

REVIEW

Nanotechnology in sustainable value addition to Sri Lankan minerals

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Summary: Sri Lanka is an Island with high quality natural resources such as precious minerals, endemic flora, and fauna, abundantly available throughout its land and sea. However, the country is among those with the poorest national economies in the world. The economy of the country is progressively declining due to the lack of a focused programme which would direct the country towards an improved economy. We, as academics and researchers, have devoted our time and energy towards developing value-added products from local minerals. This review describes some important natural minerals of Sri Lanka and our research activities on adding value to these natural treasures. The review begins with discussing natural resources of Sri Lanka focusing on industrial minerals. It then reveals the importance of adding value to these natural resources. Quoting our own research publications, the review describes the methodologies and benefits of adding value to Sri Lankan minerals. The review emphasizes the importance of preventing the export of valuable minerals in their raw forms by analysing market research on value added minerals.

Keywords: Apatite, feldspar, graphite, ilmenite, natural resources, quartz.

NATURAL RESOURCES OF SRI LANKA

Sri Lanka is gifted with several Natural Resources which include very high-quality natural minerals and endemic flora and fauna. Sri Lankan earth accommodates precious gemstones, pearls, very high-quality graphite, 100% pure quartz, mineral sands containing ilmenite, rutile and monazite, massive deposits of calcite, dolomite, apatite and iron phosphates and valuable clay minerals and so on. Some of these minerals are shown in Figure 1.

Sri Lankan graphite

Sri Lanka is one of five countries where high purity natural vein graphite is abundantly available. The other four countries where vein graphite localities available are Great Britain (Borrowdale and Cumberland), USA (North-western New Jersey, Dillion in Montana, and Ticonderoga), India (Kerala and Korani), and Madagascar (Ambohijanaka village in the Andramasina region). The vein graphite is known as crystalline vein, plumbago, Sri Lankan graphite, and Ceylon graphite; the latter names are due to the fact that Sri Lanka is the only country in the world where vein graphite is commercially produced in large quantities for the export market. This has occurred since the Dutch colonization era and peaked during the period of the second World War. There are reports to the effect that unusual graphite deposits of Ceylon have been known, and apparently used locally, since the middle of the 1600s. The fact that Sri Lanka is exporting its valuable highest quality natural vein graphite without any value addition should not be encouraged. Although, recently, Sri Lankan graphite mines are considering adding value to graphite by developing various products and making graphite aqueous dispersions, expanded graphite and graphene products, most of such work is done elsewhere in other countries such as Germany and Australia because some of the famous Sri Lankan graphite mines have been sold to companies from these countries. Therefore, their contribution to the national economy is minimal. The graphite market has escalated recently due to their use in batteries for electrical cars and a new market avenue is

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opening at the Tesla company. We have developed novel processes to convert graphite to expanded graphite and

graphene products. This will be discussed in detail in a latter section.

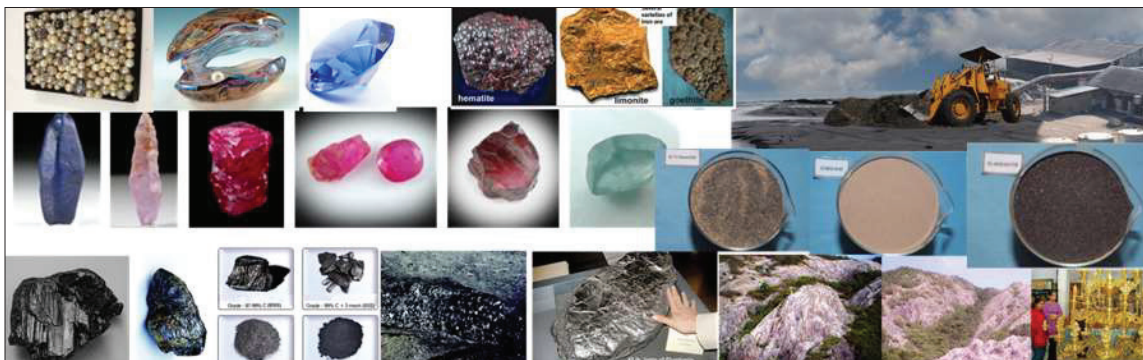


Figure 1: Some of the minerals naturally found in Sri Lanka. Photographs were taken from websites of respective industries.

Sri Lankan quartz

Sri Lanka is also gifted with high purity quartz containing over 98% pure silica. Such vein quartz deposits of high purity (over 98% silica) are found in Galaha (Kandy), Rattota, Balangoda, Pelmadulla, Embilipitiya and Ratnapura. Quartz has many technological applications including filters and absorbents, foundry sand, fillers, abrasives, specialized glassware used in laboratories, cuvettes for UV-visible spectroscopy, high tech products of ultrapure quartz for optical fibres, and for solar grade silicon manufactured for use in the electronics industry and photovoltaic cells. The silicon production increased from 35 ktonnes in 2005 to 105 ktonne in 2010. Although Sri Lankan scientists have already developed technologies to produce industry-specific quartz raw material using Sri Lankan vein quartz, these technologies are yet to be incorporated on a commercial scale (Pathirage *et al.*, 2019; Udawatte *et al.*, 2020). The conversion of quartz into solar grade silicon involves heating with coke at high temperatures. For each tonne of silica converted to silicon, ten tonnes of carbon dioxide are emitted to the atmosphere. We are developing an electrochemical process that does not require coke for the conversion of silica in quartz to silicon. This will eliminate undesirable environmental consequences due to excessive carbon dioxide emission. This will be discussed in detail later.

Sri Lankan ilmenite

Ilmenite is a commonly found in Sri Lankan mineral sands particularly in the Pulmudai area. Ilmenite is composed of iron titanate FeTiO_3 and is a major source used to extract titanium dioxide particles and

titanium metal. The common industrial processes are the so-called sulphate process and processes which demand concentrated sulphuric/hydrochloric acid and temperatures exceeding 1000 °C hence making the processes environmentally hazardous. Titanium dioxide particles are the common base material used in paints, pigments, and nanoparticles which are used in reducing toxicity of dyes and pharmaceutical drugs, wastewater treatment, reproduction of silkworm, space applications, food industries, and in dye-sensitized and perovskite solar cells. The iron component can be used to make magnetite, haematite, and zero-valent iron nanoparticles. We have developed a novel process to break down the strong ilmenite structure at 170 °C with the aid of mechanical energy using dilute hydrochloric acid enabling separation of titanium and iron components and silica impurities and converting them to useful nanomaterials.

