

FABRICATION OF PERIODIC NANOPARTICLE ARRAYS USING  
NANOSPHERE LITHOGRAPHY TECHNIQUE AND THIN FILM GOLD AS  
ELECTRICALLY ENHANCED CATALYSTS

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## ABSTRACT

Nanosphere lithography (NSL) is a versatile, facile and parallel nanofabrication technique, especially in fabrication of periodic nanoparticle arrays (PNPAs) such as nanotriangles, nanohole arrays (PNHAs) and nanocups (NCs). In this research, single layer polystyrene nanospheres (PSNs) are chosen as templates thus be manipulated and modified using reactive ion etching (RIE). Ultrasonic agitation and sticking tape technique are used as lift-off process during fabrication of PNPAs. The morphology of PNPAs and confirmation element was characterized by field emission-scanning electron microscopy (FE-SEM) and energy dispersive x-ray spectroscopy (EDS or EDX) respectively. In this report, thin film gold supported by PSNs used as electrically enhanced catalysts for the chemical reaction of oxidation of styrene. The products were characterized by using gas chromatography (GC). Oxidation of styrene produced three main products which are benzaldehyde (B), phenylacetaldehyde (PA) and styrene oxide (SO). From the GC analysis, the catalyst which was given 3V positive bias voltage selectively increased the products. The products increased about 494.12%, 926.67% and 1162.10% for B, PA and SO, respectively.

## ABSTRAK

Nanosphere Lithography (NSL) merupakan teknik yang mudah, serba guna dan teknik nanofabrikasi yang selari khususnya dalam fabrikasi zarah-zarah kecil yang bersaiz nano (PNPAs) seperti segitiga, lubang (PNHAs) dan cawan (NCs). Dalam penyelidikan ini, lapisan pertama *polystyrene nanospheres* (PSNs) telah dipilih sebagai template dan dijadikan sebagai pemalar dan manipulasi dengan menggunakan *reactive ion etching* (RIE). Getaran *ultrasonic* dan pita pekat digunakan sebagai proses *lift-off* semasa fabrikasi PNPAs. Morfologi PNPAs telah dicirikan dengan menggunakan *field emission-scanning microscopy* (FE-SEM) dan pengesanan unsur dicirikan oleh *electron dispersive x-ray spectroscopy* (EDS atau EDX). Dalam laporan ini, filem nipis emas disokong oleh PSNs digunakan sebagai *electrically enhanced catalysts* untuk reaksi kimia pengoksidaan *styrene*. Produk akhir pengoksidaan *styrene* telah dicirikan dengan menggunakan gas chromatography (GC). Pengoksidaan *styrene* menghasilkan 3 produk utama iaitu *benzaldehyde* (B), *phenylacetaldehyde* (PA) dan *styrene oxide* (SO). Filem nipis *electrically enhanced catalysts* telah diberi 3V beza upaya elektrik dan kadar reaksi telah meningkat sebanyak 494.12 % untuk B, 926.67 % untuk PA dan 1162.10 % untuk SO berbanding dengan reaksi tanpa menggunakan beza upaya elektrik.

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**LIST OF SYMBOLS AND ABBREVIATIONS**

AFM	-	Atomic Force Microscopy
Ar	-	Argon gas
Au	-	Gold
B	-	Benzaldehyde
CaF <sub>2</sub>	-	Calcium fluoride
CN	-	Coordination number
Cr	-	Chromium
Cu	-	Copper
DDA	-	Discrete Dipole Approximation
DI	-	Deionized
EB	-	Binding energy
EBL	-	Electron beam lithography
E <sub>c</sub>	-	Conduction band
EDX or EDS	-	Electron Dispersed X-Ray Spectroscopy
E <sub>F</sub>	-	Fermi level/energy
E <sub>K</sub>	-	Kinetic energy
E <sub>v</sub>	-	Valence band
FESEM	-	Field Emission Scanning Electron Microscopy
FIB	-	Focused ion beam
GC	-	Gas Chromatography
IR	-	Infrared
ITO	-	Indium-tin oxide
LED	-	Light emitting diode
LSPR	-	Localized Surface Plasmon Resonance
NCs	-	Nanocups
NPs	-	Nanoparticles



NSL	-	Nanosphere Lithography
NSPL	-	Nanosphere photolithography
O <sub>2</sub>	-	Oxygen gas
PA	-	Phenylacetaldehyde
PEDOT:PSS	-	Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate)
PL	-	Photolithography
PLD	-	Pulse laser deposition
PMMA	-	Polymethyl methacrylate
PNHAs	-	Periodic nanohole arrays
PNPAs	-	Periodic Particle Arrays
PSNs	-	Polystyrene Nanosphere
Pt	-	Platinum
PV	-	Photovoltaic
PVD	-	Physical vapor deposition
PZT	-	Lead zirconium titanate
RF	-	Radio frequency
RIE	-	Reactive ion etching
SERS	-	Surface Enhanced Raman Spectroscopy
SF <sub>6</sub>	-	Sulfur hexafluoride
Si	-	Silicon
SO	-	Styrene Oxide
STM	-	Scanning Tunneling Microscopy
SWCNTs	-	Single wire carbon nanotubes
TBHP	-	Tert-butyl hydroperoxide
TEOS	-	Tetraethoxysilane
TiO <sub>2</sub>	-	Titanium dioxide
UV	-	Ultra violet
V	-	Volt (bias voltage)
VLS	-	Vapor-liquid-solid
VS	-	Vapor-solid
XPS	-	X-ray photoelectron spectroscopy
XRL	-	X-ray lithography

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## CHAPTER 1

### INTRODUCTION

#### 1.1 Background of Research

Advances in nanofabrication technique are basically categorized in two: the top-down and bottom-up approach (Masahide, et al., 2008). The bottom-up approach is to construct a micro/nano structures by piling up atoms based on the material design which adopts the concept of molecular self-assembly (Jennifer et. al, 2000), molecular recognition (Sarikayam, et al., 20003) and enzymatic assembly (Liu et al., 2010). This process however, is not useful for practical production because its production rate is very low where from the industrial point of view, productivity and cost is very important factor.

The top-down nano fabrication technique used bulk materials and crafts it into nanosize patterns. One of well known top-down fabrication technique is photolithography (PL) or optical lithography is using light in transferring pattern to a substrate surface coated with photosensitive or photo resist material. Series of photomasks can be used to further complex patterns and lines. Reactive ion etching (RIE) are also introduce in the PL process to further fabricate nanosizes materials or patterns on substrate and are the vital technologies in fabrication of integrated circuit (IC). PL is the cornerstone technology used to pattern the components of computer chips and is largely responsible for the growth of the semiconductor industry over the past 50 years. Present commercial optical lithography allows mass replication of nanostructures with  $\sim 130$  nm resolutions but is approaching its fundamental limit, where it is set by diffraction of light which cannot go smaller than 100 nm of UV wavelength (Kuo et al, 2003). Although PL is a powerful tool, it is not a universally relevant fabrication technique because of its inherent limitations: it is expensive due

to a number of masks, limited in resolution by the fundamental limit diffraction of light, restricted to planar substrates, low particle throughput and incompatible with many organic (Moon et al., 2005) and biological materials (Dhananjay et al., 2007). PL patterning is essentially two-dimensional; it does not allow control over geometric parameters in the third dimension such as the surface profile and curvature (the topography) of fabricated features (Subramaniam et al., 2010). Although PL continues to achieve reductions in feature sizes (which are currently smaller than 100 nm), this reduction comes at great expenses.

