



Structural and optical properties of ZnS/niobate composites synthesized by exfoliation/self-assembly processing

Yufeng Chen^{a,*}, Songhua Zhou^a, Xiaojing Yang^b, Yi Ou-Yang^c

^a Department of Chemistry, Nanchang University, Jiangxi 330031, China

^b College of Chemistry, Beijing Normal University, Beijing 100875, China

^c Nanchang Institute of Technology, Jiangxi 330099, China

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ABSTRACT

A new ZnS/niobate composite was first synthesized through two processes: (1) self-assembly of $[\text{Ca}_2\text{Nb}_3\text{O}_{10}]_n^{n-}$ nanosheets in $\text{Zn}(\text{NH}_3)_4^{2+}$ solution; (2) formation of ZnS/niobate composite by adding Na_2S to the former reacting system. X-ray diffraction (XRD) result shows that the as-prepared ZnS/niobate composite can be indexed to tetrahedral symmetry with $a=5.450(2)$ and $c=16.904(7)$ Å. The uniform distributions of Zn, Ca, Nb, S and O element in the particles were demonstrated by scanning electron microscope (SEM) and energy dispersive spectrometer (EDS). The optical property of the composite was characterized by photoluminescence spectra and UV-vis absorption spectra.

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1. Introduction

As an important II–VI semiconductor, ZnS has wide bandgap energy of 3.6 eV [1]. It is used as a key material for ultraviolet light-emitting diodes, thin film electroluminescence, flat-panel display and IR windows, etc [2,3]. Chemical stability was important because ZnS nanoparticles were easily agglomerated and oxidized during heat treatment in air. Even with the existence of traces of oxygen, the surface of ZnS nanoparticles would be oxidized into ZnO dead layers, which reduced luminescence intensity significantly [4], or even may degrade the performance of the devices over years of operation [5]. One strategy is to employ a protective layer on ZnS surface to enhance the chemical stability and avoid the agglomeration and oxidation of ZnS at high temperatures [6,7]. A typical example is coating ZnS with silica [8–11], and reported to be more stable against electron beam or UV light irradiation compared to uncoated ZnS [12,13], or embedding ZnS in polymers [14,15].

In this paper, we propose an alternative host material, layered perovskite niobate, to embed ZnS, which was selected as host because of not only its excellent chemical and thermal stabilities, but also its structural stability of layers after being exfoliated. The PL spectrum of the dehydrated composite shows markedly UV emission blue shift attributed to quantum sizes effects, indicating that the size of ZnS particles can be confined by niobate host.

Although we measured the optical property of the ZnS/niobate composite, one would be interested in their other properties, such as chemical stability, photo-catalysis, etc. So that it is expectable that the relatively convenient preparation method and the material itself would be potentially application in optical field or other application in materials related fields.

2. Experimental procedure

2.1. Exfoliation of protonated $\text{KCa}_2\text{Nb}_3\text{O}_{10}$

Layered perovskite, $\text{KCa}_2\text{Nb}_3\text{O}_{10}$, was prepared by solid-state reaction method as reported in the literature [16]. The protonation of the perovskite (2.0 g) was performed by soaking in 50 mL of a HNO_3 aqueous solution (6 mol L^{-1}), stirred for 6 days, and then filtered, water-washed, and dried at 110°C . The obtained sample is refined as $\text{HCa}_2\text{Nb}_3\text{O}_{10} \cdot 0.5\text{H}_2\text{O}$ by a Rietveld refinement [17]. A colloidal suspension of nanosheets was obtained by adding a specific amount of protonation powder (2.0 g) in 1 L of a tetramethylammonium hydroxide (TMAOH) aqueous solution at a molar ratio of $\text{TMAOH}/\text{HCa}_2\text{Nb}_3\text{O}_{10}=10$, and stirred at room temperature for about 20 days.

2.2. Synthesis of ZnS/niobate composites

The colloidal suspension ($\sim 0.6 \text{ g L}^{-1}$ 500 mL for a batch) of $[\text{Ca}_2\text{Nb}_3\text{O}_{10}]_n^{n-}$ nanosheets was concentrated by centrifugation at

* Corresponding author. Fax: +86 791 830 4441.
E-mail address: yfchen@ncu.edu.cn (Y. Chen).

