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교육학석사 학위논문

**The mechanism of catalyzing reduction of
4-nitrophenol by quasimetallic nanoparticles
and the critical function of NaBH₄**

준금속 나노 입자의 촉매반응에 의한
4-니트로페놀 환원 반응에서 수소화붕소나트륨의
역할 및 메커니즘 분석

2015 년 8 월

서울대학교 대학원

과학교육과 화학전공

정 유 진

**The mechanism of catalyzing reduction of
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이 논문을 교육학석사 학위논문으로 제출함

2015 년 6 월

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Abstract

The mechanism of catalyzing reduction of 4-Nitrophenol by quasimetallic nanoparticles and the critical function of NaBH₄

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Catalytic reduction of environmental pollutant 4-nitrophenol (4NP) into useful 4-aminophenol (4AP) with sodium borohydride have been widely used. Noble metal nanoparticles have been highlighted for this catalytic reductions, but the mechanism was not fully revealed yet. Meanwhile the function of sodium borohydride has been ignored and regarded that excessive NaBH₄ has no specific function besides acting as an electron donor. Generally it is believed

quasimetallic nanoparticles and 4NP determine the reaction rate.

We investigated the mechanism and the crucial function of NaBH_4 decomposition via NMR, mass spectrometry, zeta-potential and UV-vis and, found that the reduction rate and induction time depended on the decomposition of NaBH_4 and detected possible reactive intermediate. We suggested a mechanism that quasimetallic nanoparticles accelerated NaBH_4 decomposition and the generated neutral intermediate adsorbed on the surface of nanoparticles easily without repulsion from the negative charged surface. We investigated that induction time was the period for the production of reactive intermediates from the hydrolysis of NaBH_4 and determined some factors affecting the reaction.

Our results not only solved the mechanism of 4NP reduction in the presence of catalytic quasimetallic nanoparticles under sodium borohydride, but also showed a basic guideline to the synthesis of quasimetallic nanoparticles as superior catalysts. These results suggested the useful reasoning of the relation between hydrogen generation and chemical reduction. It also has potential application in industries.

Key words: Quasimetallic nanoparticles, Catalysis, 4-Nitrophenol, Reduction, Mechanism, Sodium borohydride, Decomposition

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I. Introduction

1.1. Reasons to study 4NP reduction

1.1.1. Necessary of 4NP removal

Nitrophenols (NPs) are common environmental pollutants in many natural water and wastewater^{1, 2}. They are anthropogenic, toxic and inhibitory nature^{3, 4, 5} but extensively used in chemical industries and for the manufacture of pesticides, pharmaceutical and synthetic dyes^{6, 7, 8}. Among the NPs, 4-nitrophenol (4NP) is found in textile industry wastewater and agricultural waste as well as in rainwater in many locations due to tropospheric transformation of alkyl benzenes⁹. 4NP is notified as hazardous wastes and priority toxic pollutants by U.S. Environmental Protection Agency (EPA)^{10, 11}. Because 4NP can damage the central nervous system, liver, kidney and blood of animals and humans.^{12, 13} It was reported to damage mitochondria and inhibit energy metabolism in human and animal.^{14, 15} Therefore, removal of 4NP is necessary as an environmental issue. As the high consumption of 4NP in industries, environmentally and industrially, the research on the conversion of 4NP is very essential and

highlighted¹⁶.

1.1.2. Methods of 4NP removal

These concerns have led to stricter regulations on the wastewater containing 4NP and the further development of efficient treatment technologies to remove these hazardous pollutants^{17, 18}. Scientists have developed techniques for 4NP removal, for example microbial degradation, adsorption, photo-catalytic degradation, microwave-assisted catalytic oxidation, electrocoagulation, electro-Fenton method, and electrochemical treatment^{19, 20, 21, 22}. However, the traditional treatment of 4NP contaminated wastewater is very difficult and not viable due to their high stability and solubility of 4NP in water²³. Frequently those techniques need another organic solvent that contaminates again. Moreover long period of incubation is necessary for the microbial degradation of 4NP, becoming energy-consuming and time-consuming²⁴.

1.1.3. 4NP ‘reduction’ methods

1.1.3.1. Advantage of 4NP reduction and the product

Reduction treatment methods have been highlighted because there is no extraction or pre-treatment required²⁵. Moreover those methods can save the energy, avoid the organic solvents and be operated safely.

Unlike 4NP, the reduced product 4-aminophenol (4AP) is very useful in life science applications. 4AP can be used as antipyretic drugs, analgesic, photographic developer, anticorrosion lubricant and corrosion inhibitor^{26, 27, 28, 29}. Hence, the development of more appropriate processes for the reduction of 4NP to 4AP in aqueous solutions under mild conditions is important³⁰.

In addition, the reduction of 4-nitrophenol by NaBH₄ has been widely used as a model reaction since it is easy to monitor the reaction kinetics, and there are no by-products. This reaction is also valuable in the view of green chemistry since 4NP, one of the toxic substance in the wastewater, is converted into a commercially important substance, 4-aminophenol (4AP)³¹.

1.1.3.2. Kinetic study of 4NP reduction

Under acidic or neutral condition, 4-nitrophenol shows an absorption peak at 317 nm. Immediately after adding NaBH₄ aqueous solution, the absorption peak of 4NP red-shifted from 317 to 400 nm because of the generation of 4-

nitrophenolate ion that is the dominating species.

In the presence of a catalyst, the absorption peak at 400 nm decreases quickly. At the same time a new peak at 290 nm starts to increase corresponding to 4-aminophenol. At the same time the solution color of this reaction shows a significant change from yellow to colorless. The isosbestic peak at 317nm also proves the disappear of 4NP and the formation of 4AP as the product from 4NP reduction. We decided to measure the absorption peak of 4-nitrophenolate ions at 400nm because the peak at 400 nm is much stronger than that at 317 nm. Therefore we examined the progress and kinetics of the reaction by monitoring the change of absorbance at 400 nm^{32, 33}.

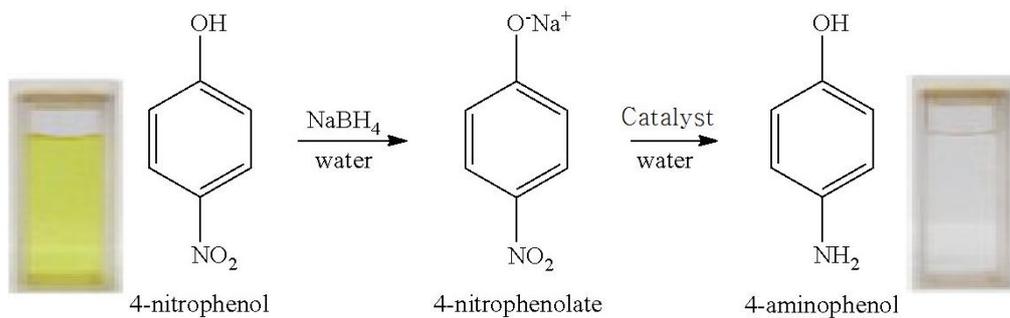


Figure 1. Reaction scheme of the conversion of 4-nitrophenol to 4-aminophenol by sodium borohydride.