“Unconventional” methods to fabricate micro and nanostructures are developed to overcome one or more of these limitations. "Unconventional fabrication" is broadly defined as any fabrication method that provides some advantage over conventional patterning. Conventional patternings are usually referred to PL and unconventional nanofabrication technique were such as electron beam lithography (EBL), focused ion beam lithography (FIB) and etc. The best technique to produce nanoparticles (NPs) should be concerned about mass production, parallel nanofabrication system, precise in shape, size and position, cheap, easy to fabricate and materials general either the substrate or the NPs.

Electron beam lithography (EBL) technique (Tseng et al, 2003) has several advantages where the scale patterning is possible towards  $\sim 20$  nm compared to the resolution of  $\sim 100$  nm for conventional photolithography. EBL can be operated directly without using physical mask such as in PL, thus eliminating cost and time delays associated with mask production. Pattern of nanostructures can be optimized and changed using flexible CAD software. However there are disadvantages of EBL where electron beam must be scanned across patterned areas pixel by pixel. The patterning nanostructures therefore may take long hours to complete. Generally, EBL is an expensive tool with sophisticated accessories, thus high in maintenance costs.

Changing the radiation source from electron beam to ion beam, scientists have developed a new lithography tools called focused ion beam (FIB) (Frey et al, 2003), where it uses ions to modified substrates or polymer resist. In EBL/scanning electron microscopy (SEM) and FIB a common setup where the radiation source, electron (EBL/SEM) or ion (FIB) beam are scan across the substrate surface and expose and modified the polymer resists. A grid of pixels is superimposed on the substrate surface, where each pixel has a unique address. The pattern data is

transferred to the controlling computer, which then directs the electron/ion beam as to realize the pattern on the substrate pixel by pixel.

## 1.2 Problem Statements

The technical development of nanofabrication is driven by the demand of miniaturization of device features with improved performance and lower cost in the electronic and information industry. This development would provide new opportunities for fundamental research in low dimensional physics. Particularly, regular arrays of nanoparticles (NPs) can exhibit interesting physics and chemical properties. Physical properties mostly studied in characterization of optical and electrical (Su et al., 2009) areas however chemical properties usually studied in biomedical (Wood, 2007) and catalysis (Johnson, 2003). Polystyrene nanospheres (PSNs) in this research act as templates in fabrication of periodic nanoparticle arrays (PNPAs) i.e. nanotriangles, periodic nanoholes arrays (PNHAs) and nanocups (NCs).

One problem in nanopattern or nanoparticles (NPs) is about precise location of NPs. Wedge-shaped region between the spheres and the planar substrate provides a convenient location for the deposition of the nanoparticles. The direct formation of templates on the substrate enables us to avoid the problem such as inhomogeneous contact between rigid template and substrates, frequently issued during the patterning transfer in PL process. Using NSL technique, the NPs will be located precisely and periodically on the substrate which PSNs were easily self-assembled. PNPAs are unique materials as they exhibit different characteristic compared to the bulk properties due to high surface-to-volume ratios (corresponded to their shape and size) and high surface energies. These are some of characteristic to be good catalysts which in turn their surface atoms to be highly active (Zhou et al., 2005).

Transition metal surfaces such as Au, Ag, Pt, Pd, etc are known to have very efficient catalytic properties for many important reactions. Since NPs have a good fraction of their atoms present on the surface, their potential use in catalysts is obvious. A catalyst is a substance that increases the rate of a chemical reaction by reducing the required activation energy, but is left unchanged by the reaction

without being consumed or chemically altered. Catalysts are classified as homogeneous if they are present in the same phase as the reactant mean that catalysts are present as solutes in a liquid reaction mixture. Catalysts are heterogeneous if both catalysts and reactant are present in a different phase, usually the catalysts in solid phase and the reactant in liquid or gas phase. Heterogeneous catalyst is a type that industry preferred due to the temperature of the reaction is not high and easily separate the catalysts from the end product.

The themes of this research are enhancing the catalytic activity by applying positive bias voltage to the thin film catalysts supported on PSNs and to show the versatility of NSL technique by producing periodic nanoparticle arrays (PNPAs) in controlling manner (shape, size and position), cheap and easy to fabricate, materials generals and parallel nanofabrication system.

### **1.3 Research Objectives**

Objectives of the research are as follow:

1. To fabricate periodic nanoparticles arrays (PNPAs) using Nanosphere Lithography (NSL) technique with different sizes and shapes of periodic nanoparticle arrays (PNPAs) on Si substrate.
2. To control the size of polystyrene nanospheres (PSNs) using Reactive Ion Etching (RIE) technique by controlling time exposure in several of gases such as argon (Ar) and oxygen (O<sub>2</sub>).
3. To study effect of positive bias voltage (dc current) applied to the thin film gold catalysts in the oxidation of styrene as chemical reaction model using PSNs as intermediate layer between thin film of metal and silicon substrate.

### **1.4 Research Scope**

The scopes of this study are to fabricate tunable PNPAs using NSL technique where the original diameter of polystyrene nanospheres (PSNs) were used is 500 nm as

templates. Several gas during RIE process i.e. Ar, O<sub>2</sub> or mixture of Ar and O<sub>2</sub> gas with same parameters such as power, pressure and gas rate but differ in etching time used for controlling the opening of the deposition channels. The best gas/gases during in RIE process will be chosen to fabricate PNPAs depend on etching rate and shape of PSNs after bombardment (PSNs shape maintain in circle).

Thin layer of Au and Pt then sputtered onto the original and modified PSNs (after RIE bombardment). Subsequently, upper layer of PSNs need to be removed in order to produce PNHAs or nanotriangles on Si substrate using ultrasonic agitation. Ordinary sticking tape used as easy and cheapest alternative technique in fabricating of NCs. The morphologies and conformation elements of PNPAs and templates from the NSL technique will be characterized using Field Emission-Scanning Electron Microscopy (FE-SEM) and Electron Dispersed X-Ray Spectroscopy (EDX or EDS).

Effect of positive bias voltage which was applied to the Au catalysts was tested in oxidation of styrene. The oxidation products will be determined using Gas Chromatography (GC) to identify the chemical element involved as production of the reaction. There are three main products in oxidation of styrene which are benzaldehyde (B), phenylacetaldehyde (PA) and styrene oxide (SO). Positive bias voltage applied to the catalysts here to increase the reaction rate, to know which one product more dominant (selectively) and/or increased amount of products (activity) compare to the catalysts without apply positive bias voltage.

