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Preparation of Gold/Silver Core-Shell Nanoparticles for Colorimetric Sensing and as Photocatalyst in the Degradation of Organic Dye

Ai Chia Patrick Melet,[a] Sheela Chandren,[a]* and Wijitar Dungchai[b]

[a]*Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 Johor Bahru, Malaysia*
[b]*Department of Chemistry, Faculty of Science, King Mongkut's University of Technology Thonburi, Bangkok Thailand*
**Corresponding Author: sheela@kimia.fs.utm.my*

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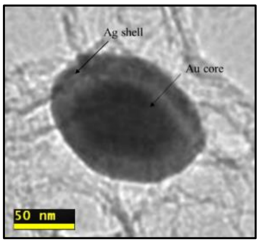
GRAPHICAL ABSTRACT



TEM image of gold/silver core-shell

ABSTRACT

Bimetallic gold/silver core-shell nanoparticles (Au/Ag core-shell NPs) were prepared by chemical reduction in aqueous solution, using an environmental-friendly and economical method. Core Au NPs (~20 nm) were synthesized in the presence of citrate ions as the reducing agent and stabilizing agent. Synthesis of Ag shell was carried out by reducing Ag^+ over Au sol in the presence of ascorbic acid (AA) as the reducing agent. Localized surface plasmon resonance (LSPR) of Au (~520 nm) obtained from ultraviolet-visible (UV-Vis) spectra, confirmed the formation of the NPs, while the formation of core-shell structure was proven by the presence of blue-shifting in the spectrum after the addition of AA into the Ag precursors. Transmission electron microscopy (TEM), field-emission scanning electron microscopy (FESEM) and X-ray diffraction (XRD) analyses confirmed the presence of Au core and Ag shell in the core-shell structure. The synthesized Au/Ag core-shell NPs were utilized in the application of colorimetric sensing of Vitamin C (also known as AA) and photocatalytic degradation of an organic dye, methyl orange (MO). For colorimetric sensing, the distance-based paper sensor was designed to determine a high-resolution colorimetric protocol. Au/Ag core-shell NPs in solution form was used as the indicator on the sensor to detect AA, where the quantification of AA has been achieved by measuring the length of the yellow colour band, and it was shown that the yellow colour band length was proportional to the concentration of AA. In the photocatalytic degradation of MO, it was found that the Au/Ag core-shell NPs were inactive under visible light irradiation, contrary to the characterization results. This could be caused by the lower surface area of the agglomerated NPs and the change in the oxidation state of the metals. Hence, modification to the synthesis step must be undertaken in order to allow visible light photocatalytic activity.

Keywords: Gold nanoparticles, silver nanoparticles, core-shell, colorimetric sensing, photocatalytic

1. INTRODUCTION

Over the last years, many technologies have been developed in the field of nanotechnology, which involves particles in the size range of 1 to100 nm [1]. In the last century, nanoparticles (NPs) have been extensively used in the field of research due to their significant chemical and physical characteristics of their size and structure [2]. There are several well-known classes of NPs, such as metal NPs, carbon-based NPs, ceramic NPs, semiconductor NPs, polymeric NPs and lipid-based NPs. Typically, metal NPs are the most flexible NPs due to their synthetic control of size, encapsulation, structure, shape and tunable optical properties [4].

In particular, gold and silver nanoparticles (AuNPs and AgNPs) have been extensively used in photocatalysis [5] and electrocatalysis, as sensors in the field of chemistry and biology [6], in medicine [7], and surface-enhanced Raman scattering [8]. This is due to their unique optical properties [9] and the remarkable localized surface plasmon resonance (LSPR) band. The plasmonic absorptions for both of these metal NPs are generally restricted to around 520 nm and 400 nm, respectively LSPR band is induced by the interaction between free electrons and light, which creates a strong electromagnetic field around the NP at specific resonance wavelength. The shape and wavelengths position (λ_{LSPR}) depend on the size and shape of the NPs, degree of agglomeration, and local refractive index around the NPs. In addition, both metals have the characteristics of a face-centered cubic (fcc) crystal structure and lattice constants [10], which make the synthesis of Au/Ag core-shell structures very simple. In other words, the combination of two metal NPs, known as bimetallic NPs, has gained a lot of interest among researchers. According to previous study [11], the bimetallic core-shell nanostructure of Au and Ag are very well known due to their plasmonic, catalytic and sensor-based applications.

