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# **Metal-oxide nanomaterials recycled from E-Waste and metal industries: a concise review of applications in energy storage, catalysis, and sensing.**

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## **SUMMARY**

There are abundant sources of metal-oxide based wastes from industries such as electronics and metal production, which generally have a detrimental effect on the environment when not recycled. In this concise review, we aim to provide a brief overview of the state-of-the-art research on how these metal oxide wastes are being used by the scientific community in the applications of energy storage, catalysis, and sensing. We focus on three important waste streams: e-waste, waste from the production of metals, such as red mud and slag, and waste from metal recovery, for example, rusted wires and discarded capacitors. We review some promising routes for obtaining high-quality metal oxide nanoparticles and nanowires and critically review potential pitfalls that hinder the wide-scale application of these waste-streams.

## **KEYWORDS**

Waste, Metal oxides, Energy storage, Catalysis, Electrochemistry

## 1. INTRODUCTION

As our planet's population increases in the coming decades, we require innovative methods to deal with all our distinct types of waste, including metal-oxide inorganic wastes from the electronics and metal production industries. However, growing awareness among populations worldwide is leading to pressure on governments and intergovernmental bodies to take action on waste reduction. Whilst the re-use and recycling of biomass <sup>1-3</sup>, paper <sup>4</sup>, cardboard <sup>5</sup>, and, increasingly, plastics <sup>6</sup> and polymers <sup>7</sup> have received a significant amount of research and publicity <sup>8</sup>, the re-use of many inorganic metal-oxide materials is relatively embryonic. Meanwhile, there is a wealth of research in the synthesis of metal-oxide nanomaterials for many applications, but especially in electrochemical energy storage, catalysis, and sensors. Thus, we hope to encourage more research on how some metal oxide wastes can be increasingly recycled for usage in these applications.

The sheer overall mass of inorganic waste produced each year poses a significant challenge to our environment but, correspondingly, offers a significant opportunity if these can be usefully re-used. A summary of the dominant types of wastes, estimated current production, and current usage is shown in table 1. For example, the electronics industry was estimated to produce 35 million tonnes of waste in 2014 <sup>9</sup>. In metal production industries, aluminium production yields a waste by-product of around 120 million tonnes of waste 'red mud' each year, adding to a stockpile of around 3 billion tonnes <sup>10</sup>. Red mud is an iron-oxide rich mixture of several metal oxides, including SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> <sup>11</sup>. Meanwhile, the estimated annual global production of iron slag is 300 to 360 million tonnes, along with 190 to 290 million tonnes of steel slag.<sup>12</sup>

**TABLE 1** Summary of the current production and utilization of the wastes focused on in this review.

<b>Class of waste</b>	<b>Estimated current production</b>	<b>Current use of wastes</b>
Electronic waste	~ 35 million tonnes <sup>9</sup>	Some raw metals (copper, gold, etc.) are recovered.
Metal production (Red mud)	~ 120 million tonnes of waste <sup>10</sup>	Largely stored in red mud lakes <sup>13</sup> , some research for use in building materials <sup>14</sup> and dye removal <sup>15</sup>
Metal production (Slags)	~490 to 650 million tonnes <sup>12</sup>	Currently either used for making cement, iron recovery <sup>16</sup> or deposited in storage yards <sup>17</sup>

One issue arising from the ‘production’ of this high quantity of waste is how it is stored. The storage of such an extensive amount of waste has damaged and degraded the environment in many countries. For example, infamously in 2010, a lake, holding around a million tonnes of red mud sludge spilled out into the environment near Kolontar, Hungary<sup>13</sup>. Nine people died from contact with the highly alkaline sludge and over 100 were injured, whilst an area of some 800 hectares of land was damaged. Thus, the environmental and human cost of metal-oxide based wastes is becoming more recognizable, and scientific interest is growing to tackle this issue.

The recycling and so-called ‘urban mining’ of e-wastes and other wastes into *pure metals* is well-reviewed elsewhere, for example by Zeng *et al.*<sup>18</sup>. Here, we wish to encourage research into how waste-based metal oxides, rather than being purified into metals, may be used. In this review, we focus on methods to help utilize some sources of waste that damage our environment and convert them into materials that help our planet. Mainly, we aim to highlight

some of the sources, processing methods, and applications for metal-oxide waste-based materials in electrochemical energy storage (batteries and supercapacitors), in catalysis, and also as electrode materials for electrochemical sensors.

