Development of electroless plating processes for low cost plastic-metallization and area-selective metal coating of three-dimensional structures

Zhan, Jing

2020

Zhan, J. (2020). Development of electroless plating processes for low cost plastic-metallization and area-selective metal coating of three-dimensional structures. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/143663>

<https://doi.org/10.32657/10356/143663>

This work is licensed under a Creative Commons Attribution-NonCommercial 4.0 International License (CC BY-NC 4.0).

Downloaded on 26 Apr 2023 19:43:06 SGT

**DEVELOPMENT OF ELECTROLESS
PLATING PROCESSES FOR LOW COST
PLASTIC-METALLIZATION AND AREA-
SELECTIVE METAL COATING OF
THREE-DIMENSIONAL STRUCTURES**

ZHAN JING

School of Mechanical and Aerospace Engineering

2020

**DEVELOPMENT OF ELECTROLESS
PLATING PROCESSES FOR LOW COST
PLASTIC-METALLIZATION AND AREA-
SELECTIVE METAL COATING OF
THREE-DIMENSIONAL STRUCTURES**

Submitted by:

ZHAN JING

Supervised by:

Associate Professor HIROTAKA SATO

School of Mechanical and Aerospace Engineering

A thesis submitted to the Nanyang Technological University in

partial fulfilment of the requirements for the degree of

Doctor of Philosophy

March 2020

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

2020 March 06

.....

Date

.....

Zhan Jing

Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

March 16th, 2020

.....

Date

.....

Hirotaka Sato

Authorship Attribution Statement

*(B) This thesis contains material from 1 paper(s) published in the following peer-reviewed journal / and 2 papers on the way to submission in which I am listed as an author.

Chapter 3 is published as Jing Zhan, Desmond CL Tan, Swaek Prakrititanon, Ming Lin, and Hirotaka Sato. "Extremely low catalyst loading for electroless deposition on a non-conductive surface by a treatment for reduced graphene oxide." Chemical Communications 53, no. 66 (2017): 9198-9201.

The contributions of the co-authors are as follows:

- Asso. Prof. Hirotaka Sato provided the initial project direction and drafted the manuscript.
- I prepared the manuscript drafts (experiment, and result section). The manuscript was revised by Dr. Tan CL Desmond, Mr. Prakrititanon Swaek and Dr. Lin Ming.
- I co-designed the study with A/Prof Hirotaka Sato and performed all the laboratory work at the School of Mechanical and Aerospace and Engineering and the Singapore, I also analysed the data.
- All microscopy, XRD, QCM, electroless nickel plating, including sample preparation, were conducted by me for Analysis, Characterization, and Testing.
- Dr. Tan CL Desmond assisted in the starting set up of the initial experiment and gave some suggestions during the whole project.
- Mr. Prakrititanon Swaek provided the initial project direction.
- Dr Lin Ming assisted in the analysis some of the TEM data.

Chapter 4 contains material from Jing Zhan, Takayuki Tamura, Gytong Ri, Zhenghao Ma, Shinjiro Umezu, Hirotaka, Sato “Metal hybrid plastic-3D-printer using catalyst-loaded filament and electroless plating” (Submitted).

The contributions of the co-authors are as follows:

- Asso. Prof Hirotaka Sato provided the initial project direction and drafted the manuscript.
- Mr. Ma Zhenghao, Mr. Tamura Takayuki and I wrote the experiment part and results parts of the manuscript drafts. The manuscript was revised together with Mr. Ri Gytong and Prof. Umezu Shijiro.
- I performed the materials testing, electroless nickel plating, carried scanning electron microscopy, and conducted data evaluation.
- Mr. Tamura Takayuki and Mr. Ri Gytong synthesised the ABS microfibers with electrospinning
- Mr. Ma Zhenghao prepared the Pd loaded ABS filaments and conducted additive manufacturing.

Chapter 5 contains material from Jing Zhan, Ming Lin, Satoshi Arai, Keitaro Sou, Hirotaka Sato. “Triggering electroless deposition by separately encapsulating metal ion and reducing agent with thermo-sensitive liposomes” (Submitted).

The contributions of the co-authors are as follows:

- Asso. Prof Hirotaka Sato provided the initial project direction and edited the manuscript drafts.

- I wrote the drafts of the manuscript (results and discussion parts).
The manuscript was revised together with Dr. Lin Ming, Dr. Arai Satoshi, and Dr. Sou Keitaro.
- I performed the materials synthesis, stability test, DLS analysis and UV-vis spectra, carried scanning electron microscopy, and conducted data evaluation.
- Dr. Lin Ming carried transmission electron microscopy and gave some suggestions on TEM results analysis.
- Dr. Arai Satoshi conducted the microscopic observation of the reaction.

2020 March 06

.....
Date

.....
Zhan Jing

Abstract

To spread out the application of electroless plating, several methods were developed to improve the efficiency, cost effectiveness and environmental aspects of the electroless plating process. The author found three exist problems could limit the applications of electroless plating: 1) high market prices and low earth abundance of the catalyst materials (platinum, palladium, etc.); 2) strong or even hazardous acids are used in the surface preparation step; 3) challenged for triggering the electroless deposition on demand. For the initialization of electroless nickel deposition with fewer catalyst nanoparticles (palladium), a pre-treatment process that induces a conductive surface of reduced graphene oxide (rGO) on substrates was added prior to the surface activation step (Pd catalyzation). We confirmed that the rGO treatment enhanced the Pd catalytic activity and achieved a sufficient rate in the electroless deposition with extremely low Pd loading ($3.94 \times 10^{-2} \text{ g/cm}^2$). In the second project, to avoid environmental contamination and hazards of the whole electroless deposition process, the catalyst palladium was pre-loaded onto Acrylonitrile Butadiene Styrene copolymer (ABS) by an appropriate solvent. The use of Pd-loaded ABS material in additive manufacturing technology eliminated the surface etching steps and maintained sufficient adhesion of metal coating on ABS substrates. In the third project, the author achieved area-selective electroless palladium deposition by separating the reducing agents and metal salts with thermosensitive liposome. With the local thermal treatment above 40 °C, the electroless Pd deposition can be triggered at any exposed or internal surface of the given three-dimensional structures. These three projects had achieved improving the cost-effectiveness of current electroless plating technology, and also extending the applications of electroless plating for localized surface metallization of three-dimensional structures by cooperating with additive manufacturing technology and liposome structures.

Acknowledgement

The author would like to take this opportunity to express her highest appreciation and gratitude to Assoc. Prof. Hirotaka Sato, the author's supervisor for his dedication, wisdom and guidance in helping the author throughout the project.

Next, the author would like to thank Mr. Swaek Prakritritanon from Okuno-Auromex Co. Ltd, Assoc. Prof. Shinjiro Umezu from Waseda University, Dr. Keitaro Sou from Waseda University and Dr. Satoshi Arai from Kanazawa University for their support and suggestion in helping the author in these projects.

Also, the author would like to appreciate Ms. Koh Joo Luang, Ms. Yong Mei Yoke and Mr. Leong Kwok Phui at School of Mechanical & Aerospace Engineering, NTU, for their continuous effort to set up and maintain the excellent experimental environment.

Lastly, the author would like to thank those who were not mentioned here but helped the author during this project.

Table of Content

Abstract	viii
Acknowledgement	ix
Figure list	xiii
Abbreviation List.....	xviii
CHAPTER 1: INTRODUCTION.....	1
1.1 Background and motivation.....	1
1.1.1 Electroless nickel deposition.....	1
1.1.2 Additive manufacturing.....	3
1.1.3 Electroless deposition and electrochemical deposition of palladium group metals.	4
1.1.4 Motivation	7
1.2 Objectives and scope.....	10
1.3 Organization of the report	11
CHAPTER 2: LITERATURE REVIEW	13
2.1. Electroless deposition	13
2.1.1. Electroless nickel (EN) deposition	13
2.1.2. Pd catalyst used in electroless nickel deposition	15
2.1.3. Application of electroless nickel deposition.....	17
2.2. Reduced graphene oxide	19
2.2.1. Reduction methods for graphene oxide	20
2.2.2. Determine the reduction of graphene oxide.....	22
2.2.3. Methods to coat rGO films on non-conductive substrates.....	24
2.3. Additive manufacturing.....	26
2.3.1. Additive manufacturing of polymers	28
2.3.2. Additive manufacturing of metals.....	29
2.3.3. Additive manufacturing of composite.....	31
2.4. Acrylonitrile butadiene styrene (ABS) plastic	32
2.4.1. Surface treatment of ABS	33
2.4.2. Additives for ABS plastic	36
2. 5. Liposome	38

2.5.1.	Factors affecting lipids selection.....	40
2.5.2.	Preparation methods of liposome structure.....	41
2.5.3.	Thermosensitive liposome	44
CHAPTER 3: USE RGO TO ENHANCE PD CATALYTIC ACTIVITY IN ELECTROLESS NICKEL DEPOSITION.....		46
3.1	Experimental Procedure	46
3.1.1.	Solution Preparation.....	46
3.1.2.	Electroless nickel plating on local catalyst conductive surface.....	47
3.1.3.	Reduced graphene oxide (rGO) pre-treatment	48
3.1.4.	Characterization of the rGO reduced by NaH_2PO_2	49
3.1.5.	Stepwise loading of Pd nanoparticles for electroless deposition	49
3.1.6.	In situ measurement of nickel deposition by quartz crystal microbalance (QCM). 50	
3.1.7.	Apply rGO layers to enhance the silver catalytic activity and measure the Ni deposition speed by QCM	51
3.1.8.	Analysis the enhancement effect of rGO layer at different rGO loadings 52	
3.2	Results and discussion	52
3.3	Conclusion.....	64
CHAPTER 4: PRE-LOADED PD IN ABS FOR LOCAL METALLIZATION OF 3D PRINTED STRUCTURE.....		66
4.1	Experimental procedure.....	66
4.1.1	Solution preparation	66
4.1.2	Compatibility of ABS solute and different organic solvents:	67
4.1.3	Synthesis of Pd ion loaded ABS microfibers by electrospinning.	67
4.1.4	Pd ion loaded ABS coating on additive manufactured ABS structure: .	68
4.1.5	Electroless nickel plating:	69
4.2	Results and discussion	70
4.2.1.	Solvent choice for dissolving catalyst precursor (PdCl_2) and ABS	70
4.2.2.	Confirm catalytic activity of solidified ABS & PdCl_2 mixture (sol.2) with tangled fibers structures.....	72
4.2.3.	Area-selective metallization of 3D printed plastic structure	75

4.2.4.	Catalyst precursor (Pd elements) distribution in ABS.....	77
4.2.5.	Characterization of the metallization layer at Pd ion loaded ABS surface after electroless plating.....	79
4.3	Conclusion.....	80
CHAPTER 5: TRIGGER ELECTROLESS DEPOSITION ON SELECTED AREA WITH THERMO-SENSITIVE LIPOSOME		82
5.1	Experimental Procedure	82
5.1.1	Chemical Preparation.....	82
5.1.2	Synthesis of liposome encapsulated structures (Lipo-P; Lipo-Pd; Lipo-PBS)	83
5.1.3	The analysis of liposome structures' stability	83
5.1.4	Characterization of liposome structures	85
5.1.5	Demonstration of area-selective electroless deposition	85
5.2	Results and discussion	86
5.2.1	Thermotropic phase behavior of liposomes.....	86
5.2.2	Characterization of liposome capped reducing agent before and after heating	90
5.2.3	Duration stability test of liposome structures.....	92
5.2.4	Area-selective deposition of Pd on substrates.....	93
5.3	Conclusion.....	96
CHAPTER 6: SUMMARY.....		98
6.1.	Summary.....	98
6.1.1	Use rGO to enhance Pd catalytic activity in electroless nickel deposition	99
6.1.2	ABS-Pd for selective-area metallization on complex ABS structure	100
6.1.3	Trigger electroless deposition on selected area with thermo-sensitive liposome	101
6.2.	Future work	102
References.....		114

Figure list

Figure 1 Electroless nickel deposition process.....	1
Figure 2 A) Set up for electrochemical deposition; B) set up for electroless deposition.	6
Figure 3 Electroless deposition models on (A) non-conductive substrate, (B) conductive substrate and (C) reduced graphene (rGO) coated nonconductive substrate.	8
Figure 4 SEM observations of (A) hypophosphate reduced Pd (Pd-P), (B) hydrazine reduced Pd (Pd-N ₂ H ₄) and (C) tin chloride reduced Pd (Pd-Sn/AA); (D) Cyclic voltammograms of various Pd nanoparticle electrocatalysts in solution (pH 9) with NaH ₂ PO ₂ normalized by Pd load (mass activity) [32]	16
Figure 5 Applications of electroless nickel depositions: A) Wear and corrosion resistance of aluminum connectors are enhanced by electroless nickel plating,[33] B) giant magnetoresistive head made with electrodeposited CoNiFe,[34] C) Cu/Ni/ Au electrodes array,[35] D) SEM images of Ni plated microtubules with 1 min of metallization.[36]	17
Figure 6 In the thermal annealing, structure model of GO changes at different stages A) room temperature; B) 100 °C; C) 220 °C; D) 500 °C.[54]	21
Figure 7 (A) the original GO film; (B) GO reduced in HI acid at 100 °C for 1 hr (C) GO reduced by hydrazine vapor.[62]	23
Figure 8 Photographs of (A) GO, (B) rGO dispersion in water and (C) rGO dispersion in DMF[48].....	23
Figure 9 AFM images and height profiles of the rod-coating fabricated GO films at different GO concentrations: A) 0.05 mg/mL; B) 0.1 mg/mL; C) 0.2 mg/mL; D) 1 mg/mL. (The rod used in this experiment with diameter at 0.2 mm. The red squares in AFM images were areas used to obtain the film's root-mean-square roughness.) [68]	26
Figure 10 The basic stages in AM technology.[71].....	27
Figure 11 Generic illustration of A) AM powder bed system; B) AM wire feed system.[80].....	29
Figure 12 The optical micrograph of SLS processed A) bronze-nickel samples; B) bronze-nickel samples sintered at 1030 °C.(B = bronze, N = nickel, P = pores, S = solid solution).[82]	30
Figure 13 A) FEF machine with triple-extruder; B) FEF fabricated composite with a gradient from 100 % Al ₂ O ₃ to 50 % Al ₂ O ₃ and 50 % ZrO ₂ . [70]	32
Figure 14 chemical structure of Acrylonitrile; 1,3 Butadiene; Styrene; and ABS.	33
Figure 15 Schematic illustration of chromium dynamics in soil.[94]	34
Figure 16 Surface treatment process of ABS A) tradition ABS etching with chromic acid; B) surface treatment process with PAA graft.[18]	36
Figure 17 Fracture surface of different ABS samples in the XYZ print orientation A) Pure ABS resin; B) ABS/Jute composite; C) ABS/MayaCorm composite; D) ABS/TiO ₂ composite; E) ABS/ZnO composite; F) ABS/SrTiO ₃ composite; G)	

ABS/Al ₂ O ₃ composite; H) ABS/styrene ethylene butadiene styrene (SEBS) blend with 80:20 ratio; I) ABS/ultra-high molecular weight polyethylene (UHMWPE)/SEBS blend with 90:10:10 weight ratio. (The white arrows indicate the micro-voids within polymer matrix.) [100]	37
Figure 18 A) The typical liposomes structure with a shell consisting in a lipid bilayer; B) some water-soluble polymer lipids exist in the “stealth” liposomes for drug-delivery applications; C) the common cationic liposome–DNA complexes with DNA (purple rods) sandwiched between cationic membranes D) a new liposome structure that the bilayer assembles from cavitands — vase-shaped molecules — to which the authors attached hydrophobic and hydrophilic chains. [106]	39
Figure 19 Schematic illustration of the behavior of the thermosensitive polymers cooperated liposome below and above their low critical solution temperature. [114]	45
Figure 20 Electroless deposition on (A) domain catalyzed Copper and (B) no catalyzed Copper foil.	53
Figure 21 The appearances of GO solutions after mixing it with DI water, N ₂ H ₄ and NaH ₂ PO ₂ respectively for different durations.	54
Figure 22 XRD patterns of graphene oxide and NaH ₂ PO ₂ reduced graphene oxide.	56
Figure 23 Raman Spectra of graphene oxide and NaH ₂ PO ₂ reduced graphene oxide.	57
Figure 24 STEM image of A) 160 ppm Pd, B) 3.2 ppm Pd and C) 3.2 ppm Pd & rGO. (See Table 5 for the denotations of these samples)	58
Figure 25 Deposition amount in Ni electroless deposition on a SiO ₂ coated QCM electrode after different catalysation processes: 160ppm Pd, 3.2ppm Pd, 3.2ppm Pd & rGO and no catalysation (blank).	59
Figure 26 Mass activity, Ni deposit normalised by Pd loadings of 160ppm Pd and 3.2ppm Pd & rGO	60
Figure 27 Electroless plating process at A) t = 0s; B) t = 20 mins (The sample on the left is 3.2ppm Pd and the sample on the right is 3.2ppm Pd & rGO).	61
Figure 28 A) Deposition amount in Ni electroless deposition on a SiO ₂ coated QCM electrode after different catalysation processes: 10 mM AgCl, 200 μM AgCl, , 200 μM AgCl & rGO and no catalysation (blank). B) Ni coating on 10 mM AgCl catalyzed sample; C) Ni coating on 200 μM AgCl catalyzed sample; D) Ni coating on 200 μM AgCl & rGO treated sample;	62
Figure 29 Mass activity, Ni deposit normalized by Pd loading of Pd catalyzation process using different GO concentrations.	64
Figure 30 A) conventional method of metallization of 3D printed plastic structure; B) new method has been proposed in this study to deposit metal of interest over the selected area of a 3D printed plastic structure.	70
Figure 31 Solvent test by mixing different solvents with solute ABS (acetone) and PdCl ₂ respectively.	71

Figure 32 SEM images of (A) electro-spun microfibers using Pd ion pre-loaded ABS acetone solution after Ni electroless deposition. (B) electro-spun ABS fibers after the treatments for Pd catalyzation (using PdCl ₂ and SnCl ₂ solutions) and Ni electroless deposition.....	73
Figure 33 A) Designed multi-layer tangled fiber structure (white color is printed with pure ABS solute; orange color is printed with ABS & PdCl ₂ mixture – sol.2); B) the multi-layer tangled fiber structure printed with electrospinning; C) the multi-layer tangled fiber structure after 10 mins electroless nickel plating.	75
Figure 34 3D printed ABS structures with different catalyzing methods: (A) conventional method shown in Figure 30A: immersion in Pd ion solution (two steps PdCl ₂ / SnCl ₂ catalyzation). The double-sided arrow indicates the depth of immersion. (B) an area-selective catalyzation: pasting ABS & PdCl ₂ mixture solution (sol.2) through a nozzle with air-pressure, (C) another area-selective catalyzation: pasting Pd-ion loaded ABS through FFF (fused filament fabrication) 3D printer using a Pd-ion preloaded ABS filament. (The top images are those 3D printed structures after different Pd catalyzation processes while the bottom images are the catalyzed 3D structures after electroless deposition.).....	77
Figure 35 A) 3D printed ABS structure with area-selective catalyzed with Pd-pre-loaded ABS solution; The cross-sectional view of Pd ion loaded ABS layer (the red circle in A) under (B) optical microscope; (C) SEM; (D) EDX mapping of Pd element.	78
Figure 36 A) ABS-Pd coated ABS structure after electroless nickel deposition; B) FESEM observation at the boundary of catalyzed region and non-catalyzed region; (red circle area in A) C) EDX analysis of the metalized area (black color area of B).	79
Figure 37 Mixture of A) Lipo-PBS and PdCl ₂ solution; (B) Lipo-P and PdCl ₂ solution; C) NaH ₂ PO ₂ solution and Lipo-Pd; D) Lipo-P and Lipo-Pd; at 20 °C, 30 °C, 40 °C, 50 °C, 60 °C, 70 °C and 80 °C, respectively.	88
Figure 38 UV-Vis spectrum of DI water, mixture of Lipo-P & PdCl ₂ after thermal treatment at 20 °C, 30 °C, 40 °C, and the mixture of Lipo-PBS & PdCl ₂ at room temperature. (The spectra were measured after removing Lipo-P and dark black deposition by centrifugation.).....	89
Figure 39 TEM of A) Lipo-PBS & PdCl ₂ at room temperature; B) Lipo-PBS & PdCl ₂ heated to 70 °C; C) Lipo-P & PdCl ₂ at room temperature; D) Lipo-P & PdCl ₂ heated to 70 °C at different magnification.....	91
Figure 40 DLS analysis results of Lipo-P at room temperature; Lipo-P after heating up to 70 °C for 1 min; and the mixture of Lipo-P & PdCl ₂ after heating up to 70 °C for 1 min.....	92
Figure 41 Mixture of Lipo-P and PdCl ₂ at 25 °C (left) and 70 °C (right) after the liposome was synthesized for A) 0 days, B) 1 days, C) 10 days, D) 40 days, E) 160 days.	93

Figure 42 SEM observations of A) heat triggered Pd deposition on Silicon wafer (Lipo-P & PdCl ₂ mixture); B) Silicon surface at room temperature (Lipo-P & PdCl ₂ mixture); C) the boundary between heat triggered area and untriggered Si substrate at low magnification.	94
Figure 43 Demonstration of triggered Pd deposition process at inner surface of glass capillary tube: A1) blank glass capillary tube; A2) inject the Lipo-P and PdCl ₂ solution into capillary tube; A3) local thermal treatment from the outside of tube (two black color regions); A4) remove the mixture and wash the capillary tube with DI water; B) SEM observation of heat triggered area; C) SEM observation of the area without heat treatment.....	95
Figure 44 The sheet resistances of the multilayer films S-1, S-2, and S-3 (different GO concentration samples) on fused silica versus the number of PANi/rGO bilayers (HI reduction). (Tested with a standard four-point probe method)[130]	103
Figure 46 Optical microscopy observation of tangled fibers after washing with different concentration of acetone solution.	107
Figure 47 electroless nickel plating appearances of solidified ABS & PdCl ₂ with and without TiO ₂ additives.	108
Figure 48 TEM observation of A) Lipo-P & PdCl ₂ mixture at room temperature; B) Lipo-P & PdCl ₂ mixture at room temperature for 20 hours.	111

Table list

Table 1 Typical components, operation, conditions and application of different EN bath[24]	14
Table 2 Working principle of different AM process.[67]	27
Table 3 Melting point of commonly used metal and alloys.	29
Table 4 Summary of Passive loading techniques. [105]	42
Table 5 Pd loadings and mass activities of the samples prepared under different PdCl ₂ concentrations	55
Table 6 Resultant rGO coverage and Pd loading from different GO concentrations....	63

Abbreviation List

3D -- three-Dimensional

3DP -- three-dimensional printing

ABS -- acrylonitrile butadiene styrene copolymer

AM -- Additive manufacturing

CAD -- Computer-Aided Design

DI water -- Deionized water

DLS -- Dynamic light scattering

DMAB -- dimethylamine borane

DMF -- dimethylformamide

DPPC -- 1,2-dipalmitoyl-sn-glycero-3-phosphocholine

EBM -- Electron Beam Melting

EDTA -- Ethylenediaminetetraacetic acid

EDX -- Energy-Dispersive X-ray Spectroscopy

EN plating -- Electroless nickel plating

FDM -- Fused Deposition Modeling

FEF -- freeze-form Extrusion fabrication

FESEM -- Field Emission Scanning Electron Microscope

FFF -- fused filament fabrication

GO -- graphene oxide

ICP-MS -- Inductively Coupled Plasma-Mass Spectroscopy

LCST -- low critical solution temperature

LENS -- Laser Engineered Net Shaping

LMD -- Laser Metal Deposition

LOM -- laminated Objective Manufacturing

MEK -- methyl ethyl ketone

MJM -- Multi-Jet Modeling Systems

m_{Ni} -- mass of Ni deposited

m_{Pd} -- mass of Pd deposited

NTP - Non-thermal plasma

PAA -- Poly(acrylic acid)

PANi – polyaniline

PBS – Phosphate buffered saline

PEG-DSPE -- 1,2-Distearoyl-sn-glycero-3-phosphoethanolamine-N-[monomethoxy poly(ethylene glycol)]

PET - polyethylene terephthalate

PGM -- platinum group metals

PLA -- polylactic acid

PP - polypropylene

QCM – Quartz Crystal Microbalance

rGO -- reduced graphene oxide

SA -- L-glutamic acid, N-(3-carboxy-1-oxopropyl)-, 1,5-dihexadecyl ester

SEM – Scanning Electron Microscope

SDS -- Sodium dodecyl sulfate

SLA -- Stereolithography

SLM -- Selective Laser Melting

SLS -- Selective Laser Sintering

TEM -- Transmission Electron Microscope

UV - Ultraviolet

UV-Vis – Ultraviolet-Visible Spectrophotometers

XRD -- X-ray Powder Diffraction

CHAPTER 1: INTRODUCTION

1.1 Background and motivation

1.1.1 Electroless nickel deposition

Electroless nickel (EN) plating is the most important catalytic chemical reduction process upon which the plating of metals depends through the catalytic reduction of metal ions in an aqueous solution. Since its invention by Brenner and Riddell in 1947,[1] electroless plating has been widely used as a deposition method in the industrial and commercial sectors for metal coating processes.

