CHAPTER II

SYNTHESIS OF PLATINUM NANOPARTICLES
VIA GREEN NANOTECHNOLOGY

2.1 Introduction

Platinum nanoparticles (Pt NPs) are attractive for research in nanotechnology because it displays the particularly properties, which suitable used in many applications, e.g., catalyst,[3, 4] fuel cell,[3, 4, 21] electro-optical device,[3, 4, 22] and magnetic device.[5, 22] It is well known that the properties of platinum metal depend on particle size, shape, compositions, and structure.[21] Therefore numerous of methods have been reported for preparation of Pt NPs with controllability of its morphologies.

2.1.1 Conventional methods for synthesis of Pt NPs

The main synthetic routes of Pt NPs are chemical reduction method, physical reduction method and photo reduction method. The chemical reduction methods involve the reduction of metal ion to metal nanoparticles by using the chemical reducing agent such as sodium borohydride ($NaBH_4$) and ethanol.[23, 24] The physical reduction method used non-chemical reagent as an electron source for the reduction of metal ion to metal nanoparticles such as laser and microwave.[25, 26] For the photo reduction method, the metal ion can be reduced to metal nanoparticles by exposure in light source such as UV-light.[26] However, in order to prepare metal nanoparticles with small size, narrow size distribution, and long-term stability, the protection agent/stabilizer, e.g., oxygen containing (sodium citrate),[27] nitrogen containing (poly(vinyl pyrrolidone)) and phosphorus containing (polyphosphate) have been used.[28]

2.1.1.1 Literature reviews

Authors/ Year	Precursor[a]	Surfactant / Reductant[b]	Condition[c]	Pt shape / size[d]	Application
Teranishi T. et al.[29] (1999)	$H_2PtCl_6\ 6H_2O$ (6 mM)	PVP/ alcohol	Reflux, 3 h	NPs 19-33 Å	Electrode
Chen D.-H. et al.[30] (1999)	$H_2PtCl_6\ 6H_2O$ (0.1 M)	Hydrazine (N_2H_5OH) in AOT/isooctane reverse micellar solutions	15-35°C, 1-2 h	NPs 7.4±1.5 nm	-
Kimura Y. et al.[31] (2003)	$H_2PtCl_6 \cdot 6H_2O$, $Na_2PtCl_6 \cdot 6HO$	PVP/ethanol and water-ethanol mixtures	25 MPa, 300°C	NPs 2.6±0.5 nm	-
Kim N. H. et al.[25] (2004)	Pt plate (1 mm thickness)	Laser ablation (YAG laser:1064 nm)	60 min	NPs 2 nm	Surface-enhanced Raman scattering
Herricks T. et al.[32] (2004)	$H_2PtCl_6 \cdot 6H_2O$ (80 mM)	PVP/ ethylene glycol and $NaNO_3$	160°C	NPs (3-5 nm), tetrahedra, octahedra	-

a: $H_2PtCl_6 \cdot 6H_2O$ = Hexachloroplatinic acid hexahydrate, $Na_2PtCl_6.6H_2O$ = Sodium hexachloroplatinate (IV) hydrate
b: PVP = Poly(N-vinyl-2-pyrrolidone)
c: AOT = Sodium di-2-ethylhexylsulfosuccinate
d: NPs = Nanoparticles

Authors/ Year	Precursor[a]	Surfactant / Reductant[b]	Condition	Pt shape / size[c]	Application
Zhang L. et al.[33] (2006)	$[PtCl_4]^{2-}$	$NaBH_4$/(PAA-b-PS)$_6$ in THFwith NaOH	Room temperature, overnight	NPs 2–4 nm	-
Liu Z. et al.[34] (2007)	$C_{10}H_{14}O_4Pt$	1,2-hexadecanediol and diphenylether/oleylamine	Room temperature to 110°C under N_2 atmosphere	NPs 3.5-11.5 nm	Fuel cell electrocatalysts
Shironita S. et al.[26] (2008)	H_2PtCl_6	UV-light irradiation (high-pressure Hg lamp)/framework of mesoporous silica	295 K, for 24 h	NPs 2 to 30 nm	-
Guo J. et al.[35] (2009)	H_2PtCl_6	Arc-discharge-in solution method	Voltage: 30A and 22–28 V,	NPs 5 nm	Catalyst
Chang S-H. et al.[36] (2011)	H_2PtCl_6	$NaBH_4$/PVP (hot-injection method)	CO-Argon gas	nanocluster (Pt/C NPs) 1.7-4.8 nm	Clectrocatalyst for methanol oxidation reaction

a: $C_{10}H_{14}O_4Pt$ = Platinum acetylacetonate, $H_2PtCl_6 \cdot 6H_2O$ = Hexachloroplatinic acid hexahydrate,
b: (PAA-b-PS)$_6$ = Poly(t-butyl acrylate), THF = Tetrahydrofuran
c: NPs = Nanoparticles

The reviews express the concern with the synthesis of platinum nanostructures using extreme conditions (e.g., high pressure, high temperature), hazardous reagent, organic solvent, and stabilizer. Presently, many researches tend to make environmental friendly method, green nanotechnology to design the reaction or choose the environmental benign for synthesis of Pt NPs.

2.1.2 Synthesis of platinum nanoparticles by green nanotechnology

2.1.2.1 Green chemistry principles

The 12 green chemistry principles are summarized in **Table 2.1**. Green chemistry principles are applied to design substance, product and process with the aims of reducing or preventing of the waste, hazardous chemical, and pollutant.

Table 2.1 12 green chemistry principles.[1, 37]

Green chemistry principles	Design to greener nanomaterial and production method
1. Prevent waste	design to prevent waste than to treat or clean up waste after it has been created
2. Atom economy	design to maximize all of the materials use in the synthetic process to final product
3. Less hazardous chemical synthesis	design to a little use or generate the hazardous substance
4. Designing safer chemicals	design the desire product with minimizing their toxicity
5. Safer solvents/reaction media	design to make a necessary use of substances (e.g., solvents)
6. Design for energy efficiency	design to minimize energy using.
7. Renewable feed stocks	design to used renewable raw material or feedstock
8. Reduce derivatives	design to minimize or avoid the using of unnecessary derivative (e.g., protection
9. Catalysis	design to use the catalytic reagent which as selective as possible
10. Design for degradation/ design for end of life	design to gain the product which non-toxic and environmentally benign
11. Real-time monitoring and process control	design to develop the real-time analysis for prevention of the formation of hazardous substances
12. Inherently safer chemistry	design to use the potential substance for minimizing of an accident

2.1.2.2 Green nanotechnology

Green nanotechnology is applied green chemistry principles to design material and process for the creation of nanomaterial and its applications, including to minimizing or preventing of the consumption or releasing of hazardous substances. [1] Now, it plays a prominent role in nanotechnology researches by employing the opportunity to design of the reagents (e.g., solvent, reducing agent, and stabilizing agent) and the reaction conditions. Many different nanostructures have been synthesized via green nanotechnology, especially by chemical reduction method which using green reagent such as Raveendran P. et al.[12] synthesis of silver nanoparticles by using β-D-glucose as a reducing agent and soluble starch as a protecting agent with aqueous solution, Huang H. et al. reported the synthesis of gold nanoparticles by using chitosan both as reducing/protecting agent,[38] Adlim M. et al. using methanol or $NaBH_4$ as a reducing agent and chitosan as a stabilizing agent for synthesis of platinum nanoparticles and palladium nanoparticles,[6] and Mallikarjuna N. N. using vitamin B_2 as a reducing agent for synthesis of platinum nanoparticles under solvent such as ethylene glycol, acetic acid, N-methylpyrrolidinone, isopropanol, and acetonitrile.[2]

Here in, it is of interests in the green synthesis of platinum nanostructure, therefore other works which using green reagents such as amino-terminated ionic liquid (1-(3-aminopropyl)-methylimidazolium bromide, IL-NH_2),[13] dextran,[39] β-D-glucose,[40] and aminodextran[41] are summarized in literature reviews section.

