitate oxidation and reduction reactions. At the photoanode, water molecules undergo oxidation, producing oxygen, protons, and electrons. Concurrently, at the photocathode, protons accept electrons to form hydrogen gas. The efficiency of this method is contingent upon the properties of the semiconductor, the effectiveness of charge separation, and the implementation of catalysts to accelerate reaction rates. This innovative clean energy technology aspires to produce renewable hydrogen fuel, contributing significantly to sustainable energy solutions [1–5].

OBJECTIVES

The main objectives of this research are:

1. Design and synthesize semiconductor nanocomposites with improved photoelectrocatalytic properties for better efficiency in processes like water splitting and pollutant degradation.
2. To characterize the structural, optical, and electronic properties of these nanocomposites.
3. To evaluate the performance of the synthesized nanocomposites in PEC water splitting applications.

METHODOLOGY

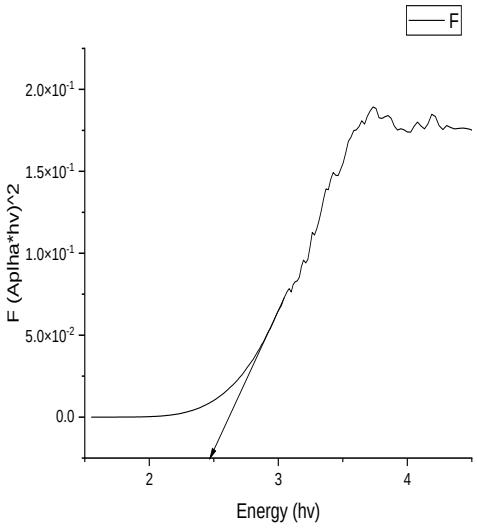
Synthesis of Semicondu0ctor Nanocomposites

Various materials were synthesized, like TiO_2, Ag-TiO_2, and $BiVO_4$.

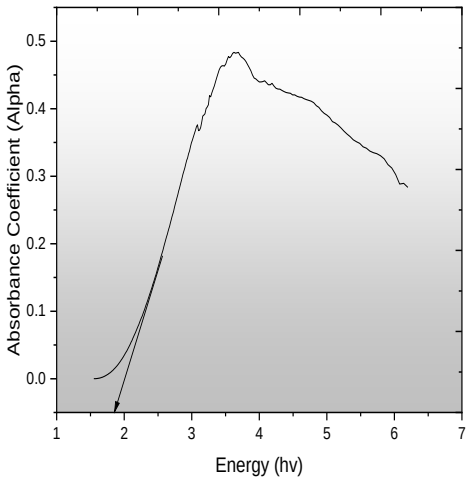
- *For the synthesis of $BiVO_4$,* Bismuth nitrate pentahydrate ($Bi(NO_3)_3$ $5H_2O$, 99.99+% purity) was combined with ammonium metavanadate (NH4VO3, 99% purity). Both materials were used without any further purification. Typically, the precursor solution was prepared by dissolving $Bi(NO_3)_3$ $5H_2O$ and NH_4VO_3 in a 1:1 molar ratio in an approximately 3 M nitric acid solution. The precursors were added to achieve a final concentration of 0.2 M [6–9].
- *For synthesis of TiO_2,* we took Titanium (IV)Oxide and mixed it in distilled water.
- *For synthesis of Ag-TiO_2,* Ag nanoparticles were anchored onto commercially available TiO_2 via photoreduction using $AgNO_3$. We did this by anchoring different concentrations of Ag nanoparticles onto commercially available TiO_2, i.e., 0.25% Ag-TiO_2, 0.5% Ag-TiO_2, 1% Ag-TiO_2, 1.5% Ag-TiO_2 [10].

Characterization Technique

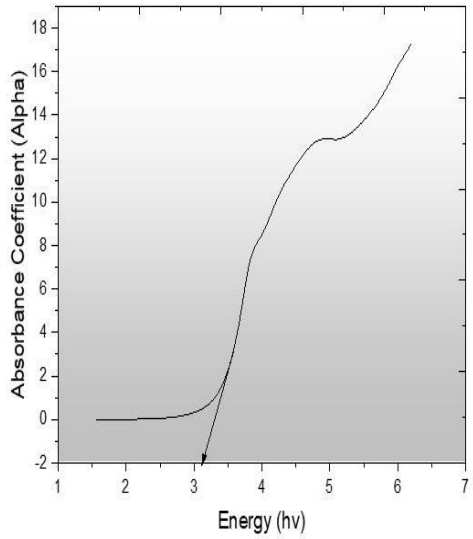
The characterization technique used is UV-Visible spectroscopy. Tauc Plots were added (Figure 1(a–j)).



