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Recovery of metal oxide nanomaterials from electronic waste materials

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Abstract

The exploitation of spent battery and electronic waste for the recovery and preparation of metal oxide nanomaterials (MONMs) is vital for technology, economical, sustainable, and environmental research. The recovery of MONMs through recycling waste materials reduces environmental pollutions and saves the primary resources due to industrial consumption. However, the economic benefits of recycling electronic waste for the recovery of these high-value MONMs have still been debated because of the low purity and stability of recovered materials restricting their commercial use. In this chapter, we discuss the motivation and importance of waste recycling for the recovery of nanomaterials, focusing on the possible techniques that can be applied for the efficient synthesis of commercial-grade MONMs (e.g., ferrites, zinc oxides, indium oxides, tin oxides, etc.) with high purity at a minimal cost. Besides, the profit of recovered MONMs in potential applications for wastewater remediation and renewable energy production are addressed.

Keywords: Nanomaterials, Metal oxides, Waste recycling, Environmental pollution. Renewable energy.

1. Introduction

Recycling waste materials to recover high-value end-products is probably the most effective environmental preservation [1]. The goals of recycling are to achieve less natural spent

consumption and reduce the amount of trash, as illustrated in Fig. 1. It is important to recycle waste materials with the lowest possible energy consumption [2]. Thus, the raw materials can be recovered several times through the recycling processes. Recycling is designed to reduce the consumption of energy and save natural resources. Up to date, we are far uptake from a locked-loop material cycle because we are not able to recycle all the waste materials (Fig. 2). A closed-loop platform has three fundamentals as following: gathering, processing, and purchase. The gathering is rerouting and collecting spent wastes for recycling and treatment. In the processing, the collected spent wastes are re-manifested for fabricating a new output. Finally, the freshly synthetic output is then sold to a tertiary party before reprocessing and repeat the operation once more. Regarding the entire closing of the spent recycle, the most crucial aspect is to beat several restrictions enjoined in reprocess like output layout, process thermodynamics, recovery methods, social behavior, and economics [3].

It could be announced that recovery and the up-scale recycling for several spent wastes (e.g., newspapers, glass bottles, cans, polymers, electronics, and batteries) are recently echoed in many countries of all the world [4]. Converting waste into fresh, valuable, and vendible products might be an essential strategy in boosting earnest recovery efforts to prospect desirable economic feedback with polity subsidization [5-10]. Several nanomaterials (metals, metal oxides and hydroxides) such as ferrites, TiO_2 , Ag, Fe, Fe-O, Au, ZnO, SiO_2 and hydroxyapatite have been recovered from waste materials by different recycling processes [11]. These recovered nanomaterials could be extensively used in many applications, such as in renewable energy solar cells, catalysis, water remediation, and supercapacitors [12]. Many researchers have reported nanomaterials recovery from electronic waste by different recycling processes under available conditions in most research laboratories, as revealed in Table 1.

The spent batteries are the most predominant waste materials recycled to recover different nanomaterials [13-18]. Nowadays, batteries are widely used as mobile sources of energy for many purposes. Annual battery consumption is estimated at 8, 6, and 1 billion units annually in Europe/United States, Japan, and Brazil, respectively [19]. Despite these batteries made of many valuable materials that can be recovered, they are usually disposed of as spent waste after their end life. Nevertheless, scientists recently made some attempts to recover these valuable metal and metal oxides from the spent batteries waste, such as wastes of Zn-C, Li-ion, Ni-MH, and zinc-manganese oxide alkaline batteries [8, 20-22]. Several nanoparticles (NPs) such as Fe, Co, Mn, Li, Ag, Au, Zn, Ti, Pd, Ni, Cu, and rare earth elements could be recovered from the spent batteries wastes [8, 21, 23, 24]. Analogous with these, various oxide nanomaterials such as Co_3O_4 , MnO_2 , ZnO , ZnMn_2O_4 , Ni-Mn-Co-Zn ferrites, and MnO_2/RGO could also be synthesized from recovered materials from the spent batteries wastes [8, 20, 21, 24, 25].

