Synthesis of well-aligned ZnO nanorod arrays from mixed sulfide-oxide lead and zinc ore

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Abstract: A novel process of recovery of zinc from mixed sulfide-oxide lead and zinc ore was presented in this paper. ZnO nanorod arrays (ZNRAs) on FTO substrate pre-coated with a layer of ZnO seeds was synthesized successfully from the mixed ore via the oxidative ammoniacal leaching process and a two-step process including precipitation and hydrothermal synthesis. The characterization results from the XRD, SEM and UV-vis spectrophotometer analysis showed that the as-prepared ZNRAs was well-aligned, large-scale, perpendicular to the FTO substrate and had a reduced band gap energy of 3.03 eV. XPS analysis indicated that the grown ZNRAs were doped by a small quantity of carbon and did not contain any other impurities particularly Fe and Pb. The total zinc extraction can reach 92.4% after the oxidative ammoniacal leaching process and the precipitation process. The elimination of conventional purification process in zinc production was achieved due to the efficient and selective oxidative ammoniacal leaching process.

Keywords: mixed sulfide-oxide lead and zinc ore, oxidative ammoniacal leaching, ZnO nanorod arrays

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1. Introduction

As one kind of zinc mineral resources, mixed sulfide-oxide lead and zinc ore typically has a complex mineralogy being composed of various ore minerals and gangue minerals [1-2] and is very often left untreated due to the difficult beneficiation. As the increasing consumption of zinc resources, efficient extraction of zinc and preparation of good performance products from mixed ore will be of great significance. However, it seems to have not received much attention and only one paper reported the leaching research about mixed ore in sulfuric acid [2].

The hydrometallurgical processes of zinc ores mainly include acid leaching and ammoniacal leaching. In comparison with acid system, ammoniacal system has many advantages [3-5] such as no excessive reagent consumption, absence of filtration problem, high selectivity and simple purification in that impurities like Fe_2O_3 , SiO_2 , CaO and MgO are insoluble at the relatively high pH value. The addition of oxidant is essential in the leaching process in consideration of the dissolution of the sulfide part of mixed ores. Persulfate ($\text{S}_2\text{O}_8^{2-}$) has a high redox potential and can decompose to be sulfate radicals ($\text{SO}_4^\bullet$) and hydroxyl radicals ($\text{HO}^\bullet$) both with more stronger oxidability through thermal activation when the pH value is 7 to 12 [6, 7]. Therefore, leaching of mixed ore in ammoniacal solution with ammonium sulfate as oxidant could be a selective and efficient approach.

As for the treatment of ammoniacal leaching solution, different methods have been investigated to separate zinc and obtain products. The leaching-electrowinning process [8-10] in ammoniacal system has been proposed and studied in which high-purity zinc can be obtained after removing the impurities of As, Sb, Cu, Pb and Cd in lixivium by the addition of oxidant and zinc

powder. But zinc concentration in ammoniacal leaching liquor tend to be lower which lead to a low current efficiency in the electrowinning process. Therefore, solvent extraction [11-13] instead of purification before electrodeposition was also researched. β -Diketones are perceived as the most alternative for recovering zinc from ammoniacal media owing to high stability and low ammonia co-extraction. But the extraction efficiency is still too low for industrial application as well as susceptible to ammonia concentration because zinc is extracted as free zinc ion and zinc ammine complexes are not extracted [14, 15]. J. Vazquez-Arenas et al. [16] evaluated the feasibility of zinc electrorecovery at different pH values in $\text{NH}_4\text{Cl-NH}_3$ electrolytes and indicated that higher current efficiencies are obtained on the Glassy Carbon, and Ti cathodes as the pH value is increased. Activated zinc oxide [4, 17, 18] was produced as well by precipitating the dissolved Zn in solution then calcinating the precipitate which was usually basic zinc carbonate. From the above, the present treatment methods are difficult or complicated, and synthesis of higher performance products like nanostructured zinc-containing materials from the ammoniacal leaching liquor would be more significant.

ZnO is a significant semiconductor with a direct wide band gap (3.37 eV), large excitation binding energy (60 meV) and high optical gain (300 cm^{-1}). Nanostructured ZnO has received remarkable interest due to its wide and promising application like chemical sensors [19], photodetectors [20], solar cells [21], catalysis [22] and piezoelectric materials [22], and the well-aligned ZNRAs are critical for scientific and technological applications [23, 24]. Various approaches such as thermal evaporation [25], chemical vapour deposition (CVD) [26], electrochemical process [27] and hydrothermal process [28] were used to prepare ZNRAs.

