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A facile chemical route for recovery of high quality zinc oxide nanoparticles from spent alkaline batteries

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ABSTRACT

Recycling of spent domestic batteries has gained a great environmental significance. In the present research, we propose a new and simple technique for the recovery of high-purity zinc oxide nanoparticles from the electrode waste of spent alkaline Zn–MnO_2 batteries. The electrode material was collected by the manual dismantling and mixed with 5 M HCl for reaction with a phosphine oxide reagent Cyanex 923® at 250 °C for 30 min. The desired ZnO nanoparticles were restored from the Zn-Cyanex 923 complex through an ethanolic precipitation step. The recovered particle product with about 5 nm diameter exhibited fluorescent properties (emission peak at 400 nm) when excited by UV radiation (excitation energy of 300 nm). Thus, the proposed technique offered a simple and efficient route for recovering high purity ZnO nanoparticles from spent alkaline batteries.

1. Introduction

Recycling industry in the area of e-waste management has not been successful enough to catch a fancy of entrepreneurs because of low paybacks (Cucchiella et al., 2015). Nonetheless, the problem of e-waste generation has become unprecedentedly significant, especially in the developing countries (Breivik et al., 2014). In light of such significance, government agencies in many countries have been supporting the research focusing on the recovery of high-cost end products from waste materials (waste to wealth) to attract more investors in the recycling industry. Spent lithium ions and domestic alkaline batteries form a sizable fraction of e-waste (Barik et al., 2015; Sun et al., 2015; Wakolbinger et al., 2014). These wastes are generally recycled by pyrolysis to produce metal oxides or by leaching of metals to produce usable salts/complexes (Ebin et al., 2015; Calgaro et al., 2015). In some studies, the use of liquid-liquid extraction technique for the recovery of pure metals from spent batteries has been projected as an industrially applicable and economically feasible option (Salgado et al. 2003; Deep et al., 2011).

Approximately 85% of all batteries used commercially are alkaline batteries (dry cell batteries) (Smith et al., 2014). Some manufacturing factories are known to produce more than hundred million pieces of alkaline batteries annually (Ma et al., 2014). As such, a large production of alkaline batteries inevitably leads to a huge accumulation of their waste. To date, the extent of such problem is too large to be ignored (Ma et al., 2014). In some countries, collection systems have been established to manage spent batteries (Xara et al., 2015). However, a significant amount is still left to be discarded along with household wastes. Landfilling, incineration, and recycling are the three major management strategies for the waste alkaline batteries (Xara et al., 2015). Due to limited availability of landfills, the incineration and recycling are obviously the more feasible routes. The incineration based recycling technologies mainly process the waste powder fraction in a Waelz kiln to convert zinc into crude zinc oxide, that can be re-used in the metal industry. The by-product of vitreous slag can be used for construction purposes. Both the landfilling and incineration management routes of alkaline battery wastes however cannot mitigate the increasing concerns of terrestrial ecotoxicity and marine eutrophication (Xara et al., 2015). Therefore, the recycling is one of the meaningful options to resolve many problems associated with waste batteries.

With the growing attention on environmental preservation and the advancements in manufacturing technologies, Zn–Mn batteries that can avoid mercury as additive have been introduced in the market. This has somehow eased the recycling procedure to eliminate a treatment step for mercury (Ma et al., 2014). Hence, if recycling technologies are employed properly, around 20,000 tonnes of zinc and manganese are estimated be restored per year rather than landfilling or incineration (Gallegos et al., 2013). Thus, the

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recycling of spent alkaline batteries may offer definite economic and environmental benefits. Their technical feasibility may depend on many factors such as transport, recycling processes, type of restoring target, and the cost/marketability of the recovered product. The recovered products of zinc or manganese can be used again for various industrial applications (Gallegos et al., 2013).

Researchers have proposed different recycling approaches for the spent alkaline batteries based on pyrometallurgy and hydrometallurgy routes (Gallegos et al., 2013). The former requires much higher energy consumption than the latter. In the case of the former, the recovered zinc may occasionally contain undesirable impurities from other heavy metals. However, some pyrometallurgy techniques have been reported to offer high recovery of zinc to directly use as the feed of electrolytic plants for the production of zinc (Ippolito et al., 2016). Nonetheless, more efforts are desirable to improve the overall efficiency and economic/environmental feasibility of pyrometallurgy processes.

In hydrometallurgical processes, zinc is leached with sulfuric acid solutions as a common practice. It can provide high zinc recoveries (up to 95%), while manganese remains in the solid mass. These processes take advantage of the fact that manganese in the oxidation state IV would not easily be solublized in acidic media. Hydrometallurgical leaching of zinc with ammonium carbonate solutions is also reported (Nogueiraa and Margarido, 2015). This type of leaching process is applied to oxidized zinc materials via the application of ammonium carbonate/ammonia reagent. Zinc is recovered as a precipitated carbonate. The method is selective for zinc with respect to many other impurities, including manganese. Liquid–liquid extraction based hydrometallurgical routes are also beneficial to some industrial scale applications (e.g. Modified ZINCEX process) due to their favorable economics, efficiency, low energy consumption, high metal selectivity, and the least emission to cause air pollution (Salgado et al., 2003). These processes, while involving the use of commercial extractants (such as DEHPA and CYANEX 272), can be used to produce high quality zinc electrolyte solution which can be converted further into pure zinc metal or zinc salts.

