

Removal of Heavy Metals (Lead, Cadmium and Iron) from Low-Grade Nanoscale Zinc Oxide using Ammonium Carbonate Solution as a Leaching Agent

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Abstract. This study investigated purification and refining methods for producing a nanometer size zinc oxide (ZnO) from low-grade ZnO commercial powder using low cost ammonium carbonate solution as a leaching agent. The atomic absorption spectroscopy results show that the concentration of lead, cadmium and iron can be significantly reduced by ammonium carbonate leaching and washing. X-ray diffraction and scanning electron microscope results show that structural properties can improve the degree of the preferential c-axis orientation, grain size, and surface morphology of ZnO by solvent evaporation. All physical and chemical results are of particular significance for the preparation of purified ZnO for device fabrication in photovoltaic industry, functional ZnO coatings, and polymer nanocomposite applications.

Introduction

Today zinc oxide is highly demanded and an active material as key ingredient in several mineral sunscreens, vitamin supplements, diaper rash creams and acne treatments sold in drug stores [1]. Heavy metal impurities such as cadmium, lead and iron in the commercial ZnO can be considered a problem when used in medicines and other pharmaceutical products. Technologies such as the hydrothermal (HT), pressurized melt growth and gas or vapor transport are traditionally used for high quality zinc oxide production [2]. The most viable method used in industry to produce crystalline bulk ZnO is HT technique, which is scalable and produces high quality material but it has some possible disadvantages such as the high energy consumption and possible contaminations from the milling media. Other production techniques for crystalline bulk material include vapour phase which can produce high quality and has low impurity concentrations, however it is costly and not simply ascendable [3]. Thus, it is not appropriate for high volume production.

The leach-solvent p-extraction process route is a latest economical method used for the removal of heavy metal impurities from commercial low-grade ZnO [4]. Low grade ZnO can also be treated with conventional acidic heap leaching process [5] but ammonia and alkaline leaching is the selective system for purification of ZnO because of significant operating cost and environmental concern [6].

In this work, the effect of temperature on the leaching of ZnO from low grade commercial zinc oxide in the ammonium carbonate solution system was studied. The aim of this work was to develop a simple process, which intends to provide economical method to purify ZnO from low-grade commercial zinc oxide.

Experimental Details

Chemicals. Low grade commercial ZnO (PARS ROOY, Iran) and ammonium carbonate (BDH Laboratory supplies) were used as received without further purification.

Refining of Low Grade Commercial ZnO. Firstly, the raw ZnO was heat-treated at 600° C for two hours in a muffle furnace at an atmospheric pressure in the presence of air. Resulted sample was then cooled in ambient conditions to 200° C, then to 25° C in a desiccator. Secondly, the treated ZnO was leached in an aqueous ammonium carbonate solution. The leaching solution was prepared by mixing with 30 g (2M) ammonium carbonate in 100 mL H₂O and heated gradually under vigorous stirring. 15 g of treated ZnO was added in the 50 ml of ammonium carbonate solution and stirring was allowed for one hour with occasional addition of gaseous ammonia to control the pH between 10 and 11 at temperature of 50° C. The purified ZnO was separated by centrifugation for 5 minutes and resulting residue was washed with de-ionized H₂O for 3 times. Finally, Separated ZnO was dried at 100°C for one hour in oven to evaporate water and remove residuals. This is shown in Fig. 1.



Fig. 1. Schematic illustration of refining process for low grade commercial ZnO.

Characterization. The microstructural investigation was carried out by scanning electron microscopy (SEM, Hitachi S4700) with energy-dispersive X-ray spectroscopy (EDS), Crystallinity of the ZnO was examined by X-ray diffraction (XRD, Rigaku) with Cu-K α . An AAS Hitachi atomic absorption spectrophotometer model Z-8000, equipped with a graphite furnace (HGA-400) and an auto-sampler plus high intensity deuterium lamp for background correction was used. The electro- thermal parameters and thermal program are listed in Table 1.