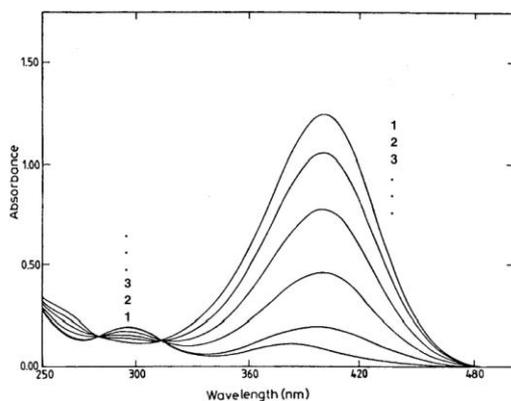


Figure2. UV-vis spectra of the reduction of 4-nitrophenol by sodium borohydride with catalyst³⁴.

1.2. Quasimetallic NPs as catalyst

1.2.1. General feature of quasimetallic NPs

Nanotechnology refers to the science and engineering of materials that have dimensions in the order of 100th of nm or less³⁵. As a result of the search for new materials, the quasimetallic nanoparticles have drawn intense attention. With the decreasing size of a materials, its properties change dramatically³⁶. The change in the physical properties of nanomaterials can be ascribed to their high surface-to-volume ratios of nanoparticles. Because of those unique properties, they have the excellent potential that can be used for solar energy conversion³⁷, optical data

storage, ultrafast data communication^{38, 39} and catalysts⁴⁰. Quasimetallic nanoparticles have been utilized in biotechnology⁴¹, preconcentration and magnetic separation of target analytes and vehicles for drug delivery^{42, 43}. Synthesis of nanoparticles with various functional groups opens even wider applications⁴⁴. There have been a lot of researches conducted about the synthesis of nanoparticles because all nanoparticles are not made equally and the size and shapes are all different, resulting in different efficacy⁴⁵.

Quasimetallic nanoparticles have been intensively highlighted during recent years due to their potential in use as catalysts^{46, 47, 48, 49}. Especially redox reactions catalyzed by nanoparticles have drawn much attention^{50, 51, 52, 53, 54}.

Among the quasimetallic nanoparticles, Ag is an excellent and promising catalyst because of its much lower cost, better selectivity and higher activity.⁵⁵

1.2.2. Quasimetallic NPs as catalyst

Quasimetallic nanoparticles have got intense attention during the recent years due to their potential use in catalysis⁵⁶. Their significant properties of excellent efficiency, high activity⁵⁷, and higher Fermi potential decreasing the reduction potential value draw scientists' attention to their application as active catalysts for various electron-transfer reactions⁵⁸.

Especially quasimetallic nanoparticles in solution can be used for the reduction and degradation of dyes like 4NP under mild condition^{59, 60, 61, 62, 63, 64}.

Particularly the reduction of 4NP to 4AP with NaBH₄ has been used as a model reaction to test the catalytic activity of quasimetallic nanoparticles⁶⁵. Such a reduction forms no by-product and fully reduced that clearly proved by isosbestic points in reacting mixtures spectra⁶⁶ and it is easy to monitor the degree of conversion via a simple and fast technique⁶⁷.

1.2.3. Factors determining the 4NP reduction

Most of the research in this field have focused on which nanoparticles have better ability in catalyzing 4NP reduction⁶⁸. Studies have suggested catalytic ability is determined by the 4NP concentration and surface area⁶⁹, consequently the efficient reduction is depend upon the nanoparticle size and stabilization⁷⁰.

Joseph et al.⁷¹ have investigated that the slope of ln[A] versus time plot for different amounts of catalyst shows the first order rate as Table 1. As increasing the concentration of catalyst, the reaction time decreases. These reactions exactly follow pseudo-first order kinetics. Furthermore, the relation between the rate constant and concentration of the catalyst is strictly linear.⁷²

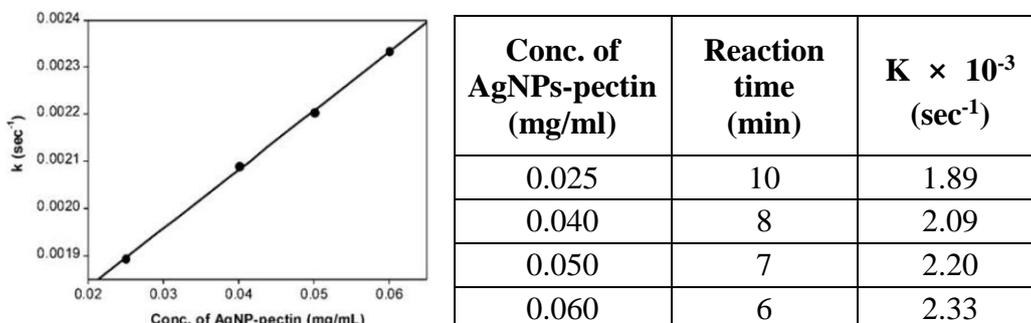


Figure 3. Plot of rate constant against amount of catalyst in 4NP reduction⁷³.

Table 1. Pseudo-first order rate constants of 4NP reduction by different amount of AgNPs-pectin catalyst⁷⁴.

1.3. Reported mechanisms of catalytic reduction of 4NP

1.3.1. Mechanism of catalytic reduction of 4NP

Even though 4NP reduction catalyzed by quasimetallic nanoparticle is highlighted, the catalytic reduction mechanism is not fully revealed yet. The most received mechanism is Langmuir-Hinshelwood model.

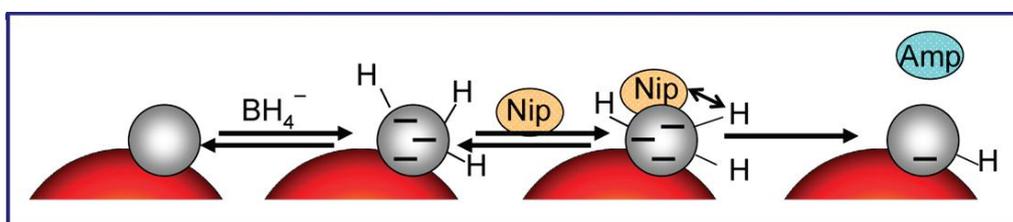


Figure 4. Mechanistic model (Langmuir-Hinshelwood mechanism)⁷⁵ of the

reduction of 4NP by borohydride with quasimetallic nanoparticles (gray spheres).

Zhang et al.⁷⁶ suggested that catalytic reduction takes place on the surface of the quasimetallic nanoparticles. They assume that firstly hydrogen species are transferred to the quasimetallic nanoparticles by borohydride so that the nanoparticles form the metal hydride. 4NP adsorbs on the metal surface as well. Here, 4NP and BH_4^- have strong interaction on the surface of quasimetallic nanoparticles at the same time. It implies that both reactants need to be adsorbed on the surface. This mechanistic studies indicate the adsorption of borohydride on metal nanoparticle is a fast and the reduction of absorbed 4NP to 4AP is the rate-determining step⁷⁷. The key point of an effective catalytic process is the strong interaction between the catalyst surface and substrates⁷⁸.

Esumi et al.⁷⁹ have concluded that the reaction is diffusion controlled by observing the catalytic activity of dendrimer-stabilized nanoparticles. Saha et al.⁸⁰ have demonstrated that the reduction of 4NP should proceed on the surface of the nanoparticles.