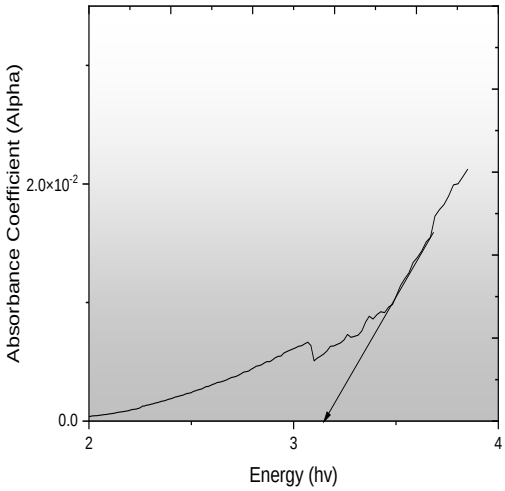
(a). 20 uL 0.25% Ag-TiO_2.



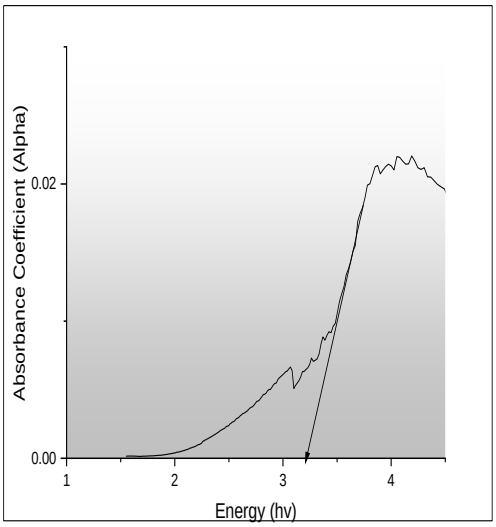
(b). 40 uL 0.25% Ag-TiO_2.



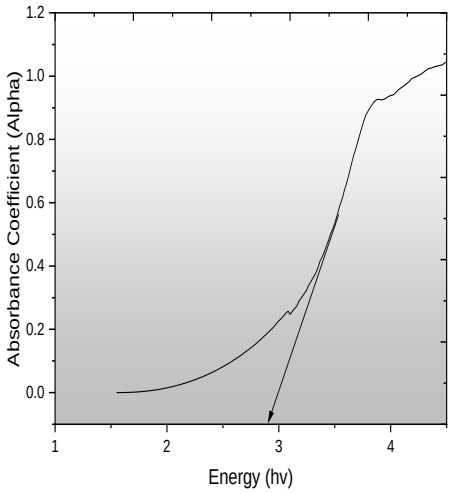
(c). 20 uL 0.5% Ag-TiO_2.



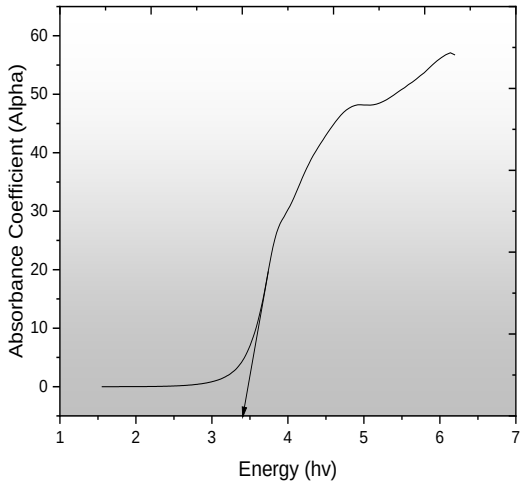
(d). 40 uL 0.5% Ag-TiO_2.



