CHAPTER 1: INTRODUCTION

1.1 Introduction to Nanoscience

Nanoscience and nanotechnology involve studying and working or manipulation of matter on an ultra-small scale, generally with at least one dimension sized from 1 to100 nanometers or smaller. On the definition of nanoscience, the word itself is a combination of *nano*, from the Greek “nanos” (or Latin “*nanus*”), meaning “Dwarf”, and the word "Science". The concepts that seeded nanotechnology were first discussed in 1959 by Richard Feynman, in which he described the possibility of synthesis via direct manipulation of atoms. The term "nano-technology" was first used by Norio Taniguchi in 1974, though it was not widely known. K. Eric Drexler, in 1986, independently used the term "nanotechnology" which proposed the idea of a nano-scale "assembler”. Emergence of nanotechnology as a field occurred through convergence of Drexler's theoretical and public work, which developed and popularized a conceptual framework for nanotechnology, and high-visibility experimental advances that drew additional wide-scale attention to the prospects of atomic control of matter.

During the past decade, nanoscience and nanotechnologies have made the most influential conceptual impact on the scientific community and they are seen as having huge potential to bring benefits in areas as diverse as drug development, water decontamination, information and communication technologies and the production of stronger, lighter materials [1].

1.2 Ultrafast Lasers in Optical Communications

The backbone of communication and information technology is composed of optical devices, which allow optical pulses to carry the data that renders information exchanges possible. Materials with nonlinear optical and electro-optical properties are needed [2-5]. Laser sources producing nanosecond to sub-picosecond optical pulses are a major

component in the portfolio of leading laser manufacturers. Ultrafast lasers are used in a variety of applications, ranging from optical communications [6] to medical diagnostics [7] and industrial materials processing [8]. Regardless of wavelength, the majority of ultrashort laser systems employ a mode-locking technique, whereby a nonlinear optical element called saturable absorber (SA) turns the laser continuous wave output into a train of ultrashort optical pulses [9]. Development of new gain media and mode-locking technologies (e.g. Kerr-lens mode-locking [6-8][10] and Semiconductor Saturable Absorber Mirrors (SESAMs) [5][10][11]) have changed the outlook of ultrafast lasers over the past two decades. These advances have pushed the applications of ultrafast pulses to a realm broader than ever before.

Nevertheless, current mode-locking technologies suffer from some drawbacks. For example, Kerr-lens mode-locked lasers usually require external perturbations in order to start[6][8][11] and are extremely sensitive to misalignment [6][8]. As for SESAM devices, most standard devices are based on traditional semiconductor technology. The key requirements for nonlinear materials are fast response time, strong nonlinearity, broad wavelength range, low optical loss, high power handling, low power consumption, low cost, and ease of integration into an optical system. Current existing technologies and solutions do not meet all these needs. Heterostructures of SESAM devices are expensive to package. They can usually be optimised only for a specific wavelength range, and hence, are not very flexible. SESAMs are complex quantum well devices as well, typically fabricated by molecular beam epitaxy on distributed Bragg reflectors [5][10-13]. Post-growth processing [5][10-12] is normally required to reduce their response time [5][10-12]. However, this has hit a limit given by materials and fabrication restrictions. The search for alternative SA materials has intensified, as other traditional SAs (organic dyes, colour filter glasses, ion-doped crystals) have also severe limitations in terms of stability and performance, specifically in their slow response

time [11], narrow operation wavelength [9][12], expensive fabrication and integration methods [11], and low damage threshold [11]. These limitations motivate research on new materials, novel designs and technologies.

1.2.1 Single Wall Carbon Nanotubes

Single wall carbon nanotubes (SWNTs) have emerged as new SA material for practical ultrafast photonic applications due to its superior performance, such as sub-picosecond recovery time [9][14-20], mechanical [9][21][22] and environmental robustness [21][23]. It has been shown that SWCNT mode lockers have many other advantages as well, such as large saturable absorption, easy to fabricate, and low cost. In particular, as SWCNTs are direct band gap materials with a gap that depends on the nanotubes' diameter and chirality. Through mixing SWCNTs with different diameters, a broadband saturable absorption mode-locking device could be made. SWNT mode-locked ultrafast lasers have been demonstrated for various applications [23][24], for instance industrial measurements [24], material processing [23], optical sampling [25], data-pattern recovery [25], optical frequency metrology [26, 27] and optical coherence tomography [28]. Since then, passive mode locking of fibre lasers with SWCNTs has attracted considerable attention [29-35]. Diversified nonlinear SAs based on CNTs have been realized for the passive laser pulsation producing high-quality femtosecond pulses, and the laser pulsation mechanism by the CNT mode-locker has been made known.