12 000 rpm to a slurry of 20 mL with pH of 12.30. The slurry was dispersed into the $\text{Zn}(\text{NH}_3)_4^{2+}$ solutions (0.1 mol L^{-1} , 200 mL) to form a mixed suspension, and stirred overnight. The pH of the mixed suspension was 12.54, at which the hydrolysis of $\text{Zn}(\text{NH}_3)_4^{2+}$ is avoided [18]. In order to get rid of the excess $\text{Zn}(\text{NH}_3)_4^{2+}$, the sediment from the mixed suspension was filtered, washed, and quickly dispersed into deionized water (200 mL) to form a new suspension, then Na_2S (0.1 mol L^{-1} , 20 mL) solution was gradually added to the new suspension, continuously stirring. The as-prepared composite of ZnS/niobate was obtained after the precipitation was filtered, washed with deionized water, and dried at 40°C in vacuum overnight. In order to compare with the as-prepared ZnS/niobate, a intercalated- $\text{Zn}(\text{NH}_3)_x$ sample prepared by $[\text{Ca}_2\text{Nb}_3\text{O}_{10}]^{n-}$ reaction with $\text{Zn}(\text{NH}_3)_4^{2+}$ solution and a ZnS sample prepared with Na_2S and $\text{Zn}(\text{NH}_3)_4^{2+}$ solutions, were supplied for the study.

2.3. Characterization

Powder X-ray diffraction (XRD) patterns were collected using a Bruker D8 Focus diffractometer with $\text{CuK}\alpha$ radiation. The generator setting is 40 kV and 40 mA. The XRD patterns of the samples were measured at room temperature with step size of 0.02, scan rate $2^\circ/\text{min}$ step, and 2θ ranging from 4.0 to 80° . The Fourier Infrared spectra of the samples were recorded on a Nicolet-380 Fourier-transform infrared spectrometer using the KBr method.

Chemical contents of Ca, Nb, Zn and S were determined by inductively coupled plasma (ICP) (Jarrel-ASH, ICAP-9000), and CHN element analysis was performed with element analyzer (Germany elemental vario EL). The chemistry formula was estimated from the results of ICP and CHN analysis. Thermal gravimetric (TG) and differential thermal analysis (DTA) data were collected using synchronous thermal analyzer (PYRIS DIAMOVD, AMERICAN PE COMPANY).

The morphological features of supported ZnS/niobate composite particles were examined by recording scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM) images. The TEM images were obtained on a JEM-200CX equipped with emission gun (FEG) high-resolution transmission electron microscope (supplied by JEOL Company, Japan). Scanning electron microscope (SEM) and energy dispersive spectrometer (EDS mapping) observation was carried out using a mode S-4800 (Hitachi, Ltd.), operating at 5.0 kV.

The information about oxidation state of Zn as a function of sample composition was obtained by X-ray photoelectron spectroscopy (XPS) analysis. A ESCALAB MKII spectrometer (UK), equipped with a $\text{AlK}\alpha$ radiation (1486.6 eV) source and operating at $12 \text{ kV} \times 12 \text{ mA}$ under ultrahigh vacuum (5×10^{-9} mbar.), was employed for this purpose. The charge compensation was accomplished by using C 1s signal at 284.8 V for reference.

The optical properties were characterized by photoluminescent spectra (PL, AFS-230E) and UV-vis absorption spectra (U-4100 Spectrophotometer). The $\text{Ca}_2\text{Nb}_3\text{O}_{10}^{n-}$ nanosheets were observed by SEM after restacking or coating on a Si wafer by layer-by-layer method and frozen drying method, respectively. The specimen for the layer-by-layer method was prepared as following: polished Si (111) wafer (n-type) was cleaned with acetone, rinsed with methanol and ionized water, respectively, and then dried by high pure N_2 gas. The sample of $\text{Ca}_2\text{Nb}_3\text{O}_{10}/\text{PEI}/\text{Si}$ was obtained by the layer-by-layer method. The Si wafer was primed by a treatment with a polyethylenimine solution (PEI, $M_w \sim 750,000$; 1.08 g L^{-1}) for 20 min to introduce a positive charge to the wafer surface. The wafer was deposited into a suspension of the $\text{Ca}_2\text{Nb}_3\text{O}_{10}^{n-}$ ($\sim 0.6 \text{ g L}^{-1}$) and after 20 min, the excess $\text{Ca}_2\text{Nb}_3\text{O}_{10}^{n-}$ sheets and other ions were removed

thoroughly by water-washing. The specimen for the frozen drying method was prepared as following: a mount of $\text{Ca}_2\text{Nb}_3\text{O}_{10}^{n-}$ ($\sim 0.6 \text{ g L}^{-1}$) nanosheets suspension was frozen and dried under liquid nitrogen for 48h, then the obtained nanosheets jelly was coated on a Si wafer for observation.

