ChemistrySelect

Research Article
doi.org/10.1002/slct.202401201

Chemistry Europe
European Chemical Societies Publishing

www.chemistryselect.org

Structural Preferences of Metal Chalcogenide based Nanothreads (MX; M = Au, Ag; X = S, Se): A Computational Study

Marutheeswaran Srinivasan,*[a] Ramesh Sivasamy,[a, b] Kulwinder Kaur,[c] K. N. Hima Sindhu,[a] Shakeel Ahmad Khandy,[d] and Lokanath Patra[e]

This study investigates the structural stability and electronic properties of α-MX nanothreads and β-MX nanosheets (M=Au, Ag; X=S, Se) using density functional theory. Our findings confirm the thermal and dynamic stability of all nanostructures, with β-MX phases being more stable than α-MX, albeit with minimal energy differences between the two phases. Electron localization analysis reveals predominantly ionic bonding character between M (Ag and Au) and X (S and Se) atoms. All the phase exhibits metallophilic interactions (Argentophilic and Aurophilic), with α-MX nanothreads demonstrating a higher level of interaction compared to β-MX nanosheets, attributed to the curvature inherent in the nanothreads. Significantly, these interactions are effectively small and do not compromise the relative stability between the α-MX and β-MX phases. Additionally, both α-MX and β-MX structures exhibit characteristics of indirect bandgap semiconductor behaviour. The band gap values do not significantly differ between α-MX and β-MX phases. Fermi analysis reveals that α-MX phases exhibit small effective electron masses and large hole mobility along the uniaxial direction. These findings suggest promising prospects for α-MX nanothreads as 1D semiconductors in nano-electronics and nano-optoelectronics applications in the future.

Introduction

Low-dimensional (D) nanomaterials have drawn much attention among materials scientists because of unique characteristics that cannot be found in bulk or macro-scale materials.[1] The distinctive properties of low-dimensional nanostructures are inherently linked to their small size and low dimensionality, enabling their utilization in a range of fields, such as photodetectors,[2] gas sensors,[3] solar cells,[4] secondary batteries,[5] and electrocatalysts.[6] Owing to their intriguing chemical and physical characteristics, many researchers are looking for new directions to adaptively synthesize 2D or 1D nanomaterials. Among the several classes of nanomaterials, Group-11 chalcogenide materials have garnered significant research interest in high-performance transistors and sensors due to their exceptionally high carrier mobilities and promising applications in photocatalysis.[7] Due to advances in experimental fabrication and computational methods, numerous two- and one-dimensional materials composed of group-11 elements, such as copper (Cu), silver (Ag), and gold (Au), combined with different chalcogen elements, have been discovered. Recent studies show that two-dimensional M_2X and MNX (M, N=Cu, Ag, Au; X=S, Se, Te) have been shown to have high stability, auxetic behavior, and excellent electronic properties.[7h,i,8] The presence of Cu(I), Au(I), and Ag(I) metals in both the M_2X and MNX nanostructures reveals the existence of metallophilic interactions, which play a crucial role in stabilizing the nanosheets.[8b]

First experimental reported on single-crystal AuSe which exist two distinct crystalline α- and β-phase structures.[9] Among them the β-AuSe phase has a layered van der Waals (vdW) structure whereas in the α-AuSe phase shows a tube-like structure (Figure 1). Computational studies have revealed that monolayers of β-MX (M=Au, Ag; X=S, Se, Te) exhibit remarkable light-capturing capabilities and hold promise as photocatalysts for oxygen evolution reactions (OER).[7b] Furthermore, these 2D β-MX monolayers demonstrate in-plane anisotropic behaviour regarding absorption coefficients, photoconductance, and carrier mobility.[7f,h,10] Similarly, the bulk α-MX phase has been studied in both experiment and computation, which are energetically stable and act as a promising photocatalyst.[7e,10b,11]

There is a paucity of research on α-MX tube-like nanostructures. In this study, we have used computational techniques to explore the stability, atomic interactions, electronic properties, and optical characteristics of single-strand α-MX nanothreads, where M=Au, Ag, and X=S, Se. Additionally, we

[a] M. Srinivasan, R. Sivasamy, K. N. Hima Sindhu
School of Physical Sciences, Amrita Vishwa Vidyapeetham Mysuru Campus, Mysore 570026, India
E-mail: rsivasamy@ing.uchile.cl
maruthees.waran@gmail.com

[b] R. Sivasamy
Department of Chemical, Biotechnology and Materials Engineering, Faculty of Sciences and Mathematics, University of Chile, Beauchef 851, Santiago, Chile

[c] K. Kaur
Department of Physics, Mehr Chand Mahajan DAV College for Women, Sector 36, Chandigarh 160036, India

[d] S. A. Khandy
ZJU-Hangzhou Global Scientific and Technological Innovation Center, School of Micro-Nano Electronics, Zhejiang University, Hangzhou 311200, China

[e] L. Patra
Department of Mechanical Engineering, University of California, Santa Barbar, California 93106, United States

Supporting information for this article is available on the WWW under https://doi.org/10.1002/slct.202401201