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Recovery of Pure ZnO Nanoparticles from Spent Zn-MnO$_2$ Alkaline Batteries

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S Supporting Information

ABSTRACT: The recovery of pure ZnO (zinc oxide) nanoparticles from spent Zn—Mn dry alkaline batteries is reported. Spent batteries were dismantled to separate the contained valuable metals of the cell electrodes in the form of black powder. Treatment of this black powder with 5 mol L^{-1} HCl produced leach liquor, primarily containing 2.90 g L^{-1} Zn and 2.02 g L^{-1} Mn. Selective and quantitative liquid—liquid extraction of Zn(II) was then carried out in three counter current steps by using Cyanex 923 (0.10 mol L^{-1} in n-hexane). Zn(II) distributed in the organic phase as complex ZnCl$_2$·2R (R = Cyanex 923 molecule). The metal loaded organic phase was subjected to combust at 600 °C to yield pure ZnO nanoparticles (40—50 nm). Important characteristics of the synthesized nanoparticles were investigated by field emission scanning electron microscopy (FESEM), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction spectroscopy (XRD), and atomic force microscopy (AFM).
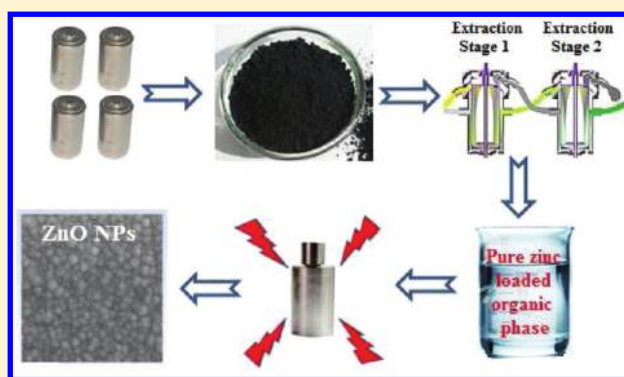
INTRODUCTION

Zinc—manganese oxide dry alkaline batteries are frequently used to operate many electronic and electrical appliances. Recycling of spent Zn-MnO$_2$ batteries is very important to minimize the risk of environmental pollution. However, recycling with an unadorned purpose of waste treatment is not an attractive business, particularly in developing countries where economic interests supersede environmental obligations. In this scenario, the idea of recovering a valuable product (e.g., pure ZnO nanoparticles) from spent batteries may be useful to promote their recycling due to the projected economic benefits.

Several pyrometallurgical and hydrometallurgical processes have been suggested to recover valuable metal components from different kinds of spent batteries, including Ni—Cd,[1−3] Ni metal hydride,[2−4] and lithium ion.[3,5−8] The recycling of Zn—Mn- and Zn—C-based batteries has also been a topic of research interest.[9] The recovery of contained valuable metals from spent batteries is generally carried out by ammoniacal and acidic leaching[10−12] processes. Precipitation[12−14] and thermal[15,16] treatments have been cited to yield reusable oxides or ferrites. Most of the above-reported processes do not necessarily catch the fancy due to limited applicability and low commercial value of the end product.

The liquid—liquid extraction of metals from spent batteries[5−8] is a simple technique to recover high purity products. Using this technique, some researchers have proposed the separation of valuable metals from spent Zn—Mn[17,18] batteries with the application of phosphonic and phosphinic acid extractants, namely Cyanex 272 and Cyanex 301. In these processes, the metal loaded organic phase needs to be treated with HCl solution in order to back-extract the desired metals. In an earlier published study,[19] we identified Cyanex 923 (a mixture of four tri alkyl phosphine oxides) as a very useful reagent for the extraction of 3d transition metals. Cyanex 923 proved to be a better choice over Cyanex 272 and Cyanex 301 as the studied extractant offered faster extraction kinetics, better loading capacity and improved phase separations. Moreover, Cyanex 923 does not solidify at low ambient temperatures and is free from foul smell.