Sri Lankan apatite

The apatite-bearing carbonate rocks are found in Eppawala, Sri Lanka and are generally known as Eppawala rock phosphate (ERP). Apatite occurs as massive, discontinuous bodies in a Precambrian, high-grade metamorphic terrain. When these apatite-bearing carbonate rocks are weathered they form economically important phosphate deposits. The naturally occurring Eppawala rock phosphate contains 28% to 42% phosphorus as P_2O_5 (Pitawala *et al.*, 2002). Its usability as a phosphorus source in agriculture is limited by its low water solubility though the solubility can be increased using concentrated phosphoric acid or concentrated sulphuric acid to form triple superphosphate (TSP) and single superphosphate (SSP). Various researchers over

several decades have extensively investigated these processes and satisfactory results were obtained. The finely ground raw phosphate product is used as a direct application as a fertilizer for perennial crops such as tea, rubber, and coconut. Studies have shown that the EPR is composed of an indiscriminate mixture of more water-soluble primary crystals and a less soluble secondary phosphate matrix rich in ferruginous and aluminous compounds, the latter being insoluble in water. Researchers have realized that the primary crystals can be easily separated from the rest of the components by mechanical separation, and they coined the term selectively mined primary crystals of Eppawala rock phosphate (SERP). The SERP has a high P_2O_5 content of 35% to 42% and much lower (less than 1%) trivalent metal oxides such as iron and aluminium oxides. The SERP is therefore water soluble and hence can be used directly for short-term crops such as rice and vegetables (Dahanayake *et al.*, 1995). Eppawala apatite is impure hydroxycalcium phosphate with some hydroxyl groups exchanged for fluoride and carbonate ions. We have developed a method to convert this impure Eppawala apatite to pure hydroxyapatite nanoparticles for making metal and alloy prostheses used in orthopaedic transplants, which are biocompatible, osteo-integrating, non-toxic, and resistant to natural rejection by the human body.

Sri Lankan dolomite

Dolomite is basically a 1:1 mole ratio of $CaCO_3:MgCO_3$, though there can be small amounts of impurities such as silica. Both $CaCO_3$ and $MgCO_3$ occur naturally in their pure form also in calcite and magnesite, respectively. The three minerals, dolomite, calcite, and magnesite are generally called limestone minerals. Dolomite is abundant in Sri Lanka and is found in Highland - Southwestern, Vijayan, and Wannu complexes. The limestone deposits are found in Anuradhapura, Habarana, Matale, Kandy, Ratnapura, Balangoda, Badulla, Bibile, Welimada, Ambilipitiya, Hambantota and Kataragama. Dolomitic mineral is the most abundant. The major use of dolomitic limestone is as quicklime and slaked lime for the building industry. Its minor uses are as a raw material in the ceramic and glass industry. Powders of dolomite are also used in the rubber and paint industries as filler material and to produce wall finishing materials. We have developed a methodology to separate the Ca and Mg carbonate components of dolomite and silica impurities, and then convert the Ca and Mg fractions to $CaCO_3$ and $MgO/Mg(OH)_2$ nanomaterials for various applications, as presented in a later section.

Sri Lankan clays

Clay is not considered a primary mineral, but it is a weathered product of various aluminosilicate minerals. Clays can be generally categorized as weathered hydrated aluminosilicate minerals. The major minerals present in clay are kaolinite, montmorillonite, and micaceous clay minerals. The major use of clay is for the ceramic industry, though there are many other applications such as in pottery. Clays are excellent materials to be used as clarifiers, absorption and adsorption materials, and in paper, paint, petroleum, ceramic, cement, adhesive, asphalt, food, and health-care industries. We have developed montmorillonite/ electronically conducting polymer nanocomposites for various technological applications as presented later.

Sri Lankan feldspar

Feldspar is an aluminosilicate mineral containing potassium, sodium, and calcium inclusions. Feldspar deposits are abundantly found throughout Sri Lanka, particularly, in Rattota, Namaloya, Koslanda, and Balangoda localities. Feldspar's major use is as a refractory mineral in ceramic and glass industries. However, some feldspar deposits are rich in potassium with over 10% w/w natural abundance. We are currently developing methodologies to extract potassium from feldspar using microorganisms such as bacteria and fungi.

CONVERSION OF SRI LANKAN MINERALS TO VALUE-ADDED MATERIALS

Graphite to expanded graphite and graphene products

We have developed a chemical-free flotation method to purify Sri Lankan vein graphite. The purified graphite obtained was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), infrared and Raman spectroscopic techniques, and by elemental analysis (Kumara *et al.*, 2021). The silicate minerals with copper and iron that are present in raw samples have been removed via the flotation. Due to this, the carbon percentage has increased to 97% from 86% in the original mineral. This is a low-cost and environmentally friendly process for purifying natural vein graphite samples. We have also developed an acid mixture to delaminate graphite attached to pieces of rock of the graphite vein banks of the Bogala graphite mine, and selectively take it into the suspension

to make expanded graphite and graphene products. The expanded graphite thus produced has an extremely high oil absorption capacity of 120 g of oil per 1 g of expanded graphite. This capacity is 20 times higher than that of biochar. The data obtained are summarized in Figure 2. In the conversion of graphite to graphene, graphite is first oxidized to graphene oxide (GO), and then reduced to produce reduced graphene oxide (rGO). Depending on the extent of oxidation followed by reduction, multi-layer graphene products are formed. In our research, the crystallite size of graphene is 1.2 nm. Graphene is the thinnest known material, made of only a one carbon atom thick layer, and is the lightest material known with the surface density of $7.710^{-4} \text{ g m}^{-2}$. Graphene is the strongest material ever discovered with a fracture strength of 130 GPa (Lee, 2008), the second- and third-order elastic

stiffnesses of 340 N m^{-1} and -690 N m^{-1} , respectively, and a Young's modulus of 1.0 TPa. Graphene is highly thermally conductive, exhibiting a thermal conductivity of $\sim 4000 \text{ W m}^{-1} \text{ K}^{-1}$ (Nair *et al.*, 2008; Chen *et al.*, 2010). The electrical conductivity of graphene is 10^8 S m^{-1} and is 1.68 times higher than that of copper.

Additionally, we have developed a technology to produce graphite electrodes using montmorillonite clay as the binder. The electrodes prepared are shown in Figure 2(b). These electrodes have conductivities of 27, 227, 454, 625, and 1250 S cm^{-1} , and are suitable not only for bulk electrolysis but also in electroanalytical chemistry in both aqueous and molten salt electrolytes (Karunadasa, 2019a)

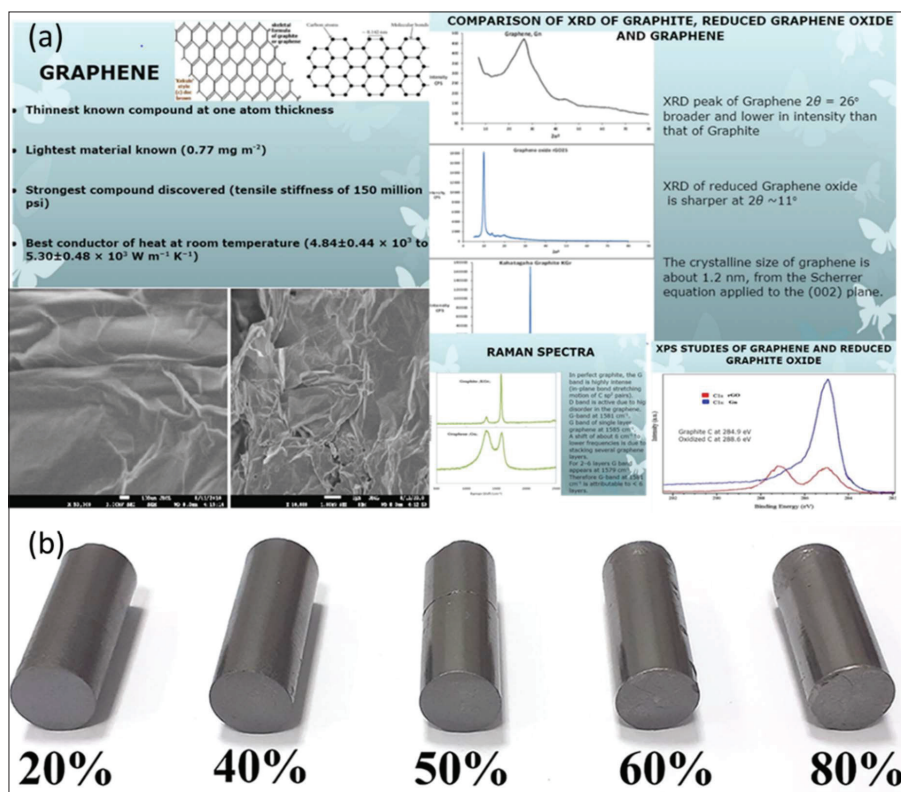


Figure 2: (a) Properties of graphene produced from Sri Lankan vein graphite. (b) The graphite electrodes prepared by using montmorillonite clay as the binder and firing the mixtures at 550°C . The percentages shown are the percentages of graphite in the mixture used to prepare electrodes. (Reproduced with permission from Karunadasa, 2019a)