Compared with other routes, the hydrothermal synthesis involves a simpler, lower temperature, more controllable process and the structure fabricated is more uniform [29]. Y. Tak et al. [30] reported that ZNRAs were grown on zinc-coated silicon substrate in aqueous solution containing zinc nitrate and ammonia by multistep growth concepts. Y. Fang et al. [31] prepared uniform, aligned and ultrathin ZnO nanofiber arrays (3-10 nm) by hydrothermal treatment of Zn foil in an ammonia/alcohol/water mixed solution at 95 °C for 24 h. To our knowledge, nanostructured ZnO has been synthesized all by using various chemical reagents so far and none of the effort has been taken on obtaining it from natural mineral, especially producing well-aligned ZNRAs. Therefore, preparation of nanostructured ZnO from mixed sulfide-oxide lead and zinc ore in this ammoniacal system would be an attractive and promising technology in view of the favorable conditions for growth of ZnO and the resource utilization.

In this paper, well-ordered ZNRAs on FTO substrate was prepared from the mixed sulfide-oxide lead and zinc ore by using oxidative ammoniacal leaching process and a two-step process including precipitation and hydrothermal synthesis. The leaching efficiency of zinc and selectivity in oxidative ammoniacal leaching process were analyzed under the optimal conditions. The as-prepared ZNRAs was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), UV-vis spectrophotometry and X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1 Materials

The mixed sulfide-oxide lead and zinc ore in this study was composed of sulfide ore and oxide ore on the basis of the molar ratio of zinc sulfide to zinc oxide 3:1 by ball mill according to the

oxidation ratio 30%, after the sulfide ore and oxide ore were milled into powders of $-38.5\ \mu\text{m}$. Both these two kinds of zinc ore were from Lanping town in Yunnan province of China. The main chemical compositions and XRD pattern of mixed sulfide-oxide zinc ore are shown in Table 1 and Fig. 1, respectively. It is indicated that the mixed sulfide-oxide lead and zinc ore mainly contains sphalerite (ZnS , 23.6%), smithsonite (ZnCO_3 , 10.1%), galena (PbS , 12.3%), pyrite (FeS_2 , 12%) and a considerable amount of gangue minerals such as calcite (CaCO_3 , 35.3%) and silica (SiO_2 , 12.3%).

All the chemicals were analytical grade and purchased from the Sinopharm Chemical Reagent Co., Ltd. The FTO conductive glass ($10\text{-}14\ \Omega \cdot \text{cm}^{-2}$) was used as the substrate and cleaned by standard procedures prior to use.

Table 1

Fig. 1.

2.2 Methods and procedure

Fig. 2 illustrated the flow chart of preparation of ZNRAs from mixed sulfide-oxide lead and zinc ore. It can be seen from Fig. 2 that the experimental procedure included two parts: the oxidative ammoniacal leaching process and a two-step process, i.e., the hydrothermal synthesis process followed by a simple precipitation step.

Fig. 2.

2.2.1 Oxidative ammoniacal leaching process

Leaching experiments of mixed sulfide-oxide lead and zinc ore were performed in a 500 ml round-flask equipped with a mechanical stirrer and temperature was controlled through electro-thermostatic water bath. The samples and leaching agents prepared with ammonia (25~28%),

ammonium sulfate ((NH₄)₂SO₄), ammonium persulfate ((NH₄)₂S₂O₈) and deionized water were added into the reactor when the set temperature was reached. When the leaching operation was terminated, the slurry was filtered to acquire filtrate and residue. The residue was washed and filtrate was diluted to constant volume with ammonia, which pH value was adjusted to 9, other than water considering the hydrolysis precipitation. The concentration of zinc, iron and lead in leaching solutions were measured and the mineralogical composition of leach residue was determined after residue was washed and dried.

2.2.2 Precipitation and hydrothermal synthesis process

(1) Precipitation of hexahydrated ammonium zinc sulphate ((NH₄)₂Zn(SO₄)₂·6H₂O)

The leaching solution obtained under the optimum leaching conditions was utilized to prepare ZNRAs on FTO substrate pre-coated with a layer of ZnO seeds. Firstly, sulfuric acid (4 mol/L) was added drop-wise into the stirring leach liquor till the pH value of 2.0 was obtained. The solution was filtered after 30 minutes to acquire the white precipitate for next use, simultaneously, which phase was measured after being dried in the air. The content of zinc in the filtrate was also determined.

