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A low-cost and large-scale synthesis of nano-zinc oxide from smithsonite

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ABSTRACT

Nano-zinc oxide was prepared through a series of complex chemical reactions from smithsonite ores and the sensitivity of products to alcohol was measured. The smithsonite ores were calcined and decomposed into ZnO at 400 °C, and then were leached by sodium hydroxide solution. The leaching solution was purified by adding sodium sulfide, and the amount ratio of lead removal agent to lead ions ($Na_2S·9H_2O$/Pb) was 4.37. The zinc ions were precipitated in the form of $Zn(OH)_{2(s)}$ by regulating the pH. Finally, the precipitate was calcined in muffle furnace at 500 °C and decomposed into nano-ZnO. The optimum operating temperature of sensitivity to alcohol was 160 °C, and the sensitivity of the products with polyethylene glycol (PEG) rose at lower temperature and attained higher maximum value than that of the product without PEG. Especially, the sensitivity of ZnO prepared with 3 wt.% PEG to alcohol could be about 35 at 160 °C.

Zinc oxide is an important direct band gap semiconductor with $E_g = 3.37$ eV at room temperature and large excitonic (electron–hole) binding energy of 60 meV, larger than the thermal energy at room temperature (26 meV) [1,2]. ZnO has been widely investigated in recent years due to its excellent light emitting properties in UV and visible, piezoelectric properties, chemical stability and biocompatibility. These properties make ZnO an interesting material with potential applications such as sensors, UV lasers, piezoelectric, luminescent phosphor, photonic crystals, and photovoltaics [3,4]. The properties of nano-metal oxide with different structures have been investigated, especially, the gas-sensing property, in many literatures [5–9]. Varied methods have been employed by researchers for synthesis of ZnO nanocrystals [10]. Thereinto, because of its simple operation, cheap source, short reaction time and low product cost, precipitation is a very promising process.

In this work, we developed a route of alkaline leaching–precipitation–calcination to prepare nano-zinc oxide from smithsonite ores. With this abundant source, large scale production could be realized. However, there are many noteworthy chemical reactions in each step, due to the complex components and phase structure of the ores. These transformations were investigated carefully to elaborate the basic principles in this route. Furthermore, we discussed the gas sensitivity of products to alcohol. All these works would be useful for the utilization of resource and the scale production of zinc oxide.

The XRD pattern of the ores (Fig. 1) shows that the major components are the zinc-bearing mineral smithsonite ($ZnCO_3$) and gangue, such as calcite ($CaCO_3$) and quartz (SiO_2). For this kind of zinc oxide ores, acid leaching will cause two serious problems: the large acid consumption and the complex components of leaching solution. As amphoteric compound, both $ZnCO_3$ and ZnO can dissolve in the alkaline solution, while many other metal elements deposit. So the alkaline solution has been considered as leaching agent to treat the zinc oxide ores [11,12].

Due to the low reaction activity of smithsonite ($ZnCO_3$) with sodium hydroxide in the solution, the ores were calcined and decomposed $ZnCO_3$ into ZnO. The thermogravimetry (TG) (Model Labsys Evo, SETARAM, France) of smithsonite ore was carried out, and the result was given in Fig. 2. It could be found that there were three main decrease stages in the TG curve with the increase of temperature. The first one is the volatilization of adsorbed water, while the second and the third one are the decomposition of $ZnCO_3$ and $CaCO_3$ in the ore, respectively. The $ZnCO_3$ decomposed into ZnO completely as Eq. (1) when the ores were calcined at ca. 400 °C [13].

$$ZnCO_3 = ZnO + CO_2\uparrow. \quad (1)$$

In the leaching process, with a higher reaction activity than $ZnCO_3$, the ZnO dissolves more easily in the alkaline solution as Eq. (2).

$$ZnO + 2OH^- + H_2O \rightarrow Zn(OH)_4^{2-}. \quad (2)$$

Meanwhile, most part of the Pb compounds would dissolve into the solution from ores. These lead ions could be quantitatively separated from zinc ions by adding sodium sulfide [14]. At 25 °C, the solubility products of zinc sulfide and lead sulfide are $Ksp_{ZnS} = 8.9 \times 10^{-22}$ and

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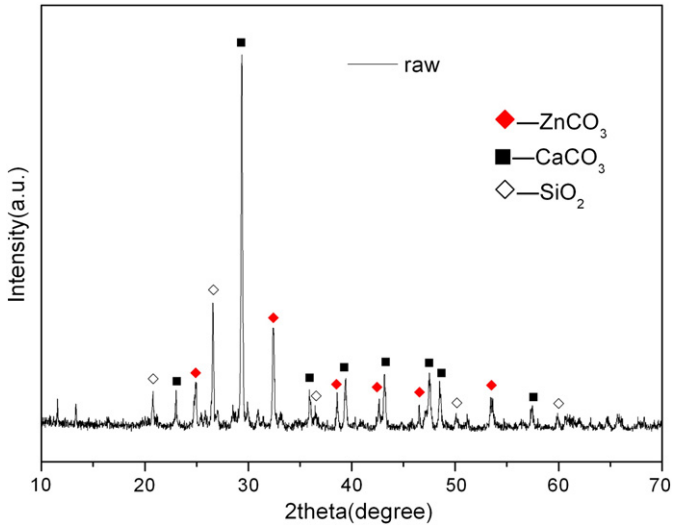

Fig. 1. The XRD pattern of the smithsonite ores.

