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Hydrogen evolution reaction: The role of arsenene nanosheet and dopant

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ABSTRACT

The state-of-the-art density functional theory (DFT) is employed to study the catalytic activity of arsenene for hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). We have included dispersion correction to get accurate adsorption energy on the individual catalytic surface (top site). Using binding energy calculation, arsenene is shown to be a potential candidate for HER. Here we investigate the stability and electronic properties of the honeycomb structure of the arsenene system using first-principles calculation to find the effect of different dopants on the fundamental band gap, which is one of the primary parameters in the photocatalytic water splitting. Further, we sieved the dopant for better HER catalytic activity by substituting one of the arsenene (As) atoms by B, N, O, Ge, Ga and Se atoms to make arsenene a better candidate for HER. Our studies depict that HER activity is increased by 82% for O-doped arsenene and OER activity by 87% for B-doped arsenene as compared to pristine arsenene.

Introduction

In today's world, as the modern society turns more towards renewable methods for its energy supply, energy storage and transport have become a more prevalent consideration. The lack of correlation between renewable sources of energy and energy demand create many challenges for the buffering of supply and demand. One of the most promising ideas for storing renewable energy is to use the excess electricity generated from renewables to split water into oxygen and hydrogen. Simple water splitting devices can be used to convert spare (renewable) electrical energy into green hydrogen gas which can be transported, stored and used on demand for domestic, commercial and transport applications [1–4]. Emergence of sustainable clear energy is one of the most important and necessary requirements due to harmful effect of fossil fuels [1–4]. To overcome demand of energy, production of hydrogen becomes essential as hydrogen molecule is considered as one of the cleanest energy suppliers. Among several methods simplest and promising approach to produce hydrogen efficiently is photocatalytic water splitting [5–7]. The water splitting mechanism consists of two half reaction: hydrogen evolution reaction (HER) which is reduction half reaction ($2H^+ + 2e^- \rightarrow H_2$) and oxygen evolution reaction (OER) which is oxidation half reaction ($2H_2O \rightarrow 4H^+ + 4e^- + O_2$). A good photocatalytic material should have properties like high stability, low toxicity, abundance and less expensive [8]. Up to date nickel (Ni) alloys, platinum (Pt), its alloys and other noble metals were

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Hydrogen evolution reaction of metal di-chalcogenides: ZrS_2, $ZrSe_2$ and Janus ZrSSe

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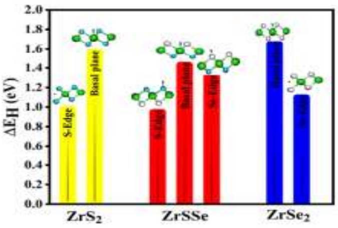
HIGHLIGHTS

- A high asymmetric arrangement of Janus leads to enhancement in catalytic activity.
- ZrSSe Janus shows more catalytic activity at the sulphur edge than selenide edge.
- Increase in basal plane catalytic activity depends on the selectivity of dopants.
- Nb-doped $ZrSe_2$ has low open circuit potential of 0.37 V.
- Nb-doped $ZrSe_2$ shows the best catalytic activity for hydrogen evolution reactions.

GRAPHICAL ABSTRACT



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ABSTRACT

Transition metal di-chalcogenides with stoichiometry MX_2 (M: Mo, V, W, Pt and X: S, Se) are considered as one of the non-precious and effective catalysts for the production of clean hydrogen energy via water-splitting mechanism. The major drawback of these materials is their inactive basal plane as compared to their edge sites. Recently, Janus MoSSe-a novel sandwiched structure has been synthesized and predicted theoretically to obtain increased catalytic activity by applying strain, external electric field and by creating vacancy. In this work, we have used *state-of-the-art* density functional theory with dispersion correction (DFT-D3) to study the catalytic activity for hydrogen evolution reaction (HER) of ZrS_2, $ZrSe_2$ and Janus ZrSSe. From our calculations, we conclude that among these three systems, the Janus ZrSSe ($\Delta G = 1.19\ eV$; ΔG : *Gibbs free energy*) is a good catalyst and can be utilized for HER at edge site. Janus ZrSSe shows enhanced catalytic activity at S-edge as compared to its basal plane and Se-edge site; whereas $ZrSe_2$ shows good catalytic activity at Se-edge rather than at the basal plane. The ZrS_2 shows good catalytic activity at S-edge. Further, we have doped Nb, Pt and W atoms in ZrS_2, $ZrSe_2$ and Janus ZrSSe to see their effect on catalytic activity of pristine compounds and found that the Nb-doped $ZrSe_2$ shows good catalytic activity for HER and is best among all considered systems with $\Delta G = 0.63$ eV

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Strain and layer modulated electronic and optical properties of low dimensional perovskite methylammonium lead iodide: Implications to solar cells

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ABSTRACT

In the present work we report the effect of quantum confinement, biaxial and uniaxial strains on electronic properties of two dimensional (2D), one dimensional (1D) and layered system of Methylammonium lead iodide (MAPI) in cubic phase using first principles calculations based on density functional theory for its implications to solar cell. Our studies show that the bandgap of MAPI is dimension dependent and is maximum for 1D. We also found that the band gap of 2D MAPI can be modulated through application of biaxial strain, which shows linear relation with strain; compressive strain decreases the band gap whereas tensile strain increases the band gap. 1D MAPI shows near parabolic response towards strain which increases with compressive and tensile strain. Our studies show that the 2D MAPI is better for a solar cell due to lower effective mass of electron and hole arising from the strong s-p anti-bonding coupling. The calculated solar cell parameters suggest that the 2D MAPI is best suited for solar cell applications. The calculated open circuit voltage, fill factor and efficiency are highest for 2D MAPI. The highest theoretical efficiency of 2D MAPI is 23.6% with mesoporous (mp)-TiO_2 electrode.

1. Introduction

Perovskite crystals with chemical formula ABO_3 are known for their complex landscape and useful physical properties such as magnetic, ferroelectric and two dimensional electronic conductivity (Cohen, 1992; Peña and Fierro, 2001). Last few years have witnessed a tremendous effort for the organic – inorganic perovskites not only due to their more complicated structure than that of organic perovskites arising due to many possible orientation of organic materials (Baikie et al., 2013) but also due to phenomenal advancement in the solid state solar cells (Burschka et al., 2013; Jeon et al., 2014; Jung and Park, 2015; Kim et al., 2012; Lee et al., 2012; Stoumpos et al., 2013; Zhou et al., 2014). The photovoltaic efficiency in the solid state solar cells has reached its maximum about 21% (Jung and Park, 2015; "Natl. Renew. Energy Lab" https://www.nrel.gov/pv/assets/images/efficiency-chart.png.; Zhou et al., 2014). Further, it is observed that the organic cations and substitution of metal halides affect the bandgap through alternation of inorganic framework (Eperon et al., 2014; Filip et al., 2014; Noh et al., 2013). The organic-inorganic halide perovskites have unit cell generally composed of AMX_3 (where $A = CH_3NH_3{}^+$, or $(H_2N)_2CH^+$, Cs^+; $M = Sn^{2+}$, Pb^{2+} and $X = Cl^-$, Br^-, I^-) (Mitzi, 2004, 2001). The best example of this alternation is Cs which is largest atom in the group I to hold cubic perovskite structure but the molecule CH_3NH_3 is larger than Cs, which makes $CH_3NH_3PbI_3$ (MAPI where MA represents CH_3NH_3 cation) more stable and perform better than $CsPbI_3$ (Zhang et al., 2015). Furthermore, they are known for many interesting properties such as high optical absorption spectra range, a long carrier diffusion and most importantly tuneable bandgap (Dong et al., 2015; Stranks et al., 2013) which leads them to be useful in various applications of optoelectronics and photonic devices including solar cells, photodetectors, light emitting diodes, field effect-transistors (FET), waveguides and nano lasers (Chin et al., 2015; Kojima et al., 2009; Snaith, 2013; Tan et al., 2014; Wang et al., 2015, 2016; Zhu et al., 2015). MAPI which was first reported by Weber (Weber, 1978) in the cubic crystal structure consequently has been studied intensively as a solid state solar cell due to its high photovoltaic efficiency over 20%

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Strain Effect on Electronic and Lattice Dynamical Behaviour of Two Dimensional Bi, BiAs and BiSb

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Abstract. The present study investigates the electronic band structure and lattice dynamical stability of 2D monolayer sheet of Bi, BiAs and BiSb using density functional theory based on first principles calculation. All these systems are semiconductor with direct bandgap. Under tensile strain the bandgap reduces and no bandgap closing is observed upto +5% strain whereas a direct-indirect-metal transition is observed for compressive strain in all these systems. The lattice dynamical stability of these materials has been studied under strain.