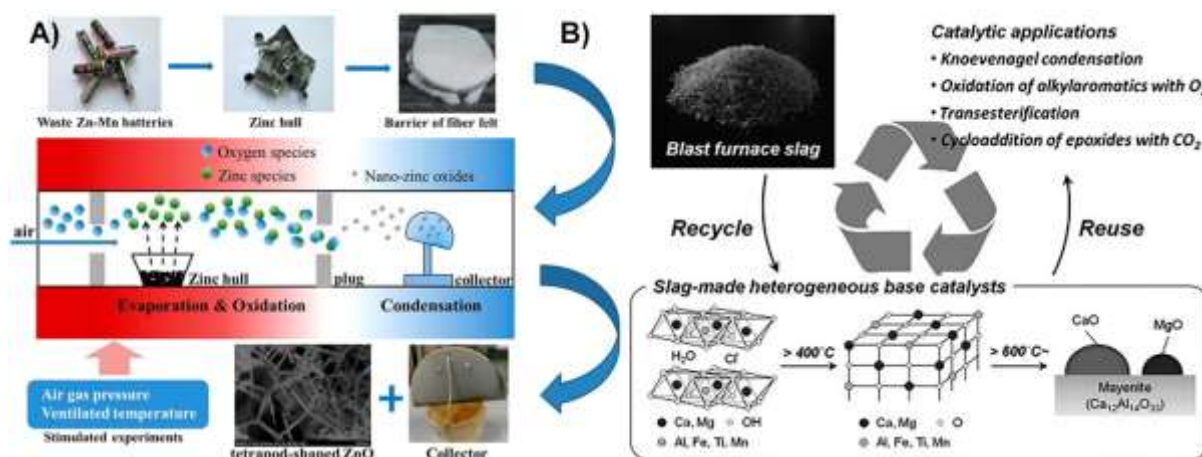
## **2. SOURCES, PROCESSING, AND APPLICATIONS OF INORGANIC WASTE**

### **2.1. E-waste**

The revolution in information communication technology has led to an abundance of E-wastes in many countries, but innovative ways to deal with this waste are appearing. The re-use of waste manganese batteries is attracting research as an abundant source of waste metal oxides: some 60 billion manganese-based batteries are produced annually<sup>19</sup>. For example, Lu Zhan *et al.*<sup>20</sup> recently produced nano-zinc oxide for potential sensing and catalysis applications, from discarded zinc-manganese batteries as shown in Figure 1 A). Initially, the zinc hull of the battery was removed and loaded into a corundum crucible and heated in a furnace under airflow and condensed onto a silicon steel sheet. Oxidation was controlled using a fibre-felt wrap around the crucible, which enabled a high (90.94 %) recovery of zinc to nano-zinc oxide on the steel substrate. The nano-zinc oxide had a crystalline, whisker morphology of ~80 nm diameter. Whilst this work demonstrated a potentially promising route for the re-use of Zinc manganese batteries, the material was not used in an application and cannot be compared with virgin materials, and no overall cost or environmental analysis was performed. Furthermore, Farzana *et.al*<sup>21</sup> recovered  $Mn_3O_4$  by initially pulverizing spent Zn-C battery powder, which contained  $MnO_2$ , in a ball milling machine, and subsequent thermal transformation of the powder up to 900 °C. The treated  $Mn_3O_4$  powder showed promising performance as supercapacitor electrodes, with a specific capacitance of  $125\text{ F g}^{-1}$  at  $5\text{ mV s}^{-1}$  scan rate and 80 % retention after 2100 cycles ( $1.2\text{ Ag}^{-1}$  current density), it should be noted that a  $Mn_3O_4$  synthesised from a commercial precursor<sup>22</sup> showed a significantly higher capacitance: 416

$F g^{-1}$  at  $5 mV s^{-1}$  which raises questions whether this waste-based material currently would be preferable to commercially produced competitors.

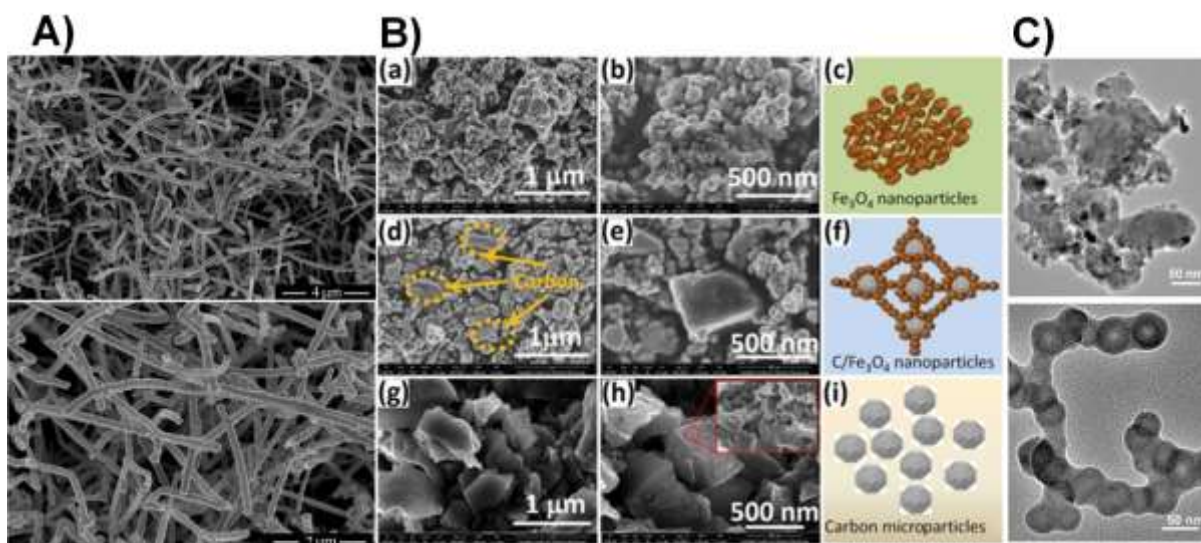
Waste film resistors are increasingly being recognized as valuable sources for the production of nanomaterials. Ruan *et al.*<sup>23</sup> showed how both the major components of metallic film resistors (~33 % ceramic and ~ 65 % nickel) may be recovered in an efficient process. The film was initially sheared using an industrial shearing machine (capacity of 5 kg/min) into macroscopic particles and then separated using a magnetic drum separator (capacity of 25 kg /min) with a 100 % separation rate of nickel and ceramic materials. XRD analysis showed that the ceramic matrix was  $Al_2O_3$  which was then ball milled (capacity 0.41 kg/hour) to nanoparticles (NPs) from 100 to 500 nm diameter. The recovery of  $Al_2O_3$  NPs from film resistors is a promising method for recovering a valuable resource, though progress may be made by increasing the throughput of ball milling such that it better matches the earlier processes and also improving the homogeneity in size of the NPs.



**Figure 1** Summary of two scheme for recycling: A, nano-zinc oxide from waste zinc-manganese batteries via thermal evaporation (Reprinted from the work of Zhan *et al.* ref. 13, Copyright (2018) American Chemical Society, B, Blast furnace slag into heterogeneous base catalysts, reprinted with permission from ref. 32, Copyright 2012 Wiley.