#### **1.4 Organization of Thesis**

Chapter 1 provides a broad overview of the thesis, covered the background of study, problem statements, objectives, scope and the theme of research. Chapter 2 discussed on literature review, past and recent researches which are related to NSL technique. The purpose of PSNs used in the study instead of the other nanospheres such as silica and polymethyl methacrylate (PMMA) has been discussed in the thesis. Various applications which have potential to be implement such as solar cells, flexible battery, organic photovoltaic, fuel cell considered in study are

reviewed. The basic operations of the main instruments which are reactive ion etching (RIE) and gas chromatography (GC) were briefly discussed in the thesis.

In chapter 3, research methodology and flow chart of research were discussed. Research methodology includes the techniques of NSL in formation of PNHAs and NCs by decreasing the size of PSNs as templates using the concept of electron bombardment during RIE processes. On the other hand, the thin film gold (Au) layered with PSNs supported on Si substrate were tested in oxidation of styrene inside reflux. The 5 experiments have been conducted using four different of samples as catalysts and one experiment without catalysts as reference.

In chapter 4, all results will be discussed include the morphology of PNPAs i.e. PNHAs, nanotriangles, nanopillars, NCs etc. Two different metals used in this study which is gold and platinum were characterized by using EDX. The products from oxidation of styrene have been characterized using GC machine and some calculation needed from GC analysis to get the percentage increment of products. Drift velocity of valence electrons, several related researches and effect of electric field to the Fermi circle were discussed.

The conclusions based on the objectives have been elaborate in the chapter 5. Several shapes of PNPAs have been achieved in the end of research. Contribution of bias voltage towards the catalysts increased the thin film catalyst's activity and selectivity. In future, the positive and negative bias voltage, will be implemented onto these PNPAs



## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Introduction

Nanoparticles (NPs) are considered as advance materials as they behave differently from their bulk structures, posses unique chemical and physical properties compared to their corresponding bulk or isolated atoms and molecules. At the nm (nanometer) scale, in range of 1 – 100 nm, although it can be said as a flat surface from mesoscopic point of view, at this scale there are many properties changed drastically. One example is surface to volume ratio ( $A/V$ ), which determine the uniqueness of the physical and chemical properties of NPs, therefore at nanoscale regime sizes, shapes and orientation of the nanoparticles become an important parameters as shown in equation 2.1 (Roduner, 2006). Assuming that spherical particles of diameter ( $d$ ) with radius ( $r$ ), the equation 2.1 gave an idea that the shrinkage of NPs will increase its surface atoms, therefore creating more sites for physical and chemical interaction. The relationship between total surface area and diameter of NPs shown in figure 2.1 where the total surface area inversely proportional to the diameter of NPs.

$$\frac{A}{V} = \frac{4\pi r^2}{4\pi r^3/3} = \frac{3}{r} = \frac{6}{d} \quad (2.1)$$

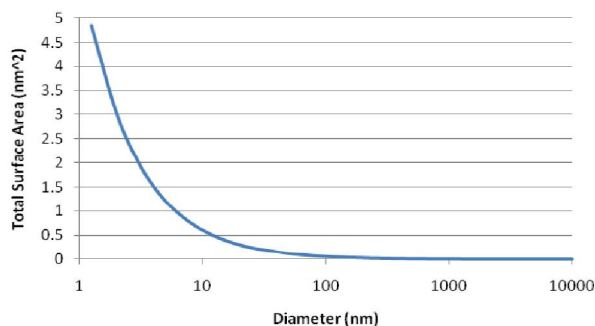


Figure 2.1: Size dependent of total surface area (Huang et al., 2010).

Nanotechnology has become the new scientific field as it is found that the smaller the materials were fabricated, they will have unique and interesting physical and chemical characteristic. Nanotechnology have vast and infinity potentiality application such as quantum dot computing, nanopillars as electron emitters for liquid crystal display application and persistent current in nanoring for future energy devices. Scientists have fabricating devices down to atomic precision and the era of fabricating materials at atomic precision were said to be led by Nanotechnology. Table 2.1 shows some of the major research activities at nanoscale regime.

Table 2.1: Characteristic lengths in solid state science model (Murday, 2006).

Field	Property	Scale Length (nm)
Electronic	Electronic wavelength	10 – 100
	Inelastic mean free path	1 – 100
	Tunnelling	1 – 10
Magnetic	Domain wall	10 – 100
	Exchanged energy	0.1 – 1
	Spin-flip scattering length	1 - 100
Optics	Quantum well	1 – 100
	Evanescent wave decay length	10- 100
	Metallic skin depth	10 – 100
Superconductivity	Cooper pair coherence length	0.1 – 100
	Meisner penetration depth	1 – 100
Mechanics	Dislocation interaction	1 – 1000
	Grain boundaries	1 – 10
Nucleation/Growth	Defect	0.1 – 10
	Surface corrugation	1 – 10
Catalysis	Localized bonding orbital	0.01 – 0.1
	Surface topology	1 – 10
Supramolecules	Primary structure	0.1 – 1
	Secondary structure	1 – 10
	Tertiary structure	10 – 1000
Immunology	Molecular recognition	1 - 10

At the bulk state, materials show their collected atom's physical and chemical behaviour and the smaller the sizes of the materials fabricated, their physical and chemical properties will be determined more by the individual atoms such the behaviour of gold that is the main material in this report. At the bulk state, gold is well a known inert, shiny, yellow noble metal that does not tarnish (Hammer & Norskov, 1995) has a face centred cubic (fcc) structure, diamagnetic materials where melts at 1064.18°C which is physical and chemically will not react with other substances at room temperature.

Gold will cease its inert or nobility at nm regime, such as at 3 -5 nm size gold NPs, about few hundred of atoms, they will become an active substances (Haruta et. al, 1997). Gold NPs size less than 2 nm exhibits considerable magnetic properties which turns to ferromagnetic properties (Yamamoto et al., 2006) due to the unpaired electron configuration of their surfaces. Gold NPs about 10 nm sizes will cease its stability of its fcc structure, thus they are arranged in icosahedral, decahedral or defective fcc structures form. By being able to fabricate and control the structure of NPs, scientists and engineers can influence the resulting properties and, ultimately, design materials to give desired properties.

At room temperature, Au was classified as diamagnetism materials where under the influence of an applied field (H) the spinning electrons precess and this motion, which is a type of electric current, produces magnetism (M) in the opposite direction to that of the applied field. However, with the mean diameter of 2.5 nm of Au NPs, they show the unexpectedly superparamagnetic properties (Nakae et al., 2000). Furthermore, catalytic activity of gold NPs are strongly dependent on their shapes beside their sizes. Such in figure in 2.2, the corner and edge atom were identical exhibit increment of catalysts reaction due to the low coordination number (CN) of gold atoms. Low CN atoms have high lying metal d states, which are in a better position to react with the adsorbate valence state than the low laying states of the high CN states of the close packed surface (Janssens et al., 2007), which is one of the factors for good catalysts.