There are three major steps involved in the electroless nickel deposition process:

1) surface preparation; 2) catalyst activation; 3) electroless plating (Figure 1).

Figure 1 Electroless nickel deposition process

In comparison with electrodeposition, which requires the use of external electrical power, electroless plating shows a huge improvement in terms of its application on any surfaces, regardless of the surface conductivity of substrates. Since electroless deposition is a dip-coating process by chemical reduction, it is relatively easy to obtain a uniform coating with the same composition, thickness, physical and mechanical properties. In other words, electroless deposition will achieve a uniform surface metallization for the non-conductive substrates.

Electroless plated nickel has some unique properties that correspond to its structure. When sodium hypophosphite is used as the reducing agent, a typical composition of 8% phosphorus was detected in the final composites and contributed to amorphous structures.[2] The phosphorus content can vary over a wide range (3% to 12%), and this leads to great variations of both physical properties and mechanical properties of deposits.

Electroless nickel coating is a chemical process that is widely used in industry to provide consistent and reliable performance to innovative and less expensive substrate materials. In general terms, electroless deposited nickel with a low phosphorus content would have a better corrosion resistance in the strong alkaline environment; whereas a high phosphorus containment for the nickel deposits would give a better resistance to the easily hydrolyzed chemical environment. In addition, the electroless deposited nickel shows obvious advances in the mechanical properties, such as hardness, galling resistance and wear resistance.

The uniform thickness of electroless nickel deposits with good corrosion resistance and enhanced mechanical properties are widely used in a wide range of applications which include valve installation, rail car components, and the food, automotive, oil and gas, aerospace and electronics industries.

1.1.2 Additive manufacturing

Nowadays, it is much easier to design and manufacture three-dimensional (3D) structures with geometrical and material complexity by using advanced additive manufacturing technologies, which are also known as rapid prototyping and 3D printing technology.[3] The underlying principle of the additive manufacturing technology involves combining raw materials to build a 3D object under the complete regulation of a computer. The most conventional and fundamental method in constructing the target structure is through the localized pasting of the molten raw material at designed and defined sites layer by layer such that liquid layers would fuse and form 3D object after solidification. [4-6]

Initially, additive manufacturing technology gives manufacturers the ability to develop a wide range of 3D structures and complex geometries to appeal in the aesthetic and functional application. In recent years, the cost of 3D printers has been significantly reduced, thereby its applications are widely expanding to homes, schools, libraries and laboratories. Additive manufacturing makes it possible for manufacturers to 3D print small quantities of customized products

with low costs. The growing consensus of applying the additive manufacturing technique is attributed to several advantages including fabrication of complex geometric structures with high precision capability, high design flexibility, maximum material savings, and high customization for personal use.

Source materials for additive manufacturing are primarily plastics and metals. However, these materials are always used individually in additive manufacturing. Generally, it is practically not possible to merge 3D plastic and 3D metal printers and print metal over plastic to construct a 3D printed structure, due to the high temperature required in metal 3D printer.[7-9] However, there is often a strong demand to deliver the lustrous appearance or conductive layers at specific positions or over the entire 3D printed plastic workpiece.[10] Is there a possibility of metalizing selected areas of 3D printed plastic? What is the most suitable technique for such area-selective metal coating over the 3D printed plastic surface?

1.1.3 Electroless deposition and electrochemical deposition of palladium group metals.

Platinum group metals (PGM) are comprised of 6 types of noble metal elements, namely ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir), and platinum (Pt). These metals are precious metals with electromotive force (emf) values between +0.680 to +1.188, that are extremely easy to be reduced to their metallic states.[11] The noble character of these PGM elements gives them excellent corrosion resistance; these metals offer proper cathodic protection to

other base materials when they work as coating layers. The PGMs are relatively inert with respect to chemical attack by many acids or by oxygen. Palladium and platinum are more reactive than other elements of the group, hence they are widely used as electrocatalysts in various chemical reactions, such as methanol oxidation and photo catalysts for splitting water on TiO_2 surface.

Electrochemical deposition, also known as electrodeposition, is a versatile technique which employs electrical current to reduce cations of a desired metal from an aqueous solution and coats a thin metallic film onto the target surface of the conductive substrates (Figure 2A).[12] Electroless deposition is a facile method that chemically reduces the metal ions or its complexes to a metallic state and forms a desired coating layer on the “activated” substrates surface (Figure 2B).

The deposited metal layer obtained from both the electrodeposition and electroless deposition has many applications. The primary application is to improve the corrosion resistance of the underlying layers. Other applications include improving surface wear resistance, decorative coating for aesthetic appearance, and enhancing the electrical conductivity for electrical contacts. Electrodeposited metal layers are fine structured and have shown valuable physical properties such as high reflectivity and high hardness.[13] The metal deposited by electroless deposition shows a great advantage of having the thickness of the deposit layers being controlled at the micrometer level.

Figure 2 A) Set up for electrochemical deposition; B) set up for electroless deposition.

The main difference in these two solution-based metallization processes is their different reduction approaches. In the electrochemical deposition, the external power source supplies the electron, and this results in both the anode and cathode being conductive for electrons. For the electroless deposition, the electron used for metal ion reduction is supplied by the reducing agent, and this even applies to the substrates of insulated materials. Hence, electroless deposition is the most widely used method for the metallization of plastic materials.

Many area-selective metal coating processes have been engineered through the use of electroless deposition, and the research on X-ray activation of electroless copper deposition and patterning has been widely studied.[14] However, all of these processes require harsh conditions, especially high temperatures, which is not readily usable for general or even industrial uses.

1.1.4 Motivation

Catalyst in electroless nickel deposition: To initiate complete and homogenous metallization on non-conductive substrates such as glass, plastic, and ceramic, it is necessary to achieve a dispersion of catalysts (Pd nanoparticles) with a 50-nm diameter and 20% coverage at the surface of substrates.[15] The high market price of Pd posed a significant cost barrier to the adoptability of Pd catalysts in electroless deposition. On the surface of a non-conductive substrate with Pd catalyzation treatment, oxidation of the reducing agent and electron discharge occur locally on the nanoparticle catalysts. Hence, only the metal ions surrounding the Pd nanoparticles will receive the electrons and will be deposited locally in the proximity of the Pd nanoparticle domains, as illustrated in Figure 3A. As such, to uniformly metallize a non-conductive surface, there must be a dense distribution of Pd nanoparticles loaded with large quantity, in the order of a few mg / cm², and this will result in the high cost in the electroless nickel deposition.[16] For conductive substrates that were catalyzed with Pd nanoparticles, electrons that were discharged from the oxidation of reducing agents are transferred away or pushed over the conductive substrate, thus resulting in complete and homogeneous Ni deposition on the surface, as shown in Figure 3B.[17] If a non-conductive substrate could be facilely functionalized with a conductive material for electron transfer, the electroless deposition will occur efficiently throughout the surface even with low Pd loading or treatment of a sparsely deposited Pd catalyst (Figure 3C). With conductive pre-coating,

uniform nickel plating can be achieved on the non-conductive substrates with a less than 20 % coverage of dispersed Pd nanoparticles.

Figure 3 Electroless deposition models on (A) non-conductive substrate, (B) conductive substrate and (C) reduced graphene (rGO) coated nonconductive substrate.

Metallization of 3D printed structure: To construct shiny or conductive layers locally or throughout the 3D printed plastic structure, an additional metallization technique is required after the onset of additive manufacturing. In the dry or vacuum metallization processes such as sputtering and evaporation, a complex 3D printed structure cannot be fully metallized due to poor step-coverage. In the dipping or solution-based metallization process, where a substrate is dipped or

immersed in the solution for metal deposition, a complete and uniform metallization of the 3D printed structure can be achieved as a result of homogeneous flow of solution occurring throughout the surface of the three-dimensional structure. In the typical dipping metallization process, such as electroplating and electroless plating, metal ions are reduced to metal by electrons, which form uniform metal layers on the substrates. In consideration of plastic materials with low electrical conductivity being commonly used in additive manufacturing, electroless deposition is a much-preferred metallization process due to the use of a reducing agent for the reduction of metal ions and an external power source is not required. Take acrylonitrile butadiene styrene (ABS) copolymer as an example. The dipping of plastic in chromic acid and the use of complicated pre-treatment processes are required for the catalyst nanoparticles and plated metal trapping well.[18-20] However, the use of chromic acid for the etching of ABS plastics has been refrained due to the social constraint placed on the reduction of hexavalent chromium.[21, 22] Therefore, there is a strong demand for the deposition of metal over 3D printed structure without pre-etching.

Triggered electroless deposition on demand: To achieve trigger deposition on demand, X-ray activation of less noble metal deposition has been studied.[23] However, the highly exothermic reaction of using an X-ray would result in high temperatures at the target area. Hence, this process is not feasible for plastic

substrates with low melting points. On the contrary, the X-ray activation process is only applicable for the electroless deposition of less noble metals (such as copper or nickel), which does not go through a direct deposition. The method to trigger the electroless deposition of noble metals (such as palladium or platinum) involves the insulation of both metal ions and a reducing agent with a separation layer before reaction takes place, and this separation layer should be easily broken on demand.

1.2 Objectives and scope

Use rGO to improve Pd catalyzed activity in EN deposition: A pre-treatment process is added before the surface activation step (Pd catalyzation), which helps in the initialization of EN deposition with much reduced loading of Pd nanoparticles:

To form a continuous conductive layer on the surface of non-conductive substrates.

To simplify the pre-treatment process and be appropriate for the solution process.

To reduce the overall cost in the whole EN process.

Pre-loaded Pd in ABS for local metallization of 3D printed structure: A method was invented and demonstrated for the pre-loading Pd source into 3D printing or ABS structures. Pre-loaded Pd works as a catalyst in EN deposition and the final

ABS-based product is designed with the area-selective surface metallization on the targeted area:

To achieve mask-less and area-selective surface metallization on 3D printed structures.

To achieve uniform metal coating with good adhesion on ABS plastic surface without the use of hazardous pre-treatment process.

Triggering electroless deposition on selected area with thermo-sensitive liposome: A new method was proposed for the separation of reducing agents and metal salts with thermosensitive liposomes. No reaction occurs between reducing agents and metal salts at a stable condition, and electroless depositions can happen under certain conditions:

To achieve area-selective electroless deposition not limited at exposed surface or even flat surface.

To achieve electroless deposition on the target substrates without any limitations on melting points of the substrates.

1.3 Organization of the report

This graduation thesis has been organized into 6 chapters.

Chapter 1 is the introductory chapter which contains background, motivation, objectives and the scope of this report, with the organisation of the report also being mentioned in this chapter.

Chapter 2 covers a comprehensive literature review that has been carried out for this project, which includes: 1) the basic process of electroless nickel deposition and the Pd catalyst being used; 2) the reduction methods and analysis of reduced graphene oxide; 3) the additive manufacturing process used in polymer, metal and composites fabrication; 4) the current etching methods used for plastic (ABS) and the problem of these etching methods; 5) preparation methods of liposome and thermosensitive liposome.

Chapter 3 discusses the work done for the reduced Graphene Oxide's enhancement on the palladium nanoparticles catalyst for electroless nickel plating.

Chapter 4 discusses the work done related to the pre-loading of Pd ions into plastic for metallization of electrospun fibres and 3D printed structure without pre-etching and catalysation process.

Chapter 5 discusses the work done for triggering electroless plating on selected area by separately encapsulating metal ions and reducing agents with thermosensitive liposomes structures.

Chapter 6 provides a summary of this graduation thesis, and also lists ideas for future research works.

CHAPTER 2: LITERATURE REVIEW

2.1. Electroless deposition

Electroless deposition (or electroless plating process) is the auto-catalytic deposition of metals (such as copper, nickel, cobalt, gold, iron, silver, palladium) or their alloys on substrates based on the reduction of metallic ions or metal complexes to the metallic state without applying any external electrical potential. This is a highly selective method that allows the patterning of embedded and isolated layers on corresponding substrates, such as plastic, ceramic and glass.[24] Due to its relatively low working temperature (usually lower than 100 °C), electroless deposition technology has been widely adopted for surface metallization of complex structures.

2.1.1. Electroless nickel (EN) deposition

Firstly, substrates go through a surface treatment process that improves the mechanical adhesion, surface area and hydrophilicity for the surface seeding of the catalyst. Secondly, the catalyst of either palladium (Pd) or platinum (Pt) nanoparticles are pre-coated on the target region to initialize the first layer of nickel seeding:

The subsequent nucleation of nickel only starts on the catalytic sites on the substrates' surface. After the first nickel layer has covered the whole catalyst surface, the nickel on the top surface catalyzes the following chemical deposition

and impels a continuous build-up of thick deposits. It has been reported that after the catalyzation with Pd/Sn nanoparticles, the surface of the substrates would experience growth of spherical island-type Ni-P in the early deposition stage, and the coating becomes continuous as the growth proceeds.[25]

In general, the solutions used in electroless deposition are more complex than the conventional electroplating baths. For the electroless nickel deposition, the typical electrolytes being used contain a few components as follows: the source of nickel ions, reducing agents, stabilizers and suitable complexing agents. As detailed in Table 1, the choice of different compounds and the different working conditions will deposit pure nickel or a nickel alloy film in the target region.

Table 1 Typical components, operation, conditions and application of different EN bath[26]

Electroless bath	Pure nickel	Acid nickel-P/B	Alkaline nickel-P/B
pH	10.5–11	4.5–5.5 Medium and high P/B; 6.0–6.5 low P/B	8.5–14
Temperature (°C)	85–90	75–95	25–95
Deposition rate (μm/h)	6–12	10–25	10–15
Metal salts or source	Nickel acetate	Nickel sulfate, nickel chloride	Nickel sulfate, nickel chloride
Reducing agents	Hydrazine	Sodium hypophosphite, sodium borohydride, dimethylamine (DMAB)	Sodium hypophosphite, sodium borohydride, dimethylamine (DMAB), hydrazine
Complexing agents	EDTA (tetra sodium salt), glycolic acid	Citric, lactic, glycolic, propionic acids, sodium citrate, succinic acid	Citric, lactic, glycolic, propionic acids, sodium citrate, sodium acetate, sodium pyrophosphate
Stabilizers		Thiourea, lead acetate, heavy metal salts, thioorganic	Thiourea, lead acetate, heavy metal salts, thioorganic compound, thallium, selenium
pH adjusters		Sodium hydroxide, sulfuric acid	Sodium hydroxide, sulfuric acid, ammonium hydroxide

2.1.2. Pd catalyst used in electroless nickel deposition

In the electroless nickel (EN) plating, the reduction of nickel ions strongly depended on the catalytic reduction process in the aqueous solution. Approximately 70% of the EN solution uses sodium hypophosphite as the reducing agent. At the catalytic surface, the sodium hypophosphite can reduce the nickel ions and react with water to form orthophosphate, which accrues in solution and precipitates as nickel phosphate in the end. Until now, palladium (Pd) is the most widely used catalyst in electroless nickel (EN) deposition.[27, 28] Due to the high market price of palladium, the Pd catalyst deposited on substrate poses a significant cost barrier to the widespread electroless deposition in industry.

Currently, surface catalyzation is commonly attained by depositing one layer of Pd/Sn colloid onto the substrates' surface. After the etching process, substrates were dipped into a palladium chloride (PdCl_2) solution and a stannous chloride (SnCl_2) solution to coat the Pd-Sn catalyst for surface activation. However, this process presents a drawback in that the catalyst must go through an "acceleration" process to remove the outer Sn layer and thereafter to expose the reactive Pd core. In this acceleration process, insufficient dipping time cannot remove all the Sn shells and results in some inactive sites, while excessive dipping also removes Pd inside and results in low activity and loss of adhesion.[29]

To avoid the creation of Pd/Sn core-shell structures, some researchers investigated the tin-free Pd catalysts by changing the reducing agent, thus, the catalyzation of the substrates' surface could be achieved without the acceleration

process. Susan L. Brandow et al. used dimethylamine borane (DMAB) as a reducing agent to produce Pd oligomers, which can achieve a complete and homogenous metallization with 20% surface catalyst coverage.[15] Chien-Liang Lee et al. prepared high activated Pd nanoparticles by using hydrazine to reduce palladium acetate($\text{Pd}(\text{OAc})_2$) in a mixed aqueous solution consists of sodium dodecyl sulfate (SDS) and nitric acid.[30] Desmond C.L. Tan et al. posted a step-wise method of synthesizing Pd-P amorphous catalyst with sodium hypophosphite (NaH_2PO_2), which displayed superior mass activity compared to Pd/Sn and Pd- N_2H_4 , as illustrated in Figure 4 below.[31, 32]

Figure 4 SEM observations of (A) hypophosphate reduced Pd (Pd-P), (B) hydrazine reduced Pd (Pd- N_2H_4) and (C) tin chloride reduced Pd (Pd-Sn/AA); (D) Cyclic voltammograms of various Pd nanoparticle electrocatalysts in solution (pH 9) with NaH_2PO_2 normalized by Pd load (mass activity) [32]

2.1.3. Application of electroless nickel deposition.

Traditionally, electroless plating technology was used to metalize the surface of insulators, such as plastics and glass for applications such as magnetic media and interconnects.[24] In the late 20th century, electroless plating followed an evolution in the microelectronics field and started to produce many micro and nano scale coatings on the semiconductor, which supported the product requirements of Integrated Circuits.

Figure 5 Applications of electroless nickel depositions: A) Wear and corrosion resistance of aluminum connectors are enhanced by electroless nickel plating,[33] B) giant magnetoresistive head made with electrodeposited CoNiFe,[34] C) Cu/Ni/ Au electrodes array,[35] D) SEM images of Ni plated microtubules with 1 min of metallization.[36]

Nickel and its alloys, which show much lower electric conductivity compared to copper, are commonly coated on the interconnects as capping layers and diffusion

barriers.[37] The highly selective nickel alloys deposited by electroless deposition are uniform in thickness, and can serve their function even as an ultra-thin film (10-20 nm). When di-methyl-amino-borane (DMAB) or hypophosphite works as reducing agents in the electroless nickel deposition, the reducing agent oxidation boron (B) or phosphorus (P) will integrate with nickel and form alloys into the deposit. Moreover, the refractory metals such as tungsten (W, by tungsten-phosphoric acid), molybdenum (Mo), or rhenium (Re) can also be introduced into the plating solutions to enhance the diffusion properties and thermal stability of Ni deposits.[38]

The electroless deposition method also attracts considerable interests for coating uniform ferromagnetic films with complex geometries, which can be applied as magnetic recording materials. The CoNiFe film prepared by the electrochemical method can develop a high saturation flux density B_s (2.0-2.1 T) with low coercivity.[39] These ternary alloys can work as base materials for write-head cores in the perpendicular magnetic recording system. Furthermore, some researchers used electroless plated NiFeB as a magnetic flux inducing film for “proximity switches”, which had significant enhancement regarding the detection distance.[40] Such a component has been widely used with more than 50 percentages of the market share and achieved total sales of \$135 million over the world in 2014.

The electroless deposition method has also been intensively investigated for the application in micro electromechanical systems, such as actuators, sensors, micro batteries, and micro-machined fuel cells.[35] The deposit coated with electroless deposition shows advantages in conformity, selectivity, has relatively low cost and a high aspect ratio deposition.