The present work demonstrates the use of Cyanex 923 for the extraction of zinc from the waste black powder of exhausted Zn-MnO$_2$ dry alkaline batteries. After extraction and a subsequent washing step, the pure zinc loaded organic phase has been

Table 1. Composition of Digest and Leach Liquors Processed from the Black Powder "S1" of Spent Batteries[a]

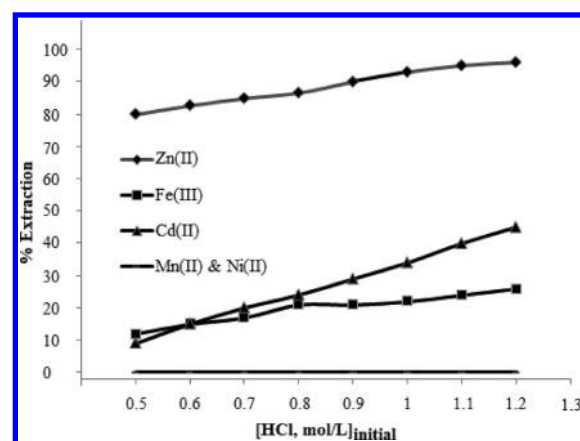| metal	concentration in digested sample g L^{-1}	concentration in leaching sample g L^{-1}	% leaching
Zn	3.05 ± 0.05	2.93 ± 0.04	96.1
Mn	7.05 ± 0.10	2.03 ± 0.04	28.8
Ni	$(3.1 \pm 0.05) \times 10^{-3}$	$(3.07 \pm 0.05) \times 10^{-3}$	≥ 99
Fe	$(51 \pm 1) \times 10^{-3}$	$(50.5 \pm 1) \times 10^{-3}$	≥ 99
Cd	$(2.5 \pm 0.02) \times 10^{-3}$	$(2.47 \pm 0.02) \times 10^{-3}$	≥ 99

[a] Sample concentration =20 g L^{-1}, dissolving medium = aqua regia for digestion, 5 mol L^{-1} HCl for leaching.

Figure 1. Extraction of metals from the leach liquor with varying concentrations of Cyanex 923 in *n*-hexane. [Cyanex 923] = 0.01, 0.05, 0.075, 0.10, 0.125, 0.15 mol L^{-1}; *A/O* ratio =1; *t* = 5 min; *T* = 25 °C.

Figure 2. Extraction of metals as a function of initial aqueous phase acidity. [Cyanex 923] = 0.10 mol L^{-1}; [HCl] = 0.50, 0.60, 0.70, 0.80, 0.90, 1.0, 1.1, 1.2 mol L^{-1}; *A/O* ratio =1; *t* = 5 min; *T* = 25 °C.

X-ray spectroscope (FESEM-EDX, Hitachi, 4800 SE), X-ray diffractometer (XRD, Shimadzu, 6000), and atomic force microscope (AFM, Park Systems, XE-NSOM).

Dismantling of Spent Batteries and Study of Elemental Composition. Spent Zn-MnO$_2$ dry alkaline cells (AA size, 1.5 V, electrolyte-KOH) of a particular brand were collected from the local sources. A set of 20 spent batteries was manually dismantled. The desired electrode material (black powder) was carefully separated from the scrap paper, plastic film, outer metallic body, and membrane. The black powder thus collected was washed with water to remove entrained electrolyte. The moist sample was dried at 120 °C (24 h), followed by manual milling to obtain fine particles (S1). One g of this sample "S1" was mixed with 20 mL of aqua-regia, heated to boil for 1 h, cooled, and then appropriately diluted with double-distilled water. The above digested sample solution was assayed by AAS for the determination of metal contents.

Leaching of Zinc from Black Powder. Ten g sample (S1) of the black powder was treated with 100 mL of 5 mol L^{-1} HCl for 2 h at 70 °C. The contents were allowed to cool and then filtered. Residual mass was washed in four steps with a total of 100 mL of double distilled water. Final volume of the leach liquor was made up to 500 mL (L1).