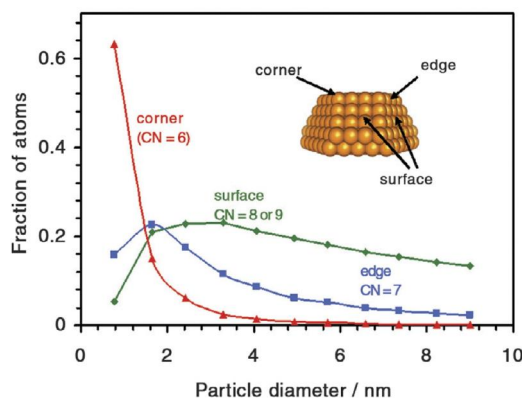


Figure 2.2: Calculated fraction of Au atoms at corners (red), edges (blue) and crystal faces (green) in uniform NPs consisting of the top half of a truncated octahedron as a function of Au particle diameter. The insert shows a truncated octahedron and the position of representative corner, edges and surface atom (Janssens et al., 2007).

Thin film of gold is an intermediate state between bulk and NPs state where the thickness is in the range nanometers to several micrometer. Thin film gold is readily produced on almost any solid substrate either chemical or physical deposition. The example of chemical deposition such as chemical vapor deposition (CVD), electroplating, electroless deposition and so on while the physical deposition include the physical vapor deposition (PVD), pulse laser deposition (PLD) and others. Due to the nobility of gold, such films will generally remain unoxidized, and can be prepared down to a thickness of a few tens of nanometers.

Films of less than 80 nm or so in thickness will transmit an appreciable fraction of any blue to green light that falls on them, with red light and the near-infrared being selectively blocked. This is due to the position of the band edge at about 2.4 eV (Blaber et al., 2009). The properties are not only controlled by thin film thickness, but also by the morphology of the film. Thin continuous coating of gold have highest known reflectivity in the infrared, a feature that leads to application of nanoscale gold coating in applications as diverse architectural windows (Holiday & Corti, 2009). Thus in this research, about 50 nm thin film of gold will be deposited on the substrate using sputtering method due to the fast and provide good thickness control without incurring excessive raw material.

## 2.2 Technique of Fabricating Nanoparticles

Lithography-based techniques are classified according to the tools used and the method of image transfer. These are mainly either direct write type or transfer of a pattern through a photo mask using conventional exposure and development routes. The lithography names varied depends on source of light introduced during the exposure process. For instance, during patterning of masks/ nanoparticles such as using uv light named Photolithography (PL), x-ray as source called X-Ray lithography (XRL), using electron as source of patterning that called Electron Beam Lithography (EBL) and so on. In this discussion, there are several types of patterning technique which will be further discussed in this chapter.

PL technique is a conventional patterning pattern on the substrate by allowing uv light passing through the mask and the patterning appear on the resist either positive resist or negative resist. Pattern which is exposed on the positive resist will become insoluble in developer or organic solvent. However, pattern exposed on the negative resist will become insoluble in the developer and the pattern will become inversed compared to it patterning mask (Jaeger, 2002). PL technique is costly and time consuming due to the series of masking required during the synthesis and the mass production is low.

Another lithography technique is X-ray Lithography technique which replaced the UV light with x-ray as radiation source thus the patterned masks/nanostructures revealed on the substrate. Although the cost of making mask using x-ray source is very low but mass-production of nanostructures still requires substantial effort (Wisitsoraat et al., 2010). EBL used as lithographic machine that shows the versatility of direct writing ELB technique to create masks depends on design to create nanostructures and the size are less than 100 nm. On the other hand, the fine tuning and improvement of resolution and precision is needed when critical dimension below 10 nm was used. Operating conditions also vary widely by changing the parameters including beam energy, beam current, beam deflection rate, type of resist and etc. As a result, the patterns on the substrate or the fabricated nanostructure significantly affected by these parameters and design of equipment either the stage of sample move or stationary (Tseng et al., 2003). Nevertheless, EBL is a comparatively slow process and often has difficulty in patterning harder

materials without suffering from considerable distortion effects due to local charge build up (Yao, 2007).

Focused Ion Beam (FIB) technique has same principle as Scanning Electron Microscopy (SEM) or in EBL process; they consist of charged particles that are focused by a series of lenses and aperture onto a sample and employ similar method to produce and accelerate the particles from their source. But in FIB technique, they used bombardment of ion compare to the SEM/EBL which is using electron as source. The FIB have 4 basic function which is milling, deposition, implantation and imaging process. One of the major advantages with FIB compared to an electron beam, especially in patterning nano-magnetic devices, is that the electron beam tends to show physical shifting to an extent of 100 nm due to the interaction between the beam of charged electrons and the magnetic thin film on the substrate to be patterned, which is almost negligible with an ion beam. Apart from these, the heavier mass of the ions allows direct etch or deposition, thus avoiding the patterning steps used in optical or electron beam (Yao, 2007).

Advances in existing production techniques are improving the quality and yields, providing a clear prospect of commercially viable volume production. World scientists, through investigating of various techniques at nanoscale regime, have shows new trend in nanotechnology research as can be seen in the figure 2.3. The self assemble technique in fabricating nanoparticles have been found to lead others techniques such as Atomic Force Microscopy (AFM) and Scanning Tunnelling Microscopy (STM), since it has these features to offer for future technological advancement.

1. Easy in fabricating nanoparticles.
2. Mass production
3. Versatile in shapes, sizes and materials
4. Cost and energy saving technique due to promoting self-assemble naturally.

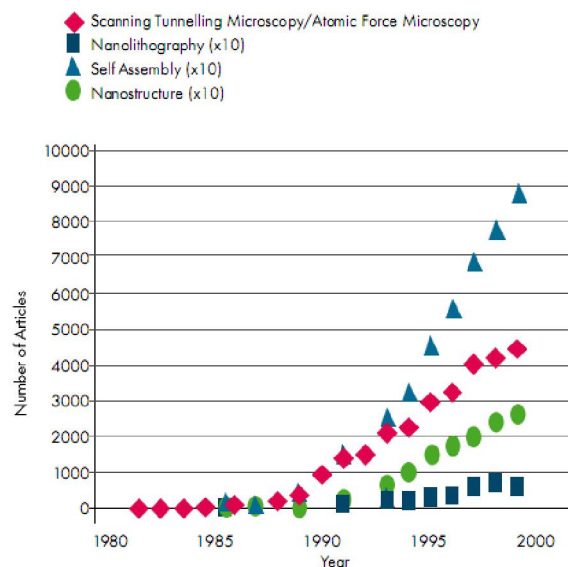


Figure 2.3: Nanoscience Literature Citation Counts (Murday, 2006)

Simple approaches of growing multidimensional nanostructures by self-assembly phenomena are vapor-liquid-solid (VLS) and vapor-solid (VS) process. VLS process include 2 step processes which is 1) formation of small liquid droplet as catalysts and 2) the alloying, nucleation and growth of nanostructure. However, VS process does not involve the 1<sup>st</sup> step of VLS process which is liquid droplet as catalysts. In many cases, the growth of 1D nanostructures such as ZnO nanowires were fabricated by decomposing ZnO powder in high temperature assisted by suitable flow gas under atmosphere pressure in the reaction chamber. Both techniques revealed fine nanostructures by controlling temperature, duration time, pressure, size of powder, vapor pressure and etc to vary the length, size and amount of ZnO powder (Fan et al., 2006). In particular, to fulfil the complex requirements and demands of a current nanotechnology, the challenges lie not only in growth themselves but also in the controlling of position makes them arrange in periodic arrays.

