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ARTICLE OPEN

Liquid exfoliation of electronic grade ultrathin tin(II) sulfide (SnS) with intriguing optical response

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Two-dimensional (2D) tin(II) monosulfide (SnS) with strong structural anisotropy has been proven to be a phosphorene analog. However, difficulty in isolating a very thin layer of SnS poses challenges in practical utilization. Here, we prepare ultrathin SnS via liquid-phase exfoliation. With transmission electron microscopy, we identify the buckled structure of 2D SnS. We employ temperature dependent Raman spectroscopy to elucidate electron–phonon interactions, which reveals a linear phonon shifts. The active Raman modes of ultrathin SnS exhibit higher sensitivity to temperature than other 2D materials. Moreover, we demonstrate strong light-matter interaction in ultrathin SnS using Z-scan and ultrafast spectroscopy. Rich exciton–exciton and coherent exciton–photon interactions arising from many-particle excited effects in ultrathin SnS eventually enhances the nonlinear optical properties. Our findings highlight the prospects for the synthesis of ultrathin anisotropic SnS towards the betterment of thermoelectric and photonic devices.

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INTRODUCTION

Successful isolation of 2D materials beyond graphene, such as boron nitride (BN), transition metal dichalcogenides (TMDs) and phosphorene opens up a new horizon in material research.[1–3] The unique optical properties that arise with strong light-matter interaction at their 2D quantum limit can provide a plethora of opportunities for future energy conversion and photonic applications.[4–7] Of a particular note, the structural anisotropy of ultrathin 2D phosphorene has sparked the revival of fundamental research.[8–10] The intriguing in-plane anisotropy due to the difference in electronic structure along the armchair and zigzag directions gives rise to different refractive index along these directions.[11] Strong anisotropy can also lead to the formation of quasi excitons, biexcitons, trions, and phonons.[8–10,12] In spite of a number of exotic phenomena, chemical stability of phosphorene is a critical issue.[13–15]

2D SnS, a member of emerging layered metal monochalcogenide (MX, M=Ge, Sn, etc.; X=chalcogen) family has recently been recognized as an analog of phosphorene.[16] Theoretical investigations revealed a sizeable band gap, odd-even quantum confinement effect, high carrier mobility and large absorption coefficient in few-layer SnS.[17] The first-principle simulations based on the modern theory of polarization predicted enormous, piezoelectric effect of monolayer SnS. One or two orders of magnitude larger value of the piezoelectric coefficient of SnS than other 2D materials was attributed to its unique puckered C_{2v} symmetry and electronic structure.[18] The buckled layered structure of SnS (Fig. 1a) gives rise to the structural anisotropy, which is manifested in the Raman response,[19] nonlinear optical property,[20] electrical mobility[16], and photoactivity.[21] More importantly, SnS layers are environmentally, thermally and dynamically stable.[17,22] Previous reports on layered SnS are mainly theoretical, but experimental investigations are on the rise. O'Brien and coworkers[23] have reported exfoliation of thin SnS nanosheets containing 3–4 bilayers. In the first report on light-matter interaction in multilayer SnS sheets, Raman spectroscopic investigations have been carried out to know the thermal properties.[19] However, the revelation of the ultrathin layer (monolayer/bi-layer) SnS nanosheets and their thermal properties are yet to be explored.

In a system of reduced dimensionality,[24–27] exciton–exciton annihilation (EEA), a many-body process in which one exciton disappears by donating its energy, is particularly significant. Recently, Nardeep et al.[28] noticed strong density-dependent initial decay of the excitonic population in $MoSe_2$ monolayer which was well illustrated by EEA. The annihilation process was also apparent in monolayer MoS_2, mono-, bi- and tri-layer WS_2.[27,29] In layered WS_2, annihilation rate was found to be faster in monolayer than in bi- or tri-layer due to reduced many-body interaction and phonon-assisted annihilation of indirect excitons.[29] Nonetheless, 2D layered materials possess nonlinear optical properties that determine the performance of nanophotonic devices. Wang et al. observed the much better saturable response in MoS_2 than graphene.[30] The broadband and enhanced saturable absorption response of multilayer black phosphorous (BP) could be used to develop broadband ultrafast mode-locker, passive Q-switcher and optical switcher.[31–33] Linear and nonlinear ultrafast absorption behaviors of chemically exfoliated phosphorene have also been investigated. Ultrashort pulse generation has been demonstrated by taking advantage of their unique nonlinear absorption.[34] However, further study of light-matter interaction in anisotropic 2D materials is very important to exploit them in energy conversion and laser applications.

In this study, we report for the first time the preparation of ultrathin SnS nanosheets via liquid-phase exfoliation (LPE). Cryogenic Raman spectroscopy, pump-probe spectroscopy, and Z-scan techniques were employed to investigate the electron–phonon and exciton–exciton interactions in layered SnS sheets. A linear behavior of phonon energy shift with temperature is observed for ultrathin SnS. Our femtosecond transient absorption studies reveal strong quasiparticle interaction in ultrathin SnS leading to EEA, which in turn enhances nonlinear

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