Liquid–Liquid Extraction Studies. Equal volumes of the leach liquor (L1) and the extractant solution (Cyanex 923 in n-hexane) were equilibrated in separatory funnels for 5 min at 25 °C to attain optimum mass transfer. The emulsion was allowed to settle (2 min) for a clear phase separation followed by the collection of aqueous and organic fractions in separate vials. The concentration of metals in aqueous phase was determined by AAS, whereas the concentration of metals in organic phase was estimated by mass balance. The zinc loaded organic fraction was equilibrated with 2.0 mol L^{-1} HCl in order to cleanse it from other coextracted metal impurities.

Synthesis of ZnO Nanoparticles. Ten mL of the zinc loaded organic phase was taken in a platinum crucible and then thermally treated for 1 h at elevated temperature (300 °C, 400 °C, 500 °C, 600 °C). Thus synthesized nanoparticles were characterized by FESEM-EDX, XRD, AFM, and UV–vis spectrometry,

subjected to combust at 600 °C for the synthesis of high purity ZnO nanoparticles. Some important structural characteristics of the synthesized nanoparticles have been ascertained by field emission scanning electron microscopy (FESEM), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction spectroscopy (XRD), atomic force microscopy (AFM), and ultraviolet–visible (UV–vis) spectrometry. The recovered pure ZnO nanoparticles may find applications in piezoelectric transducers, gas sensors, photonic crystals, light-emitting devices, photodetectors, photodiodes, optical waveguides, transparent conductive films, varistors, and solar cells.

■ EXPERIMENTAL PROCEDURES

Materials and Equipment. Metal standards for the atomic absorption spectroscopy were purchased from Merck Chemicals, India. Other reagents, solvents, and titration indicator were A.R. grade materials from Fisher Scientific/Sigma Aldrich. Cyanex 923 was received from Cytec Canada Inc., Canada. This extractant was a 93% pure mixture of four trialkylphosphine oxides: $R_3P{=}O$, $R'R_2P{=}O$, $R_2R'P{=}O$, and $R'_3P{=}O$, where R and R' represent *n*-octyl and *n*-hexyl hydrocarbon chains, respectively. The concentrations of different metals in aqueous solutions were determined by Atomic Absorption Spectrometer (AAS, Perkin-Elmer, AAnalyst 200). Spectral and topographical features of the synthesized nanoparticles were studied by UV–vis spectrometer (Varian, Cary 5000), field emission scanning electron microscope – energy dispersive

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■ RESULTS AND DISCUSSION

Composition of Spent Zn-MnO₂ Dry Alkaline Batteries and Leaching Tests. AAS analysis (average of 3 measurements) of the digested black powder solution (1 g "S1" in 50 mL of final volume) revealed the metallic contents in following concentrations: Zn: 3.05 ± 0.05 g L^{-1}, Mn: 7.05 ± 0.10 g L^{-1}, Ni: $(3.1 \pm 0.05) \times 10^{-3}$ g L^{-1}, Fe: $(51 \pm 1.0) \times 10^{-3}$ g L^{-1}, Cd: $(2.5 \pm 0.02) \times 10^{-3}$ g L^{-1}. Black powder samples from the different sets of spent batteries were studied in the above manner for establishing their average metallic composition as follows: $15 \pm 0.3\%$ Zn, $35 \pm 0.5\%$ Mn, $0.015 \pm 0.005\%$ Ni, $0.25 \pm 0.03\%$ Fe, $0.012 \pm 0.005\%$ Cd.

Data on the leaching of metals from the black powder "S1" with 5 mol L^{-1} HCl solution (solution 'L1') are given in Table 1. It can be estimated that the implemented leaching step has transferred almost 96% of the zinc content into the aqueous phase. Nickel, iron, and cadmium were almost completely dissolved, whereas the recovery of manganese was around 30%. The concentration of free HCl in the final leach liquor was estimated by acid—base titration using bromophenol blue indicator; and found to be 0.82 ± 0.05 mol L^{-1}.