Dry cell batteries (i.e., alkaline batteries) represent about 89% of commercially available batteries globally, whereas hundreds of million pieces of dry batteries are manufactured per year [26, 27]. Thus, the disposal of the spent dry batteries is a huge issue that can not be neglected [20, 27, 28]. In various countries, gathering ways were established to manage the spent dry batteries wastes. However, a considerable quantity is still left to be castaway along with household spent. Burying, burning, and recycling are the three main administration routes for the spent dry batteries [29]. The highest practical strategies for the finite availability of sites were incineration and recycling. Recycling is also a viable solution for addressing these serious problems associated with spent waste [30-32].

Accordingly, this chapter aims to discuss the most novel and environmentally friendly technologies for recycling various batteries and electronic wastes to recover valuable metals oxide

nanomaterials such as metal ferrites, zinc oxide, and indium tin oxide. The possible applications of recovered nanomaterials in different fields such as catalysis, water treatment, photocatalyst, electrocatalysis, supercapacitors will also be demonstrated.

Fig. 1 Recycling and recovery of waste.

Fig. 2 Closed-loop materials cycle.

Table 1 Nano metal oxides recovered from recyclable waste

Waste	Oxides	Methods	Recovery (%)	Ref.
Zn-C, Zn-Mn batteries	Ni-Mn-Zn/Mn-Zn ferrites	Co-precipitation, Sol-gel, and leaching	56 Fe and 97 of Mn and Zn	[13, 33, 34]
Li ion batteries	Co Ferrites	Sol-gel, coprecipitation, hydrothermal	--	[35-37]
MnO ₂ -Zn dry batteries	ZnO NPs	Liquid extraction, precipitation, and Hydrometallurgy-	99	[38-40]
Zn-MnO ₂ batteries	Zn _x Mn _{1-x} O NPs	Hydrometallurgy	57	[41]
Furnace slag, Red mud, Fly ash	TiO ₂ , SiO ₂	-	-	[42]
Pickling waste	Fe ₃ O ₄ NPs	Co-precipitation	-	[43]
Waste silver chloride	Ag NPs	Precipitation and reduction	-	[44]

2. Recent categories and strategies of metal oxide recovery

In the present sub-sections, we discuss a vast range of waste items regenerated and recovered to recuperate precious metals and metal oxides such as electrical machines, batteries, and sludges. As illustrated in Fig. 3, these waste materials can be categorized into three elementary classes, e.g., batteries (Category A), used instruments (Category B), and wastes and sludges (Category C). Several metal nanoparticles, ferrites, and metal oxides could be recovered by recycling these three categories of waste materials using several step methods of solid/liquid spent, as discussed in several literature studies. However, the hydrometallurgical and pyrometallurgical approaches are the most popular processes that yield reusable oxides or ferrites at a considerable quantity. They work on co-precipitation methods and thermal handling. Fig. 4 depicts and summarizes the main steps of the recycling and recovery processes of ultra-pure NPs from combustible wastes such as dry batteries, electronics, etc. using hydrometallurgical or pyrometallurgical approaches. The main fundamentals of those pathways are discussed in the next sections.

Fig. 3 Categories of recycling and fabrication of nanosized metals oxides and metals from spent/waste.

2.1 Hydrometallurgical approach pathway

The hydrometallurgical process is one of the most powerful ways of recycling nanosized metals and metal oxides. As illustrated in Fig. 4, the hydrometallurgical process is divided into several steps, including the dismantlement of the life end products, washing and cleaning with water to uptake all undesirable digestion, alkali/alkaline salts, extraction, thermal treatment, and filtration [45]. The selective leaching of metals could be done in acid (e.g., HCl and H_2SO_4) or alkaline (e.g., NH_3/NaOH) solutions. Similarly, efficient mineral extraction depends on several parameters such as the acid and base concentration, saturation solubility of the metal, solution pH, and reaction temperature. Furthermore, the effect of oxidants agents (e.g., H_2O_2 , KMnO_4) and reductants agents