3. Results and discussion

3.1. Chemical composition and structure

The XRD patterns of the nanosheets-aggregation, intercalated- $\text{Zn}(\text{NH}_3)_x$ sample, as-prepared ZnS/niobate composite and its dehydrated product are shown in Fig. 1. As shown, a typical wavy and broad curve corresponding to exfoliated state was observed for $[\text{Ca}_2\text{Nb}_3\text{O}_{10}]^{n-}$ nanosheets-aggregation (Fig. 1a). The intercalated- $\text{Zn}(\text{NH}_3)_x$ ($x \leq 4$) sample was obtained after the $[\text{Ca}_2\text{Nb}_3\text{O}_{10}]^{n-}$ reaction with $\text{Zn}(\text{NH}_3)_4^{2+}$ solution. The intercalated compound with interlayer ions of NH_4^+ and $\text{Zn}(\text{NH}_3)_x^{2+}$ has been studied in detail [19]. It can be indexed to tetragonal structure with $a=5.462(1)$ and $c=17.227(6)$ Å (Fig. 1b).

The as-prepared ZnS/niobate composite was obtained after Na_2S solution addition into the intercalated- $\text{Zn}(\text{NH}_3)_x$ compound suspension and S^{2-} reaction with interlayer $\text{Zn}(\text{NH}_3)_x^{2+}$. Namely, $\text{Zn}(\text{NH}_3)_x^{2+} + \text{S}^{2-} = \text{ZnS} + x\text{NH}_3$, equilibrium constant: $K=1/(K_f \cdot \text{Zn}(\text{NH}_3)_x \cdot K_{sp, \text{ZnS}})$. if $x=4$, $K=1/(2.9 \times 10^9 \times 1.6 \times 10^{-24})=2.1 \times 10^4$; if $x < 4$, $K > 2.1 \times 10^4$, so the trend of the reaction was forward to form ZnS. Analyzed by ICP and CHN element analysis, the composition is estimated to be $\text{NH}_4(\text{ZnS})_{0.41}\text{Ca}_2\text{Nb}_3\text{O}_{10} \cdot 1.8\text{H}_2\text{O}$. So the interlayer species are possibly a part of ZnS and NH_4^+ ions solvated by water molecules. However, the Zn 2P core level with binding energies of 1020.0 and 1042.9 eV corresponding to the Zn(II) chemical state of ZnS (Fig. 2) [20,21] were observed from the XPS spectra of the as-prepared sample. And the band at 3260 contributed to NH_4^+ or NH_3 [22,23] was observed from the FT-IR spectra of the intercalated- $\text{Zn}(\text{NH}_3)_x$ sample and as-prepared ZnS/niobate composite (Fig. 3). These results suggest the reasonable chemical formula of the as-prepared ZnS/niobate composite. The as-prepared ZnS/niobate composite can also be indexed to tetrahedral symmetry with

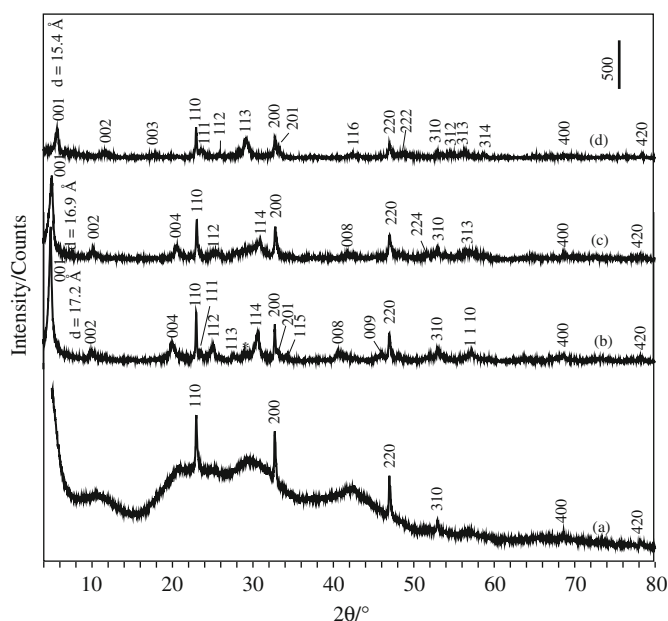


Fig. 1. XRD patterns of (a) nanosheets-aggregation, (b) $\text{Zn}(\text{NH}_3)_x$ -intercalated niobate, (c) as-prepared ZnS/niobate composite and (d) dehydrated ZnS/niobate composite.