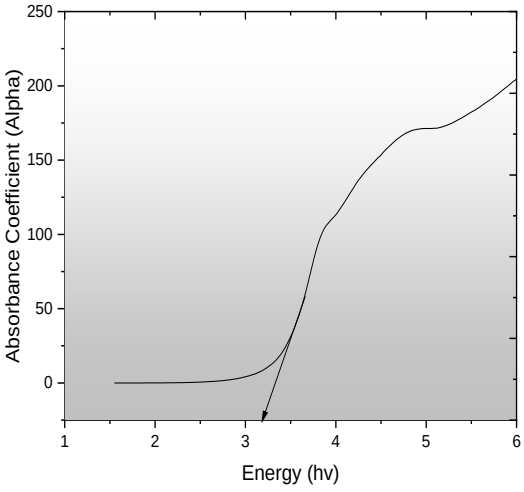
(e). 20 uL 1% Ag-TiO_2.



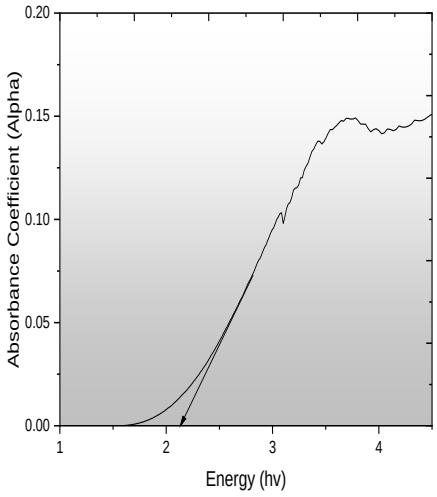
(f). 40 uL 1% Ag-TiO_2.

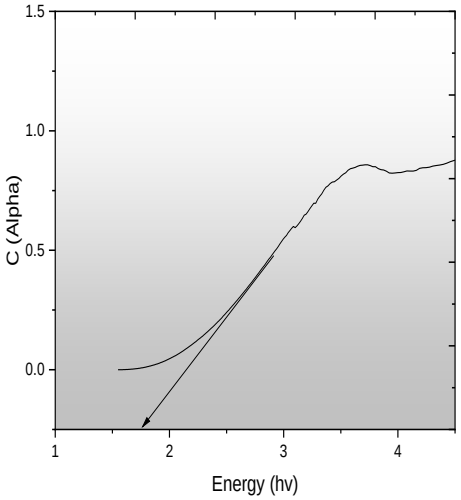


(g). 20 uL 1.5% Ag-TiO_2.



(h). 40 uL 1.5% Ag-TiO_2.





(i). 20 uL TiO_2. (j). 40 uL TiO_2.

Figure 1(a–j). The tauc plot of the uv spectroscopy data is used to calculate the band gap of the material at different doping percentages of Ag on TiO_2.

Photoelectrochemical Testing

The PEC performance of the nanocomposites was rigorously tested using a standard three-electrode setup. The detailed setup and testing procedures are as follows:

Electrode Preparation

- *Photoanode:* Different concentrations of Titanium dioxide (TiO_2) and silver-doped titanium dioxide (Ag-TiO_2), and $BiVO_4$ samples were used as semiconductor materials for the photoanode. These materials were deposited on a fluorine-doped tin oxide (FTO) substrate. The preparation involved:
  - Cleaning the FTO substrate thoroughly to remove any contaminants.
  - Depositing a thin layer of TiO_2, Ag-TiO_2, $BiVO_4$ onto the FTO substrate using techniques, such as spray pyrolysis, and drop casting.
  - Anneal the coated substrate at high temperatures to improve the crystallinity and adhesion of the semiconductor layer.
- *Counter electrode:* A platinum electrode was used as the counter electrode due to its excellent conductivity and catalytic properties for the hydrogen evolution reaction.
- *Reference electrode:* A silver (Ag) wire was used as the reference electrode, offering a stable reference potential for precise measurement of the photoanode's performance [11, 12].

Photoelectrochemical Cell Setup

The PEC cell was assembled with the prepared electrodes:

- The FTO substrate with the TiO_2 or Ag-TiO_2 or $BiVO_4$ layer acted as the working photoanode.
- The platinum electrode functioned as the counter electrode.
- The Ag wire served as the reference electrode.

Electrolyte

An aqueous solution, typically containing a suitable electrolyte, such as sodium sulfate (Na_2SO_4) or potassium hydroxide (KOH), was used to facilitate ion transport between the electrodes [13].

Readings: Readings at Different Concentrations

LSV

Key Observations

- All samples exhibit a positive photocurrent, meaning they are photoactive under applied potential.
- The undoped TiO_2 shows moderate photocurrent response compared to the doped samples.