(e.g., citric acid, acidic oxalate, and ascorbic acid) on the selective co-precipitation of metal ions was also inquired [46, 47]. Toro *et al.* [48] have reported a patented hydrometallurgical method for the large-scale production of the most valuable products using spent alkaline batteries. This method was based on alkaline batteries dissociation to split up fine (mostly manganese, graphite, and zinc) and coarse materials (paper, plastic, and steel), followed by washing and liquidation co-precipitation, cementing, and recrystallization. An agriculture fertilizer such as potassium sulfate was recovered [49]. While the leftover reagents, including acid, reagents, and water, were directed back to leaching's reactor. The residue reagents were regenerated via simple strategies to reduce the wastes generated through the nanomaterial fabrication. In this case study, the reagent solvents utilized to generate the nanomaterials were recycled and used later several times in the same preparation. Several other modern examples of lab-bench scale hydrometallurgical preparation of NPs exist as MnO_2 /graphene nanocomposites [17], ZnO NPs [38, 39], $\text{Zn}_x\text{Mn}_{1-x}\text{O}$ NPs [41], Zn substituted MnFe_2O_4 NPs [34], Co-ferrites [34, 37], and Ni-Zn-Mn ferrites [50]. In the hydrometallurgy, we mostly use acid to leach the waste batteries and form soluble salts and then disinfect the product by adjusting the pH, extraction, co-precipitation, etc. [51]. Similarly, some valuable Zn and Mn could be extracted from spent Zn–Mn batteries using bio-hydrometallurgy, whereas bioleaching bacteria species were used to reduce the extraction time to 24 h regardless of energy source types [52].

2.2 Pyrometallurgical approach pathway

The pyrometallurgical approach pathway is an alternative conventional operation for the recycling and recovering precious metals and metal oxides from the spent electronic equipment wastes. Pyrometallurgical recovery and regenerating operations include mainly the following sequences:

pyrolysis, reduction, distillation, and incineration [53]. Unlike hydrometallurgy, pyrometallurgical processes need high temperatures to generate metals and metal oxides. For instance, Umicore chemical company (Belgium) could regenerate seventeen different metals from spent electrical and electronic equipment by extracting the metal slags at high temperatures (i.e., 1200 °C).

Nevertheless, the formation of toxic or harmful fumes and gases meets a major barrier in the current period [54]. The pyrometallurgy recovery process can be performed under vacuum (i.e., vacuum metallurgy) or different atmospheric pressure (i.e., pressurized metallurgy). Although pressurized metallurgy has been used to recycle and recover zinc oxide from spent waste batteries, it is highly costly due to the latest tail gas treatment equipment. Thus, the vacuum metallurgy recovery process has recently received more attention due to its environmentally friendly advantages [55-60]. Because of the metals lower boiling points during vacuum, metal recycling by vacuum mining reduces energy compared to traditional thermal mining operations (pyrometallurgy processes) [61, 62].

2.3 Physical separation approach

Although wet recycling has attracted complete attention due to its mild reaction conditions, it shows high energy consumption and serious subaltern contamination, limiting its widespread application [63]. Subsequently, low-cost, high-efficiency, and environmentally friendly recovery processes should be considered. Physical separation is an alternative process applied to retrieve useful components from the spent fluorescent lamp, printed circuit board, and batteries. For instance, rare earth phosphorus could be recovered from the spent fluorescent lamps with a recovery efficiency of about 70-90% by the flotation method [64]. Similarly, polyvinyl chloride (PVC) could be recovered completely (i.e., 100%) from spent electronic plastics by froth flotation separation after treating the E-waste with Ca/CaO composite to hydrophilize the surface of PVC

[65]. The electrode materials (e.g., LiCoO_2 and graphite) could also be recovered from the spent dry batteries wastes with a recovery rate of 98.99% via Fenton reagent-assisted flotation [66].

Fig. 4 Strategies of metal oxide recovery from spent/waste.