2.1.2.3 Literature reviews

Authors/ Year	Precursor[a]	Surfactant / Reductant[b]	Condition[c]	Pt shape / size[d]	Application
Adlim M. et al.[6] (2004)	K_2PtCl_4 (0.1 M)	Chitosan/ methanol, Chitosan/NaBH$_4$, Chitosan/N$_2$H$_4$	Reflux, 30min, Room temperature, Room temperature	NPs 1.9–2.2	Catalysis on cyclooctene hydrogenation
Mallikarjuna N. N. et al.[2] (2006)	Metal salt	Vitamin B$_2$ in organic media (i.e., EG, acetic acid, NMP, i-PrOH, acetone, MeCN, and water)	Room temperature	NPs (7-11 nm) NWs (10 nm) NRs (100-200 nm)	-
Chun A. L. et al.[42] (2006)	H_2PtCl_6	Cyanobacterial (*Plectonema boryanum*)	29°C, 60-80°C, 100°C, 180°C	NPs (30-300 nm), Bead like chain, Crystalline NPs, Dendrite or branch	-
Yang W. et al.[13] (2007)	K_2PtCl_4	amino dextran (in potassium acetate buffer)	80°C, 2 h	NPs 1-2.2 nm	Catalyst
Shin Y. et al.[40] (2009)	$H_2PtCl_6 \cdot H_2O$	β-D-glucose (in aqueous solution, pH 8)	Autoclave (100°C), 4-24 h	NPs (3.8 nm) NWs (∅ -3.8 nm, long 10-20 nm)	-

a: $H_2PtCl_6 \cdot 6H_2O$ = Hexachloroplatinic acid hexahydrate, K_2PtCl_4 = Potassium chloroplatinite
b: N_2H_4 = hydrazine, EG = ethylene glycol, NMP = *N*-methylpyrrolidinone, i-PrOH = isopropanol, MeCN = acetonotrile
c: AOT = Sodium di-2-ethylhexylsulfosuccinate
d: NPs = Nanoparticles, NWs = Nanowires, NRs = Nanorods

Authors/ Year	Precursor[a]	Surfactant / Reductant[b]	Condition[c]	Pt shape / size[b]	Application
Li F. et al.[41] (2009)	H_2PtCl_6	$NaBH_4$/1-(3-aminopropyl)3-methylimidazo lium bromide	Room temp, 30 min (pH adjust to 9)	NPs 2 nm	Electrocatalyst for dioxygen reduction and methanol oxidation
Yang W. et al.[39] (2009)	K_2PtCl_4	Amino dextran	80°C, 2 h	NWs 1.7-2.5 nm	Electrocatalyst for reduction of oxygen
Benaissi K. et al.[43] (2010)	H_2PtCl_6	Cellulose nanowhiskers (acid hydrolysis of cellulose)	Auto clave, Room temp-100°C, pressure ≤ 100 bar	NPs 5-30 nm	-
Engelbrekt C. et al.[44] (2011)	H_2PtCl_6	Glucose/starch (in phosephate, MES, ammonium acetate buffer)	85-100°C, 3-20 h	5.8-6 nm	electrochemically (reduction of H_2O_2 and oxidation of dihydrogen
Lin X. et al.[45] (2011)	H_2PtCl_6	Wood nanomaterials (disk-mill: 15 cycle-treatment)	Reflux 100°C, 16 h	NPs, < 10 nm	Catalyst for reduction of p-nitrophenol

a: $H_2PtCl_6 \cdot 6H_2O$ = Hexachloroplatinic acid hexahydrate
b: NPs = Nanoparticles, NWs = Nanowires

There are plenty of papers concerned with the synthesis of shape-controlled Platinum NPs. However, they required extreme conditions (e.g. high pressure, high temperature), extra reducing agent, added stabilizer, complicated apparatus and the size of generated particles are uncontrollable.

Therefore, the production of stable and well-defined shape with controllable size of metal nanoparticle with green synthesis method, the polysaccharide (i.e., starch, carbohydrate, and cellulose base material) is a renewable reagent which widely used as a protecting agent or stabilizer. For example, a starch was used as a stabilizer for synthesis of silver nanoparticles published in a few reports.[46, 47] In addition, some of the literatures reported the using of polysaccharides served both as reducing/stabilizing agent for synthesis of metal nanoparticles. For instance, soluble starch was used for synthesis and stabilization of silver nanoparticles, which the reaction carried out in autoclave at 15 psi, 121°C for 5 min.[48] Carboxymethyl cellulose which achieved from the alkaline and perborate treatment of cotton and hydroxypropyl cellulose prepared by etherification reaction with propylene oxide were served for synthesis and stabilization of silver nanoparticles.[49]

It has been reported that the reducing end group (aldehyde and α-hydroxy ketone) can be obtained from the degradation of polysaccharide under alkaline condition.[51–53] Soluble starch is polysaccharide which forms a linear polymer by the α-(1→4) linkages between D-glucose units (Scheme 2.1) which can be generated the reducing end group under alkaline degradation.[50] Moreover, the hydroxyl rich on the starch structure can provide the complexation of metal ion to prevent the aggregation or precipitation of metal particles.[40, 49] Although, the soluble starch have been served for synthesis and stabilization of Ag NPs, however, the reaction is carried out in strong condition, which involves high pressure (15 psi) and high temperature (121°C). In addition, the clarification of reduction reaction mechanism for using degraded products of soluble starch under alkaline condition serving as a reducing agent for the metal reduction has not been reported.
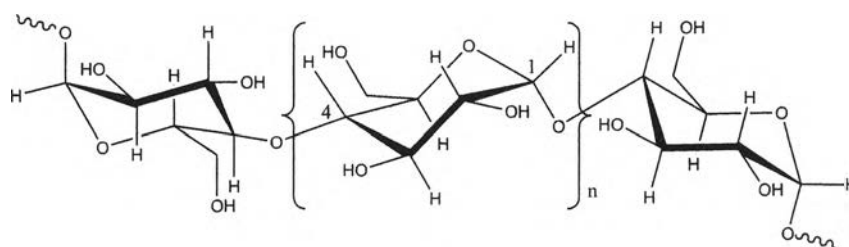
Scheme 2.1 Long chain polymer of D-Glucose unit of soluble starch structure.[48]

In this research, we reveal another green approach to synthesize Pt NPs at one step by using soluble starch as an efficient reducing and protecting agent. Our results indicated that the alkaline condition was the key step to yield the generated Pt NPs without aggregation. Only at optimized concentration of alkaline, soluble starch could be degraded to reducing species which is used to reduce platinum ion into Pt NPs and protecting species to stabilize the particles. To confirm these species, the degradation of starch under acidic/alkaline conditions was investigated by attenuated total reflection Fourier transform infrared (ATR FT-IR) spectroscopy. For the advantages of this work, the synthesis procedure is very simple and completely green with a rapid reaction time with no complex instruments or any toxic chemicals are involved.

2.2 The goal of the research

1. To develop a novel green technique for synthesis of Pt NPs with controllable size and shape via green nanotechnology.

2. To investigate the suitable conditions for preparation of Pt NPs which well-defined shape and size using soluble starch served both as reducing/stabilizing agents in aqueous solution.

2.3 Experimental section

2.3.1 Chemicals and materials

Soluble starch, sodium hydroxide (NaOH), and hydrochloric acid (HCl, 37% w/v) were purchased from Merck (Thailand). All chemicals were analytical grade and were used without any additional purification. De-ionized water was used as a solvent. All glassware and magnetic bars were cleaned with detergent and rinsed with de-ionized water followed by aqua regia, and finally rinsed again with de-ionized water before using.

2.3.2 Hexachloroplatinic acid (H_2PtCl_6) preparation

Platinum metal (99.99%) was purchased from a local retailer (Umicore precious metals (Thailand), Ltd). Platinum salt stock solution (100,000 ppm or 0.5 M platinum ion) in the form of hexachloroplatinic acid (H_2PtCl_6) was prepared by dissolving 10 g of cut platinum plates ($0.5 \times 0.5 \times 0.3$ cm^3) in aqua regia (with an excess hydrochloric acid) under a vigorous stirring and heating (80–100°C). After a prolong heating of ~8 h, all platinum plates were completely dissolved and the solution was further heated until dry. De-ionized water was added into the solution and the volume was adjusted to 100 mL. The concentrated platinum salt solution was employed for further investigation.

2.3.3 Synthesis of platinum nanoparticles (Pt NPs)

Pt NPs were synthesized by chemical reduction using soluble starch as both stabilizer and reducing agent. Briefly, a 20 mM platinum salt solution was prepared from hexachloroplatinic acid. The pH of the solution was adjusted to neutral with 1 M NaOH. Separately, 5 mL fractions of the solution was again individually pH adjusted to acidic, neutral, and alkaline conditions, respectively, with an equal volume of 2×10^{-6}–2 M HCl, water, and 2×10^{-6}–2 M NaOH. A 4% w/v soluble starch solution was prepared by dissolving 4 g of soluble starch in hot water (100 mL). After cooling down, 5 mL fractions of starch solution were mixed with an equal volume of 2×10^{-6}– 2 M HCl, water, and 2×10^{-6}–2 M NaOH. The platinum solutions and the starch solutions with the same acidic/alkaline treatment were heated at 100°C for 20 min before mixing under a vigorous stirring. The mixed solution was kept at the controlled

temperature for another 20 min before cooling down to room temperature. The total volume was kept constant at 20 mL by an addition of de-ionized water at the same temperature. In addition, time-dependent studies on the generation of Pt NPs were conducted at 1, 3, 5, 10, 15, 30, and 40 min incubation time.

