



Hydrothermal treatment of electric arc furnace dust

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ABSTRACT

In this study, ZnO crystals were fabricated from electric arc furnace dust (EAFD) after alkaline leaching, purification and hydrothermal treatment. The effects of temperature, duration, pH, and solid/liquid ratio on ZnO crystal morphology and size were investigated. Results show a high reaction temperature capable of accelerating the dissolution of ZnO precursor, expediting the growth of 1D ZnO, and increasing the L/D ratio in the temperature range of 100–200 °C. ZnO crystals with high purity can also be obtained, using the one-step hydrothermal treatment with a baffle that depends on the different solubility of zincite and franklinite in the hydrothermal conditions.

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1. Introduction

The treatment and recovery of electric arc furnace dust (EAFD) has been intensively studied, triggering the development of many recycling and recovery processes during the past decades [1–5]. Most of the pyrometallurgical processes focus on the recovery of zinc oxide and direct-reduced iron, using the carbon-thermal reduction process. Hydrometallurgical methods, notably EZINEX and ZINCEX, have also been developed to reclaim heavy metals such as zinc; many of these methods, however, fail to be commercialized [6–15].

In Taiwan, the supply of metal zinc and zinc oxide has relied exclusively on import. This problem of overreliance on imported zinc can be mitigated if the zinc in EAFDs can be effectively recycled. However, due to the absence of zinc resources, it is unlikely for Taiwan to establish a zinc refinery such as IPS to mass-produce metal zinc at low cost. Small-scale zinc hydrometallurgical process is thus a more feasible solution for the treatment and refinement of zinc in a smaller amount. In general, the hydrometallurgical process incorporates leaching, purification and electrolysis.

As varistors and additives in ceramics, glass, pigments and paints, zinc oxide boasts extensive industrial applications, particularly in the form of 1D ZnO nanorods that hold a promising key to the world of nanotechnology. With wide band gap (3.37 eV), large excitonic binding energy (60 meV) and high breakdown strength, ZnO nanorods possess several advantages for applications

in electronic and photonic devices. Hydrothermal synthesis of ZnO nanorods and its mechanism have accordingly attracted substantial research interests [16–23].

Therefore, one of the major purposes of this study is to fabricate 1D ZnO from EAFD. Alkaline leaching was performed to recover zinc, and after the separation of impurities, the produced precipitate was used to synthesize 1D ZnO nanorods with hydrothermal treatment. To achieve crystallization of 1D ZnO from the precursor, the effects of temperature, pH, S/L ratio, and duration on the ZnO crystal morphology and size were investigated.

For understanding one of the mechanisms of hydrothermal reaction, i.e. the dissolving–precipitating behavior of EAFD in the hydrothermal environment, direct hydrothermal treatment of EAFD without previous separation and purification was further conducted. A novel hydrothermal device for a one-step process of separating, purifying, and synthesizing ZnO from EAFD was developed as shown in Fig. 1. This apparatus is similar to the hydrothermal equipment for single crystal growth of quartz and ZnO, in which a baffle is used to separate the dissolving and crystallizing zones.

2. Materials and methods

The EAFD used in this study was sampled from a steel company in Taiwan with its chemical composition incorporating approximately 18.6% Fe, 33.48% Zn, 3.78% Pb, 1.33% Mn, and 0.071% Cd in the form of oxides, and 3.71% Ca, 1.79% Na and 1.11% Mg in the form of chlorides, and other impurities (Table 1). Franklinite (zinc ferrite) and zincite (ZnO) are the two major Zn-rich phases in EAFD.