3. Recovery of ferrites

Ferrites are a ceramic-like substance that has magnetic properties useful in many types of electronic devices. Ferrites are iron-based materials, generally gray or black, and exist in a polycrystalline form of many small crystals. Several other transition metals can be present in ferrites materials. For instance, Zn-Mn-Co-ferrites consists of iron oxide and one or more other cations of these transition metals. Magnetic ferrite is widely valued in different fields due to its high electrical resistance, excellent magnetic properties, chemical stability, mechanical rigidity, and relatively low cost; these materials' properties vary significantly from the properties of bulk materials [67-70]. As illustrated in Table 1, the recycling and recovery of ferrites NPs from the spent wastes started in the last decade, approximately in 2004. Xi *et al.* are among the pioneering groups that established Zn-Mn magnetic ferrite NPs recovery from dry Zn-MnO₂ batteries after

end life via co-precipitation process [71]. They found that the recovery process could be affected by several factors, such as co-precipitation pH and temperature of co-precipitation and calcination processes. Their studies showed that Zn-Mn magnetic ferrite NPs could be appropriately recovered using a co-precipitation pH of about 7.0–7.5 at 50 °C and calcination temperatures between 1100 – 1150 °C. As illustrated in Fig. 5, magnetic manganese ferrite (MnFe_2O_4) could be successfully synthesized from manganese solution recycled and recovered by leaching the cathode material of spent wastes of zinc-manganese oxide batteries with 0.5 mol/L nitric acid and 30 % (v/v) H_2O_2 at 80 °C, followed by reaction with ferric chloride and calcination of obtained coprecipitate at 450 °C [16]. The obtained MnFe_2O_4 materials were a promising catalyst for heterogeneous photo-Fenton photodegradation of methylene blue dye, which accomplished 92% dye decolorization within 120 min irradiation [16].

Fig. 5 (a) The equation mechanis of MnFe_2O_4 recovery via leaching the electrode material of spent zinc-manganese oxide batteries with nitric acid. (b) Schematic representation of effieciency of MnFe_2O_4 for water remidation. (c) X-ray diffractogram of MnFe_2O_4 synthesized from spent batteries. Adapted with permission from Ref. [16] (Copyright 2020, Elsevier).

Chang-hong *et al.* [72] have reported the synthesis of Mn–Zn light magnetic ferrite NPs from the waste of Zn-Mn batteries (e.g., spent scrap iron and pyrolusite MnO_2) via leaching, purification, and co-precipitation processes. In the first step, the leaching of the spent materials in H_2SO_4 has yielded about 92.02, 96.14, and 98.34% of Fe, Mn, and Zn, respectively. They have then washed the leached solutions with ammonia, ammonium sulfhydrylate, and ammonium sulfide to remove the heavy metals, Ca^{2+} , and Mg^{2+} by vulcanized and fluorination precipitations (i.e., double salt precipitation deep purification). This deep purification process has led to high removal efficiencies of most of the impurities. For instance, 99.7, 96.5, 92.3, 63.6, 99.9, 53.0, and 78.7% of Ca, Al, Mg, Si, Cu, Cd, and Ni, respectively, have been removed after the purification process. Thus, the obtained Mn–Zn soft magnetic ferrite powders after the co-precipitation process have been found to contain Zn 4.49%, Mn 13.92%, and Fe 41.41% with the mass ratio of Mn:Zn:Fe equals to 7.5:23.3:69.2 (theoretical mass ratio Zn:Mn:Fe = 8.3:24.4:67.3). The low content of impurities in recovered Mn–Zn soft magnetic ferrite made them better than the synthetic PC30 produced by the Japanese TDK company [72]. Nan *et al.* [33] have also fabricated Zn-Mn ferrites from the spent Mn-Zn batteries by chemical co-precipitation using ammonium oxalate. They first dismantled spent zinc manganese dioxide batteries with a mechanical machine. The dismantling materials were watered, and the iron battery components were collected using a magnet, and the remaining residual materials were baked and griddled to obtain zinc and manganese species. The separated Fe-, Zn- and Mn-species were dissolved in H_2SO_4 to obtain FeSO_4 , ZnSO_4 , and MnSO_4 solution, respectively, that were used in the synthesis of Zn–Mn ferrite magnetic materials with the composition of $\text{Mn}_{0.26}\text{Zn}_{0.24}\text{FeO}_2$ after the calcination of the co-precipitated precursor at 850–1250 °C [33]. Xi *et al.* [15] have fabricated nanocrystalline ferrites from the spent alkaline Zn–Mn batteries using sol-gel and combustion methods. The gel containing Fe, Mn, and Zn cations was