Meanwhile Khalavka et al.^{81, 82} recently investigated the Eley-Rideal mechanism in which only hydrogen needs to be adsorbed on the surface and reacts with the 4-nitrophenol from solution.

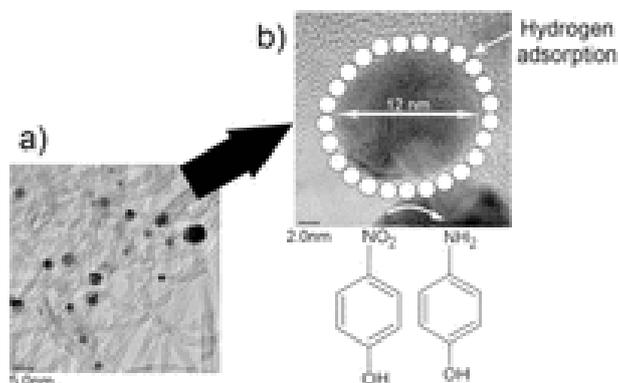


Figure 5. Mechanistic model (Eley-Rideal mechanism)⁸³ of the reduction of 4NP by borohydride with quasimetallic nanoparticles.

Generally it is believed that the catalyst reduces the kinetic barrier created by mutual repulsion between 4-nitrophenolate anion and BH_4^- anion. The metal nanoparticle make it easy to transfer electrons from BH_4^- to 4-nitrophenolate ion by giving them an appropriate reaction surface with lower activation energy caused by the catalytic activity of metal nanoparticle⁸⁴.

Most of the mechanisms have been done in the electro-chemistry field and they simply suggested catalysis brings down the kinetic barrier created by mutual repulsion between both negatively charged 4-nitrophenolate ion and BH_4^- ion⁸⁵. Even though reduction of 4NP under NaBH_4 is regarded as benchmarks for the catalytic activity of quasimetallic nanoparticles and good solution for contamination of 4NP, a comprehensive mechanism analysis of this reaction is still lacking⁸⁶.

Even the latest research just simply showed the mechanism that once the silver catalyst entered the reaction medium, there was a successive decrease in absorption peak at 400 nm. There have been no appropriate idea about the reaction medium yet so just used lump expression as 'the reaction medium'⁸⁷. Therefore a detailed mechanistic study of this catalyzed 4NP reduction is essential for understanding of the catalysis⁸⁸.

Therefore, we investigated the mechanism by assessing the function of each component and found that the reduction depends on the activity of NaBH₄. These results suggested the useful reasoning of catalyst synthesis for 4NP and it can be potential applied in industries. Moreover this study about 4NP reduction catalyzed by quasimetallic nanoparticles is good for both technology and environment. This reduction has been used as the parameter of general catalytic activity of the nanoparticles. It will help us to design and synthesize quasimetallic nanoparticles as good catalysts.

1.3.2 Properties of NaBH₄

The solubility of NaBH₄ in water is pretty high. At 25 °C, 55 g is soluble in 100 g of water.

The stability of sodium borohydride in water depends on the temperature and

pH. The hydrolysis reaction is accelerated under high temperature and low pH (Table 2).



It is alkaline, under 1.0 M concentration of NaBH₄, the pH of solution is 10.48±0.02 and under 0.01M concentration, the pH of solution is 9.56±0.02.⁸⁹

The hydrolysis reaction is pseudo-first order.⁹⁰ And the decomposition rate of NaBH₄ aqueous solution can be conveniently estimated using the below equation.

$$\text{Log}_{10}t_{1/2(\text{mins})} = \text{pH} - (0.034T - 1.92)^{91}$$

(t_{1/2} is the half-life in minutes, T is the temperature (kelvin scale))

Table 2. The relation between pH and the half-life of NaBH₄ in an aqueous solution at 25°C. At high pH there is obviously no decomposition and stable⁹².

pH	NaBH ₄ half life
4.0	0.0037 sec
5.0	0.037 sec
6.0	0.37 sec
7.0	3.7 sec
8.0	36.8 sec
9.0	6.1 mins
10.0	61.4 mins
11.0	10.2 hours
12.0	4.3 days
13.0	42.6days
14.0	426.2 days

Noble metals, cooper and nickel catalyze the decomposition. Some of the

borohydride will be consumed by reducing water. But it does not have any adverse effect on the desired reduction reaction, if sufficient borohydride is present. This is the main reason why excess of reduction agent is used in hydride reductions^{93, 94}.

The reaction of borohydride with metal nanoparticles and its decomposition with metal nanoparticles have been intensively highlighted because of the potential of borohydrides as the hydrogen generation in fuel cells⁹⁵.

1.3.3. Induction time

In 4NP reduction reaction, there is special attention to the induction time in which no 4NP reduction takes place and obviously no change in the absorbance at 400 nm. Many authors have observed the induction time with different carrier systems^{96, 97}. Some interpreted it as the time for the reactants diffusing to the nanoparticle surfaces⁹⁸. The rate of adsorption of 4NP is regarded as the main factor to the induction time⁹⁹. Xia et al.^{100,101} demonstrated that the larger catalyst surface area help the reactant to be activated faster so the induction time is also shorter. Meanwhile, Wunder et al. have observed the induction time is independent of the NaBH₄ concentration. They have suggested that the induction time is clearly not related to any reaction involving borohydride or the transfer of

a surface-hydrogen species to NPs¹⁰².

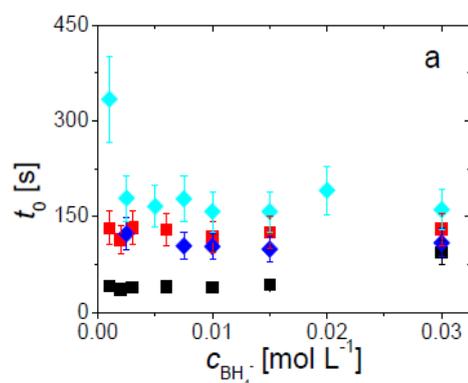


Figure 6. Induction time versus the concentration of BH_4^- and of 4NP. It shows that the induction period is independent of the concentration of BH_4^- . The squares show the data obtained for the Pt-NPs and circles for the Au-NPs.¹⁰³

Literatures suggest that the induction time can be generally regarded as a slow surface reconstruction of the nanoparticles related to the 4NP and the kinetic constant k ¹⁰⁴. The induction time only depends on the concentration of 4-nitrophenol on the surface of the nanoparticles and is clearly independent on the concentrations of borohydride¹⁰⁵.

However, the surface reconstruction is not revealed and researchers just assumed that it is related to rearrangement of bound surface atoms or a shift of single atoms¹⁰⁶. The induction time is still remain to be explained.

II. Experimental section

2.1. Chemicals

Chemicals. Silver nitrate (anhydrous, 99.999%), 4-nitrophenol ($\geq 99\%$), sodium borohydride (powder, $\geq 98.0\%$), (3-aminopropyl)trimethoxysilane, copper(II) sulfate pentahydrate, gold(III) chloride trihydrate, methyl alcohol (anhydrous, $\geq 99.8\%$), poly(acrylic acid) (=PA) (average Mn 1800, powder), poly(acrylic acid) (average Mn 8000, 45 wt. % in water), sodium citrate tribasic dihydrate ($\geq 99\%$), poly(ethyleneimine) solution (average Mn $\sim 1,200$, 50 wt. % in H₂O) and sodium carbonate (anhydrous) were purchased from Sigma-Aldrich Aldrich and used without further purification. Sulfuric acid was purchased from Kanto chemical. Co.. Zinc metal drop ($\geq 85.0\%$) was purchased from Samchun. Sodium Hydroxide (Powder) and sodium phosphate tribasic were purchased from Daejung chem.Co.. TEM grids (Carbon Grid Type-A, 300Mesh, Cu) were purchased from TedPella.

