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Facile synthesis of tin phosphite nanosheets via exfoliated bulk crystals: Electronic structure and piezoelectric property

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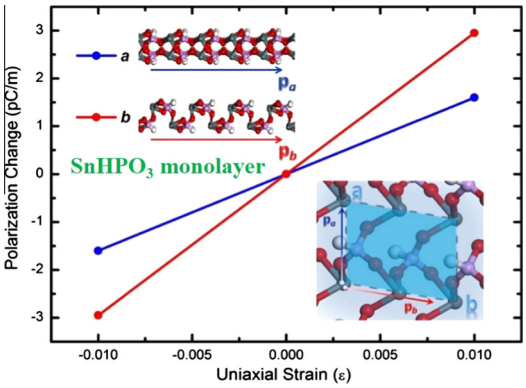
HIGHLIGHTS

- $SnHPO_3$ nanosheets were obtained by a facile exfoliation method.
- $SnHPO_3$ nanosheets exhibit blue-shift in UV absorbance.
- The piezoelectric coefficients of $SnHPO_3$ monolayer were calculated.
- The piezoelectric coefficients of $SnHPO_3$ monolayer are larger than h-BN monolayer.

GRAPHICAL ABSTRACT

$SnHPO_3$ monolayer exhibits good intrinsic piezoelectricity properties based on DFT calculations.



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ABSTRACT

Tin phosphite nanosheets were synthesized by a facile exfoliation method. $SnHPO_3$ nanosheets with a thickness of ~2.6 nm readily form a stable colloidal suspension in ethanol using ultrasonic method. Structures and optical properties of the obtained nanosheets were investigated. The prepared $SnHPO_3$ nanosheets exhibit an obvious blue-shift in UV absorbance compared with bulk $SnHPO_3$ crystal materials. Moreover, the piezoelectric coefficients of $SnHPO_3$ monolayer were calculated based on density functional theory, which are larger than that of h-BN monolayer, indicating this material could be a good candidate for designing electro-optical nano-devices.

1. Introduction

Immense research has been made in atomically thick two-dimensional (2D) nanosheets owing to their unique properties such as high surface area and quantum size effect, the wide potential applications in ultrathin nano-devices such as switches, tweezers as well as displacement sensors [1–7]. Compared with its bulk counterparts, nanostructured materials generally show excellent chemical and physical properties. Furthermore, 2D materials with atomic thickness would greatly expand their species, resulting in the relevant unprecedented excellent properties. It has been

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demonstrated that "bottom-up" or "top-down" methods both offer strategies to obtain inorganic-organic hybrid nanosheets [8–10]. Particularly, it is a cost-effective and readily available approach to discover the corresponding nanosheets via exfoliation of bulk materials with layered structure.

Metal phosphites, closely similar to the metal phosphates, have attracted increasing attention during the past two decades because they possess varied types of structures and show potential applications in catalysis, proton conductivity, electric devices, and second-order nonlinear optical (NLO) properties [11–17]. In addition, the HPO_3 anion offers three P—O bonds and one P—H bond, which could be beneficial to the forming of compounds with layered structures [18–23]. Thus, the corresponding metal phosphite nanosheets would be easily obtained by exfoliating the bulk material. It has been found that very stable colloidal dispersions of zirconium phosphates and phosphonates could be obtained by intercalation or exfoliation in water/acetone mixtures and the nanosheet-materials exhibit great value for applications in drug delivery and dye sensitized solar cells [13,16]. The first lanthanum 1,3,5-benzenetriphosphonate with layered structure was successfully exfoliated resulting in the nanosheets of this compound and both the bulk and exfoliated samples show photoluminescence [24]. Furthermore, the exfoliation of layered copper phosphonate shows enhanced adsorption capability towards Pb ions [25].

However, to our best knowledge, there have been no reports to date on inorganic nanosheets containing metal phosphites to exploit their applications though they possess similar property with metal phosphates. Recently, we reported preparation of a series of new alkali metal and alkali-earth metal phosphites with 2D layered structure, which might be favorable to result in inorganic-phosphites nanosheets and discover new physical properties [12,23].

Here, we prepared the first example of tin phosphites nanosheets by exfoliation of the corresponding layered bulk materials. The preparation, crystal structure and their optical properties in bulk form, and dispersion solutions were reported. The piezoelectric coefficients of $SnHPO_3$ monolayer were studied by means of density functional theory (DFT) calculations.

2. Material and methods

2.1. Preparation of bulk crystals of $SnHPO_3$

$SnCl_2$ (0.189 g, 1.0 mmol) and H_3PO_3 solution (1.0 mL) were mixed in H_2O (10.0 mL) and sealed in an autoclave equipped with a Teflon liner (20 mL) and heated at 210 °C for 4 days. The initial and final pH values are 1.5 and 1.0, respectively. The colorless lamellar-shaped $SnHPO_3$ crystals were obtained in a yield of ca. 70% based on Sn.