first prepared by dissolving the spent battery materials in an HNO_3 solution containing 2.5 wt.% H_2O_2 , followed by the addition of citric acid and ammonia and drying at 135°C for 2 h. The XRD, TGA, DTA, SEM, ICP, and FTIR characterizations showed that the dried gels are self-propagating combustion led to the nanocrystalline formation of manganese zinc ferrites with the stoichiometry $\text{MnZn}_{0.85}\text{Fe}_2\text{O}_4$ [15]. However, it is worth mentioning that they have used analytical grade manganese nitrate, zinc nitrate, and iron nitrates to adjust the concentration of Mn, Zn, and Fe to obtain this stoichiometric spinel.

Similarly, Mylarappa *et al.* [14] have also prepared nanocrystalline zinc-manganese ferrites from the spent Zn-C batteries as raw materials by dissolution in H_2SO_4 followed by co-precipitation in NaOH at 100°C . They used the obtained zinc-manganese ferrites to decorate rGO by using a solvothermal route. Their GO/Mn-Zn ferrite nanocomposite showed excellent photoactivity performance to decompose acid orange 88 dye in wastewater under ultraviolet irradiated, as illustrated in Fig. 6 [14].

Fig. 6 (a) Schematic representation of recovery of nanosized Mn-Zn ferrites using Zn-C dry batteries. (b) The mechanism of acid orange 88 decomposition for Mn-Zn ferrite-rGO nanocomposite. Adapted with permission from Ref. [14] (Copyright 2019, Elsevier).

Several harmful byproducts can be produced in the stainless-steel industries, such as fly ash and ultrafine particle, which can easily bioaccumulate leak and snuff, and pose a critical menace to the humans and environment of the world [73-76]. Magnetic ferrites have also been recovered and purified from industrial fly ash wastes. The magnetic ferrites (e.g., $\gamma\text{-Fe}_2\text{O}_3$ and Fe_3O_4) from fly ash waste depend on the interactions between magnetic ferrites with the applied magnetic field [75]. Lin *et al.* have utilized a magnetic separator to separate magnetic Ni-ferrites NPs from a steel industrial fly ash (RFSIF) with a good separation factor of 74%. These Ni-ferrites NPs were found suitable for various applications, especially as a catalyst for the hydrolysis and methanation of CO_2 using fluid hydrogen gas, as shown in Fig. 7 [77].

Fig. 7 Recovery of magnetic ferrite from fly ash for decomposition/methanation of CO_2 . Adapted with permission from Ref. [77] (Copyright 2018, Elsevier).

Magnetic cobalt-ferrites are another class of ferrites materials with distinct chemical, physical and mechanical properties [37, 78, 79]. For instance, they typically demonstrate a low-frequency magnetic permeability and a high magnetic polarization angle in visible light at ambient temperature [37, 78, 79]. Cobalt-ferrite also has excellent chemical consistency and high wear resistance to corrosion [80]. Magnetic cobalt ferrites have also been applied as a microwave absorber [81]. As shown in Fig. 8, spinel cobalt ferrites, NPs with the composition of $\text{Co}_{0.8}\text{Fe}_{2.2}\text{O}_4$, have been fabricated from the spent cathode of lithium-ion batteries as raw materials by sol-gel route using ethylene glycol as a gelling agent [37]. TEM, XRD, XPS, FTIR, SEM, and VSM characterizations showed that the synthesis parameters could influence the cobalt ferrites' chemical structure, morphology, and magnetic properties. Spinel $\text{Co}_{0.8}\text{Fe}_{2.2}\text{O}_4$ NPs with a saturated magnetization of around 61.96 emu.g/L could be obtained at the optimum synthesis parameters of metal ion to ethylene glycol ratio $\sim 1:0.8$, annealing temperature $\sim 800^\circ\text{C}$, and the annealing time about 6 h [37].