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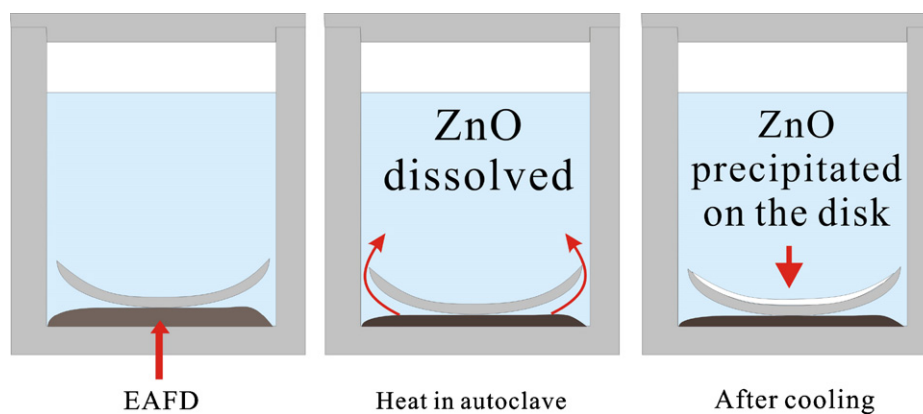


Fig. 1. Sketch for the hydrothermal equipment for one step synthesis of ZnO from EAFD.

EAFD was first washed with distilled water to separate the soluble chlorides which could cause unpredictable troubles and complexities in reactions during the unit operation of the purification and hydrothermal processes. Once washed, two major processes were conducted.

In the first major process to grow ZnO crystal of a specific morphology, the EAFD was treated with 5 M NaOH solution (S:L = 1:10) at 70 °C for 2 h to leach the Zn, Si, Pb, and other elements soluble in alkaline solution. The leaching solution with a pH exceeding 14 was adjusted to pH = 12.5 with 2 N HCl solution to generate precipitates of ZnO, including impurities of Si and Pb.

The precipitates were dissolved again in HCl solution at pH = 4, and metal zinc powder was added to precipitate Pb. To further purify the zinc solution, $\text{Ca}(\text{OH})_2$ was then added till pH of the solution reached 5 for reacting with Si to form CaSiO_3 precipitates, or 0.5 g activated carbon was added to absorb the residual Si. The precipitates with Si and Pb impurities were filtered and separated.

After each step of purifying Pb and Si, the solutions were adjusted to pH = 12.5 with 2 M NaOH solution to obtain precipitates for XRD analysis, so the effects of purification can be quickly examined.

The final purified solution was then adjusted to pH = 12.5 with 2 M NaOH solution. The precipitate was separated and dried in an electric oven at 80 °C, and the dried powder was preserved for use as the ZnO precursor for the hydrothermal process in order to grow 1D ZnO. The experimental parameters are summarized as follows: pH 10 or 12, temperature 100–200 °C, duration 12 h, and solid/liquid ratio 0.2 g:30 ml.

In the second major process, the washed EAFD was directly treated with hydrothermal process. A steel autoclave with Teflon lining under autogenously pressure was used to facilitate the hydrothermal reaction. A baffle was used in this process. 0.5 M ammonium carbonate was used as mineralizer. The hydrothermal temperature and duration are respectively 150 °C and 24 h.

Subsequently, the final ZnO products were separated, dried, and then characterized by XRD (X-ray diffraction, Rigaku D/MAX-B) and SEM (HITACHI S4700). The chemical compositions were analyzed with ICP and EDX (Oxford INCA 7060).

3. Results and discussion

3.1. Purification and growth of 1D ZnO crystal from EAFD

The XRD of the washed EAFD (Fig. 2(a)) shows a large amount of zinc ferrite. The XRD of ZnO powders precipitated from the dilution of the first alkaline leaching solution indicates that the zinc ferrite was separated; and the main phase is zincite as shown in Fig. 2(b). The broadening diffraction peaks suggest a low crystallinity of zincite.

When the unpurified ZnO precipitates were treated with hydrothermal process without a baffle under the conditions of 200 °C, 6 h, and pH = 12, the diffraction peaks were narrowed down while the phases consisted of ZnO, Zn_2SiO_4 and PbZnSiO_4 as shown in Fig. 2(c). This result indicates that the existence of impurities like Pb and Si may lead to the emergence of secondary phases.