INTRODUCTION

The identification of 2D sheets of semiconductors particularly the layered compounds of group-V elements with different bandgap energies is of utmost importance for their particular applications in optoelectronic and spintronic devices[1-2]. However, their properties are sensitive to biaxial strain induced from the substrate which is inherent while dealing with 2D materials in practical situations[3]. The semimetal-semiconductor and semiconductor-to-topological transitions under strain have been subjects of active studies [2, 4]. Recent studies on bismuthene includes the finding of Rashba-type spin splitting due to strong spin orbit coupling (SOC) in Bi and dependence of surface states on film thickness[1, 5]. Recently, the interfacial properties of the bismuthene–metal contacts have been studied in detail where it was shown that the bismuthene on the metal surface undergoes metallization, and Ohmic contact occurs in the vertical direction [6]. However, the effect of strain induced on Bi monolayer by the metal substrate has not been considered which is of utmost important since the change in bandgap of bismuthene or bismuthene compounds due to strain will alter the choice of metal electrodes in monolayer bismuthene devices. Strain dependence of electronic band structure Bi, BiAs and BiSb has been studied recently but the stability of free standing BiAs and BiSb is in question[1, 2] due to imaginary frequency of out of plane acoustical branch (ZA) near zone centre. Further, the lattice dynamical property of these materials under strain has not been considered yet which makes the study of these materials incomplete. In the present work, we systematically calculated the electronic band structure of two dimensional Bismuth (Bi), bismuth arsenide (BiAs) and bismuth antimonide (BiSb) and investigated the dynamical stability of these materials by studying phonon dispersion curves using density functional theory calculations. The objective is to understand the modification of electronic band structure of 2D Bi, BiAs and BiSb with compressive and tensile strain, to know the stability limit of monolayer Bi, BiAs and BiSb under strain and occurrence of any transition or unusual behaviour of phonon modes with the application of strain.

METHODS

The structural, electronic and lattice dynamical properties of Bi, BiAs and BiSb were studied using first principle calculations based on Density Functional Theory within the plane wave pseudopotentials as implemented in Quantum Espresso code[7]. The exchange correlational functional of Perdew-Burke-Ernzerohf (PBE)[8] for the Generalised Gradient Approximation was adopted. To mimic the 2D system, vacuum of about 15 Å is used along Z

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First Principles Study of the Structural and Electronic Properties of Hetero-Structure Silicene/SnSe2: Using Lattice Match Model

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Abstract. In this study, we investigate the structural and electronic properties of Silicene, SnSe2, and hetero-structure Silicene/SnSe2 (Si/SnSe2) using first-principles calculations based on dispersion corrected density functional theory. It is found that the structural, electronic properties are significantly modified when silicene is put together with $SnSe_2$. The electronic properties of silicene exhibit metallic nature similar to high buckled silicene (HB-Si). The calculated formation energy and cohesive energy of $Si/SnSe_2$ show energetically favorable configuration and suggests the possibility of growth of silicene on monolayer $SnSe_2$ is possible.

INTRODUCTION

The two-dimensional (2D) materials have received a lot of attention after the isolation of graphene [1]. However, the semimetal nature graphene limits its utility in electronic devices. This stimulates the search for other 2D materials mainly to find an optical band gap which is difficult in graphene [2]. Many two-dimensional materials with similar and/or better properties than graphene have been experimentally and theoretically developed in the recent years [1,3-7]. However, some of the 2D materials such as silicene, germanene and stanene do not occur naturally and need to be synthesized. The isolation of silicene is the major challenge due to its strong interaction between silicene and metal substrates [8]. Recently, experimentally high buckled (HB) silicene has been synthesized on MoS_2. Furthermore, theoretically the tailoring of electronic properties of HB silicene and low buckled (LB) silicene on MoS_2 and $MoTe_2$ substrates are reported [9,10]. Tailoring of the electronic properties depends on the interface effect which are of two types: lattice match (lattice constants differ slightly) and lattice mismatch (lattice constants differ ~1.8 %) model. In the present study, we have performed density functional theory calculations on the structural and electronic properties of hetero-structure silicene/$SnSe_2$ under lattice match model approach as the mismatch between lattice constants is 0.48 %. We have also included the dispersion correction (DFT-D2) and found that interaction DFT-D2 turns hetero-structure to metal can be attributed to strong interaction between silicene and $SnSe_2$. The lattice match model has been used in many interfaces such as graphene/BN, LB silicene/GaS, HB silicene/MoS_2 and LB silicene/$PtSe_2$ [10-14].

METHODOLOGY

First principles calculations were performed within the density functional theory (DFT) using generalized gradient approximation (GGA), a plane wave pseudo-potential method proposed by Perdew, Burke and Ernzerh(PBE-GGA) [15] as exchange correlation functional as implemented in Quantum espresso code [16]. The electronic wave functions

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ARTICLE

A Comparative Study of Hydrogen Evolution Reaction on WS_2 and PtS_2 pseudo-monolayer: Insight based on Density Functional Theory

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In this work, we have envisaged the Hydrogen Evolution Reaction activity on ultrathin nano structures of PtS_2 and WS_2 based on spin-polarised density functional theory aided electronic structure calculations. We have also explored the effect of van der walls interactions for the surface adsorbate interactions. Using adsorption free energy of H_2 as the activity descriptor, we have tuned the photocatalytic water splitting activity of PtS_2 and WS_2 by functionalizing the individual systems with different transition metals such as Ru, Rh, Pd, Ag, Ir, Au and Hg. Density of states have been calculated along with the band structure to find the effect of the different dopants on fundamental band gap which is one of the primary parameter of the water splitting phenomena.

Introduction

Sustainable clean energy is becoming more and more essential requirement for the modern human society because of the scarcity and harmful side effects of fossil fuels[1]. Hydrogen production through the photocatalytic water splitting, therefore, plays a defining role for the quest of such clean energy with least environmental hazards[2-4]. For a promising photocatalytic material, the fundamental band gap should be around 2 eV and the band edge positions must be properly aligned in order to include the redox potential of water[5]. Titanium dioxide (TiO_2) is the first semiconductor that was used for the photocatalytic water splitting[6]. Since the discovery of TiO_2, plenty of attempts have been made to develop efficient photocatalysts for hydrogen evolution reaction (HER). The metal oxides, metal alloys, transition metal carbides and phosphides, carbon nanotubes, different enzymes and biomolecules are among these attempts[6-13]. But, the primary concern regarding the recombination possibilities of electrons and holes decreasing the photocatalytic efficiency has not been completely resolved.

The photocatalytic properties have also been explored on two-dimensional (2D) materials to control the charge carrier recombination process, since when the essential role of dimensionality in determining the fundamental properties of materials was realized[14]. The rapid advancements in graphene technology and the successful exfoliation of ultrathin materials have led to the exploration of novel 2D materials[4,15-25]. Although, the first 2D material graphene is technologically relevant for a wide range of applications, but its applications are restricted due to the absence of band gap in its electronic structure[26]. Therefore, other atomically thin 2D materials such as hexagonal boron nitride, transition metal dichalcogenides (TMDCs) have been investigated intensively because of their unique and intriguing electronic properties and also due to the fact of synthesizing them over a large surface area[22].

TMDCs having the structural formula X-M-X (where M is the transition metal and X = S, Se, Te) have attracted a significant amount of attention because of the distinctive crystal

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First Principles Calculation Of Two Dimensional Antimony And Antimony Arsenide

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Abstract. This work focuses on the strain dependence of the electronic properties of two dimensional antimony (Sb) material and its alloy with As (SbAs) using density functional theory based first principles calculations. Both systems show indirect bandgap semiconducting character which can be transformed into a direct bandgap material with the application of relatively small strain.