Results and Discussion

Detailed structural Analysis. Fig. 2 indicates the surface images of SEM analysis for un-treated and treated ZnO powder samples. The SEM images show an improved morphology of the ZnO powder after leaching by an ammonium carbonate solution. Fig. 2a and 2a-1 shows the large grains with several voids of the structures surrounded by small grains in un-treated form. On the other hand, the leached sample is found to exhibit good uniformity and well-defined crystal faces with an average size of approximately 200 ~ 300 nm as shown in Fig. 2b and 2b-1. It can be seen that this leaching process has not only improved crystal quality of the ZnO powder but also there is no effect on the ZnO phase. The elemental composition of both un-treated and treated ZnO powder samples are observed by EDS as shown in Fig. 2a-2 & b-2. The resulted EDS spectrum confirmed the presence of zinc oxide (ZnO) powder and mostly strong energy peaks are associated for zinc (Zn) atoms and weak energy peak of oxygen (O) atom. In addition, the mass percentage of zinc and oxygen values is tabulated along with impurities present in both samples in the Table 2.

The crystallinity and purity of un-treated and treated ZnO powders were further characterized by XRD analysis and shown in Fig. 3. Both samples exhibited the highly crystalline and stable well indexed hexagonal wurtzite ZnO (JCPDS card No. 36-1451) phase [7, 8]. However, it was observed

that without treatment of the raw commercial ZnO powders, the additional impurity peaks of Pb, Cd and Fe, Fig. 3a, were seen while ZnO powders treated in ammonium carbonate solution, Fig. 3b, display a sharp and intense peak indicating a fine crystalline wurtzite structure without any impurities. Generally, leaching of low quality ZnO in Ammonium an ammonium solution system follows the kinetic law of shirking-core model and concentration of leaching agent causing the removal of impurities from ZnO [9].

Table 1. Measurement conditions for atomic absorption spectroscopy (AAS).

Conditions	Pb	Cd	Fe
Lamp current [mA]	7.5	7.5	10
Wave length [nm]	283.3	228.8	240.3
Slit width [nm]	1.3	1.3	0.2
Cuvette	Tube	Tube	-
Atomizer	-	-	STD burner
Carrier gas argon [ml/min]	200	200	-
Sample volume [μ L]	20	20	-
Burner height [mm]	-	-	7.5
Acetylene pressure [kg/cm^2]	-	-	0.3

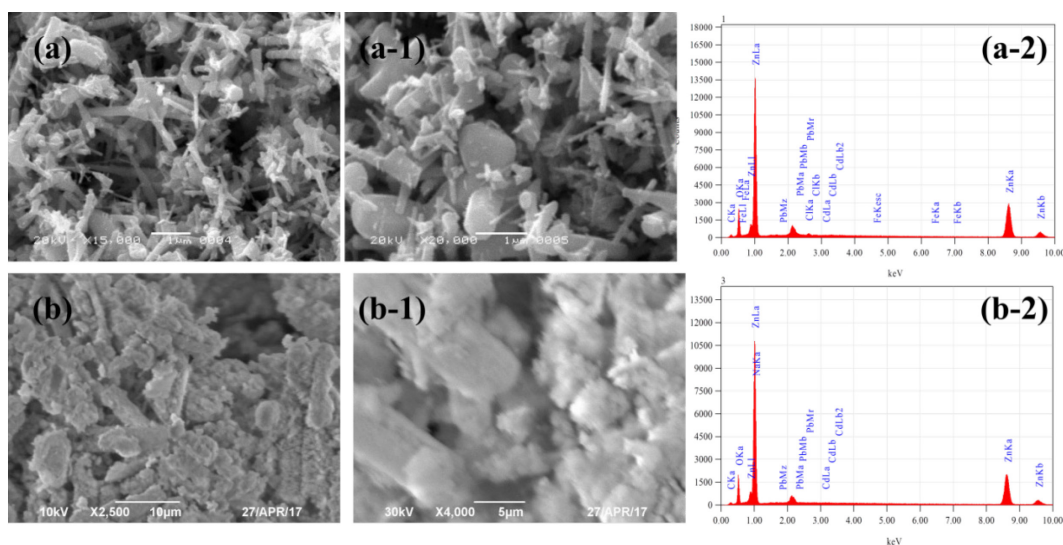


Fig. 2. SEM images and EDS analysis of Un-treated ZnO (a), (a-1), (a-2) and treated ZnO (b), (b-1), (b-2).

