SYNTHESIS AND CHARACTERIZATION OF LANTHANUM OXIDE-POLYVINYL ALCOHOL PHOSPHOR NANOFIBERS FOR WHITE LIGHT EMITTING DIODE

HASMAIFARAHATUL HIDAYAH BINTI ABDUL WAHAB

UNIVERSITI SAINS MALAYSIA

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SYNTHESIS AND CHARACTERIZATION OF LANTHANUM OXIDE-POLYVINYL ALCOHOL PHOSPHOR NANOFIBERS FOR WHITE LIGHT-EMITTING DIODE (WLED)

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HASMAIFARAHATUL HIDAYAH BINTI ABDUL WAHAB

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TABLE OF CONTENTS

CHAPTER 4 SYNTHESIS OF La_2O_3-PVA PHOSPHOR NANOFIBERS USING FIVE DIFFERENT SIZES OF NEEDLE DIAMETER……………………………………………...... 59

CHAPTER 5 SYNTHESIS OF La_2O_3-PVA PHOSPHOR NANOFIBERS BY ELECTROSPINNING PROCESS USING DIFFERENT SOL-GEL VOLUMES AND ANNEALING TEMPEATURES………………………………………………... 80

LIST OF TABLES

LIST OF FIGURES

Page

LIST OF SYMBOLS

Abs%	Absorption
c	Speed of light
d_{hkl}	Inter-plane distance between the two neighboring lattice planes
E_g	Energy gap
G	Gauge
$h\nu$	Energy of photon
k	Boltzmann’s constant
n	Photon’s frequency
T%	Transmittance percentage
T	Temperature
wt%	Weight percentage
W	Watt
θ	Bragg’s angle
λ	Wavelength

LIST OF ABBREVIATIONS

au	Arbitrary unit
CIE	Chromaticity coordinates
CRI	Color rendering index
CCT	Correlated color temperature
CuKα	Kα wavelength of copper
eV	Electron volt
Es	Electrospinning
EDX	Energy-dispersive X-ray
FESEM	Field emission scanning electron microscopy
H. V	High voltage
HPC-2	Lightsource Colorimeter
LED	Light-emitting diode
NIR	Near-infrared
PVA	Polyvinyl alcohol
RT	Room temperature
UV-VIS	Ultraviolet-visible spectroscopy
UV	Ultraviolet
WLED	White light-emitting diode
XRD	X-ray Diffraction

SINTESIS DAN PENCIRIAN FOSFOR NANOFIBER LANTHANUM OKSIDA-POLIVINIL ALKOHOL UNTUK DIOD PEMANCAR CAHAYA PUTIH

ABSTRAK

Kajian ini melibatkan aplikasi novel La_2O_3-PVA sebagai fosfor nanofiber untuk diod pemancar cahaya putih (WLED). Fosfor nanofiber La_2O_3-PVA disintesis dengan kaedah elektroputaran dan diaplikasikan sebagai fosfor nanofiber untuk menghasilkan cahaya putih. Nilai koordinat kromatik (CIE), suhu warna korelasi (CCT) dan indeks pemberian warna (CRI) telah diperolehi. Potensi fosfor nanofiber (La_2O_3-PVA) disiasat menggunakan tiga parameter iaitu saiz diameter jarum yang berbeza, ketebalan yang berbeza dan suhu penyepuhlindapan yang berbeza. Fosfor nanofiber La_2O_3-PVA disintesis di atas permukaan substrat kaca dengan menggunakan proses elektroputaran dengan jarak 17 cm daripada hujung muncung, 11.7 mm diameter picagari, 17 kV bekalan voltan dengan kadar aliran 0.5 ml/jam. Lima saiz diameter jarum yang berbeza digunakan untuk memperoleh nanofiber yang stabil dan seragam. Fosfor nanofiber La_2O_3-PVA dengan ketebalan yang berbeza dihasilkan dengan menggunakan isipadu larutan pelopor sebanyak 2, 4, 6, dan 10 ml dengan ketebalan masing-masing sebanyak 2.0, 6.0, 13.0, dan 59.0 µm. Setiap sampel disepuhlindap pada suhu yang berbeza, iaitu 100, 200, 300, 500 °C. Kajian kromatik terhadap fosfor nanofiber La_2O_3-PVA dilakukan dengan mengepam sampel dengan diod pemancar cahaya dengan jarak gelombang 365 nm untuk aplikasi diod pemancar cahaya putih (WLED). Nilai CRI yang optimum sebanyak 70.2 diperoleh dengan nilai CIE 0.3536, 0.407 dan CCT sebanyak 4890 K.