Moreover, the electroless deposition method has been considered as one of the candidates for both “top-down” and “bottom-up” approached metallization of nano-scale features. For the “top-down” approached metallization, electroless Ni alloys with refractory metals (such as W, Re) could be deposited as a very thin layer over large areas with good uniformity and secretiveness.[41] Regarding the “bottom-up” approach, the electroless deposition method has been investigated for metallization on biological templates to deposit nano-size structures, such as nanowire from microtubules, protein and DNA.[36]

2.2.Reduced graphene oxide

Graphite is one type of naturally occurring crystalline form of carbon atoms arranged in honeycomb lattice layers and overlaid to the hexagonal structure. Graphene is a simple single layer of graphite that is stable under ambient conditions. In graphene, the sp^2 hybridized carbon atoms layer forms a two-dimensional (2D) structure, which results in its superconductive properties for both electrons and heat.[42] The extraordinary electrical conductivity and

acceptable market price of graphene makes it widely used in electronic products such as batteries, solar panels and electrodes.

Coating or depositing graphene would make a plastic or ceramic surface conductive. However, graphene is not suitable for solution processes because of its hydrophobicity; graphene easily coagulates and precipitates in water. Graphene oxide (GO) has a layered structure similar to that of graphene, and with some of the carbon being decorated with hydroxyl and epoxy (1,2-ether) functional groups,[43] which make GO hydrophilic and it readily dissolves or disperses well in water.

One of the most significant properties of GO lies in its ability to be switched to a graphene-like sheet by reducing the oxygen-containing group, and thereafter to recover to a conjugated structure. Thus, reduced graphene oxide (rGO) can be considered as chemically modified graphene.[44] For the formation of continuous and conductive rGO layers on substrates, it is necessary for the solid substrate to be immersed in a GO solution and to go through the GO reduction process.[45]

2.2.1. Reduction methods for graphene oxide

With different reduction strategies, the reduction of graphene oxide methods can be divided into three groups: (1) chemical reduction (2) thermal reduction (3) multi-step reduction.[46]

For chemical reduction, chemical reagents such as hydrazine,[47] hypophosphite (sodium hypophosphite),[48] metal hydride (sodium borohydride),[49] ascorbic

acid (Vitamin C),[50] and hydriodic acid [51] have been proven in the effective reduction of hydroxyl and epoxy (1,2-ether) functional groups in graphene oxide.

During the thermal annealing, the oxygen-containing functional groups attached on graphite oxide are decomposed into CO or CO₂ gases, and enormous pressure is generated under rapid heating (>2000 °C/min) to 1050 °C.[52] The heating temperature is the critical factor that affects the reduction on GO, as higher annealing temperature impels GO into higher stages of reduction with higher C/O ratio and higher electron conductivity, as shown in Figure 6.[52-54] Besides thermal irradiation, microwave irradiation and photo-irradiation also work as heating resources in the thermal reduction of graphene oxides.[55, 56]

Figure 6 In the thermal annealing, structure model of GO changes at different stages A) room temperature; B) 100 °C; C) 220 °C; D) 500 °C.[54]

With the chemical reduction and thermal reduction methods, the reduction of graphene oxides is achieved with only one step. To further reduce the graphene oxide for high conductivity, multi-step methods with the combination of chemical reduction and thermal reduction have been proposed. In Haiqun Chen's experiment, the graphene paper produced by reducing GO with hydrazine would

experience slight weight loss when the heat treatment falls in the temperature ranges of between 200 and 500 °C.[57] This meant that the subsequent thermal annealing could further reduce the oxygen-containing groups on hydrazine reduced GO. Goki Eda et al. tested the rGO film reduced by hydrazine and annealing at a temperature of 200 °C and determined it has higher electron conductivity than the GO reduced with 550 °C thermal annealing alone.[58]

2.2.2. Determine the reduction of graphene oxide

The successful reduction of graphene oxide can be judged by its carbon to oxygen atomic ratio (C/O ratio), electrical conductivity, optical appearance and hydrophilicity.

Graphene ideally has no C-O bond, so it has a very low O/C intensity ratio. Depending on the preparation method and oxidation time, the O/C intensity ratio of GO has a value ranging from 0.430 to 0.683.[59, 60] Thus, we can confirm the reduction of GO through the clear observation of the drop in O/C ratio by X-ray photoelectron spectroscopy (XPS).[54]

The long-conjugated network of the graphitic lattice is the key factor that decides the electrical conductivity of graphene structure. The existence of oxygen-containing groups in GO destroyed the long-chain networking and significantly lowered the electrical conductivity to a few MΩ/sq. It has been reported that the rGO-based TCF produced chemical reduced GO and hence, it can achieve a sheet resistance as low as 0.84 kΩ/sq with 78% optical transmittance.[61]

Optical observation can be a direct way to observe the reduction of GO. The electrical conductivity of GO was significantly improved after the reduction process, and with the enhancement of visible light reflection due to an increased charge carrier mobility and concentration, the dark-toned surface of the rGO film showed a shiny metallic outlook (as illustrated in Figure 7).[62]

Figure 7 (A) the original GO film; (B) GO reduced in HI acid at 100°C for 1 hr (C) GO reduced by hydrazine vapor.[62]

However, the hydrophilicity of rGO dramatically decreases with the reduction of oxygen-containing function groups in GO during the reduction process. Similar to graphene, the solubility of rGO in water is very low, but it can be dispersed well in polar solvents such as dimethylformamide (DMF) (Figure 8).

Figure 8 Photographs of (A) GO, (B) rGO dispersion in water and (C) rGO dispersion in DMF[48]

2.2.3. Methods to coat rGO films on non-conductive substrates.

Due to its excellent conductivity, low price, high flexibility, chemical and thermal stability, reduced graphene oxide is widely used to coat on different materials to improve the electrical conductivity of the base materials.

There are two important approaches to coat the reduced graphene oxide or graphene film on the substrates. One is the dry approach, the chemical vapor deposition method can fabricate a graphene film on the hard substrate at high temperatures.[63, 64] With the hydrophilicity property of the graphene oxide, the rGO coating on the substrates can also be achieved by the solution-based approach at room temperature.[51]

Recently, many researchers have investigated the fabricate of rGO films from a solution, such as dip coating, spin-coating, spray-coating, rod coating and self-assembly methods.[61, 65-68] However, it is still a big challenge to form a continuous large-scale uniform rGO layer with high quality. The critical problems we faced are a) dispersing high-quality graphene in the solvent homogeneously; b) chemically reducing the graphene oxide film with high efficiency; c) continuously fabricating the large-scale rGO film with a reproducible technique.[68]

For the combination of solution-based methods and thermal annealing, Xue Wang's group presented a dip-coating method to fabricate the conductive and

transparent rGO film from thermal reduction (500 to 700 °C) of graphene oxide.[65] The obtained rGO film exhibit a high electric conductivity of 550 S/cm with only 10 nm thickness. Hector A. Becerril's group deposited an up to 150 nm rGO film with a sheet resistance at $10^2 - 10^3 \Omega/\text{sq}$ through repeated spin-coating for high-concentration GO solution followed by reduction with hydrazine vapor and thermal annealing (400 °C).[66] Viet Hung Pham's group sprayed to coat the GO-hydrazine (synthesized GO with excessive hydrazine monohydrate) dispersion on the pre-heated substrate (240 °C). The obtained rGO film showed a low sheet resistance of $2.2 \times 10^3 \Omega/\text{sq}$. [67] Joon-Suk Oh's group self-assembled the GO layer on the polyethylene terephthalate film by evaporation, the following chemical and thermal reduction (200 °C for 24 hours) converted the GO layer to rGO layer with sheet resistance as low as $100 \Omega/\text{sq}$. [69] All these studies show that the minimum annealing temperature to effectively reduce graphene oxide is a few hundred degrees centigrade, which is higher than the glass transition temperature of many plastic materials such as acrylonitrile butadiene styrene (ABS) and polylactic acid (PLA).

In the low-temperature approaches, Jie Wang's group investigated the formation of uniform large-scale rGO films on poly(ethylene terephthalate) substrates by a rod-coating technique.[68] With the Meyer rod, they were able to coat a single layer to 10 layers of rGO films on the flat poly(ethylene terephthalate) substrate

with sheet resistances from 20.1 to 1.68 k Ω sq⁻¹. However, the drawback of this method is that this rod-coating technique can only apply on a flat surface.

Figure 9 AFM images and height profiles of the rod-coating fabricated GO films at different GO concentrations: A) 0.05 mg/mL; B) 0.1 mg/mL; C) 0.2 mg/mL; D) 1 mg/mL. (The rod used in this experiment with diameter at 0.2 mm. The red squares in AFM images were areas used to obtain the film's root-mean-square roughness.) [68]

2.3. Additive manufacturing

Additive manufacturing (AM) is the process that joins materials to a target object from layer to layer building with the designed three-dimensional (3D) model data; this building process can be used to assemble parts with geometrical and material complexity that subtractive manufacturing processes cannot produce. It is also known as additive process, additive fabrication, rapid manufacturing, rapid prototyping, layer manufacturing, direct digital manufacturing, and solid freeform fabrication.[70] The basic principle of this technology is the generation of a model using a three-dimensional Computer-Aided Design (3D CAD), and

the fabrication of this model directly without the need for process planning (as shown in Figure 10).[71]

Figure 10 The basic stages in AM technology.[71]

The additive manufacturing process was investigated in the late 1980s, and it has since been applied in automotive, aerospace, biomedical and architectural design fields. Based on different applications and research needed, many different technologies have been developed with different working principles (Table 2).

Table 2 Working principle of different AM process.[70]

State of starting material	Process	Material preparation	Layer creation technique	Phase change	Typical materials	Applications
Liquid	Stereolithography (SLA)	Liquid resin in a vat	Laser scanning/ light projection	Photopoly-merization	UV curable resin, ceramic suspension	Prototypes, casting patterns, soft tooling
	Multi-Jet Modeling Systems (MJM)	Liquid polymer in jet	Ink-jet printing	Cooling & photopolymerization	UV curable acrylic plastic, wax	Prototypes, casting patterns
	Rapid Freeze Prototyping (RFP)	Liquid droplet in nozzle	On-demand droplet deposition	Solidification by freezing	Water	Prototypes, casting patterns
Filament/ Paste	Fused Deposition Modeling (FDM)	Filament melted in nozzle	Continuous extrusion and deposition	Solidification by cooling	Thermoplastics, waxes	Prototypes, casting patterns
	Robocasting	Paste in nozzle	Continuous extrusion	---	Ceramic paste	Functional parts
	Freeze-form Extrusion Fabrication (FEF)	Paste in nozzle	Continuous extrusion	Solidification by freezing	Ceramic paste	Functional parts
Powder	Selective Laser Sintering (SLS)	Powder in bed	Laser scanning	Partial melting	Thermoplastics, waxes, metal powder, ceramic powder	Prototypes, casting patterns, metal and ceramic preforms (to be sintered and infiltrated)
	Selective Laser Melting (SLM)	Powder in bed	Laser scanning	Full melting	Metal	Tooling, functional parts
	Electron Beam Melting (EBM)	Powder in bed	Electron beam scanning	Full melting	Metal	Tooling, functional parts
	Laser Metal Deposition (LMD)	Powder injection through nozzle	On-demand powder injection and melted by laser	Full melting	Metal	Tooling, metal part repair, functional parts
	Three-Dimensional Printing (3DP)	Powder in bed	Drop-on-demand binder printing	---	Polymer, Metal, ceramic, other powders	Prototypes, casting shells, tooling
Solid sheet	Laminated Objective Manufacturing (LOM)	Laser cutting	Feeding and binding of sheets with adhesives	---	Paper, plastic, metal	Prototypes, casting models

2.3.1. Additive manufacturing of polymers

A polymer is a large molecule formed from polymerization of small repeating units. Based on the pliable or moldable properties at elevated temperature, most polymers can be classified into categories of thermoset and thermoplastic.

Thermosetting polymers have many extensive cross-links between polymer chains, which results in the cured thermoset being infusible and insoluble even at elevated temperatures. The hardening process of thermosetting polymers involves the curing of viscous liquid pre-polymer or resin by inducing heat or suitable radiation. Currently, Stereolithography (SLA) and Multi-Jet Modeling Systems (MJM) are the rapid prototype technology used to photo-polymerize the liquid resin to target structures with laser scanning.[72-74]

The thermoplastic, with only intermolecular forces between polymer chains, easily becomes pliable, moldable and remains in molten form after heating to a certain temperature and gradually solidifies upon cooling. Based on this thermo-changeable property, thermoplastic materials are the most widely used polymers in the additive manufacturing technology. In the Fused Deposition Modeling (FDM) process, the thermoplastic polymer such as acrylonitrile butadiene styrene (ABS) is heated slightly above its melting point using a movable heater. The melted material is extruded through the nozzle to the target point on a substrate and solidified after cooling down, with the final products being printed layer by layer through material building.[4, 5]

2.3.2. Additive manufacturing of metals

The melting points of the most commonly used metal vary from 660 to 1770 °C (as shown in Table 3). For the metal alloys with comparable lower melting points, the melting temperatures are still much higher than the glass transition temperature of commonly used plastic (around 200 °C).

Table 3 Melting point of commonly used metal and alloys.

Melting point (°C)	Aluminum	Cobalt	Copper	Gold	Iron	Nickel	Platinum	Silver	Titanium
Pure metal	660	1495	1085	1064	1538	1453	1770	961	1668
Alloy	463-671	---	865-1000	---	1127-1540	875-1200	---	562-893	---

The “direct” way to build up a metal product with additive manufacturing is to fully melt the metal and to directly manufacture the final part with AM power bed system or AM wire feed system (as illustrated in Figure 11), such as the Selective Laser Melting (SLM), [75, 76] Electron Beam Melting (EBM), [77, 78] and Laser Metal Deposition (LMD) processes. [6, 79]

Figure 11 Generic illustration of A) AM powder bed system; B) AM wire feed system. [80]

There is another “indirect” way to produce metal components with AM by bonding metal particles with selected binders and by removing the exceeded part

by post-processing. The Selective Laser Sintering (SLS) process works through the fabrication of metal parts by melting the choice material (usually polymers) as binders to bond the metal particles together.[81] In the post-processing process, the printed bronze-nickel structure was heated up to 840 °C by liquid phase sintering technique to have a full-density part (as illustrated in Figure 12).[82] The three-dimensional printing (3DP) process printed metal part (called “green part”) with 60 vol% metal powder, 10 vol% binder material, and 10 vol% open porosity.[83] This green part undergoes appropriate thermal treatment to remove undesirable binder components and allow the formation of inter-particle necks for strengthening the part with minimum dimensional changes. With the laminated Objective Manufacturing (LOM) method, metal sheets can be cut with the use of laser-induced high thermal energy and gradually stacked layer by layer to form metallic products.[84, 85] This shows that both the “direct” and “indirect” AM methods for metal parts fabrication need to be proceeded at very high working temperature.

Figure 12 The optical micrograph of SLS processed A) bronze-nickel samples; B) bronze-nickel samples sintered at 1030 °C. (B = bronze, N = nickel, P = pores, S = solid solution).[82]

2.3.3. Additive manufacturing of composite

Additive manufacturing can also be used to fabricate the structures with more than one constituent materials (composites).

For composites with uniform compositions (such as fiber-reinforced composite), respective mixtures of proper materials are pre-prepared, with the fabrication of composites prepared filaments, taps or laminated using in FDM and LOM technologies.[86] In addition, uniform composites can be produced by infiltrating metal or alloy into porous 3DP performs.[87]

For the fabrication of functionally graded materials (non-uniform composition) with a variation of composition for different properties requirements, the AM process usually delivers different materials through multiple feeding systems and the composition is controlled during the building process. Bandyopadhyay's group used Laser Engineered Net Shaping (LENS) process to coat Co-Cr-Mo on porous Ti6Al4V for wear resistance improvement.[88] Ming C. Leu printed a gradient Al_2O_3 and ZrO_2 component with the Freeze-form Extrusion Fabrication (FEF) process (Figure 13).[89] These methods are only applicable to substrates with all the constituents having closed melting points or molding temperatures.

Figure 13 A) FEF machine with triple-extruder; B) FEF fabricated composite with a gradient from 100 % Al₂O₃ to 50 % Al₂O₃ and 50 % ZrO₂. [70]

2.4. Acrylonitrile butadiene styrene (ABS) plastic

Acrylonitrile butadiene styrene (ABS) is a widely used thermoplastic polymer that is made by polymerizing acrylonitrile and styrene in the presence of polybutadiene (Figure 14). The commercially-interested ABS terpolymers contain 15 to 35 wt% acrylonitrile and 10 to 40 wt% butadiene.[90] The ABS polymer consists poly(styrene-co-acrylonitrile) (SAN) copolymer constituted continuous phase (matrix) and polybutadiene constitutes the dispersed phase, a layer of SAN grafted onto polybutadiene surface which makes two phase compatible.[91] The nitrile groups on side chains attract the same groups on neighboring chains and bind together, making ABS having a higher strength compared to pure polystyrene. The styrene provides the waterproof surface to ABS plastic, while the rubbery substance, polybutadiene, induces a good toughness even at low temperatures.

Figure 14 chemical structure of Acrylonitrile; 1,3 Butadiene; Styrene; and ABS.

ABS polymers are widely used in industry due to its ease-of-processing condition, chemical resistance, excellent toughness and low cost. After metallization, the additional properties such as abrasion resistance, electrical conductivity, reflectivity, and a variety of decorative effects broaden the applications of ABS ranging from the decorative coating to printed circuits in microelectronics.

2.4.1. Surface treatment of ABS

For the surface metallization using a plating process on ABS plastics, the substrate needs to go through appropriate surface conditioning in order to improve the mechanical adhesion, surface area and hydrophilicity for the surface seeding of the catalyst. The most widely used method is etching the substrates with a mixture of chromic acid and sulfuric acid at elevated temperatures, which creates micro-pores and increases the wettability of ABS through oxidation of the

surface.[20, 92] After immersing in the acid-based etching solution for 20 mins, the first layer of ABS plastic is completely swept away, thus revealing the internal morphology of the material.[93]

However, the use of chromium in industry poses serious environmental contamination risks in agricultural and animal products if the by-products are being intermittently released from the factory as illustrated in Figure 15. [21, 94] An earlier investigation on the quantity of irrigation wells, irrigation reservoirs and agricultural land in villages within 10 kilometers of a chromate chemical factory (Tamilnadu chromate and chemicals, Ranipet, N.A. Dist, Tamilnadu, India), there was shown to be chromium contamination affecting whole underground aquifers from the effluent lagoon.[95] Furthermore, the chromate ions easily diffuse into the human body through the epidermis, respiration and the gastrointestinal tract, which results in nephritis, lung cancer and fatality due to acute chromate toxicity.[22]

Figure 15 Schematic illustration of chromium dynamics in soil.[94]

Alternative methods have been investigated to replace etching by chromic acid, with the aim to improve both the entrapment of catalyst nanoparticles and the adhesion of metal coating on ABS surfaces. Garcia Alexandre demonstrated the activation of ABS surface through the process of chelating the metallic seed on the pre-grafted thin polymer film (poly(acrylic acid), PAA) (as illustrated in Figure 16).[18] Tang Xuejiao used a mixture of hydrogen peroxide (30%) and sulfuric acid (98%) with a volume ratio 1:4 to etch the ABS surface, and etched foils were then dipped into chitosan (CTS) to have ligands containing amine functional group, which can covalently bind to palladium easily.[96] Similarly, Li Zhixin had posted an etching system with sulfuric acid-manganese dioxide ($\text{H}_2\text{SO}_4\text{-MnO}_2$) colloid at 70 °C.[97] On the other hand, Li Dapeng has invented a direct method of seeding ABS plastic by coating enamel pastes that contains aluminum-carbon seeds.[19] However, all these pre-treatment methods are complicated and very time-consuming, which is not feasible for industrial mass production.

Figure 16 Surface treatment process of ABS A) tradition ABS etching with chromic acid; B) surface treatment process with PAA graft.[18]

2.4.2. Additives for ABS plastic

Acrylonitrile butadiene styrene plastic has broad processing windows because of its respectable mechanical strength, reasonable chemical resistances, striking surface aspect and high cost-effectiveness. Commonly, the addition of additives is used to modify some specific material properties of the final products, such as fire retardancy, plastification, processability, oxidative stability, stiffness, impact resistance and dimensional stability.[98]

Take Antimony trioxide (Sb_2O_3) as an example. It is a common additive for the flame retardant property of the plastics, the additions of different grades and different concentrations of Sb_2O_3 have different effects on the mechanical property due to the changes of microscopical property.[99] Angel R. Torrado's group had evaluated the effect of additives on anisotropic mechanical properties by tensile testing these specimens printed with additive manufacturing

technology.[100] In the SEM observation of the fracture surface of these specimens (as shown in Figure 17), the addition of additives changed the number of micro-voids and altered the fracture morphology of the 3D printed samples. All these microstructure changes altered the variation of tensile strength, elongation modules, complex viscosity and anisotropy of the ABS composites, which resulted in broader applications in the future 3D printable materials system.

Figure 17 Fracture surface of different ABS samples in the XYZ print orientation A) Pure ABS resin; B) ABS/Jute composite; C) ABS/MayaCorm composite; D) ABS/TiO₂ composite; E) ABS/ZnO composite; F) ABS/SrTiO₃ composite; G) ABS/Al₂O₃ composite; H) ABS/styrene ethylene butadiene styrene (SEBS) blend with 80:20 ratio; I) ABS/ultra-high molecular weight polyethylene (UHMWPE)/SEBS blend with 90:10:10 weight ratio. (The white arrows indicate the micro-voids within polymer matrix.) [100]

2. 5. Liposome

Liposomes are concentric bilayer vesicles that entirely enclose an aqueous volume with natural or synthetic phospholipids bilayers. Due to the size and hydrophilic/hydrophobic character of the liposome, it is a promising system for drug delivery. Also, the liposome can be processed and formulated to different structures, charges, sizes and lamellarity for different applications to achieve controlling delivery in biotechnology, medicine and pharmacology, etc.

