Synthesis of Silica-Silver Core-Shell Nanoparticles and Catalytic Effect

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Silica nanoparticles were synthesized using the Stöber's method under ultrasonic condition at room temperature. Silver nanoparticles were prepared by reacting an aqueous silver nitrate solution with glucose and poly(vinyl alcohol) (PVA) under microwave condition. 3-Mercaptopropyl trimethoxysilane (MPTMS) and 3-aminopropyl trimethoxysilane (APTMS) were used as a linker to combine the silica and silver nanoparticles. The synthesized silica-silver core-shell nanoparticles were characterized by X-ray diffraction, scanning electron microscopy and UV-VIS spectroscopy. UV-VIS spectroscopy was used to monitor the effect of the synthesized silica-silver core-shell nanoparticles as a catalyst for reducing various nitrophenols, such as 2-nitrophenol, 3-nitrophenol and 4-nitrophenol.

Key Words: Silica nanoparticles, Silver nanoparticles, Silica-Silver nanoparticles, Core-Shell nanoparticles, Nitrophenols.

INTRODUCTION

Hollow SiO_2 spheres have attracted considerable attention because of their high surface area, unique morphology and non-toxicity[1-3]. Hollow SiO_2 spheres can be used as catalysts, drug release materials and for water retention[4,5]. The synthesis of hollow SiO_2 spheres can be classified according to the approach used, such as hard sacrificial cores, micelle directed synthesis and layer-by-layer self-assembly techniques, *etc.*[6-8]. In this study, hollow SiO_2 spheres were synthesized using a modified Stöber method with tetraethyl orthosilicate (TEOS) under ultrasonic condition.

Silver nanoparticles are also important in nanochemistry because of their electrical conductivity, antimicrobial effects, optical properties and applicationsin oxidative catalysis[9-13]. The preparation and characterization of silver nanoparticles have been discussed in many publications[14,15]. In the present study, a silver nanocolloid was synthesized from silver nitrate, glucose and poly(vinyl alcohol) (PVA) under ultrasonic condition. One of the main reason for the considerable work on silver colloids is to produce uniform surface coatings, such as those made from silica, which might make it possible to control the surface characteristics of materials[16-18].

In recent years, multi-phase nanocomposites have attracted a great deal of attention in advanced materials because multi-phase nanocomposites have improved or altered physical and chemical properties compared to their single component. Core-shell structured nanoparticles are one famous example of multi-phase nanocomposites. Several types of core-shell nanostructures, such as heterogeneous metal/metal, metal/semiconductor, metal/polymer and other combinations have been studied[19]. The shell coating of the core not only stabilizes a colloidal dispersion but also adjusts the core particle properties, such as the optical, magnetic and catalytic properties, *etc*, depending on the shell composition. For example, poly(acrylic acid)-stabilized silver nanoclusters have higher catalytic activity than commercial silver catalysts[20]. Some functional core-shell nanoparticles are renown in technological areas, such as microelectronics, optic, magnetic, photoactive devices and biomedical areas[21,22].

Since the original work of silica-coated gold nanoparticles by Mulvaney *et al.* in 1996, silica-coated colloidal nanoparticles, including other noble-metal nanoparticles and luminescent quantum dots, have been studied extensively to enhance their colloidal stability in a wide range of solvents, from polar to non-polar[23-29]. Silica-metal core-shell particles have attracted considerable attention because of their unique properties due to a combination of the mechanical and thermal stability of silica and the magnetic, electronic, optical and catalytic properties of metal nanocrystals, such as silver, gold, *etc*.