The photocurrent significantly increases as the concentration of Ag in Ag-TiO_2 increases (1% Ag-TiO_2 showing the highest current density). This indicates that silver doping in TiO_2 enhances the PEC activity, likely due to improved charge separation and better light absorption.

The $BiVO_4$ sample also shows improved performance but does not exceed the best-performing Ag-TiO_2 samples (Figure 2).

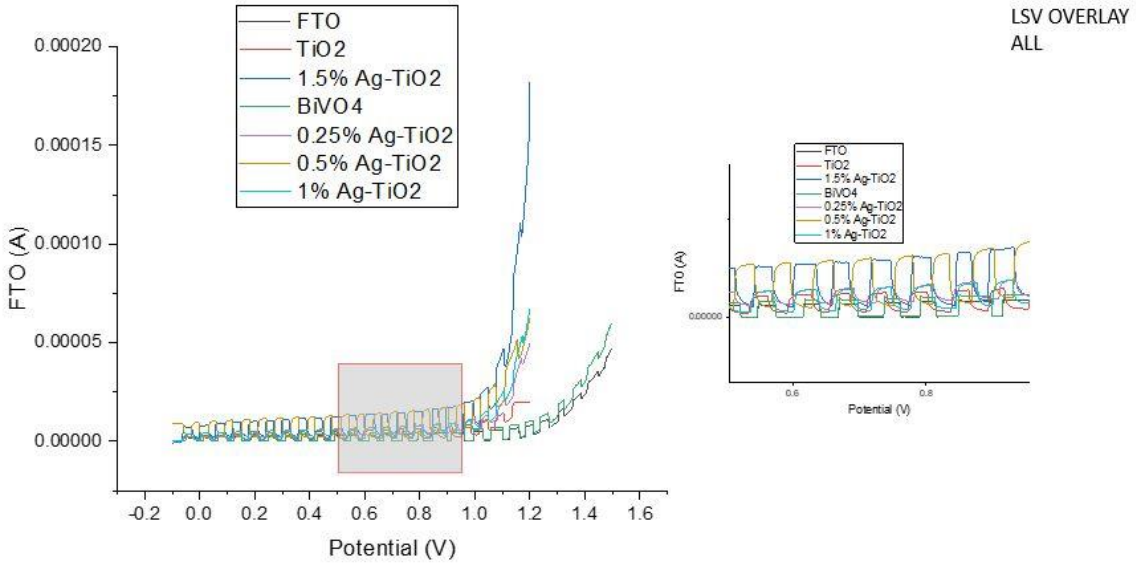


Figure 2. The LSV graph presents the current density (I) versus potential (V) for different photoanode materials: FTO, TiO_2, Ag-TiO_2 at different concentrations, and $BiVO_4$.

Interpretation

Ag-TiO_2 composites outperform both pure TiO_2 and $BiVO_4$ due to the synergistic effect of silver doping. This can be attributed to the fact that Ag enhances electron mobility and reduces charge recombination, thus improving the photoelectrochemical activity of TiO_2 [14].

I-T Chopped Overlay

Key Observations

The current spikes every time the light is turned on and drops when the light is off, which indicates the photocurrent generation and the light-driven nature of the PEC process.

Ag-TiO_2 samples, particularly at higher doping concentrations (0.5% and 1%), show higher and more stable photocurrents under illumination compared to pure TiO_2 and $BiVO_4$.

The pure FTO and lower-concentration Ag-TiO_2 samples (0.25%) show relatively lower photocurrent values and less stable performance under intermittent light (Figure 3).

Interpretation

The chopped photocurrent measurement highlights the effectiveness of Ag-TiO_2 in maintaining

higher and more stable photocurrent densities during light exposure. This suggests enhanced charge transport and reduced recombination rates in Ag-doped samples, making them more efficient for PEC applications under light-chopping conditions [15].