Bo Niu *et al.* <sup>24</sup> used a similar resource, multi-layer ceramic capacitors (MLCC), to recover NbPb co-doped and Ag-Pd-Sn-Ni loaded BaTiO<sub>3</sub>. The processing method was an efficient one-step process: MLCCs were disassembled and pulverized using a ball mill and obtained irregular NPs of 100 to 200 nm diameter. XRD showed the recycled material was BaTiO<sub>3</sub> and XPS investigation of the doping showed Nb-Pb co-doping and loading with Ag-Pd-Sn-Ni. Comparing this, in a photocatalyst application, to a commercial BaTiO<sub>3</sub> powder showed that the recycled material had a higher charge transfer and separation efficiency, with H<sub>2</sub> evolution and rhodamine blue degradation rate of 156.7 μmolg<sup>-1</sup> h<sup>-1</sup> and 0.06207 min<sup>-1</sup> respectively: 3.08 and 4.5 times higher than the commercial BaTiO<sub>3</sub> powder.

Another widely discarded E-waste is computer monitors. Maroufi *et al.* <sup>25</sup> used both the glass (used as a source of silica) and polymer shell (used as a source of carbon) of discarded computer monitors to produce ‘green’ Si<sub>3</sub>N<sub>4</sub> nanowires for future heterocatalysis applications as shown in figure 2 A). The glass screen was pulverized into a powder, whilst the polymer was pyrolyzed under a nitrogen purge at 1550 °C. The resultant Si<sub>3</sub>N<sub>4</sub> nanowires, which were predominantly β-Si<sub>3</sub>N<sub>4</sub> crystalline phase, and with a twisted nanowire morphology of 75 to 250 nm diameter. The nanowires showed favorable photocatalytic degradation of methylene blue compared with Si<sub>3</sub>N<sub>4</sub> nanoparticles though since these were not fully benchmarked against ‘gold standard’ materials, the question of whether this synthesis route may translate into industry is unclear and requires further investigation.



**FIGURE 2** Examples of synthesis of nanomaterials using waste-based metal oxides: A,  $\text{Si}_3\text{N}_4$  nanowires from computer screens, adapted with permission from ref. 18, Copyright (2018) American Chemical Society, B, (a-h) processing of  $\text{Fe}_3\text{O}_4$  – carbon microparticles, image adapted with permission from ref. 26, Copyright 2018 Wiley, C, TEM images showing the comparison of raw red mud in the raw, un-processed state (a-b) and (c-d) after 10 hour ball milling, spherical NPs have been obtained, image adapted with permission from ref. 29, Copyright 2019 Wiley.

The supply of LCD screens reached 683.5 million units in 2016, and discarded units are often incinerated or buried in landfills. Kang *et al.*<sup>26</sup> used such waste LCDs as a promising source of silicon NPs for lithium-ion battery anodes. Initially, they crushed and sieved the waste LCD glass through a 200 mesh into a fine powder. The white silicon powder was then further processed through ball milling, then treating with  $\text{HNO}_3$  to remove impurities such as Al, Ca, Sr, and B, followed by magnesiothermic reduction at 650 °C. After processing, >99% pure silicon was obtained with a few aluminium contents and NPs size distribution of 400 to 550 nm. The Lithium-ion half-cell test using the purified LCD screen wastes had a gravimetric capacity of 1710 mAh  $\text{g}^{-1}$  after 100 cycles at a current density of 0.5 A  $\text{g}^{-1}$ . Comparable work by Sun *et al.* using non-waste stream Silicon nanoparticles yielded a gravimetric capacity of 954 mAh  $\text{g}^{-1}$  after 200 cycles at a current density of 0.6 mA h  $\text{g}^{-1}$ , which suggests a



reasonably similar performance between the waste and non-waste based silicon nanoparticle performance.<sup>27</sup>

## 2.2 Recovered waste metal

Rapid industrialization and a massive improvement in our lifestyle have produced extensive metal-based industrial and domestic wastes. The recycling of such waste is beneficial to the sustainable development of society. Motivated by this, Wang *et al.*<sup>28</sup> converted waste stainless-steel (SS) recovered from window screens into porous, anodized SS mesh with a high surface area under hydrothermal atmosphere. Briefly, the mesh was cleaned in a mixture of a base solution of NaOH, Na<sub>2</sub>SiO<sub>3</sub>, sodium dodecyl sulfate, and polyoxyethelene octyphenol ether at 60 °C for 4 h. To remove the oxide layer, the mesh was further electrochemically polished for 20 s using an aqueous acid mixture of sulfuric acid and citric acid at a current density of 5 A/dm<sup>-2</sup>. Finally, the cleaned mesh was kept in a modified hydrothermal chamber and was anodized at 120 °C for 30 min using a current density of 5 A/dm<sup>-2</sup> and dried in a vacuum oven. As a result of this anodization, a nanocomposite of Fe<sub>2</sub>O<sub>3</sub>/NiO was fabricated and was utilized as a negative electrode for electrochemical energy storage as a supercapacitor. They used a 3-electrode assembly using the anodized mesh as working, Hg/HgO reference, and platinum slide as a counter electrode in 1M KOH solution. The mesh exhibited a high maximum areal capacitance of 1.22 F cm<sup>-2</sup> at a current density of 0.5 mA cm<sup>-2</sup> with remarkable cyclic stability of 93.3% of retention of initial capacitance even after 10,000 cycles and good flexibility. The waste-derived porous activated material, therefore, can be used as an effective negative electrode for flexible energy storage application. But, it is to be noted that a similar material (the core-branch Fe<sub>2</sub>O<sub>3</sub>@NiO nanorods arrays directly grown on flexible carbon cloth) synthesized using hydrothermal route exhibited better performance with an exceptional cycling performance of 96.8% initial capacitance retention at a current density of 20 mA cm<sup>-2</sup> even after 16,000 cycles.<sup>29</sup>

