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Recycling of indium from waste LCD: A promising non-crushing leaching with the aid of ultrasonic wave

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ABSTRACT

The tremendous amount of end-of-life liquid crystal displays (LCDs) has become one of the prominent sources of waste electrical and electronic equipment (WEEE) in recent years. Despite the necessity of safe treatment, recycling indium is also a focus of waste LCD treatment because of the scarcity of indium. Based on the analyses of the structure of Indium Tin Oxide (ITO) glass, crushing is demonstrated to be not required. In the present research, a complete non-crushing leaching method was firstly adopted to recycle indium from waste LCDs, and the ultrasonic waves was applied in the leaching process. The results demonstrated that indium can be leached efficiently with even a low concentration of chloride acid (HCl) without extra heating. About 96.80% can be recovered in 60 mins, when the ITO glass was leached by 0.8 M HCl with an enhancement of 300 W ultrasonic waves. The indium leaching process is abridged free from crushing, and proves to be of higher efficiency. In addition, the ultrasonic wave influence on leaching process was also explained combing with micron-scale structure of ITO glass.

1. Introduction

Indium is known as a scarce metal because of its extremely low concentration in the crust of earth (merely less than 200 ppb) (Alfantazi and Moskalyk, 2003); despite the scarcity of indium, its compounds have been applied comprehensively because of their favorable semi-conductive and optoelectronic performances. In particular, indium oxide combined with tin oxide (at an approximate mass ratio of 9:1) can be employed to produce the Indium Tin Oxide (ITO) films used in liquid crystal display (LCD) panels; this application accounts for nearly 80% of the total consumption of indium (Park et al., 2009). Because of the lack of independent indium ores, the world-wide indium production primarily depends on the by-product of Sphalerite and lead mineral ores, especially in China (Frenzel et al., 2016; Gupta et al., 2004; Zhang et al., 2016). Moreover, driven by the growing LCD market, the increasing indium demand further provides a challenge for the sustainable application of indium deposits. The recycling of secondary resources of indium would be an effective approach to mitigate the exhaustion of the primary minerals of indium. Furthermore, the low grade (featuring indium content as low as 0.002%) of raw ores that are considered to be worthy of smelting (Kumar et al., 2013) also makes them less satisfactory resources compared with indium-containing wastes. In fact, the end-of-life LCD monitors have prospects of being a reliable resource for indium production, given their indium concentration and colossal amounts. The indium content of end-of-life LCD monitors exceeds that of the primary ores, with the indium concentration covering a range from 102 mg/kg to 968.5 mg/kg for the various LCD display processing techniques of different companies (Dodbiba et al., 2012;Yang et al., 2013; Savvilotidou et al., 2015). Moreover, the massive number of waste LCD electronic products, including TVs, computers and laptops, has accumulated to become an enormous amount of waste material. According to the Chinese Statistical Yearbook of the Electronic Information Industry (2004–2012), approximately 9500 million of LCD monitors were sold in China between 2005 and 2010. With an average lifespan of 5–6 years, the useful electronic appliances inevitably reach their end-of-life state and are transformed into hazardous wastes (Schmidt, 2005). Furthermore, because of the cytotoxicity of soluble ITO to our respiratory system, the proper disposition of waste LCD monitors and indium recycling is necessary to avoid the adverse environmental influence of indium (Chou and Huang, 2009;Lim and Schoenung, 2010). Instead of being tackled as merely wastes, these end-of-life LCD products could also be a reliable potential indium resource, covering about half of the total indium demand in 2035 (Wang et al., 2015).

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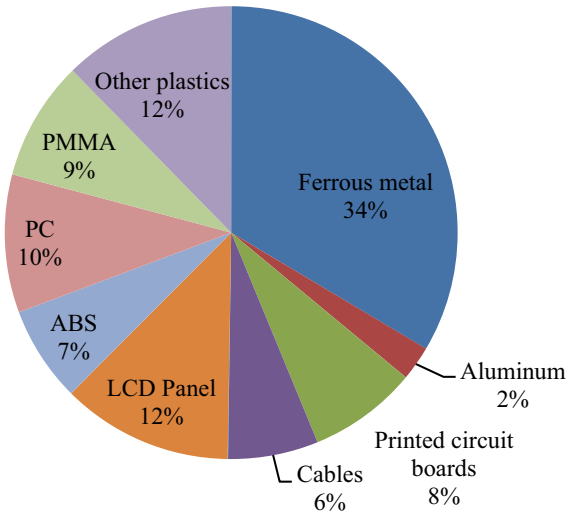

Fig. 1. The main composition and proportion of a computer monitor in terms of mass.