2.2. Preparation of samples

Preparation of stock solution

- i. Sodium borohydride stock solution for nanoparticle synthesis (1 mg/mL). For example, sodium borohydride (3 mg) was dissolved in DI water (3 mL).
- ii. Sodium borohydride stock solution for 4NP reduction (0.0192 g/200 μ l)
- iii. 4-Nitrophenol stock solution for 4NP reduction (0.0006 g/ml)
- iv. Silver stock solution for 4NP reduction (3×10^{-4} M).

Synthesis of PA-AgNDs. Briefly, AgNO_3 and 3-aminopropyl trimethoxysilane were mixed at a 3-aminopropyl trimethoxysilane / Ag^+ ratio of 2:1 based on methanol and left in the dark with stirring for 2~3 hours to make silane-silver stock solution. The silane-silver stock solution (65 μ l) and 1.1mM poly(acrylic acid) (average Mn 8000, 45 wt. % in water) stock solution (62.7 μ l) were mixed in DI water (2898.6 μ l) and left in the dark with stirring for 1 hour, followed by reducing with fresh sodium borohydride stock solution (34.7 μ l). The sample was used after an overnight incubation in the dark. The sample was then diluted in DI water to be 3×10^{-4} M.

Synthesis of PA-AgNPs. 3mM AgNO_3 solution (630 μ l) and poly(acrylic acid) (average Mn 1800, powder) (1.1 mg) were mixed in DI water (5370 μ l)

and left in the dark with stirring for 1 hour, followed by reducing with fresh sodium borohydride stock solution (210 μ l). The sample was used after an overnight incubation in the dark. The sample was then diluted in DI water to be 3×10^{-4} M.

Synthesis of citrate-AgNPs. The mixture of 1 mM AgNO₃ solution and 1 mM sodium citrate tribasic dihydrate were heated at 75°C in the dark with stirring for 10 mins. The sample was used after cooling down for 1hr in the dark. The sample was then diluted in DI water to be 3×10^{-4} M.

Synthesis of AgNPs. 2 mM sodium borohydride added drop by drop into 5mM AgNO₃ solution under stirring at a sodium borohydride /Ag⁺ volume ratio of 3:1. The sample was then diluted in DI water to be 3×10^{-4} M.

Synthesis of PA-AgNPs with different amount of PA. 3 mM AgNO₃ solution (630 μ l) and poly(acrylic acid) (average Mn 1800, powder) (0.4 mg) were mixed in DI water (5370 μ l) and left in the dark with stirring for 1 hour, followed by reducing with fresh sodium borohydride stock solution (210 μ l). The sample was incubated for overnight in the dark. And 0 mg, 0.7 mg, 2.9 mg and 10.6 mg

of PA is more added into each sample. The samples were used after 1hr incubation in the dark with stirring. The sample was then diluted in DI water to be 3×10^{-4} M.

Synthesis of AuNPs. 0.3 mM gold(III) chloride trihydrate solution is reduced by fresh sodium borohydride stock solution (22.7 μ l). The sample was then diluted in DI water to be 3×10^{-4} M.

Synthesis of PEI-AuNPs. 2.4 M polyethyleneimine solution (66.7 μ l) added drop by drop into pre-heated 0.34 mM gold(III) chloride trihydrate solution (6 ml) with stirring in the dark for 5mins at 75 °C. After cooling down for 25 mins in the dark, more polyethyleneimine solution (533.3 μ l) added into the solution and the sample was used after 1hr incubation in the dark with stirring. The sample was then diluted in DI water to be 3×10^{-4} M.

Synthesis of PA-AuNPs. Briefly, the mixture of 6.2 mM gold(III) chloride trihydrate solution and 6.2 mM Sodium citrate tribasic dihydrate were heated at 75°C in the dark with stirring for 10 mins to make citrate-AuNPs. After cooling down for 1hr in the dark, the mixture (210 μ l) of PA (0.0185 g) and sodium

carbonate (0.0311 g) in DI water (3 ml) added drop by drop into citrate-AuNPs (7 ml). The sample was used after an overnight incubation in the dark. The sample was then diluted in DI water to be 3×10^{-4} M.

2.3. Instruments

Instruments. TEM images were obtained on JEM-2100 (JEOL) transmission electron microscope. A Field-Emission Scanning Electron Microscope (JSM-6700F, JEOL) was used to obtain SEM images and EDS analysis. Absorbance spectra were obtained on UV-Visible spectrophotometer (S-4100, Sinco Co., LTD). Nuclear Magnetic Resonance spectra were obtained on Avance-500 (Bruker) with 500 MHz. Zeta potential was analyzed with a Zetasizer Nano2000 (Malvern Instruments, USA). HR-MS is analyzed with LC/MS System (Q Exactive, Thermo Scientific).

2.4. Methods

Comparison of catalytic ability. In the standard quartz cuvette, 1ml of DI water, 1 ml of 0.3 mM catalyst and 30 μ l of 4NP stock solution were taken.

Then, 50 μl of sodium borohydride stock solution for 4NP reduction is added into the mixture and close the lid of cuvette. Right after adding, the mixture is shaken once quickly. The absorption spectra were recorded on a SCINCO S-4100 Scan UV–visible spectrophotometer (Seoul, Korea) at room temperature.

The reduction can be visualized by the disappearance of the 400 nm peak of 4NP with the appearance of a new peak at 300 nm of 4AP. We observe the progress and kinetics of the reaction by recording the change of absorbance at 400 nm of the 4-nitrophenolate ions via UV-vis.

Comparison of hydrogen generation from samples. Briefly, 3 ml of catalyst is put in the flask with sidearm. About 50 μl of detergent is injected into the burette with 0.8 cm in diameter to make the thin bubble film at the specific height marked. Burette is connected with the sidearm of the flask with the hose sealed well by paraffin. Then, open the cock of burette and 50 μl of sodium borohydride stock solution for 4NP reduction is added into the catalyst and close the lid of flask with high vacuum grease. The bubble film went up as hydrogen gas is generated from decomposition of NaBH_4 in catalyst. The height of bubble film site is read and written once every 3 seconds.

Hydrogen bubbling. Zinc metal drop added into sulfuric acid ($\text{Zn} + \text{H}_2\text{SO}_3 \rightarrow$

ZnSO₄ + H₂) in the sealed flask with sidearm. It was connected to a syringe with paraffin sealing. Hydrogen gas generated from the chemical reaction came out to the sample through the syringe.

III. Results and discussion

3.1. Crucial function of NaBH₄ in the 4NP reduction

In many studies, it has been assumed and demonstrated that the 4NP reduction rate is independent of the concentration of NaBH₄ under an excess of NaBH₄¹⁰⁷,¹⁰⁸. Researchers have ignored the NaBH₄ factor when investigating the catalytic ability of quasimetallic nanoparticles in 4NP reduction because usually an excess NaBH₄ is used. However, we found that NaBH₄ was the crucial effect factor on catalyzing 4NP reduction.

