Effect of Stabilizers in the Synthesis of Silver Nanoparticles and Methylene Blue Oxidation

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Abstract. Metal nanocatalysts have received increasing attention in catalysis due to their higher reactivity and surface area-to-volume ratio at nano-size. Silver nanoparticle (AgNP) is among metal nanocatalysts that have been studied in various catalytic reactions (e.g., hydrogenation and oxidation). However, the high reactivity of AgNPs at nano-size caused instability and aggregation. Therefore, stabilizing molecules (or stabilizers) are always applied to maintain the nano size of AgNPs and prevent aggregation. Herein, the effects of different types and molar ratio of stabilizers-to-Ag precursor, to the synthesized AgNPs (i.e., size and concentration) were investigated. Two types of stabilizers, polyvinylpyrrolidone (PVP) and citrate were used in this study. The roles of stabilizers to the catalytic performance of synthesized AgNPs were then elucidated by using methylene blue oxidation as the model reaction. The UV-Vis absorption analyses showed that both stabilizers produced slightly different size and concentration of AgNPs based on the different wavelength and absorption intensity of the peak. We also found that the molar ratio of stabilizers-to-Ag precursor that produced better yield of AgNPs was 1:1 and 1:3 for PVP and citrate, respectively. Then, AgNPs stabilized by citrate was found having slightly higher catalytic activity in the methylene blue oxidation than AgNPs stabilized by PVP. This study provides insights to the roles of stabilizers for the synthesis of stable AgNPs with efficient catalytic reaction and can be used as guideline to other metal nanocatalysts.

1. Introduction

The advancement of nanotechnology has significantly increased the number of innovation and studies of nanomaterials, including metal nanocatalysts. Metal catalysts at nano-size are more reactive and thus nanocatalysts with higher reactivity and surface area-to-volume ratio are more favourable in catalysis as only lower amount is needed for higher catalytic activity. These metal nanocatalysts are not only applied for chemical transformations of value-added products but also to the catalytic removal of hazardous pollutants in the environment. For instance, a worrying amount of hazardous pollutants (especially, organic pollutants) are generated daily by many industries, thus require sustainable and efficient technology for their removal. Silver nanoparticle (AgNP) is among noble metals (e.g., platinum and gold) which have been applied as catalysts and it is preferable because it is cheaper than other noble
metals. AgNPs have been also reported as a good catalyst for the removal of organic pollutants (e.g., 4-nitrophenols and methylene blue) in wastewater [1].

Size of metal NPs is important to control their physical and chemical properties, including luminescence, conductivity, and catalytic activity. Thus, the ability to control the size of metal NPs during their synthesis is of crucial importance [2]. The size of metal NPs is usually depending on the synthesis parameters and conditions such as (e.g., stabilizers, reductant, temperature, pH, reaction time, etc). Among all, stabilizers are the most significant ingredients to modulate the size of the metal NPs during the synthesis and to maintain its stability by passivating and reducing the high surface charge of metal NPs, thus prevent further growth and aggregation [3]. Types of stabilizers used in the synthesis of metal NPs are polymers, dendrimers, anionic molecules and ligands. Polyvinylpyrrolidone (PVP), a water-soluble polymer and citrate, an anionic molecule are commonly used as stabilizers for the synthesis of metal NPs including AgNPs. In some studies, they were reported to serve as reductant, stabilizer as well as complexing agent [4].

The possibility of a precise control of size and mass production remains the most attractive goal for the synthesis of AgNPs [5]. Therefore, in this study, we investigated the effects of different type and amount of stabilizer (i.e., molar ratio of stabilizer-to-Ag precursor) to the synthesis of AgNPs and their catalytic activities. Methylene blue (MB) oxidation was used as a model reaction because methylene blue is the common dye in the wastewater. Therefore, its removal by catalytic oxidation is of high interest in wastewater treatment as the AgNPs could be incorporated into the existing materials (e.g., adsorbents and filter membranes) used in the wastewater treatment to improve the capability of those materials in removing the dyes in wastewater.

2. Materials and Methods

2.1. Preparation of chemicals

Silver precursor (silver nitrate, AgNO₃), polyvinylpyrrolidone (PVP) and trisodium citrate (Na₃C₆H₅O₇) and reductant (NaBH₄) were purchased from Sigma Aldrich while methylene blue (MB) and 50% hydrogen peroxide (H₂O₂) were purchased from local suppliers. For all experimental works, solutions were prepared using ultrapure water (denoted by UPW; 18.2 MΩ.cm @ 25°C). Beaker, volumetric flask, and other glassware were rinsed with UPW before use.

