The shape conversion of silver nanoparticles through heating and its application as homogeneous catalyst in reduction of 4-nitrophenol

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Abstract. The shape conversion of silver nanoparticles (AgNPs) through heating and its application as a homogeneous catalyst in the reduction of 4-nitrophenol is reported here. Synthesis of AgNPs by reduction of AgNO$_3$ using NaBH$_4$ and sodium citrate as reducing agent were successfully conducted. The addition of PVP was used as stabilizing agent. The synthesized AgNPs were heated at 95 °C and observed using UV-Vis spectrophotometer, transmission electron microscopy (TEM), Fourier-transformed infrared (FTIR) spectroscopy and particle size analyzer (PSA). Characteristics of AgNPs before heated were blue with UV-Vis absorbance spectrum at $\lambda_{\text{max}} = 786$ nm and the shape was pseudo nano prism sized ± 28 nm. During the heating process, the color changed gradually from blue ($\lambda_{\text{max}} = 786$ nm) to orange ($\lambda_{\text{max}} = 486$ nm) and also its shape from nano prism to nanodisk. Silver nano prism has a lattice constant, 4.160 Å, larger than the silver nanodisk, 4.081 Å, which was possibly achieved through rearrangement of silver atoms on the surface of AgNPs. Both silver nanodisk and nano prism were tested as a homogeneous catalyst for the reduction of 4-nitrophenol (4-NP) with NaBH$_4$.

1. Introduction
Silver nanoparticles (AgNPs) received much attention from researchers in the world due to its unique. Besides having a good antimicrobial ability [1,2], AgNPs also have unique optical properties, namely LSPR (Localized Surface Plasmon Resonance). The LSPR properties lead AgNPs to have an attractive color and luminescence [3,4]. Therefore, AgNPs have many benefits such as chemical sensors, biological sensors, catalysts, as well as the diagnosis and cure of disease.

Differences synthesis conditions will produce different shapes and sizes of AgNPs. Generally, the synthesis of AgNPs with reduction method produces spherical particles at a maximum wavelength ($\lambda_{\text{max}}$) 395 nm [7]. However with certain techniques such as photochemical, thermochemical and biochemical [8-10], the resulting nanoparticles can be deformed. Tang et al. [11] reported shape conversion mechanism of AgNPs from triangular to spherical shapes with heating (thermochemical). Shape conversion of AgNPs can be monitored via color change from blue (triangular) to orange (spherical) at $\lambda_{\text{max}}$ 655 nm to 472 nm.

Metal nanoparticles are often used in redox catalysis process because they have a large surface area. Even though silver is not the best redox catalyst, silver can be used as an active component of the catalyst for the partial oxidation [12]. AgNPs are effectively used as a homogeneous catalyst and can
be immobilized on a suitable support material such as silica, alumina, carbon, zeolites and metal oxides as heterogeneous catalysts [13]. In this research, we studied the effect of the shape conversion of AgNPs through heating to their catalytic activity for the first time. Reaction model used to test the catalytic activity of AgNPs was the reduction reaction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP). Previous studies have been made out in order to optimize the 4-NP reduction using AgNPs catalyst with a wide variety of reactant conditions [5]. But until this day, there has never been a report about the effect of the shape conversion of AgNPs to their catalytic activity for 4-NP reduction.

2. Experimental

2.1. Materials

AgNO₃, Trisodium citrate, Polivinilpirolidon (PVP), H₂O₂ 30 wt%, NaBH₄ and 4-nitrofenol were purchased from Merck. All chemicals were of analytic grade and were used without further purification. MilliQ water (18.2 Ω cm⁻¹) was used to make aqueous solutions.

2.2. Heat assisted shape conversion of AgNPs

The initial triangular AgNPs were synthesized according to the Mirkin’s method [14]. An aqueous solution of 100 mL AgNO₃ 0.1 mM, 1.8 mL trisodium citrate 100 mM, 0.06 g PVP, and 0.24 mL hydrogen peroxide 30 wt% were mixed and vigorously stirred under ambient condition. Then, 1.5 mL NaBH₄ solution 100 mM was rapidly injected into the mixtures. After about 30 min, colloidal blue silver nano prism was obtained.