1.1. Disposal status quo of LCD fragments

The current disposal of used LCDs including incineration and landfill, is not only a waste of potential resources, but also brings in tremendous environment risks (Kolias et al., 2014; Kiddee et al., 2013). In fact, different parts in a certain monitor can be used with proper methods. Taken one unit of waste LCD display for example, the composition and individual components are shown in Fig. 1.

1.2. Characterization of the LCD samples

In the existing research studies concerning indium recycling from waste LCDs, hydrometallurgy involving leaching and extraction has been the most common method used. Because the appropriate extractant (P204, Cyanex923, PC88A) and techniques for leaching are well established in the massive indium production industry (Gupta et al., 2004; Jinhui et al., 2012;Kang et al., 2013), leaching can be the foremost step to recycle indium effectively from waste LCD. To liberate ITO efficiently and facilitate the subsequent leaching among the glass particles with acid, the mainstreams of research studies inevitably involved various crushing methods and applicable tools hammer (Hasegawa et al., 2013), ball mills (Rocchetti et al., 2015) and even high-energy ball milling (Lee et al., 2013) and explored the crushing time and optimum particle sizes (Ghosh et al., 2009).

However, some confusing aspects were also revealed among the available research studies. As shown in Table 1, the optimum size, directly related to the maximum recovery percentages, varied over a great span: from 10 μm to 5 mm; thus, these sizes appear to be too inaccurate to be legitimate. Besides, some researchers have reported that excessive grinding may cause indium loss (Rocchetti and Beolchini, 2015). Considering ITO layer to be reported as thin as 125 nm, a non-crushing way is proposed in the paper, and ultrasonic wave were applied to improve leaching efficiency (Li et al., 2009). Moreover, It had been report recently to leach indium from ITO glass without crushing as ITO layer is on the present side (Fontana et al., 2015). Without involving crushing, the entire leaching process can be simplified to free from filtering, and thus to be appropriate for industrial application.

The use of ultrasonic waves has gradually become a practical method to facilitate waste recycling, primarily for sludge and other organic samples (Álvarez Sánchez et al., 2008;Wang et al., 2010). For example, Huang et al. (2011) reported the recovery of copper (Cu) and iron (Fe) from the generated sludge of waste Printed Circuit Boards (PCBs) production. With the enhancement of ultrasonic wave energy, the recycling process of Fe and Cu proved to be more cost-efficient and consume a smaller amount of chemicals (Huang et al., 2011). Li et al. (2014) applied organic acid to the leaching of cobalt (Co) and lithium (Li) from the cathode active materials of spent Lithium-ion Batteries, the ultrasonic-assisted leaching method is demonstrated to be environmentally friendly and to leach both Li and Co efficiently (Li et al., 2014).

The paper aims to propose a non-crushing leaching method for efficient recycling of indium from waste LCDs. Considering the structure of waste LCD glass, the misconceptions about the necessity of crushing are explained. With the aid of ultrasonic waves, high-efficiency indium leaching can be attained with a low concentration of HCl and without extra heating. Different parameters that are crucial to indium leaching, including concentration of HCl, leaching time, and power of ultrasonic power, were all considered, and the appropriate leaching condition was obtained accordingly. The process was proved to be of high efficiency while avoiding excessive leaching of impurities. In addition, the influence and the mechanism of ultrasonic wave agitation on leaching were explained by considering the structure of the waste ITO glass in the study.

Table 1
Study of crushing for the indium leaching from waste LCD.

References	Polarizing film removal	Factors	Optimum Particle size	Explanations
Li et al. (2009)	Yes	Particle sizes 10 mm, 5 mm, 1 mm	5 mm	Higher dissolved indium/power consumption during crushing
Lee et al. (2013)	Yes	Milling time: 30 s, 1 min, 5 min, 10 min, 30 min	7.5 μm 1 min	Larger surface area (excessive fining milling may cause particles to agglomerate)
Silveira et al. (2015)	Yes	Ball mill, knife mill, hammer mill Time 30 min, 1 h, 2 h Removal/without removal	0.15 mm (41%)	Ball mill (less loss of materials) Removal (polarizer won't be adhered to ITO glass) Milling for 2 h Smaller average particle sizes
Rocchetti et al. (2015)	Yes	Particle sizes 0.125, 0.25, 0.50, 1.25 mm, 10 mm	Whole stocks	Higher leaching efficiency for the reduction of particle size (avoiding indium loss)
Kato et al. (2013)	Not available	Not available	2–3 mm	Not available
Ruan et al. (2012)	Yes	Not investigated	1 mm	Not available