Keywords: Two dimensional antimony, Density Functional Theory, band structure, indirect-direct band gap, strain.
PACS: 31.15.A-, 81.05.zx, 68.65.-k, 81.05.ue

INTRODUCTION

The excellent properties such as high electron mobility, heat conduction and mechanical strength in graphene[1] a great deal of attention is being diverted to other two dimensional (2D) materials such as silicene, germanene[2], boron nitride (BN)[3-4], dichalcogenides (XY_2; X=Mo and W and Y=S and Se))[5-6] monolayer and few layer black phosphorus[6-7]. However, the electronic band structure of graphene, silicene and germanene shows zero band gap, which reduces their ability to switch current on and off in transistors even though the functonalization, electric field and strain can create a gap. The identification of 2D semiconductors with different bandgap energies for their particular applications in light emitting and optoelectronic devices is of utmost importance.

Recently, after successful experimental studies on phosphorene[8-9], the atomically thin 2D arsenic and antimony known as arsenene and antimonene respectively have received great attention and been actively studied[10-11]. These systems exist in three structural configurations namely planar, buckled and puckered among which the later two configurations are found to be stable by investigation [10]. The arsenene and antimonene both have indirect bandgap which limits their use in light emitting and optoelectronic devices. However the application of strain to arsenene makes indirect to direct bandgap transition [12]. In this work, we investigate the electronic properties of 2D planer and buckled antimonene by employing density functional theory (DFT) based electronic structure calculations. We also study the effect of strain to see and study the effect of strain on band structure of these 2D systems to find out any possible indirect-direct band transition.

METHODS

The computational approach to gain insight into the energetic, structural and electronic properties of layered antimony and antimony arsenide has been studied using first principle calculations based on Density Functional Theory within the plane wave pseudopotentials as implemented in Quantum Espresso code[12].The exchange correlation interaction was treated within the generalised gradient approximation (GGA) given by Perdew-Burke-Ernzerhof (PBE)[14]. Both materials are periodic in X and Y directions and to mimic 2D system, vacuum of about $15A^0$ is used along Z direction to avoid interaction between adjacent models. An energy cutoff of 45Ry and 180Ry were used for electronic wave function and charge density respectively. The reciprocal space for both was sampled by a grid of 25x25x1 and Brillouin zone integration was performed using Monhorst-Pack scheme. Both energy cutoff and k-point sampling value are determined by performing extensive convergence analysis. The energy convergence value between two consecutive steps was chosen as 10^{-5}eV

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Structural, Electronic and Dynamical Properties of Binary Alloy Zr-Al Using Density Functional Theory

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Keywords: alloy, structure, electronic, phonon

Abstract. The structural, electronic, dynamical and thermodynamical properties of binary Zr-Al alloy (Zr_3Al) with its end members are studied using the first principles calculations based on density functional theory. We have employed the Perdew-Zunger local density approximation as the exchange correlational functional in these calculations. There is a good agreement between present and available and experimental and other theoretical data. The calculated electronic band structure and density of states suggest that the Zr-Al alloy and its end members are metallic in nature consistent with earlier studies. Full phonon dispersion curves and phonon density of states are also calculated which show the dynamical stability of these compounds at zero pressure. The temperature dependence of the thermodynamical functions are also presented.

Introduction

During last few decades zirconium based compounds and zirconium based alloys have received great attention due to their unique and superior properties such as high strength, light weight and high melting temperature useful for various industrial application [1-7]. The zirconium aluminium (Zr-Al) alloys which have attracted as practical material exhibit good mechanical properties, low absorption cross section for thermal neutrons and corrosion resistance at high temperature suitable for air turbine energy and nuclear reactors[8-11]. The structural, mechanical, electronic and thermodynamic properties of Zr-Al alloys have been extensively studied in recent past [8-9]. However, to our knowledge the phonon properties of these alloys except for Zr_3Al [12] are not reported. Recently five ordered phases Zr_3Al, Zr_2Al, ZrAl, $ZrAl_2$ and $ZrAl_3$ in the group of Zr-Al alloys have been reported [13-15]. While Yuan *et al.* [10] have studied the pressure depend thermodynamic properties of Zr_2Al. Duan *et al.* [11] and Nakamura [16] have studied the mechanical and Debye temperature for $ZrAl_3$ respectively.

In the present work, we aim to analyse the ground state properties such as lattice constants, bulk modulus, electronic and phonon properties of Zr_3Al together with the two end members Zr and Al from the group of five experimentally reported Zr-Al alloy by density functional theory.

Computational method

All calculations in the present study were performed with the plane wave pseudopotential method of density functional theory (DFT) within the local density approximation (LDA) using the scheme of PZ (Perdew-Zunger) [17] parameterization for exchange correlation functional implemented in the Quantum espresso code [18]. The single particle functions were expanded in a plane waves basis set up to kinetic energies cut off 40 Ry, 50 Ry, and 60 Ry respectively for Zr, Al and Zr_3Al which is sufficient to fully convergeall properties. The electronic charge density was evaluated up to kinetic energy cut off 400 Ry, 500 Ry and 600 Ry respectively for Zr, Al and Zr_3Al. The Brillouin zone (BZ) integration is sampled on uniform Monkhorst-Pack grids of sizes 10x10x10, 15x15x15, and 8x8x8 respectively for Zr, Al and Zr_3Al. The tolerance for the geometry optimization is selected as the difference in total energy within 10 eV/atom, the maximum ionic

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Structural, Electronic and Dynamical Properties of Curium Monopnictides: Density Functional Calculations

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The structural, electronic, dynamical and thermodynamical properties of CmX (X = N, P, As, Sb, and Bi) compounds are studied using first principles calculations within density functional theory. The Perdew–Burke–Ernzerhof spin polarized generalized gradient approximation and Perdew–Wang (PW) spin polarized local density approximation as the exchange correlational functionals are used in these calculations. There is a good agreement between the present and previously reported data. The calculated electronic density of states suggests that the curium monopnictides are metallic in nature, which is consistent with earlier studies. The significant values of magnetic moment suggest their magnetic nature. The phonon dispersion curves and phonon density of states are also calculated, which depict the dynamical stability of these compounds. There is a significant separation between the optical and acoustical phonon branches. The temperature dependence of the thermodynamical functions are also calculated and discussed. Internal energy and vibrational contribution to the Helmholtz free energy increases and decreases, respectively, with temperature. The entropy increases with temperature. The specific heat at constant volume and Debye temperature obey Debye theory. The temperature variation of the considered thermodynamical functions is in line with those of other crystalline solids.

Key words: Density functional theory, structural and electronic properties, phonon dispersion curve, thermodynamical properties

INTRODUCTION

During the last few decades, the rare-earth monopnictides have attracted considerable interest due to their diverse structural, magnetic, transport and vibrational properties.[1–21] Like most of the actinide compounds curium monopnictides CmX (X: N, P, As, Sb, and Bi) crystallize in NaCl type (B1) structure at ambient conditions with space group Fm3 m (225)[12–14] and transform to CsCl type (B2) structure with space group Pm3 m (221) at high pressure.[12,14,15,22] The tracks along the B1 → B2 phase transition under pressure; electronic and mechanical properties have been widely reported for CmX.[12–15] Rached et al.[12] have studied the structural phase transition and elastic properties of curium monobismuthides (CmBi) together with the uranium monobismuthides (UBi) at high pressure using the full potential linear muffin tin orbital (FP-LMTO) method within local density approximation (LDA) for the exchange correlation (XC) potential. These authors found good agreement with the only available theoretical result at that time[22] and the experimental result[7] on structural data, but the phase transition pressure was almost half of the experimental value. Singh et al.[14] have studied the pressure induced phase transition and spin polarized electronic structure of five curium pnictides (CmX: X = N, P, As, Sb, and Bi) using self-consistent tight binding linear muffin tin orbital

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Sensing Behavior of a Graphene Quantum Dot Phenalenyl Towards Toxic Gases

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Abstract. In the present work, by studying the interaction of graphene quantum dot (GQD) Phenalenylwith toxic gases hydrogen cyanide (HCN) and phosgene ($COCl_2$) using density functional theory, we are aiming to evaluate the possibility of using GQD phenalenyl in the detection of HCN and $COCl_2$. Owing to strong interactions between HCN/$COCl_2$ and the GQD Phenalenyl, dramatic changes in the electronic properties of the graphene quantum dots together with highest occupied molecular orbitals and lowest unoccupied molecularorbitals (HOMO-LUMO) gap variationsare observed.The findings show that the GQD phenalenyl can be used as chemical nanosensor to detect HCN and $COCl_2$ toxic gases.