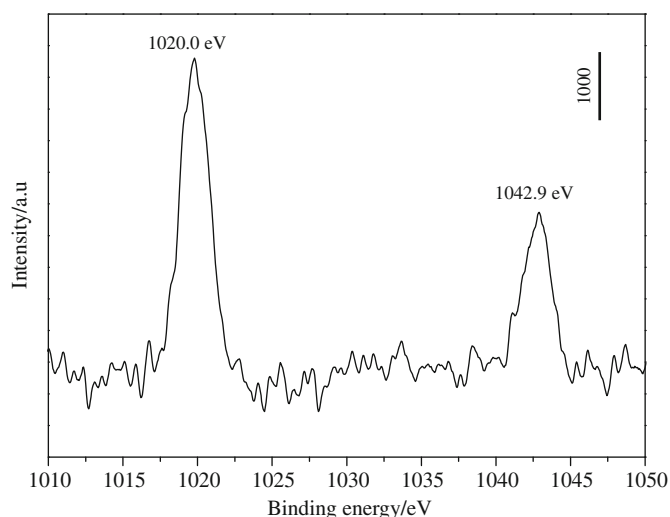


Fig. 2. XPS of the as-prepared ZnS/niobate composite for the Zn chemical valence state.

$a=5.450(2)$ and $c=16.904(7)$ Å (shown in Fig. 1c). The basal spacing (d_{basal}) of 16.9 Å for the composite suggests that it is analogous to the restacked $\text{KCa}_2\text{Nb}_3\text{O}_{10} \cdot 1.3\text{H}_2\text{O}$ compound ($d_{\text{basal}}=16.9$ Å) with a bilayer-hydrate interlayer gallery [24].

After the as-prepared sample was dehydrated at 150 °C for 3 h., the layered structure is well retained and the interlayer distance changed markedly from 16.9 to 15.4 Å, indicating the loss of interlayer water molecules. The dehydrated sample can also be indexed to tetrahedral symmetry with $a=5.440(4)$ and $c=15.4320(2)$ Å (seen in Fig. 1d). The unchanged feature of symmetry is different from the self-assembled K-form niobate, whose tetrahedral structure begins to change to orthorhombic as temperature over 100 °C [24]. This difference shows the influence of the present interlayer ions on the layer weaker than K^+ ions, which is consistent with the result [24]. The restacked K-form niobate without interlayer water has a d_{basal} of 14.7 Å [24]. The ZnS particles possibly intercalated in the interlayer of the niobate host according to the synthesis route conducted in the experiment. If does so, from the d_{basal} difference between the dehydrated composite containing ZnS (15.4 Å) and the K-form sample, the size of the ZnS particles can be estimated to ~ 3.4 Å, i.e. K^+ diameter (2.7) + 0.7 Å, close to the value calculated from covalent radius of Zn (1.25 Å) and covalent diameter of S (1.02 Å). Such ZnS particles is possibly 2D-array along the orientation paralleling to the layer in the interlayer, but the size along the orientation perpendicular to the layer was confined in the dimension of the atom level. Another case is that the ZnS particles are possibly analogous to that of the planar CdSe microclusters attached to sheets [25]. This arraying may be lack of lattice periodicity, so no trace of XRD reflections attributed to ZnS crystalline was observed (shown in Fig. 1). However, HRTEM pictures of a cross section for the ZnS/niobate composite taken at different magnifications (seen in Fig. 3) show that the interlayer ZnS was hardly observed and discerned, possibly due to the extremely small ZnS. Meanwhile, no ZnS possibly absorbed on the layers of the host was observed except for the clearly layered structure of the host materials. The result indicates that our deduction on the sizes of interlayer ZnS may be reasonable. But the mode of ZnS particles embedded in the niobate host was very complicated and should be studied further.

3.2. FT-IR spectrum, TG and SEM/EDS mapping

The FT-IR spectra of the as-prepared ZnS/niobate composite and its precursors are shown in Fig. 4. No vibration band concerning TMA^+ can be found in the spectra of the products.