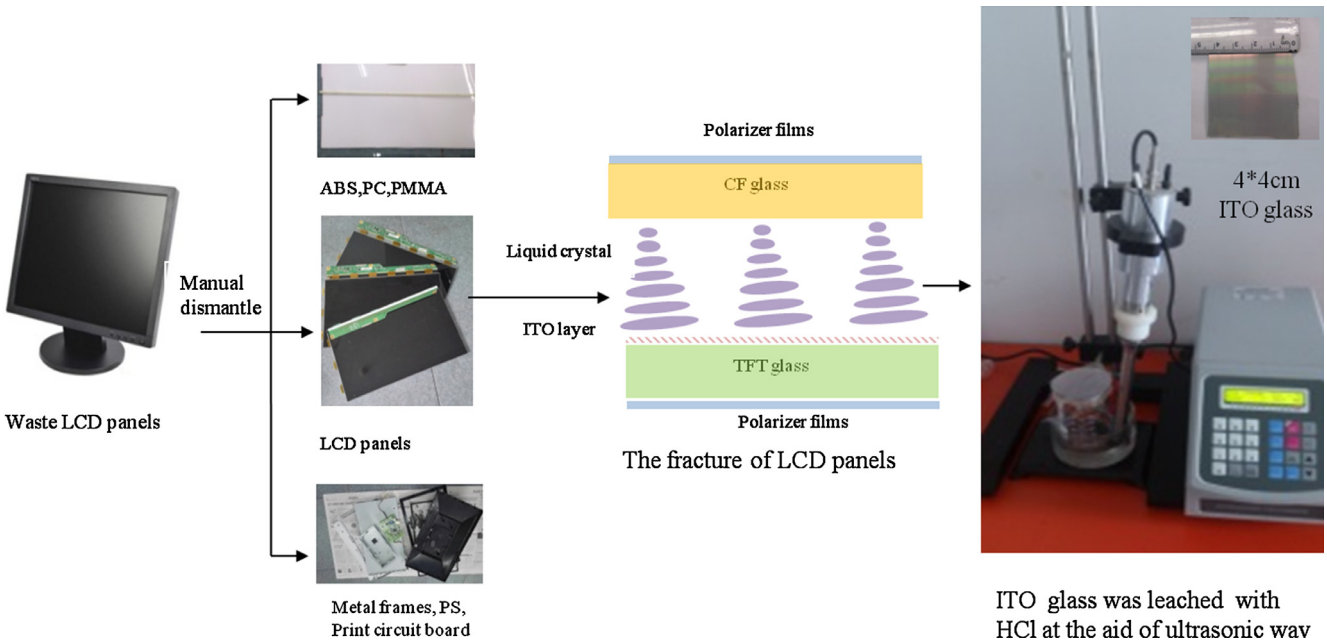

Fig. 2. Non-crushing process for indium recycling from waste LCDs.

2. Materials and experimental

2.1. Pretreatment processing and experimental procedure

A schematic of the process of indium recycling, extending from dismantling to leaching, is shown in Fig. 2. Initially, a waste computer monitor was dismantled manually to obtain the main functional LCD panel. Regarding the other components, including ferrous metals, aluminum frames and different types of plastics (PMMA, PC, and ABS) in the backlight, they can be recycled and sent to a factory for subsequent reuse. The remaining LCD panel was of a sandwich structure, which was composed of two different types of glass substrates (TFT part and CF part) with the adhered polarizing films, and liquid crystal contained in between the two glass substrates. The polarizer films were peeled manually before the LCD panel was immersed in the pure alcohol to make the adhesive bonding far less sticky. Next, the sealants between the two glasses were broken by a knife, and these pieces of glasses were soaked into acetone for 4 h to dissolve the liquid crystal, and pure liquid crystal can be recovered and purified using distillation at a subsequent stage. The upper glass substrate, which is denoted as ITO glass in the rest of this paper, was the primary source of indium. In industrial application, ITO glass has promise to be leached as a whole. However, confined by the common breakers in the laboratory, the piece of ITO glass was reduced into a size of approximately 4 cm × 4 cm. For the leaching process, the coated surfaces were ensured to be placed upward; as a result, the ultrasound and acid could contact with the ITO film directly.

2.2. Chemicals and apparatus measurements

All regents in this research study were of analytic grade and were not further purified. Hydrochloric acid (HCl) and nitric acid (HNO_3) were used as the leaching agents, both supplied by Beijing Chemical Works. Acetone was used to dissolve the liquid crystals. Deionized water was produced in the laboratory to prepare all the solutions. The waste LCD displays were the product of Lenovo. The chemical analysis of the ITO glass before and after milling was conducted using X-ray Diffraction (XRD) (D8 ADVANCE, BRUKEA) and X-ray fluorescence (XRF) (Magix PW2403, PANalytical) to determine the constituents and compositions, and a Scanning Electron Microscope (SEM) (HITACHI, SU-820) was used to observe the structure of the ITO glass. An ultrasonic processor (UBOLA GE750-50, frequency 20 kHz) was used to provide ultrasonic agitation. The concentration of metals, including Al, Fe, In, Ca, Mo, Fe, Mg, Sr, and Mo, in the leaching solution was inspected using ICP-OES (Optima8000, Perkin Elemer).