SYNTHESIS AND CHARACTERIZATION OF LANTHANUM OXIDE-POLYVINYL ALCOHOL PHOSPHOR NANOFIBER FOR WHITE LIGHT EMITTING DIODE

ABSTRACT

This study involves the novel application of La_2O_3-PVA as phosphor nanofibers for white light-emitting diode (WLED). The synthesized of La_2O_3-PVA phosphor nanofibers by electrospinning process were then applied as phosphor to produce white light. The chromaticity coordinates (CIE), correlated color temperature (CCT) and color rendering index (CRI) value were obtained. The potential of La_2O_3-PVA phosphor nanofiber was investigated by using three parameters which are different sizes of needle diameter, different thicknesses of nanofiber, and different annealing temperatures. The La_2O_3-PVA phosphor nanofibers were synthesized on glass substrates using electrospinning process at a distance of 17 cm from the nozzle tip, 11.7 mm diameter of the syringe, 17 kV of voltage supply with a flow rate of 0.5 ml/hour. Five different sizes of needle diameter were used to obtain the most stable and uniform nanofiber. Different thicknesses of La_2O_3-PVA phosphor nanofibers were prepared using 2, 4, 6, and 10 ml volume of precursor solution with thickness of 2.0, 6.0, 13.0, and 59.0 µm, respectively. Each sample was annealed at different temperatures which were 100, 200, 300 and 500 °C. The chromatic study of the obtained La_2O_3-PVA phosphor nanofibers was carried out by pumping the samples with 365 nm LED wavelengths for the WLED application. An optimum CRI value of 70.20 was obtained with CIE values of 0.3536, 0.407 and CCT of 4890 K.

CHAPTER 1

INTRODUCTION

1.1 Overview

In recent years, many observations have been focused to the preparation and characterization of one-dimensional (1D) nanostructures (including nanorods, nanowires, nanotubes, nanobelts, etc.) and Quasi-one-dimensional (Q-1D) nanostructures (e.g., nanofibers) because of their eccentric physical and chemical properties. For fields of high efficiency luminescent devices, catalysts, and other practical devices based on their optical, chemical, and electrical characteristics arising from their 4f electrons, rare-earth-doped materials have been greatly indispensable (Song et al., 2012). Photoluminescence in solids mainly from lanthanide, which also called rare-earth or transition metal (TM) is from ions emission center which have been included in crystal and given rise to energy levels within the gap isolate by optical energies. Materials showing photoluminescence are defined as luminescence materials or phosphor. Photoluminescence phenomena is caused by excitation of electromagnetic radiation which is commonly in violet spectrum, cathodoluminescence by a beam of energetic electrons, electroluminescence by an electric voltage, triboluminescence by mechanical energy, X-ray luminescence by X rays and chemiluminescence by the energy of a chemical reaction.

Currently, the attention has focused on the design, production, and advance of the multi-color-emitting phosphor for application in white light-emitting diode (WLED) technology (Xia et al., 2016). An alluring characteristic of luminescent lanthanide compounds is their line like emission, which results in a high color purity of the emitted light. The emission color depends on the lanthanide ion but is largely independent of the environment of a given lanthanide ion which means the resulted emission color was fully developed by lanthanide ion itself but rarely acquired due to environmental factors . Several studies on these compounds have been limited to either inorganic compounds (lanthanide phosphors) or molecular lanthanide compounds (Binnemans, 2009), for example $Tb[Ph_2P(O)NP(O)Ph_2]_3$ ($Tbpip_3$) (Christou et al., 2000). The unique photophysical properties of the lanthanide cations (long luminescence lifetime and a very sharp emission bands), rare earth metal complexes, especially europium (III) complexes, as luminescent material have received increasing attention for applications such as analytical sensor, imaging techniques, display, and organic light-emitting diode. Recently europium complexes have attracted more interest in organic light-emitting diode for their saturated red emission. Also, several europium complexes have been applied as red emitters in electroluminescent devices.

Nowadays, white LED use advanced technology that can participate with traditional incandescent and compact fluorescent lamps, which have countless advantages over the latter such as small size, high lifetime, robustness, fast switching and efficiency which starts to advance towards theoretical limits. The typical operating range for an LED is approximately 10-30 mA and 1.5-3 V. Therefore, the finding of new photoluminescent color converting material will be presented in the LED light source and this topic also opens up new avenues for spectroscopy physics (Paquin et al., 2011; Li et al., 2009; Wang et al., 2014). Sol-gel method was used in this work because of its benefits comprising cost-effectiveness, safe and easy to assemble in the laboratory, and controllable experimental parameters. Sol-gel preparation, involves the formation of a sol followed by formation of a gel, commonly uses either colloidal dispersions or inorganic precursors as the starting material (Ward & Ko, 1995).

In this research, the electrospinning method was used to produce phosphor nanofibers due to the easy method and setup. Electrospinning is a fibers spinning method that produces polymer fibers of nanometer to micrometer size in diameters. Typically, a polymer solution is placed into a container and is subjected to electric fields of several kilovolts up to 40 kV. The polymer is ejected through the nozzle under the applied electrostatic force which is then deposited on a template, on which the template also acts as the electrical charges grounding. More than 20 different types of polymer fibers have been generated by electrospinning method (Demir et al., 2002). Various parameters that affected the electrospinning process which is solution viscosity, size of needle diameter, voltage supply, thickness, temperature, types of substrate used, distance of needle tip to collector plate, and flow rate (Gomes et al., 2007).