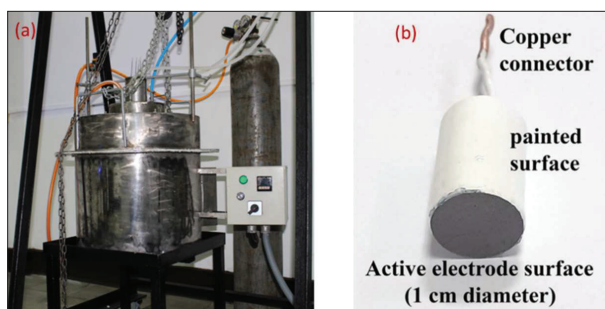
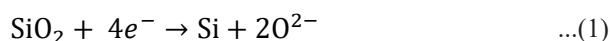


Figure 3: (a) The stainless electrolyser used to reduce silica to silicon at molybdenum anode and graphite cathode. (b) The graphite cathode fabricated. (Reproduced with permission from Karunadasa, 2018a)

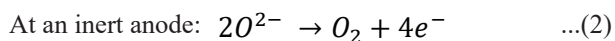
Value addition to Sri Lankan quartz

We are developing an electrochemical process for the reduction of silica to silicon under inert atmosphere maintained with an argon flow, in molten CaCl_2 and/or a CaCl_2 - NaCl salt mixture, at its eutectic point as shown in Figure 3(a). The stainless electrolyser was developed by fixing heat-stable tiling in the inside walls to maintain required the temperature without significant heat loss at a high temperature of 750°C . The graphite anode shown in Figure 3 (b) was used and the cathode material used was a molybdenum wire which was wrapped around the silica pellets. At the molybdenum cathode, silica is reduced to silicon while producing oxide ions [Equation (1)].

At the molybdenum cathode:



The ions produced at the cathode are diffused to the graphite anode and react with graphite oxidizing some C to CO and CO_2 . To eliminate the evolution of CO_2 , a molten CaCl_2 - CaO mixture is used where CaO reacts with CO_2 forming CaCO_3 . If an inert anode material is used instead of graphite, then the anodic oxidation process will be the oxidation of ions to $\text{O}_2(\text{g})$ as shown in Equation (2).



This is an environmentally friendly process. This process is similar to the FFC Cambridge Process, and the electrolysis is carried out at an applied voltage of 2.3 V. The thermal decomposition of the calcium carbonate used was extensively studied using high-temperature P-XRD measurements (Karunadasa, 2019b). The relative

stability of hydrated/anhydrous products of the calcium chloride used was also studied using high-temperature P-XRD (Karunadasa, 2018b). The composition, unit cell parameters and microstructure of quartz during phase transformation from α to β was examined by *in situ* high-temperature P-XRD (Karunadasa, 2018a). Having extensively characterized all the materials used, electrodes fabricated, and the electrolyser developed, we are currently investigating the conversion of silica micro-particle-based pellets to silicon via electrochemical reduction. All the apparatus shown in Figure 3 was fabricated locally at the Industrial Technology Institute (ITI) and the stainless-steel electrolyser can withstand high temperatures up to 1000°C . Therefore, the electrolysis can be easily carried out at the melting temperatures of calcium chloride and its eutectic mixtures with other chlorides.

Value addition to Sri Lankan ilmenite

Ilmenite is composed of iron titanate with the formula unit FeTiO_3 , and we have developed a mechanical method based on rotating autoclave to break down the ilmenite structure, separate the titanium and iron components, and convert them into phase-specific nanomaterials. This process happens at 170°C , thus making it very low-cost. The final discharge contains only sodium chloride solution, which can also be recovered in a saltern. Therefore, the process is environmentally friendly also. We have applied for two NIPO patents and one WIPO patent, and two ACS Omega publications. Figure 4 shows schematic representation of the process of making phase specific TiO_2 nanomaterials and characterization of materials synthesized. As can be observed from atomic percentage data the nanomaterials contain only Ti and O in 1:2 atomic ratio thus confirming 100% purity of the TiO_2 nanomaterials prepared (Rajakaruna, 2020). When the separated titanium sol obtained was mixed with the surfactant hexadecyltrimethylammonium bromide (HDTMA) at a concentration above its critical micelle concentration and subjected to hydrothermal treatment in a closed system of an autoclave, a disordered phase of $\text{Na}_2\text{Ti}_3\text{O}_7$ was obtained. Since these particles are formed within the micelle structure, the product has a flowerlike morphology of rods emerging in all directions starting from one point. The as-synthesized TiO_2 nanoparticles are in an amorphous state that can be converted into over 99% pure anatase phase with 90% crystallinity and 100% pure rutile phase nanorods with 98% crystallinity by calcining at 350°C and 650°C , respectively. The direct band gaps of the three materials determined using Tauc plots are 3.40 eV, 3.60 eV, and 3.15 eV, respectively.

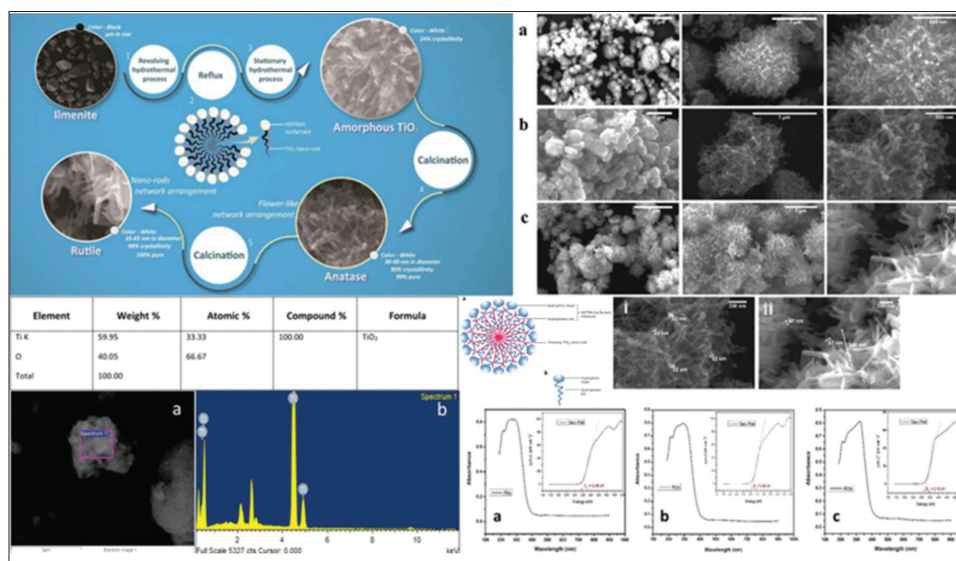


Figure 4: Schematic illustration for the conversion of ilmenite to pure titanium dioxide nanomaterials and their characterization. (Reproduced with permission from Rajakaruna, 2020)