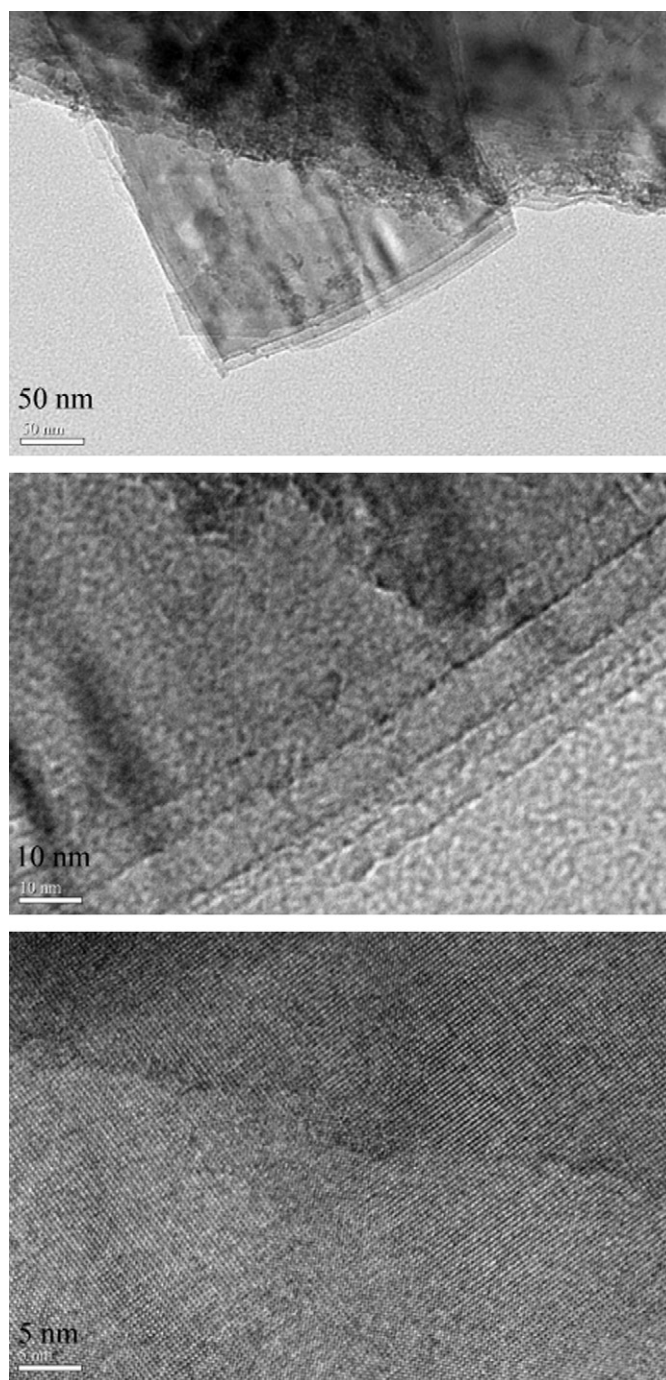


Fig. 3. HRTEM images at different magnifications for the ZnS/niobate composite.

Very similar IR spectra of the intercalated- $\text{Zn}(\text{NH}_3)_x$ sample and as-prepared ZnS/niobate composite were observed, obviously different from the precursor $\text{HCa}_2\text{Nb}_3\text{O}_{10}$. The bands at 928, 772, and 586 cm^{-1} for the intercalated- $\text{Zn}(\text{NH}_3)_x$ sample and as-prepared ZnS/niobate composite are assigned to the stretching vibrations of $\text{Nb}-\text{O}_{\text{terminal}}$ vibrations [26,27], asymmetric stretching vibrations of $\text{Nb}-\text{O}_{\text{bridge}}$ in terminal NbO_6 octahedron [28], asymmetric stretching vibrations of $\text{Nb}-\text{O}_{\text{bridge}}$ in central NbO_6 octahedron [26,28], and the bands at 3420 and 1640 cm^{-1} are recognized as the stretching and bending vibrations of hydroxyl groups, respectively [29]. The split bands were observed for the $\text{HCa}_2\text{Nb}_3\text{O}_{10}$ which has ever been discussed [24]. The characteristic peaks of Zn-S-Zn bonds did not appear in

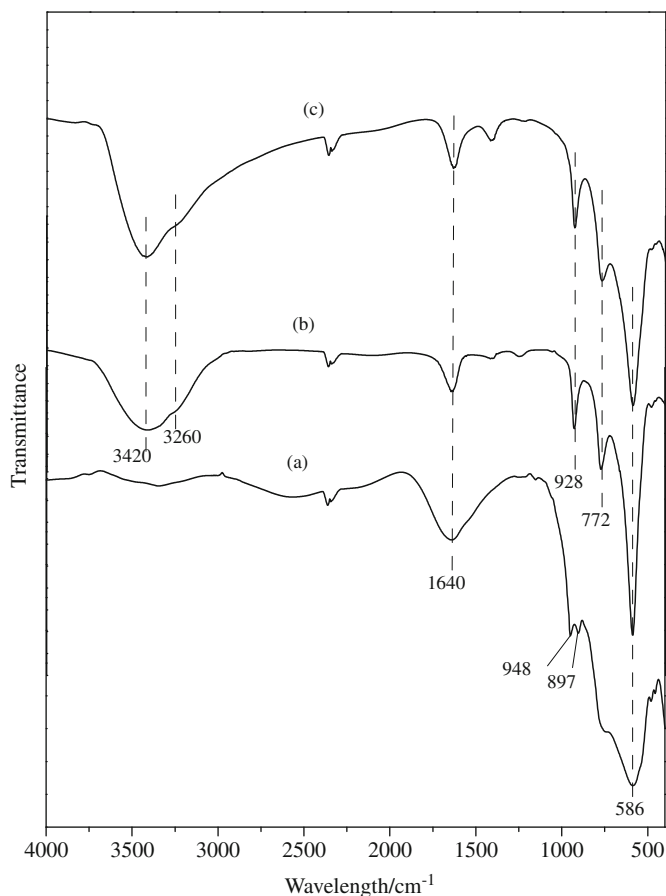


Fig. 4. FT-IR spectra of the (a) precursor $\text{HCa}_2\text{Nb}_3\text{O}_{10}\cdot 0.5\text{H}_2\text{O}$, (b) $\text{Zn}(\text{NH}_3)_x$ -intercalated niobate and (c) as-prepared ZnS/niobate composite.

the range of $595\text{--}620\text{ cm}^{-1}$ [30]. So the ZnS particles may be covered by the layered niobate, analogous to the previous report [9].