Extraction of Metals from Leach Liquor of Spent Batteries by Cyanex 923. The leach liquor "L1" was equilibrated with varying concentrations (0.01, 0.05, 0.075, 0.10, 0.125, 0.15 mol L^{-1}) of Cyanex 923. As shown in Figure 1, the extraction of Zn(II) in Cyanex 923 was higher than that of Fe(III) and Cd(II). Around 87% extraction of Zn(II) was achieved in a single extraction step with 0.10 mol L^{-1} Cyanex 923. Around 22% of Fe(III) and 25% of Cd(II) were coextracted with the above extractant solution. The extraction of Mn(II) and Ni(II) remained negligible (<1%) in all the investigated extractant concentrations. 0.10 mol L^{-1}

Figure 3. Extraction isotherm of Zn from the leach liquor. [Cyanex 923] = 0.10 mol L^{-1}; A/O ratio =4, 3, 2, 1, 0.5, 0.33, 0.25; t = 5 min; T = 25 °C.

concentration of Cyanex 923 was preferred for all further liquid—liquid extraction studies. This selected extractant concentration provided a reasonably high extraction of the desired metal ion and limited the coextraction of Fe(III) and Cd(II) to a tolerable level.

Since the HCl content in the leach liquor could influence the metal distribution in Cyanex 923, the extraction patterns of Zn(II), Mn(II), Ni(II), Fe(III), and Cd(II) were further investigated with respect to the initial aqueous phase acidity (Figure 2). Synthetic solutions were used for this particular study, whose elemental compositions matched with the leach liquor but the acid content varied (0.50—1.2 mol L^{-1}). Better extractions of Zn(II), Fe(III) and Cd(II) were observed vis-à-vis the aqueous phase acidity. This pattern may be attributed to the fact that the mechanism of the metal distribution in Cyanex 923 is governed through the solvation of neutral Zn chloro species. At low HCl acidity (e.g., 0.60—0.90 mol L^{-1}), the predominating presence of anionic ZnCl$^-$ species over the neutral ZnCl₂ species accounted the realization of lower metal extractions. Higher HCl acidity (1.0 mol L^{-1} or more) of the aqueous phase facilitated the predominance of neutral ZnCl₂ species; and consequently, the Zn extraction improved to 90% and more. Similar extraction mechanism also governs the distribution of Fe(III) and Cd(II) in Cyanex 923, and therefore, the coextraction of Fe(III) and Cd(II) also increases with the increasing aqueous phase acidity.

Extraction Equilibrium. The extraction of Zn(II) with Cyanex 923 (R) proceeds according to the following reaction:

$$Zn^{2+} + 2Cl^- + nR \rightleftharpoons ZnCl_2 \cdot nR \qquad (1)$$

The stoichiometric extraction constant K_{ex} of above reaction can be represented as follows:

$$K_{ex} = \frac{ZnCl_2 \cdot nR}{[Zn^{2+}][Cl^-]^2[R]^n} \qquad (2)$$

Defining the term $(ZnCl_2 \cdot nR)/[Zn^{2+}]$ as the distribution ratio D, the eq 2 can be rearranged as under the following:

$$\log D = \log K_{ext} + 2\log Cl^- + n\log R \qquad (3)$$

A graphical illustration ($\log [R]$ vs $\log [D]$, Figure 1) of eq 3 has been used to estimate the value of n. On the basis of this obtained value (n = 2), the distribution of Zn in Cyanex 923 is proposed in the form of complex ZnCl₂·2R. Further, solving eq 3 for different extractant concentrations have estimated the value of conditional average extraction constant K_{ex} as $(1.92 \pm 0.04) \times 10^4$.