1.2 Problem Statement

White light-emitting diode (WLED) has devoted increasing attention as a light source for the next generation of general lighting owing to low energy consumption. Commercial WLED is obtained mainly by combining InGaN LED with yellow emitting Yttrium aluminum garnet ($Y_3Al_5O_{12}$: Ce^{3+}) phosphor. Low color rendering index, low color reproducibility, and luminous efficiency had been reported with this composition. As a remedial measure for these problems, the use of a combination of red and green phosphor instead of a yellow has been proposed (Jang et al., 2007). The application of lanthanum oxide-Polyvinyl alcohol (PVA) green-emitting phosphor nanofiber for WLED synthesized by electrospinning has not been investigated. From past work, the luminescent properties of Terbium-doped lanthanum oxide (La_2O_3: Tb^{3+}) (Song et al., 2012) nanofibers were investigated but not for WLED. The value of color rendering index (CRI), correlated color temperature (CCT), chromaticity coordinates (CIE) were not investigated. To handle this problem of low luminescent properties, many phosphor nanofibers were investigated from past research, various red, blue and green phosphor nanofibers had been explored. However, green phosphor has been less explored. Over the past few years, several phosphors were studied and several synthesizing techniques had been practiced. Electrospinning was found to be a promising option for synthesizing nanofibers as the electrospinning parameters can be manipulated to produce phosphor of desired properties. Electrospinning offers a simpler, convenient, versatile and cost-effective method for synthesizing nanoparticles compared to other methods (Yim et al., 2013). Electrospinning process supports the formation of uniform fibers and beads-like with preferred morphologies under different conditions. In order to investigate lanthanum oxide (La_2O_3), the suitable polymer needs to be chosen that will help to support the material and formed a nanofiber. Terbium-doped lanthanum oxide (La_2O_3: Tb^{3+}) (Song et al., 2012) used polyethylene oxide (PEO) as a polymer and many literature studies used PEO as the pore former to enhance enrichment ability (Khosari et al., 2016) which means inherent characters, for examples strength and stability of the modified foam were also improved. This material acted as a porogen to increase the adsorption capacity of the metal-organic frameworks foam. The polymer itself has various types that can be used in specific applications. One of those biodegradable polymers are PVA due to its favourable properties; high tensile, compressive strengths, abrasion resistance and tensile modulus, made possible because it possesses the highest crystalline lattice modulus (Masuda et al., 1999). The main benefit of PVA used in this work includes its biodegradability in physiological environments. In other words, PVA is a harmless material, has no negative effects on animals, and does not cause any damages to the skin (Seema et al., 2009). Even though the properties of each polymer have been studied extensively by analysing the parameters of the electrospinning process, the data obtained is inadequate to support the electrospinning of ultra-thin nanometer-scale polymer fibers. Thus, more investigation is needed for parameter studies (Li et al., 2016).

1.3 Aim of the Study

This research aims to explore the potential of novel La2O3-PVA as a phosphor nanofiber for WLED, hence forth to fabricate nanofiber. The structural, morphological and optical properties are investigated by using different sizes of needle diameter, different thicknesses and all nanofibers were annealed at different temperatures. This parameter will present the perfect needle size that formed and placed nanofiber in uniform arrangement and perfect shape, capable to determine the best thickness and appropriate annealing temperature for novel La_2O_3-PVA phosphor nanofiber. Hence at the same time resulting in high luminescent properties.

1.4 Objective of the Study

1. To synthesize a La_2O_3-PVA phosphor nanofibers by electrospinning method.
2. To examine the structural and morphological properties of the La_2O_3-PVA phosphor nanofiber
3. To investigate the electroluminescence properties of La_2O_3-PVA phosphor nanofiber for white light-emitting diode (WLED).

1.5 Novelty of the Works

This is the earliest research to synthesize La_2O_3-PVA phosphor nanofiber by electrospinning method under different conditions and environments. Since La_2O_3-PVA had never been used in previous studies, not much information can be found about the production of white light using La_2O_3-PVA. Therefore, the investigation of the value of chromaticity coordinates (CIE), correlated color temperature (CCT) and color rendering index (CRI) of the La_2O_3-PVA phosphor nanofiber for WLED is a novel concept.

1.6 Scope of the Study

This work includes the preparation of La_2O_3-PVA phosphor nanofiber by means of electrospinning method. The synthesized nanofibers were then applied as phosphor nanofibers and the samples were pumped by 365 nm LED for the white WLED application. This study also entails the process of sol-gel to form a homogeneous precursor solution to undergo the electrospinning process and formed La_2O_3-PVA phosphor nanofibers. The sol-gel techniques and electrospinning method were expected to improve and enhance the formation of novel La_2O_3-PVA phosphor nanofibers.

1.7 Outline of the Thesis

This thesis consists of six chapters. Chapter 1 presents a synopsis of the work, problem statement, the aim of the study, objectives, and the novelty of the works. Chapter 2 provides a wide review of phosphor nanofiber, their characteristics, sol-gel techniques, electrospinning method, the theoretical background of lanthanum oxide and polyvinyl alcohol, and various parameters that can affect the electrospinning process. Methods and the system used for deposition was illustrated in Chapter 3, as well as the equipment used to characterize the La_2O_3-PVA phosphor nanofibers and optical system. Chapter 4 presents the results of the La_2O_3-PVA phosphor nanofibers synthesized via the electrospinning method by using five different sizes of needle diameters (0.45 mm, 0.55 mm, 0.65 mm, 0.75 mm, 1.1 mm). The findings of the effects of needle diameter were also discussed in this chapter. Chapter 5 focuses on two-parameter which is the investigation by using different thicknesses and different annealing temperatures on the properties of La_2O_3-PVA phosphor nanofibers. The final choices of the best condition will be considered for La_2O_3-PVA phosphor nanofibers for WLED application. Chapter 6 presents the conclusions of the study and recommendation for future study.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter points toward reviewing the relevant kinds of literature and general principles related to the method of deposition of nanofiber using electrospinning process and the sol-gel technique. The advantages of lanthanum in optical material and the significance of rare-earth metals in WLED were studied. The conditions and parameters that affected electrospinning process in terms of solution properties, processing conditions and ambient parameters were briefly explained. Different lighting terms were explained for WLED.

