Synthesis and Characterization of Silver/Clay/Starch Bionanocomposites by Green Method

[1]Mansor Bin Ahmad, [1]Kamyar Shameli, [1]Wan Md Zin Wan Yunus,
[1]Nor Azowa Ibrahim and [2]Majid Darroudi,

[1]Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang,
Selangor, Malaysia
[2]Advanced Materials and Nanotechnology Laboratory, Institute of Advanced Technology,
Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia

Abstract: In this study, we report an effective process for preparing silver nanoparticles (Ag NPs) by using Green reduction method of $AgNO_3$ in interlamellar space of Montmorillonite/Starch Bionanocomposites (MMT/Stc BNCs) suspension with moderate temperature. In here MMT, Starch, β-D-glucose and $AgNO_3$ were used as a solid support, stabilizer, green reducing agent and silver precursor, respectively. Bionanocomposites material based on MMT, starch and silver nanoparticles (Ag/MMT/Stc BNCs) were prepared by adding starch and silver nitrate respectively into montmorillonite (MMT) dispersions in double distill water solution. The crystalline structure, d-spacing of interlayer of MMT, the size distributions, surface Plasmon resonance and functional groups of synthesized Ag NPs in the MMT/Stc BNCs were characterized using Powder X-Ray Diffraction (PXRD), Transmission Electron Microscopy (TEM), UV-visible spectroscopy and Fourier Transform Infrared Spectroscopy (FT-IR). The results obtained from TEM showed that the Ag NPs prepared in the extra surface of MMT layers have larger than Ag NPs intercalated between MMT layers, the particle size of nanoparticles synthesized by this processes were from 9 to 39 nm. Powder X-Ray Diffraction analysis showed that the synthesized Ag NPs crystallized in face centered cubic (fcc) symmetry. With gentle heating, this system is a mild, renewable, inexpensive, and nontoxic reducing agent. The synthesized bionanocomposites are very stable in aqueous solution over a long period of time (i.e., 3 months) without any sign of precipitation. Silver nanoparticles in MMT/Stc suspension could be suitable to use various medical applications. Since MMT is viewed as ecologically and environmentally inert material and used for biological application such as cosmetics and pharmaceutical usage.

Key word: Green chemistry, Silver nanoparticles, Bionanocomposites, powder X-ray diffraction.

INTRODUCTION

Bionanocomposites (BNCs), a novel invention of nanocomposite materials, indicate a promising field in the frontiers of nanotechnology, materials and life sciences (Darder *et al.,* 2007). BNCs are composed of a natural polymer matrix and organic/inorganic filler with at least one dimension on the nanometer scale. In addition to these characteristics, BNCs show the extraordinary advantages of biocompatibility and biodegradability in various medical, drug release packaging, and agricultural applications (Mangiacapra *et al.,* 2006).

Among natural polymers, starch is one of the most promising biocompatible and biodegradable materials because it is a renewable resource that is universally available and of low cost. A number of researchers have presented work in the field of starch-based BNCs, which can be obtained by filling a thermoplastic starch matrix with nanofillers such as layer silicates; Montmorillonite (Huang *et al.,* 2006 and Kampeerapappun *et al.,* 2007) and kaolinite (Zhao *et al.,* 2008) are the usual layer silicates used in starch-based BNCs. MMT as

Corresponding Author: Mansor Bin Ahmad, Department of Chemistry, Faculty of Science, Universiti Putra Malaysia,
43400 UPM Serdang, Selangor, Malaysia
Tel.: (603) 89466793 Fax: (603)89435380
E-mail: mansorahmad@science.upm.edu.my