Metal nanoparticles have been used in the hydrogenation of various compounds on account of their higher catalytic efficiency than their bulk counterparts owing to their large surface-to-volume ratios[30-35]. Metal nanoparticles are employed as catalysts to synthesize aromatic amine compounds, which are used widely in industry as intermediates for the synthesis of agrochemicals and dyes[36,37]. They are normally prepared by the reduction of aromatic nitro compounds through catalytic

hydrogenation and stoichiometric reduction[38-41]. Catalytic hydrogenation is a convenient method for reducing aromatic nitro compounds in high yield. In this study, two different silica-silver core-shell nanoparticles with an 3-aminopropyl trimethoxysilane (APTMS) linker and 3-mercaptopropyl trimethoxysilane (MPTMS) linker were evaluated as a reduction catalyst for various nitrophenols, such as 2-nitrophenol, 3-nitrophenol and 4-nitrophenol.

EXPERIMENTAL

Ammonium hydroxide, tetraethyl orthosilicate, AgNO₃, 3-aminopropyl trimethoxysilane (APTMS), 3-mercaptopropyl trimethoxysilane (MPTMS), NaBH₄, 2-, 3- and 4-nitrophenol were purchased from Sigma-Aldrich. Poly(vinyl alcohol) (PVA), glucose and ethanol were obtained from Samchun Chemicals.

Silica nanoparticles, Ag nanoparticles and Si-Ag core-shell nanoparticles were treated under a range of condition by ultrasonic irradiation using an ultrasonic generator (UGI1200, Hanil Ultrasonic Co., Ltd.) with a frequency 20 kHz and nominal power of 750 W. The ultrasonic generator was a horn type system with a horn tip diameter of 13 mm.

The surfaces of the Si-Ag core-shell nanoparticles with APTMS and MPTMS linkers were observed by scanning electron microscopy (SEM, Hitachi S4700) at an accelerating voltage of 0.5 to 15 kV. The structures of the nanomaterials were examined by X-ray diffraction (XRD, Rigaku, Rigaku DMAX PSPC MDG 2000). The samples were analyzed by UV-VIS spectroscopy (UV-VIS, Shimadzu UV -1601PC).

Chemical modification of silica nanoparticles: Modification Stöber method: In a typical experiment, 3 mL of ammonium hydroxide was mixed with 4 mL of tetraethyl orthosilicate (TEOS) in 50 mL of ethanol and stirred for 0.5 h. The resulting solution was ultrasonicated for 1 h. After 1 h, 10 µL of APTMS or MPTMS was added and the mixed solution was ultrasonicated for a further 1 h.

To obtain a powder of silica nanoparticles, the mixed solution was centrifuged 5 times, washed with ethanol and allowed to dry on a watch glass.

Synthesis of silver nanoparticles: In a typical experiment, 10 mg of AgNO₃ was placed into 20 mL of distilled water with 5 mg of poly(vinyl alcohol) and 4 g of glucose, which were the dispersing and reducing, respectively. Subsequently, the mixed solution was placed on a microwave and heated until its colour had changed from colourless to yellow. The mixed solution was heated at 1 min intervals because the interval heating methods showed greater efficiency to synthesize silver nanocolloids.

Synthesis of silica-silver core-shell nanoparticles: Silica (10 mg) with organic groups, APTMS or MPTMS, was placed in 10 mL of distilled water. The silica solution was ultrasonicated for 1 h. 1 mL of the silica nanocolloids were dispersed into 13 mL of silver nanocolloid, and the mixture was ultrasonicated. For the comparison group (silica-APTMS/MPTMS-Ag nanocolloids), 1 mL of each APTMS or MPTMS was mixed with 13 mL of the silver nanocolloid and ultrasonicated. Every 15 min, the silica-silver nanocolloids with the APTMS or MPTMS linkers and their comparison groups were examined by UV-vis spectroscopy.

When the spectrum of the silica-silver nanocolloids with organic groups did not change, half of the nanocolloids were dried for further SEM and XRD analysis. To obtain a powder of silica-silver nanocomposite, the silica-silver colloids were centrifuged 5 times, washed with ethanol and left them to dry on a watch glass.