(2) Preparation of ZnO seed layers on FTO substrate

The ZnO films were prepared by the sol-gel spin coating method. A accurate amount of Zinc acetate dihydrate [Zn(CH₃COO)₂·2H₂O] was added to the solution which was prepared by 2-Methoxyethanol (C₃H₈O₂) and monoethanolamine (MEA) with the molar ratio of MEA to [Zn(CH₃COO)₂·2H₂O] maintaining at 1:1 under a constant 0.5 mol/L of zinc acetate, then stirred for 3 h at 60 °C. The solution was then transformed onto the 1.0×3.0 cm² FTO substrate's

conductive side using a spin coater which was rotated at two steps (1000 rpm for 5 seconds, 3000 rpm for 30 seconds) simultaneously. After that, the as-coated FTO substrate was heated at 350 °C for 10 min to evaporate the solvent and remove organic residuals.

(3) Hydrothermal synthesis process

The precursor solution for synthesis of ZNRAs was prepared as follows: a certain amount of the precipitate ((NH₄)₂Zn(SO₄)₂•6H₂O)) derived from the leach liquor was dissolved in deionized water depending on the zinc concentration of 0.04 mol/L. Then, ammonia (25~28%) was added drop-wise into the solution till the white floccule appeared in this process just completely dissolved, thus the precursor solution which pH value was 9.2 was obtained. The precursor solutions with pH value of 10.0 and 11.0 were also prepared by continuing adding ammonia into the solutions. After stirring for 10 min, 20 mL of the precursor solutions were transferred into a 35 mL Teflon-lined autoclave then the FTO substrate pre-coated with ZnO seed was put into the autoclaves with the seed layer down. Hydrothermal treatment was carried out at 95 °C for 4 h. After the reaction finished, the autoclave was cooled down to the room temperature naturally. Subsequently, the as-deposited substrate was rinsed repeatedly with deionized water and dried in air for further characterization.

2.2.3 Analysis and characterization

The chemical composition and phase structure were characterized by X-ray fluorescence (XRF-1800, Japan) and X-ray diffraction (XRD, Japan, Rigaku). Zinc content in leaching solution and the precursor were analyzed by EDTA titration method. The analysis of other metal concentrations in leaching solutions was conducted by Inductively Coupled Plasma Atomic

Emission Spectrometer (ICP-AES, America, Varian). The surface morphology of as-prepared ZNRAs was observed by a field emission scanning electron microscope (FESEM, Zeiss Supra-55, operated at 10 kV). The ultraviolet and visible (UV-vis) absorption spectrum was measured by Doublebeam UV-vis spectrophotometer (Beijing Purkinje General Instrument Co., Ltd., TU-1901) using BaSO₄ as background and creating the baseline from 230 to 900 nm. X-ray Photoelectron Spectroscopy studies were performed using an AXIS ULTRA spectrometer with monochromatic Al K α (1486.6 eV) radiation.

3. Results and discussion

3.1 Oxidative ammoniacal leaching of the mixed sulfide-oxide lead and zinc ore

The phases of the mixed sulfide-oxide lead and zinc ore in this study are mainly sphalerite, smithsonite, galena, pyrite, calcite and silica. The main chemical reactions taken place in the leaching process are given in Eqs.1-4.

The investigation of the effects of various factors on zinc extraction showed that the optimal conditions were as follows: stirring speed of 900 rpm, NH₃ concentration of 2.0 mol/L, (NH₄)₂SO₄ concentration of 0.25 mol/L, (NH₄)₂S₂O₈ concentration of 1.5 mol/L, leaching temperature 60 °C and leaching time 240 min. Under the conditions, the extraction of zinc can be as high as 93.2%.

The main metal content in the leaching solution and the chemical phase analysis of the leaching residue were shown in Table 2 and Fig. 1, respectively.

Table 2

According to the XRD patterns of mixed ore and leaching residue given in Fig.1, galena was oxidized to lead dioxide completely, pyrite seemed not be attacked and the gangues including calcium carbonate and silica remained insoluble in the residue, which is coincide with the result from Table 2 that only extremely small amounts of iron and lead entered into the solution after leaching mixed ore. Therefore, the ammoniacal leaching method for mixed ore using ammonium persulfate as oxidant proves to be efficient and selective. Moreover, it has a strong operability because it proceed under mild conditions (atmospheric pressure and relatively low temperature) while previous studies on ammoniacal leaching of sulfides almost need high pressure and/or high temperature [32-34].