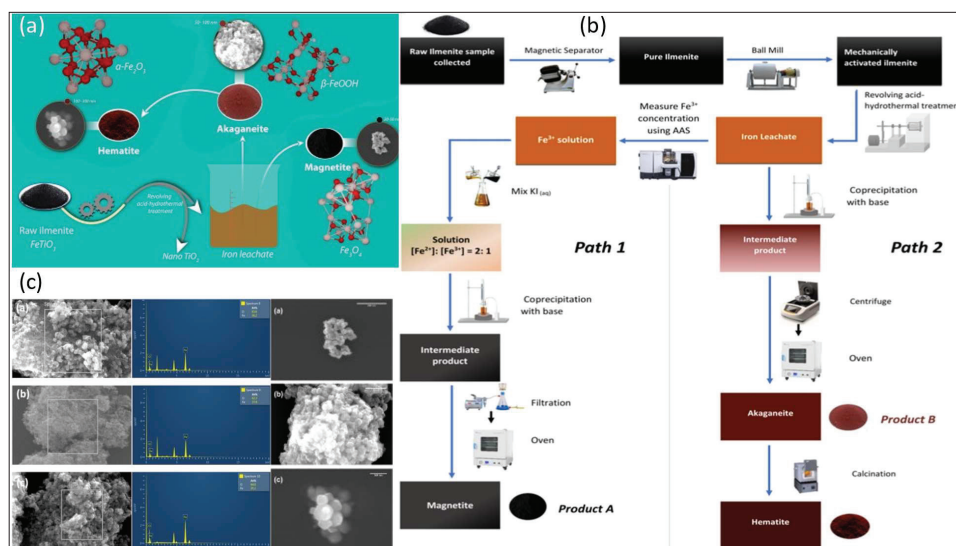


Figure 5: (a) Schematic illustration of the processes involved in converting iron component of the ilmenite to akaganeite, magnetite and haematite nanomaterials, (b) the paths used and (c) characterization of the products obtained. (Reproduced with permission from Rajakaruna, 2021).

We have already demonstrated applications of titanium dioxide nanomaterials in dye-sensitized and perovskite solar cells and in many other application (Jayaweera *et al.*, 2015, 2017; Ranasinghe *et al.*, 2015; Senevirathne *et al.*, 2016; Wanninayake *et al.*, 2016; Kumarasinghe *et al.*, 2019; Uthayaraj *et al.*, 2019; Kumarasinghe *et al.*, 2021).

When the titanium component was removed, the remaining iron component was converted into iron oxide (magnetite and haematite) and iron oxy-hydroxide (akaganeite, β-FeOOH) nanoparticles (Rajakaruna, 2021). Figure 5 shows the process used and the characterization of the products formed. Figure 5(a) schematically shows the process for the conversion of

the iron component into the akageneite phase of iron oxyhydroxide, and the magnetite and haematite phases of iron oxide nanomaterials. Figure 5(b) illustrates the paths used and 5(c) shows morphological and elemental characterizations. When both titanium and iron components are removed, the wastewater contains only sodium chloride that can be recovered in a saltern eventually releasing pure water to the environment. This is a very low-cost and environmentally friendly process that should be utilized to convert our natural ilmenite present in mineral sands into such highly value-added products demanded by many industries.

Value addition to Sri Lankan apatite

In our research, we have developed technologies to synthesize and to convert local apatite to pure hydroxyapatite nanomaterials. In the synthesis of pure hydroxyapatite nanomaterials, we used a calcium source, a phosphate source, and a base to provide hydroxyl ions (Somarathna *et al.*, 2016; Gamagedara *et al.*, 2018; Wijesinghe *et al.*, 2019). For the conversion of local apatite to pure hydroxyapatite nanomaterials, we used urea as the fuel in the combustion method (Somarathna, 2016). In this method, powdered apatite was digested and combusted to produce calcium phosphate nanoparticles. The calcium phosphate nanoparticles thus produced were then hydrothermally treated to convert them into high purity hydroxyapatite (HA) nanoparticles [Figure 6(a)].

The HA nanoparticles were characterized using XRD, FT-IR spectroscopy, SEM [Figure 6(b)] and TEM [Figure 6(c)]. The synthesized HA nanoparticles are nontoxic according to the cytotoxicity results, which confirmed their potential usage in biomedical applications. As such, we developed technology to chemically attach HA nanoparticles to stainless steel and titanium alloy (Ti-6Al-4V) prosthesis materials [Figure 6(d)]. The prostheses thus produced were evaluated for their toxicity, biocompatibility, osteo-integration, and corrosion in the body fluidic environment. Having obtained satisfactory results, two such custom-made prostheses were manufactured and transplanted into needy patients [Figure 5(e)] (Rajapakse, 2016; Wijesinghe, 2014a).

Value addition to Sri Lankan dolomite

Dolomite is $\sim 50:50$ $\text{CaCO}_3:\text{MgCO}_3$ with some silica impurities. When calcined at a temperature above 350°C , MgCO_3 undergoes decomposition according to the reaction $\text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2$ with an enthalpy of reaction, ΔH_{dec} of $+118 \text{ kJ mol}^{-1}$. However, CaCO_3 requires a higher temperature for the decomposition; it starts slowly at 650°C and occurs fast beyond 750°C , with a ΔH_{dec} of $+178.1 \text{ kJ mol}^{-1}$. Therefore, when dolomite is heated above 750°C , both CaCO_3 and MgCO_3 undergo rapid decomposition forming $\text{CaO}:\text{MgO}$ that can be converted to Ca(OH)_2 and Mg(OH)_2 upon hydration. The solubility product constant of Mg(OH)_2

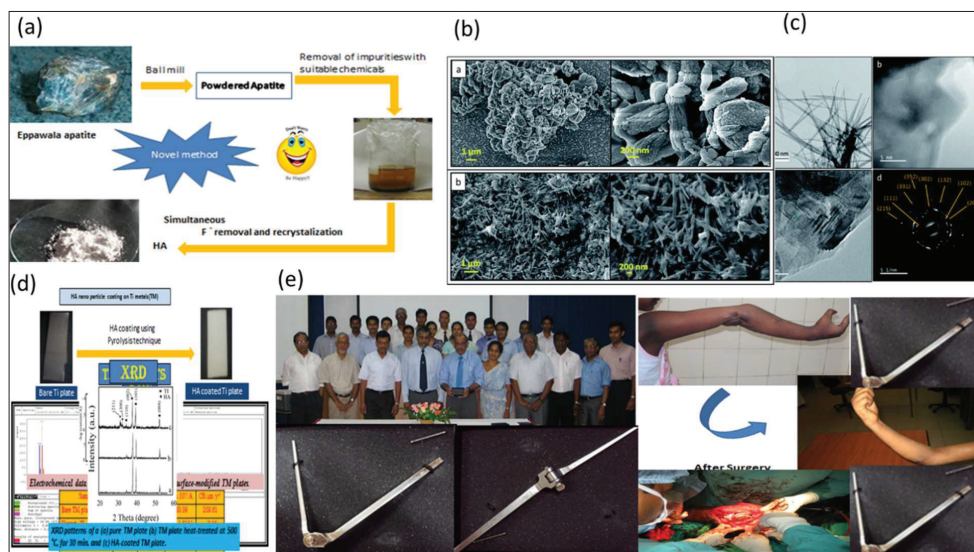


Figure 6: (a) Schematic representation of the combustion process used to convert Eppawala apatite into pure hydroxyapatite nanomaterials; (b) SEM and (c) TEM images of the final product; (d) coating of the hydroxyapatite nanomaterials on to titanium prosthesis material and characterization and (f) orthopaedic transplantation of the custom-made prostheses in needy patients. (Reproduced with permission from Wijesinghe *et al.*, 2014b and Rajapakse *et al.*, 2016)