Fig. 8 (a) Schematic chart of magnetic cobalt-ferrite spinel prepared from spent Li-ion batteries. (b) TEM analysis of the magnetic cobalt-ferrite spinel elaborated from Li-ion batteries. Adapted with permission from Ref. [37] (Copyright 2016, Elsevier).

4. Recovery of zinc oxide

ZnO has shown remarkable implementation prospects in treating environmental contamination, particularly in organic wastewater remediation [82]. Researchers worldwide have proposed different recovery methods of Zn-based materials, which can mainly be divided into pyrometallurgy and hydrometallurgy. In China, about 373 Gg of ZnO have been utilized to manufacture batteries in 2003 and have increased to 535 Gg in 2005 [83]. NPs could be effectively-prepared from the spent Zn-Mn dry batteries by high-temperature evaporation-separation and oxygen control oxidation using air as both carrier gas and oxidizer [84]. Although carbon powder or lead powder were used as additional materials to isolate the oxygen, zinc's oxidation rate was still fast. However, Zn could be first evaporated and recovered from the zinc hull covered with fiber mat with a recovery efficiency of ~98.99% and then oxidized into nanotetrapod ZnO by using a heating temperature of 1123 K, air pressure of 3 kPa, and blowing airflow at 723 K [84]. Nevertheless, due to the unstable content and flow rate of oxygen, the morphology of the substance obtained in this way is not standardized. ZnO NPs with variable morphologies have been obtained from the spent Zn-Mn battery by vacuum evaporation and oxygen control method [85]. In this method, the morphology of ZnO NPs could be controlled by adjusting the flow rate of the N₂ conveyor, the content of O₂ oxidizer, calcination temperature, used substrate, and condensing distance. For instance, nanotetrapod ZnO photocatalyst could be formed on a glass plate at 1123 K under 12.5% oxygen content and a nitrogen flow rate of 21 Lmin⁻¹ [85].

Fig. 9 Recovery of zinc oxide by high-temperature evaporation-separation and oxygen control oxidation. Adapted with permission from Ref. [84] (Copyright 2018, American Chemical Society).

Deep and his co-worker [39] have recently proposed a novel and easy method for the recovery of highly-pure ZnO NPs from the electrode waste of spent alkaline zinc-manganese oxide batteries. The spent electrode materials were gathered using manual disassembly and mixed with 5M HCl to interact with the phosphine oxide reagent Cyanex923[®] at 250°C for 30 min to form Zn-Cyanex 923 complex, as illustrated in Fig. 10. With approximately 5 nm diameter, ZnO NPs were then

prepared from the Zn-Cyanex 923 complex by an ethanolic precipitation process. Therefore, the proposed process provides an easy and efficient way to regenerate ultra-pure ZnO NPs from the spent dry waste batteries compared with other high-temperature evaporation-separation techniques oxygen control oxidation.

Fig. 10 (a) Schematic flowchart of ZnO nanoparticles recovery from spent alkaline batteries. (b) The equation mechanism of ZnO nanoparticles recovery. (c) AFM topography, line analysis, and 3-D view of the recovered ZnO nanoparticles. (d) XRD analysis of the recovered ZnO nanoparticles. Adapted with permission from Ref. [86] (Copyright 2018, CNKI).

5. Recovery of indium tin oxide

Recently, the world's indium reserves are around 12,000-13,000 tons, representing only 1/6 of the gold reserves; access to 0.03% indium content is considered a mining value [87, 88]. The binary

and ternary indium oxides have recently attracted much scientific and technological interest among indium compounds due to their fascinating structural chemistry and promising functionalities [89-92]. Indium-based materials are widely applied in radioelectronic, spintronic, and semiconductor manufacturing processes due to its special electrical, chemical, and physical properties [93-95]. Thus, it is considered an essential strategic resource in recent industrial growth [96]. More than 80% of extracted indium in the world is employed in the fabrication of indium tin oxide (ITO) materials [97] that contain more than 90% indium oxide and less than 10% tin oxide [98]. ITO is widely used to fabricate the touch display of smartphones and liquid crystal display panels (LCD) [99]. Thus, the amount of indium in the world is reduced with time, and it is getting expensive due to its scarcity on the earth [100]. The recovery of indium from the wastes of LCD devices should be urgently regulated [101].