Becoming a superior catalyst. Scientist have put a lot of efforts on finding better nanoparticles for the catalytic reduction of 4NP. Almost all the papers about catalyzing 4NP reduction are related to this. Good catalyst should have fast reaction rate and short time delay (IT).

However we found a more efficient methods to make better catalyst. It is decomposition of NaBH₄.

Surprisingly with decomposed NaBH₄, every quasimetally nanoparticles became very efficient catalyst. Silver ions were the weak catalyst which did not

finish the reaction fast and have a low reaction rate (Figure 7a). But if using NaBH_4 decomposed for 8min, even only silver ions alone could finish the reaction faster (Figure 7b) than PA-AgNPs that using fresh NaBH_4 . The latter was an excellent catalyst as shown in Figure 7a. Citrate-AgNPs did the same if using NaBH_4 decomposed for 8min. Thus decomposition of NaBH_4 can accelerate the catalytic reduction .

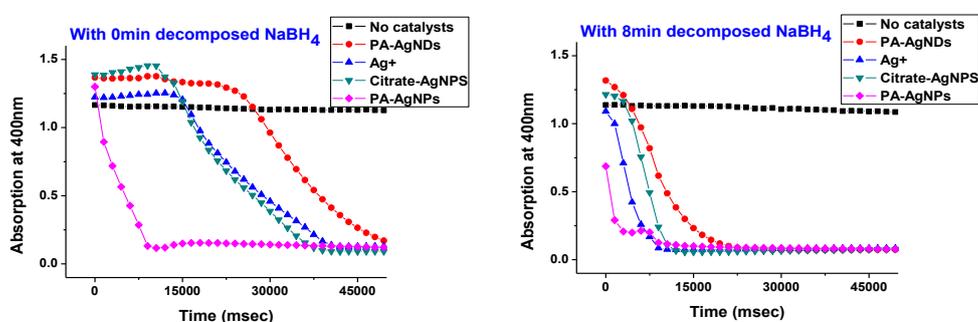


Figure 7. The comparison of catalytic ability of silver nanoparticles with decomposed NaBH_4 for 0 min and 8 mins. The Figures show the time dependence of the absorption of 4-nitrophenolate ions at 400 nm of UV-visible spectra for the catalytic reduction of 4NP in the presence of same concentration of quasimetallic nanoparticles by NaBH_4 decomposed for different time period.

Decreasing the amount of catalyst. As mentioned in introduction part (1.2.3.), it is widely observed that increasing concentration of quasimetallic nanoparticles can decrease the reaction time and it follows pseudo-first order kinetics¹⁰⁹. But it is hard to adjust this reaction at a huge industrial level, because it is not cost efficient.

However we suggest the better solution to be efficient catalyzing 4NP reduction than using more amount of catalyst inefficiently in reaction. That is the decomposition of NaBH_4 .

In case of silver ions, with low concentration of silver ions it was hard to catalyze 4NP reduction. But if using higher amount of the catalyst, the reaction became faster (Figure 8a) as many researches have demonstrated. But after NaBH_4 decomposed for 15 mins, silver ions catalyzed the reduction in a much shorter time with a faster reaction rate. Decomposed NaBH_4 made the catalytic activity of silver ions enhanced: the reaction rate was much faster than the case in which 4-fold more catalyst was used (Figure 8a). This decomposition could speed up the catalytic ability of other silver nanoparticles as well. PA-AgNDs showed just weak catalytic activity, meanwhile with decomposed NaBH_4 it became a stronger catalyst than using double concentration of PA-AgNDs (Figure 8b). Therefore decomposition of NaBH_4 might be a good solution to save cost in 4NP treatment industry and use catalysts efficiently.

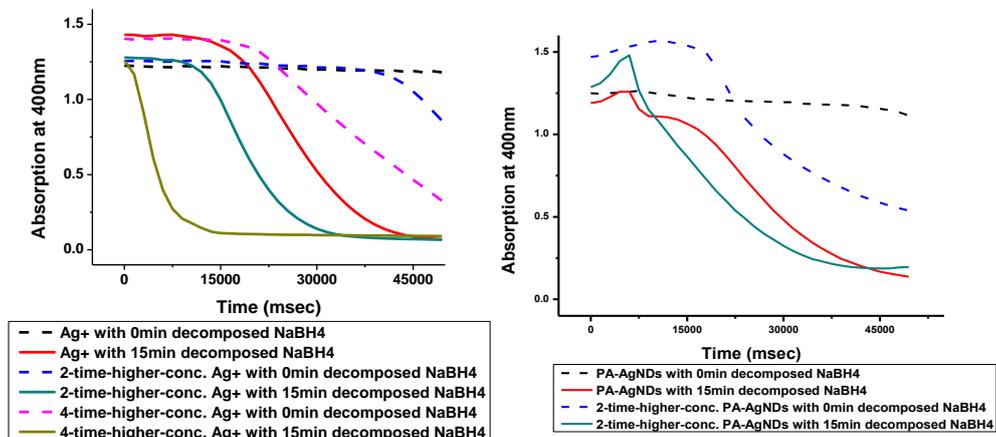


Figure 8. The comparison of catalytic ability of increasing catalyst amount to increasing decomposed time of NaBH₄. The Figures show the time dependence of the absorption of 4-nitrophenolate ions at 400 nm of UV-visible spectra for the catalytic reduction of 4NP in the presence of each concentration of quasimetallic nanoparticles by NaBH₄ decomposed for different time period.

Decomposition time period of NaBH₄. When decomposition period of NaBH₄ was changed, their reduction rates changed as well (Figure 9). With fresh NaBH₄, silver ions worked as a weak catalyst. But with NaBH₄ decomposed for 3min, it showed better catalytic ability. Further with decomposed for 12min the 4NP reduction was finished in very short time amazingly and there was no induction time. There have been many reports to find the effective factor in 4NP reduction catalyzed by quasimetallic nanoparticles. However it was the first observation of relation between NaBH₄ decomposition time and reaction rate.

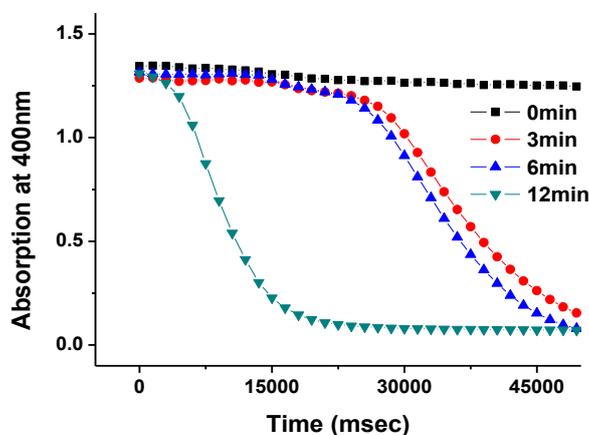


Figure 9. Catalyzing ability difference of silver ions according to decomposition time period of NaBH₄. The longer the decomposition time of NaBH₄, the faster the reduction reaction at the same concentration of catalyst (1.5×10^{-4} M silver catalyst).