is 1.2×10^{-11} whereas that of $\text{Ca}(\text{OH})_2$ is 5.5×10^{-6} . Due to the comparatively high solubility of $\text{Ca}(\text{OH})_2$ in water, we found that when a mixture of CaO and MgO is stirred in a sucrose solution, CaO selectively dissolves but MgO is converted to insoluble $\text{Mg}(\text{OH})_2$ and remains as a precipitate together with silica impurities. Therefore, we were able to separate the Ca component into the aqueous solution. The Mg component was separated from silica impurities by dissolving $\text{Mg}(\text{OH})_2$ in dilute HCl and thereby we were able to separate Ca and Mg components and silica impurities. The calcium component was converted to phase-specific CaCO_3 nanoparticles and the magnesium component to MgO and $\text{Mg}(\text{OH})_2$ nanoparticles. The nanoparticles synthesized were used to encapsulate several anticancer drugs for targeted delivery and slow release to eliminate cytotoxicity of the drugs to healthy cells and to reduce dosage, while increasing the bioavailability and efficacy of the drugs. The laboratory studies were extended to scaling up research at the Department of Chemical and Process Engineering, Faculty of Engineering, University of Peradeniya, under the National Science Foundation's Technology Grant No. TG/2016/Tech-D/02, where a spinning disc reactor was developed to synthesize

CaCO_3 nanoparticles on a large scale. In this research, superhydrophobic calcium carbonate nanoparticles were also prepared for various industrial applications. The superhydrophobic CaCO_3 nanoparticles were stabilized with polyacrylate polymer, and the composite was used as a water-repellent wall paint (Mantilaka *et al.*, 2014a; 2014b; 2014c; Wijesinghe *et al.*, 2014b; Abeywardena *et al.*, 2020; Gunathilake *et al.*, 2020).

We have also developed methods to prepare porous vaterite spherical nanoparticles and magnesium oxide nanoflakes starting from dolomite. These nanomaterials, and also many other oxide nanomaterials were used to encapsulate anticancer drugs such as cisplatin, doxorubicin, paclitaxel, and vinblastine for targeted delivery and slow release only at the cancerous sites to eliminate cytotoxicity of the drugs to healthy cells, to reduce wastage of the drug due to toxic adduct formation, and hence to reduce the dosage requirement while increasing the bioavailability and efficacy of the drugs (Dunuweera & Rajapakse, 2017; Weerasuriya *et al.*, 2017; Ranathunge *et al.*, 2019; Wimalasiri *et al.*, 2021)

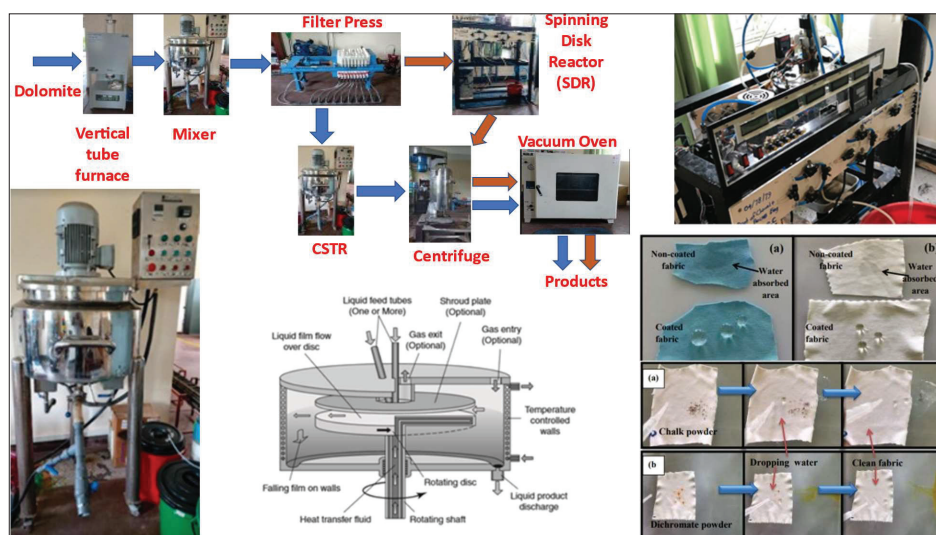


Figure 7: (a) The process flow demonstrating conversion of dolomite to final calcium carbonate products; (b) the Continuous Stirred Tank Reactor (CSTR); (c) the mechanism of the spinning disc reactor; (d) superhydrophobic calcium carbonate produced and demonstration of the stain resistance of superhydrophobic calcium carbonate attached cotton fabric. (Reproduced with permission from Abeywardena *et al.*, 2020). Scaling up research is led by Prof. D.P.P. Karunaratne, Prof. H.M.T.G.A. Pitawala, Prof. R.M.G. Rajapakse, Dr Aruna Manipura and Dr M.M.M.G.P. Mantilaka.

Value addition to Sri Lankan montmorillonite clay

Montmorillonite (MMT) is an aluminosilicate clay with negatively charged clay sheets formed due to isomorphic substitution of aluminium by silicon and magnesium or other divalent cations. The interlayer spaces accommodate hydrated cations to counterbalance the excess negative charge. These cations are usually Na^+ in Na^+ -MMT, and these cations are easily exchangeable with other cations such as H^+ to form H^+ -MMT or organic cations to form organoclay. We made use this exchangeability to incorporate anilinium ions within the interlayer spaces of MMT clay and to chemically polymerize it using an oxidant such as persulphate or iron (II), to form polyaniline (PANI) in its conducting state. The PANI-MMT clay-polymer nanocomposites thus formed were extensively characterized. Additionally, we made PPY-MMT, PEDOT-MMT nanocomposites where PPY and PEDOT stand for polypyrrole and polyethylenedioxythiophene, respectively. Various oxidants were used instead of the two oxidants quoted above. There, we used oxidizing metal cations such as Ag^+ , Hg_2^{2+} , Pd^{2+} , etc. to form nanocomposites of metal atoms/ECP/MMT where ECP stands for ‘electronically conducting polymer,’ such as PANI, PPY, and PEDOT. These novel nanocomposites were found to be excellent cathode materials for alkaline and phosphoric acid fuel cells to replace expensive platinum by the low-cost metal atoms/ECP/MMT nanocomposites (Krishantha *et al.*, 2005, 2006; Rajapakse *et al.*, 2005, 2006; Bandara *et al.*, 2016; Senevirathne *et al.*, 2016). The MMT clay is also found to be an excellent material for improving mechanical properties such as abrasion resistance of gloves produced in the Sri Lankan glove industries.