As aforementioned, the recycling of metals from spent alkaline batteries needs to be made more attractive in an economical sense. The recovery of widely marketable nanomaterials (particularly ZnO) is a viable option in this regard. ZnO nanoparticles characterized with high exciton binding energy (60 meV) and wide bandgap (3.34 eV) have the advantages of nontoxicity and chemical stability. This product has an extensive market potential due to broad applicability such as the materials for room-temperature UV lasers, light-emitting diodes, sensors, solar cells, and biolabeling (Zhang et al, 2015).

Various chemical methods have been reported for the synthesis of ZnO particles into different sizes and morphologies. Some more important techniques include conventional solid-state process, hydrolysis, precipitation, hydrothermal methods, pyrolysis, and sol–gel (Davar et al., 2015). These methods can be employed to synthesize different sizes and morphologies of ZnO crystallites through the optimization of pH, temperature, reaction media, additives, and counter ions. Generally, pure precursors are required to synthesize nano-ZnO for most of the above-mentioned methods. Presence of other metals (for example, Mn) is hence essentially undesirable. In this research work, we have proposed the recovery of pure ZnO nanoparticles from the waste electrode material of spent alkaline batteries using a one-pot solvothermal process. The use of a selective extractant provided the separation of pure Zn product from Mn. This simplified procedure helped reduce processing steps, leading to the efficient production of nanosized ZnO.

2. Experimental

2.1. Materials

Spent Zn–MnO_2 batteries were collected after their complete exhaustion in domestic electronic appliances. Reagent Cyanex 923® was a product of Cytec Canada Inc. and received as a gift sample. This extractant was a 93% pure mixture of four trialkylphosphine oxides: $R_3P=O$, $R'R_2P=O$, $R'_2RP=O$, and $R'_3P=O$, where R and R′ represent n-octyl and n-hexyl hydrocarbon chains, respectively. All other reagents were laboratory grade chemicals from Merck/Loba.

2.2. Recovery process for ZnO nanoparticles

Several spent batteries were manually dismantled to obtain their electrode material. After acid digestion, the composition of the powder (estimated by atomic absorption spectroscopy, AAS) was found as follows: Zn- 3.1 ± 0.1 g/L (15 ± 0.2 wt%), Mn- 7.0 ± 0.1 g/L (35 ± 0.5 wt%), Fe- 50 ± 2 mg/L (<0.5 wt%), Ni- 4.0 ± 0.5 mg/L (<0.05 wt%), Cd- 3.0 ± 0.5 mg/L (<0.05 wt%), and Cu- 5.0 ± 1 mg/L (<0.05 wt%). The recovery of the ZnO nanoparticles from the electrode powder was optimized based on our preliminary studies on the effect of several parameters controlling the yield rate of the final product (ZnO). These parameters included the effect of solid/leaching solution (w/v) ratio, solid/extractant ratio (w/v), reaction temperature, and reaction time. After optimizing the experimental conditions for quantitative recovery of ZnO, the desired product could be quantitatively ($\geqslant$95%) recovered in following stepwise procedures: (i) 5 g of the powder sample was mixed with 20 mL of 5 M HCl in a Teflon beaker to form a slurry. The selection of 5 M concentration of HCl was based on an earlier work in which these conditions were reported for the quantitative leaching of Zn from batteries' waste electrode material (Deep et al., 2011) (ii) A 25 mL of 0.1 M Cyanex 923 in reagent (hexane) solution was added and the beaker was properly sealed. (iii) It was then placed in a furnace for heating at 250 °C for 30 min (without the requirement of controlling pressure conditions). (iv) The left-over organic phase was collected by centrifugation after the above reaction. (v) The dissolved ZnO-Cyanex 923 complex was precipitated by the addition of 70% methanol to yield ZnO nanoparticles. (vi) The product was repeatedly washed with methanol and then resuspended in dimethylformamide for further characterizations. These whole processes are summarized in the form of a flowchart (Fig. 1). For the assessment of purity and total yield of the recovered ZnO nanoparticles, a sample was digested in acid and then diluted for quantitation by AAS.

The residue left after the centrifugation removal of ZnO-Cyanex 923 complex was collected from the reaction mixture. The separated mass was neutralized with 5 M NaOH, washed with water, and treated in a furnace at 500 °C for 4 h.

2.3. Characterizations

The properties of the synthesized nanoparticles were characterized by UV–vis spectrophotometer (Varian, Cary 5000), Photoluminescence (PL) spectrophotometer (Cary, Varian), X-ray diffractometer (Bruker, D8 Advance), confocal laser scanning microscope (LSM, Zeiss), atomic force microscope (AFM, Park Systems, XE-NSOM), and TEM (Hitachi, 7500). The composition of the batteries' waste electrode sample and the yield/purity of the finally recovered ZnO product were analyzed with Atomic Absorption Spectrophotometer (AAS, Perkin-Elmer, AAnalyst 200).

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