INTRODUCTION

Graphene being a very special 2D nanomaterial ever since its discovery has acquired a great attention as numerous graphene based nanomaterials have been synthesized and shown the positive use at doped graphene as sensors[1-3]. Graphene quantum dots (GQDs) are one of these materials which are zero dimensional and can be viewed as nanosized graphene fragments that show new and excellent properties like size dependent energy band gap, photoluminescence and electron transport ability. Due to these properties absorption of environmental molecules by them shows changes in optical and electrical properties which can be used as sensing alert[3].Raeyani et al.[4]and Chen et al.[5]have shown that the GQDs can be a potential material for optical and NH_3 gas sensors respectively. Cutting the graphene sheet results into the several nanosized graphene, in which one can see various structures of polycyclic aromatic hydrocarbons (PAHs) like anthracene, pyrene, coronene, triangulene, phenalenyl and ultimately benzene. That means the properties of PAHs are closely related to nanographenes[6-7]. Many of these PAHs have a closed-shell electronic configuration in their ground state. However, due to the topology of π electron arrangements[8], there are some PAHs which possess high spin, open-shell radical character in their ground state[9] and are also termed as open shell non -Kekulé polynuclearbenzenoid. For example phenalenyl is one of the most fundamental structure which contains an odd number of π electrons in its ground state. The simple and symmetric structure of phenalenyl, together with the alluring properties in solution and in crystalline state,researchers have been attracted for the graphene quantum dots for a long time[10-11]. Due to the arising interest for PAHs which are related to nanographene we have checked its sensing properties with hydrogen cyanide (HCN) and phosgene ($COCl_2$) using density functional calculation. HCN and $COCl_2$ are colourless, extremely poisonous, flammable

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Enhancing the potency of surface hydroxyl groups of graphene oxide for selective oxidation of benzyl alcohol

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ABSTRACT

A chemo-selective oxidation of benzyl alcohol (BzA) to benzaldehyde (BzH) was built up using transition metal immobilized amino functionalized graphene oxide [ML-*f*-GO (M = VO^{4+}, Co^{2+}, Cu^{2+})] as heterogeneous catalysts. Surface hydroxyl groups on GO are engaged fundamentally in the fabrication of ML-*f*-GO, was confirmed by density functional theory (DFT), Fourier-Transform Infrared (FTIR), electronic spectra and X-ray photoelectron spectroscopy (XPS) results, besides these X-ray diffraction (XRD), thermogravimetric analysis (TGA), Brauner-Emmett-Teller (BET) results, Raman, scanning electron microscope (SEM) and transmission electron microscopy (TEM) were employed to corroborate the successful fabrication. DFT study was executed in an attempt to elucidate the replacement of hydroxyl groups by amino groups. The propensity of binding energy was $-COOH > C{-}O{-}C > -NH_2 > -OH$ which very well corroborate the belief developed from different characterization techniques that the amino groups of substituted amino functionalized moiety replace only surface hydroxyl groups of GO. Energy gap, global hardness and softness were also calculated. Catalytic aptitude of the as-prepared catalysts was weigh-up against oxidation of BzA using 30% H_2O_2 as a greener oxidant. The impact of distinct parameters influencing catalytic activity has also been studied. Under the optimized conditions, CuL-*f*-GO exclusively promoted this transformation with excellent activity to yield 99.5% BzH.

1. Introduction

Developing dynamic, choosy and energy proficient heterogeneous catalytic processes are extremely indispensable to an inexhaustible future because heterogeneous catalysis is at the central part of the chemicals and pharmaceutical industries. The fabrication and execution of selective heterogeneous catalytic processes could have a marvelous encouraging impact on the globe as it may perform the catalytic reaction at a lower temperature, pressure and/or in less time thus wealth can be saved in up-scale reactions. Contrast to this, catalyst deactivation is the subject of considerable seriousness [1], which is the major impediment to research, design and advancing stable catalysts. That's why it is necessary to be acquainted with the reason and remedy for catalytic deactivation. Research on the catalyst deactivation has been spreading gradually across-the-board, since last three decades [2–15]. Deactivation broadly classifieds into three type viz. chemical, mechanical and thermal which includes metal poisoning, foiling, thermal degradation, leaching, solid-solid interactions and mainly support [16–18]. However, it can be lessened by vigilant control of process conditions and by a cautious choice of support materials.

According to archaic aphorism "prevention is better than cure", we have to be more careful in choosing the support. In this days and age of rising, heaps of supports are available but most of them are inept due to deactivation [17,18]. With the determination to overcome this ineptness, the pursuit of the heterogeneous acid catalyst has resulted in the consideration of carbon-based nanomaterials (CNMs) [19,20]. Interestingly, this era was lessened with graphite as the eye-catching scientific significance of graphene as a catalyst and catalytic support in heterogeneous catalysis has grown very impressively over the past several years [21]. Characteristically, graphene has a two-dimensional crystal structure, *sp*^{2} bonded carbon atoms densely packed in a hexagonal honeycomb-shaped lattice and plenty of functional groups on its basal plane and edges. During the recent time, chemically modified graphene (CMG) as graphene oxide (GO) based research has gained a stupendous strength owing to their latent outstanding quality especially in the field of catalysis [22,23]. Unique properties like high surface area [24] of ~2630 m^2/g, promising high thermal stability, elevated tensile strength [25], promotes mass transfer and superior resistivity towards

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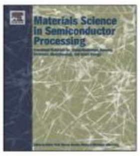

Investigation of structural, electrical and optical properties of $Sb_XW_{1\text{-}X}Se_2$ single crystals

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ABSTRACT

This article presents systematic studies of $Sb_XW_{1\text{-}X}Se_2$ (X = 0, 0.1) single crystals grown by direct vapour transport technique. The purity and stoichiometry were tested by energy dispersive analysis of X-ray (EDAX). To explore lattice structure of grown compounds, powder X-ray diffraction was performed. A surface morphology of $Sb_{0.1}W_{0.9}Se_2$ crystals was checked by optical microscope and scanning electron microscope. The transmission electron microscopy was also used to verify the crystallinity of grown samples. The variations of electrical resistivity parallel and perpendicular to c-axis were measured in the temperature range from 303 to 673 K. The results showed semiconducting behaviour and anisotropic charge conduction of grown single crystals. The n-type semiconducting nature was confirmed by Hall-effect measurements. The optical band gap was determined by UV–Visible-NIR spectroscopy. The Raman spectrum was also taken from grown $Sb_XW_{1\text{-}X}Se_2$ (X = 0, 0.1) single crystals using excitation of 785 nm. The obtained results suggest the substitutional doping of Sb^{+5} on W^{+4} lattice site.

1. Introduction

Recently, two dimensional transition metal dichalcogenides (2D-TMDC) have shown great potential for applications in the field of electronics, optoelectronics and spintronics [1–5]. The 2D-TMDCs have high on/off ratio and band gap emission which make them more suitable for field effect transistors (FETs) [6]. These compounds with generalized formula MX_2 have hexagonal lattice structure with metal plane is sandwiched between two chalcogen atom planes [6–9]. TMDCs hold great promise for various intended applications due to their tuneable band gap. This can be achieved by different elemental compositions and presence of dopant or impurity [10–14]. The doping or intercalation is the key material parameter to modify physical and chemical properties of TMDCs. The properties such as carrier concentration, electrical conductivity, mobility of charge carriers, etc. can be significantly altered by this way [11,13,15–19]. Further, substitutional doping by Nb can alter the n-type conduction of material into p-type [13]. Besides this, TMDCs also show application as electro-catalyst in hydrogen evolution and doping improves the reactivity of host materials [19]. However, concentration of dopant is most critical parameter and at high doping level there may be possibility of fall in quality of material. As per literature survey, research has been carried out on doped materials with different concentration of dopant elements and researchers have found drawbacks of doping process [20]. The growth, structural characterizations and various excitonic mechanisms in vanadium doped WSe_2 single crystals have also been demonstrated [14]. In present article, efforts have been applied to grow single crystals of Sb doped WSe_2 which is completely unexplored. The Sb was added to tune electrical and optical properties of WSe_2. The grown single crystals were characterized by different sophisticated techniques and discussed in detail.

