## Engineering vertical heterostructure of Bi<sub>2</sub>Se<sub>3</sub>-VSe<sub>2</sub>: A novel wet chemical synthetic approach

Naveen Goyal<sup>1</sup>, Rajeev Rai<sup>2</sup>, Ranit Ram<sup>3</sup> and N Ravishankar<sup>1</sup>

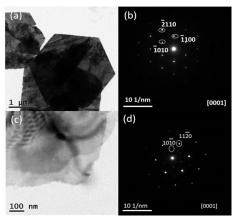
<sup>1</sup>Indian Institute of Science, United States, <sup>2</sup>Indian Institute of Science, Bangalore, Karnataka, India, <sup>3</sup>Indian Institute of Science, Kharagpur, West Bengal, India

Owing to the combined advantageous property and emergence of non-trivial features, vertical heterostructures based on layered two dimensional (2D) materials have been extensively explored in micro/nano electronics,1 opto-electronic devices,¹ and catalysis.² Due to van der Waal interaction between the layers, layered materials can be stacked in desired sequences with required properties. Tailoring the property of layered materials chalcogenides via heterostructure formation are promising for both band alignment engineering and improvements of existing applications and also for the discoveries of completely new phenomena.

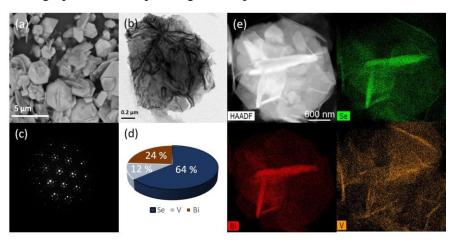
Both VSe<sub>2</sub> and Bi<sub>2</sub>Se<sub>3</sub> belongs to the class of layered materials. Crystallographically, VSe<sub>2</sub> has Se-V-Se layers and Bi<sub>2</sub>Se<sub>3</sub> has quintuple Se-Bi-Se-Bi-Se layers and are held together by van der Waal forces. From electronic point of view, individually VSe<sub>2</sub> is semi-metallic in nature and Bi<sub>2</sub>Se<sub>3</sub> is a well-known topological insulator. Recently, Sinkovic et. al. have shown the emergence of flat band on formation of heterostructure based on VSe<sub>2</sub>- Bi<sub>2</sub>Se<sub>3</sub>.3 The flat band electronic states are predicted to achieve various quantum states of matter at high temperature such as high temperature superconductivity,<sup>4</sup> fractional quantum hall effect<sup>5</sup> and ferromagnetism.<sup>6</sup> However, synthesis of such heterostructure via a facile wet-chemical method is challenging in terms of obtaining high quality crystals. Herein, using microwave method we have synthesized Bi<sub>2</sub>Se<sub>3</sub> nanosheets and Schlenk line method has been used to synthesize single crystalline VSe<sub>2</sub> nanosheets. Further, we have extended our Schlenk line method to synthesize Bi<sub>2</sub>Se<sub>3</sub>-VSe<sub>2</sub> vertical heterostructure, using the Bi<sub>2</sub>Se<sub>3</sub> nanosheets as template.

Synthesized nanostructures are characterized using different techniques. Microstructural characterization has been performed using (scanning)-transmission electron microscopy ((S)- TEM). Figure 1(a) shows lowmagnification bright-field TEM micrograph of Bi<sub>2</sub>Se<sub>3</sub> nanosheets and corresponding SAED pattern is shown in figure 1(b). Regular hexagonal pattern and single diffraction spots reveals the single crystalline nature of as-synthesized Bi<sub>2</sub>Se<sub>3</sub> nanosheets. Figure 1(c, d) shows microstructure of as-synthesized VSe2 nanosheets. Low-magnification bright-field TEM micrograph of VSe<sub>2</sub> is shown in figure 1(c) which shows the ultra-thin sheet morphology of VSe<sub>2</sub> nanostructure. Diffraction pattern shown in the figure 1(d) shows the single crystalline nature of the nanosheets. Figure 2 shows the microstructures of as-synthesized Bi<sub>2</sub>Se<sub>3</sub>-VSe<sub>2</sub> heterostructures. SEM micrograph of the heterostructure reveals the formation of sheets as shown in figure 2(a). Low-mag bright field transmission electron microscope image of heterostructure is shown in figure 2(b) showing the formation of VSe<sub>2</sub> sheets over regular hexagonal Bi<sub>2</sub>Se<sub>3</sub>. Corresponding SAED pattern as shown in figure 2(c), reveals the double diffraction pattern with regular hexagonal pattern around each primary spots indicating the formation of vertical heterostructures. In order to further confirm the heterostructure formation HAADF-STEM imaging was performed. Figure 2(e) shows the HAADF-STEM micrograph and elemental distribution map of V, B, Se. The elemental map confirms the presence of all three elements Bi, V and Se through-out the heterostructure with the atomic percent ratio close to 24:12:64 showing the formation of heterostructure with 1:1 ratio of Bi<sub>2</sub>Se<sub>3</sub> and VSe<sub>2</sub>. Similarly, these wet chemical synthetic approaches could be further extended to synthesize large number of heterostructures using two different 2D layered materials.





**Figure 1.** Microstructural characterization of Bi<sub>2</sub>Se<sub>3</sub> and VSe<sub>2</sub>. (a, and b) Low-mag bright-field TEM micrograph and corresponding SAED pattern of Bi<sub>2</sub>Se<sub>3</sub> respectively; (c, and d) Low-mag bright-field TEM micrograph and corresponding SAED pattern of VSe<sub>2</sub>.



**Figure 2.** Microstructural characterization of Bi<sub>2</sub>Se<sub>3</sub>-VSe<sub>2</sub> heterostructure. (a, b, and c) SEM micrograph, low-mag bright-field TEM micrograph and corresponding SAED pattern of heterostructure showing double-diffraction pattern respectively; (d) pie chart showing the elemental composition of Bi, V and Se in the heterostructure; (e) HAADF-STEM micrograph and elemental distribution map of Bi, V, and Se in the heterostructure.

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