2.3. Acid leaching treatments

The pure ITO was composed of several oxides of indium and tin. Although the dominant constituents are SnO_2 and In_2O_3, SnO_2 is notably difficult to dissolve using a common mineral acid. Thus, the main reactions of the soluble contents of the ITO in acid solution are as follows (Li et al., 2011):

$$In_2O_3 + 6H^+ \rightarrow 2In^{3+} + 3H_2O \quad (1)$$

$$SnO + 2H^+ \rightarrow Sn^{2+} + H_2O \quad (2)$$

The composition of ITO glass in waste LCDs was more complex than the traditional ITO waste target because of the various coated layers on the special glass substrate. Regarding the acid selection to leach indium from ITO glass, the common mineral acids, including hydrochloric acid (HCl, sulfuric acid (H_2SO_4), nitric acid (HNO_3), and their mixtures, have all been studied; the indium concentration in the leaching solution was found to vary slightly for the different acids considered (Kato et al., 2013; Swain et al., 2016; Pu et al., 2012). Because HCl is of much lower cost among the common mineral acids, it was chosen in the study, as it has potential for use in massive industrial application. A recent trend is the use of organic acids, such as citric acid ($C_6H_8O_7{\cdot}H_2O$), acetic acid (CH_3-COOH), and lactic acid ($C_3H_6O_3$), in metal recycling (Li et al., 2015, 2014). Organic acids were not considered in the paper because of the complexity of organic acids hindering the separation and purification in the extraction.

With the ultrasonic wave providing energy to activate the reaction, the initial temperature was kept at room temperature. Each ITO glass sample was leached in 20 ml of HCl while ensuring the

following: ITO glass was completely submerged, the L/S is around 10:1. The transmission and absorption of ultrasonic waves was unimpeded during leaching, and the coated surface was facing upward to ensure direct contact with the hydrochloric acid. Then, transfer 20 ml of the leachate to a volumetric flask, dilute with purified water to volume and mix for the preparation of ICP test sample, the concentrations of metals in the HCl solution is remarked as C_1 (mg/L), and the volumes of the HCl solution is remarked as V_1 (ml), Next, the same piece of glass was leached in 20 ml of aqua regia to dissolve indium fully for the calculation of the indium recovery percentage, then heat the aqua regia to drive acids, and prepare the ICP test samples as the test sample of HCl solution. The indium concentration in aqua regia is remarked as C_2 (mg/L), and the volume of aqua regia solution was remarked as V_2 (ml). The indium concentration of the batch of ITO glass was approximately 120 mg/kg.

The indium recovery percentages (μ) can be determined via Eq. (3). Because the total dissolution of the other elements was difficult to ascertain without digestion, the leaching capacity (β) was calculated using Eq. (4) to evaluate the leaching reaction, where m (kg) is the mass of ITO glass. To determine the appropriate leaching time, the proportion of a particular element among the leaching solution (w) was calculated using Eq. (5) by substituting the concentration of a particular element (C_n) and the concentration of the examined metals (C_i):

$$\mu = \frac{C_1 V_1}{C_1 V_1 + C_2 V_2} \times 100\% \tag{3}$$

$$\beta = \frac{C_1 V_1}{m \times 10^{-3}} (\text{element} - \text{mg/ITOglass} - \text{kg}) \tag{4}$$

$$w = \frac{C_n V_1}{\sum C_i V_1} \times 100\% = \frac{C_n}{\sum C_i} \times 100\% \tag{5}$$

3. Results and discussion

3.1. Characteristics of leaching in a non-crushing manner

The interior side of the ITO glass was with various coated layers, according to the XRF elemental analysis of the ITO glass substrate shown in Table 2, indium only comprised approximately 3%. Crushing appeared to be a reasonable and necessary step when simply considering the composition of ITO glass. The use of smaller particles was expected to increase the contacting surface area with the acid, thereby improving leaching efficiency. Thus, finer particle size was pursued in hydrometallurgy. However, the above-described analysis is not appropriate for ITO glass because of its structure, i.e., it is not composed of components of uniform elemental composition.

Table 2
XRF results: the composition of ITO glass before milling.

Elements	Concentration (mass ratio %)
Si	55.10%
Al	10.50%
Ca	9.24%
In	3.00%
Sr	1.36%
Sn	0.40%
Mg	0.57%
Fe	0.02%
Mo	0.06%
O	19.30%
Others	0.45%

Various functional layers, including Al, Mo and ITO, are involved in the fabrication of an ITO glass substrate (Yu, 2008). In addition, as shown in Fig. 3a, from the XRD results of the ITO glass substrate, indium oxide is found to be the dominant phase. Despite the low contents of In and Sn, this XRD result provides a clue that ITO is deposited on the outmost surface. No phase of tin oxide was observed because the radius of Sn^{4+} is similar to In^{3+}, and tin ions enter into the crystal lattice of indium oxide. As a result, ITO could come into contact with acid efficiently without further crushing.