One of the best known self assemble techniques is Nanosphere Lithography (NSL) and the figure 2.4 shows the versatility of NSL in diversifying into various researches included fabricating of nanodot for quantum dot computing researches. The precise location of NPs in array arrangement makes the properties become differ compared to non-arrangement NPs. Bartlett and co-workers (2003) prepared thin

film highly ordered, 3D macroporous magnetic networks based on the polystyrene template and the results revealed the higher coercivity and irreversible field than non-templated samples of the same film.

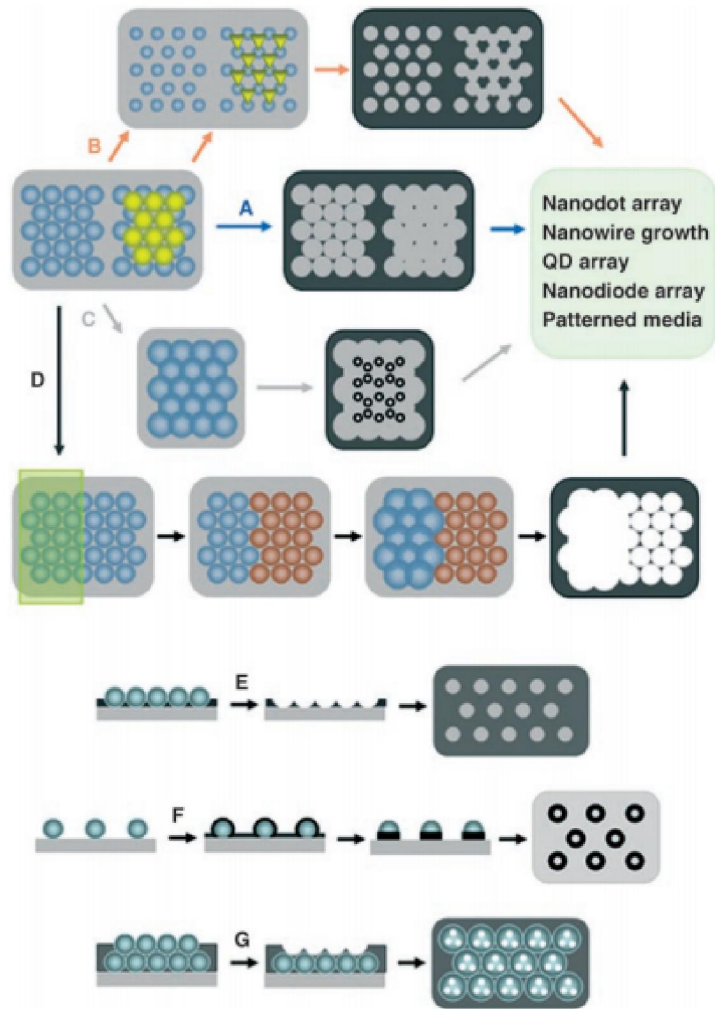


Figure 2.4: Typical nanofabrication routes of NSL (Yang, et al., 2006).



## 2.3. Polystyrene Nanospheres as source of carbon based materials

### 2.3.1 Type of Nanospheres

There are several different materials made of nanospheres such as silica, polystyrene and polymethyl methacrylate (PMMA) beads. Silica or  $\text{Si}_2\text{O}$  nanosphere is absolutely made from silica which is semiconductor material. Not many researchers have done experiments using silica nanospheres due to the limitation of modification of chemical and physical properties. One solution of the limitation was introduced (Vossen et al., 2005) where the silica nanospheres were deformed by ion bombardment and expanded in the plane perpendicular to the ion beam. In 2008, Vossen and co-workers have been introduced the chemical modification of silica nanospheres which is more accurate tuning the hole size by controlling amount of tetraethoxysilane (TEOS) added. This method more easy to use, fast and inexpensive compares the previous method. However, PSNs was chosen in our research due to the advantages as describe below.

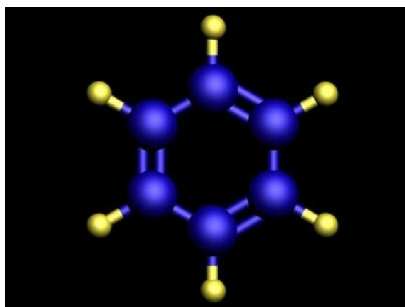


Figure 2.5: Chemical model of benzene ring (Hellroy, 2008)

Polystyrene's chemical formula is  $(\text{C}_8\text{H}_8)_n$ ; where each styrene monomer consists of 8 carbon and 8 hydrogen atoms, where the  $n$  in the formula refers to the number of styrene monomers in the polystyrene chain (Peacock and Calhoun, 2006). In benzene, each carbon atom uses one electron to bond with each of two neighbouring carbon atoms and one hydrogen atom. This leaves one of the carbon atom's four electrons hanging around, unused. The atomic orbitals that contain these extra electrons overlap with orbitals on the adjacent carbon atoms, forming an orbital represented by the ring-shaped cloud above and below the ring of carbon atoms

shown in Figure 2.5. This orbital allows the electrons to move freely around the ring of carbon atoms (delocalized electrons). Nanotechnologists have demonstrated that molecules such as benzene because they contain these handy delocalized electrons can be used to conduct electrical current in nano-scale electronic devices.

We have long accepted that diamond and graphite are different allotropic forms of carbon (Mannion, 2006) which have distinctly different structures, bonding characteristics and therefore grossly different chemical and physical properties. However, graphite (the tip of pencil), also conducts electricity. A graphite molecule is, like benzene, a collection of carbon rings but it's built differently: The same electrons that benzene uses to bond each carbon atom to a hydrogen atom are used instead to bond carbon atoms to other carbon atoms in adjacent carbon rings. As shown in figure 2.6 (1-c), in this structure, each carbon atom bonds covalently to three other carbon atoms. As with benzene, each carbon atom in graphite has an “extra” electron — one more than the number of atoms it's bonded to. The atomic orbitals for these electrons overlap to form a molecular orbital that allows delocalized electrons to move freely throughout entire graphite sheet makes graphite conducts electricity.