Reduction of nitrophenols with nanomaterials: The catalytic activity of the silica-Ag core-shell nanocomposites with two different linkers were examined using various nitrophenols; 2-, 3- and 4-nitrophenol. In addition, the Ag nanocolloids were examined as comparing with silica-Ag core-shell nanocomposites. 1 mL of each nanomaterial solution was mixed with 15 mL of water containing 0.02 mM of either of the nitrophenol solutions. All mixture solutions were monitored with 5 min interval by UV-VIS spectrometer.

RESULTS AND DISCUSSION

Fig. 1 shows the UV-VIS spectra of the APTMS-silver (a), MPTMS-silver (b), silica-silver with APTMS linker (c) and silica-silver with MPTMS linker nanocolloids (d) at various temporal stages. A general point of (a) to (d) is that the peaks increased and shifted to the right, which means that the silver nanoparticles had encapsulated other materials. This suggests that silver nanoparticles are more likely to coat APTMS and silica with APTMS linker particles than MPTMS and silica with a MPTMS linker.

Fig. 2. SEM images of (a) silica-silver nanocomposites with APTMS linkers and (b) silica-silver nanocomposites with MPTMS linkers
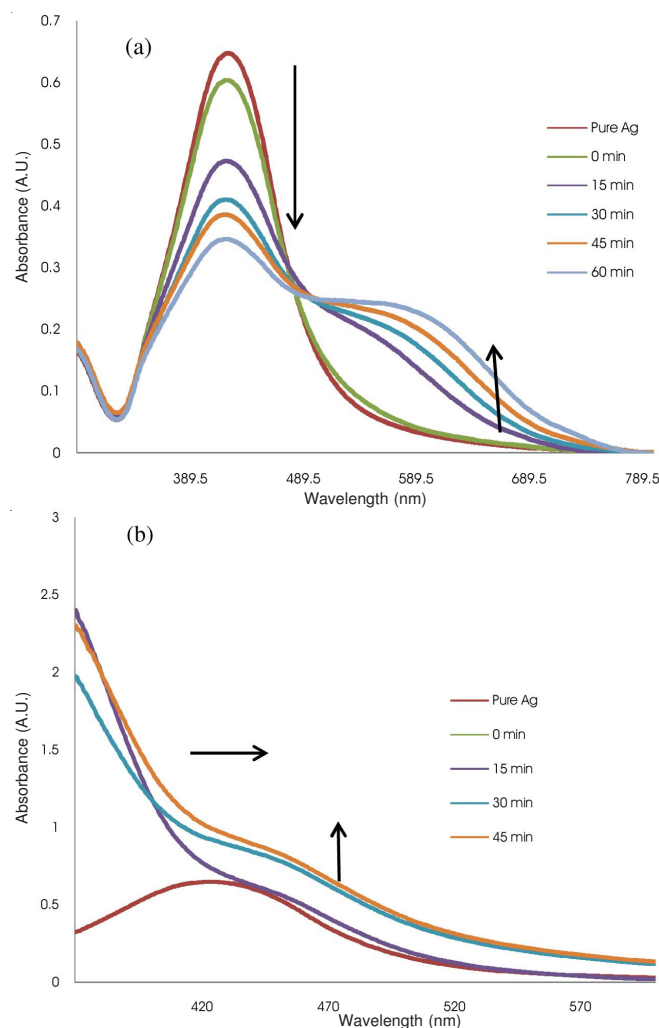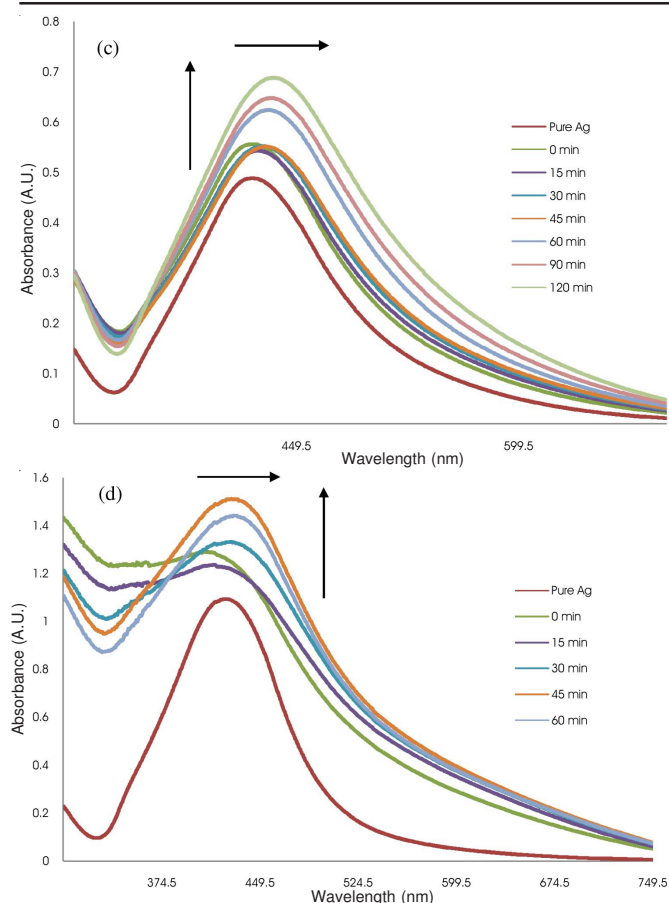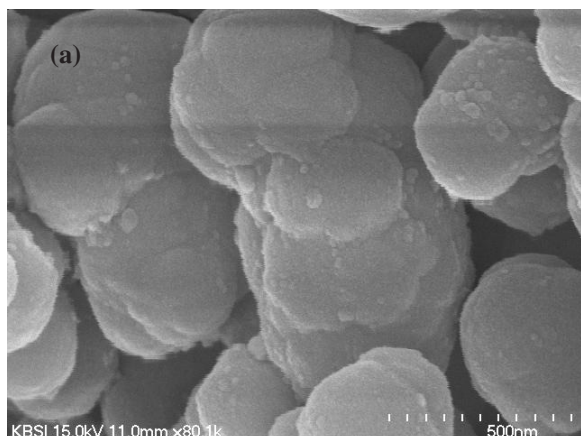
Fig. 1. UV-VIS spectra of (a) APTMS-silver nanocolloids, (b) MPTMS-silver nanocolloids (c) silica-silver nanocolloids with APTMS linkers and (d) silica-silver nanocolloids with MPTMS linkers