Next, from the XRD results after crushing ITO glass particles (hundreds of micrometers), shown in Fig. 3b, the former prominent phases, including Al, Mo and indium oxide, are no longer apparent, whereas the amorphous phase was clearly observed. The exposure of glass powder from excessive crushing caused the amorphous phase to cover the previously outermost surface of ITO, thereby interfering with the X-rays interacting with ITO. With the transformation of the sample after size reduction, the effect of grinding on the contact between particles and acid is detrimental when considering the destruction of the ITO film structure. In addition, with grinding of the ITO glass substrates, more acid might be consumed to dissolute the trapped impurities, thereby resulting in extra consumption of the extractant for indium separation and purification

As for the special glass substrate, it is potential to reuse in the future production treated in the non-crushing way (Wang et al., 2013), rather than applying as raw materials of ceramics and bricks (Lin et al., 2009; Wang, 2009).

3.2. Orthogonal experiment design

A three-level orthogonal experiment was designed, as given in Table 3, to explore these unknown key matters (the concentration of HCl, the power of ultrasonic wave, and the reaction time) and to determine the interactions of the separating factors. Rather than traditional heating, the use of ultrasonic waves was chosen to provide energy and stimulate the acid leaching. With ultrasonic excitation, only low concentrations of HCl were considered to dissolve the ITO layer. From the results of the orthogonal experiment listed in Table 3, the indium recovery percentages (μ) positively corresponded to all the individual parameters. Thus, level 3, which reflected the maximum value for all the parameters, appeared to be the optimal setting, with the corresponding indium recovery percentages exceeding 90%. From a comparison of the maximum deviation, the reaction time was found to have the most influence on indium leaching, whereas the ultrasonic power had the least influence. Taking into account the recovery percentages of (Nos. 3, 5 and 7) ($\mu > 95\%$), the base condition was set as 0.8 mol/L HCl with the aid of ultrasonic agitation at a power of 300 W for 60 min; the ultrasonic agitation can effectively reduce the energy consumptions and decrease the acid concentration.

3.3. Effect of acid and reaction temperature

Because ultrasound itself provides energy to the leaching system, it is difficult to maintain a constant temperature in the solution; thus, no additional heating was given in the leaching system. In addition, selective leaching was attained, as Mo was not detected in the leaching solution. The leaching of Mo can be averted by leaching with HCl at room temperature initially. This selective leaching was also beneficial for the subsequent extraction, because Mo is easily co-extracted with indium by using a common extractant D_2EHPA (Zimmermann et al., 2014).

3.4. Effect of the concentration of HCl

Considering indium concentration on the ITO glass was of a low amount (120 mg/kg), low concentrations of HCl (<1 M) was able to

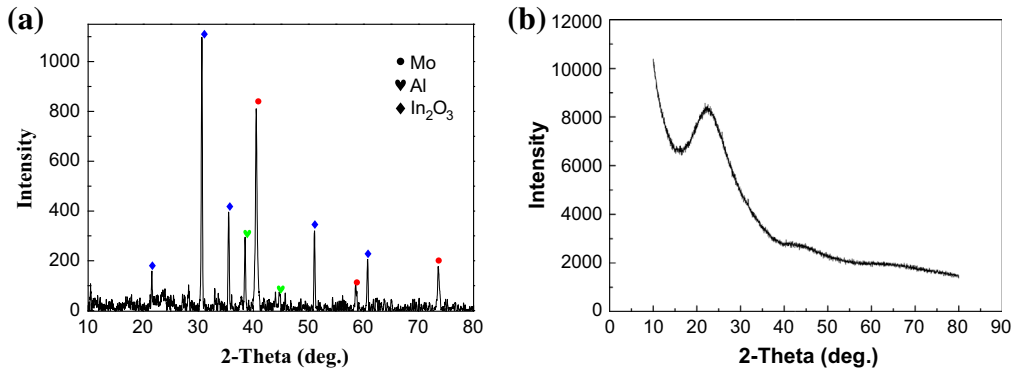

Fig. 3. XRD analysis for (a) ITO glass and (b) ITO glass powder after crushing (<100 μm).

Table 3
Experimental results and analysis for orthogonal design.