a lamellar clay has intercalation, swelling and ion exchange properties. Its interlayer space has been used for the synthesis of material and biomaterial nanoparticles, as support for anchoring transition-metal complex catalysts and as adsorbents for cationic ions (Belova *et al.,* 2008 and Kozak *et al.,*2004). Ag NPs possess many interesting and unique properties. It is found in various applications, such as catalysis, electronics, non-linear optics, antimicrobial and biomaterial applications (Twu *et al., 2008*). Several methods have been reported for the synthesis of Ag NPs, e.g., photochemical reduction (Darroudi *et al.,* 2009 and Ahmad *et al.,* 2009*a*), microwave (Yin *et al., 2004*), chemical reduction (Khanna *et al.,* 2005 and Ahmad *et al.,* 2009*b*), and γ-irradiation (Chen *et al.,* 2007). The concept of green Ag NPs preparation was first developed by (Raveendran *et al.,* 2003), who used β-D-glucose as the reducing agent and starch as a capping agent to prepare starch Ag NPs. A green method for nanoparticles preparation should be evaluated from three aspects: the solvent, the reducing agent and the stabilizing agent. In this paper, we present a simple and green method for the synthesis of Ag/MMT/Stc BNCs. In here MMT, Starch, β-D-glucose and $AgNO_3$ were used as a solid support, stabilizer, green reducing agent and silver precursor, respectively. TEM images show that Ag NPs prepared in the edge and extra surface of MMT layers have large size (39±14.09 nm) and Ag NPs intercalated between MMT layers have small size (9±3.39 nm). The Ag/MMT/Stc BNCs are very stable in aqueous solution over a long period of time (i.e., 3 months) without any sign of precipitation and have potential for various medical applications.

MATERIALS AND METHODS

Materials:

All reagents were of analytical grades and were used as received without further purification. $AgNO_3$ (99.98%), used as silver precursor, was provided by Merck, Germany. MMT, used as a solid support for Ag NPs, was purchased from Kunipa-F, Japan. Soluble starch, used as a stabilizer agent, was supplied from Hamburg Chemicals, Germany. β-D-Glucose powder, used as a green reducing agent, was obtained from, BDH-AnalaR, UK. All aqueous solutions were prepared with double distilled water (DD-water).

Synthesis of Ag/MMT/Stc BNCs:

Schematic illustration of the synthesis of the Ag NPs on MMT/Stc is shown in Fig. 1. Starch solution (100 mL, 1.0 wt %) was prepared by solubilizing starch in the moderate temperature (~40°C) under constant stirring for 1 h. 10 ml of $AgNO_3$ (1.0 M) was added to the starch solution under constant stirring for preparation of $AgNO_3$/Stc sol. For preparation of MMT suspension, 3.0 g of MMT was dispersed in 200 mL DD-water and was vigorously stirred for 1 h. The $AgNO_3$/Stc sol was added into the MMT suspension and the mixture was further vigorously stirred for more than 3 h at 40°C to obtain [Ag(MMT/Stc)] $^+$. After completed dispersion of this composite, a 20 ml aliquot of a 1.0 M aqueous solution of β- D-Glucose was added and stirred. The mixture was heated to 40 °C and was maintained at this temperature for 24 h. The suspension turned of light brown to dark brown after 3 h, indicating the initial formation of Ag NPs. Then, obtained suspensions of Ag/MMT/Stc BNCs was separated by centrifugation at speed of 15,000 rpm for 15 min, washed with double distilled water twice and dried under vacuum overnight. Unless stated otherwise, all experiments were conducted at ambient temperature.

Characterization Methods and Instrumentation:

The Ag/MMT/Stc BNCs were characterized using ultraviolet–visible (UV–vis) spectroscopy, transmission electron microscopy (TEM), powder X-ray diffraction (PXRD) and Fourier transform infrared spectroscopy (FT-IR). The UV–vis spectra were recorded over the range of 300–700 nm with a UV-vis spectrophotometer Lambda 25, Perkin Elmer (USA). Transmission electron microscopy (TEM) observations were carried out on A Hitachi H-7100 electron microscope and the particle size distributions were determined using the UTHSCSA Image Tool version 3.00 program. The structure of Ag/MMT/Stc BNCs has been studied using powder X-ray diffraction (PXRD-6000 SHIMADZU). The change in interlamellar spacing of MMT and Ag/MMT/Stc BNCs was also studied by PXRD in the angle range of $2° < 2\theta < 10°$. The interlamellar space was calculated from the PXRD peak positions using Bragg's law. A wavelength (λ) equal to 0.15418 nm was used for these measurements. The PXRD patterns were recorded at a scan speed of 2°/min. FT-IR spectra were recorded over the range of (400-4000 Cm^{-1}) with a Series 100 Perkin Elmer FT-IR 1650 spectrophotometer. After reactions the samples were centrifuged by using high speed centrifuge machine (Avanti J25, Beckman).
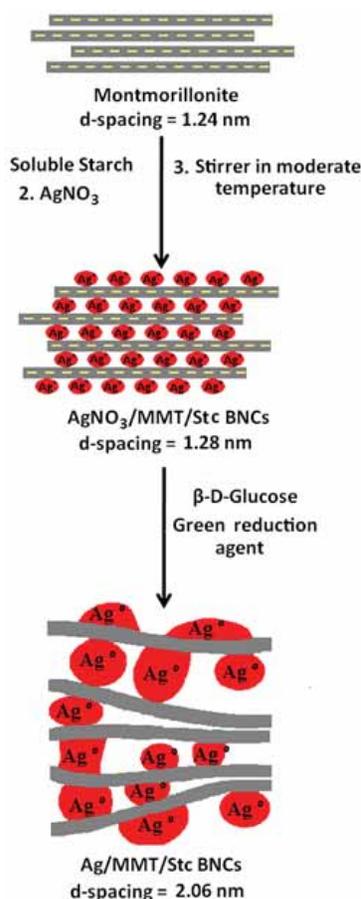
Fig. 1 Schematic illustration of the synthesis of the Ag NPs on MMT/Stc BNCs.