Fig. 2 presents SEM images of the silica-silver nanocomposites. The silver nanoparticles were attached to the silica nanoparticles. The silica-silver core-shell figure was difficult to observe using APTMS as a linker (a). On the other hand, the silica-silver core-shell figure using MPTMS as a linker was observed clearly (b). Furthermore, silver nanoparticles were more attached to the silica nanoparticles with MPTMS than those with APTMS linker.

Fig. 3 shows TEM images of the silica-silver nanocomposites. Figs. 3(i) and 3(ii) show that the silver nanoparticles are attached to the silica nanoparticle surfaces. Fig. 3(i) and Fig. 3(ii) show two different magnifications: 1 μm (a) and 200
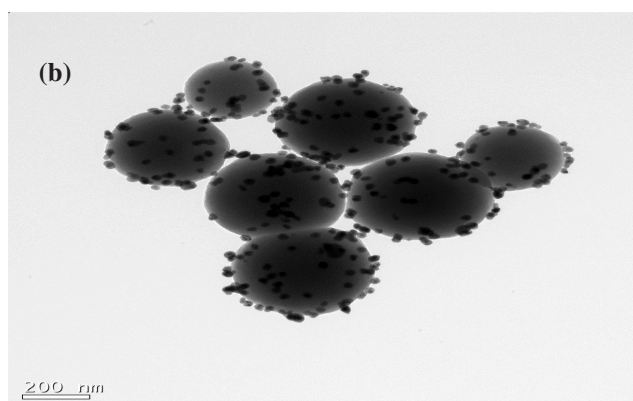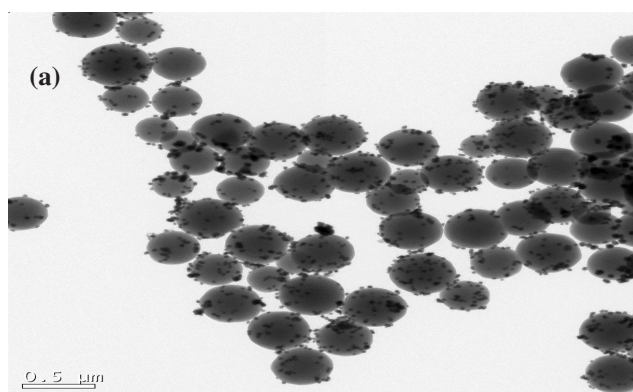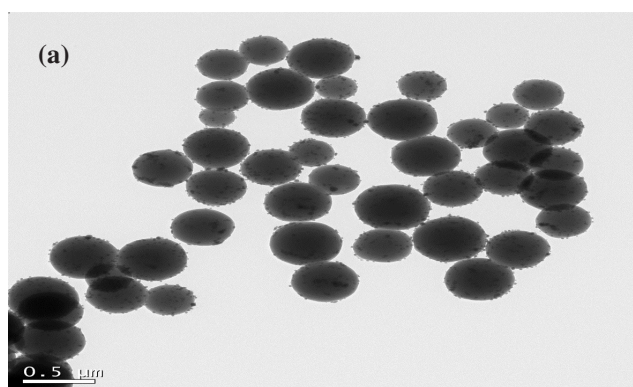
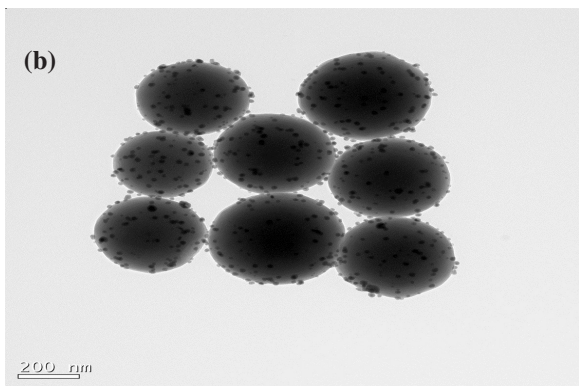Fig. 3(i). TEM images of silica-silver nanocomposites with APTMS linkers