Table 2. Chemical composition of un-treated and treated ZnO observed by EDS Analysis.

Elements	C	O	Cl	Zn	Pb	Cd	Fe	Total
Un-treated ZnO (wt.%)	5.24	17.66	4.34	71.74	0.64	0.15	0.22	100
Treated ZnO (wt.%)	4.99	21.08	0.80	72.86	0.14	0.09	0.02	100

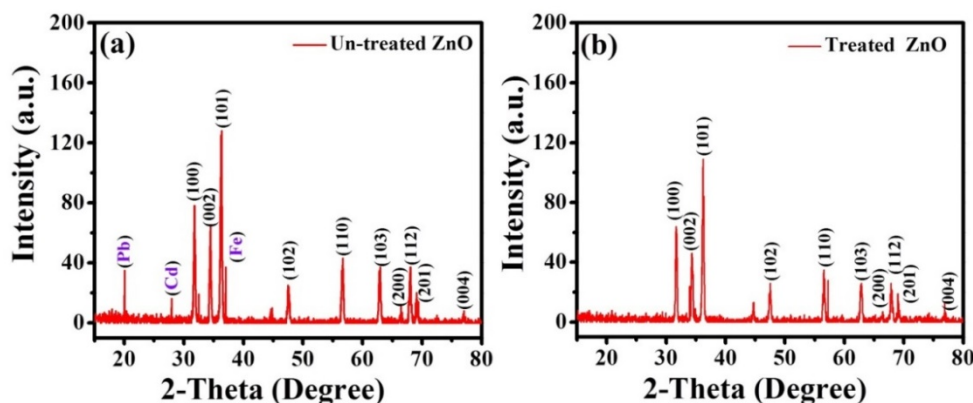


Fig. 3. XRD patterns of an un-treated (a) and (b) treated ZnO powders.

Elemental Analysis by FAAS. For further confirmation of leaching effect, un-treated and treated ZnO samples were investigated by flammable atomic absorption spectroscopy (FAAS) for three elements (Fe, Cd & Pb). The results indicate that treated ZnO powder contains lower concentrations of impurities (Fe: 129 mg kg^{-1} , Cd: 19.7 mg kg^{-1} and Pb: 141 mg kg^{-1}) than that of untreated ZnO powder (Fe: 515 mg kg^{-1} , Cd: 308 mg kg^{-1} and Pb: 1449 mg kg^{-1}), shown in Table 3. Interestingly, the reduction in Pb ion concentration was observed as 1308 mg kg^{-1} which is higher than that of Fe and Cd i.e. 288.3 mg kg^{-1} and 386 mg kg^{-1} , respectively. The differences in values suggest that the ammonium carbonate solution is adsorbent for the Pb-adsorption because Pb ion is the harder Louise acid than other heavy metal ions [10].

Table 3. Chemical analysis of treated and un-treated ZnO based of FAAS analysis.

Elements	Pb	Cd	Fe
Un-treated ZnO [mg/kg]	1449	308	515
Treated ZnO [mg/kg]	141	19.7	129

Conclusions

The present research work examined the effect of ammonium carbonate solution on the removal of heavy metals from low grade commercial ZnO powder at laboratory scale. The absorbing capacity of ammonium carbonate solution was found up to 1308 mg.kg^{-1} for the removal of Pb in low grade commercial ZnO powder that was characterized by FAAS. The removal process was also noted to be effective for other heavy metals like Fe and Cd, which showed reduction capacity of 288.3 mg.kg^{-1} and 386 mg.kg^{-1} , respectively. In addition, removal of heavy metals was also confirmed by using SEM, XRD and EDS techniques. These results are promising and confirm the advantage of the approach adopted presently. Therefore, such ammonium carbonate solution can be a suitable material for leaching of the low grade commercial ZnO powder for removal of heavy metal ion since the method is simple, fast, effective and economically viable for large production of ZnO.

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