After the unpurified ZnO precipitates were dissolved in HCl solution, zinc powder was added into the raw leaching solution to reduce Pb^{2+} into metallic Pb precipitates and to avoid the formation of PbZnSiO_4 . As shown in Fig. 2(d), the diffraction peaks of PbZnSiO_4 were nowhere in sight in the sample's diffraction patterns, indicating that the Pb was separated.

To ensure the separation of Si, $\text{Ca}(\text{OH})_2$ and activated carbon were respectively added into the HCl solution of ZnO in the separation process so as to compare their efficiencies.

The Si was successfully removed from the precipitate after the pH was adjusted to 12.5 by adding CaCO_3 , as shown in the X-ray pattern of Fig. 2(e). However, the residual $\text{Ca}(\text{OH})_2$ appeared to transform into CaCO_3 in the hydrothermal process.

On the other hand, addition of activated carbon into the solution was observed to effectively remove Si without producing $\text{Ca}(\text{OH})_2$ residue. According to the result of chemical analysis, the purified HCl solution contains nearly all Zn (Table 1). After the solution was treated, more pure ZnO precipitates were obtained. The XRD pattern as shown in Fig. 2(f) indicates the disappearance of the CaCO_3 peaks.

The chemical composition of ZnO hydrothermal product after the purification was analyzed with ICP, and the result shows that about 99 wt% of the ZnO content can be obtained (Table 1).

Table 1
Chemical composition of samples.

	Fe	Zn	Pb	Mn	Cd	Ca	Na	Mg	Si
EAFD	18.6%	33.48%	3.78%	1.33%	0.071%	3.71%	1.79%	1.11%	1.2%
Solution ^a	<10 ppb	3794 ppm	653 ppb	<5 ppb	<0.5 ppb	321 ppb	687 ppm	<50 ppb	426 ppb
ZnO crystal	0.02%	80.18%	0.02%	0.05%	0.001%	0.05%	0.25%	0.01%	0.07%

^a Final purified leaching solution.

Table 2
Morphology of ZnO crystal fabricated with hydrothermal process under various conditions (0.2 g:30 ml, duration = 12 h).

S:L ratio (g:ml)	Duration (h)	pH	Temp. (°C)	Crystal morphology	Crystal aggregate	Length and diameter	L/D ratio
0.1:30	6	10	200	Rod	Radiating	L: 5 μm, D: 1 μm	5
		12		Granular	Radiating	D: 50 nm	~1
		13		Rod	Radiating	L: 1.5 μm, D: 300 nm	5
	12	10	Rod	Radiating	L: 12 μm, D: 1 μm	12	
		12	Rod	Radiating	L: 900 nm, D: 300 nm	3	
0.2:30	12	10	100	Granular	Dispersive	~50nm	~1
			150	Rod	Dispersive	L: 600 nm, D: 80 nm	7.5
			200	Rod	Dispersive	L: 1 μm, D: 50 nm	20
		12	100	Rod	Dispersive	L: 400 nm, D: 80 nm	5
			150	Rod	Dispersive	L: 800 nm, D: 90 nm	9
			200	Rod	Dispersive	L: 900 nm, D: 40 nm	22.5

The purified precursor went through the hydrothermal processes under various parameters, including temperature and pH. The morphology of the fabricated ZnO crystals is shown in Table 2.

With the S/L set at 0.1 g/30 ml, the ZnO crystals fabricated from the hydrothermal process appeared in the form of radiating aggregates. This aggregation may cause difficulty of dispersion and cripple the crystals for further industry use. However, with S/L = 0.2 g/30 ml, the fabricated substance emerged to be dispersive.

The results indicate that different duration of hydrothermal treatment can affect the length/diameter (L/D) ratio of ZnO crystals. The L/D ratio of 6 h duration range from 1 to 5, and that of 12 h

reads 3–12. It is therefore obvious that a longer duration leads to a higher L/D ratio of the fabricated ZnO crystals. Further experiments were then performed with the S/L set at 0.2 g/30 ml and the duration 12 h.