Unfortunately, in spite of the extremely high nonlinearity of CNTs, they still have drawbacks including but not limited to the following:

(i) agglomeration of individual nanostructures

(ii) difficult control of alignment and morphological factors including chirality and diameter for energy band gap design

(iii) poor stability and long term reliability due to their high surface energy

1.2.2 Graphene

Recently, graphene is emerging as one leading material towards the new class carbon optoelectronics and photonics. Graphene is a single two-dimensional (2D) atomic layer of carbon atoms arranged in a hexagonal lattice. An isolated graphene is a zero bandgap semiconductor with a linear energy dispersion relation for both electrons and holes near Dirac point [36]. Saturable absorption in graphene is achieved due to the Pauli blocking of the electrons and holes for occupation of the energy levels in the conduction and valence bands that are resonant with the incident photons [37]. Recent advances in graphene research have shown that graphene saturable absorption has a ultrashort recovery time [37]. Moreover, different from the SWCNT, which is a small diameter tube and has large surface tension, graphene has no or at least less surface tension due to its unique 2D structure. As high surface tension contributes to a lower damage threshold, we believe that graphene should have a higher damage threshold than the SWCNTs. For SWCNTs, the unavoidable bundles, catalysts, attached amorphous carbon are the main factors that could cause non-saturable loss. For graphene, these flaws are totally avoided. A graphene based mode-locking device is made with a 2D flat graphene thin film closely attached onto the end facet of a fibre pigtail via Van der Waals forces. The scattering is much smaller compared to the bundled SWCNTs. Graphene also provides the ultrafast nonlinear saturable absorption, overcoming the inherent problems found in CNTs. Graphene has also come to the fore with ultra-broadband operation as well [31][38-41]. Therefore, it is expected that using graphene as a laser mode-locking material, large energy ultrashort pulses could be generated. *Q*-switching and mode-locking of erbium-doped fibre laser (EDFL) at around 1550 nm using graphene as a SA has been demonstrated. The applications of few layers graphene [42-44] as well as graphene-polymer composite [45, 46] as SAs were achieved in mode-locked lasers.

Following, mode-locking of lasers using chemically processed graphene film [47] and graphene-polymer composites [38] as SAs were confirmed.

1.3 Broadband Polarizer

On the other hand, silicon photonics has been hailed as the technology of promise which will make super high speed internet access a reality. The main challenge in photonics driven circuit is the down-scaling and integration of optolelectronic hardware. Silicon remains a favourite choice in photonics due to its amenability to the monolithic integration of optics and electronics. Silicon based photonic components ranging from passive devices to modulators, detectors and light amplifiers and sources have been developed. In the midst of the high demand of broadband data transferring, it is unlikely that all of these photonic components can be silicon based. Silicon, having an indirect band gap, is not a broadband optical material even though its absorption edge can be tuned by controlling the doping level. Other drawbacks include low electro-optic coefficient, low light emission efficiency and high propagation loss due to scattering off the side walls of the waveguide. In the case, the wonderful properties of graphene allow multiple functions of signal emitting, transmitting, modulating and detecting to be realized in one material. Graphene shows superior properties compared to silicon in terms of its high thermal conductivity, high optical damage threshold and high third order optical nonlinearities. These properties are important for photonic devices. Deposition of graphene directly on insulators such as SiO_2 will open up a route for monolithic integration of graphene and silicon photonics. Motivated by all the mentioned interesting optical properties of graphene, many graphene based photonic and optoelectronic applications have been developed recently, such as a graphene waveguide, broadband polarizer [48], graphene modulator [49], graphene photodetector [50-55], surface Plasmon enhanced photodetector [56, 57], broadband optical limiter [58] and many others, where most of these exhibit broadband performance, ranging

from visible to near-infrared wavelength. The massless Dirac fermions in graphene modify the Plasmon and Plasmon polariton spectra introduce some new features [59-62]. These features make graphene able to selectively support either the transverse magnetic (TM) or transverse electric (TE) electromagnetic modes, depending on its Fermi level and incident energy. This provides the basis for the development of graphene/silica hybrid waveguide, which supports either a TM or TE surface wave selectively, thus transforming unpolarized incident light into polarized light. Such polarization is vital to reducing signal fading and error in coherent optical communications.

