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 nanoparticles 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, sulfonyleurea 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
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
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 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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