2.2 Electrospinning Deposition Method

The technique based upon the use of electrostatic forces to fabricate continuous fibers with the diameter between ten nanometres to some micrometres is known as electrospinning. As for the manufacturing of nonwoven fibers, traditional methods cannot be used to achieve high quality and exceptional fibers. The nanofibers formed with electrospinning have an extraordinarily large active surface area per mass unit and the spinning process itself enables a planned formation of the web structure (e.g planned size of pores in the web by tuning the nanofibre diameter and fiber thickness).

Nanofibers can be produced by electrospinning from natural or synthetic polymers and combinations of both, from polymers with numerous nanoparticles (metal, ceramic, etc), active substances, and many more. Individual fibers, as well as webs with a random or planned fiber arrangement can be mass-produced. This method has become a significant part of research in various fields of use of technical textiles, e.g shielding materials, air and oil filters in the car industry, agro textiles and most of all medical textiles.

Poly(methyl methacrylate) (PMMA) nanofibers were produced in past work through electrospinning and produced pure, surface-roughened and coaxial hollow nanofibers which the presence of lanthanides into the transparent PMMA enhances and broadens its applications (Table 2.1), as they combine the advantages of both polymers (good processability and good mechanical properties) and inorganic luminescent materials (high luminescence efficiency and long-term chemical stability (Philip et al., 2021).

Electrospinning is a desired process for manufacturing ultrathin fibres using polymer solution or melt due to the presence of electrostatic forces (Lyons et al., 2016). During the process, a conducting liquid that flows out of a nozzle under prominent voltage will be sprayed into every single drop by repulsive forces. The liquid act as the precursor will be subsequently precipitated slowly on the opposite electrode. Electrospinning techniques have also been used to produces various nanofibers for different aims of study (Table 2.1).

For example, study on luminescence properties of terbium-doped lanthanum oxide (Song et al., 2012) followed by study on effect of La^{3+} doping on optical and photocatalytic properties (Pascariu et al., 2019) (Table 2.1). In 1902, patents about the production of fibre materials by electrospinning from solution were published (Malakhov et al., 2009).

The approach of using polymer melts to obtain fibre was attempted for the first time in 1981 (Zhou et al., 2006).The electrospinning process is advantageous because of its ability to manage all stages at one time in order to yield the product at the end.

Besides, it provides a wide range of parameters, which allows a broad-spectra of material. As well as the adjustability of the method to control the structure of the materials. Past research showed that electrospinning methods have also been used to generate white light (Dhakal et al., 2005; Lakshmi et al., 2019). Currently, the interest in producing polymer fibres by electrospinning has increased drastically. Nevertheless, majority of the studies and manufacturing processes were carried out for electrospinning of polymer melts.

Innumerable polymers, such as poly ethylene terephthalate, polyolefins, and polyamides are highly expensive and are only soluble in solvents and at very high temperatures. Because of the safety hazard that these polymers could assimilate due to its unsafe characteristics, such as dangerous, toxic and hazardous to the environment, the polymers are limited for use in the fibre production.

Lanthanide-doped sodium yttrium fluoride ($NaYF4;La^{3+}$) had been fabricated from past work by electrospinning (Table 2.1). The study showed that small reduction of upconversion efficiency for the upconverting nanoparticles (UCNPs) in nanofibers were formed, signifying that upconversion properties of the UCNPs are largely preserved in the nanofibrous films. (Bao et al., 2012).

Additional drawback about solution technology is due to solvent evaporation, which is a waste and thus is not economically advantageous. However, the melt technology is better because the fibres obtained from the melt are more uniform in size with less imperfection and finer physical mechanical properties (Malakhov et al., 2009). Nanoparticles and nanofibers of bimetallic oxides ($LaNiO_3$, $SmCoO_3$ and $DyFeO_3$) were fabricated by electrospinning (Branco et al., 2017) and all bimetallic oxides present a morphology that is very similar and better described has a homogeneous solution and their specific areas and particles size more favorable (Table

2.1). Besides, the fibres obtained by electrospinning were also used to fabricate filters and textile material for manufacturing of work clothing (Lee & Obendorf, 2006). However, many factors determining the usefulness of the electrospinning method remain unexplored.

Table 2.1 Lanthanide materials used in electrospinning with different aims of study

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Materials	Year	Aim of study	References
Poly(methyl methacrylate), (PMMA) doped with La^{3+} ions	2021	Studies on the structural and optical properties of pure and structurally modified electrospun poly(methyl methacrylate) nanofibers incorporated with lanthanide complex	Philip et al.
La_2O_3: Tb^{3+}	2012	The preparation and luminescence properties of terbium-doped lanthanum oxide nanofibers by electrospinning	Song et al.
ZnO doped with La^{3+} ions (0.02%, 1%, 2% and 4%).	2019	Investigation on preparation of La-doped ZnO ceramic nanostructures by electrospinning–calcination method: Effect of La^{3+} doping on optical and photocatalytic properties	Pascariu et al.
Lanthanide-doped sodium yttrium fluoride (NaYF4;La^{3+})	2012	Upconversion polymeric nanofibers containing lanthanide-doped nanoparticles via electrospinning	Bao et al.
$LaNiO_3$, $SmCoO_3$ and $DyFeO_3$	2017	Lanthanide bimetallic oxide nanoparticles and nanofibers for partial oxidation of methane	Branco et al.
(La)-doped zinc oxide (ZnO)	2019	Study of chemically modified electrospun nanofiber for high adsorption and effective photocatalytic decontamination of organophosphorus compounds	Lakshmi et al.