Many methods to synthesize Au/Ag core-shell NPs, have been described and one of them is by using the micro-emulsion technique. The synthesis of different sizes and morphologies of Ag layers onto Au core by using a microwave mediated polyol reduction. It was proven that the selective adsorption of polyvinylpyrrolidone (PVP) influenced the morphology of the particles during the Ag deposition. In addition, a group of researchers has also reported the deposition of Ag and ascorbic acid (AA) onto Au seeds in the presence of different capping agents, prepared on the aqueous medium. This method has been extendedly used in the preparation of Au/Ag core-shell nanostructures either to modify the particle size and morphology or to improve the dispersion stability.

Moreover, detection of sulfide and cyanide have been investigated based on Au/Ag core-shell NPs as colorimetric sensing probes. Most of the works only focused on one usage, instead of using the synthesized Au/Ag core-shell NPs for both AA detection and as photocatalyst in the degradation of organic dye.

In this study, AuNPs were synthesized by encapsulating Au in AgNPs, where AA was used as the reducing agent. Following the synthesis procedures, colorimetric sensing in the detection of AA and photocatalytic activity were tested out in the degradation of methyl orange (MO) dye as the model for organic pollutant under visible light irradiation.

2. EXPERIMENTAL

The LSPR wavelength of Au-NPs formed was measured by using UV-Vis spectroscopy (Lamda 35, Perkin 15 Elmer Instruments, USA) at the wavelength range of 200 - 900 nm. The morphology of Au/Ag core-shell NPs photocatalysts were analyzed by using TEM (JEOL, JEM-2100F) at an accelerated voltage of 200 kV and FESEM-EDX (JEOL, 6701F) at an accelerated 15 kV. The crystallinity analysis was done using XRD (Rigaku SmartLab X-Ray Diffractometer) with a Cu Kα radiation (1 = 1.5406 Å) operated at 40 kV and 30 mA.

3. RESULTS AND DISCUSSION

3.1. Synthesis of AuNPs

The first step was preparing $HAuCl_4$ solution at the concentration of 0.25 mM. The next step was reducing $HAuCl_4$ with $Na_3C_6H_5O_7$ as the reducing agent to obtain AuNPs in colloid state. The process colloidal gold formation involved three steps: ligand exchange reaction, decarboxylation, and reduction of Au (III) species. The colour of the solution was changed moderately, starting from transparent, to grey, to dark purple and eventually stabilized as red wine colour, as the colour of Au NPs. Figure 1 shows $HAuCl_4$ in the starch solution that changed to red wine colour after $Na_3C_6H_5O_7$ was added. Figure 2 shows $HAuCl_4$ in deionized water that changed to red wine colour after adding $Na_3C_6H_5O_7$.

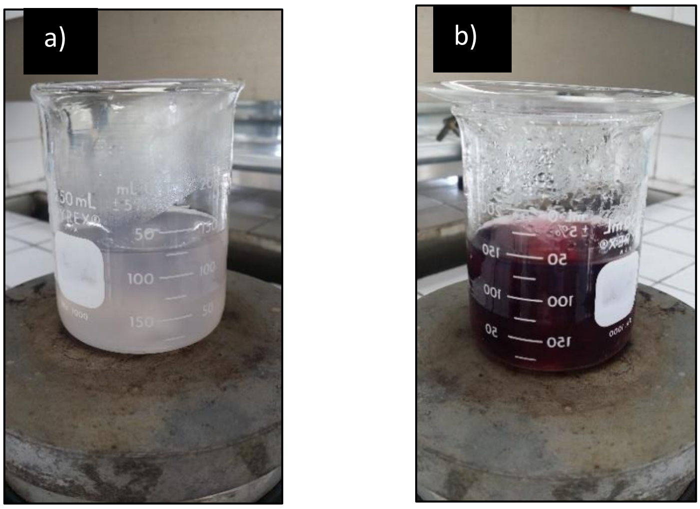


Figure 1. (a) Cloudy solution changed to (b) red wine-coloured solution after the addition of $Na_3C_6H_5O_7$