Fig. 3 presents the SEM photos of the hydrothermal product obtained under the conditions of S/L = 0.2 g/30 ml, pH = 10 and 12, and duration = 12 h, and it also presents reaction temperature ranging from 100 to 200 °C at an interval of 50 °C.

By comparing the three pairs of samples a and b, c and d, and e and f at the reaction temperatures of 100, 150, and 200 °C respectively, the effect of temperature on the growth of 1D ZnO crystal can be observed. The production, the size in length, and the length/diameter ratio (L/D) of 1D ZnO basically grow with the rising reaction temperature. The L/D ratio is about 1–5 at 100 °C, 7.5–9 at 150 °C, and more than 20 at 200 °C (Table 1). Higher temperatures tend to accelerate the dissolution of ZnO precursor in platelet form and speed up the diffusion rate of Zn²⁺ and/or Zn(OH)₂ molecules, thereby increasing the growth of 1D ZnO.

Examining the effect of pH on the growth of 1D ZnO, the study finds that the hydrothermal solution with pH = 12 is capable of promoting the 1D ZnO's growth, especially in the radial direction. A higher pH increases the concentration of Zn(OH)₂, leading to the enhanced growth in the radial direction. Also to be noted is that the ZnO rod reports a higher L/D ratio at a lower pH as shown in Fig. 3(b), (d) and (f).

As summarized in Table 3, the cost of this procedure of hydrothermally growing 1D ZnO crystal with the precursor from the purified leaching solution of EAFD is estimated to be approximately US\$1213 per metric ton which is much lower than the price of pure ZnO nano crystals.

3.2. Direct hydrothermal treatment of EAFD

To obtain a better understanding of the ZnO crystal growth mechanism in the hydrothermal reaction, direct hydrothermal treatment of EAFD without purification was performed, and the products were observed by SEM with the results shown in Fig. 4.

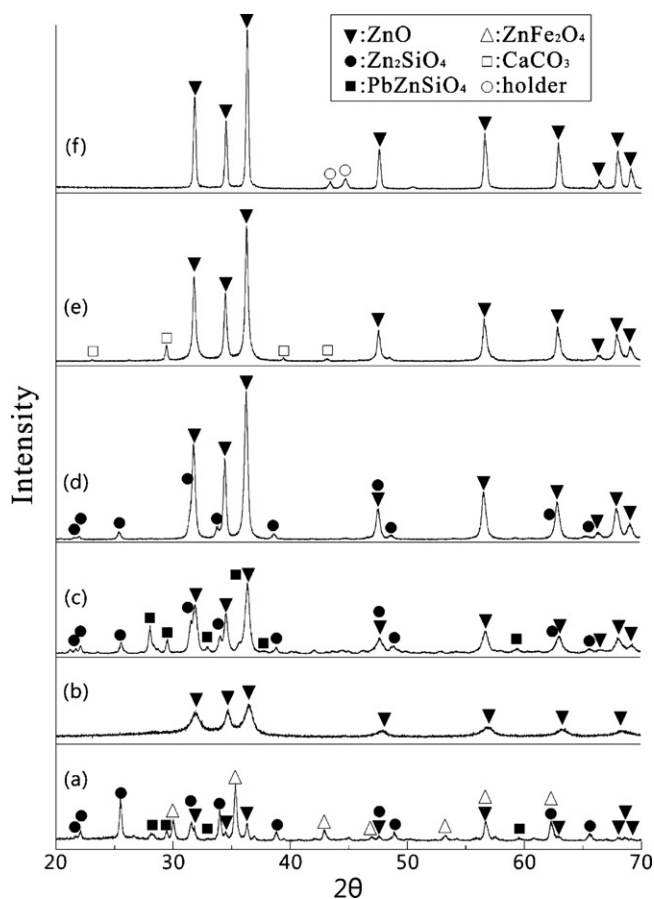


Fig. 2. The X-ray diffraction patterns of the samples after different purification processes: (a) washed EAFD, (b) precipitates from the first alkali leaching solution without purification, (c) hydrothermal treatment of the precipitates from alkali leaching solution without baffle, (d) hydrothermal treatment, adding Zn powder to separate Pb, (e) hydrothermal treatment, adding Zn powder and Ca(OH)₂ to separate Pb and Si respectively, and (f) hydrothermal treatment, adding Zn powder and active carbon to separate Pb and Si respectively.