The above obtained values of n and K_{ex} have been deduced by taking the [Cl$^-$] as 0.82 mol L^{-1} (the acidity of the herein used leaching solution). Since the selection of acid concentration for
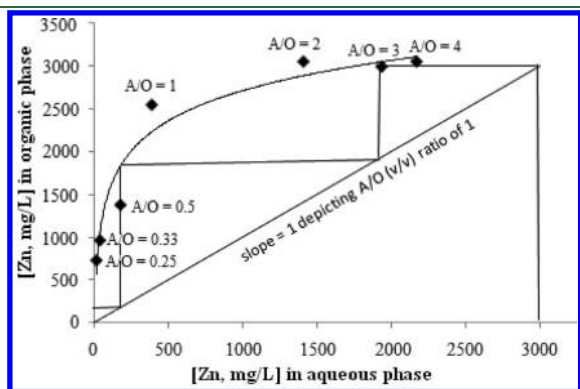
Table 2. Extraction of Zn from the Leach Liquor "L1" by Using Cyanex 923

metal	concentration in leach liquor (g L^{-1})	concentration in aqueous phase after extraction (g L^{-1})	estimated concentration in organic phase after extraction (g L^{-1})	concentration in organic phase after scrubbing with 2.0 mol L^{-1} HCl (g L^{-1})	% recovery of Zn in organic phase with purity
Zn	2.93 ± 0.04	0.04 ± 0.01	2.89	2.88 ± 0.02	≥98% (recovery)
Mn	2.03 ± 0.04	2.03 ± 0.05	<0.01	not detected	
Ni	$(3.07 \pm 0.05) \times 10^{-3}$	$(3.07 \pm 0.05) \times 10^{-3}$	<0.01	not detected	≥99 (relative purity)
Fe	$(50.5 \pm 1) \times 10^{-3}$	$(20.0 \pm 0.50) \times 10^{-3}$	30.5×10^{-3}	<0.01	
Cd	$(2.47 \pm 0.02) \times 10^{-3}$	$(1.25 \pm 0.02) \times 10^{-3}$	1.22×10^{-3}	<0.01	

^{a} Aqueous phase =200 mL of leach liquor, organic phase =200 mL of 0.10 mol L^{-1} Cyanex 923, no. of extraction stages =3, impurity scrubbing solution =2.0 mol L^{-1} HCl (A/O = 0.25).

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the leaching step is a conditional parameter, the significance of the above calculated values of n and K_{ex} depends upon their constancy for other $[Cl^-]$. Therefore, the values of n and K_{ex} have also been computed for some other $[Cl^-]$, e.g., 0.6, 0.8, 1.0, and 1.2 mol L^{-1}. Graphical representations of log $[R]$ vs log D (Figure S-1, Supporting Information) and necessary computations have revealed the values of n (= 2 in each case) and K_{ex} {$K_{ex,0.6\ M\ HCl} = (1.93 \pm 0.02) \times 10^4$; $K_{ex,0.8\ M\ HCl} = (1.97 \pm 0.02) \times 10^4$; $K_{ex,1.0\ M\ HCl} = (1.97 \pm 0.03) \times 10^4$; $K_{ex,1.2\ M\ HCl} =$

$(1.96 \pm 0.03) \times 10^4$}. It is clear that the values of n and K_{ex} remain more or less constant irrespective of the aqueous phase acidity. This observation proves the effectiveness of Cyanex 923 for the recovery of Zn from the leach liquors of varying acidity.

Extraction Isotherm. The loading capacity of Cyanex 923 was investigated by recording the distribution of Zn(II) at varying (4, 3, 2, 1, 0.5, 0.33, and 0.25) aqueous (leach liquor) to organic (0.10 mol L^{-1} Cyanex 923) phase ratios. Graphical illustration (Figure 3) of the collected data is useful to estimate the required number of extraction stages for the complete extraction of Zn(II) from the leach liquor at any desired A/O ratio. The study has indicated that the complete extraction of Zn(II) at an A/O ratio of 1 requires three counter-current extraction steps.