2. Materials and methods for crystal growth

The $Sb_XW_{1\text{-}X}Se_2$ (X = 0, 0.1) single crystals were grown by direct vapour transport technique in dual zone horizontal furnace. For growth, antimony (Sb), tungsten (W) and selenium (Se) (99.99%, Alfa Aesar) were weighed in stoichiometric proportion and the mixture was loaded in quartz ampoule. This ampoule was slowly evacuated to around 10^{-6} Torr pressure and sealed off. The ampoule was then placed in high temperature furnace controlled by temperature controller with an accuracy of ± 1 K. The source material was kept at one

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Research articles

Magnetic behavior study of samarium nitride using density functional theory

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ABSTRACT

In this work, the state-of-art density functional theory is employed to study the structural, electronic and magnetic properties of samarium nitride (SmN). We have performed calculation for both ferromagnetic and antiferromagnetic states in rock-salt phase. The calculated results of optimized lattice parameter and magnetic moment agree well with the available experimental and theoretical values. From energy band diagram and electronic density of states, we observe a half-metallic behaviour in FM phase of rock salt SmN in while metallicity in AFM I and AFM III phases. We present and discuss our current understanding of the possible half-metallicity together with the magnetic ordering in SmN. The calculated phonon dispersion curves shows dynamical stability of the considered structures. The phonon density of states and Eliashberg functional have also been analysed to understand the superconductivity in SmN.

1. Introduction

The rare-earth nitrides (RENs) are a fascinating group of materials combining theoretical and experimental challenges with the promise of extensive technological applications [1–20]. As the field of spintronic develops and the potential of harnessing electron spin in electronics approaches realisation, there is a growing need for materials that show a strong coupling between their magnetic and electronic properties [21–23]. The rare-earth elements comprising the series with atomic number 58–71 across which the 4*f* shell is filled, have been of particular interest for nearly a century. Trivalent state among the rare earth compounds is commonly observed.

Members of the rare earth nitride series show a range of electronic and magnetic properties that would be advantageous to the development of spintronic devices. For pnictides it is seen that the series vary from being ferromagnetic semiconductors to half metals or completely metallic in nature. Applications derived from exchange splitting of the bands have recently been demonstrated in EuO, where it acts as an efficient electron spin filter [24]. The exchange splitting of the conduction bands in some of the rare earths is of a similar size to that of EuO, and Ref. [25] has pointed out that the splitting of the valence bands as well as the conduction bands may make the RENs even more suitable to spin filter device applications. The rare-earth metals, also known as the lanthanides, are a group of metals unified by the progressive filling of their tightly bound 4*f* shell. Electrons in the 4*f* level are the origin of the magnetic properties, but do not participate directly in the bonding or transport in rare earth compounds; an interesting state of affairs. A surge of interest in the rare-earth pnictides (group 15 elements) and chalcogenides (group 16 elements) during the 1960's and 70's was driven by the prospect of ferromagnetic semiconductors [26]. These compounds allowed a large expanse of parameter space to be studied. The effect of the 4*f* level could be investigated by substituting one RE for another. NaCl rock salt (RS) structure is the most favoured phase in vast majority of these rare earth compounds [27]. However, research into the bulk electronic and magnetic properties of the RENs was hampered by difficulties in the preparation of stoichiometric and oxygen free samples [28]. Due to this problem in synthetic techniques, the stoichiometric study for rare earth compounds was partially known. Confusion and conflicting results remained over the fundamental magnetic and electrical properties [29–30]. The last fifteen years has seen a renewal of interest in these materials for three reasons [4–5]. Firstly, contaminant free sample fabrication methods have been developed, making it possible to obtain relatively clear stoichiometric samples. Advances in theory and improvements in band structure calculations have predicted a range of interesting properties in these materials [4,5,31–36]. With the theoretical and experimental investigations achieving maturity, it has led to the

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Tailoring the Electronic and Magnetic Properties of Peculiar Triplet Ground State Polybenzoid "Triangulene"

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In the present work we have studied the structural and electronic properties of recently synthesized elusive free standing triangulene using density functional theory. Triangulene, which is a type of graphene quantum dot, is a molecule with an even number of electrons and atoms but the structure of molecule is such that it is impossible to pair all these electrons. The spins of these two unpaired electrons have two possible orientations: triplet (ferromagnetic) and singlet (antiferromagnetic) state. From the first principles study of free standing triangulene, we found energetically, by koopman's theory of global reactivity descriptors and frequency calculations that triplet (ferromagnetic) is more stable than singlet (antiferromagnetic) which is in good agreement with the previous results. These elementary studies are technologically compatible as open shell graphene quantum dots could be useful in spintronic and magnetic carbon materials. Further we have also studied the influence of magnetic elements Fe, Co, Ni and Cu on triangulene for their applications in spintronics. Our results suggest that the transitional metal (TM) doped graphene quantum dot is interesting for information readout devices where the TM-ion spin states can be used to store information.

Introduction

Over the past decade, among all the nanomaterials, graphene[1] takes a special place because of its sumptuous properties which results in wide range of applications[2] such as organic semiconductors, chemical sensors, biological engineering, composite materials, energy storage devices, photovoltaic cells, in spintronic and nonlinear optics.[2–3] However, the major problem with the graphene is its direct electronic applications and due to the absence of electronic band gap in it. The band gap in graphene can be opened by controlling the size, such as a nano-ribbon strip and by introduction of other hetero atoms and defects into the graphene moiety.[4] The graphene quantum dots (GQDs) that consist of nanometer-scaled graphene particles with sp^2 carbon bonds show great potential in this regard. At this stage most of the applications for GQDs are focused on photoluminescence (PL) related fields energy and display.[5–6] The graphene quantum dots regarded as small piece of graphene are a kind of zero dimensional (0D) material with characteristics derived from both graphene and carbon dots (CDs).[7–8] The GQDs are superior in terms of high photostability, biocompatibility and low toxicity than organic dyes and semiconducting quantum dots (SQDs) due to quantum confinement and edge effects.[7–9] The tiny fragments of graphe ne sheet results into the nanographene with various polycyclic aromatic hydrocarbon (PAH) units. Therefore the properties of PAHs are closely related to nanographenes.[10–11] These PAHs are made up of fused aromatic rings which lead to the features with almost infinite possibilities that can lead to a rich variety of compounds. There are types of PAHs which acquires a high-spin open-shell radical character in their ground state.[11] For example, phenalenyl[12] contains an odd number of carbon atoms with an odd number of π electrons which makes it a radical in its neutral ground state. The extension of benzene rings in a triangular form can lead to several π-conjugated phenalenyl derivatives such as triangulene (also known as clar's hydrocarbon). Triangulene is the smallest triplet-ground-state polybenzoid, exists as a diradical containing an even number of carbons (22, in fused benzene rings), has been an obscure molecule ever since it was first hypothesized.[13] It is impossible to draw kekulè structure for the whole molecule, two unpaired valence electrons results in every attempt. It is a system containing even number of π-electrons although the topology of the system means that it is impossible to write a resonance structure in which each π-electron is paired with one on a neighboring carbon.[14] Due to its extreme reactivity,[13] synthesis and the characterization of free standing triangulene has not been achieved. Recently, triangulene by manipulating a precursor molecule (from a mixture of dihydrobenzo[cd,mn] pyrene isomers) has been successfully created on Cu (111), NaCl (100) and Xe (111).[15] They showed that STM, DFT and AFM calculations confirmed that the triangulene keeps its free molecule properties on the surface and exists in threefold symmetric molecular structure.[15] The expected, aligned spins-the quantum-mechanical property that gives electrons a magnetic orientation due to two unpaired electrons, has inquested triangulene's magnetic properties. This property could make triangulene useful in electronics, applications in quantum computing, quantum information processing and spintronics.[16–17] Though the supportive DFT calculations clearly brings out the free molecule properties of triangulene

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Investigation of morphological and structural properties of V incorporated $SnSe_2$ single crystals

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ABSTRACT

The unique ternary compositions $V_xSn_{1-x}Se_2$ (x = 0, 0.15, 0.25 and 0.5) have been grown in single crystal form by direct vapour transport technique. The as-grown crystals have been examined under Carl Zeiss optical microscope for morphological studies. The tiny flakes have also been observed by scanning electron microscope and it reveals the layered structure of as-grown ternary alloys. The powder XRD pattern infers hexagonal lattice structure with 2H poly type and $P\bar{3}m1$ space group. The XRD pattern shows shifting of diffraction peaks on higher angle side as content of vanadium (V) increases, confirms substitution of V-atoms on tin (Sn)-atom sites. Using transmission electron microscope, the nano-structures have been found in sono-chemically exfoliated samples. The selected area electron diffraction pattern has been obtained using 200 kV electron beam and reveals the single crystalline nature of $V_xSn_{1-x}Se_2$ (x = 0, 0.15, 0.25 and 0.5) ternary alloys. The Raman spectra show $SnSe_2$ type A_{1g} and E_g vibrational modes and on increasing V content blue shift in A_{1g} peak indicates that the V-atoms well substitutes on Sn-site.