RESULTS AND DISCUSSIONS

The colour of prepared sample, $[Ag(MMT/Stc)]^+$ suspensions through green reduction process by β-D-glucose at different periodic times gradually changed from colourless to light brown, then to brown and finally to dark brown, indicating the formation of Ag NPs in MMT/Stc suspension. The stability of synthesized Ag/MMT/Stc BNCs suspensions was studied and indicated that this suspension prepared in the moderate temperature for 24 h, was very stable over a long time (i.e., 3 months) in aqueous solution without any sign of precipitants. The possible reaction between β-D-glucose, silver ion and starch (in the MMT suspensions) can be written as follows (Hongshui *et al.,* 2005).

$$Ag^+ \; + Stc + MMT \rightarrow [Ag\,(MMT/Stc)]^+ \tag{1}$$

$$R\text{-}CHO + 2[Ag\,(MMT/Stc)]^+ \rightarrow R\text{-}COOH + 2[Ag\,(MMT/Stc)] \downarrow \tag{2}$$
$$R = (CHOH)_4\,CH_2OH \; ; \; Stc = Starch$$

In the suspension containing MMT/Stc, silver ions were reduced with glucose in two possible reactions. In the Eq. (1) Ag^+ was compounded with starch in MMT firstly and complex ions were generated $[Ag\,(MMT/Stc)]^+$. In the Eq. (2) glucose is changed to gluconic acid and then it reduces silver ions in $[Ag\,(MMT/Stc)]^+$ suspension to Ag/MMT/Stc BNCs.

As shown in Fig. 2, the original d-spacing (d_L) of MMT is 1.24 nm, and in MMT/Stc is constant to 1.28 nm at same 2θ angles (2θ= 7.12° for MMT and 2θ= 6.90° for MMT/Stc) by starch intercalation. The d_L in Ag/MMT/Stc BNCs also was increase to 2.06 nm at smaller 2θ angles (2θ= 6.14°) by silver intercalation.

These d_L values are direct proof of the fact that, in the path of ion exchange, Ag^+ ions are bound not only on the external surfaces and edges of MMT but also in the interlamellar space. Metallic nanoparticles formed at the latter location are the cause of the increase in basal spacing. In these samples the intensities of the reflections are significantly lower whereas their half-widths are larger than those of undoped clay minerals: the highly ordered parallel lamellar structure of the mineral is disrupted by particle formation (Patakfalvi *et al.,* 2003). The PXRD peaks at 2θ of 38.15°, 44.31°, 64.40° and 77.43° in Fig. 3, can be attributed to the (111), (200) (220) and (311) crystallographic planes of face-centered cubic (fcc) silver crystals, respectively (Temgire *et al.,* 2004). The PXRD peak broadenings of Ag NPs are mostly because of existing of nano-sized particles (Prasad *et al.,* 2006). In addition there is a characteristic peak at about 2θ= 62.43° that related to MMT clay (PXRD Ref. No. 00-003-0010) as a stable substrate.