		Concentration (mol/L)	Ultrasonic power (W)	Reaction time (min)	Indium recovery percentages (μ) (%)
Level	1	0.6	225	30	
	2	0.8	300	45	–
	3	1	375	60	
No.	1	0.6	225	30	24.32%
	2	0.6	300	45	73.14%
	3	0.6	375	60	100.00%
	4	0.8	225	45	56.53%
	5	0.8	300	60	98.58%
	6	0.8	375	30	82.11%
	7	1	225	60	100.00%
	8	1	300	30	75.76%
	9	1	375	45	100.00%
	Level 1	65.82%	60.28%	60.73%	–
	Level 2	79.07%	82.49%	76.56%	
	Level 3	91.92%	94.04%	99.53%	
	Max deviation	26.10%	33.75%	38.80%	

leach indium efficiently. The ITO glass was leached at room temperature for 60 min when 300 W of ultrasonic power was applied. As shown in Fig. 4, the indium recovery percentages (μ) positively correlated with the concentration of HCl. This result is explained easily by the increasing amount of H^+ available to attach to the ITO layer in dissolution: the indium recovery percentages reached to 96.82% when the concentration of HCl was 0.8 M. Therefore, 0.8 M of HCl was chosen as the most appropriate concentration for indium leaching. Indium was certainly the most privileged constituent, and the increase of H^+ had a great effect on the leaching of In and Al. Regarding these elements, including Fe, Mg and Ca, the leaching capacity was less than one-tenth that of indium, and their concentrations showed little enhancement after the acid concentration reached 0.6 M.

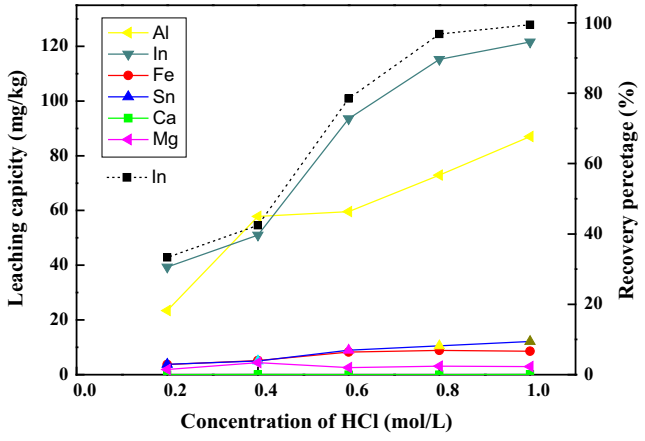

Fig. 4. Effect of the concentration of HCl on indium leaching. (20 ml HCl, 25 °C; dotted line: recovery percentage; straight line: leaching capacity).

3.5. Effect of the leaching time

As layers of different compositions were coated to produce the ITO glass, certain layers are dissolved in a certain sequence. Thus, the leaching time was the key condition to ensure the dissolution of indium to be the major reaction; otherwise excessive impurities are added into the solution. The pieces of ITO glass used in this research group were leached by 0.8 M HCl with the aid of 300 W of ultrasonic agitation at room temperature for leaching times that varied from 15 min to 75 min. As shown in Fig. 5, the proportions of certain elements are related to distributions and amounts. In and Al were of a dominating proportion in the leaching solution which indicates that they are the main components in the leaching solution. The proportion of Al In particular, indium was the primary constituent in the solution from 30 min to 90 min. Although the proportion of In was greater than 45% after 30 min, the short interval may not be an appropriate parameter for the relatively higher compositions of impurities. The proportion of Al reaches to its maximum in 15 min, since it is of greater amount than other substances. As for the proportions of impurities, including (magnesium) Mg, (Iron) Fe and (Calcium) Ca, attained an apparent increase in 30 min and did not show a clear change afterward. Therefore, it can be concluded that a fraction of these impurities might still be

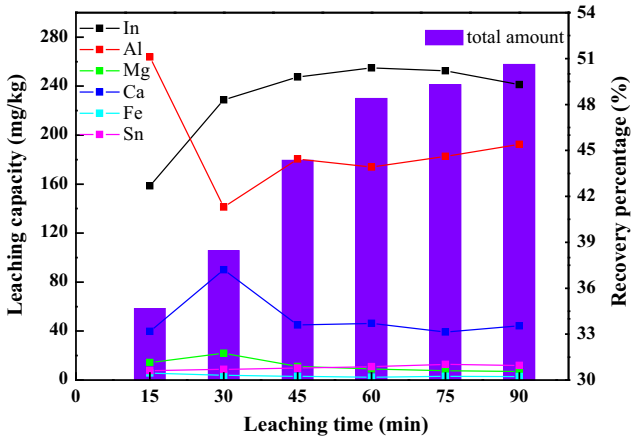

Fig. 5. Effect of leaching time on indium recycling. (20 ml HCl, 25 °C; total leaching capacity covering In, Al, Ca, Mg, Sn, Fe, Sn, and Mo; the main elements shown in XRF; the straight line: the proportion of certain elements in the leaching solution).