1.4 Graphene Oxide

Though graphene is an ideal fast saturable absorber in the application of lasers and photonics, solubility and processability are some of the issues for many perspective applications of graphene-based materials. In the process of fabrication of pristine graphene by chemical means, the exfoliation of graphite oxide produces atomically thin graphene oxide (GO) sheets that are dispersible in basic media. Graphene oxide (GO) has traditionally served as a precursor for graphene. It can be considered as the insulating and disordered analogue of highly conducting crystalline graphene. It is covalently decorated with oxygen containing functional groups – it contains a mixture of sp^2 and sp^3 hybridized carbon atoms. This causes GO to have defects that brings about its insulating nature. However, the availability of several types of oxygen-containing functional groups on the basal plane and the sheet edge allows GO to interact with a wide range of organic and inorganic materials in non-covalent, covalent or ionic manner so that functional hybrids and composites with unusual properties can be readily synthesized. Furthermore, GO is an electronically hybrid material that features both conducting π-states from sp^2 carbon sites and a large energy gap (carrier transport gap) between the σ-states of its sp^3 bonded carbons. The tunability of the ratio of the sp^2 and sp^3 fractions by reduction chemistry is a powerful way to tune its bandgap and therefore

controllably transform GO from an insulator to a semiconductor and to a graphene-like semi-metal. Manipulation of the size, shape and relative fraction of the sp^2 hybridized domains of GO by reduction chemistry provides opportunities for tailoring its optoelectronic properties. Controlled deoxidation on GO leads to an electrically and optically active material that is transparent and conducting. Furthermore, in contrast to pristine graphene, GO is fluorescent over a broad range of wavelengths, owing to its heterogeneous electronic structure.

It is possible to improve the solubility and preserve some of unique properties of the pristine material simultaneously. It has been shown that the fast carrier relaxation and large saturable absorption of GO in *N*,*N*-dimethylmethanamide (DMF) solution indicate that oxidation mainly exists at the edge areas and has ignorable effect on ultrafast dynamics and optical nonlinearities [63]. The solution-processability and fast nonlinear response of GO offer unique advantage since it is readily amenable by spin-coating, spray-casting, drop-casting, or inkjet printing onto substrates for large-scale production of graphene optoelectronics [63]. By using GO as a SA, passive *Q*-switching and mode-locking in fibre lasers and free-space solid state lasers have been realized [64-89].

Compared with the fast development and research on CNT and graphene in mode-locking, the development of applications using GO in *Q*-switching of fibre lasers has been relatively low. It is due to the fact that loss of carbon from the basal plane that limits the electronic quality – carrier mobility. sp^3 hybridized carbon atoms bonded with oxygen groups disrupt the sp^2 conjugation of hexagonal graphene lattice and thus destroy the linear dispersion of the Dirac electrons and influence its unique optical properties. Several *Q*-switched fibre lasers using GO as a SA were demonstrated; the detailed studies and evaluation on the performance and resonator design of GO-based *Q*-switched fibre lasers are limited. The forms of GO-based SA devices exist in various kinds. Throughout the course of study of the work in this thesis, depositing GO directly

onto the end face of fibre ferrules had been adapted to fabricate a simple and cost effective new SA devices and thus the experiment carried out in this work is limited to GO-based SA in this format.

On one hand, despite graphene being a much more sought-after and desirable material as SA devices in photonics and optoelectronics, the drawbacks in the preparation of graphene is a challenge – to produce the material in a scalable quantity. Thus a simple and efficient method for the preparation of GO, a precursor for pristine graphene, is greatly desired to address the issues. Most of the works on GO preparation method produced GO with small area and lateral dimension [90, 91]. In order to achieve commercial value, the synthesis process of GO needs to be simplistic and cost effective. Conventional methods of producing GO using chemical oxidation like Hummer's method [92, 93], Staudeumaier's method [93] and Brodie's method [94] involved tedious and long experimental time.

Results from [48], [95] and [96] show that graphene plays an important role in optical waveguide device technology. To date, the graphene layer(s) used in graphene-based waveguide polarizers have usually been deposited by the chemical vapour deposition (CVD) technique, which requires careful transfer of the graphene layer from its initial growth substrate onto the waveguide. In addition, achieving a uniform few-layer or single layer graphene coating over large areas with a minimal amount of defects and discontinuities remains a challenge.

Recently, uniform coating of GO layers through drop-casting has been reported. The method provides a simple alternative for uniform coating of thin graphene-based films over a finite area [97]. By increasing the concentration of the GO solution, it becomes possible to produce GO 'paper' at micrometre scale thickness [98]. Also, it has recently been shown that GO exhibits a strongly anisotropic complex dielectric function [99]. At

optical frequencies, the dielectric anisotropy may be expected to lead to differences in the propagation loss for different polarization states, which can be used to provide the function of polarization selection in an optical waveguide. It is therefore logical for these properties of GO to be explored for applications such as waveguide polarizers.