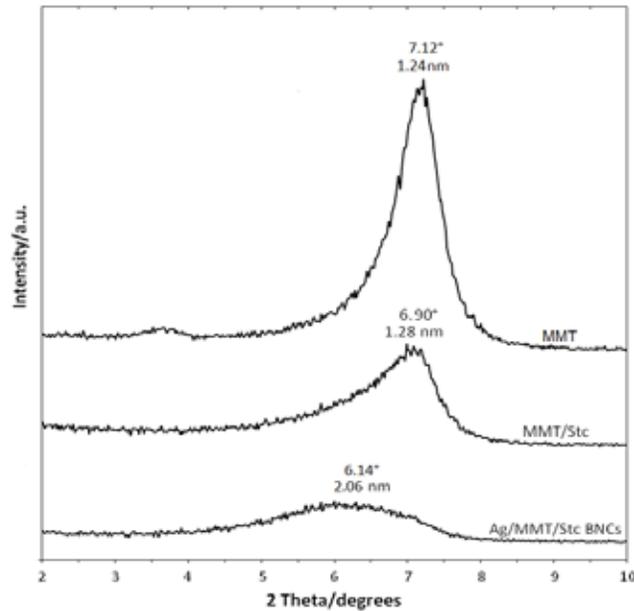**Fig. 2** PXRD patterns of MMT, MMT/Stc and Ag/MMT/Stc BNCs between 2-10/2Theta.
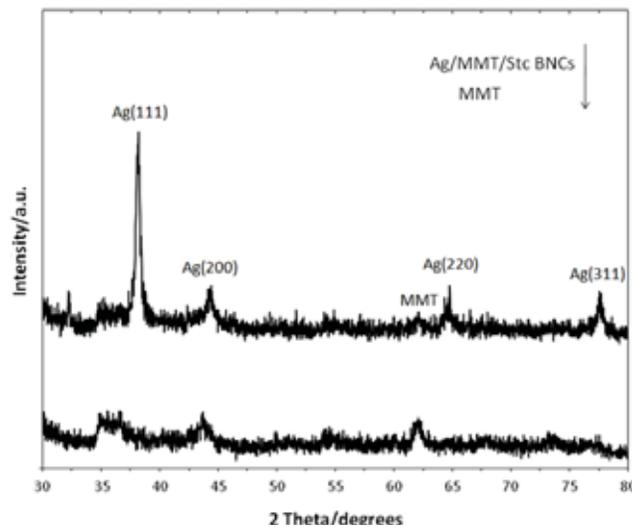

Fig. 3 PXRD patterns of MMT and Ag/MMT/Stc BNCs between 30-80/2Theta.

The formation of Ag NPs in MMT/Stc BNCs suspension was observed by TEM images. Fig. 4 shows the TEM micrographs and size distributions of the Ag NPs was based on diameter of >100 particles on TEM micrographs by using Image Tools (IT, 3 version) software. TEM image and their size distribution of Ag NPs show the mean diameter and standard deviation of the nanoparticles almost 39±14.09 nm for large Ag NPs prepared in the edge and extra surface of MMT layers (Fig. 4a, b) and 9±3.39 nm for small Ag NPs intercalated between MMT layers (Fig. 4c, d).
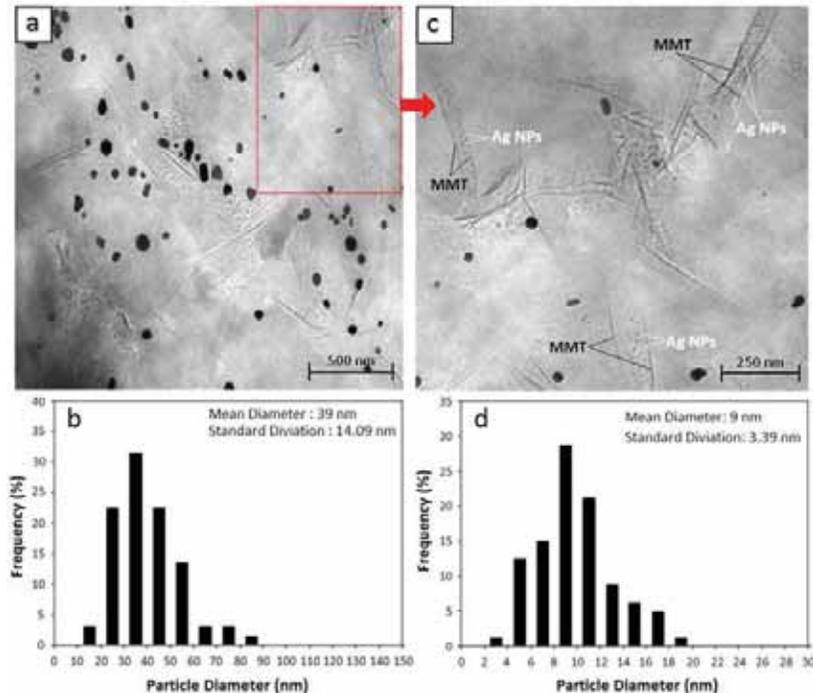

Fig. 4: TEM images and their corresponding particle size distributions of Ag NPs in MMT/Stc BNCs for large particles in the extra surface (a and b), and (c and d) for small particles intercalated between MMT layers.