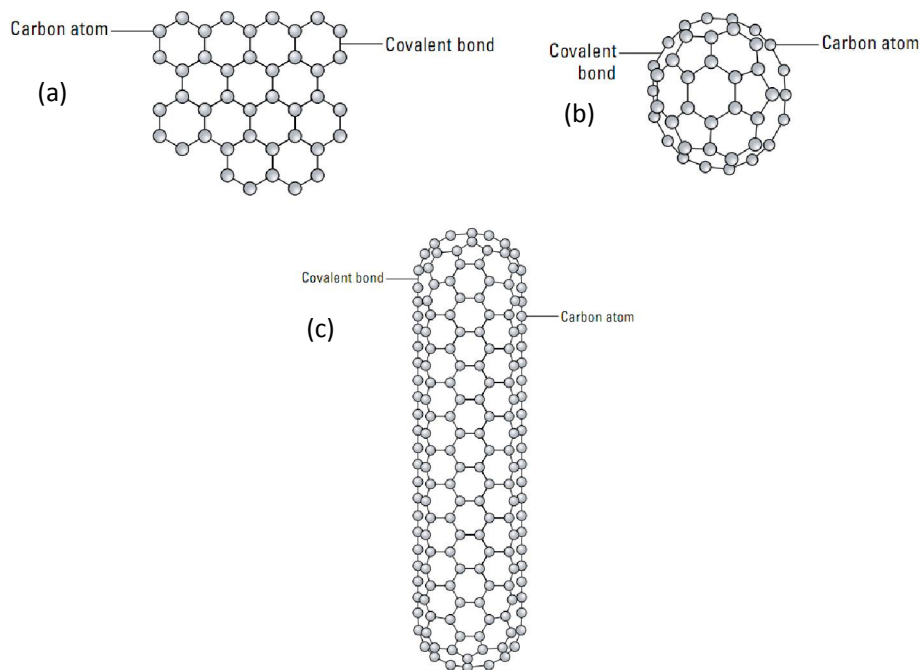


Figure 2.6: Structure of carbon atoms connected by covalent bond in a (a) graphite's sheet, (b) buckyball and (c) single wall of carbon nanotubes (SWCNTs).

Two properties of carbon group make them especially useful in nanotechnology: their strength and their ability to conduct electricity. Buckyballs and single wall carbon nanotubes (SWCNTs) are two types of simplest molecules composed of carbon atoms that have wide applications in nanotechnology such in electronics, biology, chemistry, medical, mechanical and etc (Harris, 2009). The simplest structure of buckyballs contain 60 carbon atoms form a single stable molecule only if they are arranged in 20 hexagons and 12 pentagons that are linked to form a sphere (Mitin et al., 2008) about 1 nm diameter.

Like bulkyballs, SWCNTs are combination of carbon atom instead of forming the shape of a sphere, the lattice forms the shape of a cylinder as illustrated on figure 2.4(c) which conduct electricity better than metals. When electrons travel through metal there is some resistance to their movement. This resistance happens when electrons bump into metal atoms. When an electron travels through a SWCNT, it's travelling under the rules of quantum mechanicals with low or without scattering event thus travel in maximum mobility of bulk materials. Therefore the movement of electron in SWCNT called ballistic transport (O'Connell, 2006).

Why is carbon material very important? This is due to the carbon materials relate to the chemistry, physics and biology of this versatile element described previously. Chemically, carbon is highly reactive and can be combined with many other elements to produce a wide variety of compound, either simple or complex compound (Jones, 2001). Nevertheless, carbon is very important in terms application because it has industrial and social uses and so are component of wealth generation. Figure 2.7 shows a summary of nanomaterials used in consumer as product. Carbon was selected as the most demanded by consumers as it is inexpensive materials and the ability to bond or easily join, some of the reasons why carbon include carbon compounds are common in our universe (Saucerman, 2005).

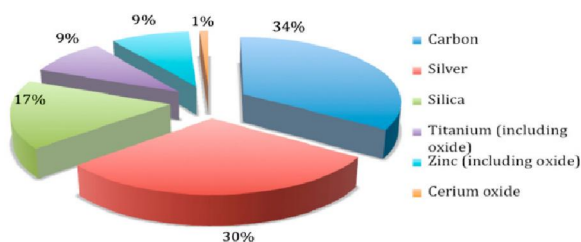


Figure 2.7: Nanomaterials used in consumer products (Maynard, 2006).

Nevertheless polymethyl methacrylate (PMMA) is a type of polymer, it can be fabricated in sphere shape or in liquid matter. PMMA does not have benzene ring in chemical structure as shown in figure 2.8 and to a certain extent, researchers not give much attention in modification of physical and chemical structures of PMMA nanospheres. For instance, magnetic hollow of PMMA nanospheres were successfully developed via in situ emulsion polymerization in the presence of oleic acid-modified  $\text{Fe}_3\text{O}_4@/\text{CaCO}_3$  composite NPs and obtain the magnetic hollow by etching the  $\text{CaCO}_3$  as templates.  $\text{Fe}_3\text{O}_4$  was proved to be existed in the hollow of PMMA nanosphere which endowed the PMMA nanospheres with magnetic properties. The magnetic properties have been shown by PMMA nanospheres could be applied in various fields of controlled release, drug delivery, target delivery and so on (Chunlei et al., 2010).

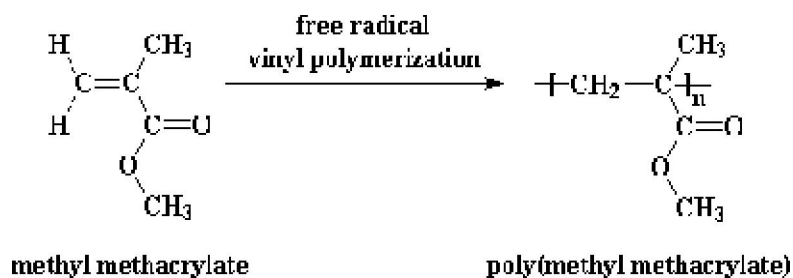


Figure 2.8: Model of polymerization of methyl methacrylate.

### 2.3.2 A flexible technology of polymer electronics

Polymer can be defined as the large chain of repeating structural unit called monomer. Polymers can be classified as natural if they made from nature such as rubber or protein and synthetic if they are human made such as polystyrene. In semiconductor industry, polymer as PMMA used as the polymer resist either positive or negative as previously described.

The famous characteristic property of polymer is the ability to form freestanding thus promises the thin, lightweight, flexible and environment environmentally friendly and enables a wide range of electrical components to be produced and directly integrated into low cost process. For example in application of

solar cells (Pagliaro, 2008) which the polymer used as the substrate in a sandwich layer of solar panel as shown in figure 2.9.