Tan *et al.*<sup>30</sup> presented a novel approach to recycle heavy metal-contaminated sewage sludge into an effective energy storage material. They used an effective route to remove toxic Cu (II) from wastewater and subsequently produced a Cu-doped carbon electrode for supercapacitor applications. They synthesized a carboxyl group functionalized starch derivative and used that as a flocculant for Cu (II) removal. The dosage of the flocculant was optimized, and they employed the subsequent pyrolytic conversion method used to produce Cu-doped porous carbon. More than 99% of Cu (II) removal was achieved. The electrochemical performance was examined in a 3-electrode configuration with the active material as working, platinum foil as counter, and saturated calomel electrode (SCE) in 6M KOH electrolyte. The electrode exhibited a high specific capacitance of 389.9 F g<sup>-1</sup> at a current density of 1 Ag<sup>-1</sup> along with 96% retention of initial capacitance after 2500 cycles indicating its suitability as a supercapacitor electrode. This work focuses on an equilibrium state between heavy metal removal efficiency and specific capacitance of the derived electrode; and it was found that a better specific capacitance can only be achieved at the expense of poor removal efficiency and thus limits its applicability.

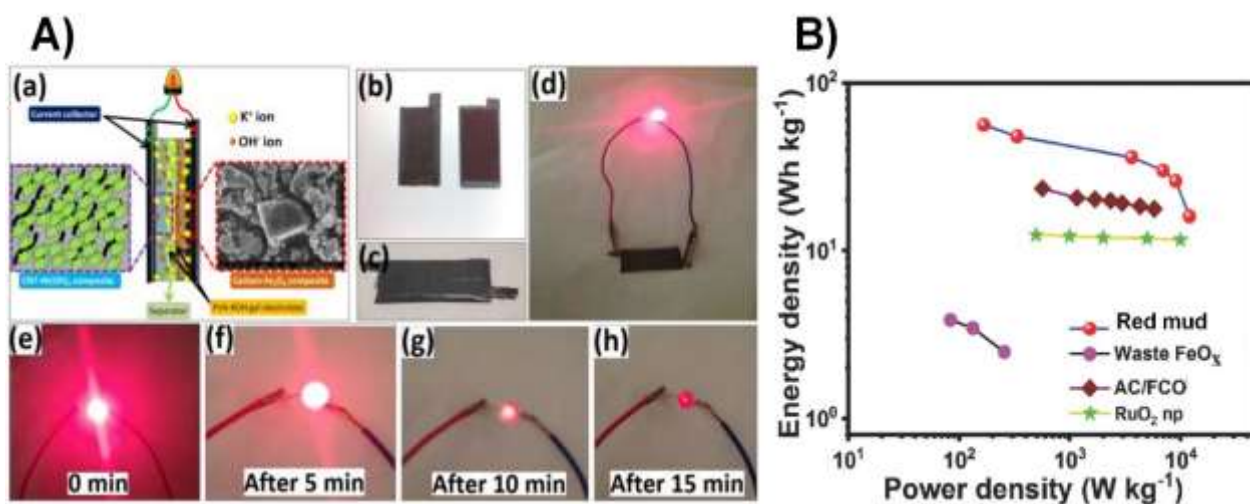
Deganello *et al.*<sup>31</sup> collected rust waste from a transmission line tower manufacturing unit and used it as a cheap, eco-friendly source of iron. They synthesized an iron-rich LaFeO<sub>3</sub> perovskite-type powder by a solution combustion technique using the scraped rust. Their work represents a novel approach for direct conversion of insoluble inorganic waste precursors into nanomaterials avoiding any complex activation/extraction process and the rust precursor directly transforms into the end-product. The waste-derived perovskite nanomaterial was used to determine its catalytic activity towards propylene oxidation. The activity was studied as a function of waste-rust loading and iron-rich samples exhibited increased catalytic activity. According to the report, the methodology can be easily extended to other iron perovskites with

different chemical compositions for different applications. Although the catalytic performance is encouraging, and the synthesis process does not need any activation, the solution conversion process is complex and expensive.

Mhamane *et al.*<sup>32</sup> collected waste rusted wires from scrap and converted them into surfactant-free interconnected hematite phase iron oxide. To produce the NPs, they cut and washed the as-collected wires and treated with a concentrated HCl at an elevated temperature (65 °C) under constant stirring. The as-obtained pale yellow color solution was further treated with concentrated HNO<sub>3</sub> for the conversion of Fe<sup>2+</sup> into Fe<sup>3+</sup>. NH<sub>4</sub>Cl, NH<sub>3</sub>, and DI water were further added to the solution mixture to obtain a brown precipitate of iron oxyhydroxide (FeOOH). The mixture was washed, centrifuged, and annealed to obtain the hematite NPs. The applicability of the as-synthesized  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> as anode for Li-ion battery applications was further studied, where the NPs served as a low-cost conversion type anode material for the fabrication of Li-ion cells with an eco-friendly LiMn<sub>2</sub>O<sub>4</sub> cathode. In a half-cell configuration, the as-synthesized hematite NPs exhibited a capacity of ~1119 mAh g<sup>-1</sup> at a current density of 0.05 Ag<sup>-1</sup> with a high power capability and cyclic stability. A pre-lithiation of the NPs decorated electrode was carried away before the full cell assembly. In the full cell configuration, the device displayed an initial reversible capacity of 737 mAhg<sup>-1</sup> with 78 % retention after 40 cycles. Whilst, the work showed an effective recycling method and an efficient conversion pathway to produce a high-performance energy storage device, the performance of a conventionally synthesized  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticle is much higher than that of the waste-derived nanoparticle.