Value addition to Sri Lankan feldspar

Sri Lankan feldspar is rich in potassium with at least 10% by mass natural abundance in the aluminosilicate clay material. We are currently working on a green method to extract potassium present in clay using microorganisms such as bacteria and fungi. We have found that *Aspergillus* fungi species isolated from the wastewater of cattle farms can release potassium from feldspar. We are working on developing organically produced potassium fertilizer from our natural clay minerals.

Current Market Analysis for Nanomaterials Produced from Sri Lankan Minerals and the Products Developed

The global market for prosthetics and orthotics was around USD 6.11 billion in 2020. It is expected to reach USD 6.39 billion in 2021, and also expected to grow

at an annual growth rate of 4.2% and reach USD 8.6 billion by 2028 [Prosthetics & Orthotics Market Size, Share & Trends Analysis Report by Type (Orthotics, Prosthetics), By Region (North America, APAC), And Segment Forecasts, 2021 - 2028, n.d.]. The global oil spill management market size was USD 131.16 billion in 2015. Based on estimates done in 2015, the market size value in 2020 was USD 159.62 billion with a revenue forecast in 2025 of USD 177.63 billion when calculated at the growth rate of CAGR of 4.0% from 2018 to 2025 (Oil Spill Management Market Size & Share Report, 2018-2025, n.d.-a). The global Nano TiO_2 market was USD 3.4 billion in 2016. With an expected growth rate at CAGR of 20.7% in the next six years, the projected global market in 2022 is USD 16.862 billion (Oil Spill Management Market Size & Share Report, 2018-2025, n.d.-b). The pigment only market for iron oxide/iron nanoparticles in 2021 was USD 2.3 billion. With a growth rate CAGR of 4.7% from 2021 to 2028, the revenue forecast for 2028 is 3.1 billion (Iron Oxide Pigments Market Size | Industry Report, 2021-2028, n.d.). The global silicon metal market size will increase to 9170 million USD by 2025, from 6520 million USD in 2018, at a CAGR of 4.4% during the forecast period. In this study, 2018 has been considered as the base year and 2019 to 2025 as the forecast period to estimate the market size for silicon metal (Global Silicon Metal Market Size In 2021: Growth by Forthcoming Developments, Industry Scope, Opportunity, Business Strategy and COVID-19 Market Scenario | Report by Industry Research Biz - MarketWatch, n.d.). These are some of the examples of the billion-to-trillion-dollar global market available for the materials and devices made starting from local minerals. It is unfortunate that the responsible authorities in Sri Lanka are not considering these developments and taking steps to develop the national economy of the country. The political leadership we had since we obtained independence in 1948 never had a right vision to develop the national economy of the country and as a consequence Sri Lanka is now a country where survival of the nation has become problematic. If our natural resources can be managed in a proper manner by adding value to them then Sri Lanka could become one of the developed countries in the world.

CONCLUSION

Although Sri Lankan researchers have developed novel technologies to add high value to local minerals through low-cost processes and invented novel devices and materials, the incorporation of research output in the industrial processes and integrating scientific advances in the export market are lacking. As this review highlights,

Sri Lanka is a country with naturally abundant high-quality minerals, and their processing to improve purity and to convert them to highly value-added products has been limited to research publications and patents without utilizing these developments in real world applications. This is due to short-sighted political leadership of the country throughout its history since receiving independence in 1948. It is time that the political leadership of the country realized the importance of adding value to local minerals at least by understanding the market research described in section 3. If the country had a leadership with a correct vision and mission, the country could have been among the most developed countries of the world. Currently, we are among the poorest nations of the world despite having such natural treasures and devoted academics and researchers who have contributed enormously towards adding value to these natural resources. It is emphasized that the country should gear towards adaptation of scientific developments in order to stand along as a developed nation.

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REFERENCES

- Abeywardena M.R., Elkaduwe R.K.W.H.M.K., Karunaratne D.G.G.P., Pitawala H.M.T.G.A., Rajapakse R.M.G., Manipura A. & Mantilaka M.M.M.G.P.G. (2020). Surfactant assisted synthesis of precipitated calcium carbonate nanoparticles using dolomite: Effect of pH on morphology and particle size. *Advanced Powder Technology* **31**(1): 269–278.
DOI: <https://doi.org/10.1016/J.APT.2019.10.018>
- Bandara W.M.A.T., Krishantha D.M.M., Perera J.S.H.Q., Rajapakse R.M.G. & Tennakoon D.T.B. (2016). Preparation, characterization and conducting properties of nanocomposites of successively intercalated polyaniline (PANI) in montmorillonite (MMT) **39**(9): 759–774.
DOI: <https://doi.org/10.1177/0021998305048155>
- Chen S. *et al.* (11 authors) (2010). Raman measurements of thermal transport in suspended monolayer graphene of variable sizes in vacuum and gaseous environments. *ACS Nano* **5**(1): 321–328.
DOI: <https://doi.org/10.1021/NN102915X>
- Dahanayake K., Ratnayake M.P.K. & Sunil P.A. (1995). Potential of Eppawala apatite as a directly applied low-cost fertilizer for rice production in Sri Lanka. *Fertilizer Research* **41**(2): 145–150.
DOI: <https://doi.org/10.1007/BF00750756>
- Dunuweera S.P. & Rajapakse R.M.G. (2017). Encapsulation of anticancer drug cisplatin in vaterite polymorph of calcium carbonate nanoparticles for targeted delivery and slow release. *Biomedical Physics and Engineering Express* **4**(1): 015017.
DOI: <https://doi.org/10.1088/2057-1976/AA9719>
- Gamagedara T.P., Rathnayake U.M. & Rajapakse R.M.G. (2018). Facile synthesis of hydroxyapatite nanoparticles by a polymer-assisted method: morphology, mechanical properties and formation mechanism. *Journal of Clinical Investigation and Studies* **1**(1).
DOI: <https://doi.org/10.15761/JCIS.1000101>
- Global Silicon Metal Market Size in 2021: Growth by Forthcoming Developments, Industry Scope, Opportunity, Business Strategy and COVID-19 Market Scenario | Report by Industry Research biz-MarketWatch. (n.d.). Available at <https://www.marketwatch.com/press-release/global-silicon-metal-market-size-in-2021-growth-by-forthcoming-developments-industry-scope-opportunity-business-strategy-and-covid-19-market-scenario-report-by-industry-research-biz-2021-11-09>. Accessed 29 December 2021.
- Gunathilake C.A., Ranathunge G.G.T.A., Dassanayake R.S., Illesinghe S.D., Manchanda A.S., Kalpage C.S., Rajapakse R.M.G. & Karunaratne D.G.G.P. (2020). Emerging investigator series: synthesis of magnesium oxide nanoparticles fabricated on a graphene oxide nanocomposite for CO₂ sequestration at elevated temperatures. *Environmental Science: Nano* **7**(4): 1225–1239.
DOI: <https://doi.org/10.1039/C9EN01442J>
- Iron Oxide Pigments Market Size | Industry Report, 2021-2028 (n.d.). Available at <https://www.grandviewresearch.com/industry-analysis/iron-oxide-pigment-market>. Accessed 29 December 2021.
- Jayaweera E.N., Kumara G.R.A., Pitawala H.M.G.T.A., Rajapakse R.M.G., Gunawardhana N., Bandara H.M.N., Senarathne A., Ranasinghe C.S.K., Huang H.H. & Yoshimura M. (2017). Vein graphite-based counter electrodes for dye-sensitized solar cells. *Journal of Photochemistry and Photobiology A: Chemistry* **344**: 78–83.
DOI: <https://doi.org/10.1016/J.JPHOTOCHEM.2017.05.009>
- Jayaweera E.N., Ranasinghe C.S.K., Kumara G.R.A., Wanninayake W.M.N.M.B., Senarathne K.G.C., Tennakone K., Rajapakse R.M.G. & Ileperuma O.A. (2015). Novel method to improve performance of dye-sensitized solar cells based on quasi-solid gel-polymer electrolytes.