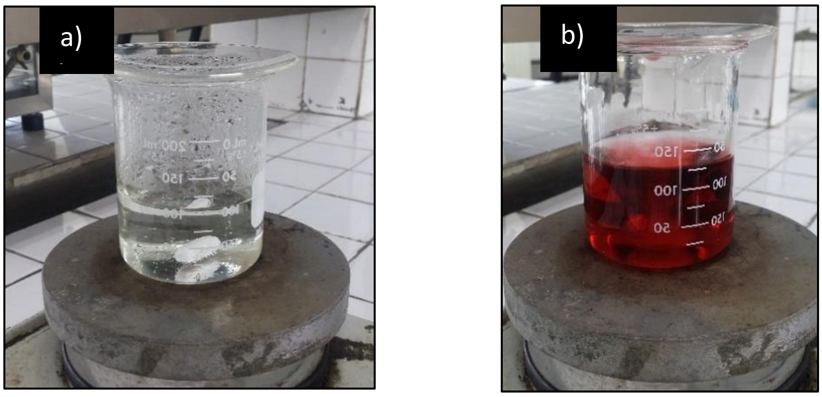


Figure 2. (a) Colourless solution changed to (b) red wine-coloured solution after the addition of $Na_3C_6H_5O_7$

$Na_3C_6H_5O_7$ acted as the reducing agent and capping agent, whereby it reduced Au^{3+} to Au^0, changing a soluble cation into an insoluble metal atom. This shows that solid atomic species have been generated in a liquid medium. A research [12] reported that due to the high separation of atomic species, large surface energy has been produced. Hence, it cannot stabilize the system and the formation of colloidal aggregates is promoted. It has been proven that $Na_3C_6H_5O_7$ solution has the ability to be a good stabilizing agent, which is electrostatically bonded to the surface of the NPs by cationic intermediates, and electrostatic repulsion is generated through its surface charge.

The number of particles with enough energy to overcome the critical barrier increases with temperature. For this reason, the synthesis of AuNPs was carried out at the boiling point of the mixture through heating at 100 ^{o}C. NPs have large surface to volume ratios implying that NPs display high surface energy which makes them thermodynamically unstable or metastable. Hence, to overcome their large surface energy and prevent NPs from agglomerating, stabilization must be employed. Stabilization in this study was accomplished by using $Na_3C_6H_5O_7$, which is electrostatically bonded to the surface of the NPs by cationic intermediates and generated electrostatic repulsion through its surface charge.

Au/Ag core-shell NPs can be identified by UV-Vis spectroscopy. Initially, AuNPs exhibit the distinct black colour line, resulting from LSPR where maximum absorption took place approximately at 520 nm and shown in Figure 3. The value of the LSPR wavelength for Ag in the core-shell structure was found to be approximately 400 nm, which is within the expected range of 400 to 410 nm. The LSPR of Au as seed and as part of the core-shell structure, shows red shifting. However, the addition of AA into the dispersion containing Ag precursor influenced the wavelength causing blue shifting. When AA with the concentration of 500 ppm and 1000 ppm were added into the solutions of AuNPs and $AgNO_3$, core-shell NPs were formed. This is due to the optical properties called plasma resonance.

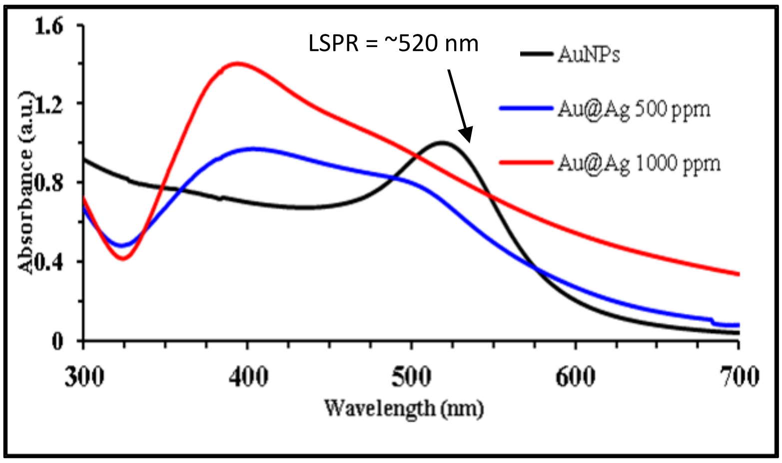


Figure 3. Absorption spectra of AuNPs and Au/Ag core-shell NPs with the concentration of AA at 500 ppm and 1000 ppm