Because of the amphipathic (both hydrophilic and hydrophobic) property of lipids in aqueous media, the thermodynamic phase properties of lipids force them to be self-assembling into various types of colloid particles according to different temperatures, environmental and preparation conditions. As a carrier, liposomes can trap both hydrophilic and hydrophobic compounds without any decomposition of the entrapped combination until it is released at the designated target.[101, 102]

The liposome structure was fortuitously discovered in 1964, the liposome was a simple spherical bilayer structure when phospholipids dispersed in the water, and this structure showed reliable encapsulation properties due to electrostatic stress developed at the lipid-water interface (Figure 18A).[14] In the therapeutic applications of liposomes, the ‘stealth’ liposome with some water-soluble polymers were attached to lipid polar heads was invented to protect the liposome from the immune system and allow the liposome to be targeted at specific

biological sites (Figure 18B).[103] The generation of cationic liposomes forms electrostatic complexes with DNA, and this liposome-DNA complexes exhibited a variety of liquid-crystalline phases (Figure 18C).[104] Kubitschke et al. used cavitands – vase-shaped molecules that attached hydrophobic and hydrophilic changes to assemble a new bilayer structure (Figure 18D), therefore these vesicles encapsulate guest molecules of different sizes in the cavitands, the bilayer and the liposome’s interior.[105]

Figure 18 A) The typical liposomes structure with a shell consisting in a lipid bilayer; B) some water-soluble polymer lipids exist in the “stealth” liposomes for drug-delivery applications; C) the common cationic liposome–DNA complexes with DNA (purple rods) sandwiched between cationic membranes D) a new liposome structure that the bilayer assembles from cavitands — vase-shaped molecules — to which the authors attached hydrophobic and hydrophilic chains. [106]

2.5.1. Factors affecting lipids selection

A large number of natural and synthetic phospholipids, steroids, polymeric materials, charge-inducing lipids can all be used as raw materials or additives in the formation of lipid bilayers. Based on applications of the liposomes, the phase transition temperature of lipids, charges or specific functional groups on the lipids and liposomes stability are all considered in the liposome raw materials selection.

The phase transition temperature is defined as the temperature required to change a lipid's physical state from the ordered gel phase to the disordered liquid crystalline phase. The packed liposome structures go through a temperature change from below phase transition temperature to above phase transition temperature, which would provide a means of releasing packaged material as the hydrocarbon chains in the lipid become randomly oriented and fluid.[107]

Consider the lipid application, where the phase transition temperature should be set in between the normal temperature at delivery status and acceptable temperature at the released status.

In some controlled delivery systems, it requires some special functions on the liposome membrane for target matches. Positive or negative charges on the lipid membranes are always essential for some blood coagulation cascade steps. The assembling of protein onto the surface of platelets requires the platelets to have a negatively charged surface. Within the prothrombin to thrombin conversion, it requires phosphatidylserine (PS) and phosphatidic acid (PA) lipids on the surface

to provide a negative charge condition.[108] Therefore, to meet the requirements in some application systems, both the surface charge and the system specificity for particular species should be satisfied.

The primary concern in the development of liposome applications is liposomes' stability, including the physical, chemical and biological stability of liposomes. The physical stability of liposome depends on the particle size, bilayer constituents, encapsulated cargos, ionic strength of the medium and environmental temperatures. The chemical stability of liposome dominantly includes the stability of phospholipids under the hydrolytic and peroxidation reactions. The significant events are responsible for biological destabilization of the liposome, including membrane fusion, protein binding and simple aggregation in the organic environment.

2.5.2. Preparation methods of liposome structure

Generally, synthesizing the liposomes involves four basic steps: 1) drying down lipids from the organic solvent; 2) dispersing the lipid powder in selected aqueous media; 3) purifying the resultant liposome; 4) analyzing the final liposome product. The preparation methods can be grouped into a passive loading technique and an active loading technique base on the time of loading cargos (before or the same as the liposome preparation time).

A. Passive loading technique

According to the different loading principles, passive loading techniques can be grouped into three different groups, which are named as solvent dispersion, mechanical dispersion, and detergent solubilization.[109]

Table 4 Summary of Passive loading techniques. [109]

Solvent dispersion method	Mechanical dispersion method	Detergent solubilization method
<ul style="list-style-type: none"> • Lipid hydration by hand shaking or freeze • drying • Micro emulsification • Sonication • French pressure cell • Membrane extrusions • Dried reconstituted vesicle • Freeze thawed liposome 	<ul style="list-style-type: none"> • Ethanol injection • Ether injection • Double emulsion vesicle • Reverse phase evaporation vesicle • Stable plurilamellar vesicle 	<ul style="list-style-type: none"> • Detergent (cholate, alkyl, glycoside, Triton x-100) removed from mixed micelles • Dialysis • Column chromatography • Dilution • Reconstituted sendai virus enveloped vesicle

All the methods under the solvent dispersion category dissolve the lipids into an organic solvent, followed by contact with an aqueous phase solution that contains target molecules to be entrapped. The lipids can align themselves at the organic-aqueous interface phase and form a monolayer of phospholipids. Based on the miscibility of aqueous solution and organic solvents, the solvent dispersion methods can be categorized into excess in organic solvents or the excess in latter beings.

In the mechanical dispersion method, the synthesizing begins at lipid solution in an organic solvent while ending up as lipid dispersion in the water. All the lipids components are mixed and dissolved in the selected organic solvent, followed by

removing the organic solvent with film deposition in the vacuum. The hydration of solvent dispersion mixture is done with an aqueous buffer after removing all the organic solvent, then the film spontaneously swells and hydrates to form liposome structures.

In the detergent removal method, the detergent (such as cholate, alkyl glycoside, Triton X-100) contacts with phospholipid molecules and serves to screen the hydrophobic portion from water. The size and the shape of formed liposome structures rely on the lipid concentration, and the chemical nature of the detergent.

B. Active loading technique

The active loading technique includes methods that stimulate the utilization of liposome structures with efficient encapsulation procedures. Ions and large hydrophilic molecules can permeate through the membrane bilayers as a result of transmembrane gradients, such as pH, electric or specific salt gradient. The concentration difference in proton can also drive the amphipathic molecules across the membrane of liposomes. Compared with the passive encapsulation technique, the active loading method shows advantages at: reduced leakage of the cargo compounds; high encapsulating capacity and efficiency; flexibility of constitutive lipid; and avoidance of biologically active compounds during the preparation steps.

2.5.3. Thermosensitive liposome

To elevate the usefulness, researchers have designed a variety of stimulus-sensitive liposomes that can release entrapped compounds as a response of different chemical or physical stimuli, such as temperature, pH, and light.[110-112] The thermosensitive liposomes (also known as temperature-sensitive liposomes) can be considered as a prospective tool for site-specific cargo delivery. The lipids used in the thermosensitive liposomes form a membrane that undergoes a gel-to-liquid crystalline phase transition when the temperature is above their physiological temperature.[113]

In the design of temperature-sensitive liposomes, the selected lipids in the bilayer structure turn to highly leaky to the water-soluble contents when the temperature is increased to their gel-to-liquid crystalline phase transition temperature. For example, the dipalmitoylphosphatidylcholine (DPPC) lipids are commonly used as the primary liposomal lipid as it exhibits phase transition at 41 °C.[113]

Another strategy to synthesize the thermosensitive liposome is incorporating the stimuli-sensitive molecules, which display as a low critical solution temperature (LCST) into the liposomal membranes. The temperature-sensitive polymers are insoluble in water when the temperature is above their LCST, while they become soluble in water when the temperature lower than the LCST (as shown in Figure 19). At the molecular level, the chains in the temperature-sensitive polymers undergo a coil-to-globule transition when the environmental temperature reaches

the LCST. Also, the stabilization and destabilization of the liposomes changed when the polymer chain changes from hydrophilic to hydrophobic at their LCST.[114]

Figure 19 Schematic illustration of the behavior of the thermosensitive polymers cooperated liposome below and above their low critical solution temperature. [114]

CHAPTER 3: USE RGO TO ENHANCE PD CATALYTIC ACTIVITY IN ELECTROLESS NICKEL DEPOSITION

3.1 Experimental Procedure

3.1.1. Solution Preparation

Graphene oxide (GO; 200 ppm) was prepared by mixing graphene oxide solution (dispersion in water, 2 mg/ml, Sigma Aldrich) and deionized water (DI water) with a corresponding ratio of 1:9.

Potassium hydroxide solution (KOH; 2 M) (Sigma Aldrich) was prepared by dissolving 12.22 g of KOH pellets in 100 mL of deionized (DI) water.

Sodium hypophosphite monohydrate (NaH_2PO_2 ; 0.2 M) (98% wt, Alfa Aesar) solution was prepared by dissolving 2.12 g of NaH_2PO_2 powder in 100 mL of DI water.

Hydrazine (N_2H_4 ; 0.2 M) (35% wt in water, Sigma Aldrich) solution was prepared by mixing 18.09 ml of N_2H_4 solution with 81.91 mL of DI water.

Dimethylamine borane (DMAB; 0.2 M) (Sigma Aldrich) solution was prepared by dissolving 1.18 g of DMAB powders in 100 mL of DI water.

A stock solution of palladium (II) chloride (PdCl_2 ; 20 mM) (99% wt, Sigma Aldrich) was prepared by dissolving 0.36 g of PdCl_2 into the solvent with 99 mL of DI water and 1 mL of concentrated hydrochloric acid (37% HCl). Other

specified PdCl_2 solutions with lower concentration were diluted by mixing the stock solution of palladium chloride (20 mM) with DI water.

A hypophosphite-nickel bath solution (sol.1) contains 0.2 M of sodium citrate (Sigma Aldrich), 0.5 M of boric acid (Strem Chemicals, Inc.), 0.06 M of nickel (II) sulfate hexahydrate (BDH Prolabo Chemicals) and 0.24 M of sodium hypophosphite (Sigma Aldrich), and the pH was adjusted to 9.0 by sodium hydroxide powder (NaOH) (Sigma Aldrich) for the electroless nickel plating.

3.1.2. Electroless nickel plating on local catalyst conductive surface

The copper foil was cut into small sheets with dimensions of 2 cm x 5 cm. The two copper foil substrates were immersed in 2 M KOH solution for surface activation for a duration of 1 hour. Two droplets (0.5 mL for each droplet) of 2 mM PdCl_2 were dropped on one of the substrates and left for 1 min. The excess of PdCl_2 on the substrate was removed and an air gun was used to dry the surface. Subsequently, the substrate was washed with DI water and dipped in 0.2 M NaH_2PO_2 solution to achieve Pd catalyzation on the localized region. Thereafter, the locally Pd-catalyzed copper foil was immersed in hypophosphite-nickel bath solution (Sol. 1) at 60 °C for electroless nickel deposition. Another copper foil without any catalyst was also immersed in the same nickel bath for comparison.

3.1.3. Reduced graphene oxide (rGO) pre-treatment

The solution-based chemical reduction method was chosen to get the reduced graphene oxide coating layers on the substrates surface. For the reducing agent selection, 3 bottles of 10 mL of 0.2 g/L graphene oxide solution were mixed with 10 mL of DI water, 10 mL of 0.2 M NaH_2PO_2 , and 10 mL of 0.2 M N_2H_4 respectively. The mixture solution was left at room temperature for 20 hours and the reduced graphene oxide (rGO) / graphene oxide (GO) solutions were observed.

The process of reduced graphene oxide (rGO) pre-treatment forms a rGO conductive layer on the non-conductive substrate before the palladium (Pd) catalyzation. The polyimide (PI) substrates were being pre-immersing in 2 M KOH solution for 1 hour to make the surface hydrophilic. The substrate was then washed with DI water and dried with air gun before processing with the rGO coating. The hydrophilic treated substrate was dipped in the GO solution (200 ppm) for 1 minute. The substrate was air-blown and dried to remove the excess solution adhered to it. Thereafter, the substrate was dipped in the NaH_2PO_2 solution (0.2 M) for 1 minute, which reduced the GO to rGO. The above-mentioned sequence was repeated five times to form a continuous rGO conductive layer on the substrate.

For other hydrophobic substrates such as acrylonitrile butadiene styrene copolymer (ABS), it was necessary to go through the pre-treatment to increase the surface hydrophilicity.

3.1.4. Characterization of the rGO reduced by NaH_2PO_2

Since rGO deposited on quartz substrate is not thick enough for XRD and Raman spectroscopy, the reduction of GO (0.2 mg/ml) by NaH_2PO_2 (0.2 M) was tested after achieving the mixing ratio of 1:9 to obtain a sufficient amount of rGO mixture in the solution. The mixture gel was separated from water by centrifugation and filtration. Subsequently, the mixture was dried in a dry box for subsequent characterization, using X-ray powder diffraction (XRD) and Raman spectroscopy, of the graphitic structure. The same amount of GO (0.2 mg/mL) was also dipped on glass slices and put in a dry box to obtain GO powder.

3.1.5. Stepwise loading of Pd nanoparticles for electroless deposition

The synthesis of Pd nanoparticles on substrate relies on stepwise deposition, which is similar to that of the rGO pre-treatment. The rGO-coated substrate was sequentially dipped in PdCl_2 (1.5 mM or 30 μM with 1% HCl) for 10 seconds followed by dipping into NaH_2PO_2 (0.2 M), for another 10 seconds. The substrate was air-blown after every step. The aforementioned stepwise Pd catalyst loading

process was repeated a second time; the substrate was then washed with DI water and dried by air blowing.

3.1.6. In situ measurement of nickel deposition by quartz crystal microbalance (QCM).

A SiO₂-coated AT-cut quartz crystal substrate was being washed with ethanol, then followed by rGO pre-treatment and Pd catalyzation. Thereafter, the QCM quartz was assembled with Dip Cell (Seiko Eg&G QA-CL3) before electroless nickel deposition. Before the testing, the assembled unit was immersed in 0.2 M NaH₂PO₂ for 7 minutes to maintain the activity of the Pd nanoparticles under aqueous conditions. The electroless nickel deposition was conducted in the hypophosphite-nickel bath solution (Sol. 1) at 60 °C. During the QCM measurement, the assembled Dip Cell with quartz substrate was immersed in the Ni bath solution to detect the frequency change during electroless deposition. In addition, a blank quartz substrate was treated with 2 cycles of Pd (in 30 µM PdCl₂ solution) before being dipped into the bath solution in which the composition, pH and temperature remained the same as those of the Ni bath solution except that nickel (II) sulphate hexahydrate was not contained.

QCM was being used to measure the amount of Ni being deposited during the Ni electroless deposition.[115-117] The changes in the mass of the substrate due to the deposition of Ni was being detected by QCM, which uses the Sauerbrey

equation to calculate the drop in the frequency of the quartz .[118] The mass activity is expressed in terms of the mass of Ni deposited, m_{Ni} , normalized by the loading of Pd nanoparticles, m_{Pd} , [119] with the following equation being used:

$$\text{Mass Activity} = \frac{m_{Ni}}{m_{Pd}}$$

The Pd loading, or m_{Pd} , was measured by ICP-MS.

3.1.7. Apply rGO layers to enhance the silver catalytic activity and measure the Ni deposition speed by QCM

A SiO₂-coated AT-cut quartz crystal substrate was washed with ethanol, then followed by rGO pre-treatment. The silver catalyzation process was achieved by step-wisely dipping the quartz substrate into the silver chloride (AgCl, 10 mM as initial concentration and 200 μ M as 50 times diluted concentration) and 0.2M dimethylamine borane (DMAB) solutions for 2 cycles with 10 seconds in each solution. To record the deposition speed of Ni on quartz substrates: 1) preheated the DI water & Ni bath to 60 °C; 2) assembled the QCM substrate into Dip Cell unit; 3) Immersed the Dip Cell unit into DI water for 7 mins – wetting the surface; 4) started QCM recording and changed the Dip Cell unit into Ni bath solution. The electroless nickel bath used in this test contained 0.2 M sodium citrate, 0.5 M boric acid, 15 g/L Nickel (II) sulphate hexahydrate, and 2g/L DMAB.

3.1.8. Analysis the enhancement effect of rGO layer at different rGO loadings

The SiO₂-coated AT-cut quartz crystal substrates had been measured the basic frequency in the NaH₂PO₂ solution with QCM. After drying with an air-gun, these quartz substrates were stepwise coated rGO layer with different concentration of graphene oxide solution at 2 g/L, 0.2 g/L, 0.02 g/L and 0 g/L (blank sample) respectively. After catalyzation with 3.2 ppm Pd solution, these quartz substrates were immersed into the NaH₂PO₂ solution to measure the frequency after coating. The rGO loadings were counted as mass difference on the substrates (the Pd loading was negligible), which can be calculated from the drop in the frequency of the quartz under QCM with Sauerbrey equation. Finally, these quartz substrates were immersed into the Ni bath solution for the in situ electroless nickel deposition measurement.

3.2 Results and discussion

For conductive surface demonstration, electroless Ni deposition occurred on the entire copper sheet regardless of the position catalyzed with Pd. As illustrated in Figure 20A, only two domains (as indicated with red concentric dots) on copper foil were Pd catalyzed. The copper foil was then dipped into the electroless deposition bath (see the experimental section). Since the substrate (copper foil) used in this test was electric conductive, electroless deposition occurred not only at the Pd catalyzed domains but everywhere on the foil (see Figure 20A as well). As shown in Figure 20B, electroless deposition did not occur on blank substrate

without Pd catalyzation. Since the Ni redox potential is lower than that of Cu, the deposition of Ni will not occur on Cu substrate via galvanic displacement deposition. In addition, it has been proven that since Cu does not catalyze the oxidation of NaH_2PO_2 , the reducing agent that was used in the deposition bath, Ni electroless deposition would similarly not occur on Cu substrate by NaH_2PO_2 . [120]

Figure 20 Electroless deposition on (A) domain catalyzed Copper and (B) no catalyzed Copper foil.

To select the appropriate reducing agent for the continuous conductive layer formed on the non-conductive substrate, hydrazine (N_2H_4) and sodium hypophosphite (NaH_2PO_2) were compared in this study predominantly for the reduction of the palladium catalyst. Visible changes observed on the mixed solutions confirmed the reduction of graphene oxides took place after mixing with hydrazine and sodium hypophosphite for 1 hour at room temperature (as in Figure 21). The N_2H_4 reduced graphene oxide turned to a darker color as a result

of the enhancement of visible light reflection, which was due to the increase of charge carriers' mobility and concentration in rGO.[62] The hydrophilicity of NaH_2PO_2 reduced graphene oxide dramatically decreased with the reduction of the oxygen-containing functional group in GO during the reduction process. After leaving both rGO solutions to settle overnight for a duration of 20 hours at room temperature, it could be observed that all the rGO settled at the bottom of two bottles due to the decrease of hydrophilicity. The N_2H_4 reduced graphene oxide showed higher hydrophobicity. Since the Pd catalyzation and Ni plating are solution-based processes, it is crucial that the rGO possessed good electrical conductivity and certain hydrophilicity. Hence, NaH_2PO_2 was chosen as the reducing agent for the reduction of graphene oxide on substrates to form the rGO layer.

Figure 21 The appearances of GO solutions after mixing it with DI water, N_2H_4 and NaH_2PO_2 respectively for different durations.

A non-conductive substrate (SiO₂ coated QCM quartz) has gone through the rGO pretreatment and Pd catalyzation at an extremely low concentration of 30 mM (3.2 ppm) PdCl₂ solution. This sample was denoted as '3.2 ppm Pd & rGO' as shown in Table 5. Two control samples were also prepared. One was prepared using the same PdCl₂ (3.2 ppm) solution, while another was prepared with highly concentrated PdCl₂ (160 ppm - this concentration level is conventionally used in the Pd catalyzation for electroless plating). The functionalization of rGO was skipped for these two control samples, which are denoted '3.2 ppm Pd' and '160 ppm Pd', respectively. Expectedly, Pd loadings were very low for the 3.2 ppm Pd & rGO and the 3.2 ppm Pd while 160 ppm Pd had a high Pd loading (see Table 5). The Pd loadings from the low PdCl₂ concentration were less than 2% of the one from the high PdCl₂. These catalyzed samples were dipped into a Ni electroless deposition bath to evaluate the catalytic activity (mass activity of deposition amount per Pd loading) by QCM.[117, 119]

Table 5 Pd loadings and mass activities of the samples prepared under different PdCl₂ concentrations

Sample name	160 ppm Pd	3.2 ppm Pd	3.2 ppm Pd & rGO
PdCl ₂ solution concentration (μM)	1.5 x 10 ³	3.0 x 10	3.0 x 10
Resultant Pd loading (μg cm ⁻²)	2.12	2.81 x 10 ⁻²	3.94 x 10 ⁻²
Loading ratio to 160 ppm Pd (%)	100	1.33	1.86
Mass activity at t = 10 s	1.41	--	47.5

We confirmed that GO was reduced by the NaH_2PO_2 treatment to rGO. The results of an X-ray diffraction (XRD) analysis (Figure 22) showed a GO peak of 9.731° , which corresponds to an interlayer spacing of 0.9083 nanometers, disappearing after the reduction treatment. A broad peak appears at 26.221° and was attributed to typical well-ordered graphitic (001) sheets associated with an interlayer spacing of 0.3 nm, as observed in the XRD profile of regular graphene or rGO.[121] The lower shift observed in NaH_2PO_2 -treated GO (26.221°) as compared to pure graphene (26.51°) implied that phosphorus released via the decomposition (oxidation) of NaH_2PO_2 , was impregnated into the rGO structure, thus resulting in the expansion of the graphene lattice.

Figure 22 XRD patterns of graphene oxide and NaH_2PO_2 reduced graphene oxide.

The reduction of GO to rGO by NaH_2PO_2 was further confirmed with the Raman spectra of GO before and after the treatment (Figure 23). The peak for rGO ($\sim 1600 \text{ cm}^{-1}$) at the G-band was low-shifted compare with that of GO before the treatment, this represented the recovery of the hexagonal network of carbon

atoms with defects. The I_D/I_G ratio of exhibited a significant increase from 0.886 (before treatment) to 1.112 (after the treatment), indicating that the structure of graphene oxide was changed during the NaH_2PO_2 reduction process.

Figure 23 Raman Spectra of graphene oxide and NaH_2PO_2 reduced graphene oxide.