As illustrated in Fig. 11, the board of LCD consists of two polarizing films, two glasses substrate covered by the ITO layer, a color filter film, and a liquid crystal band. Because of the large indium content in an ITO film, the waste LCD is considered a potential secondary source of indium [102]. However, the recovery of In from LCD screens faces some problems due to the harmful impurities and components in the display (e.g., liquid crystals, plastics, and mercury) that can be released during the dismantling process of the LCD [103]. To date, most of the studies on the recovery of indium from waste LCD panels focused on the aqueous hydrometallurgical pathway. For instance, Li and his co-workers [104] have reported the recovery of indium from the waste LCD screens using a multi-step process, including the removal of LCD polarizing film and liquid crystals by thermal shock at 230-240 °C and the ultrasonic cleaning at 40 KHz, respectively, and the recovery of indium from ITO glass by acid dissolution. This multi-step process led to the recovery of 92 wt% of indium metal when a solution mixture of HCl and HNO₃ acids with the

ratio of $\text{HCl}:\text{HNO}_3:\text{H}_2\text{O} = 45:5:50$, and aging temperature and time of $60\text{ }^\circ\text{C}$ and 30 min, respectively, are used. Lee *et al.* [105] have reported that the particle size of ITO materials crushed by high energy ball milling and the amount of HCl in the acidic solution could strongly affect the recovery efficiency of indium from the waste LCD panels. They could rapidly recover 86% of the indium in the waste materials after 1 min of ball milling using the acid solution ($\text{HCl}:\text{H}_2\text{O} = 50:50$). Solvent extraction, which is based on sulphuric acid leaching, di(2-ethylhexyl)phosphoric acid extraction, and HCl back extraction, is another alternative approach to recover indium from thin-film-transistor liquid-crystal display (TFT-LCDs) waste [106]–[Bekheet, 2013–#89]. In this method, 97% of indium in the raw materials could be recovered by leaching the waste materials H_2SO_4 (1:1, v/v) acid solution, followed by two extraction process using 30% of di(2-ethylhexyl)phosphoric acid solution (O/A=1:5) for 5 min, and 4M HCl acid solution. Hsieh and his co-worker [107] have reported the recovery of highly pure sponge indium (>99%) from spent ITO waste using hydrometallurgical in 30 vol.% HCl solution at $80\text{ }^\circ\text{C}$ for 30 min, followed by hot immersion in KOH solution at $300\text{ }^\circ\text{C}$ for 10 min.

In addition to the hydrometallurgical method, chlorination, vacuum carbon reduction, sub-critical water have also been applied to recover indium from ITO waste. For instance, Ma and Xu [108] have recovered 99.97% of indium in the ITO waste as indium chloride by using vacuum pyrolysis at $300\text{ }^\circ\text{C}$ and 50 Pa to separate oil and organic materials, followed by vacuum chlorinated separation using 50 wt% NH_4Cl at $450\text{ }^\circ\text{C}$. Similarly, 66.7 and 54.1% of indium could be recovered from LCD waste in the form of indium chloride by chloride volatilization process under air and N_2 , respectively, using polyvinyl chloride (PVC) as chlorine agent at $350\text{ }^\circ\text{C}$ and a Cl/In a molar ratio of 11 [109]. Zhang and his co-worker [110] could also prepare indium chloride with 36% of indium from waste LCD panels containing 0.02 wt% in a multi-step process including mechanical

stripping, a series of pyrolysis separation, chlorinated vacuum separation, and substitution reaction. He *et al.* [111] have reported that 90 wt% of indium could be recovered from waste LCD panel by vacuum carbon-reduction using 30 wt% carbon as additives at 1223 K and 1 Pa for 30 minutes. Yoshida *et al.* [112] have demonstrated that 83 and 10% of indium could be recovered from stained glass (CF) and TFT glass of LCD waste, respectively, using semi-critical water 360 °C. They also found that NaOH's addition during the recovery process could increase the recovery efficiency of indium from both CF and TFT glasses to 99 and 95%, respectively, at 220 °C after 5 min. Indium could also be recovered as In^{3+} ions from LCD waste via the microbial adsorption method, whereas a gram-negative bacterium could adsorb In^{3+} ions generated by leaching the spent LCD panel in HCl solution under hydrothermal conditions (120 °C, 0.198 MPa, 5 min) [113].