3.2. Encapsulation of AuNPs core with AgNPs outer shell

In the process of heterogeneous nucleation on the surface of AuNPs, $AgNO_3$ was reduced due to the presence of Au core. In this part, the experiment was conducted at room temperature. Hence, the activation energy for nucleation of the solid phase is smaller. Since the energy barrier is higher, the number of Ag nuclei to overcome the barrier was lower, followed by migration to reduce the total free energy and growth on the surface of AuNPs. In the presence of AA, AA was oxidized, and Ag ions are reduced to metallic Ag. At a later stage, AA was degraded by decarboxylation and Ag takes over as growth agent for the NPs, hence core-shell structure was obtained. Figure 4 shows the formation of Au/Ag core-shell NPs.

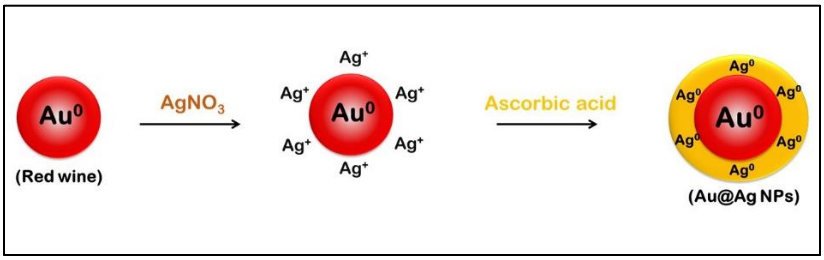


Figure 4. Formation of Au/Ag core-shell NPs

3.2.1. Morphological Study of Au/Ag Core-Shell NPs

The morphology of Au/Ag core-shell NPs was observed by using TEM with high resolution at accelerated voltage of 200 kV. TEM images of Au/Ag core-shell NPs are presented in the Figure 5. In Figure 5 (a), as can be seen, the coating of Ag shell towards Au core can be clearly identified. However, in Figure 5(b), it can be seen that there were some relatively round granular uncoated particles which were identified to be AuNPs. Hence, this shows that some AuNPs have not been encapsulated by Ag and might have agglomerated if left alone. It was found that after the addition of $AgNO_3$ and AA, the particle size of Au that formed the core-shell structure is larger. After the Ag ions were reduced by AA, the Ag particles then captured the surface area of AuNPs.

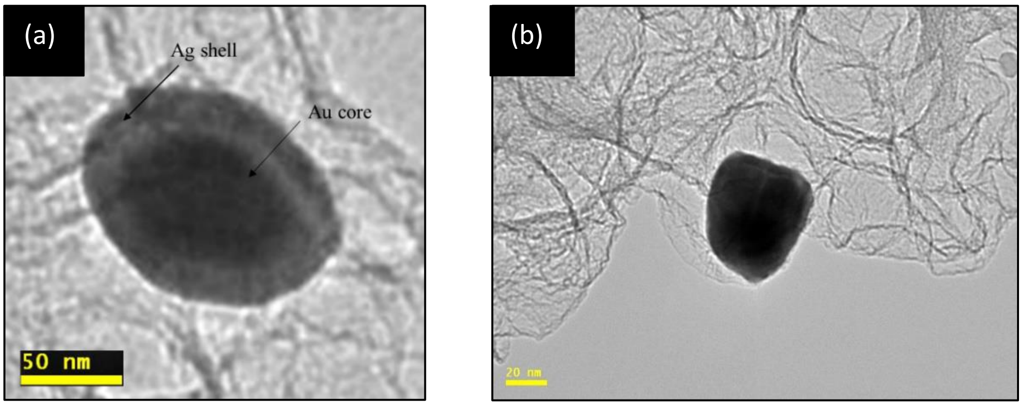


Figure 5. TEM images (a) Au/Ag core-shell NPs (b) AuNPs

Apart from TEM, FESEM has also been carried out and the spherical shape of NPs can be clearly seen, as shown in Figure 6. Agglomeration can also be clearly seen. EDX analysis was also carried at in order to determine the elements present in the sample. Based on the analysis, the results are presented in Table 1. it was revealed that the element present in the highest percentage is Ag. Au present in a much smaller percentage as the core-shell structure consists of Ag in the outer layer. Hence, more Ag was detected.