Vadiyar and co-workers<sup>33</sup> produced activated carbon-Fe<sub>3</sub>O<sub>4</sub> nanocomposite from local waste thermocol sheets and rusted iron wires and used as the electrode material for supercapacitor application. A reflux precipitation method was employed to synthesize strongly interconnected Fe<sub>3</sub>O<sub>4</sub> NPs on the carbon microparticle backbone as shown in figure 2 B). Initially, the

electrochemical property of the as-synthesized  $c\text{-Fe}_3\text{O}_4$  was studied in a 3-electrode set up in a 6M KOH aqueous solution and a specific capacitance of  $1,375 \text{ Fg}^{-1}$  was achieved at a current density of  $1 \text{ Ag}^{-1}$ . A detailed electrochemical study revealed the storage mechanism was capacitive. Finally, an all-solid-state asymmetric supercapacitor was fabricated, as shown in Figure 3 A) (a-h) using the as-synthesized  $c\text{-Fe}_3\text{O}_4 / \text{Ni}(\text{OH})_2/\text{CNT}$  in a PVA-KOH gel electrolyte assembly where the as-synthesized  $c\text{-Fe}_3\text{O}_4$  worked as the negative electrode and the device exhibited a high specific capacitance of  $256 \text{ Fg}^{-1}$  at a current density of  $1 \text{ Ag}^{-1}$  along with a high energy density of  $91.1 \text{ Wh kg}^{-1}$  at a power density of  $0.8 \text{ kW kg}^{-1}$  with excellent capacitance retention of 98% after 10000 cycles. The work thus shows an alternative recycling pathway for the sustainable, inexpensive easy to fabricate supercapacitor device for electrochemical energy storage and as the performance of the device is comparable to the similar conventional devices, the method can be suitable for practical application.



**FIGURE 3** A, Device schematic (a) and (b-h) Application of waste-derived carbon- $\text{Fe}_3\text{O}_4$  nanocomposite as a supercapacitor device for glowing an LED (Adapted with permission from ref. 26, Copyright 2018 Wiley), B, Ragone plot demonstrating that waste-based red mud and waste  $\text{FeO}_x$  show superior behavior as supercapacitors to non-waste based AC/FCO (mixed metal) based and  $\text{RuO}_2$  supercapacitors (Adapted with permission from ref. 29, Copyright 2019 Wiley).

### 2.3. By-products of metal production

The present-day metal extraction and processing industries generate a huge amount of waste byproducts that are rich in mixed metal oxides. Metal oxides have been used extensively in energy storage and other applications due to their exotic properties. Inspired by the idea of utilization of metal oxide waste obtained from metal processing, Fu *et al.*<sup>34</sup> utilized mill scale, a steel industry waste, and a rich source of iron oxide with other mixed metal-oxides. They fabricated a supercapacitor electrode from suspension by spray deposition over SS and Cu current collectors. In their work, they used ball-milling to produce fine particles of  $\sim 1\mu\text{m}$ . To induce porosity in the samples, the as-prepared powders were treated in hydrochloric acid. The resulting powder consisted of a combination of  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_{0.942}\text{O}$ , and metallic iron. The electrochemical measurements were carried using a 3-electrode cell configuration with spray deposited mill scale working, Ag/AgCl reference, and a platinum sheet reference electrode in a 0.5 M  $\text{Na}_2\text{SO}_3$  aqueous electrolyte. The assembly exhibited a maximum capacitance of  $25 \text{ Fg}^{-1}$  at a current density of  $0.25 \text{ Ag}^{-1}$ . The long-term stability test was also performed and 83% of the initial capacitance was found to be retained after 5000 cycles. In this work, they also assessed the cost of the device and compared with the commercially available electrodes and showed the promising potential of the low cost, easy to fabricate recycled iron oxide electrode in large scale energy storage applications. Although the material itself exhibited a promising electrode performance, all the measurements were carried out in a 3-electrode test setup and it is difficult to compare its performance with a complete device.

In their next work, Fu *et al.*<sup>35</sup> employed a novel strategy to synthesize a rectangular, hollow, and porous  $\text{Fe}_2\text{O}_3$  micro-rods by a facile combination of ball-milling and chemical treatment using oxalic acid. The applicability of the produced metal oxide in electrochemical energy storage

(supercapacitors and lithium batteries) were examined. A similar 3-electrode cell set up as mentioned in their previous work was employed and a maximum specific capacitance of  $346 \text{ Fg}^{-1}$  at  $2 \text{ mVs}^{-1}$  was obtained with an 88% capacitance retention after 5000 cycles. After pre-lithiation, the battery electrode delivered an initial reversible specific capacity of  $933 \text{ mAh}^{-1}$  at  $0.1 \text{ C}$  which was retained after 100 cycles. Their study revealed that the porous and hollow nature of the  $\text{Fe}_2\text{O}_3$  NPs not only created higher surface area but also facilitated swift ion mobility throughout the electrode which enhances the charge storage capability and also provided remarkable strain accommodation during lithiation and de-lithiation. According to the report, the proposed method can be used as an attractive route to produce grid-scale energy storage devices. Though it is noteworthy to mention that the long-term supercapacitor performance showed that 88% of the initial capacitance had been retained after 5000 cycles.