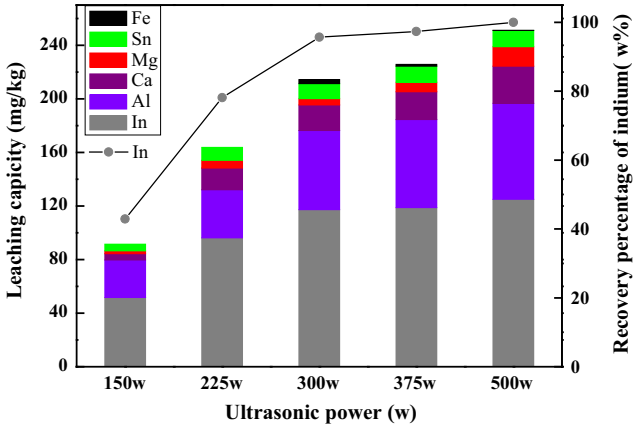

Fig. 6. Effect of ultrasonic power on indium recycling (20 ml HCl, 25 °C; straight line: recovery percentage).

on the outermost surface, their dissolution can be accomplished initially, and despite that they cannot be detected by XRD. The leaching of impurities cannot be avoided by adjusting the leaching time. The total leaching capacities increase with more layers dissolved. The proportion of (indium) In reached a peak at 60 min, and declined hereafter, while the proportion of (aluminum) Al kept increasing, because the main reaction after 60mins did not involve the leaching of ITO but Al. As a result, the leaching was performed for 60 min, i.e., when the recovery percentage of indium exceeded 95%.

3.6. Character of leaching with the ultrasonic-wave

The influence of ultrasonic power was investigated when each piece of ITO glass in the research group was leached by 0.8 M of HCl for 60 min at room temperature. As shown in Fig. 6, the recovery percentage of indium is positively correlated with the ultrasonic power and reached up to 95.69% when the power of ultrasonic agitation was 300 W. Although the complete dissolution of indium oxide could be further achieved increasing the ultrasonic power to 375 W, 300 W was chosen as the most appropriate ultrasonic power to assist the indium leaching to reduce the energy consumption.

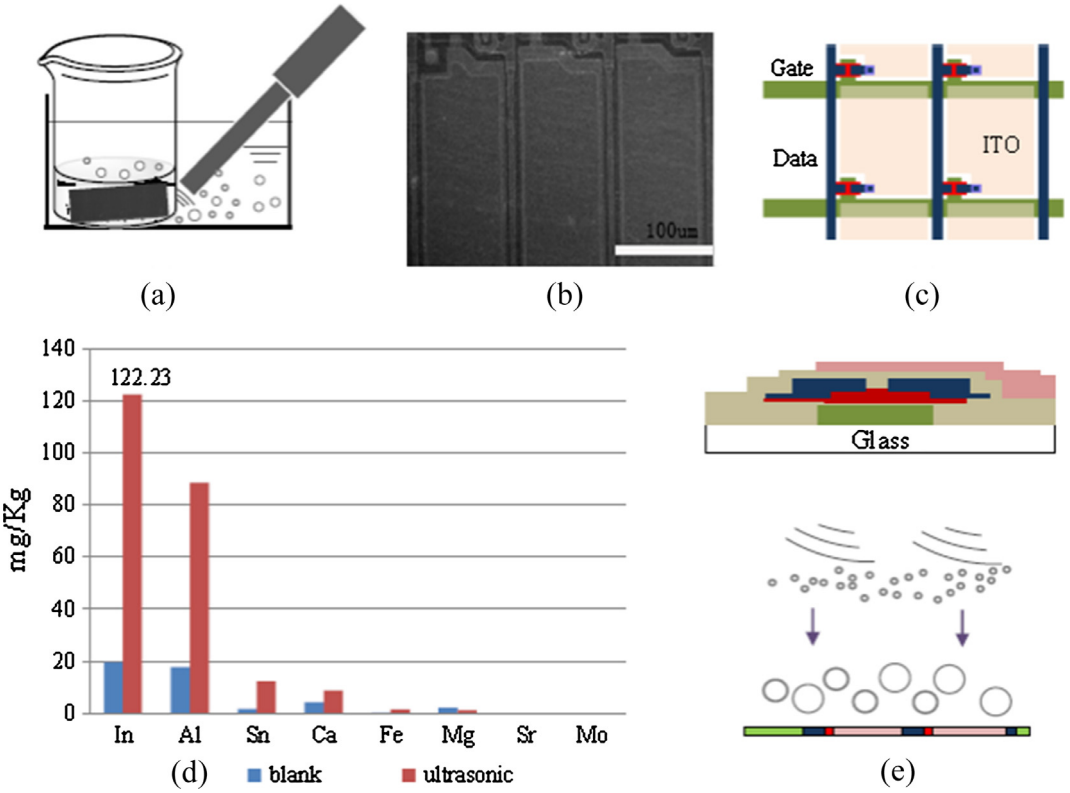

Fig. 7. Mechanism of ultrasonic-assisted leaching indium from waste ITO glass. (a) Schematic of the setup for leaching assisted by ultrasonic wave agitation; (b) SEM image of ITO glass; (c) graphical illustration of the TFT components; (d) effects of ultrasonic agitation on the leaching capacity of individual elements; (e) influence of the cavitation effect on ITO glass.