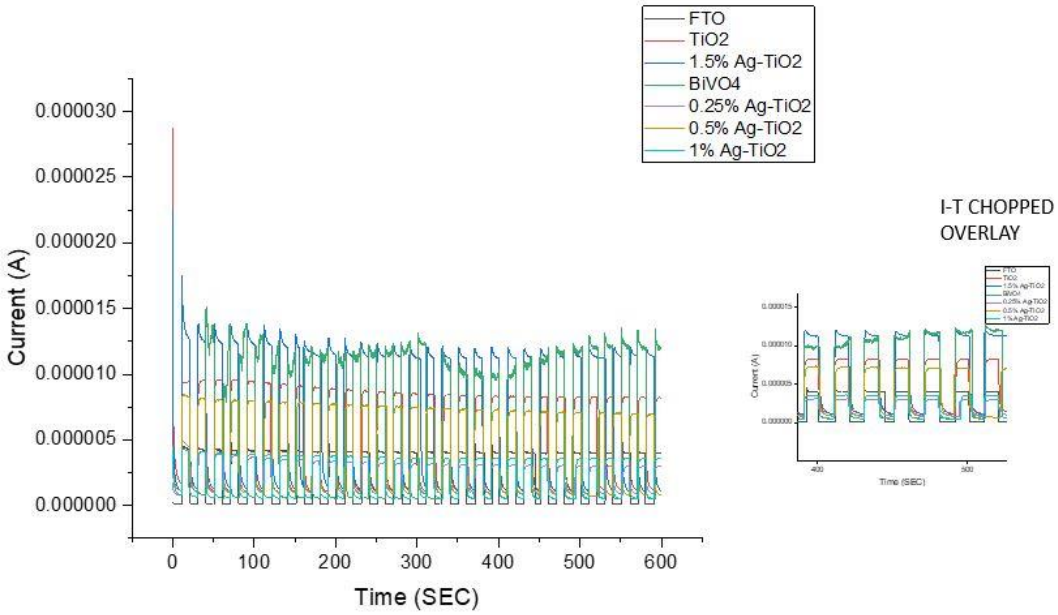


Figure 3. This graph represents the transient photocurrent response (current vs. time) under chopped illumination (periodically switching the light on and off) for the same set of materials (FTO, TiO_2, Ag-TiO_2, $BiVO_4$).

RESULTS

Both the LSV and I-T chopped overlay graphs suggest that silver-doped TiO_2 nanocomposites outperform pure TiO_2 and $BiVO_4$ in terms of photoelectrochemical water splitting performance. The enhanced photocurrent densities, along with more stable and higher transient photocurrent responses, demonstrate the improved PEC efficiency with Ag doping, particularly at higher doping concentrations (1%). These findings align with the study's goal of enhancing hydrogen production through solar-driven water splitting using advanced semiconductor materials.

CONCLUSION

In this research, the design and development of semiconductor nanocomposites for photoelectrocatalytic (PEC) water splitting were thoroughly examined. The main objective was to improve the efficiency of hydrogen production through solar-driven water splitting by employing advanced semiconductor materials.

Key Findings from the Study Include

1. *Successful synthesis of nanocomposites:* Various semiconductor nanocomposites, including $BiVO_4$, TiO_2 and Ag-TiO_2, were effectively synthesized using methods, such as sol-gel and hydrothermal synthesis. Structural and morphological characterizations verified the creation of well-defined nanostructures with a uniform particle distribution.
2. *Enhanced optical and electronic properties:* The nanocomposites demonstrated strong light absorption in the visible spectrum and efficient charge separation, as shown by UV-Vis and photoluminescence spectroscopy. Silver doping in TiO_2 significantly enhanced its properties, leading to improved overall photocatalytic performance.
3. *Improved PEC performance:* Photoelectrochemical testing indicated that the synthesized nanocomposites surpassed conventional semiconductor materials in performance. The TiO_2 and

Ag-TiO_2 photoanodes on FTO substrates exhibited higher photocurrent densities and hydrogen production rates. This improvement was attributed to superior light absorption, efficient charge carrier dynamics, and enhanced catalytic activity facilitated by the nanocomposite structure.

4. *Mechanistic insights:* The research provided valuable insights into the mechanisms behind the improved PEC performance. The synergistic effects of the nanocomposite components, especially at the interfaces, were crucial in enhancing charge separation and reducing recombination rates, this enhances the overall efficiency of the PEC water splitting process.

In conclusion, this study highlights the potential of semiconductor nanocomposites as promising materials for PEC water splitting applications. The significant enhancements in photocatalytic activity highlight the feasibility of using these materials for sustainable hydrogen production. Future research should aim at scaling up the synthesis process, exploring additional semiconductor combinations, and investigating the long-term stability and durability of the nanocomposites to further their practical application in clean energy technologies.

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