

Tannic Acid Stabilized Silver Nanoparticles and its Sensing Application to Pyrazosulfuron Ethyl Herbicide

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Abstract: Tannic acid-stabilized silver nanoparticles were synthesized using various initial pH conditions ranging from 5.0-9.0 under UV exposure for 60 min. At pH of 5.0, the color of the silver nanoparticles colloids changed from yellow to greenish blue and the characteristic peak shifted from 420-635 nm as the amounts of pyrazosulfuron-ethyl herbicide increased from 0-400 ppm. On the other hand, those nanoparticles colloids synthesized at pH of 6.0 showed the color change from yellow to red. However, at neutral and alkali conditions, the obtained nanoparticles colloids did not exhibit the sensing ability to this herbicide. The results indicated that UV radiation assisted method can be used for the synthesis of the nano particles at various pH conditions using tannic acid as both reducing agent and stabilizer. This can increase the opportunity to use silver nanoparticles in sensing applications, especially for pH dependent chemicals such as this herbicide.

Key words: Silver nanoparticles, tannic acid, herbicide, sensor, Thailand

INTRODUCTION

Conventional techniques used for herbicide detection such as gas chromatography and high performance liquid chromatography are time consuming processes (Congress, 1988). New techniques based on the sensing Ability of silver Nanoparticles (AgNPs) have been developed since these techniques use shorter time in detection process (Dubas and Pimpan 2008a, b; Filippo *et al.*, 2013; Han *et al.*, 2014). It is known that Localized Surface Plasmon absorption (LSPR) of the nanoparticles can be shifted to other wavelengths by changing the dielectric constants of their mediums or surroundings (Silva *et al.*, 2010). Consequently, the change in the colors of AgNPs colloids is observed. This strategy can be done by employing a stabilizer that contains oxygen-rich functional groups such as carboxylic, carbonyl and hydroxyl groups in order to make the nanoparticles sensitive to ionic strength of the targeting chemicals (Dubas and Pimpan 2008a, b). One stabilizer which exhibits this potential is Tannic Acid (TA).

Generally, the reducing agents such as sodium citrate, citric acid ascorbic acid and sodium borohydride in conjunction with a stabilizer are used in the synthesis of AgNPs. However, there are problems based on these chemical reduction methods such as the difficulty in

removing unreacted reducing agent and/or stabilizer which can affect the characteristics and properties of the obtained AgNPs. Therefore, many techniques have been developed such as irradiation assisted (Dubas and Pimpan, 2008a, b; Silva *et al.*, 2010; Azawi *et al.*, 2015) and thermal assisted methods (Akaighe *et al.*, 2011; Hebeish *et al.*, 2010) in order to reduce the chemicals used in the reaction.

Several researchers have made significant progress in the syntheses of TA-stabilized AgNPs by adjusting pH of the precursor solutions (Han *et al.*, 2014; Silva *et al.*, 2010; Azawi *et al.*, 2015; Akaighe *et al.*, 2011; Hebeish *et al.*, 2010; Yi *et al.*, 2011; Sivaraman *et al.*, 2009; Tian *et al.*, 2007). In their research, it was found that TA can act as both reducing agent and stabilizer. At alkali condition, TA dissociates into gallic acid and gallic acid can rapidly reduce silver ions in the system (Sivaraman *et al.*, 2009). On the other hand, at acidic condition, TA is known to be a weak reducing agent (Han *et al.*, 2014). However, varying pH conditions of AgNPs colloids can increase the opportunity to use the silver nanoparticles in sensing applications. This is because some chemicals are pH dependent. For example, sulfonylurea herbicide is more rapidly soluble in water at acidic condition but stable in neutral solution (Brown, 1990; Sarmah and Sabadie, 2002; Watcharaporn *et al.*, 2014). To overcome the limitation of

less reduction of TA at acid condition, UV radiation was applied in order to drive the reduction rate of the synthesis process. Preliminary results indicated that TA-stabilized AgNPs were successfully synthesized at acidic and neutral conditions with the assistance of UV radiation (Watcharaporn *et al.*, 2014). Therefore, in this research, the effect of pH used in the synthesis of AgNPs on its sensing ability to Pyrazosulfuron-Ethyl herbicide (PSE) which is one of the widely used herbicide was studied. The main objective was to find the suitable pH condition in the synthesis that can yield AgNPs which can be used for PSE detection. TA-stabilized AgNPs were synthesized by UV radiation assisted method. Initial pH of TA solutions were varied from 5.0, 6.0, 7.0, 8.0-9.0. The formation of AgNPs was confirmed by UV-Vis spectroscopy and transmission electron microscopy. Herbicide sensing application was tested based on the change in the optical properties after exposing to the increasing amounts of PSE herbicide.

MATERIALS AND METHODS

Tannic acid ($C_{76}H_{52}O_{46}$) having molecular weight of 1701.2 gmol^{-1} (Sigma-Aldrich), silver nitrate (Merck) and potassium carbonate (Merck) were analytical grade. Pyrazosulfuron-ethyl herbicide which was commercial grade was obtained from Sotus International Ltd., Thailand. They were used as received without further purification.