The synthesized silver nano prism was placed in a water bath at 95 °C. The color of colloidal AgNPs changed from blue to purple, red and then orange during the heating process. The AgNPs colloid were monitored using ultraviolet-visible spectrophotometer (Shimadzu 2600), Fourier transmits infrared (FTIR) (Shimadzu Prestige 21), particle size analyzer (PSA) Malvern ZEN 1600 and TEM (JEM 1400).

2.3. Catalytic activity test of 4-NP reduction

The catalytic activity of AgNPs as a homogeneous catalyst was determined by adding 1 mL of NaBH₄ 0.1 M into 5 mL of 4-NP 8,6x10⁻⁵ M in a centrifuge tube. The solution showed a change in color of 4-NP which are colorless into yellow. Blue (AgNPs-blue) and orange (AgNPs-orange) homogeneous catalysts were added to the mixture, vortexed at the variation of time and characterized using UV-Vis spectrophotometer.

3. Results and discussion

3.1. Shape conversion of AgNPs

The AgNPs-Blue colloid gradually changed into purple, maroon and orange during heated at 95 °C as shown in figure 1. The color changes related to the SPR (surface plasmon resonance) properties of AgNPs. Color changes which are accompanied by changes in UV-Vis absorption spectra indicate that heating could lead to the shape conversion of AgNPs [9].
The AgNPs-Blue colloidal have an absorbance at $\lambda_{\text{max}}$ 786 nm. The increasing of heating time (every 10 min) caused the blue shift at $\lambda_{\text{max}}$ 534 nm (AgNPs-Purple), 501 nm (AgNPs-Marun), and 486 nm (AgNPs-Orange), which indicates that the nanoparticle size decreases (figure 2).

TEM characterization has been used to clarify the shape conversion of AgNPs through the differences of heating time. Figure 3 and 4 shows the differences in morphology between AgNPs-blue and AgNPs-orange. AgNPs-blue was the initial color after synthesis while AgNPs-orange was the last color change of AgNPs colloidal after heating ± 30 minutes.
The Morphology of AgNPs-blue showed that most AgNPs have pseudo triangular shape with side length ± 25 nm while AgNPs-orange is almost spherical with diameters ± 12 nm. Based on the results, (1) AgNPs morphology can be converted from triangular to spherical by heating at 95 °C, (2) AgNPs size get smaller with increasing heating time. Shape and size conversion process of AgNPs by heating are illustrated in figure 1.

Shape conversion of AgNPs likely to occur because of the migration of silver atoms from the less stable sides to the more stable, thereby causing surface energy difference and selective adsorption of citrate. According to Tang et al. [11], the sharp edges on the triangular AgNPs have a larger surface energy and less stable, so it can lead to changes the shape of triangular become spherical with heating. This raises the idea that spherical AgNPs can be formed because of the displacement of the silver atoms on the less stable side with a high surface energy and the rearrangement of the atoms that have been "dissolved" in the spherical AgNPs colloidal formed by heat-assisted. Displacement of the silver atom from sharp edges on triangular particles to colloids causes the formation of very small and unstable AgNPs to allow the rearrangement of these particles on spherical AgNPs surfaces. Rearrangement of the silver atoms can be proved through the analysis of SAED data from TEM characterization. Based on the diffraction pattern (Figure 5 and 6), the crystal structure of AgNPs can be determined.
The rings patterns with plane distances from Table 1 are consistent with the plane families of pure face-centered cubic (fcc) silver structure (JCPDS, File No. 4-0787).

| Plane distances (Å) | Hkl |
|---------------------|-----|
| 2.32                | 2,36| 2,34|
| 2.05                | 2,17| 2,006|
| 1.44                | 1.44| 1.47|
| 1.22                | 1.28| 1.239|
| 1.18                | 1.002| 1.001|

The Fcc structure of AgNPs-Blue and AgNPs-Orange in this study have lattice parameter values 4.160 Å and 4.081 Å, respectively. Decrease in the value of the lattice parameter of triangular AgNPs-Blue to spherical AgNPs-Orange indicates rearrangement of the AgNPs atoms which was initially shaped triangular then atoms on the edges "detached" and undergo rearrangement into spherical nanoparticles.