The images of scanning electron microscope (SEM) were shown in Fig. 5. The difference of shape was observed between the precursor $\text{HCa}_2\text{Nb}_3\text{O}_{10}$ and the as-prepared ZnS/niobate composite. A typical image of exfoliated nanosheets exhibited as in Fig. 5b and c, respectively [31]. The energy dispersive spectrometer (EDS) observation (Fig. 6) demonstrates the uniform distributions of Zn, Ca, Nb, S and O in the particles, indicating the ZnS particles highly dispersed in the niobate host.

The thermal stability of the ZnS/niobate composite (ZnS coated with niobate) was characterized by TG (shown in Fig. 7). As shown, the weigh loss (%) curve of the ZnS/niobate composite was always above that of the ZnS without coating, indicating the thermal stability of the ZnS/niobate composite better than that of the ZnS without coating.

3.3. Optical properties

Fig. 8 shows the room temperature photoluminescence of ZnS/niobate composites using an excitation wavelength of 300 nm. A broad strong UV emission around at 360 nm was observed for the as-prepared ZnS/niobate composite. After the as-prepared sample was dehydrated at 150°C for 3 h, a weak UV emission at 330 nm occurred, and the strong broad UV emission slightly shifted to 364 nm. A weak UV emission at 330 nm and a strong UV emission at 364 nm were observed at the room temperature PL of the ZnS embedded in silica host [9]. The emission at 330 nm was attributed to recombination of free excitons [9,32] or shift-blue of bandgap due to quantum confinement [33]. The emission at 360 or 364 nm could be ascribed to a recombination of electrons at the sulphur vacancy donor level with holes trapped at the zinc vacancy acceptor level

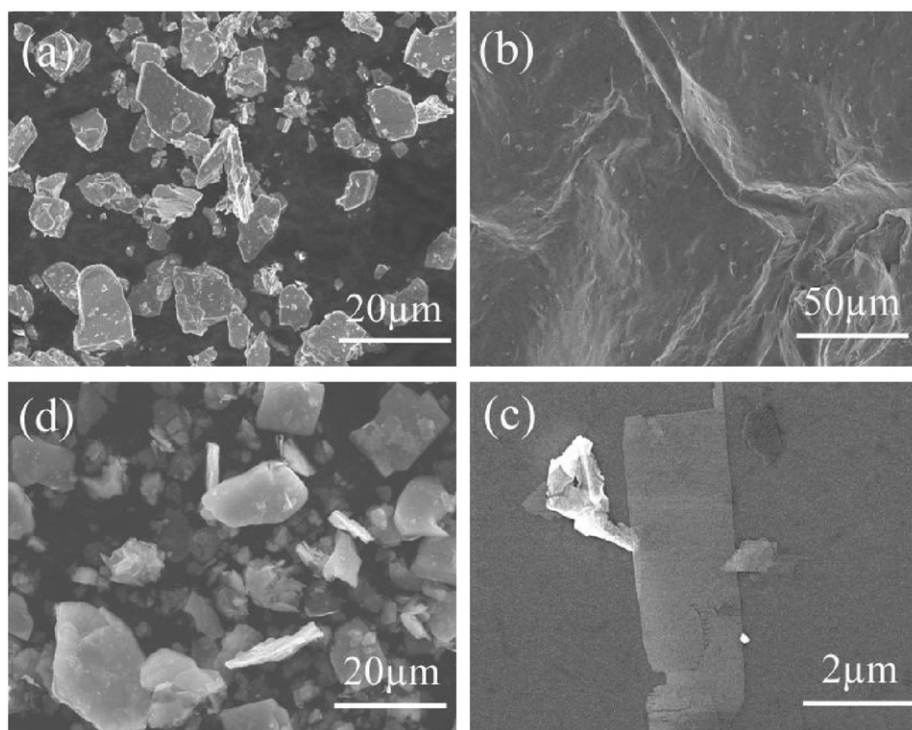


Fig. 5. SEM images of (a) precursor $\text{HCa}_2\text{Nb}_3\text{O}_{10}$, (b) freeze-dried nanosheets under liquid nitrogen, (c) nanosheets/PDDA/Si wafer, and (d) as-prepared ZnS/niobate composite.