Table 3
Cost estimation of the procedure of this study (US dollar/metric ton).

Variable costs	
Chemical materials (NaOH, HCl, zinc powder, and activated carbon)	200
Utility	35
Others (packaging, transportation, waste and water processing)	70
Energy costs	45
Fixed costs (depreciation, labor, maintenance, insurance, taxes, and service)	830
Sales and management expenses	33
Total	1213

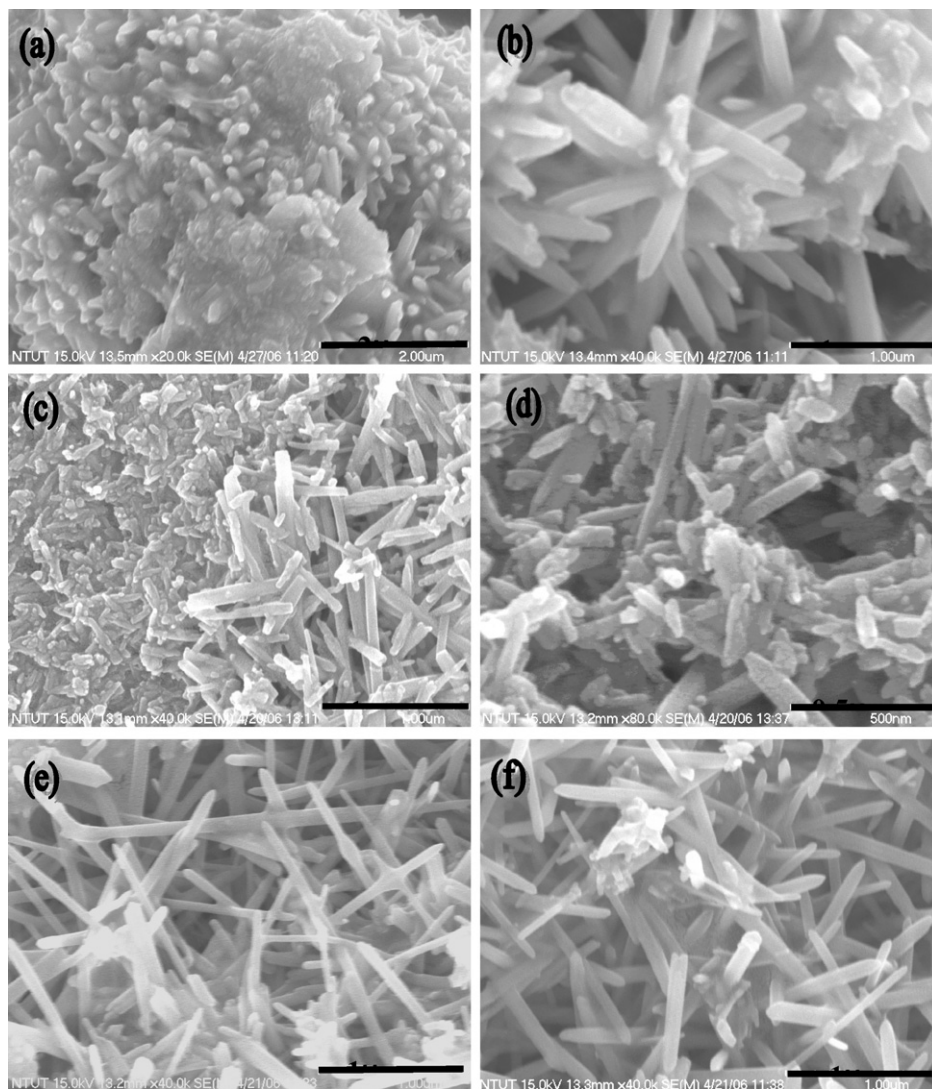


Fig. 3. SEM photos of the products from the hydrothermal treatment of purified precursor