The formation of Ag NPs was also followed by measuring the surface Plasmon resonance (SPR) of the MMT/Stc suspensions containing Ag NPs at the wavelength ranged from 300-700 nm as shown in Fig. 5a. SPR band was observed when $[Ag (MMT/Stc)]^+$ composite was reacted with β-D-glucose, heated at 40 °C for 24 h. The characteristic silver surface Plasmon resonance (SPR) band was detected around 429 nm. However, Fig. 5b does not show any peak before reaction $[Ag (MMT/Stc)]^+$ with β-D-glucose.

The chemical structure of the MMT/Stc and Ag/MMT/Stc BNCs were analyzed by using FT-IR spectroscopy (Figs. 6 and 7). The FT-IR spectrum of MMT (Fig. 6a) shows the vibration bands at 3619 cm^{-1} for O–H stretching, 3425 cm^{-1} due to interlayered O–H stretching (H-bonding), at the 1637 and 1502 cm^{-1} for H–O–H bending, 984 and 896 cm^{-1} for Si–O stretching, 594 cm^{-1} for Al–OH, 896 cm^{-1} due to (Al, Mg)–OH vibration modes, and 518 and 430 cm^{-1} for Si–O bending (Alemdar *et al.,* 2005). The spectrum of starch (Fig. 6c) shows absorption bands at 3277 cm^{-1} due to the O–H group stretching bands, The band at 2988 cm^{-1} corresponded to the C–H stretching, while the bands at 1637 cm^{-1} and 1425 cm^{-1} were assigned to the δ(O–H) bending of water and CH$_2$, respectively (Mano *et al.,* 2003). The absorption bands at 1425 and 1344 cm^{-1} correspond to the C-H bending, at 1131 and 1007cm^{-1} in the fingerprint region correspond to –C–O–C– stretching vibration in glucose bonds (Fang *et al.,* 2003). The absorption bands at 833, 563 and 422 cm^{-1} are attributed to the whole glucose ring stretching vibrations.

The spectrum of the MMT/Stc (Fig. 5b) shows the combination of characteristic absorptions due to the MMT and C-H stretching and bending groups of starch. The peaks of C-H groups in pure starch at 2988, 1425 and 1344 cm^{-1} are shifted to 2915, 1417 and 1350 cm^{-1} in the MMT/Stc, corresponding to the deformation vibration of C-H group of starch. These results are in agreement with the data from PXRD, revealing the combination of starch in the MMT structure. As shown in Fig. 7, there is no significant change in the spectra

of MMT/Stc and Ag/MMT/Stc BNCs, except for the appearance of the peak at 1423 and 1359 cm^{-1} for Ag/MMT/Stc with increase peak intensity and the existence of the peak at 1229 cm^{-1} due to the complexation between the hydroxyl groups of the starch and Ag NPs in the layer of MMT as sample support. The Ag NPs were successfully prepared in the extra and interlamellar space of MMT/Stc BNCs by using Green reducing agent and moderate heat treatment in 40°C and was maintained at this temperature for 24 h. The Ag NPs were found to be stabilized by starch molecules. Mean diameter and standard deviation for Ag NPs prepared in the edge and extra surface of MMT layers were 39±14.09 nm and for Ag NPs intercalated between MMT layers were 9±3.39 nm. Therefore syntheses of Ag NPs in the interlamellar space of MMT have small size distribution and standard deviation. The Ag/MMT/Stc BNCs are very stable in aqueous solution over a long period of time (i.e., 3 months) without any sign of precipitation and have potential for various medical applications.
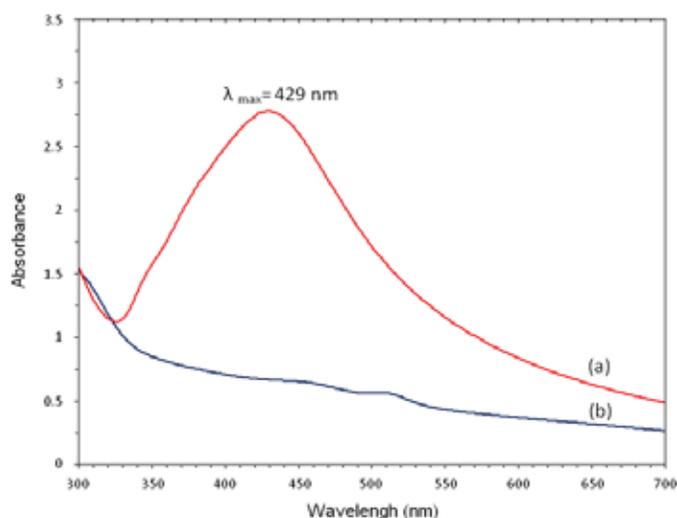