2.3.4 Characterization

2.3.4.1 UV/vis spectroscopy (UV/vis)

The product with 5 mM Pt NPs content was investigated by UV/vis spectroscopy to ensure the formation of Pt NPs colloids. The absorption spectra of platinum ion and the colloidal Pt NPs were measured with a portable fiber optics UV/vis spectrometer (USB4000 Ocean Optics) equipped with a deuterium/halogen lamp light source (DH-2000, Micropack). Solution of platinum salt and Pt NPs colloid were diluted to 0.05 mM with de-ionized water before analysis.

2.3.4.2 Attenuated Total Reflection Fourier Transform Infrared spectroscopy (ATR FT-IR)

A Nicolet 6700 FT-IR spectrometer attached to the Continuµm infrared microscope equipped with a mercury-cadmium-telluride (MCT) detector and a built-in 15X Schwarzschild-Cassegrain infrared objective was employed for all infrared spectral acquisition. A slide-on Ge µATR accessory with a cone shape Ge IRE was employed as the sampling probe.[54] To acquire an infrared spectrum, starch solution and starch-stabilized Pt NPs colloid were dropped onto a glass slide and dried under an ambient condition. The dried film on the glass slide was mounted onto the sample stage beneath the infrared objective. The spectral acquisition at a defined position was conducted by raising the sample stage until the film on the glass slide contacted the tip of the Ge µIRE. The degree of contact was monitored and controlled by a built-in pressure sensor. All ATR spectra were collected at 4 cm^{-1} with 128 co-addition scans.

2.3.4.3 Transmission electron microscopy (TEM)

The colloidal Pt NPs were diluted to 0.25 mM and dropped onto a carbon-coated copper grid. The excess liquid was removed by a lint-free paper. The specimen was dried overnight in a desiccator. The morphology of Pt NPs was captured by a

transmission electron microscope (H-7650, Hitachi High-Technologies Corporation) operated at 100 kV accelerating voltage.

2.4 Results and discussion

2.4.1 Synthesis of platinum nanoparticles (Pt NPs)

Platinum solution (hexachloroplatinic acid, H_2PtCl_6) has an orange-yellow color with a strong absorption in UV/vis region at 263 nm, as shown in Figure 2.1.[39] Figures 2.1A and 2.1B show digital images of platinum salt in the presence of 1% w/v starch under various acid/alkaline treatments. The absorption at 263 nm shows a significant decrease with an increase of alkalinity. The change is more pronounced than that observed in the system without starch. The decrease of peak intensity is expected to be due to the changes of Pt complex ion. Pt salt is known to undergo hydrolysis from $[PtCl_6]^{2-}$ to $[PtCl_5(H_2O)]^-$ and $[PtCl_4(H_2O)_2]$ with a gradual increase in alkalinity.[55] An indication of the reduction of platinum ions platinum ionsto Pt NPs was observed as the color of the solution changed from yellow to black colloid at 0.01 M NaOH. The existence of Pt NPs was confirmed by the baseline shift of UV/vis spectra (Figures 2.1C) and TEM images, as shown in Figures 2.1D–2.1E. However, under stronger alkaline treatments (0.1 and 1 M), the Pt NPs aggregated and precipitated within a few minutes. This observed phenomenon suggests that the platinum ion could be reduced by *in situ* generated reducing species under an alkaline degradation of starch.

2.4.2 Influence of acidic-alkaline treatment for platinum complex

In order to gain an insight understanding on the influence of acidic-alkaline treatment for platinum complex, the platinum salt (H_2PtCl_6) adjusted at different alkalinity were performed. In our work, the initial H_2PtCl_6 (20 mM, pH ~1) was pH adjusted with NaOH until the solution became neutral (pH 7) and used as a stock solution. The UV/vis absorption at 260 nm, presenting to $[PtCl_5(H_2O)^{-1}]$ or $[PtCl_4(H_2O)_2]$ was observed.[55, 56] Under acidic treatment, the stock solution was adjusted to the difference pH by using HCl solution (10^{-5}–1 M). The UV/vis spectra reveal the peak maxima blue shift to 263 nm as the HCl concentration increased to 1

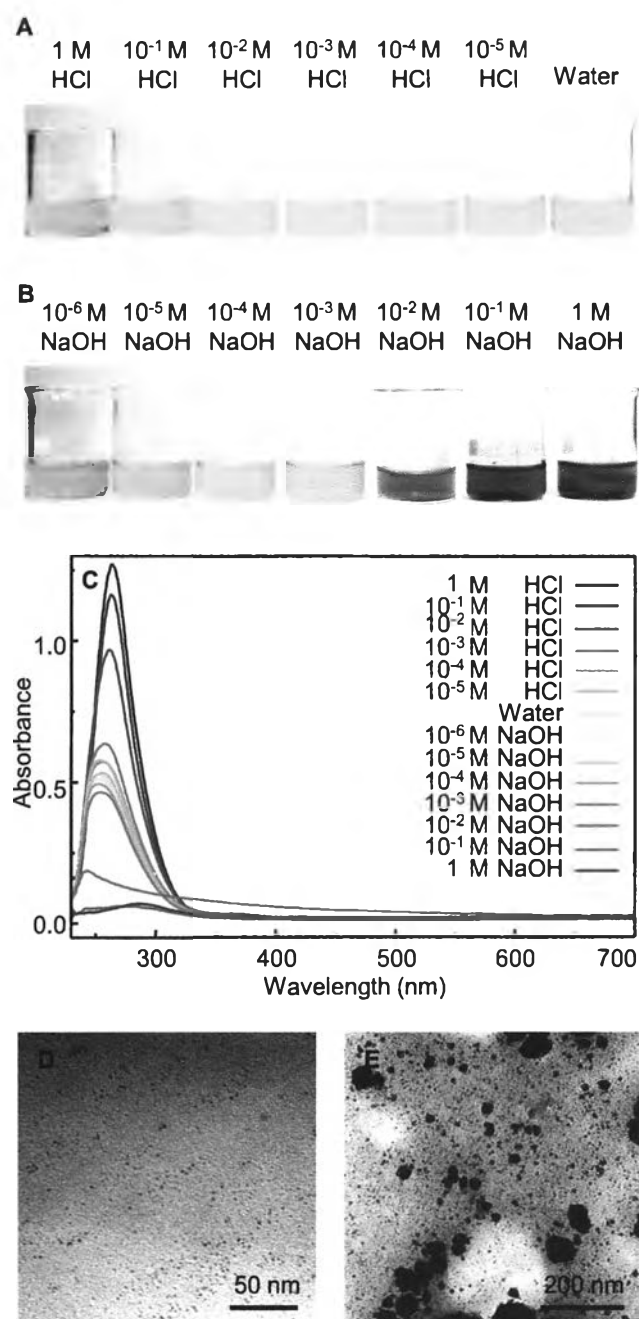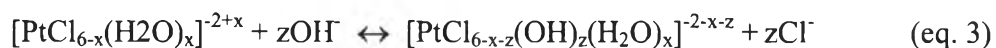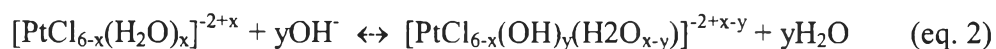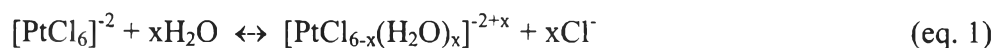M. These phenomena represented to the aquo ligand exchange chloride to form H_2PtCl_6.

Figure 2.1 (A) Digital image of platinum solution in acidic condition adjusted by addition of HCl ($1-10^{-5}$ M) and water, (B) digital image of platinum solution in alkaline condition, (C) UV/vis spectra of platinum solution at various acidic-alkaline conditions after reduction, (D) TEM image of platinum solution at 10^{-2} M, and (E) TEM image of platinum solution at 10^{-1} M.