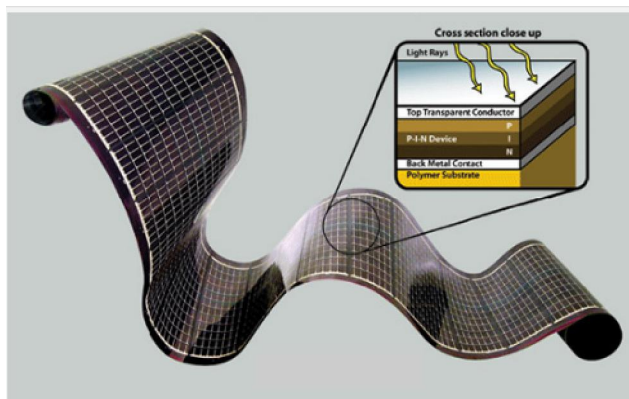


Figure 2.9: Flexible solar panels used polymer as substrate (Pagliaro, 2008).

Organic electronics, sometimes called plastic electronic or polymer electronic is a branch of electronics which is use the principle of conductive polymer. Over the last few years, significant progress has been made in improving the performance of devices, enabling a first generation of products to become available. The roadmap in figure 2.10 shows the nine selected applications, products are shown according to the timescale at which it is expected that they will reach the market, either in the short term (2009-2012) or medium (2012-2017), along with a forecast beyond 2018. For instance, figure 2.11 shows the chemical structure of an organic conductor, poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS), that is widely used for electrodes which make it transparent, has high ductility and is less expensive than inorganic conductors such as copper or aluminium (Groenendaal et al., 2000).

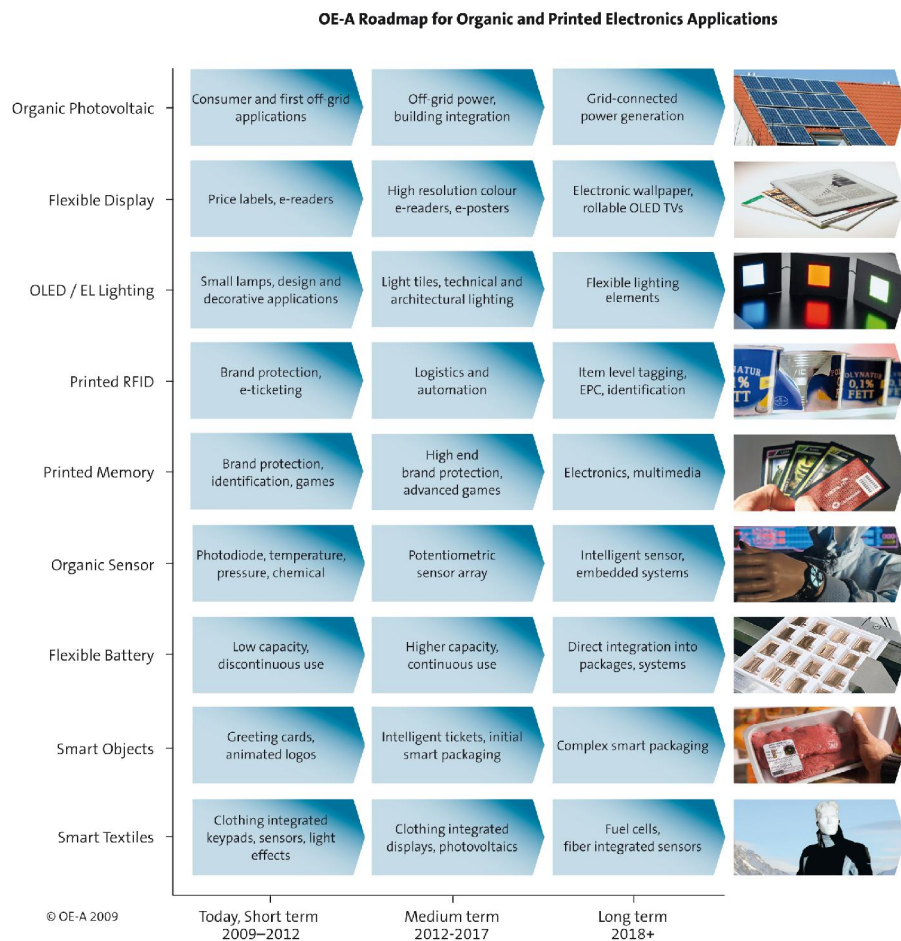


Figure 2.10: Third Organic Electronic Association (OE-A) Roadmap describes future focus of the industry (Hecker, 2009).

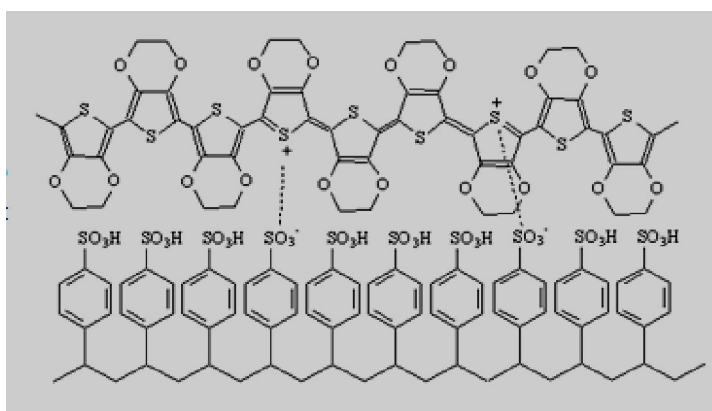


Figure 2.11: Chemical structure of PEDOT:PSS

In practise, the photoactive organic layer is placed between two different electrodes, the upper being transparent (figure 2.12 (a) and (b)). Charge separation takes place in the organic phase, the anode and cathode being chosen to have largely different (asymmetric) work functions, and thus to enhance modest charge separation. In photovoltaic (PV), light is absorbed mainly in the so-called donor material, a hole-conducting small molecule or conjugated polymer. The photogenerated singlet excitons diffuse within the donor towards the interface to the second material, the acceptor, which is usually strongly electronegative for example  $C_{60}$ . However, mechanism in light emitting diode (LED) is opposite mechanism in PV by releasing light as shown in figure (a).

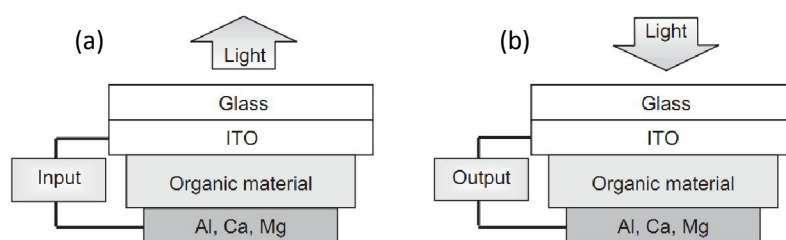


Figure 2.12: Organic materials sandwiched between two electrodes can work as (a) LED or (b) PV devices. In the former case electrons are collected at the metal electrode and holes at the iodine-tin oxide (ITO) electrode (Spanggaard & Krebs, 2004).