Red mud is an iron-rich, mixed metal oxide composite, rich in hematite ( $\text{Fe}_2\text{O}_3$ ) which is a byproduct of the aluminium extraction process using Bayer's method. In the quest towards waste management and sustainability and to use red mud as an effective energy storage material Bhattacharya *et al.*<sup>36</sup> used ball milling to produce spherical red mud NPs of size  $\sim 30\text{-}50 \text{ nm}$  for samples milled for 10 hours. The comparison of unprocessed material and ten-hours milled is shown by TEM in Figure 2 C). They employed a 3 electrode set up using GCE modified-red mud as working,  $\text{Ag}/\text{AgCl}$  as a reference, and a platinum wire counter electrode in a  $6\text{M KOH}$  aqueous electrolyte assembly and achieved a specific capacitance of  $317 \text{ Fg}^{-1}$  at a scan rate of  $10 \text{ mV s}^{-1}$ . The modified electrode exhibited remarkable capacitance retention of 97% after 5000 cycles (at a current density of  $6 \text{ Ag}^{-1}$ ). The detailed electrochemical analysis revealed a diffusion dominated storage mechanism and a battery-like pseudocapacitance. A high energy density of  $6 \text{ Wh kg}^{-1}$  at a specific current density of  $1 \text{ Ag}^{-1}$  and a maximum power density of  $12 \text{ kW kg}^{-1}$  at a higher current density of  $20 \text{ Ag}^{-1}$ . Figure 3 B) shows the Ragone plot of the red mud supercapacitors, which is a key metric of energy and power density for supercapacitors

and shows a good relative performance of the waste-based red-mud compared to other traditional materials. Though it is noted that the performance of red mud nanoparticles was promising and slightly better than that of chemically synthesized  $\text{Fe}_2\text{O}_3$  nanoparticles, characterization of the red-mud derived supercapacitor device may be of more practical interest but was not present.

In later work, Bhattacharya et al.<sup>37</sup> fabricated a planar, interdigitated, hybrid flexible micro-supercapacitor using a polyimide derived laser-induced graphene (LIG), decorated with red mud NPs with a solid-state ionogel electrolyte consisting of PVDF, [EMI][TFSI] and [EMIM][BF<sub>4</sub>]. The 2-electrode-based device produced an energy density of 0.018 mWh/cm<sup>2</sup> at a power density of 0.66 mW/cm<sup>2</sup> and exhibited 81% retention of capacitance after 4000 cycles in an ambient atmospheric condition, and could withstand bending and flexing. According to the report, the presence of red-mud NPs improved the charge transfer kinetics compared with the pristine LIG device. A prototype device successfully illuminated a white-LED. This prototype device thus is a positive development in the field and further optimization, passivation and encapsulation may lead to a real-time large scale device production for practical applications.

Suryavanshi *et al.*<sup>38</sup> used red mud as an efficient anode material in Li-ion batteries. The red mud was extracted using a simple magnetic separation method and applied as the anode material without further processing. The extracted material was  $\text{Fe}_2\text{O}_3$  rich and also contained inter-dispersed phases of other metal oxides of Titanium Aluminum and Silicon. The half-cell assembly exhibited a reversible capacity of 697 mAh g<sup>-1</sup> with excellent stability. They hypothesized that the presence of other electrochemically inactive metal oxides, could provide the strain and accommodate release during the charge-discharge processes in the  $\text{Fe}_2\text{O}_3$  site. Finally, they fabricated a full cell assembly using environmentally benign  $\text{LiMn}_2\text{O}_4$  cathode by optimizing the mass loading. To overcome the irreversible capacity loss pre-lithiation was

carried out on the anode material. The optimized full cell exhibited a capacity of  $100 \text{ mA h g}^{-1}$  with ambient capacitance retention of 61% after 2000 cycles. The performance of the electrode is still not as good as conventionally synthesized hematite nanoparticles<sup>39</sup> and the non-uniform particle size may be a route cause of it.

Deshmukh *et al.*<sup>40</sup> produced a reduced graphene oxide (rGO)- red mud nanocomposite using ball milling for the electrochemical detection of arsenic. They utilized square wave anodic stripping voltammetry technique and modified the commercial glassy carbon electrode with as-synthesized nanocomposite and used as the working electrode. After optimizing various parameters (milling time, deposition potential, deposition time, pH of the solution), they achieved a high sensitivity of  $2.49 \mu\text{A ppb}^{-1}$  and a low limit of detection of 0.07 ppb towards  $\text{As}^{3+}$  detection, which is among the best performing electrochemical sensors for arsenic. An interference study showed high selectivity of  $\text{As}^{3+}$  in the presence of other common cations ( $\text{Cd}^{2+}$ ,  $\text{Cr}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Hg}^{2+}$ ). They also demonstrated the applicability of the electrode for the detection of arsenic in a spiked- real groundwater sample. The excellent performance of the electrode was attributed to the high adsorption capacity of the hematite ( $\text{Fe}_2\text{O}_3$ ) phases in the red mud nanoparticles and the rGO dominated enhanced electron-transfer kinetics. They concluded that the milling time also played a significant role in the electrochemical performances and imputed to the formation of functionalized nanocomposites which provided many adsorptive active sites and accelerated the electron-transfer kinetics. Though the ball- milling process is simple, the preparation of rGO is time-consuming and required complex sonication-assisted chemical exfoliation of graphite. The material displayed excellent performance, but the performance of a prototype device was not presented and thus can't be utilized in the present state for practical applications. The repeatability of red mud from different sources and sites in this type of sensing application has not yet been proven, and this could be a significant drawback in how red mud can be used in industrial products.



Blast furnace slag (BFS), a high-volume byproduct that is produced from the pig iron-making processes. Kuwahara *et al.*<sup>41</sup> used the BFS as a potent low-cost highly abundant precursor and synthesized Calcium-based layered double hydroxide (LDH) termed 'hydrocalumite'. A combination of ball-milling and subsequent chemical treatment was carried out to produce the recycled material, and a schematic of the processing is shown in figure 1 B). As this hydrocalumite has the property to incorporate Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> counterions these derivatives were also synthesized during the crystallization process. The as-prepared materials worked as effective heterogeneous base catalysts towards Knoevenagel condensation, transesterification, oxidation of alkyl aromatics with O<sub>2</sub>, and cycloaddition reaction of epoxides with atmospheric CO<sub>2</sub>. The activity was found to be affected by surface basicity, co-ordination geometry, and impurity elements. The presence of metal impurities and counterions in the slag- derived samples worked as active sites to enhance the catalytic activity. The catalyst could be easily recoverable and exhibited excellent recyclability and the catalytic efficiency was restored in multiple processes. The as-synthesized LDH thus can be used as an effective catalyst and can replace the commercial LDH. Though the catalytic activity is impressive, the complex and time-consuming two-step synthesis process limits its global applicability.