Recovery of Pure Zn(II) from Leaching Solution. 200 mL aliquot of the leach liquor "L1", containing 2.93 g L^{-1} Zn(II), 2.03 g L^{-1} Mn(II), 3.07×10^{-3} g L^{-1} Ni(II), 50.5×10^{-3} g L^{-1} Fe(III), and 2.47×10^{-3} g L^{-1} Cd(II) was equilibrated with 0.10 mol L^{-1} Cyanex 923 in three stages of counter-current extraction ($A/O = 1$). The composition of the leach liquor before and after the extraction is shown in Table 2. The estimated composition (by mass balance) of the organic phase is also given. Zn(II) was almost completely transferred into the organic phase with some coextraction of Fe(III) and Cd(II). Mn(II) and Ni(II) remained in the aqueous raffinate. After phase separation, the zinc loaded organic phase was washed with 50 mL of 2.0 mol L^{-1} HCl (four times) in order to scrub out the impurities and recover a pure Zn(II) loaded organic phase (O1). The relative recovery and purity of the extracted Zn(II) were confirmed by taking out a small (1.0 mL) sample from the "O1" and stripping the loaded metal content into an aqueous phase (1.0 mL of 2.0 mol L^{-1}
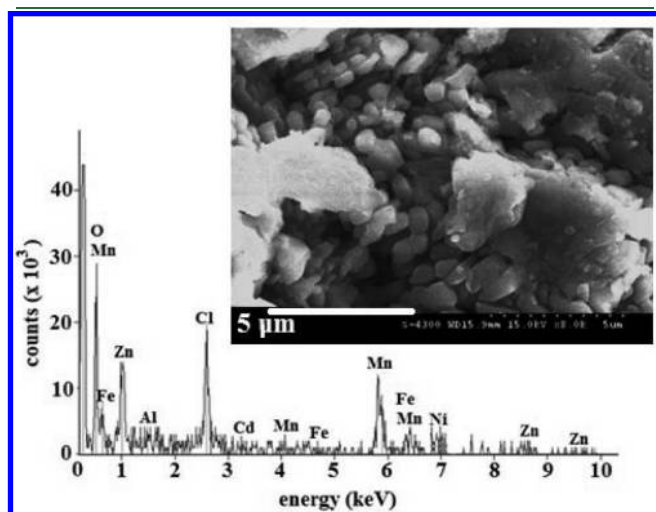

Figure 4. Surface morphology (FESEM) and elemental composition (EDX) of the black powder from spent batteries.
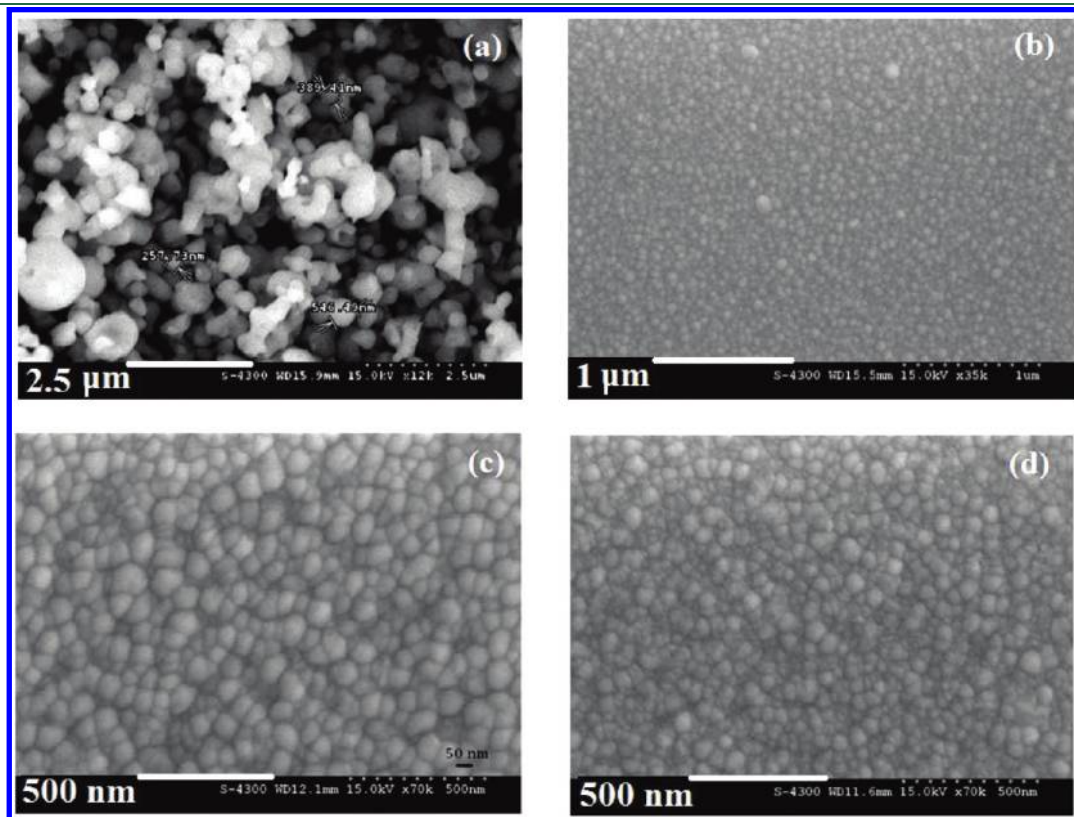