Similarly with alkaline treatment, the platinum stock solutions were pH adjusted by using NaOH solution (10^{-6}–1 M). The UV/vis spectra showed the peak maxima red shift. These phenomena explained by the hydroxide ion ligand exchange of chloride and aquo ligand leading to the formation platinum hydroxo complex (i.e., $[Pt_4(OH)_2]^{-2}$). However, result in Figure 2.2 shows the peak maxima shift to nearly 263 nm while the peak intensity lowers than the initial solution instead of the appearance of the platinum aquo complex. It is due to the initial hydrolysis reaction of aquo ligand exchange (eq. 1) of chloride and aquo are fast and reversible (eq. 2–3) while the hydroxide ion ligand exchange of chloride and aquo ligand are relatively slow.[55] Spieker, W.A. et al.[55] reports that H_2PtCl_6 is a strong acid which undergoes rapid and extensive hydrolysis. The set of reactions are as follows:

$$[PtCl_6]^{-2} + xH_2O \leftrightarrow [PtCl_{6-x}(H_2O)_x]^{-2+x} + xCl^- \qquad \text{(eq. 1)}$$

$$[PtCl_{6-x}(H_2O)_x]^{-2+x} + yOH^- \leftrightarrow [PtCl_{6-x}(OH)_y(H2O_{x-y})]^{-2+x-y} + yH_2O \qquad \text{(eq. 2)}$$

$$[PtCl_{6-x}(H2O)_x]^{-2+x} + zOH^- \leftrightarrow [PtCl_{6-x-z}(OH)_z(H_2O)_x]^{-2-x-z} + zCl^- \qquad \text{(eq. 3)}$$

In our work, platinum nanoparticles were formed in the alkaline treatment when platinum ions and starch solution were adjusted with NaOH over 0.01 M. However, the precipitated Pt NPS were found when those solutions over 0.05 M NaOH. Hence, the proper alkaline condition for the formation of platinum nanoparticles in the range of 10^{-2} M to 10^{-1} M NaOH was investigated. Although, the UV/vis result in Figure 2.2 confirmed that the alkalinity had an influence on the platinum complex and Yu, Y.-T. et al. reported that the product of H_2O/Cl^- ligand exchange could be more easily reduced than $PtCl_6^{2-}$ for the synthesis of platinum nanocrystals by reduction with H_2.[57]

However, under the window of the observation (in the range of 10^{-2} M to 10^{-1} M NaOH) the UV/vis spectra no significantly changed both of peak maximum and intensity. It means that the initial platinum complex adjusted with above alkaline concentrations seem to be the same.
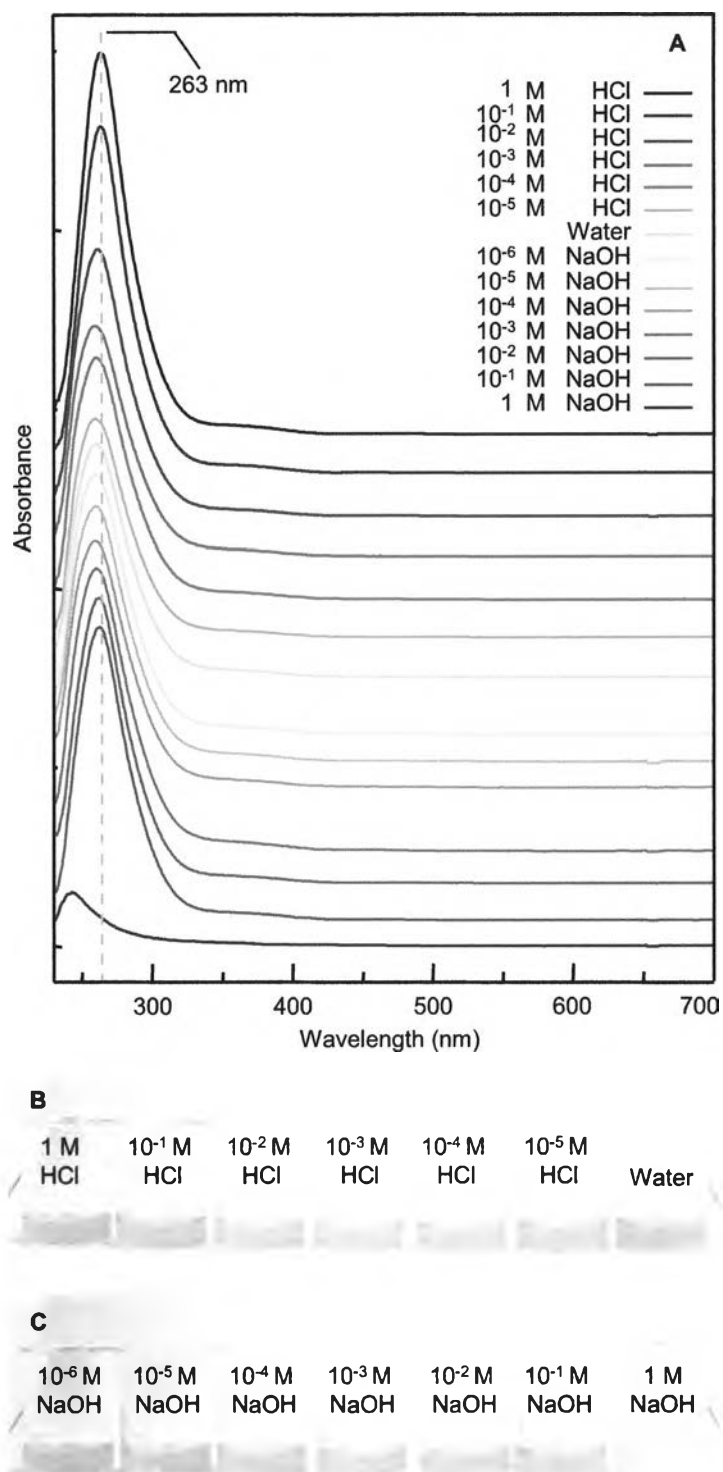
Figure 2.2 (A) UV/vis spectra of platinum at various acidic-alkaline conditions after reduction, (B) digital image of platinum solution in acidic condition adjusted by addition of HCl (1–10^{-5} M) and water, and (C) digital image of platinum solution in alkaline condition.

2.4.3 Investigation of starch degradation under and alkaline treatment

It is well-known that starch molecules are degraded and broken down to small organic acid (e.g., formic acid, acetic acid, glycolic acid, and lactic acid) under an alkaline treatment.[58] Since, the organic acid possesses no reducing potential, the degraded intermediates are expected to be responsible for the reduction of platinum ions to Pt NPs. Aldehyde and α-hydroxy ketone in alkaline media are well-known function as efficient reducing species. There are reports indicating that the degraded species of glucose and cellulose under alkaline condition contain aldehyde, ketone and acid moiety.[53–58] Figure 2.3 shows attenuated total reflection Fourier transform infrared (ATR FT-IR) spectra of products obtained after the acidic/alkaline treatments of soluble starch.
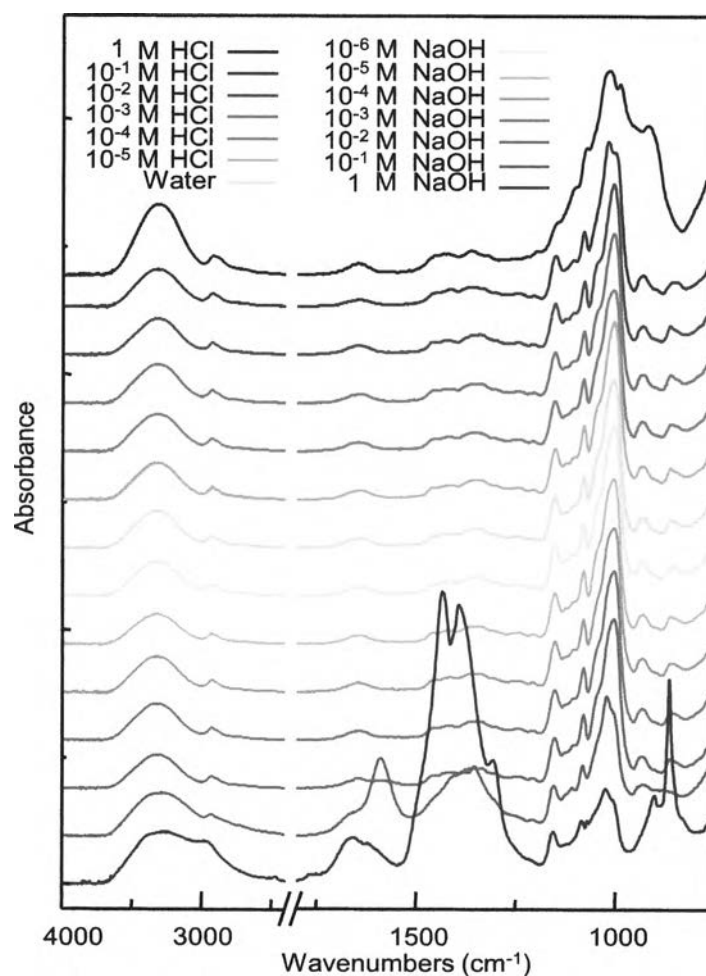
Figure 2.3 Normalized ATR FT-IR stack spectra of soluble starch at various acidic-alkaline conditions adjusted by HCl, water, and NaOH solutions.