1. Introduction

Recently, discovery of two dimensional materials including graphene, boron nitride and transition metal chalcogenides have open up new opportunities in research and technical applications of these materials due to extraordinary advancement in the properties [1–6]. Besides this, important features like multiple exciton generation and presence of band gap make these compounds suitable for field effect transistors (FET). The theoretical investigations on IV–VI semiconductors for renewable energy resources have also been demonstrated [6]. The most extensively explored member of IV-VI group, $SnSe_2$ has shown potential for the applications in the field of optoelectronics, photovoltaic, infrared optoelectronic devices, holographic recording systems, and memory switching devices [7–14]. Currently, there is a growing interest in band gap engineering by atomic doping and substitution. The characteristics have also been significantly tailored by alloying different semiconductors [15–26]. More precisely, modulation of band gap have been demonstrated with tenability of few hundreds of meV in ternary compounds for example, $WSe_{2(1-x)}S_{2x}$ and $MoS_{2(1-x)}Se_{2x}$ by a variation of S and Se contents [22–24]. In order to produce high performance electronic device, improvement in electronic transport have been demonstrated in atomically doped semiconductors and even transformation of semiconductor type from n-type to p-type in $MoSe_2$ has been reported [27].

The layered s-p metal chalcogenide of IV-VI group, $SnSe_2$ crystallize in 2-H and 1-T poly-types, as shown in Fig. 1(a). The 2H-$SnSe_2$ has hexagonal lattice structure with $P\bar{3}m1$ space group [28,29]. The 2H-$SnSe_2$ is structurally similar to $MoSe_2$ and WSe_2 and exhibiting anisotropic structure in which Sn-atom layer is sandwiched between two Se-atom layers, as shown in Fig. 1(b). Within each stacked set of trilayers, a plane of Sn atoms is sandwiched between two Se planes with strong covalent metal–anion bonds in the basal plane. The formed Se–Sn–Se layers are stacked by weak van der Waals interactions along the c axis. The unit cell of 2H-$SnSe_2$ is shown in Fig. 1(b). In present research, ternary alloys 2H-$V_xSn_{1-x}Se_2$ (x = 0, 0.15, 0.25 and 0.5) have been grown in single crystal form by direct vapour transport technique. The atomic size mismatch between vanadium (1.34 Å) and tin (1.40 Å) is estimated to be ~ 4%. Since, atomic size of vanadium is smaller than tin, it is predicted that the vanadium atom take substitutional doping at Sn-sites owing to their comparable atomic size, exhibiting strain assisted unit cell contraction.

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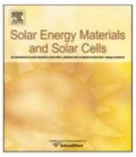

Tunable and anisotropic photoresponse of layered $Re_{0.2}Sn_{0.8}Se_2$ ternary alloy

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Keywords:
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Tunable and anisotropic photodetection

ABSTRACT

In order to produce high-performance optoelectronic devices, alloy engineering has been exploited in ternary transition metal dichalcogenides. In the present study, we demonstrated the effect of rhenium incorporation on the structural and electrical response in $SnSe_2$ layered crystals grown by direct vapour transport technique. Elemental conformation was characterized by EDAX. The powder X-ray diffraction shows the hexagonal phase and high crystallinity of grown compounds, which is also confirmed by the TEM SAED pattern. Perfectly hexagonal shaped microcrystals are shown in SEM surface micrograph. Raman spectra indicate the redshift in the vibrational mode peaks of $SnSe_2$ with the rhenium doping. Current-time characteristic was measured to study to the effect of alloy engineering on the photoresponse ability of the grown compound. Among all, $Re_{0.2}Sn_{0.8}Se_2$ ternary alloy shows the enhanced photoresponse under polychromatic illumination, showing the suppression of deep-level defect states after incorporation of Re in $SnSe_2$ lattice structure. These materials have a layered structure and exhibit the anisotropic conductivity. Hence the anisotropic photodetection characteristics of $Re_{0.2}Sn_{0.8}Se_2$ ternary alloy based photodetectors are further studied in detail. Photocurrent and photo responsivity are higher along the symmetric contacts, whereas along the asymmetric contacts both the quantities are lower in magnitude because the photogenerated carriers have to cross the perpendicular resistance of is layers stacked together by the weak Vander Waal's forces. Increasing the bias voltage enhances the photoresponsivity from $5.141\,mAW^{-1}$ to $67.231\,mAW^{-1}$ and photodetectivity 0.971 to 3.452×10^9 Jones. Anisotropic photoresponse was also studied under the monochromatic light. Results provide the significant understanding of tunable and layered structure dependent anisotropic photoresponse ability of TMDC materials.

1. Introduction

Recently, transition metal dichalcogenides (TMDCs) have been widely investigated in the fields of optoelectronics and electronics due to their enrolled properties imposing great promise for future applications in high-performance devices. Due to their chemical and thermal stability, TMDC materials have a tremendous contribution in the field of sensing applications including a gas sensor, photodetector, field effect transistors, solar cell [1–4]. In the TMDC family, Tin Diselenide ($SnSe_2$) exhibits great potential for the optoelectronic application due to its unique band structure and high carrier mobility [5]. Xing Zhou et al. fabricated the single-layered $SnSe_2/MoS_2$ heterojunction based photodetector with high photoresponsivity [5]. Prathiban Ramasamy at. el. show applications of SnSe and $SnSe_2$ nanosheets as a counter back electrode in the dye-sensitized solar cell for the better energy conversion [6]. Extreme variation in the electronic properties of TMDC materials can be carried out to fit application criteria by bandgap engineering and thickness variation up to a single layer [7,8]. Besides these, properties of the TMDC material like semiconductor type, band gap etc, can be manipulated through doping by appropriate dopant elements [9].

Rhenium (Re) is Group 7 metal and prominent dopant in TMDC binary alloys. Doping of Re in WS_2 and MoS_2 leads to higher strain, improved photocatalytic activity, enhanced electric conductivity for sodium ion-batteries [9–11]. Re substitution in MoS_2 also induced the change in structure from 2H to 3R and strongly influence the separation of excitons [12]. The effect in photoresponse ability of TMDC layered material with the incorporation of Re is still not well explored as far as

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Temperature Dependence of vibrational properties of $Sb_xSn_{1-x}Se_2$(x=0, 0.1, 0.2 & 0.3) ternary alloy

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Abstract:

We report the Raman spectroscopy of $Sb_xSn_{1-x}Se_2$ (x= 0, 0.1, 0.2, 0.3) single crystals in temperature range 78K to 468K. The strong peak, assigning A_{1g} vibrational mode is found. The frequency of A_{1g} peak decreases on increasing Sb concentration. The down shift is observed on increasing the temperature from 78K to 468K.. For the quantitative analysis, Temperature co-efficient (χ_o), peak position at 0K (ω_0), Anharmonic constant (Γ_0), and peak broadening at 0K (C) are computed from the temperature dependence of frequency and peak width. The present findings provide good scientific significance to qualitative and quantitative analysis of transition metal dichalcogenides.

Keywords: Crystal growth; Raman spectroscopy; Semiconductors; alloys; tin diselenide.

