

Comment on "Rapid Solid-Phase Sulfurization Growth and Nonlinear Optical Characterization of Transfer-Free TiS₃ Nanoribbons"



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Zhang et al.¹ have done a commendable job of developing a highly time-efficient method for the synthesis of TiS₃. While the experimental data presented in their work¹ are of high quality, the current fits to their high-resolution X-ray photoemission spectroscopy (XPS) data for the S 2p core level (Figure 3b of ref 1) are in line with neither prior work^{2–6} nor expectations.

Several prior studies focused on the photoemission spectroscopy characterization of TiS₃ contain rigorous discussions on the S 2p core level XPS spectra.^{2–6} The expectation is that there is more electron donation between Ti and S^{2–} (sulfide) than between Ti and S₂^{2–} (disulfide). This phenomenon manifests itself in higher binding energy for the S₂^{2–} 2p core-level doublet than that of the S^{2–} 2p core-level doublet,^{2–6} as opposed to what is reported in ref 1.

Moreover, in accordance with the multiplicity of the 2p_{1/2} and 2p_{3/2} electronic states, the XPS peak intensity ratio of the fitted 2p_{1/2} core level to the fitted 2p_{3/2} core level associated with each sulfur species should be 1:2, which is not what the current fits indicate. It is also worth noting that, given the high quality of their data,¹ better fits might indicate whether it is the S^{2–} sulfur vacancies or the S₂^{2–} sulfur vacancies that render TiS₃ n-type.^{7,8} In other words, a thorough analysis of such high-quality high-resolution XPS (shown in Figure 3b of ref 1) may actually help single out the exact kind of sulfur vacancies that are responsible for making TiS₃ n-type. This could be accomplished by analyzing the XPS peak ratio of S^{2–} to S₂^{2–}, as for TiS₃ any XPS peak ratio of S^{2–} to S₂^{2–} besides 1:2 would imply preferential sulfur vacancies. For now, a superficial examination of the current fits¹ hints toward the existence of sulfur vacancies among the S₂^{2–} species.

In conclusion, to fix the existing internal inconsistencies in the paper¹ and to strengthen its message, further analysis and careful refitting of the data presented in Figure 3b of ref 1 is strongly recommended. Not only will redoing the current fits correctly help improve the quality of science that is being communicated by the paper in its present form, but it may also unveil what kind of sulfur vacancies are liable for the observed n-type behavior of TiS₃.^{7,8}

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Notes

The author declares no competing financial interest.

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