under the conditions of $S/L=0.2\text{ g}/30\text{ ml}$ and 12 h at (a) $100^\circ\text{C}/\text{pH}=10$, (b) $100^\circ\text{C}/\text{pH}=12$, (c) $150^\circ\text{C}/\text{pH}=10$, (d) $150^\circ\text{C}/\text{pH}=12$, (e) $200^\circ\text{C}/\text{pH}=10$, and (f) $200^\circ\text{C}/\text{pH}=12$.

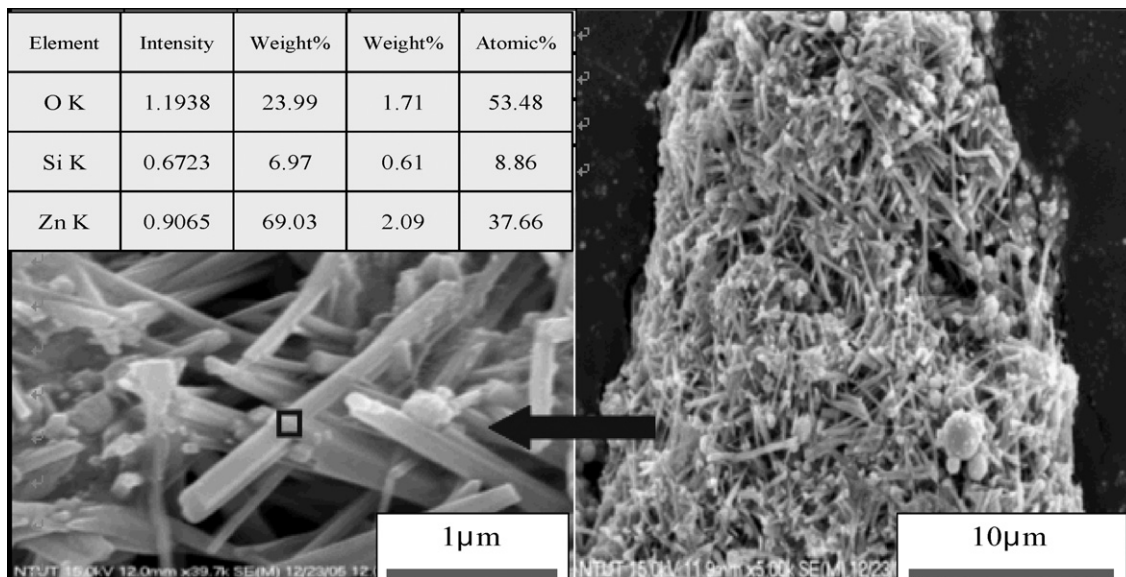


Fig. 4. SEM photos of the products from direct hydrothermal treatment of EAFD without purification under the condition of $200^\circ\text{C}/48\text{ h}$, $\text{pH}=10$.