Synthesis and characterizations: About 5 mL of 4.00 mM silver nitrate was poured into 20 mL of 0.1 mM of TA aqueous solution. Its pH was adjusted to the desired pH by adding potassium carbonate solution. After stirring in the dark for 5 min, the mixture were stirred for 60 min under UV radiation at room temperature using 8 watts of UV lamp. The obtained AgNPs were stored in the dark bottles at room temperature and they were found to be stable for >1 month. UV-Vis absorption spectra of AgNPs were recorded by a SPECORD250 Spectrophotometer in the wavelength range between 250-700 nm. Their morphology were analyzed using a JEOL JEM 2100 Transmission Electron Microscope (TEM). The sensing ability to PSE of the obtained AgNPs colloids were tested by mixing 1 mL of various PSE concentrations of 0, 50, 100, 200 and 400 ppm using acetone as solvent with 1 mL of the synthesized AgNPs colloids. The mixtures were shaken for 5 min and then 5 mL of deionized water was added. The mixtures were then analyzed with UV-Vis spectroscopy and TEM using the same instruments as previously mentioned.

RESULTS AND DISCUSSION

Optical characteristics of the synthesized silver nanoparticles: The synthesis of AgNPs was achieved by UV radiation assisted method in the presence of TA solution at pH ranging from 5.0-9.0. It was reported that at least two hydroxyl groups at the ortho or para position of the polyphenolic compound structure gave out two electrons oxidation and changed to quinone form while silver ions were reduced (Yoosaf *et al.*, 2007; Dutta and Dolui, 2011). Moreover, another work revealed that at initial pH of TA solution of 6.0 and without UV exposure, the obtained AgNPs were agglomerated (Han *et al.*, 2014). Figure 1 shows UV-Vis spectra of the synthesized AgNPs. The spectra show that the main characteristic peaks of AgNPs are divided into two groups. First group of the characteristic peaks occur around 424 nm which can be attributed to AgNPs stabilized with TA. These characteristic peaks at this position were observed in every pH condition. The characteristic peaks of the second group occur at about 350 nm, observed in the products synthesized using pH conditions of 7.0, 8.0 and 9.0. This group can be attributed to AgNPs stabilized with gallic acid. This can be explained by the occurrence of gallic acid in these systems. The results suggested that the nanoparticles synthesized using pH of 7.0, 8.0 and 9.0 showed the increasing amounts of nanoparticles stabilized with gallic acid as pH was elevated. Their spectra also suggested that their sizes were smaller than those obtained from pH of 5.0 and 6.0 which were then confirmed by TEM images as shown in Fig. 2.

Sensing ability of the synthesized silver nanoparticles: Due to pH dependent nature of PSE, it was observed that only AgNPs synthesized using initial pH of 5.0 and 6.0 exhibited the sensing ability to PSE as shown in Fig. 3 and 4. The colors of these TA-stabilized AgNPs significantly changed when exposed to the increasing amounts of PSE in acetone solution. At pH of 5.0, the color of the AgNPs colloids changed from yellow to greenish blue (sample of pH 5.0) and the characteristic peak shifted from 420-635 nm as PSE amounts were increased from 0-400 ppm as shown in Fig. 3. At pH of 6.0, the color of the AgNPs colloids changed from yellow to red and UV-Vis characteristic peak shifted from 420-540 nm as PSE amounts were increased from 0-400 ppm as shown in Fig 4. This is due to the fact that PSE can be hydrolyzed in acidic condition and forms sulfonamide, heterocyclic amine and carbon dioxide as shown in Reaction 1 (Sarmah and Sabadie, 2002; Singh and Singh, 2013). Later, the heterocyclic amines probably accept hydronium ions in acidic condition and then form cationic species at primary

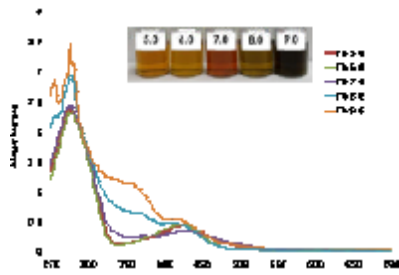


Fig. 1: The UV-Vis spectra of AgNPs colloids synthesized using various initial pH of TA solutions (inset picture displays the appearances of AgNPs colloids)

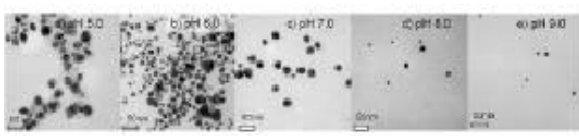


Fig. 2: TEM images of AgNPs synthesized using various initial pH of TA solutions

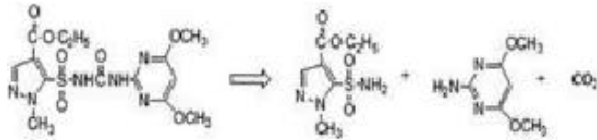


Fig. 3: Cationic species

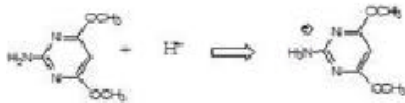


Fig. 4: Primary amine position

amine position as shown in Reaction 2 (Sarmah and Sabadie, 2002; Singh and Singh, 2013); The effect of the surrounding medium on the optical properties resulting in the shift of the absorption spectra to higher wavelength when changing the surrounding medium from water to acetone were reported (Silva *et al.*, 2010; Tilaki and Mahdavi, 2006; Pyatenko, 2010). However, in the sensing test with 0 ppm of PSE in acetone solution, there was no significant change in the color when AgNPs colloids were mixed with acetone solution. This can be concluded that acetone did not significantly affect the color change of the synthesized AgNPs, at all pH range used in this study.