2.2. Synthesis of AgNPs with different type and amount of stabilizers

At a room temperature (~27 ± 1°C), 0.05 mL of 40 mM AgNO₃ solution was mixed with UPW with 40 mM PVP solution in a 15 mL vial. The volume of UPW and PVP was varied based on the different molar ratio of AgNO₃-to-PVP (1:1, 1:3, 1:5 and 1:7) which are summarized in table 1. The UPW was added to the mixture to make-up the total volume of 3 mL. The mixture was shaken using hand for 10 seconds and allowed to mix for 10 minutes. After 10 minutes, 0.02mL NaBH₄ (prepared by dissolving 0.04 g in 10 mL UPW) was added into the solution and the mixture was left for etching at room temperature for 70 minutes.

| Table 1. The molar ratios and volume of reagents used for the synthesis of AgNPs |
|---------------------------------|-----------------|-----------------|-------|
| Molar ratio of AgNO₃:Stabilizer | AgNO₃ (40 mM) | Stabilizer (40 mM) | UPW |
| 1:1 | 0.05 | 0.05 | 2.9 |
| 1:3 | 0.05 | 0.15 | 2.8 |
| 1:5 | 0.05 | 0.25 | 2.7 |
| 1:7 | 0.05 | 0.35 | 2.6 |

The colour of the solution turns into yellowish colour and the yellow colour became brighter after longer reaction time, indicating the formation of AgNPs. The as-synthesized AgNPs were then
characterized by UV-Vis spectroscopy whereby 0.2 mL sample was diluted with 1.8 mL UPW. The above-mentioned steps were repeated for the synthesis of AgNPs stabilized by citrate. Of note, the concentration of the as-synthesized AgNPs is based on the mol of Ag precursor in the 3 mL total solution, which is 0.67 mM. Due to high sensitivity of AgNPs, all synthesis process and AgNO$_3$ solution were kept in the dark to avoid any photochemical reaction during experimental work. All the experiments were done in duplicates.

2.3. Methylene blue (MB) oxidation
The catalytic activity of as-synthesized AgNPs was determined using methylene blue (MB) oxidation with hydrogen peroxide (H$_2$O$_2$) as oxidizing agent. Briefly, in 7 mL vial, 0.2 mL of 0.05M MB was mixed with 0.2 mL AgNPs (0.67 mM). Then 1.7 mL of oxidizing agent (50% H$_2$O$_2$ solution) was added to the mixture and was shaken by hand to start the oxidation. The mixture was analysed using UV-Vis spectroscopy at 0, 20, 40 and 60 minutes. The blue colour of mixture due to the MB gradually changed in intensity and finally to colourless after the oxidation completed. The catalytic tests were done in duplicates. Two control experiments were done which one of them was without oxidant and catalyst (also called as blank control) and another control was without the catalyst only. The blank control was measured by UV-Vis to determine the initial absorbance of the MB (A$_o$) before catalytic reaction occur. The catalytic tests were carried out at ambient temperature and under the present or normal light. The values of UV-Vis absorption were recorded and compared. The catalytic tests were done in duplicates.

3. Result and Discussion
3.1. Effects of stabilizers amount to the formation of AgNPs
The formation AgNPs can be observed by colour appearance and characterization by UV-Vis absorption peak. Colourless solution turns into yellowish brown after addition of NaBH$_4$ which gave a maximum absorbance at ~400 nm as shown in figure 1(a-b). It is well known that this yellowish brown color arises owing to excitation of surface plasmon resonance (SPR) vibration in the AgNPs [6].

![Figure 1. Color of (a) AgNPs-PVP and (b) AgNPs-Citrate solution and the UV-Vis absorption spectra for (c) AgNPs-PVP and (d) AgNPs-Citrate solution.](image)
Figure 1(a-b) also shows that the colour of solution looks similar for both AgNPs stabilized by PVP (AgNPs-PVP) and citrate (AgNPs-Citrate), except for AgNPs-Citrate with 1:1 molar ratio of AgNO$_3$-to-Citrate. The colour is darker and more to brownish, probably due to formation of more and bigger AgNPs [7]. In general, the surface plasmon resonance of AgNPs produces a UV-Vis absorption peak at around 400 nm as can be seen in figure 1(c-d), but may slightly vary depending on the size of AgNPs [8].

Results in figure 1(c-d) also indicates that the highest peak of AgNPs synthesized by PVP and citrate were obtained when using AgNO$_3$-to-stabilizer molar ratio of 1:1 and 1:3, respectively. The highest peak at particular molar ratio of (AgNPs-PVP) and (AgNPs-Citrate), indicating those amounts are sufficient to form higher AgNPs than other molar ratio. As PVP has bigger structure than citrate based on molecular weight, the molar ratio of 1:1 (PVP) and 1:3 (citrate) is comparable to produce the highest amount of AgNPs. The higher molar ratio (i.e 1:5 and 1:7) for both PVP and Citrate produce lower AgNPs due to excessive amount of stabilizer, hence hinder the stabilizer to form complex with Ag$^+$. 