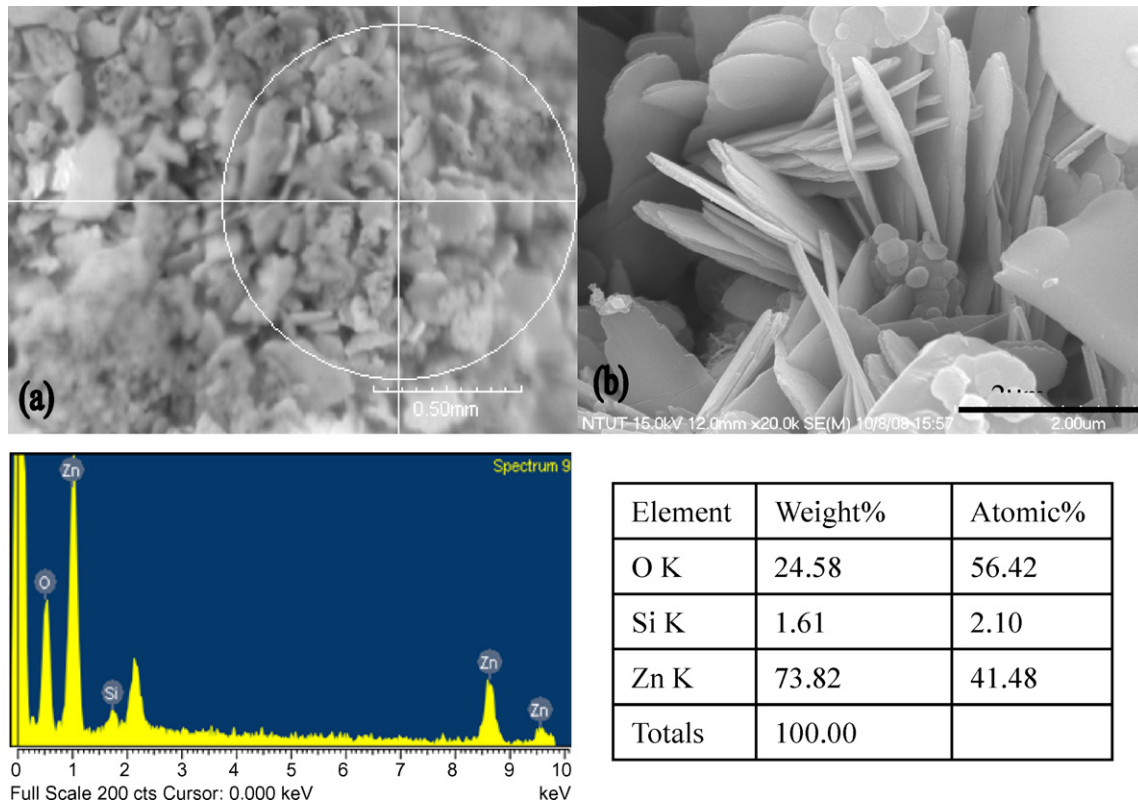


Fig. 5. Optical (a) and SEM (b) photos of the products from direct hydrothermal treatment of EAFD without purification under the condition of 150 °C, pH=8.7, and with a baffle. (c) and (d) show the EDX analytical results of SEM (b).

The recrystallized ZnO rod was observed while the round particles of zinc ferrite remained unchanged. The result suggests that the mechanism of ZnO crystal growth is mainly based on dissolution–precipitation, and the zinc ferrite shows no reaction in the hydrothermal temperature range of 100–200 °C.

In response to this observation, the study designed an auto-clave shown in Fig. 1, in which a baffle was set up to collect the precipitates of recrystallized ZnO. During the heating stage of the hydrothermal process, the ZnO was dissolved into the solution; however, the zinc ferrite stayed below the baffle at the bottom of the Teflon jar. After cooling, the ZnO was precipitated and fall on the baffle.

The ZnO crystals are shown in Fig. 5, and the platelet ZnO could be observed under SEM. The chemical analysis with EDX shows that only impurity of Si could be found. The ZnO with a purity higher than 98% can be directly obtained from EAFD, using this one step hydrothermal process with a baffle.

4. Summary

The experimental results indicate that ZnO nanorods with a length/diameter larger than 22 and a high purity of 99% can be obtained by the multiple-step processes of alkaline leaching, purification, and hydrothermal synthesis. A high reaction temperature helps expedite the dissolution of ZnO precursor, accelerate the growth of 1D ZnO, and raise the L/D ratio in the temperature range of 100–200 °C.

Moreover, ZnO crystals with 98% purity can also be obtained using the one-step hydrothermal treatment and a baffle depending on the different solubility of zincite and franklinite in the hydrothermal conditions.

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