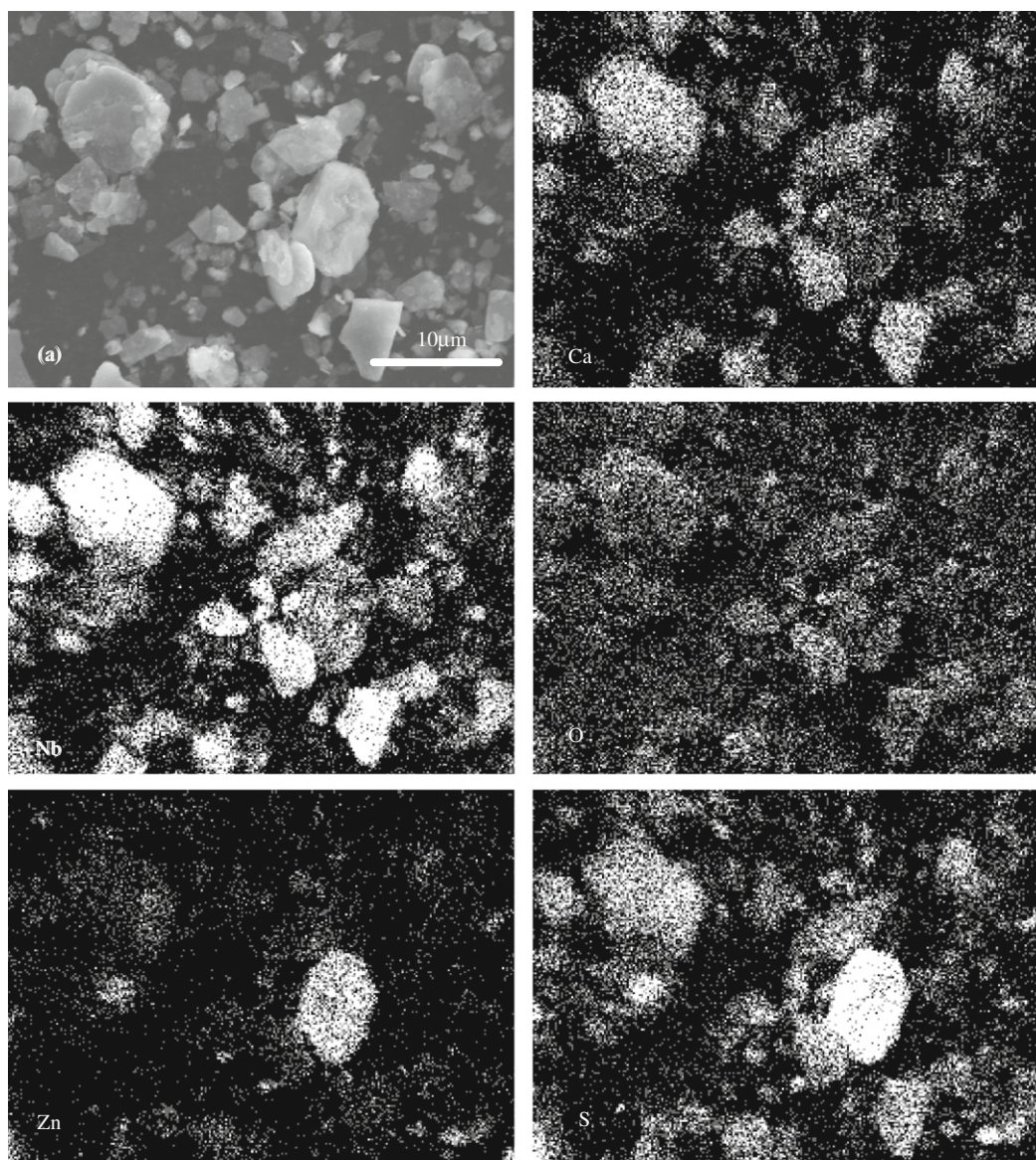


Fig. 6. SEM image of the as-prepared ZnS/niobate composite-(a) and its EDS-mapping scans of Ca, Nb, O, Zn, and S.

[9,34]. These results show that the photoluminescent property of ZnS embedded in layered niobate can be improved as that of the ZnS embedded in silica. UV-vis absorption spectra show that the absorbed edge of the as-prepared ZnS/niobate composite slightly shifted to low energy after dehydration (Fig. 9), consistent with the result of PL.