From the TEM observations of the catalyzed samples, we confirmed that a small amount of Pd particles was deposited on the samples of 3.2 ppm Pd (Figure 24B) and 3.2 ppm Pd & rGO (Figure 24C) as compared to 160 ppm Pd (Figure 24A). This confirmed the trend in the Pd loading as measured with ICP MS (as illustrated in the third row of Table 5). The 160 ppm Pd sample had relatively dense Pd particles that were coagulated to form large particles (50–100 nm, Figure 24A).[122] Coagulation was also observed in the 3.2 ppm Pd sample as well (Figure 24B). For the Pd deposition, electrons discharged from the oxidation of hypophosphite reduced Pd ions to Pd metal. Since both 160 ppm Pd and 3.2 ppm Pd samples did not have an rGO layer, and when the hypophosphite oxidized,

the discharged electrons would not travel widely and the Pd deposition would occur locally. On the other hand, for the 3.2 ppm Pd & rGO, the majority of the particles were small (~ 5 nm) and well dispersed. This could be due to the wide distribution of electrons over the rGO layers covered on the 3.2 ppm Pd & rGO sample, which is similar as discussed and illustrated in Figure 3C.

Figure 24 STEM image of A) 160 ppm Pd, B) 3.2 ppm Pd and C) 3.2 ppm Pd & rGO. (See Table 5 for the denotations of these samples)

The rGO coating enhanced electroless deposition on the substrates with extremely low Pd loading, and the electroless deposition rate was comparable to that of the conventionally used Pd loading. For comparison, a conventionally employed PdCl_2 concentration level, i.e., 1.5 mM ('160 ppm Pd' sample in Table 5) was used for Pd catalyzation in the conventional Ni electroless deposition, which resulted in regular Pd loading (2.12 mg cm^{-2}) and consistent Ni deposition rate, as shown in Figure 25.[30] Once the PdCl_2 concentration was reduced to 30

μM (3.2 ppm Pd sample), the Pd loading was consequently dropped to $2.81 \times 10^{-2} \text{ mg cm}^{-2}$ and, as expected, the deposition rate drastically dropped and no Ni deposition was observed. The QCM result of the reduced Pd concentration experiment was similar to that of the surface with no applied catalysts (“blank samples” in Figure 25). In principle, electroless Ni deposition will not occur without catalyzation. Thus, no Ni was deposited in the electroless deposition process when $30 \mu\text{M}$ of PdCl_2 solution was used.

Figure 25 Deposition amount in Ni electroless deposition on a SiO_2 coated QCM electrode after different catalysation processes: 160ppm Pd, 3.2ppm Pd, 3.2ppm Pd & rGO and no catalysation (blank).

With rGO pre-treatment (3.2 ppm Pd & rGO), the Pd loading ($3.94 \times 10^{-2} \text{ mg cm}^{-2}$) for $30 \mu\text{M}$ of the PdCl_2 solution was relatively minimal; however, the deposition rate was notably competitive to that of 160 ppm Pd without rGO (Figure 26). The low Pd loading and high deposition rate indicated the effectiveness of rGO in enhancing the catalyzation process for electroless deposition, even with a low amount of Pd nanoparticle catalysts being used.

Quantitatively, the mass activity, the amount of Ni deposited in mg normalized by Pd loading in mg,[119] was 47.5 at a deposition time (t) of 10 s; this value is 34 times higher than that obtained when 160 ppm Pd (the mass activity was 1.41 at t = 10 s) was used, as shown in Figure 26.

Figure 26 Mass activity, Ni deposit normalised by Pd loadings of 160ppm Pd and 3.2ppm Pd & rGO

Similarly, the enhancement of Ni deposition was demonstrated using another non-conductive substrate, polyimide. For 3.2 ppm Pd & rGO (the sample at the right in Figure 27), it was clearly shown that Ni deposited over the catalyzed area. In contrast, for 3.2 ppm Pd without rGO (the sample at the left in Figure 27), the appearance of the polyimide substrate did not change, indicating insufficient Ni deposition without rGO. The rGO coating of a non-conductive surface would induce electroless deposition at regular deposition rates even with extremely small Pd loading.

Figure 27 Electroless plating process at A) $t = 0s$; B) $t = 20 mins$ (The sample on the left is 3.2ppm Pd and the sample on the right is 3.2ppm Pd & rGO).

Certainly, the rGO pre-coated layer also enhanced the silver catalytic activity in the electroless Ni plating. For the Ni coating appearance, almost no Ni deposition was observed on the 200 μM AgCl sample (Figure 28C), the 10 mM AgCl catalyzed sample showed Ni partially deposited at the bottom area (Figure 28B), while the 200 μM & rGO sample showed very continuous and flat Ni coating (Figure 28D). It has been reported that Ag can work as catalysts in the electroless Ni plating but with low catalytic activity and low stability.[123] Ag could be easily oxidized to Ag_2O in air or O_2 contained water (heated) before the QCM measuring process. Before transferring all of the substrates into the Ni bath, the silver existed on the top surface in the form of Ag_2O . Thus, the reducing agent in the plating bath needed to reduce the Ag_2O to Ag before electroless Ni deposition happened, and this stage resulted in a substantial decrease of mass for the QCM substrates (as shown in Figure 28A). In comparison to the following mass

changing curve measured by QCM, the 200 μM & rGO sample showed the highest deposition speed amount all samples.

Figure 28 A) Deposition amount in Ni electroless deposition on a SiO_2 coated QCM electrode after different catalysation processes: 10 mM AgCl, 200 μM AgCl, , 200 μM AgCl & rGO and no catalysation (blank). B) Ni coating on 10 mM AgCl catalyzed sample; C) Ni coating on 200 μM AgCl catalyzed sample; D) Ni coating on 200 μM AgCl & rGO treated sample;

As expected, the coverage fraction of rGO film over the substrate surface increased when the concentration of GO solution increased. As shown in Table 6, with 2000ppm GO solution, the coverage was over 200 % indicating the rGO layer is double over the surface while the coverage was drastically decreased down to 22.5 % and 12.7 % with 200ppm and 20ppm GO solutions respectively. This was due to more GO remaining on the substrates after the drying when

higher concentrations of GO dispersion were used in the rGO dip-coating process. However, interestingly, the Pd loading of all the with GO samples (2000ppm, 200ppm, and 20ppm) were very closed and the values were slightly higher than the “no rGO” sample. The rGO conductive layer can promote the Pd catalyzation process, but the enhancement was very small when the catalyzation duration was very short (2 cycles with 10 seconds per cycle).

Table 6 Resultant rGO coverage and Pd loading from different GO concentrations.

Sample name	2000ppm GO	200ppm GO	20ppm GO	No GO
GO concentration [g/L]	2.00	0.20	0.02	0.00
Fractional coverage [%]	218.5	22.5	12.7	0
Pd loading [$\mu\text{g}/\text{cm}^2$]	5.63×10^{-2}	6.85×10^{-2}	5.98×10^{-2}	2.03×10^{-2}

As shown in Figure 29, “2000ppm GO” sample exhibited the highest mass activity compared with the other samples with low GO coverage. As observed previously, the “200ppm GO) samples showed 50 times higher mass activity compare with the “No GO” samples. On the other hand, the Ni mass activity of “20ppm GO” sample was closed to “No GO” sample, suggesting that 12.7 % of rGO coverage is too low to have significant enhancement of the Pd catalytic activity. The calculation of fraction coverage showed in Table 6 was based on the mass of loaded rGO on the substrates surface and assuming the rGO sheets on the substrates surface were equally distributed. The 218.5 % coverage in “2000ppm GO” sample meant the whole substrate surface was covered with a few layers of

conductive film. This fully conductive surface showed the highest enhancement on the Pd catalytic activity in the electroless nickel plating. Overall, the rGO loading and coverage changed when the concentration of GO solution varied, and it had a significant impact on the enhancement of catalytic activity of Pd nanoparticles in the electroless deposition.

Figure 29 Mass activity, Ni deposit normalized by Pd loading of Pd catalyzation process using different GO concentrations.

3.3 Conclusion

In electroless nickel plating on non-conductive substrates, high concentration and high coverages of the catalyst are required to initialize the nickel deposition. The conductive nature of a substrate would result in the transfer of electrons, generated from the oxidation of reducing agents, across the entire surface. This approach would result in the initialization of the nickel deposition with a much

lower catalyst loading. Thus, we induced rGO to form a conductive coating on non-conductive surfaces in order to achieve electron transfer required for the initializing of the electroless nickel deposition with low catalyst loading. With the selected reducing agents, we have a pre-coated rGO layer formed on the substrates' surface with the solution-based wet process.

The QCM was used for the in-situ analysis of the deposition speed of nickel by measuring the difference in frequency caused by weight change during the deposition process. We confirmed that the layer of rGO coating which enhanced catalytic activity of palladium, would achieve a similar nickel deposition speed with a relatively low Pd loading of 1/50. This result indicated that our rGO pretreatment process proposed and demonstrated in this study improves the cost-effectiveness of industrial metallization processes because Pd pre-deposition has been employed in all electroless deposition processes over the last 50 years.

Furthermore, we have demonstrated the enhancement method also applies to the silver catalyst in electroless plating. With the rGO pre-treatment, nickel coating that has been initialized with an Ag catalyst would result in better uniformity and higher deposition speed in comparison with the substrate treated with 50 times concentrated Ag solution (Figure 28). It further proved our hypothesis that the rGO pre-coated layer can improve the substrates' surface electrical conductivity and achieve fully electroless nickel plating with extremely low catalyst loading.

CHAPTER 4: PRE-LOADED PD IN ABS FOR LOCAL METALLIZATION OF 3D PRINTED STRUCTURE

4.1 Experimental procedure

4.1.1 Solution preparation

The ABS solute was prepared by cutting 9 g of ABS plastic into small pieces, mixed with 50 mL acetone in a closed container and left for overnight.

The ABS & PdCl₂ acetone solution (sol.2) was prepared by dissolving 2 g of ABS (Plasil, FA17510WT) in 2 g of acetone (Wako Pure Chemical, 016-00346), followed by mixing with 4 g of acetone that dissolved 1 g of PdCl₂ (Kanto Chemical, 32009-60).

A stock solution of palladium (II) chloride (PdCl₂; 20 mM) (99% wt, Sigma Aldrich) was prepared by dissolving 0.36 g of PdCl₂ into the solvent with 99 mL of DI water and 1 mL of concentrated hydrochloric acid (37% HCl). The PdCl₂ (1.5 mM) solution was diluted from stock palladium chloride (20 mM) by mixing with DI water at ratio 3:37.

Tin (II) Chloride (SnCl₂; 0.2 M) (Alfa Aesar) solution was prepared by dissolving 3.79 g of SnCl₂ powder into the solvent with 90 mL of DI water and 10 mL of concentrated hydrochloric acid (37% HCl).

Sodium hydroxide (NaOH; 1 M) (Sigma Aldrich) solution was prepared by dissolving 4.00 g of NaOH powder in 100 mL of DI water.

The hypophosphite-nickel bath solution (sol.1) contains 0.2 M of sodium citrate (Sigma Aldrich), 0.5 M of boric acid (Strem Chemicals, Inc.), 0.06 M of nickel (II) sulfate hexahydrate (BDH Prolabo Chemicals) and 0.24 M of sodium hypophosphite (Sigma Aldrich), and the pH was adjusted to 9.0 with sodium hydroxide powder (NaOH) (Sigma Aldrich) for the electroless nickel plating.

4.1.2 Compatibility of ABS solute and different organic solvents:

One milliliter of ABS solute was drawn out and mixed individually with the following solvents: 0.5 ml of DI water, ethanol, glacial acetic acid, toluene, O-xylene, methyl ethyl ketone (MEK) and acetone, respectively. This is to observe the compatibility of ABS solute and different solvent. Similarly, the PdCl_2 solubility in different solvent was tested by adding 10 mg of PdCl_2 powder into 1 mL each of: DI water, ethanol, glacial acetic acid, toluene, O-xylene, MEK and acetone, respectively.

4.1.3 Synthesis of Pd ion loaded ABS microfibers by electrospinning.

The freshly prepared ABS & PdCl_2 acetone solutions (sol.2) were left overnight and were subsequently mixed and poured into a polypropylene syringe (17 mm in diameter and 82 mm in length, 10 ml in capacity) with a sharp nozzle (polyethylene, 0.25 mm in inside diameter and 0.51 mm in outer diameter and 31 mm in length). In order to eject the mixed solution (Pd ion and ABS in acetone)

by electrospinning, an enamel-coated wire (electrode) was inserted into the solution and air pressure was also exerted as well with another syringe. The metal surface at the other end of the wire was exposed by polishing the enamel, and the exposed metal tip was connected to the positive end-terminal of a high-voltage power supply (Green Techno, GS30). This unit was set up on a stage with the nozzle being vertically pointed down to the stage. A metal plate (100 mm x 100 mm, 1 mm thick) was placed on the stage, and connected to the ground of the high-voltage power supply. A glass plate (18 mm x 18 mm, 0.17 mm thick) was set on the metal plate with 25 mm gap (working distance) between its top surface and the tip of the nozzle. The power supply was turned on to supply 9.0 V between the mixed solution and the metal plate to drive the electrospinning to coat the Pd ion loaded ABS microfibers over the glass plate. This experiment was set at room temperature and humidity.

4.1.4 Pd ion loaded ABS coating on additive manufactured ABS structure:

With the designed structure, a pure ABS filament (Plasil, FA17510WT) was also used to form three-dimensional ABS structures by additive manufacturing (Fused Deposition Modeling process). For the sample prepared with air-pressure based Pd loaded ABS solution, the mixed solution (sol.2) as described in the 4.1.1 section was prepared and directly used for coating the ABS layer (loaded with Pd ions) on pre-determined areas of 3D ABS structures. The coating process that we

adopted was the same set up as in the electrospinning (described in the 4.1.3 section) without the electric power supply unit. For the sample printed with ABS filaments and Pd loaded ABS filaments, the entire sample was printed employing a dual nozzle printer that can extrude pure ABS material and Pd loaded ABS material at the same time. The Pd loaded ABS filaments was prepared by: 1) mixing the PdCl_2 powder and ABS powder with a weight ratio of 1:10; 2) heating the powder mixture up to 260 °C and extruding them through filament extruder.

4.1.5 Electroless nickel plating:

The nickel bath (sol.1) was maintained at 60 °C during the electroless deposition. The prepared Pd ion loaded ABS sample (microfiber or three-dimensional structure) was washed with DI water and followed by the electroless nickel deposition (as illuminated in Figure 30B). For comparison, the pure ABS sample (microfiber or three-dimensional structure) was also used for electroless plating. It was first washed with DI water, before being catalyzed with conventional Pd/Sn catalyst, as described in steps as follow: (1) dipped into 1.5 mM palladium (II) Chloride for 2 mins, (2) DI water washing to prevent contamination, (2) followed by dipping in 0.2 M Tin (II) Chloride for 2 mins, (4) DI water washing to prevent contamination, (5) immersed into 1 M NaOH for 3 mins as acceleration process, (6) DI water washing to remove excess solution on the substrate surface.

After the Pd/Sn catalyzation, the ABS samples were immersed in the nickel bath (sol.1) for electroless nickel deposition (as illuminated in Figure 30A).

Figure 30 A) conventional method of metallization of 3D printed plastic structure; B) new method has been proposed in this study to deposit metal of interest over the selected area of a 3D printed plastic structure.

4.2 Results and discussion

4.2.1. Solvent choice for dissolving catalyst precursor (PdCl₂) and ABS

Firstly, acetone was chosen as the solvent for both ABS resin and Pd catalyst precursor (PdCl₂). We have surveyed varieties of solvents (listed and shown in Figure 31) according to their PdCl₂ solubility and compatibility with ABS. Methyl ethyl ketone (MEK) or acetone works as polar protic solvents that would dissolve the SAN (styrene-acrylonitrile) matrix and some of polybutadiene disperse inside ABS and transfer ABS plastic into ABS solute.[124] On the

palladium source compatibility test, PdCl_2 was partially dissolved in acetone but less so for MEK. DI water and ethanol are solvents that are usually used for PdCl_2 . However, both solvents resulted in the solidification of the solute ABS once contact was made with acetone solute ABS. The possibility of swelling of ABS caused by glacial acetic acid, toluene, and o-xylene, but all of these solvents showed extremely low solubility of PdCl_2 . Moreover, glacial acetic acid was responsible for the solidification of acetone solute ABS. Ultimately, acetone was chosen after considering the solvent compatibility with both PdCl_2 and the solute ABS.

Figure 31 Solvent test by mixing different solvents with solute ABS (acetone) and PdCl_2 respectively.

4.2.2. Confirm catalytic activity of solidified ABS & PdCl₂ mixture (sol.2) with tangled fibers structures

When Pd ions were dissolved in the ABS solute (sol.2), a uniform distribution of these ions would occur over the material, including the whole surface after solidification. While the Pd ion was reduced to Pd(0), it functioned as a catalyst for electroless nickel plating. In the catalytic activity test of these surface Pd elements in electroless nickel plating, some microfibers were printed by electrospinning with ABS & PdCl₂ mixture (sol.2) and the subsequent SEM characterization would show the appearance of the nickel coating.

Before the onset of electroless nickel plating, Pd ion loaded ABS fibers were previously printed through electrospinning with the ABS & PdCl₂ mixture (sol.2). After solidification, those fibers were immersed in Ni electroless plating bath, and uniform and conformal nickel coating can be observed on the nanofiber structures. As shown in Figure 32A, every individual fiber was uniformly coated with Ni after 5 minutes plating. When the plating time was increased to 15 minutes, the Ni coating thickness significantly increased and still predominantly occurred on the fiber surface. This indicates that the pre-loaded Pd ions were uniformly distributed in the ABS fibers, and they indeed functioned as a catalyst for electroless nickel plating occurring only at the catalytic area.

Figure 32 SEM images of (A) electro-spun microfibers using Pd ion pre-loaded ABS acetone solution after Ni electroless deposition. (B) electro-spun ABS fibers after the treatments for Pd catalyzation (using PdCl_2 and SnCl_2 solutions) and Ni electroless deposition.

Notably, the uniform and conformal nickel coatings on the solidified ABS & Pd fiber are attributed to the pre-loaded Pd element. For comparison, some pure ABS microfibers were printed through the same electrospinning machine with pure ABS solute (ABS powders dissolved with acetone). In the conventional electroless nickel plating process, the catalyst or catalyst precursor was coated by immersing the workpiece into a Pd ion solution and a reducing agent solution alternatively (PdCl_2 and SnCl_2 used in this study, respectively). Thus, the distribution of Pd catalyst over the substrate surface depended on the substrate's surface morphology and hydrophilicity. Due to the overlapping of fibers in the tangled fiber, more Pd nanoparticles would be deposited in between the gaps of

fibers compared to the fiber surfaces in the conventional dip-coating method. After 5 minutes electroless plating in the nickel bath, the conventional Pd catalyzed pure ABS fiber illustrated the Ni coating without order and structures, and these nickel deposits even destroyed the original tangled fiber structures due to low adhesion between fibers and nickel coating (as shown in Figure 32B). After further plating, the thickness of the metal depositions over the fibers increased and changed the fiber structures into plate configuration. This indicated the Pd catalysts are more likely to stay in between the gaps than on the fibers because catalyst solutions were trapped by the tangled fibers.

In addition, a multi-layer tangled fiber structure with 2 layers of pure ABS and 2 layers of Pd loaded ABS fibers (as shown in Figure 33A) was designed to examine the nickel coating boundary between Pd pre-loaded area and the pure ABS area. After 10 minutes plating in the electroless nickel bath, the nickel deposits only occurred at the 2nd and 4th layers while the 1st and 3rd layers remained white (pure ABS). This result showed the pre-loaded Pd element sticks only on the target ABS surface and can be used as catalysts for pinpoint nickel coating.

Figure 33 A) Designed multi-layer tangled fiber structure (white color is printed with pure ABS solute; orange color is printed with ABS & PdCl₂ mixture – sol.2); B) the multi-layer tangled fiber structure printed with electrospinning; C) the multi-layer tangled fiber structure after 10 mins electroless nickel plating.

4.2.3. Area-selective metallization of 3D printed plastic structure

Electroless plating was area-selectively induced over the 3D printed ABS structure coated with Pd ion loaded ABS. Three different 3D ABS structure samples were tested with different catalyst coating methods through the following processes: (A) immersion of a 3D ABS structure sample in Pd ion solution (PdCl₂ solution) and reducing agent solution (SnCl₂ solution) in sequence, (B) air-pressure based additive manufacturing (ejection of ABS & PdCl₂ mixture solution with air pressure), (C) fused filament fabrication (FFF) by a dual extrusion printer with pure ABS filaments and Pd ion loaded ABS filaments.

For the sample denoted (A), the top half of the structure was immersed in a Pd/Sn solution for catalyzation, but the deposition of Pd catalysts was affected by the structure's surface morphology and surface hydrophilicity, which resulted in partial Ni deposition on the catalyzed region. Moreover, the hydrophobicity of

the ABS material resulted in poor adhesion between the ABS surface and the catalyst nanoparticles, also with the metal coating (Figure 34 A). For the sample denoted (B), the electroless nickel deposition occurred at Pd ion loaded domains with sufficient adhesion (Figure 34 B). This indicated the loaded Pd ion was reduced into Pd metal by the reducing agent (sodium hypophosphite monohydrate) in the electroplating bath (sol.1), and the Pd metal functioned as a catalyst for subsequent electroless Ni deposition. For the sample denoted (C), only the parts printed with Pd ion loaded ABS filaments (the black region in Figure 34 C – after printing) initialized the Ni plating in the electroless Ni bath, which indicated the pre-loaded Pd element acting as a catalyst for electroless Ni plating on the target area. Notably, the invented metallization using the ABS & PdCl₂ mixture for coating over ABS is environment-friendly and cost-effectively as it precluded the process of chromic acid etching. In general, we achieved area-selective, environmentally friendly metallization with strong adhesion over the 3D printed ABS structure using the ABS & PdCl₂ mixture solution.

Figure 34 3D printed ABS structures with different catalyzing methods: (A) conventional method shown in Figure 30A: immersion in Pd ion solution (two steps PdCl_2 / SnCl_2 catalyzation). The double-sided arrow indicates the depth of immersion. (B) an area-selective catalyzation: pasting ABS & PdCl_2 mixture solution (sol.2) through a nozzle with air-pressure, (C) another area-selective catalyzation: pasting Pd-ion loaded ABS through FFF (fused filament fabrication) 3D printer using a Pd-ion preloaded ABS filament. (The top images are those 3D printed structures after different Pd catalyzation processes while the bottom images are the catalyzed 3D structures after electroless deposition.)