2.3 Sol-gel Techniques Overview

In order to prepare and understand catalytic materials, sol-gel is one of the most flexible methods. Sol-gel product’s structural and chemical properties can be controlled by large scale group of available synthetic parameters. The controllable parameters help catalytic researcher to plan and study the consequence of composition, homogeneity, pore structure and metastable phases on catalytic performance with more detailed. As starting material, the colloidal distribution or inorganic precursors were used in sol-gel process which involve the formation of a sol and then by formation of a gel (Ward & Edmond, 1996). Alkoxide route was the main focus in the past research. In addition, sol-gel preparation can be achieved excellently with various precursors. For example, when alkoxide (M(OR)J) acts as a precursor, the chemistry reactions of the sol-gel can be expressed by two category which is hydrolysis and condensation.

Two suggestions were stated in sol-gel chemistry reactions. The first reaction is formation of a gel due to the condensation of partially hydrolyzed species to three-dimensional polymeric network. Next, the properties of the gel will be affected by both of these factors. To distinguish sol-gel process from other methods, these parameters act as important criteria. For example, type of precursor, type of solvent, water content, acid or base content, precursor concentration, and temperature. The characteristics of the materials in all processing steps were controlled by these parameters. To separate the solvent, dehydrated gel needs to be obtained (Ward & Edmond, 1996). Aging is one of the important parameters, which is a process in the middle of formation of a gel and its drying time. The hydrolysis and condensation processes will take over as a gel unchanged in the middle of aging process. Additionally, the process of synthesis will occur which involves the splitting up and reprecipitation of particles and the removal of the solvent. All of these are due to the roughness and diminishing of a gel (Doshi & Reneker, 1995). The chemical and structural properties of a gel can be affected by this situation after its starting to form. Drying is one of the parameters that give impact to sol-gel process. Standard evaporative drying induces capillary pressure connected with the liquid-vapor interface within a pore and process of gel annealed inside oven. The samples with normal distribution of pore sizes, drying process tend to deteriorate the porous network and the resultant differential capillary tension occurred.

Xerogel is one of the dried samples that failed to be classified as catalytic interest due to small distribution of surface area and pore volume. To reduce the effect of conventional drying, the development of xerogels with large surface areas and pore volumes needs to be formed in detail. Supercritical drying is used to bypass the complication of differential capillary pressure which was explored in the past researches (Moulton & Moulton, 1947). The first application of sol-gel methods was antireflection (AR) coatings. Wet chemical methods had been applied to develop single, multi-layer and graded-index antireflection (AR) coating. Sol-gel synthesis route has been recounted to be a viable approach to combine organic-inorganic components at the nanoscale and/ or molecular level. The objective is the insertion of polymer chains into the sol while the inorganic network is being formed. The structure and properties of the hybrids were affected by the type of polymer used and causes chemical interactions established between the organic and inorganic components (Tin & Ato, 2011; Larsen et al., 2003). Unluckily, owing to their poor solubility, countless of biodegradable polymers cannot be established into the sol. Therefore, researcher studied only a nondegradable and water-soluble polyvinyl alcohol (PVA) for sol-gel process in order to synthesize polymer/ bioactive glass (BG) hybrid materials (Allo et al., 2010). From past works, several types of lanthanide material had been explored using sol-gel process with different types of solvent (Table 2.2). Lanthanide oxide-based aerogels were synthesized utilizing the so-called epoxide addition sol-gel method using propylene oxide as a solvent, which resulted in aerogels remained monolithic with a variety of appearances and were fairly stable and able to undergo gentle handling without calving or cracking (Wittstock et al.,2012). Fabrication of lanthanide doped zinc sulphide (ZnS) using dimethyl sulfoxide (DMSO) as a solvent appears to avoid undesired particle aggregation during the sol-gel process (Julian-lopez & Julia., 2008). Lanthanide ion containing garnet had been prepared with sol-gel method based on in-situ generation of mixed-metal chelates by complexing metal ions with ethane-1,2-diol in an aqueous solution.

Table 2.2 The preparation of the lanthanide materials using different types of solvent

Material	Solvent	References
($LnCl^3.xH_2O$ and $Ln(NO_3)_3$ xH_2O; x = 6, 7)	Propylene oxide (PO)	Wittstock et al
Ln doped ZnS, $Zn(NO_3)_2$.6H2O, $Eu(NO_3)_3$	Dimethyl sulfoxide (DMSO), $(CH_3)_2SO$	Julian-lopez & Julia
$[NH_4]_2[Ce(NO_3)_6]$, La_2O_3	Nitric acid (HNO_3)-ethane-1,2-diol ($HOCH_2CH_2OH$)	Dubnikova et al.
$[Tb(bpy)_2]Cl_3.2H_20$ and $[Eu(phen)_2]Cl_3.2H_20$	N,N-dimethylformamide (DMF)	Jin et al
Tetraethylorthosilicate (TEOS) and $Al(NO_3)_3.9H_2O$	Distilled water and HCl as a catalyst	Rojas-hernandez & Santos
$Tb(NO_3)_3.6H_2O$ and 2,2-bipyridine	Dimethyl sulfoxide (DMSO), $(CH_3)_2SO$ and Tetraethyl orthosilicate (TEOS)	Yu et al
$TbCl_3.6H_20$ and $EuCl_3.6H_20$	Toluene(C6H5CH3)	Lessard et al