Fig. 3(ii). TEM images of silica-silver nanocomposites with MPTMS linkers

nm (b). TEM of the silica-silver nanocomposites showed no differences between the APTMS and MPTMS linkers, where as SEM revealed significant differences.

Fig. 4 showed XRD patterns of the silica-silver nanocomposites with (a) APTMS linkers and (b) MPTMS linkers. The locations of the peaks were similar in the APTMS linkers and MPTMS linkers silica-silver nanocomposites. In contrast, the intensity of some peaks are different; the APTMS linker silica-silver nanocomposites have higher peaks than the MPTMS one. The XRD patterns of the APTMS linker silica-silver nanocomposites show peaks at 38.12, 44.34, 64.50 and 77.43 as a 2θ shown in Fig. 4(a). The peaks for MPTMS linker silica-silver nanocomposites at 38.14, 43.96, 64.36 and 77.25 as a 2θ shown in Fig. 4(b).
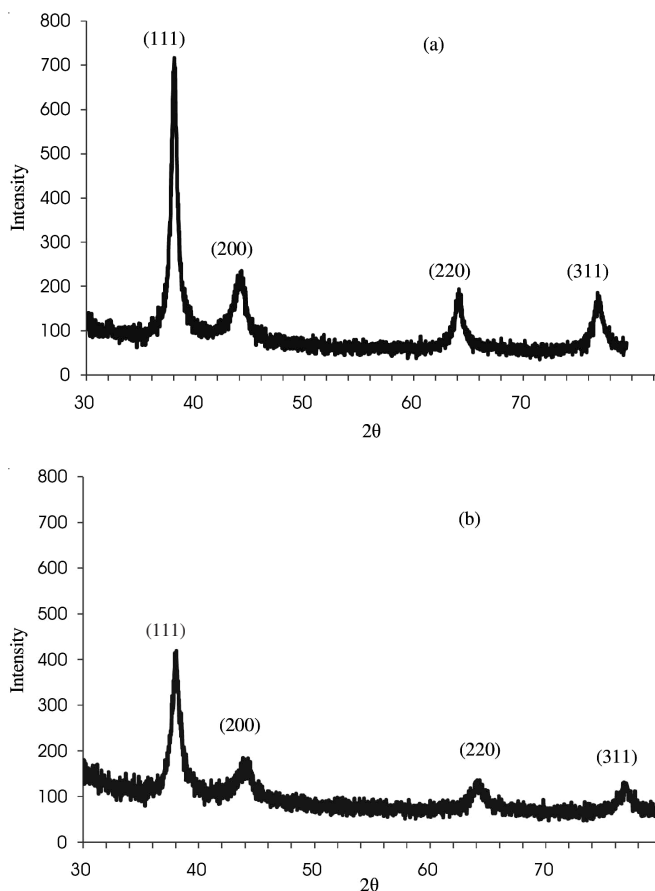