4.2.4. Catalyst precursor (Pd elements) distribution in ABS

Acetone has sufficient solubility to Pd ions and ABS material, and this ensures an equal distribution of Pd ions over the ABS & PdCl_2 acetone solution (sol.2). Furthermore, a large amount of Pd ions also equally existed on the outer surface of the solidified ABS & Pd material. Figure 35 showed the visualized cross-section images of the Pd ion loaded ABS substrate. From the optical microscope image (Figure 35A), the brown color primarily appeared on the peripheral surface of the ABS substrates and barely penetrated a few micrometers due to the contact

and penetration of the acetone solution (dissolved Pd ions) on the ABS plastic. This brown distribution was the same as the Pd element mapping as illustrated in Figure 35C, which indicated the presence of Pd²⁺ ions. The Pd metals existed over the top outer surface of the final substrate after the loading of Pd ions, and the ions were not lost through deep penetration. This implied the solidification of ABS & PdCl₂ mixture on the 3D printed ABS structure would result in a high Pd concentration on the outlying surface. The Pd layer served as a catalyst for the electroless plating: the Pd ions over the surface were reduced to Pd metals by the reducing agents in the electroless plating bath, and the Pd metals, in turn, induced the oxidation of the reducing agents and initialized the electroless Ni plating.

Figure 35 A) 3D printed ABS structure with area-selective catalyzed with Pd-pre-loaded ABS solution; The cross-sectional view of Pd ion loaded ABS layer (the red circle in A) under (B) optical microscope; (C) SEM; (D) EDX mapping of Pd element.

4.2.5. Characterization of the metallization layer at Pd ion loaded ABS surface after electroless plating

To characterize the metalized surface on the ABS structure, a Field Emission Scanning Electron Microscope (FESEM) has been used to observe the nickel deposition at the boundary between Pd ion loaded ABS and pure ABS regions. After 5 minutes electroless nickel deposition, a clear boundary was observed between the ABS-Pd (sol.2) activated region and original ABS substrates as shown in Figure 36B. Figure 36C illustrated the result of the energy-dispersive X-ray spectroscopy (EDX) result showed the nickel occupying 94% of the deposition surface (black region). This implied the exact nickel metallization had been achieved on the target area of the three-dimensional ABS structure.

Figure 36 A) ABS-Pd coated ABS structure after electroless nickel deposition; B) FESEM observation at the boundary of catalyzed region and non-catalyzed region; (red circle area in A) C) EDX analysis of the metalized area (black color area of B).

4.3 Conclusion

In order to achieve area-selective metallization on 3D printed plastic structures with the exclusion of conventional pretreatments such as surface etching, roughening, and the use of toxic chemicals, we proposed and adopted electroless plating for fused filament fabrication (FFF) 3D printing. We also custom-fabricated a new ABS filament-containing Pd ions (precursor of the catalyst for electroless plating) using ABS & PdCl₂ acetone mixture solution. A FFF 3D printer with dual nozzles was employed for fabricating the 3D printed ABS structure and having Pd ion loaded ABS deposited at selected regions of interest: the main component was manufactured by one nozzle using a regular ABS filament (pure ABS, no Pd ion) while Pd ion loaded ABS layers were deposited at selected zones of interest by the second nozzle using the new ABS filament with Pd ions. The ABS workpiece with Pd ion loaded ABS was then immersed into a Ni electroless plating bath. We confirmed that the Ni was deposited at the selected regions and the Ni adhered sufficiently onto the ABS. This result indicates that the proposed 3D printing technology coupled with the new ABS filament with Pd ion and the electroless plating enables the area-selective metallization. This novel technology offers many advantages and efficiencies because it does not require (i) any customized design of regular FFF 3D printing (commercial compatibility is offered), (ii) any surface etching or roughening (damage less to 3D printed structure is guaranteed), (iii) any toxic chemical, for

example, chromic acid which is often employed for etching of ABS workpiece in electroless plating.

Furthermore, we have confirmed that injection of ABS & PdCl₂ mixture solution on selected areas of 3D printed ABS structure is also applicable for metallization through electroless plating. Although this method has disadvantages compared with the method using the Pd ion loaded ABS filament: it is not compatible with a regular 3D printer and it could damage the surface of the injected ABS region because the acetone dissolves the ABS, it has potential applications. For example, we have demonstrated uniform and conformal metal coating over the surface of microfibers fabricated through electrospinning using the solution followed by electroless plating (Figure 32 A).

Generally, since varieties of metals (not only Ni but also Co, Cu, Au, Ag, Pd, Pt, etc.) and their alloys can be deposited by electroless plating, the 3D printing technology demonstrated in this study is widely applicable for the manufacturing of three-dimensional structures with varieties of metal features (including circuits, metal catalysts, lustrous appearances, hardness, etc.) at selected regions.

CHAPTER 5: TRIGGER ELECTROLESS DEPOSITION ON SELECTED AREA WITH THERMO-SENSITIVE LIPOSOME

5.1 Experimental Procedure

5.1.1 Chemical Preparation

A sodium hypophosphite monohydrate (NaH_2PO_2 ; 0.2 M) (98% wt, Alfa Aesar) solution was prepared by dissolving 2.12 g of NaH_2PO_2 powder in 100 mL of DI water.

Sodium chloride (NaCl ; 300 mM) (>99% wt, Sigma Aldrich) was prepared by dissolving 17.53 g of NaCl powder in 1L of DI water

A solution of palladium (II) chloride (PdCl_2 ; 20 mM) (99% wt, Sigma Aldrich) was prepared by dissolving 0.36 g of PdCl_2 into the solvent with 100 mL of sodium chloride (300 mM) solution.

Phosphate buffered saline (PBS) buffer was purchased from Sigma Aldrich and directly used in following experiment.

Lipid membranes were prepared using 1,2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC), L-glutamic acid, N-(3-carboxy-1-oxopropyl)-, 1,5-dihexadecyl ester (SA), and 1,2-Distearoyl-sn-glycero-3-phosphoethanolamine-N-[monomethoxy poly(ethylene glycol) (5000)] (PEG-DSPE) with a molar ratio of 9/1/0.06, and the mixture solution was freeze-dried to obtain a mixed lipid powder

5.1.2 Synthesis of liposome encapsulated structures (Lipo-P; Lipo-Pd; Lipo-PBS)

The dried lipid mixture powder was hydrated with the reducing agent solution (0.2 M NaH_2PO_2). After complete and homogeneous mixing, the dispersion was introduced into a syringe and was extruded through membrane filters (0.45 μm final pore size, Durapore®; Millipore Corp., Tokyo, Japan) above the phase transition temperature of DPPC under pressure. The non-encapsulated NaH_2PO_2 solution was removed twice by Beckman Optima TL Ultracentrifuge with PBS solution. The prepared liposomes encapsulating reducing agent (Lipo-P) were stored at room temperature (22 °C). The liposome capped Pd ion (Lipo-Pd) was prepared by changing 0.2 M NaH_2PO_2 to 20 mM PdCl_2 in 300 mM NaCl solution. Another blank sample (Lipo-PBS) was prepared by capping PBS solution in liposome for comparison.

5.1.3 The analysis of liposome structures' stability

The critical temperature to trigger the release of calcein from DPPC liposomes is determined at 40 °C, which is corresponding to the phase transition temperature of DPPC liposomes.[126] The temperature stability tests of liposome-covered chemical (reducing agent) were conducted by heating the mixture of lipo-P and PdCl_2 to different temperatures and hence, to test the remaining Pd^{2+} ions in the

solution. The UV/Vis spectroscopy was used to evaluate the unreacted Pd^{2+} concentration in the solution and to finally confirm the critical temperature to induce the release of NaH_2PO_2 from Lipo-P and then the deposition of Pd.[127] Seven glass bottles (2 ml) with the mixture were prepared by adding 200 μL of liposomes encapsulated NaH_2PO_2 (Lipo-P) and 100 μL of 2 mM PdCl_2 solution (dissolved in 300 mM NaCl). The glass bottles were heated in a water bath to 20 $^\circ\text{C}$, 30 $^\circ\text{C}$, 40 $^\circ\text{C}$, 50 $^\circ\text{C}$, 60 $^\circ\text{C}$, 70 $^\circ\text{C}$, and 80 $^\circ\text{C}$ respectively. Also, the control group samples were prepared with 200 μL of liposomes encapsulated PBS (Lipo-PBS) and 100 μL of 2 mM PdCl_2 solution (dissolved in 300 mM NaCl) in each glass bottle. Each sample was moved into the 1.5 mL microcentrifuge tube and centrifuged at 1000 rpm for 5 mins. After that, 100 μL of the supernatant was taken into a new microcentrifuge tube and diluted to 10 times with Deionized (DI) water. The diluted solution was centrifuged at 1000 rpm for 10 mins and the supernatant was taken for UV-Vis scanning with a range of 300 nm to 600 nm.

The stability and activity of Lipo-P structures were tested after keeping the Lipo-P dispersion in the fridge at 3 $^\circ\text{C}$ for certain durations. After 1 day, 10 days, 40 days and 160 days respectively, 200 μL of liposomes encapsulated NaH_2PO_2 (Lipo-P) was taken out from the fridge and mixed with 100 μL of 2 mM PdCl_2 solution (dissolved in 300 mM NaCl), and the encapsulation stability of liposomes can be visually observed through the change in color. Then, the

mixture was heated up to 70 °C to test the activity of reducing agent and thermal sensitivity of liposomes.

5.1.4 Characterization of liposome structures

DLS analysis was used for measuring the size of both the lipo-P structures and Pd nanoparticles. The 10 μ L freshly prepared Lipo-P dispersion was diluted with 990 μ L of PBS buffer solution, then scanned under monochromatic light to get the size distribution curve. The heated lipo-P sample was prepared by heating the same batch of Lipo-P to a temperature of 70 °C, and thereafter diluted 100 times with PBS solution for DLS analysis. The mixed sample was prepared by mixing the Lipo-P dispersion and PdCl₂ solution (20mM in 300mM NaCl) with a ratio of 1:2 and heating the mixture to the temperature of 70 °C, followed by 100 times dilution with PBS solution.

5.1.5 Demonstration of area-selective electroless deposition

An aliquot of Lipo-P dispersion (200 μ L) was mixed with 100 μ L of 2 mM PdCl₂ solution (dissolved in 300 mM NaCl) before the reaction. The Pd electroless deposition was initiated on the silicon wafer surface which was dropped cast with 50 μ L of the reaction mixture, and heat was applied on the flipped surface directly opposite to the targeted area with a soldering iron. After washing with DI water,

a black coating remained on the target area. The black deposition was observed under FESEM/EDX for element analysis. Another inner surface Pd local plating was initiated within the glass capillary tube (inner dimension 1.1-1.2 mm, outer dimension 1.5-1.6 mm, Marienfeld). The pre-immersion of the glass capillary tube into 8 vol% (3-aminopropyl)triethoxysilane for 3 hours for surface treatment. The Lipo-P & PdCl₂ mixture solution was injected into a capillary tube via one of its two ends. The pretended coating area was heated on the external surface with a soldering iron. After excluding all the solution out of capillary tube and washing it with DI water, the Pd coating was only applied on the expected inner surface area.

5.2 Results and discussion

5.2.1 Thermotropic phase behavior of liposomes

Once the Pd²⁺ ion came into contact with the reducing agent (NaH₂PO₂), the drastic change in color (from orange to dark black) could be observed and interpreted as a result of the reduction reaction from Pd²⁺ ions to Pd(0). The color of mixtures in Figure 37A (Lipo-PBS & PdCl₂) represented the original color of DPPC liposome & PdCl₂ mixture without any chemical reaction at any temperatures from 20 to 80 °C. In Figure 37B, the color of lipo-P and PdCl₂ mixture first started to darken at 40 °C, and gradually turned dark black when the mixture solution was heated to a temperature above 50 °C. This color change

indicated the release of reducing agents from liposome, which reduced Pd^{2+} ions to $\text{Pd}(0)$ once the temperature reached 40 °C. When the temperature was set at 30 °C and below, the color of the solution was the same as that of the blank sample (Figure 37A lipo-PBS and PdCl_2). This observation showed the well encapsulation of reducing agent inside the liposomes in the temperature range below 40 °C. For the mixture of NaH_2PO_2 and Lipo-Pd (Figure 37C), the entire solution changed to dark black and released small bubbles after mixing for 10 mins, and the effervescence of mixture solution reaction was still visible after 2 hours. When the 0.2 M of NaH_2PO_2 dissolved in the water, it dissociated a large amount of Na^+ and H_2PO_2^- in water and resulted in the solution at a faint acid condition. This acidic environment affected the membrane fluidity of DPPC liposome structure, which resulted in a lower phase transition temperature.[128] For the Lipo-P and Lipo-Pd mixture (Figure 37D), the color of the solution started to change at 60 °C, and it gradually turned dark black when the temperature of the mixture solution exceeded 70 °C. The reaction of Pd^{2+} ion and NaH_2PO_2 happened after the temperature of the mixture solution reached the threshold temperatures of both the Lipo-P and the Lipo-Pd. The threshold temperature to release reducing agent from Lipo-P was between 40 °C to 50 °C, which can be observed from Figure 37B. Hence, the threshold temperature to release Pd^{2+} ion from Lipo-Pd was regarded to fall between 60 °C to 70 °C (Figure 37D). This increase in threshold temperature of Lipo-Pd was caused by the absorbance of positively charged Pd^{2+} ions on negatively charged liposome membrane (as

shown in Figure 39), which resulted in less Pd^{2+} ions released from Lipo-Pd at 40 °C to 60 °C. Another reason could be that the combination of Lipo-P and Lipo-Pd needs a higher release efficiency at the higher temperature due to the much lower concentration of both Pd^{2+} ions and the reducing agent. Overall, the combination of lipo-P and PdCl_2 was chosen in this research.

Figure 37 Mixture of A) Lipo-PBS and PdCl_2 solution; (B) Lipo-P and PdCl_2 solution; C) NaH_2PO_2 solution and Lipo-Pd; D) Lipo-P and Lipo-Pd; at 20 °C, 30 °C, 40 °C, 50 °C, 60 °C, 70 °C and 80 °C, respectively.

The UV-Vis spectrum (Figure 38) showed the Pd^{2+} concentration of the solution of Lipo-P and PdCl_2 to be comparable with that of Lipo-PBS and PdCl_2 when the

temperature was maintained at 20 °C and 30 °C. It further proved that the “safety temperature” for stable encapsulation of reducing agent with DPPC liposome fell in the temperature range of 30 °C and lower. However, a small reduction of Pd^{2+} concentration occurred once the mixture temperature reached 40 °C, which implied a small amount of NaH_2PO_2 was released from liposomes which helped in the reduction of Pd^{2+} ions to $\text{Pd}(0)$. This UV/Vis spectroscopic data supported the change of color from orange to dark black (as shown in Figure 37) was caused by the Pd deposition which consumed Pd^{2+} ions in solutions. The encapsulation of NaH_2PO_2 inside the liposome would not affect the change in phase transition temperature of the DPPC liposome, which was maintained at around 40 °C.

Figure 38 UV-Vis spectrum of DI water, mixture of Lipo-P & PdCl_2 after thermal treatment at 20 °C, 30 °C, 40 °C, and the mixture of Lipo-PBS & PdCl_2 at room temperature. (The spectra were measured after removing Lipo-P and dark black deposition by centrifugation.)

5.2.2 Characterization of liposome capped reducing agent before and after heating

Inside the TEM image, the Pd element showed the darkest color due to its high atomic mass. In the sample of Lipo-PBS & PdCl₂ at room temperature (Figure 39A), a clear spherical shape with black boundary was observed predominantly due to electrostatic attraction between the positive charge of Pd²⁺ ion and the negative charge of SA lipid. After heating the mixture to a temperature of 70 °C (Figure 39B) and waiting for it to cool back to room temperature, all the lipids became disordered during heating and regained the similar spherical shape with a broad size range. However, the Pd element remained both within and out of the liposome structure due to the reconstruction of SA lipids inside liposome structure. Similarly, the Lipo-PBS, the mixture of Lipo-P & PdCl₂ (Figure 39C) also clearly showed the spherical shape clearly with a black boundary at high magnification. However, a drying process was required in the preparation of TEM samples, and this resulted in the breakage of certain liposome structures and the reduction of palladium ions (many black colloids). However, for the heated Lipo-P & PdCl₂ sample that was prepared by drying the thermally treated mixture with all the Lipo-P was broken before the drying process, the TEM images only showed a large quantity of dispersed nanoparticles structures (Figure 39D), which had been confirmed are Pd and P elements with EDX analysis. After the temperature of Lipo-P significantly exceeded the transition point, the liposome

structures were quickly broken up and this released the reducing agent NaH_2PO_2 , which reduced all Pd^{2+} ions to Pd nanoparticles within a short period. Once all Pd^{2+} ions formed Pd nanoparticles and were released from the SA lipids, the remaining liposome structures became “invisible” under TEM observation due to the low atomic mass of the basic elements in the lipids (hydrogen, carbon, nitrogen, oxygen, and phosphorus).

Figure 39 TEM of A) Lipo-PBS & PdCl_2 at room temperature; B) Lipo-PBS & PdCl_2 heated to 70 °C; C) Lipo-P & PdCl_2 at room temperature; D) Lipo-P & PdCl_2 heated to 70 °C at different magnification.

Moreover, the DLS analysis results (Figure 40) showed the re-construction of liposome-encapsulated reducing agent sample (Lipo-P) during the thermal treatment by analyzing the particle size in Lipo-P before and after heating. The average size of lipo-P was around 224 nm before the thermal treatment, and the size curve of the heated Lipo-P sample illustrated a wider distribution. During the

synthesis of the Lipo-P structure, the size of liposome structures had been unified with a 0.45 μm filter. The thermal treatment was carried out at a temperature above its transition point, resulting in the reconstruction of the liposome structures that gave a broader size distribution. When the PdCl_2 was added into the Lipo-P solution (Lipo-P & PdCl_2 sample) and heated to a temperature of 70 $^\circ\text{C}$, the DLS curve showed two peaks at 111 nm and 514 nm. The 111 nm peak indicated the newly formed Pd nanoparticles, while the 514 nm peak indicated the re-constructed liposome structures that were “invisible” in TEM observation.

Figure 40 DLS analysis results of Lipo-P at room temperature; Lipo-P after heating up to 70 $^\circ\text{C}$ for 1 min; and the mixture of Lipo-P & PdCl_2 after heating up to 70 $^\circ\text{C}$ for 1 min.

5.2.3 Duration stability test of liposome structures

Based on the duration stability test results of liposome structures, the mixture of lipo-P and PdCl_2 remained orange in color at room temperature even when the

lipo-P structures were synthesized 160 days before (as shown in Figure 41). On the other hand, the mixture solution turned dark black within 1 minute after heating to above the transition temperature. This change in color indicated the activity of the reducing agent within the liposome was maintained even with prolonged storage. Therefore, this test showed the NaH_2PO_2 was well encapsulated within the liposome even after 160 days of storage, and this liposome-encapsulated reducing agent structure could maintain high stability and activity even after storing it for a long period of time.

Figure 41 Mixture of Lipo-P and PdCl_2 at 25 °C (left) and 70 °C (right) after the liposome was synthesized for A) 0 days, B) 1 days, C) 10 days, D) 40 days, E) 160 days.

5.2.4 Area-selective deposition of Pd on substrates

A demonstration of heat-triggered electroless deposition of palladium by the mixture of Lipo-P and PdCl_2 was conducted on the silicon wafer and inner glass tube. In Figure 42, the SEM images showed the palladium deposited in the thermally treated area, and the non-treated region remained blank after washing. Also, a clear boundary was observed between the heat triggered area and the non-triggered area. This demonstration indicated the Lipo-P and

PdCl_2 mixtures could achieve accurate electroless Pd deposition at the exposed surface with controlled thermal triggering.

Figure 42 SEM observations of A) heat triggered Pd deposition on Silicon wafer (Lipo-P & PdCl_2 mixture); B) Silicon surface at room temperature (Lipo-P & PdCl_2 mixture); C) the boundary between heat triggered area and untriggered Si substrate at low magnification.

As shown in Figure 43A, this demonstrated the triggered electroless Pd deposition at the inner surface of a capillary glass tube. This glass tube was being injected with Lipo-P & PdCl_2 solution, and the external heat was applied on the two target regions from outside the capillary glass tube. The coating remained at the interior surface after washing and air blowing, which indicated a strong adhesion of the palladium coating. In Figure 43B and Figure 43C, the SEM images confirmed that uniform deposition only occurred at the inner surface of the capillary tube with the external thermal

treatment. Additionally, the EDX showed the presence of Pd/P nanoparticles through analysis of the black deposits on the thermal-treated region. The demonstration implied that NaH_2PO_2 was released from lipo-P at the thermally treated regions, and this resulted in area-selective deposition of Pd/P on the target region. Overall, any substrates can be trigger-deposited with Pd at any surface through the selective thermal treatment. Therefore, the combination of thermosensitive liposome and electroless deposition would lead to a triggered local metal deposition on different substrates at comparably low temperature with minimal restrictions.

Figure 43 Demonstration of triggered Pd deposition process at inner surface of glass capillary tube: A1) blank glass capillary tube; A2) inject the Lipo-P and PdCl_2 solution into capillary tube; A3) local thermal treatment from the outside of tube (two black color regions); A4) remove the mixture and wash the capillary tube with DI water; B) SEM observation of heat triggered area; C) SEM observation of the area without heat treatment.

5.3 Conclusion

To achieve triggering electroless deposition of palladium at any exposed or internal surface of the given structures, we developed a new method that used a thermosensitive liposome to separate the reducing agents and metal ions in the plating solution. The reducing agents and the metal ions were separated by DPPC thermosensitive liposome which has a phase transition temperature at 40 °C; thus, excellent stability of the plating solution could be maintained at room temperature (stable state). When the mixture of liposome-encapsulated reducing agent (Lipo-P) and PdCl₂ was heated to a temperature above the transition point, the reducing agent was released from the liposome which reduced Pd²⁺ ions to Pd nanoparticles. We have demonstrated triggered electroless Pd deposition at both the exposed surface and internal surface, and the results showed accurate and uniform deposition of Pd occurring only at the thermal triggered regions.