Fig. 5: UV-vis adsorption spectra of [Ag (MMT/Stc)]$^+$ in 0h (a) and Ag/MMT/Stc BNCs after 24h (b).
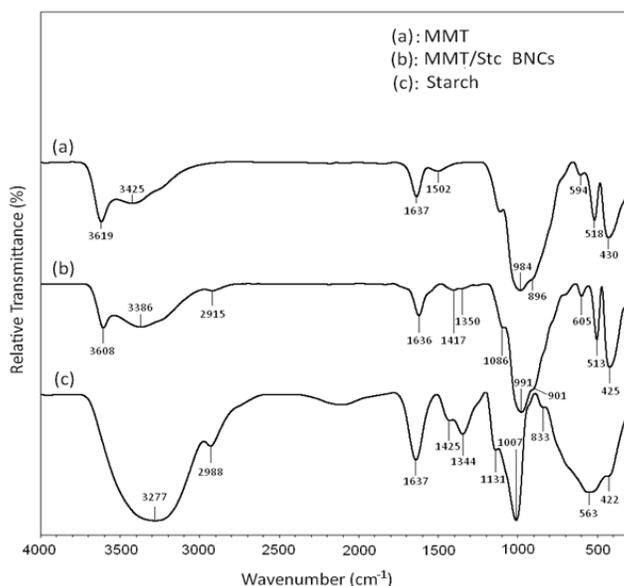

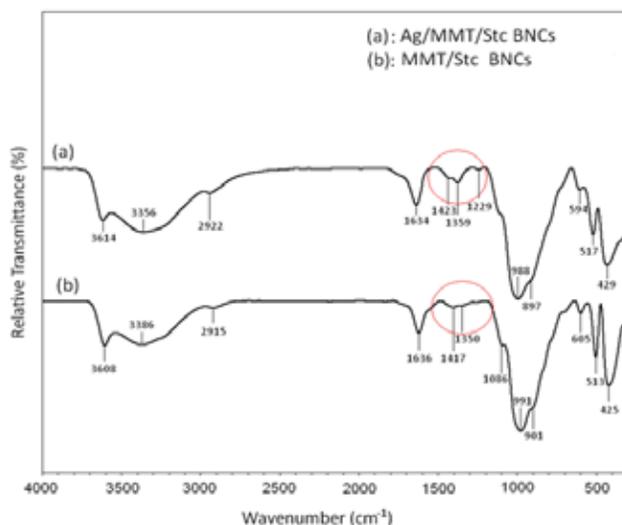**Fig. 6:** FT-IR spectra of MMT, MMT/Stc and Starch (a) MMT (b) MMT/Stc (c) Starch

Fig. 7: FT-IR spectra of MMT/Stc and Ag/MMT/Stc BNCs (a) MMT/Stc/Ag BNCs (b) MMT/Cts

REFERENCES

Ahmad, M.B., K. Shameli, M. Darroudi, W.M.Z.W. Yunus, and N.A. Ibrahim, 2009a. Synthesis and Characterization of Silver/Clay/Chitosan Bionanocomposites by UV-Irradiation Method. Am. J. Appl. Sci., 6 (12): 2030-2035.

Ahmad, M.B., K. Shameli, M. Darroudi, W.M.Z.W. Yunus and N.A. Ibrahim, 2009b. Synthesis and Characterization of Silver/Clay Nanocomposites by Chemical Reduction Method. Am. J. Appl. Sci., 6 (11): 1909-114.