3.2. Comparing the roles of different stabilizer to the formation of AgNPs

The UV-Vis absorption spectra of the AgNPs-PVP and AgNPs-Citrate solution were also compared with the control experiment whereby the AgNPs were produced without addition of stabilizers. However, AgNPs were still formed in the control experiments due to the presence of borohydride anions (BH$_4^-$) from the reductant (NaBH$_4$) which are not only capable to reduce the Ag$^+$ into Ag$^0$ but also to form complex and stabilize Ag$^+$ cations and AgNPs in the solution [9]. Based on the UV-Vis absorption spectra in figure 2(a), when other parameters and synthesis conditions were held constant, it can be seen that different stabilizers lead to the formation of AgNPs with different size and concentration which indicated by the different wavelength and intensity for the highest absorption peak. The highest absorption peak of AgNPs-PVP was found at higher wavelength (404 nm) than that of AgNPs-Citrate (388 nm), indicating the size of AgNPs-PVP could be slightly higher than AgNPs-Citrate. However, the intensity of the absorption peak of AgNPs-PVP is lower than that of AgNPs-Citrate, meaning there were more AgNPs species in AgNPs-Citrate solution than in AgNPs-PVP. The reason could be due to the more Ag-citrate complex can be formed with citrate anions which has more oxygens (in form of O$^-$ and =O moieties) which are able to stabilize and reduce more Ag$^+$ cations, thus forming more AgNPs in the solution.
AgNPs-citrate (388 nm). Interestingly, the absorption intensity of AgNPs-control is the lowest which suggest that there was insufficient reducing capability of NaBH₄ to reduce Ag⁺ into AgNPs and both stabilizers, PVP and citrate are not only stabilizing the AgNPs, but also act as the reductant in the synthesis of AgNPs, leading to more formation of AgNPs in the solution.

3.3. Comparing the catalytic activity of AgNPs
The cationic MB dye is one of the water pollutants, which consumes the dissolved oxygen in water and endangers the aquatic system [10]. The catalytic ability of as-synthesized AgNPs was investigated with degradation of MB with presence of H₂O₂ for oxidation reaction figure 3. H₂O₂ generates OH radicals and oxidize the MB by generating discoloration. MB typically shows absorption maxima band at about 664 nm in aqueous solution due to n / n* and n / n* transitions and UV Vis absorption peak of MB is at 631nm wavelength from figure 3.

After one hour of reaction, it was found that the UV-Vis absorption peak of MB decreased, and the blue color of MB solution reduced. MB degrade faster with catalyst (i.e AgNPs) as compared to H₂O₂ alone (without catalyst) and by comparing between two stabilizers, citrate performs better catalytic degradation as compared to PVP towards MB oxidation. One of the possible reasons is due bigger size and presence of alkyl chain of PVP that reduce accessibility to substrate (MB) hence reducing catalytic activity.

4. Conclusion
In the present study, stable silver nanoparticles were successfully prepared by a stabilizers PVP and citrate. The procedure was relatively easy, rapid, inexpensive, eco-friendly. Furthermore, this study demonstrated the effect of different molar ratio and type of stabilizers to produce AgNPs. It was found that the best molar ratio of stabilizers-to-Ag precursor for the highest yield of AgNPs synthesized using PVP and citrate was 1:1 and 1:3, respectively. It was also found that with similar molar ratio of stabilizers-to-Ag precursor, the yield and morphology of the Gaps such as size and shape could be different due to the different wavelength of the UV-Vis absorption peak. TEM analysis can be further done to confirm the different size and shape of the AgNPs produced by different stabilizers. Catalytic activity was demonstrated on MB to check the effectiveness of AgNPs as catalyst. The reduction of MB dye at was done at ambient conditions. The MB dye degraded within 60 min, signifying the
usefulness of the synthesized AgNPs as a good catalyst for wastewater treatment. Different stabilizers also affect the catalytic activity as PVP is a polymer with a longer chain length reduced the accessibility of the substrate to the catalyst, thus leading to lower catalytic activity than AgNPs stabilized by citrate. This study provides a guideline in the selection of stabilizers for the synthesis of AgNPs nanocatalysts.

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References
[1] Fundneider T, Acevedo Alonso V, Wick A, Albrecht D, and Lackner S, 2021, Water Res., 189, 116588
[2] Xue Y, Chen S, Yu J, Bunes B R, Xue Z, Xu J, Lu B, and Zang L, 2020, J. Mater. Chem. C, 8, 108319
[3] Das S, Bandyopadhyay K, and Ghosh M M, 2021, Inorg. Chem. Commun., 123, 108319
[4] Zeng S, Vahidzadeh E, VanEssen C G, Kar P, Kisslinger R, Goswami A, Zhang Y, Mahdi N, Riddell S, Kobryn A E, Gusarov S, Kumar P, and Shankar K, 2020, Appl. Catal. B: Environ., 267, 118644
[5] Yaqoob A A, Umar K, and Ibrahim M N M, 2020, Appl. Nanoscience, 10, 1369
[6] Saha J, Begum A, Mukherjee A, and Kumar S, 2017, Sustain. Environ. Res., 27, 245
[7] Deshpande J B, Chakrabarty S, and Kulkarni A A, 2020, Chem. Eng. J.l, 127753
[8] Ganash E A and Altuwirqi R M, 2021, Materials, 14, 2326
[9] Iravani S, Korbekandi H, Mirmohammadi S V, and Zolfaghari B, 2014, Res. Pharm. Sci., 9, 385-406
[10] Atta A M, Moustafa Y M, Al-Lohedan H A, Ezzat A O, and Hashem A I, 2020, ACS Omega, 5, 2829-2842