Fig. 4.   XRD images of (a) silica-silver nanocomposites with APTMS linkers and (b) silica-silver nanocomposites with MPTMS linkers

Fig. 5(i) to 5(ii) shows the reduced catalytic activities of silver nanoparticles and silica-silver nanocomposites with APTMS and MPTMS linkers. Silica-silver nanocomposites with APTMS linkers were the most effective reduction catalyst for all the nitrophenols examined. They reduced the nitrophenols to lower levels at a faster rate than when using the other nanomaterials. The second effective reduction catalyst was silica-silver nanoparticles with a MPTMS linker. In particular, for 2-nitrophenol, they reached a lower levels than the silica-silver nanocomposites with an APTMS linker. All nanomaterials showed better reductive catalytic effects to 4-nitrophenol than other nitrophenols.
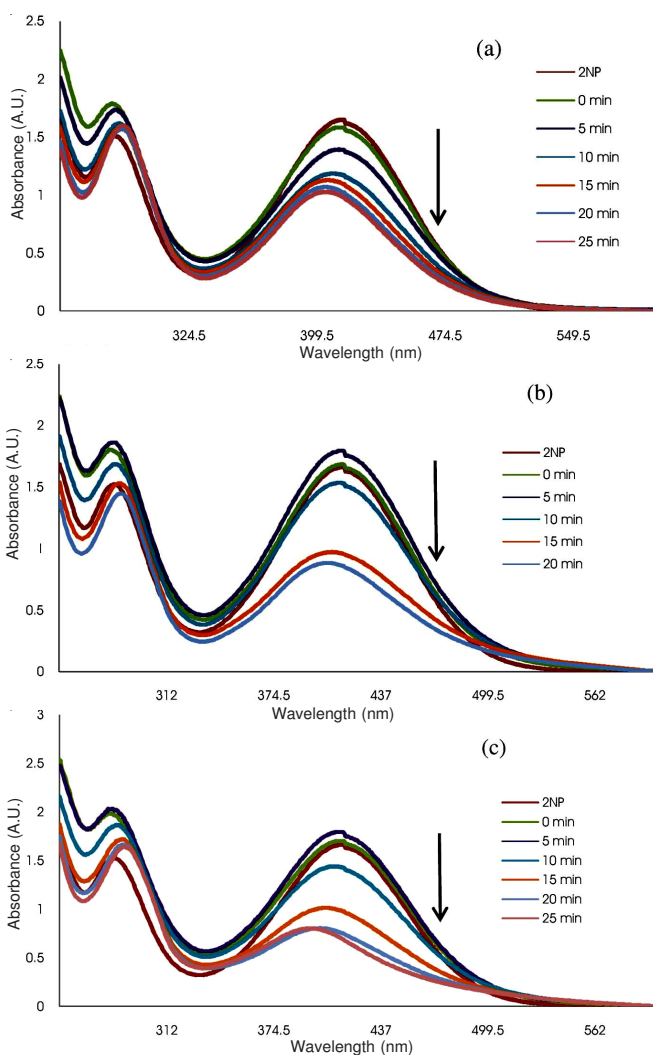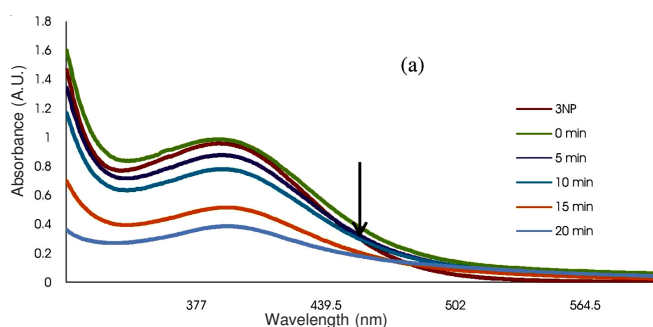