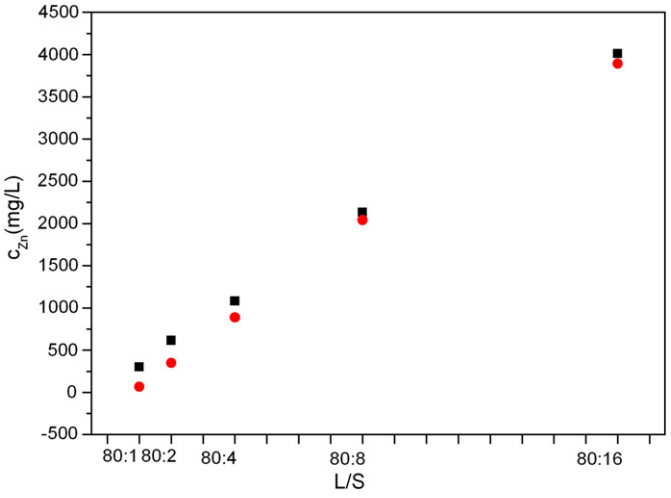

Fig. 4. The zinc ion contents before (■) and after (●) addition of sodium sulfide.

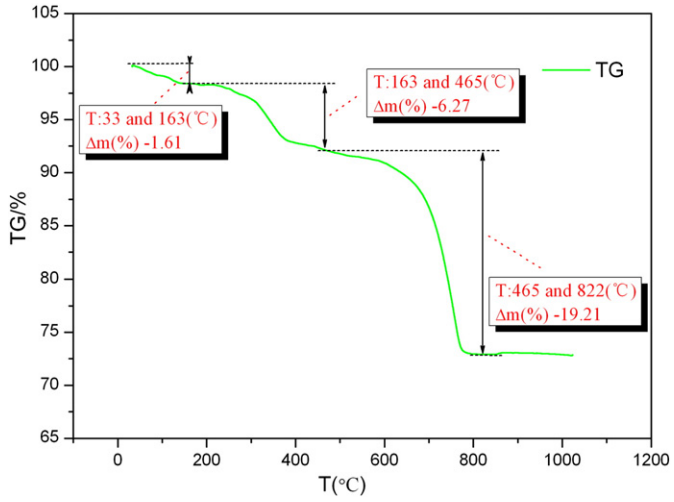

Fig. 2. The TG pattern of the smithsonite ores.

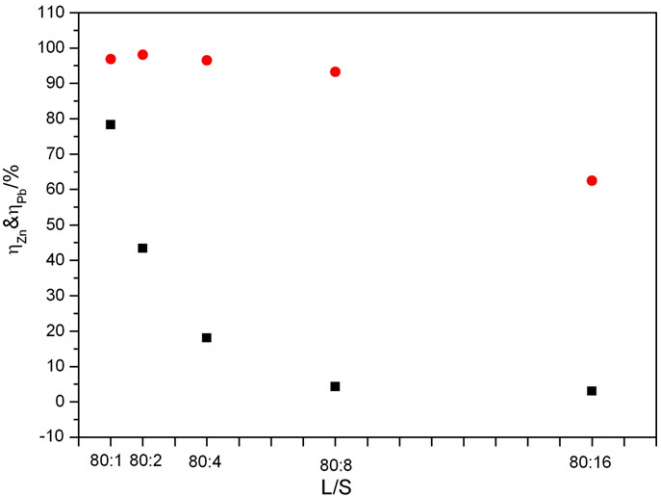

Fig. 5. The removal ratio of lead ions (●) and zinc ions (■).

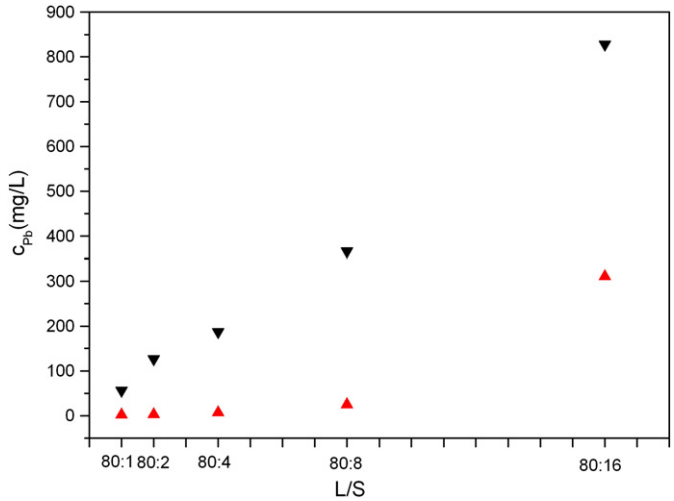

Fig. 3. The lead ion contents before (▼) and after (▲) addition of sodium sulfide.

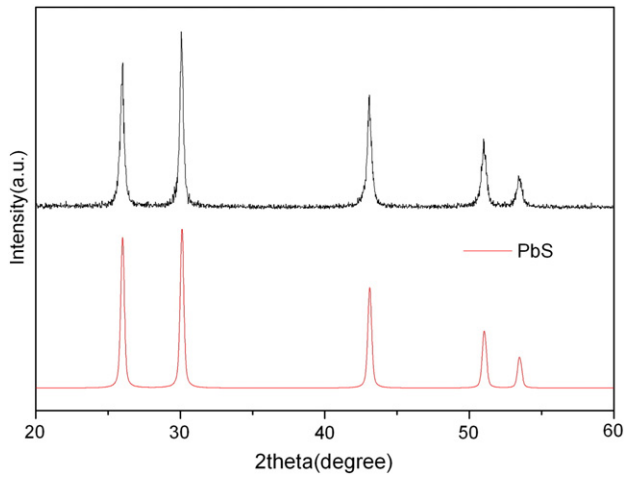

Fig. 6. The XRD pattern of the lead removal slag.