All the results indicated that extremely small ZnS particles formed in the niobate host by the novel route. ZnS was possibly inserted in interlayer of niobate with a 2D structure, or attached to the $\text{Ca}_2\text{Nb}_3\text{O}_{10}$ sheets as that of the CdSe microclusters attached to the $\text{Ca}_2\text{Nb}_3\text{O}_{10}$ sheets [25], or embedded in the host with other modes.

4. Conclusions

In conclusion, a new composite of ZnS/niobate was synthesized through the two processes. XRD, IR, PL, HRTEM, XPS, and SEM/EDS mapping results indicate that the extremely small ZnS particles may be formed in the host niobate. The PL spectroscopy of the dehydrated sample shows markedly UV emission blue shift

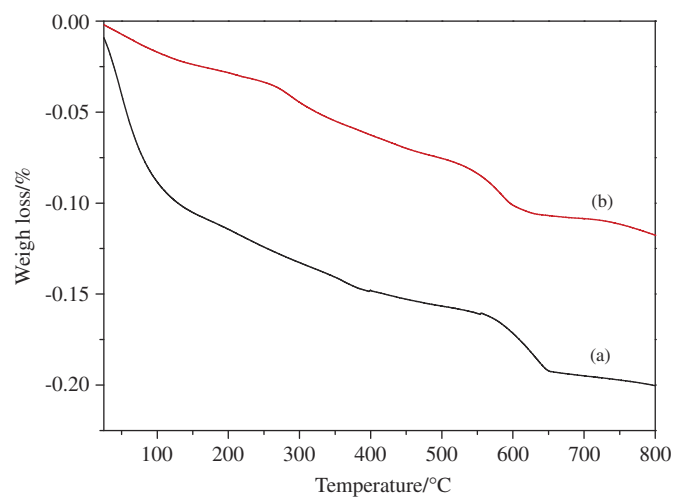


Fig. 7. TG curves of (a) ZnS without coating and (b) as-prepared ZnS/niobate composite.

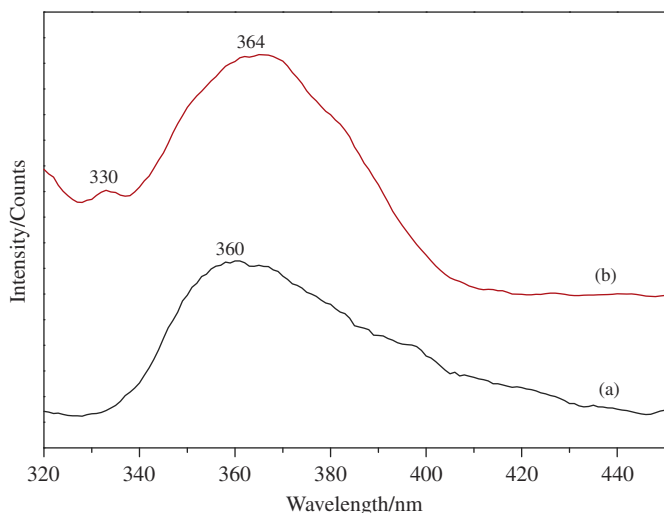


Fig. 8. Room-temperature PL spectra of (a) as-prepared ZnS/niobate composite and (b) dehydrated ZnS/niobate composite ($\lambda_{\text{ex}}=300$ nm).

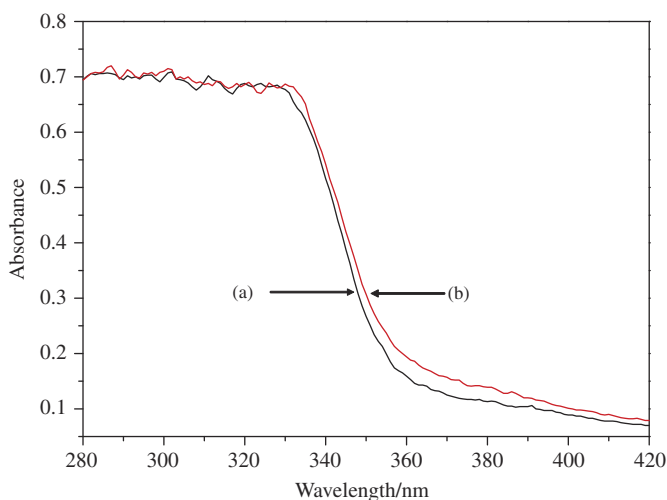


Fig. 9. UV-vis spectra of (a) as-prepared ZnS/niobate composite and (b) dehydrated ZnS/niobate composite.

attributed to quantum confinement, indicating the layered niobate can confine the size of ZnS particles as that of the silica host materials conducted by other methods. The thermal stability of the as-prepared ZnS/niobate (ZnS coated with niobate) was obviously higher than that of the ZnS particles without coating. The mode of ZnS particles embedded in the niobated host should be studied further.

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