- Electrochimica Acta* **152**: 360–367.
DOI: <https://doi.org/10.1016/J.ELECTACTA.2014.11.156>
- Karunadasa K.S.P., Manaratne C.H., Pitawala H.M.T.G.A., & Rajapakse R.M.G. (2018a). The composition, unit cell parameters and microstructure of quartz during phase transformation from α to β as examined by in-situ high-temperature X-ray powder diffraction. *Journal of Physics and Chemistry of Solids* **117**: 131–138.
DOI: <https://doi.org/10.1016/J.JPCS.2018.02.028>
- Karunadasa K.S.P., Manaratne C.H., Pitawala H.M.T.G.A. & Rajapakse R.M.G. (2018b). Relative stability of hydrated/anhydrous products of calcium chloride during complete dehydration as examined by high-temperature X-ray powder diffraction. *Journal of Physics and Chemistry of Solids* **120**: 167–172.
DOI: <https://doi.org/10.1016/J.JPCS.2018.04.034>
- Karunadasa K.S.P., Manaratne C.H., Pitawala H.M.T.G.A. & Rajapakse R.M.G. (2019a). A potential working electrode based on graphite and montmorillonite for electrochemical applications in both aqueous and molten salt electrolytes. *Electrochemistry Communications* **108**: 106562.
DOI: <https://doi.org/10.1016/J.ELECOM.2019.106562>
- Karunadasa K.S.P., Manaratne C.H., Pitawala H.M.T.G.A. & Rajapakse R.M.G. (2019b). Thermal decomposition of calcium carbonate (calcite polymorph) as examined by in-situ high-temperature X-ray powder diffraction. *Journal of Physics and Chemistry of Solids* **134**: 21–28.
DOI: <https://doi.org/10.1016/J.JPCS.2019.05.023>
- Krishantha D.M.M., Rajapakse R.M.G., Tennakoon D.T.B. & Dias H.V.R. (2005). Polypyrrole-montmorillonite nanocomposite: a composite fast ion conductor **40**(11): 1009–1021.
DOI: <https://doi.org/10.1177/0021998305056388>
- Krishantha D.M.M., Rajapakse R.M.G., Tennakoon D.T.B. & Dias H.V.R. (2006). AC impedance analysis of polyaniline-montmorillonite nanocomposites. *Ionics* **12**: 287–294.
DOI: <https://doi.org/10.1007/S11581-006-0049-8>
- Kumara G.R.A., Pitawala H.M.G.T.A., Karunaratne B., Mantilaka M.M.M.G.P.G., Rajapakse R.M.G., Huang H.H., de Silva K.K.H. & Yoshimura M. (2021). Development of a chemical-free floatation technology for the purification of vein graphite and characterization of the products. *Scientific Reports* **11**: Article number 22713.
DOI: <https://doi.org/10.1038/s41598-021-02101-9>
- Kumarasinghe K.D.M.S.P.K., Kumara G.R.A., Rajapakse R.M.G., Liyanage D.N. & Tennakone K. (2019). Activated coconut shell charcoal based counter electrode for dye-sensitized solar cells. *Organic Electronics* **71**: 93–97.
DOI: <https://doi.org/10.1016/J.ORGEL.2019.05.009>
- Kumarasinghe K.D.M.S.P.K., Karunaratne B.C., Dunuweera S.P., Gamini Rajapakse R.M., Tennakone K. & Asoka Kumara G.R. (2021). Impact of 4-tertiary-butylpyridine in imidazolium iodide/triiodide redox couple-based dye-sensitized solar cells. *ACS Applied Energy Materials* **2021**: 9393–9401.
DOI: <https://doi.org/10.1021/acsaem.1c01587>
- Lee C., Wei X., Kysar J.W. & Hone J. (2008). Measurement of the elastic properties and intrinsic strength of monolayer graphene. *Science* **321**(5887): 385–388.
DOI: https://doi.org/10.1126/SCIENCE.1157996/SUPPL_FILE/LEE-SOM.PDF
- Mantilaka M.M.M.G.P.G., Pitawala H.M.T.G.A., Karunaratne D.G.G.P. & Rajapakse R.M.G. (2014a). Nanocrystalline magnesium oxide from dolomite via poly(acrylate) stabilized magnesium hydroxide colloids. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **443**: 201–208.
DOI: <https://doi.org/10.1016/J.COLSURFA.2013.11.020>
- Mantilaka M.M.M.G.P.G., Pitawala H.M.T.G.A., Rajapakse R.M.G., Karunaratne D.G.G.P. & Upul Wijayantha K.G. (2014b). Formation of hollow bone-like morphology of calcium carbonate on surfactant/polymer templates. *Journal of Crystal Growth* **392**: 52–59.
DOI: <https://doi.org/10.1016/J.JCRYSGRO.2014.02.007>
- Mantilaka M.M.M.G.P.G., Rajapakse R.M.G., Karunaratne D.G.G.P. & Pitawala H.M.T.G.A. (2014c). Preparation of amorphous calcium carbonate nanoparticles from impure dolomitic marble with the aid of poly(acrylic acid) as a stabilizer. *Advanced Powder Technology* **25**(2): 591–598.
DOI: <https://doi.org/10.1016/J.APT.2013.09.008>
- Nair R.R., Blake P., Grigorenko A.N., Novoselov K.S., Booth T.J., Stauber T., Peres N.M.R. & Geim A.K. (2008). Fine structure constant defines visual transparency of graphene. *Science* **320**(5881): 1308.
DOI: <https://doi.org/10.1126/science.1156965>
- Oil Spill Management Market Size & Share Report 2018-2025. (n.d.). Available at <https://www.grandviewresearch.com/industry-analysis/oil-spill-management-market>. Accessed 29 December 2021,
- Pathirage S.S., Hemalal P.V.A., Rohitha L.P.S. & Ratnayake N.P. (2019). Production of industry-specific quartz raw material using Sri Lankan vein quartz. *Environmental Earth Sciences* **78**(3): Article number 58.
DOI: <https://doi.org/10.1007/S12665-019-8060-3>
- Pitawala A., Schidlowski M., Dahanayake K. & Hofmeister W. (2002). Geochemical and petrological characteristics of Eppawala phosphate deposits, Sri Lanka. *Mineralium Deposita* **2003** **38**(4): 505–515.
DOI: <https://doi.org/10.1007/S00126-002-0327-Y>
- Prosthetics and orthotics market size, share and trends analysis report by type (orthotics, prosthetics), by region (North America, APAC), and segment forecasts, 2021-2028. (n.d.). Available at <https://www.marketresearch.com/Grand-View-Research-v4060/Prosthetics-Orthotics-Size-Share-Trends-14436369/>. Accessed 29 December 2021.
- Rajakaruna T.P.B., Udawatte C.P., Chandrajith R. & Rajapakse R.M.G. (2020). Nonhazardous process for extracting pure titanium dioxide nanorods from geogenic ilmenite. *ACS Omega* **5**(26): 16176–16182.
DOI: <https://doi.org/10.1021/ACSOMEGA.0C01756>
- Rajakaruna T.P.B., Udawatte C.P., Chandrajith R. & Rajapakse R.M.G. (2021). Formulation of iron oxide and oxy-hydroxide nanoparticles from ilmenite sand through a low-temperature process. *ACS Omega* **6**(28): 17824–17830.