Induction time. As mentioned in introduction part (1.3.3.), IT means the induction time that the time period taken before obvious any change in the absorbance at 400 nm. Our results (Figure 7, 8, 9, 10) obviously indicated that IT was related to the decomposition of NaBH₄. This was opposite to the previous reports that the induction time has no relation with borohydride^{110, 111}. Our result cannot be fully explained as a surface reconstruction of the nanoparticles related to the 4NP¹¹².

With fresh NaBH₄, there was a long induction time. But with decomposed NaBH₄ for 6min, the IT became much shorter. With NaBH₄ decomposed for 12min, there was almost no induction time we could detect. It proved NaBH₄ was closely related to the induction time as well (Figure 9).

Not only with silver, this interesting result also can be applied to the other metals. Among metal nanoparticles, especially silver, gold and copper have attracted more attention because of their useful and interesting properties and potential applications in technical fields¹¹³. Same as silver, originally gold or copper ions alone was a weak catalyst (Figure 10a), but under decomposed NaBH_4 they became good catalysts with much faster reaction rate but without any induction time (Figure 10b).

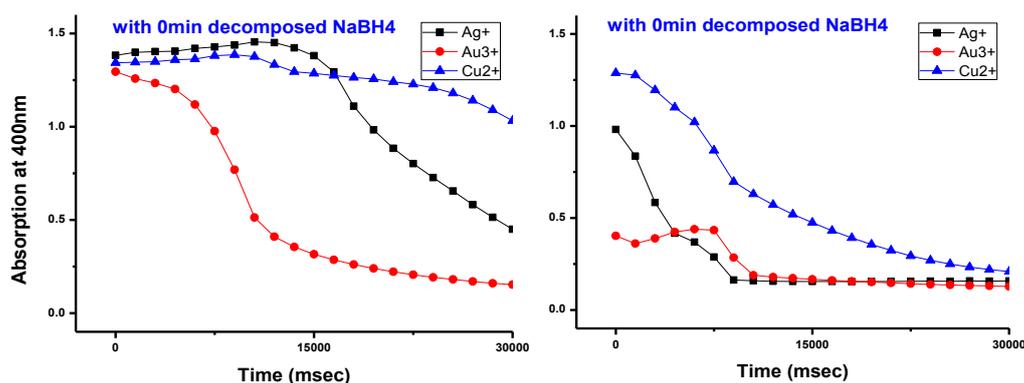


Figure 10. The catalytic ability of several novel metals with decomposed NaBH_4 for 0 min and 8 mins. (a) The pretty slow reduction reaction of the catalyst such as silver, gold and copper ions with 0 min decomposed NaBH_4 . (b) The much faster reduction reaction of the catalyst such as silver, gold and copper ions with 8 min decomposed NaBH_4 .

Prevent decomposing NaBH_4 . We investigated whether this was really caused by decomposition of NaBH_4 .

The decomposition of sodium borohydride is very low at high pH (introduction part 1.3.3.).

Figure 11 showed that if NaBH_4 was not decomposed due to high pH, then the 4NP reduction was not proceeded. In other words, there should have been some ‘specific product’ generated from the decomposition of NaBH_4 and which was the crucial reactive group in this reaction. This was highly noted because so far NaBH_4 has been ignored in the study of catalytic 4NP reduction and even it is generally regarded that the excess of NaBH_4 is needed in 4NP reduction due to its hydrolysis. But we found that decomposition of NaBH_4 was a key point in 4NP reduction.

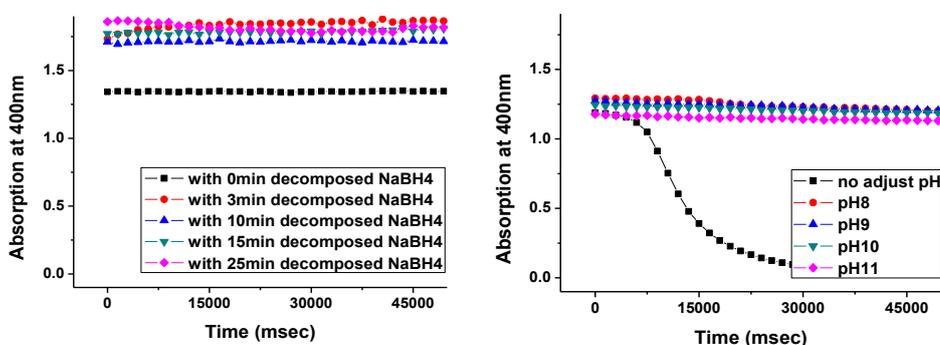


Figure 11. 4NP reduction is not proceeded if preventing decomposition of NaBH_4 . (a) The absorption of 4-nitrophenol under NaBH_4 dissolved in pH 10 buffer made by sodium phosphate tribasic (Na_3PO_4) to prevent decomposition. (b) The absorption of 4-nitrophenol under NaBH_4 dissolved in different pH solution each made by sodium phosphate tribasic (Na_3PO_4).

3.2. Mechanism of NaBH₄ in the catalytic reduction

Since the decomposition of NaBH₄ was the key point in this catalytic reduction, we investigated in detail about decomposition of NaBH₄ to study why the decomposition of NaBH₄ accelerated 4NP reduction reaction and reduced the induction time.

Reactive group. First of all, we assumed H₂ generated from decomposition of NaBH₄ worked as the reactive group in the reaction. Khalavka et al.^{114, 115} suggested the mechanism that only hydrogen needs to be adsorbed on the surface and reacts with the 4-nitrophenol. However, 4NP was not reduced to 4AP with bubbling hydrogen gas continuously (Figure 12). Therefore hydrogen generated from the decomposition of NaBH₄ was not the reactive group in this reduction.

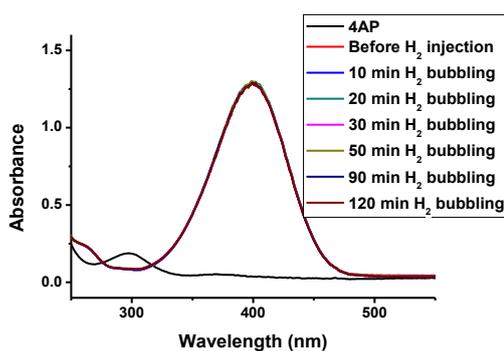


Figure 12. Absorbance spectra of 4NP and silver nanoparticles with H₂ bubbling without NaBH₄. Comparing to absorbance spectra of 4AP, 4NP cannot be

produced only with H_2 .

The surface charge supported that something intermediate was needed to start this reaction. Reported mechanisms have suggested that the catalysis reduces mutual repulsions between both negatively charged 4-nitrophenolate ion and BH_4^- ion¹¹⁶. But the zeta potential measurement (Figure 13) showed that the surface of silver nanoparticle was also negatively charged at pH 10 at which the reduction was proceeded. Both 4-nitrophenolate ion and borohydride ion were negatively charged^{117, 118}. So something else was needed as intermediates to overcome those repulsion force caused by the surface charge.

