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Synthesis of 2D Rare earth elements oxide nano-sheets from Nd-Fe-B magnets

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ABSTRACT

With rising global demand for rare earth elements (REEs) in a range of emerging clean energy technologies such as hybrid electric vehicles, and the uncertainty in their supply, REEs are now under severe risk. The development of new technologies for the recovery of REEs from waste and also replacing the conventional resources with the alternative renewable sources is urgently needed. Currently, Nd-Fe-B magnets are known as one of the most extensively used types of REE magnets which can be used as a potentially valuable and rich source of REEs (i.e., Nd, Pr and Dy). In the present paper, using REEs (i.e., Nd, Pr and Dy) recovered from the end-of-life Nd-Fe-B magnets, we applied homogeneous precipitation technique at low temperature and synthesised REEs (i.e., Nd, Pr and Dy) hydrate oxalate which was then utilised as a precursor for the synthesis of REO nano-sheets. FE-SEM and TEM images showed that the synthesised REO nano-sheets were in the dimension of ~1μm × 0.5μm × 17 nm made from nano-particles. From X-ray diffraction spectrum, several strong peaks assigning to the cubic phase of Nd_2O_3 and small peaks corresponding to cubic phases of $NdPrO_3$ and Pr_2O_3 were detected. This paper confirms the feasibility of transforming waste materials such as end-of-life Nd-Fe-B magnets into valuable nano-structured products through a simple pathway.

1. Introduction

The use of nano-scale rare earth oxides (REOs) has gained attention as a result of their remarkable optical, chemical and electronic properties (Hadi and Yaacob, 2007; Xiao et al., 2009) deriving from their 4*f*-orbital partially shielded (Dhamale et al., 2016; Qu et al., 2009) and also because of their low toxicity, high stability, high efficiency in excitation and longer lifetime of their luminescence property (Kaczmarek et al., 2015). The lanthanide series have been widely applied for synthesis of phosphors, particularly for the emission of the three primary colors (Zhao et al., 2008), catalysts (He et al., 2013;Parac-Vogt et al., 2004) and biological labels (Zhang et al., 2007;Li and Lin, 2010;Beaurepaire et al., 2004). Neodymium (Nd), Praseodymium (Pr) and Dysprosium (Dy) are key rare earth elements in the lanthanide family with extensive applications in a range of areas such as magnetic and luminescent devices, dielectrics, catalysts and protective coatings (Işıldar et al., 2018), (Xueping et al., 2012; Abdelkader et al., 2010;Yu et al., 2007;Mohan et al., 2007;Shylesh et al., 2005).

In their nanostructure form, REOs not only possess the outstanding properties of their bulk counterpart but display their own unique properties (Behnamfar et al., 2016; Dhamale et al., 2016; Xu et al., 2003; Wu et al., 2004;Fang et al., 2003) such as improved catalytic activity and excellent chemical stability. A variety of methods have been attempted and investigated to synthesize REO in nanoscale with different morphologies (e.g. nano-spherical particles (Yan and Yan, 2008), nano-wire (Yin et al., 2008), nano-rod (Zhao et al., 2008), nano-cubes (Yang and Gao, 2006) and nano-plates (Si et al., 2007). These techniques include hydrogen plasma metal reaction (Li et al., 2003), the colloidal precipitation route (Bazzi et al., 2003), the solvothermal reaction route (Zawadzki and Kpiński, 2004; Yin et al., 2008), the hydrothermal reaction (Que et al., 2001;Bazzi et al., 2003;Kępiński et al., 2004), the solution combustion method (Yu et al., 2007;Chavan et al., 2008;Umesh et al., 2011), the tartrate route (Zhaorigetu et al., 2007), the microwave assisted hydrothermal method (Kępiński et al., 2004;Zawadzki, 2008), radiofrequency inductively coupled thermal plasma technique (Dhamale et al., 2016), inverse micro-emulsion route (Que et al., 2001), direct and quick precipitation from polyalcohol solutions (Bazzi et al., 2003), electron-beam evaporation (Jeon et al., 2001) and thermal evaporation (Kosola et al., 2005).