The spectra show a significant break down of glycosidic linkage of starch bridge β C^1-O-C^4 in the region 1200–900 cm^{-1}(i.e., C-O, C-C stretching (1163 cm^{-1}), C-O-H bending (1094 cm^{-1}), C^1-H bending (1067 cm^{-1}), and skeleton mode vibration of α-1,4 glycosidic linkage, C-O-C (930 cm^{-1})) under alkalinity greater than 0.01 M as the absorption was significantly decreased.[53–58] In fact at 0.01 M a slight degradation was observed. At a greater alkalinity (0.1 M), an indication for the generation of the carboxylate group is observed at 1587 cm^{-1}.
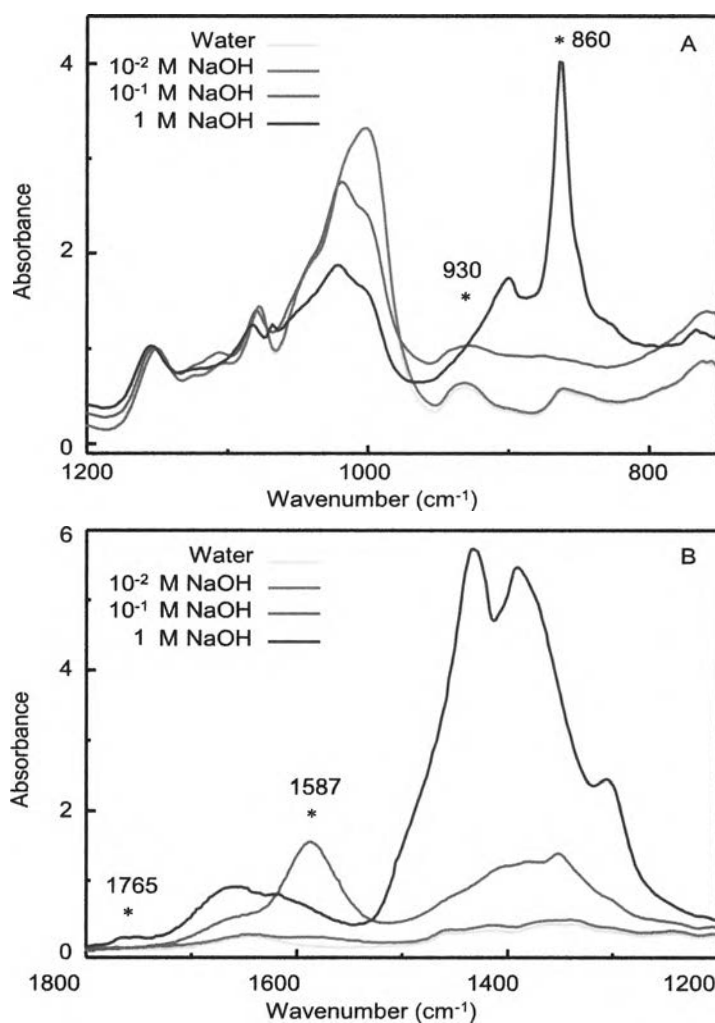
Figure 2.4 Normalized ATR FT-IR stack spectra of soluble starch at 10^{-2}–1 M NaOH in the region of (A) 1200–750 cm^{-1} and (B) 1800–1200 cm^{-1}.

At an extremely high alkaline condition (1 M), the extensive destruction of starch molecule and evolution of collective carbonyl group (e.g., carboxylic acid and aldehyde) were indicated by a development of a broad absorption band at 1770–1550

cm^{-1}, as shown in Figure 2.4.[62] The observed infrared spectra demonstrate the formation of carbonyl species after an alkaline treatment. These species are expected to be responsible for the formation of Pt NPs observed in Figure 2.1D-2.1E. The detail infrared band assignment is shown in Table 2.2.[53–58]

Table 2.2 Infrared bands assignment of starch.

Infrared band (cm^{-1})	Infrared band assignment
860	CH_2 deformation
930	Skeleton mode vibration of α-1,4 glycosidic linkage (C-O-C)
1200 - 900	Bridge β C^1-O-C^4 stretching
1500 - 1300	Vibration band related to the carbon and hydrogen atoms
1610 – 1550/1420-1300	COO^- stretching vibration (carboxylic acid salt)
1642	Water adsorbed in the amorphous region of starch
1765	C=O stretching vibration of carboxylic acid
3000 - 2800	C-H stretching
3600 - 3100	O-H stretching
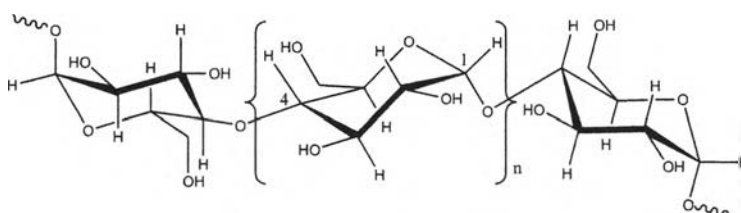
Long chain polymer of D-Glucose unit represent to soluble starch structure

The observed infrared spectral changes are in good agreement with the alkaline degradation of polysaccharide given by the Nef-Isbell mechanism.[51] In this work, soluble starch, a linear polymer of glucose units, was used as both the reducing and the stabilizing agent. The degradation of starch under alkaline treatment involves a β-elimination reaction followed by a series of rearrangement before liberation of a glucose unit. A simplified mechanism of starch degradation is shown in Scheme 2.2.[51–53, 58, 63, 64] The glucose unit undergoes further degradations before breaking down to smaller organic species containing carbonyl moiety. Previous works show that the final products of starch/polysaccharide degradation are small organic acid.[58] However, the intermediates involve the formation of organic species with reducing potential containing carbonyl species (i.e., aldehyde and α-