3.2. Catalytic activity of AgNPs for 4-NP reduction

The catalytic activity of AgNPs as homogeneous catalysts was tested using reaction reduction model of 4-NP into 4-AP. The reaction model was used because in addition to the interest of reducing the harmful compounds into the medicinal raw materials compounds, also due to the two compounds can be easily detected using UV-Vis spectrophotometer on a laboratory scale. Reduction reaction of 4-NP into 4-AP in the presence of NaBH$_4$ can occur thermodynamically when the value of potential standard (E$_0$) for 4-NP / 4-AP = -0.76 V and for H$_3$BO$_3$ / BH$_4$ = -1.33 V. But in kinetics, the reaction without the presence of catalyst restricted (no changes absorbance for approximately 2 days) [15]. Therefore, the presence of AgNPs as catalyst expected the reaction runs more effectively.
Figure 7. UV-Vis absorption spectra of the reduction of 4-NP in aqueous solution using 1 mL AgNPs-Blue as a catalyst.

4-NP (λ\text{max} 317 nm) was reduced to nitrophenolate ions (λ\text{max} 400 nm) in the presence of NaBH₄. However, with the presence of AgNPs catalyst, absorbance peak decreased, and a new peak appeared at λ\text{max} 300 nm which is the absorbance of 4-AP (Figure 7). The reaction was assumed to be a pseudo-first order reaction because of the excessive amount of NaBH₄ in comparison to 4-NP [6]. A graph with a plot of ln [A] versus time, where [A] is the absorbance of 4-NP at t time, will give a linear correlation with the rate constant as slope. The kinetic equation can be drawn in equation (1), (2), and (3).

\[
\frac{d[A]}{dt} = -k[A] \quad (1)
\]

\[
ln\frac{[A]}{[A]₀} = -kt \quad (2)
\]

\[
ln[A] = -kt + ln[A]₀ \quad (3)
\]

Figure 8 shows the decrease of 4-NP’s concentration against reaction time using AgNPs-Blue and AgNPs-Orange catalyst, in which the rate constant k are 0.0458 min⁻¹ and 0.0356 min⁻¹, respectively. Based on TEM characterization, the AgNPs-Blue catalyst that showed higher catalytic activity in this study has pseudo triangular particles shape. While AgNPs-Orange catalyst has a spherical shape.
Although AgNPs-Blue catalyst has a larger particle size than AgNPs-Orange catalyst, based on its shape, AgNPs-Blue has more active side than AgNPs-Orange catalyst so that the catalytic activity in the electron-transfer process becomes larger. Mahmoud et al. [16] state that the catalytic activity of metal nanoparticles that have sharper edges and corners are more active than the smooth and blunt. That is because particles with sharper edges and corners have more valence-unsatisfied surface atoms, atoms that do not have the complete number of bonds that they can chemically accommodate, which will act as active side than fine and blunt particles.

Accordingly, the catalytic activity of AgNPs with triangular shape was better than AgNPs with a spherical shape for 4-NP reduction despite larger particle size. Triangular shape has sharp edges that act as an active site on the catalyst as electron transfer media due to more valency-unsatisfied surface atoms than spherical AgNPs catalysts. The amount of the active side of triangular AgNPs accelerates the 4-NP reduction in the presence of NaBH₄.

4. Conclusions
Shape conversion of AgNPs have been done through the heating at 95°C and applied for reduction catalyst of 4NP to 4-AP. TEM characterization results show the occurrence of morphological changes of triangular to spherical AgNPs. The catalytic activity of triangular AgNPs was better than a spherical one.

Acknowledgement
This work was funded by Hibah Penelitian Unggulan Perguruan Tinggi (PUPT) 2015 from the Directorate General of Higher Education, Ministry of Research, Technology and Higher Education of Indonesia through the Directorate of Research and Community Services, Universitas Indonesia (No. 0544/UN2.R12/HKP.05.00/2015).
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