The significance of rare earth elements (REEs) has rapidly grown as new technologies made with these elements entered the market. Due to the high demand in the market and limited supply of REEs worldwide, the price of these elements increased which put pressure on natural resources. In 2015 and 2016, China processed 105,000 mt of REEs (about 80% of the world REE production). Other countries such as Australia (14,000 mt), Russia (3000 mt), India (1700 mt), and Brazil

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(1100 mt) also produced REEs from their mines (Ganguli and Cook, 2018).

Currently, less than one percent of REEs are extracted via recycling. Nd-Fe-B with the content of almost 30 wt. % REEs is one of the most extensively used type of REEs magnets which are applied in a variety of electronic devices such as laptop and computer hard drive and also in electrical and hybrid vehicles (Machacek et al., 2015;Al and Razi, 2016;Nakamoto et al., 2012;Saito et al., 2006). Demand for such magnets is forecasted to continue to grow, as the demand for light-weight devices with strong magnetic property mainly in the sectors of the clean energy/transport (Widmer et al., 2005) is growing. The global sales of such magnets are forecasted to reach US$ 12.7 billion by 2019.

The rapidly growing stockpile of end-of-life Nd-Fe-B permanent magnet, is a rich secondary source of REEs which can be extracted and utilised in other applications (Schulze et al., 2018;Schulze and Buchert, 2016). In a research paper published recently by authors (Maroufi et al., 2017), we successfully recovered REEs (i.e., Nd, Pr and Dy) in oxide form from waste Nd-Fe-B permanent magnets via novel thermal isolation process. Nd-Fe-B magnets were dismantled manually from obsolete hard drives sourced from e-waste. After pulverisation, the powder was oxidized at 1000 °C for 60 min followed by reduction at high temperatures (1450 °C for 90 min) using the activated carbon derived from waste tyre rubber as a reducing agent. Oxides of Fe, Co and Ni, were reduced to the metallic phase and separated from the oxide phase leading to the formation of oxide and Fe-based metal phases with a clear interface. The oxide phase dominantly contained REEs (i.e., Nd, Dy and Pr) with a minor amount of B and Al.

In this study, the recovered REEs from the previous work was utilised for synthesising 2D RE (i.e., Nd, Dy and Pr) oxide nano-sheets. First, using a simple technique (i. e., homogeneous precipitation at low temperature), nano-sheets of RE (i.e., Nd, Pr and Dy) hydrate oxalate was synthesised. The synthesised RE (i.e., Nd, Pr and Dy) hydrate oxalate was then applied as a precursor for the synthesis of REO nanoparticles. The processes detailed here prove the possibility of synthesising nano-sized REO with high quality from waste materials.

2. Experimental procedure

The REEs extracted from spent Nd-Fe-B permanent magnets were pulverised first. The crushed powder was then analysed using Inductively Coupled Plasma mass spectrometry (ICP-MS) technique. The elemental analysis of the separated oxide phase is presented in Table 1. A thorough characterisation examination of the separated REE is reported in our previous paper (Maroufi et al., 2017).

100 mg of pulverised REE was added to 4 mL of concentrated HCl at temperature of 100 °C, and the mixture was then stirred for 30 min to have a complete digestion. The resulting solution was filtered to separate the insoluble impurities, followed by adding 10 mL of deionised water. The solution's pH was then adjusted to 2 by adding dropwise solution of ammonia (3 M). To obtain a crystalline precipitant, 10 mL solution of oxalic acid (0.1 M) was added as a precipitating agent to the prepared REE solution. The final product was separated by centrifugation, washed with distilled water and ethanol, and the resulting blue precipitate was allowed to be dried at room temperature.

Table 1
ICP data of REEs recovered from the Nd-Fe-B permanent magnet (wt %).