The preparation of particular phases is possible at ambient and mild conditions due to the reactivity of such precursors while starting from a solid state precursor either in high temperatures or pressure (Dubnikova et al., 2010). Organic lanthanide complexes were prepared and dissolved in N,N-dimethylformamide (DMF) and resulting composite materials also possessed excellent mechanical strength, hydrolytic stability and consequently good durability for the emissions from the lanthanide compositions (Jin et al., 1998). Lanthanide (Ln)-doped luminescent layers were deposited using sol-gel method on cell materials to attain spectral conversion by methods like chemical vapor deposition (CVD) or physical vapor deposition (PVD). Sol-gel processing is a low-cost technology that may be a good alternative to achieve this purpose (Rojas-hernandez & Santos, 2020). A group of silica gel electrolytes with lanthanide luminescent hybrid materials were investigated using sol-gel process. The emission of characteristic narrow-lined luminescence even in sulfuric acid solutions of gel electrolytes from their siliceous hybrid materials can also be observed (Yu et al., 2017). Molecular composites that possess unique emission properties had been prepared by introducing luminescent molecules into sol-gel based silica glasses which resulted in lanthanide cryptates in an aqueous solution and the sol-gel matrix is intensely luminous (Lessard et al., 1989).

2.4 The Advantages of Lanthanum as an Optical Material

The development of nanoscale materials and devices are widely affected by metal and semiconductor nanoparticles (NPs) as the critical material. To obtain range of NP architectures, including two- and three-dimensional film assemblies, designed colloidal aggregates, NP-based photovoltaic, electroluminescence, and sensing devices, the nanoscale materials were applied as a building block. An essential characteristic of such NPs is their size-dependent physicochemical properties which is optical, electrical, magnetic, and catalytic properties.

Rare-earth-doped lanthanum phosphates ($LaPO_4$) contains different class of NPs that reveal distinctive optical properties (Zhang & Guan, 2005). In recent years, $LaPO_4$ NPs undergo a synthetic route in organic solvent for high monodisperse fluorescent and the work was reported (Riwotzki et al., 2000). Next, by using various preservative agents, NPs were then transferred to an aqueous phase (Schuetz & Caruso, 2016). The fluorescence of $LaPO_4$ NPs was developed from a distinct nature with same size range (≈5 nm) as quantum dots (QD NPs), whereas, due to size-dependent band gaps, semiconductor NPs turn into fluorescent. The bulk properties (i.e., transitions between d and f electron states and their local symmetry) are the main effect for the growth of fluorescence of $LaPO_4$ NPs (Riwotzki et al., 2000; Bourcet & Fong, 1974; Qin & Wang, 2006). With the use of the rare-earth dopant, the absorbance and emission properties of quantum dots can be adjusted to yield NPs with different optical properties regardless of their sizes. $LaPO_4$ NPs are acceptable in biological labelling applications because $LaPO_4$ NPs have high quantum yield, up to 61%, high chemical stability, and expected low toxicity (W. Li et al., 2001). A simple thermal decomposition route has been developed to prepare La_2O_3 and $La_2O_2CO_3$ nanoparticles and the result shows that lanthanum oxy-carbonate nanoparticle is a promising material in photocatalytic applications such as waste water purification (Ghiasi & Malekzadeh, 2015). Novel luminescent and amorphous $La_2O_3ZrO_2:Eu^{3+}$(LZE) nanofibrous membrane with robust softness are fabricated for the first time via a simplistic electrospinning technique and exhibit excellent softness and luminescent properties, which make the materials have potential applications in fluorescent lamps and field emission displays (Weidong et al., 2013).

Moreover, as coatings for luminescent lamps, the use of rare-earth-doped $LaPO_4$ thin films from micrometer-sized powders have been recorded, to accentuate their high constancy toward bleaching. Main requirement for the preparation of functional thin film devices are the build layered structures of fluorescent NPs with nanoscale precision and tuned properties. Layer-by-layer (LbL) assembly technique is one of the most important approaches for achieving vertically structured thin films with control at the nanometer scale which is very compromising. The successive deposition is a basic method for substrate with oppositely charged species (Junxing Li et al., 2005). Lanthanum oxide (La_2O_3) has the potential to be more beneficial material in a wide range of optical and electronic applications due to their large energy band gap, Eg > 4 eV and also contains the lowest lattice energy with high dielectric constants of $\varepsilon = 27$ pF/m (Ramjeyanthi et al., 2018).

2.5 Polyvinyl Alcohol (PVA) Overview

Polyvinyl alcohol (PVA) is a semi-crystalline, hydrophilic polymer with good chemical and thermal stability. The main beneficial property of PVA includes its biodegradability in physiological environments. PVA is a non-hazardous material, has no negative effects on animals, and does not cause any injuries to the skin upon contact (Seema et al., 2009). Polyvinyl alcohol (PVA) has been of interest because of its good properties and various usages and was obtained by the saponification of polyvinyl ester or poly (vinyl ether).

