Advancing Antimony Selenide Nanostructures for Electrocatalysis, Desalination and Nonlinear Optical Applications

Thesis submitted for the degree of

Doctor of Philosophy (Science)

By

Nabanita Sen

Department of Physics

Jadavpur University

Kolkata -700032

India

February, 2025

Abstract:

This work explores the untapped potential of antimony selenide (Sb_2Se_3) in emerging fields such as the hydrogen evolution reaction (HER), desalination, and nonlinear optics. This investigation is significant, as Sb_2Se_3 has primarily been recognized for its applications in solar cells due to its advantageous properties, including an optimal band gap (direct: 1.17 eV, indirect: 1.03 eV) for efficient solar light absorption, a high absorption coefficient of 10^5 cm^{-1} at shorter wavelengths, and a favourable crystal structure (space group Pbnm(62)). Its ribbon-like structure is held together by weak van der Waals forces, while strong covalent bonds exist within the ribbons. The absence of dangling bonds along the covalent bonds, along with concentrated electron density in these regions, contributes to excellent electrical conductivity along the [001] direction. Additionally, crystalline Sb_2Se_3 exhibits a high dielectric constant (~19), which reduces exciton binding energy and facilitates efficient separation of photogenerated carriers. Beyond its role in photovoltaics, Sb_2Se_3 is also valued for its thermoelectric properties, owing to its high Seebeck coefficient, as well as its potential applications in photoelectrochemical processes.

The motivation behind this thesis is to harness the full potential of Sb_2Se_3 by improving its weaker properties while also utilizing its inherent beneficial characteristics. A brief overview of the thesis is provided below.

The global shift toward clean hydrogen energy necessitates earth-abundant, noble-metal-free hydrogen evolution electrocatalysts. In this work, Chapter 4 presents a straightforward solvothermal strategy for designing Sb_2Se_3/rGO heterointerfaces to enhance electrocatalytic hydrogen evolution performance. The resulting hybrid demonstrates an improved onset potential of -0.32 V and a two-fold reduction in the Tafel slope compared to pure Sb_2Se_3.Experimental findings confirm that heterointerface engineering significantly enhances interfacial electron transport, leading to better HER performance. Density functional theory (DFT) calculations reveal that the heterointerfacial interaction lowers hydrogen adsorption energy on the (001) and (230) planes. Essentially, rGO facilitates charge redistribution at the

Sb_2Se_3/rGO interface, increasing H^+ adsorption at selective sites and thereby optimizing electrocatalytic HER activity.

The field of nonlinear optics continues to evolve, driven by the discovery of new materials with unique optical properties. In this work, chapter 5 presents, spatial self-phase modulation (SSPM) experiments using the anisotropic, layered Sb_2Se_3 material in a liquid suspension for all-optical diode and switching applications. Through a 671 nm laser beam, we determined the third-order broadband nonlinear optical susceptibility ($\chi(3)$single layer ~10^{-9} e.s.u) and nonlinear refractive index (n_2 ~10^{-6} cm^2/W) of Sb_2Se_3. These findings can be attributed to the material's anisotropic hole mobility, which plays a key role in the formation of diffraction patterns through nonlocal hole coherence, as evidenced by the linear relationship between $\chi(3)$ and carrier mobility. The time evolution of the diffraction rings aligns with the "Wind-Chime" model.

Furthermore, we demonstrate a novel photonic diode based on Sb_2Se_3/SnS_2, leveraging the nonreciprocal propagation of light. Using the self-phase modulation (SPM) technique with varying laser wavelengths and intensities, we successfully implement all-optical logic gates, particularly the OR logic gate. This exploration of Sb_2Se_3's nonlinear optical properties open new opportunities for optical information processing and communication.

Chapter 6 presents a theoretical and experimental validation of Sb_2Se_3 nanorods (NRs) as a promising candidate for solar thermal heat generation. Through customized water droplet experiments, the light-to-heat conversion efficiencies of Sb_2Se_3 were determined to be approximately 57.8% and 58% for red (671 nm) and green (532 nm) lasers, respectively. Building on this, we developed PVDF(M)/Sb_2Se_3 NRs hybrid membranes for solar desalination, which achieved a temperature of ~59°C within 15 minutes of illumination. The primary mechanism driving heat generation is electron/hole-acoustic phonon scattering.

Despite the superior visible-NIR absorption and heat localization of Sb_2Se_3 NRs, the hybrid membranes exhibited a limited evaporation rate of 1.72 kg m^{-2} h^{-1}, even with increased mass loading. This limitation arises from the hydrophobic nature of the

Sb_2Se_3 NRs layer, which restricts uniform water diffusion to hot zones, thereby reducing solar evaporation efficiency. To overcome this challenge, we introduced a novel mechanical imprinting strategy to create macro-channels in the hybrid membranes. These macro-channels significantly enhance water transport to hot zones, leading to an improved mass loss rate of ~2.37 kg m^{-2} h^{-1} and a solar evaporation efficiency of 148% under a mercury vapor lamp with an intensity of 1000 W m^{-2}.

Furthermore, outdoor sunlight experiments demonstrated a commendable solar evaporation efficiency of ~108%. The steam generated through this solar thermal process effectively removes heavy metal ions, ensuring compliance with the World Health Organization (WHO) standards for potable water. This study highlights macro-channel imprinting as a viable strategy for improving desalination efficiency in hydrophobic materials, with potential applicability to other similar systems.

This thesis highlights the potential benefits of using Sb_2Se_3 in research areas such as HER, desalination and nonlinear optics. It is believed that further opportunities remain in these fields with continued exploration of Sb_2Se_3.

Nabanita Sen
Signature of the candidate

Date: 05.02.2025

Signature of the supervisor

Date: 5.2.2025

Dr. K. K. Chattopadhyay
Professor
Department of Physics
Jadavpur University
Kolkata-700 032