Table 1. EDX elemental analysis of Au/Ag

Element	**Weight (%)**
Au	13.08
Ag	86.92

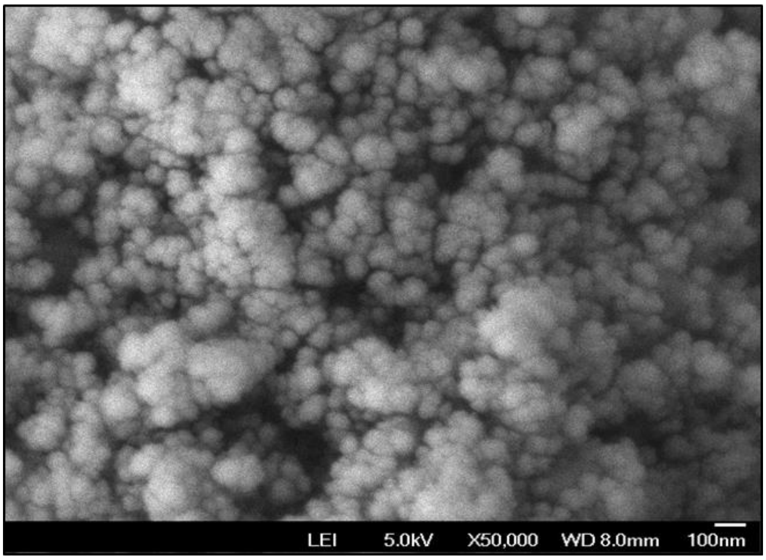


Figure 6. FESEM image of Au/Ag core-shell NPs

3.2.2. Crystallinity of Au/Ag core-shell NPs

The powder XRD pattern of Au/Ag core-shell (Figure 7 (a)) shows the sharp peaks corresponding to the fcc of Au(0) and Ag(0). However, some overlapping can be seen due to the similar miller indices of both NPs. The diffraction peaks at 2θ of 38.04º, 44.24º, 64.38º and 77.35º, are characteristics of (111), (200), (220) and (311) planes, respectively. The results obtained was in good agreement with previous study [13]. It can be observed that the composition of this sample did not alter the structural properties of both NPs. In addition to this, the d-spacing for 38.04º (111) is found to be 0.236 nm for both Au and Ag. This d-spacing value has been obtained from the Bragg's Law equation, shown in Equation 1, where n is the integer.

$$n\lambda = 2d\sin\theta \qquad (1)$$

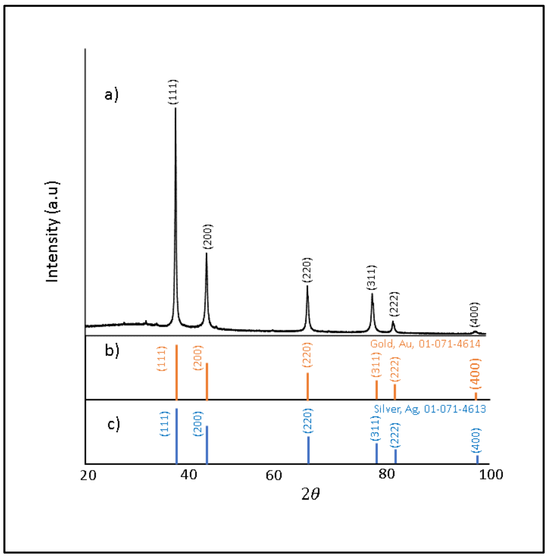


Figure 7. XRD patterns of (a)Au/Ag core-shell NPs (b) reference of Au ICDD (PDF-2 Release 2105 RDB) (c) reference of Ag ICPP (PDF-2 Release 2015 RDB)

3.3. Application of Colorimetric Sensing

In this study, a distance-based paper sensor on PADs was developed for the detection AA with the reaction of Au/Ag core-shell NPs. Investigation of oxygen effect towards AA and analytical performance have been run to validate this assay for the detection of AA in real samples of Vitamin C.

3.3.1. Calibration performance of the paper sensor

From the results, the changes in colour for AA corresponded to the concentration of AA as shown in Figure 8 and Figure 9, which show that the distance was affected by the concentration of AA. The calibration equation obtained from the graph was y =20.04x - 37.691 and the correlation coefficient (R^2) was 0.9891. The results obtained can be considered as accurate and precise since it was close to 1.