Fig. 5(i). UV-vis spectra of the reduction of 2-nitrophenol with (a) pure silver (b) silica-silver nanocolloids with APTMS linkers, (c) silica-silver nanocolloids with MPTMS linkers
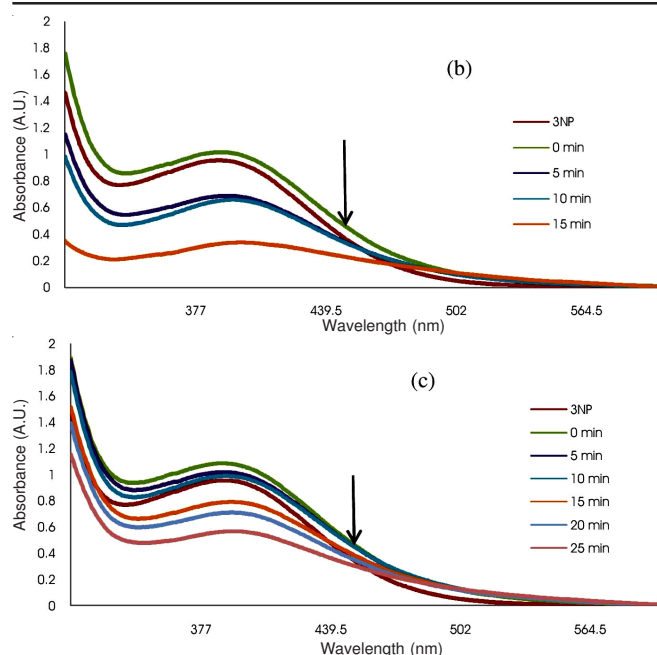
Fig. 5(ii). UV-vis spectra of the reduction of 3-nitrophenol with (a) pure silver (b) silica-silver nanocolloids with APTMS linkers, (c) silica-silver nanocolloids with MPTMS linkers

Conclusion

Silica nanoparticles were synthesized using the Stöber's method under ultrasonic condition at room temperature. 3-Mercaptopropyl trimethoxysilian (MPTMS) and 3-amino-propyl trimethoxysilane (APTMS) were used as a linker to combine the silica and silver nanoparticles. The synthesized silica-silver core-shell nanoparticles were characterized by XRD, SEM and UV-VIS spectroscopy. XRD and UV-VIS spectroscopy revealed the silica-silver nanocomposites with an APTMS linker to have clearer corresponding peaks with silver nanoparticles. On the other hand, the silica-silver nanoparticles with the MPTMS linker showed better SEM images than those with the APTMS linker.

The synthesized silica-silver core-shell nanoparticles were used as a reduction catalyst for various nitrophenols. Silica-silver nanocomposites with an APTMS linker were found to be the most effective reduction catalyst for all nitrophenols examined.

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