As resource accessibility and global sustainability become important aspects of the design and application of electronic devices such as sensors, green synthesis of devices with recycled waste is an important research area. Abdelbasir *et al.*<sup>42</sup> synthesized spherical cuprous oxide (Cu<sub>2</sub>O) NPs from waste electric cables employing a surfactant-assisted chemical reduction approach. They reported that the choice of surfactant played a crucial role in nanoparticle size, bandgap, and other properties. The nanosensors were fabricated by anchoring the as-synthesized nanoparticle over laser-induced graphene electrodes by a magnet assisted electrodeposition technique. The device was used for the detection of dopamine and mercury (Hg). The dopamine detection was carried out using DC potential amperometry (DCPA) and

the sensors exhibited linearity within a range of 300 nM to 5  $\mu$ M with a detection limit, response time, and sensitivity of 200 nM,  $2.4 \pm 0.7$  s, and  $30 \text{ nA } \mu\text{M cm}^2$  respectively. The Hg sensor was investigated using linear sweep stripping voltammetry (LSSV) and linearity from 0.02 - 2.5 ppm was achieved with a detection limit of 25 ppb, response time  $< 3$  min and sensitivity of  $10 \text{ nA ppm}^{-1}$ . In this work, the authors correlated the enhanced electrochemical performance with the nanoscaled-Cu<sub>2</sub>O structure where the anchoring with the LIG provided a reduced series and charge transfer resistance due to the crystallinity of the mesospheric NPs.

### **3. OVERVIEW AND FUTURE DIRECTIONS**

In this review, we have summarised some of the recent publications which take metal-oxide based wastes and recycle them into useful nanomaterials. The most promising applications appear to be energy storage materials, and there is a significant body of work in this area. Work by two separate groups, using red mud-based electrodes for both supercapacitors and batteries, showed how impurities may help to facilitate increased capacitance retention compared with a purer comparative material<sup>36, 38</sup>. Meanwhile, other studies<sup>41</sup> have shown how impurities in a predominantly calcium-based heterogeneous catalyst aided the catalytic activity by acting as active sites. Whilst there is a growing body of knowledge and many promising applications for recycled waste-based metal oxides, here we will outline and overview some of the future challenges and directions.

We have earlier grouped reported works by the sources of waste, all of which have the potential to be more widely recycled and utilized. In Table 2, in critically summarising some of the work and grouping by the processing route ‘output’, we hope to illustrate the challenges and pathways for the future.

**TABLE 2** Summary of some of the processing routes used to obtain metal oxide nanomaterials from recycled wastes, including pros and cons.

<b>Processing route</b>	<b>Input Waste</b>	<b>Process PROS</b>	<b>Process CONS</b>
Ball Milling	Red mud <sup>36</sup> Mill scale waste <sup>34</sup> Zn-C batteries <sup>21</sup>	<ul style="list-style-type: none"> <li>• May be used to obtain uniform spherical NPs</li> <li>• Tunable shape and size of NPs</li> </ul>	<ul style="list-style-type: none"> <li>• Input material composition (E.G. Red mud) is variable in both time and location</li> <li>• Throughput of ball milling is low</li> <li>• Regularity and size of NPs is time dependant: slower processing for smaller, more uniform NPs</li> </ul>
Magnetic Separation	Metallic film resistors <sup>23</sup> Red mud <sup>38</sup>	<ul style="list-style-type: none"> <li>• Some magnetic separators are high throughput (25 Kg/Min drum separator)</li> </ul>	<ul style="list-style-type: none"> <li>• Magnetic separation can only separate magnetic particles</li> </ul>
Thermal processing	Zinc-manganese batteries <sup>20</sup> Rust waste <sup>31</sup>	<ul style="list-style-type: none"> <li>• Thermal processing may be scaled towards industrial scale</li> <li>• Nanomaterials of innovative morphology may be obtained</li> </ul>	<ul style="list-style-type: none"> <li>• Thermal evaporation may only remove impurities if the evaporation temperatures are different</li> <li>• Some metal oxides require very high temperatures</li> </ul>
Chemical processing	Rusted wires <sup>32,22</sup>	<ul style="list-style-type: none"> <li>• May remove impurities and obtain a uniform output</li> <li>• Can obtain novel micro and nanostructures</li> </ul>	<ul style="list-style-type: none"> <li>• Chemical reactions may not be repeatable if the input material varies widely</li> </ul>
Mixed processing	Mill scale <sup>35</sup> Blast furnace slag <sup>41</sup>	<ul style="list-style-type: none"> <li>• Enables tunable morphology and property</li> <li>• Enables a combination of industrial-scale techniques</li> </ul>	<ul style="list-style-type: none"> <li>• Bottlenecks in multi-stage processes may occur in low-throughput steps</li> <li>• Complex extraction may give variable output if the input material differs</li> </ul>

The composition of metal production-based wastes often varies significantly, for example, red mud  $\text{Fe}_2\text{O}_3$  content, even within a single country (India), may vary from between 18 and 55 % of the total<sup>43</sup>. Thus, to produce consistent outputs, such waste must be processed in innovative routes, such as the oxalic acid treatment of mill-scale waste, showed by Fu *et al.*<sup>35</sup> which enabled the production of hollow micro-rods of predominantly crystalline  $\text{Fe}_2\text{O}_3$ .