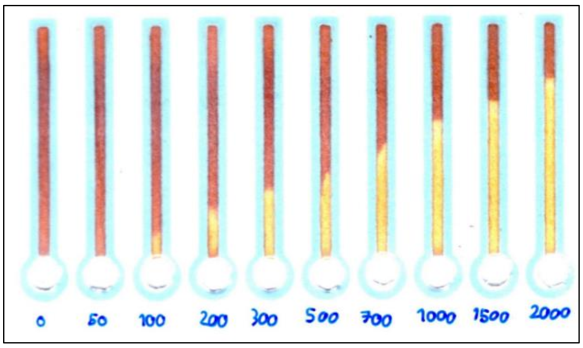


Figure 8. The corresponding relationship between the increasing colour band length and the increasing concentration of AA in ppm

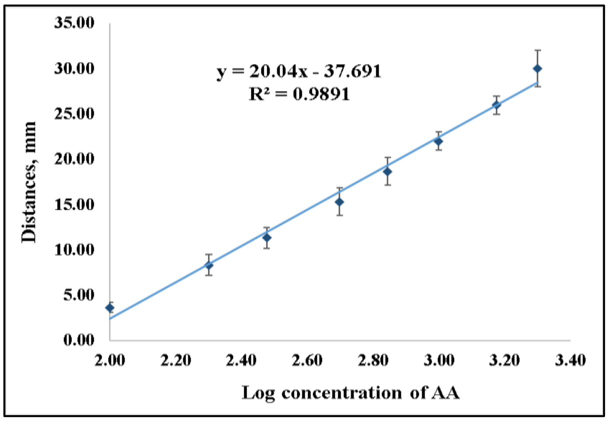


Figure 9. The calibration curve of AA between 100 and 2000 mg/L using distance-based paper sensor

3.3.2. Colorimetric testing for AA detection

To validate that Au/Ag core-shell NPs can act as sensor for the determination of AA in real samples, 2 different brands of vitamin C tablets were bought from a local pharmaceutical shop and were analysed. The changes of colour and the length were measured which corresponded to the concentration of AA, as shown in the Figure 11. From the results obtained, sample A (ASCEE 500) show 98% of accuracy while sample B (Vita-c) show 83% of accuracy. These high values indicate that high content of AA was present in these 2 types of real samples.

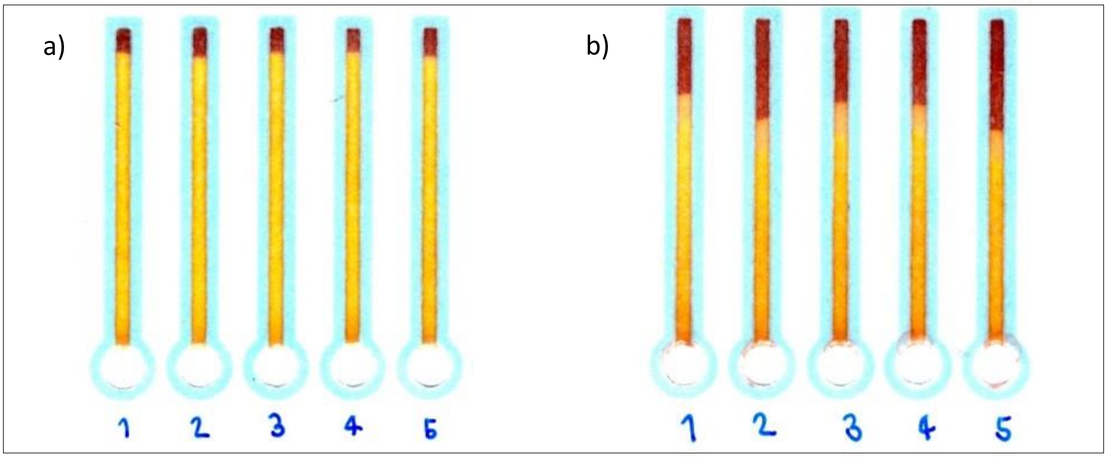


Figure 10. Detection of AA in real samples in 5 readings (a) Sample A (b) Sample B

3.4. Photocatalytic Activity of Au/Ag Core-Shell NPs

Photodegradation study is important to determine the efficiency of the photocatalyst synthesized. In this study, MO dye has been chosen as the model of organic pollutant and the catalytic activity of Au/Ag core-shell NPs was tested out under visible lamp irradiation. The UV-Vis spectra of MO with different concentrations are shown in Figure 11. The UV-Vis spectra show the increasing intensity of MO dye's peak located at 464 nm for different concentrations, which has also been reported by other researchers [14,15]. The calibration curve was used to determine the concentrations of MO at certain period interval based on mathematical relationship given.