Figure 5. Surface morphology of ZnO nanoparticles synthesized by the combustion of Zn loaded Cyanex 923 phase at (a) 300 °C, (b) 400 °C, (c) 500 °C, and (d) 600 °C.
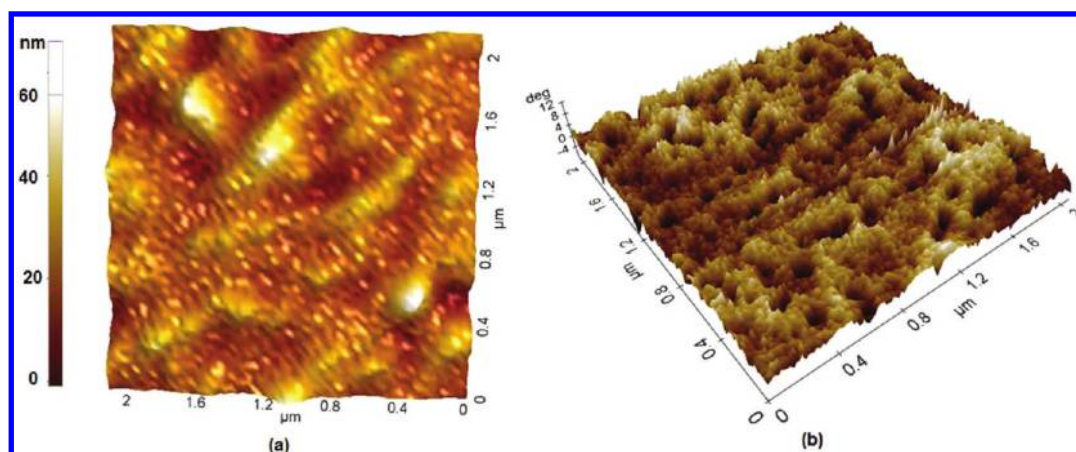
Figure 6. Noncontact AFM topography and 3-dimensional NCM phase of $ZnO_{600}{}^{0}C$ nanoparticles.

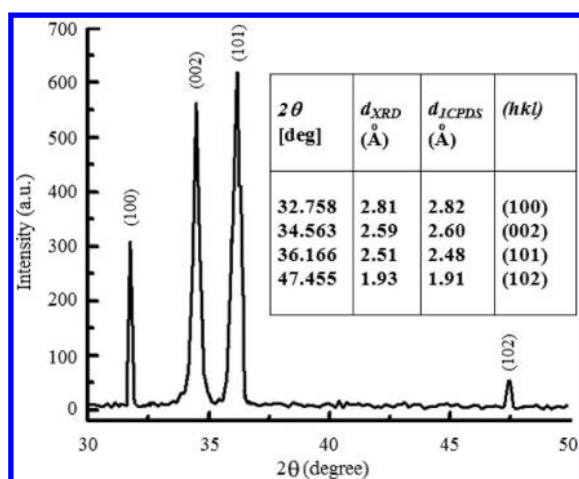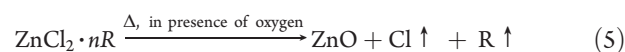**Figure 7.** XRD spectrum of $ZnO_{600}{}^{0}C$ nanoparticles with interplanar spacing (experimental and JCPDS data card) and corresponding (*hkl*) values.