hydroxy ketone). A simplification of starch degradation products with different carbon number are shown in Scheme 2.3.[51–53, 58, 63, 64] Some of the intermediates have aldehyde or α-hydroxy ketone moiety which can function as powerful reducing species under an alkaline condition. There are at least 17 reported reducing species of different carbon number (as shown in Table 2.3). Aldehyde and α-hydroxy ketone can be efficient reducing specie under the employed alkaline condition (Scheme 2.4A). As a result, platinum ions could be reduced to Pt NPs as indicated by Scheme 2.4B.
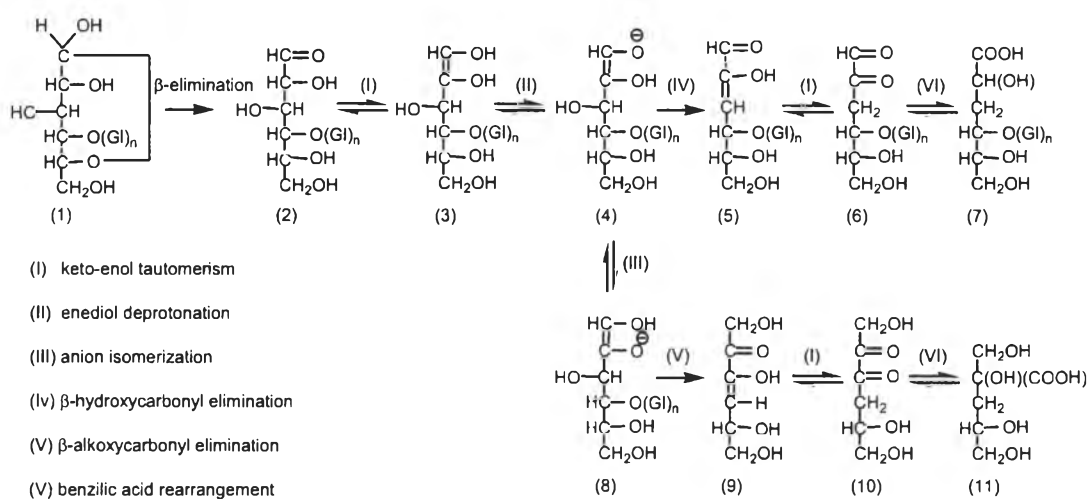
Scheme 2.2 The possible process of starch under alkaline degradation to generate reducing end groups adapted from Nef-Isbell mechanism.
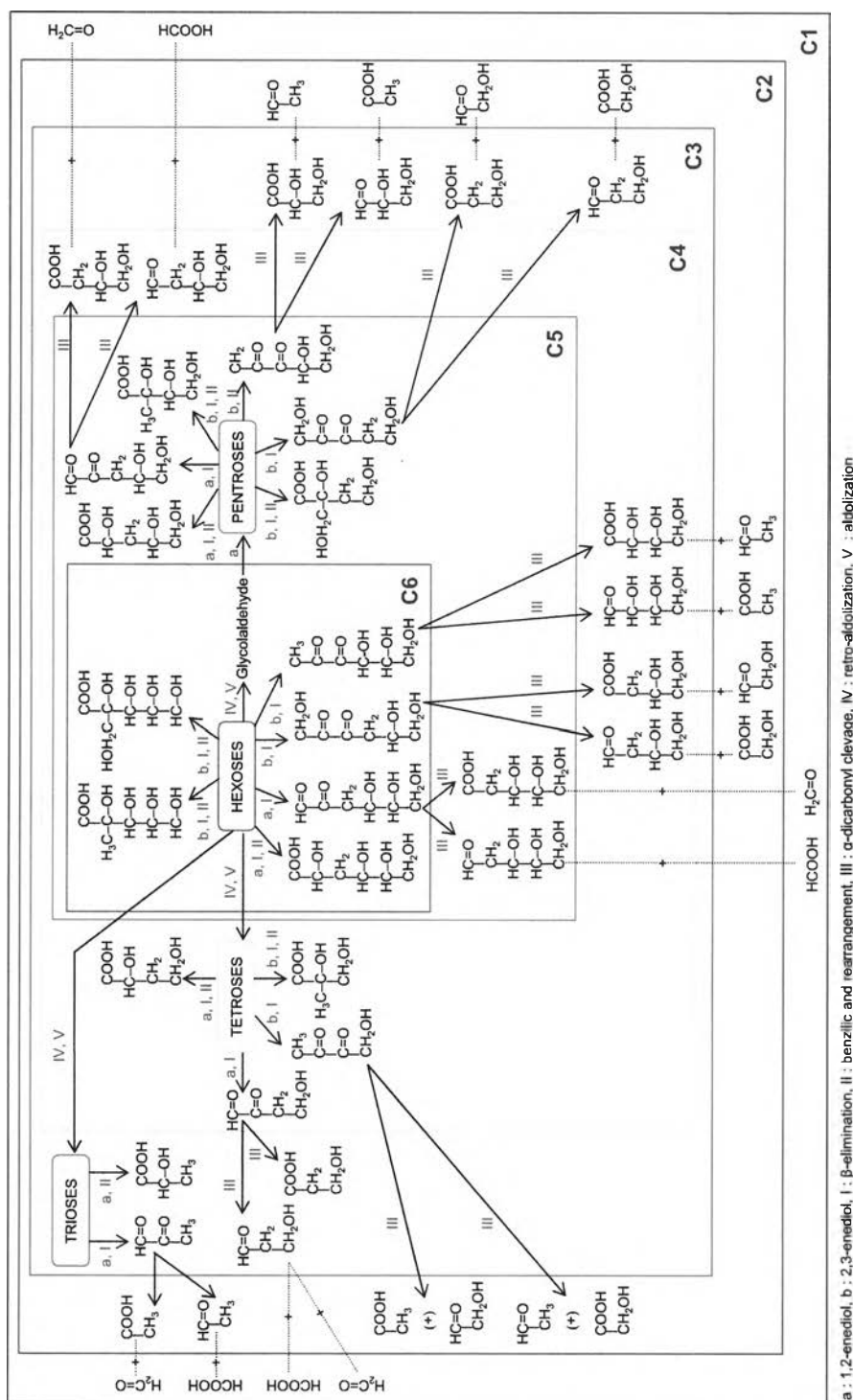
Scheme 2.3 The reaction pathways of monosaccharide under alkaline degradation. Classification of the degraded products based on carbon number was simplified (adapted from references 51–53, 58, 62, 63). Some of the degradation intermediates contain functional groups with reduction potential (i.e., aldehyde and α-hydroxy ketone moieties).
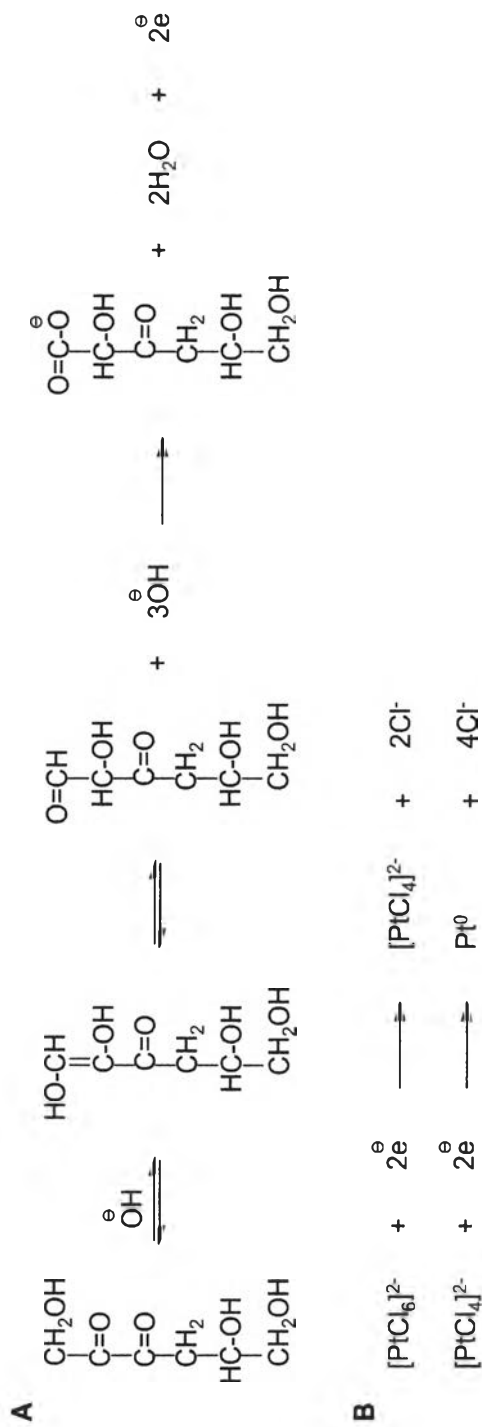
Scheme 2.4 (A) Example of reducing species (C_6) from starch degraded intermediates and (B) reduction of platinum ions into Pt NPs.

Table 2.3 The possible degradation products of starch in alkaline solution those act as reducing species. [51–53, 58, 62, 63]

Numbers of Carbon	Structure	Product name
6	HC=O C=O CH₂ HC–OH HC–OH CH₂OH	4,5,6-trihydroxy-2-oxohexanal
6	CH₂OH C=O C=O CH₂ HC–OH CH₂OH	1,5,6-trihydroxyhexane-2,3-dione
6	CH₃ C=O C=O HC–OH HC–OH CH₂OH	4,5,6-trihydroxyhexane-2,3-dione
5	HC=O C=O CH₂ HC–OH CH₂OH	4,5-dihydroxy-2-oxopentanal
5	CH₃ C=O C=O HC–OH CH₂OH	4,5-dihydroxypentane-2,3-dione
5	CH₂OH C=O C=O CH₂ CH₂OH	1,5-dihydroxypentane-2,3-dione
5	HC=O CH₂ HC–OH HC–OH CH₂OH	3,4,5-trihydroxypentanal

Numbers of Carbon	Structure	Product name
4	HC=O C=O CH₂ CH₂OH	4-hydroxy-2-oxobutanal
4	CH₃ C=O C=O CH₂OH	1-hydroxybutane-2,3-dione
4	HC=O CH₂ HC–OH CH₂OH	3,4-dihydroxybutanal
4	HC=O HC–OH HC–OH CH₂OH	2,3,4-trihydroxybutanal
3	HC=O HC–OH CH₂OH	2,3-dihydroxypropanal
3	HC=O CH₂ CH₂OH	3-hydroxypropanal
3	HC=O C=O CH₃	2-oxopropanal
2	HC=O CH₂OH	2-hydroxyacetaldehyde
2	HC=O CH₃	Acetaldehyde
1	H₂C=O	formaldehyde

2.4.4 Investigation of stabilization power of starch

According to the observed phenomena in Figure 2.1, an onset efficient reduction was observed at the alkaline concentration greater than 0.01 M. It is imperative to gain an in-depth understanding of the influences of alkalinity on the formation of reducing species and Pt NPs with NaOH concentration in the range of 0.01–0.1 M. The obtained Pt NPs were investigated by TEM as shown in Figure 2.5. Spherical Pt NPs with an average size of 2–4 nm were generated under all examined conditions. The particle size does not significantly change with increasing NaOH concentration (Figure 2.5A–2.5E). However, using NaOH solution with a concentration greater than 0.05 M, large aggregation of primary particles was observed. Those aggregated particles with domain size of 20–80 nm can be deaggregated into primary particles by ultrasonic (Figure 2.5D2 and 2.5E2). The observed phenomena suggested that small Pt NPs were formed and were stabilized at the early stage of the reduction process. Those primary particles do not grow bigger due to starch stabilization. The complete reduction of platinum ions to Pt NPs occurs before the aggregation. The aggregations of Pt NPs at high alkaline concentration (Figure 2.5C2–2.5E2) induce a precipitation within a few minutes. The prolonged reaction breaks down glycosidic linkages and diminishes of stabilization potential of starch at high alkaline concentration. The breakdowns of glycosidic linkage shorten the starch chain and trigger precipitation.