1.5 Objectives, Scope of Study and Methodology

The objectives of the study are to employ a modified available method to synthesize GO, and fabricate a simple fibre-based GO SA device using a simple transfer method, to study its viability in *Q*-switching of fibre lasers. The anisotropic dielectric properties of GO is studied briefly as well, and the GO is used as a polarizing element in a waveguide polarizer.

The scope of study includes the following:

(1) demonstrate a simple and cost effective way of synthesizing of large area GO chemically;

(2) present a systematic characterization of the morphological, physical, linear and nonlinear optical properties of GO;

(3) evaluate the performance of GO-based *Q*-switched fibre lasers with various SA device format, and compare with that of reduced graphene oxide (rGO);

(4) apply GO on a polymer waveguide, characterize it and inspect its performance as a polarizer.

On the synthesis of GO, the work comprises of experimental work conducted at the Low Dimensional Research Centre, located at the Department of Physics, Faculty of Science, University of Malaya. It was carried out for 3 days, without any temperature control. When the GO is used as a SA, a ring fibre laser was set up, and all common optical instrument/components and devices, such as optical spectrum analyser, optical

power meter, photodetector and many others were used to characterize and study the light pulses produced. Lastly, on the use of GO in a polarizer, a polymer waveguide was fabricated at the Cleanroom (Class 10K) facilities of the Planar Lightwave Circuit (PLC) Laboratory, Photonics Research Centre, University of Malaya. All experimental work was carried out at the PLC Laboratory, including the simulation and modelling of the field distribution of the polarized light modes.

A brief description for all chapters is as seen below:

Chapter 1: An introduction to nanoscience and nanotechnology. The need for ultrafast pulsed lasers and broadband light polarizers in optical communications is presented. The drawbacks of using conventional methods and devices for generating ultrafast light sources and fabricating light polarizers and modulators are also discussed in details. A brief history of the discovery, development, and recent advances in carbon based materials – CNT and graphene, and their applications in photonics and optoelectronics is included. The chapter also highlights the challenges and limitations of CNT and graphene in optics and photonics applications and hence the need for further studying and developing an alternative material – graphene oxide..

Chapter 2: The chapter serves mainly as a literature review for *Q*-switched fibre laser using graphene oxide as a passive saturable absorber. It consists of two major areas: (1) the principles of optical pulse generation via *Q*-switching and (2) a review of the recent developments in GO-based *Q*-switched lasers.

Chapter 3: The chapter presents the basic theory of linearly polarized light. It consists also recent developments in optoelectronic devices, typically on light polarizers using graphene.

Chapter 4: Chemical synthesis of GO using simplified Hummer's method is presented. The method uses graphite flakes as the raw material. Sulphuric acid, phosphoric acid,

potassium permanganate and hydrogen peroxide were used. The area, size and morphology of the GO obtained using Atomic Force Microscopy (AFM) and Field Emission Scanning Electron Microscopy (FESEM) are shown and discussed in details. X-ray diffraction (XRD), Raman spectroscopy, Fourier Transform Infrared (FTIR) spectroscopy and thermogravimetric analysis (TGA) results are presented and discussed as well. Linear and nonlinear optical properties studies of the GO are done by using a set of power dependent transmission measurements. The modulation depth of the transmission and absorption loss of the GO is determined and the results are discussed.

Chapter 5: The GO based SA is first used to demonstrate a *Q*-switched erbium-doped ring fibre laser. Important parameters of a *Q*-switched laser such as average output power, pulse repetition rate, pulse energy and pulse duration are recorded in details. Comparison of laser *Q*-switching performance between GO-based ring fibre laser with rGO-based ring laser is carried out. Lastly, short resonator length tunable ring fibre lasers using Bismuth based erbium-doped fibre (Bi-EDF) as the laser gain medium is set up and included in the studies.

Chapter 6: The chapter presents mainly the use of GO in broadband waveguide polarizer. The fabrication of a polymer waveguide, as well as the deposition of GO onto the waveguide, are discussed in details. The physical and optical properties of the GO based waveguide polarizer are shown and illustrated with both experimental results and computer simulation. The underlying principles of the polarization dependent propagation loss and anisotropic complex dielectric function of GO are studied and verified. The light coupling efficiency and guided light propagation in the GO-based polymer waveguide are discussed.

Chapter 7: Conclusions and suggestions for future work are outlined in the chapter.

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