- DOI: <https://doi.org/10.1021/ACSOMEGA.1C00938>
- Rajapakse R.M.G., Krishantha D.M.M., Tennakoon D.T.B. & Dias H.V.R. (2006). Mixed-conducting polyaniline-Fuller's Earth nanocomposites prepared by stepwise intercalation. *Electrochimica Acta* **51**(12): 2483–2490.
- DOI: <https://doi.org/10.1016/J.ELECTACTA.2005.07.035>
- Rajapakse R.M.G., Tennakoon D.T.B., Perera J.S.H.Q., Bandara W.M.A.T. & Krishantha D.M.M. (2005). Electrochemical impedance spectroscopic and other studies of polyaniline-montmorillonite intercalate. *Journal of Composite Materials* **39**(22): 1985–1999.
- DOI: <https://doi.org/10.1177/0021998305052023>
- Rajapakse R.M.G. et al. (12 authors) (2016). Preparation of bone-implants by coating hydroxyapatite nanoparticles on self-formed titanium dioxide thin-layers on titanium metal surfaces. *Materials Science and Engineering: C* **63**: 172–184.
- DOI: <https://doi.org/10.1016/J.MSEC.2016.02.053>
- Ranasinghe C.S.K., Jayaweera E.N., Kumara G.R.A., Rajapakse R.M.G., Bandara H.M.N. & Yoshimura M. (2015). Low-cost dye-sensitized solar cells based on interconnected FTO-activated carbon nanoparticulate counter electrode showing high efficiency. *Journal of Materials Science and Engineering A* **5**(10).
- DOI: <https://doi.org/10.17265/2161-6213/2015.9-10.005>
- Ranathunge T.A., Karunaratne D.G.G.P., Rajapakse R.M.G. & Watkins D.L. (2019). Doxorubicin loaded magnesium oxide nanoflakes as pH dependent carriers for simultaneous treatment of cancer and hypomagnesemia. *Nanomaterials* **9**(2): 208.
- DOI: <https://doi.org/10.3390/NANO9020208>
- Senevirathne A.M.C., Seneviratne V.A., Ileperuma O.A., Bandara H.M.N. & Rajapakse R.M.G. (2016). Novel quasi-solid-state electrolyte based on γ -butyrolactone and tetrapropylammonium iodide for dye-sensitized solar cells using fumed silica as the gelling agent. *Procedia Engineering* **139**: 87–92.
- DOI: <https://doi.org/10.1016/J.PROENG.2015.08.1117>
- Somarathna Y.R., Mantilaka M.M.M.G.P.G., Karunaratne D.G.G.P., Rajapakse R.M.G., Pitawala H.M.T.G.A. & Wijayantha K.G.U. (2016). Synthesis of high purity calcium carbonate micro- and nano-structures on polyethylene glycol templates using dolomite. *Crystal Research and Technology* **51**(3): 207–214.
- DOI: <https://doi.org/10.1002/CRAT.201500190>
- Udawatte C.P., Panagoda P.V.A., Wickramasinghe W.M.A.D.B., Wijewardena J.D.H., Sirisena D.N., Emtiyagoda S. & Bandara H.R.U.D. (2020). Use of single superphosphate fertiliser produced using eppawala rock phosphate as a source of phosphorous for rice cultivation. *Journal of the National Science Foundation of Sri Lanka* **48**(2): 131–142.
- DOI: <https://doi.org/10.4038/jnsfsr.v48i2.9264>
- Uthayaraj S., Karunaratne D.G.B.C., Kumara G.R.A., Murugathas T., Rasalingam S., Rajapakse R.M.G., Ravirajan P. & Velauthapillai D. (2019). Powder pressed cuprous iodide (CuI) as a hole transporting material for perovskite solar cells. *Materials* **12**: 2037.
- DOI: <https://doi.org/10.3390/MA12132037>
- Wanninayake W.M.N.M.B., Premaratne K., Kumara G.R.A. & Rajapakse R.M.G. (2016). Use of lithium iodide and tetrapropylammonium iodide in gel electrolytes for improved performance of quasi-solid-state dye-sensitized solar cells: Recording an efficiency of 6.40%. *Electrochimica Acta* **191**: 1037–1043.
- DOI: <https://doi.org/10.1016/j.electacta.2016.01.108>
- Weerasuriya D.R.K., Wijesinghe W.P.S.L. & Rajapakse R.M.G. (2017). Encapsulation of anticancer drug copper bis(8-hydroxyquinoline) in hydroxyapatite for pH-sensitive targeted delivery and slow release. *Materials Science and Engineering: C* **71**: 206–213.
- DOI: <https://doi.org/10.1016/j.msec.2016.10.010>
- Wijesinghe W.P.S.L., Mantilaka M.M.M.G.P.G., Karunaratne T.S.E.F. & Rajapakse R.M.G. (2019). Synthesis of a hydroxyapatite/poly(methyl methacrylate) nanocomposite using dolomite. *Nanoscale Advances* **1**(1): 86–88.
- DOI: <https://doi.org/10.1039/C8NA00006A>
- Wijesinghe W.P.S.L., Mantilaka M.M.M.G.P.G., Premalal E.V.A., Herath H.M.T.U., Mahalingam S., Edirisinghe M., Rajapakse R.P.V.J. & Rajapakse R.M.G. (2014a). Facile synthesis of both needle-like and spherical hydroxyapatite nanoparticles: Effect of synthetic temperature and calcination on morphology, crystallite size and crystallinity. *Materials Science and Engineering: C* **42**: 83–90.
- DOI: <https://doi.org/10.1016/j.msec.2014.05.032>
- Wijesinghe W.P.S.L., Mantilaka M.M.M.G.P.G., Premalal E.V.A., Herath H.M.T.U., Mahalingam S., Edirisinghe M., Rajapakse R.P.V.J. & Rajapakse R.M.G. (2014b). Facile synthesis of both needle-like and spherical hydroxyapatite nanoparticles: Effect of synthetic temperature and calcination on morphology, crystallite size and crystallinity. *Materials Science and Engineering: C* **42**: 83–90.
- DOI: <https://doi.org/10.1016/J.MSEC.2014.05.032>
- Wimalasiri V.W., Dunuweera S.P., Dunuweera A.N. & Rajapakse R.M.G. (2021). Noyes-Whitney dissolution model-based pH-sensitive slow release of paclitaxel (taxol) from human hair-derived keratin microparticle carriers. *BioMed Research International* **2021**: Article ID 6657482.
- DOI: <https://doi.org/10.1155/2021/6657482>