HNO_3). The analyses have indicated that the above developed process for the extraction of Zn(II) from the leaching solution "L1" provides more than 98% recovery of the desired metal ion with a purity of more than 99%. The whole process is simple, fast and can be accomplished in commonly existing industrial mixer-settlers or column extractors. Remaining metals in raffinate and scrubbing solutions can be recovered by standard cementation/precipitation (e.g., Cd, Fe) or electrolytic deposition (e.g., Mn). The left-over solutions after the leaching, extraction and other involved processes can be reused in closed process loop to maintain water balance. All of the suggested leaching, extraction, and washing steps construct a standard hydrometallurgical engineering setup. Modern day engineering advancements in such systems are well capable of minimizing the waste and byproduct generation.

Treatment of Loaded Organic Phase to Yield ZnO Nanoparticles. FESEM and EDX (Figures 4) investigations of the starting material (black powder of spent batteries) revealed macroscopic structures of Zn, Mn, Fe, Cd and Ni with no particular orientation or shape. Thermal treatment (300 °C, 400 °C, 500 °C, 600 °C) of the Zn(II) loaded Cyanex 923 phase "O1" has yielded ZnO particles. Morphological (Figure 5) and

elemental (Figure S-2 of the Supporting Information) studies of the recovered products have indicated that the combustion at 300 and 400 °C delivers ZnO particles of more than 100 nm diameter. These products were also contaminated with phosphorus, which might have surfaced due to incomplete vaporization of Cyanex 923. Solution combustion at a higher temperature (500 and 600 °C) resulted into the formation of the ZnO nanoparticles. These nanoparticles were also free from any metallic or nonmetallic impurity. In overall, the formation of ZnO nanoparticles from the leach liquor can be represented by the following reactions.

$$Zn^{2+} + 2Cl^- + nR \Longrightarrow ZnCl_2 \cdot nR \qquad (4)$$

$$ZnCl_2 \cdot nR \xrightarrow{\Delta, \text{ in presence of oxygen}} ZnO + Cl\uparrow + R\uparrow \qquad (5)$$

Combustion of "O1" at 600 °C has produced good quality ZnO nanoparticles (35−50 nm). It may be pertinent to mention here that the treatment of vapors evolved during the combustion process may be required for the safety of the environment. The boiling points of the involved chemicals, i.e., *n*-hexane (69 °C) and Cyanex 923 (310 °C), are fairly distinct from the final annealing temperature (600 °C). During practical operations, the whole setup can easily be designed to recycle the used reagents by introducing two fractional distillation steps before the final annealing. A rough estimation of the process cost (Sheet 1 of Supporting Information) indicates that the described recovery of the ZnO nanoparticles is economically beneficial. The use of recycled chemicals may further improve the process economics.

AFM data of the synthesized ZnO nanoparticles are shown in Figure 6. True Non-Contact AFM surface topographic scanning confirmed the particle size to be in the range of 40−50 nm. Three dimensional view of the scan area also supports our claim of nanoparticle formation. Figure S-3 of Supporting Information shows the energy absorption characteristics of the $ZnO_{600}{}^{0}C$ nanoparticles. Maximum absorption at 351 nm with a sharp onset represents the crystalline semiconducting ZnO nanostructure. XRD spectrum (Figure 7) of the synthesized nanoparticles is also characterized with well-defined diffraction peaks for a hexagonal crystalline structure. Clearly, the product was free from impurities.

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■ ASSOCIATED CONTENT

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■ ACKNOWLEDGMENT

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