PVA resins are widely used in various applications such as a fibers for cloth industries, adhesives and binders, films, membranes, materials for drug delivery system, and cancer cell-killing embolic materials (Masuda et al., 1991; Lyoo et al., 1997) due to their excellent chemical resistance, physical properties, and biocompatibility. PVA fiber has high tensile and compressive strengths, tensile modulus, and abrasion resistance due to its highest crystalline lattice modulus. Molecular parameters that can be controlled to optimize the physical properties of PVA are molecular weight, degree of saponification, and syndiotactic (Choo et al., 1999; Lee et al., 2003). Especially, molecular weight is a fundamental parameter affecting the physical properties of PVA (Lyoo & Ha, 1999; Lyoo & Blackwell, 1998).

For specific applications, the optimization of biodegradable polymeric fiber structures can provide a large surface area, and a relatively high porosity. Due to the structural similarity between electrospun polymeric mats and the collagen fiber arrangement in the natural extracellular matrix component of bone, the electrospinning process has drawn a great deal of attention in scaffold processing for tissue engineering (Greiner & Wendorff, 2007; Li et al., 2001; Matthews et al., 2002).

In addition, electrospinning is regularly used to fabricate nano-fibrous structures from a number of natural synthetic polymers, such as collagen chitosan (Min et al., 2004; Ohkawa et al., 2004; Jin et al., 2002), silk fibroin (Li et al., 2005) hyaluronic acid (Yoshimoto et al., 2003), poly(L- lactide) (Zhang & Chang, 2008) and polycaprolactone (Yoshimoto et al., 2003; Venugopal et al., 2008; Rujitanaroj et al., 2008). In recent years, as for biomedical applications, including tissue engineering of scaffolds, wound dressings, drug delivery, and in other fields such as medical implants (Bader et al., 2012; Barhate & Ramakrishna, 2007; Sill & Recum, 2008; Rao et al., 2006; John & Thomas, 2008; Lutolf & Hubbell, 2005), the electrospinning technique has proven to be exceptionally suitable.

Biodegradable polymers have gained a large amount of attention and also been proposed as a viable option to other tissue engineering materials. These polymers can be easily classified into three-dimensional porous structures with proper degradation behavior and mechanical strength (Wang et al., 2014). The incorporation of nanofibers of PVA into the novel nanocomposite membranes with a nafion matrix (NAF/PVA) is a proper approach in order to reduce methanol crossover. The nanofibers have been obtained by electrospinning of a water solution of the polymer with a cationic surfactant additive.

In order to maintain high proton conductivity of composite membranes prepared with nafion, the external surface of PVA nanofibers had been utilized with sulfonic groups and had been proven that the infiltration of such polymer into the porous structure of the nanofibers mat is achievable by means of successive steps of wetting and evaporation.

The advantages exhibited by the nanofibers come from the obtaining of reinforced composite films, much thinner than commercial nafion (Reneker & Chun, 1996), and with an attractive potential as methanol barriers for membranes applied to Direct Methanol Fuel Cells (DMFCs) (Greiner & Wendorff, 2007).

2.6 The Significance of Rare-Earth for White Light-Emitting Diode (WLED) Application

With the rapid development of lighting equipment, WLEDs have attracted increased attention in both industrial and scientific research fields due to their long lifetime, low energy consumption, mercury-free composition, good reliability and high efficiency (Suryamas et al., 2012). The combination of blue InGaN LED chip with a yellow YAG: Ce phosphor forms traditional two-color WLEDs (K. Song et al., 2015). However, due to the deficiency of red components in the emission spectra of YAG: Ce, these two-color WLEDs exhibit a poor color rendering index (CRI) and high correlated color temperature (CCT). As a result, warm WLED cannot be achieved. The combination of ultraviolet (UV) chip with red, green, and blue (RGB) phosphors to fabricate tri-color WLED is one of alternative methods that can be used (Jiang et al., 2014; Xia et al., 2016). The exploration of high-efficiency red phosphors excited by near-UV or blue light had been actively investigated. As the price of some of the activators are expensive, their applications in optoelectronic devices were limited.

Consequently, the development of new efficient, less-expensive, environmentally friendly and rare-earth-free phosphors is of particular urgency. Due to the facile preparation and chemical stability, the oxide-based compounds doped with rare-earth ions gaining major attention for the application of luminescence under vacuum ultraviolet (VUV) excitation. One-dimensional (1D) nano phosphors can play a crucial role in optoelectronic device applications and had been revealed on past research work. To develop new functionalities based on the quantum effects and improve the emission intensity and efficiency of the devices, uniform nanofiber phosphors need to be applied (Yim et al., 2014; Park et al., 2014). Many types of rare-earth which were described in Table 2.3 below including $CaSi_2O_2N_2:Eu^{2+}$ (Hou et al., 2011), $Tb_2(WO_4)_3$: Eu^{3+} (Dong et al., 2009), $Y_2O_3:Eu^{3+}$ (Cheng et al., 2010), $Y_3Al_5O1_2:Ce^{3+}$(Song et al., 2012) $SrAl_2O_4:Eu^{3+}Dy^{3+}$(Dali et al., 2010), $NaGdF_4:Eu^{3+}$ (Wang et al., 2009) and $ZnGa_2O_4:Mn^{2+}$ (Wang et al., 2017) have been prepared by electrospinning technique. High luminescent intensity and quantum efficiency had been documented from prepared 1D luminescent materials compared to corresponding bulk materials (Park et al., 2014; Yim et al., 2014). The investigation on potential application in warm WLED of $CaAl_{12}O_{19}$: Mn^{4+} and both electrospinning technique and the luminescent properties of $CaAl_{12}O_{19}$: Mn^{4+} nanofiber phosphors are very commendable (Liu et al., 2008).