2.2. Preparation of $SnHPO_3$ nanosheets

The bulk sample of $SnHPO_3$ is easy to disperse in polar solvents such as water, ethanol and ethylene glycol. Typically, the bulk sample of $SnHPO_3$ (1 mg) suspended in an ethanol solution (5 mL) was subjected to ultrasonic treatment (300 W) for 6 h at room temperature and then the $SnHPO_3$ nanosheets were obtained.

2.3. Computational descriptions

The electronic structure, optical and piezoelectric properties regarding monolayer $SnHPO_3$ were generalized gradient approximation with the Perdew-Burke-Ernzerh of functional [26] and the projector augmented-wave method [27] as implemented in VASP code[28,29]. To ensure high accuracy, the Brillouin zone was sampled with $7 \times 7 \times 1$ Monkhorst-Pack k-point grids, and the energy cutoff was set to be 550 eV for geometric optimization and electronic structure calculations. The vacuum space of 15 Å is large enough to avoid the interaction of periodic images. The convergence criterion in energy was 10^{-5} eV. All the structural relaxations were performed until the Hellmann-Feynman force on each atom reduces by less than 10^{-2} eV/Å. Atomic positions are relaxed at each strain state to generate the so-called relaxed-ion coefficients that are expected to be experimentally observable. We calculate the change in polarization along a and b per unit cell using the geometric phase approach [30,31]. The relaxed-ion piezoelectric coefficients are subsequently obtained by least-squares fitting of the polarization change per unit area.

2.4. Characterizations

X-ray powder diffraction (XRD) patterns were collected on a Rigaku MiniFlex II diffractometer using Cu-Kα radiation in the angular range of $2\theta = 5–80°$ with a step size of 0.1° (Fig. S1). Thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC) analyses were carried out with a NETZCH STA449C unit at a heating rate of 15 °C min^{-1} under N_2 and air atmosphere (Fig. S2). IR spectra were recorded on a Magna 750 Fourier transform infrared (FT-IR) spectrometer as KBr pellets in the range of 4000–450 cm^{-1} with a resolution of 2 cm^{-1} at room temperature (Fig. S3). Optical diffuse reflectance and UV spectra were measured at room temperature with a Perkin-Elmer Lambda 900 UV–vis–NIR spectrophotometer and a $BaSO_4$ plate was used as a standard (100% reflectance). The absorption spectrum was calculated from reflectance spectra using the Kubelka-Munk function: $\alpha/S = (1 - R)^2/2R$, where α is the absorption coefficient, S is the scattering coefficient (which is practically wavelength independent when the particle size is larger than 5 μm), and R is the reflectance [32].

3. Results and discussion

Scanning electron microscope (SEM) measurement was carried out for the bulk crystalline $SnHPO_3$, showing the bulk stacking of the $SnHPO_3$ nanosheets (Fig. 1a). The multilayered nanostructure also was clearly observed from TEM image (Fig. 1b). According to single crystal XRD analysis, $SnHPO_3$ displays a layer structure similar to graphite sheets as shown in Fig. 1c. The inter-layer interaction in $SnHPO_3$ is weak, thus it is possible to exfoliate the layers via a conventional exfoliation approach. The precipitates of the ultrasonicated sample of $SnHPO_3$ were investigated by atom force microscopy (AFM). As a result, $SnHPO_3$ nanosheets with a thickness of ~2.6 nm readily form a stable colloidal suspension in ethanol, as shown in Fig. 1d. In other words, the bulk sample could be successfully exfoliated into nanosheets with ~four-layer overlapped stack (2.5 nm) estimated from the single crystal data. The supernatant in ethanol after ultrasonication exhibits a Tyndall effect (Fig. 1e) [25,33].

Optical properties of the bulk and nanosheets $SnHPO_3$ were characterized by UV absorption spectrum. Fig. 2 shows the repeatable absorption spectrum of these two materials. A strong absorption at about 220 nm and 250 nm for bulk and nanocrystals $SnHPO_3$, respectively, could be observed, originating from charge-transfer between the O_{2p} and Sn_{5s} states in O^{2-} and Sn^{2+}. Compared with bulk $SnHPO_3$ material, there is an obvious blue-shift in UV absorbance for the prepared $SnHPO_3$ nanosheet, which could be ascribed to the size quantization effects [34,35].

$SnHPO_3$ crystallizes in the polar monoclinic space group Cc (No. 9). As we all know, compounds with polar structures usually have excellent physical properties, such as second order nonlinear optical, ferroelectric, piezoelectric properties, etc. We investigated the