Al	B	Co	Fe	Ni	Nd	Pr	Dy
1.3	2.4	0.01	0.60	0.01	64.2	11.9	1.97

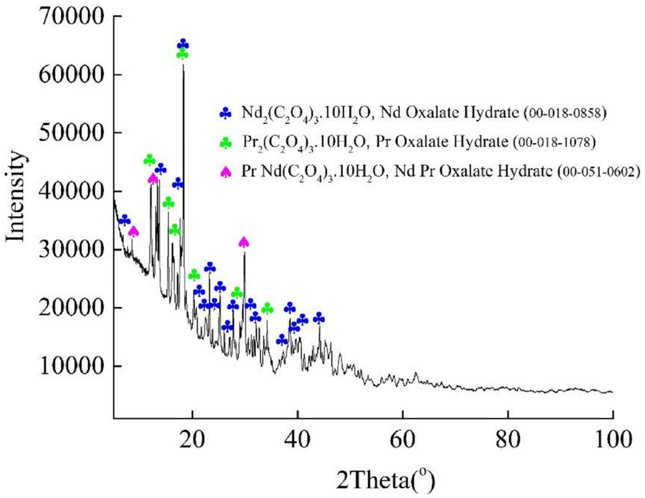

Fig. 1. a) XRD pattern of the as-synthesized precipitate using oxalate.

3. Results and discussion

3.1. Characterization and thermal decomposition of the synthesised $RE_2(C_2O_4)_3.10H_2O$

The resulting precipitate was subjected to X-ray diffraction analysis for the identification of the crystalline phases. Fig. 1 illustrates X-ray diffraction spectrum of the precipitate with several intensive peaks corresponding to Neodymium oxalate Hydrae [$Nd_2(C_2O_4)_3.10H_2O$], Praseodymium oxalate hydrate [$Pr_2(C_2O_4)_3.10H_2O$] and Praseodymium-Neodymium oxalate hydrate [Pr Nd $(C_2O_4)_3.10H_2O$].

It has been reported that a varying amount of hydrate water is dependent on the temperature of the precipitation (Wendlandt, 1959). No diffraction peak assigning to Dy was found in the X-ray diffraction pattern.

The structure and morphology of the produced $RE_2(C_2O_4)_3.10H_2O$ were studied using FE-SEM analysis. The FE-SEM image of the synthesised $RE_2(C_2O_4)_3.10H_2O$, in Fig. 2a, indicates that the $RE_2(C_2O_4)_3.10H_2O$ was in the form of 2D thin nano-sheets with approximate dimensions of ~1 μm × 0.5 μm × 25 nm. The whole process of $RE_2(C_2O_4)_3.10H_2O$ nano-sheets can be simply explained by the following reaction:

$$2NdCl_3.\ nH_2O + 3H_2C_2O_4 \rightarrow Nd_2(C_2O_4)_3.\ nH_2O + 6HCl \qquad (1)$$

The oxalate as chelating ligands connects to Nd^{3+} /Pr^{3+}ions to form a one-dimensional polymeric structure. Inter-polymeric chain hydrogen bonding (H-bonding) interactions between the O atoms of the oxalate and OH groups of water, organises the one-dimensional polymer into two-dimensional layers in which water acts as a good coordinating ligand, and a driving force for the formation of 2D nano-sheets. The role of water in the adjustment of the morphology of metal oxalate has been proved (Kim et al., 2016).

The synthesised RE hydrate oxalate can be used as a precursor for the final synthesis of REOs. This is the simplest form of carboxylate which has been prepared through a simple and cost- effective route. It also possesses a homogeneous composition which can be easily decomposed at low temperature. To indicate the temperature of decomposition and oxidation, thermal decomposition of the synthesised hydrated RE oxalate was performed.

The thermal decomposition behavior of hydrated RE oxalates [$RE_2(C_2O_4)_3.10H_2O$] was examined by thermogravimetric analysis technique (TGA); the sample was heated from ambient temperature to 1000 °C with slow heating rate (20 °C.min^{-1}) under nitrogen (20 ml.min^{-1}). Thermogravimetric analysis (Fig. 2b) reveals three decomposition stages while sample is gradually heating. From Fig. 2, total