Furthermore, stability tests of the liposome-encapsulated reducing agent (Lipo-P structures) were conducted at different temperatures and also after prolong storage. When the temperature was maintained at 30 °C or even lower, the reducing agents would be encapsulated well within the liposome structures. The Lipo-P would start to release reducing agents at a temperature of 40 °C, and the reaction between Pd ions and reducing agents would occur within one minute when the surrounding temperature reached 50 °C. Hence, Pd deposition on the target surface can be achieved with a couple of minutes of local thermal treatment.

In addition, the duration stability test showed the Lipo-P structures were able to retain its high stability and remain usable even with prolonged storage. With this applicable phase transition temperature and long-term storage capability, this invention can be applied on most substrates and structures for area-selective surface metallization.

CHAPTER 6: SUMMARY

6.1. Summary

The aim of this graduation thesis “Development of electroless plating processes for low cost plastic-metallization and area-selective metal coating of three-dimensional structures”, is to improve the cost-effectiveness of current electroless plating technology, and also to extend the application of electroless plating for localized surface metallization of the complex structures by cooperating with additive manufacturing technology and liposome structures. Electroless plating technology has been developed and widely used in industry for more than 60 years, but the catalyst is still the cost barrier in this process because of the limited resources in the earth and difficulty in recycling.[129, 130] For this reason, the author decided to reduce the palladium catalyst required for initializing the electroless nickel plating, with the aim of improving the cost-effectiveness of this technology for further development. Additionally, the current electroless plating process involves three major steps: surface preparation, catalyst activation and electroless plating. However, the traditional handling method of these three steps limits the applications of electroless plating because of the environmental contamination caused by the etching solution or the complexity of target structures. Thus, the author combined the electroless deposition process with other technologies for area-selective metal deposition on any complex structures with low environmental contamination.

This thesis has three major purposes: (1) to investigate the enhancement of palladium catalytic activity in electroless nickel plating by pre-loading a layer of reduced graphene oxides (rGO) on non-conductive substrates; (2) to demonstrate an environmentally friendly method for surface metallization of three-dimensional structures that are fabricated with additive manufacturing technology; (3) to develop the method for triggering area-selective electroless palladium deposition at any surface (exposed surface or internal surface) of three-dimensional materials.

6.1.1 Use rGO to enhance Pd catalytic activity in electroless nickel deposition

This project presented a viable process to enhance the catalyst activity of palladium nanoparticles for electroless nickel plating by inducing a layer of pre-coated conductive layer. The advantages of this proposed method for electroless deposition can be summarized as follow:

- The pre-treatment process is simple and widely applicable: sequential dipping in the graphene oxide solution and reducing agent solution in sequence;
- Significant increase in the mass activity of the Pd catalyst in electroless nickel deposition. The samples pre-coated with conductive rGO shows a

47-times increase in mass activity as compared with the Pd-only loaded sample;

- Due to the huge price difference between graphene and palladium, the rGO pre-treatment proposed and demonstrated in this study will improve the cost-effectiveness of industrial metallization processes.

Overall, the proposed rGO pre-coating method changes the surface conductivity of the substrates which leads to huge improvements for catalyst.

6.1.2 ABS-Pd for selective-area metallization on complex ABS structure

This report proposed a method to achieve selective-area metallization on complex ABS structures through the use of additive manufacturing technology followed by electroless deposition. The advantages of this proposed method for electroless deposition can be summarized as follows:

- The additive manufacturing technology can be used in the direct fabrication of complex structures;
- The final metallization surface retains its excellent adhesion capability, even without the use of chromic acid which makes the overall process environmentally viable and timesaving through the elimination of complicated process steps;
- With the precise control of the activated area, accurate metallization on the selective region can be achieved.

Overall, the proposed ABS-Pd catalyzation process for three-dimensional ABS structures has been shown to achieve selected area metallization with good adhesion and accuracy.

6.1.3 Trigger electroless deposition on selected area with thermosensitive liposome

This report developed a new method for triggering electroless deposition of palladium on selected area with thermosensitive liposome. The advantages of this proposed method for electroless deposition can be summarized as follows:

- Heat triggered electroless Pd deposition in selected areas is achieved;
- The triggering temperature of electroless Pd deposition is only 40-50 °C, which is applicable for all the plastic substrates;
- The liposome-capped structure can be storage stable for at least 160 days;
- The proposed method can be applied to any surface regardless of exposed or internal surface.

Overall, the proposed separating reducing agents and metal ions with thermal sensitive liposome structures for triggering palladium deposition has been shown to achieve area-selective metallization on both exposed and internal surfaces with respectable accuracy.

6.2. Future work

Even though our current projects have presented significant advances in both the catalyst enhancement as well as applications of the electroless deposition method, there are still further areas of interest and improvements which can be made. The further research areas can be divided into three different groups, catalyst enhancement with the conductive layer, apply electroless deposition in the additive manufacturing technology, and area-selective palladium deposition with thermosensitive liposome.

For the palladium catalyst enhanced by rGO conductive layer, the areas of improvement/ research directions are listed and explained as follows:

- a. Varying the rGO coating methods. The enhancement of the Pd catalytic activity is limited by the conductivity and continuity of the rGO layers. The technology for reducing GO to rGO are chemical reduction method, thermal reduction method and multi-step method (chemical reduction followed by thermal reduction). Currently, we used a stepwise dipping method to coat a few layers of rGO on the plastic to help the electrons transferring on the substrates surface and the rGO coating showed sheet resistance of a few $M\Omega/sq$. As shown in Figure 44, a single layer of chemically reduced graphene oxide layer (PANI/rGO bilayers) showed

extremely high sheet resistance up to $10^8 \Omega/\text{sq}$ and continues 5 layers of rGO showed low sheet resistance at $5.3 \text{ k}\Omega/\text{sq}$. [131] Normally, the sheet resistance of GO is $400 \text{ M}\Omega/\text{sq}$ and few layers of chemical reduce GO film can only achieve the sheet resistance at $\sim 4 \text{ M}\Omega/\text{sq}$ due to the discontinuity and poor uniformity. [45]

Figure 44 The sheet resistances of the multilayer films S-1, S-2, and S-3 (different GO concentration samples) on fused silica versus the number of PANi/rGO bilayers (HI reduction). (Tested with a standard four-point probe method) [131]

In the thermal reduction methods, the heating temperature is the critical factor that affects the reduction on GO, as higher annealing temperature impels GO into higher stages of reduction with higher C/O ratio and higher electron conductivity, refer to Figure 6. [54] Thus, the formation of

rGO always requires very high working temperatures ($\sim 1000\text{ }^{\circ}\text{C}$) for a few hours, which is not applicable for most plastic substrates.[52]

It has been proved that the subsequent thermal annealing could further reduce the oxygen-containing groups on hydrazine reduced GO.[57]

Hector A. Becerril's group deposited up to 150 nm rGO film with sheet resistances as low as $10^2 - 10^3\text{ }\Omega/\text{sq}$ through repeated spin-coating for high-concentration GO solution followed by reduction with hydrazine vapor and thermal annealing ($400\text{ }^{\circ}\text{C}$).[66] Viet Hung Pham's group sprayed to coat the GO-hydrazine (synthesized GO with excessive hydrazine monohydrate) dispersion on the pre-heated substrate ($240\text{ }^{\circ}\text{C}$), the obtained rGO film showed a low sheet resistance of $2.2 \times 10^3\text{ }\Omega/\text{sq}$. [67]

Joon-Suk Oh's group self-assembled the GO layer on the polyethylene terephthalate film by evaporation, the following chemical and thermal reduction ($200\text{ }^{\circ}\text{C}$) converted the GO layer to rGO layer with sheet resistance as low as $100\text{ }\Omega/\text{sq}$. [69]

Compare with thermal reduction methods, the multi-steps reduction methods require heating the substrates to $200\text{-}400\text{ }^{\circ}\text{C}$, which is still acceptable for some non-conductive materials such as thermoset plastics and silicon oxide. If we induce the thermal annealing process after the chemical reduction process, the electric conductivity of the rGO layer could be further improved and the required palladium to initialize the electroless nickel plating could be further reduced.

- b. Induce stronger bonding between the conductive layer and the substrates.

There are four types of intermolecular forces from strongest to weakest: ionic forces, dipole forces, hydrogen bonding, and induced dipole force (including van der Waals force). So far, the bonding between the rGO conductive layer and different substrates is the relatively weak force - van der Waals force, and it could possibly result in the peeling of nickel coating layers after bending the substrates.

Non-thermal plasma (NTP) is widely used to create various chemically active agents (ions, electrons, photons and excited atoms, etc.) on the surface of polymeric materials.[132, 133] It has been proved that after exposing the polypropylene (PP) and polyethylene terephthalate (PET) under ultraviolet (UV) light for several hours, lots of oxygen-containing functional groups (including carboxyl groups $-(OH)C=O$) formed on the modified surface layer.[134] This negatively charged surface can easily be coated PANi-GO bilayer by immersing into the positively charged 30 polyaniline (PANi) solution and negative-charged GO solution (pH 3.5) sequentially for multi-cycles.[131, 135] The assembled five bilayers of PANi-rGO on PET substrate represented excellent adhesion and sheet resistance as low as $5.3 \text{ k}\Omega/\text{sq}$ after being exposed in $\text{HI}/\text{H}_2\text{O}$ vapor for chemical reduction.

Once we can induce negative charged functional groups on the surface of plastic substrates with non-thermal plasma, the ionic bonding between the substrate and PANi-rGO bilayers will result in respectable adhesion of the conductive layer on substrates.

Next, the areas of improvements for the palladium loaded ABS materials in the additive manufacturing are stated accordingly:

- a. Adding additives to the mixture materials. Currently, the Pd concentration in the mixture material is too high (6 wt%) for commercialization of this method, and only the exposed Pd element can work as the catalyst for surface metallization. According to our primary results, the addition of additives (TiO₂ powders) into the ABS & PdCl₂ mixture can initialize the electroless Ni plating even with lower Pd concentration (3 wt%).

As shown in the solvent compatibility test, the acetone solute ABS solidified when it contacted with DI water. So, we did an ABS's solubility test with different concentrations of acetone solvent (diluted with DI water) by observing the structure changes of tangled ABS fibers after washing different acetone solvents. As shown in the optical microscope observation (Figure 46), the tangled fibers started to dissolve and coagulate to thick shape when they were washed with a mixture solution with more than 30 vol% of acetones. When the acetone concentration in

the washing solution reached 60 vol%, most fibers dissolved and coagulated together. Overall, we got the conclusion that 20 vol% of acetone solvent can be used to wash the ABS structure without changing its microstructures and 60 vol% of acetone solvent would be used to etch the ABS surface.

Figure 45 Optical microscopy observation of tangled fibers after washing with different concentration of acetone solution.

In the additive test, we added different concentrations of TiO_2 powders into the ABS & PdCl_2 mixture (with 3 wt% of Pd), the solidified surfaces were washed with acetone solvent at different concentrations (diluted with 0.2 M NaH_2PO_2) and immersed into electroless nickel bath to observe the coating appearance. As shown in Figure 47, the solidified ABS & PdCl_2 (without additives) cannot initialize the electroless nickel plating when the weight ratio of Pd and ABS is 3:97. When the TiO_2 powders were added into the mixture as an additive, the solidified

mixtures with only 3 wt% of Pd were able to initialize the electroless nickel plating on the plastic surface.

Figure 46 electroless nickel plating appearances of solidified ABS & PdCl₂ with and without TiO₂ additives.

From our experiment result, adding TiO₂ powder as additives into the ABS & PdCl₂ mixture could help to initialize the electroless Ni deposition at comparable lower Pd concentration. In the literature's explanation, adding different additives (such as TiO₂, ZnO, Al₂O₃ powders) into the ABS plastics will change the physical properties as well as the microstructures of ABS plastics.[100] Since the palladium element and acetone solvent cannot penetrate the additive particles, the addition of additives will result in a new distribution of palladium elements and possibly reduce the required Pd amount to initialize the metallization.

- b. Inducing the conductive materials (such as carbon nanoparticles) into the ABS mixture. As we have proved in the first project, the conductive materials required less palladium to initialize the electroless nickel coating. The addition of conductive materials can increase the electric conductivity of the mixture, as a result, the Pd required in the mixture can be reduced.

In the case of triggering area-selectively Pd deposition, the possible enhancements are:

- a. Varying the lipids contents of the thermosensitive liposome. Currently, our thermosensitive liposome was prepared using DPPC, SA, and PEG-DSPE lipids with a molar ratio of 9/1/0.06. The SA lipid contains a negatively charged group and would attach the Pd^{2+} ions during the synthesizing of liposome structures (Lipo-Pd in this project), which results in the uncapped Pd^{2+} ions out of liposome structure even after washing for a few times.

To replace the SA lipids in current liposome structures, the neutral polymer can be considered. The poly(N-iso- prepropylacrylamide) [poly(NIPAM)] is one type of thermosensitive polymer that exhibits drastic water-solubility change at its low critical solution temperature (LCST) which is around 32 °C in aqueous solution.[136, 137] It has been

reported that the coating of this thermosensitive polymer on the DPPC liposome would not change the release behavior of the thermosensitive liposome.[138] Also, the polymer-coated liposome has a more intensive release near its phase transition temperature than the unmodified liposomes because the dehydrated polymer chains enhanced the destabilization of the structural defects in the DPPC membrane.[139] Thus, the NIPAN-coated DPPC liposomes exhibit a high thermal sensitivity at its transition temperature which is 42 °C.

As a result, by using this NIPAN-coated DPPC liposome to encapsulate the PdCl₂ chemical, we possible can achieve triggering electroless Pd deposition for some harsh conditions (like in cell culture) because the transition temperature of both Lipo-P and Lipo-Pd are close to 40 °C.

- b. Synthesizing the metal nanostructures with the Lipo-P and metal ions mixture. According to our previous research, we found that the thermosensitive liposome structures can separate the metal ions and reducing agents in the solution to prevent the directly electroless Pd deposition, but the Pd²⁺ ions could slowly diffuse into the liposome and react with reducing agents after mixing at room temperature for a long time (as shown in Figure 48). Also, the size of these synthesized metal nanoparticles fully depended on the liposome size, which could be controlled by varying the filter size during synthesizing.

Figure 47 TEM observation of A) Lipo-P & PdCl₂ mixture at room temperature; B) Lipo-P & PdCl₂ mixture at room temperature for 20 hours.

It required at least 10 hours for the metal ions (Ag⁺, Au⁺, Pd²⁺, Pt²⁺, etc.) to diffuse through liposome bilayers and react with reducing agents.[140] And the Pd (0) can be used as catalysts to initialize the reaction between Ni²⁺ ions, Cu²⁺ ions and reducing agents. It is possible to form some unique metal-alloy nanostructures (such as Pd-Ni, Pd-Cu core-shell structures) by adjusting the metal composition in the aqueous solution during the 10 hours mixing time (for example, we mix the Lipo-P with low concentration Pd²⁺ solution, then add Ni²⁺ or Cu²⁺ ions one hour after mixing). Since the transition temperature of DPPC liposome is around 40 °C, these metal nanostructures would not have obvious structure change during the thermally release.

Currently, most bimetallic nanoparticles are synthesizing with multistep, including chemical reduction, microemulsion techniques, sonochemical reactions, γ -ray irradiation and laser ablation.[141, 142] The reported one-

pot synthesizing methods always require refined handling, accurate control in time, temperature and string speed.[143] The synthesizing of bimetallic nanostructure with thermosensitive liposome is much simple (one step), and controllable (varying the liposome size to control the nanoparticle size).

- c. Using a laser as the thermal treatment method. So far, our thermal treatment method is transferring heat from the contact surface (such as water bath, direct heat). Direct shooting with laser can also generate heat locally at the target region with high accuracy. With the help of laser, we can achieve triggering electroless Pd deposition at intricate structures with high accuracy.
- d. Varying the reducing agents. Palladium ions can be reduced by lots of reducing agents such as hydrazine, sodium borohydride, ethylene glycol, and DMAB. So far, we used sodium hypophosphite as reducing agents in current research and it generates a weak acid environment that resulted in lipo-Pd structures broke in the solution of reducing agents. By testing the DPPC liposomes with different reducing agents (such as hydrazine, sodium borohydride, ethylene glycol and DMAB), we can get the liposome structures with different transition temperatures for more extensive applications.

Publication and patent

Publication:

Jing Zhan, Desmond CL Tan, Swaek Prakrititanon, Ming Lin, and Hirotaka Sato. "Extremely low catalyst loading for electroless deposition on a non-conductive surface by a treatment for reduced graphene oxide." *Chemical Communications* 53, no. 66 (2017): 9198-9201.

Jing Zhan, Takayuki Tamura, Gytong Ri, Zhenghao Ma, Shinjiro Umezu, Hirotaka, Sato "Metal hybrid plastic-3D-printer using catalyst-loaded filament and electroless plating" (Accepted by Additive Manufacturing).

Jing Zhan, Ming Lin, Satoshi Arai, Wan Wei Yang, Keitaro Sou, Hirotaka Sato. "Electrochemical System Encapsulated by Nanoscale Liposomes Enabling On-Demand Triggering of Electroless Deposition at Selected Areas." *ACS Appl. Nano Mater.* 2020, 3, 6, 5098–5106

Patent:

Hirotaka S. **Jing Z.** Chun Long Desmond T. "Plated object and method of forming the same cross-reference to related application". Worldwide applications WO2018186804A1. Issued Oct 11, 2018.

References

1. Daniel, E.D., C.D. Mee, and M.H. Clark, *Magnetic recording: the first 100 years*. 1999: John Wiley & Sons.
2. Parkinson, R., *Properties and applications of electroless nickel*. Nickel Development Institute, 1997. **37**.
3. Mueller, B., *Additive manufacturing technologies–Rapid prototyping to direct digital manufacturing*. Assembly Automation, 2012. **32**(2).
4. Ahn, S.-H., et al., *Anisotropic material properties of fused deposition modeling ABS*. Rapid prototyping journal, 2002. **8**(4): p. 248-257.
5. Perez, A.R.T., D.A. Roberson, and R.B. Wicker, *Fracture surface analysis of 3D-printed tensile specimens of novel ABS-based materials*. Journal of Failure Analysis and Prevention, 2014. **14**(3): p. 343-353.
6. Lewis, G.K. and E. Schlienger, *Practical considerations and capabilities for laser assisted direct metal deposition*. Materials & Design, 2000. **21**(4): p. 417-423.
7. Murr, L., *Metallurgy of additive manufacturing: Examples from electron beam melting*. Additive Manufacturing, 2015. **5**: p. 40-53.
8. Prashanth, K., et al., *Production of high strength Al85Nd8Ni5Co2 alloy by selective laser melting*. Additive Manufacturing, 2015. **6**: p. 1-5.
9. Lee, Y. and W. Zhang, *Modeling of heat transfer, fluid flow and solidification microstructure of nickel-base superalloy fabricated by laser powder bed fusion*. Additive Manufacturing, 2016. **12**: p. 178-188.
10. White, J., et al., *Environmentally benign metallization of material extrusion technology 3D printed acrylonitrile butadiene styrene parts using physical vapor deposition*. Additive Manufacturing, 2018. **22**: p. 279-285.
11. Rao, C.R. and D. Trivedi, *Chemical and electrochemical depositions of platinum group metals and their applications*. Coordination Chemistry Reviews, 2005. **249**(5-6): p. 613-631.
12. Schlesinger, M. and M. Paunovic, *Modern electroplating*. Vol. 55. 2011: John Wiley & Sons.
13. Kanani, N., *Electroplating: basic principles, processes and practice*. 2004: Elsevier.
14. Bangham, A.D. and R. Horne, *Negative staining of phospholipids and their structural modification by surface-active agents as observed in the electron microscope*. Journal of molecular biology, 1964. **8**(5): p. 660-IN10.
15. Brandow, S.L., et al., *The morphology of electroless Ni deposition on a colloidal Pd (II) catalyst*. Journal of the Electrochemical Society, 1995. **142**(7): p. 2233-2243.
16. Homma, T., et al., *Transmission electron microscopy study of electroless NiP and Cu films at initial deposition stage*. Journal of the Electrochemical Society, 1991. **138**(5): p. 1269-1274.