It can be concluded that the leaching solution contains nearly no impurity elements, which is significant to eliminate the following purification process and simplify the product preparation process.

3.2 Preparation of ZNRAs by the two-step process including precipitation and hydrothermal synthesis

3.2.1 Precipitation of hexahydrated ammonium zinc sulphate ((NH₄)₂Zn(SO₄)₂•6H₂O) from the leaching solution

The white solid substance was precipitated easily by dropping H₂SO₄ (4 mol/L) into the leaching solution. The XRD pattern was shown in Fig. 3.

Fig. 3.

It indicates that the precipitate is hexahydrated ammonium zinc sulphate ((NH₄)₂Zn(SO₄)₂•6H₂O) and no other phases involved in it. The precipitation reaction is presented as Eq.5.

Based on the zinc contents in the solution before and after precipitating operation, it can be calculated that 99.2% of zinc in leach liquor transformed into (NH₄)₂Zn(SO₄)₂•6H₂O. That is to say, a high zinc extraction 92.4% from mixed sulfide-oxide lead and zinc ore to the precipitate hexahydrated ammonium zinc sulphate can be achieved.

3.2.2 Preparation and characterization of ZNRAs on FTO substrate

The precursor solution was obtained rapidly through dissolving the precipitate ((NH₄)₂Zn(SO₄)₂•6H₂O) into the deionized water then adding ammonia (25~28%) into the solution. Subsequently, ZNRAs were synthesized via a hydrothermal treatment at 95 °C for 4 h. The ZnO formation involved the following dissolution and chemical reactions:

The crystallinity of the grown ZNRAs on FTO substrate was investigated and shown in Fig. 4. In addition to the diffraction peaks of SnO₂ derived from the FTO substrate, all other peaks match the wurtzite ZnO structure for the lattice parameters $a = 0.324$ nm and $c = 0.519$ nm (JCPDS 01-075-0576). The substantially higher intensity of the (002) diffraction peak indicates that the ZNRAs are oriented perfectly with their c axes perpendicular to the FTO substrate.

Fig. 4.

The SEM analysis indicated that the ZNRAs could be obtained when the pH value of the precursor solution was 9.2 as well as 10.0 while it did not grow with the pH value of 11.0. Fig. 5 gave the SEM images of the as-prepared ZNRAs prepared in the condition of pH value of 9.2 and the statistical distribution of the diameter. It can be seen that ZnO nanorods were hexagonal structure and grew vertically, uniformly on the substrate, which corresponded well to the result of XRD analysis. The growth density and the average diameter of ZnO nanorods were calculated to be 4.11×10^9 rods/cm² and 142 nm, respectively. The statistical data indicated that the diameter of nanorods distributed in a narrow range.

Fig. 5.

The room temperature UV–vis absorption spectrum of the synthesized ZNRAs was presented as Fig. 6. Fig. 6 (a) indicated that there was a large absorbancy of nano-ZnO structure when the wavelength was less than 400 nm while the absorbance gradually decreased and tend to be stable as the wavelength increased in the range of more than 400 nm. Fig. 6 (b) exhibited the relationship between $(ah\nu)^2$ and $h\nu$, which was drawn on the basis of the well-known Tauc relation presented by Eq.9 [35].

$$ah\nu = C(h\nu - E_g)^{1/2} \quad (9)$$

where a is the absorption coefficient of the ZnO at a certain value of wavelength, h is Planck's constant, ν is the frequency of light, C is the proportionality constant, E_g is the band gap energy and $n=1/2$ since ZnO is considered as a direct band gap semiconductor. The value obtained for the band gap energy of 3.03 eV reduces noticeably when compared with the bulk ZnO (3.37 eV) [36]. This

may indicate that the obtained ZNRAs might be efficient in photocatalysis application.

Fig. 6.

In order to understand the element composition and chemical bonding state, the as-synthesized ZNRAs was also characterized by X-ray photoelectron spectroscopy and the corresponding spectra were given in Fig. 7. The peak positions were referenced to carbon at 284.6 eV. Fig. 7 (a) showed the wide scan spectrum of the sample, where peaks of Zn, O and C could be identified obviously, and remarkably, no other elements existed especially Fe and Pb. The doublet spectral lines of Zn2p remarked in Fig. 7 (b) were observed at the binding energy of 1021.2 eV (Zn2p_{3/2}) and 1044.3 eV (Zn2p_{1/2}), which are very close to the standard bulk ZnO binding energy values [37]. The narrow scan spectra for Fe and Pb were also further analyzed. The result displayed no peaks of them were detected, which demonstrated that the as-synthesized ZNRAs did not contain any other metal impurities.