The mass of discarded metal oxides from metal production is vast, however, the bottleneck for metal oxide waste processing is the conversion from raw waste to usable nanomaterials: for example, lab-scaled ball milling may be too slow and small-scaled for industrialization. Whilst large-scaled ball mills exist, there is currently limited evidence of high throughput, low-cost nanomaterial production. Some of the promising methods include chemical treatment, for example, oxalic acid treatment of mill scale waste<sup>35</sup> and hydrochloric acid and nitric acid-treated  $\alpha\text{-Fe}_2\text{O}_3$  rusted wires<sup>32</sup>. Whilst this has mainly been shown on the lab-scale thus far, chemical treatments have the potential for scale-up, for some certain nanomaterials.

Further to the considerations of nanomaterial purity, the consistency of the output, and the scalability of the process; the overall monetary cost of obtaining nanomaterials from waste sources is a key determining factor in increasing the utilization of wastes. Fu *et al.*<sup>34</sup> have attempted to quantify the cost implications of using waste-based nanomaterials compared with commercially available alternatives. They estimated a total cost of mill-scale based supercapacitor electrodes as ~23 USD per kg, and calculated a capacitance cost (USD per Farad), energy cost (USD per kWh), and power costs (USD per kW) energy cost, and compared these to values obtained from commercially available  $\text{Fe}_3\text{O}_4$  powders. They noted that the minimum energy cost of mill-scale based supercapacitors is significantly higher than that of the commercial supercapacitor ~ 8000 compared with ~ 6000 USD per kWh. Thus, in the case of mill-scale waste, the performance of the waste-based material needs to be improved before it can become competitive. This example shows the difficulty for waste-based materials, even

when free, or near-freely available, to compete with pure, commercial alternatives if the performance of the material is relatively poor. However, many other materials discussed in this review have shown comparable and even improved performance over pure equivalents; and thus, provide solid evidence that future waste-based nanomaterials may be commercially viable.

One downside to the majority of work summarised in this review is that few materials benchmark themselves against commercial or gold-standard material competitors. The supplemental table in S1 shows a comparison, between the performance of recycled nanomaterials and the research or commercial alternatives., Most of the current research does not provide a cost-benefit or environmental analysis of their work. Whilst this is understandable since most material scientists are not economists or environmentalists. However, when the issues of cost and environmental improvement are the main, or even sole, justifications of undertaking and publishing research (as is the case of many of the reviewed papers), the overall impact and buy-in from the wider scientific community, and industry, would potentially increase if quantitative data on the money saved and positive environmental impact were more widely available.

### **3.1 Key future directions for Energy storage**

In this paper, we have reviewed a range of energy storage materials derived from waste-based metal oxide nanomaterials. Some of this high-quality research has shown promising performance which is comparable to commercially available materials and we believe that in particular (i) red mud<sup>36-37</sup> and (ii) thermocol sheets<sup>33</sup> may warrant further research, as they have both been shown in working supercapacitor devices, suggestive that these could be scaled up. However, the outlook for future work is uncertain due to two main areas. Firstly, very few of the waste-based energy materials here have had in-depth cost-analysis completed on them,

and this is a major drawback: if this is not made clear in published work then the uptake may not increase. There should be greater collaboration with economists and waste-production companies. This may also help to attract government support and subsidies which would make waste-based energy much more financially attractive. For example, in Taiwan, the concept of sustainable materials management <sup>44</sup> was used to encourage recycling enterprises to increase material circulation as a solution to the resource scarcity issue.

Finally, the performance of waste-based materials should not just be compared to similar materials, they should be compared to the overall best-performing materials to give readers a clearer view of the relative performance. For example, the overall goal of 15-minute charging time for batteries should be a key goal for waste-based batteries, as it is for the battery industry overall <sup>45</sup> however this is rarely discussed in the context of waste-based energy nanomaterials. The combined performance and cost-benefit of waste-based energy nanomaterials will be the driving factors to usefully recycle these damaging wastes.

### **3.2 Key future directions for Catalysis**

As with waste-based nanomaterials for energy storage, the recycling of metal-oxides for use in catalysis should include real cost-benefit analysis and focus on the highest value streams. Cost should be minimized and simplified by reducing the number of steps taken in processing and innovation in this area may be a key step in increasing the volume of recycled products in catalytic applications. Furthermore, the overall environmental benefit of the recycling process should be analyzed and the environmental harm caused by the recycling process. For example, the damage caused by any solvents or toxic additives <sup>46</sup> should be considered against the potential benefit of recycling.

### **3.3 Key future directions for Sensing**

Compared with energy storage and catalysis, the field of waste-based sensors is relatively young and the volume of work is lower. As this field progresses, some initial feasibility studies should be undertaken. Compared with the volume of material required in energy storage and catalysts (driven, for example, by industry and transportation) the overall mass of sensing material is considerably lower. Thus the benefit of saving money, and usefully removing material from the waste-cycle, are much lower for sensors. Furthermore, sensors require a high level of precision and accuracy that may be greatly affected by the changing composition of the waste-based materials. For example, red-mud rGO nanocomposites showed very high performance for sensing arsenic, however, since the composition of red mud can vary widely across different sites<sup>43</sup>; this would greatly alter the relative performance of sensors comprising nominally similar red mud. Another key aspect regarding low-cost sensors is how they can be miniaturized and work in remote settings. Currently, this is an area that has not been sufficiently addressed.

## **4. CONCLUSIONS**

In this review, we have given a brief overview of the state of the art of research into the recycling of waste-based metal oxides into nanomaterials for energy storage, catalysis, and sensing. We have seen that the impurities in some of these materials, notably red mud, and calcium-based catalysts, may improve the performance over more purified materials. There are abundant sources of waste, that, if under-used, will continue to degrade the quality of the environment in many countries. However, if these sources are more widely utilized, especially in energy storage materials, and further innovations in large-scale manufacturing are realized,

then these environmental liabilities may become a source of wealth for many communities. However, a lack of quantification of the positive environmental and economic impact appears to, thus far, undermined the wide-scale application of waste streams for producing metal-oxide nanoparticles.

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