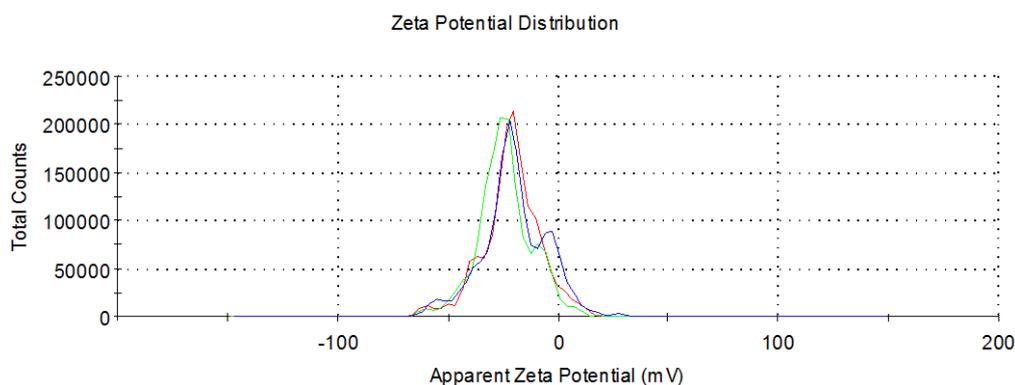


Figure 13. Zeta-potential spectra of silver nanoparticle with 4NP under the pH10 that usually reduction proceeded. It shows that surface of silver is negatively charged.

We found the reactive group via mass spectrometry (Figure 14). No matter

negative mode (Figure 14a) or positive mode (Figure 14b), we found new peaks as NaBH_4 decomposed. Likely those peaks represented reactive intermediates as shown in Figure 15. It was neutral. If assuming this predicted reactive intermediate (Figure 15) acted in the reaction, then this repulsion issue would be solved.

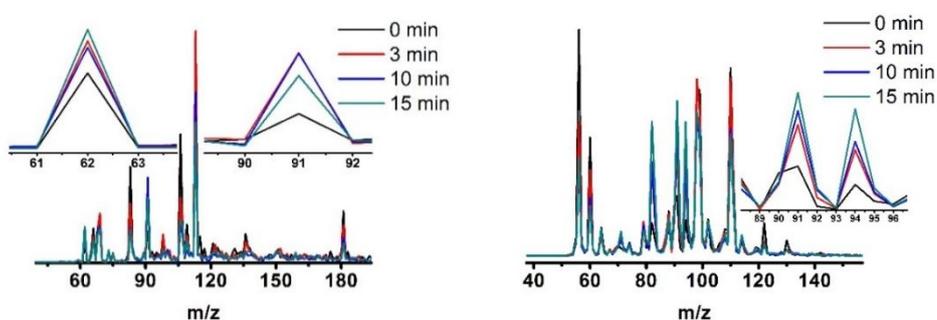


Figure 14. Mass spectrum of NaBH_4 as decomposed more. (a) Negative mode (b) Positive mode

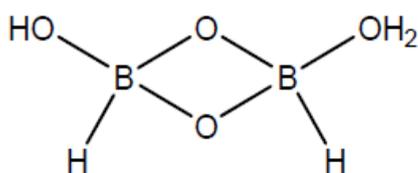


Figure 15. Predicted intermediate from decomposed NaBH_4 . The mass is 91.

The difference in the surface charge of nanoparticles proved our reactive intermediates. We synthesized almost the same size of AuNPs with different protection group (Figure 16a, b). But they showed a large difference in catalytic ability (Figure 16c). This result cannot be explained the previous conclusion that

different catalytic ability of 4NP reduction depends on size issues^{119, 120}. The surface of PA protected AuNPs is negatively charged and PEI protected AuNPs is positively charged. If BH_4^- were the reactive group as indicated in previous studies, then reactive group should have absorbed on the PEI-AuNPs faster and reaction fast¹²¹. But from the result we observed that PEI-AuNPs was slower than PA-AuNPs when aged borohydride was used (Figure 16c). However, given our reactive intermediates (Figure 15), all those experiments were explained. Fresh sodium borohydride was BH_4^- form so it is negatively charged. But decomposed sodium borohydride produced neutral intermediates. So it was not much influenced by the surface of nanoparticles. Then it was reasonable that PA-AuNPs was faster than PEI-AuNPs. Obviously in case of negatively charged PA-AuNPs, the fresh NaBH_4 due to repulsion would catalyze the reaction slowly. However, after decomposition of NaBH_4 , the neutral reactive group would bind PA-AuNPs easily. Consequently the reduction took place much faster with no induction time. On the other hands, PEI-AuNPs was not affected much (Figure 16c). This result also proved our hypothesis that there should be intermediates from the decomposition of NaBH_4 as reactive groups.

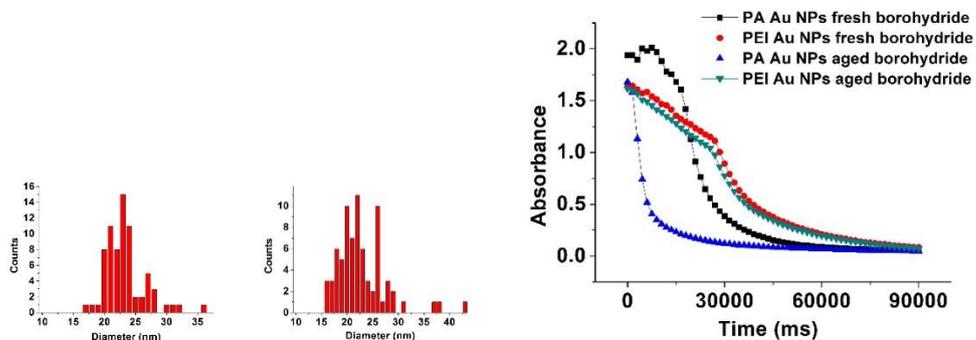


Figure 16. The surface charge as effect factor on 4NP reduction. (a) The size distribution from TEM pictures of PA-AuNPs and average size is 23.8 nm. (b) The size distribution from TEM pictures of PEI-AuNPs and average size is 23.2 nm. (c) The catalytic ability of 4NP reduction of PA-AuNPs and PEI-AuNPs with fresh and decomposed NaBH_4 .

On metal surface. If only decomposition was the point, then with the decomposed NaBH_4 , 4NP should have been reduced without catalysts. However, the 4NP was not reduced in the absence of nanoparticles (Figure 17). It indicated that the intermediate must adsorbed on the nanoparticle surface.

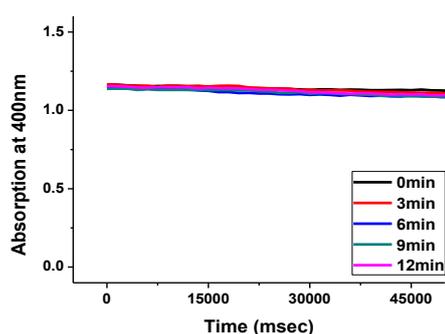


Figure 17. 4NP reduction without metal nanoparticle under NaBH_4 .

We observed through zeta-potential that at the very beginning there was no interactions between quasimetallic nanoparticles and borohydride because of the repulsive force from both the negatively charged. Only H_2 could not reduce 4NP in the presence of AgNPs as well. So we suggested that intermediates was produced from the $NaBH_4$ decomposition. This reactive intermediate would follow the previous mechanism in which the intermediate absorbs on the silver nanoparticle surface and form active centers. 4NP might diffuse to the surface and react¹¹⁷. We also observed that sodium borohydride decomposition also can be the rate determining step. It is opposite to the researches have mentioned so far that borohydride function have been regarded as a fast step and ignored in the rate-determining step¹¹⁷.