17. Hwang, B.J. and S.H. Lin, *Reaction mechanism of electroless deposition: observations of morphology evolution during nucleation and growth via tapping mode AFM*. Journal of The Electrochemical Society, 1995. **142**(11): p. 3749-3754.
18. Garcia, A., et al., *ABS polymer electroless plating through a one-step poly (acrylic acid) covalent grafting*. ACS applied materials & interfaces, 2010. **2**(4): p. 1177-1183.
19. Li, D., K. Goodwin, and C.-L. Yang, *Electroless copper deposition on aluminum-seeded ABS plastics*. Journal of Materials Science, 2008. **43**(22): p. 7121-7131.
20. Gui-xiang, W., et al., *Process of direct copper plating on ABS plastics*. Applied Surface Science, 2006. **253**(2): p. 480-484.
21. Khasim, D.I., N.N. Kumar, and R. Hussain, *Environmental contamination of chromium in agricultural and animal products near a chromate industry*. Bulletin of environmental contamination and toxicology, 1989. **43**(5): p. 742-746.
22. Nriagu, J.O. and E. Nieboer, *Chromium in the natural and human environments*. Vol. 20. 1988: John Wiley & Sons.
23. Hsu, P.-C., et al., *X-ray-induced Cu deposition and patterning on insulators at room temperature*. Journal of synchrotron radiation, 2015. **22**(6): p. 1524-1527.
24. Krulik, G., *Electroless plating of plastics*. Journal of Chemical Education, 1978. **55**(6): p. 361.
25. Marton, J. and M. Schlesinger, *The Nucleation, Growth, and Structure of Thin Ni-P Films*. Journal of The Electrochemical Society, 1968. **115**(1): p. 16-21.
26. Sudagar, J., J. Lian, and W. Sha, *Electroless nickel, alloy, composite and nano coatings—A critical review*. Journal of alloys and compounds, 2013. **571**: p. 183-204.
27. Severin, J., R.v. Hokke, and H. Van der Wel, *A study on changes in surface chemistry during the initial stages of electroless Ni (P) deposition on alumina*. Journal of the Electrochemical Society, 1993. **140**(3): p. 682-687.
28. Li, L., et al., *Pretreatment and deposition process of electroless Ni plating on polyimide film for electronic field applications*. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2015. **477**: p. 42-48.
29. Bae, S., et al., *Roll-to-roll production of 30-inch graphene films for transparent electrodes*. Nature nanotechnology, 2010. **5**(8): p. 574.
30. Lee, C.-L., et al., *Mesoporous, self-assembled palladium nanospheres: High efficiency activator for electroless nickel deposition*. Electrochemistry communications, 2006. **8**(5): p. 697-702.
31. Poon, K.C., et al., *Newly developed stepwise electroless deposition enables a remarkably facile synthesis of highly active and stable amorphous Pd*

- nanoparticle electrocatalysts for oxygen reduction reaction*. Journal of the American Chemical Society, 2014. **136**(14): p. 5217-5220.
32. Tan, D.C., et al., *A facile synthesized highly active Pd nanoparticle electrocatalyst for electroless deposition process*. RSC Advances, 2015. **5**(108): p. 88805-88808.
 33. Parkinson, R., *Properties and applications of electroless nickel*. Nickel Development Institute, 1997. **37**: p. 1-33.
 34. Osaka, T., *Electrodeposition of highly functional thin films for magnetic recording devices of the next century*. Electrochimica Acta, 2000. **45**(20): p. 3311-3321.
 35. Lee, S.-R., et al., *Development of a disposable glucose biosensor using electroless-plated Au/Ni/copper low electrical resistance electrodes*. Biosensors and Bioelectronics, 2008. **24**(3): p. 410-414.
 36. Yang, Y., et al., *Electroless metal plating of microtubules: Effect of microtubule-associated proteins*. Journal of materials science, 2004. **39**(6): p. 1927-1933.
 37. Paunovic, M., et al., *Electrochemically deposited diffusion barriers*. Journal of The Electrochemical Society, 1994. **141**(7): p. 1843-1850.
 38. Kohn, A., et al., *Evaluation of electroless deposited Co (W, P) thin films as diffusion barriers for copper metallization*. Microelectronic engineering, 2001. **55**(1-4): p. 297-303.
 39. Osaka, T., et al., *A soft magnetic CoNiFe film with high saturation magnetic flux density and low coercivity*. Nature, 1998. **392**(6678): p. 796.
 40. TAKAI, M., et al., *Magnetic properties of electroless-deposited NiFeB and electrodeposited NiFe alloy thin films*. IEICE transactions on electronics, 1995. **78**(11): p. 1530-1535.
 41. Shacham-Diamand, Y., et al., *Electroless processes for micro-and nanoelectronics*. Electrochimica Acta, 2003. **48**(20-22): p. 2987-2996.
 42. Novoselov, K., KS Novoselov, AK Geim, SV Morozov, D. Jiang, Y. Zhang, SV Dubonos, IV Grigorieva, and AA Firsov, *Science 306, 666 (2004)*. Science, 2004. **306**: p. 666.
 43. Boukhvalov, D.W. and M.I. Katsnelson, *Modeling of graphite oxide*. Journal of the American Chemical Society, 2008. **130**(32): p. 10697-10701.
 44. Eda, G. and M. Chhowalla, *Chemically derived graphene oxide: towards large-area thin-film electronics and optoelectronics*. Advanced materials, 2010. **22**(22): p. 2392-2415.
 45. Gilje, S., et al., *A chemical route to graphene for device applications*. Nano letters, 2007. **7**(11): p. 3394-3398.
 46. Pei, S. and H.-M. Cheng, *The reduction of graphene oxide*. Carbon, 2012. **50**(9): p. 3210-3228.
 47. Gómez-Navarro, C., et al., *Electronic transport properties of individual chemically reduced graphene oxide sheets*. Nano letters, 2007. **7**(11): p. 3499-3503.

48. Wang, X., et al., *A facile and cost-effective approach to the reduction of exfoliated graphite oxide using sodium hypophosphite under acidic conditions*. Journal of Materials Chemistry C, 2013. **1**(4): p. 690-694.
49. Shin, H.J., et al., *Efficient reduction of graphite oxide by sodium borohydride and its effect on electrical conductance*. Advanced Functional Materials, 2009. **19**(12): p. 1987-1992.
50. Ferná́ndez-Merino, M.J., et al., *Vitamin C is an ideal substitute for hydrazine in the reduction of graphene oxide suspensions*. The Journal of Physical Chemistry C, 2010. **114**(14): p. 6426-6432.
51. Moon, I.K., et al., *Reduced graphene oxide by chemical graphitization*. Nature communications, 2010. **1**: p. 73.
52. Schniepp, H.C., et al., *Functionalized single graphene sheets derived from splitting graphite oxide*. The Journal of Physical Chemistry B, 2006. **110**(17): p. 8535-8539.
53. Pan, D., et al., *Hydrothermal route for cutting graphene sheets into blue-luminescent graphene quantum dots*. Advanced materials, 2010. **22**(6): p. 734-738.
54. Mattevi, C., et al., *Evolution of electrical, chemical, and structural properties of transparent and conducting chemically derived graphene thin films*. Advanced Functional Materials, 2009. **19**(16): p. 2577-2583.
55. Zhu, Y., et al., *Microwave assisted exfoliation and reduction of graphite oxide for ultracapacitors*. Carbon, 2010. **48**(7): p. 2118-2122.
56. Cote, L.J., R. Cruz-Silva, and J. Huang, *Flash reduction and patterning of graphite oxide and its polymer composite*. Journal of the American Chemical Society, 2009. **131**(31): p. 11027-11032.
57. Chen, H., et al., *Mechanically Strong, Electrically Conductive, and Biocompatible Graphene Paper*. Advanced Materials, 2008. **20**(18): p. 3557-3561.
58. Eda, G., G. Fanchini, and M. Chhowalla, *Large-area ultrathin films of reduced graphene oxide as a transparent and flexible electronic material*. Nature nanotechnology, 2008. **3**(5): p. 270.
59. Hontoria-Lucas, C., et al., *Study of oxygen-containing groups in a series of graphite oxides: physical and chemical characterization*. Carbon, 1995. **33**(11): p. 1585-1592.
60. Szabó, T., et al., *Evolution of surface functional groups in a series of progressively oxidized graphite oxides*. Chemistry of materials, 2006. **18**(11): p. 2740-2749.
61. Zhao, J., et al., *Efficient preparation of large-area graphene oxide sheets for transparent conductive films*. ACS nano, 2010. **4**(9): p. 5245-5252.
62. Pei, S., et al., *Direct reduction of graphene oxide films into highly conductive and flexible graphene films by hydrohalic acids*. Carbon, 2010. **48**(15): p. 4466-4474.

63. Reina, A., et al., *Large area, few-layer graphene films on arbitrary substrates by chemical vapor deposition*. Nano letters, 2008. **9**(1): p. 30-35.
64. Sun, Z., et al., *Growth of graphene from solid carbon sources*. Nature, 2010. **468**(7323): p. 549.
65. Wang, X., L. Zhi, and K. Müllen, *Transparent, conductive graphene electrodes for dye-sensitized solar cells*. Nano letters, 2008. **8**(1): p. 323-327.
66. Becerril, H.A., et al., *Evaluation of solution-processed reduced graphene oxide films as transparent conductors*. ACS nano, 2008. **2**(3): p. 463-470.
67. Pham, V.H., et al., *Fast and simple fabrication of a large transparent chemically-converted graphene film by spray-coating*. Carbon, 2010. **48**(7): p. 1945-1951.
68. Wang, J., et al., *Rod-coating: towards large-area fabrication of uniform reduced graphene oxide films for flexible touch screens*. Advanced Materials, 2012. **24**(21): p. 2874-2878.
69. Oh, J.-S., et al., *Chemically-modified graphene sheets as an active layer for eco-friendly metal electroplating on plastic substrates*. Thin Solid Films, 2012. **521**: p. 270-274.
70. Guo, N. and M.C. Leu, *Additive manufacturing: technology, applications and research needs*. Frontiers of Mechanical Engineering, 2013. **8**(3): p. 215-243.
71. Upcraft, S. and R. Fletcher, *The rapid prototyping technologies*. Assembly Automation, 2003. **23**(4): p. 318-330.
72. Liu, B., X. Gong, and W.J. Chappell, *Applications of layer-by-layer polymer stereolithography for three-dimensional high-frequency components*. IEEE Transactions on microwave theory and techniques, 2004. **52**(11): p. 2567-2575.
73. Lipson, H. and M. Kurman, *Fabricated: The new world of 3D printing*. 2013: John Wiley & Sons.
74. Kim, Y.C., et al., *UV-curing kinetics and performance development of in situ curable 3D printing materials*. European Polymer Journal, 2017. **93**: p. 140-147.
75. Tolosa, I., et al., *Study of mechanical properties of AISI 316 stainless steel processed by "selective laser melting", following different manufacturing strategies*. The International Journal of Advanced Manufacturing Technology, 2010. **51**(5-8): p. 639-647.
76. Thomas, D., *The development of design rules for selective laser melting*. 2009, University of Wales.
77. Cormier, D., O. Harrysson, and H. West, *Characterization of H13 steel produced via electron beam melting*. Rapid prototyping journal, 2004. **10**(1): p. 35-41.

78. Otubo, J. and A.d.S. Antunes. *Characterization of 150mm in diameter NiTi SMA ingot produced by electron beam melting*. in *Materials Science Forum*. 2010. Trans Tech Publ.
79. Gasser, A., et al., *Laser Additive Manufacturing: Laser Metal Deposition (LMD) and Selective Laser Melting (SLM) in Turbo-Engine Applications*. Laser Technik Journal, 2010. **7**(2): p. 58-63.
80. Frazier, W.E., *Metal additive manufacturing: a review*. Journal of Materials Engineering and Performance, 2014. **23**(6): p. 1917-1928.
81. Agarwala, M., et al., *Direct selective laser sintering of metals*. Rapid Prototyping Journal, 1995. **1**(1): p. 26-36.
82. Agarwala, M., et al., *Post-processing of selective laser sintered metal parts*. Rapid Prototyping Journal, 1995. **1**(2): p. 36-44.
83. Allen, S.M. and E.M. Sachs, *Three-dimensional printing of metal parts for tooling and other applications*. Metals and Materials, 2000. **6**(6): p. 589-594.
84. Chiu, Y., Y. Liao, and C. Hou, *Automatic fabrication for bridged laminated object manufacturing (LOM) process*. Journal of Materials Processing Technology, 2003. **140**(1-3): p. 179-184.
85. Obikawa, T., M. Yoshino, and J. Shinozuka, *Sheet steel lamination for rapid manufacturing*. Journal of Materials Processing Technology, 1999. **89**: p. 171-176.
86. Klosterman, D., et al., *Interfacial characteristics of composites fabricated by laminated object manufacturing*. Composites Part A: Applied Science and Manufacturing, 1998. **29**(9-10): p. 1165-1174.
87. Suwanprateeb, J., et al., *Mechanical and in vitro performance of apatite-wollastonite glass ceramic reinforced hydroxyapatite composite fabricated by 3D-printing*. Journal of Materials Science: Materials in Medicine, 2009. **20**(6): p. 1281.
88. Bandyopadhyay, A., et al., *Application of laser engineered net shaping (LENS) to manufacture porous and functionally graded structures for load bearing implants*. Journal of Materials Science: Materials in Medicine, 2009. **20**(1): p. 29.
89. Leu, M.C., et al. *Freeze-form extrusion fabrication of composite structures*. in *Proceedings of the Solid Freeform Fabrication Symposium*. Austin, TX. 2011.
90. Beery, D., et al., *Shear and elongational viscosities of a thermotropic liquid crystalline polymer and its blend with polycarbonate*. Polymer Engineering & Science, 1992. **32**(1): p. 14-19.
91. Arostegui, A., et al., *Effect of dissolution-based recycling on the degradation and the mechanical properties of acrylonitrile-butadiene-styrene copolymer*. Polymer Degradation and Stability, 2006. **91**(11): p. 2768-2774.
92. McCaskie, J.E., *Plating on plastics: A survey of mechanisms for adhering metal films to plastic surfaces*. Metal finishing, 2006. **104**(5): p. 31-39.

93. Dong, L., R. Greco, and G. Orsello, *Polycarbonate/acrylonitrile-butadiene-styrene blends: 1. Complementary etching techniques for morphology observations*. Polymer, 1993. **34**(7): p. 1375-1382.
94. Choppala, G., N. Bolan, and J.H. Park, *Chromium contamination and its risk management in complex environmental settings*, in *Advances in Agronomy*. 2013, Elsevier. p. 129-172.
95. Nanda Kumar, N. and S. Rajendra Babu, *Physico chemical analysis of chromate polluted water resources from chromate chemical industry*. Poll. Res, 1984. **3**(1): p. 12-15.
96. Tang, X., et al., *Research on a new surface activation process for electroless plating on ABS plastic*. Materials Letters, 2008. **62**(6-7): p. 1089-1091.
97. Li, Z., et al., *An environment-friendly surface pretreatment of ABS resin prior to electroless plating*. Electrochemical and Solid-State Letters, 2009. **12**(12): p. D92-D95.
98. Bai, X., et al., *Effects of reprocessing on additives in ABS plastics, detected by gas chromatography/mass spectrometry*. Progress in Rubber Plastics and Recycling Technology, 2012. **28**(1): p. 1-14.
99. Seddon, R. and J.F. Harper. *Influence of flame retardant additives on the processing characteristics and physical properties of ABS*. in *Macromolecular Symposia*. 2001. Wiley Online Library.
100. Torrado, A.R., et al., *Characterizing the effect of additives to ABS on the mechanical property anisotropy of specimens fabricated by material extrusion 3D printing*. Additive Manufacturing, 2015. **6**: p. 16-29.
101. Shehata, T., et al., *Prolongation of residence time of liposome by surface-modification with mixture of hydrophilic polymers*. International journal of pharmaceutics, 2008. **359**(1-2): p. 272-279.
102. Atrooz, O., *Effects of alkylresorcinolic lipids obtained from acetonic extract of Jordanian wheat grains on liposome properties*. Int J Biol Chem, 2011. **5**(5): p. 314-321.
103. Gregoriadis, G., D. Lasic, and F. Martin, *Stealth Liposomes*. by Lasic D., Martin F., CRC Press, Boca Raton, 1995: p. 7-12.
104. Safinya, C., K. Ewert, and C. Leal, *Cationic liposome-nucleic acid complexes: liquid crystal phases with applications in gene therapy*. Liquid crystals, 2011. **38**(11-12): p. 1715-1723.
105. Kubitschke, J., S. Javor, and J. Rebek, *Deep cavitand vesicles-multicompartmental hosts*. Chemical Communications, 2012. **48**(74): p. 9251-9253.
106. Safinya, C.R. and K.K. Ewert, *Materials chemistry: liposomes derived from molecular vases*. Nature, 2012. **489**(7416): p. 372.
107. Sato, K., *Crystallization behaviour of fats and lipids—a review*. Chemical engineering science, 2001. **56**(7): p. 2255-2265.

108. Jones, M.E., et al., *Comparison of the abilities of synthetic and platelet-derived membranes to enhance thrombin formation*. Thrombosis research, 1985. **39**(6): p. 711-724.
109. Mansoori, M., et al., *A review on liposome*. IJARPB, 2012. **2**(4): p. 453-64.
110. Weinstein, J.N., et al., *Liposomes and local hyperthermia: selective delivery of methotrexate to heated tumors*. Science, 1979. **204**(4389): p. 188-191.
111. Maeda, M., A. Kumano, and D.A. Tirrell, *H⁺-induced release of contents of phosphatidylcholine vesicles bearing surface-bound polyelectrolyte chains*. Journal of the American Chemical Society, 1988. **110**(22): p. 7455-7459.
112. Frankel, D.A., et al., *Photoinduced destabilization of bilayer vesicles*. Journal of the American Chemical Society, 1989. **111**(26): p. 9262-9263.
113. Papahadjopoulos, D., et al., *Phase transitions in phospholipid vesicles fluorescence polarization and permeability measurements concerning the effect of temperature and cholesterol*. Biochimica et Biophysica Acta (BBA)-Biomembranes, 1973. **311**(3): p. 330-348.
114. Kono, K., *Thermosensitive polymer-modified liposomes*. Advanced drug delivery reviews, 2001. **53**(3): p. 307-319.
115. Matsubara, H., et al., *The observation of the nucleation and growth of electrolessly plated nickel deposited from different bath pH by TEM and QCM method*. Electrochimica Acta, 2006. **52**(2): p. 402-407.
116. Ashassi-Sorkhabi, H., M. Moradi-Haghighi, and M. Hosseini, *Effect of rare earth (Ce, La) compounds in the electroless bath on the plating rate, bath stability and microstructure of the nickel-phosphorus deposits*. Surface and Coatings Technology, 2008. **202**(9): p. 1615-1620.
117. Ashassi-Sorkhabi, H., A. Mirmohseni, and H. Harrafi, *Evaluation of initial deposition rate of electroless Ni-P layers by QCM method*. Electrochimica acta, 2005. **50**(28): p. 5526-5532.
118. Bard, A.J. and L.R. Faulkner, *Fundamentals and applications*. Electrochemical Methods, 2001. **2**: p. 482.
119. Lee, C.-L., Y.-L. Tsai, and C.-W. Chen, *Specific and mass activity of silver nanocube and nanoparticle-based catalysts for electroless copper deposition*. Electrochimica Acta, 2013. **104**: p. 185-190.
120. Barke, H.-D., A. Hazari, and S. Yitbarek, *Misconceptions in chemistry: Addressing perceptions in chemical education*. 2008: Springer Science & Business Media.
121. Tang, P., et al., *The microwave adsorption behavior and microwave-assisted heteroatoms doping of graphene-based nano-carbon materials*. Scientific reports, 2014. **4**: p. 5901.
122. Demir, M.M., et al., *Palladium nanoparticles by electrospinning from poly (acrylonitrile-co-acrylic acid) – PdCl₂ solutions. Relations between preparation conditions, particle size, and catalytic activity*. Macromolecules, 2004. **37**(5): p. 1787-1792.

123. Lu, Y., L. Xue, and F. Li, *Adhesion enhancement between electroless nickel and polyester fabric by a palladium-free process*. Applied Surface Science, 2011. **257**(7): p. 3135-3139.
124. Kubota, H., *Flow properties of ABS (acrylonitrile-butadiene-styrene) terpolymer*. Journal of Applied Polymer Science, 1975. **19**(8): p. 2299-2308.
125. Garg, A., A. Bhattacharya, and A. Batish, *On surface finish and dimensional accuracy of FDM parts after cold vapor treatment*. Materials and Manufacturing Processes, 2016. **31**(4): p. 522-529.
126. Arai, S., et al., *Thermosensitive nanoplateforms for photothermal release of cargo from liposomes under intracellular temperature monitoring*. RSC Advances, 2015. **5**(113): p. 93530-93538.
127. Rastogi, L., S.R. Beedu, and A.J. Kora, *Facile synthesis of palladium nanocatalyst using gum kondagogu (Cochlospermum gossypium): a natural biopolymer*. IET nanobiotechnology, 2015. **9**(6): p. 362-367.
128. Sułkowski, W., et al., *The influence of temperature, cholesterol content and pH on liposome stability*. Journal of Molecular Structure, 2005. **744**: p. 737-747.
129. Shacham-Diamand, Y., et al., *30 years of electroless plating for semiconductor and polymer micro-systems*. Microelectronic Engineering, 2015. **132**: p. 35-45.
130. Mandich, N., *The evolution of a process: Fifty years of electroless nickel*. Metal finishing, 1992. **90**(5): p. 25-27.
131. Sarker, A.K. and J. Hong, *Layer-by-Layer Self-Assembled Multilayer Films Composed of Graphene/Polyaniline Bilayers: High-Energy Electrode Materials for Supercapacitors*. Langmuir, 2012. **28**(34): p. 12637-12646.
132. Kuvaldina, E. and D. Shutov, *Kinetic characteristics of the interaction of oxygen atoms with certain polymers*. Surface Engineering and Applied Electrochemistry, 2007. **43**: p. 94-99.
133. Dorai, R. and M.J. Kushner, *A model for plasma modification of polypropylene using atmospheric pressure discharges*. Journal of Physics D: Applied Physics, 2003. **36**(6): p. 666-685.
134. Akishev, Y.S., et al., *On Hydrophilicity Ageing of PP and PET Films Induced by Ultraviolet Radiation and Hydrogen Atoms*. The Open Plasma Physics Journal, 2013. **6**(1): p. 19-29.
135. Sarker, A.K. and J. Hong, *Flexible and Transparent Plastic Electrodes Composed of Reduced Graphene Oxide/Polyaniline Films for Supercapacitor Application*. Bulletin of The Korean Chemical Society, 2014. **35**(6): p. 1799-1805.
136. Schild, H.G. and D.A. Tirrell, *Microcalorimetric detection of lower critical solution temperatures in aqueous polymer solutions*. The Journal of Physical Chemistry, 1990. **94**(10): p. 4352-4356.

137. Heskins, M. and J.E. Guillet, *Solution Properties of Poly(N-isopropylacrylamide)*. Journal of Macromolecular Science, Part A, 1968. **2**(8): p. 1441-1455.
138. Kono, K., H. Hayashi, and T. Takagishi, *Temperature-sensitive liposomes: liposomes bearing poly (N-isopropylacrylamide)*. Journal of Controlled Release, 1994. **30**(1): p. 69-75.
139. Kim, J.-C., S.K. Bae, and J.-D. Kim, *Temperature-Sensitivity of Liposomal Lipid Bilayers Mixed with Poly(N-Isopropylacrylamide-co-acrylic Acid)*. The Journal of Biochemistry, 1997. **121**(1): p. 15-19.
140. Lee, J.-H., et al., *General and programmable synthesis of hybrid liposome/metal nanoparticles*. Science Advances, 2016. **2**(12): p. e1601838.
141. Lu, L., et al., *Fe@Ag core-shell nanoparticles with both sensitive plasmonic properties and tunable magnetism*. Materials Letters, 2010. **64**(15): p. 1732-1734.
142. Ghosh Chaudhuri, R. and S. Paria, *Core/Shell Nanoparticles: Classes, Properties, Synthesis Mechanisms, Characterization, and Applications*. Chemical Reviews, 2012. **112**(4): p. 2373-2433.
143. Carroll, K.J., et al., *One-Pot Aqueous Synthesis of Fe and Ag Core/Shell Nanoparticles*. Chemistry of Materials, 2010. **22**(23): p. 6291-6296.