Based on the observed phenomena, the reducing and stabilizing potential of starch was investigated by the ATR FT-IR spectroscopy. Figure 2.6 shows overall changes associated with starch degradation under 0.01–0.1 M NaOH treatment. Increase of the carbonyl absorption at 1770–1550 cm^{-1} indicates the extensive decomposition of glucose unit which imply the increasing of reducing species. A rapid reduction was observed at high alkaline concentration. At the same time, a decrease in the absorption of glycosidic linkage (bridge β C^1-O-C^4 stretching) in the region 1200–900 cm^{-1} indicates the progressive break down of the starch skeleton. As a result, stabilization via steric hindrance was drastically decreased after the glycosidic linkage breakdown. The observed phenomena are in good agreement with previously reported works that the extensive number of hydroxyl groups present in soluble starch can facilitate the complexation of metal ion to molecular matrix.[12,

48] platinum ions were reduced on the starch chain and were stabilized. Steric hindrance imposed by starch molecules prevents Pt NPs aggregation and result in a small size (2–4 nm) and narrow size distribution. However, when starch chain was later damaged, the shorter chain cannot provide an adequate stabilization of Pt NPs. Particles aggregate without further fusion or particles grow as platinum ions were completely consumed.
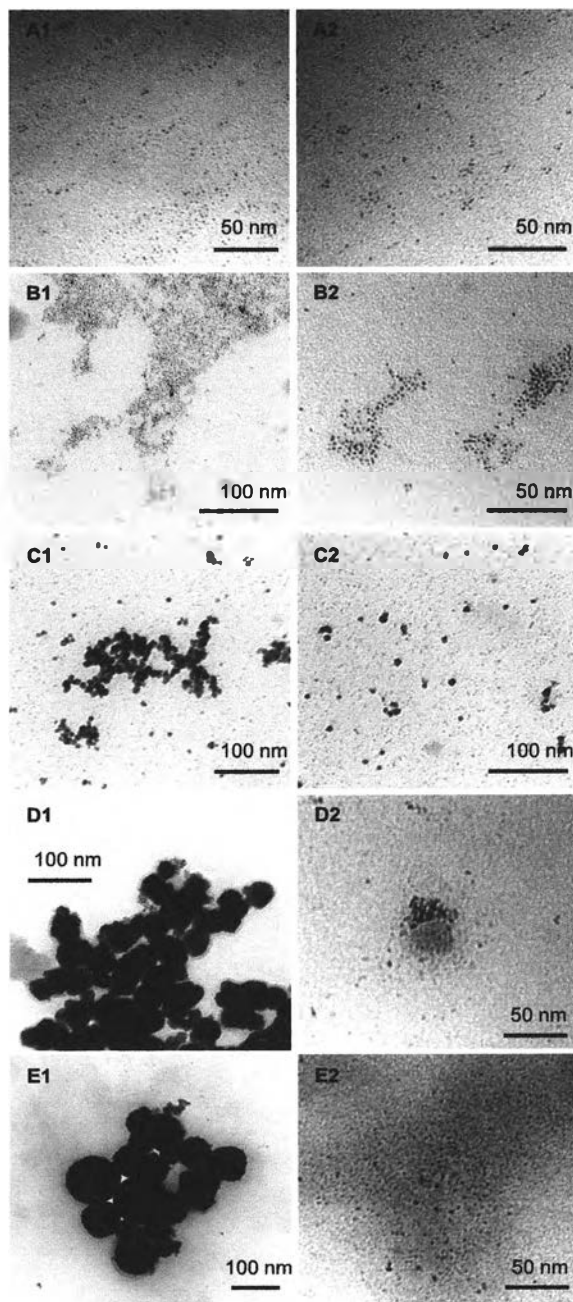

Figure 2.5 TEM images of synthesized Pt NPs at various concentrations of NaOH solution (A) 0.01, (B) 0.025, (C) 0.05, (D) 0.075, and (E) 0.1 M.
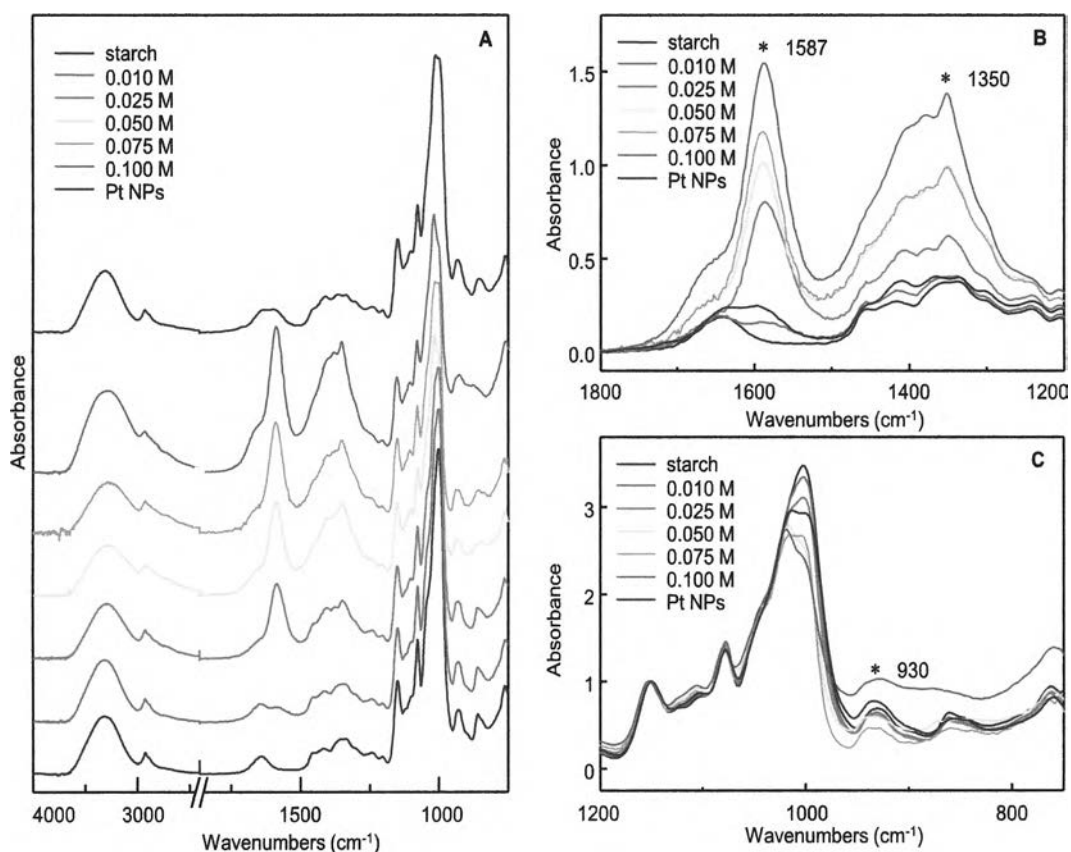
Figure 2.6 Normalized ATR FT-IR (A) stack spectra, (B) overlay spectra in the region of 1800–1200 cm^{-1}, and (C) overlay spectra in the region of 1200–750 cm^{-1} of soluble starch after a 20 min incubation with 0.01–0.1 M NaOH.

2.4.5 Efficiency of the *in situ* reducing species

In order to investigate the reducing efficiency of the *in situ* generated species, a time dependent UV/vis experiment was conducted and the results are shown in Figure 2.7. Since, the quantitative analysis of generated Pt NPs is commonly monitored through the baseline shift at 500 nm, a plot of time dependent baseline shift is shown in Figure 2.8.[24] The reduction profile show sigmoidal shape. An increasing absorbance in the first period corresponded to the seed nucleation, followed by a rapid particle growth (as suggested by LaMer[65] in colloidal growth mechanism). In our case, due to the high efficiency of the *in situ* generated species, the nucleation is very fast and the reaction was completed within 5 min. As a result, very small particles with narrow size distribution (2–4 nm) were obtained. The synthesized Pt NPs using appropriate (0.025 M) NaOH concentration can be stabilized in the solution for 3