3.7. Brief explanation of the influence of the ultrasonic wave agitation

The leaching capacities of various elements were enhanced with the increase of ultrasonic wave power. The enhancement provided by ultrasonic wave agitation on leaching can be primarily explained as the combination of energy input and percussion. First, the energy input to leaching system is reflected by the temperature increase of the solution, 25–46 °C. In addition, the ultrasonic waves also affected the convective motions among the solution, allowing fresh H^+ to come into contact with the ITO glass particles and transport the dissolved metal ions away, thus promoting diffusion that improved the recovery percentages.

Further comparison of the leaching experiment with certain similar conditions (0.8 M HCl for 1 h at room temperature without the aid of ultrasonic agitation), the heterogeneous influence of different elements was clear: the enforcement of ultrasonic waves mainly reflected the leaching capacity of In, Al, Sn and Ca, as shown in Fig. 7(d). In contrast, for the elements of low percentage, such as Fe and Mg, the contents remained extremely low and were barely impacted by ultrasonic agitation. In fact, this result was related to one of the distinctive characteristics of ultrasonic waves - the cavitation effect, which acts directly on the outermost surface.

The integrated structure of ITO glass was preserved in the leaching process due to the adoption of non-crushing method. From the SEM image of the ITO glass in Fig. 7(b), it was observed to be composed of repeated units. To display the structure of different layers explicitly, a schematic of the functional components is shown in Fig. 7(c). Those multiple layers of various compounds were deposited onto soda-lime-silica glass (main body) during the course of fabrication: the ITO was sputtered deposited at the outmost surface via a magnetron sputtering system; the Mo and Al layers appeared alternately and repeatedly reacting as the Gate and Data layers; many dielectric protective layers (SiNx, etc.) had been deposited using plasma enhanced chemical vapor deposition. The sequence and distribution of those layers was shown in Fig. 7 (e) (upper part) by a schematic of the parallel compositions of the ITO glass after being cut longitudinally. When it comes to the contact of acid and influence by the ultrasonic wave, it can be the outermost surface, and it was shown in Fig. 7(e) (lower part) (Rack and Holloway, 1998;Yu, 2008).

As shown in Fig. 7(a), the ultrasonic wave was generated by an ultrasonic amplitude transformer, and the ultrasonic wave impacted the outermost surface of the ITO glass. During the transmission, an enormous number of micro vacuum holes were produced in the solution, and the bubbles enlarged gradually as the sound pressure continually increased via transmission of the ultrasonic wave (Eskin, 1995). These growing bubbles attack the outermost surface, and finally burst during the stage of negative process in only 0.1 μs. Thus, high pressure (tens of thousands pounds per square inch) is directly applied to the outermost layer, thereby accelerating leaching of In, Sn and Al. The leaching of Ca can be facilitated because the glass substrate inevitably also comes into contact with the ultrasonic wave. Indeed, the increase of ultrasonic power enhances the cavitation effect as the reaction time lengthens and the intervals shorten. Therefore, the application of ultrasonic agitation was suitable for the leaching of ITO glass, with enhanced leaching mainly for In and Al and with little impact on the other impurities.

4. Conclusions

The average indium content of the present series of waste LCD is approximately 120 mg/kg, and is notably suited for recycling. On the basis of structure analyses, the ITO layer is proved to be sputtered at the outermost surface. Despite the low concentration of indium (less than 3%), the ITO layer might be leached as a whole. Therefore, an innovative non-crushing approach was proposed to leach indium from waste LCD, and ultrasonic wave agitation is used to accelerate the indium leaching. In the case, the leaching process can be conducted without extra heating. Moreover, the chosen of HCl, as the leaching agent avoids the dissolution of Mo, and thus reduces acid consumption and impurities in the leaching solution. The optimal parameters were confirmed to be 0.8 M HCl with the aid of 300 W of ultrasonic wave agitation for 60 min, and the recovery percentage of indium was approximately 96% for the optimal conditions. The mechanism of ultrasonic wave agitation on the leaching process was explained by exploring cavitation effect and the layered-coating structure of the ITO glass. This work illustrates the potential of ultrasonic wave enhancement to leach indium from waste LCD, meanwhile the non-crushing method proves to be efficient regarding the design of analysis of the waste ITO glass, i.e. a recycling method for waste LCD with less steps and high efficiency.

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