Table 2.3 Past research works on the synthesis of phosphor nanofibers doped with various rare-earth metals with different aims of study

Materials	Aim of study	References
$CaSi_2O_2N_2$: Eu^{2+}	Study of $CaSi_2O_2N_2$: Eu nanofiber mat based on electrospinning: facile synthesis, uniform arrangement, and application in white LED	Hou et al
$Tb_2(WO_4)_3$: Eu^{3+}	Study of electrospinning- derived $Tb_2(WO_4)_3$: Eu^{3+} nanowires for energy transfer and tunable luminescent properties	Dong et al
Y_2O_3: Eu^{3+}	Investigation of structural and photoluminescence properties of europium-doped titania nanofibers prepared by electrospinning method	Cheng et al
$Y_3Al_5O1_2$: Ce^{3+}	Study of photoluminescent and crystalline properties of $Y_{3-x}Al_5O_{12}$:$Cex^{3+}$$Y_{3-x}Al_5O_{12}$: Ce^{3+} phosphor nanofibers prepared by electrospinning	Suryamas et al
$NaGdF_4$: Eu^{3+}	To investigate electrospinning preparation and properties of $NaGdF_4$: Eu^{3+} nanowires	Want et al
$CaAl_{12}O_{19}$: Mn^{4+}	Study the electrospinning, optical properties and white LED applications of one- dimensional $CaAl_{12}O_{19}$: Mn^{4+} nanofiber phosphors	Liu et al
$ZnGa_2O_4$: Mn^{2+}	Study the preparation and luminescence properties of Mn^{2+}-doped $ZnGa_2O_4$ nanofibers via electrospinning process	Wang et al
TiO_2: Eu^{3+}	Study structural and photoluminescence properties of europium-doped titania nanofibers prepared by electrospinning method	Zhao et al

2.7 Conditions and Parameters that Affected Electrospinning Process

To fabricate continuous nanofibers, electrospinning had been one of the uncomplicated, versatile and favourable processes. The nanofibers demonstrate high porosity, large surface area per unit mass, high gas permeability and small inter-fibrous pore size (Saeed & Park, 2010).

Solution properties were one of parameter that affected electrospinning process (Table 2.4). Concentration, viscosity, electrical conductivity, surface tension, and dielectric properties are the parameters pertaining to solvent solution. Numerous variables including electrical field strength, fluid flow rate, and distance to the collector plate also should be taken into account. Additionally, ambient parameters such as humidity and temperature are also deemed as important (Bhardwaj and Kundu, 2010, Deitzel et al., 2001, Liu et al., 2010, Theron et al., 2004, Ying et al., 2005).

To comprehend the nature of electrospinning and the conversion of polymer solutions into nanofibers through electrospinning, functional parameters play a very important role in data analysis. Solution properties, processing conditions had been investigated by many of researchers (Table 2.4) (Fong et al., 1999; Demir et al., 2014), under ambient condition, each of the parameters has been discovered to affect the morphology structure of the electrospun fibers (Doshi & Reneker, 1993). By manipulating each of the parameters, the fibers' morphologies will be affected, and hence the changes can be studied, examined, and analyzed. Electrospinning process supports the formation of uniform fibers and beads-like with preferred morphologies under different conditions. Even though the properties of each polymer have been studied extensively by analysing the parameters of the electrospinning process, the data obtained is inadequate to support the electrospinning of ultra-thin nanometer-scale polymer fibers. Thus, more investigations are needed (Li et al., 2016). All processing parameters will be discussed in section 2.8.

Table 2.4 Processing parameters in electrospinning (Kuehn & Lunkenheimer, 1985)

Solution properties	Processing conditions	Ambient conditions
Viscosity	Applied voltage	Temperature
Polymer concentration	Distance from needle to collector	Humidity
Molecular weight of polymer		Atmospheric pressure
Electrical conductivity	Volume feed rate	
Elasticity	Needle diameter	
Surface tension		

2.8 Solution Properties

2.8.1 Concentration

Polymer solution concentration which was stated in Table 2.4 is one of the main parameters that can widely impact the formation of fiber during the electrospinning process. There are four critical concentrations that will be emphasized, step by step, from low to high. The polymeric micro (nano)-particles will be produced when the concentration is very low. During this process phase, due to the low viscosity and high surface tensions of the solution, electrospray occurs instead of electrospinning (Deitzel et al., 2001; Eda & Shivkumar, 2007). A mixture of beads and fibers was obtained when the concentration is higher, (Eda & Shivkumar, 2007; Fong et al., 1999; Lee et al., 2003). When the concentration is at the suitable condition, smooth nanofibers can be observed (Yang et al., 2004). If the concentration is very high, not nanoscaled fibers, helix-shaped micro ribbons will be observed (Koshi et al.,