Fig. 11 The configuration of the LCD panel.

Even if indium tin oxide is the target, the CF glass is the primary medium because ITO adheres to the CF, easily removed by crushing from the glass (Figure 11). The flotation process has also been

utilized to recover ITO from color filter (CF) glass in waste LCD panels, as illustrated in Figure 12 [114]. ITO could be easily separated from glass for indium recycling by the floatability of CF due to its hydrophobicity caused by hydrophobic methyl groups and aromatic ring. The separation of CF containing ITO from the glass substrate was found to depend on the feed size of crushed materials, and the recovery of indium and ITO increased with decreasing feed size. For instance, 85.21% of ITO containing 0.61% indium could be recovered for particles with a size smaller than 0.025 mm. In addition, the indium oxide concentration and the recovery of indium tin oxide increased with increasing grinding time. The 92.51% of ITO containing 0.60% indium was recovered after 80 minutes of milling.

Fig. 12 (a) Flowsheet of ITO recovery by flotation. (b) Schematic diagram for ITO and glass separation by flotation. Adapted with permission from Ref. [114] (Copyright 2018, Elsevier).

Thermal decomposition is another approach that has been applied to recover ITO from the waste color filter (CF) glass, as illustrated in Fig. 13 [115]. The ITO layer could be first separated from the glass substrate after the color layer's thermal oxidation. Although the yield of recovered ITO

was found to decrease with increasing temperature and time of the thermolysis process, the recovery and enrichment ratio was increased. After thermolysis at 600 °C for 8 min, 98% of ITO could be efficiently recovered with yield and enrichment ratio of 0.06% and 1669, respectively. Moreover, the crystal structure of recovered ITO has not been changed during the thermolysis process. It is worth noting that the authors have used activated carbon during thermolysis to adsorb the released toxic mixed flue gas that might harm the atmospheric environment [115].

Fig. 13 Recovery of ITO by thermal decomposition of waste color filter glass. Adapted with permission from Ref. [115] (Copyright 2020, Elsevier).

6. Conclusions

There is no dispute concerning the significance of recycling spent waste and the recovery and regeneration of high-value products, including minerals, nanoparticles, and other materials.

Nevertheless, the literature in this work remains to be explained inappropriate technology due to the limitation of cost-effectiveness. Moreover, although recycling is beneficial from an environmental point of view, economic sustainability cannot often be achieved for an advanced process without subsidizing the country due to low or non-existent profits. However, new methods appear more favorable, perhaps for modern trade models to become more profitable than debris. With the scheme increasing by 21% annually in global depletion of metal oxides by 2019, there is a critical need to generate potential metal oxide supplies. Conventional processes for converting bulk materials into metal oxides (NPs) can increase supply slightly. Recycling such materials from recycled expenses thus opens up the possibility that some of the most important materials will create a secondary supply chain. Overall, we have found that most of the currently available recycling technologies need more refinement to produce finished commercial goods.

7. Future prospective

Furthermore, the reproduction of specific recovery methods and stability should be dealt with more widely. Reuse of materials that have been produced or degraded after application for various treatment purposes is crucial, especially as production costs for NPs with high-purity metal oxides are generally high. The replication and degradability or reuse of recycled metal oxides should be given greater importance to close existing research gaps. For the nanostructures to survive, a systematic approach is also required to determine risks associated with the use and disposal of the major metal oxides associated with the product. The evolution of the process for assessing toxicity that predicts potential impacts on human health and the environment is still critical. Finally, applying a green process may significantly raise the benefits of pilot projects, and it should be taken into consideration.

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