Generally, the presence of C was attributed to the atmospheric contamination and ambient exposure of the sample. Nevertheless, it is possible that carbon in solution was also entered into the ZnO nanostructure in the hydrothermal synthesis process. For the sake of ascertaining the source of carbon, the narrow scan spectra of O1s peaks after etching the sample for 0 s, 20 s and 80 s (etching rate: 0.05 nm/s) were analyzed and shown in Fig. 7 (c). In these three cases, the O1s core level all can be fit to yield two Gaussian curves, at binding energy 530.2 eV and 531.7 eV, respectively. The component at binding energy 530.2 eV was assigned to oxygen atom (O^{2-}) in the ZnO lattice that formed a strong bond in the manner Zn-O. The second peak at 531.7 eV corresponded to the C-O bond and the intensity decreased with the increasing etching time but did

not disappeared finally. This suggested that carbon doped into the ZnO nanorods during the hydrothermal growth process, which was probably the reason why the band gap energy of as-prepared ZNRAs decreased by 0.34 eV significantly. The carbon in the precursor solution may stem from the carbonate ion (CO_3^{2-}) because smithsonite in the mixed ore dissolved and formed zinc ion and carbonate ion in the leaching process.

Fig. 7.

Based on the above analysis, it can be concluded that large-scale ZNRAs with well orientation was rapidly obtained from the leaching solution. In the preparation process, none of other impurities particularly Fe, Pb entered into the ZnO nanorods except that a small quantity of carbon doped, leading to a reduced band gap energy.

4. Conclusions

Well-ordered ZNRAs was synthesized successfully on FTO substrate pre-coated with a layer of ZnO seeds from the mixed sulfide-oxide lead and zinc ore via the oxidative ammoniacal leaching process and a two-step process including precipitation and hydrothermal synthesis. In the oxidative ammoniacal leaching process, the optimal zinc extraction was as high as 93.2% and nearly no other metal elements entered into the leach liquor, thus the following purification process could be eliminated. The as-prepared ZNRAs was well-aligned, perpendicular to the FTO substrate and had a reduced band gap energy of 3.03 eV. After the leaching of mixed ore and precipitation of hexahydrated ammonium zinc sulphate, the total zinc recovery can reach 92.4%. The grown ZnO nanorods was doped by a small quantity of carbon and did not contain any other impurities particularly Fe and Pb, which confirmed that this approach to production of nano-ZnO was feasible

and had a high selectivity. The entire process was also simple and easy to operate due to the elimination of purification and the mild conditions for each step. The method this paper proposed was innovative and significant for effective utilization of mixed sulfide-oxide lead and zinc ore as well as large-scale production of nanostructured ZnO.

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Table captions

Table 1 The main chemical compositions of mixed sulfide-oxide lead and zinc ore.

Table 2 Main metal content in the leaching solution under the optimum leaching conditions.

Figure captions

Fig. 1. X-ray diffraction patterns of mixed sulfide-oxide zinc and lead ore and leaching residue.

Fig. 2. The flow chart of preparation of ZNRAs from mixed sulfide-oxide lead and zinc ore.

Fig. 3. X-ray diffraction pattern of the precipitate obtained from the leaching solution.

Fig. 4. X-ray diffraction pattern of the as-synthesized product on FTO substrate.

Fig. 5. (a), (b) Different magnification SEM images of the as-synthesized product on FTO substrate, (c) the statistical distribution of the diameter.

Fig. 6. (a) The room temperature UV–vis absorption spectrum of the as-synthesized ZNRAs, (b) Tauc plot of the as-prepared ZNRAs.

Fig. 7. XPS spectra of the as-synthesized ZNRAs: (a) wide scan survey, (b) core level spectrum for Zn2p region, (c) core level spectrum for Zn2p region after etching the sample for 0 s, 20 s and 80 s, respectively.

Table 1 The main chemical compositions of mixed sulfide-oxide lead and zinc ore.

Compositions	Zn	S	Pb	Fe	Si	Ca	Al	Mg
Content (wt%)	21.15	6.06	10.63	5.53	5.74	14.12	1.60	0.44

Table 2 Main metal content in the leaching solution under the optimum leaching conditions.

Element	Zn	Fe	Pb
Content (mg/L)	7392	0.157	0.067