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Growth and application of $Sb_{0.5}Mo_{0.5}Se_2$ ternary alloy as photodetector

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Raman
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Responsivity and detectivity

ABSTRACT

Presently, ternary alloy engineering holds ability in promoting high performance photo detecting devices. In the present investigation, we have employed direct vapor transport technique (DVT) to grow $Sb_{0.5}Mo_{0.5}Se_2$ multilayer crystal for its use as photodetector. To confirm the composition of the grown crystals, energy dispersive analysis of x-ray (EDAX) is performed. To explore the morphological properties, optical microscopy and scanning electron microscopy (SEM) are used and the growth from vapor phase that is initiated due to screw dislocation is observed. The phase composition and optical properties of the as grown crystals are examined by transmission electron microscopy (TEM) and UV–Visible spectroscopy providing indirect energy band gap of 1.22 eV. Raman spectra of both pure $MoSe_2$ and $Sb_{0.5}Mo_{0.5}Se_2$ show the presence of the out of plane A1g vibrational mode at 243 cm^{-1}. In addition, to study photo conduction property, the mechanically exfoliated crystal was illuminated by polychromatic source having intensity of 50 $mWcm^{-2}$ at different bias voltages.

1. Introduction

Electronic devices with quick response to light, fast switching capability and better performance are preferred for industrial and research sectors. There are numerous materials possessing the photo-sensing properties such as black phosphorous, graphene, graphene oxide and transition metal dichalcogenides (TMDCs). Properties such as flexibility in synthesis, mobility, environmental stability, carrier concentration, structural, vibrational and highly crystalline nature have made TMDCs the most fascinating material [1–8]. Recently, the photo-sensing properties and energy band gap of TMDCs material were altered for achieving high photoresponsivity and detectivity by alloy engineering [9]. The semiconducting layered TMDCs are in great demand due to their robust material properties and as quick switching photosensors [10]. TMDCs have also shown great potential in its use as photo sensors, field effect transistors (FET), humidity sensors, gas sensors, touch less positioning systems and many more as optoelectronic, photonic and photovoltaic devices [11–14]. Within the TMDCs family, MoS_2 and $MoSe_2$ materials are widely investigated due to their excellent photo conducting properties. The highly oriented and crystalline TMDCs are composed of stacks of MX_2 tri-layers along c-axis [15]. Alloy engineering (i.e. doping) has great deal of influence over the performance of the photo detector. The quick response of the photo detector was achieved by alloying vanadium and antimony in $SnSe_2$ material [9,16]. This became the sole reason to grow $Sb_{0.5}Mo_{0.5}Se_2$ single crystals by DVT technique concerning vapor transport crystal growth [17]. Then, the morphological, structural, optical and vibrational properties of the grown crystals were studied. The photoconduction property of mechanically exfoliated crystal along the basal plane is studied under polychromatic source of intensity 50 $mWcm^{-2}$ and its other photo-sensing parameters are reported here in detail.

2. Experimental

In the present investigation to grow single crystals of $Sb_{0.5}Mo_{0.5}Se_2$, constituent material such as antimony (Sb), molybdenum (Mo), and selenium (Se) all 99.99% pure are procured from Alfa Aesar. These materials are mixed in stoichiometric proportion weighing 10 g and placed in a clean dry quartz ampoule of dimensions 250 mm long, 25 mm outer diameter and 22 mm inner diameter and sealed at a pressure 10^{-5} torr. Afterwards, the sealed ampoule is loaded in a temperature controlled dual zone horizontal furnace. The temperatures at the two zones i.e. source zone and growth zone are increased at the rate of 24 K/h till they reach

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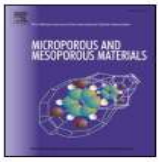

Zeolite-Y entrapped metallo-pyrazolone complexes as heterogeneous catalysts: Synthesis, catalytic aptitude and computational investigation

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ABSTRACT

Transition metal [M = VO(IV) and/or Co(II)] complexes with Schiff base ligand (Z)-3-methyl-1-phenyl-4-(2,2,2-trifluoro-1-(2-hydroxyphenyl)imino)ethyl)-1H-pyrazol-5-ol (H_2L) have been entrapped in the super cages of zeolite-Y by Flexible Ligand Method. These nanohybrid materials have been characterized by preferential physico-chemical techniques such as ICP-OES, elemental analyses, (FT-IR, ^1H and ^{13}C-NMR and electronic) spectral studies, BET, scanning electron micrographs (SEMs), AAS, X-ray diffraction patterns (XRD) and thermogravimetric analysis. The density functional theory calculations are performed to find optimized structures together with the bond angles, bond lengths, dihedral angles and electronic properties of ligand and neat complexes. The catalytic competence of zeolite-Y entrapped metallo-pyrazole complexes was examined by the oxidation of olefins viz. limonene, cyclohexene, styrene, and α-pinene using H_2O_2 as an oxidant. So as to ensure the shielding effect of the nanohybrid over the active center on the catalytic properties, the performance of the entrapped complexes (heterogeneous system) was weighing up against the neat complexes (homogeneous system). The effect of experimental variables (such as solvents, mole ratio of substrate and oxidant, the amount of catalyst and reaction time) with their probable justification on the conversion of limonene was discussed. Under the optimized reaction conditions, $[VO(L)\cdot H_2O]$-Y was found to be potential candidate, achieving 87.44%, 90.01%, 82.01%, and 85.44% conversions of limonene, cyclohexene, styrene, and α-pinene oxidation reactions, respectively.

1. Introduction

Now-a-days the oxidation of olefins has pulled up a great meaning as its oxygen functionalized derivatives are fateful intermediates used in various fields like fragrant, pharmaceutical, plasticizer, coating material etc. [1–4]. Due to significance of selective and partial oxidations, catalytic oxidation of olefins has achieved enormous attention because it is the most enviable pathway for the synthesis of highly selective and vital industrial products such as epoxides, carbonyl compounds, diols and products obtained by cleavage of C-C bond.

Merely in attendance of this, there is an eagle-eye to discover a catalyst which can adequately carry out such oxidation reactions with generous yield and stability besides first-rate conversion with desired selectivity. For this rationale, great efforts are being put to build up solid support based catalytic systems and different approaches were being applied such as grafting on polymers [5], immobilization in polysiloxanes [6], sulfonic acid-functionalized mesoporous SBA-15 [7], silica-based mesoporous organic–inorganic hybrid materials like MOFs [8,9] and zeolites [10–13].

In today's era, zeolite-Y has acquired attention to great extent as solid support [14–16] due to properties like high surface area, large pore volume and well-defined arrays of channels as well as cavities made it suitable support for entrapment of transition metal complexes. Madadi and Rahimi [17] reported zeolite-Y entrapped Fe(III), Mn(III) and/or Co(III) complexes with 5,10,15,20-tetra(4-methoxyphenyl)porphyrin as heterogeneous catalysts for the epoxidation of monoterpenes. The catalytic results showed that Fe(III) complexes were more efficient ((R)-(+)-limonene conversion: 81%) than Mn(III) and Co(III) complexes. Xia et al. [18] have studied numerous heterogeneous Mn^{2+}-zeolite catalysts for instance, Mn-beta, Mn-Y, Mn-ZSM-5 and/or Mn-A for the epoxidation of alkenes with 30% H_2O_2 in sodium hydrocarbonate solution. Amongst all, Mn-Y has demonstrated high conversions of 98.5–99.9 mol%. Low active oxygen content is another critical concern for the sustainability of the reactions, for this reason, numerous oxidants have been employed such as oxygen, hydrogen peroxide, *tert*-butyl hydroperoxide (TBHP) and iodosobenzene diacetate ($PhI(OAc)_2$) [17]. Owing to ecologically aware oxidant, H_2O_2 is more desirable, as the active oxygen content is around 50% with producing no- or only

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Hydrogen evolution and oxygen evolution reactions of pristine and alkali metal doped $SnSe_2$ monolayer

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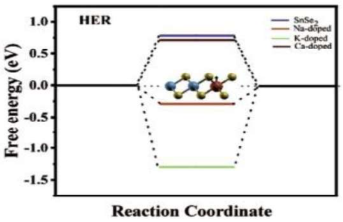
HIGHLIGHTS

- The analysis of HER and OER activity is done for $SnSe_2$ and alkali atoms doped $SnSe_2$ monolayers.
- $SnSe_2$ having optical bandgap of 1.2 eV can be used as photo-electro catalyst.
- Basal plane activity of $SnSe_2$ is dopant dependent.
- Edge site of Na-doped $SnSe_2$ is best suited for hydrogen evolution reaction.
- Basal plane of Ca-doped $SnSe_2$ is best suited for oxygen evolution reaction.