months without any sign of aggregation. The complete reduction was confirmed by a NaBH₄ test, results are shown in Figure 2.9. A complete reduction of platinum ions is signified by an insignificant spectral change after an addition of NaBH₄.
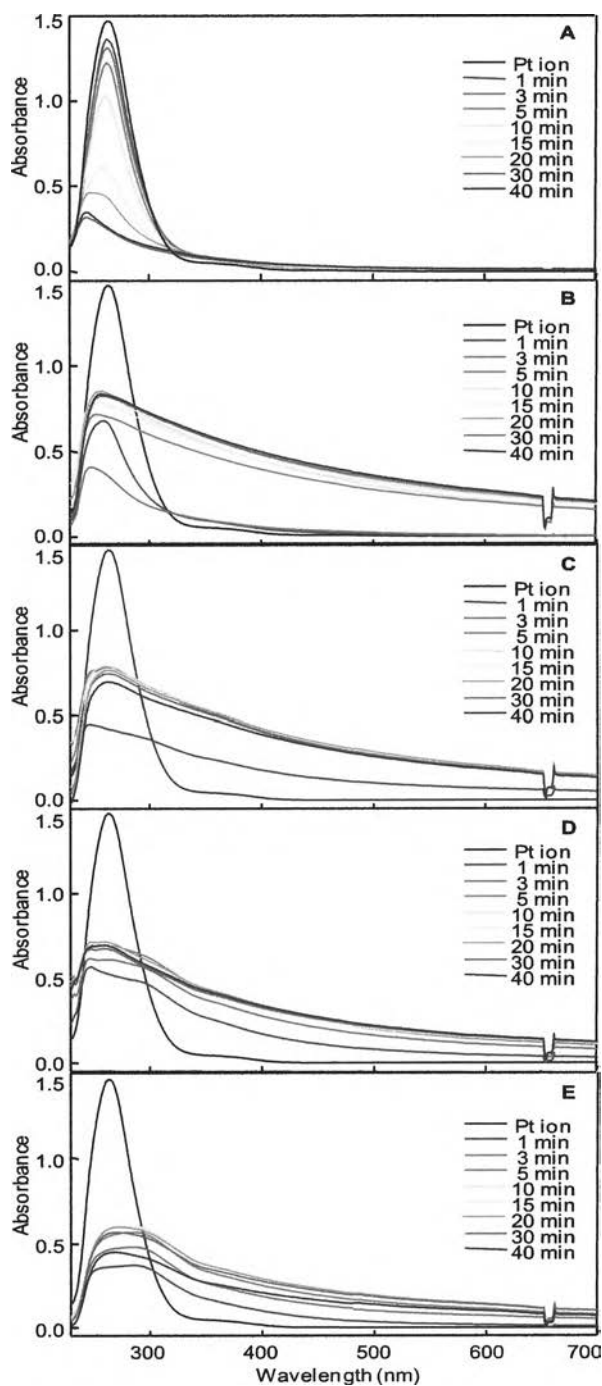

Figure 2.7 Time-resolved UV/vis spectra of synthesized platinum nanoparticles with (A) 0.01 M NaOH, (B) 0.025 M NaOH, (C) 0.50 M NaOH, (D) 0.075 NaOH, and (B) 0.10 NaOH.
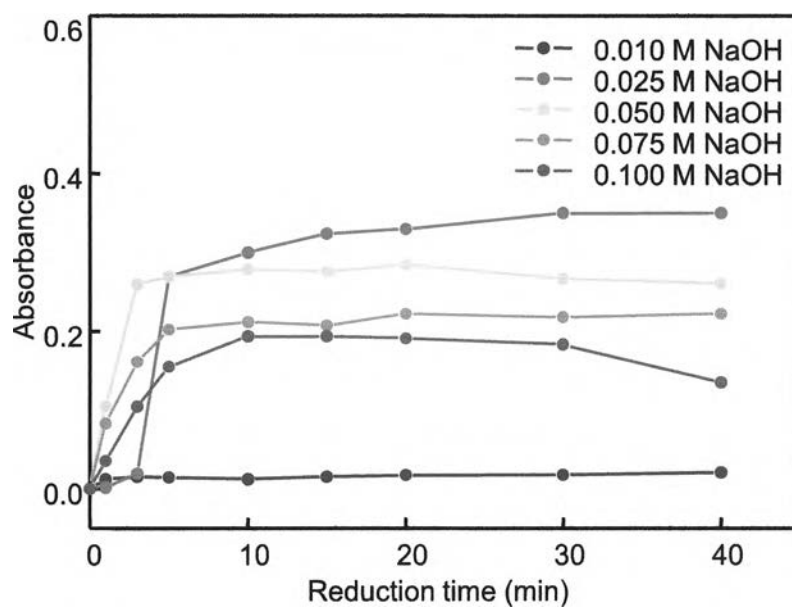
Figure 2.8 Time-dependent baseline shift at 500 nm of colloidal platinum nanoparticles after treatment under various alkaline conditions.
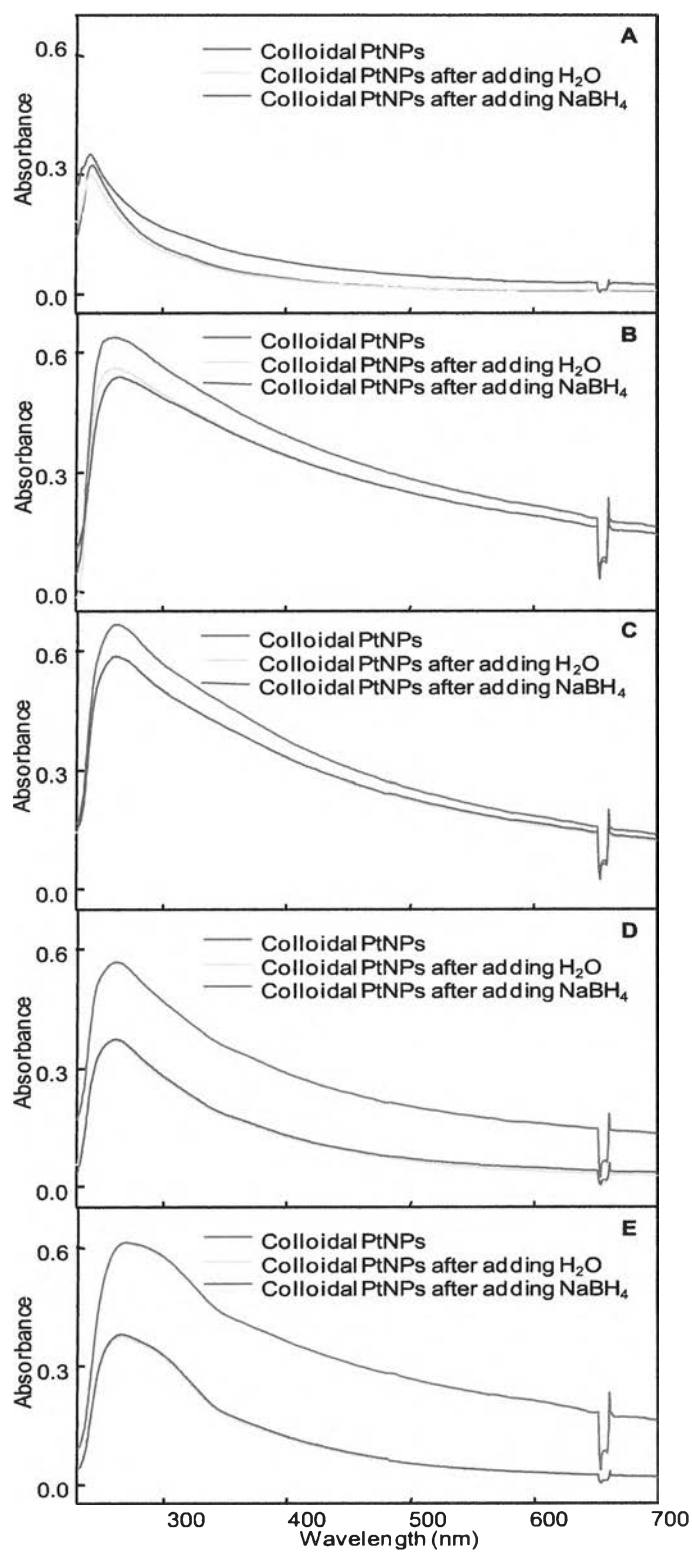
32

Figure 2.9 UV/vis spectra of colloidal Pt NPs at (A) 0.01 M NaOH, (B) 0.025 M NaOH, (C) 0.05 M NaOH, (D) 0.075 M NaOH, and (E) 0.10 M NaOH before and after checking the completely of the reduction with NaBH$_4$.

2.5 Conclusion

We have successfully synthesized Pt NPs via a "Green" synthesis approach using starch as the reducing and stabilizing agent. Uniform spherical Pt NPs (2–4 nm) were obtained. The reduction efficiency of the soluble starch was enhanced by an alkaline treatment. The active reducing species were expected to be the degraded intermediates containing aldehyde and α-hydroxy ketone moiety. The system is rapid and very efficient as all platinum ions (20 mM) were completely reduced to Pt NPs within 5 min. The obtained Pt NPs are expected to have a good catalytic activity. The ongoing glycerol oxidation by this green Pt NPs is being investigated.