Alemdar, A., N. Güngör, Ö.I. Ece. and O. Atici, 2005. The rheological properties and characterization of bentonite dispersions in the presence of non-ionic polymer PEG. J. Mater. Sci., 40: 171-177.

Belova, V., H. Möhwald and D.G. Shchukin, 2008. Sonochemical intercalation of preformed gold nanoparticles into multilayered clays. Langmuir., 24: 9747-9753.

Chen, P., L. Song, Y. Liu, and Y. Fang, 2007. Synthesis of silver nanoparticles by [gamma]-ray irradiation in acetic water solution containing chitosan. Radiat. Phys. Chem., 76: 1165-1168.

Darder, M., P. Aranda, and E. Ruiz-Hitzky, 2007. Bionanocomposites: A new concept of ecological, bio-inspired, and functional hybrid materials. Advanced Materials, 19: 1309–1319.

Darroudi, M., M.B. Ahmad, K. Shameli, A.H. Abdullah, and N.A. Ibrahim, 2009. Synthesis and characterization of UV-irradiated silver/montmorillonite nanocomposites. Solid State Sci., 11: 1621-1624.

Fang, J.M., P. A. Fowler, C. Sayers and P. A. Williams, 2004. The chemical modification of a range of starches under aqueous reaction condition. Carbohyd Polym., 55: 283–289.

Hongshui, W., X. Qiao, J. Chen, and S. Ding, 2005. Preparation of silver nanoparticles by chemical reduction method. Colloids and Surfaces A: Physicochem. Eng. Aspects, 256: 111–115.

Huang, M. F., J. G. Yu, and X. F. Ma, 2006. High mechanical performance MMT-urea and Formamide-plasticized thermoplastic cornstarch biodegradable nanocomposites. Carbohyd. Polym., 63: 393–399.

Kampeerapappun, P., D. Aht-Ong, D. Pentrakoon, and K. Srikulkit, 2007. Preparation of cassava starch/montmorillonite composite film. Carbohyd. Polym., 67: 155–163.

Khanna, P.K., N. Singh, S. Charan, V.V.V.S. Subbarao, R. Gokhale and U.P. Mulik, 2005. Synthesis and characterization of Ag/PVA nanocomposite by chemical reduction method. Mater. Chem. Phys., 93: 117-121.

Kozak, M. and L.J. Domka, 2004. Adsorption of the quaternary ammonium salts on montmorillonite. J. Phys. Chem. Solids., 65: 441-445.

Mangiacapra, P., G. Gorrasi, A. Sorrentino, and V. Vittoria, 2006. Biodegradable nanocomposites obtained by ball milling of pectin and montmorillonites. Carbohyd. Polym., 64: 516–523.

Mano, J.F., D. Koniarova, and R.L. Reis, 2003. Thermal properties of thermoplastic starch/synthetic polymer blends with potential biomedical applicability. J. Mater. Sci.: Mater. Med., 14: 127–135.

Patakfalvi, R., A. Oszko and I. Dékány, 2003. Synthesis and characterization of silver nanoparticle/kaolinite composites. Colloid Surface A., 220: 45-54.

Prasad, V., C.D. Souza, D. Yadav, A.J. Shaikh, and N. Vigneshwaran, 2006. Spectroscopic characterization of zinc oxide nanorods synthesized by solid-state reaction. Spectrochim. Acta A., 65: 173-178.

Raveendran, P., J. Fu, and S. L, Wallen, 2003. Completely "Green" Synthesis and Stabilization of Metal Nanoparticles. J. Am. Chem. Soc., 125: 13940–13941.

Temgire, M.K. and S.S. Joshi, 2004. Optical and structural studies of silver nanoparticles. Radiat. Phys. Chem., 71: 1039-1044.

Twu, Y.K., Y.W. Chen, and C.M. Shih, 2008. Preparation of silver nanoparticles using chitosan suspensions. Powder Technol., 185: 251-257.

Yin, H., T. Yamamoto, Y. Wada and S. Yanagida, 2004. Large-scale and size-controlled synthesis of silver nanoparticles under microwave irradiation. Mater. Chem. Phys., 83: 66-70.

Zhao, X.P., B.X. Wang and J. Li, 2008. Synthesis and electrorheological activity of a modified kaolinite/carboxymethyl starch hybrid nanocomposite. J. Appl. Polym. Sci., 108: 2833–2839.