## 2.4 Nanosphere Lithography Technique

NSL also has other names: natural lithography (Deckman et al., 1982), colloidal lithography (Yang, et al., 2006), shadow nanosphere lithography (Kosiorsek et al., 2005) and nanosphere photolithography (Wei, 2007). In 1981, Fischer and Zingsheim reported the use of a simple drop-coated, colloidal monolayer with diameter of 312 nm onto a glass plate as a lithographic mask for preparation of platinum (Pt) nanostructures. The size and the periodicity of the Pt patterns were smaller than the visible light (Fischer et al., 1981). However, the focus of this work was on replication of submicroscopic patterns using visible light and not realization of lithographic colloidal masks.

One year later, Deckman and Dunsmuir have extended the idea of this technique. They have shown results of two-fold mask preparation: using

electrostatic adsorption and the spinning coating technique. Because the mask preparation process was based on the naturally occurring self-assembly phenomenon, they named this strategy as “Natural Lithography” (Deckman et al., 1982). Over the last ten years Van Duyne et al. have popularized natural lithography under the name of “nanosphere lithography” (Haynes et al., 1995). Since the pioneering works of Fischer et al. and Deckman et al., many groups have started to develop new approaches and to improve established methods in order to fabricate better quality colloidal masks and more sophisticated nanostructures depending on application.

#### **2.4.1 Modification of polystyrene nanospheres (PSNs)**

Thermal energy is a simplest way or source of energy in modification of PSNs whether using oven, hot plate or microwave treatment.  $\text{Fe}_2\text{O}_3$  and silica hexagonal periodic triangular prism nanopillars were successfully fabricated by heat-induced deformation of PSNs using oven. Unheated PSNs will result truncated-hollow sphere  $\text{Fe}_2\text{O}_3$  due to position of PSNs in close-packed lattice structures and contact with each other by quasi style in monolayer. However heating PSNs makes the contact of PSNs change from quasi point contact to facet contact resulting triangular prism nanopillars. Interestingly, the morphologies are different from those obtained by the templates with heating and without heating. However, over-heating PSNs will make the channel between PSNs will disappear, therefore no nanopillars were fabricated (Li et al., 2005).

Au thin layer was coated PSNs before introduced microwave heating to investigate of Surface Enhanced Raman Spectroscopy (SERS) performance. Wirelike structures are generated in the PSNs coated Au after 200 s treated under microwave, leading to more effective SERS activities via the localization of electromagnetic waves on the sharp structures. Au can be vaporized from the surface and condensed to form wirelike structures. In addition, the space between PSNs reduced and the shape of PSNs changed into a polyhedral shape. In contrast, with the hot plate heating (200 °C for 200s), the periodic structures of substrate are disturbed, and the PSNs bead structures is deformed. Some PSNs are fused together indicating



the inefficiency of selectivity heating by hot plates. Additionally, no wirelike structures are formed because the arching of metal is inefficient. By employing the conventional heating source to anneal Au-polystyrene beads substrate is not effective in modifying the morphology of metals because high annealing temperature leads to the serve deformation of PSNs. Well-controlled postgrowth microwave treatment on the Au-PSNs for effectively improving the SERS performance. This method enables the selective modification and discharging of Au films while minimizing the thermal effect on PSNs, thereby promoting greatly enhanced SERS activities (Clement et al., 2008).

The changes of physical properties of PSNs have been investigated by Agam and Guo (2007) by radiating the PSNs to the electron radiation under room temperature. The shrinkage of PSNs offers a new route in modification of NSL technique where the diameter of PSNs linearly decreased by increasing the duration time exposed. The shrinkage is likely to be caused by electron-induced damage of the polymer chain, resulting in partial loss of hydrogen and the formation of amorphous carbon like structures (Agam et al., 2007).

Wu and colleagues (2008) developed a maskless PL named nanosphere photolithography (NSPL) utilizing the silica micro-sphere (1  $\mu\text{m}$ ) to focus uv light for fabricating periodic metallic nanoholes perforated in gold and aluminium films. Silica micro-spheres were spun on a standard commercial positive and negative photoresist before exposing UV light. Metal layers of Au were deposited by electron-beam evaporator. After development, the positive resist will result in gold nanopost whereas the negative resist will result in gold nanoholes. The diameters of Au nanoholes and nanoposts about 180 nm. The simulation results show that even smaller nanoholes with tunable periods can be generated with a shorter wavelength.

To get a good uniformity of microspheres/nanospheres on a photoresist, the surface property of photoresist need to modify by dipping them into the developer for a few seconds before spread the microspheres/nanospheres on a photoresist. Photoresist here acts as substrate for dispersion of microspheres/nanospheres and developer as agent to make hydrophilic surface of photoresist (Wu et al., 2008).

### 2.4.2 NSL as versatile technique to produce periodic Nanoparticle Arrays (PNPAs).

Nanotriangles is a basic shape of nanostructure arrays fabricated using PSNs as templates by deposition of metal using metal deposition evaporator, electron-beam evaporator and etc., filled the voids between the arrangements of PSNs in hexagonal closed pack. Deckman et al. (1982) evaporated silver over hexagonal closed pack arrays of 0.4  $\mu\text{m}$  PSNs and the nanotriangles left on the substrate after dissolved in methylene chloride. Haes et al (2005) have extended the basic shape of nanotriangles by releasing them in solution rather than on the substrate. They discovered that the nanoparticles are weakly attracted to the glass surface, therefore they take these advantages to released the nanotriangles and become suspended in the solution, which is ethanol. Later, they investigate the Localized Surface Plasmon Resonance (LSPR) spectrum of the nanotriangles suspended in the bulk ethanol and reported that there are two maximum peaks LSPR spectrums at 417.9 and 682.1 nm compared to nanotriangles on substrate that has only an extinction maximum at 645.6 nm. Later they tried to simulate the experimental results as they are interested to understand why nanoparticles in suspension solution showed two peaks at LSPR spectrum.

They started with Mie theory to model the LSPR spectrum of suspended nanoparticles in solution. They started with hexadecanethiol-coated Ag nanosphere with radius ranging from 5, 10, 15 and 20 nm. As the size of sphere radius increases the LSPR extinction maximum increase from  $\sim 390$  nm to 410 nm. The model are further investigated using Discrete Dipole Approximation (DDA) to model the nanoparticles with different sizes and shapes, where the nanotriangles nanoparticles were represented as cubic lattice to formed as polarized points. From both theoretical results, the intense local maximum centered at  $\sim 420$  nm (experimental) arises from the combined effect from the absorption of small spherical nanoparticles and the out-of-plane polarization of truncated tetrahedral nanoparticles are better explained (Haes et al., 2005).

Li et al. (2009) later shows the NSL is a versatile lithography technique as they managed to grow hexagonally patterned arrays of well-aligned, regular ZnO nanopillars with controlled size, shape and orientation where they directly fabricated

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