3.3. Effective factors of the catalytic reduction

The surface area. It was believed that different catalytic ability of 4NP reduction are due to the size issue. Smaller nanoparticles tend to show a higher catalytic ability because they have a much higher surface-to-volume ratio. No aggregation was observed to get a high surface-to-volume ratio. Thus, much

attention has been focused on the synthesis of small sized and highly dispersed nanoparticles^{122, 123}.

Citrate-AgNPs (Figure 18a, c) had much bigger size and smaller surface-to-volume ratio than PA-AgNPs (Figure 18b, d). And PA-AgNPs shows much faster catalytic ability than citrate-AgNPs (Figure 7).

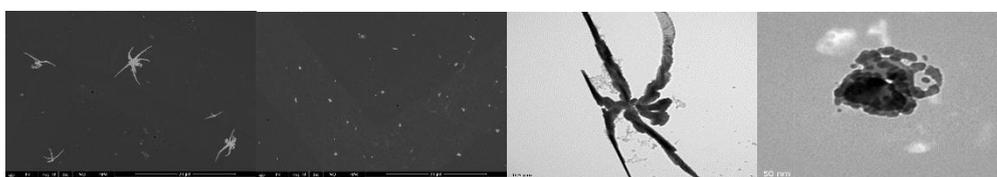


Figure 18. The image of silver nanoparticles. (a) The SEM image of the citrate-AgNPs under 2,500 \times magnification. (b) The SEM image of the PA-AgNPs 2,500 \times magnification. (c) The TEM image of the citrate-AgNPs with 500nm scale bar. (d) The SEM image of the citrate-AgNPs with 50nm scale bar.

Dispersion. Well dispersed nanoparticles showed better catalytic ability even though consisting of same elements (Figure 19). With a 10-fold- more polymer stabilizer, the PA-AuNPs showed the best catalytic ability. With a third-amount of polymer stabilizer, the PA-AuNPs showed the weakest catalytic ability. It suggested that well dispersed PA-AuNPs showed the better catalytic ability. This would result from the size dependent metal redox potential and the surface-to-volume ratio that influences electron transfer from metal nanoparticles surface to 4NP in the presence of more electron donor¹²⁴.

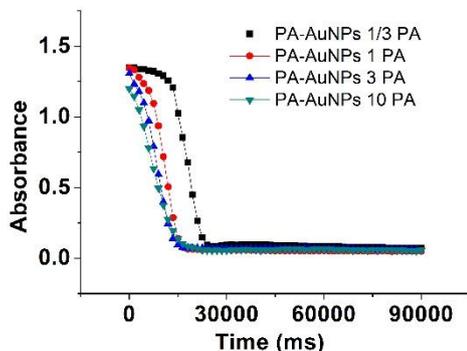


Figure 19. Catalyzing ability difference of PA-AuNPs according to the distribution. The more amount of PA added to make disperse better, the higher catalytic ability of reduction. After first synthesis PA-AuNPs, more PA added to make sure that the same amount of PA was inside of each sample.

pH as the effect factor on decomposition of NaBH₄. We investigated which factor affected the decomposition of NaBH₄. And we suggested pH of nanoparticle solution decided it. As mentioned in introduction part (1.3.2.) and Table 2, at lower pH, decomposition of NaBH₄ is much faster. PA-AgNPs which have the lowest pH (Table 3) showed the best catalytic ability (Figure 7). PA-AgNDs which had the highest pH (Table 3) shows the lowest catalytic ability (Figure 7). Others also followed this pattern. The pH of all solutions got quickly changed to about 10 right after adding NaBH₄ into the solution, so researchers have not cared about this pH of the catalyst. But we observed the nanoparticle indicating the lower pH had better ability of NaBH₄ decomposition and more decomposed NaBH₄ led to the higher catalytic ability of 4NP reduction. It proved

our hypothesis that decomposition of NaBH_4 was the crucial key in the catalytic 4NP reduction. We suggested that the pH value was the effective factor on determining the ability of decomposition of NaBH_4 . In other words, pH was another factor to influence the catalytic 4NP reduction.

Table 3. The pH value of catalyst solution before adding NaBH_4 .

Catalyst	pH of the catalyst solution
PA-AgNPs	5
Citrate-AgNPs	6
Ag^+	6
PA-AgNDs	7

IV. Conclusion

In summary, we found the catalyst could have better catalytic ability by using decomposed NaBH_4 . With decomposed one, we might save the cost and expand to the huge industry efficiently.

We suggested the quasimetallic nanoparticles and pH accelerated the decomposing. We observed the reactive intermediate generated from the decomposition of NaBH_4 . The surface charge factors played an important role. The neutral intermediate adsorbed on the surface of nanoparticles easily with less repulsion from negative charged surface. We showed that negatively charged nanoparticles prevented the approach of borohydride anions, resulting in a delay of reaction (IT) and induction time was the period of the reactive intermediate produced from NaBH_4 decomposition. The longer time NaBH_4 decomposed, the shorter the induction time. Surface area, dispersion and pH of catalysts determined the catalytic activity.

Our results not only provided methods to enhance the catalytic activity, but also helped us to explain the mechanism of catalytic 4NP reduction. It can be dramatically expanded to hydrogen cell as well that have highlighted nowadays.

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국문초록

수소화붕소나트륨을 사용하여 환경 오염 물질인 4-니트로페놀을 유용한 4-아미노페놀로 환원 시키는 촉매 반응이 널리 사용되고 있다. 금속 나노 입자를 촉매로 활용하는 것이 큰 관심을 받고 있지만, 여전히 메커니즘은 제대로 밝혀지지 않았다. 반면 이 환원 반응에서 수소화붕소나트륨의 역할은 고려되지 않아왔고, 대량을 사용하기 때문에 전자 제공 이외에는 다른 어떤 역할도 하고 있지 않다고 여겨져 왔다. 일반적으로 준금속 나노 입자와 4-니트로페놀이 반응 속도를 결정한다고 알려져 있다.

이 연구에서는 수소화붕소나트륨이 이 반응에서 아주 중요한 역할을 하고 있음을 찾아내었고, 이를 바탕으로 반응 메커니즘을 조사하였다. 그 결과 환원 반응 속도와 반응 지연 시간은 수소화붕소나트륨의 가수분해가 결정함이 드러났고, 중요한 반응성 중간체를 발견하였다. 이 연구는 준금속 나노 입자가 수소화붕소나트륨의 가수분해를 촉진시키고, 이때 생성된 중간체는 중성이므로 반발력이 사라져서 나노 입자 표면에 흡착되기 쉬워진다는 메커니즘을 제시한다. 또한 반응 지연 시간은

수소화붕소나트륨이 가수분해되며 반응성 중간체를 생성해내는 시간임을 밝혀냈다.

본 연구는 4-니트로페놀의 환원 반응의 메커니즘을 설명해낼 수 있게 해줄 뿐만 아니라 훌륭한 촉매 역할을 수행하는 준금속 나노 입자의 합성에 대한 기본적인 원리를 제공해준다. 또한 수소 생성과 환원 반응의 연관 관계에 대한 원리를 제시해주며 이는 실제 산업에서 유용한 가능성을 가지고 있다.

주요어 : 준금속 나노 입자, 촉매 반응, 4-니트로페놀, 환원 반응, 메커니즘, 수소화붕소나트륨, 가수분해

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