GRAPHICAL ABSTRACT



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ABSTRACT

Many transition metal di-selenides such as $MoSe_2$ and WSe_2 show good catalytic activity on their edges with limited active orientations. These metal di-selenides are actively being used as target material for increasing the number of electrocatalytic active sites and in turn to improve the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) activities by increasing the ratio of edges to the basal plane. In present work, we have studied the activity of pristine and alkali atoms (Na, K and Ca) doped-$SnSe_2$ for HER and OER catalyst. The *state-of-art* density functional theory (DFT) based computations are performed for estimating the catalytic activity of the pristine and doped $SnSe_2$ by means of evaluating the adsorption and Gibbs free energies subjected to hydrogen and oxygen adsorption. Further, to get better prediction of adsorption energy on the individual catalytic surface, we have included the dispersion correction term to exchange-correlation functional. Results show that the pristine $SnSe_2$ is not a good HER catalyst when hydrogen is adsorbed on its basal plane. However, edge-sites show the good hydrogen adsorption and

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Paper-Based Flexible Photodetector Functionalized by WSe_2 Nanodots

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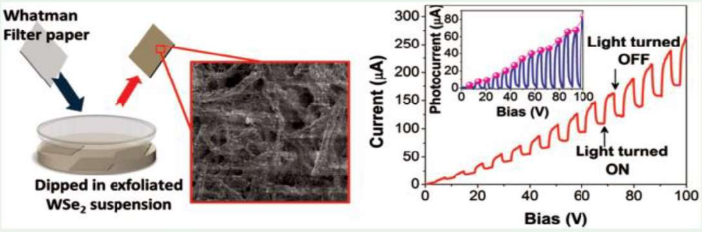
S *Supporting Information*



ABSTRACT: Ultrathin two-dimensional WSe_2 has attracted huge attention due to its potential applications in future wearable electronics. Here, we demonstrate the flexible and high-performance photodetector using high-yield sonochemical exfoliation technique. An efficient and low cost fabrication strategy using Whatman filter paper is adopted for the first time for fabrication of a photodetector based on WSe_2 nanodots (NDs). The WSe_2 NDs have hexagonal lattice structure with $P6_3/mmc$ and have indirect band gap of 1.63 eV. The exfoliation and number of layers in WSe_2 NDs is confirmed by Raman, absorption, and photoluminescence spectroscopy. Subsequently, the photodetector based on WSe_2 NDs is fabricated. The device shows excellent photoresponse with response time of 0.68 s and photoresponsivity of 17.78 mAW^{-1} and detectivity of 5.86×10^{10} Jones for 5 V. The device is analyzed for bias of 0 to 100 V and responsivity is enhanced up to 796.18 mA W^{-1} at 100 V bias. Furthermore, the paper-based detector exhibited great flexibility and air stability. The performance of the photodetector was also recorded in the spectral range 390 to 880 nm. Over all, the performance paper-based device advocates a novel pathway for flexible and intelligent electronics.

KEYWORDS: *WSe_2 nanodots, sonochemical exfoliation, paper -based photodetector, flexible photodetector, air stability, oxygen-assisted mechanism*

1. INTRODUCTION

Two-dimensional transition metal dichalcogenides (2D-TMDCs) exhibits fascinating properties including layer-dependent band gap, exotic band structure, exceptionally high chemical inertness, and so forth.[1−5] The excellent electrical and optical properties including strong light matter interaction, moderated carrier mobility, and favorable band gap of 1−2 eV make TMDCs most appropriate for fabrication of high-performance optoelectronic devices.[6−11] Besides, mechanical flexibility originating from the layered structure is the most important property of TMDCs which can be utilized for future flexible electronics.[12−15] The most intensively explored member of TMDC family, WSe_2, holds good promise for future flexible, wearable, and transparent electronic and optoelectronic devices due to its superior physical, electrical, and optical properties.[16,17] It crystallizes in the van der Waals layered structure in which the W atom plane is sandwiched between two Se-atom planes and Se−W−Se slabs are stacked one upon another to form bulk crystals.[18−20] The individual single layer can be cleaved from bulk crystal and isolated as graphene-like 2D-crystal using techniques of mechanical and chemical exfoliation.[1] The large scale synthesis of 2D-crystals is not possible using mechanical exfoliation but it can be facilitated easily by chemical exfoliation due to availability of variety of solvents including water, acetone, *N*-methyl 2-pyrrolidinone, *N*-*N*-methyl formaldehyde, and so forth.[21]

Recently, nanostructured photodetectors have been spotlighted in modern electronics as they efficiently convert optical signal into electrical signal.[22,23] The 2D-TMDCs seem to be the most appropriate materials for high-performance photo-

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Photovoltaic activity of WSe_2/Si hetero junction

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ABSTRACT

Propelled by the development of layered transition metal dichalcogenides, heterojunctions have captivated tremendous attention due to various excitonic mechanisms assisted strong light-matter interaction. We demonstrate liquid phase exfoliation of WSe_2 and fabrication of fast switchable WSe_2/Si heterojunction. The heterojunction device showed obvious rectifying nature with ideality factor of 1.21 and it is explored under white illumination at power intensities varying from 5 to 18 mW/cm^2. The WSe_2/Si heterojunction photovoltaic device exhibited excellent transient photoresponse with highest responsivity of 86.11 mA/W and 23 ms response time under white light. Besides, heterojunction exhibited excellent photoresponse in broad spectral range from 390 to 1088 nm with highest photoresponsivity of 122.2 mA/W for 780 nm illumination. The device showed excellent response in temperature range 200 to 300 K. Eventually, the results advocate the huge significance of WSe_2/Si heterojunction for photovoltaic cell and photodetection.

1. Introduction

Transition metal dichalcogenides (TMDCs) with generalised formula MX_2 (where, M is the metal atom and X is the chalcogen atom) have typical layered structure in which each layer consists of three atomic planes covalently bonded in the sequence of X—M—X with a separation of about 0.6 nm governed by weak van der Waal's interactions [1,2]. Apart from earth-abundant nature and environmental stability, the unique thickness dependent properties make TMDCs more attractive for technical applications [3,4]. TMDCs have shown great potential applications for next generation electronics and optoelectronics owing to proper electronic properties, inherent semiconducting characteristics and high carrier mobility [5–7]. The semiconducting members of TMDCs attract considerable attention for photoconducting and photovoltaic applications on account of their strong light matter interactions, proper band gap, dangling bond free surfaces, variety of excitonic mechanisms, high carrier life time and so forth [8–13]. After the discovery of graphene, huge research has been demonstrated on 2D-TMDCs, as the weak interlayer van der Waal's interaction allows easy separation of atomically thin sheets through exfoliation techniques. Huge development in exfoliation techniques has been demonstrated for the high yield synthesis of quality nanostructures [14]. The micromechanical exfoliation yields isolated atomically thin layers with excellent optical features [15–17]. However, it became less attractive due to smaller lateral dimension and low yield. Although, the chemical vapour deposition is an alternative of mechanical exfoliation as it allows the growth of atomically thin film having larger lateral dimensions, it demands typical experimental set up which significantly raises the production cost [18–23]. Among all the techniques, the liquid phase exfoliation is the most attractive technique as it allows the high yield synthesis of mono and few layer nano sheets using simple and economically low cost experimental tools. The typical liquid phase exfoliation technique is top to down approach, enables the size controlled synthesis of Nanosheets. The liquids like N-methyl 2-Pyrollidon (NMP), di-methyl formaldehyde (DMF), water, acetone, Dimethyl sulfoxide (DMSO), etc. can effectively be employed for exfoliation of TMDCs [18–23].

The realization of optoelectronic devices is important in technical research because of their potential applications in photo-electronic energy conversion and optical communication. Among various photosensitive devices, photovoltaic cells have shown great potential in power generation and photodetection as they work without external power sources [9]. The TMDC semiconductors whose band gap lies between 1.2–2.0 eV have been intensively exploited in fabrication of photovoltaic cells. The atomically thin candidates such as tungsten diselenide (WSe_2) [9,24], tungsten disulphide (WS_2) [9,25], molybdenum diselenide ($MoSe_2$) [26] and molybdenum disulphide (MoS_2) [27,28] are widely employed as photosensitive materials. MoS_2 based

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