Those heterocyclic amine cations can change the dielectric constant of the surrounding medium by their nature of basic substance (Robert and Robert, 1992). This can cause the shift of LSPR band of those AgNPs as shown in Fig. 5 and 6. However, the

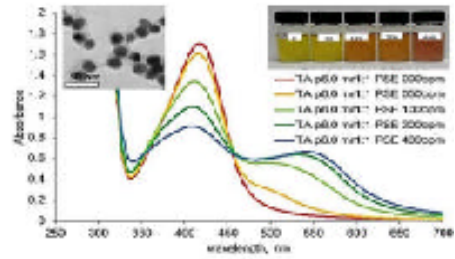


Fig. 5: UV-Vis spectra of AgNPs colloids synthesized using initial pH of TA solution at 5.0, after exposed to various amounts of PSE (inset pictures; left: TEM image of AgNPs after exposed to 400 ppm of PSE, right: the color change with increasing herbicide concentrations)

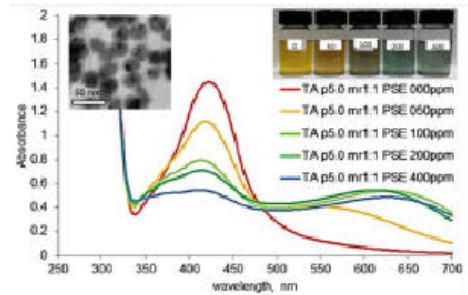


Fig. 6: UV-Vis spectra of AgNPs colloids synthesized using initial pH of TA solution at 6.0, after exposed to various amounts of PSE (inset pictures; left: TEM image of AgNPs after exposed to 400 ppm of PSE, right: the color change with increasing herbicide concentrations)

results show that UV-Vis characteristic peaks of the samples synthesized at pH of 5.0 shift to longer wavelength than those of the samples synthesized at pH of 6.0. These results were confirmed with TEM images as shown in both figures. This is because the more acidity of the surrounding medium, the more heterocyclic amine cations formed. Those cations affect the dielectric constant of the medium. From these results, it can be explained that in acid condition, TA molecules turn poly phenols parts on their surface, to make particles stable in aqueous solution. Then, the heterocyclic amine cations can solvate around the nanoparticles surface with the electrostatic force. The inset pictures of TEM images showed that after exposed to PSE, there was thin layer of those stabilizers. These layers coated around the nanoparticles surface which made LSPR bands shifted to higher wavelength. The schematic picture representing how PSE interacts with silver nanoparticles is shown in

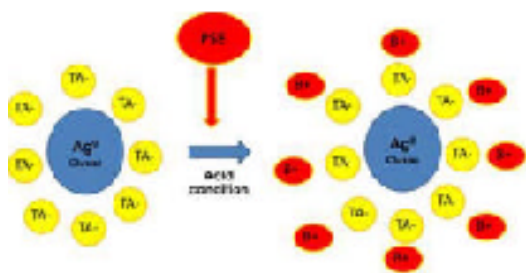


Fig. 7: Schematic picture representing the interaction between pyrazosulfuron ethyl herbicide and TA-stabilized silver nanoparticles (TA = Tannic Acid, PSE = Pyrazosulfuron Ethyl, B⁺ = Cationic of heterocyclic amine)

Fig. 7. When PSE is in acidic solution, it is hydrolyzed as previously mentioned. Then the cationic heterocyclic amines surround TA-stabilized silver nanoparticles with the electrostatic attraction. This results in the formation of the bigger nanoparticles. This results in the observation in UV-Vis spectra that the absorbance of the original peak decreases and a new peak formed at the longer wavelength due to bigger particles formation. Moreover, the increasing amount of PSE solution can make the characteristic peaks of AgNPs shifted to the higher wavelength. Those synthesized using pH of 5.0 and 6.0 of TA exhibit the maximum positions at 625 and 550 nm, respectively as shown in Fig. 3 and 4.

CONCLUSION

UV radiation assisted method can be used to support the formation of AgNPs in wide range of pH conditions. PSE sensing test results showed that pH conditions of the synthesized AgNPs colloids affected the ability to detect PSE. It was indicated that the colorimetric detection of PSE can be achieved when TA-stabilized AgNPs synthesized using initial pH of TA solution at 5.0 and 6.0. The results showed that the synthesized AgNPs exhibited the sensitivity to the herbicide at low concentration as 50 to 400 ppm. This system could be fabricated to simple herbicide detection application which is easily to carry on for onsite service with quick response result.

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