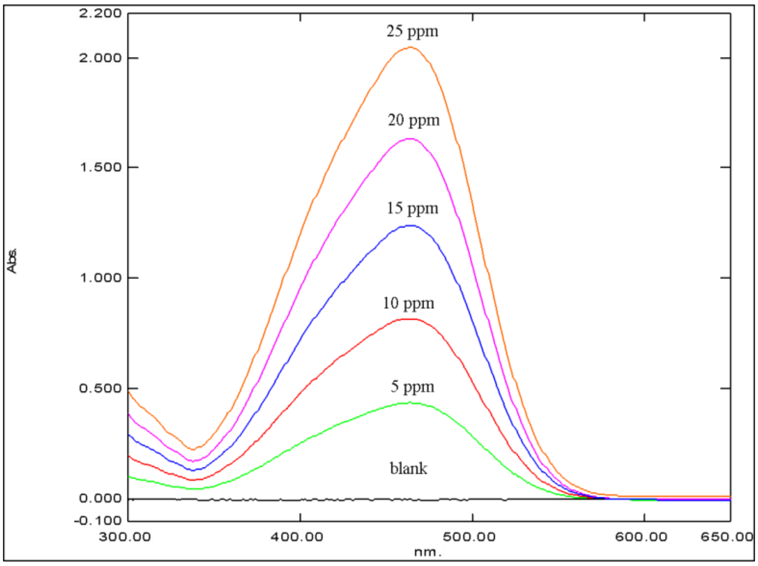


Figure 11. Graph of absorbance obtained for different MO's concentrations

In this study, regrettable, the Au/Ag core-shell NPs have failed to degrade MO under visible light irradiation, contrary to the characterization and predicted results. This could be caused by the lower surface area of the agglomerated NPs. Agglomeration is a process which resulted in a reduction of surface free energy by increasing size and decreasing surface area. Agglomeration of NPs occurred due to adhesion of particles to each other by weak forces leading to dispersed particles. In addition, it is speculated that changes in the oxidation state of the metals may have taken place where Au(0) and Ag(0) changed back to higher oxidation state. Hence, there was no active sites for the MO to undergo degradation.

4. CONCLUSION

In this study, Au/Ag core-shell NPs have been successfully synthesized by using Turkevich method, where trisodium citrate acted as the reducing agent and stabilizing agent. UV-Vis spectroscopy has been used to determine the LSPR band of Au/Ag core-shell NPs. TEM, FESEM and XRD were used to study the physicochemical properties of the synthesized Au/Ag core-shell NPs. Colorimetric sensing application of the Au/Ag core-shell NPs was used to detect 2 types of Vitamin-C (AA) in the distance-based paper sensor has also been successfully carried out. For the last part, photodegradation of MO dye has been carried out under visible light irradiation in the presence of photocatalyst, which was analyzed by using a UV-Vis spectrometer.

Based on the results obtained, it has been proven that encapsulation of AuNPs as core with AgNPs shell has been successfully carried out and the morphology was confirmed by the TEM images. The XRD patterns revealed that AuNPs and AgNPs have been detected in the composite which showed crystallinity. The optical properties of Au/Ag core-shell NPs showed the increment of wavelength towards visible light region that could prove the potential application of the photocatalyst under visible light irradiation.

The colorimetric sensing ability of Au/Ag core-shell NPs as the indicator sensor for AA (Vitamin C) detection was proven by using the distance-based paper sensor, which is low cost, rapid, easy to operate, instrument free and portable. The changes in colour of AuNPs in red wine to orange-yellow colour of the Au/Ag core-shell NPs was due to the altered LSPR. Yellow colour band length, which corresponds to the quantity of AA due to strong changes in colour, can be easily detected by the naked eye. However, for the photocatalytic activity testing, even after 6 h of visible light irradiation, no MO was degraded, showing the inactiveness of the synthesized Au/Ag core-shell NPs in visible light range.

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